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MO- $\pi$ -Bindungsordnung-Bindungslängen-Beziehungen für Hetero- $\pi$ -Systeme, V<sup>1)</sup>

## $\pi$ -Systeme mit NO-Bindungen

Aus dem Lehrstuhl für Organische Chemie der Universität Tübingen

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Für NO- $\pi$ -Bindungen werden aus HMO- $\pi$ -Bindungs-Bindungs-Polarisierbarkeiten mittels der zuvor ermittelten HMO- $\pi$ -Bindungsordnung-Bindungslängen-Beziehungen und den entsprechenden experimentellen Bindungsabständen folgende empirische Resonanzintegralparameter abgeleitet:

$$k_{\text{N}=\text{N}-\text{O}} = 0.8; \quad k_{\text{N}=\text{N}^{\oplus}-\text{O}^{\ominus}} = 1.9; \quad k_{\text{N}=\text{N}=\text{O}} = 1.4$$

Die nach der Methode der kleinsten Fehlerquadrate aus den mit diesen Parametern berechneten HMO- $\pi$ -Bindungsordnungen und den experimentellen Bindungslängen ermittelte Ausgleichsgerade beträgt

$$R_{\text{rs}}^{\text{HMO, NO}} [\text{\AA}] = 1.474 - 0.371 p_{\text{rs}}$$

mit einer Standardabweichung ( $\sigma$ ) von 0.034 Å und einem Korrelationskoeffizienten ( $k$ ) von 0.902 für 159 Punkte.

Für die CN-Bindungen dieser NO- $\pi$ -Systeme ergibt sich die Ausgleichsgerade

$$R_{\text{rs}}^{\text{HMO, CN in NO}} [\text{\AA}] = 1.512 - 0.263 p_{\text{rs}}$$

mit  $\sigma = 0.043$  Å und  $k = 0.795$  für 114 Werte, deren relativ hohe Lage daher kommt, daß

die  $\text{C}-\text{N}^{\oplus}=\text{N}^{\ominus}$ -Bindungen, z. B. in Nitroverbindungen, extrem lang sind.

Die Zusammenfassung aller bisherigen CN- $\pi$ -Bindungen liefert die Beziehung:

$$R_{\text{rs}}^{\text{HMO, CN}} [\text{\AA}] = 1.478 - 0.234 p_{\text{rs}}$$

mit  $\sigma = 0.030$  Å und  $k = 0.772$  für 479 Punkte.

Für NN-Bindungen in NO-Systemen ergibt sich

$$R_{\text{rs}}^{\text{HMO, NN in NO}} [\text{\AA}] = 1.497 - 0.271 p_{\text{rs}}$$

mit  $\sigma = 0.028$  Å und  $k = 0.914$  für 11 Werte.

Für die Gesamtheit der NN-Bindungen gilt:

$$R_{\text{rs}}^{\text{HMO, NN}} [\text{\AA}] = 1.443 - 0.190 p_{\text{rs}}$$

mit  $\sigma = 0.027$  Å und  $k = 0.900$  für 48 Punkte.

## MO- $\pi$ -Bond Order-Bond Length Relations for Hetero- $\pi$ -Systems, V<sup>1)</sup>

### $\pi$ -Systems with NO-Bonds

For NO- $\pi$ -bonds the following empirical resonance integral parameters have been derived by means of HMO- $\pi$ -bond-bond polarizabilities in combination with the previously obtained HMO- $\pi$ -bond order-bond lengths relation and experimentally determined bond lengths:

$$k_{\text{N}=\text{N}-\text{O}} = 0.8; \quad k_{\text{N}=\text{N}^{\oplus}-\text{O}^{\ominus}} = 1.9; \quad k_{\text{N}=\text{N}=\text{O}} = 1.4$$

<sup>1)</sup> IV. Mitteil.: G. Häfelinger, Chem. Ber. 103, 3289 (1970).

The linear equation derived by the method of least squares which represents the relationship between HMO- $\pi$ -bond orders calculated with these new parameters and experimental bond lengths is

$$R_{rs}^{\text{HMO, NO}} [\text{\AA}] = 1.474 - 0.371 p_{rs}$$

with a standard deviation ( $\sigma$ ) of 0.034 Å and a correlation coefficient ( $k$ ) of 0.902 for 159 points. For CN-bonds in these NO- $\pi$ -systems the following linear equation results

$$R_{rs}^{\text{HMO, CN in NO}} [\text{\AA}] = 1.512 - 0.263 p_{rs}$$

with  $\sigma = 0.043$  Å and  $k = 0.795$  for 114 points.

The values for the bond lengths in this equation are relatively high because  $=\text{C}-\text{N}^{\text{B}}-$ -bonds, for instance in nitro compounds, are extremely long. The combination of all CN-bonds in  $\pi$ -systems treated in the previous communications gives the relation

$$R_{rs}^{\text{HMO, CN}} [\text{\AA}] = 1.478 - 0.234 p_{rs}$$

with  $\sigma = 0.030$  Å and  $k = 0.772$  for 479 points.

For NN-bonds in NO- $\pi$ -systems the equation

$$R_{rs}^{\text{HMO, NN in NO}} [\text{\AA}] = 1.497 - 0.271 p_{rs}$$

with  $\sigma = 0.028$  Å and  $k = 0.914$  for 11 points is obtained.

Combination with the NN-bonds of the previous contribution<sup>1)</sup> leads to

$$R_{rs}^{\text{HMO, NN}} [\text{\AA}] = 1.443 - 0.190 p_{rs}$$

with  $\sigma = 0.027$  Å and  $k = 0.900$  for 48 points



In der Literatur sind nur wenige Angaben über HMO- $\pi$ -Bindungsordnung-Bindungslängen-Beziehungen für NO-Bindungen zu finden, die in Tab. 1 zusammen-

Tab. 1.  $\pi$ -Bindungsordnung-Bindungslängen-Beziehungen für NO-Bindungen

$$R_{rs} [\text{\AA}] = S - B p_{rs} \quad (1)$$

| $S [\text{\AA}]$<br>$N_{sp^2}-O-$<br>Einfachbindungs-<br>abstand für $p=0$ | $D [\text{\AA}]$<br>$N_{sp^2}=O-$<br>Doppelbindungs-<br>abstand für $p=1.0$ | Steigung $B$<br>in Gl. (1) | Kurventyp | Methode*) | Lit. |
|----------------------------------------------------------------------------|-----------------------------------------------------------------------------|----------------------------|-----------|-----------|------|
| 1.43                                                                       | 1.15                                                                        | 0.28                       | linear    | HMO       | 2)   |
| 1.44                                                                       | 1.21                                                                        | 0.23                       | linear    | HMO       | 3)   |
| 1.326                                                                      | 1.156                                                                       | 0.166                      | linear    | HMO + PPP | 4)   |
| 1.430                                                                      | 1.200                                                                       | 0.230                      | linear    | PPP       | 5)   |
| 1.325                                                                      | 1.145                                                                       | 0.180                      | linear    | PPP       | 6)   |

\*) Berechnungsmethode für  $\pi$ -Bindungsordnungen: HMO = Berechnung nach der einfachen Hückelmethode ohne Berücksichtigung der Überlappung und eines induktiven Hilfsparameters<sup>7a)</sup>; PPP = Berechnung nach der empirischen SCF-Methode nach *Pariser, Parr* und *Pople*<sup>7b)</sup>.

2) *J. H. Bryden*, Acta crystallogr. [Copenhagen] **12**, 581 (1959).

3) *G. Tsoucaris*, Acta crystallogr. [Copenhagen] **14**, 914 (1961).

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6) *O. Gropen* und *P. N. Skancke*, Acta chem. scand. **23**, 2685 (1969).

7a) *A. Streitwieser jr.*, Molecular Orbital Theory for Organic Chemists, J. Wiley & Sons, New York 1962.

7b) *R. Pariser*, J. chem. Physics **21**, 568 (1953); *J. Pople*, Trans. Faraday Soc. **49**, 1375 (1953); *R. G. Parr*, The Quantum Theory of Molecular Electronic Structure, W. A. Benjamin, New York 1966.

gestellt sind. Diese Beziehungen beruhen jeweils auf einer geringen Zahl experimentell bestimmter Bindungsabstände. Außerdem besteht keine Klarheit über die Wahl der benötigten HMO-Parameter, wie ein Blick auf Tab. 2 zeigt.

Tab. 2. HMO-Heteroatomparameter für NO-Bindungen

$$\alpha_X = \alpha_C + h_X \beta_{CC} \quad (2); \quad \beta_{XY} = k_{XY} \cdot \beta_{CC} \quad (3)$$

| $h-\ddot{N}-h-\ddot{N}-h-\overset{\oplus}{N}-h-\ddot{O}-h-\ddot{O}-h-\ddot{O} \leftrightarrow kC \equiv N \quad kC-\ddot{N}-\quad kC-\overset{\oplus}{N}-\quad k-N \equiv O \quad k-\overset{\oplus}{N}-\overset{\ominus}{O} \quad \text{Verbindungs-}$ |      |     |      |      |      |      |      |     |      |               | Lit.                    |        |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------|-----|------|------|------|------|------|-----|------|---------------|-------------------------|--------|
| 0.5                                                                                                                                                                                                                                                     | 1.5  | 2.0 | 1.0  | 2.0  | 2.0  | 1.0  | 0.8  | —   | —    | —             | allgemein               | 7a)    |
| 0.5                                                                                                                                                                                                                                                     | —    | 0.6 | —    | —    | 1.0  | 1.0  | —    | —   | —    | 0.5; 1.0; 1.5 | Pyridinoxid             | 8)     |
| —                                                                                                                                                                                                                                                       | 1.2  | 0.8 | —    | —    | 1.2  | 1.0  | 0.7  | —   | —    | 1.0           | Pyridinoxide            | 9)     |
| 0.6                                                                                                                                                                                                                                                     | 0.7  | 0.8 | 2.3  | 2.1  | 2.2  | 1.0  | 1.0  | —   | 1.17 | —             | allgemein               | 10,11) |
| 1.0                                                                                                                                                                                                                                                     | 2.0  | 2.5 | 2.0  | 3.2  | —    | 1.0  | —    | —   | 1.2  | 0.7           | Nitro-<br>verbindungen  | 12)    |
| 0.5                                                                                                                                                                                                                                                     | 0.65 | 1.8 | —    | —    | 1.5  | 1.0  | 0.9  | 1.1 | —    | 1.6           | Nitro-<br>substituenten | 13)    |
| 0.55                                                                                                                                                                                                                                                    | 1.5  | 2.0 | 1.0  | 2.5  | 1.0  | —    | 0.7  | —   | —    | 0.7           | Nitro-<br>substituenten | 14)    |
| 0.45                                                                                                                                                                                                                                                    | —    | 1.1 | —    | —    | 0.7  | 0.8  | —    | 0.5 | —    | 1.0           | Nitro-<br>substituenten | 15)    |
| 0.5                                                                                                                                                                                                                                                     | 0.8  | 0.8 | —    | —    | 1.2  | 1.0  | 1.2  | 0.8 | —    | 1.2           | Nitro-<br>substituenten | 16)    |
| —                                                                                                                                                                                                                                                       | —    | 1.6 | —    | —    | 0.8  | —    | —    | —   | —    | 1.0           | N-Oxide                 | 17)    |
| 0.83                                                                                                                                                                                                                                                    | 1.47 | —   | 1.18 | 1.96 | 2.06 | 1.06 | 1.30 | —   | 1.95 | —             | allgemein               | 18)    |

Die in den vorhergehenden Mitteilungen<sup>19,20)</sup> beschriebene Methode zur Bestimmung der Resonanzintegralparameter aus HMO- $\pi$ -Bindungs-Bindungs-Polarisierbarkeiten und experimentell bestimmten Bindungsabständen in Kombination mit empirisch bestimmten HMO- $\pi$ -Bindungsordnung-Bindungslängen-Beziehungen soll zur Ermittlung der benötigten Bindungsparameter  $k_{NO}$  benutzt werden.

In Tab. 3 sind die experimentell mit einer Standardabweichung von höchstens 0.015 Å bestimmten Bindungsabstände von NO-Bindungen enthaltenden Hetero- $\pi$ -Systemen zusammengestellt, gemeinsam mit den Ergebnissen von HMO- $\pi$ -Bindungsordnungsberechnungen mit dem Parametersatz (4) \*\*,\*)).

\*) Die Berechnungen wurden mit einem HMO-Programm von I. Brauman und A. Streitwieser jr. am Zentrum für Datenverarbeitung der Universität Tübingen mit dem Computer CDC 3300 durchgeführt.

\*\*) Die Coulombintegral-Heteroatomparameter  $h_X$  sind die Werte von Derflinger und Lischka<sup>18)</sup>. Die  $k_{CN}$ - und  $k_{CO}$ -Werte sind in den vorherigen Mitteilungen abgeleitet worden<sup>19,20)</sup>.

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9) G. Tsoucaris, J. Chim. physique **58**, 613 (1961).

10) G. Rasch, Z. Chem. **2**, 347 (1962).

11) G. Rasch, Z. Chem. **2**, 382 (1962).

12) A. J. Owen, Tetrahedron [London] **23**, 1857 (1967).

13) P. Schuster, Mh. Chem. **98**, 1310 (1967).

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15) D. Beltrame, P. L. Beltrame und M. Simonetta, Tetrahedron [London] **24**, 3043 (1968).

16) J. Kroner und H. Bock, Chem. Ber. **101**, 1922 (1968).

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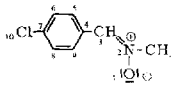
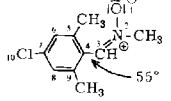
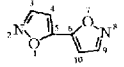
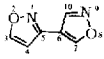
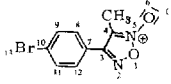
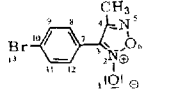
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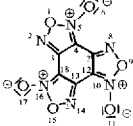
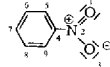
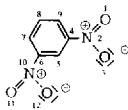
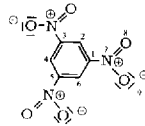
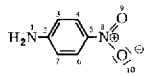
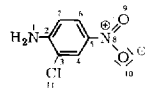
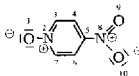
Tab. 3. Bindungsabstände und  $\pi$ -Bindungsordnungen von NO-Bindungen enthaltenden Hetero- $\pi$ -Systemen

| Nr.                   | Verbindung                                                                                                                       | Bindung<br>is                                                       | Abstand<br>R <sub>is</sub> [Å]                                                         | Standard-<br>abweichung<br>σ · 10 <sup>3</sup> [Å] | Methode *) | Lit. | π-Bindungsordnungen p <sub>rs</sub>                                                    |                                                                                        |                |      |
|-----------------------|----------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------|----------------------------------------------------------------------------------------|----------------------------------------------------|------------|------|----------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------|----------------|------|
|                       |                                                                                                                                  |                                                                     |                                                                                        |                                                    |            |      | HMO**) HMO***)                                                                         | PPP                                                                                    | Lit.           |      |
| I. NO-Abstände        |                                                                                                                                  |                                                                     |                                                                                        |                                                    |            |      |                                                                                        |                                                                                        |                |      |
| 1                     | HN = O<br>                                      | 1-2                                                                 | 1.212                                                                                  | 2                                                  | MW         | a)   | .9806                                                                                  | .9899                                                                                  |                |      |
| 2                     | Natriumnitrit<br>                               | 1-2                                                                 | 1.240                                                                                  | 3                                                  | N          | b)   | .6796                                                                                  | .6873                                                                                  |                |      |
| 3                     | Salpetrige Säure<br>                            | 1-2<br>2-3                                                          | 1.433<br>1.177                                                                         | 3                                                  | MW         | c)   | .3783<br>.8994                                                                         | .3340<br>.9309                                                                         |                |      |
| 4                     | Nitromethan <sup>1)</sup><br>                   | 1-2                                                                 | 1.204                                                                                  | 10                                                 | MW         | d)   | .6738                                                                                  | .6974                                                                                  |                |      |
| 5                     | Salpetersäure<br>                               | 1-2<br>2-4                                                          | 1.206<br>1.405                                                                         | 5                                                  | MW         | d)   | .6094<br>.4266                                                                         | .6691<br>.2817                                                                         |                |      |
| 6                     | Pentaerythrit-<br>tetranitrat <sup>1)</sup><br> | 1-2<br>2-4                                                          | 1.214<br>1.404                                                                         | 14<br>12                                           | X          | e)   | .6094<br>.4266                                                                         | .6691<br>.2817                                                                         |                |      |
| 7                     | Methylguanidi-<br>niumnitrat<br>                | 1-2                                                                 | 1.244                                                                                  | 10                                                 | X          | f)   | .5588                                                                                  | .5720                                                                                  |                |      |
| 8                     | Natriumnitrat<br>                               | 1-2                                                                 | 1.234                                                                                  | 3                                                  | X          | g)   | .5588                                                                                  | .5720                                                                                  |                |      |
| 9                     |                                                                                                                                  | 1-2                                                                 | 1.250                                                                                  | 2                                                  | X          | h)   | .5588                                                                                  | .5720                                                                                  |                |      |
| 10                    |                                                                                                                                  | 1-2                                                                 | 1.258                                                                                  | 2                                                  | X          | i)   | .5588                                                                                  | .5720                                                                                  |                |      |
| II. CN- + NO-Abstände |                                                                                                                                  |                                                                     |                                                                                        |                                                    |            |      |                                                                                        |                                                                                        |                |      |
| 11                    | Formaldoxim<br>                                | 1-2<br>2-3                                                          | 1.408<br>1.276                                                                         | 5<br>5                                             | MW         | j)   | .1695<br>.9416                                                                         | .1967<br>.9409                                                                         | .4498<br>.8311 | uuu) |
| 12                    | Cyclohexandion-<br>(1,4)-dioxim<br>           | 1-2<br>2-3                                                          | 1.411<br>1.276                                                                         | 3<br>3                                             | X          | k)   | .1695<br>.9416                                                                         | .1967<br>.9409                                                                         | .4498<br>.8311 | uuu) |
| 13                    | Formamidoxim<br>                              | 1-2<br>2-3<br>3-4                                                   | 1.415<br>1.288<br>1.334                                                                | 7<br>8<br>8                                        | X          | l)   | .1128<br>.8079<br>.4919                                                                | .1318<br>.8128<br>.4829                                                                |                |      |
| 14                    | Glyoxim<br>                                   | 1-2<br>2-3<br>3-4                                                   | 1.397<br>1.284<br>1.449                                                                | 4<br>5<br>6                                        | X          | m)   | .2004<br>.8644<br>.4053                                                                | .2286<br>.8583<br>.4158                                                                |                |      |
| 15                    | Diacetyl-<br>dioxim <sup>1)</sup><br>         | 1-2<br>2-3<br>3-4                                                   | 1.321<br>1.253<br>1.479                                                                | 21<br>11<br>15                                     | N          | n)   | .2004<br>.8644<br>.4053                                                                | .2286<br>.8583<br>.4158                                                                |                |      |
| 16                    | syn-p-Chlor-<br>benzaloxim<br>                | 1-2<br>2-3<br>3-4<br>4-5<br>5-6<br>6-7<br>7-8<br>8-9<br>4-9<br>7-10 | 1.408<br>1.260<br>1.486<br>1.367<br>1.382<br>1.396<br>1.367<br>1.396<br>1.396<br>1.728 | 7<br>8<br>9<br>8<br>8<br>8<br>8<br>8<br>8<br>6     | X          | o)   | .1646<br>.8494<br>.4125<br>.6064<br>.6817<br>.6518<br>.6518<br>.6817<br>.6064<br>.1302 | .1925<br>.8507<br>.4114<br>.6069<br>.6814<br>.6520<br>.6520<br>.6814<br>.6069<br>.1295 |                |      |

Tab. 3 (Forts.)

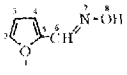
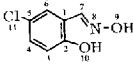
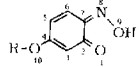
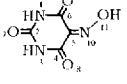
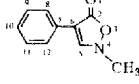
| Nr. | Verbindung                                                                                                                                                                | Bindung<br>rs | Abstand<br>$R_E$ [Å] | Standard-<br>abweichung<br>$\sigma \cdot 10^3$ [Å] | Methode *) | Lit. | $\pi$ -Bindungsordnungen $p_{rs}$ |       |      |  |
|-----|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------|----------------------|----------------------------------------------------|------------|------|-----------------------------------|-------|------|--|
|     |                                                                                                                                                                           |               |                      |                                                    |            |      | HMO**) HMO***)                    | PPP   | Lit. |  |
| 17  | <i>N</i> -Methyl- <i>p</i> -chlor-<br>benzaldoxim <sup>(1)</sup><br>                     | 1-2           | 1.284                | 6                                                  | X          | o)   | .2048                             | .5217 |      |  |
|     |                                                                                                                                                                           | 2-3           | 1.309                | 7                                                  |            |      | .8022                             | .7669 |      |  |
|     |                                                                                                                                                                           | 3-4           | 1.464                | 8                                                  |            |      | .4255                             | .4297 |      |  |
|     |                                                                                                                                                                           | 4-5           | 1.401                | 8                                                  |            |      | .6021                             | .6014 |      |  |
|     |                                                                                                                                                                           | 5-6           | 1.391                | 8                                                  |            |      | .6831                             | .6816 |      |  |
|     |                                                                                                                                                                           | 6-7           | 1.363                | 8                                                  |            |      | .6506                             | .6521 |      |  |
|     |                                                                                                                                                                           | 7-8           | 1.363                | 8                                                  |            |      | .6506                             | .6521 |      |  |
|     |                                                                                                                                                                           | 8-9           | 1.388                | 9                                                  |            |      | .6831                             | .6816 |      |  |
|     |                                                                                                                                                                           | 4-9           | 1.411                | 8                                                  |            |      | .6021                             | .6014 |      |  |
|     |                                                                                                                                                                           | 7-10          | 1.768                | 7                                                  |            |      | .1318                             | .1204 |      |  |
| 18  | <i>anti</i> -4-Chlor-2,6, <i>N</i> -<br>trimethyl-<br>benzaldoxim <sup>(1)</sup><br>     | 1-2           | 1.298                | 7                                                  | X          | p)   | .2123                             | .5050 |      |  |
|     |                                                                                                                                                                           | 2-3           | 1.299                |                                                    |            |      | .8633                             | .8205 |      |  |
|     |                                                                                                                                                                           | 3-4           | 1.473                |                                                    |            |      | .2588                             | .2633 |      |  |
|     |                                                                                                                                                                           | 4-5           | 1.408                |                                                    |            |      | .6432                             | .6426 |      |  |
|     |                                                                                                                                                                           | 5-6           | 1.389                |                                                    |            |      | .6732                             | .6727 |      |  |
|     |                                                                                                                                                                           | 6-7           | 1.383                |                                                    |            |      | .6577                             | .6581 |      |  |
|     |                                                                                                                                                                           | 7-8           | 1.376                |                                                    |            |      | .6577                             | .6581 |      |  |
|     |                                                                                                                                                                           | 8-9           | 1.391                |                                                    |            |      | .6732                             | .6727 |      |  |
|     |                                                                                                                                                                           | 4-9           | 1.403                |                                                    |            |      | .6432                             | .6426 |      |  |
|     |                                                                                                                                                                           | 7-10          | 1.742                |                                                    |            |      | .1260                             | .1220 |      |  |
| 19  | 1,2,5-Oxadiazol<br>                                                                      | 1-2           | 1.380                | 3                                                  | MW         | q)   | .3172                             | .3563 |      |  |
|     |                                                                                                                                                                           | 2-3           | 1.300                |                                                    |            |      | .8277                             | .8116 |      |  |
|     |                                                                                                                                                                           | 3-4           | 1.421                |                                                    |            |      | .4781                             | .5051 |      |  |
| 20  | 5,5'-Bi-isoxazol<br>                                                                     | 1-2           | 1.418                | 11                                                 | X          | r)   | .2894                             | .3124 |      |  |
|     |                                                                                                                                                                           | 2-3           | 1.291                | 14                                                 |            |      | .7563                             | .7529 |      |  |
|     |                                                                                                                                                                           | 3-4           | 1.423                | 12                                                 |            |      | .5843                             | .5906 |      |  |
|     |                                                                                                                                                                           | 4-5           | 1.323                | 12                                                 |            |      | .7034                             | .7014 |      |  |
|     |                                                                                                                                                                           | 5-1           | 1.343                | 11                                                 |            |      | .4337                             | .4406 |      |  |
|     |                                                                                                                                                                           | 5-6           | 1.483                | 18                                                 |            |      | .3998                             | .3992 |      |  |
| 21  | 3,4'-Bi-isoxazol<br>                                                                     | 1-2           | 1.432                | 6                                                  | X          | s)   | .2695                             | .2934 |      |  |
|     |                                                                                                                                                                           | 2-3           | 1.346                |                                                    |            |      | .4680                             | .4751 |      |  |
|     |                                                                                                                                                                           | 3-4           | 1.341                |                                                    |            |      | .7780                             | .7754 |      |  |
|     |                                                                                                                                                                           | 4-5           | 1.428                |                                                    |            |      | .5338                             | .5396 |      |  |
|     |                                                                                                                                                                           | 1-5           | 1.322                |                                                    |            |      | .6992                             | .6999 |      |  |
|     |                                                                                                                                                                           | 5-6           | 1.477                |                                                    |            |      | .3752                             | .3700 |      |  |
|     |                                                                                                                                                                           | 6-7           | 1.372                |                                                    |            |      | .7018                             | .7033 |      |  |
|     |                                                                                                                                                                           | 7-8           | 1.342                |                                                    |            |      | .4962                             | .4997 |      |  |
|     |                                                                                                                                                                           | 8-9           | 1.421                |                                                    |            |      | .2810                             | .3049 |      |  |
|     |                                                                                                                                                                           | 9-10          | 1.321                |                                                    |            |      | .7756                             | .7719 |      |  |
|     |                                                                                                                                                                           | 6-10          | 1.394                |                                                    |            |      | .5338                             | .5396 |      |  |
| 22  | 4-Methyl-3-[ <i>p</i> -brom-<br>phenyl]-1,2,5-oxa-<br>diazol-5-oxid <sup>(1)</sup><br> | 1-2           | 1.386                | 6                                                  | X          | t)   | .2998                             | .2315 |      |  |
|     |                                                                                                                                                                           | 2-3           | 1.309                | 6                                                  |            |      | .7238                             | .6894 |      |  |
|     |                                                                                                                                                                           | 3-4           | 1.415                | 7                                                  |            |      | .5096                             | .5582 |      |  |
|     |                                                                                                                                                                           | 4-5           | 1.313                | 7                                                  |            |      | .7720                             | .6609 |      |  |
|     |                                                                                                                                                                           | 1-5           | 1.425                | 6                                                  |            |      | .4054                             | .3389 |      |  |
|     |                                                                                                                                                                           | 5-6           | 1.236                | 7                                                  |            |      | .3028                             | .5916 |      |  |
|     |                                                                                                                                                                           | 3-7           | 1.462                | 7                                                  |            |      | .3641                             | .3601 |      |  |
|     |                                                                                                                                                                           | 7-8           | 1.391                | 7                                                  |            |      | .6190                             | .6206 |      |  |
|     |                                                                                                                                                                           | 8-9           | 1.382                | 7                                                  |            |      | .6778                             | .6773 |      |  |
|     |                                                                                                                                                                           | 9-10          | 1.360                | 7                                                  |            |      | .6558                             | .6562 |      |  |
|     |                                                                                                                                                                           | 10-11         | 1.378                | 7                                                  |            |      | .6558                             | .6562 |      |  |
|     |                                                                                                                                                                           | 11-12         | 1.384                | 8                                                  |            |      | .6778                             | .6773 |      |  |
|     |                                                                                                                                                                           | 7-12          | 1.392                | 7                                                  |            |      | .6190                             | .6206 |      |  |
|     |                                                                                                                                                                           | 10-13         | 1.908                | 5                                                  |            |      | .1135                             | .1127 |      |  |
| 23  | 4-Methyl-3-[ <i>p</i> -<br>brom-phenyl]-1,2,5-<br>oxadiazol-2-oxid <sup>(1)</sup><br>  | 1-2           | 1.221                | 6                                                  | X          | u)   | .2528                             | .5752 |      |  |
|     |                                                                                                                                                                           | 2-3           | 1.322                | 6                                                  |            |      | .7237                             | .6239 |      |  |
|     |                                                                                                                                                                           | 3-4           | 1.428                | 7                                                  |            |      | .4560                             | .5361 |      |  |
|     |                                                                                                                                                                           | 4-5           | 1.309                | 7                                                  |            |      | .8297                             | .7697 |      |  |
|     |                                                                                                                                                                           | 5-6           | 1.355                | 6                                                  |            |      | .2974                             | .2555 |      |  |
|     |                                                                                                                                                                           | 2-6           | 1.439                | 6                                                  |            |      | .3768                             | .3380 |      |  |
|     |                                                                                                                                                                           | 3-7           | 1.471                | 6                                                  |            |      | .2871                             | .3796 |      |  |
|     |                                                                                                                                                                           | 7-8           | 1.390                | 7                                                  |            |      | .3768                             | .6147 |      |  |
|     |                                                                                                                                                                           | 8-9           | 1.382                | 8                                                  |            |      | .6148                             | .6781 |      |  |
|     |                                                                                                                                                                           | 9-10          | 1.377                | 7                                                  |            |      | .6790                             | .6556 |      |  |
|     |                                                                                                                                                                           | 10-11         | 1.369                | 8                                                  |            |      | .6548                             | .6556 |      |  |
|     |                                                                                                                                                                           | 11-12         | 1.380                | 8                                                  |            |      | .6548                             | .6781 |      |  |
|     |                                                                                                                                                                           | 7-12          | 1.387                | 7                                                  |            |      | .6790                             | .6147 |      |  |
|     |                                                                                                                                                                           | 10-13         | 1.899                | 4                                                  |            |      | .1137                             | .1062 |      |  |

Tab. 3 (Forts.)

| Nr. | Verbindung                                                                                                             | Bindung<br>$R_2$                                                    | Abstand<br>$R_{rs}$ [Å]                                                                | Standard-<br>abweichung<br>$\sigma \cdot 10^3$ [Å]      | Methode *) | Lit. | $\pi$ -Bindungsordnungen $p_{rs}$                                                      |                                                                                        |                                              |      |                                      |      |
|-----|------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------|----------------------------------------------------------------------------------------|---------------------------------------------------------|------------|------|----------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------|----------------------------------------------|------|--------------------------------------|------|
|     |                                                                                                                        |                                                                     |                                                                                        |                                                         |            |      | HMO**)                                                                                 | HMO***)                                                                                | PPP                                          | Lit. | PPP                                  | Lit. |
| 24  | Benzotrifuroxan<br>                   | 1-2<br>2-3<br>3-4<br>4-5<br>1-5<br>5-6<br>4-7                       | 1.389<br>1.322<br>1.425<br>1.335<br>1.478<br>1.232<br>1.448                            | 17<br>13<br>14<br>11<br>9<br>7<br>9                     | X          | v)   | .3467<br>.7123<br>.4495<br>.6901<br>.4089<br>.2987<br>.4204                            | .2020<br>.6601<br>.4498<br>.6125<br>.3295<br>.6043<br>.4728                            |                                              |      |                                      |      |
| 25  | Nitrobenzol<br>                       | 1-2<br>2-4<br>4-5<br>5-6<br>6-7                                     | 1.208<br>1.486<br>1.367<br>1.426<br>1.363                                              | 14<br>20<br>14<br>14<br>14                              | X          | w)   | .5100<br>.5603<br>.5344<br>.7032<br>.6351                                              | .6545<br>.3122<br>.6282<br>.6747<br>.6613                                              | .6841<br>.1675<br>.6483<br>.6709<br>.6636    | vvv) | .650<br>.233<br>.644<br>.656<br>.672 | www) |
| 26  | <i>m</i> -Dinitrobenzol<br>           | 1-2<br>2-3<br>2-4<br>4-5<br>4-9<br>8-9                              | 1.271<br>1.225<br>1.493<br>1.384<br>1.384<br>1.392                                     | 6<br>6<br>6<br>6<br>6<br>7                              | X          | x)   | .5132<br>.5132<br>.5547<br>.5183<br>.5608<br>.5608                                     | .6545<br>.6545<br>.3115<br>.6230<br>.6361<br>.6361                                     |                                              |      |                                      |      |
| 27  | <i>sym</i> -Trinitrobenzol<br>       | 1-2<br>2-3<br>1-6<br>1-7<br>7-8                                     | 1.388<br>1.382<br>1.380<br>1.468<br>1.236                                              | 7<br>10<br>6<br>6<br>11                                 | X          | y)   | .4839<br>.4839<br>.4839<br>.5471<br>.5203                                              | .6310<br>.6296<br>.6610<br>.3112<br>.6550                                              |                                              |      |                                      |      |
| 28  | <i>p</i> -Nitranilin<br>            | 1-2<br>2-3<br>3-4<br>4-5<br>5-8<br>8-9                              | 1.371<br>1.412<br>1.375<br>1.393<br>1.460<br>1.247                                     | 7                                                       | X          | z)   | .4679<br>.5447<br>.7546<br>.5008<br>.6158<br>.4532                                     | .3855<br>.6060<br>.6950<br>.6134<br>.3341<br>.6469                                     | .422<br>.605<br>.667<br>.640<br>.256<br>.638 | www) |                                      |      |
| 29  | 2-Chlor-4-nitranilin<br>            | 1-2<br>2-3<br>3-4<br>4-5<br>5-6<br>6-7<br>2-7<br>5-8<br>8-9<br>3-11 | 1.386<br>1.400<br>1.401<br>1.407<br>1.392<br>1.395<br>1.425<br>1.471<br>1.240<br>1.766 | 12<br>14<br>12<br>12<br>15<br>13<br>13<br>13<br>13<br>9 | X          | aa)  | .4677<br>.5386<br>.7514<br>.5012<br>.4999<br>.7536<br>.5461<br>.6164<br>.4508<br>.1133 | .3823<br>.6022<br>.6918<br>.6122<br>.6144<br>.6928<br>.6087<br>.3341<br>.6468<br>.1117 |                                              |      |                                      |      |
| 30  | 4-Nitro-pyridin- <i>N</i> -oxid<br> | 1-2<br>2-3<br>3-4<br>4-5<br>5-8<br>8-9                              | 1.260<br>1.383<br>1.336<br>1.423<br>1.472<br>1.188                                     | 9                                                       | X          | bb)  | .2639<br>.6136<br>.6774<br>.5553<br>.5185<br>.5364                                     | .4853<br>.5737<br>.6911<br>.6164<br>.3273<br>.6490                                     |                                              |      |                                      |      |



Tab. 3 (Forts.)

| Nr. | Verbindung                                                                                                                                            | Bindung<br>$r_s$ | Abstand<br>$r_s$ [Å] | Standard-<br>abweichung<br>$\sigma \cdot 10^3$ [Å] | Methode *) | Lit. | $\pi$ -Bindungsordnungen $p_{rs}$ |         |     |      |
|-----|-------------------------------------------------------------------------------------------------------------------------------------------------------|------------------|----------------------|----------------------------------------------------|------------|------|-----------------------------------|---------|-----|------|
|     |                                                                                                                                                       |                  |                      |                                                    |            |      | HMO**)                            | HMO***) | PPP | Lit. |
| 38  | <i>anti</i> -Furfuraldoxim<br>                                       | 1-2              | 1.376                | 7-16                                               | X          | jj)  | .4613                             | .4589   |     |      |
|     |                                                                                                                                                       | 2-3              | 1.346                |                                                    |            |      | .7491                             | .7510   |     |      |
|     |                                                                                                                                                       | 3-4              | 1.432                |                                                    |            |      | .6037                             | .6016   |     |      |
|     |                                                                                                                                                       | 4-5              | 1.364                |                                                    |            |      | .6899                             | .6916   |     |      |
|     |                                                                                                                                                       | 1-5              | 1.389                |                                                    |            |      | .3900                             | .3912   |     |      |
|     |                                                                                                                                                       | 5-6              | 1.438                |                                                    |            |      | .4618                             | .4584   |     |      |
|     |                                                                                                                                                       | 6-7              | 1.305                |                                                    |            |      | .8167                             | .8200   |     |      |
|     |                                                                                                                                                       | 7-8              | 1.384                |                                                    |            |      | .1526                             | .1791   |     |      |
| 39  | 5-Chlor-salicyl-<br>aldoxim<br>                                      | 1-2              | 1.379                | 17                                                 | X          | kk)  | .5728                             | .5737   |     |      |
|     |                                                                                                                                                       | 2-3              | 1.412                | 17                                                 |            |      | .6353                             | .6361   |     |      |
|     |                                                                                                                                                       | 3-4              | 1.428                | 15                                                 |            |      | .6734                             | .6727   |     |      |
|     |                                                                                                                                                       | 4-5              | 1.375                | 16                                                 |            |      | .6428                             | .6436   |     |      |
|     |                                                                                                                                                       | 5-6              | 1.390                | 16                                                 |            |      | .6798                             | .6789   |     |      |
|     |                                                                                                                                                       | 1-6              | 1.421                | 16                                                 |            |      | .6040                             | .6052   |     |      |
|     |                                                                                                                                                       | 1-7              | 1.474                | 16                                                 |            |      | .4308                             | .4284   |     |      |
|     |                                                                                                                                                       | 7-8              | 1.237                | 16                                                 |            |      | .8380                             | .8402   |     |      |
|     |                                                                                                                                                       | 8-9              | 1.385                | 13                                                 |            |      | .1573                             | .1842   |     |      |
|     |                                                                                                                                                       | 2-10             | 1.345                | 15                                                 |            |      | .3251                             | .3234   |     |      |
|     |                                                                                                                                                       | 5-11             | 1.777                | 12                                                 |            |      | .1156                             | .1156   |     |      |
| 40  | 5-Propyloxy- <i>o</i> -<br>benzochinon-2-<br>oxim <sup>13)</sup><br> | 1-2              | 1.270                | 8                                                  | X          | ll)  | .7732                             | .7662   |     |      |
|     |                                                                                                                                                       | 2-3              | 1.410                |                                                    |            |      | .4553                             | .4596   |     |      |
|     |                                                                                                                                                       | 3-4              | 1.357                |                                                    |            |      | .7403                             | .7370   |     |      |
|     |                                                                                                                                                       | 4-5              | 1.458                |                                                    |            |      | .4569                             | .4626   |     |      |
|     |                                                                                                                                                       | 5-6              | 1.344                |                                                    |            |      | .8056                             | .8035   |     |      |
|     |                                                                                                                                                       | 6-7              | 1.442                |                                                    |            |      | .4468                             | .4491   |     |      |
|     |                                                                                                                                                       | 2-7              | 1.482                |                                                    |            |      | .2885                             | .2977   |     |      |
|     |                                                                                                                                                       | 7-8              | 1.319                |                                                    |            |      | .8031                             | .7969   |     |      |
|     |                                                                                                                                                       | 8-9              | 1.353                |                                                    |            |      | .2418                             | .2838   |     |      |
|     |                                                                                                                                                       | 4-10             | 1.344                |                                                    |            |      | .3498                             | .3490   |     |      |
| 41  | 5-[2-Chlor-äthoxy]-<br><i>o</i> -benzochinon-2-<br>oxim <sup>13)</sup>                                                                                | 1-2              | 1.253                | 7                                                  | X          | mm)  | .7732                             | .7662   |     |      |
|     |                                                                                                                                                       | 2-3              | 1.430                | 8                                                  |            |      | .4553                             | .4596   |     |      |
|     |                                                                                                                                                       | 3-4              | 1.358                | 8                                                  |            |      | .7403                             | .7370   |     |      |
|     |                                                                                                                                                       | 4-5              | 1.457                | 8                                                  |            |      | .4569                             | .4626   |     |      |
|     |                                                                                                                                                       | 5-6              | 1.345                | 8                                                  |            |      | .8056                             | .8035   |     |      |
|     |                                                                                                                                                       | 6-7              | 1.435                | 8                                                  |            |      | .4468                             | .4491   |     |      |
|     |                                                                                                                                                       | 2-7              | 1.502                | 8                                                  |            |      | .2885                             | .2977   |     |      |
|     |                                                                                                                                                       | 7-8              | 1.306                | 7                                                  |            |      | .8031                             | .7969   |     |      |
|     |                                                                                                                                                       | 8-9              | 1.365                | 6                                                  |            |      | .2418                             | .2838   |     |      |
|     |                                                                                                                                                       | 4-10             | 1.343                | 7                                                  |            |      | .3498                             | .3490   |     |      |
| 42  | Violursäure<br>                                                    | 1-2              | 1.361                | 8                                                  | X          | nn)  | .3937                             | .3940   |     |      |
|     |                                                                                                                                                       | 2-3              | 1.378                | 8                                                  |            |      | .3937                             | .3940   |     |      |
|     |                                                                                                                                                       | 3-4              | 1.377                | 6                                                  |            |      | .4070                             | .4061   |     |      |
|     |                                                                                                                                                       | 4-5              | 1.467                | 8                                                  |            |      | .2980                             | .3049   |     |      |
|     |                                                                                                                                                       | 5-6              | 1.504                | 8                                                  |            |      | .2980                             | .3049   |     |      |
|     |                                                                                                                                                       | 1-6              | 1.371                | 6                                                  |            |      | .4070                             | .4061   |     |      |
|     |                                                                                                                                                       | 2-7              | 1.230                | 9                                                  |            |      | .7660                             | .7657   |     |      |
|     |                                                                                                                                                       | 4-8              | 1.230                | 20                                                 |            |      | .7987                             | .7958   |     |      |
|     |                                                                                                                                                       | 6-9              | 1.200                | 20                                                 |            |      | .7987                             | .7958   |     |      |
|     |                                                                                                                                                       | 5-10             | 1.284                | 9                                                  |            |      | .8657                             | .8581   |     |      |
|     |                                                                                                                                                       | 10-11            | 1.335                | 12                                                 |            |      | .2399                             | .2782   |     |      |
| 43  | 2-Methyl-4-phenyl-<br>isoxazolon-(5) <sup>14)</sup><br>            | 1-2              | 1.215                | 5                                                  | X          | oo)  | .7329                             | .7267   |     |      |
|     |                                                                                                                                                       | 2-3              | 1.387                | 6                                                  |            |      | .3876                             | .3934   |     |      |
|     |                                                                                                                                                       | 3-4              | 1.403                | 4                                                  |            |      | .1257                             | .1396   |     |      |
|     |                                                                                                                                                       | 4-5              | 1.335                | 6                                                  |            |      | .5410                             | .5490   |     |      |
|     |                                                                                                                                                       | 2-6              | 1.427                | 6                                                  |            |      | .4327                             | .4375   |     |      |
|     |                                                                                                                                                       | 6-7              | 1.454                | 6                                                  |            |      | .3938                             | .3937   |     |      |
|     |                                                                                                                                                       | 7-8              | 1.398                | 6                                                  |            |      | .6106                             | .6106   |     |      |
|     |                                                                                                                                                       | 8-9              | 1.392                | 6                                                  |            |      | .6789                             | .6789   |     |      |
|     |                                                                                                                                                       | 9-10             | 1.388                | 6                                                  |            |      | .6583                             | .6582   |     |      |
|     |                                                                                                                                                       | 10-11            | 1.403                | 6                                                  |            |      | .6583                             | .6582   |     |      |
|     |                                                                                                                                                       | 11-12            | 1.368                | 6                                                  |            |      | .6789                             | .6789   |     |      |
|     |                                                                                                                                                       | 7-12             | 1.418                | 6                                                  |            |      | .6106                             | .6106   |     |      |
|     |                                                                                                                                                       | 5-6              | 1.380                | 6                                                  |            |      | .7104                             | .7064   |     |      |

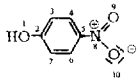
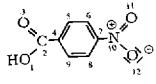
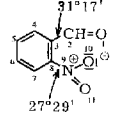
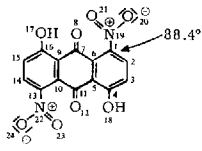
Tab. 3 (Forts.)

| Nr. | Verbindung                                                        | Bindung<br>$r_s$ | Abstand<br>$R_{rs}$ [Å] | Standard-<br>abweichung<br>$\sigma \cdot 10^3$ [Å] | Methode*) | Lit. | $\pi$ -Bindungsordnungen $p_{rs}$ |         |     |      |
|-----|-------------------------------------------------------------------|------------------|-------------------------|----------------------------------------------------|-----------|------|-----------------------------------|---------|-----|------|
|     |                                                                   |                  |                         |                                                    |           |      | HMO**)                            | HMO***) | PPP | Lit. |
| 44  | 4-Brom-2-methyl-3-phenyl-isoxazolon-(5) <sup>±</sup>              | 1-2              | 1.200                   | 7                                                  | X         | pp)  | .7179                             | .7115   |     |      |
|     |                                                                   | 2-3              | 1.402                   | 7                                                  |           |      | .3849                             | .3917   |     |      |
|     |                                                                   | 3-4              | 1.421                   | 6                                                  |           |      | .1231                             | .1375   |     |      |
|     |                                                                   | 4-5              | 1.342                   | 8                                                  |           |      | .4966                             | .5115   |     |      |
|     |                                                                   | 5-6              | 1.369                   | 8                                                  |           |      | .7537                             | .7585   |     |      |
|     |                                                                   | 2-6              | 1.416                   | 7                                                  |           |      | .4729                             | .4771   |     |      |
|     |                                                                   | 5-7              | 1.470                   | 7                                                  |           |      | .2549                             | .2049   |     |      |
|     |                                                                   | 7-8              | 1.418                   | 11                                                 |           |      | .6441                             | .6522   |     |      |
|     |                                                                   | 8-9              | 1.455                   | 12                                                 |           |      | .6714                             | .6697   |     |      |
|     |                                                                   | 9-10             | 1.342                   | 17                                                 |           |      | .6635                             | .6646   |     |      |
|     |                                                                   | 10-11            | 1.350                   | 14                                                 |           |      | .6635                             | .6646   |     |      |
|     |                                                                   | 11-12            | 1.369                   | 10                                                 |           |      | .6714                             | .6697   |     |      |
|     |                                                                   | 7-12             | 1.374                   | 12                                                 |           |      | .6441                             | .6522   |     |      |
|     |                                                                   | 6-13             | 1.843                   | 6                                                  |           |      | .0782                             | .0771   |     |      |
| 45  | 3-Phenyl-isoxazolon-(5) <sup>±</sup>                              | 1-2              | 1.207                   | 7                                                  | X         | qq)  | .8510                             | .8503   |     |      |
|     |                                                                   | 2-3              | 1.371                   | 5                                                  |           |      | .3946                             | .3947   |     |      |
|     |                                                                   | 3-4              | 1.449                   | 9                                                  |           |      | .1685                             | .1956   |     |      |
|     |                                                                   | 4-5              | 1.283                   | 9                                                  |           |      | .8472                             | .8475   |     |      |
|     |                                                                   | 5-6              | 1.476                   | 9                                                  |           |      | .4114                             | .4108   |     |      |
|     |                                                                   | 6-7              | 1.400                   | 7                                                  |           |      | .6074                             | .6077   |     |      |
|     |                                                                   | 7-8              | 1.391                   | 11                                                 |           |      | .6796                             | .6795   |     |      |
|     |                                                                   | 8-9              | 1.402                   | 10                                                 |           |      | .6579                             | .6579   |     |      |
|     |                                                                   | 9-10             | 1.395                   | 8                                                  |           |      | .6579                             | .6579   |     |      |
|     |                                                                   | 10-11            | 1.392                   | 10                                                 |           |      | .6796                             | .6795   |     |      |
|     |                                                                   | 6-11             | 1.402                   | 8                                                  |           |      | .6074                             | .6077   |     |      |
| 46  | 3-Hydroxy-5-phenyl-isoxazol                                       | 1-2              | 1.341                   | 5                                                  | X         | rr)  | .3389                             | .3321   |     |      |
|     |                                                                   | 2-3              | 1.313                   | 7                                                  |           |      | .7049                             | .7057   |     |      |
|     |                                                                   | 3-4              | 1.417                   | 5                                                  |           |      | .2420                             | .2641   |     |      |
|     |                                                                   | 4-5              | 1.372                   | 6                                                  |           |      | .4276                             | .4350   |     |      |
|     |                                                                   | 5-6              | 1.372                   | 6                                                  |           |      | .7196                             | .7171   |     |      |
|     |                                                                   | 2-6              | 1.408                   | 6                                                  |           |      | .5463                             | .5523   |     |      |
|     |                                                                   | 5-7              | 1.439                   | 6                                                  |           |      | .3890                             | .3875   |     |      |
|     |                                                                   | 7-8              | 1.416                   | 6                                                  |           |      | .6130                             | .6135   |     |      |
|     |                                                                   | 8-9              | 1.377                   | 7                                                  |           |      | .6781                             | .6780   |     |      |
|     |                                                                   | 9-10             | 1.380                   | 8                                                  |           |      | .6589                             | .6591   |     |      |
|     |                                                                   | 10-11            | 1.395                   | 7                                                  |           |      | .6589                             | .6591   |     |      |
|     |                                                                   | 11-12            | 1.383                   | 8                                                  |           |      | .6781                             | .6780   |     |      |
|     |                                                                   | 7-12             | 1.410                   | 7                                                  |           |      | .6130                             | .6135   |     |      |
| 47  | 3-Benzoyl-anthranil                                               | 1-2              | 1.412                   | 7-9                                                | X         | ss)  | .3161                             | .3438   |     |      |
|     |                                                                   | 2-3              | 1.357                   |                                                    |           |      | .4949                             | .4990   |     |      |
|     |                                                                   | 3-4              | 1.394                   |                                                    |           |      | .6058                             | .6031   |     |      |
|     |                                                                   | 4-5              | 1.425                   |                                                    |           |      | .4686                             | .4725   |     |      |
|     |                                                                   | 1-5              | 1.344                   |                                                    |           |      | .6473                             | .6459   |     |      |
|     |                                                                   | 5-6              | 1.390                   |                                                    |           |      | .5132                             | .5128   |     |      |
|     |                                                                   | 6-7              | 1.364                   |                                                    |           |      | .7473                             | .7477   |     |      |
|     |                                                                   | 7-8              | 1.430                   |                                                    |           |      | .5772                             | .5782   |     |      |
|     |                                                                   | 8-9              | 1.376                   |                                                    |           |      | .7415                             | .7412   |     |      |
|     |                                                                   | 4-9              | 1.416                   |                                                    |           |      | .5331                             | .5340   |     |      |
|     |                                                                   | 3-10             | 1.473                   |                                                    |           |      | .3387                             | .3453   |     |      |
|     |                                                                   | 10-11            | 1.221                   |                                                    |           |      | .8536                             | .8504   |     |      |
|     |                                                                   | 10-12            | 1.520                   |                                                    |           |      | .1792                             | .1788   |     |      |
|     |                                                                   | 12-13            | 1.399                   |                                                    |           |      | .6548                             | .6549   |     |      |
|     |                                                                   | 13-14            | 1.393                   |                                                    |           |      | .6692                             | .6692   |     |      |
|     |                                                                   | 14-15            | 1.372                   |                                                    |           |      | .6649                             | .6650   |     |      |
|     |                                                                   | 15-16            | 1.374                   |                                                    |           |      | .6649                             | .6650   |     |      |
|     |                                                                   | 16-17            | 1.421                   |                                                    |           |      | .6692                             | .6692   |     |      |
|     |                                                                   | 12-17            | 1.398                   |                                                    |           |      | .6548                             | .6549   |     |      |
| 48  | 3,4-[Bis- <i>p</i> -chlor-benzoyl]-1,2,5-oxdiazol- <i>N</i> -oxid | 1-2              | 1.209                   | 10                                                 | X         | tt)  | .2735                             | .5941   |     |      |
|     |                                                                   | 2-3              | 1.478                   |                                                    |           |      | .3864                             | .4012   |     |      |
|     |                                                                   | 3-4              | 1.376                   |                                                    |           |      | .3384                             | .2868   |     |      |
|     |                                                                   | 4-5              | 1.298                   |                                                    |           |      | .7910                             | .7365   |     |      |
|     |                                                                   | 5-6              | 1.430                   |                                                    |           |      | .5255                             | .5315   |     |      |
|     |                                                                   | 2-6              | 1.310                   |                                                    |           |      | .7544                             | .5991   |     |      |
|     |                                                                   | 6-7              | 1.492                   |                                                    |           |      | .1157                             | .3703   |     |      |
|     |                                                                   | 7-8              | 1.201                   |                                                    |           |      | .8566                             | .7879   |     |      |
|     |                                                                   | 7-9              | 1.467                   |                                                    |           |      | .3586                             | .3412   |     |      |
|     |                                                                   | 9-10             | 1.389                   |                                                    |           |      | .6195                             | .6232   |     |      |
|     |                                                                   | 10-11            | 1.394                   |                                                    |           |      | .6785                             | .6775   |     |      |
|     |                                                                   | 11-12            | 1.384                   |                                                    |           |      | .6541                             | .6548   |     |      |
|     |                                                                   | 12-13            | 1.396                   |                                                    |           |      | .6541                             | .6548   |     |      |

Tab. 3 (Forts.)

| Nr. Verbindung                                                     | Bindung | Abstand<br>$R_{rs}$ [Å] | Standard-<br>abweichung<br>$\sigma \cdot 10^3$ [Å] | Methode *) | $\pi$ -Bindungsordnungen $pr_s$ |         |          |      |      |
|--------------------------------------------------------------------|---------|-------------------------|----------------------------------------------------|------------|---------------------------------|---------|----------|------|------|
|                                                                    |         |                         |                                                    |            | Lit.                            | HMO **) | HMO ***) | PPP  | Lit. |
| 48 Fortsetzung                                                     | 13-14   | 1.416                   |                                                    |            |                                 | .6785   | .6775    |      |      |
|                                                                    | 9-14    | 1.422                   |                                                    |            |                                 | .6195   | .6234    |      |      |
|                                                                    | 5-15    | 1.496                   |                                                    |            |                                 | .1047   | .2823    |      |      |
|                                                                    | 15-16   | 1.205                   |                                                    |            |                                 | .8581   | .8244    |      |      |
|                                                                    | 15-17   | 1.475                   |                                                    |            |                                 | .3590   | .3490    |      |      |
|                                                                    | 17-18   | 1.445                   |                                                    |            |                                 | .6194   | .6202    |      |      |
|                                                                    | 18-19   | 1.416                   |                                                    |            |                                 | .6785   | .6785    |      |      |
|                                                                    | 19-20   | 1.363                   |                                                    |            |                                 | .6541   | .6539    |      |      |
|                                                                    | 20-21   | 1.409                   |                                                    |            |                                 | .6541   | .6539    |      |      |
|                                                                    | 21-22   | 1.395                   |                                                    |            |                                 | .6785   | .6785    |      |      |
|                                                                    | 17-22   | 1.416                   |                                                    |            |                                 | .6194   | .6202    |      |      |
|                                                                    | 12-23   | 1.726                   |                                                    |            |                                 | .1306   | .1296    |      |      |
|                                                                    | 20-24   | 1.778                   |                                                    |            |                                 | .1306   | .1306    |      |      |
| 49 Myxin <sup>1)</sup>                                             | 1-2     | 1.352                   | 4                                                  | X          | uu)                             | .3198   | .3149    |      |      |
|                                                                    | 2-3     | 1.373                   |                                                    |            |                                 | .6969   | .6898    |      |      |
|                                                                    | 3-4     | 1.406                   |                                                    |            |                                 | .5972   | .5996    |      |      |
|                                                                    | 4-5     | 1.379                   |                                                    |            |                                 | .7262   | .7250    |      |      |
|                                                                    | 5-6     | 1.409                   |                                                    |            |                                 | .5421   | .5444    |      |      |
|                                                                    | 6-7     | 1.414                   |                                                    |            |                                 | .4772   | .5000    |      |      |
|                                                                    | 2-7     | 1.439                   |                                                    |            |                                 | .5000   | .5204    |      |      |
|                                                                    | 7-8     | 1.368                   |                                                    |            |                                 | .5778   | .5298    |      |      |
|                                                                    | 8-9     | 1.323                   |                                                    |            |                                 | .2502   | .4584    |      |      |
|                                                                    | 8-10    | 1.368                   |                                                    |            |                                 | .5631   | .5237    |      |      |
|                                                                    | 10-11   | 1.426                   |                                                    |            |                                 | .4772   | .5000    |      |      |
|                                                                    | 11-12   | 1.380                   |                                                    |            |                                 | .5778   | .5298    |      |      |
|                                                                    | 12-13   | 1.288                   |                                                    |            |                                 | .2502   | .4584    |      |      |
|                                                                    | 6-12    | 1.392                   |                                                    |            |                                 | .5632   | .5237    |      |      |
|                                                                    | 11-14   | 1.444                   |                                                    |            |                                 | .5000   | .5204    |      |      |
|                                                                    | 14-15   | 1.380                   |                                                    |            |                                 | .6969   | .6898    |      |      |
|                                                                    | 15-16   | 1.408                   |                                                    |            |                                 | .5972   | .5996    |      |      |
|                                                                    | 16-17   | 1.360                   |                                                    |            |                                 | .7262   | .7250    |      |      |
|                                                                    | 10-17   | 1.413                   |                                                    |            |                                 | .5421   | .5444    |      |      |
|                                                                    | 14-18   | 1.358                   |                                                    |            |                                 | .3198   | .3149    |      |      |
| 50 Jodinin                                                         | 1-2     | 1.352                   | 3                                                  | X          | vv)                             | .3198   | .3149    |      |      |
|                                                                    | 2-3     | 1.368                   | 4                                                  |            |                                 | .6969   | .6898    |      |      |
|                                                                    | 3-4     | 1.406                   | 4                                                  |            |                                 | .5972   | .5996    |      |      |
|                                                                    | 4-5     | 1.374                   | 4                                                  |            |                                 | .7262   | .7250    |      |      |
|                                                                    | 6-7     | 1.422                   | 4                                                  |            |                                 | .4772   | .5000    |      |      |
|                                                                    | 5-6     | 1.409                   | 4                                                  |            |                                 | .5421   | .5444    |      |      |
|                                                                    | 2-7     | 1.441                   | 4                                                  |            |                                 | .5000   | .5204    |      |      |
|                                                                    | 7-8     | 1.364                   | 4                                                  |            |                                 | .5778   | .5298    |      |      |
|                                                                    | 8-9     | 1.306                   | 3                                                  |            |                                 | .2502   | .4584    |      |      |
|                                                                    | 8-10    | 1.379                   | 4                                                  |            |                                 | .5631   | .5237    |      |      |
| 51 <i>p</i> -Methoxy-indo-<br>phenol- <i>N</i> -oxid <sup>1)</sup> | 1-2     | 1.248                   | 5                                                  | X          | ww)                             | .7778   | .6794    | .762 | ww)  |
|                                                                    | 2-3     | 1.456                   | 6                                                  |            |                                 | .3752   | .4648    |      |      |
|                                                                    | 3-4     | 1.357                   | 6                                                  |            |                                 | .8430   | .7769    |      |      |
|                                                                    | 4-5     | 1.438                   | 6                                                  |            |                                 | .4258   | .5147    |      |      |
|                                                                    | 5-6     | 1.437                   | 6                                                  |            |                                 | .4258   | .5147    |      |      |
|                                                                    | 6-7     | 1.357                   | 6                                                  |            |                                 | .8430   | .7769    |      |      |
|                                                                    | 2-7     | 1.454                   | 6                                                  |            |                                 | .3752   | .4648    | .593 |      |
|                                                                    | 5-8     | 1.357                   | 4                                                  |            |                                 | .7122   | .5547    | .656 |      |
|                                                                    | 8-9     | 1.266                   | 5                                                  |            |                                 | .2925   | .6911    | .204 |      |
|                                                                    | 8-10    | 1.450                   | 5                                                  |            |                                 | .2144   | .2403    |      |      |
|                                                                    | 10-11   | 1.384                   | 6                                                  |            |                                 | .6433   | .6386    |      |      |
|                                                                    | 11-12   | 1.393                   | 6                                                  |            |                                 | .6800   | .6818    |      |      |
|                                                                    | 12-13   | 1.401                   | 6                                                  |            |                                 | .6274   | .6267    |      |      |
|                                                                    | 13-14   | 1.383                   | 6                                                  |            |                                 | .6274   | .6267    |      |      |
|                                                                    | 14-15   | 1.396                   | 6                                                  |            |                                 | .6800   | .6818    |      |      |
|                                                                    | 10-15   | 1.397                   | 6                                                  |            |                                 | .6433   | .6386    |      |      |
|                                                                    | 13-16   | 1.361                   | 5                                                  |            |                                 | .3094   | .3117    | .354 |      |
| 52 Kalium-4,4-dinitro-<br>butensäure-(2)-amid                      | 1-2     | 1.243                   | 7-9                                                | X          | xx)                             | .3714   | .6020    |      |      |
|                                                                    | 2-3     | 1.237                   |                                                    |            |                                 | .3714   | .6020    |      |      |
|                                                                    | 2-4     | 1.391                   |                                                    |            |                                 | .6956   | .4591    |      |      |
|                                                                    | 4-5     | 1.386                   |                                                    |            |                                 | .4266   | .3721    |      |      |
|                                                                    | 5-6     | 1.263                   |                                                    |            |                                 | .4962   | .6048    |      |      |
|                                                                    | 5-7     | 1.247                   |                                                    |            |                                 | .4962   | .6048    |      |      |
|                                                                    | 4-8     | 1.424                   |                                                    |            |                                 | .4501   | .5760    |      |      |
|                                                                    | 8-9     | 1.347                   |                                                    |            |                                 | .8244   | .7476    |      |      |
|                                                                    | 9-10    | 1.479                   |                                                    |            |                                 | .3785   | .4107    |      |      |
|                                                                    | 10-11   | 1.326                   |                                                    |            |                                 | .4233   | .3722    |      |      |
|                                                                    | 10-12   | 1.233                   |                                                    |            |                                 | .7578   | .7806    |      |      |

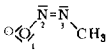
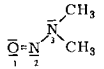
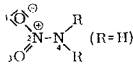
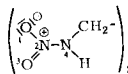
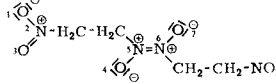
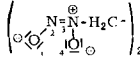
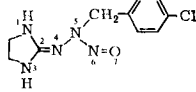
Tab. 3 (Forts.)

| Nr. Verbindung                                                                                                                            | Bindung<br>$R_{\Sigma}$ | Abstand<br>$R_{\Sigma}$ [Å] | Standard-<br>abweichung<br>$\sigma \cdot 10^3$ [Å] | Methodc *) | Lit. | $\pi$ -Bindungsordnungen $p_{rs}$ |          |     |      |
|-------------------------------------------------------------------------------------------------------------------------------------------|-------------------------|-----------------------------|----------------------------------------------------|------------|------|-----------------------------------|----------|-----|------|
|                                                                                                                                           |                         |                             |                                                    |            |      | HMO **)                           | HMO ***) | PPP | Lit. |
| 53 <i>p</i> -Nitro-phenol<br>$\alpha$ -Modifikation<br>  | 1-2                     | 1.351                       | 6                                                  | X          | yy)  | .3785                             | .3202    |     |      |
|                                                                                                                                           | 2-3                     | 1.390                       |                                                    |            |      | .5701                             | .6219    |     |      |
|                                                                                                                                           | 3-4                     | 1.379                       |                                                    |            |      | .7400                             | .6890    |     |      |
|                                                                                                                                           | 4-5                     | 1.386                       |                                                    |            |      | .5099                             | .6180    |     |      |
|                                                                                                                                           | 5-8                     | 1.442                       |                                                    |            |      | .6011                             | .3282    |     |      |
|                                                                                                                                           | 8-9                     | 1.234                       |                                                    |            |      | .4727                             | .6491    |     |      |
|                                                                                                                                           |                         |                             |                                                    |            |      |                                   |          |     |      |
| 54 <i>p</i> -Nitro-phenol<br>$\beta$ -Modifikation                                                                                        | 1-2                     | 1.361                       | 5                                                  | X          | zz)  | .3785                             | .3202    |     |      |
|                                                                                                                                           | 2-3                     | 1.398                       |                                                    |            |      | .5701                             | .6219    |     |      |
|                                                                                                                                           | 3-4                     | 1.380                       |                                                    |            |      | .7400                             | .6890    |     |      |
|                                                                                                                                           | 4-5                     | 1.394                       |                                                    |            |      | .5099                             | .6180    |     |      |
|                                                                                                                                           | 5-8                     | 1.450                       |                                                    |            |      | .6011                             | .3282    |     |      |
|                                                                                                                                           | 8-9                     | 1.242                       |                                                    |            |      | .4727                             | .6491    |     |      |
|                                                                                                                                           |                         |                             |                                                    |            |      |                                   |          |     |      |
| 55 <i>p</i> -Nitro-<br>benzoesäure<br>                   | 1-2                     | 1.319                       | 7                                                  | X          | aaa) | .3698                             | .3682    |     |      |
|                                                                                                                                           | 2-3                     | 1.222                       |                                                    |            |      | .8090                             | .8023    |     |      |
|                                                                                                                                           | 2-4                     | 1.501                       |                                                    |            |      | .3101                             | .3245    |     |      |
|                                                                                                                                           | 4-5                     | 1.402                       |                                                    |            |      | .6084                             | .6255    |     |      |
|                                                                                                                                           | 5-6                     | 1.393                       |                                                    |            |      | .7005                             | .6790    |     |      |
|                                                                                                                                           | 6-7                     | 1.393                       |                                                    |            |      | .5393                             | .6266    |     |      |
|                                                                                                                                           | 7-10                    | 1.480                       |                                                    |            |      | .5463                             | .3054    |     |      |
|                                                                                                                                           | 10-11                   | 1.216                       |                                                    |            |      | .5181                             | .6504    |     |      |
|                                                                                                                                           |                         |                             |                                                    |            |      |                                   |          |     |      |
|                                                                                                                                           |                         |                             |                                                    |            |      |                                   |          |     |      |
|                                                                                                                                           |                         |                             |                                                    |            |      |                                   |          |     |      |
| 56 <i>o</i> -Nitro-<br>benzaldehyd<br>                   | 1-2                     | 1.200                       | 9                                                  | X          | bbb) | .8878                             | .8849    |     |      |
|                                                                                                                                           | 2-3                     | 1.490                       |                                                    |            |      | .2999                             | .3057    |     |      |
|                                                                                                                                           | 3-4                     | 1.377                       |                                                    |            |      | .6697                             | .6413    |     |      |
|                                                                                                                                           | 4-5                     | 1.390                       |                                                    |            |      | .6374                             | .6669    |     |      |
|                                                                                                                                           | 5-6                     | 1.367                       |                                                    |            |      | .6441                             | .6604    |     |      |
|                                                                                                                                           | 6-7                     | 1.388                       |                                                    |            |      | .6856                             | .6659    |     |      |
|                                                                                                                                           | 7-8                     | 1.380                       |                                                    |            |      | .5650                             | .6453    |     |      |
|                                                                                                                                           | 3-8                     | 1.382                       |                                                    |            |      | .5325                             | .6055    |     |      |
|                                                                                                                                           | 8-9                     | 1.468                       |                                                    |            |      | .5121                             | .2753    |     |      |
|                                                                                                                                           | 9-10                    | 1.226                       |                                                    |            |      | .5363                             | .6640    |     |      |
|                                                                                                                                           | 9-11                    | 1.234                       |                                                    |            |      | .5363                             | .6640    |     |      |
| 57 <i>o</i> -Nitro-benzaldehyd                                                                                                            | 1-2                     | 1.204                       | N                                                  |            | ccc) | .8878                             | .8849    |     |      |
|                                                                                                                                           | 2-3                     | 1.506                       |                                                    |            |      | .2999                             | .3057    |     |      |
|                                                                                                                                           | 3-4                     | 1.377                       |                                                    |            |      | .6697                             | .6413    |     |      |
|                                                                                                                                           | 4-5                     | 1.390                       |                                                    |            |      | .6374                             | .6669    |     |      |
|                                                                                                                                           | 5-6                     | 1.367                       |                                                    |            |      | .6447                             | .6604    |     |      |
|                                                                                                                                           | 6-7                     | 1.388                       |                                                    |            |      | .6856                             | .6659    |     |      |
|                                                                                                                                           | 7-8                     | 1.380                       |                                                    |            |      | .5650                             | .6453    |     |      |
|                                                                                                                                           | 3-8                     | 1.382                       |                                                    |            |      | .5325                             | .6055    |     |      |
|                                                                                                                                           | 8-9                     | 1.474                       |                                                    |            |      | .5121                             | .2753    |     |      |
|                                                                                                                                           | 9-10                    | 1.241                       |                                                    |            |      | .5363                             | .6640    |     |      |
|                                                                                                                                           | 9-11                    | 1.249                       |                                                    |            |      | .5363                             | .6640    |     |      |
| 58 1,5-Dinitro-4,8-<br>dihydroxy-anthra-<br>chinon<br> | 1-2                     | 1.383                       | 5                                                  | X          | ddd) | .6516                             | .6519    |     |      |
|                                                                                                                                           | 2-3                     | 1.351                       |                                                    |            |      | .6765                             | .6764    |     |      |
|                                                                                                                                           | 3-4                     | 1.395                       |                                                    |            |      | .6192                             | .6193    |     |      |
|                                                                                                                                           | 4-5                     | 1.385                       |                                                    |            |      | .5984                             | .5988    |     |      |
|                                                                                                                                           | 5-6                     | 1.418                       |                                                    |            |      | .5856                             | .5853    |     |      |
|                                                                                                                                           | 1-6                     | 1.368                       |                                                    |            |      | .6410                             | .6411    |     |      |
|                                                                                                                                           | 6-7                     | 1.470                       |                                                    |            |      | .3354                             | .3351    |     |      |
|                                                                                                                                           | 7-8                     | 1.219                       |                                                    |            |      | .7981                             | .7986    |     |      |
|                                                                                                                                           | 7-9                     | 1.456                       |                                                    |            |      | .3591                             | .3590    |     |      |
|                                                                                                                                           | 16-17                   | 1.336                       |                                                    |            |      | .3276                             | .3275    |     |      |
|                                                                                                                                           | 1-19                    | 1.477                       |                                                    |            |      | .0234                             | .0096    |     |      |
|                                                                                                                                           | 19-20                   | 1.185                       |                                                    |            |      | .6738                             | .6975    |     |      |
|                                                                                                                                           | 19-21                   | 1.180                       |                                                    |            |      | .6738                             | .6975    |     |      |

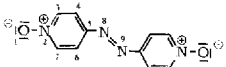
Tab. 3 (Forts.)

| Nr. Verbindung                                        | Bindung<br>$r_{\pi}$ | Abstand<br>$R_{\pi}$ [Å] | Standard-<br>abweichung<br>$\sigma \cdot 10^3$ [Å] | Methode *) | Lit. | $\pi$ -Bindungsordnungen $p_{rs}$ |          |     |      |
|-------------------------------------------------------|----------------------|--------------------------|----------------------------------------------------|------------|------|-----------------------------------|----------|-----|------|
|                                                       |                      |                          |                                                    |            |      | HMO **)                           | HMO ***) | PPP | Lit. |
| 59 2,4,6-Trinitro-phenetol <sup>†)</sup>              | 1-2                  | 1.368                    | 7                                                  | X          | eee) | .4616                             | .3402    |     |      |
|                                                       | 2-3                  | 1.388                    |                                                    |            |      | .5411                             | .6109    |     |      |
|                                                       | 3-4                  | 1.360                    |                                                    |            |      | .6802                             | .6787    |     |      |
|                                                       | 4-5                  | 1.379                    |                                                    |            |      | .5055                             | .6142    |     |      |
|                                                       | 5-6                  | 1.369                    |                                                    |            |      | .5399                             | .6280    |     |      |
|                                                       | 6-7                  | 1.389                    |                                                    |            |      | .5993                             | .6537    |     |      |
|                                                       | 2-7                  | 1.385                    |                                                    |            |      | .4803                             | .5920    |     |      |
|                                                       | 3-8                  | 1.479                    |                                                    |            |      | .3418                             | .1649    |     |      |
|                                                       | 8-9                  | 1.200                    |                                                    |            |      | .6153                             | .6855    |     |      |
|                                                       | 8-10                 | 1.199                    |                                                    |            |      | .6153                             | .6855    |     |      |
|                                                       | 5-11                 | 1.467                    |                                                    |            |      | .5799                             | .3268    |     |      |
|                                                       | 11-12                | 1.215                    |                                                    |            |      | .4912                             | .6477    |     |      |
|                                                       | 11-13                | 1.222                    |                                                    |            |      | .4912                             | .6477    |     |      |
|                                                       | 7-14                 | 1.462                    |                                                    |            |      | .4877                             | .2854    |     |      |
|                                                       | 14-15                | 1.205                    |                                                    |            |      | .5286                             | .6614    |     |      |
|                                                       | 14-16                | 1.234                    |                                                    |            |      | .5286                             | .6614    |     |      |
| 60 5-Nitro-uracil-monohydrat                          | 1-2                  | 1.384                    | 6                                                  | X          | fff) | .3715                             | .3937    |     |      |
|                                                       | 2-3                  | 1.370                    |                                                    |            |      | .4032                             | .4063    |     |      |
|                                                       | 3-4                  | 1.382                    |                                                    |            |      | .4054                             | .4002    |     |      |
|                                                       | 4-5                  | 1.453                    |                                                    |            |      | .3401                             | .4066    |     |      |
|                                                       | 5-6                  | 1.358                    |                                                    |            |      | .5326                             | .7233    |     |      |
|                                                       | 1-6                  | 1.335                    |                                                    |            |      | .6085                             | .5063    |     |      |
|                                                       | 2-7                  | 1.222                    |                                                    |            |      | .7712                             | .7580    |     |      |
|                                                       | 4-8                  | 1.236                    |                                                    |            |      | .7793                             | .7494    |     |      |
|                                                       | 5-9                  | 1.431                    |                                                    |            |      | .6815                             | .3781    |     |      |
|                                                       | 9-10                 | 1.251                    |                                                    |            |      | .4265                             | .6340    |     |      |
|                                                       | 9-11                 | 1.263                    |                                                    |            |      | .4265                             | .6340    |     |      |
| 61 5-Nitro-barbitur-säure                             | 1-2                  | 1.366                    | 5                                                  | X          | ggg) | .4008                             | .4054    |     |      |
|                                                       | 2-3                  | 1.361                    |                                                    |            |      | .3785                             | .3948    |     |      |
|                                                       | 3-4                  | 1.348                    |                                                    |            |      | .5402                             | .4735    |     |      |
|                                                       | 4-5                  | 1.408                    |                                                    |            |      | .4543                             | .6369    |     |      |
|                                                       | 5-6                  | 1.452                    |                                                    |            |      | .3457                             | .4331    |     |      |
|                                                       | 1-6                  | 1.382                    |                                                    |            |      | .4029                             | .3938    |     |      |
|                                                       | 2-7                  | 1.225                    |                                                    |            |      | .7693                             | .7583    |     |      |
|                                                       | 4-8                  | 1.302                    |                                                    |            |      | .4681                             | .4086    |     |      |
|                                                       | 5-9                  | 1.406                    |                                                    |            |      | .7211                             | .4099    |     |      |
|                                                       | 9-10                 | 1.259                    |                                                    |            |      | .3969                             | .6238    |     |      |
|                                                       | 9-11                 | 1.222                    |                                                    |            |      | .3969                             | .6238    |     |      |
|                                                       | 6-12                 | 1.223                    |                                                    |            |      | .7780                             | .7256    |     |      |
| 62 Ammonium-nitrilit                                  | 1-2                  | 1.222                    | 7                                                  | X          | hhh) | .5196                             | .4195    |     |      |
|                                                       | 2-3                  | 1.424                    |                                                    |            |      | .5372                             | .6245    |     |      |
|                                                       | 3-4                  | 1.443                    |                                                    |            |      | .3459                             | .3932    |     |      |
|                                                       | 4-5                  | 1.184                    |                                                    |            |      | .8378                             | .8078    |     |      |
|                                                       | 3-6                  | 1.404                    |                                                    |            |      | .6579                             | .3652    |     |      |
|                                                       | 6-7                  | 1.245                    |                                                    |            |      | .4458                             | .6381    |     |      |
|                                                       | 6-8                  | 1.231                    |                                                    |            |      | .4458                             | .6381    |     |      |
|                                                       | 4-9                  | 1.553                    |                                                    |            |      | .2686                             | .2836    |     |      |
| 63 8-Nitro-6-methoxy-5-acetoxy-chinolin <sup>†)</sup> | 1-2                  | 1.314                    | 5                                                  | X          | iii) | .6784                             | .6897    |     |      |
|                                                       | 2-3                  | 1.408                    |                                                    |            |      | .6120                             | .6046    |     |      |
|                                                       | 3-4                  | 1.365                    |                                                    |            |      | .7152                             | .7223    |     |      |
|                                                       | 4-5                  | 1.416                    |                                                    |            |      | .5559                             | .5537    |     |      |
|                                                       | 5-6                  | 1.423                    |                                                    |            |      | .5193                             | .5152    |     |      |
|                                                       | 1-6                  | 1.371                    |                                                    |            |      | .5590                             | .5417    |     |      |
|                                                       | 6-7                  | 1.416                    |                                                    |            |      | .5051                             | .5425    |     |      |
|                                                       | 7-8                  | 1.371                    |                                                    |            |      | .6597                             | .7160    |     |      |
|                                                       | 8-9                  | 1.410                    |                                                    |            |      | .6014                             | .5761    |     |      |
|                                                       | 9-10                 | 1.379                    |                                                    |            |      | .6607                             | .6865    |     |      |
|                                                       | 5-10                 | 1.422                    |                                                    |            |      | .5533                             | .5593    |     |      |
|                                                       | 7-11                 | 1.472                    |                                                    |            |      | .3968                             | .1735    |     |      |
|                                                       | 11-12                | 1.245                    |                                                    |            |      | .5808                             | .6839    |     |      |
|                                                       | 11-13                | 1.252                    |                                                    |            |      | .5808                             | .6839    |     |      |
|                                                       | 9-14                 | 1.373                    |                                                    |            |      | .3043                             | .3025    |     |      |
|                                                       | 10-15                | 1.389                    |                                                    |            |      | .0611                             | .0540    |     |      |
|                                                       | 15-16                | 1.365                    |                                                    |            |      | .3927                             | .3929    |     |      |
|                                                       | 16-17                | 1.211                    |                                                    |            |      | .8540                             | .8532    |     |      |

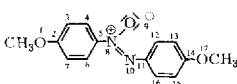
Tab. 3 (Forts.)

| Nr.                          | Verbindung                                                                                                                                                   | Bindung<br>rs                                 | Abstand<br>R <sub>rs</sub> [Å]                              | Standard-<br>abweichung<br>σ · 10 <sup>3</sup> [Å] | Methode *) | Lit. | π-Bindungsordnungen p <sub>rs</sub>                         |                                                             |            | Lit. |
|------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------|-------------------------------------------------------------|----------------------------------------------------|------------|------|-------------------------------------------------------------|-------------------------------------------------------------|------------|------|
|                              |                                                                                                                                                              |                                               |                                                             |                                                    |            |      | HMO **)                                                     | HMO ***)                                                    | PPP        |      |
| IV. CN-, NO- und NN-Abstände |                                                                                                                                                              |                                               |                                                             |                                                    |            |      |                                                             |                                                             |            |      |
| 64                           | Kalium-syn-methyldiazotat <sup>†)</sup><br>                                 | 1-2<br>2-3                                    | 1.306<br>1.246                                              | 7<br>8                                             | X          | ijj) | .2458<br>.9692                                              | .4451<br>.8946                                              |            |      |
| 65                           | Dimethyl-nitrosamin <sup>†)</sup><br>                                       | 1-2<br>2-3                                    | 1.2345<br>1.3440                                            | 2.1<br>2.4                                         | ED         | kkk) | .8711 <sup>++</sup><br>.4753                                | .7454<br>.6533                                              | .86<br>.48 | kkk) |
| 66                           | Nitramid<br>                                                                | 1-2<br>2-4                                    | 1.206<br>1.427                                              | 2<br>2                                             | MW         | lll) | .5041<br>.6786                                              | .6574<br>.3380                                              |            |      |
| 67                           | Dimethylnitramin <sup>†)</sup><br>(R = CH <sub>3</sub> )                                                                                                     | 1-2<br>2-4                                    | 1.2230<br>1.3823                                            | 2.0<br>3.2                                         | ED         | mmm) | .5041<br>.6786                                              | .6574<br>.3380                                              |            |      |
| 68                           | N,N'-Dinitro-äthylendiamin <sup>†)</sup><br>                                | 1-2<br>2-3<br>2-4                             | 1.240<br>1.236<br>1.301                                     | 3<br>3<br>4                                        | X          | nnn) | .5041<br>.5041<br>.6786                                     | .6574<br>.6574<br>.3380                                     |            |      |
| 69                           | 2-Nitro-nitroso-athan <sup>†)</sup> (dimer)<br>                              | 1-2<br>2-3<br>4-5<br>5-6                      | 1.205<br>1.198<br>1.262<br>1.304                            | 5<br>4<br>4<br>6                                   | X          | ooo) | .6738<br>.6738<br>.2428<br>.9371                            | .6974<br>.6974<br>.3630<br>.8439                            |            |      |
| 70                           | Methylen-bis-nitrosohydroxylamin-dikaliumsalz <sup>†)</sup><br>           | 1-2<br>2-3<br>3-4                             | 1.323<br>1.297<br>1.266                                     | 6<br>4<br>4                                        | X          | ppp) | .2236<br>.8472<br>.2236                                     | .2595<br>.8788<br>.3837                                     |            |      |
| 71                           | 2-[2-Nitroso-2-(4-chlor-benzyl)-hydrazono]-imidazolidin <sup>†)</sup><br> | 1-2<br>2-3<br>2-4<br>4-5<br>5-6<br>6-7        | 1.360<br>1.327<br>1.303<br>1.393<br>1.300<br>1.250          | 5                                                  | X          | qqq) | .4734<br>.4734<br>.6155<br>.4451<br>.7404<br>.4572          | .4465<br>.4465<br>.6640<br>.3684<br>.6742<br>.6216          |            |      |
| 72                           | 4,4'-Dichlor-3,3'-äthylen-bis-sydnon <sup>†)</sup><br>                    | 1-2<br>2-3<br>3-4<br>4-5<br>1-5<br>4-6<br>5-7 | 1.313<br>1.389<br>1.407<br>1.395<br>1.344<br>1.215<br>1.679 | 5                                                  | X          | rrr) | .6827<br>.3223<br>.4852<br>.6382<br>.6481<br>.3764<br>.1090 | .6826<br>.3486<br>.4895<br>.6474<br>.6416<br>.3666<br>.1089 |            |      |

Tab. 3 (Forts.)

| Nr. Verbindung                                                                                                                             | Bindung<br>i-j | Abstand<br>$R_{ij}$ [Å] | Standard-<br>abweichung<br>$\sigma \cdot 10^3$ [Å] | Methode *) | Lit. | $\pi$ -Bindungsordnungen $p_{rs}$ |          |     | Lit. |
|--------------------------------------------------------------------------------------------------------------------------------------------|----------------|-------------------------|----------------------------------------------------|------------|------|-----------------------------------|----------|-----|------|
|                                                                                                                                            |                |                         |                                                    |            |      | HMO **)                           | HMO ***) | PPP |      |
| 73 4,4- <i>trans</i> -Azo-<br>pyridin- <i>N</i> -oxid<br> | 1-2            | 1.283                   | 11                                                 | X          | sss) | .2178                             | .4678    |     |      |
|                                                                                                                                            | 2-3            | 1.364                   | 12                                                 |            |      | .6152                             | .5792    |     |      |
|                                                                                                                                            | 3-4            | 1.352                   | 13                                                 |            |      | .6727                             | .6835    |     |      |
|                                                                                                                                            | 4-5            | 1.373                   | 11                                                 |            |      | .6389                             | .6316    |     |      |
|                                                                                                                                            | 5-6            | 1.378                   | 11                                                 |            |      | .6389                             | .6316    |     |      |
|                                                                                                                                            | 6-7            | 1.365                   | 12                                                 |            |      | .6727                             | .6835    |     |      |
|                                                                                                                                            | 2-7            | 1.351                   | 16                                                 |            |      | .6152                             | .5792    |     |      |
|                                                                                                                                            | 5-8            | 1.419                   | 12                                                 |            |      | .2645                             | .2744    |     |      |
|                                                                                                                                            | 8-9            | 1.228                   | 15                                                 |            |      | .9316                             | .9247    |     |      |

## V. CN-, NO-, NN- und CO-Abstände

|                                                                                                               |       |       |   |   |      |       |       |  |  |
|---------------------------------------------------------------------------------------------------------------|-------|-------|---|---|------|-------|-------|--|--|
| 74 <i>p</i> -Azoxyanisol<br> | 1-2   | 1.352 | 5 | X | ttt) | .3085 | .3081 |  |  |
|                                                                                                               | 2-3   | 1.390 | 5 |   |      | .6287 | .6294 |  |  |
|                                                                                                               | 3-4   | 1.370 | 6 |   |      | .6805 | .6795 |  |  |
|                                                                                                               | 4-5   | 1.372 | 6 |   |      | .6347 | .6383 |  |  |
|                                                                                                               | 5-6   | 1.386 | 5 |   |      | .6347 | .6383 |  |  |
|                                                                                                               | 6-7   | 1.392 | 6 |   |      | .6805 | .6795 |  |  |
|                                                                                                               | 2-7   | 1.394 | 5 |   |      | .6287 | .6294 |  |  |
|                                                                                                               | 5-8   | 1.496 | 5 |   |      | .2662 | .2468 |  |  |
|                                                                                                               | 8-9   | 1.279 | 4 |   |      | .2298 | .4271 |  |  |
|                                                                                                               | 8-10  | 1.218 | 5 |   |      | .8963 | .8388 |  |  |
|                                                                                                               | 10-11 | 1.496 | 6 |   |      | .2822 | .2805 |  |  |
|                                                                                                               | 11-12 | 1.373 | 6 |   |      | .6322 | .6339 |  |  |
|                                                                                                               | 12-13 | 1.401 | 6 |   |      | .6809 | .6782 |  |  |
|                                                                                                               | 13-14 | 1.380 | 5 |   |      | .6285 | .6307 |  |  |
|                                                                                                               | 14-15 | 1.394 | 5 |   |      | .6285 | .6307 |  |  |
|                                                                                                               | 15-16 | 1.365 | 6 |   |      | .6809 | .6782 |  |  |
|                                                                                                               | 11-16 | 1.398 | 6 |   |      | .6322 | .6339 |  |  |
|                                                                                                               | 14-17 | 1.359 | 5 |   |      | .3083 | .3026 |  |  |

## Anmerkungen zu Tabelle 3:

\*) Strukturbestimmungsmethoden: MW = Mikrowellenspektroskopie, N = Neutronenbeugung, X = dreidimensionale Röntgenstrukturbestimmung, ED = Elektronenbeugung.

\*\*) HMO-Berechnungen mit dem Parametersatz (4).

\*\*\*) HMO-Berechnungen mit den neuen NO-Resonanzintegralparametern (12).

<sup>†)</sup> Alkylsubstituenten nicht berücksichtigt.

<sup>††)</sup> Berechnung mit  $k_{N=O} = 1.60$ .

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- b) M. J. Kay und B. C. Frazer, *Acta crystallogr.* [Copenhagen] **14**, 56 (1961).
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$$\begin{aligned}
 h\ddot{N} &= 0.8 & k_{C-N} &= 1.0 \\
 h\ddot{N} &= 1.5 & k_{C=N} &= 1.1 \\
 h\overset{\ominus}{N} &= 1.2 & & \\
 h\ddot{O} &= 1.2 & k_{C-O} &= 1.0 \\
 h\ddot{O} &= 2.1 & k_{C=O} &= 1.6
 \end{aligned} \tag{4a}$$

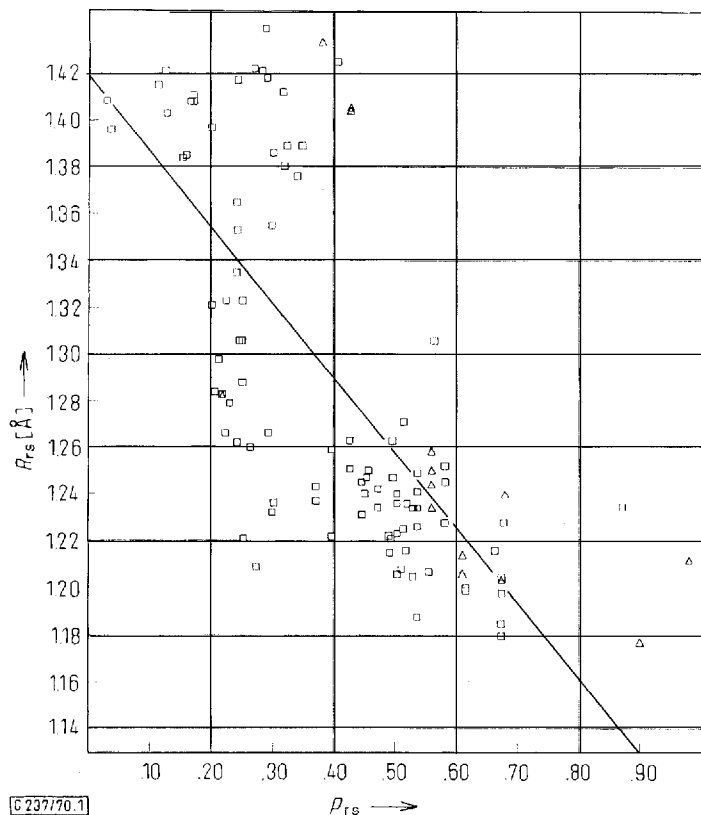
$$\begin{aligned}
 h_{Cl} &= 2.0 & k_{C-Cl} &= 0.4 \\
 h_{Br} &= 1.5 & k_{C-Br} &= 0.3 \\
 k_{N-O} &= 0.7 \\
 k_{\overset{g}{N}-\overset{\ominus}{O}} &= 1.0 \\
 k_{N=O} &= 1.0
 \end{aligned} \tag{4b}$$

Die mit den Parametern (4) berechneten HMO- $\pi$ -Bindungsordnungen für die NO- $\pi$ -Bindungen sind in Abbild. 1 graphisch dargestellt.

Die Gleichung der nach der Methode der kleinsten Fehlerquadrate bestimmten Ausgleichsgeraden (5) lautet

$$R_{rs} [\text{\AA}] = 1.418 - 0.320 \rho_{rs} \quad (5)$$

mit einer Standardabweichung von 0.054  $\text{\AA}$  für 159 Punkte und einem Korrelationskoeffizienten von 0.728.



Abbild. 1. HMO- $\pi$ -Bindungsordnung-Bindungslängen-Beziehung (5) für NO-Bindungen der Tab. 3, berechnet mit den Heteroatomparametern (4) ( $\Delta$  = Verbindungen, die nur NO-Bindungen besitzen)

Diese Beziehung ist hoffnungslos schlecht. Es ist daher unbedingt notwendig, einen neuen Parametersatz für NO-Bindungen zu bestimmen. Besonders die Parameterwerte für die NO-Bindungen in Nitrogruppen sind falsch, da die mit (4b) berechneten Bindungsordnungen eindeutig zu niedrig sind.

### Bestimmung der Resonanzintegralparameter $k_{\text{NO}}$ für NO-Bindungen

Bei den Verbindungen der Tab. 3 treten 5 Typen von NO-Bindungen auf, die durch entsprechende Resonanzintegralparameter behandelt werden müssen:

- a)  $=\bar{\text{N}}-\bar{\text{O}}-$  in Oximen, s. Tab. 4
- b)  $=\overset{\oplus}{\text{N}}-\overset{\ominus}{\text{O}}|$  in Aminoxiden, s. Tab. 5
- c)  $=\overset{\oplus}{\text{N}}\begin{smallmatrix} \diagup \text{O} \\ \diagdown \text{O} \end{smallmatrix}\overset{\ominus}$  in Nitroverbindungen, s. Tab. 6
- d)  $=\bar{\text{N}}-\bar{\text{O}}-$  in Hydroxylaminen, s. Tab. 7
- e)  $=\bar{\text{N}}=\bar{\text{O}}$  in Nitrosoverbindungen, s. Tab. 8

Nach dem bereits beschriebenen Verfahren<sup>19,20)</sup> werden aus Bindungs-Bindungs-Polarisierbarkeiten<sup>21)</sup>  $\pi_{\text{tu,rs}}$  nach (6) und den empirisch bestimmten HMO- $\pi$ -Bindungsordnung-Bindungslängen-Beziehungen (7)<sup>22)</sup>, (8)<sup>23)</sup>, (9)<sup>20)</sup> und (10)<sup>1)</sup>

$$\Delta p_{\text{rs}} = \pi_{\text{tu,rs}} \Delta \beta_{\text{tu}} = \pi_{\text{NO,rs}} (k_{\text{NO}}^{\text{neu}} - k_{\text{NO}}^{\text{alt}}) \quad (6)$$

$$R_{\text{rs}}^{\text{CC}} [\text{\AA}] = 1.585 - 0.295 p_{\text{rs}} \quad (7)$$

$$R_{\text{rs}}^{\text{CN}} [\text{\AA}] = 1.460 - 0.209 p_{\text{rs}} \quad (8)$$

$$R_{\text{rs}}^{\text{CO}} [\text{\AA}] = 1.431 - 0.256 p_{\text{rs}} \quad (9)$$

$$R_{\text{rs}}^{\text{NN}} [\text{\AA}] = 1.436 - 0.177 p_{\text{rs}} \quad (10)$$

die neuen Resonanzintegralparameter  $k_{\text{NO}}$  bestimmt. Die zur Berechnung der  $k_{\text{NO}}$ -Werte benötigten Größen sind in den Tabellen 4–8 angeführt.

Die Mittelung der Werte für die einzelnen Bindungen, die mit einem unterschiedlichen Fehler behaftet sind, geschah mit Hilfe der statistischen Formeln<sup>24)</sup> (11).

$$\bar{\Delta \beta} = \frac{\sum_i \frac{\Delta \beta_i}{\sigma_i^2}}{\sum_i \frac{1}{\sigma_i^2}}; \quad \bar{\sigma} = \sqrt{\frac{1}{\sum_i \frac{1}{\sigma_i^2}}} \quad (11)$$

Die neuen Parameterwerte sind in (12) zusammengestellt.

$$\begin{aligned} k_{\text{--}\ddot{\text{N}}\text{--}\ddot{\text{O}}\text{--}} &= 0.8 \\ k_{\text{--}\overset{\oplus}{\text{N}}\text{--}\overset{\ominus}{\text{O}}\text{--}} &= 1.9 \\ k_{\text{--}\ddot{\text{N}}\text{--}\ddot{\text{O}}\text{--}} &= 1.4 \end{aligned} \quad (12)$$

Die Parameterwerte für NO-Bindungen in Aminoxiden (s. Tab. 5) und in Nitroverbindungen (s. Tab. 6) weichen voneinander ab. Da die letzteren Werte aber mit größerer Genauigkeit bestimmt sind, scheint es gerechtfertigt, für die NO-Bindungen in beiden Verbindungstypen nur den für die Nitroverbindungen bestimmten Wert von 1.9 zu verwenden.

Im Fall der  $\text{--}\ddot{\text{N}}\text{--}\ddot{\text{O}}\text{--}$ -Bindungen versagt die Parameterbestimmungsmethode, da die Auswirkung des Wertes für die N–O-Bindungen auf die Nachbarbindungen nur gering ist und nicht eine genügende Zahl genauer experimenteller Werte zur Verfügung steht.

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Tab. 4. Werte zur Bestimmung des Resonanzintegralparameters  $k = \bar{N} - \bar{O} -$ 

| Verbindung                                                | Bindung*)<br>$r_s$ | $p_{rs}^{HMO}$ | $p_{rs}^{exp}$ | $\Delta p_{rs} =$<br>$p_{rs}^{exp} - p_{rs}^{HMO}$ | $\pi_{HMO}$ | $\Delta \beta_{rs} =$<br>$\Delta p_{rs}$<br>$\pi_{HMO}$ | Fehler**) =<br>$\sigma_{R_{rs}}$<br>$B \cdot \pi_{HMO}$ |
|-----------------------------------------------------------|--------------------|----------------|----------------|----------------------------------------------------|-------------|---------------------------------------------------------|---------------------------------------------------------|
| Formaldoxim                                               | 2-3                | .9416          | .881           | -.061                                              | -.0040      | 15.3                                                    | $\pm 6.0$                                               |
| Cyclohexandion-<br>(1.4)-dioxim                           | 2-3                | .9416          | .881           | -.061                                              | -.0040      | 15.3                                                    | $\pm 3.6$                                               |
| Formamidoxim                                              | 2-3                | .8079          | .823           | .015                                               | .0481       | 0.312                                                   | $\pm 0.79$                                              |
|                                                           | 3-4                | .4919          | .603           | .111                                               | -.0834      | -.0133                                                  | $\pm 0.46$                                              |
|                                                           |                    |                |                |                                                    | Mittelwert: | -.002                                                   | $\pm 0.40$                                              |
| Glyoxim                                                   | 2-3                | .8644          | .843           | -.021                                              | -.0581      | 0.362                                                   | $\pm 0.41$                                              |
|                                                           | 3-4                | .4053          | .460           | .055                                               | .1039       | 0.528                                                   | $\pm 0.196$                                             |
|                                                           |                    |                |                |                                                    |             | 0.493                                                   | $\pm 0.18$                                              |
| 1,2,5-Oxadiazol                                           | 2-3                | .8277          | .765           | -.063                                              | .0038       | -16.6                                                   | $\pm 3.79$                                              |
|                                                           | 3-4                | .4781          | .556           | .078                                               | .2684       | 0.29                                                    | $\pm 0.04$                                              |
|                                                           |                    |                |                |                                                    |             | 0.29                                                    | $\pm 0.04$                                              |
| 3,4'-Bi-isoxazol                                          | 2-3                | .4680          | .332           | -.136                                              | .0651       | -2.09                                                   | $\pm 0.36$                                              |
|                                                           | 3-4                | .7780          | .827           | .049                                               | -.0154      | -3.19                                                   | $\pm 1.32$                                              |
|                                                           | 4-5                | .5338          | .533           | -.001                                              | .0444       | -.0023                                                  | $\pm 0.46$                                              |
|                                                           | 1-5                | .6992          | .660           | -.039                                              | -.0110      | 3.54                                                    | $\pm 2.60$                                              |
|                                                           | 5-6                | .3752          | .366           | -.009                                              | -.0051      | 1.77                                                    | $\pm 4.00$                                              |
|                                                           | 6-7                | .7018          | .722           | .020                                               | -.1597      | -0.13                                                   | $\pm 0.13$                                              |
|                                                           | 7-8                | .4962          | .348           | -.148                                              | .3045       | -0.49                                                   | $\pm 0.086$                                             |
|                                                           | 9-10               | .7756          | .665           | -.111                                              | -.0836      | 1.33                                                    | $\pm 3.43$                                              |
|                                                           | 6-10               | .5338          | .647           | .113                                               | .1177       | 0.96                                                    | $\pm 0.17$                                              |
|                                                           |                    |                |                |                                                    |             | -.028                                                   | $\pm 0.06$                                              |
| 5-Propyloxy- <i>o</i> -<br>benzochinon-2-<br>oxim         | 1-2                | .7732          | .629           | -.144                                              | -.0660      | 2.18                                                    | $\pm 0.47$                                              |
|                                                           | 2-3                | .4533          | .594           | .141                                               | .0404       | 3.49                                                    | $\pm 0.67$                                              |
|                                                           | 3-4                | .7403          | .808           | .068                                               | -.0310      | -2.19                                                   | $\pm 0.88$                                              |
|                                                           | 4-5                | .4569          | .430           | -.027                                              | .0523       | -.052                                                   | $\pm 0.52$                                              |
|                                                           | 5-6                | .8056          | .817           | .011                                               | -.0165      | -0.67                                                   | $\pm 1.64$                                              |
|                                                           | 6-7                | .4468          | .484           | .037                                               | .0180       | 2.06                                                    | $\pm 1.51$                                              |
|                                                           | 2-7                | .2885          | .349           | .060                                               | .0853       | .70                                                     | $\pm 0.32$                                              |
|                                                           | 7-8                | .8031          | .674           | -.129                                              | -.0507      | 2.54                                                    | $\pm 0.76$                                              |
|                                                           | 4-10               | .3498          | .339           | -.011                                              | -.0074      | 1.49                                                    | $\pm 4.23$                                              |
|                                                           |                    |                |                |                                                    |             | 1.03                                                    | $\pm 0.20$                                              |
| 5-[2-Chlor-<br>äthoxy]- <i>o</i> -benzo-<br>chinon-2-oxim | 1-2                | .7732          | .694           | -.079                                              | -.0660      | 1.20                                                    | $\pm 0.41$                                              |
|                                                           | 2-3                | .4533          | .525           | .072                                               | .0404       | 1.78                                                    | $\pm 0.66$                                              |
|                                                           | 3-4                | .7403          | .769           | .029                                               | .0310       | -0.94                                                   | $\pm 0.88$                                              |
|                                                           | 4-5                | .4569          | .434           | -.023                                              | .0523       | -.044                                                   | $\pm 0.52$                                              |
|                                                           | 5-6                | .8056          | .780           | -.026                                              | -.0165      | 1.58                                                    | $\pm 1.64$                                              |
|                                                           | 6-7                | .4468          | .474           | .027                                               | .0180       | 1.50                                                    | $\pm 1.50$                                              |
|                                                           | 2-7                | .2885          | .288           | -.0005                                             | .0853       | -0.006                                                  | $\pm 0.32$                                              |
|                                                           | 7-8                | .8031          | .736           | -.067                                              | -.0507      | 1.32                                                    | $\pm 0.66$                                              |
|                                                           | 4-10               | .3498          | .344           | -.006                                              | -.0074      | 0.81                                                    | $\pm 3.69$                                              |
|                                                           |                    |                |                |                                                    |             | 0.48                                                    | $\pm 0.20$                                              |
| Violursäure                                               | 1-2                | .3937          | .473           | .079                                               | .0026       | 30.4                                                    | $\pm 14.7$                                              |
|                                                           | 2-3                | .3937          | .393           | -.001                                              | .0026       | -0.39                                                   | $\pm 14.7$                                              |
|                                                           | 3-4                | .4070          | .397           | -.010                                              | -.0085      | 1.18                                                    | $\pm 3.38$                                              |
|                                                           | 4-5                | .2980          | .400           | .102                                               | .0640       | 1.59                                                    | $\pm 0.42$                                              |
|                                                           | 5-6                | .2980          | .274           | -.024                                              | .0640       | -0.38                                                   | $\pm 0.42$                                              |
|                                                           | 1-6                | .4070          | .426           | .019                                               | -.0085      | -2.24                                                   | $\pm 3.38$                                              |
|                                                           | 2-7                | .7660          | .784           | .018                                               | -.0026      | -6.93                                                   | $\pm 13.5$                                              |
|                                                           | 4-8                | .7987          | .784           | -.015                                              | -.0268      | 0.57                                                    | $\pm 3.81$                                              |
|                                                           | 6-9                | .7987          | .902           | .103                                               | -.0268      | -3.84                                                   | $\pm 3.81$                                              |
|                                                           | 5-10               | .8657          | .842           | -.024                                              | -.0669      | 0.36                                                    | $\pm 0.65$                                              |
|                                                           |                    |                |                |                                                    |             | 0.53                                                    | $\pm 0.27$                                              |
| 3-Hydroxy-5-<br>phenyl-isoxazol                           | 1-2                | .3389          | .351           | .012                                               | -.0668      | -0.18                                                   | $\pm 0.29$                                              |
|                                                           | 2-3                | .7049          | .704           | -.001                                              | .0101       | -0.099                                                  | $\pm 3.31$                                              |
|                                                           | 4-5                | .4276          | .231           | -.197                                              | .0752       | -2.62                                                   | $\pm 0.31$                                              |
|                                                           | 5-6                | .7196          | .722           | .002                                               | -.0234      | -0.086                                                  | $\pm 0.87$                                              |
|                                                           | 2-6                | .5463          | .600           | .054                                               | .0591       | 0.91                                                    | $\pm 0.34$                                              |
|                                                           | 5-7                | .3890          | .494           | .105                                               | -.0164      | -6.40                                                   | $\pm 1.24$                                              |
|                                                           | 7-8                | .6130          | .573           | -.040                                              | .0059       | -6.77                                                   | $\pm 3.45$                                              |
|                                                           | 8-9                | .6781          | .705           | .027                                               | -.0017      | -15.9                                                   | $\pm 14.0$                                              |
|                                                           | 9-10               | .6589          | .695           | .036                                               | .0014       | 25.7                                                    | $\pm 19.4$                                              |
|                                                           | 10-11              | .6589          | .644           | -.015                                              | .0014       | -10.7                                                   | $\pm 17.0$                                              |
|                                                           | 11-12              | .6781          | .684           | .006                                               | -.0017      | -3.53                                                   | $\pm 16.0$                                              |
|                                                           | 7-12               | .6130          | .593           | -.020                                              | .0059       | -3.39                                                   | $\pm 4.02$                                              |
|                                                           |                    |                |                |                                                    |             | -.080                                                   | $\pm 0.17$                                              |

\*), \*\*) siehe Tab. 8.

Mittelwert:  $\Delta \beta = (k_{N-O}^{neu} - 0.7) = 0.13$   $\pm 0.03$

Tab. 5. Werte zur Bestimmung des Resonanzintegralparameters  $k_{\text{N}-\text{O}}^{\oplus}$ 

| Verbindung                                                  | Bindung*)<br>rs | $p_{\text{rs}}^{\text{HMO}}$ | $p_{\text{rs}}^{\text{exp}}$ | $\Delta p_{\text{rs}} =$<br>$p_{\text{rs}}^{\text{exp}} - p_{\text{rs}}^{\text{HMO}}$ | $\pi^{\text{HMO}}$ | $\Delta\beta_{\text{rs}} =$<br>$\frac{\Delta p_{\text{rs}}}{\pi^{\text{HMO}}}$ | Fehler**) =<br>$\sigma_{R_{\text{rs}}}$<br>$B \cdot \pi^{\text{HMO}}$ |
|-------------------------------------------------------------|-----------------|------------------------------|------------------------------|---------------------------------------------------------------------------------------|--------------------|--------------------------------------------------------------------------------|-----------------------------------------------------------------------|
| N-Methyl-p-chlor-benzaldoxim                                | 2-3             | .8022                        | .722                         | -.080                                                                                 | .0507              | -1.58                                                                          | $\pm 0.66$                                                            |
|                                                             | 3-4             | .4255                        | .410                         | -.016                                                                                 | -.0226             | 0.71                                                                           | $\pm 1.20$                                                            |
|                                                             | 4-5             | .6021                        | .623                         | .021                                                                                  | .0091              | 2.31                                                                           | $\pm 2.98$                                                            |
|                                                             | 5-6             | .6831                        | .657                         | -.026                                                                                 | -.0036             | 7.23                                                                           | $\pm 7.55$                                                            |
|                                                             | 6-7             | .6506                        | .752                         | .101                                                                                  | .0031              | 32.6                                                                           | $\pm 8.75$                                                            |
|                                                             | 7-8             | .6506                        | .752                         | .101                                                                                  | .0031              | 32.6                                                                           | $\pm 8.75$                                                            |
|                                                             | 8-9             | .6831                        | .666                         | -.017                                                                                 | -.0036             | 4.72                                                                           | $\pm 8.48$                                                            |
|                                                             | 4-9             | .6021                        | .590                         | -.012                                                                                 | .0091              | -1.32                                                                          | $\pm 2.98$                                                            |
|                                                             |                 |                              |                              |                                                                                       | Mittelwert:        | -0.58                                                                          | $\pm 0.56$                                                            |
|                                                             |                 |                              |                              |                                                                                       |                    |                                                                                |                                                                       |
| 4-Chlor-2,6-N-trimethyl-benzaldoxim                         | 2-3             | .8633                        | .771                         | -.092                                                                                 | .0364              | -2.53                                                                          | $\pm 0.92$                                                            |
|                                                             | 3-4             | .2588                        | .380                         | .121                                                                                  | -.0129             | -9.38                                                                          | $\pm 1.84$                                                            |
|                                                             | 4-5             | .6432                        | .599                         | -.054                                                                                 | .0029              | -18.6                                                                          | $\pm 8.18$                                                            |
|                                                             | 5-6             | .6732                        | .664                         | -.009                                                                                 | -.0012             | 7.49                                                                           | $\pm 19.8$                                                            |
|                                                             | 6-7             | .6577                        | .685                         | .027                                                                                  | .0010              | 27.0                                                                           | $\pm 23.7$                                                            |
|                                                             | 7-8             | .6577                        | .708                         | .050                                                                                  | .0010              | 50.0                                                                           | $\pm 23.7$                                                            |
|                                                             | 8-9             | .6732                        | .657                         | -.016                                                                                 | -.0012             | 13.3                                                                           | $\pm 19.8$                                                            |
|                                                             | 4-9             | .6432                        | .617                         | -.026                                                                                 | .0029              | -9.0                                                                           | $\pm 8.18$                                                            |
|                                                             |                 |                              |                              |                                                                                       |                    | -3.74                                                                          | $\pm 0.82$                                                            |
|                                                             |                 |                              |                              |                                                                                       |                    | 0.88                                                                           | $\pm 0.33$                                                            |
| Dimeres 2-Nitro-nitrosoäthan<br>p-Methoxy-indophenol-N-oxid | 5-6             | .9371                        | .746                         | -.091                                                                                 | -.1031             | 0.88                                                                           | $\pm 0.33$                                                            |
|                                                             | 1-2             | .7778                        | .715                         | -.063                                                                                 | -.0929             | 0.68                                                                           | $\pm 0.21$                                                            |
|                                                             | 2-3             | .3752                        | .438                         | .063                                                                                  | .0866              | 0.73                                                                           | $\pm 0.23$                                                            |
|                                                             | 3-4             | .8430                        | .774                         | -.069                                                                                 | -.0395             | 1.75                                                                           | $\pm 0.53$                                                            |
|                                                             | 4-5             | .4258                        | .498                         | .072                                                                                  | .0459              | 1.60                                                                           | $\pm 0.44$                                                            |
|                                                             | 5-6             | .4258                        | .502                         | .076                                                                                  | .0459              | 1.66                                                                           | 0.44                                                                  |
|                                                             | 6-7             | .8430                        | .774                         | -.069                                                                                 | -.0395             | 1.74                                                                           | $\pm 0.53$                                                            |
|                                                             | 2-7             | .3752                        | .444                         | .069                                                                                  | .0866              | 0.79                                                                           | $\pm 0.23$                                                            |
|                                                             | 5-8             | .7122                        | .493                         | -.219                                                                                 | -.0240             | 9.14                                                                           | $\pm 0.80$                                                            |
|                                                             | 8-10            | .2144                        | .048                         | -.166                                                                                 | .0077              | -21.5                                                                          | $\pm 3.11$                                                            |
|                                                             | 10-11           | .6433                        | .681                         | .038                                                                                  | -.0008             | -47.5                                                                          | $\pm 25.4$                                                            |
|                                                             | 11-12           | .6800                        | .651                         | -.039                                                                                 | .0008              | -48.8                                                                          | $\pm 25.4$                                                            |
|                                                             | 12-13           | .6274                        | .624                         | -.003                                                                                 | -.0001             | 30                                                                             | $\pm 204$                                                             |
|                                                             | 13-14           | .6274                        | .685                         | .058                                                                                  | -.0001             | -580                                                                           | $\pm 204$                                                             |
|                                                             | 14-15           | .6800                        | .640                         | -.040                                                                                 | .0008              | -50                                                                            | $\pm 25.4$                                                            |
|                                                             | 10-15           | .6433                        | .637                         | -.006                                                                                 | -.0008             | 7.5                                                                            | $\pm 25.4$                                                            |
|                                                             | 13-16           | .3094                        | .274                         | -.035                                                                                 | .0016              | -21.9                                                                          | $\pm 12.2$                                                            |
|                                                             |                 |                              |                              |                                                                                       |                    | 1.08                                                                           | $\pm 0.11$                                                            |
| Myxin                                                       | 1-2             | .3198                        | .308                         | -.012                                                                                 | -.0055             | 2.17                                                                           | $\pm 2.84$                                                            |
|                                                             | 2-3             | .6969                        | .720                         | .023                                                                                  | -.0085             | -2.71                                                                          | $\pm 1.59$                                                            |
|                                                             | 3-4             | .5972                        | .606                         | .009                                                                                  | .0111              | 0.81                                                                           | $\pm 1.22$                                                            |
|                                                             | 4-5             | .7262                        | .698                         | -.028                                                                                 | -.0018             | 15.6                                                                           | $\pm 7.52$                                                            |
|                                                             | 5-6             | .5421                        | .594                         | .052                                                                                  | .0012              | 43.3                                                                           | $\pm 12.3$                                                            |
|                                                             | 6-7             | .4772                        | .578                         | .101                                                                                  | .0432              | 2.34                                                                           | $\pm 0.31$                                                            |
|                                                             | 2-7             | .5000                        | .495                         | -.005                                                                                 | .0223              | -0.22                                                                          | $\pm 0.61$                                                            |
|                                                             | 7-8             | .5778                        | .440                         | -.138                                                                                 | -.0418             | 3.30                                                                           | $\pm 0.76$                                                            |
|                                                             | 8-10            | .5631                        | .440                         | -.123                                                                                 | -.0324             | 3.80                                                                           | $\pm 0.59$                                                            |
|                                                             | 10-11           | .4772                        | .538                         | .061                                                                                  | .0432              | 1.41                                                                           | $\pm 0.31$                                                            |
|                                                             | 11-12           | .5778                        | .383                         | -.195                                                                                 | -.0418             | 4.67                                                                           | $\pm 0.46$                                                            |
|                                                             | 6-12            | .5632                        | .325                         | -.238                                                                                 | -.0324             | 7.35                                                                           | $\pm 0.59$                                                            |
|                                                             | 11-14           | .5000                        | .478                         | -.022                                                                                 | .0223              | 0.99                                                                           | $\pm 0.61$                                                            |
|                                                             | 14-15           | .6969                        | .694                         | -.003                                                                                 | -.0085             | 0.35                                                                           | $\pm 1.59$                                                            |
|                                                             | 15-16           | .5972                        | .600                         | .003                                                                                  | .0111              | 0.27                                                                           | $\pm 1.22$                                                            |
|                                                             | 16-17           | .7262                        | .763                         | .037                                                                                  | -.0018             | -20.6                                                                          | $\pm 7.52$                                                            |
|                                                             | 10-17           | .5421                        | .583                         | .041                                                                                  | .0012              | 34.2                                                                           | $\pm 12.3$                                                            |
|                                                             | 14-18           | .3198                        | .286                         | -.024                                                                                 | -.0055             | 4.36                                                                           | $\pm 2.84$                                                            |
|                                                             |                 |                              |                              |                                                                                       |                    | 2.48                                                                           | $\pm 0.15$                                                            |
| Jodinin                                                     | 1-2             | .3198                        | .308                         | -.012                                                                                 | -.0055             | 2.17                                                                           | $\pm 2.13$                                                            |
|                                                             | 2-3             | .6969                        | .736                         | .039                                                                                  | -.0085             | 4.58                                                                           | $\pm 1.59$                                                            |
|                                                             | 3-4             | .5972                        | .606                         | .009                                                                                  | .0111              | 0.81                                                                           | $\pm 1.22$                                                            |
|                                                             | 4-5             | .7262                        | .715                         | -.011                                                                                 | -.0018             | 6.10                                                                           | $\pm 7.52$                                                            |
|                                                             | 5-6             | .5421                        | .596                         | .054                                                                                  | .0012              | 45.0                                                                           | $\pm 12.3$                                                            |
|                                                             | 6-7             | .4772                        | .583                         | .106                                                                                  | .0432              | 2.46                                                                           | $\pm 0.31$                                                            |
|                                                             | 7-8             | .5778                        | .459                         | -.119                                                                                 | -.0418             | 2.84                                                                           | $\pm 0.46$                                                            |
|                                                             | 2-7             | .5000                        | .488                         | -.012                                                                                 | .0223              | -0.54                                                                          | $\pm 0.61$                                                            |
|                                                             | 8-10            | .5631                        | .388                         | -.175                                                                                 | -.0324             | 5.40                                                                           | $\pm 0.59$                                                            |
|                                                             |                 |                              |                              |                                                                                       |                    | 2.57                                                                           | $\pm 0.22$                                                            |

\*), \*\*) siehe Tab. 8.

$$\text{Mittelwert: } \Delta\beta = (k_{\text{N}-\text{O}}^{\text{neu}} - 1.0) = 1.60 \pm 0.10$$

Tab. 6. Werte zur Bestimmung des Resonanzintegralparameters  $k_{N-O}^{\oplus}$  (in  $-\text{NO}_2$ )

| Verbindung                                       | Bindung*)<br>rs | $p_{rs}^{\text{HMO}}$ | $p_{rs}^{\text{exp}}$ | $\Delta p_{rs} =$                           |                    | $\Delta \beta_{rs} =$ | Fehler **) $\rightarrow$                     |
|--------------------------------------------------|-----------------|-----------------------|-----------------------|---------------------------------------------|--------------------|-----------------------|----------------------------------------------|
|                                                  |                 |                       |                       | $p_{rs}^{\text{exp}} - p_{rs}^{\text{HMO}}$ | $\pi^{\text{HMO}}$ | $\pi^{\text{HMO}}$    | $\sigma_{R_{rs}} / B \cdot \pi^{\text{HMO}}$ |
| Nitrobenzol                                      | 2-4             | .5603                 | .124                  | -.684                                       | -.4165             | 1.64                  | $\pm 0.23$                                   |
|                                                  | 4-5             | .5344                 | .739                  | .205                                        | .2118              | 0.97                  | $\pm 0.22$                                   |
|                                                  | 5-6             | .7032                 | .538                  | -.165                                       | -.0720             | 2.29                  | $\pm 0.66$                                   |
|                                                  | 6-7             | .6351                 | .718                  | .083                                        | .0747              | 1.11                  | $\pm 0.63$                                   |
|                                                  |                 |                       |                       |                                             | Mittelwert: 1.33   |                       | $\pm 0.15$                                   |
| <i>p</i> -Nitranilin                             | 1-2             | .4679                 | .426                  | -.042                                       | -.2080             | 0.22                  | $\pm 0.15$                                   |
|                                                  | 2-3             | .5447                 | .587                  | .042                                        | .1618              | 0.26                  | $\pm 0.15$                                   |
|                                                  | 3-4             | .7546                 | .713                  | -.042                                       | -.1325             | 0.32                  | $\pm 0.18$                                   |
|                                                  | 4-5             | .5008                 | .650                  | .149                                        | .2254              | 0.66                  | $\pm 0.11$                                   |
|                                                  | 5-8             | .6158                 | .000                  | -.616                                       | -.4138             | 1.49                  | $\pm 0.08$                                   |
|                                                  |                 |                       |                       |                                             |                    | 0.89                  | $\pm 0.05$                                   |
| <i>N</i> -[4-Methylbenzyliden]-4-nitranilin      | 2-4             | .5743                 | -.053                 | -.627                                       | -.4255             | 1.47                  | $\pm 0.08$                                   |
|                                                  | 4-5             | .5252                 | .705                  | .280                                        | .1090              | 2.57                  | $\pm 0.22$                                   |
|                                                  | 5-6             | .7184                 | .688                  | -.030                                       | -.0938             | 0.32                  | $\pm 0.25$                                   |
|                                                  | 6-7             | .6019                 | .688                  | .086                                        | .0994              | 0.87                  | $\pm 0.24$                                   |
|                                                  | 7-10            | .3002                 | .287                  | -.013                                       | -.0956             | 0.14                  | $\pm 0.35$                                   |
|                                                  | 10-11           | .8001                 | .914                  | .114                                        | .0416              | 2.73                  | $\pm 0.86$                                   |
|                                                  | 11-12           | .4294                 | .377                  | -.052                                       | -.0208             | 2.50                  | $\pm 1.14$                                   |
|                                                  | 12-13           | .5998                 | .671                  | .071                                        | .0112              | 6.24                  | $\pm 2.12$                                   |
|                                                  | 13-14           | .6819                 | .671                  | -.011                                       | -.0038             | 2.89                  | $\pm 6.25$                                   |
|                                                  | 14-15           | .6557                 | .687                  | .031                                        | .0040              | 7.75                  | $\pm 5.94$                                   |
|                                                  |                 |                       |                       |                                             |                    | 1.41                  | $\pm 0.05$                                   |
| 9-Nitro-anthracen                                | 1-2             | .7353                 | .630                  | -.105                                       | .0220              | 4.76                  | $\pm 1.23$                                   |
|                                                  | 2-3             | .5872                 | .502                  | -.085                                       | -.0150             | 5.66                  | $\pm 2.48$                                   |
|                                                  | 1-6             | .5375                 | .513                  | -.025                                       | -.0174             | 1.44                  | $\pm 1.56$                                   |
|                                                  | 5-6             | .4856                 | .583                  | .097                                        | .0056              | 17.3                  | $\pm 6.65$                                   |
|                                                  | 6-7             | .6023                 | .628                  | .026                                        | .0272              | 0.96                  | $\pm 0.98$                                   |
|                                                  | 7-15            | .1177                 | -.153                 | -.271                                       | -.4900             | 0.55                  | $\pm 0.15$                                   |
|                                                  |                 |                       |                       |                                             |                    | 0.52                  | $\pm 0.15$                                   |
| <i>p</i> -Nitro-phenol<br>$\alpha$ -Modifikation | 1-2             | .3785                 | .312                  | -.067                                       | .1471              | 0.46                  | $\pm 0.16$                                   |
|                                                  | 2-3             | .5701                 | .660                  | .090                                        | .1396              | 0.65                  | $\pm 0.15$                                   |
|                                                  | 3-4             | .7400                 | .698                  | -.042                                       | -.1182             | 0.36                  | $\pm 0.17$                                   |
|                                                  | 4-5             | .5099                 | .674                  | .164                                        | .2273              | 0.72                  | $\pm 0.09$                                   |
|                                                  | 5-8             | .6011                 | .086                  | -.515                                       | -.4237             | 1.22                  | $\pm 0.07$                                   |
|                                                  |                 |                       |                       |                                             |                    | 0.89                  | $\pm 0.05$                                   |
| <i>p</i> -Nitro-phenol<br>$\beta$ -Modifikation  | 1-2             | .3785                 | .274                  | -.105                                       | -.1471             | 0.71                  | $\pm 0.13$                                   |
|                                                  | 2-3             | .5701                 | .633                  | .063                                        | .1396              | 0.45                  | $\pm 0.12$                                   |
|                                                  | 3-4             | .7400                 | .694                  | -.046                                       | -.1182             | 0.39                  | $\pm 0.14$                                   |
|                                                  | 4-5             | .5099                 | .647                  | .137                                        | .2273              | 0.60                  | $\pm 0.08$                                   |
|                                                  | 5-8             | .6011                 | .048                  | -.553                                       | -.4237             | 1.31                  | $\pm 0.06$                                   |
|                                                  |                 |                       |                       |                                             |                    | 0.90                  | $\pm 0.04$                                   |
| <i>p</i> -Nitro-benzoesäure                      | 1-2             | .3698                 | .438                  | .068                                        | -.0030             | 22.7                  | $\pm 9.12$                                   |
|                                                  | 2-3             | .8090                 | .816                  | .007                                        | -.0146             | 0.48                  | $\pm 1.88$                                   |
|                                                  | 2-4             | .3101                 | .285                  | -.025                                       | .0305              | 0.83                  | $\pm 0.90$                                   |
|                                                  | 4-5             | .6084                 | .620                  | .012                                        | .0542              | 0.22                  | $\pm 0.50$                                   |
|                                                  | 5-6             | .7005                 | .650                  | -.051                                       | -.0587             | 0.87                  | $\pm 0.46$                                   |
|                                                  | 6-7             | .5393                 | .650                  | .111                                        | .2018              | 0.55                  | $\pm 0.13$                                   |
|                                                  | 7-10            | .5463                 | -.096                 | -.642                                       | -.4141             | 1.55                  | $\pm 0.14$                                   |
|                                                  |                 |                       |                       |                                             |                    | 0.86                  | $\pm 0.10$                                   |
| 5-Nitro-uracil                                   | 1-2             | .3715                 | .364                  | -.007                                       | .0392              | 0.18                  | $\pm 0.73$                                   |
|                                                  | 2-3             | .4032                 | .431                  | .028                                        | .0056              | 5.0                   | $\pm 5.13$                                   |
|                                                  | 3-4             | .4054                 | .374                  | -.031                                       | -.0092             | 3.37                  | $\pm 3.12$                                   |
|                                                  | 4-5             | .3401                 | .448                  | .108                                        | .1203              | 0.90                  | $\pm 0.17$                                   |
|                                                  | 5-6             | .5326                 | .769                  | .236                                        | .3548              | 0.66                  | $\pm 0.06$                                   |
|                                                  | 1-6             | .6085                 | .598                  | -.011                                       | -.1862             | 0.06                  | $\pm 0.15$                                   |
|                                                  | 2-7             | .7712                 | .816                  | .045                                        | -.0232             | 1.94                  | $\pm 1.02$                                   |
|                                                  | 4-8             | .7793                 | .762                  | -.017                                       | -.0550             | 0.31                  | $\pm 0.43$                                   |
|                                                  | 5-9             | .6815                 | .139                  | -.543                                       | -.3940             | 1.38                  | $\pm 0.07$                                   |
|                                                  |                 |                       |                       |                                             |                    | 0.98                  | $\pm 0.04$                                   |

\*), \*\*) siehe Tab. 8.

Tab. 6 (Forts.)

| Verbindung                | Bindung *)<br>rs | $p_{rs}^{HMO}$ | $p_{rs}^{exp}$ | $\Delta p_{rs}^{rs} =$<br>$p_{rs}^{exp} - p_{rs}^{HMO}$ | $\pi^{HMO}$ | $\frac{\Delta \beta_{rs}}{\pi^{HMO}} =$<br>$\frac{\Delta p_{rs}}{\pi^{HMO}}$ | Fehler **) =<br>$\frac{\sigma_{R_{rs}}}{B \cdot \pi^{HMO}}$ |
|---------------------------|------------------|----------------|----------------|---------------------------------------------------------|-------------|------------------------------------------------------------------------------|-------------------------------------------------------------|
| 5-Nitro-<br>barbitursäure | 1-2              | .4008          | .450           | .049                                                    | .0073       | 0.15                                                                         | $\pm 3.28$                                                  |
|                           | 2-3              | .3785          | .474           | .095                                                    | .0261       | 3.64                                                                         | $\pm 0.65$                                                  |
|                           | 3-4              | .5402          | .537           | -.003                                                   | -.1119      | 0.03                                                                         | $\pm 0.15$                                                  |
|                           | 4-5              | .4543          | .600           | .146                                                    | .3092       | 0.47                                                                         | $\pm 0.06$                                                  |
|                           | 5-6              | .3457          | .451           | .105                                                    | .0432       | 0.73                                                                         | $\pm 0.12$                                                  |
|                           | 1-6              | .4029          | .374           | -.029                                                   | -.0145      | 2.00                                                                         | $\pm 1.17$                                                  |
|                           | 2-7              | .7693          | .804           | .035                                                    | -.0173      | -2.02                                                                        | $\pm 0.98$                                                  |
|                           | 4-8              | .4681          | .500           | .032                                                    | -.0938      | -0.34                                                                        | $\pm 0.13$                                                  |
|                           | 5-9              | .7211          | .258           | -.463                                                   | -.3533      | 1.31                                                                         | $\pm 0.05$                                                  |
|                           | 6-12             | .7780          | .813           | .035                                                    | -.0642      | -0.54                                                                        | $\pm 0.26$                                                  |
|                           |                  |                |                |                                                         |             | 0.78                                                                         | $\pm 0.03$                                                  |

\*,\*\*) siehe Tab. 8.

Mittelwert:  $\Delta \beta = (k_{NO}^{neu} - 1.0) = 0.91 \pm 0.02$ Tab. 7. Werte zur Bestimmung des Resonanzintegralparameters  $k-N-\bar{O}-$ 

| Verbindung                                      | Bindung *)<br>rs | $p_{rs}^{HMO}$ | $p_{rs}^{exp}$ | $\Delta p_{rs}^{rs} =$<br>$p_{rs}^{exp} - p_{rs}^{HMO}$ | $\pi^{HMO}$      | $\frac{\Delta \beta_{rs}}{\pi^{HMO}} =$<br>$\frac{\Delta p_{rs}}{\pi^{HMO}}$ | Fehler **) =<br>$\frac{\sigma_{R_{rs}}}{B \cdot \pi^{HMO}}$ |
|-------------------------------------------------|------------------|----------------|----------------|---------------------------------------------------------|------------------|------------------------------------------------------------------------------|-------------------------------------------------------------|
| Hydroxy-<br>harnstoff                           | 1-2              | .4172          | .646           | .229                                                    | -.0123           | -18.6                                                                        | $\pm 3.12$                                                  |
|                                                 | 2-3              | .7395          | .649           | .081                                                    | -.0225           | -3.61                                                                        | $\pm 1.39$                                                  |
|                                                 | 2-4              | .4360          | .593           | .157                                                    | .0430            | 3.65                                                                         | $\pm 0.67$                                                  |
|                                                 |                  |                |                |                                                         | Mittelwert: 1.52 |                                                                              | $\pm 0.59$                                                  |
| O-Carbamoyl-<br>hydroxylamin                    | 1-2              | .4280          | .656           | .228                                                    | -.0107           | -21.3                                                                        | $\pm 2.24$                                                  |
|                                                 | 2-3              | .7596          | .738           | -.022                                                   | -.0197           | 1.12                                                                         | $\pm 0.99$                                                  |
|                                                 | 2-4              | .3741          | .347           | -.027                                                   | .0402            | -0.67                                                                        | $\pm 0.49$                                                  |
|                                                 |                  |                |                |                                                         |                  | -1.10                                                                        | $\pm 0.43$                                                  |
| 2-Methyl-4-phenyl-<br>isoxazolon-(5)            | 1-2              | .7329          | .844           | .111                                                    | -.0598           | -1.86                                                                        | $\pm 0.33$                                                  |
|                                                 | 2-3              | .3876          | .172           | -.216                                                   | .0567            | -3.81                                                                        | $\pm 0.41$                                                  |
|                                                 | 4-5              | .5410          | .598           | .057                                                    | .0769            | 0.74                                                                         | $\pm 0.37$                                                  |
|                                                 | 5-6              | .7104          | .696           | -.014                                                   | -.0365           | 0.38                                                                         | $\pm 0.56$                                                  |
|                                                 | 2-6              | .4327          | .536           | .003                                                    | .0466            | 0.06                                                                         | $\pm 0.44$                                                  |
|                                                 | 6-7              | .3938          | .443           | .049                                                    | -.0016           | -30.6                                                                        | $\pm 12.7$                                                  |
|                                                 | 7-8              | .6106          | .633           | .022                                                    | .0002            | 110                                                                          | $\pm 102$                                                   |
|                                                 | 8-9              | .6789          | .654           | -.025                                                   | -.00002          | -1250                                                                        | $\pm 1020$                                                  |
|                                                 | 9-10             | .6583          | .668           | .010                                                    | -.00003          | -333                                                                         | $\pm 680$                                                   |
|                                                 | 10-11            | .6583          | .617           | -.041                                                   | -.00003          | 1370                                                                         | $\pm 680$                                                   |
|                                                 | 11-12            | .6789          | .736           | .043                                                    | -.00002          | 2150                                                                         | $\pm 1020$                                                  |
|                                                 | 7-12             | .6106          | .566           | -.045                                                   | .0002            | 225                                                                          | $\pm 102$                                                   |
|                                                 |                  |                |                |                                                         |                  | -1.07                                                                        | $\pm 0.18$                                                  |
| 4-Brom-2-methyl-<br>3-phenyl-<br>isoxazolon-(5) | 1-2              | .7179          | .903           | .185                                                    | -.0638           | -2.90                                                                        | $\pm 0.43$                                                  |
|                                                 | 2-3              | .3849          | .113           | -.272                                                   | .0620            | -4.38                                                                        | $\pm 0.44$                                                  |
|                                                 | 4-5              | .4966          | .565           | .068                                                    | .0782            | 0.87                                                                         | $\pm 0.49$                                                  |
|                                                 | 5-6              | .7537          | .733           | -.021                                                   | -.0370           | 0.57                                                                         | $\pm 0.73$                                                  |
|                                                 | 2-6              | .4729          | .573           | .100                                                    | .0500            | 2.00                                                                         | $\pm 0.48$                                                  |
|                                                 | 5-7              | .2549          | .389           | .134                                                    | -.0098           | -13.7                                                                        | $\pm 2.43$                                                  |
|                                                 | 7-8              | .6441          | .565           | -.079                                                   | .0022            | -35.9                                                                        | $\pm 16.9$                                                  |
|                                                 | 8-9              | .6714          | .441           | -.230                                                   | -.0006           | 384                                                                          | $\pm 67.7$                                                  |
|                                                 | 9-10             | .6635          | .823           | .159                                                    | .0005            | 317                                                                          | $\pm 115$                                                   |
|                                                 | 10-11            | .6635          | .796           | .132                                                    | .0005            | 264                                                                          | $\pm 94.5$                                                  |
|                                                 | 11-12            | .6714          | .733           | .062                                                    | -.0006           | -104                                                                         | $\pm 56.4$                                                  |
|                                                 | 7-12             | .6441          | .716           | .072                                                    | .0022            | 32.7                                                                         | $\pm 18.5$                                                  |
|                                                 |                  |                |                |                                                         |                  | -1.29                                                                        | $\pm 0.22$                                                  |

\*,\*\*) siehe Tab. 8.

Mittelwert:  $\Delta \beta = (k_{NO}^{neu} - 0.7) = -1.01 \pm 0.13$ 

Die Bestimmung in Tab. 7 liefert mit  $-0.3$  einen negativen Wert für diese  $N-O$ -Bindung, was ein sinnloses Ergebnis darstellt. Die mit dem  $NO$ -Parameter für Oxime  $k_{NO} = 0.8$  berechneten Bindungsordnungen sind schon kleiner als 0.10, so daß es wohl möglich, aber nicht notwendig ist, einen kleineren Wert für die Aminoxidbindungen anzusetzen.

Tab. 8. Werte zur Bestimmung des Resonanzintegralparameters  $k_{\text{N}=\text{O}}$ 

| Verbindung                                              | Bindung <sup>*)</sup><br>rs | $\rho_{\text{rs}}^{\text{HMO}}$ | $\rho_{\text{rs}}^{\text{exp}}$ | $\Delta \rho_{\text{rs}} =$<br>$\rho_{\text{rs}}^{\text{exp}} - \rho_{\text{rs}}^{\text{HMO}}$ |        | $\pi^{\text{HMO}}$ | $\Delta \beta_{\text{rs}} =$<br>$\Delta \rho_{\text{rs}} / \pi^{\text{HMO}}$ |  | Fehler <sup>**) :</sup><br>$\sigma_{R_{\text{rs}}} / B \cdot \pi^{\text{HMO}}$ |
|---------------------------------------------------------|-----------------------------|---------------------------------|---------------------------------|------------------------------------------------------------------------------------------------|--------|--------------------|------------------------------------------------------------------------------|--|--------------------------------------------------------------------------------|
|                                                         |                             |                                 |                                 |                                                                                                |        |                    |                                                                              |  |                                                                                |
| Dimethyl-nitrosamin                                     | 2-3                         | .4753                           | .519                            | .044                                                                                           | -.2051 | -.021              |                                                                              |  | $\pm 0.07$                                                                     |
| 2-[2-Nitroso-2-(4-chlor-benzyl)-hydrazono]-imidazolidin | 1-2                         | .4348                           | .478                            | .043                                                                                           | -.0543 | -.079              |                                                                              |  | $\pm 0.44$                                                                     |
|                                                         | 2-3                         | .4348                           | .636                            | .201                                                                                           | -.0543 | -.371              |                                                                              |  | $\pm 0.44$                                                                     |
|                                                         | 2-4                         | .6837                           | .751                            | .067                                                                                           | .0889  | .076               |                                                                              |  | $\pm 0.28$                                                                     |
|                                                         | 4-5                         | .3384                           | .243                            | -.095                                                                                          | -.1337 | .071               |                                                                              |  | $\pm 0.21$                                                                     |
|                                                         | 5-6                         | .6345                           | .769                            | .134                                                                                           | -.2018 | -.067              |                                                                              |  | $\pm 0.14$                                                                     |
|                                                         |                             |                                 |                                 |                                                                                                |        | -.032              |                                                                              |  | $\pm 0.10$                                                                     |

$$\text{Mittelwert: } \Delta \beta_{\text{N}=\text{O}} = (k_{\text{N}=\text{O}}^{\text{neu}} - 1.60) = -0.25 \quad \pm 0.06$$

<sup>\*)</sup> siehe Tab. 3.

<sup>\*\*) B</sup> in Gl. (1);  $\sigma_{R_{\text{rs}}}$  Standardabweichung der experimentellen Bindungslängenbestimmung.

In Tab. 3 sind die Ergebnisse der HMO- $\pi$ -Bindungsordnungen mit den Parametern (4a) und den neuen NO-Bindungsparametern (12) angeführt. Die graphische Darstellung in Abbild. 2 ergibt die Ausgleichsgerade (13)

$$R_{\text{rs}}^{\text{HMO, NO}} [\text{\AA}] = 1.474 - 0.371 \rho_{\text{rs}} \quad (13)$$

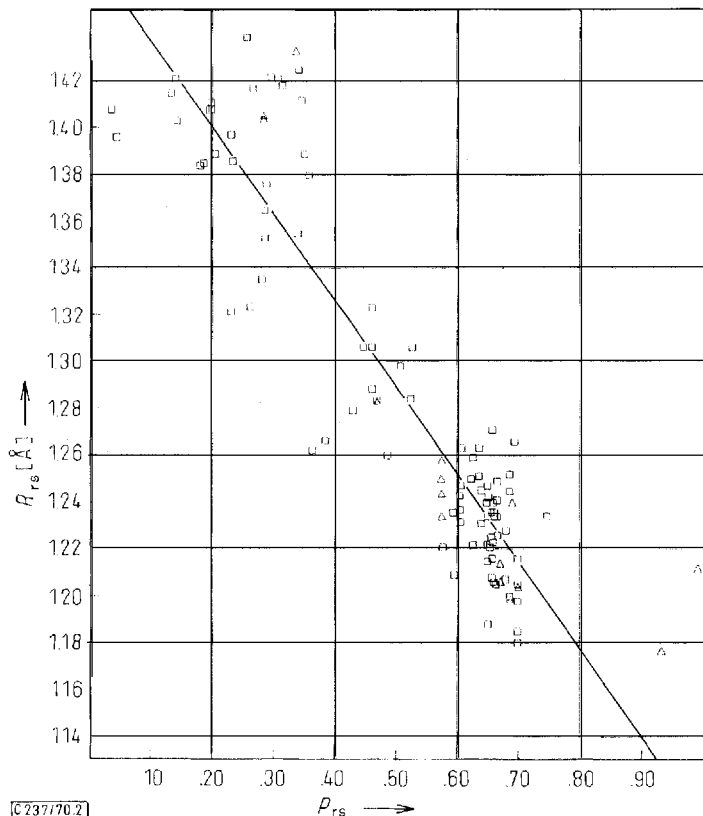
mit einer Standardabweichung von 0.034  $\text{\AA}$  und einem Korrelationskoeffizienten von 0.902 für 159 Werte. Die Berechnung (13) zeigt somit eine wesentliche Verbesserung gegenüber (5), die mit den alten NO-Parametern (4b) berechnet wurde.

Die Ergebnisse der Bestimmung der Bindungsordnung-Bindungslängen-Beziehungen für die anderen  $\pi$ -Bindungen in den NO- $\pi$ -Systemen der Tab. 3 sind in Tab. 9 zusammengestellt.

Tab. 9. HMO- $\pi$ -Bindungsordnung-Bindungslängen-Beziehungen für die  $\pi$ -Bindungen der Verbindungen der Tab. 3

| Bindungstyp                                   | Parametersatz für die HMO-Berechnung | $R_{\text{rs}} [\text{\AA}]$     | $\sigma [\text{\AA}]$ | $k$   | Zahl der Punkte |
|-----------------------------------------------|--------------------------------------|----------------------------------|-----------------------|-------|-----------------|
| CN in NO-                                     | (4)                                  | $1.510 - 0.231 \rho_{\text{rs}}$ | 0.056                 | 0.621 | 114             |
| CN in NO-                                     | (4a) + (12)                          | $1.512 - 0.263 \rho_{\text{rs}}$ | 0.043                 | 0.795 | 114             |
| CN in NO-, NN-, CN-, CO- und CN + CO-Systemen | (4a) + (12)                          | $1.478 - 0.234 \rho_{\text{rs}}$ | 0.030                 | 0.772 | 479             |
| CO in NO-                                     | (4)                                  | $1.432 - 0.259 \rho_{\text{rs}}$ | 0.039                 | 0.821 | 55              |
| CO in NO-                                     | (4a) + (12)                          | $1.424 - 0.252 \rho_{\text{rs}}$ | 0.041                 | 0.801 | 55              |
| CO in NO-, NN-, CN-, CO- und CN + CO-Systemen | (4a) + (12)                          | $1.430 - 0.255 \rho_{\text{rs}}$ | 0.027                 | 0.894 | 296             |
| NN in NO-                                     | (4)                                  | $1.526 - 0.282 \rho_{\text{rs}}$ | 0.045                 | 0.753 | 11              |
| NN in NO-                                     | (4a) + (12)                          | $1.497 - 0.271 \rho_{\text{rs}}$ | 0.028                 | 0.914 | 11              |
| NN in NO + NN-Systemen                        | (4a) + (12)                          | $1.443 - 0.190 \rho_{\text{rs}}$ | 0.027                 | 0.900 | 48              |
| CC in NO-                                     | (4)                                  | $1.538 - 0.234 \rho_{\text{rs}}$ | 0.021                 | 0.800 | 358             |
| CC in NO-                                     | (4a) + (12)                          | $1.572 - 0.285 \rho_{\text{rs}}$ | 0.018                 | 0.867 | 358             |
| CC in reinen CC-Systemen                      |                                      | $1.585 - 0.295 \rho_{\text{rs}}$ | 0.017                 | 0.895 | 137             |

Die neuen NO-Parameter (12) führen jeweils zu einer deutlichen Verbesserung der statistischen Angaben für die Ausgleichsgeraden. Eine Ausnahme bilden nur die CO-Verbindungen, die eine geringfügige Verschlechterung zeigen.



Abbild. 2. HMO- $\pi$ -Bindungsordnung-Bindungslängen-Beziehung (13) für die NO-Bindungen der Tab. 3, berechnet mit den Parametern (4a) und (12). ( $\Delta$  = Verbindungen, die nur NO-Bindungen enthalten)

Bemerkenswert ist die Verschiebung der Ausgleichsgeraden für die CN-Bindungen in NO-Systemen nach großen Bindungslängen. Dies kommt daher, daß die  $=C-\overset{\oplus}{N}$ -Bindungen, z. B. in Nitroverbindungen wegen der Bindungsaufweitung infolge der positiven Formalladung (vgl. Lit.<sup>20)</sup>) extrem lang sind.

Die wenigen Werte für SCF- $\pi$ -Bindungsordnungen der Tab. 3 genügen nicht zur Aufstellung einer Bindungsordnung-Bindungslängen-Beziehung.

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[237/70]