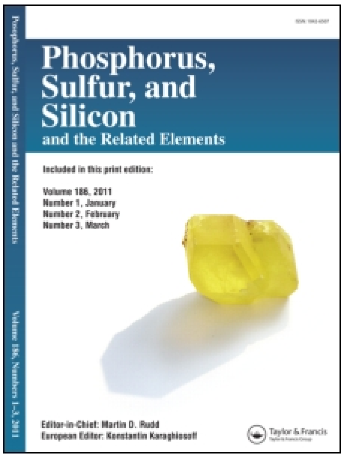


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

BOND LENGTHS AND BOND ORDERS IN π-ELECTRON HETEROCYCLES

Cyril Párkányi[a]; William C. Herndon[a]
[a] Department of Chemistry, The University of Texas at El Paso, El Paso, Texas

To cite this Article Párkányi, Cyril and Herndon, William C.(1978) 'BOND LENGTHS AND BOND ORDERS IN π-ELECTRON HETEROCYCLES', Phosphorus, Sulfur, and Silicon and the Related Elements, 4: 1, 1 — 7
To link to this Article: DOI: 10.1080/03086647808079955
URL: http://dx.doi.org/10.1080/03086647808079955

Phosphorus and Sulfur
1978, Vol. 4, pp. 1–7

BOND LENGTHS AND BOND ORDERS IN π-ELECTRON HETEROCYCLES[1]

CYRIL PÁRKÁNYI and WILLIAM C. HERNDON

Department of Chemistry, The University of Texas at El Paso, El Paso, Texas 79968

(Received May 11, 1977)

A comparison of bond orders calculated by different methods (Pauling, HMO, PPP, SCF–MO) with experimental bond lengths has been made for representative sets of sulfur and nitrogen π-electron heterocycles and statistical treatment of the results has been presented. Bond orders obtained by simple techniques (Pauling, HMO) are equally effective in predicting and correlating bond lengths in these heterocycles as those calculated by more sophisticated methods (PPP, SCF–MO).

Because the bond order is related to the strength of the respective bond, it is related to the bond length as well. The relationship between theoretical π bond orders and experimental bond lengths in unsaturated hydrocarbons is well-known and the agreement between predicted bond lengths in benzenoid hydrocarbons and the corresponding experimental values is usually considered as a support for the concept of a bond order.[2]

A bond order can be defined in several different ways. In a recently published paper,[3] we have compared the actual correlative abilities of the bond orders calculated by different methods and evaluated the results by using statistical techniques. Previous discussions of the relationship between calculated bond orders and experimental bond lengths were limited to qualitative statements regarding accuracy or, at most, only a few experimental bond lengths were compared with the calculated values.

The results of our recent study indicate that Pauling bond orders, HMO bond orders (Coulson), and SCF–MO bond orders are equally effective in predicting and correlating bond lengths in π-electron hydrocarbons.[3]

It is often believed that simple theoretical methods give an unsatisfactory account of many physical and chemical properties of π-electron systems other than alternant hydrocarbons, in particular those containing heteroatoms.[4]

This assumption is not justified, at least not in practice. We have demonstrated in many of our previous papers that simple quantum-chemical methods, such as the HMO method or the empirical structure-resonance theory, work very well for various types of π-electron systems and give results for many properties of unsaturated compounds which are comparable with the results of SCF–MO calculations.

The purpose of the present contribution is to show that, even in the case of π-electron systems with heteroatoms, bond orders calculated by simple methods lead to an equally good agreement with experimental bond lengths as bond orders calculated by more sophisticated methods.

Two groups of heterocyclic systems were selected for this study, viz., sulfur heterocycles and pyridine-like nitrogen heterocycles. Both groups are the heterocyclic analogs of the corresponding π-electron hydrocarbons, with sulfur atoms replacing a –CH=CH– group in the parent hydrocarbon and contributing two π electrons into the π-electron system, whereas an sp^2-hybridized nitrogen atom replaces a CH group in nitrogen heterocycles and contributes just one π electron into the delocalized system.

The bond orders used in the study are Pauling bond orders, Coulson HMO bond orders, PPP (SCF–MO) bond orders, and Dewar's SPO and SCF–MO bond orders.

DEFINITIONS OF BOND ORDER AND CALCULATIONS

Pauling bond orders. According to Pauling, the bond order is defined as the ratio of Kekulé structures in which a particular bond is double (ND) to the total number of possible Kekulé structures (SC).[5]

$$p_{rs}^{P} = \mathrm{ND}/\mathrm{SC} \qquad (1)$$

These bond orders can be determined from simple drawings of the molecular graph. Various methods of obtaining bond orders and structure counts (SC) are summarized in several recently published articles.[6-9]

Pauling bond orders used for the pyridine-like azaheterocycles are the same as those for the corresponding benzenoid hydrocarbons and were taken from one of our previous publications.[8]

HMO bond orders. Coulson defined the bond order in terms of the HMO method by Eq. (2).[10]

$$p_{rs}^{C} = \sum n_j c_{jr} c_{js} \qquad (2)$$

The sum is over j occupied MO's, n_j is the number of electrons in the j-th MO, and the coefficients of the bonded atoms are c_{jr} and c_{js}.

To calculate the HMO (Coulson) bond orders, models of the heterocycles were treated by the simple HMO method using a standard program. The calculations were performed on an IBM 360/50 computer. In the case of sulfur heterocycles, the model neglecting the participation of the d orbitals of sulfur in conjugation was employed.[11] The following parameters were used.[12,13]

$$\alpha_S = \alpha + \beta \qquad \beta_{CS} = 0.7\,\beta$$

$$\alpha_N = \alpha + 0.5\,\beta \qquad \beta_{CN} = \beta$$

$$\beta_{NN} = \beta$$

In the above expressions, α stands for the Coulomb integral of the carbon $2p_z$ orbital, β is the resonance integral of the C–C bond in benzene, and α_X and β_{CX} are the corresponding quantities for the heteroatom X and the C–X bond, respectively.[14]

Bond orders for most of the nitrogen heterocycles were taken from a previously published paper.[13]

PPP bond orders. Bond orders in various semiempirical methods (Pariser–Parr–Pople, PPP,[15,16] CNDO/2,[17-19] MINDO[20-22]) are calculated according to Eq. (2) and thus the interpretation of an SCF bond order is analogous to that of the Coulson HMO bond order.

In the PPP treatment, the usual version of the method was used.[23] Interactions between monoexcited configurations formed by promotion of one electron from one of the four highest occupied MO's to one of the four lowest vacant MO's were considered. The systems studied were assumed to be planar and to have idealized geometry. All C-C, C-N, and C-S bond lengths were assumed to be 1.40 Å. The rings were taken as regular pentagons, hexagons, and heptagons. SCF MO's served as the basis for CI calculations. Only resonance integrals between nearest neighbors were considered. No participation of the sulfur d orbitals in conjugation was assumed. The following parameters were used (values in eV).[12,24]

Atom, r	I_r	A_r	γ_{rr}	Z_r	β_{C-r}
C	11.22	0.69	10.53	1	−2.318
S	20.27	10.47	9.80	2	−1.623
N	14.10	1.80	12.30	1	−2.318[a]

[a] $\beta_{N-N} = -2.318$ eV.

I_r and A_r are the ionization potential and electron affinity of atom r in the atomic valence state, respectively. The monocentric repulsion integrals and core integrals between nearest neighbors are represented by γ_{rr} and β_{C-r}, respectively, and Z_r is the core charge at atom r. The bicentric electronic repulsion integrals have been calculated using the Mataga-Nishimoto formula.[25]

$$\gamma_{rs} = \frac{14.399}{R_{rs} + 1.328}\ \text{eV},$$

where R_{rs} (Å) is the distance between atoms r and s.

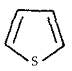
The calculations were performed on an IBM 360/50 computer.[14]

Other bond orders. The SCF-MO bond orders for the sulfur heterocycles and the SPO bond orders for the nitrogen heterocycles also used in our correlations are those calculated by Dewar and co-workers.[4,26]

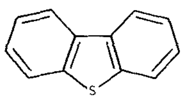
COMPOUNDS AND EXPERIMENTAL BOND LENGTHS

Sulfur and nitrogen π-electron heterocycles for which the experimental bond lengths are known have been chosen for the correlations.

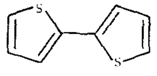
The first group consisted of eleven π-electron sulfur heterocycles, **1-11**, all of which are analogs of alternant



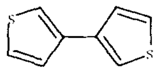
1



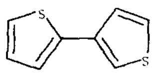
2



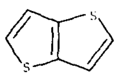
3



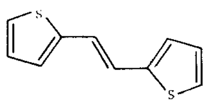
4



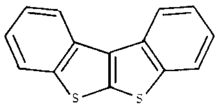
5



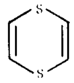
6



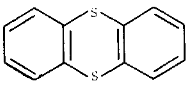
7



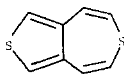
8



9



10



11

hydrocarbons. Their names, the method by which the bond lengths were determined, and the corresponding references are given in Table I.

The second group were pyridine-like nitrogen heterocycles, **12-27**, which are analogs of the corresponding benzenoid hydrocarbons. The information on these heterocycles is summarized in Table II.

Calculated π-bond orders were correlated with the experimental bond lengths using the linear relationship

$$l_{rs} = ap_{rs} + b, \tag{3}$$

where l_{rs} is the experimental bond length (in Å), p_{rs} is the respective bond order, a is the slope and b is the intercept.

RESULTS AND DISCUSSION

The methods commonly used for the determination of the crystal and molecular structure of organic compounds are x-ray diffraction, electron diffraction, neutron diffraction, and microwave spectroscopy. It is important to realize that the experimental bond lengths determined by these techniques are not necessarily the same. The differences are due to the methods themselves. Thus, e.g., neutrons are scattered by atomic nuclei, whereas with x-rays the centers of electronic charge clouds are determined. In the case of benzenoid hydrocarbons, we have established a roughly linear relationship given by Eq. (4).

$$\Delta r(\text{Neutron} - \text{x-ray}) = 0.032\, p^P - 0.007. \tag{4}$$

Another factor which one has to consider is the age of the data—many of the older determinations are not too accurate. Because of the above factors, we have tried to use the best sets of data possible, e.g., the most recent data and practically all of them determined by the same technique—x-ray diffraction. Microwave and electron diffraction data have been employed only in cases where no x-ray diffraction data were available.

Although there have been some previous efforts to correlate calculated bond orders and experimental bond lengths in sulfur heterocycles[24, 26, 56-59] and in nitrogen heterocycles[4, 60] (see also Ref. 61), our study represents the first attempt to systematically correlate representative sets of data for both groups and to compare the results obtained by using bond orders calculated by different methods. Among the previous studies, only Häfelinger has made a similar effort.[58]

The results of the correlations are presented in the form of the corresponding regression lines obtained

TABLE I

Sulfur Heterocycles Used in the Correlations

No.	Compound	Structure, Ref.[a]
1	Thiophene[b]	27
2	Dibenzothiophene	30
3	2,2′-Bithiophene (α,α'-dithienyl)[c]	31
4	3,3′-Bithiophene (β,β'-dithienyl)	31
5	2,3′-Bithiophene (α,β'-dithienyl)	31
6	Thieno[3,2-*b*]thiophene (1,4-thiophthene)	33
7	*trans*-1,2-Bis(2-thienyl)ethylene	34
8	[1]Benzothieno[2,3-*b*][1]benzothiophene	35
9	1,4-Dithiin (1,4-dithiadiene)	36
10	Thianthrene[d]	37
11	Thieno[3,4-*d*]thiepin	39

[a] X-ray diffraction unless stated otherwise.
[b] Electron diffraction. For microwave data, see Refs. 28, 29.
[c] For electron diffraction data, see Ref. 32.
[d] For another set of x-ray diffraction data, see Ref. 38.

TABLE II

Nitrogen Heterocycles Used in the Correlations

No.	Compound	Structure, Ref.[a]
12	Pyridine[b]	40
13	Pyrimidine	41
14	Pyrazine	42
15	*s*-Triazine	43
16	2,2′-Bipyridine	44
17	1,5-Naphthyridine[c]	45
18	1,8-Naphthyridine	47
19	2,6-Naphthyridine	45
20	2,3-Di-*t*-butylquinoxaline	48
21	Pteridine	49
22	Pyridazino[4,5-*d*]pyridazine	50
23	Phenanthridine	51
24	Acridine	52
25	Phenazine	53
26	9,10-Phenanthroline	54
27	Dibenzo[*a,h*]phenazine	55

[a] X-ray diffraction unless stated otherwise.
[b] From microwave spectra.
[c] Cf. also Ref. 46.

TABLE III

π-Bond Order-Bond Length Correlations for Sulfur Heterocycles[a]

l_{rs} (Å) = $ap_{\mathrm{rs}} + b$

No.	Method	n	a	b	d	r
C-C bonds						
1	HMO	41	−0.282	1.575	0.020	0.887
2	PPP	41	−0.243	1.552	0.021	0.879
3	SCF-MO (Dewar)[b]	25	0.818	0.253	0.020	0.874
C-S bonds						
4	HMO	15	−0.334	1.855	0.015	0.878
5	PPP	15	−0.354	1.848	0.015	0.869
6	SCF-MO (Dewar)[b]	10	1.125	−0.227	0.019	0.608

[a] n Number of bonds, a slope, b intercept, d standard error, r correlation coefficient. All data are significant on 1% probability level with the exception of the regression line No. **6.**

[b] In the case of the regression lines **3** and **6**, the linear relationship is expressed as l_{rs} (Å) = al_{rs} (calcd) (Dewar) + b.

by statistical treatment of the data (Tables III and IV). Because of the difficulties in obtaining the Pauling bond orders for sulfur heterocycles, this type of bond orders was not used in the case of sulfur-containing compounds. To conserve space, the actual data are not listed.

It can be seen from Tables III and IV that the correlation coefficients are practically identical in several cases and, in general, are somewhat better for the simplest methods (Pauling and Coulson HMO bond orders). Our conclusions are that the different bond orders compared in the present work are about equally effective in predicting and correlating bond lengths in heterocyclic π-electron systems. Hence, one would also expect the different methods to correlate well with each other and this assumption is correct. Thus, e.g., the correlation coefficients for the C-C bonds in sulfur heterocycles are HMO/SCF (Dewar) 0.958, PPP/SCF (Dewar) 0.965, and HMO/PPP 0.989.

As an example of the agreement between calculated and experimental bond lengths, a comparison is given in Table V for dibenzothiophene (**2**), pyridine (**12**), and acridine (**24**). It can be seen from the data in Table V

TABLE IV

π-Bond Order-Bond Length Correlations for Nitrogen Heterocycles[a]

l_{rs} (Å) = $ap_{\mathrm{rs}} + b$

No.	Method	n	a	b	d	r
C-C bonds						
7	Pauling	71	−0.149	1.467	0.018	0.782
8	HMO	86	−0.263	1.563	0.019	0.744
9	PPP	75	−0.240	1.547	0.018	0.771
10	SPO (Dewar)[b]	32	0.674	0.457	0.025	0.685
C-N bonds						
11	Pauling	34	−0.146	1.410	0.018	0.809
12	HMO	38	−0.314	1.538	0.018	0.790
13	PPP	36	−0.212	1.476	0.020	0.752
14	SPO (Dewar)[b]	12	1.207	−0.279	0.018	0.733

[a] For the explanation of symbols, see Table III. All data are significant on 1% probability level.

[b] In the case of the regression lines **10** and **14**, the linear relationship is expressed as l_{rs} (Å) = al_{rs} (calcd) (Dewar) + b.

TABLE V

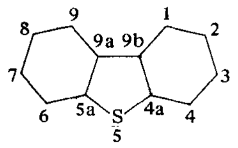
Experimental and Calculated Bond Lengths

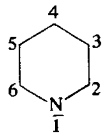
Bond, r–s	Bond length, l_{rs} (Å)[a] Exptl.	Pauling	HMO	PPP	SCF-MO	Dewar[b]
Dibenzothiophene[c] (2)						
1-2	1.370	–	1.381	1.384	1.390	1.390
1-9b	1.392	–	1.404	1.404	1.403	1.406
2-3	1.385	–	1.394	1.396	1.400	1.402
3-4	1.384	–	1.382	1.385	1.391	1.391
4-4a	1.386	–	1.398	1.400	1.401	1.403
4a-5	1.740	–	1.736	1.738	1.733	1.742
4a-9b	1.409	–	1.411	1.405	1.397	1.399
9a-9b	1.441	–	1.458	1.461	1.448	1.461
Pyridine[c] (12)						
1-2	1.338	1.337	1.333	1.337	1.330	1.333
2-3	1.394	1.393	1.387	1.387	1.401	1.401
3-4	1.392	1.393	1.388	1.387	1.398	1.396
Acridine[c] (24)						
1-2	1.356	1.355	1.369	1.364	1.374	1.360
1-9a	1.432	1.430	1.422	1.425	1.433	1.448
2-3	1.427	1.430	1.408	1.412	1.434	1.449
3-4	1.359	1.355	1.370	1.365	1.370	1.355
4-4a	1.427	1.430	1.420	1.424	1.440	1.459
4a-9a	1.432	1.430	1.435	1.427	1.412	1.417
4a-10	1.345	1.337	1.354	1.349	1.334	1.336
8a-9	1.395	1.393	1.404	1.401	1.401	1.401

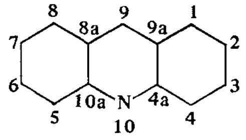
[a] Calculated using the regression lines 1–14 given in Tables III and IV.

[b] These values were calculated directly by the corresponding Dewar's programs.

[c] Numbering:

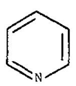




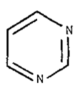


that the predictions of bond lengths based on simple methods are at least as good as those obtained by semiempirical techniques.

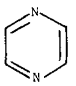
Two more points seem worth mentioning. In the case of nitrogen heterocycles, the bond lengths confirm that at least some bond fixation occurs and that some bonds are more double than other bonds. Thus, e.g., the 1-2 and 3-4 bonds in the benzene ring of acridine (cf. Table V) are "short bonds" and in the usually written Kekulé formula appear as double



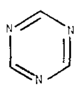
12



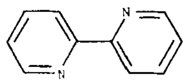
13



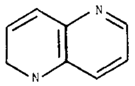
14



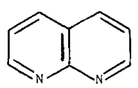
15



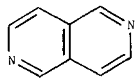
16



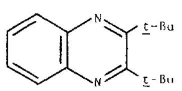
17



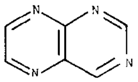
18



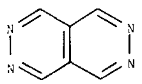
19



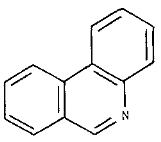
20



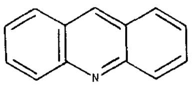
21



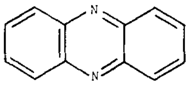
22



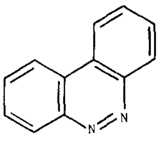
23



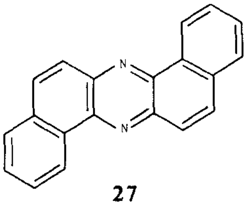
24



25



26



27

bonds. On the other hand, the 1-9a, 2-3, and 4-4a bonds are "long bonds" and are indicated as single bonds in the corresponding Kekulé structure. The C-N bonds in the nitrogen heterocycles participate in this alternation.

All the C-S bond lengths in sulfur heterocycles are long and in the 1.700-1.775 Å range and do not show significant changes with the structure of the respective heterocycles. This would seem to indicate very limited, if any, participation of the sulfur atom in the delocalized π-electron system. Thus, these results suggest that sulfur π-electron heterocycles might be much less aromatic than it is commonly assumed.[62]

ACKNOWLEDGMENT

The financial support of this work by the Robert A. Welch Foundation, Houston, Texas is gratefully acknowledged.

REFERENCES AND NOTES

1. Presented, in part, at the VIIth International Symposium on Organic Sulphur Chemistry, Hamburg, Federal Republic of Germany, July 12-16, 1976 (sulfur heterocycles), and at the 32nd Southwest Regional Meeting, American Chemical Society, Fort Worth, Texas, December 1-3, 1976 (nitrogen heterocycles).
2. A. Streitwieser, Jr., *Molecular Orbital Theory for Organic Chemists* (J. Wiley, New York, N.Y., 1961) p. 165.
3. W. C. Herndon and C. Párkányi, *J. Chem. Educ.* **53**, 689 (1976).
4. M. J. S. Dewar and G. J. Gleicher, *J. Chem. Phys.* **44**, 759 (1966).
5. L. Pauling, L. O. Brockway and J. Y. Beach, *J. Am. Chem. Soc.* **57**, 2705 (1935).
6. W. C. Herndon, *Tetrahedron* **29**, 3 (1973).
7. W. C. Herndon, *J. Chem. Educ.* **51**, 10 (1974).
8. W. C. Herndon, *J. Am. Chem. Soc.* **96**, 7605 (1974).
9. M. Randić, *Croat. Chem. Acta* **47**, 71 (1975); cf. also: M. Randić, *J. Chem. Soc., Faraday Trans. II* **72**, 232 (1976).
10. C. A. Coulson, *Proc. Roy. Soc., Ser. A* **169**, 413 (1939).
11. R. Zahradník, C. Párkányi, V. Horák and J. Koutecký, *Collect. Czech. Chem. Commun.* **28**, 776 (1963).
12. R. Zahradník, I. Tesařová and J. Pancíř, *Collect. Czech. Chem. Commun.* **36**, 2867 (1971).
13. R. Zahradník and C. Párkányi, *Collect. Czech. Chem. Commun.* **30**, 355 (1965).
14. Detailed results of the calculations are available upon request.
15. J. A. Pople, *Trans. Faraday Soc.* **49**, 1375 (1953).
16. R. Pariser and R. G. Parr, *J. Chem. Phys.* **21**, 466, 767 (1963).
17. J. A. Pople, D. P. Santry and G. A. Segal, *J. Chem. Phys., Suppl.* **43**, 5129 (1965).
18. J. A. Pople and G. A. Segal, *J. Chem. Phys.* **43**, 5136 (1965).
19. J. A. Pople and G. A. Segal, *J. Chem. Phys.* **44**, 3289 (1966).
20. N. C. Baird and M. J. S. Dewar, *J. Chem. Phys.* **50**, 1262 (1969).
21. M. J. S. Dewar and E. Haselbach, *J. Am. Chem. Soc.* **92**, 590 (1970).
22. M. J. S. Dewar and D. H. Lo, *J. Am. Chem. Soc.* **94**, 5296 (1972).
23. J. Koutecký, P. Hochman and J. Michl, *J. Chem. Phys.* **40**, 2439 (1964).
24. J. Fabian, A. Mehlhorn and R. Zahradník, *J. Phys. Chem.* **72**, 3975 (1968).
25. N. Mataga and K. Nishimoto, *Z. Physik. Chem. (Frankfurt am Main)* **13**, 140 (1957).
26. M. J. S. Dewar and N. Trinajstić, *J. Am. Chem. Soc.* **92**, 1453 (1970).
27. W. R. Harsbarger and S. H. Bauer, *Acta Crystallogr., Sect. B* **26**, 1010 (1970).
28. B. Bak, D. Christensen, J. Rastrup-Andersen and E. Tannenbaum, *J. Chem. Phys.* **25**, 892 (1956).
29. B. Bak, D. Christensen, L. Hansen-Nygaard and J. Rastrup-Andersen, *J. Mol. Spectr.* **7**, 58 (1961).
30. R. M. Schaffrin and J. Trotter, *J. Chem. Soc. A* 1561 (1970).
31. G. J. Visser, G. J. Heeres, J. Wolters and A. Vos, *Acta Crystallogr., Sect. B* **24**, 467 (1968).
32. A. Almenningen, O. Bastiansen and P. Svendsäs, *Acta Chem. Scand.* **12**, 1671 (1958).
33. E. G. Cox, R. J. J. H. Gilot and G. A. Jeffrey, *Acta Crystallogr.* **2**, 356 (1949).
34. G. Ruban and D. Zobel, *Acta Crystallogr., Sect. B* **31**, 2632 (1975).
35. S. Dayagi, I. Goldberg and U. Shmueli, *Tetrahedron* **26**, 411 (1970).
36. P. A. Howell, R. M. Curtis and W. N. Lipscomb, *Acta Crystallogr.* **7**, 498 (1954).
37. I. Rowe and B. Post, *Acta Crystallogr.* **11**, 372 (1958).
38. H. Lynton and E. G. Cox, *J. Chem. Soc.* 4886 (1956).
39. T. D. Sakore, R. H. Schlessinger and H. M. Sobell, *J. Am. Chem. Soc.* **91**, 3995 (1969).
40. G. O. Sørensen, L. Mahler and N. Rastrup-Andersen, *J. Mol. Struct.* **20**, 119 (1974).
41. P. J. Wheatley, *Acta Crystallogr.* **13**, 80 (1960).
42. P. J. Wheatley, *Acta Crystallogr.* **10**, 182 (1957).
43. P. J. Wheatley, *Acta Crystallogr.* **8**, 224 (1955).
44. L. L. Merritt and E. D. Schroeder, *Acta Crystallogr.* **9**, 801 (1956).
45. M. Brufani, W. Fedeli, G. Giacomello, F. M. Riccieri and A. Vaciago, *Atti. Accad. Naz. Lincei* **40**, 187 (1966).

46. M. Brufani, D. Duranti, G. Giacomello and L. Zambonelli, *Gazz. Chim. Ital.* 91, 287 (1961).
47. A. Clearfield, M. J. Sims and P. Singh, *Acta Crystallogr., Sect. B* 28, 350 (1972).
48. G. J. Visser, A. Vos, A. de Groot and H. Wynberg, *J. Am. Chem. Soc.* 90, 3253 (1968).
49. C. D. Shirrell and D. E. Williams, *J. Chem. Soc., Perkin II* 40 (1975).
50. C. Sabelli, P. Tangocci and P. F. Zanazzi, *Acta Crystallogr., Sect. B* 25, 2231 (1969).
51. P. Roychowdhury, *Acta Crystallogr., Sect. B* 29, 1362 (1973).
52. D. C. Phillips, F. R. Ahmed and W. H. Barnes, *Acta Crystallogr.* 13, 365 (1960).
53. F. L. Hirshfeld and G. M. J. Schmidt, *J. Chem. Phys.* 26, 923 (1957).
54. H. van der Meer, *Acta Crystallogr., Sect. B* 28, 367 (1972).
55. B. Bovio and S. Locchi, *Z. Kristallogr.* 121, 306 (1965).
56. A. Skancke and P. N. Skancke, *Acta Chem. Scand.* 24, 23 (1970).
57. A. Skancke, *Acta Chem. Scand.* 24, 1389 (1970).
58. G. Häfelinger, *Tetrahedron* 27, 1635 (1971), and references therein to previous papers.
59. J. Fabian, in *Sulfur in Organic and Inorganic Chemistry*, A. Senning (M. Dekker, New York, N.Y., 1972), Vol. 3 p. 39, and references therein.
60. R. W. Wagner, P. Hochmann and M. A. El-Bayoumi, *J. Mol. Spectr.* 54, 167 (1975).
61. P. J. Wheatley, in *Physical Methods in Heterocyclic Chemistry*, eds. A. R. Katritzky (Academic Press, New York, N.Y., 1972), Vol. V p. 1 and ff.
62. W. C. Herndon and C. Párkányi, unpublished results.