Tetrahedron Vol 32, pp 2775 to 2781 Pergamon Press 1976. Printed in Great Britain

THE n-ORBITAL SEQUENCE IN 1,3 DIAZAADAMANTANE

ROLF GLEITER* and MICHIO KOBAYASHI
Institut für Organische Chemie der Technischen Hochschule Darmstadt, D-61 Darmstadt, West Germany

and

JOSEF KUTHAN
Department of Organic Chemistry, Institute of Chemical Technology, 16628 Prague 6, CSSR

(*Received in UK* 13 *May* 1976; *Accepted for publication* 27 *May* 1976)

Abstract—The photoelectron spectra of 1,3-diazaadamantane (1) and 1,3-diaza-6-methyleneadamantane (2) have been measured. An analysis of the spectra based on a ZDO model indicates that the ordering of the n-orbitals in 1 is $b_2(n_- - \lambda\sigma)$ above $a_1(n_+ - \lambda\sigma)$. The splitting of b_2 and a_1 in 1 is dominated by the through space interaction. These results are confirmed by semiempirical calculations of the Extended Hückel and MINDO/3 type. An analysis of the PE spectrum of 1,3-diazaadamantanone(6) (5) indicates that in 5 the inductive effect of the CO group is dominant.

THE concept of through bond interaction[1,2] has been quite useful in the interpretation of PE spectra of compounds containing two centers with lone pairs separated by four σ-bonds. Particular interest has been devoted to molecules with rigid geometries.

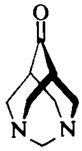
We show in this paper that the sequence of the two highest occupied molecular orbitals in 1,3-diazzaadamantane (1) most likely is b_2 above a_1. For this purpose the PE spectrum of 1,3-diaza-6-methyleneadamantane (2) is compared with the spectra of 1 and 6-methyleneadamantane (4).[3] This comparison is similar to the comparison of the PE spectrum of 1-aza-6-methyleneadamantane (3) with the spectra of 1-azaadamantane (8)[3] and 4. Furthermore, the analysis of the PE spectrum of 1 enables us to correlate the PE spectrum of 1,3-diazaadamantanone(6) (5) with the spectra of 1-azaadamantanone (6)[3] and adamantanone (7).[3]


1


2


3


4


5


6


7


8

The PE spectra of 1 and 2 are shown in Fig. 1 and the relevant data are given in Table 1.

In the interpretation of the PE spectra of 1, 2 and 5 we assume that the molecules have C_{2v} symmetry and we shall make use of Koopmans' theorem[7]

$$-\epsilon_J = I_{vJ} \qquad (1)$$

where ϵ_J is the energy of the molecular orbital from which the electron is ejected.

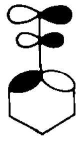
In order to assign the orbital sequence in 1, the main issue of this paper, we apply the symmetry arguments outlined by Heilbronner.[8] If we introduce a π-system at the 6 position in 1 containing either a high lying occupied π-orbital (e.g. a C–C double bond as in 2) or a low lying π*-orbital (e.g. a carbonyl group as in 5) we expect an interaction with the antisymmetric combination of the nitrogen lone pairs. This interaction must be of the through bond type[1,2] since the direct through space interaction is negligibly small.

To evaluate this through bond interaction in 2 we consider explicitly the interaction of the basis orbitals of the nitrogen lone pairs with the π-orbital of the C–C double bond and some C–C σ-orbitals of the adamantane frame. The results are found to be very sensitive to the assignment of the orbital sequence in 1. Furthermore, the predicted levels are in good agreement with the PE spectrum of 2 only when it is assumed that $b_2(n_- - \lambda\sigma)$ lies above $a_1(n_- - \lambda\sigma)$ in 1.

Basis orbital energies of π and σ orbitals. To investigate the interactions between the three basis orbitals (σ, π and *n*) we first must estimate their orbital energies. Semiempirical calculations on 4 predict a considerable interaction between $b_2(\pi)$ and the σ-frame as indicated below for the antibonding linear combination. The inequality of the $2p_\pi$ AO coefficients of the π-bond indicates that $b_2(\pi^*)$ may also take part in this interaction. In our simplified model, however, we will neglect this effect. As basis orbital energy of the $b_2(\pi)$-orbital in 4 we choose

$$A_\pi = -10.5\,\text{eV}, \qquad (2)$$

the ionization potential of ethylene,[9] which incorporates


$b_2(\pi - \lambda\sigma)$

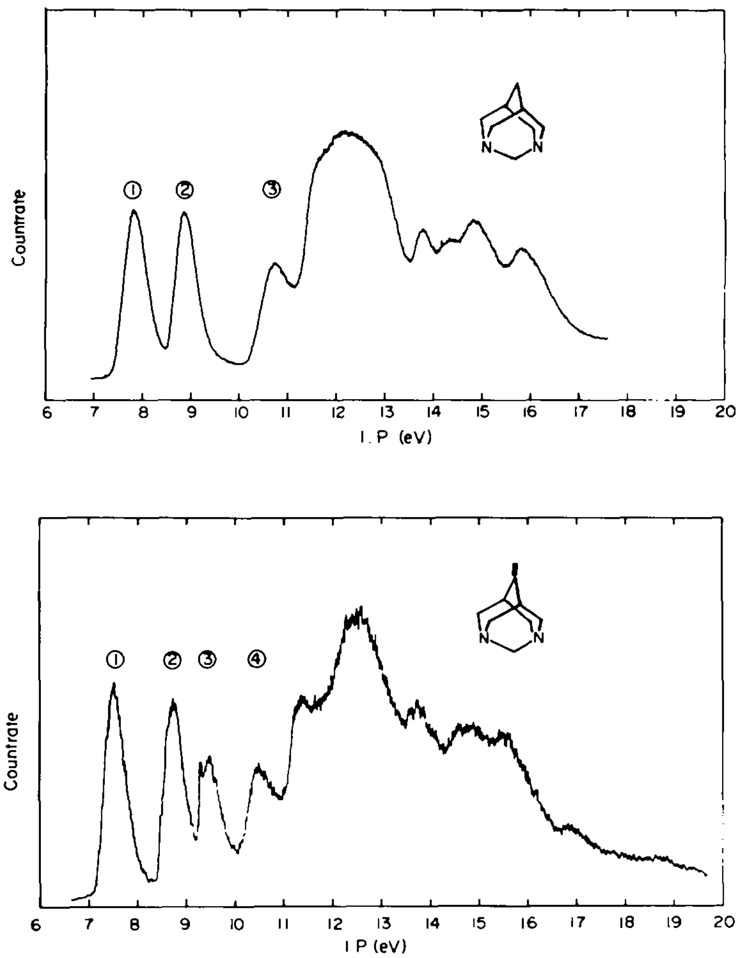


Fig. 1. Photoelectron spectra of **1** and **2**.

Table 1. Comparison between vertical ionization potentials $I_{v,J}$ of **1**, **2** and **5** with orbital energies. All values are given in eV

Compound	band	$I_{v,J}$	assign-ment	EH^4	$MINDO/3^5$	$CNDO/S^6$
1	①	7.75	$b_2(n_-)$	-12.15	-7.95	-10.05
	②	8.78	$a_1(n_+)$	-12.51	-8.77	-10.69
	③	10.66	σ	-13.20	-9.89	-11.69
2	①	7.53	$b_2(n_-)$	-12.04	-7.79	-9.52
	②	8.74	$a_1(n_+)$	-12.52	-8.79	-10.62
	③	9.52	$b_2(\pi)$	-13.08	-9.71	-10.82
	④	10.72	σ	-13.00	-9.70	-11.49
5	①	8.25	$b_2(n_-)$	-12.41	-8.41	-9.88
	②	9.10	$b_1(2p)$	-12.51	-9.18	-10.39
	③	9.25	$a_1(n_+)$	-12.67	-9.18	-11.10
	④	11.68	σ	-13.51	-10.76	-12.68

no hyperconjugation. For the $b_2(\sigma)$ orbital we take from the literature[10]

$$A_\sigma = -14.0\,\text{eV}. \tag{3}$$

This value is less reliable, but a calculation shows that the final results do not depend significantly on the precise energy of this level.

Interaction between π and σ orbitals. Having chosen the basis orbital energies of the $b_2(\pi)$ and $b_2(\sigma)$-orbitals, we can derive the corresponding interaction parameter $B_{\pi,\sigma}$ by adjusting the following secular equation

$$\begin{vmatrix} A_\pi - \epsilon & B_{\pi,\sigma} \\ B_{\pi,\sigma} & A_\sigma - \epsilon \end{vmatrix} = 0 \tag{4}$$

to yield the measured ionization potentials of **4**.

From the PE spectrum of **4** we take

$$\epsilon(b_2(\sigma - \lambda\pi)) = -8.86\,\text{eV}. \tag{5}$$

The second value $\epsilon(b_2(\sigma + \lambda\pi))$ is not available, due to the strong overlap with the bands corresponding to ionization out of σ-orbitals.

Using (2), (3) and (5) the secular eqn (4) yields

$$B_{\pi,\sigma} = -2.90\,\text{eV}. \tag{6}$$

n Orbitals. From the comparison of the PE spectra of bicyclo[2.2.2]octane, 1-azabicyclo[2.2.2]octane and 1,4-diazabicyclo[2.2.2]octane[11] one would expect the successive replacement of two tertiary carbon atoms in adamantane by N atoms to cause an increasing shift of the first σ-band in the PE spectrum towards higher energy.

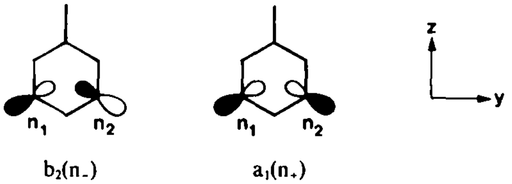
The σ-onset in 1-azaadamantane (**8**) is observed at 10.1 eV.[3] This amounts to a shift of the σ-onset of 0.35 eV since the first band in adamantane is observed at 9.75 eV.[12]

The band at 10.66 eV in **1** is attributed to the first σ-band in line with the comparison made above. In progressing from **8** to **1** we observe an increase of the ionization potential corresponding to the ejection of an electron out of the highest σ-orbital by about the same amount as progressing from adamantane to **8**.

From this discussion it seems reasonable to assign band ① (7.94 eV) of **8** and bands ① and ② (7.75 and 8.78 eV) of **1** to the ejection of an electron out of a nitrogen lone pair or a nitrogen lone pair combination, respectively.

All theoretical results listed in Table 1 predict for **1** the $b_2(n_-)$ linear combination to be above the $a_1(n_-)$ linear combination. This assignment has previously been adopted for the assignment of photolectron[13,14] and electronic[15] spectra on the basis of semiempirical calculations.

In a ZDO model we define the following symmetry adapted linear combinations of the two lone-pairs in **1**

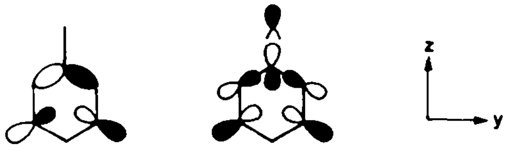


$b_2(n_-)$ $a_1(n_+)$

$$b_2(n_-) = \frac{1}{\sqrt{2}}(n_1 - n_2) \tag{7}$$

$$a_1(n_+) = \frac{1}{\sqrt{2}}(n_1 + n_2) \tag{8}$$

Semiempirical calculations predict a considerable interaction of $b_2(n_-)$ and $a_1(n_+)$ with the σ-frame as indicated below.



$b_2(n_- - \lambda\sigma)$ $a_1(n_+ - \lambda\sigma)$

The observed ionization potentials of bands ① and ② of **1** correspond to ionization out of $b_2(n_- - \lambda\sigma)$ and $a_1(n_+ - \lambda\sigma)$ levels, which are destabilized with respect to the simple lone pair combinations $b_2(n_-)$ and $a_1(n_+)$.

To determine the orbital energy of $b_2(n_-)$, A_{N^-}, we must estimate the interaction parameter for $b_2(n_-)$ and $b_2(\sigma)$, $B_{n,\sigma}$. Since the lone pair on nitrogen in **1** is sp^3 hybridized, the interaction with the C–C σ-frame is small. We therefore expect that $B_{n,\sigma} < B_{\pi,\sigma}$. As will be shown later, the best fit between model calculation and the PE spectrum of **2** is obtained when we adopt

$$B_{n,\sigma} = -1.9\,\text{eV}. \tag{9}$$

This magnitude is in line with our expectation.

The value of A_{N^-} can be derived by substituting $B_{n,\sigma}$ from (9) and the ionization potential corresponding to $\epsilon(n_- - \lambda\sigma)$ in the following secular equation:

$$\begin{vmatrix} A_{N^-} - \epsilon(n \;\; - \lambda\sigma) & B_{n,\sigma} \\ B_{n,\sigma} & A_\sigma - \epsilon(n_- - \lambda\sigma) \end{vmatrix} = 0. \tag{10}$$

Since we don't know yet the sequence of $b_2(n_- - \lambda\sigma)$ and $a_1(n_- - \lambda\sigma)$ in **1** we have the following two possibilities for $(n_- - \lambda\sigma)$:

$$\epsilon(n_- - \lambda\sigma) = \text{I.P. of band ① of } \mathbf{1} = -7.75\,\text{eV} \tag{11}$$

or

$$\epsilon(n_- - \lambda\sigma) = \text{I.P. of band ② of } \mathbf{1} = -8.78\,\text{eV}. \tag{12}$$

Substitution of (3), (9) and (11) into (10) yields

$$A_{N^-} = -8.33\,\text{eV}. \tag{13}$$

Substitution of (3), (9) and (12) into (10) yields

$$A'_{N^-} = -9.47\,\text{eV}. \tag{14}$$

Orbital sequence in **1** *and PE spectrum of* **2**. Having derived the basis orbital energies and interaction parameters, we can predict the ionization energies of **2**. By means of a comparison of the predicted and observed ionization potentials of **2**, it is possible to distinguish between the two possibilities (11) or (12) for the n-orbital sequence in **1**. The basis energies are given in (2), (3) and (13) or (14). The interaction parameters are given in (6) and (9).

With these parameters we investigate the following two cases: Case I: the orbital sequence in **1** is $b_2(n_- - \lambda\sigma)$

above $a_1(n_+ - \lambda\sigma)$. Case II: the orbital sequence in **1** is $a_1(n_+ - \lambda\sigma)$ above $b_2(n_- - \lambda\sigma)$. The secular equation for both cases is:

$$\begin{vmatrix} A_{N-}-\epsilon & 0 & B_{n-,\sigma} \\ 0 & A_{\pi}-\epsilon & B_{\pi,\sigma} \\ B_{n-,\sigma} & B_{\pi,\sigma} & A_{\sigma}-\epsilon \end{vmatrix} = 0. \qquad (15)$$

From this we obtain the following orbital energies:

Case I	Case II
$\epsilon_1 = -7.4\,\text{eV}$	$\epsilon_1 = -8.0\,\text{eV}$
$\epsilon_2 = -9.4\,\text{eV}$	$\epsilon_2 = -9.9\,\text{eV}$
$\epsilon_3 = -16.0\,\text{eV}$	$\epsilon_3 = -16.1\,\text{eV}$.

The first two orbital energies derived for Case I compare well with the measured ionization potentials for **2** ($I_{v,1} = 7.53\,\text{eV}$ and $I_{v,3} = 9.52\,\text{eV}$). This comparison is given in Fig. 2.

The comparison between calculated and experimental results is not at all satisfactory (Fig. 3) for Case II. Even a change in the interaction parameter $B_{n,\sigma}$ would not improve the agreement. We conclude that *the sequence of the symmetry adapted linear combinations of the lone pairs in* **1** *is* $b_2(n_- - \lambda\sigma)$ *above* $a_1(n_+ - \lambda\sigma)$. This means that the ordering of the n_+ and n_- levels is determined by the through space interaction; this is mainly due to the fact that the interaction of $a_1(n_+)$ and $b_2(n_-)$ with the σ-bonds is equally strong as shown in Fig. 4.

In Fig. 5 we have constructed an interaction diagram between the relevant occupied orbitals of **1** (n- and σ-orbitals) and the $b_2(\pi)$ orbital of ethylene to yield the corresponding orbitals of **2**. The energies of the highest occupied orbitals of **1** ($b_2(n_- - \lambda\sigma)$, $a_1(n_+ - \lambda\sigma)$, and $b_2(n_- \lambda\pi)$) and **2** should be compared with the observed levels indicated in Fig. 6, where the first bands in the PE spectra of **1**, **2** and **4** are correlated.

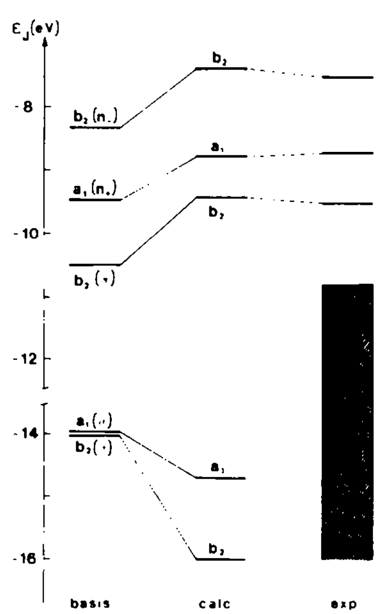


Fig. 2. Comparison between the calculated and experimental orbital sequence for **2** assuming $b_2(n_- - \lambda\sigma)$ above $a_1(n_- - \lambda\sigma)$.

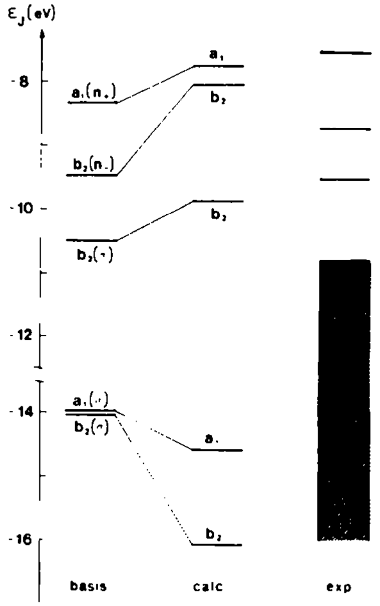


Fig. 3. Comparison between the calculated and experimental orbital sequence for **2** assuming $a_1(n_+ - \lambda\sigma)$ above $b_2(n_- - \lambda\sigma)$.

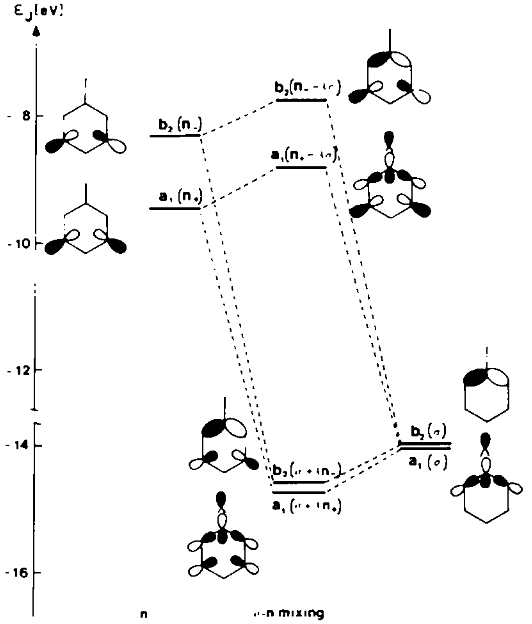
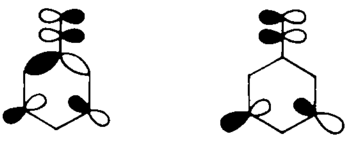


Fig. 4. σ – n interaction diagram for **1**.

Semiempirical calculations of the EH,[4] MINDO/3[5] and CNDO/S[6] type reproduce the correlation diagram of Fig. 5 quite well (see Table 1). Below are shown schematically the wave functions corresponding to the highest and third highest occupied MO's of **2**.



$b_2(n_- - \lambda\sigma - \lambda'\pi)$ $\qquad$ $b_2(\pi - \lambda n_-)$

The $b_2(\pi - \lambda n_-)$ orbital can be described as a mixing of the bonding combination of $b_2(\pi)$ and $b_2(n_- - \lambda\sigma)$ with the antibonding combination of $b_2(\pi)$ and $b_2(\sigma + \lambda n_-)$, as indicated below.

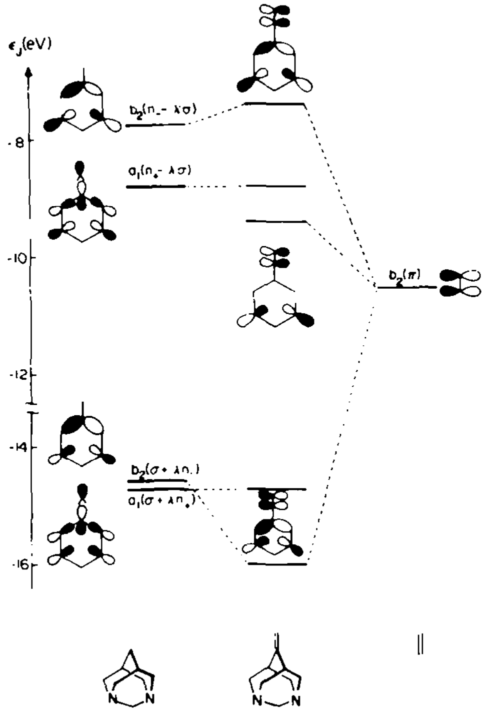
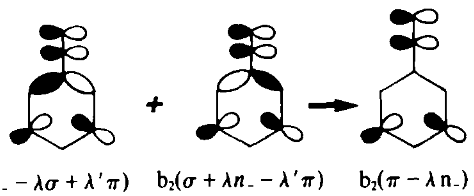


Fig. 5. Interaction diagram between the n and σ orbitals of 1 (see Fig. 4) and the $b_2(\pi)$ orbital of an ethylene unit to yield the corresponding MO's of 2.



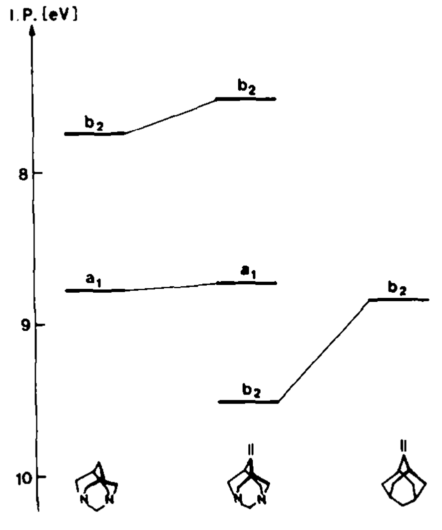


Fig. 6. Correlation between the first PE bands of 1, 2 and 4.

Accordingly we would expect the energy of the $b_2(\pi - \lambda n_-)$ orbital approximately half way between the basis orbital energies of $b_2(\pi)$ and $b_2(n_-)$ in our ZDO model. This expectation is confirmed as seen in Fig. 5.

PE spectrum of 5. Knowing the orbital sequence in 1 and 2 we are able to discuss the PE spectrum of 5.

In the PE spectrum of 5 we find two peaks (Fig. 7) with ionization potentials lower than 10 eV. The second peak we assign to two independent ionization processes (bands ② and ③). This assignment is based on the comparison of the half height widths of the first and second peak and on the assumption that the first peak corresponds to a single ionization process. The calculated results listed in Table 1 predict for the orbital sequence of 5: b_2, b_1 and a_1.

In Figs. 8 and 9 we have shown two possible correlations between the first bands of 5 with those of 1 and 7. The two ionization potentials to the left are due to the ionization from the $b_2(n_- - \lambda\sigma)$ and $a_1(n_+ - \lambda\sigma)$ orbitals of 1 as discussed in the preceding pages. The band to the right is due to an ionization from the 2p lone pair of the oxygen atom of 7.

According to these diagrams there are two interpretations likely for bands ② and ③: Either b_1 is on top of a_1 (Fig. 8) or *vice versa* (Fig. 9).

If we assume that the inductive effect of the CO group on the a_1 combination is the same as on the b_2 combination we derive from Fig. 8 the following parameters:

inductive effect:

$$\Delta I = a_1(n_+ - \lambda\sigma) \text{ of } 1 - a_1(n_+ - \lambda\sigma) \text{ of } 5$$

$$\Delta I = 8.78 - 9.25 = -0.47\ \text{eV}$$

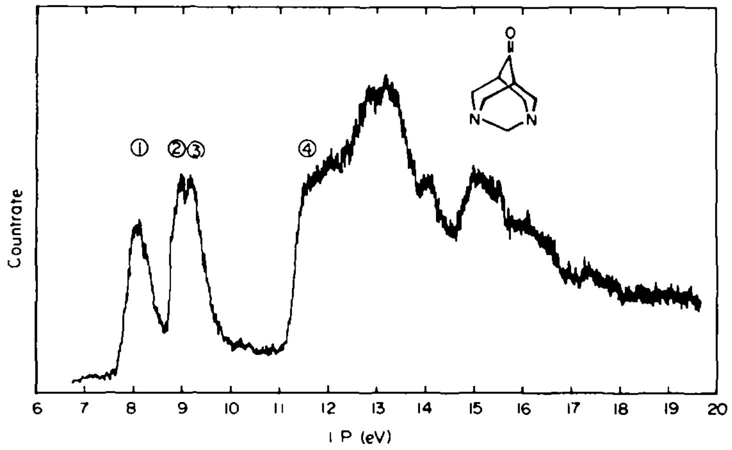


Fig. 7. Photoelectron spectrum of 5.

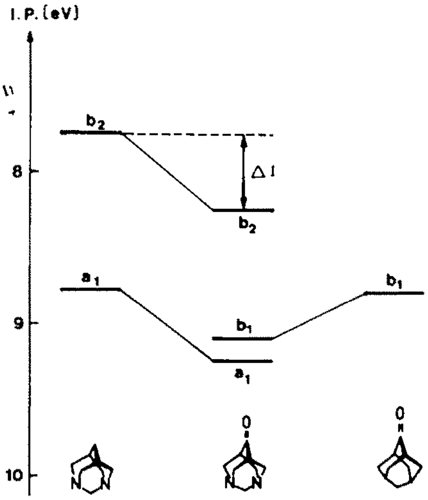


Fig. 8. Possible correlation diagram between the first bands of **1**, **7** and **5** to assess the inductive (ΔI) effect. For the sake of clarity the through bond effect has been neglected.

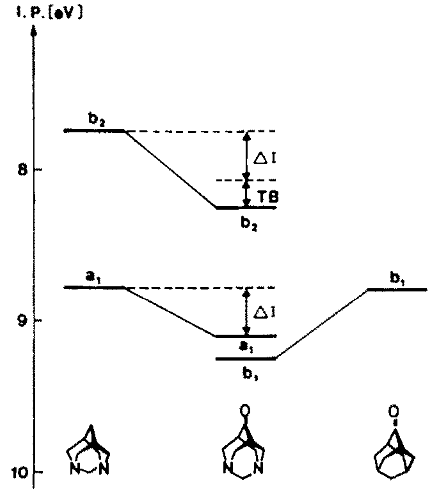


Fig. 9. Possible correlation diagram between the first bands of **1**, **7** and **5** to assess the inductive (ΔI) and through bond (TB) effect.

through bond effect:

$$TB = b_2(n_- - \lambda\sigma) \text{ of } \mathbf{1} - \Delta I - b_2(n_- - \lambda\sigma) \text{ of } \mathbf{5}$$

$$TB = 7.75 + 0.47 - 8.25 = -0.03\,\text{eV}$$

from Fig. 9:

inductive effect:

$$\Delta I = a_1(n_+ - \lambda\sigma) \text{ of } \mathbf{1} - a_1(n_+ - \lambda\sigma) \text{ of } \mathbf{5}$$

$$\Delta I = 8.87 - 9.10 = -0.32\,\text{eV}$$

through bond effect:

$$TB = b_2(n_- - \lambda\sigma) \text{ of } \mathbf{1} - \Delta I - b_2(n_- - \lambda\sigma) \text{ of } \mathbf{5}$$

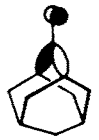
$$TB = 7.75 + 0.32 - 8.25 = -0.18\,\text{eV}$$

Both possible assignments reveal that the inductive effect of the carbonyl group is dominant.

According to the assignment given in Fig. 9 the through bond interaction with $b_2(\pi^*)$ of the carbonyl group is quite sizeable. However, we favour the assignment given in Fig. 8 for the following reasons: The comparison of the ionization potentials in the PE spectra of **6**, **7** and **8** reveals[3] that the band which is due to an ionization out of the b_1 orbital remains constant while the band which is due to the ionization out of the lone pair on the nitrogen is increased in its ionization potential in going from **8** ($I_{V,1} = 7.94$ eV) to **6** ($I_{V,1} = 8.21$ eV) by 0.27 eV.

We expect therefore that the orbital energy of the b_1 lone pair of the oxygen atom does not change very much in going from **6** to **5**. The orbital energies of the lone pair combinations b_2 and a_1 on the other hand should be affected to a larger extent. This in accordance with the assignment given in Fig. 8.

Accepting this assignment we find a stabilization of the orbital energy of the b_1 lone pair by comparing the PE spectra of **7** and **5**. We attribute this to a decrease of the hyperconjugative effect of the σ-orbitals. The orbital energy of the $b_1(\sigma)$ orbital is lowered due to the inductive effect of the N atoms and thus its interaction with the $b_1(2p)$ orbital to yield $b_1(2p - \lambda\sigma)$ indicated below is diminished.



$b_1(2p - \lambda\sigma)$

EXPERIMENTAL

The preparation of compounds **1**, **2** and **5** was reported in previous studies.[15] All compounds used were analytically pure. The PE spectra were recorded on a PS 18 photoelectron spectrometer (Perkin-Elmer Ltd., Beaconsfield, England). The recording conditions were for **1**: 36°, for **2**: 23° and for **5**: 47°. For the EH and MINDO/3 calculations standard bond lengths and angles[16] were used.

Acknowledgements—This work was supported by the Deutsche Forschungsgemeinschaft, Fonds der Chemischen Industrie and by the Otte Röhm Stiftung. We also wish to express our gratitude to Dr. J. Paleček (Institute of Chemical Technology, Prague) for the purification of the studied compounds.

REFERENCES

[1] R. Hoffmann, A. Imamura and W. J. Hehre, *J. Am. Chem. Soc.* **90**, 2499 (1968); R. Hoffmann, *Accounts Chem. Res.* **4**, 1 (1971).
[2] R. Gleiter, *Angew. Chem.* **86**, 770 (1974); *Ibid.* Int. Ed. Engl. **13**, 696 (1974).
[3] C. Worrell, J. W. Verhoeven and W. N. Speckamp, *Tetrahedron* **30**, 3525 (1974).
[4] R. Hoffmann, *J. Chem. Phys.* **39**, 1397 (1963); R. Hoffmann and W. N. Lipscomb, *Ibid.* **36**, 2179, 3489 (1962); **37**, 2872 (1962).
[5] R. Bingham, M. J. S. Dewar and D. H. Lo, *J. Am. Chem. Soc.* **97**, 1285 (1975).
[6] J. DelBene and H. H. Jaffé, *J. Chem. Phys.* **48**, 1807 (1968); H. H. Jaffé, *Accounts Chem. Res.* **2**, 136 (1969).
[7] T. Koopmans, *Physica* **1**, 104 (1934).
[8] E. Heilbronner, *Israel J. of Chem.* **10**, 143 (1972); E. Heilbronner and H. D. Martin, *Helv. Chim. Acta* **55**, 1490 (1972).
[9] D. W. Turner, C. Baker, A. D. Baker and C. R. Brundle, *Molecular Photoelectron Spectroscopy*. Wiley-Interscience, New York (1970).
[10] E. Heilbronner and J. P. Maier, *Helv. Chim. Acta* **57**, 151 (1974); R. Gleiter, *Tetrahedron Letters* 4453 (1969).
[11] P. A. Bischof, J. A. Hashmall, E. Heilbronner and V. Hornung, *Ibid.* 4025 (1969).

[12] N. Bodor, M. J. S. Dewar and S. D. Worley, *J. Am. Chem. Soc.* **92**, 19 (1970); R. Boschi, W. Schmidt, R. J. Suffolk, B. T. Wilkins, H. J. Lempka and J. N. A. Ridyard, *J. Electron Spectroscopy* 2, 373 (1973); S. D. Worley, G. D. Mateescu, C. W. McFarland, R. C. Fort and C. F. Sheley, *J. Am. Chem. Soc.* **95**, 7580 (1973); L. L. Miller, V. R. Kock, T. Koenig and M. Mittle, *Ibid.* **95**, 5076 (1973); and Refs therein.

[13] S. F. Nelsen and J. M. Buschek, *Ibid.* **96**, 7930 (1974).

[14] T. Sasaki, S. Eguchi, T. Kiriyama, Y. Sakito and H. Kato, *J. Chem. Soc.* Chem. Comm. 725 (1974).

[15] J. Kuthan, J. Palecek and L. Musil, *Coll. Czech., Chem. Comm.* **38**, 3491 (1973); **39**, 750 (1974).

[16] *Tables of Interatomic Distances and Configuration in Molecules and Ions.* Special Publication No. 18, The Chemical Society, London (1965).