

NITROGEN LONE PAIR INTERACTION IN 1,4-DIAZA-BICYCLO[2.2.2]OCTANE

(DABCO) (1)

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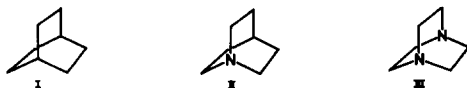
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In a paper concerned with the theoretical investigation of the interaction of orbitals separated by a number of σ -orbitals R. Hoffmann, A. Imamura and W. J. Hehre (2) made the following predictions:

a) The interaction of the nitrogen lone pairs in DABCO (III; symmetry D_{3h}) should manifest itself by a split of 1.573 eV between the orbital energies of the two topmost occupied orbitals $\epsilon(\mathbf{a}'_1) = -11.849$ eV and $\epsilon(\mathbf{a}''_2) = -13.422$ eV.

b) The mean of $\epsilon(\mathbf{a}'_1)$ and $\epsilon(\mathbf{a}''_2)$ ($1/2(\epsilon(\mathbf{a}'_1) + \epsilon(\mathbf{a}''_2)) = -12.636$ eV) should be lower than the orbital energy of the highest occupied orbital \mathbf{a}_1 of quinuclidine (II; symmetry C_{3v}) which occurs at $\epsilon(\mathbf{a}_1) = -12.261$ eV. Hence the splitting of \mathbf{a}'_1 and \mathbf{a}''_2 of III relative to \mathbf{a}_1 of II is not symmetrical, the split ratio being $|-11.849 + 12.261| : |-13.422 + 12.261| = 0.412 : 1.161$ eV or roughly 1 : 3.



Even though the extended Hückel model (3) used by Hoffmann and his coworkers (2) is bound to yield ionization potentials (IP) the absolute values of which may be seriously in error, one might expect their relative values to be representative. We wish to show that this is indeed the case in the particular example under discussion.

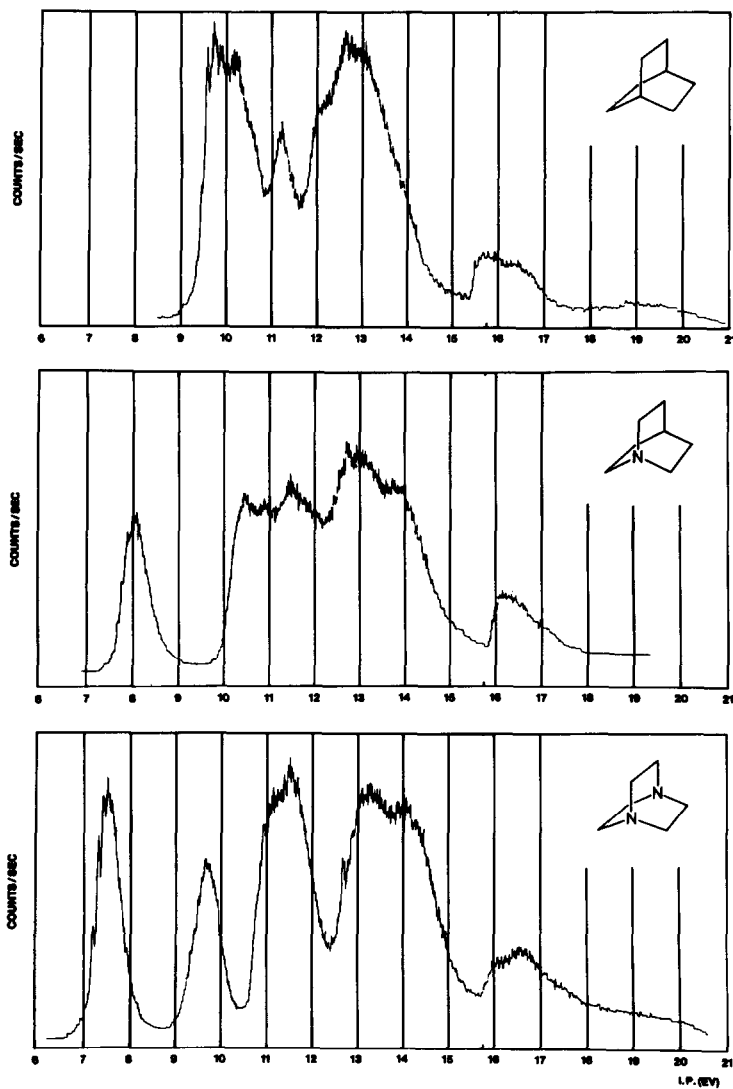


Figure 1. Photoelectron spectra of I, II and III. Abscissa: IP in eV. Ordinate: Count rate in arbitrary units. Characteristic IP (in eV) measured at the maxima:

I : 9.71; 11.20; 12.61; 15.77; 18.79 compare with (4)

II : 8.02; 10.45; 11.41; 12.66; 13.70; 16.10

III : 7.52; 9.65; 11.50; 13.26; 14.05; 16.56

In figure 1 are given the photoelectron (PE) spectra of bicyclo[2. 2. 2]octane (I) (4), quinuclidine (II) and DABCO (III). The relevant data are summarized in the legend. The spectra were recorded on a modified Perkin-Elmer photoelectron-spectrometer of the type described by D. W. Turner (5) ($\pi/\sqrt{2}$ electrostatic energy analyser; excitation by photons from the 584 Å He resonance line.)

In qualitative and quantitative agreement with the results obtained by M. I. Al-Joboury and D. W. Turner (6), successive replacement of the two tertiary carbon atoms 1 and 4 of I by nitrogen atoms results in a shift of the first σ -band in the PE spectrum towards higher ionization potentials: $\Delta IP(\sigma) = 0.65$ eV in II, $\Delta IP(\sigma) = 1.4$ eV in III measured at the first observed fine structure maximum (f. o. f. s. m.) which may be taken as an approximation for the adiabatic IP. Therefore the band observed at 8 eV in the PE spectrum of II and the two bands at 7.5 eV and 9.5 eV in that of III must correspond to the ionization of the nitrogen lone pairs, or more precisely to the ionization of electrons from orbitals strongly localized on these lone pairs. These are the orbitals a_1 of II and a_1' , a_2'' of III (2). (From the calculations reported in ref. (2) one concludes that an electron in orbital a_1' of III contributes 0.58 of its charge to the electron population of the two nitrogen atoms and only 0.42 to that of the six carbon and the twelve hydrogen atoms.)

a) Assuming the validity of Koopman's theorem we deduce from the PE spectrum of III that the split between the two top occupied orbitals in DABCO is 2.11 eV (f. o. f. s. m.) or 2.13 eV (measured at the maxima). This value compares favorably with the predicted value of 1.57 eV.

b) The mean of the first two IP of III, namely $(7.23 + 9.34)/2 = 8.29$ (f. o. f. s. m.) and $(7.52 + 9.65)/2 = 8.59$ (maximum) is indeed higher than the corresponding first IP of II i. e. 7.69 eV and 8.02 eV respectively. Therefore the splits of the first two IP of III relative to the first IP of II are - 0.46 and + 1.65 eV (f. o. f. s. m.) or - 0.50 and + 1.63 eV (maximum). Their ratio is practically 1 : 3 in perfect agreement with the prediction.

To conclude we would like to add the following comments:

1) The theoretical model used by Hoffmann, Imamura and Hehre (2) considers only

electron delocalization as a mechanism for lone pair interaction, either direct N...N delocalization or via the three C - C σ -bonds. Even though the agreement of the predictions so obtained with the experimental data is excellent, it should be borne in mind that a model taking electron-electron repulsion explicitly into account may yield similarly good results, but may also interchange the two top occupied orbitals a_1' and a_2'' of III. It is therefore not possible at this stage to assign the first band in the PE spectrum of III uniquely to ionization from a_1' .

2) The first two bands in the spectrum of III show a vibrational pattern with a regular spacing of 0.093 eV and 0.082 eV respectively.

3) For comparison it should be mentioned that the lone pair interaction in cyanogen ($N\equiv C - C\equiv N$) amounts to 0.37 eV (7), in ethylene diamine ($H_2N-CH_2CH_2 - NH_2$) to roughly 0.5 eV (8) while that in piperazine ($C_4H_8N_2$) is about zero (8).

A detailed discussion will be published in *Helvetica Chimica Acta*.

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References

- (1) Part III of "Applications of Photoelectron Spectroscopy". Part II see ref. (4).
- (2) R. Hoffmann, A. Imamura and W. J. Hehre, *J. Amer. Chem. Soc.* 90, 1499 (1968).
- (3) R. Hoffmann, *J. Chem. Phys.* 39, 1397 (1963); 40, 2745, 2474, 2480 (1964); *Tetrahedron* 22, 521, 539 (1966).
- (4) P. Bischof, J. A. Hashmall, E. Heilbronner and V. Hornung, *Helv. Chim. Acta*, in print.
- (5) D. W. Turner, *Proc. Roy. Soc. A*, 307, 15 (1968).
- (6) M. I. Al-Joboury and D. W. Turner, *J. Chem. Soc. (London)* 1964, 4434.
- (7) C. Baker and D. W. Turner, private communication.
- (8) P. Bischof, J. A. Hashmall, E. Heilbronner and V. Hornung, unpublished results.