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Interaction between Lone Pair Electrons on the Nitrogen Atoms in 1,5-Diazabicyclo[3.2.1]octane

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In the course of our studies on the electronic spectra of amines,[1-3] we have been interested in the intramolecular interaction between the nitrogen lone pairs. Hoffmann *et al.*[4] made a theoretical study on the interaction of two orbitals (n_1 and n_2) separated by a number of intervening σ bonds. They showed that the interaction should be dependent only on the orientation of the σ bonds between the orbital lobes in question and the orientation of the lobes themselves, but not on the specific molecule. By extended Hückel calculations, they predicted, for example, that in arrangement (a) of Fig. 1, the antisymmetric (n_1-n_2) level should be

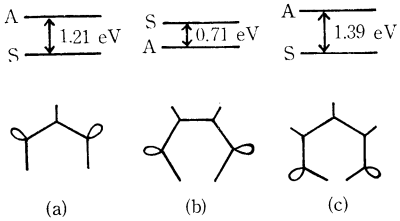
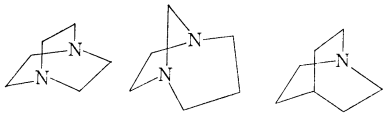


Fig. 1. Interaction patterns in some model arrangements of orbital lobes (n_1 and n_2) and intervening σ bonds, as given by Hoffmann *et al.*[4] The amount of splitting of the S (symmetric, n_1+n_2) and A (antisymmetric, n_1-n_2) levels is given in eV for each model arrangement.

higher by 1.21 eV than the symmetric (n_1+n_2) level, while in arrangement (b) the symmetric level should be higher by 0.71 eV than the antisymmetric level. Therefore, for 1,4-diazabicyclo[2.2.2]octane (I), a splitting of some 2.1 eV ($\fallingdotseq 0.71\times 3$) is expected between the two levels of the lone pair electrons. This was



(I) (II) (III)

shown to be the case by Bischof *et al.*[5] They found in the photoelectron spectrum of I two bands at 7.5 and 9.5 eV which are assignable to the ionizations of electrons from two orbitals strongly localized on the nitrogen lone pairs. The assignment was also supported by Dewar and Wasson[6] by the use of a semiempirical SCF MO procedure (MINDO/2).

We now report here the result of our similar examination on 1,5-diazabicyclo[3.2.1]octane (II), in which two nitrogen atoms are connected by three σ-bond-bridges corresponding to arrangements (a), (b), and (c) in Fig. 1 (instead of three type-(b) bridges in I). On the basis of the study of Hoffmann and his collaborators,[4] the amount of splitting should be somewhat smaller in II than in I, and the ordering of the symmetric and antisymmetric levels should be reversed. In Fig. 2, are given the photoelectron spectra of I and II observed in their gaseous states. To help the assignments of the observed peaks, we have made a semiempirical SCF MO (MINDO/2) calculation for quinuclidine (III), as well as for I and II. In the calculation for III, the orbital energy of an MO in which the nitrogen lone pair has the greatest contribution came out to be -8.64 eV, and this is in agreement with the position of the observed peak (8.02 eV) in the photoelectron spectrum of III assignable to the lone pair orbital (highest occupied MO).[5] For I and II, the calculated energy values of the MO's in which the main contributions come from the nitrogen lone

1) M. Tsuboi, A. Y. Hirakawa, and H. Kawashima, *J. Mol. Spectrosc.*, **29**, 216 (1969).

2) A. Y. Hirakawa, H. Miyazaki, and M. Tsuboi, This Bulletin, **45**, 757 (1972).

3) Y. Hamada, A. Y. Hirakawa, and M. Tsuboi, *J. Mol. Spectrosc.*, in press.

4) R. Hoffmann, A. Imamura, and W. J. Hehre, *J. Amer. Chem. Soc.*, **90**, 1499 (1968).

5) P. Bischof, J. A. Hashmall, E. Heilbronner, and V. Hornung, *Tetrahedron Lett.*, **1969**, 4025.

6) M. J. S. Dewar and J. S. Wasson, *J. Amer. Chem. Soc.*, **92**, 3506 (1970).

Table 1. Energy levels (eV) of I and II

Orbital	Molecule I Obsd	Molecule I MINDO/2	Molecule II Obsd	Molecule II MINDO/2
A vacant MO	(−2.77)[a]	—	(−2.64)[a]	—
Highest occupied MO	−7.70	− 8.27(S)	−8.24	−8.83(A)
Other lone pair combination	−9.71	−10.17(A)	−8.95	−9.10(S)
(A–S Splitting)	(2.01)	(−1.90)	(0.71)	(+0.27)

a) Obtained by adding the transition energy of the observed absorption band to the orbital energy of the highest occupied MO.

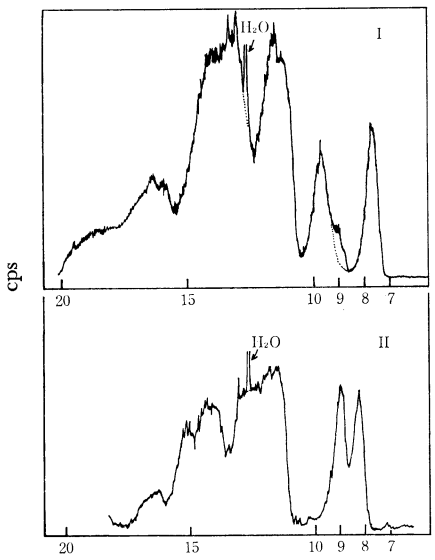


Fig. 2. Photoelectron spectra of I and II. Ordinate is the count rate in arbitrary units. The photoelectron spectrum of I was observed also by Bischof *et al.*,[5] and their result is in a good agreement with ours, shown here. A small peak at 9 eV in the spectrum of I is considered to be caused by an impurity.

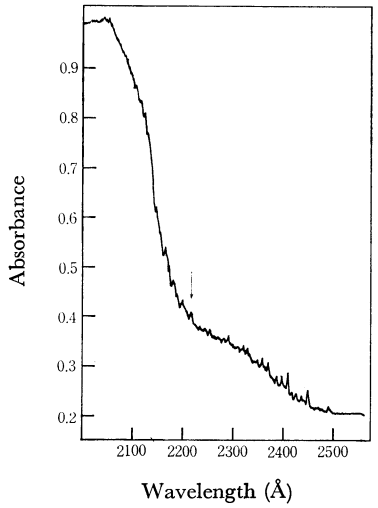


Fig. 3. Ultraviolet absorption spectrum of II in its gaseous state. The arrow indicates a band assigned to 0–0 transition.

pairs are given in Table 1. As may be seen in this table, the calculated values for I are in good agreement with the observed values. In view of such an agreement (both for III and I), we may expect an equally good prediction for our MINDO/2 calculation of the orbital energy in II. Hence, the assignments can be made on the observed peaks in the photoelectron spectrum of II as shown in Table 1. In other words, we may conclude that, assuming the validity of Koopmans' theorem, the two highest occupied MO's of II at −8.24 and −8.95 eV are attributed mostly to the nitrogen lone pairs, the higher one (E_A=−8.24 eV) to the antisymmetric MO (n_1-n_2) and the lower one (E_S=−8.95 eV) to the symmetric MO(n_1+n_2). The amount of splitting (E_A-E_S) due to the lone pair interaction is +0.71 eV. This is somewhat smaller than a simple estimate from the study of "basic coupling units" of Hoffmann *et al.*,[4] but slightly greater than the value estimated by our MINDO/2 procedure.

We like to mention here the result of our ultraviolet absorption measurement of II in its vapor phase. This is shown in Fig. 3. The apparent 0—0 transition of the strong absorption band is found at 2216 Å. By adding this transition energy to the orbital energy of the highest occupied MO (−8.24 eV), the approximate orbital energy of the vacant MO now in question is given as −2.64 eV. By a similar procedure, the corresponding orbital energy is found to be −2.77 eV in I and −2.6 eV in III. It is interesting that this vacant MO is located at almost equal height for all of these molecules (I, II, and III).

Experimental

The sample of 1,5-diazabicyclo[3.2.1]octane (II) was prepared from homopiperazine and formaldehyde by the method of Poppelsdorf.[7] Solvent used was toluene, and the product was purified by a recrystallization and sublimation procedure.

The photoelectron spectra were recorded on a Jasco PE-1 High-resolution Photoelectron Spectrometer. Excitation was made by photons from the 584 Å He resonance line. For calibration of the ionization potential (IP), H_2O (IP, 12.61_6 eV), O_2 (12.07_0), and N_2 (15.57_9) were used as internal standards.

The ultraviolet absorption spectrum was observed by the use of a Hitachi EPS-3T spectrometer with a quartz prism. The calibration was made by the absorption lines of the γ system of nitric oxide in the region from 1955 to 2270 Å.

MINDO/2 Calculation

For I and III, a set of the molecular parameters given by Yokozeki and Kuchitsu[8] (N–C, 1.472 Å;

7) F. Poppelsdorf, U.S. 3120336 (Cl. 260—239).
8) A. Yokozeki and K. Kuchitsu, This Bulletin, **44**, 72 (1971).

C–C, 1.562 Å; C–H, 1.110 Å; ∠NCC, 110.2°; ∠CNC, 108.7°; ∠HCH, 111.5°; angle of twisting ϕ defined by Yokozeki and Kuchitsu, 10°) has been used. For II, the following parameters were used: N–C, 1.472 Å; C–C, 1.562 Å; C–H, 1.110 Å; ∠NCN, 109.7°; ∠CNC, 108.7°; ∠NCC, 110.2°; ∠CCC, 109.7°; ∠HCH, 111.5°, dihedral angle HCCH, 0°. The calculation was made by the use of HITAC 5020E. The SCF procedure was repeated until the change in total electronic energy becomes smaller than 0.0005 eV.