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PHOTOELECTRON SPECTRA OF BISDIMETHYLAMINOCYCLOPROPENONE AND RELATED COMPOUNDS

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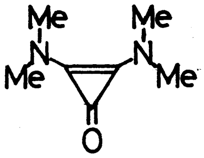
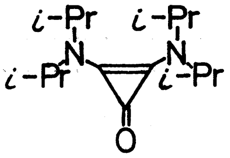
The photoelectron spectra of bisdimethylaminocyclopropenone, bisdiisopropylaminocyclopropenone, and bisdimethylaminocyclopropenethione were measured and interpreted systematically in terms of MO's obtained by the EHMO method, their energies being found to decrease in the following order: $b_1\pi >$ carbonyl or thiocarbonyl $b_2n > a_2\pi > b_1\pi$.

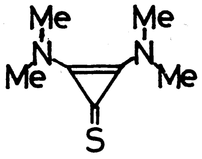
Cyclopropenone is one of the most interesting small ring compounds. This report is concerned with the photoelectron spectra (PES) of cyclopropenone derivatives with electron donating substituents, bisdimethylaminocyclopropenone (I), and bisdiisopropylaminocyclopropenone (II). The PES of bisdimethylaminocyclopropenethione (III) which is isoelectronic to I has also been studied.



I



II



III

Experimental and Calculation

The cyclopropenones, I and II, and the cyclopropenethione, III, were prepared as described in Ref. 1).

The PES of these compounds were measured using the 584 Å He(I) resonance line as excitation source. The details of the measurement were described in a previous paper.$^{2)}$ The sample inlet and target chamber system was heated to 120°C by circulating heated silicon oil.

The geometrical structures of the cyclopropenone, I, and the cyclopropenethione, III, were properly assumed on the basis of the X-ray diffraction data of trisdimethylaminocyclopropenium perchlorate,$^{3)}$ diphenylcyclopropenone,$^{4)}$ and diphenylcyclopropenethione.$^{5)}$ The EHMO$^{6)}$ calculations of these compounds were carried out on a FACOM 230-60 computer at the Institute of Physical and Chemical Research.

Results and Discussion

The PES of I and III, are shown in Fig. 1. The vertical ionization potentials, I_v's, of the compounds, I, II, and III, obtained from the PES are summarized in Table 1 together with those of their related compounds.

The cyclopropenone, I, shows four lower energy bands in the energy region from 7.4 to 10.7 eV. In view of the orbital energies, the dimethylamino lone pair (n) orbital (for example, dimethylamine: 8.9 eV[7]), the ethylenic π orbital (ethylene: 10.51 eV[8]), and the carbonyl n and π orbitals (acetone: 9.72 and 12.6 eV, respectively[8]) may be mainly related with the four lower energy bands of I. In other words, these bands may correspond to the ionization from four orbitals constructed by the interaction among the two n orbitals of the dimethylamino groups, the olefinic π orbitals, and the carbonyl n and π orbitals. Of these orbitals, the only carbonyl n orbital is of the $\bar{\pi}$ type and is expected to be independent of the other orbitals with π character.

The ionization energy of the carbonyl n orbital is 9.72 eV[8] for acetone. Since the carbonyl group is conjugated with a stronger electron donating group in I than in acetone, the band due to the carbonyl n orbital of I may be expected to appear at the lower energy region than 9.72 eV. Therefore, either the 7.43 eV band or the 8.39 eV band of I should be assigned to the carbonyl n orbital. In order to determine which band corresponds to the carbonyl n orbital, we consider the shifts of both bands caused by the replacement of the dimethylamino groups by the diisopropylamino groups. Table 1 shows that the 8.39 eV band is less sensitive to the replacement than the 7.43 eV band. This indicates that the second band is assigned to the n orbital mainly localized on the carbonyl oxygen atom. The fact that this band is rather narrower than the first band also supports this assignment.

TABLE 1. VERTICAL IONIZATION POTENTIALS IN eV

	I_v (eV)			
	1	2	3	4
Cyclopropenone I	7.43	8.39	9.81	10.70
Cyclopropenone II	6.88	8.07	9.15	10.11
Cyclopropenethione III	6.90	7.16	9.15	10.01
Dimethylamine[a]	8.9	12.6	13.3	13.8
Trimethylamine[a]	8.5	12.4	12.9	14.0
Acetone[b]	9.72	12.6	13.4	13.9
Formaldehyde[c]	10.88	14.5	16.0	16.6
Thioformaldehyde[d]	9.34	11.90		
Ethylene[b]	10.51	12.85	14.66	15.87

a) Ref. 7).
b) Ref. 8).
c) Ref. 9).
d) Ref. 10).

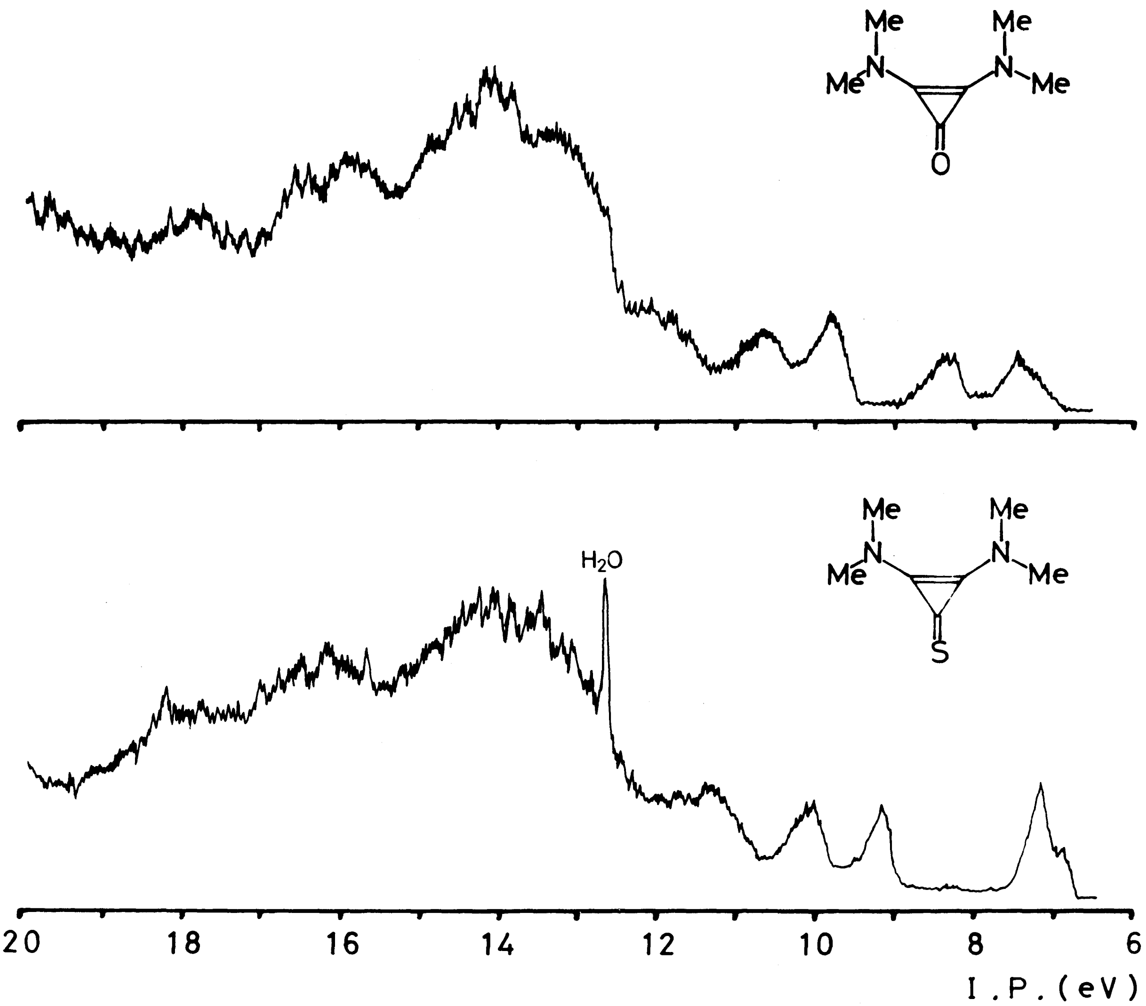


Fig. 1. Photoelectron spectra of bisdimethylaminocyclopropenone and bisdimethylaminocyclopropenethione.

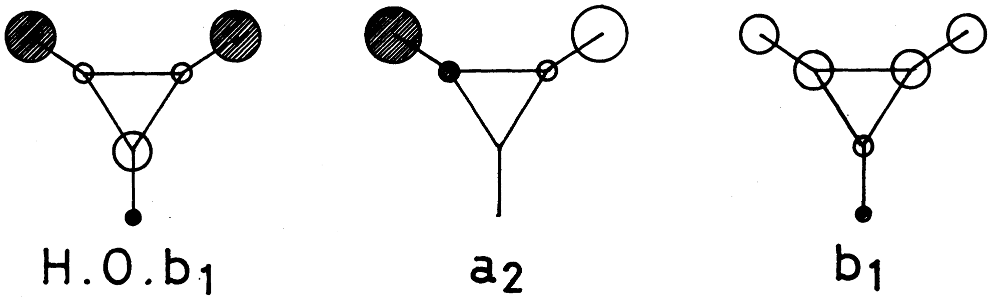


Fig. 2. The higher occupied π orbitals of aminocyclopropenone as C_{2v}.

Next, let us turn to the π molecular orbitals, $b_1\pi$, $a_2\pi$, and $b_1\pi$, constructed from the two dimethylamino n orbitals, the ethylenic π orbital, and the carbonyl π orbital. The EHMO calculation shows that their energies decrease in the following order: $b_1\pi > a_2\pi > b_1\pi$. Here we assume the C_{2v} symmetry for I and these molecular orbitals are schematically shown in Fig. 2.

A similar consideration can be applied to II. Thus, the first, second, third, and fourth bands observed with I and II correspond to the ionization from the $b_1\pi$, carbonyl n (b_2n), $a_2\pi$, and $b_1\pi$ orbitals, respectively.

The ionization energy of the carbonyl n orbital of formaldehyde is 10.88 eV$^{9)}$ and is much larger than that of the thiocarbonyl n orbital of thioformaldehyde (9.34 eV$^{10)}$). This suggests that the ionization energy of the thiocarbonyl n band of the cyclopropenethione, III, should be smaller than that of the carbonyl n band of I. Therefore, in III, as in the case of I, either the first band or the second band should be ascribed to the thiocarbonyl n band. The energy difference between the corresponding bands of I and III are 0.53, 1.23, 0.66, and 0.69 eV for the first, second, third, and fourth bands, respectively. The value for the second band is much greater than those for the other bands which are similar to one another and is close to the energy difference between the first band of formaldehyde and that of thioformaldehyde (1.54 eV). Thus, it may be reasonable to assign the second band of III to the thiocarbonyl n orbital. Sharpness of the band also supports this assignment.

The EHMO calculation predicts that the π-MO's of III decrease their energies in the same order as those of I. Thus, the first, second, third, and fourth bands observed with III correspond to the ionization from $b_1\pi$, thiocarbonyl b_2n, $a_2\pi$, and $b_1\pi$, respectively.

Table 1 shows that the energies of the corresponding π MO's obtained for II and III are almost equal to each other. This means that similar effects are given to the higher occupied π MO's of I by the substitution of isopropyl groups for methyl groups and by the substitution of a thiocarbonyl group for a carbonyl group.

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