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Photoelectron Spectra of Substituted Naphthalenes

Chikatoshi Utsunomiya, Tsunetoshi Kobayashi, and Saburo Nagakura

The Institute for Solid State Physics, The University of Tokyo, Roppongi, Minato, Tokyo 106

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The photoelectron spectra (PES) of 1- and 2-substituted naphthalenes (naphthols, aminonaphthalenes, *N,N*-dimethylaminonaphthalenes, acetylnaphthalenes, and cyanonaphthalenes) were measured in the region from 6 to 20 eV. The observed PES were assigned with the aid of the CNDO/2 calculations and the substituent effect. The lower energy bands of the compounds with the electron-donating group were found to be due to the ionization from the orbitals caused by the interaction of the highest three occupied π orbitals of the naphthalene ring with the nonbonding orbital of the substituent group. The second bands of the 1-substituted naphthalenes are commonly assigned to π orbitals almost completely localized on the naphthalene ring. The dimethylamino group of 1-dimethylaminonaphthalene was found to be twisted to a great extent from the ring plane.

Photoelectron spectroscopy is effective in getting information concerning electronic structures, especially concerning occupied orbitals, of molecules. In the preceding papers,$^{1-4)}$ we have studied the PES of substituted benzenes. In this paper we extend the study to substituted naphthalenes. The PES of substituted naphthalenes have scarcely been studied and a few papers have hitherto been published. For example, Bock and his co-workers$^{5)}$ studied the PES of 1- and 2-methoxy- and 1- and 2-methylthionaphthalenes. Maier$^{6)}$ reported quite recently on the PES of aminonaphthalenes.

Experimental and Calculations

Naphthols, aminonaphthalenes, dimethylaminonaphthalenes, acetylnaphthalenes, and cyanonaphthalenes used in the present study were purified in usual ways and their purities were checked with the aid of NMR spectra. The PES of these compounds were measured as described previously,$^{3)}$ the He I 584 Å resonance line being used as the excitation source and Xe gas as the internal standard for the energy-scale calibration. The CNDO/2$^{7)}$ calculations of these compounds were carried out by a FACOM 230-60 computer at the Institute of Physical and Chemical Research. The geometrical structures of these compounds were assumed on the basis of the data for naphthalene and the corresponding benzene derivatives given in Refs. 8 and 9.

Results and Discussion

Naphthols. The PES of 1-naphthol and 2-naphthol are shown in Fig. 1. The vertical ionization potentials, I_v, of these compounds derived from the observed PES are summarized in Table 1.

As is seen in Fig. 1, naphthols show three lower-energy bands in the region from 7 eV to 10.1 eV. This is the region for the highest three occupied π orbital I_v's of naphthalene.$^{10)}$ Therefore, these bands are reasonably due to the naphthalene π orbitals mixed with the hydroxyl n orbital, the energy of which is -10.96 eV for methanol.$^{11)}$

As is seen in Fig. 1 and Table 1, the I_v's of the first and third bands of 1-naphthol are smaller than the corresponding ones of naphthalene, but the second band I_v's agree with each other for both compounds. This fact demonstrates that the highest occupied π orbital of naphthalene (a_u) and the third one (b_{3g}) interact with the n orbital of the hydroxyl group, while the second one does not because the b_{1g} π orbital of naphthalene has nodes at the α-positions. On the other hand, the first three highest occupied orbital I_v's of 2-naphthol are smaller than the corresponding ones of naphthalene. This is because all the highest three occupied π orbitals of naphthalene have no node at the β-positions and can interact with the n orbital of the hydroxyl group. The CNDO/2 calculations (Fig. 2(b)) also support this conclusion. The orbital energy diagram given by the CNDO/2 method (Fig. 2(b)) qualitatively agrees with the observed one obtained on the assumption of Koopmans' theorem,$^{12)}$ $\varepsilon=-I_v$, (Fig. 2(a)).

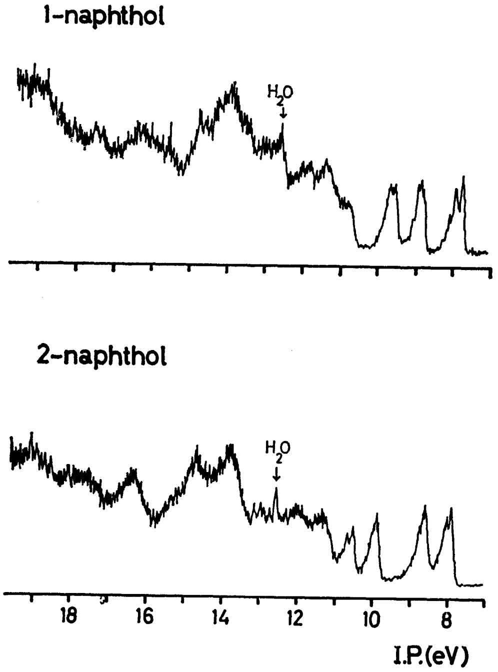


Fig. 1. Photoelectron spectra of naphthols.

Aminonaphthalenes and Dimethylaminonaphthalenes. The PES of 1-aminonaphthalene, 2-aminonaphthalene, 1-dimethylaminonaphthalene, and 2-dimethylaminonaphthalene are shown in Figs. 3 and 4, the I_v's of these compounds being summarized in Table 1. These compounds show four lower-energy bands in the region from 7 eV to 10.5 eV except for 1-dimethylaminonaphthalene; the latter apparently shows only three bands in this region, but the second band consists

Table 1. Vertical ionization potentials ($I_v(J)$ in eV) of substituted naphthalenes

	$I_v(J)$			
J	1	2	3	4
Naphthalene[a)]	8.15	8.88	10.00	10.86
1-Naphthol	7.78	8.89	9.57	
2-Naphthol	7.90	8.63	9.91	10.54
Methanol[b)]	10.96	12.62	15.21	15.64
1-Aminonaphthalene	7.46	8.66	9.26	10.49
2-Aminonaphthalene	7.56	8.32	9.65	10.14
Methylamine[c)]	9.7	13.2	14.5	15.6
1-Dimethylamino-naphthalene	7.59	8.59	8.59	9.88
2-Dimethylamino-naphthalene	7.12	8.13	9.16	9.81
Trimethylamine[c)]	8.5	12.4	12.9	14.0
1-Acetylnaphthalene	8.23	8.99	9.18	10.12
2-Acetylnaphthalene	8.31	9.00	9.21	10.19
Acetone[d)]	9.72	12.6	13.4	13.9
Acetophenone[e)]	9.37	9.55	9.77	11.91
1-Cyanonaphthalene	8.61	9.35	10.31	
2-Cyanonaphthalene	8.64	9.33	10.51	11.18
Acetonitrile[f)]	12.21	13.14		

a) Ref. 10a. b) Ref. 11. c) Ref. 13. d) C. R. Brundle, M. B. Robin, N. A. Kuebler, and H. Basch, *J. Amer. Chem. Soc.*, **94**, 1451 (1972). e) Ref. 4. f) Ref. 15.

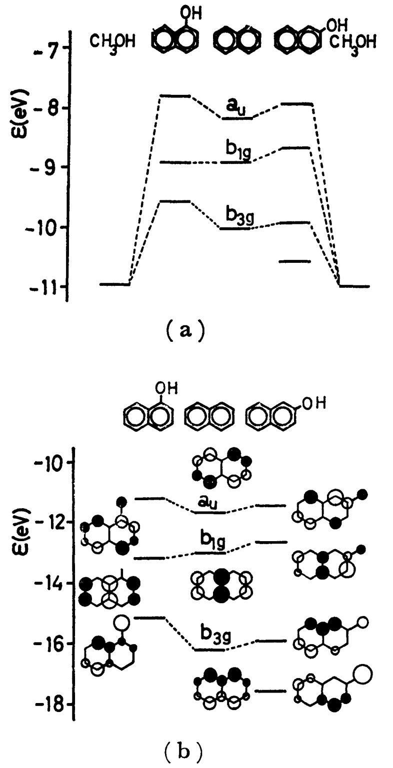


Fig. 2. Orbital energy diagrams for the higher occupied orbitals of naphthols; (a) experimental, (b) calculated.

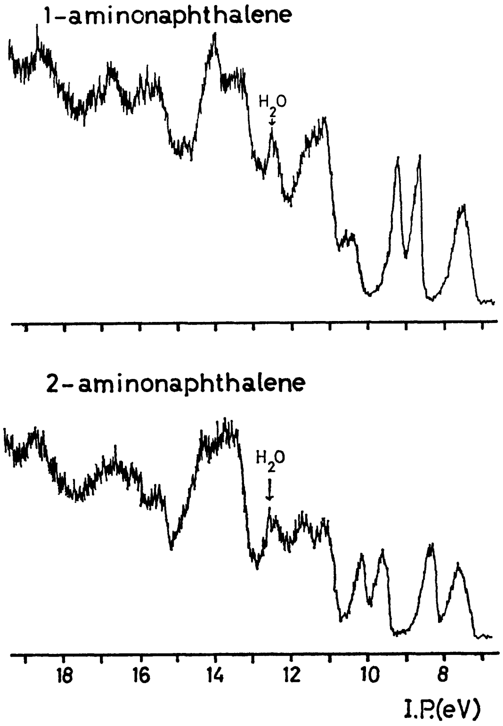


Fig. 3. Photoelectron spectra of aminonaphthalenes.

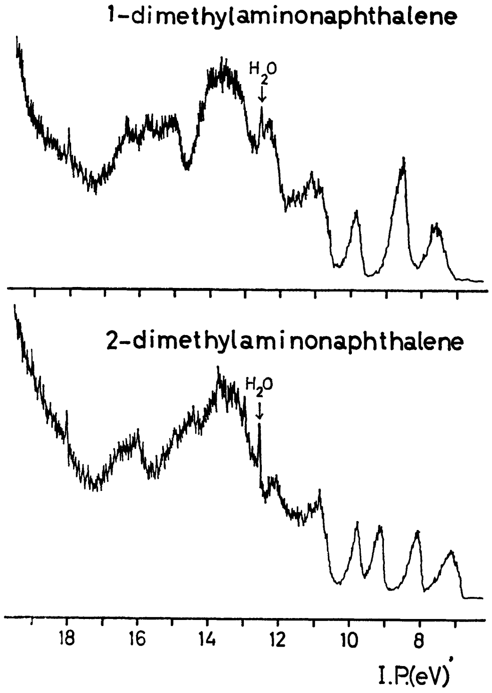


Fig. 4. Photoelectron spectra of dimethylaminonaphthalenes.

of two overlapping bands, judging from its integrated intensity. After all, all of these compounds show four bands in this region. This region includes the first three π bands of naphthalene, the methylamine n band,[13)] and the trimethylamine n band.[13)] Therefore, these bands are regarded as due to the four π orbitals constructed by the interaction between the highest three occupied π orbitals of naphthalene and the n orbital of the amino or dimethylamino group.

The observed orbital energy diagram estimated according to Koopmans' theorem and the calculated

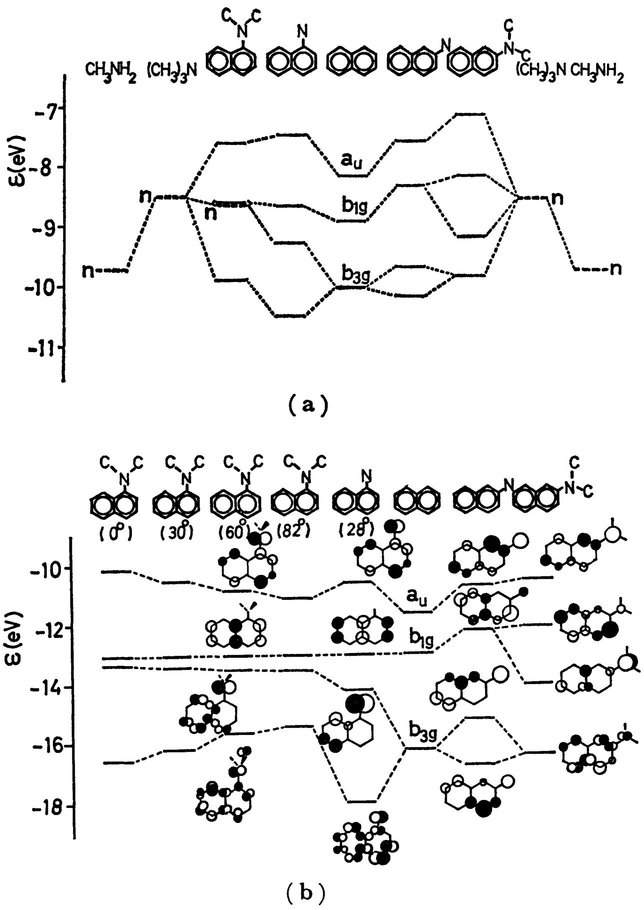


Fig. 5. Orbital energy diagrams for the higher occupied orbitals of aminonaphthalenes and dimethylaminonaphthalenes; (a) experimental, (b) calculated.

orbital energy diagram are shown in Figs. 5(a) and 5(b), respectively. In the calculations, the twist angle of the amino group from the naphthalene ring plane was assumed to be 28° for 1-aminonaphthalene on the basis of the molecular polarizability data.[14] The angle was assumed to be 0° for 2-aminonaphthalene and 2-dimethylaminonaphthalene. As for 1-dimethylaminonaphthalene, the calculations were carried out for the following twist angles of the dimethylamino group: 0°, 30°, 60°, and 82°. The last value, 82°, was estimated from van der Waals' radii.

As is seen in Fig. 5(a), the highest and second highest occupied orbitals of 1-aminonaphthalene and 2-aminonaphthalene are higher in energy than the corresponding first and second ones of naphthalene, respectively, but their fourth orbitals are lower in energy than the third highest π orbital of naphthalene. This indicates that the n orbital of the amino group is located between the second and third highest occupied π orbitals of the naphthalene ring. This is supported by the fact that the methylamine n I_v is 9.7 eV.[13] From the location of the methylamine n orbital, the third bands of 1-aminonaphthalene and 2-aminonaphthalene are due to the ionization from the orbitals which mainly consist of the nitrogen n orbital. This is supported by the fact that the band of 2-aminonaphthalene is more sensitive to *N,N*-dimethylation than the other lower-energy bands and also by the CNDO/2 calculations.

Judging from the fact that the energy of the second highest occupied orbital of 1-aminonaphthalene is scarcely changed by *N,N*-dimethylation, it is concluded that the second highest occupied π orbitals of 1-aminonaphthalene and 1-dimethylaminonaphthalene are almost completely localized on the naphthalene ring. This is supported by the sharpness of these bands and by the CNDO/2 calculations.

The first I_v of 1-aminonaphthalene can be expected to be reduced by *N,N*-dimethylation because of the electronic effect of methyl groups so long as the twist angle of the amino group from the naphthalene plane is not changed by *N,N*-dimethylation. In reality, however, the first I_v of 1-aminonaphthalene is increased by *N,N*-dimethylation. This indicates that the amino group of 1-aminonaphthalene is twisted further by the *N,N*-dimethylation because of the increment in steric hindrance. As is seen in Figs. 5(a) and 5(b), the overall pattern of the observed orbital energy diagram for the higher occupied orbitals of 1-aminonaphthalene, 1-dimethylaminonaphthalene, and naphthalene is qualitatively well reproduced by the result calculated for the 1-dimethylaminonaphthalene model with a twist angle at least of 60°. The total energy calculated by the CNDO/2 method also indicates that the 60° model is more stable than the others. These results suggest that the dimethylamino group of 1-dimethylaminonaphthalene is twisted by about 60°. This is consistent with Maier's result obtained with HMO level model calculations.[6]

According to the CNDO/2 calculations, the third highest occupied orbital of 1-dimethylaminonaphthalene consists mainly of the n orbital of the dimethylamino group. The band due to the ionization from this orbital is expected to appear around 8.5 eV, in view of the fact that the n orbital energy of trimethylamine is 8.5 eV.[13] Therefore, the band corresponds to one of the overlapping bands around 8.59 eV of 1-dimethylaminonaphthalene.

The observed I_v's of 2-aminonaphthalene and 1-dimethylaminonaphthalene agree with those reported by Maier.[6] As for 1-aminonaphthalene, however, our results are rather different from the values reported by him. We repeated the measurements carefully and confirmed our results.

Cyanonaphthalenes. The PES of 1-cyanonaphthalene and 2-cyanonaphthalene are shown in Fig. 6, the I_v's of these compounds being summarized in Table 1. We can see that cyanonaphthalenes show three lower-energy bands in the region from 8 eV to 10.6 eV. The highest three occupied π orbital bands of naphthalene fall in this region, and the first band of acetonitrile appears at 12.21 eV.[15] Therefore, the three lower-energy bands may be ascribed to the highest three occupied π orbitals of naphthalene mixed with the cyano group π orbital. According to Koopmans' theorem, the correlation diagram for these orbitals may be drawn as is shown in Fig. 7(a).

As is seen in Fig. 7(a), the third highest occupied orbital of 2-cyanonaphthalene is lower in energy than the corresponding one of 1-cyanonaphthalene. Since the third highest occupied π orbital of naphthalene has

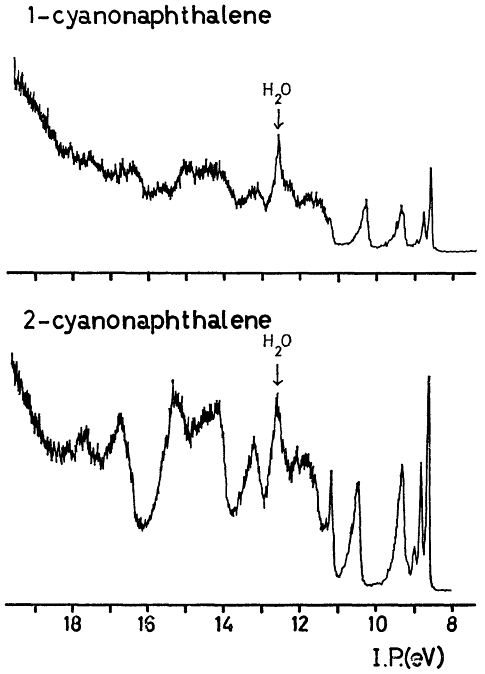


Fig. 6. Photoelectron spectra of cyanonaphthalenes.

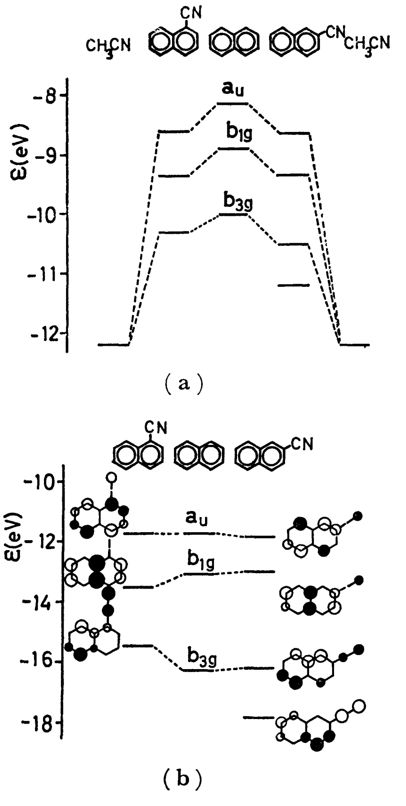


Fig. 7. Orbital energy diagrams for the higher occupied orbitals of cyanonaphthalenes; (a) experimental, (b) calculated.

a larger AO coefficient on carbon atom 1 than on carbon atom 2, this finding can be explained by considering the interaction of the orbital with the occupied π orbital of the cyano group located below. The same tendency was observed for the highest occupied π orbitals of these cyanonaphthalenes. However, the difference between the first I_v's of these compounds is considerably smaller than that between their third I_v's. This may be explained by considering the following two factors. 1) The third highest occupied π orbital of the naphthalene ring interacts more strongly with the occupied π orbital of the cyano group than the highest occupied one does. 2) The energy lowering due to the interaction with the vacant π orbital of the cyano group is more effective in the highest occupied π orbitals of the cyanonaphthalenes than in the third highest occupied ones.

In contrast with the first and third bands, the second band I_v of 2-cyanonaphthalene is smaller, though only slightly, than that of 1-cyanonaphthalene. This is because the second highest occupied π orbital of 1-cyanonaphthalene is almost completely localized on the naphthalene ring, while that of 2-cyanonaphthalene is composed of the naphthalene second highest occupied π orbital mixed with the occupied π orbital of the cyano group, as suggested by the CNDO/2 calculations (Fig. 7(b)).

As is seen in Fig. 7(a), the highest three occupied orbitals of these cyanonaphthalenes are much lower in energy than the corresponding ones of naphthalene. This indicates that the electron-withdrawing effect of the cyano group is very effective.

The fourth sharp band of 2-cyanonaphthalene at 11.18 eV may be ascribed to the fourth highest occupied π orbital constructed by the interaction of the naphthalene ring fourth highest occupied π orbital with the cyano group π orbital.

Acetylnaphthalenes. The PES of 1-acetylnaphthalene and 2-acetylnaphthalene are shown in Fig. 8, and the I_v's of these compounds are summarized in Table 1. Both compounds show three lower-energy bands in the region from 8 eV to 10.2 eV. Their

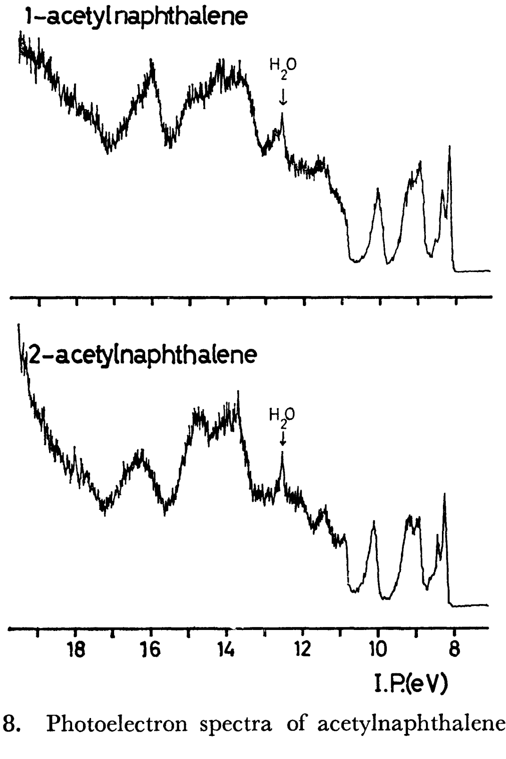
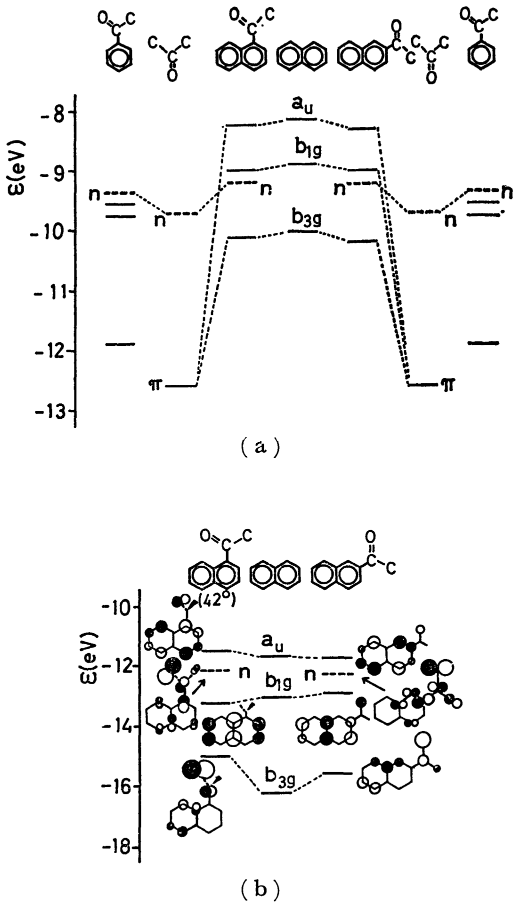


Fig. 8. Photoelectron spectra of acetylnaphthalenes.

second bands seem to consist of two overlapping bands, judging from the integrated intensities. Thus, there are four bands in the region from 8 eV to 10.2 eV for the acetylnaphthalenes. This region is for the first three π bands of naphthalene and the acetyl n orbital band (for example, acetophenone: 9.37 eV[4]). Therefore, the four observed bands may be ascribed to three orbitals caused by the interaction of the highest three occupied π orbitals of the naphthalene ring with the occupied π orbital of the acetyl group and to the acetyl n orbital.

According to the CNDO/2 calculations (Fig. 9(b)), in which the twist angle of the acetyl group was estimated to be 42° for 1-acetylnaphthalene from the polarizability data[16] and was assumed to be 0° for 2-acetylnaphthalene, the occupied orbitals of these compounds are located in the following order, from the top: π, n, π, π, $\cdots$.

First, let us consider the overlapping bands around 9.2 eV of each compound. One of them is assigned to the ionization from the n orbital of the acetyl group in view of the fact that the n orbital I_v of acetophenone is 9.37 eV.[4] According to the CNDO/2 calculations, the second highest occupied π orbital of 1-acetylnaphthalene is the orbital localized mainly on the naphthalene ring; its energy scarcely changes compared with that of naphthalene (−13.04 eV for naphthalene; −13.17 eV for 1-acetylnaphthalene). Therefore, the lower-energy band of the overlapping bands of 1-acetylnaphthalene is assigned to the ionization from this orbital. The second band at 9.00 eV of 2-acetylnaphthalene may also safely be assigned to the second highest occupied π orbital.



(a)

(b)

Fig. 9. Orbital energy diagrams for the higher occupied orbitals of acetylnaphthalenes; (a) experimental, (b) calculated.

The remaining first and fourth bands of acetylnaphthalenes are assigned to the ionization from the orbitals constructed by the interaction mainly between the first and third highest occupied π orbitals of naphthalene and the π orbital of the acetyl group, respectively.

The observed correlation diagram for the orbital energies obtained on the assumption of Koopmans' theorem is shown in Fig. 9(a). The calculated relative ordering of the n and π orbitals of acetylnaphthalenes (Fig. 9(b)) is different from the experimental one (Fig. 9(a)). This discrepancy is often found in the CNDO/2 calculation of closely located n and π orbitals.

References

1) T. Kobayashi and S. Nagakura, *Chem. Lett.*, **1972**, 903.

2) T. Kobayashi and S. Nagakura, *ibid.*, **1972**, 1013.

3) T. Kobayashi, K. Yokota, and S. Nagakura, *J. Electron Spectrosc.*, **2**, 449 (1973).

4) T. Kobayashi and S. Nagakura, This Bulletin, **47**, 2563 (1974).

5) H. Bock, G. Wagner, and J. Kroner, *Chem. Ber.*, **105**, 3850 (1972).

6) J. P. Maier, *Helv. Chim. Acta*, **57**, 994 (1974).

7) J. A. Pople and G. A. Segal, *J. Chem. Phys.*, **44**, 3289 (1966).

8) "Interatomic Distances," Sp. Pub. No. 11, ed. by L. E. Sutton, The Chem. Soc., London (1958).

9) "Interatomic Distances," Sp. Pub. No. 18, ed. by L. E. Sutton, The Chem. Soc., London (1965).

10) a) F. Brogli, E. Heilbronner, and T. Kobayashi, *Helv. Chim. Acta*, **55**, 274 (1972). b) J. H. D. Eland and C. J. Danby, *Z. Naturforsch.*, **23a**, 355 (1968).

11) M. B. Robin and N. A. Kuebler, *J. Electron Spectrosc.*, **1**, 13 (1972).

12) T. Koopmans, *Physica*, **1**, 104 (1934).

13) A. B. Cornford, D. C. Frost, F. G. Herring, and C. A. McDowell, *Can. J. Chem.*, **49**, 1135 (1971).

14) R. J. W. Le Fèvre and A. Sundaram, *J. Chem. Soc.*, **1962**, 4756.

15) D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, "Molecular Photoelectron Spectroscopy," John Wiley & Sons, London (1970), p. 346.

16) P. H. Gore, J. A. Hoskins, C. K. Thadani, R. J. W. Le Fèvre, L. Radom, and G. L. D. Ritchie, *J. Chem. Soc. (B)*, **1969**, 426.