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Photoelectron Spectra of Substituted Benzenes

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Photoelectron spectra were measured in the region between 6 and 21 eV for aniline, *N*,*N*-dimethylaniline, phenol, anisole, benzonitrile, acetophenone, nitrobenzene, and their methyl derivatives. The observed spectra were interpreted in terms of their MO's obtained by the CNDO/2 and EHMO methods, the methyl-substituent effect and the steric hindrance effect being considered. Both effects are essential for the reliable assignment of the observed photoelectron spectra. We found a general tendency that the interaction of the doubly degenerate highest occupied orbitals (e_{1g}) of the benzene ring with the highest occupied orbital of a substituent group is important for the interpretation of the observed lower energy (7～12 eV) bands. The only exceptional case is the nitrobenzenes in which the lowest vacant orbital of the substituent group is rather close to the highest occupied orbitals of the benzene ring and the interaction between them is important. The effects of the substituent groups upon the observed photoelectron spectra are classified into four types.

Photoelectron spectroscopy[1] developed in recent years gives direct information about occupied molecular orbital energies and is expected to be a useful tool to investigate the effect of substituent groups upon the electronic structures of parent hydrocarbons.

We have studied photoelectron spectra (PES) of various kinds of substituted benzenes and have already published the results of styrene and its methyl derivatives.[2] Steric hindrance of the α- or *ortho*-methyl group was found to have great effect on the PES of methyl-substituted styrenes, and the relation between the higher occupied π-orbital energies of styrene and the twist angle of the vinyl group was discussed from both experimental and theoretical points of view. Furthermore, some preliminary reports have been published on the PES of aniline, *N*,*N*-dimethylaniline, nitrobenzene, and their methyl derivatives.[3,4]

In this paper we intend to discuss systematically our results of PES obtained hitherto with substituted benzenes; phenol, anisole, benzonitrile, acetophenone, and their methyl derivatives being newly treated in addition to the molecules studied in the preliminary reports.[3,4] Main purposes of the present study are as follows: 1) to make assignments of lower energy bands in the PES of the substituted benzenes under consideration as reliably as possible, orbital energies calculated by the CNDO and EHMO methods and the effect of methyl-substituent group being considered; 2) to interpret systematically the observed PES in terms of the interaction between substituent groups and the benzene ring; 3) to clarify the correlation between the observed PES and the steric hindrance of methyl-substituent groups.

Baker *et al.*[5] measured the PES of aniline, *N*,*N*-dimethylaniline, *p*-toluidine, *N*,*N*-dimethyl-*p*-toluidine, phenol, and anisole with a relatively low-resolution magnetic deflection type photoelectron spectrometer. Thereafter, several works[6–11] on the PES of some of the compounds studied here have been published. They are discussed in comparison with our results in later parts of this paper.

Experimental and Calculation

2,4-Dimethylanisole and 2,6-dimethylanisole were synthesized according to Ref. 12 and isolated by column chromatography. All the samples were purified in usual ways and their purities were checked with the aid of gas chromatograms and NMR spectra.

The PES of these compounds were recorded on a JASCO model PE-1 photoelectron spectrometer and a newly constructed photoelectron spectrometer[2] with a sample inlet system which can be heated, if necessary, up to *ca.* 140 °C. HeI resonance line of 584 Å was used as excitation source and Xe gas as the internal standard for the calibration.

The CNDO/2[13] and the EHMO[14] calculations of these compounds were carried out by a FACOM 270—30 and a FACOM 230—60 computer at the Institute of Physical and Chemical Research. The geometrical structure of *N*,*N*-dimethylaniline was taken from Ref. 15 and the geometrical structures of the other compounds were taken from Refs. 16 and 17 or assumed based on the data given in these references.

Results and Discussion

Anilines. The PES of aniline, *o*-, *m*-, and *p*-toluidines, *N*,*N*-dimethylaniline, and *N*,*N*-dimethyl-*o*-, *m*-, and *p*-toluidines are shown in Fig. 1. The vertical ionization potentials, $I_v(J)$, of these compounds were obtained from the observed PES and are summarized in Table 1.

As is seen in Fig. 1 and Table 1, these aromatic amines commonly show three lower energy bands in the region from 7 eV to 11 eV. They are assigned to the ionizations from three π MO's, b_1 (like), a_2 (like), and b_1 (like),[3] which are caused by the interaction among the highest occupied doubly degenerate π orbitals, e_{1g}(S) and e_{1g}(A), (9.23 eV) of the ring and the lone pair (n) orbital of the corresponding alkylamine (9.7 eV[18] for methylamine and 8.5 eV[18] for trimethylamine). As is clearly seen in Fig. 2 which shows schematically the orbitals concerned, the first and third highest occupied π MO's are delocalized over both benzene ring and amino nitrogen atom, while the second highest occupied π MO is localized on the benzene ring. This assignment is supported by the fact that the first and third bands of aniline and toluidines shift much more by *N*,*N*-dimethylation than their second bands.

The shifts, $\Delta I_v(J)$ (J=1,2····), of the lowest three vertical ionization potentials of aniline and *N*,*N*-dimethylaniline by *o*-, *m*-, and *p*-methyl substitutions

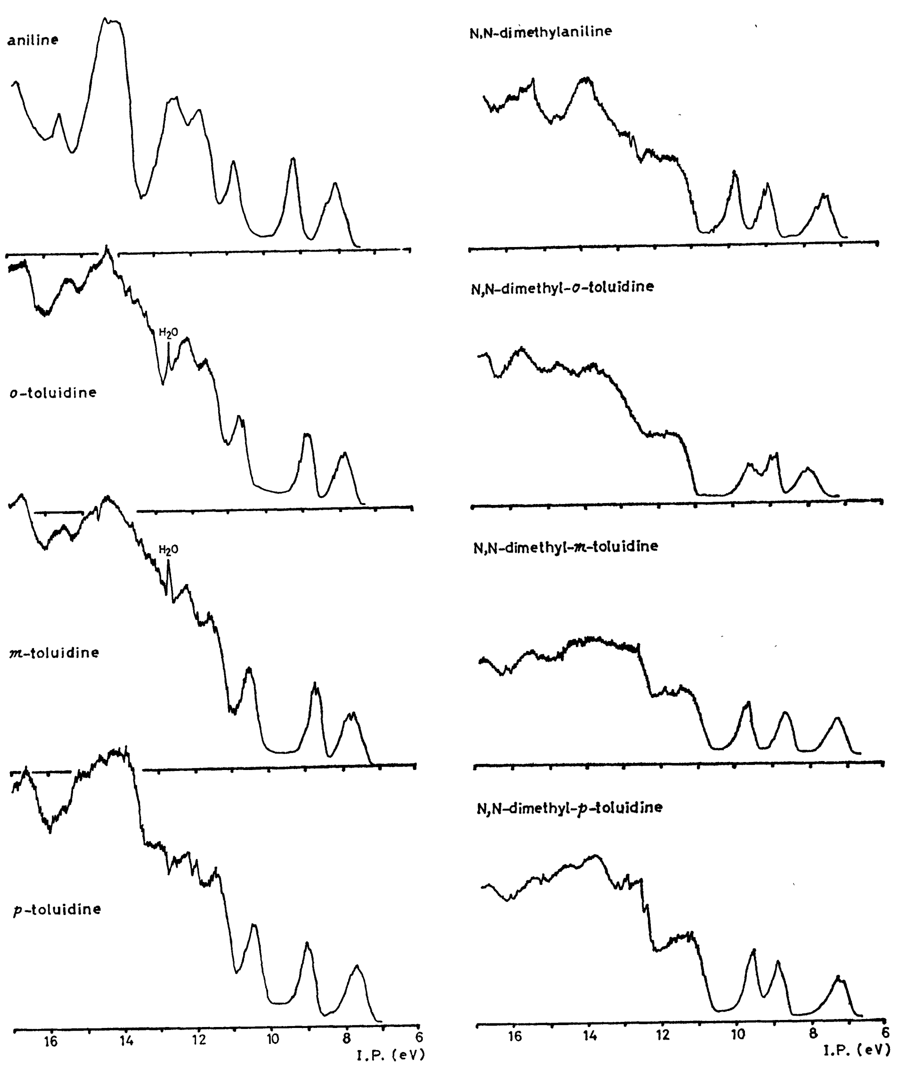

Fig. 1. Photoelectron spectra of anilines.

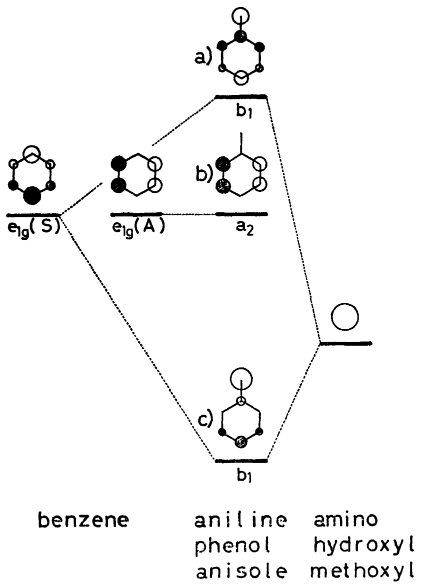

Fig. 2. Orbital energy diagram showing the correlation of the three highest occupied π orbitals of aniline (phenol or anisole) with the benzene e_{1g} π orbitals and a substituent lone pair orbital.

can be estimated by the aid of the following equation derived by the first-order perturbation theory.[19]

$$-\Delta I_v(J) = 0.0528 + 1.0110 \sum_{\zeta} (3C^2_{J\zeta} + C^2_{J\tau} + C^2_{J\tau'})/3 \tag{1}$$

Here ζ denotes the position of methyl substitution, and τ and τ' the positions of the nearest neighbours to ζ. C_{Jk} is the coefficient of the k-th AO in the J-th π MO obtained by the CNDO/2 method. The vertical ionization potentials of methyl substituted anilines and *N*,*N*-dimethylanilines were estimated by considering those of the parent compounds and the $\Delta I_v(J)$ values thus obtained. The results are listed in Table 1 (in the parentheses).

As is seen in Table 1, the estimated values agree rather well with the observed ones except for the case of *N*,*N*-dimethyl-*o*-toluidine in which the estimated values of the first and third ionization potentials are smaller by 0.73 eV and greater by 0.17 eV than the corresponding observed ones, respectively, and, therefore, the estimated splitting between them (2.49 eV) is much larger than the observed value (1.59 eV). It is known[20–23] that the dimethylamino group of *N*,*N*-dimethyl-*o*-toluidine is twisted from the benzene ring

TABLE 1. VERTICAL IONIZATION POTENTIALS ($I_v(J)$ IN eV) OF ANILINE, *N,N*-DIMETHYLANILINE, AND THEIR METHYL DERIVATIVES[a,b]

J	$I_v(J)$ (eV) 1	2	3	4
Benzene[c]	9.23	11.67	12.32	13.97
Toluene[c]	8.85	9.34	11.43	
m-Xylene[c]	8.71	9.03	11.24	
Aniline	8.05	9.21	10.81	11.79
o-Toluidine	7.83 (7.83)	8.77 (8.81)	10.70 (10.69)	11.58
m-Toluidine	7.66 (7.86)	8.71 (8.83)	10.45 (10.60)	11.52
p-Toluidine	7.62 (7.77)	8.94 (9.00)	10.40 (10.50)	11.45
N,N-Dimethylaniline	7.37	8.96	9.80	11.63
N,N-Dimethyl-*o*-toluidine	7.92 (7.19)	8.78 (8.57)	9.51 (9.68)	11.57
N,N-Dimethyl-*m*-toluidine	7.24 (7.22)	8.63 (8.58)	9.61 (9.66)	11.18
N,N-Dimethyl-*p*-toluidine	7.27 (7.15)	8.86 (8.75)	9.55 (9.60)	11.37
Methylamine[d]	9.7	13.2	14.5	15.6
Dimethylamine[d]	8.9	12.6	13.3	13.8
Trimethylamine[d]	8.5	12.4	12.9	14.0

a) The values in the parentheses denote the ionization potentials estimated with the aid of Eq. (1). b) The $I_v(J)$'s of benzene, toluene, *m*-xylene, and some aliphatic amines are also tabulated in this table. c) Ref. 4. d) Ref. 18.

TABLE 2. VERTICAL IONIZATION POTENTIALS ($I_v(J)$ IN eV) OF PHENOL, ANISOLE, AND THEIR METHYL DERIVATIVES[a,b,c]

J	$I_v(J)$ (eV) 1	2	3	4
Phenol	8.73	9.40	11.59	11.99
o-Cresol	8.48 (8.48)	9.08 (9.01)	11.42 (11.49)	11.67
m-Cresol	8.52 (8.51)	9.10 (9.02)	11.16 (11.41)	11.65
p-Cresol	8.38 (8.38)	9.25 (9.18)	11.14 (11.34)	11.68
2,4-Dimethylphenol	8.18 (8.18) [8.13]	8.89 (8.84) [8.93]	11.00 (11.30) [10.97]	11.40
2,6-Dimethylphenol	8.26 (8.28) [8.23]	8.78 (8.66) [8.76]	11.13 (11.45) [11.25]	11.51
Methanol[d]	10.96	12.62	15.21	15.64
Anisole	8.39	9.22	11.06	11.52
o-Methylanisole	8.24 (8.16)	8.93 (8.83)	10.92 (10.95)	11.37
m-Methylanisole	8·28 (8.20)	8.93 (8.84)	10.76 (10.91)	11.33
p-Methylanisole	8.18 (8.09)	9.11 (9.01)	10.75 (10.84)	11.34
2,4-Dimethylanisole	7.95 (7.92) [8.03]	8.75 (8.67) [8.82]	10.60 (10.78) [10.61]	11.12
2,6-Dimethylanisole	8.51 (8.00) [8.09]	8.71 (8.48) [8.64]	9.87 (10.89) [10.78]	11.31
Methyl ether[e]	10.04	11.91	13.43	14.2

a) See footnote a) for Table 1. b) The values in the square brackets are the I_v's estimated from those of the parent molecules and their mono-methyl derivatives. c) The $I_v(J)$ values of methanol and methyl ether are also given in this table. d) Ref. 25. e) Ref. 26.

plane by the steric hindrance effect of the *o*-methyl group. This twisting decreases the conjugation between the e_{1g}(S)-like π orbital of benzene ring and the nitrogen n orbital and, therefore, decreases the splitting between the first and third I_v's of *N,N*-dimethyl-*o*-toluidine.

In the preliminary report,[3] we estimated the lowest three I_v's of the hypothetical *N,N*-dimethyl-*o*-toluidine with no steric hindrance effect to be 7.41∼7.48 eV, 8.69 eV, and 9.85∼9.86 eV by adding the correction terms due to *N,N*-dimethylation to the corresponding values of *o*-toluidine. The splitting between the first and third ionization potentials thus obtained, 2.37—2.45 eV, is in good agreement with the value estimated with the aid of Eq. (1), 2.49 eV.

Concerning aniline, the splitting between the first and second bands is smaller than that between the second and third bands. The reverse is the case for *N,N*-dimethylaniline. This indicates that in the case of aniline, as is shown in Fig. 2, the benzene ring e_{1g} π orbitals are higher than the amino group n orbital, while, in the case of *N,N*-dimethylaniline, the relative height of both orbitals is reversed. This reversal is caused by the increase in the n orbital energy of the amino group by *N,N*-dimethylation. This means that the highest occupied and third highest occupied MO's of aniline are mainly contributed by e_{1g}(S) orbital of the ring and the n orbital on the nitrogen atom, respectively, while the reverse is the case for *N,N*-dimethylaniline. This is supported qualitatively by the CNDO/2 calculation.

The correlation diagram for the orbital energies of these aromatic amines obtained on the assumption of $\varepsilon=-I_v$ (Koopmans' theorem[24]) has already been shown in Fig. 1 of Ref. 3.

The PES of aniline, *N,N*-dimethylaniline, *o*-toluidine and *N,N*-dimethyl-*o*-toluidine have recently been reported by Maier and Turner[11] and their assignment of the three lower energy bands is consistent with that given in our preliminary report[3] and in the present paper.

Phenols and Anisoles. The PES of phenol, *o*-, *m*-, and *p*-cresols, 2,4- and 2,6-dimethylphenols, anisole, *o*-, *m*-, and *p*-methylanisoles, and 2,4- and 2,6-dimethylanisoles are shown in Fig. 3, and the observed $I_v(J)$'s of these compounds are summarized in Table 2.

Phenols and anisoles commonly show three lower energy bands in the region between 8 eV and 11.5 eV. This region corresponds to the ionization from the benzene e_{1g}(S) and e_{1g}(A) orbitals and from the n orbital on the oxygen atom of methanol (10.96 eV)[25] or methyl ether (10.04 eV).[26] Therefore, the lower three energy bands of phenols or anisoles are mainly related to the MO's caused by the interaction of the e_{1g}(S) and e_{1g}(A) orbitals of the ring with the oxygen

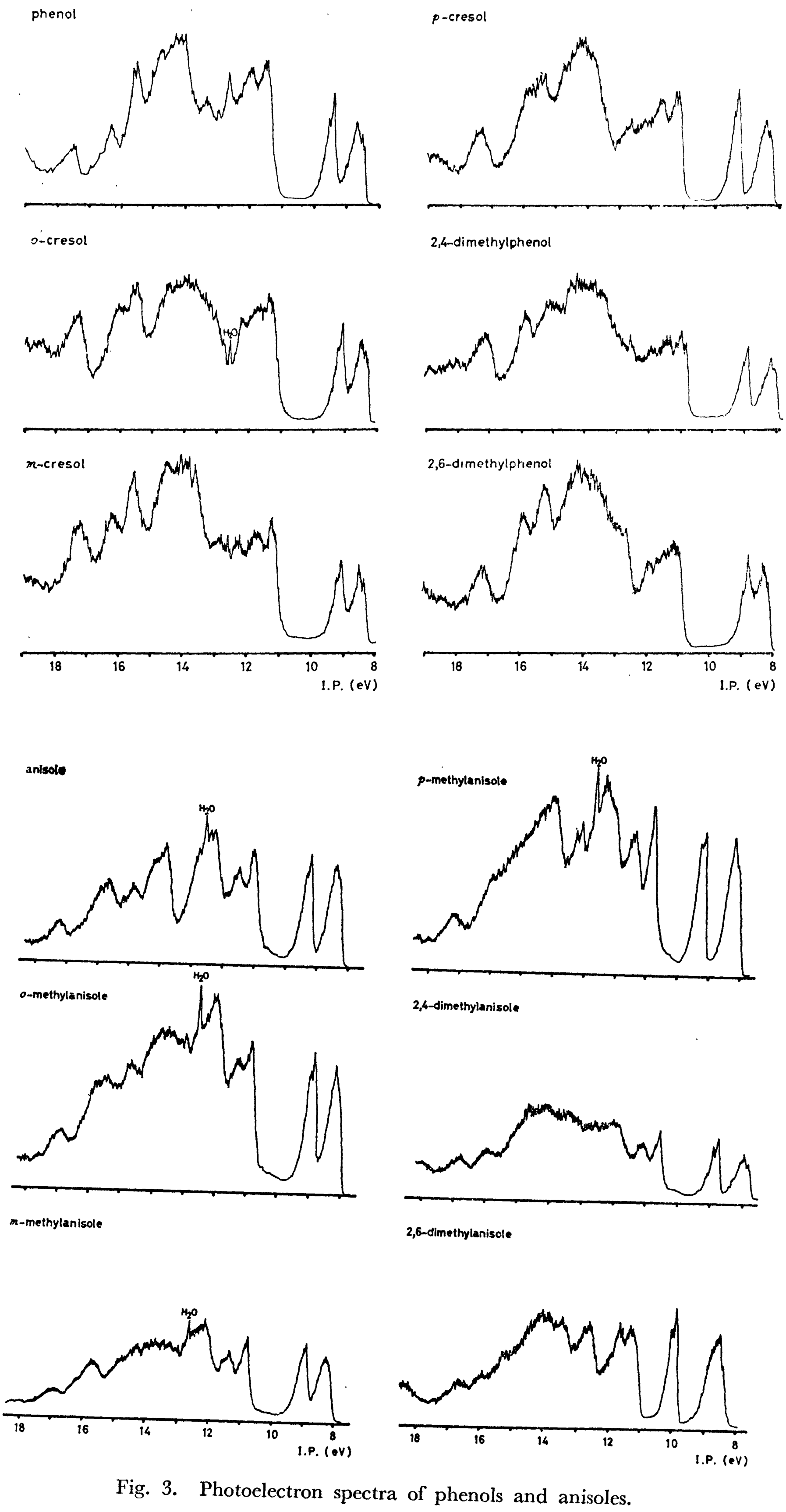

Fig. 3. Photoelectron spectra of phenols and anisoles.

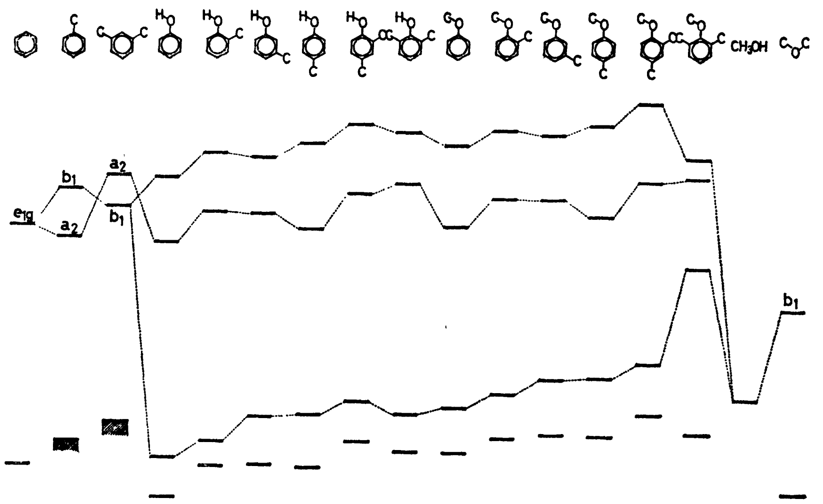

Fig. 4. Orbital energy diagram for the higher occupied orbitals of phenols and anisoles.

n orbital as schematically shown in Fig. 2. This qualitative scheme is supported by the CNDO/2 calculation. The observed orbital energy diagram estimated according to Koopmans' theorem[24] is shown in Fig. 4.

Now let us consider methyl substituent effects on the PES of phenol and anisole. The lowest three ionization potentials of some methyl substituted phenols and anisoles were estimated by two methods: one of them is to estimate the substituent effect by the aid of Eq. (1) and the other is to derive the ionization potentials of dimethyl derivatives from those of monomethyl derivatives and the parent molecules by assuming the additivity of the methyl substituent effect. The vertical ionization potentials of the methyl derivatives estimated by the aid of both methods are summarized in Table 2 (in the parentheses and the square brackets).

As is clearly seen in Table 2, the lowest three ionization potentials estimated by both methods are in good agreement with the observed values except for the case of 2,6-dimethylanisole. In particular, the agreement is better for the values estimated by the additivity rule.

The lowest and third lowest ionization potentials estimated by both methods for 2,6-dimethylanisole show large discrepancies from the observed values. The estimated values are for the planar molecule; in actuality, however, the methoxyl group of this molecule is considered to be twisted by around 90°[27,28] from the benzene ring plane because of the steric hindrance effect of the two *o*-methyl groups. This twisting decreases the conjugation between the ring π orbital and the oxygen n orbital. This is the reason why the observed lowest and third lowest ionization potentials are larger and smaller, respectively, compared with the corresponding values estimated for the hypothetical planar molecule.

The difference between the first and second ionization potentials is smaller for both phenol and anisole than that between the second and third ionization potentials. This is similar to the situation found for aniline and indicates that the highest occupied orbitals of phenol and anisole are mainly contributed by the ring $e_{1g}(S)$ orbital.

The PES of phenol, *o*-cresol, 2,6-dimethylphenol, anisole, *o*-methylanisole and 2,6-dimethylanisole were reported recently by Maier and Turner.[11] The PES

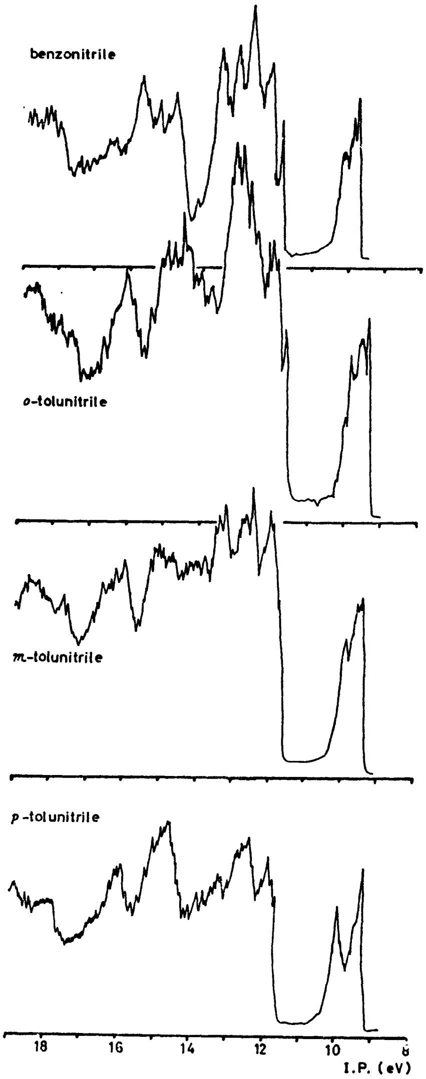

Fig. 5. Photoelectron spectra of benzonitriles.

of 2,6-dimethylanisole reported by them, however, is slightly different from ours: in their spectrum, the first band is too strong compared with the third band and an additional band appears around 9.20 eV. This additional band could not be observed for our sample which was purified by column chromatography and the purity of which was checked with gas chromatography and NMR spectrum. This band may be due to some impurities.

Benzonitriles. The PES of benzonitrile and *o*-, *m*-, and *p*-tolunitriles are shown in Fig. 5. The observed $I_v(J)$'s of benzonitriles are summarized in Table 3.

TABLE 3. VERTICAL IONIZATION POTENTIALS ($I_v(J)$ IN eV) OF BENZONITRILE AND ITS METHYL DERIVATIVES, AND ACETONITRILE[a)]

J	$I_v(J)$ (eV) 1	2	3	4
Benzonitrile	9.72	10.14	11.84	12.11
o-Tolunitrile	9.38 (9.49)	9.84 (9.75)	11.62	12.01 (12.01)
m-Tolunitrile	9.40 (9.51)	9.83 (9.75)	11.69	11.95 (11.91)
p-Tolunitrile	9.33 (9.39)	9.97 (9.92)	11.68	11.90 (11.83)
Acetonitrile[b)]	12.21	13.14		

a) See footnote a) for Table 1. b) Ref. 1.

According to the CNDO/2 and EHMO calculations, the occupied orbitals of benzonitrile are located in the following orders from the top, respectively: $b_1\pi$, $b_2\sigma$, $a_1\sigma$, $a_2\pi$.... and $a_2\pi$, $b_1\pi$, $a_1\sigma$, $b_2\sigma$..... Judging from the fact that the e_{1g}(S) and e_{1g}(A) orbitals of benzene are located at 9.23 eV while the highest occupied orbital of acetonitrile at 12.21 eV, we may safely assign the first and second bands of benzonitrile to two π($b_1\pi$ and $a_2\pi$) MO's mainly localized on the benzene ring.

Figure 6 shows the orbital energies determined from the observed ionization potentials by the aid of Koopmans' theorem.[24)] The observed first ionization potentials of *o*- and *m*-tolunitriles are similar to each other, but are larger than the corresponding value of *p*-tolunitrile. Furthermore, the second ionization potentials of *o*- and *m*-tolunitriles are smaller than that of the *p*-isomer. This tendency can be reproduced by the use of Eq. (1) on the assumption that the highest occupied π MO of benzonitrile is b_1 and the second one a_2. The ionization potentials obtained thus for *o*-, *m*-, and *p*-tolunitriles are in good agreement with the observed values as is shown in Table 3. Therefore the first and second bands of benzonitrile may be assigned to the ionizations from the $b_1\pi$ and $a_2\pi$ orbitals, respectively.

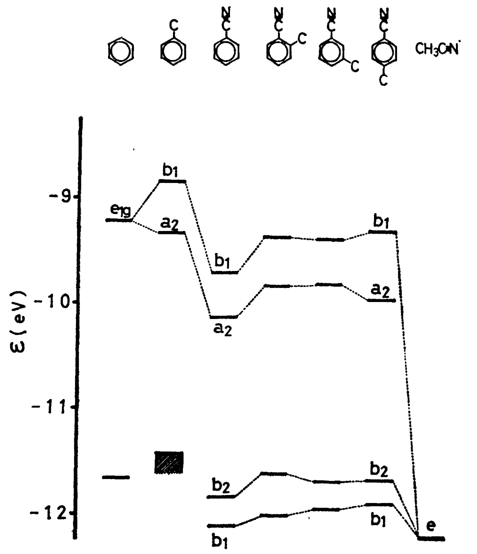

Fig. 6. Orbital energy diagram for the higher occupied orbitals of benzonitriles.

TABLE 4. VERTICAL IONIZATION POTENTIALS ($I_v(J)$ IN eV) OF ACETOPHENONE, *o*-, *m*-, AND *p*-METHYLACETOPHENONES, AND ACETONE[a)]

J	$I_v(J)$ (eV) 1	2	3	4
Acetophenone	9.37	9.55	9.77	11.91
o-Methylacetophenone	9.15 ((9.21))	9.32	9.44 ((9.47))	11.68
m-Methylacetophenone	9.14 ((9.23))	9.34	9.45 ((9.46))	11.69
p-Methylacetophenone	9.12 ((9.16))	9.36	9.56 ((9.60))	11.65
Acetone[b)]	9.72	12.6	13.4	13.9

a) The values in the double parentheses denote the ionization potentials estimated from the I_v data of acetophenone and benzonitriles on the assumption that the methyl-substitution effect upon the π orbitals of acetophenone is equal to that of benzonitrile. b) Ref. 29.

From the fact that the $b_1\pi$ orbital caused by the mixing with appropriate orbitals of the cyano group is located above the $a_2\pi$ orbital localized on the benzene ring, it is revealed that the highest occupied doubly degenerate orbitals of the ring interact more strongly with higher occupied orbitals of the cyano group than with lower vacant orbitals of the group. This scheme on the orbital interaction for benzonitrile is the same as for aniline, phenol, and anisole. There is a difference, however, between benzonitrile and aniline or phenol in the point that the first ionization potential of benzonitrile is greater than that of benzene, while the reverse is the case for aniline and phenol. This is due to the difference in the charge density on the benzene ring; the electron density on the ring is reduced by the electron-accepting group like the cyano group and is increased by the electron-donating group like amino or hydroxyl group.

Benzonitriles show commonly two sharp bands around 11.7~12.1 eV and this region is for the doubly degenerate π orbitals of the cyano group (for example, acetonitrile: 12.21 eV[1)]). Judging from the above assignment of the lowest energy band of benzonitrile, the higher energy band of the two sharp bands around 12 eV (the fourth lowest energy band) is due to the b_1-like π MO constructed by the bonding combination

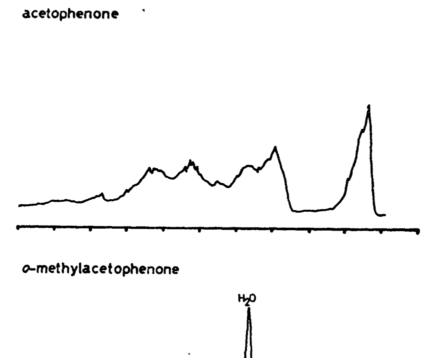

Fig. 7. Photoelectron spectra of acetophenones.

of the cyano group out-of-plane occupied π orbital and the ring $e_{1g}(S)$-type π orbital, and the other band (the third lowest energy band) is assigned to the ionization from the cyano group in-plane π orbital. The observed methyl-substitution effect on the former band supports this assignment; as is clearly seen in Table 3, the fourth ionization potentials of *o*-, *m*-, and *p*-tolunitriles estimated with the aid of Eq. (1) (the values in the parentheses in Table 3) are in excellent agreement with the observed values.

The PES of benzonitrile was recently assigned by Rabalais and Colton[9] on the basis of INDO and CNDO calculations, the assignment of the four lower energy bands being consistent with ours.

Acetophenones. The PES of acetophenone and *o*-, *m*-, and *p*-methylacetophenones are shown in Fig. 7. Their vertical ionization potentials are summarized in Table 4. Acetophenone has overlapped bands in the region of 9.3—9.8 eV. This region corresponds to the benzene e_{1g} orbital bands (9.23 eV) and the acetyl n orbital band (for example, acetone: 9.72 eV[29]). Therefore, it is quite natural to assign the overlapped bands to the acetyl n orbital and the benzene ring $e_{1g}(S)$ and $e_{1g}(A)$ orbitals perturbed by acetyl group π orbitals. The CNDO/2 calculation gives the following order for the higher occupied orbitals of acetophenone: from the top, n, π, σ, and π. This order, however, is quite improbable in the point that the σ band is expected to appear in the 9.3—9.8 eV region.

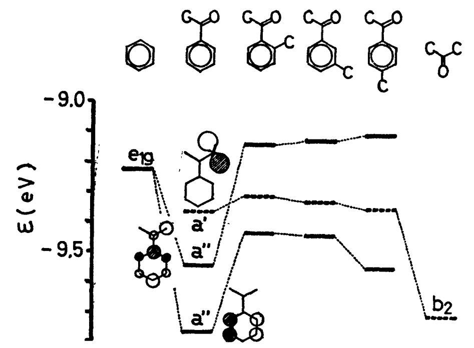

Fig. 8. Orbital energy diagram for the higher occupied orbitals of acetophenones.

Since the lowest energy peak at 9.37 eV is rather sharp, it is reasonable to assign this band to the acetyl n orbital. The second (9.55 eV) and third (9.77 eV) bands of acetophenone, which are due to the ionizations from π orbitals, change by the methyl substitution on the *o*-, *m*-, and *p*-positions with the same tendency as the first and second bands of benzonitrile, respectively. Therefore, by an analogy with the case of benzonitrile, the order of the π orbitals of acetophenone can be determined as shown in Fig. 8: namely, the π orbital localized on the ring (a″) is lower than the π orbital (a″) caused by the interaction of the ring π orbital with the highest occupied π orbital of the acetyl group.

Next, let us turn to the *o*-, *m*-, and *p*-methylacetophenones. The vertical ionization potentials from their π orbitals were estimated from the π $I_v(J)$ data of acetophenone and the benzonitriles on the assumption that the methyl-substitution effect upon the π orbitals of acetophenone is equal to that of benzonitrile: the results are given in Table 4 (in the double parentheses). The estimated values are in good agreement with the observed values for *o*-, *m*-, and *p*-methylacetophenones. It may be noticed that the a″ orbital of acetophenone is greatly pushed up by the methyl substitution while the a′ orbital is rather insensitive. Consequently, the highest and second highest occupied orbitals of acetophenone are reversed for the methyl substituted acetophenones. This is supported by the fact that the observed second ionization potentials of *o*-, *m*-, and *p*-methylacetophenones are almost constant and are close to the first ionization potential of acetophenone. The fact that these n ionization potentials are smaller than the corresponding value of acetone (9.72 eV) may be interpreted in terms of the electron migration from the benzene ring to the acetyl group and therefore the imcrement in the negative charge on the group.

Finally the orbital energy diagram estimated according to Koopmans' theorem[24] is shown in Fig. 8.

Nitrobenzenes. The PES of nitrobenzene, *o*-, *m*-, and *p*-nitrotoluenes, 2,4- and 2,6-dimethylnitrobenzenes, 2,4,6-trimethylnitrobenzene, and nitromethane are shown in Fig. 9. The vertical ionization potentials are summarized in Table 5. The correlation diagram

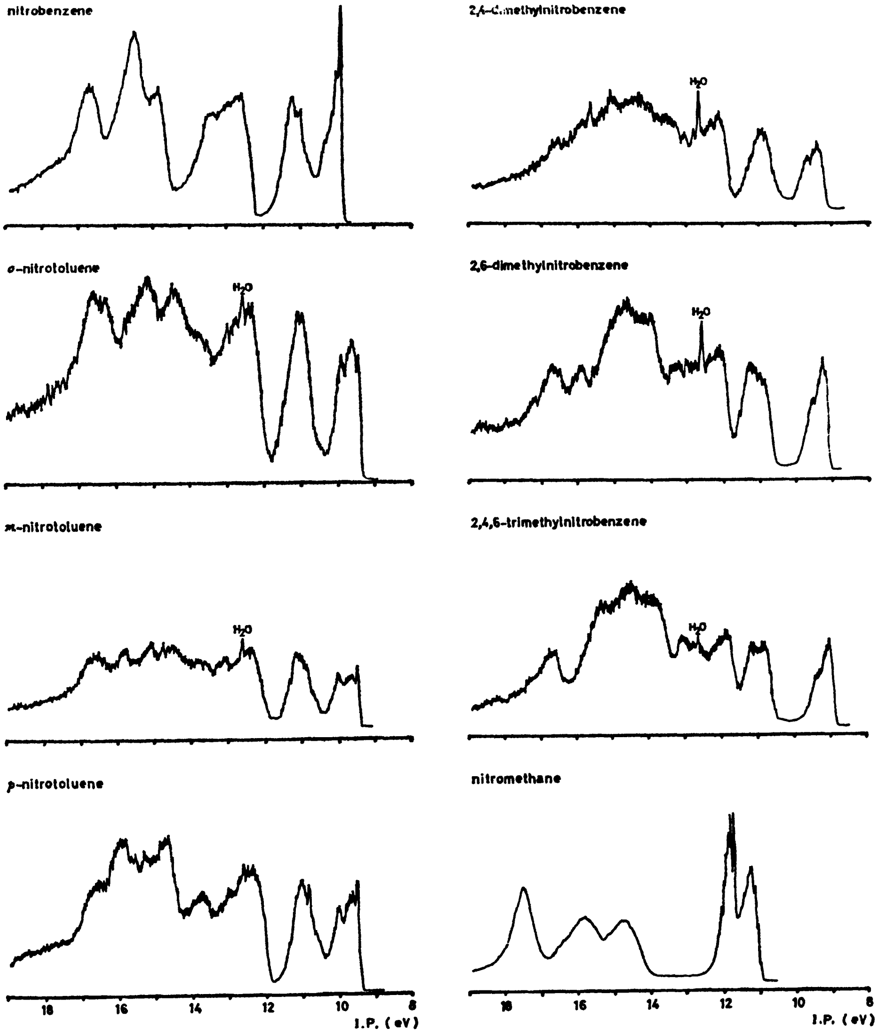

Fig. 9. Photoelectron spectra of nitrobenzenes and nitromethane.

TABLE 5. VERTICAL IONIZATION POTENTIALS ($I_v(J)$ IN eV) OF NITROBENZENE, ITS METHYL DERIVATIVES, AND NITROMETHANE

J	$I_v(J)$ (eV) 1	2	3	4	5
Nitrobenzene	9.93	10.32	11.01	11.23	12.65
o-Nitrotoluene	9.63	9.90	10.98	11.09	12.43
m-Nitrotoluene	9.48	10.03	10.90	11.08	12.42
p-Nitrotoluene	9.52	10.01	10.84	11.01	12.36
2,4-Dimethyl-nitrobenzene	9.36	9.65	10.89		12.07
2,6-Dimethyl-nitrobenzene	9.17	9.57	10.87	11.20	12.10
2,4,6-Trimethyl-nitrobenzene	9.01	9.32	10.86	11.08	11.84
Nitromethane	11.29	11.71	14.76	15.80	17.49

for the orbital energies of these compounds obtained on the assumption $\varepsilon = -I_v(J)$ (Koopmans' theorem[24]) is shown in Fig. 10.

According to the EHMO calculation, the first and second bands can be correlated, respectively, with the $a_2\pi$ orbital corresponding to the $e_{1g}(A)$ type π orbital of benzene and with the $b_1\pi$ orbital constructed by the combination of the lowest unoccupied orbital of the nitro group and the highest occupied $e_{1g}(S)$ orbital of the benzene ring. These orbitals are schematically shown in Fig. 11. The prediction derived by the first-order perturbation theory on the basis of this assignment

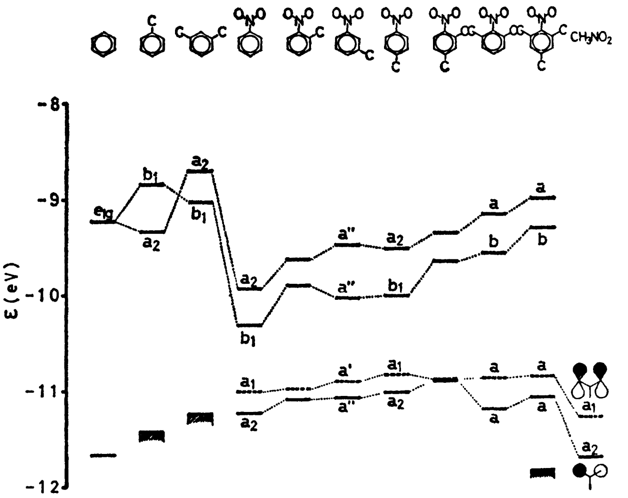

Fig. 10. Orbital energy diagram for the higher occupied orbitals of nitrobenzenes.

can well explain the observed tendency shown in Fig. 10 that the difference between the first two vertical ionization potentials is larger for *m*-nitrotoluene than for *p*-nitrotoluene and is larger for 2,6-dimethylnitrobenzene than for 2,4,6-trimethylnitrobenzene.

It may be emphasized that in the case of nitrobenzenes the first band corresponds to a_2 (like) π orbital mainly localized on the benzene ring and the second band corresponds to the b_1 (like) π orbital, while the reverse is the case for the other molecules treated in the present paper. This characteristic of nitrobenzenes is due to the fact that the mixing of the ring $e_{1g}(S)$ orbital with the lowest vacant π orbital of the nitro group is predominant for nitrobenzenes, while, in the other cases, the occupied group π orbitals of the substituents mix more significantly with the benzene $e_{1g}(S)$-(like) orbital rather than the vacant group π orbital of the substituents.

From the spectral shape and the INDO calculation, Rabalais[8)] assigned the first two bands of nitrobenzene to the $b_1\pi$ and $a_2\pi$ orbitals, respectively, but from the above discussion our assignment seems to be more reasonable.

Nitrobenzene and its methyl derivatives have commonly two bands in the range between 10.5 and 11.5 eV; lower energy bands around 10.9 eV and higher energy ones around 11.1 eV. From their positions and relative intensities, they are correlated with the 11.29 eV and 11.71 eV bands of nitromethane.[30)] The third band of nitrobenzene at 11.01 eV is insensitive to the methyl substitution on the benzene ring and may be assigned to the a_1n orbital which is the nonbonding orbital in plane (see Fig. 11). The fourth band of nitrobenzene correlated with the 11.71 eV band of nitromethane is rather sensitive to the methyl substitution on a carbon atom of the benzene ring and may be due to the $a_2\pi$ orbital shown in Fig. 11. Further details of the assignment on the bands in the 10.5—12.0 eV region observed with nitromethane, nitrobenzene and its methyl derivatives are not described here, since they have been described in the previous paper[4)]. Our assignments of the third and fourth bands are consistent with those by Rabalais.[8)]

According to the first-order perturbation theory the splitting between the first two vertical ionization potentials of *o*-nitrotoluene should be similar to that of *m*-isomer. In reality, however, the former is significantly smaller than the latter. This abnormal result is easily understood if one remembers that in the case of *o*-isomer the conjugation between the benzene e_{1g}-like orbitals and the nitro group π orbitals is diminished by the twisting of the nitro group from the benzene ring plane: this twisting of ~40° is caused by the steric hindrance of the *o*-methyl group.[4,31–40)]

The second I_v of 2,4-dimethylnitrobenzene should be greater than that of 2,6-dimethylnitrobenzene according to the first-order perturbation theory but the reverse tendency was observed. This is also explained by the decreasing conjugation between the benzene $e_{1g}(S)$-like π orbital and the b_1 type vacant π orbital of the nitro group because of the additional twisting[40)] of the nitro group from the benzene ring plane caused by the presence of two *o*-methyl groups.

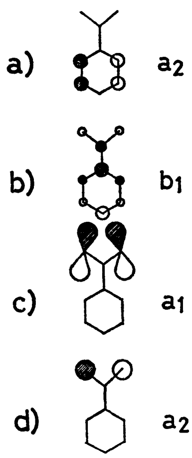

Fig. 11. Schematic representation of the higher occupied molecular orbitals of nitrobenzene.

Table 6. Classification of substituent groups

Character of substituent group	Case	Character of the H.O.[a)]	Example
Electron donating	1	Mainly n	-N(CH$_3$)$_2$
	2	Mainly $e_{1g}(S)\pi$	-NH$_2$, -OH, -OCH$_3$
Electron accepting	3	$e_{1g}(S)\pi+S\pi$ (occupied)	-CN, -COCH$_3$
	4	$e_{1g}(A)\pi$	-NO$_2$

a) H.O. means the highest occupied orbital of a substituted benzene molecule, n the highest occupied nonbonding orbital of an electron-donating group, and $S\pi$(occupied) the highest occupied π orbital of an electron-accepting group.

PES of Substituted Benzenes and Classification of Substituent Groups. From the above discussion on the PES of substituted benzenes, the substituent groups under consideration can be classified into four categories as shown in Table 6.

Substituted benzenes with such electron-donating groups as OH, OCH$_3$, NH$_2$, and N(CH$_3$)$_2$ have lower first ionization potentials than benzene, because of the increasing electron density on the benzene ring. These substituent groups are divided into two cases, cases 1 and 2, in terms of the nature of the highest occupied MO's of substituted benzenes which are mainly constructed by the mixing of the highest occupied ($e_{1g}(S)$) MO of the ring with the highest occupied n orbital of the substituent group. Two cases are separated by the relative height of the e_{1g} MO to the n orbital. In case 1, the latter is located above the former and the highest occupied and third highest occupied MO's of the substituted benzenes are mainly contributed by the n orbital and the $e_{1g}(S)$ MO, respectively. In case 2, the reverse is the case concerning the relative height of the e_{1g} MO to the n orbital and also concerning the nature of the highest occupied and third highest occupied MO's.

Substituted benzenes with such electron-accepting groups as CN, COCH$_3$, and NO$_2$ have larger first π ionization potentials than benzene, because of the decreasing electron density on the ring. From the consideration of the nature of their highest occupied π MO's, the electron-accepting groups are divided into two cases, cases 3 and 4.

In case 3, the highest occupied e_{1g}(S) MO of the ring interacts mainly with the occupied π orbital of the substituent group and, therefore, both orbitals contribute to the highest occupied π orbital of the substituted benzene molecule. On the other hand, in case 4, the e_{1g}(S) MO of the ring interacts mainly with the lowest vacant π orbital of the substituent group and the MO of the substituted benzene molecule obtained by this interaction is the second highest occupied MO: the highest occupied MO in this case is of the ring e_{1g}(A) type.

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