December, 1977] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 50 (12), 3111—3117 (1977) 3111

"Molecular Orbital Analysis" of Naphthalene Derivatives. An Application of Configuration Analysis to the Assignment of Photoelectron Spectra

Tsuneo Fujii and Satoshi Suzuki

Department of Industrial Chemistry, Faculty of Engineering, Shinshu University, Wakasato, Nagano 380

(Received February 4, 1977)

Molecular orbital analysis, which is an application of configuration analysis proposed by Baba *et al.*, has been applied to the interpretation of the photoelectron spectra of substituted naphthalenes, with particular attention paid to the dependence of the spectra on the position of substitution and on the character of the substituents. The results of MO calculations based on the Pariser-Parr-Pople method have been analyzed in terms of the π-MO's of naphthalene and the π-AO or π-MO's of a substituent. The results of the molecular orbital analysis for naphthalene derivatives with an electron-donating group are compared with the results for those with an electron-accepting group.

Since Turner first succeeded in measuring high resolution photoelectron (PE) spectra,[1] the PE spectra of many compounds have been reported. The PE spectra give precise data on the vertical ionization potentials (I_v) of atoms and molecules. Assuming Koopmans' theorem,[2] one may also easily obtain information on the orbital energies. Recently Kimura *et al.* have found a sum rule—that the sum of the experimental ionization energies may be reproduced by the sum of the calculated orbital energies of the localized orbitals.[3] Heilbronner *et al.* have calculated the π-orbital energies of naphthalene by three different approximations and compared them with experimental data.[4] Marschner and Goetz could reproduce the experimental values of the PE spectra of naphthalene by using modified Pariser-Parr-Pople (PPP) parameters.[5]

The PE spectra of substituted naphthalenes have been observed by several authors.[6–8] The changes in the π-MO energies of naphthalene caused by the introduction of a substituent depend on the position and properties of the substituent. Although the change in the energy and character of MO's due to the introduction of a substituent into the parent naphthalene is a very interesting problem for chemists, the origin of such a change in the π-MO character and energy has not been fully understood. From the experimental results on monosubstituted naphthalenes with an electron-donating group,[6–8] it has been found that the individual bands are apparently shifted to a higher energy compared with those of naphthalene. In contrast to this, the PE spectra of monosubstituted naphthalenes with an electron-accepting group are apparently shifted to a lower energy compared with that of naphthalene.

The method of configuration analysis proposed by Baba *et al.* has enabled us to give a quantitative interpretation of the electronic absorption spectra of the derivatives of aromatic hydrocarbons in terms of locally excited and charge-transfer states.[9] In the calculation process of configuration analysis, the matrix which transforms the set of MO's of a derivative into a set of reference MO's, that is, the MO's of a corresponding parent compound and a substituent, is obtained. This matrix gives us information on the correlation between the MO's of a derivative and the MO's of a parent compound and a substituent. This procedure will be called "Molecular Orbital Analysis" (MOA), by analogy with configuration analysis. The quantitative assignments of the MO's of the derivatives to their reference MO's can be made by the application of MOA.

This paper will present the assignments of the MO's of monosubstituted naphthalenes in terms of the MO's of naphthalene and a substituent and will make a comparison between the electron-donating and electron-accepting cases. In the present paper, naphthalene and its derivatives, *i.e.*, 1- and 2-naphthols, 1- and 2-naphthylamines, 1- and 2-naphthonitriles, and 1- and 2-naphthaldehydes, will be considered. The LCAO-SCF-MO calculations of the PPP type have been performed, and the results subjected to the MOA.

Procedure and Calculation

The semiempirical MO's of substituted compounds may be obtained by the PPP procedure. Although the quantitative correlation between the MO's of substituted compounds and those of the corresponding parent compounds is an interesting problem in such fields of chemistry as PE spectroscopy, such information cannot be obtained by means of the usual MO calculations. It can, though, be derived in the course of the calculation of configuration analysis. This procedure will be outlined below.

The MO's of a substituted compound, ϕ_i's, which are obtained by the usual procedure, can be written in a matrix form as

$$\boldsymbol{\phi} = \boldsymbol{\chi}\mathbf{C}, \tag{1}$$

where $\boldsymbol{\chi}$ represents the row vector of n orthonormal AO's, χ_p, and where $\mathbf{C}$ is an $n \times n$ unitary matrix, the elements of which are AO coefficients of ϕ_i's. In the present study, systems composed of naphthalene and a substituent are employed as the reference systems; therefore, the reference MO's used are the LCAO-SCF-MO's of naphthalene and the π-AO or π-MO's of a substituent. The MO's of the reference system, $\boldsymbol{\phi}^\circ$, are expressed in terms of the same basis set, $\boldsymbol{\chi}$, as well as ϕ_j's

$$\boldsymbol{\phi}^\circ = \boldsymbol{\chi}\mathbf{C}^\circ. \tag{2}$$

It follows, then, that

$$\boldsymbol{\phi} = \boldsymbol{\phi}^\circ\mathbf{B}, \tag{3}$$

with

$$\mathbf{B} = (\mathbf{C}^\circ)^\dagger\mathbf{C}, \tag{4}$$

where $(\mathbf{C}^\circ)^\dagger$ is the Hermitian conjugate of the $\mathbf{C}^\circ$ matrix. The **B** matrix represents the correlation between $\boldsymbol{\phi}$ and $\boldsymbol{\phi}^\circ$. This matrix is used in the calculation of the configuration analysis. When the configuration analysis of a certain compound has been completed, the **B** matrix of the compound has also been obtained as a matter of course.

Calculations have been made for the π-electron systems of naphthalene, naphthols, naphthylamines, naphthonitriles, and naphthaldehydes by the semiempirical LCAO-SCF-MO method. The parameters used in this study have been given elsewhere.[10,11]

Results

Tables 1 and 2 give the calculated π-MO energies, ε_i, and the I_v's for ϕ_i° and ϕ_j in the first and third rows for individual compounds; the values of I_v's were obtained from the PE spectroscopy. The MO's of the compounds are numbered in the order of increasing energy. The corrected MO energies, $\varepsilon_i^{\text{corrd}} = \varepsilon_i + 1.65$ eV, are also included in the second row of Tables 1 and 2. The correction factor of 1.65 eV is taken to give a general agreement between the experimental and theoretical data.

Table 1. SCF MO energies(ε), corrected SCF MO energies ($\varepsilon^{\text{corrd}}$), and vertical ionization potentials (I_v) in eV for naphthalene

	Photoelectron band (upper) and orbital function (lower)				
	V ϕ_1°	IV ϕ_2°	III ϕ_3°	II ϕ_4°	I ϕ_5°
ε	−14.56	−12.79	−11.86	−10.78	−9.79
$\varepsilon^{\text{corrd}}$	−12.91	−11.14	−10.21	−9.13	−8.14
I_v[a]	12.36	11.00	10.10	8.88	8.15

a) Ref. 14.

The results of MOA are shown in Tables 3—10. The reference MO's consist of $\phi_1^\circ, \phi_2^\circ, \cdots, \phi_{10}^\circ$, which are the SCF-MO's of naphthalene, and ϕ_X°'s, which represent the π-AO or the π-MO of the substituents, X being

Table 2. SCF MO energies(ε), corrected SCF MO energies ($\varepsilon^{\text{corrd}}$), and vertical ionization potentials (I_v) in eV for naphthols, naphthylamines, naphthonitriles, and naphthaldehydes

Compound	Photoelectron band (upper) and orbital function (lower)					
	VI ϕ_1	V ϕ_2	IV ϕ_3	III ϕ_4	II ϕ_5	I ϕ_6
1-Naphthol						
ε	−15.06	−13.72	−12.44	−11.29	−10.66	−9.26
$\varepsilon^{\text{corrd}}$	−13.41	−12.07	−10.79	−9.64	−9.01	−7.61
I_v[a]				9.57	8.89	7.78
2-Naphthol						
ε	−14.91	−13.89	−12.12	−11.55	−10.24	−9.42
$\varepsilon^{\text{corrd}}$	−13.28	−12.24	−10.47	−9.90	−8.61	−7.77
I_v[a]			10.54	9.91	8.63	7.90
1-Naphthylamine						
ε	−14.57	−12.95	−12.15	−10.82	−10.62	−8.99
$\varepsilon^{\text{corrd}}$	−12.92	−11.30	−10.50	−9.17	−8.97	−7.34
I_v[a,b]	12.70	11.40	10.49	9.26	8.66	7.46
2-Naphthylamine						
ε	−14.44	−13.14	−11.78	−11.26	−9.99	−9.16
$\varepsilon^{\text{corrd}}$	−12.79	−11.49	−10.13	−9.61	−8.34	−7.51
I_v[a,b]	12.50	11.70	10.14	9.65	8.32	7.56
1-Naphthonitrile						
ε	−15.02	−13.65	−12.85	−11.82	−11.04	−9.94
$\varepsilon^{\text{corrd}}$	−13.37	−12.00	−11.20	−10.17	−9.39	−8.29
I_v[a]				10.31	9.35	8.61
2-Naphthonitrile						
ε	−14.97	−13.87	−12.58	−12.05	−10.89	−10.01
$\varepsilon^{\text{corrd}}$	−13.32	−12.22	−10.93	−10.40	−9.24	−8.36
I_v[a]			11.18	10.51	9.33	8.64
1-Naphthaldehyde[c]						
ε	−15.06	−13.76	−12.99	−12.08	−11.11	−10.11
$\varepsilon^{\text{corrd}}$	−13.41	−12.11	−11.34	−10.43	−9.46	−8.46
2-Naphthaldehyde[c]						
ε	−15.06	−13.97	−12.83	−12.22	−11.09	−10.16
$\varepsilon^{\text{corrd}}$	−13.41	−12.32	−11.18	−10.57	−9.44	−8.51

a) Ref. 8. b) Ref. 7. c) The observed data are not available.

TABLE 3. ELEMENTS OF **B** MATRIX OF 1-NAPHTHOL[a)]

Reference MO	Symmetry type	Band notation	Photoelectron band (upper) and orbital function (lower)					
						III	II	I
			ϕ_1	ϕ_2	ϕ_3	ϕ_4	ϕ_5	ϕ_6
ϕ_1°	b_{1u}	B_5	0.7594	0.6327	0.1279	−0.0696	−0.0030	0.0391
ϕ_2°	b_{2g}	B_4	−0.1656	0.4008	−0.8791	0.1919	0.0131	−0.0436
ϕ_3°	b_{3g}	B_3	−0.2152	0.2875	0.3642	0.8468	0.0092	−0.1428
ϕ_o°		B_o	0.5629	−0.5557	−0.2562	0.3794	0.0053	−0.3261
ϕ_4°	b_{1u}	B_2	0.0045	−0.0044	0.0093	−0.0102	0.9997	0.0108
ϕ_5°	a_u	B_1	−0.1399	0.1760	0.0896	−0.2910	0.0077	−0.9249
ϕ_6°	b_{2g}		−0.0763	0.0901	0.0456	−0.0847	0.0026	0.0870
ϕ_7°	b_{3g}		−0.0041	0.0009	0.0033	−0.0027	−0.0119	−0.0011
ϕ_8°	b_{1u}		−0.0629	0.0685	0.0371	−0.0529	−0.0021	0.0634
ϕ_9°	a_u		−0.0405	0.0444	0.0224	−0.0378	−0.0026	0.0365
ϕ_{10}°	b_{3g}		0.0412	−0.0430	−0.0218	0.0338	−0.0013	−0.0364
Assignment[a)]			ϕ_1°		ϕ_2°	$\phi_3^\circ(B_3)$	$\phi_4^\circ(B_2)$	$\phi_5^\circ(B_1)$

a) See text for definition.

TABLE 4. ELEMENTS OF **B** MATRIX OF 2-NAPHTHOL[a)]

Reference MO	Symmetry type	Band notation	Photoelectron band (upper) and orbital function (lower)					
					IV	III	II	I
			ϕ_1	ϕ_2	ϕ_3	ϕ_4	ϕ_5	ϕ_6
ϕ_1°	b_{1u}	B_5	0.7100	0.6956	−0.0865	0.0516	0.0310	0.0286
ϕ_2°	b_{2g}	B_4	−0.3215	0.4522	0.7850	−0.2343	−0.1125	−0.0885
ϕ_3°	b_{3g}	B_3	−0.0921	0.1182	−0.3946	−0.8990	−0.1089	−0.0399
ϕ_o°		B_o	0.5774	−0.4971	0.3703	−0.2353	−0.3025	−0.2826
ϕ_4°	b_{1u}	B_2	−0.1719	0.1746	−0.2450	0.2642	−0.8640	−0.2506
ϕ_5°	a_u	B_1	−0.0862	0.0901	−0.1188	0.0705	0.3567	−0.9152
ϕ_6°	b_{2g}		0.0506	−0.0478	0.0390	−0.0322	−0.0406	−0.0514
ϕ_7°	b_{3g}		0.0677	−0.0634	0.0594	−0.0342	−0.0627	−0.0570
ϕ_8°	b_{1u}		0.0317	−0.0310	0.0269	−0.0182	−0.0204	−0.0272
ϕ_9°	a_u		0.0655	−0.0614	0.0539	−0.0351	−0.0526	−0.0478
ϕ_{10}°	b_{3g}		−0.0345	0.0305	−0.0261	0.0180	0.0239	0.0232
Assignment[a)]			ϕ_1°		$\phi_2^\circ(B_4)$	$\phi_3^\circ(B_3)$	$\phi_4^\circ(B_2)$	$\phi_5^\circ(B_1)$

a) See text for definition.

TABLE 5. ELEMENTS OF **B** MATRIX OF 1-NAPHTHYLAMINE[a)]

Reference MO	Symmetry type	Band notation	Photoelectron band (upper) and orbital function (lower)					
			VI	V	IV	III	II	I
			ϕ_1	ϕ_2	ϕ_3	ϕ_4	ϕ_5	ϕ_6
ϕ_1°	b_{1u}	B_5	0.9635	−0.1943	0.1498	−0.0920	−0.0028	−0.0526
ϕ_2°	b_{2g}	B_4	−0.0587	−0.8164	−0.5332	0.2038	−0.0163	0.0615
ϕ_3°	b_{3g}	B_3	−0.1127	−0.3134	0.7309	0.5684	0.0120	0.1757
ϕ_4°	b_{1u}	B_2	0.0036	0.0144	0.0023	−0.0111	0.9996	−0.0131
ϕ_5°	a_u	B_1	−0.0579	−0.1537	0.1361	−0.5270	0.0072	0.8220
ϕ_N°		B_N	0.2243	0.4063	−0.3639	0.5777	0.0078	0.5051
ϕ_6°	b_{2g}		−0.0265	−0.0651	0.0613	−0.1235	0.0032	−0.1332
ϕ_7°	b_{3g}		−0.0036	−0.0006	0.0038	−0.0056	−0.0132	−0.0004
ϕ_8°	b_{1u}		−0.0244	−0.0491	0.0507	−0.0782	−0.0034	−0.0912
ϕ_9°	a_u		−0.0154	−0.0322	0.0304	−0.0552	−0.0030	−0.0550
ϕ_{10}°	b_{3g}		0.0162	0.0308	−0.0295	0.0482	−0.0012	0.0521
Assignment[a)]			$\phi_1^\circ(B_5)$	$\phi_2^\circ(B_4)$	$\phi_3^\circ(B_3)$		$\phi_4^\circ(B_2)$	$\phi_5^\circ(B_1)$

a) See text for definition.

Table 6. Elements of **B** matrix of 2-naphthylamine[a)]

Reference MO	Symmetry type	Band notation	Photoelectron band (upper) and orbital function (lower)					
			VI	V	IV	III	II	I
			ϕ_1	ϕ_2	ϕ_3	ϕ_4	ϕ_5	ϕ_6
ϕ_1°	b_{1u}	B_5	0.9662	−0.2309	0.0566	0.0813	0.0356	−0.0437
ϕ_2°	b_{2g}	B_4	−0.1392	−0.8360	−0.0369	−0.3349	−0.1231	0.1330
ϕ_3°	b_{3g}	B_3	−0.0298	−0.1314	0.8374	−0.5127	−0.1129	0.0705
ϕ_4°	b_{1u}	B_2	−0.0704	−0.1866	0.2299	0.6159	−0.6373	0.3479
ϕ_5°	a_u	B_1	−0.0289	−0.0818	0.1077	0.1627	0.6309	0.7456
ϕ_N°		B_N	0.1973	0.4251	−0.2988	−0.4464	−0.3906	0.5191
ϕ_6°	b_{2g}		0.0171	0.0419	−0.0282	−0.0543	−0.0504	0.0869
ϕ_7°	b_{3g}		0.0217	0.0517	−0.0476	−0.0645	−0.0756	0.1019
ϕ_8°	b_{1u}		0.0096	0.0263	−0.0215	−0.0345	−0.0263	0.0459
ϕ_9°	a_u		0.0206	0.0505	−0.0414	−0.0634	−0.0649	0.0857
ϕ_{10}°	b_{3g}		−0.0119	−0.0256	0.0195	0.0319	0.0296	−0.0406
Assignment[a)]			$\phi_1^{\circ}(B_5)$	$\phi_2^{\circ}(B_4)$	$\phi_3^{\circ}(B_3)$			$\phi_5^{\circ}(B_1)$

a) See text for definition.

Table 7. Elements of **B** matrix of 1-naphthonitrile[a)]

Reference MO	Symmetry type	Band notation	Photoelectron band (upper) and orbital function (lower)					
						III	II	I
			ϕ_1	ϕ_2	ϕ_3	ϕ_4	ϕ_5	ϕ_6
ϕ_1°	b_{1u}	B_5	0.9398	−0.3218	0.0784	−0.0584	−0.0061	0.0082
ϕ_{CN1}°		B_{CN}	0.3005	0.6938	−0.3925	0.4482	0.0023	−0.2431
ϕ_2°	b_{2g}	B_4	−0.0955	−0.5174	−0.8385	0.1247	−0.0224	−0.0115
ϕ_3°	b_{3g}	B_3	−0.0825	−0.3316	0.3503	0.8662	0.0087	−0.0182
ϕ_4°	b_{1u}	B_2	0.0042	−0.0110	−0.0211	−0.0054	0.9996	0.0088
ϕ_5°	a_u	B_1	−0.0544	−0.1573	0.1052	−0.1442	0.0081	−0.9595
ϕ_6°	b_{2g}		−0.0284	−0.0637	0.0350	−0.0344	−0.0054	0.0062
ϕ_7°	b_{3g}		−0.0007	−0.0008	0.0025	0.0032	−0.0007	0.0063
ϕ_{CN2}°			0.0771	0.0655	0.0103	−0.0808	−0.0038	0.1401
ϕ_8°	b_{1u}		−0.0204	−0.0489	0.0264	−0.0267	0.0021	0.0035
ϕ_9°	a_u		−0.0133	−0.0304	0.0169	−0.0171	−0.0011	0.0030
ϕ_{10}°	b_{3g}		0.0129	0.0301	−0.0158	0.0170	0.0000	−0.0019
Assignment[a)]			ϕ_1°		ϕ_2°	$\phi_3^{\circ}(B_3)$	$\phi_4^{\circ}(B_2)$	$\phi_5^{\circ}(B_1)$

a) See text for definition.

Table 8. Elements of **B** matrix of 2-naphthonitrile[a)]

Reference MO	Symmetry type	Band notation	Photoelectron band (upper) and orbital function (lower)					
					IV	III	II	I
			ϕ_1	ϕ_2	ϕ_3	ϕ_4	ϕ_5	ϕ_6
ϕ_1°	b_{1u}	B_5	0.9466	0.3081	0.0745	0.0255	0.0209	−0.0027
ϕ_{CN1}°		B_{CN}	0.2733	−0.6684	−0.5208	−0.2766	−0.3010	0.1634
ϕ_2°	b_{2g}	B_4	−0.1330	0.6217	−0.7447	−0.1697	−0.0506	0.0121
ϕ_3°	b_{3g}	B_3	−0.0399	0.1293	0.3370	−0.9288	−0.0559	−0.0052
ϕ_4°	b_{1u}	B_2	−0.0541	0.1840	0.2051	0.1643	−0.9375	0.0544
ϕ_5°	a_u	B_1	−0.0323	0.0881	0.0901	0.0386	0.1127	0.9806
ϕ_6°	b_{2g}		0.0139	−0.0376	−0.0282	−0.0164	−0.0076	0.0057
ϕ_7°	b_{3g}		0.0206	−0.0515	−0.0369	−0.0197	−0.0142	−0.0018
ϕ_{CN2}°			0.0688	−0.0787	0.0334	0.0441	0.1060	−0.0923
ϕ_8°	b_{1u}		0.0098	−0.0224	−0.0151	−0.0093	−0.0079	0.0033
ϕ_9°	a_u		0.0194	−0.0474	−0.0338	−0.0156	−0.0128	0.0042
ϕ_{10}°	b_{3g}		−0.0095	0.0235	0.0166	0.0072	0.0068	−0.0034
Assignment[a)]			ϕ_1°		$\phi_2^{\circ}(B_4)$	$\phi_3^{\circ}(B_3)$	$\phi_4^{\circ}(B_2)$	$\phi_5^{\circ}(B_1)$

a) See text for definition.

Table 9. Elements of **B** matrix of 1-naphthaldehyde[a)]

Reference MO	Symmetry type	Band notation	Orbital function ϕ_1	ϕ_2	ϕ_3	ϕ_4	ϕ_5	ϕ_6
ϕ_1°	b_{1u}	B_5	0.9585	−0.2692	−0.0648	−0.0266	0.0139	0.0042
$\phi_{\mathrm{CHO}1}^{\circ}$		B_{CHO}	0.2605	0.8046	0.3533	0.3469	0.0029	−0.1758
ϕ_2°	b_{2g}	B_4	−0.0497	−0.4182	0.8994	0.0950	−0.0002	0.0046
ϕ_3°	b_{3g}	B_3	−0.0610	−0.2758	−0.2368	0.9237	−0.0178	−0.0068
ϕ_4°	b_{1u}	B_2	0.0163	0.0048	0.0039	−0.0169	−0.9996	−0.0001
ϕ_5°	a_u	B_1	−0.0316	−0.1371	−0.0630	−0.0827	0.0018	−0.9732
ϕ_6°	b_{2g}		−0.0021	−0.0604	−0.0176	−0.0190	−0.0042	−0.0129
$\phi_{\mathrm{CHO}2}^{\circ}$			−0.0716	0.0551	−0.0343	−0.0945	0.0126	0.1475
ϕ_7°	b_{3g}		−0.0036	−0.0052	−0.0010	0.0060	−0.0003	0.0023
ϕ_8°	b_{1u}		−0.0147	−0.0446	−0.0162	−0.0114	−0.0084	−0.0018
ϕ_9°	a_u		−0.0102	−0.0298	−0.0098	−0.0090	−0.0032	−0.0061
ϕ_{10}°	b_{3g}		0.0088	0.0274	0.0100	0.0086	0.0029	0.0020
Assignment[a)]			ϕ_1°	$\phi_{\mathrm{CHO}1}^{\circ}$	ϕ_2°	ϕ_3°	ϕ_4°	ϕ_5°

a) See text for definition.

Table 10. Elements of **B** matrix of 2-naphthaldehyde[a)]

Reference MO	Symmetry type	Band notation	Orbital function ϕ_1	ϕ_2	ϕ_3	ϕ_4	ϕ_5	ϕ_6
ϕ_1°	b_{1u}	B_5	0.9577	−0.2786	−0.0525	0.0023	−0.0125	0.0055
$\phi_{\mathrm{CHO}1}^{\circ}$		B_{CHO}	0.2479	0.7426	0.5254	−0.1980	0.2271	0.1115
ϕ_2°	b_{2g}	B_4	−0.1127	−0.5580	0.8128	−0.0746	0.0080	−0.0093
ϕ_3°	b_{3g}	B_3	−0.0402	−0.1211	−0.1842	−0.9727	0.0286	−0.0237
ϕ_4°	b_{1u}	B_2	−0.0377	−0.1655	−0.1344	0.0812	0.9663	0.0065
ϕ_5°	a_u	B_1	−0.0297	−0.0833	−0.0595	0.0015	−0.0402	0.9900
ϕ_6°	b_{2g}		0.0082	0.0314	0.0205	−0.0110	−0.0041	0.0053
$\phi_{\mathrm{CHO}2}^{\circ}$			0.0641	0.0697	−0.0570	0.0458	−0.1099	−0.0819
ϕ_7°	b_{3g}		0.0159	0.0462	0.0250	−0.0110	−0.0005	−0.0087
ϕ_8°	b_{1u}		0.0067	0.0182	0.0101	−0.0072	0.0036	0.0030
ϕ_9°	a_u		0.0144	0.0415	0.0233	−0.0076	0.0012	0.0010
ϕ_{10}°	b_{3g}		−0.0067	−0.0202	−0.0117	0.0033	−0.0019	−0.0025
Assignment[a)]			ϕ_1°	$\phi_{\mathrm{CHO}1}^{\circ}$	ϕ_2°	ϕ_3°	ϕ_4°	ϕ_5°

a) See text for definition.

O, N, CN, and CHO, corresponding to naphthols, naphthylamines, naphthonitriles, and naphthaldehydes respectively. The symmetry types shown in the tables are those for the naphthalene SCF-MO's, where the X- and Y-axes are chosen as the long and short axes of the naphthalene ring respectively. The band notations for the PE bands of naphthalene and the substituents, B_1, B_2,···, B_x, are also given in the tables. In columns of these tables, the elements of **B** matrix defined by Eq. 4 are given. The square of the element represents the weight of the individual ϕ_i°'s. When a reference MO, ϕ_i°, makes a contribution of more than 50% to ϕ_j, the ϕ_j is assigned to the ϕ_i°; the band notation for the ϕ_i° is given in the assignment column.

Figures 1 and 2 show the energy diagrams for the occupied π-orbitals of the compounds studied. When ϕ_i° makes a contribution of more than 50% to ϕ_j, the level of the ϕ_i° is connected to that of the ϕ_j by —·—. When the ϕ_i° makes a contribution of between 30 to 50% to the ϕ_j, the level of the ϕ_i° is connected to that of the ϕ_j by ······. The MO energy levels of monosubstituted naphthalenes with an electron-donating group look as if they are shifted toward a higher energy

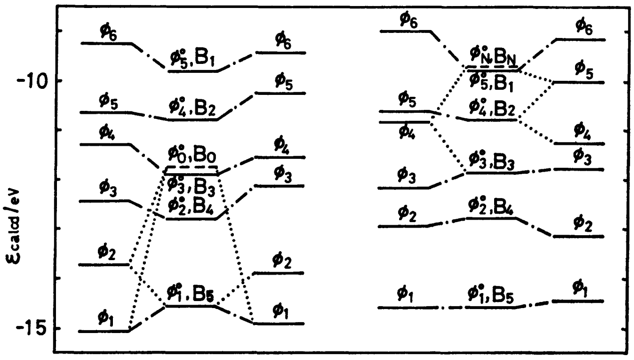

Fig. 1. Orbital energy diagram for the occupied π-orbitals of naphthalene(N), 1- and 2-naphthols(1-OH and 2-OH), and 1- and 2-naphthylamine(1-NH_2 and 2-NH_2). OH and NH_2: the π-AO of the substituents; ——: SCF-MO energies of the compounds; ——: π-AO of the substituents. A semibroken line(—·—) indicates that ϕ_i° makes a contribution higher than 50% to ϕ_j and a dotted line (······)a contribution ranging from 30% to 50%. B_1, B_2, ···, correspond to the band notation (see text).

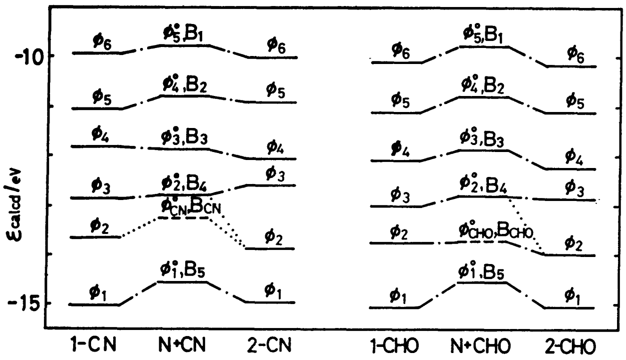

Fig. 2. Orbital energy diagram for the occupied π-orbitals of naphthalene(N), 1- and 2-naphthonitriles(1-CN and 2-CN), and 1- and 2-naphthaldehydes(1-CHO and 2-CHO). CN and CHO: the occupied π-MO of the substituents; ----: π-MO of the substituents. Other symbols are the same as in Fig. 1.

compared with those of naphthalene, although the case of naphthylamines is somewhat complicated. On the other hand, the MO energy levels of naphthonitriles and naphthaldehydes are apparently shifted toward a lower energy.

Discussion

Usually the ionization potentials are evaluated from the SCF molecular wavefunction by the use of Koopmans' theorem,[2] according to which the energy required to remove an electron from the ith orbital of a molecule, leaving the nuclei fixed and the orbital unaltered, is given by

$$I_i = -\varepsilon_i. \tag{5}$$

Tables 1 and 2 show that the $\varepsilon_i^{\mathrm{corrd}}$'s for the compounds studied in the present paper are in good agreement with the observed I_v's. The $\varepsilon_i^{\mathrm{corrd}}$ of the unoccupied orbital ϕ_6° of naphthalene is equal to 0.25 eV. The reported value of the electron affinity is 0.16 eV[12] or 0.20 eV.[13] Hence, $\varepsilon_i^{\mathrm{corrd}}$ is found to be a reasonable value for both the I_v and the electron affinity. Below, discussion will be limited to the occupied orbitals.

Orbital Assignment. Let us now proceed to discuss the results of the MOA, beginning with naphthols.

Tables 3 and 4 show that the ϕ_1, ϕ_3, ϕ_4, ϕ_5, and ϕ_6 of naphthols are assigned to the ϕ_1°, ϕ_2°, ϕ_3°, ϕ_4°, and ϕ_5° of naphthalene respectively. There is a relatively strong interaction among the ϕ_1°, ϕ_2°, and ϕ_O° of which the ϕ_2 of naphthols is composed. The most important reference MO's in the ϕ_2 of naphthols are the ϕ_1° and ϕ_O°. There is a splitting of the reference MO's. For example, the ϕ_1° splits into the ϕ_1 and ϕ_2 of nearly equal weights, the ϕ_1 lying on the lower-energy side, and the ϕ_2 on the higher-energy side, relative to ϕ_1°. The ϕ_5 of 1-naphthol has almost the same property as the ϕ_4°. The ϕ_O° makes an important contribution to the ϕ_1, ϕ_2, ϕ_4, and ϕ_6 by weights of 31.7, 30.9, 14.4 and 10.6% in 1-naphthol and to the ϕ_1, ϕ_2, and ϕ_3 by weights of 33.3, 24.7, and 13.7% in 2-naphthol, respectively.

With reference to the results shown in Tables 5 and 6, the ϕ_1, ϕ_2, ϕ_3, and ϕ_6 of naphthylamines can reasonably be assigned to the ϕ_1°, ϕ_2°, ϕ_3°, and ϕ_5° respectively. The ϕ_5° of 1-naphthylamine has almost the same property as the ϕ_4°, the situation being the same as in 1-naphthol. There is a relatively strong interaction among the ϕ_3°, ϕ_5°, and ϕ_N° of which the ϕ_4 of 1-naphthylamine is composed. They make nearly equal contributions to the ϕ_4. However, in the case of 2-naphthylamine, the interaction among the ϕ_2°, ϕ_3°, ϕ_4°, ϕ_5°, and ϕ_N° is large, yielding the ϕ_4 and ϕ_5. A splitting of the reference MO's is also found, as in the case of naphthols. For example, ϕ_4° splits into the ϕ_4 and ϕ_5 with nearly equal weights. The ϕ_4° is the most important reference MO in the ϕ_4 and ϕ_5 of 2-naphthylamine. The weight of the ϕ_4° to the ϕ_4 is larger than that of the ϕ_3°. The ϕ_4 lies on the higher-energy side, and the ϕ_5 lies on the lower-energy side, relative to the ϕ_4°. The ϕ_N° makes an important contribution to the ϕ_2, ϕ_3, ϕ_4, and ϕ_6 by weights of 16.5, 13.2, 32.2, and 25.5% in 1-naphthylamine, and to the ϕ_2, ϕ_4, ϕ_5, and ϕ_6 by weights of 18.1, 19.9, 15.3, and 27.0% in 2-naphthylamine, respectively.

It may be seen in Tables 7 and 8 that the ϕ_1, ϕ_3, ϕ_4, ϕ_5, and ϕ_6 of naphthonitriles can reasonably be assigned to the ϕ_1°, ϕ_2°, ϕ_3°, ϕ_4°, and ϕ_5° respectively and that the ϕ_5 of 1-naphthonitrile has the same property as the ϕ_4°, just as in 1-naphthol and 1-naphthylamine. The ϕ_2 of naphthonitriles is mainly composed of the $\phi_{\mathrm{CN}1}^\circ$ and ϕ_2°. The $\phi_{\mathrm{CN}1}^\circ$ makes an important contribution to the ϕ_2, ϕ_3, and ϕ_4 by weights of 48.1, 15.4, and 20.1% in 1-naphthonitrile and to the ϕ_2 and ϕ_3 by weights of 44.7 and 27.1% in 2-naphthonitrile respectively. The splitting of the reference MO's is also found, as in the case of electron-donating.

Tables 9 and 10 show that the ϕ_1, ϕ_2, ϕ_3, ϕ_4, ϕ_5, and ϕ_6 of naphthaldehydes are assigned to the ϕ_1°, $\phi_{\mathrm{CHO}1}^\circ$, ϕ_2°, ϕ_3°, ϕ_4°, and ϕ_5°, respectively, irrespective of the substitution at the 1- or 2-position. The $\phi_{\mathrm{CHO}1}^\circ$ mixes mainly with the ϕ_2°. It is also found that the reference MO's split into several MO's of naphthaldehydes. The ϕ_5 of 1-naphthaldehyde also has the same property as the ϕ_4°. The $\phi_{\mathrm{CHO}1}^\circ$ makes an important contribution to the ϕ_3 and ϕ_4 by weights of 12.5 and 12.0% respectively in 1-naphthaldehyde and to the ϕ_3 by a weight of 27.6% in 2-naphthaldehyde.

As may be seen from Tables 3, 5, 7, and 9, the weight of the ϕ_4° in the ϕ_5 is always 99.9% in the case of the naphthalene derivatives with a substitution at the 1-position. The ϕ_4° of naphthalene is little affected by the substitution at the 1-position. This situation can be well interpreted in terms of the property of the orbital. Since the ϕ_4° orbital of naphthalene has a node at the 1-position, its energy is little changed by the ϕ_O°, ϕ_N°, ϕ_CN°'s, and ϕ_CHO°'s in the cases of 1-naphthol,[8] 1-naphthylamine,[8] 1-naphthonitrile,[8] and 1-naphthaldehyde.

Assignment of the Photoelectron Spectra. The results of the orbital assignment will now be related to the PE spectra. The PE spectra of naphthalene have five bands in the region from 8 to 13 eV.[4,6,7,14] Table 1 shows that Bands I, II, III, IV, and V are assigned to the ionization corresponding to taking an electron away from the ϕ_5°, ϕ_4°, ϕ_3°, ϕ_2°, and ϕ_1° respectively. The PE bands corresponding to these ionization processes are conveniently indicated by the B_1, B_2, B_3, B_4, and B_5 notations respectively. The B_O, B_N, B_{CN}, and B_{CHO} notations indicate taking an electron away from the $\phi_O°$, $\phi_N°$, $\phi_{CN1}°$, and $\phi_{CHO1}°$ respectively (see Tables 3—10).

The PE spectra of naphthalene derivatives have been reported by several authors.[6-8] 1-Naphthol[8] has three bands, I, II, and III, in the region from 7 to 10 eV, while 2-naphthol has four bands, I, II, III, and IV, in the region from 7 to 11 eV. From Table 3, Bands I, II, and III of 1-naphthol are assigned to the B_1, B_2, and B_3 of naphthalene, while from Table 4 Bands I, II, III, and IV of 2-naphthol are assigned to the B_1, B_2, B_3, and B_4 of naphthalene respectively.

In the cases of 1- and 2-naphthylamines, there are six bands in the region from 7 to 13 eV.[7,8] Bands I, II, IV, V, and VI of 1-naphthylamine are assigned to the B_1, B_2, B_3, B_4, and B_5, while Bands I, IV, V, and VI of 2-naphthylamine are assigned to the B_1, B_3, B_4, and B_5 respectively. Band III of 1-naphthylamine is composed of the B_N, B_1, and B_3. Bands II and III of 2-naphthylamine are composed of the B_1 and B_2 and of the B_2 and B_3 respectively.

The PE bands of naphthonitriles have been reported by the same authors.[8] Bands I, II, and III for 1-naphthonitrile and Bands I, II, III, and IV for 2-naphthonitrile have been found. It may be seen from Tables 7 and 8 that they are assigned to the B_1, B_2, and B_3 for 1-naphthonitrile and to the B_1, B_2, B_3, and B_4 for 2-naphthonitrile.

Effects of the Electron-donating and Electron-accepting Properties on the Photoelectron Spectra. It is well known that the amino and hydroxyl groups have an electron-donating property, while the formyl and cyano groups have an electron-accepting property. In this subsection we will discuss the effect of these properties of the substituent on the PE spectra.

The PE spectra of naphthylamine, on the whole, are similar in appearance to the PE spectra of the corresponding naphthols. However, in passing from naphthols to naphthylamines, the individual bands undergo considerable changes in location.

The weight of the most important reference orbitals in naphthylamines is considerably smaller than that of the corresponding orbitals in naphthols. This suggests that amino substitution has a greater influence on the PE bands of naphthalene than does hydroxyl substitution. Since the calculated orbital energy is −9.7 eV for an amino group and −11.7 eV for a hydroxyl group, the higher the energy of the orbital of the substituent, the greater the mixing among the reference orbitals in the case of electron-donating substitution.

There may also be a similarity of the PE spectra between naphthonitriles and naphthaldehydes, as in the case between naphthols and naphthylamines.

It may be seen from Tables 7—10 that the weight of the most important reference orbitals in the individual orbitals of naphthaldehydes and the mixing among the local π-MO's of naphthalene and the orbital of the formyl group in naphthaldehydes are smaller than those in naphthonitriles. This suggests that the cyano substitution has a greater influence on the lower-energy PE bands of naphthalene than does the formyl substitution. The cyano and formyl groups have one occupied MO and one unoccupied MO. The calculated π-MO energies for the cyano group are $\varepsilon_{CN1} = -13.2209$ eV and $\varepsilon_{CN2} = -0.1855$ eV, while those for the formyl group are $\varepsilon_{CHO1} = -13.7252$ eV and $\varepsilon_{CHO2} = -0.7651$ eV. The energy difference between the unoccupied orbital of the formyl group and the occupied π-MO's of naphthalene is smaller than that between the unoccupied orbital of the cyano group and the occupied π-MO's of naphthalene. Therefore, the smaller the energy difference between the unoccupied orbital of the substituent and the occupied π-MO's of naphthalene, the smaller the mixing among the reference orbitals, this is in contrast with the electron-donating case.

The individual electronic absorption bands of naphthalene derivatives shift to the red relative to the corresponding bands of naphthalene whether the substituents are electron-donating or electron-accepting. The behavior of the individual electronic absorption bands of naphthalene derivatives can now be satisfactorily interpreted by the method of configuration analysis.[10,11,15] On the other hand, the PE spectra of naphthonitriles and naphthaldehydes shift to the lower energy of the corresponding bands of naphthalene. The PE spectra of naphthols and naphthylamines seem to shift to the higher energy relative to the corresponding bands of naphthalene. No simple explanation of the relationships observed in the PE spectra of naphthalene derivatives can be offered at the present time.

References

1) D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, "Molecular Photoelectron Spectroscopy," John Wiley & Sons, New York, N. Y. (1969).

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

3) K. Kimura, S. Katsumata, Y. Achiba, H. Matsumoto, and S. Nagakura, *Bull. Chem. Soc. Jpn.*, **46**, 373 (1973).

4) P. A. Clark, F. Brogli, and E. Heilbronner, *Helv. Chim. Acta*, **55**, 1415 (1972).

5) F. Marschner and H. Goetz, *Tetrahedron*, **30**, 3159 (1974).

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

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

8) C. Utsunomiya, T. Kobayashi, and S. Nagakura, *Bull. Chem. Soc. Jpn.*, **48**, 1852 (1975).

9) H. Baba, S. Suzuki, and T. Takemura, *J. Chem. Phys.*, **50**, 2078 (1969).

10) S. Suzuki, T. Fujii, and H. Baba, *J. Mol. Spectrosc.*, **47**, 243 (1973).

11) S. Suzuki, T. Fujii, and T. Ishikawa, *J. Mol. Spectrosc.*, **57**, 490 (1975).

12) R. S. Becker and E. Chen, *J. Chem. Phys.*, **45**, 2403 (1966).

13) M. Bathey, Ph. D. Thesis, University of Queensland, Australia, 1966.

14) F. Brogli, E. Heilbronner, and T. Kobayashi, *Helv. Chim. Acta*, **55**, 274 (1972).

15) S. Suzuki and T. Fujii, *J. Mol. Spectrosc.*, **61**, 350 (1976).