Electronic Spectra of Substituted Aromatic Hydrocarbons. II. Naphthols and Naphthylamines[*]

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The effect of substitutions on the electronic spectrum of a conjugated molecule depends upon the positions at which the substituents are attached to the molecule. With naphthalene, there is a noticeable difference between the spectral changes caused by substitutions at α- and β-positions. Several theoretical studies have been made to account for this interesting phenomenon[1]. The treatments, however, were limited to the framework of the LCAO molecular orbital (MO) theory in its simplest form, because substituted naphthalenes are complex molecules which have only low symmetry or none at all.

In the present study, the ultraviolet absorption spectra of naphthols and naphthylamines have been newly measured, and the effects of hydroxyl and amino substitutions upon the naphthalene spectrum have been examined on the basis of a calculation which was carried out according to the same method as that used in the preceding paper[2] (hereafter referred to as I).

Experimental

Materials.—α-Naphthol was recrystallized from ligroin, and β-naphthol from water and ligroin. Both were further purified by vacuum sublimation; m. p. 93.0~93.5°C and 119.0~119.5°C, respectively. α-Naphthylamine and β-naphthylamine were repeatedly recrystallized from ligroin, and were sublimed in vacuo; m. p. 48.5~49.0°C and 110.0~110.5°C, respectively. Each of the four samples was subjected to vacuum sublimation whenever it was used for a measurement.

Isooctane (2,2,4-trimethylpentane; Enjay Co., Inc., U. S. A.) was carefully purified by distillation and by being passed through a chromatography tube filled with dried silica-gel powder. The isooctane thus purified is transparent down to 200 mμ.

Measurement of Spectra and Results.—Ultraviolet absorption spectra were measured at controlled

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[*] Read in part at the Symposium on Electronic States in Molecules, held by the Chem. Soc. Japan, Oct. 1958. (See Abstract of the Meeting, p. 73).

[1] D. Peters, *J. Chem. Soc.*, **1957**, 646, 1993, 4182; K. Nishimoto and R. Fujishiro, This Bulletin, **32**, 445 (1959); R. Fujishiro and K. Nishimoto, Abstract of the Symposium on Electronic States in Molecules, held by the Chem. Soc. Japan, Sept. 1959, p. 14.

[2] H. Baba, This Bulletin, **34**, 76 (1961).

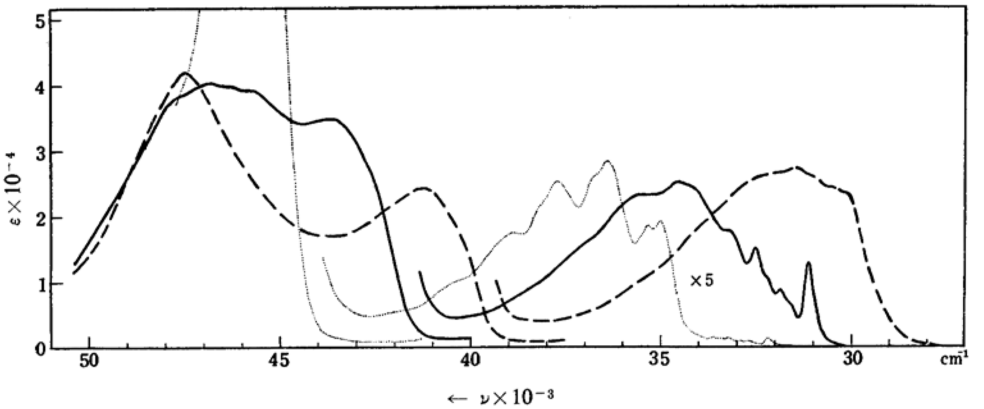

Fig. 1. Ultraviolet absorption spectra of α-naphthol (——), α-naphthylamine (----) and naphthalene (······) in isooctane.

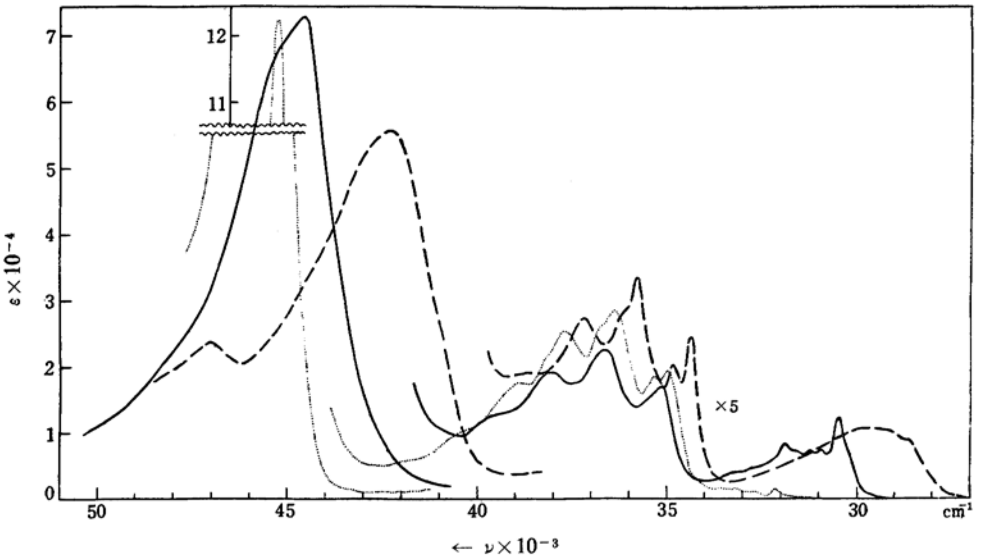

Fig. 2. Ultraviolet absorption spectra of β-naphthol (——), β-naphthylamine (----) and naphthalene (······) in isooctane.

temperatures with a Hitachi quartz spectrophotometer of type EPU-2A. Attention was paid to the width of the slit so that the effective band width of the exit beam came to be sufficiently narrow as compared with the width of the absorption bands. Silica cells of 10 mm. and 2.5 mm. lengths were used, each of which was fitted with a ground-glass stopper. It was confirmed that Beer's law holds for all the substances in isooctane over the range of concentrations ($10^{-4}\sim10^{-5}$ mol./l.) used in the present measurement.

The absorption spectra of the α- and β-derivatives are shown, respectively, in Figs. 1 and 2. The spectra were observed at 20°C except for that of α-naphthylamine, which was obtained at 17.5°C. In the figures the spectrum of naphthalene[3] is also given for ready comparison.

Calculation

Calculations have been made for α-, β-naphthols and α-, β-naphthylamines by following the same procedure as in I. Various theoretical quantities are at first presented as functions of the parameter δ_X; and then the values of the quantities for naphthols and naphthylamines are derived by assuming δ_O and δ_N to

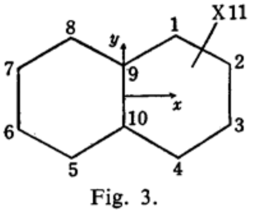

Fig. 3.

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[3] American Petroleum Institute Research Project 44, Ultraviolet Spectral Data, Serial No. 640, 654.

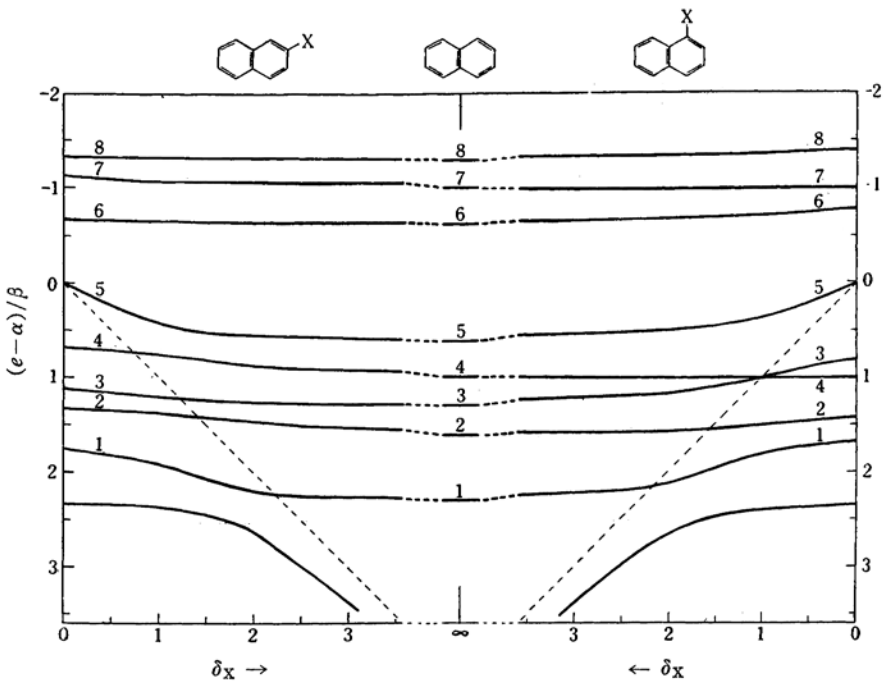

Fig. 4. Relation of MO energies to δ_X.

be equal to the corresponding parameter values determined in I for phenol and aniline. The notation used in this paper is the same as in I.

Molecular Orbitals.—The MO's of the parent hydrocarbon, naphthalene, are designated as $\phi_1^0, \phi_2^0, \cdots\cdots$ in the sequence of ascending energy. Among these the following MO's are primarily associated with the lower electronic transitions[4].

$$\phi_4^0 = a(\chi_2+\chi_3+\chi_6+\chi_7) - a(\chi_9+\chi_{10}),$$
$$e_4^0 = \alpha+\beta \qquad \text{(1a)}$$
$$\phi_5^0 = b(\chi_1-\chi_4+\chi_5-\chi_8) + c(\chi_2-\chi_3+\chi_6-\chi_7),$$
$$e_5^0 = \alpha+0.6180\beta \qquad \text{(1b)}$$
$$\phi_6^0 = b(\chi_1+\chi_4-\chi_5-\chi_8) - c(\chi_2+\chi_3-\chi_6-\chi_7),$$
$$e_6^0 = \alpha-0.6180\beta \qquad \text{(1c)}$$
$$\phi_7^0 = -a(\chi_2-\chi_3-\chi_6+\chi_7) + a(\chi_9-\chi_{10}),$$
$$e_7^0 = \alpha-\beta \qquad \text{(1d)}$$

where $a=0.4082$, $b=0.4253$, $c=0.2629$; χ_p is the pth atomic orbital (see Fig. 3 for the numbering of the positions); the superscript zeros refer to the parent hydrocarbon.

The energies of the ground-state MO's and of the lower excited MO's for the monosubstituted naphthalenes are plotted against δ_X in Fig. 4.

Configuration Interaction.—With naphthalene, configurations V_{46}^0 and V_{57}^0 belong to B_{3u}, and V_{47}^0 and V_{56}^0 to B_{2u} species of the symmetry group D_{2h}[5]. According to the simple LCAO treatment, the configuration V_{46}^0 and V_{57}^0 are degenerate, but V_{47}^0 and V_{56}^0 are not (cf. Eqs. 1a—1d). To a first approximation, interaction is included only between the degenerate configurations, V_{46}^0 and V_{57}^0[6]. The wave functions thus obtained for the lower excited states of naphthalene are shown in Table I. Using the observed excitation energies, given in Table I, one obtains

TABLE I. EXCITED STATES OF NAPHTHALENE

Symmetry	Wave function	Observed excitation energy* (eV.)
B_{3u}^-	$\frac{1}{\sqrt{2}}(V_{46}^0-V_{57}^0)$	3.99
B_{2u}	V_{56}^0	4.51
B_{3u}^+	$\frac{1}{\sqrt{2}}(V_{46}^0+V_{57}^0)$	5.62

* Taken from Ref. 3.

$$E(V_{46}^0) = E(V_{57}^0) = \frac{1}{2}\{W^0(B_{3u}^-) + W^0(B_{3u}^+)\}$$
$$= E(V_0^0) + 4.80 \text{ eV.}$$
$$E(V_{56}^0) = E(V_0^0) + 4.51 \text{ eV.}$$

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[4] R. Pariser, *J. Chem. Phys.*, 24, 250 (1956).

[5] The group-theoretical notation is the same as that used in G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Company, Inc., New York (1945), p. 108. The x and y axes are chosen as in Fig. 3 and the z axis is perpendicular to the molecular plane.

[6] M. J. S. Dewar and H. C. Longuet-Higgins, *Proc. Phys. Soc.* (*London*), A67, 795 (1954).

Hence it follows from Eq. 2 of I

$$\beta^0_{4\to6}=\beta^0_{5\to7}=-2.97\ \text{eV.}=\beta^0(B_{3u}) \tag{2a}$$

$$\beta^0_{5\to6}=-3.65\ \text{eV.} \tag{2b}$$

With the naphthalene derivatives, even the energies of V_{46} and V_{57} are no longer equal. In this calculation, only the interaction is taken into account between those configurations of the derivatives which are degenerate in the parent hydrocarbon. Thus the interaction of V_{46} and V_{57} is included; on the other hand, V_{56} is assumed to represent the wave function for an excited state without mixing with any other configurations. The energies of these configurations are obtained from Eq. 2 of I on the assumption that $\beta_{4\to6}=\beta_{5\to7}=\beta^0(B_{3u})$ and $\beta_{5\to6}=\beta^0_{5\to6}$.

The calculation of the matrix element $\{V_{46} \mid V_{57}\}$ is made in exactly the same way as in I. The integral values used in the present calculation are the same as those used in I. As a result, it follows that

naphthalene, $\{V^0_{46} \mid V^0_{57}\}=0.918$ eV.

α-derivative, $\{V_{46} \mid V_{57}\}=0.866$ and 0.782 eV.

β-derivative, $\{V_{46} \mid V_{57}\}=0.824$ and 0.693 eV.

where the values for each derivative correspond, respectively, to the paramater values $\delta_X=2.0$ and 1.2.

State Energies.—The calculated energies of the excited states are shown in Fig. 5 as functions of δ_X; the observed excitation energies of naphthalene, naphthols and naphthylamines are also indicated in the figure. In the parent hydrocarbon, naphthalene, the calculated and observed energies of the B_{2u} state are, of course, in accord with each other. The energies of the B^-_{3u} and B^+_{3u} states are calculated, respectively, to be 3.89 and 5.72 eV., both being in good agreement with the observed excitation energies (see Table I). This may be regarded as a proof that the used integrals are of suitable values.

The monosubstituted naphthalenes have no symmetry, apart from their symmetry with respect to the molecular plane. However, the wave functions or energy levels of the derivatives may be denoted by the analogy of the notation for the corresponding quantities of the parent hydrocarbon. Thus, for example, the lowest excited state of the derivatives will be designated as (B^-_{3u}), where the symbol of the symmetry type for the parent hydrocarbon is inclosed in parentheses.

Oscillator Strengths. — Oscillator strengths, f, are calculated from Eq. 12 of I. Plots of f_{calc} vs. δ_X are given in Fig. 6. It may be noted that f_{calc} values for the transitions to B^-_{3u}, B_{2u} and B^+_{3u} states in naphthalene are, respectively, 0, 0.52 and 2.14, corresponding f_{obs} values being 0.002, 0.11 and 1.70[3,7].

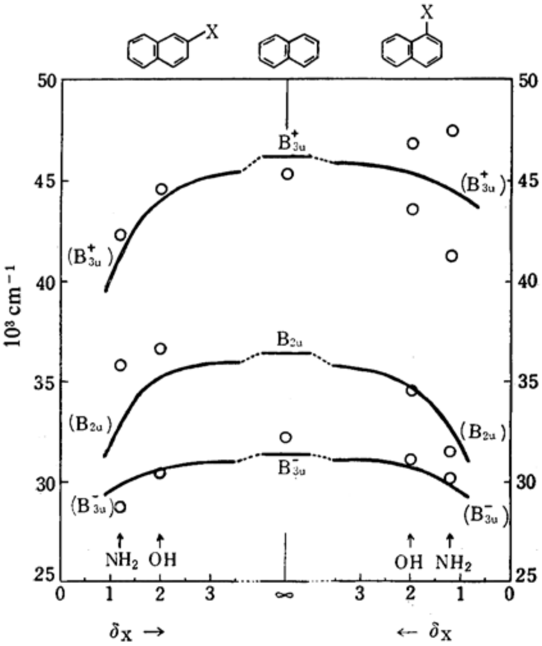

Fig. 5. Relation of the energies of the excited states to δ_X. The observed energies are represented by circles.

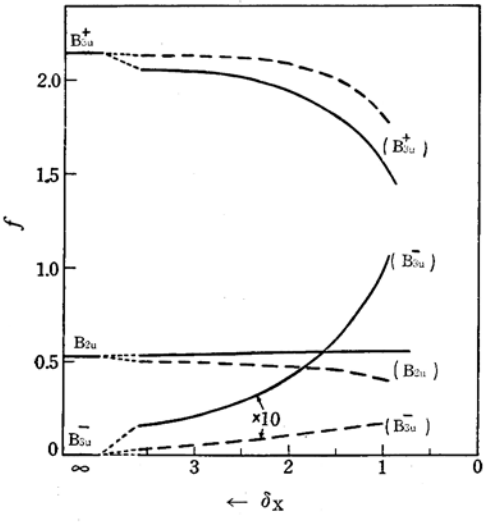

Fig. 6. Relation of f values to δ_X.
——, α-derivative; ----, β-derivative.

Summary of Calculation.—As the most appropriate values for the Coulomb integral parameters of the oxygen and nitrogen atoms,

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7) H. B. Klevens and J. R. Platt, *J. Chem. Phys.*, **17**, 470 (1949).

TABLE II. EXCITED STATES OF NAPHTHOLS AND NAPHTHYLAMINES

	State	Wave function	Excitation energy (cm^{-1})		f		Δq_X
			calc.	cbs.	calc.	obs.*	
α-Naphthol	(B_{3u}^{-})	$0.591V_{46}-0.807V_{57}$	30800	31100	0.042	0.016	−0.038
	(B_{2u})	V_{56}	34800	34570	0.55	0.102	−0.049
	(B_{3u}^{+})	$0.807V_{46}+0.591V_{57}$	45400	43570 46820	1.94	0.328 0.892	−0.010
β-Naphthol	(B_{3u}^{-})	$0.766V_{46}-0.643V_{57}$	30600	30470	0.011	0.0211	−0.056
	(B_{2u})	V_{56}	35200	36600	0.48	0.0811	−0.043
	(B_{3u}^{+})	$0.643V_{46}+0.766V_{57}$	44100	44580	2.08	1.06	−0.049
α-Naphthylamine	(B_{3u}^{-})	$0.502V_{46}-0.865V_{57}$	29900	30100	0.082	0.13	−0.13
	(B_{2u})	V_{56}	32700	31500	0.55		−0.14
	(B_{3u}^{+})	$0.865V_{46}+0.502V_{57}$	44500	41250 47440	1.68	0.34 0.82	−0.011
β-Naphthylamine	(B_{3u}^{-})	$0.778V_{46}-0.628V_{57}$	29900	28740	0.016	0.033	−0.13
	(B_{2u})	V_{56}	33000	35790	0.43	0.10	−0.16
	(B_{3u}^{+})	$0.628V_{46}+0.778V_{57}$	41300	42340	1.91	0.86	−0.14

* For the details of the determination of the observed f values see Ref. 8.

$\delta_O=2.0$ and $\delta_N=1.2$ were obtained in I. Application of these values to the case of the naphthalene derivatives leads to the results summarized in Table II, where the changes of the π-electron density, Δq_X, accompanying the electronic transitions are also given. The observed excitation energies and oscillator strengths are cited in the table.

In connection with the Δq_X values it is instructive to know the charge distribution in the ground state. Thus, from the ground-state MO's corresponding to $\delta_X=1.2$, quantities related to the charge distribution in the ground state were derived for naphthylamines. The results are collected in the molecular diagrams of Fig. 7, in which the analogous diagram for aniline is shown for the sake of comparison.

Discussion

Inspection of Fig. 4 reveals several features of the MO's of the naphthalene derivatives. In the α-derivative, orbital energies e_4 and e_7 are completely identical with e_4^0 and e_7^0, respectively, regardless of the value of δ_X; e_3 is raised with decreasing magnitude of δ_X, and consequently the sequence of the heights of e_3 and e_4 is reversed at $\delta_X=1$; e_5 is most affected by the α-substitution. In the β-derivative e_4 is strongly influenced by the substitution, while e_3 remains almost unaltered. When δ_X is large e_5 is little changed upon the β-substitution, but it is considerably affected by a substituent with a small magnitude of δ_X, i. e., by a strongly conjugating substituent. The behaviors of the orbital energies in the α- and β-derivatives may, at least in part, be understood in terms of the coefficients of the atomic orbitals in the MO's of the parent hydrocarbon (cf. Eqs. 1a—1d).

Regarding the wave functions of the excited states, it is to be noted that the degrees of configuration mixing in the wave functions of the $(B_{3u}^{\pm})$ states are appreciably changed by the substitutions.

Before proceeding to a discussion of the excitation energies, mention should be made of the spectra shown in Fig. 1. In the spectrum of α-naphthol, several minor peaks are present on the lower frequency side of the 34570 cm^{-1} band. In the light of the spectrum of naphthalene it is reasonable to regard these peaks as showing a fine structure of a definite electronic band which corresponds to the lowest frequency band of the parent hydrocarbon. No analogous band is found, at first sight, in the α-naphthylamine spectrum. However, the 31500 cm^{-1} band of α-naphthylamine exhibits relatively high extinction at the shoulder of 30100 cm^{-1}, as compared with the corresponding bands of α-naphthol and naphthalene. In view of this fact, the present authors tentatively assumed that the band in question is hidden under the more intense band of 31500

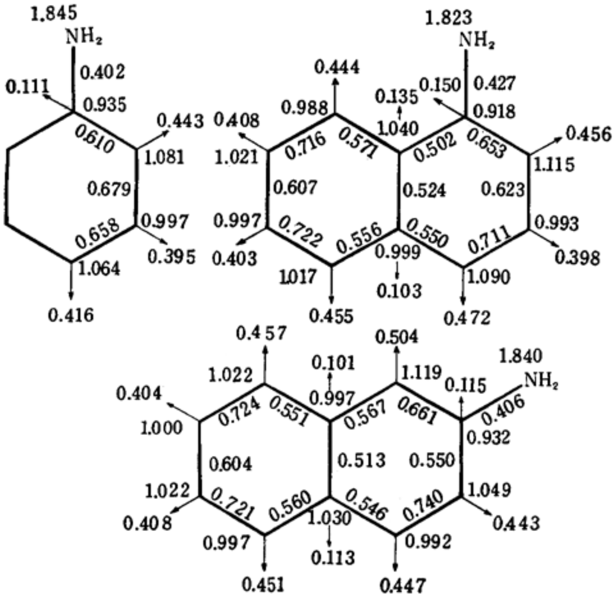

Fig. 7. Molecular diagrams for aniline, α-naphthylamine and β-naphthylamine. The π-electron density, π-bond order and free valence are shown in the usual manner for each molecule.

cm^{-1} in the neighborhood of the said shoulder.

α-Naphthol has two absorption bands ($\nu_{\max} = 43570$ and $46820\,\mathrm{cm}^{-1}$) in the higher frequency region, which are not fully separated from each other. It has been observed that, when a hydrogen bond is formed between α-naphthol and dioxane, these bands exhibit quite different behaviors: that is, the lower frequency band is displaced to the red and the other to the blue⁸⁾. This observation conclusively indicates that the bands under consideration are due to two distinct electronic transitions.

The calculated excitation energies for the (B_{3u}^-) and (B_{2u}) states of the α-derivatives are in good accord with the observed. A difficulty arises in the fact that two levels are observed near the calculated (B_{3u}^+) level of the α-derivatives. A tentative explanation for this will be given below.

According to Pariser's calculation for naphthalene, there exists a B_{1g}^+ state slightly below the B_{3u}^+ state⁴⁾. A plus state in general favors the transition from the ground state⁴⁾, but in the case of the B_{1g}^+ state the transition is forbidden, because $A_g \rightarrow B_{1g}$ is not allowed by the selection rule. To a first approximation, the B_{1g}^+ state is represented by $(1/\sqrt{2})(V_{36}^0 + V_{58}^0)$. As has already been shown, ϕ_3^0 and ϕ_5^0 are profoundly influenced by the α-substitution, so that the B_{1g}^+ state will be subjected to a considerable distortion. It is therefore probable that the B_{1g}^+ state comes to be allowed in the α-derivatives, and that a fairly strong interaction occurs between the (B_{3u}^+) and (B_{1g}^+) states to give two mixed states which can be assigned to the observed levels mentioned above. It seems reasonable to conclude that, of the two observed bands in question, the one of higher intensity, i. e., that of higher frequency, primarily corresponds to the (B_{3u}^+) state and the other to the (B_{1g}^+) state, for the transition to the B_{3u}^+ state is allowed even in the parent hydrocarbon.

Next, discussion will be turned to the excitation energies in the β-derivatives. There is a discrepancy between the calculated and observed energies of the (B_{2u}) state. It is generally accepted that the *p* band of naphthalene, which arises from the $A_g \rightarrow B_{2u}$ transition, is makedly shifted to the red by α-substitution, whereas it exhibits almost no shifts due to β-substitution¹⁾. The B_{2u} state of naphthalene is approximately represented by V_{56}^0. Also, for the coefficients of the atomic orbitals in ϕ_5^0 and ϕ_6^0, the relation $b^2 \gg c^2$ is seen to hold. Accordingly, so far as the behaviors of the *p* band are treated from the viewpoint of the perturbation theory, the calculation will lead to a result which is compatible with the observation. This is substantiated by the

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8) H. Baba and S. Suzuki, to be published in *J. Chem. Phys.*

results of Peters' perturbation treatment[1]. However, quite a different situation may be produced for strongly conjugating substituents, to which the perturbation theory fails to apply. In fact, in cases $\delta_X < 2$ the orbital energy e_5 is noticeably raised even in the β-derivatives, and hence the calculated excitation energy for $\phi_5 \rightarrow \phi_6$ becomes considerably smaller than the observed. This discrepancy is the most serious is the most serious difficulty involved in the present calculation.

From the spectra of Figs. 1 and 2, the effect of substitutions on the band intensities may be summarized as follows: the intensity of the transitions to the (B_{3u}^-) state is greatly enhanced, while that of the transition to the (B_{3u}^+) state is lowered; the transition to the (B_{2u}) state is subject to only a slight change in its intensity. These remarks are applicable to each of the α- and β-derivatives. It may be said that the f_{calc} values account, at least qualitatively, for the observed intensity variations due to the substitutions.

One may predict from the calculation of Δq_X that all transitions in both the α- and β-derivatives are accompanied by an increase of the positive charge at the substituent, and that the increment of the charge is extremely small as regards the transition to the (B_{3u}^+) state of the α-derivatives. This prediction has been verified in its essential points by experimental studies of the hydrogen bonding effect on the spectra of naphthols and naphthylamines[8].

By comparing the diagrams of Fig. 7, which are based on the molecular orbital method, with those obtained by the valence bond method[9,10], it is found that the two theoretical methods lead to essentially the same results in respect of both the charge distributions and the bond orders for aniline and the amines. It may be worthy of note that the π-electron densities at the nitrogen atoms are in the order

aniline> β-naphthylamine> α-naphthylamine

The present calculation is based on the assumption of the transferability of the parameters δ_N and δ_O from the benzene derivatives to the naphthalene derivatives. This assumption is seen to be reasonable on the inspection of Table II and Fig. 5.

Summary

The ultraviolet absorption spectra of α-, β-naphthols and α-, β-naphthylamines have been newly measured down to 200 mμ. On the basis of a calculation which was carried out in the same manner as in the preceding paper, the effect of substitutions at α- and β-positions upon the spectrum of napthalene has been explained and the assignment of the observed absorption bands has been made. It is suggested that, upon substitution at the α-position, the $A_u \rightarrow B_{3u}^+$ band of naphthalene splits into two electronic bands because of the interaction of the B_{3u}^+ state with a B_{1g}^+ state. Molecular diagrams are given for naphthylamines and for aniline.

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[9] B. Pullman, *Bull. soc. chim. France*, **1948**, 533.

[10] R. Daudel and M. Martin, ibid., **1949**, 83.