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Observation and Interpretation of Triplet-Triplet Absorption Spectra of Substituted Naphthalenes¹⁾

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Triplet-triplet (T-T) absorption spectra of naphthalene, α - and β -naphthol, and α - and β -methoxynaphthalene have been observed in rigid-glass solutions at 77°K by the rapid-scan spectrophotometric method and in fluid solutions at room temperature by the flash spectroscopic method. Hydrogenbonding effects on the T-T absorption spectra were examined for α - and β -naphthol. α -Naphthol was found to give different absorption spectra, depending upon the solvents employed. In a certain case the spectrum is attributed to a photoproduct rather than to the triplet state of α -naphthol. Analysis of the spectral data leads to the conclusion that the T-T absorption spectra in α -derivatives involve two different electronic transitions, and those in β -derivatives are due to a single electronic transition which is analogous to the transition in naphthalene. In agreement with these observations, calculations performed by the Pariser-Parr-Pople method predict that in the low-energy region, α -naphthol should have two allowed and detectable transitions, ${}^3\Psi_1 \rightarrow {}^3\Psi_7$ and ${}^3\Psi_1 \rightarrow {}^3\Psi_8$, and naphthalene and β -naphthol have only one such transition, ${}^3\Psi_1 \rightarrow {}^3\Psi_9$. The wave functions of triplet states are subjected to configuration analysis, with the result that ${}^3\Psi_7$ and ${}^3\Psi_8$ of α -naphthol are related predominantly to ${}^3\Psi_8$ and ${}^3\Psi_9$ of naphthalene, respectively.

Triplet-triplet (T-T) absorption spectra give useful information concerning the electronic structure of higher triplet states as well as of the lowest triplet of molecules. Until now a number of studies have been made both experimentally and theoretically on the T-T transitions in aromatic hydrocarbons such as naphthalene.^{2,3)} It is to be expected that we get a deeper insight into the nature of triplet states by investigating the effect of substitution on the T-T transitions. There have been, however, relatively few systematic studies of T-T absorption for substituted aromatic hydrocarbons.

The present paper deals with T-T absorption spectra of some substituted naphthalenes. The parent hydrocarbon, naphthalene, is one of the molecules whose T-T transitions have attracted much attention.^{2,3)} The naphthalene molecule shows at about 400 m μ a T-T absorption consisting of three sharp peaks. Recent studies including polarization measurements⁴⁻⁶⁾ and molecular orbital calculations^{7,8)} have demonstrated that this T-T absorption is due to a single electronic transition which has three peaks as vibrational components. In their theoretical study on T-T absorption spectra of substituted naphthalenes, Kla-

1) Presented at the Symposium on Molecular Structure, held by the Chemical Society of Japan, at Towa University, Kyushu, Oct. 1969.

2) S. K. Lower and M. A. El-Sayed, *Chem. Revs.*, **66**, 199 (1966).

3) S. P. McGlynn, T. Azumi, and M. Kinoshita, "Molecular Spectroscopy of the Triplet State," Prentice-Hall, Englewood Cliffs, New Jersey (1969).

4) M. A. El-Sayed and T. Pavlopoulos, *J. Chem. Phys.*, **39**, 834 (1963).

5) D. P. Craig and G. Fischer, *Trans. Faraday Soc.*, **63**, 530 (1967).

6) D. Lavalette, *Chem. Phys. Lett.*, **3**, 67 (1969).

7) R. L. de Groot and G. J. Hoytink, *J. Chem. Phys.*, **46**, 4523 (1967).

8) M. K. Orloff, *ibid.*, **47**, 235 (1967).

sinc and Sommer⁹⁾ paid attention to the experimental fact that the β -derivatives of naphthalene give an absorption spectrum similar to the spectrum of the parent molecule, but the α -derivatives show one or more new absorption bands.¹⁰⁾

In this study, α - and β -naphthol and α - and β -methoxynaphthalene were treated as substituted naphthalenes. Our particular attention was directed to the distinction between the absorption arising from the triplet state and that possibly from a photoproduct, as well as to the distinction between individual transitions when different electronic transitions were involved in a T-T absorption. For naphthols, hydrogen-bonding effects were investigated on the T-T absorption spectra to obtain information on the origin of the spectra and also on the electronic properties of the triplet states concerned. In addition to these experimental investigations, calculations have been made for the triplet states of naphthols by the Pariser-Parr-Pople method,^{11,12)} and the resulting wavefunctions have been subjected to the configuration analysis proposed by Baba, Suzuki, and Takemura¹³⁾ with a view to revealing the electronic structure of the triplet states and making a reasonable assignment of the observed spectra.

Experimental

Materials. Naphthalene was purified by vacuum sublimation. α -Naphthol was recrystallized from ligroin, and β -naphthol from water and ligroin; both were further purified by vacuum sublimation. α -Methoxynaphthalene was purified by high-vacuum distillation over metallic sodium, and was then passed through an activated alumina column with a mixture of petroleum ether and ethyl ether as the solvent. After eliminating the solvent by distillation in an atmosphere of nitrogen, the α -methoxynaphthalene was again subjected to high-vacuum distillation. β -Methoxynaphthalene was recrystallized from ethanol and from *n*-heptane and was sublimed *in vacuo*.

Isopentane was distilled over phosphorus pentoxide. Methylcyclohexane and *n*-hexane of spectroscopic quality were used without further purification. Ethyl ether was treated with 10% sodium bisulfite solution, dried with calcium chloride and finally distilled over metallic sodium. Triethylamine was refluxed with phosphorus pentoxide and then fractionally distilled.

Apparatus and Procedure. Triplet-triplet absorption spectra were measured by two different methods. In the first method, the spectra were obtained with a rapid-scan spectrophotometer (Hitachi Model RSP-2¹⁴⁾) in rigid-glass solutions at 77°K, as shown in Fig. 1. The spectrophotometer is a double-beam instrument, and scans from 220 to 700 m μ in 150 msec at a rate of 3 scans/sec. It is suitable for use in the present experiment since all the compounds studied have triplet lifetimes of about 2 sec.

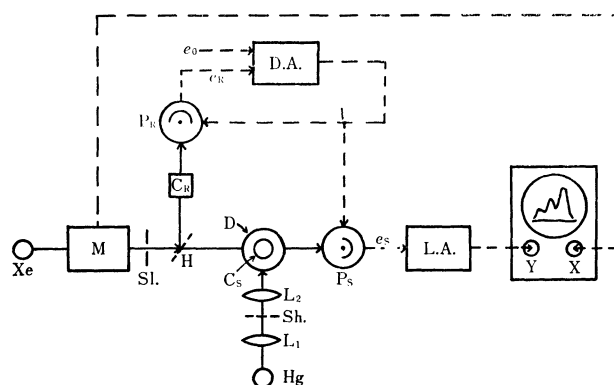


Fig. 1. A schematic diagram of the rapid-scan spectrophotometer as used for measuring T-T absorption spectra at 77°K. Xe, xenon light source; M, monochromator; Sl, slit; H, half-mirror; D, quartz Dewar; Hg, high-pressure mercury lamp for excitation; L₁ and L₂, lenses; Sh, shutter; D.A., differential amplifier; L.A., logarithmic amplifier; see text for other symbols.

Light from a 150-W xenon lamp, the source, is dispersed by a grating monochromator, and the resulting monochromatic light is divided into two beams which pass through the reference cell C_R and sample cell C_S, and then fall on the reference photomultiplier P_R and sample photomultiplier P_S, respectively. The difference between the output voltage e_R of P_R and a standard voltage e_0 is amplified, and the resulting voltage V is fed back to the cathode of P_R. By making the degree of amplification sufficiently great, e_R is held at a constant level (e_0) even if the wavelength of the monochromatic light is changed according to scanning. The voltage V is also applied to the photomultiplier P_S, so that the output voltage e_S of P_S becomes proportional to the transmittance of the sample. The output e_S is fed into a logarithmic amplifier to produce a voltage proportional to the absorbance of the sample. Absorption spectra corresponding to desired scans can be obtained on a storage oscilloscope for a desired wavelength range, with a linear wavelength scale which is calibrated with reference to the absorption spectrum of holmium.

In the T-T absorption measurements, the sample solution in a quartz cell of test-tube type was placed in a quartz Dewar and was cooled down to 77°K. An Osram HBO 100-W high-pressure mercury lamp was used for excitation. Several T-T absorption spectra were obtained in each measure-

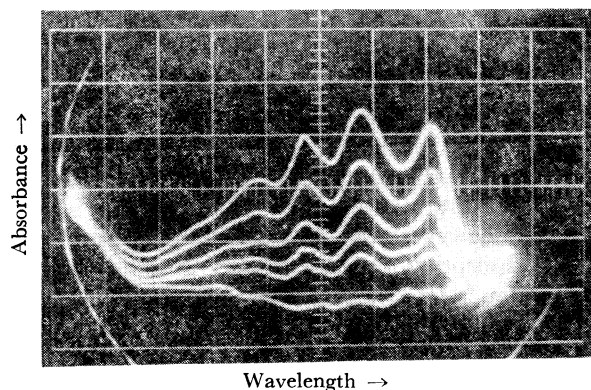


Fig. 2. T-T absorption spectra of α -naphthol in PME containing triethylamine at 77°K, measured by the rapid-scan spectrophotometer. The region of scanning is from 335 m μ to 535 m μ ; the scan time is about 60 msec for this region.

9) L. Klasinc and U. Sommer, *Chem. Phys. Lett.*, **3**, 107 (1969).

10) G. Heinrich, H. Blume, and D. Schulte-Frchlinde, unpublished work cited in Ref. 9.

11) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466, 767 (1953).

12) J. A. Pople, *Trans. Faraday Soc.*, **49**, 1375 (1953).

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

14) H. Baba and Y. Shindo, *Bunseki Kagaku*, **16**, 653 (1967).

ment. They included the spectrum corresponding to the scan immediately after shutting off the exciting light and also the spectrum (or base line) after completion of the triplet decay; allowance was made for the base line in determination of the true absorption. An example of the measurement by the rapid-scan method is shown in Fig. 2.

In the second method, T-T absorption spectra were obtained by means of flash spectroscopy. The technique and procedure were similar to those described by Porter and Windsor.^{15,16} Two xenon flash tubes for excitation were mounted parallel to a sample quartz cell, 10 mm in diameter and 10 cm in length. The cell, was connected to a reservoir where the sample solution was degassed by repeated freeze-thaw cycles. The energy of the excitation flash was about 100 J. Another xenon flash tube was used to take the T-T absorption spectrum on the X-ray film set on a Shimadzu plane-grating spectrograph, Model GE-100. The density of the film was measured by a microphotometer.

Theoretical

Calculations on the Triplet States. Molecular orbital (MO) calculations have been made for the π -electronic triplet states of naphthalene and α - and β -naphthol by the semiempirical LCAO-SCF MO method including configuration interaction (CI), the Pariser-Parr-Pople method, to obtain the excitation energies and oscillator strengths of their T-T absorption transitions.

It is assumed that all the C-C distances are 1.40 Å, all the bond angles 120°, and the C-O distance is 1.37 Å. The valence-state ionization potentials I , valence-state electron affinities A , and resonance integrals β are taken to be as follows:

$$\begin{aligned} I_C &= 11.16 \text{ eV}, & I_O &= 32.9 \text{ eV} \\ A_C &= 0.03 \text{ eV}, & A_O &= 11.7 \text{ eV} \\ \beta_{CC} &= -2.48 \text{ eV}, & \beta_{CO} &= -2.30 \text{ eV} \end{aligned}$$

The Coulomb repulsion integrals γ_{pq} are calculated in units of eV by the formula

$$\gamma_{pq} = 14.40/[a \exp(-0.3r^2) + r] \quad (1)$$

where r is the distance in units of Å between a pair of atoms p and q , and

$$a = 14.40/\{(1/2)[(I_p - A_p) + (I_q - A_q)]\}$$

with I and A expressed in units of eV. Atoms p and q may include both carbon and oxygen atoms, and Eq. (1) is used for $p=q$ as well as for $p \neq q$.

The values of I_C and A_C are taken from the data presented by Hinze and Jaffé.¹⁷ In the derivation of Eq. (1), we first assumed a general formula

$$\gamma_{pq} = 14.40/[a \exp(-br^n) + r]$$

where b and n are adjustable parameters. (The formula proposed by Nishimoto and Mataga¹⁸ is obtained by taking b as zero, while the formula by Knowlton and Carper¹⁹ corresponds to $n=1$.) The values

of b and n adopted here, together with the integral β_{CC} , are so chosen that the calculated excitation energies for the ${}^1B_{2u}$, ${}^1B_{1u}$, ${}^1E_{1u}$, and ${}^3B_{1u}$ states of benzene are in best agreement with the observed ones as measured at the maximum of the whole absorption band corresponding to each of the electronic transitions from the ground state to these singlet and triplet states. The values of I_O , A_O , and β_{CO} are determined so that the results of calculation and experiment may agree well as to the energy shifts of the lower singlet and triplet levels which are produced on going from benzene to phenol.

Twelve singly excited triplet configurations of lower energy are included in the CI calculations. If the SCF MO's of naphthalene and naphthols are numbered from 1 to 10 and from 1 to 11, respectively, in order of increasing orbital energy, the twelve configurations concerned are represented by the following one-electron transitions: for naphthalene 5→6, 7, 8, 9; 4→6, 7, 8, 9; 3→6, 7; 2→6, 7; and for naphthols 6→7, 8, 9, 10; 5→7, 8, 9, 10; 4→7, 8; 3→7, 8.

Configuration Analysis. The general procedure for configuration analysis has been described in a previous paper.¹³ The wavefunctions ${}^3\Psi_1$, ${}^3\Psi_2$, ... for the triplet states of α - or β -naphthol are collected in a row vector ${}^3\Psi$. Each of these wavefunctions is expressed in terms of the reference state wavefunctions ${}^3\Psi_1^0$, ${}^3\Psi_2^0$, ... that are built up from the MO's localized either on the naphthalene or on the substituent. The reference state wavefunctions collected in a row vector ${}^3\Psi^0$ involve locally excited states and charge-transfer states. By introducing a matrix ${}^3\mathbf{M}$, ${}^3\Psi$ is written as

$${}^3\Psi = {}^3\Psi^0({}^3\mathbf{M}) \quad (2)$$

The matrix ${}^3\mathbf{M}$ can be determined by the method developed previously.¹³

Results and Discussion

Figure 3 shows transient absorption spectra obtained by the rapid-scan method for naphthalene, α - and β -naphthol in a mixture of isopentane, methylcyclohexane and ether (PME; volume ratio, 6:1:1:

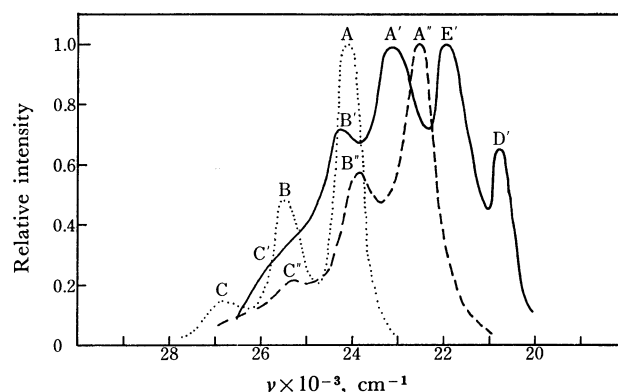


Fig. 3. Transient absorption spectra of naphthalene (.....), α -naphthol (—), and β -naphthol (---) in PME at 77°K. Concentrations of solutes: naphthalene, 8.3×10^{-4} mol/l; α -naphthol, 1.8×10^{-4} mol/l; β -naphthol, 1.7×10^{-4} mol/l.

15) G. Porter, *Proc. Roy. Soc. London*, **A200**, 284 (1950).

16) G. Porter and M. W. Windsor, *Discuss. Faraday Soc.*, **17**, 178 (1954).

17) J. Hinze and H. H. Jaffé, *J. Amer. Chem. Soc.*, **84**, 540 (1962).

18) K. Nishimoto and N. Mataga, *Z. physik. Chem. N.F.*, **12**, 335 (1957).

19) P. Knowlton and W. R. Carper, *Mol. Phys.*, **11**, 213 (1966).

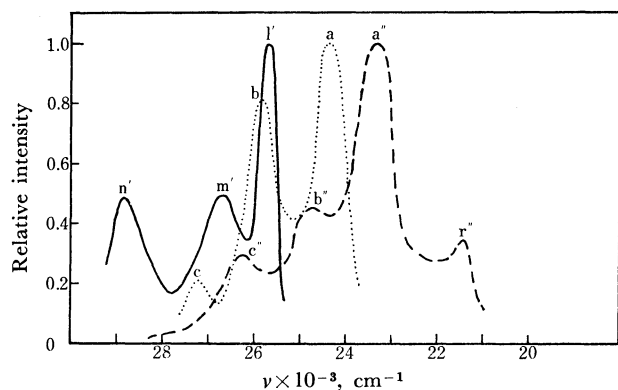


Fig. 4. Transient absorption spectra of naphthalene (.....), α -naphthol (—), and β -naphthol (---) in *n*-hexane at room temperature. Concentrations of solutes: naphthalene, 8.5×10^{-4} mol/l; α -naphthol, 3.07×10^{-4} mol/l; β -naphthol, 3.3×10^{-4} mol/l.

TABLE 1. BAND MAXIMA OF ABSORPTION SPECTRA

	Rapid-scan method in PME at 77°K			Flash method in <i>n</i> -hexane at room temperature		
	Band	$\lambda(\text{m}\mu)$	$\nu(\text{cm}^{-1})$	Band	$\lambda(\text{m}\mu)$	$\nu(\text{cm}^{-1})$
Naphthalene	A	414.5	24130	a	410.5	24360
	B	392.0	25510	b	387.5	25810
	C	372.5	26850	c	368.0	27170
α -Naphthol	D'	481.0	20790	l'	389.0	25710
	E'	455.0	21980	m'	374.5	26700
	A'	431.5	23180	n'	347.5	28780
	B'	412.0	24270			
	C'	—	—			
β -Naphthol				r''	467.0	21410
	A''	443.0	22570	a''	429.0	23310
	B''	419.0	23870	b''	404.0	24750
	C''	395.5	25280	c''	381.0	26250

0.7)²⁰ at 77°K, and Fig. 4 those obtained by the flash method in *n*-hexane at room temperature. In this paper all the spectra are given in such a way that the intensity of the maximum of the whole absorption spectrum is normalized to unity, since we are not concerned with the absolute absorption intensities. The numerical data on band maxima are presented in Table 1.

As has been mentioned, the absorption spectrum of naphthalene consists of three vibrational bands which belong to a single T-T electronic transition. In Figs. 3, 4 and Table 1, the absorption bands for naphthalene and its derivatives are denoted in the following way. The bands observed in the PME rigid glass are written in capital letters, while those observed in *n*-hexane by the flash method are written in small letters; the prime and double prime refer to α - and β -naphthol, respectively. As will be seen, bands of the same type are represented by letters of the same kind.

20) Ether was added to eliminate the possibility of association of the naphthol molecules.

Confirmation of T-T Absorption. The lifetimes of the transient absorption spectra in PME at 77°K shown in Fig. 3 were measured and found to be equal to the respective phosphorescence lifetimes of naphthalene, α - and β -naphthol observed under the same conditions. All the absorption spectra in Fig. 3 are therefore regarded as due to T-T transitions.

The T-T absorption spectra of naphthalene in Figs. 3 and 4 agree in their features, though a slight frequency shift is found. The corresponding spectra of β -naphthol also agree with each other and with the naphthalene spectra except for an additional band appearing in the spectrum of Fig. 4. Thus, on changing the solvent from the PME rigid glass to the fluid *n*-hexane, bands A'', B'', and C'' show a shift to higher frequencies, resulting in a'', b'', and c'', respectively. On the other hand, a new band referred to as r'' appears in the β -naphthol spectrum obtained by the flash method (Fig. 4). This band cannot be due to β -naphthol itself, but should be assigned to a certain molecular species produced by flash photolysis. In fact, r'' is identical with the absorption band at 21500 cm^{-1} which was found by Jackson and Porter²¹ in flash photolysis of β -naphthol in viscous paraffin and assigned to the β -naphthoxyl radical.

The absorption spectrum of α -naphthol shown in Fig. 4 is similar to the spectrum attributed to a T-T transition in α -naphthol by Porter and Windsor.²² However, the spectrum of α -naphthol in Fig. 4 differs entirely from the spectrum in Fig. 3, so that the former should not be identified with the T-T absorption. This is also supported by the following.

A rapid-scan measurement of the transient absorption spectrum was made for α -naphthol at 77°K in a hydrocarbon solvent of isopentane-methylcyclohexane (PM) mixture. In contrast to the case of Fig. 3, this did not contain ether. The spectrum thus obtained was very different from the T-T spectrum of α -naphthol in Fig. 3, and was analogous to the spectrum in Fig. 4. It was found that the absorption spectrum obtained in this way did not vanish so long as the sample was kept at low temperature, and disappeared on warming. This clearly shows that the spectrum in question, and hence the spectrum of α -naphthol in Fig. 4, cannot be due to a T-T transition, and should be attributed to a free radical produced by flash photolysis. The spectral behavior of α -naphthol thus changes with the constituent of the solvent employed, and it does not depend on the temperature or rigidity of the solvent.

In PME, the naphthol must form a hydrogen bond with ether. We assume that formation of a hydrogen bond between α -naphthol and a proton-accepting substance like ether gives rise to stabilization of the triplet state of the α -naphthol molecule and leads to the normal T-T absorption spectrum. It might be noted that a solution of α -naphthol in PME containing triethylamine as a proton acceptor also gives the T-T absorption at 77°K (*vide infra*).

21) G. Jackson and G. Porter, *Proc. Roy. Soc. London*, **A260**, 13 (1961).

22) G. Porter and M. W. Windsor, *Proc. Roy. Soc. London*, **A245**, 238 (1958).

Analysis of T-T Absorption Spectra. The three absorption bands of naphthalene (Fig. 3) belong to one and the same electronic transition and constitute a vibrational progression. Thus all these bands are known to be polarized along the long axis of the molecule,⁴⁻⁶ and the spacings A...B and B...C are equally $\sim 1400\text{ cm}^{-1}$, which can be assigned to a totally symmetric vibration of naphthalene. Similarly, the three absorption bands of β -naphthol are considered to constitute an analogous vibrational progression. The T-T absorption spectrum of α -naphthol (Fig. 3) involves five bands, which are not likely to belong to a single electronic transition. In connection with this problem, we will refer to additional experimental results.

The T-T absorption spectra at 77°K of α -naphthol in PME containing triethylamine as a proton acceptor and of α -methoxynaphthalene in PME are shown in Fig. 5, and the corresponding spectra of the β -derivatives in Fig. 6. In these figures the spectra of the naphthols in PME at 77°K are also given for comparison.

As regards the hydrogen bonding effects on electronic transitions, a thorough investigation has been carried out on the usual singlet transitions of hydroxylic compounds including α - and β -naphthol.²³ It was concluded that frequency shifts accompanying the formation of hydrogen bond differ in magnitude among different electronic transitions in a given molecule, and all the vibrational components for a given transition show a uniform shift. Intensity changes accompanying the formation of hydrogen bond also differ. These conclusions may be applied to the case of T-T transitions.

It is expected that triethylamine produces far greater hydrogen bonding effects on the T-T transitions of naphthols than does ether, since the former is known to have a much stronger proton-accepting power.^{24,25}

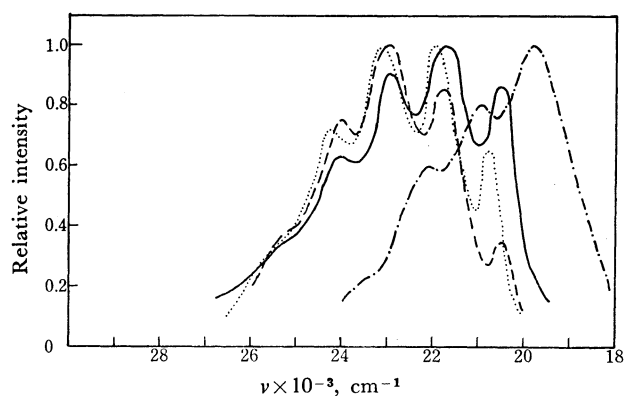


Fig. 5. T-T absorption spectra of α -substituted naphthalenes at 77°K: ·····, α -naphthol in PME; —, α -naphthol in PME containing triethylamine (0.2 mol/l); — · — ·, α -naphthol in an ethanol-methanol mixture containing potassium hydroxide (0.11 mol/l); ---, α -methoxynaphthalene in PME. Concentrations of solutes: α -naphthol, 1.8×10^{-4} mol/l in all cases; α -methoxynaphthalene, 1.7×10^{-4} mol/l.

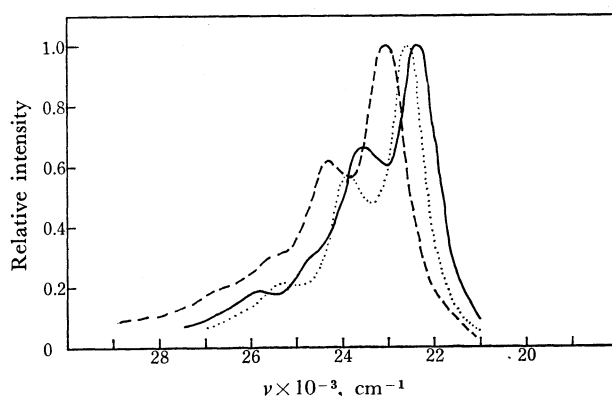


Fig. 6. T-T absorption spectra of β -substituted naphthalenes at 77°K: ·····, β -naphthol in PME; —, β -naphthol in PME containing triethylamine (0.2 mol/l); ---, β -methoxynaphthalene in PME. Concentrations of solutes: β -naphthol, 1.7×10^{-4} mol/l in all cases; β -methoxynaphthalene, 1.6×10^{-4} mol/l.

For β -naphthol (Fig. 6), the three bands show a uniform red shift on changing the proton acceptor from ether to triethylamine. Furthermore, the absorption spectrum of β -methoxynaphthalene resembles the spectrum of β -naphthol. These observations confirm the view that the absorption bands of β -naphthol or of β -methoxynaphthalene are to be associated with a single T-T transition.

In the case of α -naphthol (Fig. 5), when the proton acceptor is changed from ether to triethylamine, the two bands at lower frequencies, D' and E' (cf. Fig. 3), are red-shifted and intensified to a greater extent than the remaining three bands, A', B', and C', suggesting that D' and E' belong to a different T-T transition from that to which A', B', and C' belong. α -Methoxynaphthalene gives a spectrum which is, as a whole, similar to the α -naphthol spectrum. It is seen, however, that the bands corresponding to D' and E' are of lower intensity in α -methoxynaphthalene than in α -naphthol. In Fig. 5 is also shown the T-T absorption spectrum at 77°K of α -naphthol in an alkaline ethanol-methanol mixture (volume ratio, 5 : 1), where the naphthol molecule is converted to the naphtholate ion. Owing to the highly electron-donating character of the O^- group, the absorption spectrum of the α -naphtholate ion is markedly displaced to the red with a considerable change in appearance as compared with the spectrum of α -naphthol. It can be assumed here that in the naphtholate ion the bands D' and E' coalesce into one broad band with the maximum at 19800 cm^{-1} , and that the three bands at the higher frequencies correspond to A', B', and C', with the band at 21000 cm^{-1} assigned as A'.

Thus, all the observations for the α -derivatives of naphthalene indicate that the absorption spectrum of α -naphthol or of α -methoxynaphthalene originates in two different T-T transitions, one leading to the bands A', B', and C' and the other to D' and E'. It is to be noted that the relative intensity of the T-T transition with which D' and E' are associated increases

23) H. Baba and S. Suzuki, *J. Chem. Phys.*, **35**, 1118 (1961).

24) S. Nagakura and M. Gouterman, *J. Chem. Phys.*, **26**, 881 (1957).

25) For this reason, in PME containing triethylamine, naphthols are considered to form a hydrogen bond with triethylamine.

TABLE 2. CALCULATED STATE ENERGIES RELATIVE TO THE GROUND STATE AND f VALUES FOR THE T-T TRANSITIONS

Wave-function	Naphthalene						α -Naphthol		β -Naphthol	
	This work			Pariser						
	Symmetry	Energy (cm ⁻¹)	f	Symmetry	Energy (cm ⁻¹)	f	Energy (cm ⁻¹)	f	Energy (cm ⁻¹)	f
$^3\Psi_1$	B_{2u}^+	23360	Ref.	B_{2u}^+	17590	Ref.	21830	Ref.	22680	Ref.
$^3\Psi_2$	B_{1g}^+	30600	0	B_{1g}^+	27620	0	29940	0.002	29880	0.001
$^3\Psi_3$	B_{3u}^+	33080	0	B_{3u}^+	29360	0	31240	0.001	31960	0
$^3\Psi_4$	B_{3u}^-	36060	0	B_{3u}^-	32420	0	35440	0.002	34150	0.005
$^3\Psi_5$	A_{1g}^+	37850	0	B_{2u}^+	34040	0	38360	0.002	36930	0.004
$^3\Psi_6$	B_{2u}^+	38740	0	A_{1g}^+	35770	0	39160	0	39220	0.004
$^3\Psi_7$	B_{1g}^+	48390	0	B_{1g}^+	44580	0	47250	0.254	46440	0.081
$^3\Psi_8$	A_{1g}^-	48460	0.134	A_{1g}^-	46100	0.084	48120	0.645	48530	0.065
$^3\Psi_9$	B_{1g}^-	50560	0.990	B_{1g}^-	48280	0.451	49770	0.076	49950	0.990
$^3\Psi_{10}$	A_{1g}^+	56760	0	A_{1g}^+	48560	0	55180	0.025	56260	0.072
$^3\Psi_{11}$	A_{1g}^-	62630	0.523	B_{3u}^+	51070	0	61040	0.823	60830	0.457
$^3\Psi_{12}$	B_{1g}^-	70630	0.013	B_{2u}^+	54090	0	69250	0.008	68380	0.010

in the order: α -methoxynaphthalene < α -naphthol hydrogen-bonded with ether < α -naphthol hydrogen-bonded with triethylamine < α -naphtholate ion.

In general the frequency shift of an electronic transition produced by hydrogen bonding is due to the difference between the energies of hydrogen bond for the electronic states which are concerned in that transition.²³⁾ All the T-T absorption transitions in α - and β -naphthol treated in this study are found to be shifted to the red upon formation of the hydrogen bond. This means that in all cases the proton-donating power of the naphthols is stronger in the higher triplet state than in the lowest triplet. It should be noted that the frequency shifts for the T-T transitions of α - and β -naphthol are comparable in magnitude to those for the transitions from the ground state to excited singlet states of the naphthols.^{23,24)}

Theoretical Interpretation of T-T Transitions. The calculated energies for triplet states, relative to the ground state, and the oscillator strengths (f) for transitions from the lowest triplet state to higher triplet states are summarized in Table 2. In all cases, the triplet state wavefunctions are numbered from 1 to 12 in order of increasing energy. For naphthalene, the results of calculation by Pariser²⁶⁾ are also given in the same table. It should be noted that Pariser included all singly excited configurations in his CI calculation. Of the resulting twenty-five state wavefunctions twelve are given in Table 2. The symmetry types are shown for the wavefunctions of the naphthalene molecule (symmetry group, D_{2h}). The long and short molecular axes are chosen as x and y coordinate axes, respectively, and the plus and minus signs have the same meaning as those used by Pariser.²⁶⁾

In Fig. 7 the results of calculations are compared with the spectral data obtained at 77°K in rigid-glass solution. The magnitudes of the calculated oscillator strengths f are represented by the lengths of solid lines in such a way that the largest f value for each of the molecules is normalized to unity. However, for the

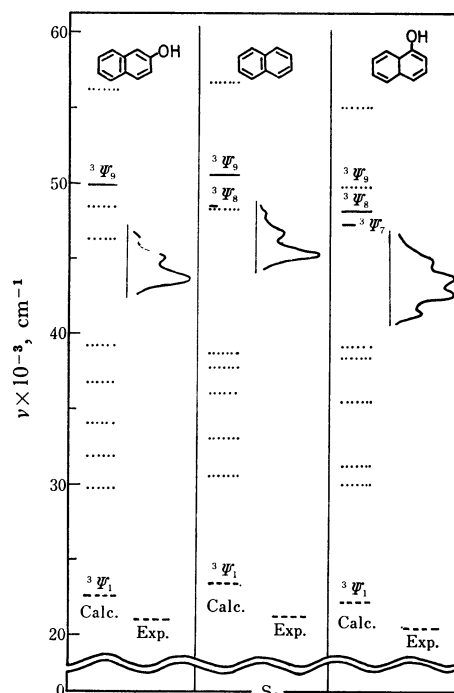


Fig. 7. Calculated and experimental energies of triplet states in naphthalene, α - and β -naphthol. Energies are expressed in wavenumbers relative to the ground state (S_0). The intensities of T-T transitions from the lowest triplet to higher triplet states are represented by solid lines of different lengths or by dotted lines according to the magnitudes of the calculated oscillator strengths; see text for the details.

triplet states with f values less than one-tenth of the largest f , only their energy levels are shown in the figure by dotted lines. In each of the molecules, the experimental energy level for $^3\Psi_1$ represents the position of the 0-0 band of the phosphorescence spectrum measured in PME at 77°K; the spacing between the experimental level for $^3\Psi_1$ and the absorption curve given in the figure corresponds to the observed T-T transition energy.

Since the lowest triplet of naphthalene is a $^3B_{2u}^+$

26) R. Pariser, *J. Chem. Phys.*, **24**, 250 (1956).

state, only the transitions to the triplet states characterized by g and minus are to be allowed. From a comparison of the f values, it follows that the T-T absorption in β -naphthol as well as in naphthalene is due to $^3\Psi_1 \rightarrow ^3\Psi_9$ transition, the adjacent transition $^3\Psi_1 \rightarrow ^3\Psi_8$ being assumed to be too weak to be observed. In the case of α -naphthol, there is no large difference between the f values for $^3\Psi_1 \rightarrow ^3\Psi_7$ and $^3\Psi_1 \rightarrow ^3\Psi_8$, so that these transitions are expected to appear in the T-T absorption spectrum. Thus, of the two transitions ob-

served for α -naphthol, the one of lower energy is assigned to $^3\Psi_1 \rightarrow ^3\Psi_7$ and the other to $^3\Psi_1 \rightarrow ^3\Psi_8$.

The triplet-state energies obtained from our calculations should in principle be related to the Franck-Condon maxima of absorption transitions which might be supposed to occur from the ground state to the triplet states concerned. If allowance is made for this fact, it might be said that the calculated energies are in general agreement with the experimental ones, at least with respect to the relative positions of the triplet levels

TABLE 3. CONFIGURATION ANALYSIS FOR α -NAPHTHOL

	$^3\Psi_1$	$^3\Psi_2$	$^3\Psi_3$	$^3\Psi_4$	$^3\Psi_5$	$^3\Psi_6$	$^3\Psi_7$	$^3\Psi_8$	$^3\Psi_9$	$^3\Psi_{10}$
$^3\Psi_1^0$	78.3	6.2		0.7		0.3	1.0	0.3		
$^3\Psi_2^0$	2.9	70.2	3.4		0.4	0.9	0.3			0.2
$^3\Psi_3^0$		2.4	54.3	27.9	0.1	0.3	2.7		0.1	
$^3\Psi_4^0$			17.6	38.6	9.6	20.1	0.6	0.5	0.4	0.4
$^3\Psi_5^0$	0.2	0.5	3.6	18.2	22.7	29.0	0.1	2.1	0.3	0.2
$^3\Psi_6^0$				0.1	53.0	34.7	0.2	0.3	0.2	0.1
$^3\Psi_7^0$					0.2		15.4	9.4	51.4	
$^3\Psi_8^0$			0.9		0.6		39.0	5.3	32.1	1.7
$^3\Psi_9^0$				0.3		0.2	11.6	60.8	2.3	0.6
$^3\Psi_{10}^0$							0.3		0.2	75.1
$^3\Psi_{11}^0$					0.2				0.1	1.8
$^3\Psi_{12}^0$										
$^3\Psi_{CTO \rightarrow 6}^0$	11.4	5.7		1.8	0.6	2.5	7.0	2.3	0.3	1.2
$^3\Psi_{CTO \rightarrow 7}^0$		0.9	9.5	1.6		0.3	10.0	2.8	1.7	3.4
$^3\Psi_{CTO \rightarrow 8}^0$	0.2	4.8	0.2	0.1		0.2	1.2	5.5		
$^3\Psi_{CTO \rightarrow 9}^0$			0.3	0.8	1.6	1.3	0.5		0.4	4.2
$^3\Psi_{3 \rightarrow 8}^0$		0.3					0.2	1.4		
$^3\Psi_{3 \rightarrow 9}^0$					0.2	0.1				0.7
$^3\Psi_{2 \rightarrow 8}^0$										
Total weight (%)	93.0	91.0	89.8	90.1	89.2	89.9	90.1	90.7	89.5	89.6

TABLE 4. CONFIGURATION ANALYSIS FOR β -NAPHTHOL

	$^3\Psi_1$	$^3\Psi_2$	$^3\Psi_3$	$^3\Psi_4$	$^3\Psi_5$	$^3\Psi_6$	$^3\Psi_7$	$^3\Psi_8$	$^3\Psi_9$	$^3\Psi_{10}$
$^3\Psi_1^0$	83.9	2.7	0.7	0.6		0.3		2.8	0.1	
$^3\Psi_2^0$	0.5	63.6	21.1	0.6	0.4		0.2	1.6		
$^3\Psi_3^0$	0.5	1.2	54.2	5.5	16.3	0.2			0.2	0.4
$^3\Psi_4^0$	1.2	3.1	2.8	46.0	5.1	22.5	8.1		0.1	
$^3\Psi_5^0$	0.4	0.9	2.4	0.2	40.9	14.7		0.8		1.1
$^3\Psi_6^0$				16.3	13.0	42.2	15.1	2.5		
$^3\Psi_7^0$				1.2	0.2		22.0	18.1		
$^3\Psi_8^0$	0.3	0.4	0.2			0.6	17.4	50.9		
$^3\Psi_9^0$					0.4	0.1	0.1	0.5	80.1	8.4
$^3\Psi_{10}^0$					0.4	0.1	0.2	0.5	1.8	56.5
$^3\Psi_{11}^0$					0.3	0.2		0.7	0.3	3.1
$^3\Psi_{12}^0$							0.4	0.3	0.6	0.9
$^3\Psi_{CTO \rightarrow 6}^0$	5.8	7.4	4.7	1.4	5.4	1.0	0.5	2.0	3.6	8.8
$^3\Psi_{CTO \rightarrow 7}^0$	0.1	0.4	0.5	9.9	1.8	1.4	4.8	1.1	0.1	2.1
$^3\Psi_{CTO \rightarrow 8}^0$	0.2	2.7			2.6	1.4	1.9	2.2	3.0	4.0
$^3\Psi_{CTO \rightarrow 9}^0$				0.2	0.5		2.7	0.5		0.7
$^3\Psi_{3 \rightarrow 8}^0$					0.1		0.2	0.4		0.3
$^3\Psi_{3 \rightarrow 9}^0$							0.1	0.2		
$^3\Psi_{2 \rightarrow 8}^0$		0.2			0.3	0.1	0.3	0.2	0.2	0.5
Total weight (%)	92.9	82.6	86.6	81.9	87.7	84.8	74.0	85.3	90.1	86.8

for naphthalene and its two derivatives.

In the T-T absorption spectrum of α -naphthol in PME at 77°K, the two transitions have almost the same intensities, whereas theory predicts that the intensity of the first transition should be about two-fifths of that of the second (Table 2). In PME, however, naphthol is linked to ether through a hydrogen bond, which will result in an increase in the relative intensity of the first transition. In fact, α -methoxynaphthalene, which is expected to have a π -electronic structure similar to that of α -naphthol and has no possibility of forming a hydrogen bond with ether, gives in PME a T-T absorption spectrum in which the first transition is weak compared with the second (see Fig. 5).

Recently Klasinc and Sommer⁹⁾ have made calculations on the T-T transitions of naphthalene and naphthols by the Pariser-Parr-Pople method. Their results differ in detail from the results of the present calculations, but they also reached the conclusion that one new transition should appear in the T-T absorption spectrum of α -naphthol.

Tables 3 and 4 give the results of configuration analysis. The triplet-state wavefunctions ${}^3\Psi_1$, ${}^3\Psi_2$, ..., ${}^3\Psi_{10}$ for the naphthols are analyzed into the wavefunctions for reference triplet states, *viz.*, the locally excited states related to naphthalene ${}^3\Psi_1^0$, ${}^3\Psi_2^0$, ..., ${}^3\Psi_{12}^0$, charge-transfer (CT) configurations ${}^3\Psi_{CTO \rightarrow k}^0$, formed by transferring an electron from the orbital localized on the oxygen atom to the k th MO of naphthalene, and some other singly locally excited

configurations ${}^3\Psi_{i \rightarrow k}^0$. The numbering of the MO's localized on naphthalene is the same as described previously. In the columns of Tables 3 and 4, the weights in percent of the ${}^3\Psi^0$'s obtained as the squares of the elements of the matrix ${}^3\mathbf{M}$ in Eq. (2), are shown for each of the ${}^3\Psi$'s, the weights less than 0.1% being omitted.²⁷⁾

It is seen from the tables that in β -naphthol the wavefunction ${}^3\Psi_9$ consists mainly of ${}^3\Psi_9^0$, while in α -naphthol ${}^3\Psi_7$ and ${}^3\Psi_8$ consist predominantly of ${}^3\Psi_8^0$ and ${}^3\Psi_9^0$, respectively. The lowest triplet state ${}^3\Psi_1$ is largely due to ${}^3\Psi_1^0$ in both α - and β -naphthol. Thus, ${}^3\Psi_1 \rightarrow {}^3\Psi_7$ and ${}^3\Psi_1 \rightarrow {}^3\Psi_8$ transitions in α -naphthol are to be related, respectively, to local transitions ${}^3\Psi_1^0(B_{2u}^+) \rightarrow {}^3\Psi_8^0(A_{1g}^-)$ and ${}^3\Psi_1^0(B_{2u}^+) \rightarrow {}^3\Psi_9^0(B_{1g}^-)$, and ${}^3\Psi_1 \rightarrow {}^3\Psi_9$ in β -naphthol to ${}^3\Psi_1^0(B_{2u}^+) \rightarrow {}^3\Psi_9^0(B_{1g}^-)$. It will be found, on closer inspection of Table 3, that the appearance of a new transition in the α -derivative of naphthalene is due to the fact that ${}^3\Psi_7$ involves the characters ${}^3\Psi_9^0(B_{1g}^-)$ and CT configurations to an appreciable extent. The total weight of CT configurations amounts to as much as 18.7%.

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27) Numbers written in boldface represent the largest weights.