Molecular Complexes and Their Spectra. XIX. Hydrogen-Bonding Complexes of Phenol and Naphthols with Trimethylamine N-Oxide[1]

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Abstract: The 1:1 hydrogen-bonding complexes of trimethylamine N-oxide with phenol, β-naphthol, and α-naphthol were studied in dichloromethane solution. The thermodynamic constants so obtained are: K(l./mole) = 3680 (20.5°), $\Delta H = -7.90$ kcal./mole, and $\Delta S = -10.6$ e.u. for phenol; and K = 6560 (20.7°) and 6310 (20.7°) for β-naphthol and α-naphthol, respectively. The ${}^1L_b$ band of the above proton donors showed a rather large red shift on hydrogen bonding (Table II). These results show trimethylamine N-oxide to be a strong proton acceptor, which is consistent with its strong electron-donor character as shown by its large iodine-complexing ability. For comparison, the K values and spectroscopic constants for hydrogen bonding of triethylamine with α- and β-naphthol were also measured in dichloromethane. At wave lengths below about 300 mμ, triethylamine in CH_2Cl_2 shows contact charge-transfer absorption.

The iodine-complexing ability of aliphatic tertiary amine N-oxides has been found[3] to be larger than that of any other n-electron donors reported hitherto in which the site of the n-donor action is at the oxygen atom. Because of the well-known parallelism between halogen molecular and hydrogen-bonding complexes,[4] and since the oxygen atom in the N→O dative bond is clearly more negative than in usual oxo compounds or aromatic tertiary amine N-oxides,[3] we may anticipate large hydrogen-bonding ability for aliphatic tertiary amine N-oxides, because a greater electron accumulation at the oxygen atom will increase both the charge-transfer (CT) force and the electrostatic force, just as for the case $(R_1R_2R_3)_3N$ discussed by Mulliken.[4a] Thus quantitative spectroscopic and thermodynamic studies of hydrogen-bonding complexes with the amine oxides seem important. In this paper the hydrogen-bonding power of trimethylamine N-oxide with phenol and α- and β-naphthols is studied spectroscopically in dichloromethane. For comparison the study of three-component systems consisting of α- or β-naphthol, triethylamine, and dichloromethane (solvent) has also been carried out. These results will be compared and discussed with other spectral and thermodynamic results reported hitherto.

Experimental Section

Materials. The trimethylamine N-oxide used was the same as that employed for the iodine-complex study. This compound was sublimed again and always kept in a desiccator with P_2O_5 in the dark. The special absolute pure grade phenol obtained from National Aniline Division, Allied Chemical and Dye Corp., was distilled twice at reduced pressure, the middle portion of the last distillate being dried in a desiccator with P_2O_5. The purification of commercial grade β-naphthol from Matheson Coleman and Bell Division, The Matheson Co. Inc., was made by recrystallizing three times from ethanol and water, m.p. 122.5–123.5°. Eastman Organic Chemical White Label α-naphthol was recrystallized four times from methanol–water, m.p. 95–96°. These naphthols, put into the P_2O_5 desiccator, were stored in the dark. The triethylamine used was Eastman Organic Chemicals White Label, refluxed for 1 day with acetic anhydride and distilled under a nitrogen atmosphere. The fraction ranging in boiling point from 88.5 to 89.5° was collected and dried with active alumina, and again distilled carefully under a N_2 atmosphere in a system protected from moisture. The middle portion of the last distillate was sealed in ampoules which had been filled with dry N_2 gas and kept in the dark. Solvents employed were CH_2Cl_2, CCl_4, $CHCl_3$, and n-heptane. Dichloromethane and carbon tetrachloride were purified by the same method as in the previous paper.[3] Fisher's spectroanalyzed chloroform, which contains about 0.75% C_2H_5OH as stabilizer, was purified by stirring twice with deionized water and by distilling from a Podbielniak column after drying with freshly burned $CaCl_2$. This chloroform was always stored in the dark and used within ~2 days since chloroform removed from the C_2H_5OH stabilizer is not stable, especially for light. Phillips pure grade (99 mole % minimum) n-heptane was washed thoroughly with concentrated H_2SO_4 several times until it showed no coloring, then washed with water, aqueous NaOH, and again water. It was dried over metallic sodium and distilled directly from the sodium–heptane mixture using a Podbielniak column. These solvents were stocked in bottles each provided with an automatic buret and $CaCl_2$ tube, and always operated with N_2 gas led through a $CaCl_2$ tube.

Method. A Beckman Model DK-2 spectrophotometer equipped with a temperature-regulated cell holder was used for recording the absorption spectra under the same conditions as in a previous paper. A temperature constant within ±0.5° was maintained by circulating water from a thermostat through the cell holder. Because of the hygroscopic nature of trimethylamine N-oxide, the sampling was always carried out in a drybox, and the weight of amine oxide was obtained by the same method as in the iodine-complex study.[3] The stock solutions of all materials for recording the spectra were freshly prepared on the day of measurement and were kept in a dark place except during sampling. The cells used were 5-cm. and 1-cm. matched quartz cells equipped with stoppers. Equilibrium constants for three-component systems were evaluated in CH_2Cl_2 solvent because of very low solubility of trimethylamine N-oxide in nonpolar solvents. The hydrogen-bonding complexes of trimethylamine oxide with phenol or naphthols in CH_2Cl_2 solvent are stable, and there is no trouble in doing the study. As will be mentioned later, relatively high concentrations of triethylamine were required to obtain equilibrium constants for the case of hydrogen bonding with the naphthols, so we always put in the reference cell the amine in the same concentration as in the sample cell.

To test the stability of triethylamine in CH_2Cl_2 solvent at room temperature, we checked the time dependence of absorption spectra of the solutions of concentrations from 2.3×10^{-2} to 7.2×10^{-1}

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[3] T. Kubota, *J. Am. Chem. Soc.*, **87**, 458 (1965).

[4] (a) R. S. Mulliken, *J. chim. phys.*, **61**, 20 (1964); (b) S. Nagakura, *ibid.*, **61**, 217 (1964); (c) R. S. Mulliken and W. B. Person, *Ann. Rev. Phys. Chem.*, **13**, 107 (1962); (d) U. Jentschura, Diplomarbeit from Laboratorium für Physikalische Chemie und Elektrochemie der Techische Hochschule, Stuttgart, 1964; and earlier references given in these.

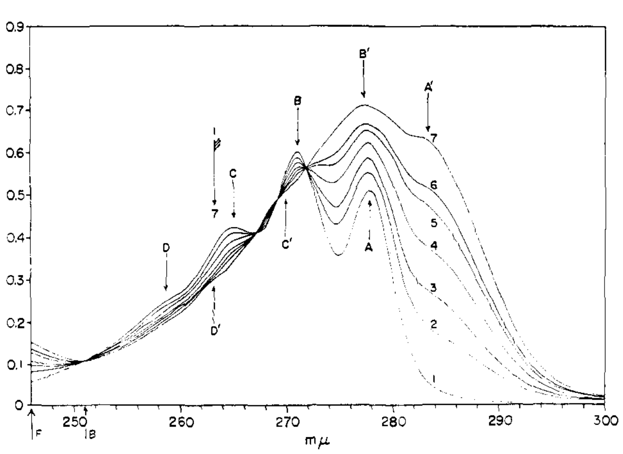

Figure 1. The near-ultraviolet absorption spectra of phenol-trimethylamine N-oxide in CH_2Cl_2 (temperature 10.0°; cell, 5 cm.). Curve 1 is for phenol, 6.006×10^{-5} mole/l. The concentrations of trimethylamine N-oxide are 5.752×10^{-5}, 11.50×10^{-5}, 23.01×10^{-5}, 46.02×10^{-5}, and 69.02×10^{-5} mole/l. for curves 2, 3, 4, 5, and 6, respectively; the phenol concentration is the same as in curve 1. Curve 7, for the absorption due solely to the hydrogen-bonded phenol, was calculated as described in the text. The signs F and B on the wave length scale mean the integration limits used in getting the oscillator strength for free phenol (f_{free}) and for hydrogen-bonded phenol ($f_{\text{H-bonded}}$). The notations A, A′, etc. shown by arrows in the figure mean vibrational structures (see text and Table II).

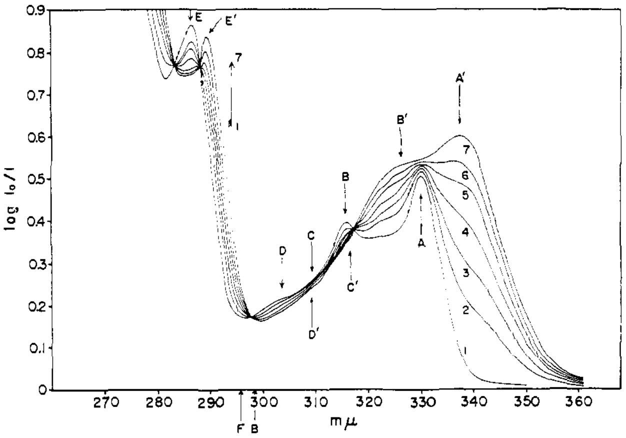

Fig. 2.

Figure 2. The near-ultraviolet absorption spectra of β-naphthol-trimethylamine N-oxide in CH_2Cl_2 (temperature 20.7°; cell, 5 cm.). Curve 1 is for β-naphthol, 4.713×10^{-5} mole/l. The concentrations of amine oxide are 7.72×10^{-5}, 15.43×10^{-5}, 30.87×10^{-5}, 61.74×10^{-5}, and 123.5×10^{-5} mole/l. for curves 2, 3, 4, 5, and 6, respectively. The naphthol concentration is the same as in curve 1. Curve 7 is for the absorption due solely to the hydrogen-bonded β-naphthol, and was calculated as described in the text. The signs F and B on the wave length scale mean the integration limits used in getting the oscillator strengths for free β-naphthol and hydrogen-bonded β-naphthol. The notations A, A′, etc., shown by arrows in the figure mean vibrational structures (see text and Table II).

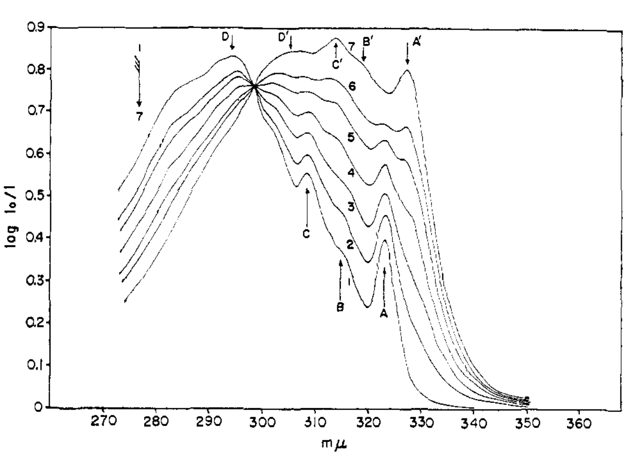

Figure 3. The near-ultraviolet absorption spectra of α-naphthol-trimethylamine N-oxide in CH_2Cl_2 (temperature 20.7°; cell, 5 cm.). Curve 1 is for α-naphthol, 3.065×10^{-5} mole/l. The concentrations of amine oxide are 0.4835×10^{-4}, 0.967×10^{-4}, 1.934×10^{-4}, 3.868×10^{-4}, and 6.769×10^{-4} mole/l. for curves 2, 3, 4, 5, and 6, respectively; the naphthol concentration is the same as in curve 1. Curve 7 is for the absorption due solely to the hydrogen-bonded α-naphthol, and was calculated as described in the text. The notations A, A′, etc. shown by arrows in the figure mean vibrational structures (see text and Table II).

mole/l., where we found absorption which we interpret as contact CT spectra beginning at ~320 mμ (7.2×10^{-1} mole/l.) and at ~285 mμ (2.3×10^{-2} mole/l.), respectively.[5] After 1 day the change of the optical density is less than 0.01. However, with much higher concentrations, some precipitation of colorless crystals was found in the flask after 4 days under usual room light (not dark), but the change is much slower than in the case of the CCl_4 solution of triethylamine, where the solution is very unstable and much formation of crystalline needles was found after 1 day. In the present study all the measurements of the spectra were made within at most 1 hr. after preparation of the mixed solution.

Results

The Effect of Trimethylamine N-Oxide on the Spectra of Phenol and Naphthols in CH_2Cl_2 and Thermodynamic Constants. Figures 1, 2, and 3 show typical spectral changes of phenol and the naphthols produced by adding a small quantity of trimethylamine N-oxide; fine isosbestic points are clearly visible. These results show that a 1:1 hydrogen-bonding complex such as $(CH_3)_3N{\rightarrow}O\cdots HO{-}C_6H_5$ is produced under the conditions stated in the caption of each figure. As is seen in these figures, the initial concentration ($C_A{}^0$) of phenol or naphthols is in most cases considerably less than that ($C_D{}^0$) of trimethylamine N-oxide, but neither of the conditions $C_D{}^0 \gg C_A{}^0$ and $C_D{}^0 \ll C_A{}^0$ is sufficiently satisfied in spite of the use of a 5-cm. cell which made it possible to employ dilute solutions of phenol or the naphthols. Hence we cannot directly apply here the well-known eq. 1[3] to evaluate the

$$\epsilon = \frac{1}{K}\left(\frac{\epsilon_A - \epsilon}{C_D{}^0}\right) + \epsilon_{DA} \qquad (1)$$

equilibrium constant K for the systems of this chapter. Here ϵ_A and ϵ_{DA} are, respectively, the molecular extinction coefficients of the proton donor (electron acceptor) and of the complex, and ϵ is an apparent extinction coefficient of the proton donor calculated using the concentration $C_A{}^0$ at a suitable wave length. Then the method used to evaluate K for the present systems was Drago's plotting method,[6] which as is well known also leads to the accurate K. Combining the equation $(1/K) = (C_D{}^0 - C_{DA})(C_A{}^0 - C_{DA})/C_{DA}$ with the well-known equation[3] $C_A{}^0(\epsilon - \epsilon_A) = C_{DA}(\epsilon_{DA} - \epsilon_A)$,

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(5) It is well known that triethylamine shows "contact charge-transfer interaction" with CCl_4, etc., as evidenced by light absorption at longer wave lengths than 300 mμ, accompanied by photochemical reaction: D. P. Stevenson and G. M. Coppinger, *J. Am. Chem. Soc.*, **84**, 149 (1962); D. P. Stevenson, *ibid.*, **84**, 2849 (1962).

(6) (a) N. J. Rose and R. S. Drago, *ibid.*, 81, 6138 (1959); (b) M. D. Joesten and R. S. Drago, *ibid.*, 84, 2037 (1962); **84**, 3817 (1962).

Table I. Thermodynamic and Some Spectral Data (See Also Table II) on the Hydrogen Bond Formation of Phenol and Naphthols with Several Proton Acceptors

Proton donor	Wave length,[a] mμ	K, l./mole (temp., °C.)	ϵ	f_{free}	$f_{\text{H-bonded}}$	$\left(\frac{f_{\text{H-bonded}}}{f_{\text{free}}}\right)^d$	$\Delta\tilde{\nu}_{1/2}$, cm.$^{-1}$ Free[e]	$\Delta\tilde{\nu}_{1/2}$, cm.$^{-1}$ H-Bonded[e]
Hydrogen Bonding with Trimethylamine N-Oxide in CH_2Cl_2								
Phenol	283	2800 (27.8)[b,c]	2110[b]	0.0222 (D = 1.13 D.)	0.0323 (D = 1.38 D.)	1.45	2560	3040
		3680 (20.5)[c]	2128					
		6460 (10.0)[c]	2101					
		6850 (7.5)[c]	2080					
		8470 (3.9)[c]	2113					
β-Naphthol	339	6650 (20.7)	2456	0.0231	0.0354	1.53	2460	3100
	337	6480 (20.7)	2534					
	Av.	6560						
α-Naphthol	329	6338 (20.7)	4907	...	...	...	...	...
	327	6210 (20.7)	5239					
	320	6367 (20.7)	5123					
	Av.	6310						
Hydrogen Bonding with Triethylamine in CH_2Cl_2								
β-Naphthol	340	52.8 (20.7)	1900	0.0231	0.0315	1.36	2460	2990
	338	54.1 (20.7)	2195					
	336	56.5 (20.7)	2336					
	Av.	54.4						
α-Naphthol	327	62.3 (20.7)	4257	...	...	...	...	...
	318	59.8 (20.7)	4630					
	314	57.8 (20.7)	5030					
	Av.	60.6						

Proton donor	Proton acceptor	Solvent	K, l./mole (temp., °C.)	$-\Delta H$, kcal./mole	$\Delta\tilde{\nu}_{\text{H-bond}}$,[f] cm.$^{-1}$	$\Delta\tilde{\nu}_{\text{ion}}$,[g] cm.$^{-1}$	Ref.
Phenol	$(C_2H_5)_3N$	n-Heptane	89 (25)	9.2	...	2330	6b
			83.8 (25)	...	580		10a
Phenol	$(CH_3)_3P{\rightarrow}O$	CCl_4	1480 (25)	7.4	...	2330	6b
Phenol	Quinoline N-oxide	CCl_4	146 (26.7) 158 (26.7)	~5.1–5.7	...	2330	11
β-Naphthol	$(C_2H_5)_3N$	n-Heptane	103 (25)	...	590	1640	10a
		Benzene	60 (~15)	...	370		14a
α-Naphthol	$(C_2H_5)_3N$	n-Heptane	121 (25)	...	280	1020	10a

[a] The largest change in intensity was observed at this wave length. [b] When Drago's plotting was tried, all the points scattered in a considerable area, so this K value was calculated by assuming that the ϵ is the average of those obtained at 20.5, 10.0, 7.5, and 3.9°, because better results were obtained by this procedure. The reason for this scattering may be some vaporization of the solvent because of the low boiling point (39.9°) of CH_2Cl_2. [c] $\Delta H = -7.9 \pm 0.5$ kcal./mole and $\Delta S = -10.6 \pm 0.5$ e.u. were derived. [d] All the values are for the ^1L_b band. [e] See ref. 18 in text. To get a transition moment D, however, the $\tilde{\nu}_{\max}$ (in cm.$^{-1}$) obtained by the latter method described in ref. 18 was used. [f] These values mean the ^1L_b band shift due solely to hydrogen bonding. [g] Here $\Delta\tilde{\nu}_{\text{ion}}$ refers to the shift of the ^1L_b band of phenol and the naphthols which occurs on complete ionization to the respective anion in water solvent.

where C_{DA} means the concentration of the complex, we have derived eq. 2. Here R is defined as $(\epsilon_{DA}$

$$(1/K) = C_D^0 R + C_A^0(1/R) - (C_A^0 + C_D^0) \quad (2)$$

$- \epsilon_A)/(\epsilon - \epsilon_A)$. Now we are able to calculate K as a function of various assumed values of ϵ_{DA}; thus many curves, almost straight lines, can be drawn. These curves cross one another in a closed area; all crossing points were picked up and averaged to get the best K. As an example, the results for the typical system, phenol + trimethylamine N-oxide + CH_2Cl_2 (solvent), are illustrated. For the experiment shown in Figure 1, K and ϵ_{DA} at 283 mμ, where the largest change in optical density was found, were 6461 and 2101, respectively. These values were obtained as the average of the crossing points, 1.569, 1.563, 1.555, 1.5325, and 1.519 for $(1/K) \times 10^4$ and 2112.5, 2110, 2105, 2090, and 2087 for ϵ_{DA}.[7]

The experimental results are included in Tables I and II. In Figures 1, 2, and 3 the spectra due solely to the hydrogen-bonded phenol or naphthols are also given. These were calculated on the basis of the concentrations of the complex obtained using K and ϵ_{DA} as stated above. From these spectra we have calculated the ϵ_{DA} at all wave lengths (see also Table II) and then the oscillator strengths (f) to compare with those of the noncomplexed species. Oscillator strengths were obtained with a planimeter after plotting the curves on a large scale. The integration (in units of cm.$^{-1}$ × ϵ) was made over the wave length range corresponding to a single electron transition, as shown in each figure.[8] For the case of the free and hydrogen-bonded α-naphthols, the longer wave length absorption is overlapped considerably by two different electronic transitions[9a,10] (^1L_b and ^1L_a in Platt's notation),[9b]

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[7] To check the accuracy of these values we also applied Lang's equation to the same system. The results for K and ϵ_{DA} at 283 mμ were, respectively, 6530 and 2100, which are almost the same values as those obtained using eq. 2, so that the calculation was made by means of Drago's plotting method for convenience's sake for the present systems: R. P. Lang, *J. Am. Chem. Soc.*, **84**, 1185 (1962).

[8] Experimental f values were calculated using the equation, $f = 4.319 \times 10^{-9}(\int\epsilon \cdot d\tilde{\nu})$: C. Sandorfy, "Electronic Spectra and Quantum Chemistry," Prentice-Hall, Inc. Englewood Cliffs, N. J., 1964, pp. 100, 103.

[9] (a) It should be noted that the effect of substituents on the electronic spectra of naphthalene, anthracene, etc., was also investigated experimentally and theoretically by many workers, and that α-substitution of OH or NH_2 groups causes a larger red shift of the ^1L_a band of

Table II. The Wave Length Shift and the Intensity Change of Spectra of Phenol and Naphthols Caused by Hydrogen Bond Formation with Trimethylamine Oxide and Triethylamine in CH_2Cl_2 Solvent

		Free species		Bonded species		
System	Band notation	λ, mμ (cm.$^{-1}$)	ε	λ, mμ (cm.$^{-1}$)	ε	$\Delta\tilde{\nu}$, cm.$^{-1}$
Phenol + tri-methylamine oxide	A	277.9 (889)	1685	~283 (713)	2105	~648
	B	271.2 (820)	1988	277.4 (988)	2351	824
	C	265.3 (917)	1405	~270 (841)	1780	~656
	D	~259	826	~264	1170	~732
β-Naphthol + trimethyl-amine oxide	A	329.7 (1375)	2156	337 (1095)	2538	657
	B	~315.4 (677)	1668	~325 (877)	2219	~937
	C	~308.8 (697)	1103	~316 (768)	1294	~737
	D	~302.3	883	~308.5	870	~666
	E	286.3	3637	289.2	3509	350
α-Naphthol + trimethyl-amine oxide	A	323 (787)	2629	327.2 (757)	5259	397
	B	315 (669)	2480	~319.3 (599)	5253	427
	C	308.5	3635	313.3	5716	497
	D	~294.5	5436	~305	5514	1169
β-Naphthol + triethylamine	A			335.1 (1071)	2371	490
	B			~323.5 (904)	2075	794
	C			~314.3 (810)	1386	567
	D			~306.5	931	454
	E			288.3	3501	242
α-Naphthol + triethylamine	A			325.9 (762)	4535	275
	B			318 (667)	4665	300
	C			311.4	5336	302
	D			301	5635	734

so the evaluation of the f values was not carried out because of the difficulty in separating these clearly.

The Effect of Triethylamine on the Spectra of Naphthols in CH_2Cl_2, and the Thermodynamic Constants of the Complex. Quantitative hydrogen-bonding studies of triethylamine with naphthols in nonpolar solvents have been reported by other investigators.[6b,10] To compare the hydrogen-bonding ability of trimethylamine N-oxide with that of triethylamine in the same solvent, we now have studied the spectral behavior of the three-component systems $(C_2H_5)_3N$ + α- or β-naphthol + CH_2Cl_2 (solvent). The change of the spectra with an addition of triethylamine is quite similar to Figures 2 and 3 except that the red shift occurring in each spectrum is a little smaller than in the case of the amine oxide. However, for these systems the spectral change occurs only at relatively high concentrations of triethylamine (for example, 0.87×10^{-2}–10.5×10^{-2} mole/l. at 20.7° for the concentration 3.007×10^{-4} mole/l. of β-naphthol and cell length 1 cm.). The conditions for validity of eq. 1 are now sufficiently well fulfilled, so the calculation of K was made using eq. 1, and a good linear relation was obtained. The spectra of hydrogen-bonded naphthols with triethylamine, the red shift due to hydrogen bonding, and other spectral constants were determined by the same methods as in the case of trimethylamine N-oxide. All the results are included in Tables I and II.

Discussion

The Hydrogen-Bonding Ability of Trimethylamine N-Oxide. As is apparent from Table I, the thermodynamic constants due to the hydrogen bond formed between trimethylamine N-oxide and phenol or the naphthols in CH_2Cl_2 are quite large, so that it seems to be now possible to say that trimethylamine oxide is a strong proton acceptor, the active center of which is an oxygen atom. In particular, the fact that K and ΔH for the system $(CH_3)_3NO$ + phenol + CH_2Cl_2 are much larger than in the case of the system quinoline N-oxide (aromatic amine oxide) + phenol + CCl_4[11] agrees well with the data which show that trimethylamine oxide is a much stronger electron donor toward iodine[3] than are the aromatic N-oxides. Since the complexing power of I_2 is clearly attributable to CT forces, the above results support the idea that the charge-transfer interaction[4,10a,12,13] expressed schematically as

$$[(CH_3)_3\overset{+}{N}\text{—}\overset{-}{O}\cdots H\text{—}O\text{—}C_6H_5] \longleftrightarrow [(CH_3)_3\overset{+}{N}\text{—}OH\cdots\overset{-}{O}\text{—}C_6H_5]$$

also plays an important role for the hydrogen-bonding mechanism. Now it is of interest to compare the results in Table I with the molecular complexing ability of triethylamine, whose I_2 and hydrogen-bonding power were extensively studied by Nagakura[10a,13] and also, for the case of hydrogen bonding, by Drago, *et al.*,[6b] and Mataga, *et al.*[14] The results showed that $(C_2H_5)_3N$ is one of the strongest electron donors to iodine on the basis of a large K (6460 l./mole at 20°) and ΔH (−12 kcal./mole) in *n*-heptane.[13] Similarly it reaches $\Delta H = -9.2$ kcal./mole for hydrogen bonding with phenol in *n*-heptane.[6b] However, the very large difference of the K values seen in Table I for hydrogen bonding of naphthols or phenol with $(C_2H_5)_3N$ as compared with

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naphthalene than that of the ^1L_b band, so that the ^1L_a and ^1L_b bands become considerably overlapping at the longer wave length region. However, β-substitution makes the separation of both bands clear[10b]; see also H. Baba and S. Suzuki, *Bull. Chem. Soc. Japan*, **34**, 82 (1961); L. S. Forster and K. Nishimoto, *J. Am. Chem. Soc.*, **87**, 1459 (1965); T. Kubota, "Progress Reports on Electronic Processes in Chemistry," Vol. 2, published by the Japanese Research Group on the Electronic States, 1960, p. 39; T. Kubota and H. Miyazaki, *Chem. Pharm. Bull.* (Tokyo), **9**, 948 (1961); R. N. Jones, *Chem. Rev.*, **41**, 353 (1947), etc.; (b) J. R. Platt, *J. Chem. Phys.*, 17, 484 (1949).

(10) (a) S. Nagakura and M. Gouterman, *ibid.*, **26**, 881 (1957); (b) H. Baba and S. Suzuki, *ibid.*, **35**, 1118 (1961).

(11) T. Kubota, *J. Pharm. Soc. Japan*, **74**, 831 (1954); **75**, 1540, (1955); *J. Chem. Soc. Japan, Pure Chem. Sect.*, **79**, 916 (1958); G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., Reinhold Publishing Corp., New York, N. Y., 1960, Appendixes B and C.

(12) (a) C. A. Coulson and U. Danielsson, *Arkiv Fysik*, **8**, 245 (1954); (b) H. Tsubomura, *Bull. Chem. Soc. Japan*, **27**, 445 (1954); (c) G. C. Pimentel, *J. Chem. Phys.*, **19**, 446 (1951).

(13) S. Nagakura, *J. Am. Chem. Soc.*, **80**, 520 (1958).

(14) (a) N. Mataga and Y. Kaifu, *Mol. Phys.*, **7**, 137 (1963); (b) N. Mataga, Y. Kawasaki, and Y. Torihashi, *Theoret. Chim. Acta*, **2**, 168 (1964).

$(CH_3)_3NO$ in the same solvent may be due to the fact that these compounds belong to quite different types of electron donor. That is, the former is a strong electron donor of the amine type while the latter belongs to the oxo compounds, so that, as was verified by Drago,[6b] the contribution from the ΔS term is quite different in both series. Therefore, if ΔH is compared at the same K value by using the relationship between ΔH *vs.* K for the hydrogen bonding of phenol with the above two series of proton acceptors, the amine compounds have a larger $-\Delta H$ than that of the oxo compounds. Particularly trimethylamine oxide is different from $(C_2H_5)_3N$ in having a large dipole moment (5.02 D.),[15] and the oxygen atom is surely very negative, so that this will increase both the effects of CT force and electrostatic force, as was mentioned in the introductory section.

Inasmuch as $(CH_3)_3PO$ has a structure similar to that of $(CH_3)_3NO$, a comparison of the hydrogen-bonding abilities of these two compounds is interesting. As is seen in Table I, $(CH_3)_3PO$ also shows large K and $-\Delta H$ values for phenol, but these values are a little smaller than those for $(CH_3)_3NO$. A reasonable explanation is that for the former compound 3d orbitals in the P atom assist in bringing about double bond P=O accompanied by a reduced negative charge at the oxygen atom, so that the interaction with phenol is reduced.

It should here be noted that our experiment for the systems $(C_2H_5)_3N$ + naphthols + CH_2Cl_2 resulted in K values which are smaller than those measured in *n*-heptane solvent but of almost the same order as in benzene solvent[14] where weak hydrogen bonding of phenol with benzene occurs. Our relatively low K values in CH_2Cl_2 solvent may be due to weak interaction of the amine with CH_2Cl_2 in the form of $(C_2H_5)_3N\cdots HCHCl_2$ type hydrogen bonding as well as the interaction of $ClH_2C{-}Cl\cdots H{-}O{-}C_6H_5$, these interactions competing with the strong hydrogen bonding of $(C_2H_5)_3N$ with the naphthols.[16]

Spectra of Hydrogen-Bonded Phenol and Naphthols. At first, attention should be paid to the spectra of phenol and naphthols alone in CH_2Cl_2 solvent. Comparing the spectra recorded at room temperature in CH_2Cl_2 with those in *n*-heptane, the vibrational structures in the ^1L_b band come out with broader maxima; an especially very sharp band appearing in *n*-heptane (designated as A in each figure) decreases in intensity compared with other vibrational structures, but the positions are almost the same as in *n*-heptane. The facts stated above are attributed to a weak interaction between solutes and the solvent (CH_2Cl_2). It is noted that the above broadening tendency generally increases in the order of CH_2Cl_2, $CHCl_3$, and CCl_4, and is parallel to increasing number of chlorine atoms. For the wave lengths, taking the ^1L_b band of phenol as an example, the following results were obtained: 277.6, 271; 277.9, 271.2; 278.1, 271.4; 279.4, 272.8 in *n*-heptane, CH_2Cl_2, $CHCl_3$, and CCl_4, respectively. Here in each set the first number is the wave length (mμ) at peak A in Figure 1 and the latter at peak B.[17] All the spectral data are given in Tables I and II (regarding the band notation A, B, C, etc., see captions of Figures 1–3). $\Delta\bar{\nu}_{1/2}$ (the half-width in cm.$^{-1}$ at half-maximum) for the complete transition was determined by a usual way (see Table I).[18] Now let us examine the results in Table II. The red shift of the ^1L_b band of phenol and the naphthols caused by hydrogen bonding with $(CH_3)_3N{\rightarrow}O$ is quite large and is somewhat larger than that found in the system $(C_2H_5)_3N$ + naphthols + *n*-heptane.[19] It is also noteworthy that the oscillator strength of the proton donors increases when hydrogen bonding occurs (the ratio ($f_{\text{H-bond}}/f_{\text{free}}$) for the amine oxide system is larger than that for the triethylamine system in CH_2Cl_2 solvent) and that at the same time $\Delta\bar{\nu}_{1/2}$ is also increased considerably. All these spectral results indicate that aliphatic amine oxides are strong proton acceptors (electron donors). From the abovementioned red shift caused by hydrogen bonding, we can infer that hydrogen bonding is facilitated in the excited ^1L_b state. This is explained as follows. Since the electron migration of 2pπ electrons on the oxygen atom of phenol or the naphthols to the aromatic ring is larger in the ^1L_b state than at the ground state,[20] the net δ^+ charge on the oxygen atom increases in the ^1L_b state. This results in an increasing proton-donor ability (increasing electron acceptor), in other words, a more stable hydrogen-bonding complex is produced in that excited state. However, it is noted that the red shift caused by complete negative ion formation as in $C_6H_5{-}O^-$ (see $\Delta\bar{\nu}_{\text{ion}}$ in Table I) is much larger than the red shift due to hydrogen bonding, so in the ground or excited Franck–Condon state the complex seems not to be in a complete ion-pair form in CH_2Cl_2 solvent. This conclusion is consistent with the result that the spectra of free and hydrogen-bonded species are recognizably similar in vibrational pattern as is shown in Figures 1–3 and Table II, although the spectrum of the hydrogen-bonding complex itself in CH_2Cl_2 solution is broader than that for the free molecule.

Let us now consider the origin of the above broadening found in the spectra of hydrogen-bonding species. The main reason for this phenomenon may be due to the nature of excited states of hydrogen-bonding systems. In connection with this problem, quite recently,

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(15) E. P. Linton, *J. Am. Chem. Soc.*, **62**, 1945 (1940).

(16) Naturally very large K and $-\Delta H$ values were reported for especially strong three-component systems including triethylamine; *e.g.*, the hydrogen bonding power of triethylamine with benzoic acid and bromophthalein magenta E in benzene solvent is, respectively, K = 5580 (20°) and ΔH = −11.0 kcal./mole for the former and K = 42,600 (20°) and −15.3 kcal./mole for the latter: M. M. Davis and M. Paabo, *J. Am. Chem. Soc.*, **82**, 5081 (1960).

(17) Here the ^1L_b band corresponds to a transition to the $^1B_{2u}$ state of benzene, where the 0–0 band is forbidden. Since it is well known that the 0–0 band is allowed in unsymmetrically substituted benzenes, the band designated A in Figure 1 (phenol) is a kind of the 0–0 band progression in the ^1L_b state. In naphthols the same would be true; see also G. Durocher and C. Sandorfy, *J. Mol. Spectry.*, **14**, 400 (1964); F. A. Matsen, W. W. Robertson, and R. L. Chuoke, *Chem. Rev.*, **41**, 273 (1947); S. Leach, R. Lopez-Delgado, and F. Delmas, *J. Mol. Spectry.*, **7**, 304 (1962).

(18) To get the half-maximum we employed the value $^1/_2\epsilon_{\max}$. $\epsilon_{\max}$ means the ϵ at the strongest vibrational band. Even if we adopt the maximum of an envelope connecting vibrational bands, we guess, for the present case, the difference between the former and the latter is small.

(19) The shift due to the hydrogen bonding of $(C_2H_5)_3N$ with naphthols observed in CH_2Cl_2 solvent is smaller than that obtained in *n*-heptane. This may be due to a competition by hydrogen bonding of the amine or naphthol to the solvent (see discussion above, an effect of solvent on K).

(20) These results, for example, can be deduced from the red shift of the ^1L_b band of benzene on introducing an OH group (phenol), and many theoretical and experimental studies have verified this conclusion: A. Weller, *Z. Elektrochem.*, **61**, 956 (1957); K. Kimura, H. Tsubomura, and S. Nagakura, *Bull. Chem. Soc. Japan*, **37**, 1336 (1964), and other papers cited in this; J. R. Platt, "Systematics of the Electronic Spectra of Conjugated Molecules," John Wiley and Sons, Inc., New York, N. Y., 1964.

Mataga, *et al.*,[14] studied the hydrogen bonding of triethylamine with β-naphthol in benzene or *n*-heptane solvent by measuring the absorption and fluorescence spectra and found that the red shift (especially in benzene solvent) of the fluorescence spectra due to the hydrogen bonding is much larger than that of the absorption spectra, the shift of the latter being similar to that in this paper. To explain these phenomena they concluded that the ^1L_b equilibrium state of the β-naphthol would be mixed considerably with the charge-transfer state of the hydrogen-bonding system that is described as the charge transfer of one of the nitrogen atom's lone-pair electrons to the antibonding orbital of an O–H group. We can now expect that this mixing would modify the potential energy surface in the excited state considerably. In addition, strong hydrogen bonding reduces the molecular symmetry, so that more coupling among various vibrations becomes possible both in excited and ground states. The changes mentioned could bring about a broadening of the spectra of hydrogen-bonding species. Also, the fact that CH_2Cl_2 is a somewhat polar solvent may cause more broadening because of interactions with the proton donors and acceptors, as was discussed at the beginning of this section.

Finally consideration should be given to expected differences in the spectral shifts caused by hydrogen bonding in different electronic excited states. The electronic density, potential energy surface, and also the mixing with the CT state due to hydrogen bonding should be different in different excited states. So, in principle, the wave length shift due to hydrogen bonding should be different in other excited states. We can see from Table II that the red shift arising from hydrogen bonding with trimethylamine oxide or triethylamine at the D band of α-naphthol is larger than that observed for the bands A, B, and C, so that we can say that the band in question belongs to a different electronic state, namely the ^1L_a state; the same conclusion has also been reached by other authors.[9a,21]

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(21) In β-naphthol, on the other hand, band E (^1L_a)[9a] shows a smaller shift than for the A, B, C, and D bands (^1L_b state). The behavior mentioned above is quite similar to the substituent effect on the absorption spectra of naphthalene,[9] the same facts having been pointed out by previous workers.[9a,10]

Microwave Spectrum of Cyclohexyl Fluoride. Structure and Dipole Moment of the Equatorial Isomer

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Abstract: The microwave spectrum of cyclohexyl fluoride has been investigated in the frequency region 10 to 25 Gc. Twenty-six transitions are reported which can be attributed to rotational absorption by the equatorial form in its ground vibrational state. Rotational constants derived from the measured frequencies are $A = 4313.38$, $B = 2188.78$, and $C = 1591.61$ Mc. Assuming that the bonded CC and CH distances are the same in equatorial cyclohexyl fluoride as they are in propane, and that the ring structure is symmetrical, the following structural parameters are obtained: CF = 1.404, CC = 1.526, CH = 1.096 Å.; $\angle$CCC = 111° 22′, $\angle$HCH = 107° 34′, $\angle$HCF = 109° 13′, $\angle$CCF = 108° 39′, $\angle$CCH = 109° 29′; $\beta = 55° 2'$, where β = the dihedral angle for alternate CC bonds. Stark effect measurements yield $|\mu_a| = 2.08 \pm 0.03$, $|\mu_c| = 0.36 \pm 0.05$, and μ(total) = 2.11 ± 0.03 D. These data indicate that the dipole moment vector makes an angle of either 29° 40′ or 10° with the CF bond axis. In view of the fact that the CF bond moment is much larger than the CH bond moment, the angle 10° seems more probable than the angle 29° 40′.

Despite the interest and correspondingly vast literature concerning cyclohexane and its derivatives,[4] there have been no previous spectroscopic investigations of the structures of six-membered rings which are presumed to have both axial and equatorial isomers. The present work is concerned with the microwave spectrum of cyclohexyl fluoride and the structural and other information which it provides. Structures as determined from electron diffraction experiments have been reported for both cyclohexane[5] and cyclohexyl fluoride.[6] In the latter investigation, the ring structure of cyclohexyl fluoride (both forms) was assumed to be

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(3) This is A.E.C. Document No. COO-38-442.

(4) See, for example, E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrisson, "Conformational Analysis," Interscience Division, John Wiley and Sons, Inc., New York, N. Y., 1965.

(5) M. Davis and O. Hassel, *Acta Chem. Scand.*, 17, 1181 (1963).

(6) P. Andersen, *ibid.*, 16, 2337 (1962).