

Studies on Intermolecular π -Hydrogen Bond

Part 1

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Received 11th January, 1965

The spectral shift in the longest wavelength π - π^* absorption band of naphthol in going from a heptane to a benzene, toluene or xylene solution has been associated with the hydrogen bond formation between the hydroxyl group of naphthol and the π -electron system of the aromatic hydrocarbons. The equilibrium constant for hydrogen bond formation was found to run parallel to the base strength of the π -electron system.

The electronic spectra of a molecule may be altered by the formation of hydrogen bonds if the chromophoric portion of the molecule is perturbed by the hydrogen-bond formation, and this is often accompanied by spectral changes, due to π - π^* and n - π^* transitions.⁴ Benzene has been used as an inert solvent but it in fact acts as a weak hydrogen-bonding base, as evidenced from the infra-red ¹ proton magnetic resonance ² spectral investigations, and from electronic spectra of aromatic alcohols.³

When a phenolic hydroxyl group enters into hydrogen bond formation with a suitable acceptor, the longest wavelength π - π^* absorption band of the phenol shows a forward shift.⁴ But if the π -electron system of a phenyl ring can act as a proton acceptor, then the longest wavelength π - π^* absorption band of a phenol dissolved in benzene should appear at a longer wavelength as compared to that in n-heptane solution. The optical density measurements at the shifted peak of the phenol absorption band for a continuous change from pure heptane to pure benzene may give useful information about the π -hydrogen bonding capacity of the phenyl ring. This paper reports an investigation of the π -hydrogen bond formation between α - and β -naphthol and the π -electron system of benzene, toluene and xylene.

EXPERIMENTAL

All chemicals were reagent quality samples of E. Merck & Co. The liquids were dried and fractionally distilled before use. The solids were chromatographed on silica gel and repeatedly crystallized from spectroscopically-pure alcohol. All measurements were taken on freshly prepared solutions. The spectral measurements were made in a Beckman Spectrophotometer model DU using 1 cm silica cells. All measurements were made at a slit width of 0.1 mm.

RESULTS AND DISCUSSION

In the fig. 1 and 2 are given the absorption spectra of α - and β -naphthol in n-heptane and in benzene. The longest wavelength absorption band of naphthol shows a red shift in going from the heptane to benzene solution. The position of this absorption band of α - and β -naphthol in different solvents is shown in table 1. The peak in toluene and in xylene appears at the same position as in benzene with α - and β -naphthols, but the extinction was different in different hydrocarbons.

The observed shift is not due to environmental perturbation alone since we cannot account for the increased extinction accompanying the shift, but if the shift is due to hydrogen bond formation, then the increased electron migration effect will cause the absorption intensity to increase in the hydrogen-bonded state.⁶ Since the hydrogen bond must be between the hydroxyl group of naphthol and the aromatic hydrocarbons, only π -hydrogen bonds can exist in such systems.

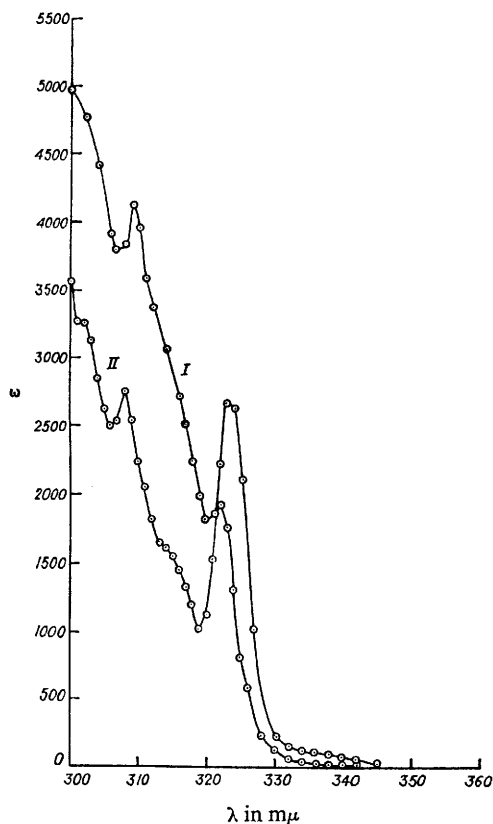


FIG. 1.—Long-wavelength absorption spectra of α -naphthol in n-heptane and in benzene.

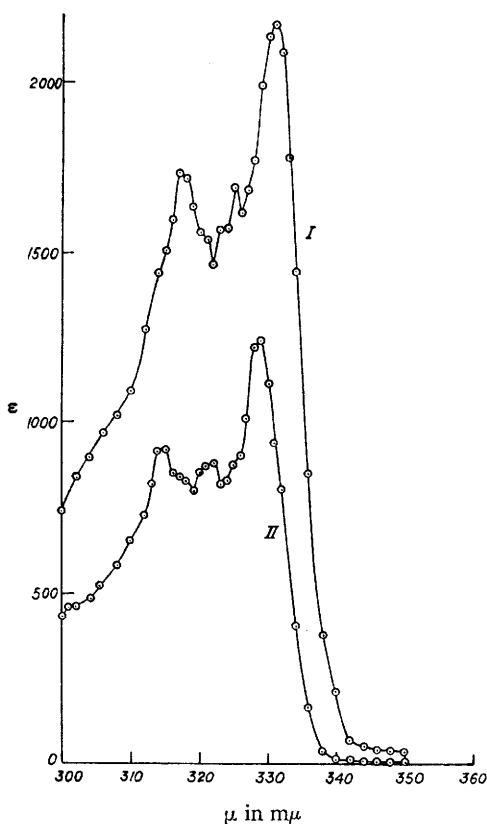
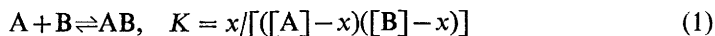


FIG. 2.—Long-wavelength absorption spectra of β -naphthol in n-heptane and in benzene.

If the hydrogen bonding is represented by an equilibrium



where $[B]$ represents the initial concentration of naphthol, $[A]$ that of the aromatic hydrocarbon and x the equilibrium concentration of the hydrogen-bonded complex, then the equilibrium constant may be estimated from the optical density

TABLE 1.—PEAK OF THE ABSORPTION BAND OF α AND β NAPHTHOL IN n-HEPTANE AND IN BENZENE

compound	n-heptane	λ_{\max} in $m\mu$	benzene
α -naphthol	322 ($\epsilon = 1900$)		326 ($\epsilon = 2700$)
β -naphthol	328 ($\epsilon = 1250$)		331 ($\epsilon = 2180$)

measurements of the shifted π - π^* band in the following manner. To a n-heptane solution of a naphthol, increasing amount of benzene was added and the shift of the π - π^* band as well as the optical density at the peak was noted. When the solute was in pure benzene, the naphthol was assumed to exist completely in the hydrogen-bonded state, while the peak in n-heptane was associated with the characteristic absorption band of the non-complexed solute. The optical density (O.D.) of a solution containing the molecular species of (1) measured at a wavelength corresponding to the peak of the shifted π - π^* band of the solute may be represented as

$$\text{O.D.} = \bar{\epsilon}[\text{B}] = \epsilon_0([\text{B}] - x) + \epsilon_1 x, \quad (2)$$

where $\bar{\epsilon}$ is the formal extinction coefficient given by $\bar{\epsilon} = D/[\text{B}]l$; where D is the measured O.D. of the solution and l is the length of the light path in cm. ϵ_0 and ϵ_1 are the extinction coefficients of the free and the complexed naphthol respectively. Combining eqn. (1) and (2),

$$\frac{[\text{A}]}{\bar{\epsilon} - \epsilon_0} = \frac{1}{\epsilon_1 - \epsilon_0} \frac{1}{K} + \frac{[\text{A}]}{\epsilon_1 - \epsilon_0} + \frac{[\text{B}]}{\epsilon_1 - \epsilon_0} + \frac{[\text{B}](\bar{\epsilon} - \epsilon_0)}{(\epsilon_1 - \epsilon_0)^2}. \quad (3)$$

If we assume that in pure benzene solution, naphthol at low concentration exists completely in the hydrogen-bonded form then from fig. 1 it is evident that $\epsilon_1 - \epsilon_0$ must be at least 1000. Further, since the concentration of A is about 1000 times that of B, the third term in (3) is negligible compared to the second. The maximum value of $\bar{\epsilon} - \epsilon_0$ is $\epsilon_1 - \epsilon_0$, hence the fourth term in (3) is about the same magnitude as the third and so may be neglected. The equation thus becomes

$$\frac{[\text{A}]}{\bar{\epsilon} - \epsilon_0} = \frac{1}{\epsilon_1 - \epsilon_0} \frac{1}{K} + \frac{[\text{A}]}{\epsilon_1 - \epsilon_0}, \quad (4)$$

which shows that a plot of $[\text{A}]/\bar{\epsilon} - \epsilon_0$ against $[\text{A}]$ should be linear (for 1 : 1 complex formation) from the intercept and the slope of which the equilibrium constant K and the molar extinction coefficient of the complex may be estimated.

In table 2 are summarized the relevant experimental data with α - and β -naphthol in n-heptane containing varying amounts of benzene, toluene and xylene, and the corresponding $[\text{A}]/(\bar{\epsilon} - \epsilon_0)$ against $[\text{A}]$ plots are given in the fig. 3 and 4.

TABLE 2.—EQUILIBRIUM CONSTANT FOR π -HYDROGEN BOND FORMATION BETWEEN NAPHTHOLS AND AROMATIC HYDROCARBONS

solute	conc. of solute (M) $\times 10^4$	hydrocarbon	range of hydrocarbon conc. (M),	$\epsilon_1 \times 10^{-3}$	K	I.P. of hydrocarbon (eV)
α -naphthol	2.578	benzene	1.13-7.89	2.118	0.04	9.52
	2.695	toluene	1.59-7.20	2.208	0.11	9.23
	2.695	xylene	0.81-5.65	1.725	0.25	8.96
β -naphthol	4.281	benzene	2.25-9.01	0.862	0.12	9.52
	4.528	toluene	0.79-5.59	1.122	0.21	9.23
	4.528	xylene	2.43-5.68	1.252	0.26	8.96

These plots are linear in all cases indicating 1 : 1 complex formation in these systems. Further, from table 2, the equilibrium constant follows the order benzene < toluene < xylene, which is in the reversed order to the ionization potential (I.P.) of the hydrocarbons. Since a lower ionization energy is associated with higher base strength, the equilibrium constants in table 2 is in the right sequence.

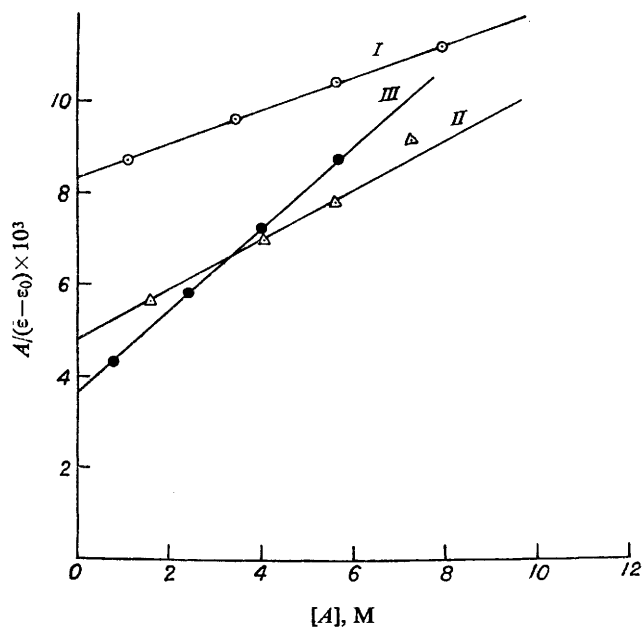


FIG. 3.—Graphical determination of equilibrium constant for α -naphthol + aromatic hydrocarbon systems. I, benzene; II, toluene; III, xylene.

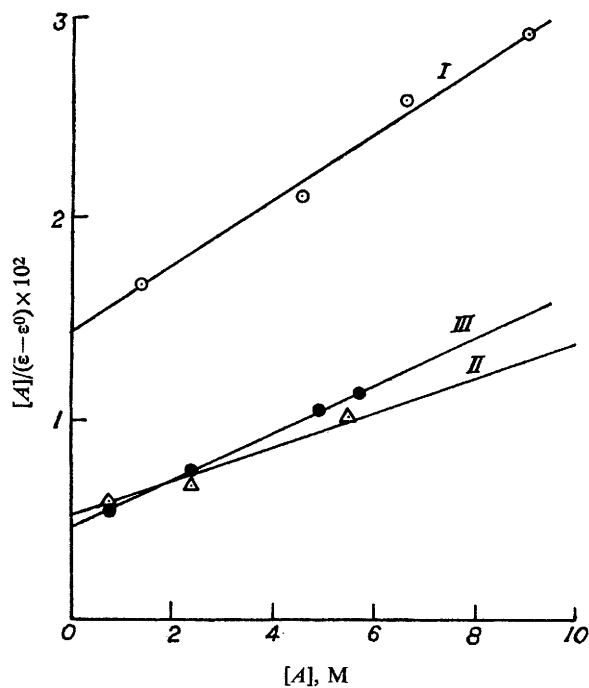


FIG. 4.—Graphical determination of equilibrium constant for β -naphthol + aromatic hydrocarbon systems. I, benzene; II, toluene; III, xylene.

Intermolecular association due to dispersive interaction may be responsible for the observed red shift and the small association constants. However, when methoxy naphthalene was dissolved in n-heptane and in benzene there was no change in the longest wavelength absorption band. Since the dispersive interaction must be equally important in the methoxy naphthalene system, the dispersive interaction is too small to be detected.

From these considerations we conclude that the spectral change induced in naphthols in presence of aromatic hydrocarbons are associated with π -hydrogen bond formation between the hydroxyl group of naphthols and the π -electron system of aromatic hydrocarbons.

Thanks are due to C.S.I.R. (India) for a Junior Research Fellowship to one of us (B. G.).

¹ Huggins and Pimental, *J. Physic. Chem.*, 1956, **60**, 1615.

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³ Trifan and Weiman, *J. Amer. Chem. Soc.*, 1957, **79**, 6566; Goldman and Crisler, *J. Org. Chem.*, 1958, **23**, 751.

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⁵ Higasi, Omura and Tsuchya, *Tables of Ionisation Potentials of Molecules and Radicals*, (Institute of Applied Electricity, Hokkaido University, 1954-7).

⁶ Nagakura and Baba, *J. Amer. Chem. Soc.*, 1952, **74**, 5693.