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Solvent Effect on Hydrogen Bonding Interaction between 5,6,7,8-Tetrahydro-2-naphthol in the Ground and Excited States and Triethylamine

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In the ground state 5,6,7,8-tetrahydro-2-naphthol (ThOH) forms with triethylamine (TEA) simple hydrogen bond, hydrogen-bonded ion pair or solvent-separated ion pair complex depending on the polarity of solvents. Fluorescence emission of ThOH is quenched by TEA in all solvents. The quenching rate constant k_q is large in weakly polar solvents than in highly polar solvents and there is no evidence of formation of solvent-separated ion pair in latter solvents. It is suggested that restricted electron delocalization in excited ThOH molecule lowers the tendency of deprotonation of the OH group. The likely pathway of energy depletion is through intermediate singlet contact CT exciplex of the type A^-D^+ between ThOH and TEA.

Hydrogen-bonding interactions between an acid A–H and a base B can be of different types depending on the polarity of the solvents in which the systems are studied and may lead to simple hydrogen-bond, hydrogen-bonded ion pair or solvent-separated ion pair complex. The present paper concerns absorption and fluorescence spectra of ThOH, a bicyclic molecule of biological interest specially in hormone biology, measured in solvents of different dielectric constant (ε_0) in the presence of TEA as the hydrogen-bond acceptor. In the ThOH molecule the π-electrons extend over one ring and the other alicyclic like ring of the molecule has a flexible distorted half-chair structure like cyclohexane. In a previous communication[1] some changes in the π-electronic absorption spectrum of ThOH and other similar molecules due to hydrogen-bonding with TEA were described. It was also reported that fluorescence of some bicyclic tetrahydronaphthols and amines is quenched by hydrogen-bonding molecules like TEA.[1–3] Hydrogen-bonding properties of molecules are generally different in the ground and excited states. The absorption and emission spectra of ThOH have been measured in the same set of solvents. One of the main objectives is to elucidate dependence of hydrogen-bonding interaction between ThOH in the ground and excited states and TEA on solvent polarity and the nature of the complexes that might be formed. Possible reaction schemes in the ground and excited states and kinetics of energy depletion have been examined.

Experimental

5,6,7,8-Tetrahydro-2-naphthol (ThOH) (Aldrich, 98% pure) was sublimed under reduced pressure before use. TEA (Fluka, AG) was distilled at atmospheric pressure. Spectroscopic grade solvents hexane, ethanol (EtOH), methanol (MeOH), dichloromethane (DCM), tetrahydrofuran (THF), *N,N*-dimethylformamide (DMF), acetonitrile (ACN) supplied by E. Merck, W. Germany were used as received. TEA and all the solvents were tested carefully for any possible interfering emission when excited at 280 nm.

The concentration of ThOH was about 2.25×10^{-4} mol dm^{-3} for both absorption and emission experiments. In ternary mixtures, the concentration of TEA in different solvents varied from 0.1 to 1 mol dm^{-3} for absorption and from 10^{-3} to 0.1 mol dm^{-3} for emission study. The excitation wavelength was 280 nm.

The absorption spectra were recorded with a Shimadzu UV-VIS spectrophotometer model 210A and the emission spectra with a Perkin-Elmer model MPF 44A fluorescence spectrophotometer attached with corrected spectra unit.

Fluorescence decay measurements were made using a time-correlated single photon-counting fluorimeter (model 199, Edinburge Instruments, U. K). The excitation source was a coaxial H_2 flash lamp giving an instrumental response function of about 1.2 ns full width at half-maximum (FWHM) at 30 kHz repetition rate. The excitation and emission wavelengths were 280 nm and 305 nm, respectively. Count versus channel number was recorded separately and fluorescence lifetime was calculated by fitting single exponential function with the experimental data and the computation was done using HCL PC Computer model BUSYBEE PC/XT.

Results and Discussion

Hydrogen-Bonding and Absorption Spectral Changes. The π-electronic absorption spectrum of ThOH in 260—310 nm region has been measured at 300 K in different nonpolar and polar protic and aprotic solvents without and with added amounts of TEA. Figure 1 shows that when TEA is added to the solution of ThOH in hexane (dielectric constant $\varepsilon_0\approx1.89$ at 300 K) the absorption spectrum undergoes a small shift towards the longer wavelength. An isosbestic point is also noted at 290 nm in the absorption spectrum (Fig. 1). TEA does not produce any change in the absorption spectrum of an analogous molecule 6-methoxy-1,2,3,4-tetrahydronaphthalene which is unlikely to have hydrogen-bonding interaction with TEA in hexane. Addition of excess amount of TEA to the tetrahydronaphthol–hexane system does not yield any band on the long wavelength side characteristic of charge transfer or ion pair formation. All this indicates that in hexane medium hydrogen-bonding

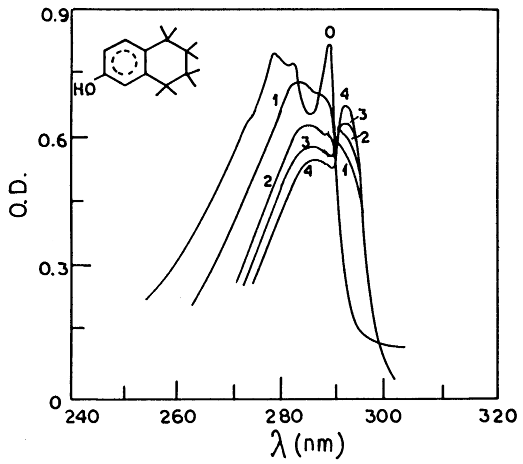


Fig. 1. Ultraviolet absorption curves for ThOH in hexane (2.23×10^{-4} mol dm^{-3}) at 300 K. Concentration (mol dm^{-3}) of TEA: (0) 0; (1) 0.10; (2) 0.67; (3) 0.83; (4) 1.0.

between ThOH and TEA is weak and a simple hydrogen-bonded complex is formed. The simple hydrogen-bonded equilibrium may be expressed as

$$\underset{C_f}{\mathrm{ThOH}}+\underset{C_A}{\mathrm{NR_3}} \xrightleftharpoons{K_1} \underset{C_b}{\mathrm{ThOH\cdots NR_3}} \qquad (1)$$

where R stands for C_2H_5.

The equilibrium constant K_1 is given by

$$K_1 = C_b/C_fC_A$$

where C_f, C_A, and C_b represent concentrations of free ThOH, TEA, and the hydrogen-bonded species respectively.

When ThOH is dissolved in polar protic solvents EtOH or MeOH or in polar aprotic solvent tetrahydrofuran (THF) the absorption bands of the molecule shift towards the red with respect to the bands observed in hexane solution. When TEA is added to the binary mixture of ThOH-alcohol or ThOH-THF, no further shift is observed. Apparently ThOH becomes engaged in hydrogen-bonding with EtOH, MeOH, or THF and when TEA is added, direct hydrogen-bonding between TEA and ThOH does not take place.

In dichloromethane (DCM) which has a relatively high dielectric constant ($\varepsilon_0 \approx 9.80$ at 300 K) compared to hexane, the tetrahydronaphthol-TEA system yields two absorption maxima at 289 and 325 nm which may be assigned to simple hydrogen-bonded species and hydrogen-bonded ion pair, respectively (Fig. 2, Table 1). This implies establishment of a tautomeric equilibrium between simple hydrogen-bonded complex and the hydrogen-bonded ion pair and the following equilibria may be assumed

$$\mathrm{ThOH+NR_3} \xrightleftharpoons{K_1} \mathrm{ThOH\cdots NR_3}$$

$$\underset{C_{HB}}{\mathrm{ThOH\cdots NR_3}} \xrightleftharpoons{K_2} \underset{C_{HBIP}}{\mathrm{ThO^-\cdots NH^+R_3}} \qquad (2)$$

where K_2 is given by C_{HBIP}/C_{HB}. Here C_{HB} and C_{HBIP} stand for concentration of simple hydrogen-bonded complex and hydrogen-bonded ion pair complex

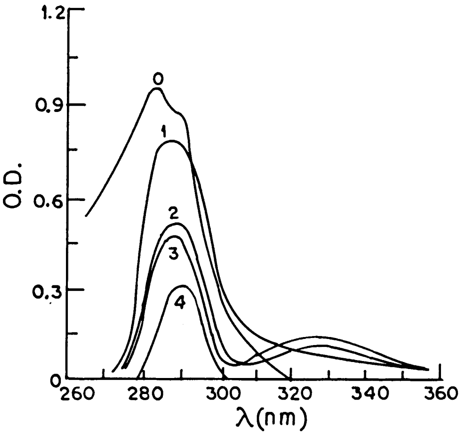


Fig. 2. Ultraviolet absorption curves for ThOH in DCM (2.25×10^{-4} mol dm^{-3}) at 300 K. Concentration (mol dm^{-3}) of TEA: (0) 0; (1) 0.23; (2) 0.67; (3) 0.83; (4) 1.0.

Table 1. Position of Absorption Maxima, λ_{max} in nm

Solvent	ε_0 a)	ThOH	ThOH···NR$_3$	ThO$^-$···HN$^+$R$_3$	ThO$^-$(solv.)N$^+$HR$_3$
Hexane	1.89	287	292	—	—
		280	286	—	—
THF	7.58	291	—	—	—
		283	—	—	—
DCM	9.08	290	—	—	—
		283	289	325	—
EtOH	24.55	289	—	—	—
		283	—	—	—
MeOH	32.70	289	—	—	—
		283	—	—	—
DMF	36.70	290	—	—	—
		283	—	—	340
ACN	37.50	289	—	—	340
		283	—	—	—

a) Values given at 300 K.

respectively. Baba et al.[3] made similar observation in the case of *p*-nitrophenol-TEA in DCM. The peak at 289 nm in DCM represents absorption by ThOH, hydrogen-bonded with TEA. The corresponding peak due to free molecule before the addition of TEA is at 283 nm (Fig. 2, Table 1). When concentration of TEA is sufficiently high ($\approx$1 mol dm^{-3}) the longer wavelength band at 325 nm assigned to hydrogen-bonded ion pair disappears and only the 289 nm band due to simple hydrogen-bonded species persists (Fig. 2). Therefore, at large concentration of TEA, the tautomeric equilibria shown by Eq. 2 are disturbed. The equilibrium under these conditions is weighted in favor of the simple hydrogen-bonded complex. Evidently when a large amount of TEA, which has a comparatively low dielectric constant ($\varepsilon_0\approx2.24$), is present in the mixture containing DCM and TEA, the effective dielectric constant is lowered and the situation tends to be the case of solution of low dielectric constant in which only simple hydrogen-bonded complex is formed.

When TEA is gradually added to solution of ThOH in highly polar aprotic solvents *N*,*N*-dimethylformamide (DMF) ($\varepsilon_0\approx36.7$) and acetonitrile (ACN) ($\varepsilon_0\approx37.0$), a single broad structureless band (Fig. 3) appears at 340 nm (Table 1) in place of the 325 nm band due to hydrogen-bonded ion pair observed in DCM. At the same time, intensity of the absorption band due to free molecules diminishes (Fig. 3). It is seen from Fig. 3 that naphtholate ion in aqueous solution absorbs near the same wavelength and therefore the 340 nm band may be attributed to absorption by deprotonated naphtholate ion ThO$^-$ in the ground state. The presence of isosbestic point in the spectrum (Fig. 3) indicates a chemical equilibrium which may be expressed as

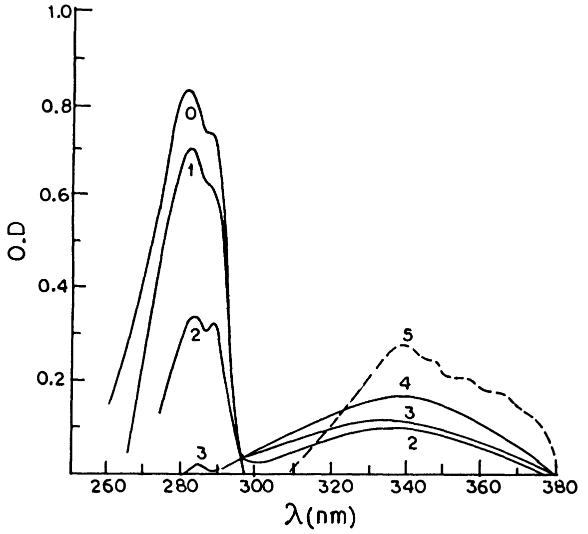


Fig. 3. Ultraviolet absorption curves for ThOH in ACN (2.31×10^{-4} mol dm^{-3}) at 300 K. Concentration (mol dm^{-3}) of TEA: (0) 0; (1) 0.10; (2) 0.67; (3) 0.83; (4) 1.0. Dotted curve (5): spectrum of tetrahydronaphtholate ion (ThO$^-$) in aqueous solution.

$$\mathrm{ThOH+NR_3} \underset{}{\overset{K_3}{\rightleftharpoons}} \mathrm{ThO^-(solv.)N^+HR_3} \qquad (3)$$

which assumes formation of solvent-separated ion pair by transfer of proton. The ions are separated by one or more solvent molecules and are linked electrostatically.

Hydrogen-Bonding and Fluorescence Spectral Changes. To sum up, absorption measurements demonstrate different types of interaction between ThOH in the ground state and TEA in different solvents depending on the dielectric constants of solvents. It would be interesting to investigate the nature of interaction between excited ThOH and TEA in the same solvents as were employed in absorption study. The fluorescence spectra of ThOH at 300 K are given in Fig. 4(a) and Fig. 4(b). It is seen that in the solvents hexane ($\varepsilon_0\approx1.89$ at 300 K), THF ($\varepsilon_0\approx7.58$ at 300 K), DCM ($\varepsilon_0\approx9.08$ at 300 K), DMF ($\varepsilon_0\approx36.7$ at 300 K), and ACN ($\varepsilon_0\approx37.5$ at 300 K), fluorescence emission of ThOH is reduced remarkably in the presence of very small amount of TEA (concentration$\approx$ 10^{-3}—10^{-2} mol dm^{-3}), but the shape and position of the bands are unchanged (Figs. 4(a) and (b)).

The absorption spectral changes described above, require comparatively large concentration of TEA (0.1 mol dm^{-3}). So, for very low TEA concentration, ranging from 10^{-3} to 10^{-2} mol dm^{-3}, used in fluorescence measurements, static quenching or innerfilter effect may be neglected and the dynamic quenching rate constant k_q may be determined from simple Stern-Volmer equation

$$f_0/f = 1 + K_{sv}[\mathrm{Q}] \qquad (4)$$

where $K_{sv}=k_q\tau_0$, τ_0 being the fluorescence decay time in absence of TEA. Plots of f_0/f versus [Q] in different solvents are found to be linear and the computed k_q's are given in Table 2. It is seen that the dynamic fluorescence quenching rate constant k_q measured in hexane is larger than the rate constants measured in more polar solvents THF, DMF, and ACN (Table 2). In DCM, k_q is slightly higher than in hexane. In this solvent, external heavy atom perturbation is likely to contribute to deactivation of the excited singlet state of ThOH. In alcoholic solvents, on addition of TEA (Fig. 4(c)), the fluorescence of ThOH is not quenched and this indicates that the nonbonding lone-pair electrons on the nitrogen atom of TEA form hydrogen-bonding of R-OH···N type with alcohols and charge transfer in ThOH-TEA system is retarded. The solvent dependence of quenching constant k_q is not very regular. But it is found to be generally high in solvents of low polarity than in solvents of high polarity (Table 2). This negates existence of solvent-separated ion pair complex in the excited state, similar to the one formed in the ground state, even in highly polar solvent like ACN. Plainly, hydrogen-bonding

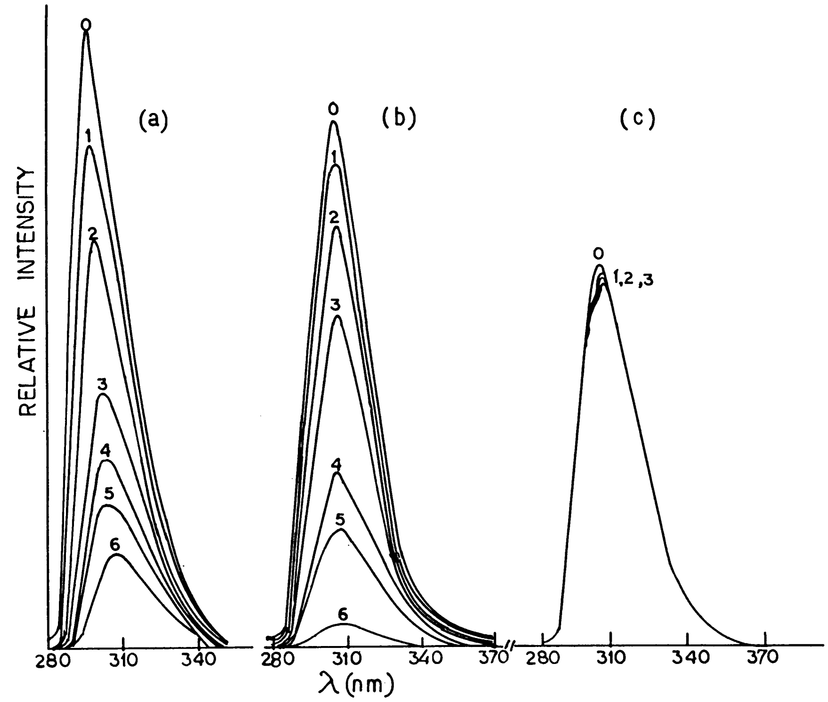
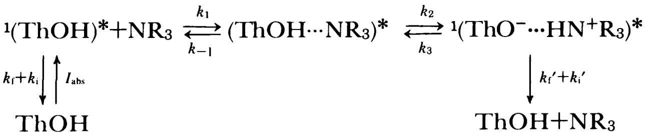


Fig. 4. (a) Fluorescence spectra of ThOH in hexane (2.23×10^{-4} mol dm^{-3}) at 300 K (excitation wavelength: 280 nm). Concentration (mol dm^{-3}) of TEA in (0) 0; (1) 3.17×10^{-3}; (2) 9.51×10^{-3}; (3) 1.90×10^{-2}; (4) 3.17×10^{-2}; (5) 4.76×10^{-2}; (6) 9.52×10^{-2}.
(b) Fluorescence spectra of ThOH in ACN (2.31×10^{-4} mol dm^{-3}) at 300 K (excitation wavelength: 280 nm). Concentration (mol dm^{-3}) of TEA in (0) 0; (1) 1.60×10^{-2}; (2) 3.20×10^{-2}; (3) 6.40×10^{-2}; (4) 1.28×10^{-1}; (5) 1.92×10^{-1}; (6) 9.52×10^{-1}.
(c) Fluorescence spectra of ThOH in EtOH (2.25×10^{-4} mol dm^{-3}) at 300 K (excitation wavelength: 280 nm). Concentration (mol dm^{-3}) of TEA in (0) 0; (1) 1.60×10^{-2}; (2) 6.40×10^{-2}; (3) 1.92×10^{-1}.

Table 2. Bimolecular Fluorescence Quenching Rate Constant (k_q) in Solvents of Varing ε_0 Values for ThOH-TEA System at 300 K

Solvent	ε_0	τ_0/ns	K_{sv}/dm^3 mol^{-1}	k_q/dm^3 mol^{-1} s^{-1}
Hexane	1.89	4.19	69.32	1.65×10^{10}
THF	7.58	5.46	8.55	1.56×10^{9}
DCM	9.08	2.00	35.29	1.76×10^{10}
EtOH	24.55		No quenching	
MeOH	32.70		No quenching	
DMF	36.70	6.83	3.18	4.65×10^{8}
ACN	37.00	4.54	9.20	2.02×10^{9}

properties of ThOH are different in the ground and excited states. The deactivation of the excited ThOH molecule may be through formation of hydrogen-bonded ion pair or contact CT exciplex and the equilibrium may be represented by



$$\begin{array}{ccccc} {}^1(\mathrm{ThOH})^*+\mathrm{NR_3} & \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} & (\mathrm{ThOH}\cdots\mathrm{NR_3})^* & \underset{k_3}{\overset{k_2}{\rightleftarrows}} & {}^1(\mathrm{ThO^-}\cdots\mathrm{HN^+R_3})^* \\ k_f+k_i \downarrow \uparrow I_{abs} & & & & \downarrow k_f'+k_i' \\ \mathrm{ThOH} & & & & \mathrm{ThOH}+\mathrm{NR_3} \end{array}$$

Scheme 1.

The energy gap between the CT state $^1(\mathrm{ThO^-}\cdots\mathrm{NH^+R_3})^*$ and the ground state of ThOH may be small enough to favor internal conversion[5] and fast non-radiative decay as pictured in Scheme 1. It is interesting to note that in the ground state, 2-naphthol, in which the π-electrons extend over both the rings, reportedly[6,7] enters into simple hydrogen-bonding with TEA in nonpolar solvents. In polar solvents bonding between TEA and unexcited 2-naphthol is supposed to be hindered[6] due to large solvation of both the acceptor and donor molecules. On the other hand, due to interaction between TEA and excited 2-naphthol in polar solvents, formation of solvent-separated ion pair complex equlibrium state from which fluorescence transition occurred was reported.[6]

Therefore hydrogen-bonding behaviors of 2-naphthol and the bicyclic tetrahydronaphthol are different, particularly in the excited state. This difference in behavior may be attributed to the lessening of electron delocalization due to the saturation of one of the rings of the bicyclic system of ThOH and consequent lowering of the number of π-bonds. The outcome of low electron delocalization is that tendency of deprotonation of OH group of ThOH decreases.

Apparently this restriction of electron delocalization is specially important in the excited state of ThOH because as has been noted above, there is no indication of solvent-separated ion pair formation in polar solvents.

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