

Investigation of H-Bond on Fluorescence Changes in Benzene Derivations and Different Acceptor Systems

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In this study, benzene derivatives of phenol and naphtol were selected as donor systems and mixed with dioxane and TEA (triethylamine), which were chosen as acceptors. H-bond formation in the phenol-triethylamine binary system was investigated by both UV absorption and emission spectroscopies. The changes in the absorption and emission spectra by H-bond formation and the equilibrium of the H-bonded complexes were studied at both the ground and excited states. In addition, equilibrium constants at different temperatures and thermodynamic properties related to equilibrium (enthalpy, free energy change and entropy values of H-bond formation) were calculated. A shift to longer wavelengths and differences in absorption and fluorescence intensities in the absorption and emission spectra were observed. Moreover, H-bond formation in various solvents with different dielectric constants was investigated. Changes in entropy related to the formation of hydrogen bonded complexes generally had negative values at both ground and excited states. These values were observed to increase with the increase in the dielectric constants of the solvent systems; therefore, H-bonded complexes grew more stable with the increase in the dielectric constants of the solvent systems.

Introduction

The examination of hydrogen bond formation by spectroscopic methods in biologically important benzene derivatives (phenol, naphtol, and prene type compounds) began in 1950. The spectroscopic investigation (UV, IR and NMR) of hydrogen bond formation of some purine and pyrimidine systems was carried out by W. Wagner et al.¹, whereas Graham et al.² investigated H-bond formation in pyridazine and benzofenon with ethylalcohol.

A number of studies on H-bond formation in polar and apolar solvent have been carried out. Mizushima et al.³ examined H-bond complexes formed by carbonyl bases in alcoholic or aqueous media. Tsubomura⁴ and Nagakura⁵ investigated acetates by examining their electronic transitions. In addition, George C. Pimentel⁶ suggested that hydrogen bond complexes formed in aqueous media were stronger than those formed in methanol. H-bonds, formed by substituted phenols and ethanols in cyclohexane, ether or other solvents, were examined by D.L. Gerrard⁷ by absorption spectroscopy.

Melvin et al.⁸ determined formation enthalpies and equilibrium constants by examining H-bond formation between phenols and amides in carbontetrachloride.

Sabura Nagakura⁹ investigated complexes formed by phenols and acetate esters in apolar solvents by UV spectroscopy, and determined their thermodynamic parameters.

Simule-emission spectroscopic examination of H-bond complex formed by phenol-water was recently carried out by Takayuki Ebata et al.¹⁰. H-bond formation by proton transfer of aromatic alcohols in non-aqueous solvents was investigated by Hasselbacher et al.¹¹ with the "Time-Resolved Fluorescence" method.

Hiroaki Baba et al.¹² investigated the influence of H-bond formation by phenol and naphthol with various proton acceptors in terms of their electronic spectra. H. Baba¹⁴, G. C. Pimental⁶, H. Tsubomure⁴, and G. J. Brealey et al.² have suggested some theoretical parameters concerning the work mentioned above. However, limited research has been conducted on the effect of solvents and dipole moments by steady-state fluorescence.

Hydrogen bonding effects on electronic spectra will give useful information about the nature of the hydrogen bond and also the nature of the electronic transitions.

Since the molecular absorption and fluorescence spectra are directly related to the electronic structure of the molecule, H-bonding would effect the UV and Vis absorption and fluorescence spectra.

As a result of these investigations, it has been recognized that the phenomenon of the hydrogen bonding effect on electronic spectra is useful in several respects. It has been suggested that thermodynamic quantities for some hydrogen bonding equilibria may be determined through this phenomenon. Moreover, when a polar substance is used as solved, and anomaly in the solvent effect on electronic spectra occurs, which could be interpreted in terms of the hydrogen bonding effect¹².

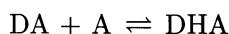
Experimental

Phenol and naphthal were selected as donors while dioxane (Sigma HPLC grade 99.9%) and triethylamine (Sigma, pure) were used as acceptors. Solvent systems chosen were n-hexane (Sigma 99%), n-heptane (Sigma, 99%), isooctane (Merck, pure) and cyclohexane (Sigma 99%).

All absorbance measurements were made with a Shimadzu UV-160A, UV-Visible Recording Spectrophotometer. For fluorescence measurements, a Fica 55 spectrofluorimeter differential absolute was used. Dielectric constant measurements were made with a Dekameter DKO3 Nach. Temperature was controlled throughout the experiment by a Poly Science 901 refrigerated circulator ($\pm 0,02$ Temperature Stability).

The Determination of H-bond formation Constants From Absorption and Fluorescence Spectra

Ground state equilibrium constants can be calculated by using absorption spectral data in the equation derived below⁸:



where (DH) is the proton donor, A is the proton acceptor, and (DHA) is the hydrogen bonded complex.

For example, if the equilibrium between phenol-dioxane,

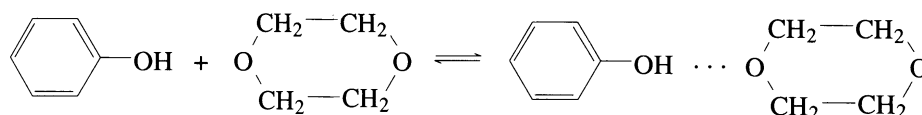
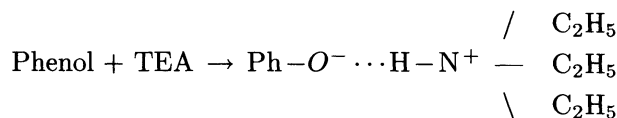


Figure 1. The equilibrium between phenol and dioxane.

or if the equilibrium between Phenol-Triethylamine are considered, then



C_d : initial concentration of the donor

C_a : initial concentration of the acceptor

C_c : concentration of H-bonded complex

Therefore, the equilibrium constant is

$$K = \frac{C_c}{(C_d - C_c)(C_a - C_c)}$$

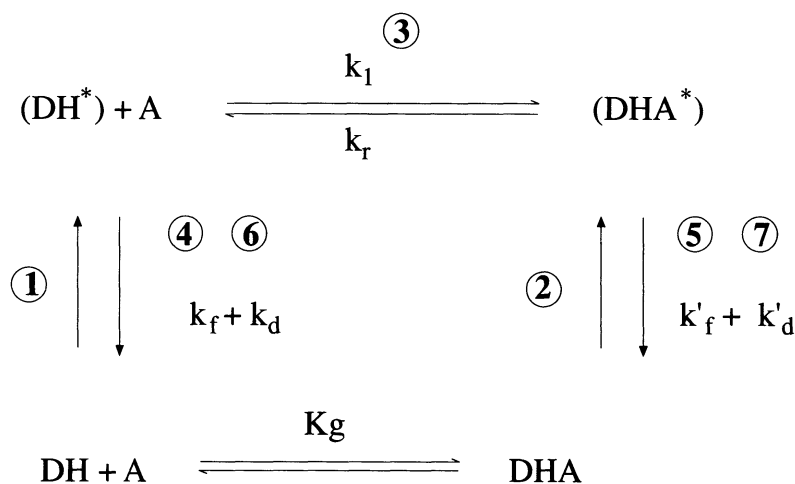
$$\frac{1}{\Delta A} = \frac{1}{\Delta A_{\max}} + \frac{1}{K_g \Delta A_{\max}} \cdots \frac{1}{C_a}$$

where ΔA is the change in optical density of the donor in the presence of C_a .

ΔA_{\max} is the maximal change in absorbance and K_g is the association constant of the ground state.

If the autoassociations are ignored, the graph of $1/\Delta A$ vs $1/C_a$ gives a linear change in which K_g and ΔA_{\max} can be found from the slope and intercept value.

When light at a certain wavelength is directed on a solution containing donor and acceptor system, the following may occur:



The asterisk indicates the excited states, while k_f and k_d radiative and radiationless decay rates for (DH^*) as are k'_f and k'_d (DHA^*) .

Rate or equilibrium constant

- | | |
|--|--|
| 1. $\text{DH} + h\nu_{abs} \rightarrow (\text{DH}^*)$ | } total I_{abs} |
| 2. $\text{DHA} + h\nu'_{abs} \rightarrow \text{DHA}^*$ | |
| 3. $(\text{DH}^*) + \text{A} \rightarrow (\text{DHA}^*)$ | $K^* = \frac{k_1}{k_r} = \frac{ (\text{DHA}^*) }{ (\text{DH}^*) \text{A} }$ |
| 4. $(\text{DH}^*) \rightarrow (\text{DH}) + h\nu_f$ | $k_f (\text{DH}^*) $ |
| 5. $(\text{DHA}^*) \rightarrow \text{DHA} + h\nu_{f'}$ | $k'_{f'} (\text{DHA}^*) $ |
| 6. $(\text{DH}^*) \rightarrow (\text{DH}) + \text{heat}$ | $k_d (\text{DH}^*) $ |
| 7. $(\text{DHA}^*) \rightarrow (\text{DHA}) + \text{heat}$ | $k'_{d'} (\text{DHA}^*) $ |

$$\frac{\frac{I}{I_o} - 1}{|A|} = \alpha K^* - K^* \frac{I}{I_o}$$

This equation was derived¹⁵ and the graph obtained with $(I/I_o) - 1/|A|$ vs I/I_o , yielding a straight line, and equilibrium constants for the excited state can be found from the slope.

In this equation, I_o and I are the fluorescence intensities of the free and hydrogen-bonded phenols.

$$\alpha = \frac{\phi'}{\phi}$$

ϕ and ϕ' are respectively the quantum efficiencies of fluorescence for the excited proton donor and the excited complex.

Preliminarily, the donor solution was optimized by recording absorption and emission at λ_{\max} for a series of selected donor solutions in varying concentrations. These measurements were made in media with no dimerisation. The absorption and emission spectra of the donor solution were investigated after the addition of various amounts of acceptor. Dielectric constants were measured for solution and the solvent separately. All measurements were repeated for different solvent and acceptor systems at different temperatures.

If the formation rate of the excited state at equilibrium is much slower than the rate of fluorescence, this may help to calculate the ground state equilibrium constant. This constant is in agreement with that obtained from absorption spectra. In the case of slower fluorescence radiation, the equilibrium constant for the excited state can be obtained¹⁶.

Determination of ΔH , ΔG and ΔS of H-Bond Formation

Change in free energy, ΔG , is defined by the following equation:

$$\Delta G = - RT \ln K$$

Change in enthalpy, ΔH , is related to the equilibrium constant (K) and temperature (T) by the following equation:

$$\Delta H = -R [d \ln K / d (1/T)]$$

The $\ln K$ values plotted against $1/T$ were found to fall on a straight line. From the slope of this line, determined by the method of least squares, the value of the change in enthalpy, ΔH , was derived, is of course to be associated with the ground state of a given molecule, so that it may be denoted by ΔH_g . The change in enthalpy of the hydrogen bond in the excited state is in general different from that in the ground state, and the former will therefore be denoted by ΔH_e . The hydrogen bonding frequency shift is given by¹²

$$\delta\nu = \Delta H_e - \Delta H_g$$

or

$$\Delta H_e = \Delta H_g + \delta\nu$$

$\Delta H_{e(cal)}$ values in Table 2 are calculated according to this equation.

$$\delta\nu = \nu_b - \nu_f$$

$\nu_b \rightarrow$ max absorbance frequency shift of a free molecule.

$\nu_f \rightarrow$ max absorbance frequency shift of a bonded molecule.

ΔS , related to H-bond formation, is calculated with the equation given below:

$$\Delta G = \Delta H - T\Delta S$$

The thermodynamic parameters of phenol-dioxane and phenol-triethylamine systems for both ground state and excited state are shown in Table 1.

Results and Discussions

The optimum concentration of phenol was found to be 4×10^{-4} M. The absorption spectra of a series of solution of phenol containing dioxane in the concentration range of 0.04-0.5 M were recorded. The effect of dioxane concentration on the absorption value was reduced off by adding the same amount of dioxane to the reference cell. The absorption spectra of this system in heptane is shown in Fig. 2. Differences in optical intensity (ΔA) were obtained from the differential spectra for 282 nm. The ground state equilibrium constant for H-bond formation, K_g , was found from the graph between the relation $1/C_a$ and $1/\Delta A$. The measurements were made in different solvents.

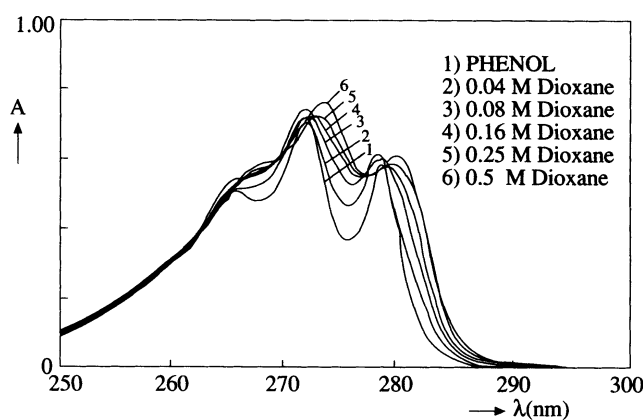


Figure 2. Absorption spectra of 4×10^{-4} M phenol solutions containing dioxane at varied concentrations in heptane at 25 °C.

For phenol-triethylamine systems, H-bond formation was examined with both absorption and fluorescence spectra. Phenol concentration was maintained at 4×10^{-5} M in all measurements. Triethylamine concentrations varied in the range of 8×10^{-4} – 0.14 M. The absorption spectra of this system in hexane are shown in Figure 3. Differences in absorbance (ΔA) were obtained from the differential spectra recorded at 284nm, and the ground state equilibrium constant for H-bond formation, K_g , was calculated from a graph drawn between $1/C_a$ and $1/\Delta A$.

Fluorescence spectra of the phenol-dioxane and phenol-triethylamine systems were recorded in apolar solvents. Figure 4 shows the fluorescence spectra of the phenol-dioxane system in n-neptane. The excited state equilibrium constant for H-bond formation, K^* , was found by the relation between $(I/I_o - 1)C_a$ and I/I_o at different dioxane concentrations.

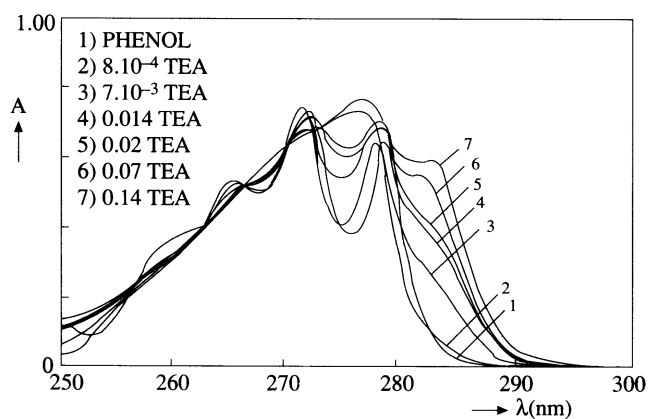


Figure 3. Absorption spectra of 4×10^{-4} M phenol solutions containing triethylamine at varied concentrations in heptane at 25°C .

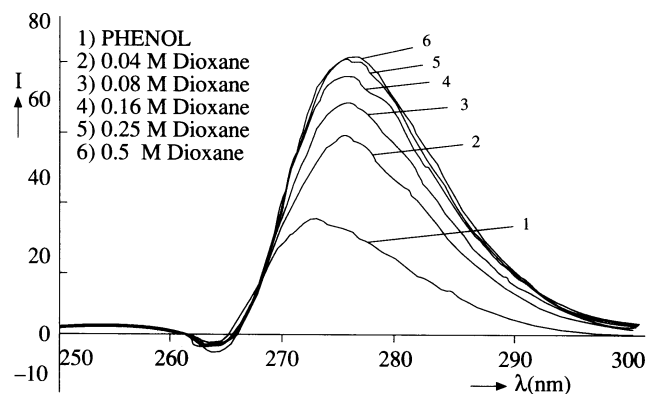


Figure 4. Fluorescence spectra of phenol-dioxane system in n-heptane at 25°C .

The recorded fluorescence spectra of the phenol-triethylamine system in hexane at 25°C are shown in figure 5. The excited-state equilibrium constant for this system was obtained by the method described above.

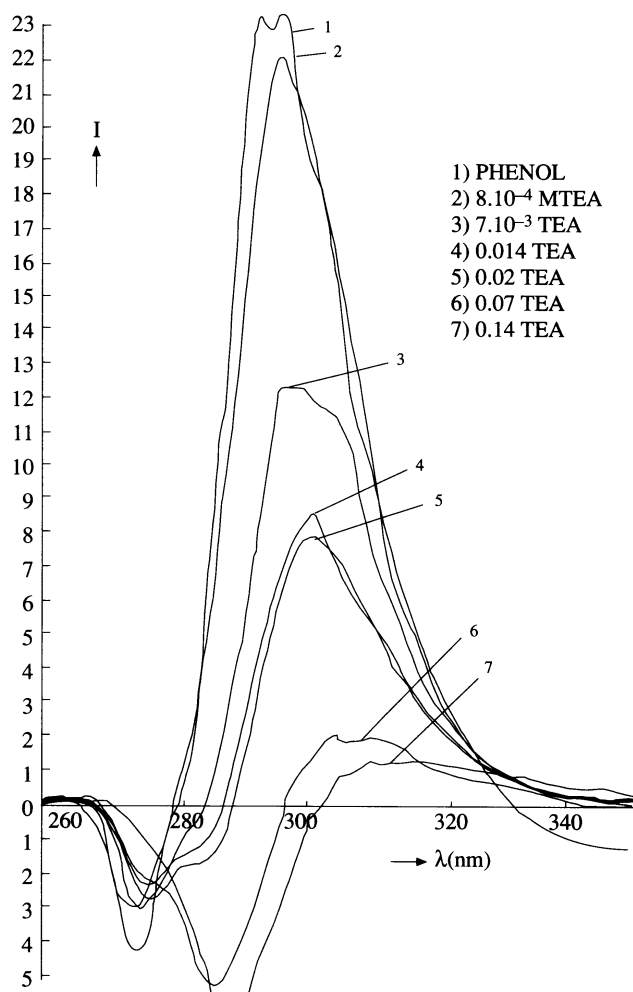


Figure 5. Fluorescence spectra of phenol-triethylamine system in hexane at 25°C .

In this study, all absorption and fluorescence spectra for phenol-systems were recorded at five different temperatures in the range 15 °C-35 °C.

The comparison of the experimental thermodynamic properties of Phenol-Dioxane and Phenol-triethylamine systems in the ground and excited states is shown in Table 1.

Table 1. The comparison of the experimental thermodynamic properties of Phenol-Dioxane and Phenol-Triethylamine systems in the ground and excited states.

Phenol-Dioxane System								
20°C	M ⁻¹		kJ/mole				J/mole K	
	K _g	K _e	ΔH _g	ΔH _e	ΔG _g	ΔG _e	ΔS _g	ΔS _e
Hexane	7	28	-13	-8.8	-4.7	-8.1	-30	-2
Heptane	9	12	-24	-8.6	-5.3	-6.0	-54	-8
Isooctane	14	38	-16	-21	-6.4	-8.9	-33	-41
Cyclohexane	13	27	-27	-25	-6.2	-8.0	-70	-57
Phenol-Triethylamine System								
Hexane	115	107	-25	-23	-12	-11	-47	-39
Heptane	80	322	-59	-31	-11	-14	-165	-58
Isooctane	80	100	-118	-52	-11	-11	-366	-140
Cyclohexane	62	222	-84	-28	-10	-13	-251	-50

The temperature dependence errors in the enthalpy changes were found to be approximately ± 0.03 kJ/mol

Calculated ΔH_e values of Phenol-Dioxane systems are given in Table 2.

Table 2. Calculated ΔH₂ values of phenol-dioxane systems.

Comp.	Frequency (cm ⁻¹)					ΔH _{e_{calc}} (kJ/mol)
	Trans	Assig	ν _f	ν _b	ν _b - ν _f	
Phenol (282nm)	I	1A1→1B2				
(Hexane)	I		35958	35702	-256	-14,6
(Heptane)	I		35958	35676	-282	-22,6
(Isooctane)	I		35984	35714	-270	-17,1
(Cyclohexane)	I		35992	35689	-244	-28

Table 3 shows shifts in frequency (δν) of UV absorption spectra for phenol and naphthol systems in H-bonded complex formation with dioxane (isooctane)¹² and triethylamine (heptane) as acceptors. For phenol, Frequency values for phenol presented in this study were obtained experimentally, whereas those for α and β-naphthol were obtained from the literature.

Table 3. Frequency shifts due to hydrogen bond formation for phenol and naphthol systems.

Compound	Transition	Frequency (cm ⁻¹)		δν (cm ⁻¹)	
		ν _f	ν _b	Dioxane	Triethylamine
Phenol	I	35984	35714	-270	580
α-Nahphtol	I	31740	31595	-145	280
β-Nahphtol	I	31180	30795	-385	590

For all systems the equilibrium constants for ground and excited states and thermodynamic properties such as change in enthalpy (ΔH), change in free energy, (ΔG) and change in entropy (ΔS) for H-bond formation were calculated and compared with those in the literature.

Phenol-Dioxane System: For phenol I ($^1A_1 \rightarrow ^1B_2$) transitions, at 282 nm, in the temperature range of 15-35°C, K_g equilibrium constants generally increase as the dielectric constants increase for all solvent systems except isooctane. The K_g values for cyclohexane¹⁷ and for isooctane¹² are both in accord with values given in the literature. It follows that the results obtained for isooctane presumably result from a deviation arising from its structure (2 dimethyl, 4 methyl pentane). ΔH_g , at 282 nm, in the temperature range of 15-35°C, increases as the dielectric constant increases for all solvents except heptane. The change in free energy for the ground state, ΔG_g , increases according to the dielectric constant of the solvent. The deviation in K_g values, is reflected in ΔG_g values only for isooctane.

At ground state, 282 nm and 20°C, the ΔS_g values of H-bond formation gradually increase as the dielectric constant of the solvent increases except in heptane).

As a result, the ΔS_g values of H-bond formation gradually shift toward negative values according to the dielectric constant of the solvent; therefore, H-bond formation for the phenol-dioxane system is stronger.

If equilibrium constants for the excited state are compared to the values obtained for the ground state, K_e values are seen to be higher; therefore, the H-bond complex for the phenol-dioxane system is stronger. ΔH_e , bond energies for the excited state, gradually increase according to the dielectric constant of the solvent. At the excited state, at temperatures of 20° and 25°C for each solvent, higher negative values of ΔS_e reveal the phenol-dioxane hydrogen-bonded complex to be more stable. The increment in negative ΔS_e values, depending on the dielectric constants of various solvents, shows the stability of H-bonded phenol-dioxane complex to increase.

The electronegativity of the hydroxyl oxygen atom of phenolic groups is affected by the increment of the dielectric constant of solvents either in the ground state or in the excited state. Thus, the interaction of the nonbonding pair of electrons in hydroxyl oxygen with the ring π -electrons will be enhanced on account of the hydrogen bond formation, which will be stronger¹².

Phenol-Triethylamine System: For phenol I transitions, at 284 nm in the temperature range of 15-35°C, K_g values for all solvents except isooctane were found to decrease as the dielectric constants of the solvents increased. In the same temperature range, bond energy for the ground state increases as the dielectric constant increases. The data obtained are in accord with the results given in the literature¹⁸. At 20 and 25°C, ΔG_g values (apart from isooctane) were found to decrease as ΔS_g values increased. As a result, the increment in ΔS_g values of H-bond formation according to the dielectric constant of the solvent reveals H-bond formation in the phenol-triethylamine system to be strong. This result is parallel to that obtained for the phenol-dioxane system. However, the increment observed in ΔS_g values (at constant temperatures) for the phenol-triethylamine system was larger than that observed for the phenol-dioxane system. This was due to the stronger proton acceptor of triethylamine.

In the excited state, at constant temperature K_e values were higher than K_g values, so that at the excited state phenol-triethylamine H-bonded complex was stronger. Using K_e values by fluorescence measurements in heptane for the phenol-triethylamine system, the K_g value was 95 M⁻¹, calculated with the equation from the literature^{11,19}. This result is in accord with the value ($K_g = 81$ M⁻¹) found experimentally.

ΔH_e H-bond energy of the phenol-triethylamine system, increased as the dielectric constant increased. At a constant temperature, ΔG_e and ΔS_e values shifted towards higher negative values with the increase of the dielectric constant. The change in entropy, an important criterion for stability, showed that in the

excited state, triethylamine complexes were stronger than dioxane complexes since triethylamine is a stronger proton acceptor than dioxane¹¹.

Naphtol-Dioxane and Naphtol-TEA (Triethylamine) Systems: The UV absorption data of the naphtol and phenol systems forming H-bonded complexes with dioxane and TEA are given in Table 3. As shown in Table 1, frequency shifts for dioxane as well as those for TEA are changed in the following order:

$$\delta\nu_{\beta\text{-Naphtol}} > \delta\nu_{\text{phenol}} > \delta\nu_{\alpha\text{-Naphtol}}$$

This observation shows that the strength of the H-bond can be given in the following order:

β -Naphtol-dioxane > phenol-dioxane > α -Naphtol-dioxane

β -Naphtol-TEA > Phenol-TEA > α -Naphtol-TEA.

The emission spectra data for the same systems shows the phenol-triethylamine complex to be weaker than β -naphtol-Triethylamine complex.

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