Articles

Solvatochromic Effects and Hydrogen Bonding Interactions of 4-(4-Nitrophenylazo)-1-naphthol Derivatives

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Solvatochromic effect and hydrogen bonding interaction of NPNOH, NPNO[−] and NPNOR were investigated. Electronic transition energies of the dyes were plotted against empirical solvent polarity parameters, Taft's π^* and Reichardt's $E_T(30)$. Good correlations were observed when the excitation energies were plotted against the energy calculated by multiple linear regression method which was developed by Taft. There is an intrinsic difference between betaine for $E_T(30)$ polarity scale and the azoderivative, which is derived from the specific hydrogen bond incurred with probe molecules and solvents. The hydrogen bonding plays a very important role for stabilization of an excited state molecule by solvents especially when a solute possesses a negative charge as with NPNO[−].

Introduction

Hydrogen-bonding interaction of excited molecules solubilized in organic solvents are closely related to those of activated complexes in organic solvents.[1~3] Many reactions failed, due to intermolecular hydrogen abstraction either from water or from organic solvents. Hydrogen bonding is, also, crucial for the formation of large biological assemblies. Understanding the dynamics and the extent of hydrogen bonding interactions observed in excited state molecules are, thus, of current interest.

4-(4-Nitrophenylazo)-1-naphthol (NPNOH) is susceptible to the hydrogen bond donor (HBD) and hydrogen bond acceptor (HBA) solvents. A hydroxy group of NPNOH has both HBD and HBA character and a nitro group locating at the other end of hydroxy group has HBA property. Since NPNOH has many hydrogen bonding sites, quantitative analysis of intermolecular hydrogen bonding in ground and excited states of NPNOH is quite complicated.

Upon irradiation, positive charge develops at the hydroxy group of NPNOH and negative charge develops at the nitro group. These charges can be dispersed throughout the conjugated aromatic system. Since the dipole moment of the charge transfer state is larger than that of the ground state, a solvent of higher polarity stabilizes the excited state to a much greater extent. The electronic transition energy (ΔE_p) in polar solvents is therfore smaller than that (ΔE_n) in nonpolar solvents for the molecules whose excited dipole moment is larger than the ground state dipole moment. When the dipole moment significantly increases in a excited state, the electronic transition energy (ΔE_p) obtained in a more polar solvent becomes small.[4~6]

As well as solvent polarity, specific interactions profoundly influence electronic transition energies. The solvent effects on electronic transition energy are determined with dielectric constant, refractive index, polarizability, hydrogen bonding interaction, long range non-bonding interactions, *etc.* Dielectric constant, refractive index, and polarizability are the major bulk physical variables that have been used to describe solvent polarity. It is, however, very difficult to describe the multitude of solvent-solute interactions and microscopic molecular interactions with bulk physical properties. Empirical solvent polarity scale replaced the theoretical expressions which were developed on the basis of the bulk physical parameters. Many empirical solvent polarity scales have been attempted. Since each solvent polarity scale has its own bias that comes from specific solvent-solute interaction, the specific interaction has to be extensively studied before applying the solvent polarity scale.

In this study, π^* scale developed by Taft and Kamlet[2,3] and $E_T(30)$ scale developed by Reichardt[1] will be used to estimate the solvent-solute interactions on electronic transitions for NPNOH, its anion NPNO[−], and O-alkylated product (NPNOR) which was synthesized by O-alkylation of NPNOH with dodecyl bromide. Since NPNOH equilibrates with NPNO[−] at both the ground state and the excited state, NPNOH shows a dynamic solvent effect. A simple transformation of NPNOH to NPNO[−] by adding small amount of a base makes these dyes useful for an investigation of solvent-solute interactions in homogeneous solvents and microheterogeneous media.

Experiments

The NPNOH (Aldrich) was recrystallized three times from dimethyl sulfoxide (DMSO), which was the solvent that could dissolve NPNOH to a reasonable amount. The NPNOH recrystallized was washed with dry ethyl ether and dried in the vacuum desiccator for one day. The ^{1}H NMR (80 MHz) and IR spectra showed characteristic functional groups of NPNOH. All the UV-visible spectroscopic measurements were done at the concentration of 1.0×10^{-5} M, which was prepared from the 1.0×10^{-3} M chloroform solution. The UV-visible absorption spectrum was obtained from a HP-diode

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Table 1. The Absorption Enrgy of NPNO⁻, NPNOH, and NP-NOR in Organic Solvents. The $E_T(30)^1$ and π^{*1} are the Empirical Solvent Polarity Parameters

| No.	Solvents	$E_T(30)$	π^*	NPNO⁻	NPNOH	NPNOR
1.	diethyl ether	34.50	0.28	—	62.99	66.20
2.	toluene	33.90	0.54	—	62.99	65.00
3.	benzene	34.30	0.59	—	62.99	64.70
4.	ethyl acetate	38.10	0.55	45.68	62.99	65.90
5.	chloroform	39.10	0.58	—	62.44	65.30
6.	acetone	42.20	0.71	44.96	62.17	65.90
7.	acetonitrile	45.60	0.75	45.25	62.44	65.90
8.	dichloromethane	40.70	0.82	43.80	62.99	64.70
9.	N,N-dimethylform-amide	43.80	0.88	43.59	60.59	64.71
10.	dimethyl sulfoxide	45.10	1.00	43.86	60.09	64.70
H1	methanol	55.40	0.60	49.14	61.64	65.90
H2	ethanol	51.90	0.54	47.19	61.64	65.60
H3	1-propanol	50.70	0.52	46.89	61.37	65.30
H4	1-butanol	50.20	0.50	46.89	60.85	65.89
H5	1-pentanol	49.10	—	46.70	61.10	65.00
H6	iso-butanol	48.60	—	47.35	61.37	65.30
H7	1-hexanol	48.80	—	46.89	61.37	64.70
H8	benzyl alcohol	50.40	0.98	45.98	59.09	64.40

array spectrophotometer (Model HP8452A).

Results and Discussion

Solvatochromic Shift. Table 1 shows visible absorption energies in kcal/mol for NPNOH, NPNO⁻, and NPNOR in various solvents. The absorption energy of NPNOH decreases as the solvent polarity increases. Due to the low solubility of NPNOH and NPNO⁻ in n-hexane and other saturated hydrocarbons, the absorption energies were not obtained. In benzene, toluene, and diethyl ether, the absorption energy is 62.99 kcal/mol, while it becomes 60.08 and 60.59 kcal/mol in DMSO and DMF, respectively. Solvent stabilization of dipolar excited state accounts for the bathochromic shift. It is quite surprising to observe high S_0 to S_1 electronic transition energy for NPNOR, which compares with that of NPNOH, since NPNOR has strong electron donating group.

The low extinction coefficient of NPNOR (40-60% lower than that of NPNOH) accounts for distortions in alkyl chain with respect to the naphthyl plane of NPNOR. The torsional angle calculated for naphthyl-O-H of NPNOH was 180° and naphthyl-O-CH₂ of NPNOR was 168°. The conjugation from the oxygen atom in an ether linkage to the nitro group can be significantly reduced due to the distortion of O-alkyl group, and the distortion would incur the low extinction coefficient and high energy absorption.

NPNO⁻ absorbs photons at the absorption maximum ranged in 43.0-49.1 kcal/mol, as shown in Table 1. It can be attributed to the good electron donating ability of hydroxide. Methanol, a strong HBD solvent, shifts the electronic transition energy of NPNO⁻ by 3.5 kcal/mol in comparison with that obtained in non-HBD solvents of comparable π^*.
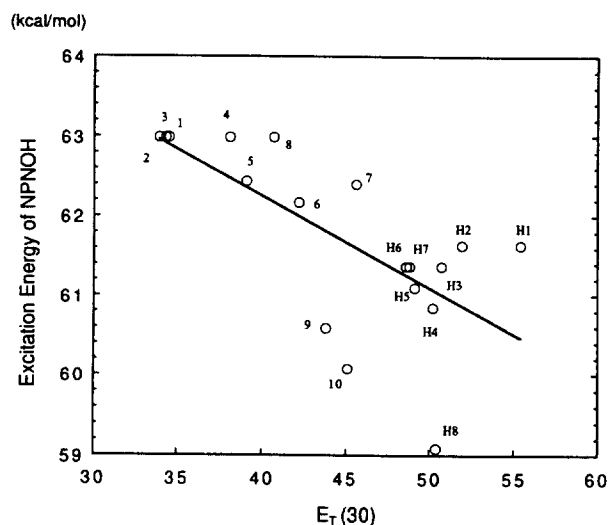
(kcal/mol)

Figure 1. Plot of Excitation Energy of NPNOH Observed in Organic Solvents *versus* $E_T(30)$.

A pronounced hypsochromic shift, 17.3 kcal/mol, was reported for a betainee when it was solubilized in methanol, which compared with that obtained in ethyl acetate.[1] Relatively small shift observed from NPNO⁻ in methanol may be caused by the hydrogen bonding interaction of nitro group of NPNO⁻.[7]

Hydrogen Bonding Interaction. The following are three important hydrogen bonding interactions available in NPNOH derivatives.[7~12]
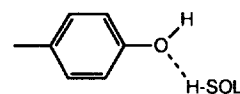
Type A Hydrogen Bonding Interaction
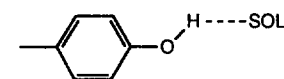
Type B Hydrogen Bonding Interaction
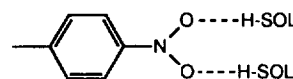
Type C Hydrogen Bonding Interaction

HBD solvents tie up to the electrons on an oxygen atom by Type A and Type C interactions which introduce positive charge on the oxygen atom. A HBA solvent binds to the hydrogen atom on a hydroxy group by Type B interaction, which introduces partially negative charge on the oxygen atom of hydroxy group. Type B and Type C interactions lower the electronic transition energy, while Type A interaction makes it higher, since Type A interaction ties up the electron available for charge transfer electronic transition.[13,14] The three types of hydrogen bonding interaction cooperatively influence the electronic transition energy of NPNOH
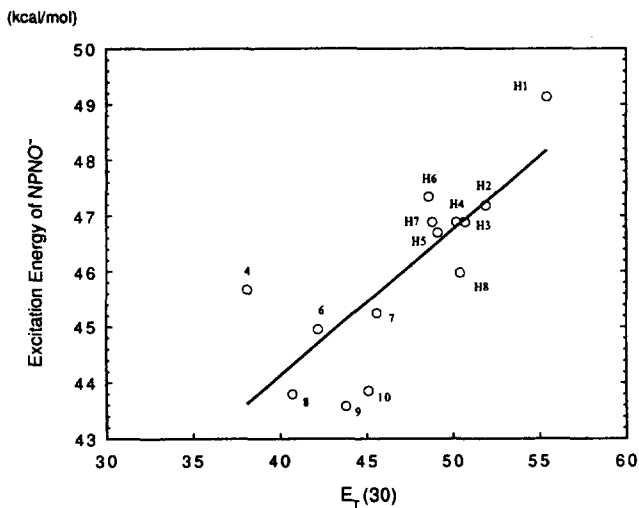
(kcal/mol)

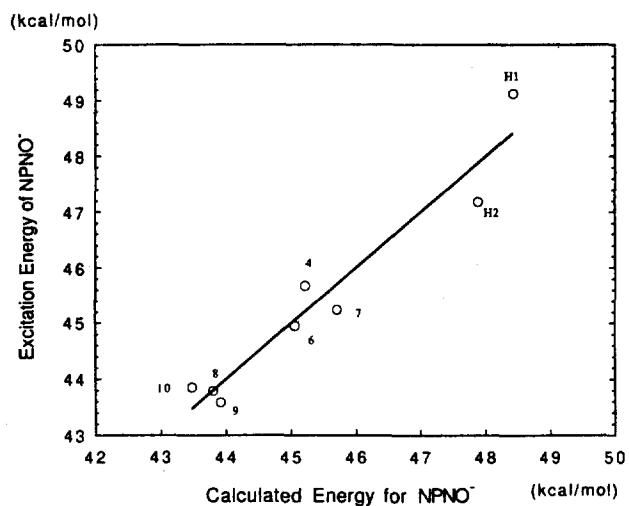**Figure 2.** Plot of Excitation Energy of NPNO⁻ Observed in Organic Solvents *versus* $E_T(30)$.

(kcal/mol)

Figure 3. Plot of Excitation Energy of NPNOH Observed in Organic Solvents *versus* Calculated Energy of NPNOH using eq. (1).

(kcal/mol)

Figure 4. Plot of Excitation Energy of NPNO⁻ Observed in Organic Solvents *versus* Calculated Energy of NPNO⁻ using eq. (1).

(kcal/mol)

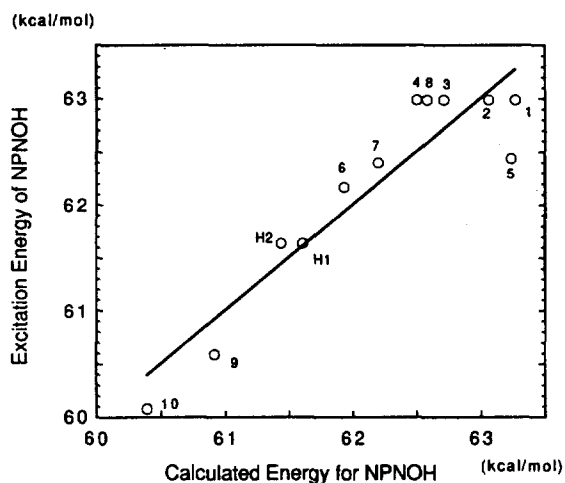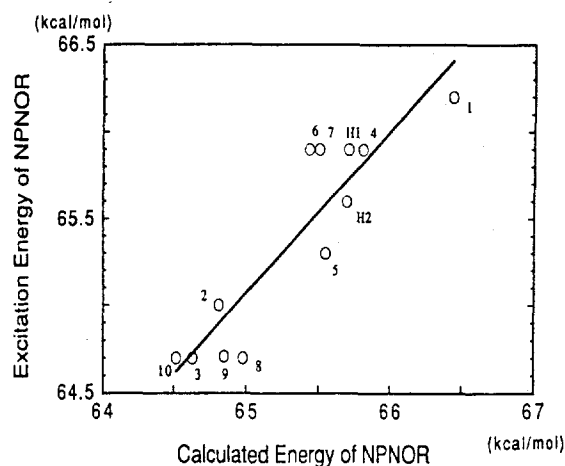**Figure 5.** Plot of Excitation Energy of NPNOR Observed in Organic Solvents *versus* Calculated Energy of NPNOR using eq. (1).

derivatives.

Figures 1 and 2 show the electronic transition energy of NPNOH and NPNO⁻ versus the $E_T(30)$ scale. The negative slope observed for the NPNOH and positive slope of NPNO⁻ indicate how solvents stabilize ground and excited state of these dyes. NPNO⁻ follows the same pattern as the betaine, which is the molecular probe used for $E_T(30)$ scale. However, the trend observed from NPNOH is opposite to that of E_T (30). There is no correlation for NPNOR. Although the solvatochromic effect is less conspicuous than in case of betaine, the NPNOH and NPNO⁻ showed solvent dependent chromic shift. The $E_T(30)$ scale is not suitable for the quantitative estimation of specific solvent-solute interaction.

Empirical Polarity Scale. The solvent acidity coefficient, α, represents hydrogen donating ability of solvents. The solvent nucleophilicity coefficient, β, is a measure of electron donating ability of solvents. The correction factor for polarizability is a function of refractive index(n) parameter, $(n^2-1)/(2n^2+1)$. The correlation factors are 1 for aro-

matic solvents, 0.5 for halogenated solvents, and 0 for others.[3] Taft and Kamlet developed a linear solvation energy relationship (LSER) for estimation of solvent polarity factors mentioned above.[15,16]

$$\Delta E = \Delta E_o + s\ (\pi^* + d\delta) + a\alpha + b\beta \tag{1}$$

Figure 3, 4, and 5 show electronic transition energy of NPNOH, NPNO⁻, and NPNOR versus the calculated electronic transition energy of these compounds through LSER. The coefficients (s, d, a and b) of the parameters (π^*, δ, α and β) listed in Table 2 were obtained by multiple linear regression using eq. (1). As shown in Table 2, and Figures 3, 4, and 5, the correlation coefficients were 0.93 for NPNOH and NPNO⁻, and 0.87 for NPNOR. These are improved from the correlation coefficients obtained from the plot of excitation energy of these compounds versus π^* itself.[17]

The **a** value of NPNO⁻ is 3.9 which compares with negative **a** value, -0.33, of NPNOH. The large **a** value of NPNO⁻

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Table 2. The Coefficients (s, d, a, and b) of the Parameters (π^*, δ, α and β) Obtained from the Multiple Linear Regressions with $\Delta E = \Delta E_o + s$ $(\pi^* + d\delta) + a\alpha + b\beta$

Coefficient	NPNO⁻	NPNOH	NPNOR
s	−3.24	−2.94	−2.27
d	−	0.11	0.38
a	3.11	−0.33	−0.06
b	−	−2.54	−
ΔE_o	47.0	65.3	67.0
correlation	0.93	0.93	0.87

Table 3. The Ratios of Coefficients (a/s, b/s, and d/s) which Represent Relative Contribution of Hydrogen Bonding and Polarizability of Solvents Compared with Solvent Polarity

Compounds	Relative ratios	
betain	a/s	1.13
	d/s	−0.02
NPNO⁻	a/s	−0.96
	b/s	0.74
NPNOH	a/s	0.11
	d/s	0.04
	b/s	0.86

indicates great sensitivity to HBD solvents. The positive **a** value could be derived from the Type A interaction with HBD solvents. Although Type C interaction influences the electronic transition energy in opposite direction, Type A interaction prevails. Since NPNO⁻ does not have a functional group for Type B interaction, Type C interaction is the one that lowers the electronic transition energy. Both Type B and C interactions can generate negative b value for NP-NOH, and the interactions may lower the electronic transition energy.[7]

It is interesting that the sign of the slopes is opposite when the electronic transition energies of NPNOH and NPNO⁻ are plotted against $E_T(30)$, whereas the s values are all negative when those were plotted against π^*. The contrast can be resolved by analyzing the specific solvent-solute interactions. The **a** and **d** values obtained from the multiple linear regression with $E_T(30)$ are 16.5 and −0.23, respectively. The multiparameter equation is given by

$$E_T(30)/(\text{kcal mol}^{-1}) = 14.6 \ (\pi^* - 0.23 \ \delta) + 16.5 \ \alpha + 30.31 \quad (2)$$

To estimate contribution of hydrogen bonding interaction and the polarizability of the solute to the solvatochromic effect, these were compared with the solvent polarity. **a/s**, **b/s** and **d/s** values for betaine, NPNOH, and NPNO⁻ were obtained, as shown in Table 3. Since **a/s** is greater than 1.0 for betaine, one would say that Type A interaction surpasses the solvent polarity. The hydrogen bonding interaction of NPNO⁻ is very strong, which results in high **a/s** value (−0.96). The negative figure means that hydrogen bonding interaction increases an electronic transition energy whereas solvent polarity lowers the energy. When electronic transition energy of NPNOH and NPNO⁻ is plotted against $E_T(30)$, solvent polarity makes

the slope negative, and hydrogen bonding interaction with HBD solvents tends to makes a positive slope, as shown in Figures 1 and 2. The negative slope shown in Figure 1 represents mainly for non-alcohols. The points that obtained in alcohols group together and show positive slope. The $E_T(30)$ scale is not considered to be suitable for the molecular probes on which hydrogen bonding interaction and solvent polarity influence against each other.

The sensitivity of NPNOH derivatives to solvent polarity falls within the range of −2.27 to −3.24, which is less than half the values that obtained for azobenzenes with amine and nitro group as substituents.[15] The contribution of hydrogen bonding interaction between solute and solvents is very large for NPNOH derivatives. Especially, for NPNO⁻, hydrogen bonding to the hydroxide makes electronic transition energy high and the contribution of hydrogen bonding is as large as that of solvent polarity. Since the charge, electron polarizability, steric effect, hydrophobicity, and hydrophilicity of probes influence the electronic transition energy of a solute, assessment of specific solute-solvent interaction should be accompanied with that of polarity. This result could be utilized to estimate characteristics of solubilization sites and molecular orientations of NPNOH derivatives in micellar media.

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