Bull. Chem. Soc. Jpn., ***69***, *2581—2584 (1996)*

Reversal in Solvatochromism: An $E_T(30)$ Switch for a New Class of Cyanine Dyes

Bijay K. Mishra,* Minati Kuanar, Amaresh Mishra, and Gopa B. Behera

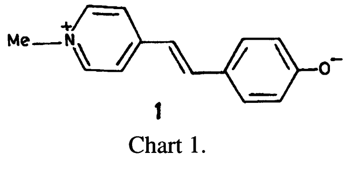
Centre of Studies in Surface Science and Technology, Department of Chemistry, Sambalpur University,
Jyoti Vihar-768019, India

(Received December 25, 1995)

This paper reports the analysis of reversal in solvatochromism of a new class of cyanine dyes by using the $E_T(30)$ scale. The point of reversion is defined as a switch that identifies the hydrogen bond donor and hydrogen bond acceptor solvents.

The effects of solvents on the shift of an electronic spectral band are coveted by the term solvatochromism. The shifting of bands is due to changes in the π–π* and n–π* transition energy because of solvation of the ground state and excited state of the probe. Hypsochromic and bathochromic shifts in the absorption spectra of the probe with increasing polarity of the solvent are termed 'negative solvatochromism' and 'positive solvatochromism' respectively.[1)] The negative solvatochromism is due to the consequence of stabilization of the ground state in increasing solvent polarity, while stabilization of excited state with increasing polarity results in positive solvatochromism. Solvatochromic dyes generally have steady positive or negative solvatochromism.

Some dyes have been reported to have reversed the sign of the solvatochromism, which has created a desire to unveil the chemistry behind it. Since the original description of the stilbene betaine dye (**1**) by Brooker et al.,[2)] the solvatochromism of this dye has been the subject of intensive research (Chart 1). Benson et al.[3)] and Botrel et al.[4)] have rationalized the solvatochromic reversal of **1** by semiempirical molecular orbital calculations, which has been confirmed by Jacques[5)] using spectroscopic measurement in mixed solvents. From the transition energy calculations of **1**, Luzhkov and Warshel[6)] have reported negative solvatochromism, but Morley[7)] has shown a positive solvatochromism for it by the CNDOVS method. Catalan et al.[8)] denied the reversal of solvatochromism of **1** outright and criticized the proposal of Botrel et al. and Jacques. They explained the observations as due to splitting of effective levels by vibrational states. Niedbalska and Gruda[9)] have also opposed the idea of reversal solvatochromism and have proposed aggregation phenomena in solution to explain the results. However, da Silva et al.[10)] have made a theoretical approach to rationalize and predict the solvatochromic behavior of vinylogous γ-pyridones and have supported the reverse solvatochromism.



1

Chart 1.

In this paper we have reported a new group of dyes (Chart 2) with reverse solvatochromism.

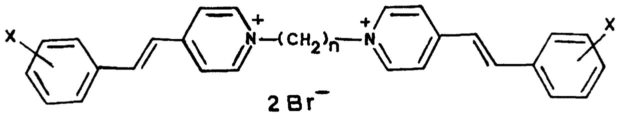
Experimental

Materials. The bischromophoric dyes (**2**—**7**) were prepared following the procedure described in Ref. 11. After recrystallization from ethanol the compounds were kept in the dark. The melting points were recorded in a sulfuric acid bath and were uncorrected. The analytical data of the compounds are given in Table 1. All the solvents were of the high purity grade available from SRL and MERCK, Bombay. The purity of the solvents were further checked from their UV spectra. Triple distilled water was used as the solvent.

Methods. The absorption spectra were measured by using a Shimadzu 160-A UV-vis. spectrophotometer and a matched pair of quartz cells of 1 cm thickness. The sample temperature was maintained at 300±0.1 K by an MK-70 cryostat. Due to poor solubility in some solvents concentrations of the compounds were not maintained. The optical density values were maintained at 1.0—1.5. The multiple regression analysis was made by using SAS package.

Results and Discussion

To study solvatochromism, two sets of solvents, namely hydrogen bond acceptor (HBA)[12)] solvents like acetone, *N*,*N*-dimethylformamide, dimethyl sulfoxide, acetonitrile, and pyridine, and amphiprotic[12)] solvents like water, methanol,



	n	X		n	X
2 :	2	p-OH	5 :	3	o-OH
3 :	3	p-OH	6 :	4	o-OH
4 :	4	p-OH	7 :	6	o-OH

Chart 2.

Table 1. Physical Constants and Analytical Data of Compounds **2**—**7**

Compd No.	*n*	X	Mp °C	Yield %	%C (Calcd)	%H (Calcd)	%Br (Calcd)
2	2	*p*-OH	220 (d)	80	57.8 (57.5)	4.72 (4.79)	27.0 (27.3)
3	3	*p*-OH	240 (d)	75	58.4 (58.5)	4.92 (5.01)	26.5 (26.7)
4	4	*p*-OH	245 (d)	75	59.3 (59.4)	5.20 (5.22)	26.0 (26.1)
5	3	*o*-OH	240	50	58.2 (58.5)	4.89 (5.01)	26.1 (26.7)
6	4	*o*-OH	271	68	59.1 (59.4)	5.17 (5.22)	25.7 (26.1)
7	6	*o*-OH	280	72	60.0 (60.3)	5.42 (5.43)	25.2 (25.5)

ethanol, 2-propanol, 1-butanol, isobutanol, and *t*-butanol have been selected. HBA solvents have one or more acceptor groups (bases) and no donor groups, while amphiprotic solvents have both donor (HBD) and acceptor groups.[13] The $\nu_{\max}$ values corresponding to the longest wavelength of the absorption bands of all the cyanine dyes (**2**—**7**) in all the above solvents are reported in Table 2. With a view to identify the light-absorbing species, all the compounds (**2**—**7**) were treated with alkali in various solvents. The absorption spectra of the resultant solutions were found to be red shifted to the extent of ($\Delta\nu_{\max}$) 4292.8 to 8631.7 cm^{-1}. The bathochromic shift may be ascribed to the betaine or neutral merocyanine species. Hence, the $\nu_{\max}$ values under study are due to the cationic dyes (**2** to **7**). These $\nu_{\max}$ values have been correlated with various solvent parameters and the correlation coefficients (R^2) have been found to be less than 0.85 (R^2: Dimorth and Richardt's $E_T(30)$ scale[14]= 0.17—0.39; Abboud, Taft, and Kamlet's π^* scale[15]= 0.59—0.76; Kosower's Z scale[16]= 0.15—0.37; Dielectric constants,[17] ε = 0.64—0.83).

The analysis of data (Table 2) reveals that with increases in the methylene chain in the spacer the $\nu_{\max}$ increases for both para and ortho series of compounds. The difference in $\nu_{\max}$ due to increase in the spacer length from C_2 to C_3 system is 857.7±150.4 cm^{-1}, and from C_3 to C_4 system is 270.3±67.3 cm^{-1} for para series of compounds. However, for the ortho series of compounds the change is 364.5±173.2 cm^{-1} (C_3 to C_4) and 151.0±98.1 cm^{-1} (C_4 to C_6). The bischromophoric dyes [R–$(CH_2)_n$–R] have two similar chromophoric groups separated by a nonabsorbing flexible chain as the spacer. One monochromophoric unit (R = substituent chromophore) with the spacer [R–$(CH_2)_n$–] acts as a substituent at the pyridine nitrogen of the other chromophoric group (R = parent chromophore). The inductive effect of the substituent chromophore on the parent chromophore decreases with increasing chain length of the spacer. This observation is in conformity with the σ_I values of Br–$(CH_2)_n$– (C_1 = 0.20, C_2 = 0.05, C_3 = 0.02).[18]

Further the $\nu_{\max}$ values for the ortho series of compounds are found to be higher than that of the para series of compounds, which may be attributed to the steric effect of the ortho hydroxy group.

Reversal Solvatochromism: Among the solvatochromic solvent-polarity parameters, $E_T(30)$, proposed by Richardt and Dimorth et al. is based on the π–π* absorption band of 4-(2,4,6-triphenylpyridinium)-2,6-diphenyl phenoxide dye. This parameter has found wide application in reaction rates,[14] dissociation constants,[19] and retention parameters in liquid chromatography.[20] Here, we have used the $E_T(30)$ scale to study the absorption behavior of the compounds.

The $\nu_{\max}$ values of the dyes in various solvents are plotted against the $E_T(30)$ scale and are shown in Figs. 1 and 2. Inspection of the figures shows that all the compounds have positive solvatochromism in solvents of low $E_T(30)$ values but undergo a reversion in the solvents at higher $E_T(30)$ values i.e. a transition in the solvatochromic effect is noted. The decreasing arm (positive solvatochromism) in the plot is due

Table 2. $\nu_{\max}$ Values of Some Bischromophoric Dyes (**2**—**7**) in Various Solvents

	$\nu_{\max}/\mathrm{cm}^{-1}$					
Solvents	**2**	**3**	**4**	**5**	**6**	**7**
Water	25220.7	26246.7	26420.1	26350.5	26809.7	27027.0
Methanol	24038.5	24721.9	25062.7	25125.6	25608.2	25740.0
Ethanol	23696.7	24509.8	24813.9	24875.6	25316.5	25380.7
2-Propanol	23310.0	24271.8	24600.2	24449.9	25094.1	25284.5
1-Butanol	23310.0	24213.1	24570.0	24600.2	25094.2	25188.9
Isobutanol	23255.8	24390.2	24691.4	24752.5	25188.9	25284.4
t-Butanol	23089.5	24875.6	25188.9	25252.5	25380.7	25575.4
Acetone	24539.9	25284.4	25542.8	25740.0	25906.7	26143.8
Acetonitrile	24691.4	25413.0	25740.0	26178.0	26595.7	26881.7
DMF	24213.1	25000.0	25252.5	25641.0	25673.9	25974.0
DMSO	24271.8	25062.7	25220.7	25608.2	25839.8	25839.8
Pyridine	23640.7	24301.3	24630.5	24844.7	25284.4	25284.4

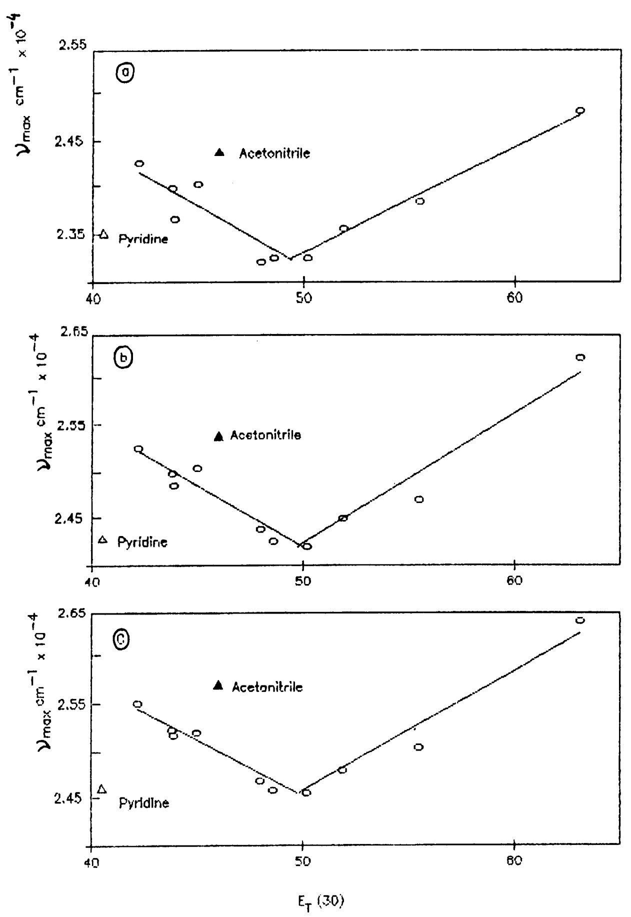
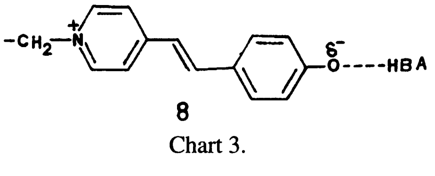


Fig. 1. Plot of ν_{max} of the bis chromophoric dyes vs. $E_T(30)$ (a): **2**, (b): **3**, (c): **4**.

to HBA and a few amphiprotic solvents while the increasing arm (negative solvatochromism) is due to amphiprotic solvents only.

The HBA solvents form hydrogen bonds with the phenolic hydrogen of the dye as a result of which the molecule becomes less polar (**8**) (Chart 3).

Therefore with increasing polarity of the solvent the excited Franck Condon state is stabilized increasingly, causing a bathochromic shift. The amphiprotic solvents have both HBA and HBD characteristics. The ground state of the dye is increasingly stabilized by decreasing polarity due to the HBA characteristic of the solvent, while a reverse situation occurs with the HBD characteristic of the solvents. It is noticed from the plots (Figs. 1 and 2) that some of the amphiprotic solvents occur clearly in the decreasing arm with compounds of higher spacer groups (C_4 and C_6) but with dyes of the lower spacer groups (C_2 and C_3) these solvents occur in the twilight zone of the plot. With the increasing hydrophobic nature of the alkyl chain the alcohols behave more as acceptors than as donors. Hence alcohols like 2-propanol, isobutanol, and tert butanol are found to be in decreasing arm of the plot. The HBA parameters, β[21] of these solvents are found to be more than the corresponding HBD parameter, α.[21] However, no good correlation is obtained by adopting multiple regression analysis of ν_{max} with $E_T(30)$, α and β values ($R^2 = 0.74$).



8

Chart 3.

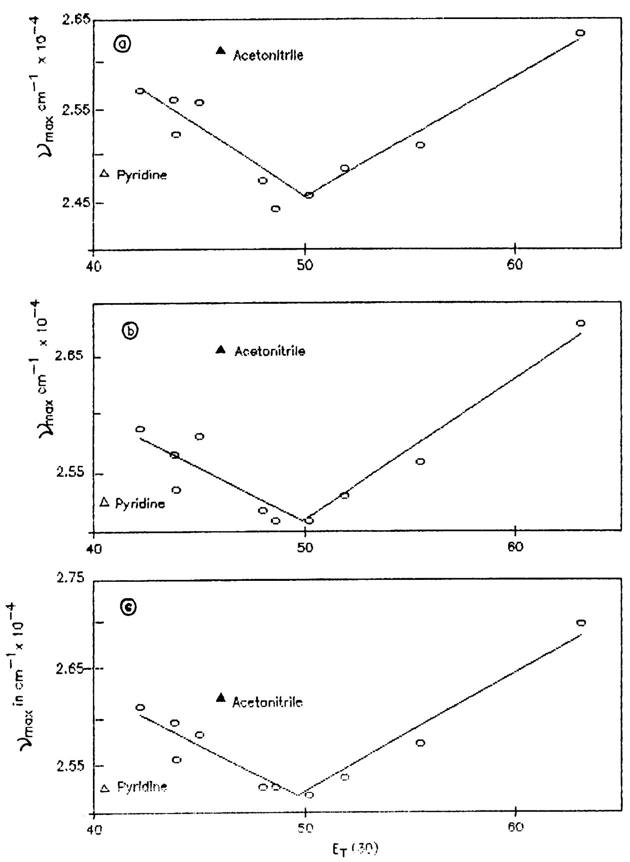


Fig. 2. Plot of ν_{max} of the bis chromophoric dyes vs. $E_T(30)$ (a): **5**, (b): **6**, (c): **7**.

The reversion in the solvatochromism is found to occur at almost a constant $E_T(30)$ value, 49.8, which is independent of the nature of the spacer group and the position of hydroxyl group in the dye. This $E_T(30)$ value behaves as a switch, below and above which the ν_{max} values increase. The solvents behave as HBD and HBA to the right and left of the switch respectively. da Silva et al.[10] have observed a reversal in the solvents like dioxane and THF for a merocyanine dye with the switch occurring at $E_T(30)$ value of around 37.0.

The $E_T(30)$ and ν_{max} values of the solvents of negative solvatochromism part (increasing arm) has been subjected to multiple regression analysis by using Eq. 1. The results of the multiple regression are presented in Table 3. The analysis of the results shows that with change in spacer there is almost no change in the sensitivity (a) of $E_T(30)$ towards the ν_{max} values.

$$\nu_{max} = \nu^{\circ}_{max} + aE_T(30) \qquad (1)$$

The multiple regression of the ν_{max} and $E_T(30)$ values of the dyes in the solvents constituting the decreasing arm by using Eq. 1 is reported in Table 4.

Table 3. The Results of Multiple Regression Analysis of $\nu_{\max}$ and $E_T(30)$ of the Solvents Constituting the Increasing Arm

Compound	$\nu^{\circ}_{\max}/\mathrm{cm}^{-1}$	*a*	$R^{2\ a)}$	SD$^{a)}$
2	16830.7	131.9±8.4	0.98	113.3
3	17951.1	128.1±21.2	0.90	269.2
4	18100.0	129.8±16.9	0.95	195.3
5	18079.0	130.1±9.8	0.98	113.0
6	19005.0	122.1±13.4	0.97	153.9
7	18835.0	127.4±17.3	0.95	200.0

a) R^2: Correlation coefficient, SD: Standard deviation.

Table 4. The Results of Multiple Regression Analysis of $\nu_{\max}$ and $E_T(30)$ of the Solvents Constituting the Decreasing Arm

Compound	$\nu^{\circ}_{\max}/\mathrm{cm}^{-1}$	*a*	$R^{2\ a)}$	SD$^{a)}$
2	31286.0	−162.5±8.4	0.82	250.0
3	31119.0	−139.1±17.2	0.92	125.0
4	30806.6	−126.1±11.9	0.96	86.6
5	33991.8	−143.4±40.4	0.85	228.5
6	30637.8	−113.2±36.9	0.70	208.9
7	31026.0	−117.5±21.6	0.86	157.7

a) R^2: Correlation coefficient, SD: Standard deviation.

The change in sensitivity is more in the case of the ortho series than for the para series of compounds. While measuring the p*K* values of ortho and para hydroxy *N*-benzylidene 2-aminobenzothiazole, Behera et al. have also observed a similar trend.[22] The sensitivity of $E_T(30)$ values towards $\nu_{\max}$ values in case of solvents in the decreasing arm, however, changes with the nature of the spacer.

In all the plots, pyridine and acetonitrile are found to have negative and positive deviations, respectively, from the normal trend in the decreasing arm. Other solvents of this group form hydrogen bonds with their C=O, S=O or lone pair of oxygen, but acetonitrile and pyridine involve the C=N pi orbital[23] and the lone pair of nitrogen respectively. This difference in characteristics of the solvent molecules may be responsible for the deviation.

In conclusion, it can be said that these dyes form a new class of cyanines with an $E_T(30)$ switch.

The authors thank the Department of Science and Technology, New Delhi for funding.

References

1) C. Reichardt, *Chem. Rev.*, **94**, 2319 (1994).

2) a) L. G. S. Brooker, C. H. Keyes, R. H. Sprague, R. H. Van Dyke, E. Van Lare, G. Van Zandt, F. L. White, H. W. J. Cressman, and S. G. Dent, *J. Am. Chem. Soc.*, **73**, 5332 (1951); b) L. G. S. Brooker, C. H. Keyes, and D. H. Heseltine, *J. Am. Chem. Soc.*, **73**, 5350 (1951).

3) H. G. Benson and J. N. Murrell, *J. Chem. Soc., Faraday Trans. 2*, **68**, 137 (1972).

4) A. Botrel, A. Le Beuze, P. Jacques, and H. Strub, *J. Chem. Soc., Faraday Trans. 2*, **80**, 1235 (1984).

5) P. Jacques, *J. Phys. Chem.*, **90**, 5535 (1986).

6) V. Luzhkov and A. Warshel, *J. Am. Chem. Soc.*, **113**, 4491 (1991).

7) J. O. Morley, *J. Mol. Struct.* (*Theochem*), **304**, 191 (1994).

8) J. Catalan, E. Mena, W. Metermans, and J. Elguro, *J. Phys. Chem.*, **96**, 3615 (1992).

9) M. Niedbalska and I. Gruda, *Can. J. Chem.*, **68**, 691 (1990).

10) L. da Silva, C. Machado, and M. C. Rezende, *J. Chem. Soc., Perkin Trans. 2*, **1995**, 483.

11) J. K. Mishra, P. K. Behera, S. K. Parida, and B. K. Mishra, *Indian J. Chem., Sect. B*, **31B**, 118 (1992).

12) M. J. Kamlet, J. L. M. Abboud, and R. W. Taft, "Progresses in Physical Organic Chemistry," ed by R. W. Taft, John Wiley and Sons, New York (1981), Vol. 13, p. 485.

13) Pimental and McClellan, "The Hydrogen Bond," Freeman, San Fransisco (1960).

14) a) K. Dimorth, C. Reichardt, T. Siepmann, and F. Bohlmann, *Liebigs Ann. Chem.*, **661**, 1 (1963); b) C. Reichardt, "Solvents and Solvent Effects in Organic Chemistry," 2nd ed, VCH, Weinheim (1988).

15) M. J. Kamlet, J. L. M. Abboud, and R. W. Taft, *J. Am. Chem. Soc.*, **103**, 1080 (1981).

16) E. M. Kosower, *J. Am. Chem. Soc.*, **80**, 5253 (1958).

17) J. A. Riddick and W. B. Bunger, in "Organic Solvents," Wiley Interscience, New York (1970).

18) M. Charton, "Progress in Physical Organic Chemistry," ed by R. W. Taft, John Wiley and Sons, New York (1981), Vol. 13, p. 119.

19) a) E. Casassas, G. Fonrodona, and A. de Jhan, *J. Solution Chem.*, **21**, 147 (1992); b) E. Bosch, C. Rafols, and M. Roses, *Anal. Chem.*, **62**, 102 (1990).

20) a) B. P. Johnson, M. G. Khalei, and J. G. Dorsey, *Anal. Chem.*, **58**, 2354 (1986); b) W. J. Cheong and P. W. Carr, *Anal. Chem.*, **61**, 1524 (1989).

21) M. Kamlet, J. Abboud, and R. W. Taft, *J. Am. Chem. Soc.*, **99**, 6027 (1977).

22) P. K. Mishra, B. K. Mishra, and G. B. Behera, *Indian J. Chem., Sect. A*, **27A**, 889 (1988).

23) S. N. Vinogradov and R. H. Linnel, in "Hydrogen Bonding," Van Nostrand Reinhold Company, New York (1971), p. 150.