1 equiv of hydrogen was absorbed. After filtration and washing of the solid with EtOH, evaporation of the combined filtrates gave **7b** (or **9b**) in 80% yield.

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Registry No. **1a**, 96852-88-9; **1b**, 7284-07-3; **1c**, 19877-09-9; **1d**, 19877-13-5; **1e**, 89755-67-9; **1f**, 17225-57-9; **1g**, 74152-53-7; **1h**, 118226-52-1; **2**, 2904-57-6; **3**, 873-67-6; **4**, 51983-62-1; **5a**, 118226-53-2; **5b**, 118226-54-3; **5b** (xanthate), 118246-93-8; **5c**, 118226-55-4; **5d**, 118332-52-8; **5e**, 118226-56-5; **5f**, 118226-57-6; **5g**, 118226-58-7; **5h**, 118226-59-8; **6a**, 118332-53-9; **6b**, 118332-54-0; **6c**, 118332-55-1; **6d**, 118332-56-2; **6e**, 118332-57-3; **6f**, 118332-58-4; **6g**, 118332-59-5; **6h**, 118332-60-8; **7b**, 118226-60-1; **7d**, 118332-61-9; **8b**, 118332-62-0; **8d**, 118332-63-1; **9b**, 118226-61-2; **9d**, 118226-62-3; **10b**, 118332-64-2; **10d**, 118374-38-2; PhC(=NOH)Cl, 698-16-8; EtOCOC(=NOH)Cl, 14337-43-0.

Supplementary Material Available: Tables of positional parameters, anisotropic thermal parameters for non-hydrogen atoms, bond distances and angles for adduct **5b**, ^{1}H NMR chemical shifts and coupling constants for adducts **5–10**, Eu(fod)$_3$-induced shifts in ^{1}H NMR spectra of **5b** and **6b**, NOE difference data on adducts **5d** and **6d**, and elemental analyses of adducts **5–10** (10 pages). Ordering information is given on any current masthead page.

Solvatochromic Studies of Novel Azo Merocyanine Dyes. The π^*_{azo} Scale of Solvent Polarity[†]

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Six novel azo merocyanine dyes (1–6) have been synthesized and their UV–vis spectra recorded in 29 solvents. These dyes exhibit positive solvatochromism (bathochromic shift) with increasing solvent polarity, i.e., $\mu_g < \mu_e$. The spectral data obtained were used as *primary data* in a parameter optimization program (Teetor Totter method) to arrive at averaged results in 19 select solvents, which led to the formulation of a new solvent polarity scale, the π^*_{azo} scale. Subsequently, π^*_{azo} values of ten secondary solvents were determined. The π^*_{azo} values thus obtained were correlated with 20 solvent polarity scales and the spectral data of 59 indicator solutes. The correlation coefficients were found to be in the region 0.900 to 0.995, indicating the overall validity of the procedure adopted in the formulation of the π^*_{azo} scale. The correlations of the π^*_{azo} scale with solvent polarity scales such as Brooker's χ_R scale, based on compounds that are structurally similar to the azo dyes, were found to be better than the correlations of Kamlet and Taft's π^* scale with the above polarity scales. The spectral data of the azo merocyanines 1–6 were also used as *secondary data* with Kamlet's π^* and α parameters as well as with 20 other polarity scales. Of the various scales considered, the π^* scale and Brooker's χ_R scale were found to correlate best with the spectral data of 1–6. The π^* value of a new solvent, *N,N'*-dimethyl-*N,N'*-trimethyleneurea (DMPU), has been determined as 1.08 (π^*_{azo} = 0.99). Various structure–spectral property relationships among the azo merocyanine dyes are considered. Based on the correlations observed in the present work, it is suggested that a "Universal primary set of solutes", comprising representative compounds from important classes of compounds, be chosen to formulate a π^*_{U} (Pi Star Universal) scale. Alternatively, though less desirably, a dozen diversified π^*_{X} scales (X representing various families of compounds) could be designed.

Introduction

Solvent as a medium for chemical and physical processes has always played a very important role in chemistry. Interest in describing solvent properties has focused mainly on the polarity aspect, a term that has not been defined precisely. In a broader sense, solvent polarity relates to the overall solvating capability of a solvent.[1,2] Numerous reports on solvent polarity scales have appeared in the literature in the past 30 years.[1–6] These scales have been designed on single and multiple parameter approaches.

The scales based on the single parameter approach include Dimroth and Reichardt's E_T,[4a] Brooker's χ_R,[4b] Drougard and Decroocq's log k_2,[4c] Walther's ϵ_K,[4d] Knauer and Napier's $\mathcal{A}_n$,[4e] Allerhand and Schleyer's G,[4f] Brownstein's S,[4g] Kosower's Z,[4h] Winstein and Grunwald's Y,[4i] Berson, Hamlet, and Mueller's Ω,[4j] Dong and Winnick's *Py*,[4k] and Dubois and Bienvenüe's ϕ scale.[4l] These scales, being based on spectral data of a single indicator dye, are

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[†] Studies of Azo and Azoxy Dyestuffs. 19. For 18, see: Buncel, E.; Onyido, I. *Can. J. Chem.* **1986**, *64*, 2115.

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of limited value when hydrogen-bonding interactions become dominant.

The scales based on the multiparameter approach include Koppel and Palm's Y and P,[5a] Krygowski and Fawcett's E_T and DN,[5b] Dougherty's IP and EA,[5c] and Kamlet, Abboud, and Taft's π^*, α, and β parameters.[5d,6] These scales invoke more than one parameter in quantifying solvent effects since the empirical polarity scales based on a single parameter approach do not account for various measurements, e.g., kinetic, spectroscopic, etc., involving diverse solute–solvent interactions. Among the above scales, the π^* scale stands out distinctly as its design is based on the averaged spectral behavior of a number of solutes, rather than on the spectral data of any single compound. This scale has received wide attention and its significance can be measured by the controversy generated by it.[7a–c]

Thus Kamlet, Abboud, Taft, and later, Abraham, have approached the complexity of solvent properties by using a novel method.[5d,6] They incorporated specific and nonspecific solute–solvent interactions in their approach, referred to as the Solvatochromic Comparison Method (SCM). They devised three scales to describe the essential properties of a solvent: a β scale of solvent Hydrogen Bond Acceptor (HBA) basicity; an α scale of solvent Hydrogen Bond Donor (HBD) acidity; and a π^* scale of solvent dipolarity/polarizability (SPP).

The classification of solvents employed in their study was based on the hydrogen-bonding capacities of solvents. Solvents such as benzene and hexane, which do not partake in hydrogen bonding, are grouped as Non Hydrogen Bonding (NHB) solvents. Solvents (containing heteroatoms) such as anisole, 1,4-dioxane, and pyridine, which participate in hydrogen bonding with a hydrogen-bond donor solute (e.g. aniline), are assembled together as Hydrogen Bond Acceptor (HBA) solvents. Solvents like alcohols, which play dual roles, i.e. as Hydrogen Bond Donors and Hydrogen Bond Acceptors, are classified as Amphiprotic Solvents (HBD-HBA).

The π^* scale together with an α scale and β scale is predicted to rationalize medium effects on various types of spectral and chemical properties through a general equation of the form,

$$\mathrm{XYZ} = \mathrm{XYZ}_0 + s\pi^* + a\alpha + b\beta \qquad (1)$$

XYZ in eq 1 may represent a reaction rate or equilibrium constant or a position or intensity of a spectral absorption; s, a, and b are measures of the susceptibility of XYZ to changing solvent polarity/polarizability, HBD acidity, and HBA basicity, respectively.

The π^* scale has been correlated by Kamlet et al. with several phenomena involving solute–solvent interactions,[8a] based on which the authors have stated that no new scales be introduced into the literature unless they show real and obvious advantages over the existing scales.[8b] Nevertheless, the basic tenets of their approach must be reexamined.

The strategy used by Kamlet et al. in the formulation of the π^* scale focuses on the averaged spectral behavior of a set of primary solutes in order to exclude any spectral anomaly arising from choosing a single solute. The primary solutes used in the design of the π^* scale are 4-nitroanisole, *N*,*N*-diethyl-3-nitroaniline, 4-methoxy-β-nitrostyrene, 1-ethyl-4-nitrobenzene, *N*-methyl-2-nitro-*p*-toluidine, *N*,*N*-diethyl-4-nitroaniline, and 4-(dimethylamino)benzophenone. The fact that six of the seven primary solutes are nitroaromatics raises questions regarding the generality of the π^* scale. Kamlet et al. recognized this possible deficiency by stating "Finally, since **1**–**6** were all nitroaromatics, 4-dimethylaminobenzophenone was included to ensure that we did not unwittingly incorporate into the π^* scale any solvent effects which were specific to the nitro group. In retrospect, we might properly have chosen a more representative variety of primary indicator types but, after reviewing all the correlations, we are satisfied that any other reasonable set of primary indicators would have led to very similar solvent π^* values to those reported here".[6]

Though a decade has passed since the introduction of the π^* scale, there have not been any reported attempts to formulate an alternative π^* scale on the basis of a different set of solutes. A solvatochromic examination of another set of solutes on the same or similar lines as the π^* scale would be a worthwhile endeavor as it could substantiate the validity of the design of the π^* scale and shed light on its generality. Furthermore, some authors[7a–g] have pointed out weaknesses in the design of the β scale and the overall solvatochromic comparison method of Kamlet et al.[6]

Our earlier work with azo dyes[9a] suggested that these could be suitable as a new set of primary solutes for solvatochromic studies. The azo dyes and pigments form the largest group of all the synthetic colorants.[10–12] Aromatic and particularly heteroaromatic azo dyes are gaining importance due to their photoimaging characteristics[13,14] and nonlinear optical properties.[15,16] However, surprisingly,

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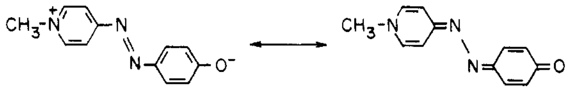
Table I. Electronic Spectral Data of Azo Merocyanine Dyes 1–6 in Various Solvents

			ν_{max}, 10^3 cm^{-1}					
no.[a]	code[b]	solvent	1	2	3	4	5	6
Select Solvent Set								
nonchlorinated aliphatics solvents								
1	0	hexanes	20.73	19.46	22.16	20.89	21.76	21.55
2	1	cyclohexane	20.49	19.36	21.89	20.69	21.62	21.62
3	4	ether	19.97	18.77	21.78	20.48	21.70	21.31
4	5	1,4-dioxane	19.75	18.67	21.22	20.26	21.43	21.01
5	7	ethyl acetate	19.52	18.45	21.40	20.23	21.29	21.04
6	8	monoglyme	19.29	18.22	21.28	20.05	21.15	21.10
7	10	methyl acetate	19.53	18.46	21.39	20.18	20.71	21.06
8	18	dimethylacetamide	18.42	17.41	20.66	19.50	20.56	20.52
9	19	dimethylformamide	18.46	17.43	20.59	19.58	20.53	20.48
10	20	dimethyl sulfoxide	18.23	17.24	20.34	19.31	20.24	20.37
11	14	2-butanone	18.63	18.14	21.06	19.92	20.87	20.87
12	17	acetone	19.26	18.09	21.04	19.97	20.93	21.05
aromatic solvents								
1	2	toluene	19.78	18.71	21.28	20.15	21.19	20.92
2	3	benzene	19.73	18.70	21.24	20.15	21.15	20.89
3	6	chlorobenzene	19.28	18.33	20.92	19.87	20.94	20.71
4	12	pyridine	18.84	17.84	20.61	19.53	20.39	20.59
5	15	nitrobenzene	18.50	17.71	20.39	19.38	20.33	20.41
6	16	benzonitrile	18.67	17.81	20.53	19.53	20.49	20.58
chlorinated aliphatic solvents								
1	10a	1,2-dichloroethane	19.08	18.12	20.80	19.79	20.97	20.71
Secondary Solvent Set								
chlorinated aliphatic solvents								
1	9	chloroform	19.29	18.46	20.78	19.94	20.71	20.58
2	13	dichloromethane	19.14	18.27	20.87	19.86	20.71	20.75
other solvents								
1	11	HMPA	18.41	17.40	20.64	19.43	20.37	20.83
2	21	acetonitrile	18.78	17.99	20.90	19.93	20.84	20.85
3	22	nitromethane	18.69	17.88	20.76	19.87	20.71	20.75
4	26	water	18.24	17.92	19.65			
5	27	DMPU	18.27	17.27	20.44	19.26	20.37	20.27
alcohol solvents								
1	23	1-propanol	18.18	17.96	20.31	19.80	20.79	20.20
2	24	ethanol	18.18	17.99	20.29	19.72	20.64	20.30
3	25	methanol	18.41	17.91	20.24	19.58	20.62	20.17

[a] The numbers indicate the number of solvents in a given set. [b] Solvent numbering based on present work.

one finds that azo dyes have received scant attention in the field of solvatochromic studies and in the design of polarity scales.

Past studies of azo and azoxy dyestuffs from this laboratory have focused on the acid-catalyzed Wallach rearrangement of azoxybenzenes and related compounds. In an extension of the Wallach rearrangement studies into the (phenylazoxy)pyridine series,[9b–e] the product obtained from the acid-catalyzed rearrangement, 4-[(4′-hydroxyphenyl)azo]-*N*-methylpyridine, bearing an electron pair donor at one terminus and at the other an electron pair acceptor, was expected to show significant solvatochromic behavior based on the extended conjugation between the two termini:



In fact, some preliminary results on the solvatochromic behavior of this compound in pyridine–water mixtures were reported by Hünig in 1965.[18] We have now synthesized a series of azo merocyanine dyes encompassing the structure of the Wallach rearrangement product in order to evaluate (a) the solvatochromic properties of these azo dyes and (b) formulate a new scale, the π^*_{azo} scale, based on the averaged spectral data of these dyes and comparing it with existing polarity scales, particularly with the π^* scale.

Results and Discussion

1. Suitability of Azo Merocyanines as Solvatochromic Indicators. A set of six azo merocyanine dyes, **1**–**6**, referred to as the primary indicator set, was used in the formulation of the π^*_{azo} scale. The dyes **1**–**6** are the following: *N*-methyl-4-pyridone 1,4-benzoquinone azine (**1**), *N*-methyl-4-pyridone (3,5-diphenyl)-1,4-benzoquinone azine (**2**), *N*-methylbenzothiazol-2-one 1,4-benzoquinone azine (**3**), *N*-methylbenzothiazol-2-one (3,5-diphenyl)-1,4-benzoquinone azine (**4**), *N*-methylbenzothiazol-2-one 1,4-naphthoquinone azine (**5**), and *N*-methylbenzothiazol-2-one 1,2-naphthoquinone azine (**6**).[17] Pertinent spectral data are given in Table I.

The suitability of the azo merocyanines **1**–**6** as primary indicator solutes is based on the following factors:

(i) These dyes were considered to be least influenced by type-B hydrogen-bonding effects in HBA solvents, allowing their inclusion in the select solvent set. Type-A hydrogen bonding relates to the hydrogen bonding arising from solvent proton donor–solute proton acceptor, whereas in

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(17) The dyes **1**–**6** can be formulated either as the dipolar zwitterionic structures or in the non-charge-separated quinoidal forms. The latter probably give a better description of the ground states of these molecules, while the dipolar structure better represent the excited states, since the azo merocyanine dyes are positively solvatochromic with $\mu_g < \mu_e$. However, for the sake of consistency, throughout this paper the structures of **1**–**6** are generally given in the dipolar form.

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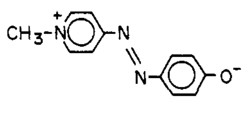
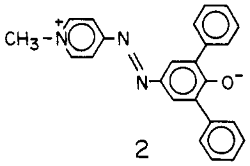
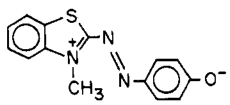


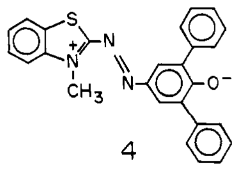
1



2



3



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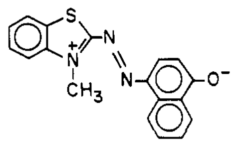
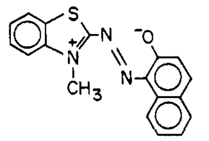


5



6

type-B hydrogen bonding the roles are reversed.

(ii) The positions of frequency maxima of the lowest energy bands for the n → π^* or $\pi \rightarrow \pi^*$ transitions are in the region 440–590 nm, far away from the cut-off points of a maximum number of solvents.

(iii) The $\nu_{\max}$ values in non-HBD solvents show linear regressions with good correlations. The following linear regressions were obtained when $\nu(\mathrm{i})_{\max}$, where i = **1** to **6** except **2**, was correlated with $\nu(\mathbf{2})_{\max}$ in non-HBD and HBA solvents, where r denotes the correlation coefficient and σ the standard deviation.

$$\nu(\mathbf{1})_{\max} = 1.12\nu(\mathbf{2})_{\max} - 1.32 \qquad n = 19, \quad r = 0.977, \qquad \sigma = 0.154 \tag{2}$$

$$\nu(\mathbf{3})_{\max} = 0.778\nu(\mathbf{2})_{\max} + 6.87 \qquad n = 19, \quad r = 0.933, \qquad \sigma = 0.190 \tag{3}$$

$$\nu(\mathbf{4})_{\max} = 0.689\nu(\mathbf{2})_{\max} + 7.40 \qquad n = 19, \quad r = 0.989, \qquad \sigma = 0.128 \tag{4}$$

$$\nu(\mathbf{5})_{\max} = 0.695\nu(\mathbf{2})_{\max} + 8.28 \qquad n = 19, \quad r = 0.907, \qquad \sigma = 0.203 \tag{5}$$

$$\nu(\mathbf{6})_{\max} = 0.684\nu(\mathbf{2})_{\max} + 6.45 \qquad n = 19, \quad r = 0.913, \qquad \sigma = 0.088 \tag{6}$$

The choice of **2** as the standard for comparison is due to its least hydrogen bonding interaction with the hydrogen-bond donor solvents. This aspect will be dealt with further in a later section.

2. Formulation of the π^*_{azo} Scale. Once the dyes chosen were found to be suitable solvatochromic dyes, exhibiting spectral shifts with solvents varying in polarity, the spectral data were treated in the following manner in the formulation of the π^*_{azo} scale.

Twenty-nine solvents comprising NHB, HBA, and HBD-HBA solvents were chosen. These were divided into two sets: *Select Solvent Set* (SSS) consisting of NHB and HBA solvents and the *secondary solvent set* (sss) containing HBD-HBA and other protic solvents.

(a) Select Solvent Set (SSS): The Teetor Totter Method. The first step in the formulation of the π^* scale was to choose solvents such as the select solvents, which have the effect of reducing eq 1 to eq 7. This was possible

$$\mathrm{XYZ} = \mathrm{XYZ}_0 + s\pi^* \tag{7}$$

with the azo merocyanines **1**–**6** (b = 0, no hydrogen-bonding interactions with HBA solvents) as primary solutes and the select solvents (α = 0, non-HBD).

Nineteen non-HBD solvents (α = 0) were chosen as the select solvent set. Acetone (α = 0.08) and 2-butanone (α = 0.06) were retained in the present select solvent set as these solvents were included in Kamlet's select solvent set.[6] The list of solvents included in the select solvent set is shown in Table I (top half).

In the procedures used by Kamlet et al. in the formulation of the π^* scale, the spectral data were treated by the so-called Round Robin parameter optimization program.[6] Unfortunately, this program has not been explained in any detail in the published works.[6] The lack of an adequate description of this important procedure caused us to design an alternative method in the formulation of the π^*_{azo} scale, the Teetor Totter method.

In the Teetor Totter method, the spectral data of the six indicator solutes **1**–**6** in 19 select solvents were treated by means of linear correlation equations in order to optimize the standard deviations (σ) of the data points. The general eq 8 is given below in terms of the frequency maxima, where i and j refer to the solute and solvent, respectively, and i varies from **1** to **6** while j varies from 1 to 19.

$$\nu(\mathrm{i,j})_{\max} = \nu_0(\mathrm{i}) + s(\mathrm{i})[\pi^*_{\text{azo}}(\mathrm{j})] \tag{8}$$

Primarily, the π^*_{azo} values for two particular solvents (cyclohexane and dimethyl sulfoxide) are defined as

$$\pi^*_{\text{azo}}(\text{cyclohexane}) = 0.00 \tag{9}$$

$$\pi^*_{\text{azo}}(\text{dimethyl sulfoxide}) = 1.00 \tag{10}$$

similar to the formulation of the π^* scale.[6] Now, in eq 8, we have two unknown variables, $\nu_0(\mathrm{i})$ and $s(\mathrm{i})$. Using the predefined π^*_{azo} values for cyclohexane and dimethyl sulfoxide, one can solve for $[\nu_0(\mathrm{i})$ and $s(\mathrm{i})]_1$ where i = **1** to **6**. The subscript indicates that these values are obtained from iteration 1.

The next step is to calculate π^*_{azo} values for the remaining 17 solvents using $\nu_0(\mathrm{i})$ and $s(\mathrm{i})$ values. This results in six sets of $\pi^*_{\text{azo}}(\mathrm{i,j})$ values with i = **1** to **6** and j = 1 to 17. The $\pi^*_{\text{azo}}(i,j)$ values are averaged in this step (Supplementary Table 1).

The $\nu(\mathrm{i})_{\max}$ values are then correlated with the averaged π^*_{azo} values. This leads to a second set of $\nu_0(\mathrm{i})$ and $s(\mathrm{i})$ values. Retaining the π^*_{azo} values of cyclohexane (0.00) and DMSO (1.00), π^*_{azo} values for the remaining 17 solvents are calculated by using $[\nu_0(\mathrm{i})$ and $s(\mathrm{i})]_1$ where i = **1** to **6**. The resulting $\pi^*_{\text{azo}}(\mathrm{i,j})$ values are averaged (Supplementary Table 1) and correlated with $\nu_{\max}(\mathrm{i})$ values. The cycle is repeated until the standard deviations obtained in each correlation between $\nu_{\max}(\mathrm{i})$ and π^*_{azo} values are minimized.

In the present work the Teeter Totter method of correlations required three iterations (Supplementary Table 2) to achieve minimal least-square deviations of data points. The resultant π^*_{azo} values for the 19 solvents from the select solvent set are given in Table II along with the π^* values for these solvents as given by Kamlet et al.[8c]

(b) Secondary Solvent Set (sss). The secondary solvent set includes alcoholic solvents, protic solvents, and chlorinated solvents. As well, HMPA, acetonitrile, nitromethane, and chloroform were included in the secondary solvent set as they have been reported to complicate simple correlations if included in the select solvent set, with π^* or other appropriate measures of solvent dipolarity/polarizability.[19,20]

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(19) Kamlet, M. J.; Taft, R. W. *J. Chem. Soc., Perkin Trans. 2* **1979**, 1723.

(20) Abboud, J. L. M.; Taft, R. W.; Kamlet, M. J. *J. Chem. Res., Synop.* **1984**, *98*.

Table II. π^* and π^*_{azo} Values of Solvents Used in This Study

primary solvent set					secondary solvent set				
no.	code	solvent	π^* RR[a]	π^*_{azo} TT[b]	no.	code	solvent	π^* [c]	π^*_{azo} [d]
1	0	hexanes	−0.08	−0.09	20	9	chloroform	0.58	0.62
2	1	cyclohexane	0.00	0.00	21	13	dichloromethane	0.82	0.62
3	4	ether	0.27	0.16	22	11	HMPA	0.87	0.85
4	5	dioxane	0.55	0.34	23	21	acetonitrile	0.75	0.63
5	7	ethyl acetate	0.55	0.37	24	22	nitromethane	0.85	0.70
6	8	monoglyme	0.53	0.45	25	26	water	1.09	1.03
7	10	methyl acetate	0.60	0.44	26	23	1-propanol	0.52	0.85
8	18	*N,N*-DiMe-acetamide	0.88	0.86	27	24	ethanol	0.54	0.86
9	19	*N,N*-DiMe-formamide	0.88	0.86	28	25	methanol	0.60	0.89
10	20	dimethyl sulfoxide	1.00	1.00	29	27	DMPU	(1.08)[e]	0.99
11	14	2-butanone	0.67	0.61					
12	17	acetone	0.71	0.53					
13	2	toluene	0.54	0.38					
14	3	benzene	0.59	0.40					
15	6	chlorobenzene	0.71	0.58					
16	12	pyridine	0.87	0.80					
17	15	nitrobenzene	1.01	0.91					
18	16	benzonitrile	0.90	0.82					
19	10a	1,-dichloroethane	0.81	0.63					

[a] RR: From Kamlet's Round Robin least-squares correlation (ref 6). [b] TT: Using the Teeter Totter method (present work). [c] Calculated from $\pi^* = (\nu_{max} - \nu_0)/s$. [d] Calculated from $\pi^*_{azo} = (\nu_{max} - \nu_0)/s$. [e] π^* value for DMPU was calculated from the spectra shifts of azo dyes 1–6 using eq 7.

1,3-Dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidone (*N,N'*-dimethyl-*N,N'*-trimethyleneurea, DMPU) has not been included in the comprehensive list of solvents reported by Kamlet et al. in 1983.[8c] Hence, the π^* as well as π^*_{azo} values of DMPU have been determined by using eq 7 and 11. The values were found to be $\pi^* = 1.08$; $\pi^*_{azo} = 0.99$. These values were determined by the method reported,[21] wherein high and low π^*_i (i = 1 to 6) values are discarded and the remainder is averaged to give a value of 1.08 and 0.99 for π^* and π^*_{azo}, respectively.

The π^*_{azo} values of secondary solvents were calculated by using the reciprocal eq 11 and averaging the values obtained from the six indicator solutes.

$$\pi^*_{azo} = [\nu_{max} - \nu_0]/s \qquad (11)$$

3. Comparison of π^* and π^*_{azo} Scales. When we compare the magnitudes of the π^* scale (based on the Round Robin optimization program of the spectral data of mostly nitroaromatic solutes) and the π^*_{azo} scale (based on the Teetor Totter optimization program of the spectral data of the azo merocyanines), the following aspects are revealed.

(a) The π^*_{azo} values are *smaller* than π^* values for 16 of the 19 select solvents, with $\Delta(\pi^* - \pi^*_{azo})$ ranging from 0.02 to 0.19 unit in the primary set. The π^* and π^*_{azo} values for cyclohexane and DMSO agree by default. The π^* value of hexane is only slightly higher than the π^*_{azo} value.

(b) Considering the secondary solvents, the π^*_{azo} values of alcohols are *higher* than the corresponding π^* values; $\Delta(\pi^* - \pi^*_{azo}) \approx -0.33$ to -0.39 unit. HMPA, acetonitrile, nitromethane, and water have π^*_{azo} values *smaller* than the corresponding π^* values: $\Delta(\pi^* - \pi^*_{azo}) \approx -0.33$ to -0.39 unit.

(c) The π^*_{azo} values of polychlorinated aliphatics fall together very closely: 1,2-dichloroethane (0.63); dichloromethane (0.62); chloroform (0.62); whereas the π^* values vary to a greater extent: $ClCH_2CH_2Cl$ (0.81); CH_2Cl_2 (0.82); $CHCl_3$ (0.58).

(d) In the case of strong HBD solvents, namely, propanol ($\alpha = 0.78$), ethanol ($\alpha = 0.83$), and methanol ($\alpha = 0.93$), π^*_{azo} values are higher than π^* values. This observation suggests that the π^*_{azo} values might include some contribution (α type) from their HBD effects. This problem has also been encountered by Kamlet et al.[3] They have stated that type-A hydrogen bonding is so pervasive that any chromophore or auxochrome that could lead to absorption of light in an experimentally accessible region of the electronic spectrum would almost necessarily contain a site of ground-state electron density sufficiently high to induce hydrogen bonding by solvents such as alcohols.[3]

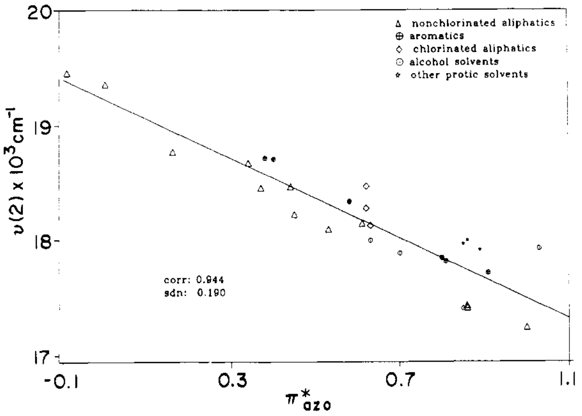

Figure 1. Representative plot of ν(i) vs π^*_{azo} for azo merocyanine dye **2** in all solvents.

(e) The response of azo dyes to the dipolarity/polarizability component of solvent properties is varying only in degree in comparison with the nitroaromatics used in the study of Kamlet et al.[6]

4. Correlation of Spectral Data of Dyes 1–6 with π^* and π^*_{azo} Scales. The spectral data (ν_{max}) obtained for the six azo merocyanines are correlated here with the π^* and π^*_{azo} scales. The correlations are carried out sequentially with (a) π^* and π^*_{azo}; (b) $\pi^* + d\delta$ and $\pi^*_{azo} + d\delta$; (c) $s(\pi^* + d\delta) + \nu_0 + a\alpha$ and $s(\pi^*_{azo} + d\delta) + \nu_0 + a\alpha$. This treatment follows Kamlet's approach in arriving at the total solvatochromic equation.[6]

A representative plot of ν(i) versus π^*_{azo} for compound **2** is shown in Figure 1. An all-data least-squares corre-

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[21] Kamlet, M. J.; Hall, T. N.; Boykin, J.; Taft, R. W. *J. Org. Chem.* **1979**, *44*, 2599.

[22] Kolling, D. W. *Anal. Chem.* **1978**, *50*, 212; **1977**, *49*, 591.

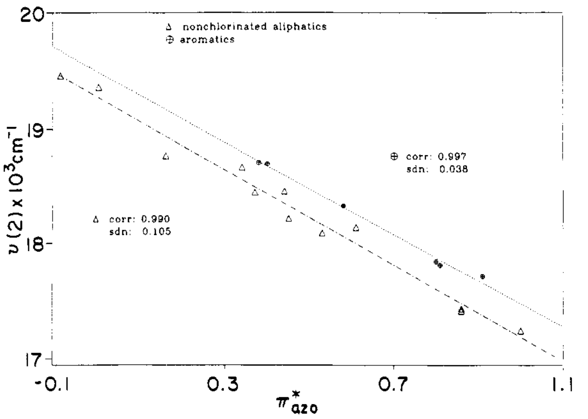


Figure 2. Plot of ν(i) vs π^*_{azo} for dye **2** in select solvents showing improved correlation with aromatic and nonchlorinated solvents, respectively.

Table III

dye no.	XYZ_{NCA}[a]	s_{NCA}[a]	XYZ_{AROM}[b]	s_{AROM}[b]	d[c]
A. Calculation of d Values from Spectral Data Correlated with the π^* Scale					
1	20.62	-2.31	21.38	-2.92	0.127
2	19.43	-2.05	20.05	-2.42	0.162
3	22.09	-1.57	22.38	-2.01	-0.010
4	20.83	-1.36	21.15	-1.79	0.012
5	21.81	-1.37	22.33	-2.05	0.026
6	21.61	-1.12	21.49	-1.05	-0.065
B. Calculation of d Values from Spectral Data Correlated with the π^*_{azo} Scale					
1	20.44	-2.36	20.68	-2.39	0.092
2	19.27	-2.09	19.48	-2.00	0.133
3	21.96	-1.58	21.89	-1.65	-0.073
4	20.73	-1.39	20.72	-1.47	-0.046
5	21.72	-1.42	21.84	-1.69	-0.044
6	21.52	-1.14	21.23	-0.85	-0.087

[a] NCA: Nonchlorinated Aliphatic solvents. [b] AROM: Aromatic solvents. [c]

$$d = 2\left[\frac{XYZ_{NCA} - XYZ_{AROM}}{s_{NCA} - s_{AROM}}\right] \text{ at } \pi^* = 0.7.$$

lation of ν(i) with solvent π^* and π^*_{azo} values leads to the following regression equations:

$$\nu(\mathbf{1}) = 20.39 - 2.02\pi^* \qquad \nu(\mathbf{1}) = 20.48 - 2.33\pi^*_{azo} \qquad (12)$$
$$n = 28,\ \sigma = 0.439,\ r = 0.787 \qquad n = 28,\ \sigma = 0.174,\ r = 0.970$$
$$\nu(\mathbf{2}) = 19.31 - 1.71\pi^* \qquad \nu(\mathbf{2}) = 19.24 - 1.77\pi^*_{azo} \qquad (13)$$
$$n = 28,\ \sigma = 0.280,\ r = 0.862 \qquad n = 28,\ \sigma = 0.213,\ r = 0.927$$
$$\nu(\mathbf{3}) = 21.96 - 1.61\pi^* \qquad \nu(\mathbf{3}) = 22.00 - 1.80\pi^*_{azo} \qquad (14)$$
$$n = 28,\ \sigma = 0.338,\ r = 0.798 \qquad n = 28,\ \sigma = 0.115,\ r = 0.974$$
$$\nu(\mathbf{4}) = 20.77 - 1.32\pi^* \qquad \nu(\mathbf{4}) = 20.72 - 1.37\pi^*_{azo} \qquad (15)$$
$$n = 27,\ \sigma = 0.172,\ r = 0.902 \qquad n = 27,\ \sigma = 0.088,\ r = 0.977$$
$$\nu(\mathbf{5}) = 21.76 - 1.37\pi^* \qquad \nu(\mathbf{5}) = 21.70 - 1.39\pi^*_{azo} \qquad (16)$$
$$n = 27,\ \sigma = 0.217,\ r = 0.862 \qquad n = 27,\ \sigma = 0.142,\ R = 0.944$$
$$\nu(\mathbf{6}) = 21.41 - 0.96\pi^* \qquad \nu(\mathbf{6}) = 21.51 - 1.22\pi^*_{azo} \qquad (17)$$
$$n = 27,\ \sigma = 0.272,\ r = 0.690 \qquad n = 27,\ \sigma = 0.158,\ r = 0.932$$

In the above correlations solvents belonging to various families are treated as one group. However, when we limit correlations to solvents with similar polarizability characteristics, such as nonchlorinated aliphatics (NCA) and aromatics (AROM), it is seen that the correlation equations improve significantly. For example, for 12 nonchlorinated aliphatic solvents, solute **2** shows the following regressions:

$$\nu(\mathbf{2}) = 19.43 - 2.05\pi^* \qquad \nu(\mathbf{2}) = 19.27 - 2.09\pi^*_{azo} \qquad (18)$$
$$n = 12,\ \sigma = 0.188,\ r = 0.964 \qquad n = 12,\ \sigma = 0.105,\ r = 0.990$$

and for six aromatic solvents:

$$\nu(\mathbf{2}) = 20.05 - 2.42\pi^* \qquad \nu(\mathbf{2}) = 19.47 - 2.00\pi^*_{azo} \qquad (19)$$
$$n = 6,\ \sigma = 0.090,\ r = 0.984 \qquad n = 6,\ \sigma = 0.038,\ r = 0.997$$

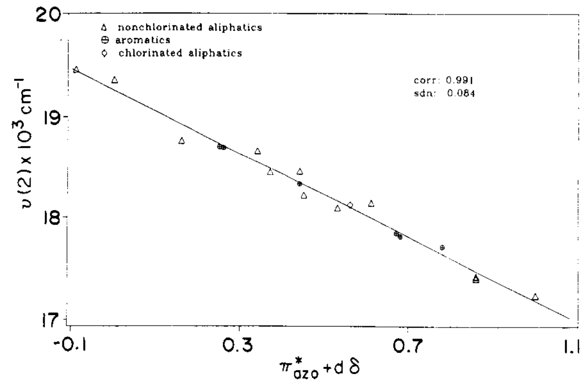


Figure 3. Plot of ν(i) vs $\pi^*_{azo} + d\delta$ for dye **2** showing the effect of inclusion of the polarizability correction factor δ.

Table IV

dye no.	n[a]	s	a	ν_0	cc[b]	σ[b]
A. Solvatochromic Coefficients Obtained by Multiple Linear Regression Analysis Using π^* Values: $\nu_{max} = \nu_0 + s\pi^* + a\alpha$						
1	27	-2.13	-1.22	20.64	0.878	0.341
2	27	-1.86	-0.40	19.44	0.869	0.272
3	27	-1.56	-1.02	22.09	0.958	0.148
4	27	-1.36	-0.38	22.85	0.939	0.135
5	27	-1.40	-0.43	21.84	0.915	0.195
6	27	-1.03	-0.83	21.57	0.935	0.134
B. Solvatochromic Coefficients Obtained by Multiple Linear Regression Analysis with the π^*_{azo} Values: $\nu_{max} = \nu_0 + s\pi^*_{azo} + a\alpha$						
1	27	-2.31	-0.21	20.48	0.982	0.129
2	27	-2.00	0.48	19.30	0.989	0.082
3	27	-1.63	-0.30	21.95	0.991	0.067
4	27	-1.44	0.26	20.73	0.992	0.049
5	27	-1.47	0.22	21.72	0.951	0.132
6	27	-1.08	-0.34	21.48	0.970	0.091

[a] Number of data points. [b] Values of cc and σ determined by least-squares correlation of $\nu(i) = \nu_0 + s(\pi^* + d\delta) + a\alpha$ with $\nu(i)_{obsd}$ (IVA) and $\nu(i)_{calcd} = \nu_0 + s(\pi^*_{azo} + d\delta) + a\alpha$ with $\nu(i)_{obsd}$ (IVB).

As was reported in Kamlet's work,[6] these correlations display significant improvement over the earlier correlations (eq 12–17). This reiterates the need for grouping together solvents belonging to the same polarizability family. A representative plot of ν(**2**) vs π^*_{azo} for NCA and AROM solvents is shown in Figure 2.

Kamlet et al. have added a polarizability parameter (δ) to include all the solvents.[6] δ equals 0.00 for all nonhalogenated aliphatic solvents, 0.50 for all polyhalogenated aliphatics, and 1.00 for all aromatic solvents. The coefficient of the polarizability parameter, d, is a measure of the differential susceptibility to solvent polarizability between ν_{max} (XYZ in general) and π–π^* electronic transitions and is calculated individually for each dye using eq 20. The d values are given in Table III,A and B.

$$d = 2\left[\frac{XYZ_{NCA} - XYZ_{AROM}}{s_{NCA} - s_{AROM}}\right] \text{ at } \pi^* = 0.7 \qquad (20)$$

The polarizability correction term δ leads to considerable improvement as seen in the correlations of ν_{max} vs $\pi^*_{azo} + d\delta$ (Figure 3). The data for the regressions for the six solutes with π^* and π^*_{azo} scales are given in the Supplementary Tables 3a and 3b.

The next step in the procedure adopted by Kamlet et al. was to include another parameter, α or β, to account for the solvent HBD acidity or HBA basicity. The following shows the incorporation of the α term to lead to the final solvatochromic equation.

The final solvatochromic equations are obtained for all the solutes by using the π^* and π^*_{azo} scales by the method

Table V. Correlations of Electronic Spectral Data for Dyes 1-6 with the π^* Scale

dye no.	n	eq[a]	slope	int	d	σ	r	type[b]	exclude
1	28	1	-2.02	20.39		0.439	0.787	All	
	27	1	-2.03	20.40		0.449	0.774	All	H_2O
	19	1	-2.19	20.65		0.248	0.937	SSS	
	12	1	-2.31	20.62		0.253	0.955	NCA	
	6	1	-2.92	21.38		0.067	0.994	AROM	
	19	2	-2.36	20.66	0.117	0.210	0.958	SSS	
	28	3	0.82	3.47		0.341	0.878	All	
	27	3	1.03	-0.73		0.248	0.936	All	H_2O
2	28	1	-1.71	19.31		0.280	0.862	All	
	27	1	-1.83	19.36		0.266	0.880	All	H_2O
	19	1	-1.88	19.45		0.231	0.930	SSS	
	12	1	-2.05	19.43		0.118	0.964	NCA	
	6	1	-2.42	20.05		0.090	0.984	AROM	
	19	2	-2.08	19.45	0.162	0.167	0.965	SSS	
	28	3	0.88	2.11		0.272	0.869	All	
	27	3	-1.07	-1.40		0.192	0.939	All	H_2O
3	28	1	-1.61	21.96		0.338	0.798	All	
	27	1	-1.47	20.90		0.328	0.777	All	H_2O
	19		-1.65	22.12		0.129	0.974	SSS	
	12	1	-1.57	22.09		0.153	0.969	NCA	
	6	1	-2.01	22.38		0.042	0.995	AROM	
	19	2	-1.63	22.12	-0.010	0.127	0.974	SSS	
	28	3	0.91	1.80		0.160	0.958	All	
	27	3	1.00	0.09		0.148	0.958	All	H_2O
4	27	1	-1.32	20.77		0.172	0.902	All	H_2O
	19	1	-1.41	20.86		0.110	0.970	SSS	
	12	1	-1.36	20.83		0.129	0.966	NCA	
	6	1	-1.79	21.15		0.049	0.991	AROM	
	19	2	-1.42	20.86	0.012	0.110	0.970	SSS	
	27	3	-1.00	2.01		0.135	0.939	All	H_2O
5	27	1	-1.37	21.76		0.217	0.862	All	H_2O
	19	1	-1.42	21.86		0.200	0.915	SSS	
	12	1	-1.37	21.81		0.224	0.914	NCA	
	6	1	-2.05	22.33		0.094	0.976	AROM	
	19	2	-1.44	21.86	0.026	0.195	0.915	SSS	
	27	3	1.01	-0.15		0.183	0.907	All	H_2O
6	27	1	-0.96	21.41		0.272	0.690	All	H_2O
	19	1	-1.15	21.61		0.100	0.963	SSS	
	12	1	-1.12	21.61		0.135	0.956	NCA	
	6	1	-1.05	21.49		0.029	0.991	AROM	
	19	2	-1.11	21.61	-0.065	0.095	0.966	SSS	
	27	3	-1.00	0.013		0.134	0.935	All	H_2O

[a] Equation 1. $\nu_{max} = \nu_0 + s\pi^*$. Equation 2. $\nu_{max} = \nu_0 + s(\pi^* + d\delta)$. Equation 3. $\nu_{max} = \nu_0 + s(\pi^* + d\delta) + a\alpha$. [b] NCA = Nonchlorinated Aliphatic solvents. AROM = Aromatic solvents. SSS = Select Solvent Set.

of multiple linear regression analysis. In this one-step procedure, ν(i) is correlated with the solvent parameters π^* and α. Similarly, ν(i) is correlated with π^*_{azo} and α:

$$\nu(\mathrm{i}) = s_i\pi^* + a_i\alpha \tag{21}$$

$$\nu(\mathrm{i}) = s_i\pi^*_{azo} + a_i\alpha \tag{22}$$

The values of s_i and a_i are given in Tables IV,A and B.

With known s_i, a_i, and d_i values, one can proceed to the final expression of the Solvatochromic Comparison Method (SCM) as given in eq 23 and 24:

$$\nu(\mathrm{i}) = \nu_0 + s_i[\pi^* + d_i\delta] + a_i\alpha \tag{23}$$

$$\nu(\mathrm{i}) = \nu_0 + s_i[\pi^*_{azo} + d_i\delta] + a_i\alpha \tag{24}$$

The regressions for eq 23 and 24 show significant improvement over the initial equations, $\nu(\mathrm{i}) = \nu_0 + s\pi^*$ and $\nu(\mathrm{i}) = \nu_0 + s\pi^*_{azo}$. The data for the regressions are tabulated in Supplementary Tables 4a, 4b, 5a, and 5b. The results of all the regressions are summarized in Tables V and VI for comparison. A plot for eq 24 incorporating these regressions is shown in Figure 4 for solute 2.

It is seen from Tables V and VI that the correlations improve considerably when the final solvatochromic equation is used to correlate with ν_{max}(i). This equation comprises the dipolarity/polarizability term, π^* or π^*_{azo}; the polarizability correction term δ; and a solvent HBD acidity term α. It follows that when the parameters δ and α are used in conjunction with the solvent dipolarity/polariza-

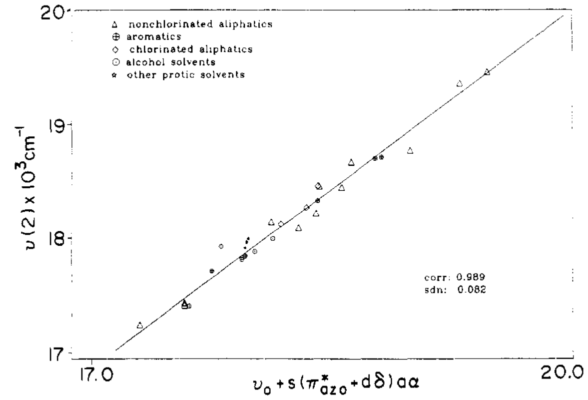


Figure 4. Plot of the expression of the total solvatochromic eq 24 for dye 2 showing a significantly improved correlation compared to plot 1 with the inclusion of the δ and α parameters.

Table VI. Correlations of Electronic Spectral Data for Dyes 1–6 with the π^*_{azo} Scale

dye no.	n	eq[a]	slope	int	d	σ	r	type[b]	exclude
1	28	1	−2.33	20.48		0.174	0.970	All	
	27	1	−2.36	20.49		0.174	0.969	All	H_2O
	19	1	−2.26	20.47		0.157	0.976	SSS	
	12	1	−2.36	20.44		0.153	0.984	NCA	
	6	1	−2.39	20.68		0.050	0.997	AROM	
	19	2	−2.36	20.44	0.092	0.120	0.986	SSS	
	28	3	0.98	−0.49		0.153	0.977	All	
	27	3	1.01	0.32		0.129	0.982	All	H_2O
2	28	1	−1.77	19.24		0.213	0.927	All	
	27	1	−1.87	19.27		0.190	0.944	All	H_2O
	19	1	−1.95	19.29		0.148	0.972	SSS	
	12	1	−2.09	19.27		0.105	0.990	NCA	
	6	1	−2.00	19.47		0.038	0.997	AROM	
	19	2	−2.08	19.26	0.133	0.084	0.991	SSS	
	28	3	1.03	−0.65		0.90	0.987	All	
	27	3	1.04	−0.88		0.082	0.989	All	H_2O
3	28	1	−1.80	22.00		0.152	0.962	All	
	27	1	−1.71	21.96		0.115	0.974	All	H_2O
	19	1	−1.65	21.95		0.094	0.984	SSS	
	12	1	−1.58	21.96		0.094	0.986	NCA	
	6	1	−1.65	21.89		0.025	0.998	AROM	
	19	2	−1.60	21.96	−0.073	0.078	0.989	SSS	
	28	3	1.00	−0.67		0.079	0.990	All	
	27	3	0.993	0.18		0.067	0.991	All	H_2O
4	27	1	−1.37	20.72		0.088	0.977	All	H_2O
	19	1	−1.44	20.73		0.044	0.995	SSS	
	12	1	−1.39	20.73		0.042	0.996	NCA	
	6	1	−1.47	20.72		0.011	0.999	AROM	
	19	2	−1.44	20.75	−0.046	0.034	0.997	SSS	
	27	3	−1.44	0.21		0.049	0.992	All	H_2O
5	27	1	−1.39	21.70		0.142	0.944	All	H_2O
	19	1	−1.47	21.74		0.140	0.957	SSS	
	12	1	−1.41	21.72		0.164	0.951	NCA	
	6	1	−1.69	21.84		0.064	0.989	AROM	
	19	2	−1.44	21.74	−0.044	0.140	0.957	SSS	
	27	3	0.99	0.29		0.132	0.951	All	H_2O
6	27	1	−1.22	21.51		0.158	0.932	All	H_2O
	19	1	−1.15	21.49		0.091	0.969	SSS	
	12	1	−1.14	21.52		0.082	0.980	NCA	
	6	1	−0.85	21.23		0.041	0.983	AROM	
	19	2	−1.10	21.49	−0.087	0.075	0.979	SSS	
	27	3	1.00	0.04		0.091	0.970	All	H_2O

[a] Equation 1. $\nu_{max} = \nu_0 + s\pi^*_{azo}$. Equation 2. $\nu_{max} = \nu_0 + s(\pi^*_{azo} + d\delta)$. Equation 3. $\nu_{max} = \nu_0 + s(\pi^*_{azo} + d\delta) + a\alpha$. [b] NCA = Nonchlorinated Aliphatic solvents. AROM = Aromatic solvents. SSS = Select Solvent Set.

bility term, π^* or π^*_{azo}, correlations with ν(i) are improved. The above results confirm the validity of Kamlet's approach of SCM using the polarizability correction term and the HBD acidity term along with the π^* scale and also the π^*_{azo} scale.

5. Comparison of π^*_{azo} Scale for 59 Indicator Solutes. In this section we examine the correlations between the π^* and π^*_{azo} scales and the ν_{max} values in 19 different solvents for the 59 indicator solutes listed in Table VII. The indicator solutes include the azo merocyanine dyes **1–6**, the nitroaromatic compounds used in Kamlet's treatment, Dimroth and Reichardt's betaine **11**, Brooker's merocyanine **12**, quinone methide dyes **24–31**, azo dyes **40–49**, polymethine dyes **50–54**, and Figueras' phenol blues **55–59**. Correlations with NHB solvents solely were not attempted as there are only six NHB solvents used in the select solvent set in the present work (hexane, cyclohexane, benzene, toluene, chlorobenzene, and 1,2-dichloroethane). Hence, the 19 select solvents were used in these correlations. The results of the correlations are summarized in Table VII.

The statistics of these correlations, i.e., the correlation coefficients (r) (Table VIII) and the standard deviations (Table IX), are informative. The standard deviation (σ) for the 59 dyes is 0.260 with the π^*_{azo} scale, which is slightly better than σ = 0.289 obtained using the π^* scale. The data in Tables VII–IX clearly show that the π^*_{azo} scale is better than the π^* scale when we consider groups of compounds such as the azo merocyanine dyes (**1–6**), Dimroth and Reichardt's betaine and Brooker's merocyanine (**11**, **12**), Nile blues A and B (**19**, **20**), 7,7-disubstituted quinone methides (**24–31**), azobenzenes (**40–49**), and Figueras' phenol blues (**56–59**). At the same time, the π^* scale is better for nitroaromatics (**7–10** and **32–39**).

6. Comparison of π^* and π^*_{azo} Scales with Other Polarity Scales. Among the various polarity scales in the literature, 20 scales were chosen wherein data was available for more than five solvents to examine correlations with the π^* and π^*_{azo} scales. The results obtained from these correlations are presented in Table X.

The correlation coefficients (r) given in Table XI show that the π^*_{azo} scale correlates just as well as the π^* scale with 20 other polarity scales. Furthermore, π^*_{azo} correlates very well with Brooker's χ_R scale (r = 0.991, σ = 0.383), compared to π^* vs χ_R (r = 0.961, σ = 0.805) for the select solvents. This is probably due to structural similarities between Brooker's merocyanine (**12**) and the azo merocyanines (**1–6**).

Table VII. Correlation of Electronic Spectral Data with the π^* and π^*_{azo} Scales in NHB and HBA Solvents

			π^* scale		π^*_{azo} scale		
no.	solute	*n*	σ	cc	σ	cc	ref
1	*N*-methyl-4-pyridone 1,4-benzoquinone azine	19	0.248	0.937	0.157	0.976	*a*
2	*N*-methyl-4-pyridone 3,5-diphenyl-1,4-benzoquinone azine	19	0.231	0.930	0.148	0.972	*a*
3	*N*-methylbenzothiazol-2-one 1,4-benzoquinone azine	19	0.129	0.974	0.094	0.984	*a*
4	*N*-methylbenzothiazol-2-one 3,5-diphenyl-1,4-benzoquinone azine	19	0.110	0.970	0.044	0.995	*a*
5	*N*-methylbenzothiazol-2-one 1,4-naphthoquinone azine	19	0.200	0.915	0.140	0.957	*a*
6	*N*-methylbenzothiazol-2-one 1,2-naphthoquinone azine	19	0.100	0.963	0.091	0.969	*a*
7	*N*,*N*-diethyl-4-nitroaniline	15	0.130	0.992	0.257	0.967	*b*
8	4-nitroaniline	15	0.772	0.896	0.670	0.918	*b*
9	4-niroanisole	10	0.115	0.993	0.209	0.977	*b*
10	4-nitrophenol	10	0.595	0.924	0.576	0.929	*b*
11	Dimroth and Reichardt's log k_2	11	0.597	0.948	0.478	0.967	*c*
12	Brooker's merocyanine	10	0.328	0.958	0.160	0.990	*c*
13	*N*,*N*-dimethyl-2-nitroaniline	9	0.270	0.936	0.242	0.949	*d*
14	2-nitroaniline	9	0.457	0.872	0.389	0.909	*d*
15	*N*,*N*-dimethyl-2-nitro-*p*-toluidine	9	0.110	0.991	0.196	0.970	*d*
16	2-nitro-*p*-toluidine	9	0.276	0.951	0.230	0.966	*d*
17	*N*,*N*-dimethyl-2-nitro-*p*-anisidine	9	0.103	0.993	0.210	0.969	*d*
18	2-nitro-*p*-anisidine	9	0.245	0.954	0.235	0.958	*d*
19	Nile Blue A Oxazone (NBAO)	7	0.199	0.942	0.128	0.977	*e*
20	Tolyl DiPropyl Nile Blue Base (TDPNBB)	12	0.186	0.931	0.134	0.965	*e*
21	*N*-methyl-4-nitroaniline	10	0.349	0.972	0.332	0.975	*f*
22	*N*,*N*-dimethyl-4-nitroaniline	10	0.174	0.991	0.320	0.969	*f*
23	*N*-methyl-2-nitroaniline	10	0.071	0.994	0.131	0.978	*f*
24	7,7-disubstituted quinone methide 1	8	0.116	0.947	0.128	0.935	*g*
25	7,7-disubstituted quinone methide 2	8	0.213	0.903	0.139	0.960	*g*
26	7,7-disubstituted quinone methide 3	8	0.167	0.886	0.133	0.929	*g*
27	7,7-disubstituted quinone methide 4	7	0.204	0.792	0.139	0.909	*g*
28	7,7-disubstituted quinone methide 5	8	0.125	0.399	0.119	0.494	*g*
29	7,7-disubstituted quinone methide 6	8	0.313	0.790	0.342	0.743	*g*
30	7,7-disubstituted quinone methide 7	8	0.092	0.692	0.083	0.763	*g*
31	7,7-disubstituted quinone methide 8	8	0.178	0.471	0.178	0.478	*g*
32	ethyl 4-aminobenzoate	9	0.699	0.872	0.633	0.896	*h*
33	4-aminobenzophenone	13	0.582	0.871	0.493	0.909	*h*
34	3,5-dinitroaniline	15	0.603	0.824	0.575	0.841	*h*
35	3-nitroaniline	15	0.625	0.856	0.538	0.896	*h*
36	*N*-ethyl-3-nitroaniline	15	0.321	0.945	0.258	0.965	*h*
37	*N*-methyl-2-nitro-*p*-toluidine	9	0.051	0.997	0.141	0.975	*i*
38	2-nitrophenol	8	0.498	0.248	0.468	0.412	*i*
39	4-nitrophenoxide anion	8	0.580	0.874	0.453	0.925	*i*
40	azobenzene	5	0.021	0.992	0.030	0.982	*j*
41	4′-methoxyazobenzene	6	0.048	0.981	0.065	0.966	*k*
42	4-nitro-4′-methoxyazobenzene	6	0.148	0.946	0.097	0.977	*k*
43	4′-*N*,*N*-dimethylazobenzene	6	0.149	0.958	0.055	0.994	*k*
44	3-nitro-4′-*N*,*N*-dimethylazobenzene	6	0.273	0.936	0.122	0.988	*k*
45	4-nitro-4′-*N*,*N*-dimethylazobenzene	6	0.310	0.957	0.244	0.973	*k*
46	2,4-dinitro-4′-*N*,*N*-dimethylazobenzene	6	0.158	0.982	0.198	0.972	*k*
47	4-nitro-2′-*N*-acetyl-4′-N(C_2H_4OH)$_2$-5′-methoxyazobenzene	6	0.079	0.966	0.075	0.970	*k*
48	2,4-nitro-2′-*N*-acetyl-4′-N(C_2H_4OH)$_2$-5′-methoxyazobenzene	5	0.087	0.945	0.102	0.924	*k*
49	2-CN-4-NO_2-6-Br-2′-*N*-acetyl-4′-N(C_2H_4OH)$_2$-5′-methoxyazobenzene	5	0.047	0.969	0.057	0.954	*k*
50	N-substituted-(4-nitrophenyl)polymethine dye 1	5	0.069	0.999	0.362	0.965	*l*
51	N-substituted-(4-nitrophenyl)polymethine dye 3	6	0.103	0.994	0.165	0.984	*l*
52	N-substituted-(4-nitrophenyl)polymethine dye 4	4	0.108	0.997	0.127	0.995	*l*
53	N-substituted-(4-nitrophenyl)polymethine dye 5	6	0.082	0.998	0.289	0.970	*l*
54	N-substituted-(4-nitrophenyl)polymethine dye 6	6	0.091	0.997	0.258	0.979	*l*
55	Figueras phenol blue 1	7	0.206	0.993	0.220	0.992	*m*
56	Figueras phenol blue 2	7	0.420	0.956	0.192	0.991	*m*
57	Figueras phenol blue 3	7	1.054	0.857	0.724	0.935	*m*
58	Figueras phenol blue 4	7	1.519	0.807	1.100	0.904	*m*
59	Figueras phenol blue 5	7	0.719	0.876	0.461	0.951	*m*

[a] This work. [b] Kamlet, M. J.; Taft, R. W. *J. Am. Chem. Soc.* **1976**, *98*, 378. [c] Kamlet, M. J.; Taft, R. W. *J. Am. Chem. Soc.* **1976**, *98*, 2886. [d] Yokoyama, T.; Kamlet, M. J.; Taft, R. W. *J. Am. Chem. Soc.* **1976**, *98*, 3233. [e] Davies, M. M.; Hetzer, H. B. *Anal. Chem.* **1976**, *38*, 451. [f] Yokoyama, T. *Aust. J. Chem.* **1976**, *29*, 1469. [g] Pavlickova, L.; Koutek, B.; Jehlicka, V.; Soucek, M. *Collect. Czech. Chem. Commun.* **1978**, *48*, 2376. [h] Kamlet, M. J.; Jones, M. E.; Taft, R. W.; Abboud, J. L. M. *J. Chem. Soc., Perkin Trans. 2* **1979**, 342. [i] Kamlet, M. J.; Taft, R. W. *J. Org. Chem.* **1982**, *47*, 1734. [j] Abboud, J. L. M.; Taft, R. W.; Kamlet, M. J. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 603. [k] Mustroph, H.; Epperlein, J. *J. Prakt. Chem.* **1980**, *322*, 305. [l] Kamlet, M. J.; Minesinger, R. R.; Kayser, E. G.; Albridge, M. H.; Eastes, J. W. *J. Org. Chem.* **1971**, *36*, 3852. [m] Figueras, J. *J. Am. Chem. Soc.* **1971**, *93*, 3255.

7. Correlations between the Transition Energies of Azo Merocyanines and Other Polarity Scales. Finally, we have examined possible correlations between the transition energies (ν_{max}) of the azo merocyanines with solvent polarity scales from the literature other than the π^* and π^*_{azo} scales. The scales include Z, E_T, χ_R, χ_B, ϕ, G, $\mathcal{A}_N$, ϵ, μ, and n_D.

In an attempt to reveal possible trends for different types of solvents, these were grouped into four categories: all solvents (ALL), nonchlorinated aliphatics (NCA), aromatics (AROM), Select Solvent Set (SSS), and hydrogen-bond donors (HBD). The results obtained from these correlations of the various solvent polarity scales with the six azo merocyanine dyes are tabulated in Supplementary

Table VIII. Comparison of Correlation Coefficients Obtained from the Linear Correlations of ν_{max}(i) vs π^* and π^*_{azo} Scales

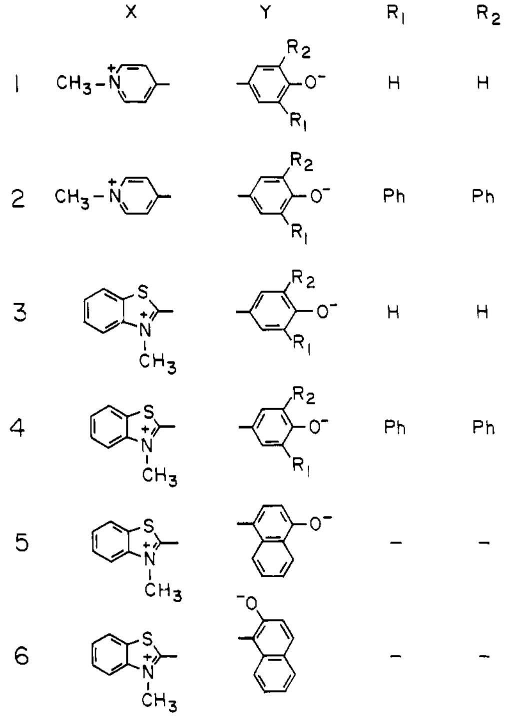
r	
ν_{max}(i) vs π^* scale	ν_{max}(i) vs π^*_{azo} scale
14 are greater than 0.99	6 are greater than 0.99
14 lie between 0.95 and 0.99	33 lie between 0.95 and 0.99
14 lie between 0.90 and 0.95	12 lie between 0.90 and 0.95
11 lie between 0.80 and 0.99	3 lie between 0.80 and 0.90
6 are lesser than 0.80	5 are lesser than 0.80

Table IX. Comparison of Standard Deviation Obtained from the Linear Correlations of ν_{max}(i) vs π^* and π^*_{azo} Scales

	$10^3\sigma$, cm^{-1}	
	ν_{max}(i) vs π^* scale	ν_{max}(i) vs π^*_{azo} scale
for all 59 dyes	0.289	0.260
for 6 azo dyes (from this work)	0.170	0.112
for 10 azo dyes (ref *m*, Table VII)	0.132	0.105
for 8 quinone methiodide dyes (ref *g*, Table VII)	0.176	0.158
for Brooker's merocyanine	0.328	0.160

Chart I

X − N=N−Y



Tables 6–11.

It is found that, considering all solvents, Brooker's χ_R scale correlates reasonably well with ν_{max} of the six azo merocyanines, the correlation coefficients (r) being 0.928 (**1**), 0.905 (**2**), 0.942 (**3**), 0.965 (**4**), 0.964 (**5**), and 0.883 (**6**). The correlation coefficients obtained from correlating E_T values of the 19 select solvents with ν_{max}(i) are 0.918 (**1**), 0.930 (**2**), 0.854 (**3**), 0.868 (**4**), 0.876 (**5**), and 0.791 (**6**).

When the solvents are grouped into NCA, AROM, and so on, the correlations improve significantly (Supplementary Tables 6–11). However, correlations with ϕ, μ, n, $\mathcal{A}_N$, and ϵ are poor.

8. **Structure–Property Relationships.** In this section we discuss the relationships between the structures of the azo merocyanine dyes and the spectral shifts in various solvents. From Kamlet's work,[6] the s parameter is believed to serve as an indicator of the interaction of a chromophore with its cybotactic environment. Also, the a/s ratio is considered to be a measure of the susceptibility of XYZ to hydrogen bonding.

The absorption maxima for [$^+$X=C(1) → C(4)=Y$^-$] electronic transitions are known to be displaced to lower energies with increasing electron-donor ability of Y and electron-acceptor ability of X. The present work deals with azo merocyanine dyes of the type XN=NY, where X correponds to the pyridyl and benzothiazolyl moieties, while Y are substituted phenyl groups (Chart I).[23] The

Table X. Correlation of Various Solvent Scales for Select Solvents with the π^* and π^*_{azo} Scales

correlation[a]	n	R	σ	ref	correlation[a]	n	R	σ
π^* vs Z	11	0.610	6.653	4h	π^*_{azo} vs Z	11	0.530	7.123
π^* vs Z	10[a]	0.839	2.453	4h	π^*_{azo} vs Z	10[a]	0.847	2.410
π^* vs E_T	18	0.900	1.962	4a	π^*_{azo} vs E_T	18	0.917	1.789
π^* vs ψ_R	15	0.961	0.805	4b	π^*_{azo} vs ψ_R	15	0.991	0.383
π^* vs ϕ	7	0.591	0.038	4l	π^*_{azo} vs ϕ	7	0.627	0.037
π^* vs ϕ	6[b]	0.880	0.020	4l	π^*_{azo} vs ϕ	6[b]	0.821	0.024
π^* vs G	9	0.986	3.618	1	π^*_{azo} vs G	9	0.951	6.686
π^* vs $a^{^{14}N}$	11	0.959	0.051	4e	π^*_{azo} vs $a^{^{14}N}$	11	0.947	0.057
π^* vs ϵ	17	0.695	11.13	1	π^{γ}_{azo} vs ϵ	17	0.824	8.765
π^* vs ϵ	15[c]	0.854	10.39	1	π^*_{azo} vs ϵ	15[c]	0.904	7.348
π^* vs μ	17	0.847	2.548	1	π^*_{azo} vs μ	17	0.910	1.983
π^* vs n_D	17	0.416	0.059	1	π^*_{azo} vs n_D	17	0.435	0.058
π^* vs E_k	9	0.922	1.529	4d	π^*_{azo} vs E_k	9	0.902	1.701
π^* vs P	9	0.908	0.400	3	π^*_{azo} vs P	9	0.925	0.363
π^* vs Ω	7	0.215	0.048	4j	π^*_{azo} vs Ω	7	0.323	0.046
π^* vs S	13	0.875	0.031	4g	π^*_{azo} vs S	13	0.808	0.038
π^* vs lg k_1	6	0.995	0.146	1	π^*_{azo} vs lg k_1	6	0.975	0.318
π^* vs log k_2	9	0.970	0.356	4c	π^*_{azo} vs log k_2	9	0.919	0.578
π^* vs π^*_n	15	0.907	0.670	7b	π^*_{azo} vs π^*_n	15	0.863	0.805
π^* vs vs PB	9	0.973	0.416	22	π^*_{azo} vs PB	9	0.988	0.278
π^* vs NBAO	9	0.909	0.786	22	π^*_{azo} vs NBAO	9	0.954	0.565
π^* vs AN	9	0.978	1.370	1	π^*_{azo} vs AN	9	0.975	1.458
π^* vs Py	15	0.887	0.202	4k	π^*_{azo} vs Py	15	0.894	0.195
π^* vs χ_B	*d*				π^*_{azo} vs χ_B	*d*		
π^* vs Y	*d*				π^*_{azo} vs Y	*d*		
π^* vs X	*d*				π^*_{azo} vs X	*d*		

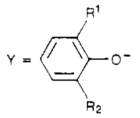
[a] Excluding acetone. [b] Excluding toluene. [c] Excluding hexanes and cyclohexane. [d] These correlations would involve less than five common solvents and were not considered.

Table XI. Comparison of Correlation Coefficients Obtained from the Linear Correlations of Other Scales vs π^* and π^*_{azo} Scales

R	
with π^* scale	with π^*_{azo} scale
1 is greater than 0.99	1 is greater than 0.99
6 lie between 0.95 and 0.99	5 lie between 0.95 and 0.99
5 lie between 0.90 and 0.95	7 lie between 0.90 and 0.95
6 lie between 0.80 and 0.90	6 lie between 0.80 and 0.90
2 are lesser than 0.80	2 are lesser than 0.80

Table XII. Structural Effects on Solvatochromic Parameters

A. Electron Donor Ability of Auxichrome

		$\nu_{max} = \nu_0 + s\pi^*$		$\nu_{max} = \nu_0 + s\pi^*_{azo}$	
dye no.		ν_0	$-s$	ν_0	$-s$
1	R_1 = H, R_2 = H	20.65	2.19	20.47	2.26
2	R_1 = Ph, R_2 = Ph	19.45	1.88	19.29	1.95
3	R_1 = H, R_2 = H	22.12	1.65	21.95	1.65
4	R_1 = Ph, R_2 = Ph	20.86	1.41	20.73	1.44
5	1,4-naphthoquinone	21.86	1.42	21.74	1.47
6	1,2-naphthoquinone	21.61	1.15	21.49	1.15

B. Electron Acceptor Terminus of Chromophore

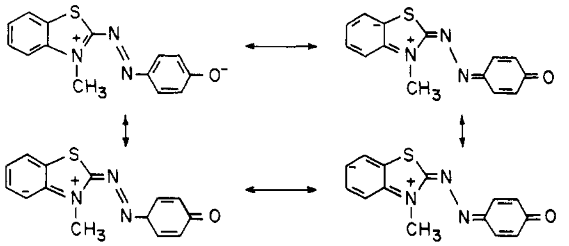
		$\nu_{max} = \nu_0 + s\pi^*$		$\nu_{max} = \nu_0 + s\pi^*_{azo}$	
dye no.	Y	$-s$	Δs^a	$-s$	Δs^a
1	*N*-methylpyridyl	2.19		2.26	
3	*N*-methylbenzothiazolyl	1.65	0.54	1.65	0.61
2	*N*-methylpyridyl	1.88		1.95	
4	*N*-methylbenzothiazolyl	1.41	0.47	1.44	0.51

[a] $\Delta s = (s_{N\text{-methylpyridyl}} - s_{N\text{-methylbenzothiazolyl}})$.

effect or varying X, Y, R_1, and R_2 on the spectral shifts of these compounds as a function of solvent character is presented below.

(a) Variation in R. When we examine the trends in the *s* and ν_0 values in Table XII, A, showing structural effects on solvatochromic parameters, we see that introduction of phenyl groups at the 3 and 5 positions (dyes **2** and 4) results in a bathochromic shift and a significant increase in the magnitude of the *s* term (Δs = 0.31 and 0.24 units for the π^* scale, and 0.31 and 0.21 units for the π^*_{azo} scale). A change in Y from 1,4-naphthoquinone to 1,2-naphthoquinone results in an increase in the *s* term by 0.27 unit for the π^* scale and 0.32 unit for the π^*_{azo} scale). This trend suggests that an increase in the *s* term is a manifestation of a lowered excited state, which is also seen from the observed bathochromic displacements of ν_0.

(b) Variation in X. Comparison of the *s* terms of dyes 1 and 3 with 2 and 4 gives an indication of the nature of the electron-acceptor terminus of the chromophore, i.e., *N*-methylpyridyl vs *N*-methylbenzothiazolyl moiety. The observed increase of 0.54 and 0.47 unit in the *s* term for the π^* scale, and 0.61 and 0.51 unit in the *s* term for the π^*_{azo} scale, on changing from *N*-methylpyridyl to *N*-methylbenzothiazolyl, strongly suggests that the *N*-methylbenzothiazolyl moiety is a better electron sink compared to *N*-methylpyridyl (Table XII). This could be raionalized by the increased low-energy resonance forms available to the fomer system:



(c) *a*/*s* Ratio. The ratio of the solvatochromic parameters *a* and *s* obtained from the multiple parameter regression analysis of ν_{max} vs π^* and α reflects the susceptiblity of ν_{max} to hydrogen bonding. On comparing the *a*/*s* values for the series of azo dyes studied, it is seen (Table XIII) that *a*/*s* is maximum for dye **6** and minimum for dye **2**.

Table XIII. Comparison of *a*/*s* Ratios for the Azo Merocyanine Dyes

dye no.	a/s^a	$a/s^{b,c}$
1	0.56	0.33
2	0.22	0.00
3	0.63	0.42
4	0.28	0.06
5	0.30	0.10
6	0.83	0.55

[a] From $\nu_{max} = \nu_0 + s^*\pi^* + a\alpha$. [b] From $\nu_{max} = \nu_0 + s\pi^*_{azo} + a\alpha$. [c] 0.24 has been added to each value to start the scale from 0.00.

The magnitude of the *a*/*s* ratio indicates that hydrogen bonding with HBD solvents for these solutes is in the order **2** < **4** < **5** < **1** < **3** < **6**. Dye **2** exhibits the minimum *a*/*s* value, which may be explained by steric factors arising due to the two phenyl groups which could inhibit solvent molecules from partaking in hydrogen bonding with the solute. This is the case with dye **4** as well. Comparing *a*/*s* values of **5** and **6**, the magnitude for **6** is significantly higher than that of **5**. This can be explained by the decreased distance between the centers of maximum and minimum electron density in the excited state, which is manifested in lower *s* values. The maximum *a*/*s* value for dye **6** may be rationalized by the availability of dual sites for hydrogen bonding in this system.

9. Conclusions. On the basis of the results obtained from the solvatochromic studies of the six azo merocyanine dyes **1**–**6**, the following conclusions may be drawn:

(1) The azo merocyanine dyes are suitable solvatochromic dyes exhibiting spectral shifts with solvents varying in polarity. These dyes exhibit positive solvatochromism, a manifestation of $\mu_g < \mu_e$.

(2) Among the various solvent polarity scales correlated with the spectral data of azo merocyanines, Kamlet, Abboud, Taft and Abraham's π^*, and Brooker's χ_R scales agree well. The π^* scale with the polarizability correction term ($d\delta$), in conjunction with the hydrogen-bonding acidity scale (α), correlates well among the polarity scales reported so far.

(3) A π^* value for a new solvent, DMPU, has been found to be 1.08.

(4) The new π^*_{azo} scale designed on the averaged spectral data of the azo merocyanine dyes agrees well with the spectral data of several indicator dyes and other polarity scales. Compared to the π^* scale, the correlations of π^*_{azo} are satisfactory with various indicator dyes.

(5) Based on structure–spectral property relationships, it was found that the *N*-methylbenzothiazolyl group is a

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(23) As an alternative to discussion of color–structure relationships in terms of a donor–azo-acceptor model, the azo-acceptor part of the molecule could be considered as a complex-acceptor moiety.[24] The conclusions of such a treatment would, however, be very similar.

(24) (a) Griffiths, J. *Color and Constitution of Organic Molecules*; Academic Press: London, 1976. (b) Fabian, J.; Hartmann, H. *Light Absorption of Organic Colorants*; Springer Verlag, 1980.

better electron sink compared to the *N*-methylpyridyl group.

(6) Some comments concerning the generality of solvent polarity scales seem appropriate. Kamlet et al.[6] have stated that any other reasonable set of primary indicators would lead to very similar solvent π^* values. It has in fact been found that a scale based on azo dyes has resulted in an overall similar set of solvent $\pi^*_{\rm azo}$ values. However, when we correlate with various phenomena dealing with solute–solvent interactions, the $\pi^*_{\rm azo}$ scale relates especially well with interactions dealing with azo compounds, while the π^* scale correlates well with interactions dealing with nitro compounds, as expected. We have certainly advanced from a situation wherein a potential investigator was faced with a plethora of solvent polarity scales based on a single parameter approach to a better stage wherein appropriate solvent polarity scales based on the averaged spectral behavior of a set of solutes, with the incorporation of specific and nonspecific interactions, are available. Nevertheless, the domain of a "reasonable solute set" is not clearly defined. Two possible avenues are thus open for future work.

(a) Proposal of a Universal Scale. It would be worthwhile to devise a representative "Universal Set" of solutes comprising representative solutes from important familes of compounds. This primary set (the Universal Set) could possibly include about 25 solutes from various families such as nitroaromatics, azo dyes, sulfur and phosphorous derivatives, polyenes, polyines, etc. This primary set of solutes could then be used to measure their spectral or chemical properties (reaction rate, equilibrium constant, position or intensity of spectral absorption, etc.) which could then be employed to design a $\pi^*_{\rm U}$ (Pi Star Universal) scale. This scale would serve as a Universal Scale, thus minimizing the burden of a potential investigator in solvent effects in choosing from a multitude of solvent property scales.

(b) Proposal of Diversified Scales. Alternatively, diversified scales pertaining to important classes of compounds could be formulated, if the Universal Scale, $\pi^*_{\rm U}$, becomes impractical. For instance, a series of $\pi^*_{\rm X}$ scales could be formulated where X represents different families of commonly occurring compounds. This set of diversified scales would probably be less desirable than a Universal scale but could more accurately predict the behavior of diverse compounds.

Experimental Section

The azo merocyanines **1**–**6** were synthesized either by known procedures or by slightly modified methods. Details of the preparation of **1**–**6** and their ^{1}H NMR characteristics are described in a separate paper.[25]

The solvents used in this study were of spectrophotometric grade quality whenever possible. The following spectrometric grade solvents were used without further purification: hexanes (M_r 86.18, bp 68–69 °C), chlorobenzene, ethyl acetate, monoglyme, methyl acetate, 1,2-dichloroethane, dichloromethane, benzonitrile, *N,N*-dimethylacetamide, *N,N*-dimethylformamide, 1-propanol, and 1,4-dioxane (Aldrich); toluene, benzene, chloroform, 2-butanone, acetone, dimethyl sulfoxide, acetonitrile, methanol, ethanol, and cyclohexane (BDH). Diethyl ether, nitrobenzene, pyridine, and nitromethane (Aldrich) were distilled before use. Hexamethylphosphoramide (HMPA) and *N,N'*-(dimethylpropylene)urea (DMPU, Fluka) were used without further purification.

The above solvents were chosen from a broad spectrum of solvents ranging from 32.6 to 63.1 in their $E_{\rm T}$ scale and grouped into three sets as follows: set 1 ($E_{\rm T}$ 30 to 40), solvent numbers 0 to 10; set 2 ($E_{\rm T}$ 41 to 50), solvent numbers 11 to 22; set 3 ($E_{\rm T}$ 51 to 65), solvents numbers 23 to 27.

Due to varying solubility of the azo merocyanines **1**–**6** in the above solvents, a cosolvent was chosen in each set to prepare stock solutions: chloroform in set 1, acetone in set 2, and ethanol in set 3. Aliquots of 5 μL of the stock solution (1×10^{-2} M) were added to 2 mL of solvent placed in a quartz cuvette and the UV–vis spectra were scanned over the range 320–780 nm using a Perkin-Elmer Lambda 5 spectrophotometer equipped with a thermostatted cell holder. The presence of the cosolvent (0.25%) did not alter the spectra detectably. The spectrophotometer was routinely calibrated and checked for wavelength accuracy by means of Holmium and Didymium filters before and after measurements. All spectral measurements were performed at 25 °C.

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Registry No. **1**, 6068-47-9; **2**, 117229-50-2; **3**, 38901-87-0; **4**, 117229-51-3; **5**, 68854-61-5; **6**, 101073-38-5; HMPA, 680-31-9; DMPU, 7226-23-5; hexane, 110-54-3; cyclohexane, 110-82-7; ether, 60-29-7; dioxane, 123-91-1; ethyl acetate, 141-78-6; monoglyme, 110-71-4; methyl acetate, 79-20-9; *N,N*-dimethylacetamide, 127-19-5; *N,N*-dimethylformamide, 68-12-2; dimethyl sulfoxide, 67-68-5; 2-butanone, 78-93-3; acetone, 67-64-1; toluene, 108-88-3; benzene, 71-43-2; chlorobenzene, 108-90-7; pyridine, 110-86-1; nitrobenzene, 98-95-3; benzonitrile, 100-47-0; 1,2-dichloroethane, 107-06-2; chloroform, 67-66-3; dichloromethane, 75-09-2; acetonitrile, 75-05-8; nitromethane, 75-52-5; water, 7732-18-5; 1-propanol, 71-23-8; ethanol, 64-17-5; methanol, 67-56-1; *N,N*-diethyl-4-nitroaniline, 2216-15-1; 4-nitroaniline, 100-01-6; 4-nitroanisole, 100-17-4; 4-nitrophenol, 100-02-7; *N,N*-dimethyl-2-nitroaniline, 610-17-3; 2-nitroaniline, 88-74-4; *N,N*-dimethyl-2-nitro-*p*-toluidine, 52262-63-2; 2-nitro-*p*-toluidine, 89-62-3; *N,N*-dimethyl-2-nitro-*p*-anisidine, 60049-83-4; 2-nitro-*p*-anisidine, 96-96-8; Nile Blue A oxazone, 7385-67-3; *N*-methyl-4-nitroaniline, 100-15-2; *N,N*-dimethyl-4-nitroaniline, 100-23-2; *N*-methyl-2-nitroaniline, 612-28-2; ethyl 4-aminobenzoate, 94-09-7; 4-aminobenzophenone, 1137-41-3; 3,5-dinitroaniline, 618-87-1; 3-nitroaniline, 99-09-2; *N*-ethyl-3-nitroaniline, 4319-19-1; *N*-methyl-2-nitro-*p*-toluidine, 4600-08-2; 2-nitrophenol, 88-75-5; 4-nitrophenoxide anion, 14609-74-6; azobenzene, 103-33-3; 4'-methoxyazobenzene, 2396-60-3; 4-nitro-4'-methoxyazobenzene, 29418-59-5; 4'-(*N,N*-dimethylamino)azobenzene, 60-11-7; 3-nitro-4'-(*N,N*-dimethylamino)azobenzene, 3837-55-6; 4-nitro-4'-(*N,N*-dimethylamino)azobenzene, 2491-74-9; 2,4-dinitro-4'-(*N,N*-dimethylamino)azobenzene, 35473-63-3; 4-nitro-2'-*N*-acetylamino-4'-N$(C_2H_4OH)_2$-5'-methoxyazobenzene, 74583-45-2; 2,4-dinitro-2'-*N*-acetylamino-4'-N$(C_2H_4OH)_2$-5'-methoxyazobenzene, 74583-46-3; 2-cyano-4-nitro-6-bromo-2'-*N*-acetylamino-4'-N$(C_2H_4OH)_2$-5'-methoxyazobenzene, 74583-47-4.

Supplementary Material Available: Tables 1–11 listing $\pi^*_{\rm azo}$ and ν(i) values for correlations (16 pages). Ordering information is given on any current masthead page.

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(25) Buncel, E.; Rajagopal, S., to be published.