

Toward a Generalized Treatment of the Solvent Effect Based on Four Empirical Scales: Dipolarity (SdP, a New Scale), Polarizability (SP), Acidity (SA), and Basicity (SB) of the Medium

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This paper reports a methodology for analyzing the solvent effect from empirical measurements of solvent acidity (SA), basicity (SB), dipolarity (SdP), and polarizability (SP). The proposed methodology departs from the traditional single-parameter procedures for estimating nonspecific solvent effects by splitting them into a polarizability term and a dipolarity term. In this work, we examined the SA, SB, SP, and SdP values for 160 solvents, the gas phase (the absence of solvent) being the origin of these scales. As shown in this paper, this information allows one not only to accurately describe the solvent effect experienced by any solute—whether polar or nonpolar and exhibiting some or no specific interaction with the solvent—but also to understand the nature of the well-known solvent parameters $E_T(30)$, π^* , S' , and SPP, which are frequently used to describe the overall nonspecific contribution of solvents in terms of a single parameter. The high potential of the proposed empirical methodology is illustrated with its application to the solvatochromic analysis of the spectroscopic behavior of molecular chromophores, thus explaining, for example, the influence of solvent effects in the twist intramolecular charge transfer (TICT), the excited-state intramolecular proton transfer (ESIPT), or LASER (light amplification by stimulated emission of radiation) emissions. Also, this methodology is applied to understanding for the indole chromophore the feasible inversion of the electronic nature for the first electronic excited state due to solvent effects.

Introduction

Ever since, in the late 19th century, Berthelot and Saint-Gilles,¹ and Menshutkin,² showed that some solvents deemed inert until then were in fact able to substantially alter the rate of some chemical reactions, the properties of solvents have aroused vast chemical interest and have been the focus of much endeavor at their accurate description. Describing the behavior of a solvent in terms of a single parameter (i.e., by using a global single-parameter scale or one restricted to nonspecific solvent effects) appears to be an inappropriate choice since the parameter in question will be so strongly dependent on the particular probe used to establish the single parameter scale concerned that it will lack the ability to predict the behavior of other solutes with significantly different properties from those of the probe.

Overall, the solvent effect can be split into two different types of contributions, namely:

(a) *Specific interactions*, which were described by Drago et al.³ as localized donor–acceptor interactions involving specific orbitals, and parametrized via Gutman's AN and DN scales,⁴ Drago's E_B and C_B scales;⁵ and as *acid–base interactions* involving hydrogen bonding by Kamlet and Taft,⁶ and parametrized via Koppel and Palm's $B(\text{MeOD})$,⁷ Arnett's ΔH_f scale,⁸ Kamlet and Taft's α and β ,⁶ Maria and Gal's $\Delta H(\text{BF}_3)$,⁹ and Catalán and co-workers' SA and SB scales.¹⁰

(b) *Nonspecific interactions* (viz., those arising from the solvent acting as a dielectric continuum), which were originally modeled by Kirkwood¹¹ and Onsager,¹² and have been empirically parametrized via, for example, Kosower's Z scale;¹³ Brooker's χ_R scale;¹⁴ Dong and Winnick's Py scale;¹⁵ Kamlet,

Abboud, and Taft's π^* scales;¹⁶ Dragos's S' scale;¹⁷ and Catalán and co-workers' SPP scale.¹⁸

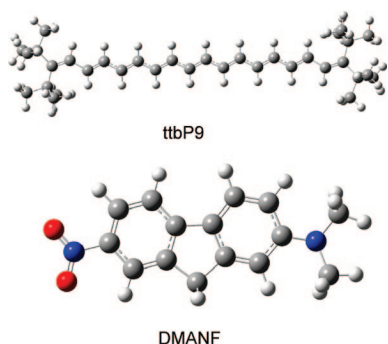
Interested readers can find a comprehensive discussion of this topic in Chapter 7 of ref 19 and also in refs 20–22.

While multiparameter procedures simultaneously using scales that describe specific and general effects have provided excellent results in the analysis of the solvent effect, there is also experimental evidence of some shortcomings especially prominent among which is their inability to describe the solvatochromic behavior of nonpolar solutes exhibiting no specific interaction with the solvent. Therefore, a solvatochromic behavior exclusively predicted in terms of changes in solvent polarizability cannot be accurately described by the parameters of the different empirical scales, which reflect a mixed effect of solvent dipolarity and polarizability at best.

One paradigmatic example of this situation was exposed in 1990 by Abe²³ in examining the 0–0 components of the $^1\text{L}_a$ transition for anthracene previously determined by Nicol et al.²⁴ in 16 solvents and finding that they were not accurately described by Kamlet and Taft's π^* parameter. Abe used the previous data for the 16 solvents to determine new π^* parameters which he designated π_2^* and expected to be more sensitive to polarizability. However, the proponents of the original π^* scale had previously considered the need to deal with solvent polarizability more flexibly by including a “polarizability correction term”, δ ,²⁵ ranging from 0.0 for nonchlorinated aliphatic solvents through 0.5 for polychlorinated solvents to 1.0 for aromatic solvents; in this way, they used an alternative ($\pi^* + d\delta$) scale. Abe's π_2^* is not the sole polarizability scale reported so far; in fact, Buncel and Rajogopal²⁶ developed their own, π_{azo}^* scale in this context.

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SCHEME 1



Abe's proposal²³ of developing a general scale (π^*) to deal with polar solvents and an alternative scale (π_2^*) for nonpolar solvents failed to solve the problem, since polar solutes need not respond identically to both solvent dipolarity and solvent polarizability. This required splitting the general effect into independent polarizability and dipolarity scales. The first successful attempt in this respect was made in 2004 by Catalán and Hopf,²⁷ who found ttbP9 (3,20-di-*tert*-butyl-2,2,21,21-tetramethyl-5,7,9,11,13,15,17,19-docosanonene) to exclusively respond to the polarizability of the medium and hence to be insensitive to the solvent acidity, basicity, and dipolarity; this made ttbP9 a useful probe for developing an empirical solvent polarizability scale (SP) based on the measured 0–0 component of its strong $^1A_g \rightarrow ^1B_u$ electronic transition. Spange et al.²⁸ have recently analyzed the solvatochromism of barbiturate dyes in 10 solvents with the SPP and SP scales, and have concluded also that it is necessary to split the two contributions of the general solvent effect, that is, solvent dipolarity and polarizability.

In this work, we expanded the original study to 163 solvents of known dipolarity and developed a general, multiparameter scale for describing the solvent scale based on two specific scales (SA and SB) and two general scales (SP and SdP). Mathematically, the new scheme can be formulated as follows:

$$A = A_0 + bSA + cSB + dSP + eSdP \quad (1)$$

where A denotes a solvent-dependent physicochemical property in a given solvent and A_0 the statistical quantity corresponding to the value of the property in the gas phase; SA, SB, SP, and SdP represent independent, yet complementary, solvent parameters accounting for various types of solute–solvent interactions; and b to e are the regression coefficients describing the sensitivity of property A to the different solute–solvent interaction mechanisms.

Application of the proposed scheme to the spectroscopic behavior of the anthracene chromophore afforded several interesting conclusions as shown later on. Also it will be applied to understanding the awkward results published either on solvatochromism of the laser dye pyrromethene 567²⁹ or of the molecular probe 10-hydroxybenzo[*h*]quinoline.³⁰ Finally, we will examine the interesting solvatochromic behavior of the indole molecule.³¹

Experimental and Theoretical Section

The ttbP9 and DMANF (2-*N,N*-dimethylamino-7-nitrofluorene) samples used in this work (see (Scheme 1) were those previously employed to develop the SP²⁷ and SPP scales.¹⁸ All solvents used were purchased in the highest available grade from either Aldrich, Fluka, or Merck. UV/vis measurements were made on a newly calibrated Cary 5 spectrophotometer with reproducibility better than 0.05 nm and a precision better than

± 0.1 nm in wavelength. The instrument was routinely checked for wavelength accuracy by using holmium oxide and didymium filters. All spectral measurements were made at 20 °C, using a matched pair of quartz cells 1 cm in path length.

The maximum absorption wavelength for the 0–0 component of the first electronic transition of ttbP9, $^1A_g \rightarrow ^1B_u$, and the absorption maximum for the first electronic transition in DMANF, in each solution were determined from derivative functions. Each result given here was the average of two spectra the maxima of which differed by not more than 0.1 nm. Also, the tabulated wavenumbers are direct conversions of the corresponding λ values. Table 1 collects the $\bar{\nu}_{\text{ttbP9}}$ and $\bar{\nu}_{\text{DMANF}}$ values in the new solvents studied.

The anthracene was 99% pure and obtained from Aldrich; the maximum absorption wavelength for its first electronic transition, 1L_a , in the solvents where ttbP9 was insoluble (viz. water, formamide, diols, and triols) was determined in the same manner as those for ttbP9. Because anthracene was additionally insoluble in water at 20 °C, we recorded its spectrum at temperatures from 40 to 60 °C, where it is partially soluble, and extrapolated the results to 20 °C. In glycerin, where anthracene is also insoluble at 20 °C, the solute was dissolved at 80 °C and the temperature then slowly lowered to the lower value. We should note that the first absorption band for anthracene in glycerin at 80 °C was not changed by the decrease in temperature, which allowed the spectrum at 20 °C to be directly obtained; also, the spectrum retained its envelope and intensity after 4 h at 20 °C.

The values for parameter SP as determined from the following expression:

$$SP_{\text{solvent}} = (\bar{\nu}_{\text{gas}} - \bar{\nu}_{\text{solvent}}) / (\bar{\nu}_{\text{gas}} - \bar{\nu}_{\text{CS2}}) = (23975 - \bar{\nu}_{\text{solvent}}) / 3530 \quad (2)$$

Table 2 collects the parameter values of the four scale parameters for all solvents; most were determined by our group in this or previous work.^{10,18,20,27,32–34}

The calculations for ANF (2-amino-7-nitrofluorene) and DMANF were done within the framework of the HF theory for the ground electronic state, S_0 , and the CIS theory³⁵ for the first singlet excited state of π, π^* nature [viz., $1(\pi, \pi^*)^1$], using the 6-31G** basis set³⁶ in the Gaussian software package.³⁷ Both the ground and the $1(\pi, \pi^*)^1$ excited electronic state were subjected to full geometry optimization and the results checked to be true minima by analyzing their respective vibrational frequencies.

Results and Discussion

This section starts by emphasizing the excellent properties of DMANF as a probe for the general solvent effect and then focuses on the development of the new empirical dipolarity scale. Finally, it examines existing single-parameter scales in the light of the four solvent scales (SA, SB, SP, and SdP) and provides a detailed description of the spectroscopic behavior of the anthracene, pyrromethene 567, 10-hydroxybenzo[*h*]quinoline, and indole chromophores.

Suitability of the Probes Used: DMANF and ttbP9. As shown previously,²⁷ ttbP9 is an excellent polarizability probe as its $^1A_g \rightarrow ^1B_u$ electronic transition at a constant temperature is exclusively affected by the polarizability of the solvent—not by its acid or basic, or dipolarity properties.^{27,38}

In 1995, our group¹⁸ found DMANF to be an also excellent probe of a high sensitivity to the general solvent effect; thus, its first electronic transition is shifted by more than 4000 cm^{-1} from perfluorohexane to DMSO. Such a high sensitivity can

TABLE 1: Wavenumber (cm⁻¹) for the 0–0 Component, and the Peak of the First Absorption Band, for the Probes ttbP9, and DMANF, Respectively, in the Solvents Studied in This Work

solvent	$\bar{\nu}_{\text{ttbP9}}$	$\bar{\nu}_{\text{DMANF}}$
3-methylpentane	21786	25232
squalane		24730
tridecane		24871
tetradecane		24839
2,2,4-trimethylpentane	21793	24975
cyclopentane	21661	24759
cycloheptane	21494	24759
cyclooctane	21435	24661
2-butanol	21660	
2-pentanol	21622	
2-hexanol	21563	
2-octanol	21520	
cyclopentanol	21363	
cyclooctanol	21234	
2-phenylethanol	20979	
2-methyl-1-propanol	21655	
2-methyl-2-propanol	21745 ^a	
1,2-propanediol		23220
1,2-butanediol	21433	
1,3-butanediol	21368	
1,4-butanediol	21283	
2,3-butanediol		23320
1,2,3-propanetriol		22693
ethylbenzene	21248	
propylbenzene	21267	
butylbenzene	21275	
tert-butylbenzene	21302	
m-xylene	21253	
p-xylene	21229	
1,2,3,5-tetramethylbenzene	21206	
aniline		22167
1-methylnaphthalene		22966
1-bromonaphthalene		22435
diisopropyl ether	21769	24648
propyl ether	21697	24614
n-butyl ether	21603	
dihexyl ether	21572	24561
triacetin	21381	
eucalyptol		24075
1,2-dimethoxyethane	21575	23895
cyclohexanone	21271	
2-butanone	21613	
tert-butyl methyl ether	21780	
γ-butyrolactone	21239	
N,N-diethylformamide	21345	
N,N-diethylacetamide	21336	
1,1,3,3-tetramethylurea	21228	
1,1,3,3-tetramethylguanidine		23202
sulfolane	21044	
butyl acetate	21595	
methyl salicylate	20999	22910
ethyl salicylate	21084	23123
chloroacetonitrile	21281	
propanenitrile	21639	
butanenitrile	21595	
pentanenitrile	21517	
trimethyl phosphate	21478	
1-methylpiperidine	21475	
1-methylpyrrolidine	21462	
piperidine	21312	
1,4-dimethylpiperazine	21399	
N-methylimidazole	21031	
butylamine	21539	
dibutylamine	21533	
1,1,1-trichloroethane		23816
1,1,2-trichloroethane	21871	
1,1,2,2-tetrachloroethane	20991	
propanoic acid	21632	
butanoic acid	21591	
pentanoic acid	21550	
hexanoic acid	21512	
heptanoic acid	21491	
2-methylpropanoic acid	21650	
2-methylbutyric acid	21552	
hexamethylphosphoramide	21347	
3-methylbutyric acid	21611	
carbon disulfide		23419

^a At 30 °C 21 773 cm⁻¹.

be ascribed to the facts that its unmethylated counterpart, ANF (2-amino-7-nitrofluorene), is a polar structure (5.8 D) in the ground electronic state, and that electronic excitation increases its dipole moment by 18 D according to Lippert.³⁹ In addition, its dipole moment in the first excited state has been measured to be 23 D.⁴⁰ Based on the foregoing, both dipole moments must retain their orientation in this stiff molecular structure;⁴¹ also, this structure, which is highly polarizable, must substantially increase in polarity by effect of electronic excitation, as indeed confirmed by theoretical results. In fact, the theoretical data of Table 3 confirm that both ANF and DMANF undergo an increase in dipole moment (by 6.1 and 6.7 D, respectively) and polarizability (by 10.5 and 12.4 Å³, respectively) upon electronic excitation. Consequently, the bathochromic shift in the transition of DMANF is clearly the result of a combined increase in solvent dipolarity and polarizability. As a result, both effects must stabilize the excited electronic state more markedly than the ground state, thereby shifting the electronic transition for the probe to the red region of the spectrum.

Solvent Dipolarity Scale (SdP). If ttbP9 allows one to measure solvent polarizability, and DMANF generously measures the dipolarity and polarizability jointly, comparing data obtained with the two probes can obviously help one identify those solvents exclusively influencing the probe via their polarizability; such solvents must exhibit a linear behavior and include the gas phase (i.e., the absence of solvent). The shift undergone by DMANF by effect of the solvent polarizability, which should be consistent with such linear behavior, would be augmented by effect of the solvent dipolarity, which would cause the measured frequency for the electronic transition of DMANF in the solvent to depart from the linear behavior. As can clearly be seen from Figure 1, the gas phase and the alkane solvents (also included in Table 2, following the numbering 1, 62, 74, 75, 83, 93, 98, 99, 112, 113, 116, 128, 130, 131, 140, 147, 148, 149, 153, 155, 158, 160, 161, 162, and 13) follow the linear trend described by eq 3:

$$\bar{\nu}_{\text{solv}}^0 = (-4887.45 \pm 44) \cdot \text{SP}_{\text{solv}} + (28224.6 \pm 28) \quad (3)$$

with $n = 25$, and $r = 0.9991$.

In fact, the points for tetrachloromethane and carbon disulfide fit this linear equation very closely. We assigned this body of 26 solvents plus the gas phase an SdP value of zero. Clearly, the points for the other solvents departed from the linear behavior to an extent increasing with increase in dipolarity. This behavior allows one to assess, via the departure from the above-described linear trend due to the solvent polarizability alone, a part of the general behavior of a solvent which, based on its largely involving the dipolarity of the solvent, we shall designate solvent dipolarity (SdP). This effect was assessed by using the following equation:

$$\text{SdP} = (\bar{\nu}_{\text{solv}}^0 - \bar{\nu}_{\text{solv}}) / (\bar{\nu}_{\text{DMSO}}^0 - \bar{\nu}_{\text{DMSO}}) = (\bar{\nu}_{\text{solv}}^0 - \bar{\nu}_{\text{solv}}) / 1611 \quad (4)$$

where $\bar{\nu}_{\text{solv}}^0$ and $\bar{\nu}_{\text{DMSO}}^0$ are the terms representing the solvent and DMSO polarizability as evaluated via eq 3, and $\bar{\nu}_{\text{solv}}$, and $\bar{\nu}_{\text{DMSO}}$ are the frequencies of the first electronic transition of the probe DMANF in the solvent concerned and in DMSO, respectively. Table 2 lists the SdP values obtained for the studied solvents; as can be seen, they spanned the range from 0.0 for the gas phase to 1.0 for DMSO.

It should be noted that various solvents including water, trifluoroethanol, formamide, and some diols and triols, precluded studying the behavior of the probes as they were insoluble in

TABLE 2: Normalized SP, SdP, SA, and SB Data Values for Each of the 163 Solvents Studied and Gas Phase

no.	solvents	SP	SdP	SA	SB	no.	solvents	SP	SdP	SA	SB
1	gas phase	0.000	0.000	0.000	0.000	83	C ₆ F ₁₄ , perfluorohexane	0.339	0.000	0.000	0.057
2	H ₂ O, water	0.681	0.997	1.062	0.025	84	C ₆ H ₄ Cl ₂ , 1,2-dichlorobenzene	0.869	0.676	0.033	0.144
3	CCl ₄ , tetrachloromethane	0.768	0.000	0.000	0.044	85	C ₆ H ₃ Br, bromobenzene	0.875	0.497	0.000	0.192
4	CS ₂ , carbon disulfide	1.000	0.000	0.000	0.104	86	C ₆ H ₅ Cl, chlorobenzene	0.833	0.537	0.000	0.182
5	CHCl ₃ , chloroform	0.783	0.614	0.047	0.071	87	C ₆ H ₅ F, fluorobenzene	0.761	0.511	0.000	0.113
6	CH ₂ Cl ₂ , dichloromethane	0.761	0.769	0.040	0.178	88	C ₆ H ₅ NO ₂ , nitrobenzene	0.891	0.873	0.056	0.240
7	CH ₃ NO, formamide	0.814	1.006	0.549	0.414	89	C ₆ H ₆ , benzene	0.793	0.270	0.000	0.124
8	CH ₃ NO ₂ , nitromethane	0.710	0.954	0.078	0.236	90	C ₆ H ₇ N, aniline	0.924	0.956	0.132	0.264
9	CH ₄ O, methanol	0.608	0.904	0.605	0.545	91	C ₆ H ₅ NO, <i>N,N</i> -dimethylacetamide	0.763	0.987	0.028	0.650
10	C ₂ Cl ₃ F ₃ , 1,1,2-trichlorotrifluoroethane	0.596	0.152	0.000	0.038	92	C ₆ H ₇ N, cyclohexanone	0.766	0.745	0.000	0.482
11	C ₂ H ₂ ClN, chloroacetoneitrile	0.763	1.024	0.445	0.184	93	C ₆ H ₁₂ cyclohexane	0.683	0.000	0.000	0.073
12	C ₂ H ₂ Cl ₄ , 1,1,2,2-tetrachloroethane	0.845	0.792	0.000	0.017	94	C ₆ H ₁₂ O ₂ , butyl acetate	0.674	0.535	0.000	0.525
13	C ₂ H ₃ Cl ₃ , 1,1,1-trichloroethane	0.737	0.500	0.000	0.085	95	C ₆ H ₁₂ O ₂ , hexanoic acid	0.698	0.245	0.465	0.304
14	C ₂ H ₃ F ₃ O, 2,2,2-trifluoroethanol	0.543	0.922	0.893	0.107	96	C ₆ H ₁₃ N, 1-methylpiperidine	0.708	0.116	0.000	0.836
15	C ₂ H ₃ N, acetonitrile	0.645	0.974	0.044	0.286	97	C ₆ H ₁₃ NO, <i>N,N</i> -diethylacetamide	0.748	0.918	0.000	0.660
16	C ₂ H ₄ Cl ₂ , 1,2-dichloroethane	0.771	0.742	0.030	0.126	98	C ₆ H ₁₄ , hexane	0.616	0.000	0.000	0.056
17	C ₂ H ₄ O ₂ , acetic acid	0.651	0.676	0.689	0.390	99	C ₆ H ₁₄ , 3-methylpentane	0.620	0.000	0.000	0.050
18	C ₂ H ₅ NO ₂ , nitroethane	0.706	0.902	0.000	0.234	100	C ₆ H ₁₄ N ₂ , 1,4-dimethylpiperazine	0.730	0.211	0.000	0.832
19	C ₂ H ₆ O, ethanol	0.633	0.783	0.400	0.658	101	C ₆ H ₁₄ O, diisopropyl ether	0.625	0.324	0.000	0.657
20	C ₂ H ₆ OS, dimethyl sulfoxide	0.830	1.000	0.072	0.647	102	C ₆ H ₁₄ O, dipropyl ether	0.645	0.286	0.000	0.666
21	C ₂ H ₆ O ₂ , 1,2-ethanediol	0.777	0.910	0.717	0.534	103	C ₆ H ₁₄ O, 1-hexanol	0.698	0.552	0.315	0.879
22	C ₃ H ₅ N, propanenitrile	0.668	0.888	0.030	0.365	104	C ₆ H ₁₄ O, 2-hexanol	0.683	0.601	0.140	0.966
23	C ₃ H ₆ O, acetone	0.651	0.907	0.000	0.475	105	C ₆ H ₁₅ N, triethylamine	0.660	0.108	0.000	0.885
24	C ₃ H ₆ O, allyl alcohol	0.705	0.839	0.415	0.585	106	C ₆ H ₁₈ N ₃ PO, hexamethylphosphoramine	0.744	1.100	0.000	0.813
25	C ₃ H ₆ O ₂ , ethyl formate	0.648	0.707	0.000	0.477	107	C ₇ H ₅ F ₃ , (trifluoromethyl)benzene	0.694	0.663	0.014	0.073
26	C ₃ H ₆ O ₂ , methyl acetate	0.645	0.637	0.000	0.522	108	C ₇ H ₅ N, benzonitrile	0.851	0.852	0.047	0.281
27	C ₃ H ₆ O ₂ , propanoic acid	0.664	0.434	0.608	0.377	109	C ₇ H ₈ , toluene	0.782	0.284	0.000	0.128
28	C ₃ H ₆ O ₃ , dimethyl carbonate	0.653	0.531	0.064	0.433	110	C ₇ H ₈ O, anisole	0.820	0.543	0.084	0.299
29	C ₃ H ₇ NO, <i>N,N</i> -dimethylformamide	0.759	0.977	0.031	0.613	111	C ₇ H ₉ O, benzyl alcohol	0.861	0.788	0.409	0.461
30	C ₃ H ₈ O, 1-propanol	0.658	0.748	0.367	0.782	112	C ₇ H ₁₄ , cycloheptane	0.703	0.000	0.000	0.050
31	C ₃ H ₈ O, 2-propanol	0.633	0.808	0.283	0.830	113	C ₇ H ₁₄ , methylcyclohexane	0.675	0.000	0.000	0.069
32	C ₃ H ₈ O ₂ , 1,2-propanediol	0.731	0.888	0.475	0.598	114	C ₇ H ₁₄ O, cycloheptanol	0.770	0.546	0.183	0.911
33	C ₃ H ₈ O ₃ , 1,2,3-propanetriol	0.828	0.921	0.653	0.309	115	C ₇ H ₁₄ O ₂ , heptanoic acid	0.704	0.238	0.445	0.328
34	C ₃ H ₉ O ₄ P, trimethyl phosphate	0.707	0.909	0.000	0.522	116	C ₇ H ₁₆ , heptane	0.635	0.000	0.000	0.083
35	C ₄ H ₆ N ₂ , 1-methylimidazole	0.834	0.959	0.069	0.658	117	C ₇ H ₁₆ O, 1-heptanol	0.706	0.499	0.302	0.912
36	C ₄ H ₆ O ₂ , γ -butyrolactone	0.775	0.945	0.057	0.399	118	C ₈ H ₈ O, acetophenone	0.848	0.808	0.044	0.365
37	C ₄ H ₆ O ₃ , propylene carbonate	0.746	0.942	0.106	0.341	119	C ₈ H ₈ O ₂ , methyl benzoate	0.824	0.654	0.000	0.378
38	C ₄ H ₇ N, butanenitrile	0.689	0.864	0.000	0.384	120	C ₈ H ₈ O ₃ , methyl salicylate	0.843	0.741	0.219	0.216
39	C ₄ H ₈ O, 2-butanone	0.669	0.872	0.000	0.520	121	C ₈ H ₁₀ , <i>o</i> -xylene	0.791	0.266	0.000	0.157
40	C ₄ H ₈ O, tetrahydrofuran	0.714	0.634	0.000	0.591	122	C ₈ H ₁₀ , <i>m</i> -xylene	0.771	0.205	0.000	0.162
41	C ₄ H ₈ O ₂ , butanoic acid	0.675	0.333	0.571	0.464	123	C ₈ H ₁₀ , <i>p</i> -xylene	0.778	0.175	0.000	0.160
42	C ₄ H ₈ O ₂ , 1,4-dioxane	0.737	0.312	0.000	0.444	124	C ₈ H ₁₀ , ethylbenzene	0.772	0.237	0.000	0.138
43	C ₄ H ₈ O ₂ , ethyl acetate	0.656	0.603	0.000	0.542	125	C ₈ H ₁₀ O, ethoxybenzene	0.810	0.669	0.000	0.295
44	C ₄ H ₈ O ₂ , propyl formate	0.667	0.633	0.000	0.549	126	C ₈ H ₁₀ O, 2-phenylethanol	0.849	0.793	0.376	0.523
45	C ₄ H ₈ O ₂ , 2-methylpropionic acid	0.659	0.302	0.515	0.281	127	C ₈ H ₁₀ O ₂ , veratrole	0.851	0.606	0.000	0.340
46	C ₄ H ₈ O ₂ S, sulfolane	0.830	0.896	0.052	0.365	128	C ₈ H ₁₆ , cyclooctane	0.719	0.000	0.000	0.068
47	C ₄ H ₉ Cl, 1-chlorobutane	0.693	0.529	0.000	0.138	129	C ₈ H ₁₆ O, cyclooctanol	0.777	0.537	0.137	0.919
48	C ₄ H ₁₀ N, butylamine	0.690	0.296	0.000	0.944	130	C ₈ H ₁₈ , octane	0.650	0.000	0.000	0.079
49	C ₄ H ₁₀ O, 1-butanol	0.674	0.655	0.341	0.809	131	C ₈ H ₁₈ , 2,2,4-trimethylpentane	0.618	0.000	0.000	0.044
50	C ₄ H ₁₀ O, 2-butanol	0.656	0.706	0.221	0.888	132	C ₈ H ₁₈ O, dibutyl ether	0.672	0.175	0.000	0.637
51	C ₄ H ₁₀ O, diethyl ether	0.617	0.385	0.000	0.562	133	C ₈ H ₁₈ O, 1-octanol	0.713	0.454	0.299	0.923
52	C ₄ H ₁₀ O, 2-methyl-1-propanol	0.657	0.684	0.311	0.828	134	C ₈ H ₁₈ O, 2-octanol	0.696	0.496	0.088	0.963
53	C ₄ H ₁₀ O, 2-methyl-2-propanol	0.632	0.732	0.145	0.928	135	C ₈ H ₁₉ N, dibutylamine	0.692	0.209	0.000	0.991
54	C ₄ H ₁₀ O ₂ , 1,2-butanediol	0.724	0.817	0.466	0.668	136	C ₉ H ₁₀ O ₃ , ethyl salicylate	0.819	0.681	0.118	0.236
55	C ₄ H ₁₀ O ₂ , 1,3-butanediol	0.739	0.873	0.429	0.610	137	C ₉ H ₁₂ , propylbenzene	0.767	0.209	0.000	0.144
56	C ₄ H ₁₀ O ₂ , 1,4-butanediol	0.763	0.864	0.424	0.598	138	C ₉ H ₁₂ , mesitylene	0.775	0.155	0.000	0.190
57	C ₄ H ₁₀ O ₃ , 2,3-butanediol	0.714	0.877	0.461	0.652	139	C ₉ H ₁₄ O ₆ , triacetin	0.735	0.686	0.023	0.416
58	C ₄ H ₁₀ O ₂ , 1,2-dimethoxyethane	0.680	0.625	0.000	0.636	140	C ₉ H ₂₀ , nonane	0.660	0.000	0.000	0.053
59	C ₅ H ₅ N, pyridine	0.842	0.761	0.033	0.581	141	C ₉ H ₂₀ O, 1-nonanol	0.717	0.429	0.270	0.906
60	C ₅ H ₉ N, pentanenitrile	0.696	0.853	0.000	0.408	142	C ₁₀ H ₇ Br, 1-bromonaphthalene	0.964	0.669	0.000	0.202
61	C ₅ H ₉ NO, 1-methyl-2-pyrrolidinone	0.812	0.959	0.024	0.613	143	C ₁₀ H ₁₂ , 1,2,3,4-tetrahydronaphthalene	0.838	0.182	0.000	0.180
62	C ₅ H ₁₀ , cyclopentane	0.655	0.000	0.000	0.063	144	C ₁₀ H ₁₄ , butylbenzene	0.765	0.176	0.000	0.149
63	C ₅ H ₁₀ O, cyclopentanol	0.740	0.673	0.258	0.836	145	C ₁₀ H ₁₄ , <i>tert</i> -butylbenzene	0.757	0.182	0.000	0.171
64	C ₅ H ₁₀ O, 2-methyltetrahydrofuran	0.700	0.768	0.000	0.584	146	C ₁₀ H ₁₄ , 1,2,3,5-tetramethylbenzene	0.784	0.203	0.000	0.186
65	C ₅ H ₁₀ O, 2-pentanone	0.689	0.783	0.010	0.537	147	C ₁₀ H ₁₈ , decalin ^a	0.744	0.000	0.000	0.056
66	C ₅ H ₁₀ O, 3-pentanone	0.692	0.785	0.000	0.557	148	C ₁₀ H ₁₈ , <i>cis</i> -decalin	0.753	0.000	0.000	0.056
67	C ₅ H ₁₀ O ₂ , 2-methylbutyric acid	0.686	0.261	0.439	0.250	149	C ₁₀ H ₂₂ , decane	0.669	0.000	0.000	0.066
68	C ₅ H ₁₀ O ₂ , 3-methylbutyric acid	0.670	0.310	0.538	0.405	150	C ₁₀ H ₁₈ O, 1-decanol	0.722	0.383	0.259	0.912
69	C ₅ H ₁₀ O ₂ , pentanoic acid	0.687	0.276	0.502	0.473	151	C ₁₀ H ₁₈ O, eucalyptol	0.736	0.343	0.000	0.737
70	C ₅ H ₁₀ O ₂ , propyl acetate	0.670	0.559	0.000	0.548	152	C ₁₁ H ₁₀ , 1-methylnaphthalene	0.908	0.510	0.000	0.156
71	C ₅ H ₁₁ N, 1-methylpyrrolidine	0.712	0.216	0.000	0.918	153	C ₁₁ H ₂₄ , undecane	0.678	0.000	0.000	0.080
72	C ₅ H ₁₁ N, piperidine	0.754	0.365	0.000	0.933	154	C ₁₁ H ₂₄ O, 1-undecanol	0.728	0.342	0.257	0.909
73	C ₅ H ₁₁ NO, <i>N,N</i> -diethylformamide	0.745	0.939	0.000	0.614	155	C ₁₂ H ₂₆ , dodecane	0.683	0.000	0.000	0.086
74	C ₅ H ₁₂ , 2-methylbutane	0.581	0.000	0.000	0.053	156	C ₁₂ H ₂₆ O, dihexyl ether	0.681	0.208	0.000	0.618
75	C ₅ H ₁₂ , pentane	0.593	0.000	0.000	0.073	157	C ₁₂ H ₂₈ N, tributylamine	0.689	0.060	0.000	0.854
76	C ₅ H ₁₂ O, butyl methyl ether	0.647	0.345	0.000	0.505	158	C ₁₃ H ₂₈ , tridecane	0.690	0.000	0.000	0.050
77	C ₅ H ₁₂ O, <i>tert</i> -butyl methyl ether	0.622	0.422	0.000	0.567	159	C ₁₄ H ₁₄ O, dibenzyl ether	0.877	0.509	0.000	0.330
78	C ₅ H ₁₂ O, 1-pentanol	0.687	0.587	0.319	0.860	160	C ₁₄ H ₃₀ , tetradecane	0.696	0.000	0.000	0.050
79	C ₅ H ₁₂ O, 2										

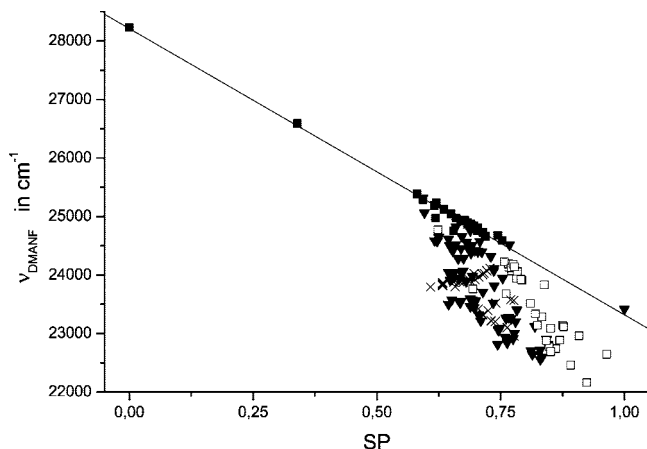


Figure 1. Dipolarity and polarizability effects (ν_{DMANF}) vs polarizability (SP) for the 163 solvents studied: (■) hydrocarbons; (×) alcohols; (□) aromatics; and (▼) other solvents.

TABLE 3: Theoretical Values for the Dipole Moments and Polarizabilities Corresponding to the Ground Electronic State, S_0 , and First Excited Electronic State, S_1 , and Their Two State Increments for the Chromophores ANF and DMANF

compound	state	dipole moment, μ (D)	$\Delta\mu$ (D)	polarizability, α (\AA^3)	$\Delta\alpha$ (\AA^3)
ANF	S_0	7.76	6.06	22.53	10.5
	S_1	13.82		33.03	
DMANF	S_0	8.46	6.74	26.5	12.4
	S_1	15.20		38.9	

some or reacted with others. These shortcomings were circumvented in various ways. Thus, SP for the solvents unable to dissolve ttBP9 were determined from the behavior of the anthracene chromophore as described below. Likewise, SdP for water was estimated from a correlation between this parameter for eleven 1-alcohols from methanol to 1-undecanol and the dipolar reaction field function $\Delta f = [(\epsilon - 1)/(\epsilon + 1)] - (n^2 - 1)/(n^2 + 2)$, where ϵ denotes the static dielectric permittivity and n the refractive index of the solvent as evaluated from the D line for sodium at 20 °C. Such a correlation (5) allows one to establish the SdP data values for water and 2,2,2-trifluoroethanol, that is, 0.997 and 0.992, respectively.

$$\text{SdP} = -2.549\Delta f + 3.913\Delta f^2 + 0.655 \quad (5)$$

with $n = 11$, and $r = 0.997$.

The SdP values for the previous two solvents should be considered secondary values as they were estimated via correlations established from analogues rather than from actual measurements with the DMANF probe. In any case, they are also included in Table 2, which shows the SP, SdP, SA, and SB values for the studied solvents.

Before splitting the general solvent effect into a polarizability term (SP) and a dipolarity term (SdP), we should check whether the two are linearly independent. Figure 2 is a plot of SP versus SdP for the studied solvents; as can clearly be seen, the two are strongly independent—in fact, least-squares fitting of the data provided a coefficient $r^2 = 0.088$.

Analysis of the $E_T(30)$, π^* , S' , and SPP Single-Parameter Scales. The $E_T(30)$ scale⁴² is based on the energy of the first electronic transition in the probe 2,6-diphenyl-4-(2,4,6-triphenylpyridinium-1-yl)phenolate; in its ground state, the charge of the probe is located largely on its oxygen site, which endows

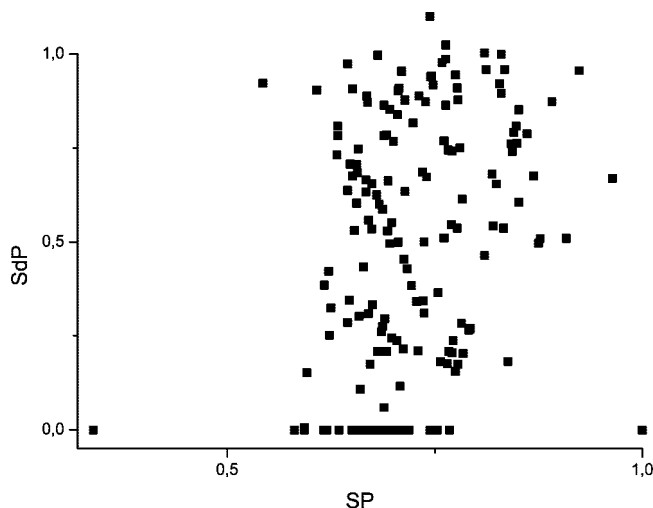


Figure 2. Dipolarity (SdP) vs polarizability (SP) for the 163 solvents studied.

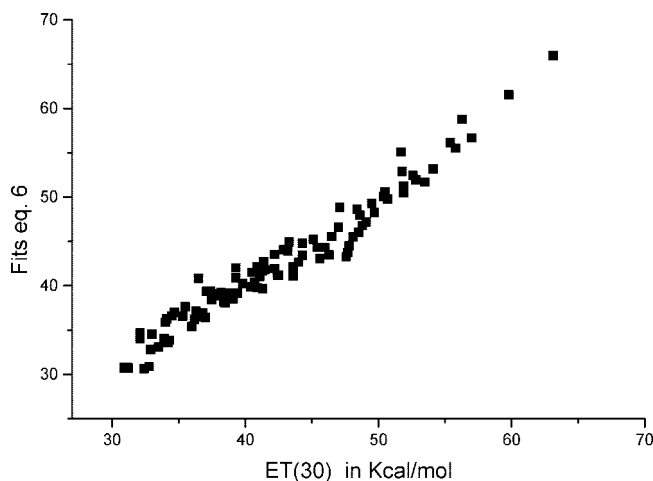


Figure 3. Fits from eq 6 vs the corresponding $E_T(30)$ data values by Reichardt.

it with basic and polar properties. Electronic excitation delocalizes the charge and reduces the dipolarity and basicity of the molecule as a result. Consequently, raising the acidity or dipolarity of the medium should help stabilize much more the ground state of the probe than its first excited electronic state; this in turn should result in a hypsochromic shift in the spectrum for the probe that will increase with increasing acidity or polarity of the medium.

Examining Dimroth and Reichardt's $E_T(30)$ values (specifically, data from Table 7.3 in ref 20 without considering the corresponding data value for the gas phase) in the light of the SA, SB, SP, and SdP values given here revealed that the $E_T(30)$ scale is negligibly sensitive to the basicity of the solvent and, even more surprisingly, insensitive to its polarizability. As can be seen from Figure 3, consistency can be deemed acceptable and, based on eq 6 (with $n = 113$, and $r = 0.9788$),

$$E_T(30) = (23.17 \pm 0.77)\text{SA} + (10.84 \pm 0.53)\text{SdP} + (3.39 \pm 0.56)\text{SB} + (30.50 \pm 0.36) \quad (6)$$

this scale is much more sensitive to the acidity of the medium than to its dipolarity.

Interestingly, based on eq 6, $E_T(30)$ for the gas phase should be 30.50 kcal/mol, which differs little from the 27.1 kcal/mol calculated by Reichardt.¹⁹ Such a value, however, is in sheer

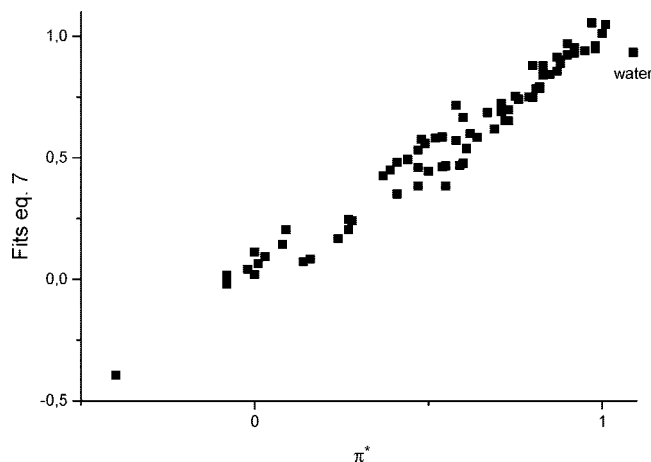


Figure 4. Fits from eq 7 vs the corresponding π^* data values by Kamlet and Taft.

contradiction with that recently estimated by Renge:⁴³ 40.3 ± 2 kcal/mol [i.e., one in the middle of the $E_T(30)$ scale, which ranges from 30.7 kcal/mol for tetramethylsilane to 63.1 kcal/mol for water].

It is important to point out that the $E_T(30)$ scale depends mostly on the acidity (eq 6), and to a lesser extent on dipolarity, which is consistent with the bibliography published. That is, on the one hand, Marcus⁴⁴ (using the Taft–Kamlet π^* , α , and β parameters) and we²⁰ (using the SPP, SA, and SB scales) show that the most important solvent interaction described by the $E_T(30)$ scale is due to solvent acidity; on the other hand, Bekárek et al.⁴⁵ and Makitra et al.⁴⁶ established, by considering a set of no acid solvents, that the $E_T(30)$ scale is mostly sensitive to the Kirkwood function, $f(\epsilon_r) = (\epsilon_r - 1)/(2\epsilon_r + 2)$, and shows little sensitivity to the Lorenz–Lorentz function, $f(n^2) = (n^2 - 1)/(n^2 + 2)$.

As can be seen from Figure 4, the π^* values of Taft and Kamlet taken from refs 25 and 47 provide a major description of solvent polarizability and dipolarity, but unexpectedly it is slightly contaminated by solvent acidity and basicity. It is also interesting to point out that the corresponding value for water deviates significantly from the correlation shown in Figure 4, and this does not occur for the $E_T(30)$ scale as shown in Figure 3.

Based on the fitting to eq 7 (with $n = 78$, and $r = 0.9798$),

$$\pi^* = (1.48 \pm 0.09)SP + (0.74 \pm 0.03)SdP - (0.11 \pm 0.03)SB + (0.08 \pm 0.04)SA - (0.89 \pm 0.06) \quad (7)$$

the π^* scale mostly reflects a mixture of solvent dipolarity and, very especially, polarizability. As a consequence, Taft's intelligent introduction of factor δ can turn artificially the π^* scale into a virtually pure polarizability scale; see eq 8.

$$\pi^* + \delta = (4.68 \pm 0.42)SP + (0.50 \pm 0.13)SdP - (0.53 \pm 0.14)SB + (0.24 \pm 0.18)SA - (2.66 \pm 0.29) \quad (8)$$

The independent term in eq 7, -0.89 ± 0.07 , can shed some light on the various attempts at placing the gas phase in the π^* scale. Thus, based on a UV/vis analysis, Bekárek⁴⁸ estimated a π^* value of -0.58 to -0.51 for the absence of solvent; Abraham et al.⁴⁹ one of -0.61 to -0.55 from the heterolytic decomposition of *tert*-butyl halides and another of -0.44 based on the equilibria of 4-*tert*-butylcyclohexanes;⁵⁰ and Essafar et al.⁵¹ one of -1.06 based on UV/vis spectroscopic data for the gas phase of some solvents originally used to construct the scale.

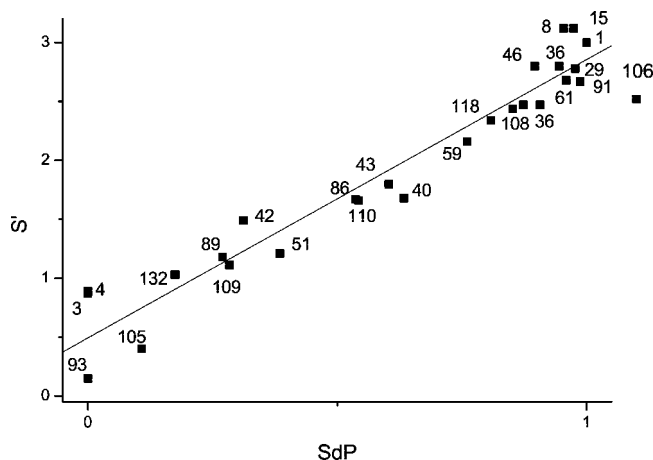


Figure 5. S' vs SdP data values for the 27 solvents originally studied by Drago (to identify the solvents see numeration in Table 2).

TABLE 4: Square Correlation Coefficients for the Fits between Each Pair of Solvent Scales

	SdP	SA	SB
SP	0.088	0.005	0.001
SdP		0.120	0.129
SA			0.034

In 1992, Drago¹⁷ proposed a new scale which he called the unified scale of solvent polarity, S' , and developed from an exhaustive statistical analysis of previously reported experimental evidence. Interestingly, the S' values for the 27 solvents he studied were exclusively dependent on SdP, with a correlation coefficient $r = 0.961$; see Figure 5. In 1994, Drago⁵² obtained the S' values for a further four solvents and corrected those previously reported for various others; in any case, the body of solvents continues to be accurately described by our SdP alone ($r = 0.968$). If the data set is expanded with the S' values for hydroxyl solvents reported in 1997,⁵³ which the authors deemed quite accurate, then the body of values continues to depend exclusively on SdP, but correlation is now significantly lower ($r = 0.8871$); this is largely a result of the S' value for acetic acid, which was clearly an outlier. Excluding such a value improves the fitting and raises correlation to $r = 0.9116$. However, if the S' values for other solvents⁵⁴ such as hydrocarbon solvents as determined by correlation with their corresponding Hildebrand solubility parameters are included, no fitting is any longer possible to any of the four scales. This clearly appears to be the result of S' being exclusively sensitive to the solvent dipolarity, so introducing any solvents where only polarizability is variable precludes a joint description of both properties.

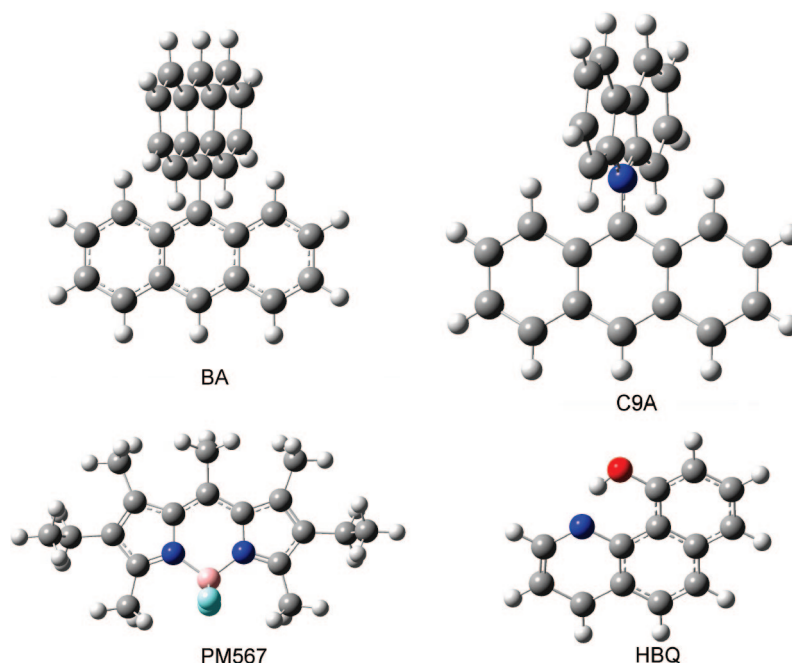
The SPP data were also highly correlated with SP and SdP for the whole body of solvents. The SPP scale is a highly balanced mixture of both effects (see eq 9, with $n = 159$, and $r = 0.9597$)

$$SPP = (0.49 \pm 0.03)SP + (0.38 \pm 0.01)SdP + (0.21 \pm 0.02) \quad (9)$$

which is probably the origin of its ability to describe the general solvent effect, provided the solute concerned exhibits both effects, obviously.

Proposed Empirical Scheme and the Anthracene Solvatochromism. Based on the r^2 values of Table 4, the four scales used to obtain an empirical description of the solvent effect (SA, SB, SP, and SdP) can be deemed orthogonal to one another.

SCHEME 2



Therefore, any solvent effect involving a polar or nonpolar solute interacting in a specific or nonspecific manner with the solvent can in theory be examined in the light of the four scales (specifically, with eq 1). Obviously, if a solvent alters the structure of a solute, such scales, and no other, should provide an accurate description of the effect. What follows is a discussion of some spectroscopic evidence for the anthracene chromophore of special significance to the solvent effect.

In 1968, Nicol et al.²⁴ determined the 0–0 component for the 1L_a transition of anthracene in 46 different solvents in order to check existing theories on the solvent effect in terms of a dielectric continuum model for the solution; they concluded that the function $(n^2 - 1)/(2n^2 + 1)$ allowed solvents to be classified into various families (viz., hydrocarbons, halogenated hydrocarbons, alcohols, and ketones). As noted earlier, accurately describing these data in terms of single-parameter scales such as $E_T(30)$, π^* , or SPP is impossible; in fact, the corresponding correlation coefficients for the three scales (0.30, 0.76, and 0.78) are too low by effect of anthracene being a nonpolar solute.

As expected, the SP and SdP scales provide a highly accurate description of the spectral behavior of anthracene in the studied solvents; also, the blue shift in the compound is largely the result of the increase in polarizability and, to a lesser extent, also in dipolarity, of the solvent:

$$\bar{\nu}_{\text{anthracene}}^{0-0} = (-1577.8 \pm 18.3)\text{SP} - (38.5 \pm 7.3)\text{SdP} + (27655 \pm 12) \quad (10)$$

with $n = 42$, and $r = 0.998$.

It should be noted that the fitting provided by the solvent polarizability alone is so acceptable (see eq 11, with $n = 42$, and $r = 0.996$)

$$\bar{\nu}_{\text{anthracene}}^{0-0} = (-1612.7 \pm 22.1)\text{SP} + (27660 \pm 15) \quad (11)$$

that the SP scale can be used to empirically estimate this property in those cases where the probe ttbP9 is insoluble or reacts with the solvent (e.g., water, formamide, 1,2-propanediol, 1,2-butanediol, 2,3-butanediol, and 1,2,3-propanetriol). Equation 11 allowed us to estimate the SP values for these solvents, which

were found to be 0.681, 0.810, 0.731, 0.724, 0.714, and 0.828, respectively, from the corresponding measured 0–0 components (viz., 26 562, 26 353, 26 481, 24 493, 26 509, and 26 324 cm^{-1} , respectively). These SP data are deemed the most appropriate for the previous solvents among those in Table 2.

Anthracene covalently bonded to another aromatic system such as another anthracene molecule in bianthracene (BA) or to a carbazole ring as in carbazole 9-anthracene (C9A) (Scheme 2) exhibits an unusual spectroscopic behavior. Because of their steric hindrance, these systems tend to have their two rings in a nearly orthogonal arrangement (i.e., at an inter-ring twist angle close to 90°).

Schneider and Lippert⁵⁵ found the fluorescence of BA to change markedly with the polarity and viscosity of the medium or even to exhibit dual fluorescence in some solvents; they assigned the new fluorescence to a mechanism called TICT. Because the greatest differences occurred in the excited electronic state, the phenomenon has usually been examined via the corresponding Stokes shifts; as a result, the effect of the solvent on the absorption of these aromatic systems has been almost invariably ignored.

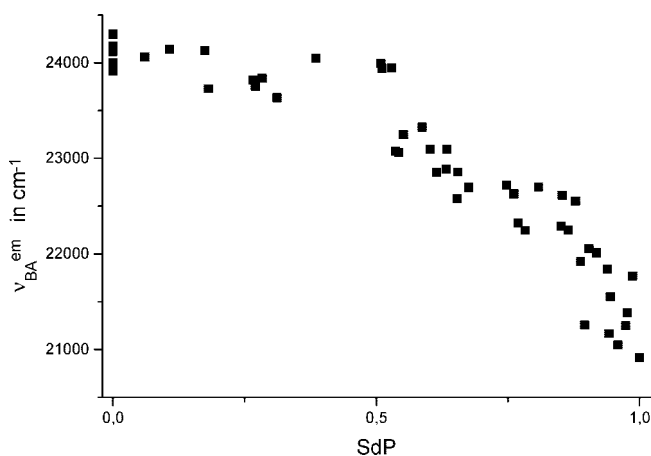


Figure 6. $\bar{\nu}_{\text{BA}}^{\text{em}}$ vs the SdP data values for 55 solvents.

It seems obvious that, if two aromatic fragments lie virtually normal to each other in the ground electronic state, their mutual perturbation must be near zero and the compound follow the same known spectroscopic patterns for the anthracene chromophore (i.e., the absorption should be largely dictated by the solvent polarizability). This is the situation reflected by eq 12 (with $n = 55$, and $r = 0.989$),

$$\bar{\nu}_{\text{abs}} = (-1543.5 \pm 35)\text{SP} - (26 \pm 9)\text{SdP} + (26740 \pm 24) \quad (12)$$

from experimental data reported in ref 56.

The situation, however, changes dramatically when one examines the emission of the compound, which is absolutely independent of the solvent polarizability and described by changes in solvent dipolarity alone. The most interesting finding, however, is that, as can be seen from Figure 6, the behavior of the compounds in the 55 solvents (experimental data from ref 55) was, as previously also found by Schneider and Lippert,⁵⁵ bilinear (see also ref 56).

The BA molecule is the result of covalently bonding two identical nonpolar aromatic fragments and its absorption behavior is identical with that of the anthracene monomer. In C9A, however, the nonpolar anthracene fragment is covalently bonded to a polar aromatic fragment at position 9; this results in decreased symmetry and increased dipolarity in its absorption relative to BA. As can be seen from eq 13 (with $n = 55$, and $r = 0.987$),

$$\bar{\nu}_{\text{abs}} = -(1428.5 \pm 37.7)\text{SP} - (100.7 \pm 10.0)\text{SdP} + (26907 \pm 26) \quad (13)$$

the weight of the SdP term for C9A is greater with respect to SP than in BA.

The most salient features of the emission of C9A are that it depends virtually identically on the solvent polarizability and dipolarity, and that, based on eq 14 (with $n = 55$, and $r = 0.975$)

$$\bar{\nu}_{\text{em}} = -(2313 \pm 335)\text{SP} - (2385 \pm 89)\text{SdP} - (25523 \pm 233) \quad (14)$$

it is linear for the whole range of solvent studied. Therefore, only the TIC mechanism seemingly operates throughout the whole solvent range for C9A.

Pyrromethene Laser Dye Solvatochromism. In 1998, López-Arbeloa et al.²⁹ studied the solvatochromism of the interesting dye BODIPY 567 (PM567) (see Scheme 2), on the basis of the empirical solvent scales π^* , α , and β , which were developed by Kamlet and Taft, and also on the SPP, SA, and SB scales designed by our research group. The fits obtained using these solvent scales are to be improved significantly; the correlation coefficients assessed by López-Arbeloa et al.²⁹ are only of 0.60 and 0.76 for absorption and of 0.46 and 0.53 for emission, respectively. By fitting the absorption and emission data values of PM567 to the eqs 15 and 16, respectively, the resultant fits have greatly improved those reported previously:

$$\bar{\nu}_{\text{abs}} = -(515 \pm 109)\text{SP} + (264 \pm 26)\text{SdP} - (84 \pm 33)\text{SA} - (54 \pm 28)\text{SB} + (19512 \pm 73) \quad (15)$$

with $n = 24$ and $r = 0.9327$.

$$\bar{\nu}_{\text{em}} = -(506 \pm 110)\text{SP} + (139 \pm 26)\text{SdP} - (168 \pm 33)\text{SA} + (38 \pm 28)\text{SB} + (19008 \pm 73) \quad (16)$$

with $n = 24$ and $r = 0.8521$.

From these solvent coefficients, we can conclude that this chromophore presents a solvatochromism dominated by non-specific interactions, and in special due to polarizability. It is interesting to point out that the solvatochromic data contributed by López-Arbeloa et al. indicate that the first absorption band and the first emission band for PM567 exhibit small wavenumber shifts, for example, on going from 2-methylbutane to methanol, its first absorption band is shifted for 156 cm^{-1} , while the corresponding emission peaks shift only 95 cm^{-1} .

Recently Boens et al.^{57,58} have bonded a pyrromethene derivative to a p-N,N-dimethylamino-benzaldehyde, generating the compound named as **a**, or to a 4-(1,4,7,10)-tetraoxa-13-azacyclopentadec-13-yl)benzaldehyde, generating the compound named as **b**, and these new fluorescent probes may be used for checking the pH or the metal cations in solution. These probes **a** and **b** are more sensitive to the solvent effect than PM567; that is, its first absorption band shifts to the red about 357 and 289 cm^{-1} , respectively, and its emission about 2772 and 2316 cm^{-1} on changing from cyclohexane to DMSO. The analysis published shows that emission energies are fitted adequately either to the Kamlet–Taft scales or to Catalán et al. scales, displaying correlation coefficients of 0.947 and 0.978 for the probe **a**, and 0.938 and 0.978 for the probe **b**, respectively; however, the absorption data are not described correctly, and their correlation coefficients are 0.381 and 0.797, by using the Kamlet–Taft or Catalán et al. scales, respectively. The multi-parametric analysis 1 included in eqs 17 and 18 for the probe **a** and in eqs 19 and 20 for the probe **b** shows, on the contrary, good fits for the same absorption data values:

$$\bar{\nu}_{\text{abs}} = -(2092 \pm 110)\text{SP} - (60 \pm 20)\text{SdP} - (138 \pm 46)\text{SA} + (181720 \pm 76) \quad (17)$$

with $n = 18$, and $r = 0.983$.

$$\bar{\nu}_{\text{em}} = -(1323 \pm 697)\text{SP} - (2440 \pm 127)\text{SdP} + (17337 \pm 483) \quad (18)$$

with $n = 18$ and $r = 0.981$.

$$\bar{\nu}_{\text{abs}} = -(1904 \pm 126)\text{SP} - (67 \pm 29)\text{SB} + (17682 \pm 91) \quad (19)$$

with $n = 18$, and $r = 0.970$.

$$\bar{\nu}_{\text{em}} = -(1084 \pm 595)\text{SP} - (1990 \pm 120)\text{SdP} + (254 \pm 240)\text{SA} - (399 \pm 158)\text{SB} + (16737 \pm 434) \quad (20)$$

with $n = 18$, and $r = 0.979$.

It is important to emphasize the good description achieved in both emission and absorption data values; both are controlled by the general solvent effects, especially for absorption by polarizability and for emission by dipolarity. This distinct behavior guides us to analyze the Stokes' shifts ($\Delta^a\bar{\nu}_{\text{abs-em}}$, and $\Delta^b\bar{\nu}_{\text{abs-em}}$) measured by the probes **a** and **b** for the same set of solvents. It is clearcut that these shifts are adequately described by dipolarity for **a** (eq 21), and by mostly dipolarity for **b** (eq 22).

$$\Delta^a\bar{\nu}_{\text{abs}} = (2346 \pm 124)\text{SdP} + (313 \pm 83) \quad (21)$$

with $n = 18$ and $r = 0.978$.

$$\Delta^b\bar{\nu}_{\text{abs}} = (2009 \pm 112)\text{SdP} - (642 \pm 532)\text{SP} + (240 \pm 125)\text{SB} + (823 \pm 394) \quad (22)$$

with $n = 18$ and $r = 0.981$.

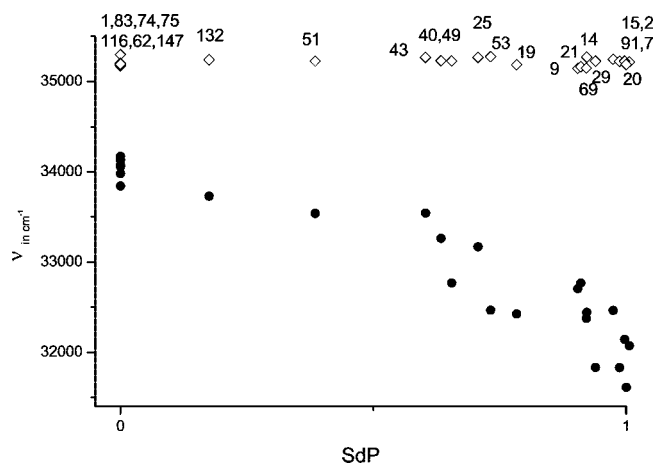


Figure 7. Plot of the $\bar{\nu}_{\text{abs}}(\text{dipolar})$ (\diamond) and $\bar{\nu}_{\text{em}}(\text{dipolar})$ (\bullet) (see text) for indole vs the SdP parameters of the solvents under study (to identify the solvents to see numeration in Table 2).

10-Hydroxybenzo[*h*]quinoline (HBQ) Solvatochromism. In 2001, our laboratory published³⁰ a solvent study on 10-hydroxybenzo[*h*]quinoline (HBQ) (see Scheme 2), a probe which was proposed as polarity calibrator in biopolymers.^{59,60} Its solvent behavior was mainly described by the dipolarity/polarizability (SPP) and acidity (SA) scales, and therefore, we did not advise its use as polarity probe. Following an ESIPT mechanism the HBQ molecule generates a proton-transfer tautomer that emits fluorescence, which is controlled mainly by the solvent acidity and to a minor extent by dipolarity/polarizability (SPP). Also, the first absorption band of HBQ was controlled by acidity to a greater extent than dipolarity/polarizability (SPP). The multiparametric fits were only dependent on SPP and, however, the statistic was not really good for absorption ($r = 0.822$), and for emission was better with $r = 0.949$. *tert*-Butyl alcohol was not included in the fit for absorption due to steric effects which could be the cause of making worse the correlation coefficient. For absorption, especially incorrect was the fit of the data values by including the hydrocarbon solvents (i.e., perfluorohexane) due to a hypothetical stacking interaction of monomers, and the gas phase. The fit of the 20 solvents, including hydrocarbon solvents, bulky alcohols, and the gas phase by using the eq 1 yields a much better statistics for both absorption (eq 23) and emission (eq 24) data values:

$$\bar{\nu}_{\text{abs}} = -(571 \pm 107)\text{SP} + (637 \pm 56)\text{SdP} + (376 \pm 64)\text{SA} + (26748 \pm 63) \quad (23)$$

with $n = 27$ and $r = 0.9675$.

$$\bar{\nu}_{\text{em}} = (289 \pm 113)\text{SP} + (854 \pm 63)\text{SA} + (160 \pm 64)\text{SB} + (15516 \pm 74) \quad (24)$$

with $n = 27$ and $r = 0.9471$.

From these analyses, in accordance with ref 30, HBQ is not an appropriate probe for polarity due to the great dependence on solvent acidity. Also, there is no need to invoke a stacking interaction since the fits provide a good linear correlation for all the solvents studied including hydrocarbon solvents and bulky alcohols. The split of the SPP scale into the two contributions solvent dipolarity and solvent polarizability has solved all the conflicts reported in ref 30.

Solvatochromism of Indole. Our group investigated the solvatochromism of indole³¹ in 2003 and concluded that using the SPP, SA, and SB scales one can discount the specific contributions and demonstrate for the first time that indole in a

media with polarity (SPP) larger than 0.8 exhibits an emission band which is no longer ascribed to ${}^1\text{L}_b \rightarrow {}^1\text{A}$ but to ${}^1\text{L}_a \rightarrow {}^1\text{A}$. We wonder which effect polarizability or dipolarity is responsible for the indole changes. Using eq 1 to describe the chromism of indole, the general solvent effect on the first absorption band is only due to polarizability (eqs 25 and 26), with some contribution of solvent acidity and basicity. For emission, however, dipolarity contributes to a greater extent than polarizability, with a significant contribution of solvent acidity which is the main interaction that dominates the solvatochromism of indole (eq 27).

$$\bar{\nu}_{\text{abs}} = -(628 \pm 59)\text{SP} + (114 \pm 36)\text{SA} - (211 \pm 41)\text{SB} + (27 \pm 36)\text{SdP} + (35242 \pm 33) \quad (25)$$

with $n = 25$ and $r = 0.9654$.

$$\bar{\nu}_{\text{abs}} = (-614 \pm 55)\text{SP} + (133 \pm 26)\text{SA} - (191 \pm 32)\text{SB} + (35237 \pm 32) \quad (26)$$

with $n = 25$ and $r = 0.9644$.

$$\bar{\nu}_{\text{em}} = -(873 \pm 449)\text{SP} - (2014 \pm 220)\text{SdP} - (2079 \pm 242)\text{SA} + (34050 \pm 258) \quad (27)$$

with $n = 25$ and $r = 0.9788$.

The distinct behavior exhibited in eqs 26 and 27 between absorption and emission data values raises that the nature of the emitting state has changed due to solvent effects. Equations 26 and 27 allow one to discount other contributions (SP, SA, and SB) than dipolar interactions from the experimental wavenumbers [$\bar{\nu}_{\text{abs}}(\text{dipolar}) = \bar{\nu}_{\text{abs}} + 614\text{SP} - 133\text{SA} + 191\text{SB}$ and $\bar{\nu}_{\text{em}}(\text{dipolar}) = \bar{\nu}_{\text{em}} + 873\text{SP} + 2079\text{SA}$]. Figure 7 shows, for the first time, the behavior of the emission data for indole versus the pure dipolar contribution.

Conclusions

A new solvent scale, the solvent dipolarity scale (SdP), has been constructed from the SP scale and the absorption wavenumber values of the probe DMANF. It is linearly independent and complementary to the other three well-known solvent scales acidity (SA), basicity (SB), and polarizability (SP).

The proposed empirical scheme, based on the solvent acidity (SA), basicity (SB), polarizability (SP), and dipolarity (SdP) scales, can seemingly predict the solvatochromic behavior of any solute. In this way, it facilitates explanation of the solvent effect.

These four solvent scales satisfactorily explain the solvatochromism of such relevant molecules as anthracene, 10-hydroxybenzo[*h*]quinoline, various BODIPY dyes, and indole.

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