Empirical Treatment of the Inductive and Dispersive Components of Solute−Solvent Interactions: The Solvent Polarizability (SP) Scale

Javier Catalán*[a] and Henning Hopf[b]

Dedicated to Professor Christian Reichardt on the occasion of his 70th birthday[‡]

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By using 3,20-di-*tert*-butyl-2,2,21,21-tetramethyl-3,5,7,9,11,13,15,17,19-docosanonaene (ttbP9) as a probe, the inductive and dispersive interactions of solvents were empirically evaluated for the first time. This probe exhibits a very strong first electronic transition with a marked vibronic structure that is very well resolved from the second electronic transition. One hundred solvents were used to construct a solvent polarizability (SP) scale ranging from zero for the gas phase (i.e. the absence of solvent) to unity for carbon disulfide. The probe was found to exhibit an ideal spectroscopic behaviour towards a variety of polar, acidic and basic solvents. The polarizability scale provides an accurate description of the solvatochromism of such interesting apolar chromophores as anthracene, molecular oxygen, and C_{60} among a wider variety of solvents spanning very broad ranges of polarity, acidity and basicity.

Introduction

Whenever solvents influence physico-chemical processes, the medium is obviously not inert and thus can play a more or less pronounced role in such processes. The influence of the reaction medium depends on the nature of the solvent or the solvent mixtures involved. For this reason, chemists have for over a century now aimed at characterizing reaction media in order to rationalize the so-called "solvent effect". Broadly speaking, the solvent effect can be either of two types depending on whether the solute−solvent interactions involved are specific or nonspecific.[1]

According to Drago,[2] specific solvent interactions can be described in terms of donor−acceptor interactions involving certain orbitals by using electrostatic (*E*) and covalent (*C*) parameters. Other authors, however, have described specific interactions in terms of acid−base hydrogen-bonding interactions by using parameters such as Kamlet and Taft's α and β,[3] or the more recent SA and SB proposed by Catalán and co-workers.[4,5]

In nonspecific interactions, also called "general interactions", each solvent is assumed to act as a dielectric continuum. The earliest models for this type of interaction were developed by Kirkwood[6] and Onsager,[7] and were later modified to correct for the effect of electrostatic saturation.[8,9] The intrinsic difficulty of these models in accurately determining the dimensions of the cybotactic region (viz. the region where solvent molecules are directly perturbed by the presence of solute molecules) around each solute molecule in the bulk solvent has raised the need for empirical approximations for the determination of a parameter encompassing solvent polarity and polarizability.

A number of general empirical solvents scales have been reported.[1] According to Drago,[10] their strong mutual discrepancies are a good proof that they reflect not only general effects, but also specific effects of variable nature depending on the particular probe used to construct each scale. In the past decade, there have been two attempts to develop a pure polarity−polarizability scale for solvents. Thus, in 1992 Drago[10] developed the "Unified Solvent Polarity Scale", also called the "S′ scale", by using least-squares minimization software to fit a series of physicochemical properties (χ) for systems, where specific interactions with the solvents were excluded to the Equation $\Delta\chi = PS' + W$. In 1995, one of our groups[11] reported the solvent polarity−polarizability (SPP) scale, based on UV/Vis measurements of the 2-dimethylamino-7-nitrofluorene/2-fluoro-7-nitrofluorene probe/homomorph couple.

[a] Departamento de Química Física Aplicada, Universidad Autónoma de Madrid,
Cantoblanco, 28049 Madrid, Spain
Fax: (internat.) + 34-914974785
E-mail: javier.catalan@uam.es
[b] Institut für Organische Chemie, Technische Universität Braunschweig,
Hagenring 30, 38106 Braunschweig, Germany
Fax: (internat.) + 49-531-391-5388
E-mail: H.Hopf@tu-bs.de
[‡] and for his important contributions to clarify solvent effects.

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Because empirical scales for general solvent effects are based on a single parameter, they must simultaneously describe solvent dipolarity and polarizability and rely on the solvatochromism of probes that undergo marked changes in dipole moment; therefore, they must be highly sensitive to dipolarity and polarizability changes in the electronic transition undergone by the probe concerned. Also, as previously noted by Abe,[12] because the scales are developed from probes the polarity of which changes upon electronic excitation, they cannot describe the solvent effect on a nonpolar solute. These issues led us to develop a pure scale for one of the two effects combined in the previous ones.

In this work, we addressed the solvent polarizability issue by using a suitable probe the UV/Vis spectroscopic behaviour of which was examined in a wide variety of solvents with the aim to develop a wide empirical solvent polarizability scale: the SP scale. Data from the scale were checked against reported evidence for nonpolar chromophores of variable molecular size (viz. C_{60}, anthracene and singlet oxygen) which has been ascribed to the effect of solvent polarizability.

Results and Discussion

Suitability of ttbP9 as a Solvatochromic Indicator and Formulation of the SP Scale

For a compound to be a suitable probe for estimating solvent polarizability, it should be nonpolar in the two electronic states involved in the transition, stable and soluble; also, it should possess the following spectroscopic characteristics: (*a*) the measured band should be strong, not overlap with other bands of the chromophore and located at a lower energy level than the cutoff points for the solvents usually employed in chemistry, (*b*) the band should be structured and its 0−0 component visible, and (*c*) the band structure should not blur in polar, acid or basic solvents.

If a probe is nonpolar in the two states involved in the transition and the transition is therefore only perturbed by dispersive interactions in both nonpolar solvents and − largely − polar solvents, the shape of the band and its vibronic structure should be preserved in any type of medium.

Figure 1 shows the UV/Vis spectra for ttbP9 in selected solvents, namely: (1) two solvents, differing markedly only

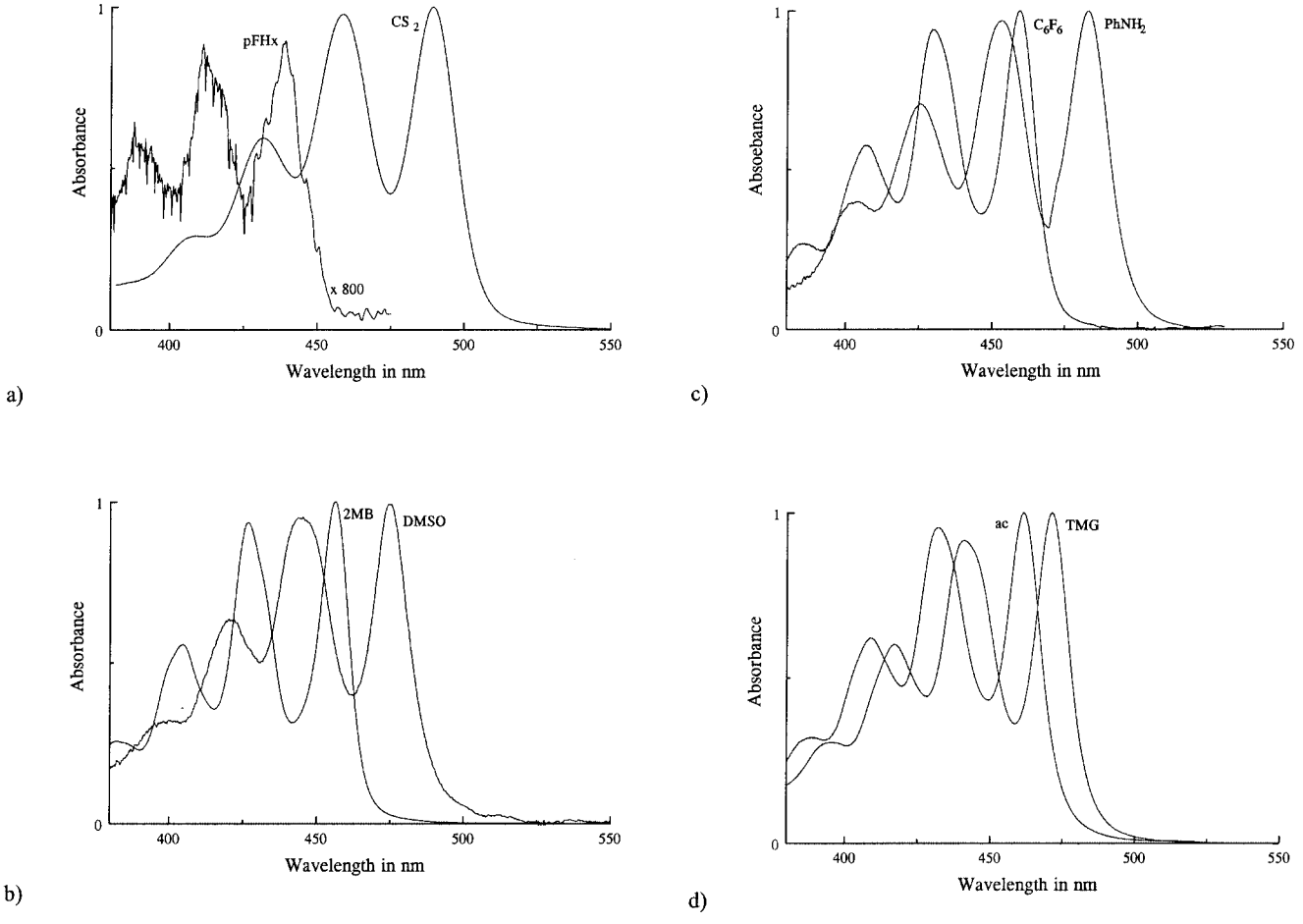


Figure 1. First electronic transition of ttbP9 at 20 °C in a) perfluorohexane (pFHx) and in carbon disulfide (CS_2), b) 2-methylbutane (2MB) and dimethyl sulfoxide (DMSO), c) hexafluorobenzene (C_6F_6) and aniline ($PhNH_2$), d) acetic acid (ac) and tetramethylguanidine (TMG)

in polarizability: perfluorohexane and carbon disulfide (their respective refractive indices are 1.2510 and 1.6270[13]); (2) two solvents of differential polarity: 2-methylbutane (SPP = 0.479) and dimethyl sulfoxide (SPP = 1.000), the latter of which possesses the largest value on the solvent polarity scale;[11] (3) two aromatic solvents with a differential donor ability: hexafluorobenzene and aniline, the respective ionization potentials of which are 9.90[14] and 7.65 eV[15]); and (4) a strongly acidic solvent (acetic acid, with SA = 0.689[16]) and a strongly basic one (tetramethylguanidine, with SB = 1.000 at the top of the solvent basicity scale).[5]

If the spectra of Figure 1 retain their structure and the relative intensity of their vibrational peaks, then ttbP9 will be highly suitable for describing the behaviour of a nonpolar chromophore the spectrum of which undergoes a red shift as the polarizability of the medium increases. (The natural product β-carotene, with its long polyene chain, exhibits a first absorption band very sensitive to the polarizability of the environment.[17,18] However, this first band of β-carotene, which is without doubt very structured in the gas phase at 20 °C, shows little structure in nonpolar solvents such as *n*-hexane, and even less structure in polar solvents like DMSO. The loss of vibronic structure reveals that in the shift of this absorption band for β-carotene other solvent effects intervene, together with the polarizability.[17] Also, the loss of structure is accompanied by blurring of the 0−0 component, therefore, it may not be utilized to locate this band but the peak wavelength at the maximum.) Also, clearly, the first band for ttbP9 is located at lower energy levels than the cutoff points for the solvents usually employed in chemistry.[1]

The molecular properties of ttbP9 precluded the recording of its spectrum in the gas phase at 20 °C; we thus determined the position of its 0−0 component by using the Lorenz−Lorentz relation as applied to linear alkanes, which had previously provided very good results with other systems.[19,20] Figure 2 illustrates the highly linear relationship [Equation (1)] for the solvents examined, with $n = 12$, $r = 0.9995$ and sd = 0.004 kK.

$$\nu^{0-0} = (-9.518\pm0.098)f(n^2) + 23.975\pm0.024 \quad (1)$$

The high quality of this relationship allows one to predict that the 0−0 component for ttbP9 in the gas phase at 20 °C must lie at 23975 ± 24 cm^{-1}.

Figure 3 illustrates the behaviour of ν^{0-0} of ttbP9 in the 100 solvents studied and in the gas phase (calculated value) in terms of the so-called "polarizability function" [viz. $(n^2 - 1)/(n^2 + 2)$]. Obviously, ttbP9 is only sensitive to the polarizability of its environment.

It should be noted that, contrary to the widespread assumption[1] that the dispersion effect involves small shifts in UV/Vis bands, ttbP9 exhibits a substantial shift (3530 cm^{-1}) from the gas phase to carbon disulfide. The information gathered can be ranked on a polarizability scale ranging from 0 for the gas phase to 1 for CS_2 and based on Equation (2). The data in question are listed in Table 1.

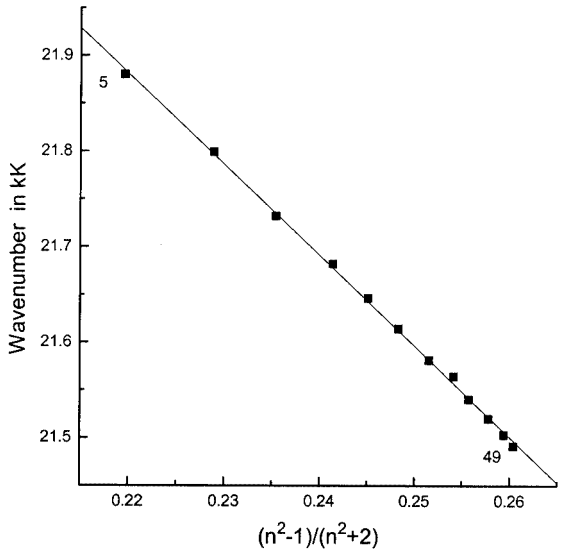


Figure 2. Lorenz−Lorentz relation between the 0−0 transition frequency of ttbP9 vs. the polarizability function in linear alkanes from *n*-pentane (5) to *n*-hexadecane (49) at 20 °C

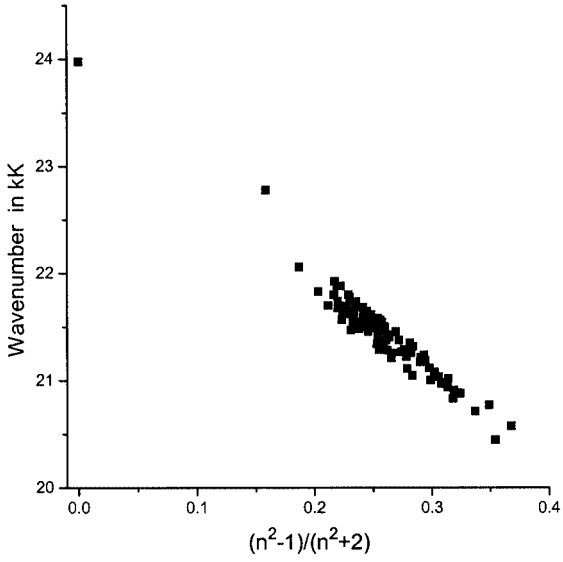


Figure 3. Correlation of the 0−0 transition frequency of ttbP9 vs. the polarizability of the solvents and gas phase at 20 °C

$$SP = (\nu_{gas} - \nu_{solvent})/(\nu_{gas} - \nu_{CS2}) \quad (2)$$

Whether the SPP scale can accurately describe the polarizability of the medium can be inferred by plotting SPP values against their SP counterparts (see Figure 4, which includes the 90 solvents for which both values were available). Interestingly, the solvents with a very small or zero dipole moment − the gas phase included − exhibit a clearly linear relationship. The prevailing solvatochromic effect is of the dispersive type, hence the linear relationship. Figure 4 allows one to draw several interesting conclusions, namely: (*a*) in this model polarizability is the dominant factor in the polarity/polarizability couple; (*b*) polar solvents depart from the linear relationship described above as their dipole

Table 1. Frequency ν [cm^{-1}] for the 0−0 component of ttbP9 in the different solvents studied, the polarizability value SP, and the refraction index *n*

No.	Solvent	ν_{ttbP9}	SP	*n*
0	gas	23975	0	1
1	perfluoro-*n*-hexane	22779	0.3388	1.251
2	2,2,2-trifluoroethanol	22058	0.5431	1.300
3	2-methylbutane	21923	0.5813	1.354
4	petroleum ether	21881	0.5932	1.363
5	*n*-pentane	21880	0.5935	1.358
6	methanol	21829	0.6079	1.329
7	*n*-hexane	21799	0.6164	1.375
8	diethyl ether	21798	0.6167	1.353
9	hexafluorobenzene	21776	0.6229	1.377
10	2-propanol	21739	0.6334	1.377
11	ethanol	21739	0.6334	1.359
12	*n*-heptane	21732	0.6354	1.387
13	acetonitrile	21699	0.6448	1.344
14	methyl acetate	21695	0.6452	1.361
15	*n*-butyl methyl ether	21690	0.6473	1.369
16	ethyl formate	21688	0.6479	1.359
17	*n*-octane	21682	0.6496	1.398
18	acetone	21677	0.6510	1.359
19	acetic acid	21676	0.6513	1.369
20	dimethyl carbonate	21671	0.6527	1.368
21	ethyl acetate	21660	0.6558	1.372
22	1-propanol	21652	0.6581	1.384
23	*n*-nonane	21646	0.6598	1.405
24	triethylamine	21644	0.6603	1.400
25	diethyl carbonate	21633	0.6635	1.384
26	*n*-propyl formate	21622	0.6666	1.375
27	propionitrile	21618	0.6683	1.366
28	*n*-decane	21614	0.6688	1.411
29	*n*-propyl acetate	21611	0.6697	1.382
30	1-butanol	21595	0.6742	1.382
31	methylcyclohexane	21591	0.6753	1.399
32	*n*-undecane	21581	0.6782	1.422
33	propionaldehyde	21567	0.6821	1.365
34	cyclohexane	21564	0.6830	1.426
35	*n*-dodecane	21564	0.6830	1.422
36	1-pentanol	21549	0.6873	1.409
37	2-pentanone	21544	0.6887	1.390
38	*n*-butyronitrile	21543	0.6889	1.383
39	tri-*n*-butylamine	21542	0.6892	1.429
40	*n*-tridecane	21540	0.6898	1.425
41	3-pentanone	21532	0.6921	1.392
42	1-chlorobutane	21529	0.6929	1.402
43	acetic anhydride	21529	0.6929	1.390
44	(trifluoromethyl)benzene	21526	0.6938	1.415
45	*n*-tetradecane	21520	0.6955	1.429
46	1-hexanol	21511	0.6980	1.418
47	2-methyltetrahydrofuran	21503	0.7003	1.406
48	*n*-pentadecane	21503	0.7003	1.432
49	*n*-hexadecane	21491	0.7037	1.434
50	allyl alcohol	21487	0.7048	1.412
51	nitroethane	21484	0.7057	1.392
52	1-heptanol	21483	0.7059	1.424
53	nitromethane	21470	0.7096	1.379
54	1-octanol	21459	0.7127	1.429
55	tetrahydrofuran	21455	0.7139	1.407
56	squalane	21455	0.7139	1.451
57	1-nonanol	21445	0.7167	1.433
58	1-decanol	21426	0.7221	1.437
59	1-undecanol	21405	0.7280	1.440
60	1,4-difluorobenzene	21405	0.7280	1.441
61	cineole	21378	0.7357	1.457
62	1,1,1-trichloroethane	21373	0.7371	1.436
63	1,4-dioxane	21372	0.7374	1.422
64	decalin	21350	0.7436	1.475
65	propylene carbonate	21342	0.7459	1.421
66	*cis*-decalin	21318	0.7527	1.480
67	dimethylformamide	21296	0.7589	1.431
68	fluorobenzene	21289	0.7609	1.465
69	dichloromethane	21288	0.7612	1.424
70	*N*,*N*-dimethylacetamide	21281	0.7632	1.438
71	tetrachloromethane	21265	0.7677	1.460
72	cycloheptanol	21257	0.7700	1.477
73	1,2-dichloroethane	21253	0.7711	1.445
74	mesitylene	21238	0.7754	1.499
75	1,1,3,3-tetramethylguanidine	21221	0.7802	1.469
76	toluene	21216	0.7816	1.493
77	chloroform	21210	0.7833	1.444
78	*o*-xylene	21183	0.7909	1.501
79	benzene	21176	0.7929	1.501
80	dibutyl phthalate	21173	0.7938	1.492
81	phenetole	21116	0.8099	1.508
82	1-methylpyrrolidin-2-one	21110	0.8116	1.470
83	anisole	21079	0.8204	1.516
84	methyl benzoate	21068	0.8235	1.517
85	dimethyl sulfoxide	21047	0.8295	1.479
86	chlorobenzene	21035	0.8329	1.524
87	tetralin	21017	0.8380	1.541
88	pyridine	21004	0.8416	1.510
89	acetophenone	20981	0.8482	1.532
90	benzonitrile	20972	0.8507	1.528
91	veratrole	20972	0.8507	1.533
92	benzyl alcohol	20935	0.8612	1.540
93	1,2-dichlorobenzene	20909	0.8686	1.551
94	bromobenzene	20885	0.8754	1.558
95	dibenzyl ether	20879	0.8770	1.562
96	nitrobenzene	20831	0.8907	1.549
97	1-methylnaphthalene	20771	0.9076	1.615
98	aniline	20714	0.9238	1.586
99	1-bromonaphthalene	20573	0.9637	1.657
100	carbon disulfide	20445	1	1.627

moments increase; and (*c*) this analysis provides an entry to the empirical resolution of the general solvent effect into its polarizability and dipolarity components.

Correlation of Experimental Data with the SP Scale

Let us now examine the solvent effect of various spectral transitions in nonpolar chromophores, namely the $^1A \rightarrow L_a^1$ transition in anthracene, the position of peak A_1 for C_{60}, and the solvatochromic shift and rate constant for the photophosphorescence from the $^1\Delta_g$ state for oxygen, in the light of the new solvent polarizability (SP) scale. The data used to this end are shown in Table 2.

$^1A \rightarrow L_a^1$ Transition in Anthracene

The solvatochromism of this electronic transition in anthracene has been thoroughly studied. Thus, in 1968, Nicol et al.[21] reported the position of its 0−0 component in 43 different solvents and used least-squares regression to fit it to Equation (3), where ν and ν_0 are the frequency of the 0−0 component in the solvent concerned and the gas phase,

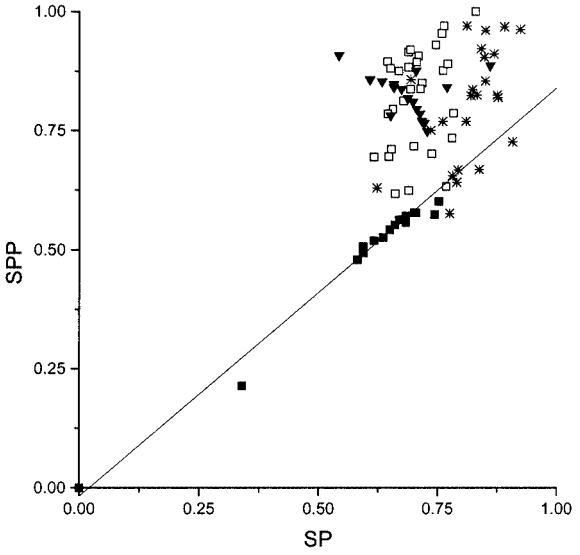


Figure 4. Correlation of the SPP parameter (polarity/polarizability) vs. the polarizability parameter for the solvents studied (filled squares: gas phase, perfluorohexane, and saturated hydrocarbons; *: aromatic solvents; filled triangles; solvents with acidic groups; open squares: other solvents)

respectively; n and ε are the refractive index and the dielectric constant of the solvent; A and B are two least-squares fitting parameters.

$$\nu = \nu_0 + A\frac{n^2-1}{2n^2+1} + B\frac{(\varepsilon-n^2)(2\varepsilon+n^2)}{(n^2+2)^2\varepsilon} \quad (3)$$

This equation allowed ν to be predicted with a precision better than 50 cm^{-1} for 38 solvents and better than 80 cm^{-1} for another five (viz. cyclohexane, carbon tetrachloride, chloroform, acetaldehyde and butyraldehyde).

In 1982, Morales[22] examined the behaviour of this transition in 15 solvents and in the gas phase and found alkanes to conform to the polarizability function $\varphi(n^2) = (n^2 - 1)/(n^2 + 2)$, and other types of solvents to depart from it with increase in their polarity; he thus claimed to have resolved the dispersive and inductive interactions of anthracene in the bulk solvent.

In 1989, Maciejewski[23] included perfluoroalkanes in the discussion and found the transition in *n*-alkanes to fit the polarizability function $(n^2 - 1)/(2n^2 + 1)$ quite closely, but in perfluoroalkanes to clearly deviate from it; between these two extremes, solvents such as CCl_4, 1,4-dioxane, 2,2,4,6,6-pentamethylheptane and 2,2,4,4,6,8,8-heptamethylnonane departed from both trends.

In 1990, Abe[12] examined this transition in the 16 solvents originally studied by Nicol et al.[21] and found the π* scale of Kamlet and Taft,[24] which is based on the change in dipole moment caused by the electronic transition in polar solutes, not to accurately describe the spectral behaviour of anthracene in such solvents. This author proposed a new, more polarizability-sensitive π* scale that he designated the π^*_2 scale and described the behaviour of anthracene in the previous solvents in terms of the Equation (4), with $r = 0.934$.

$$\nu = -774.2\,\pi^*_2 + 27\,361 \quad (4)$$

Figure 5 illustrates the behaviour of the 0−0 component of the $^1A \rightarrow L_a^1$ transition for anthracene in 42 of the solvents studied (Table 2). As can be seen, it fits Equation (5) with $n = 42$, $r = 0.9966$ and sd = 20 cm^{-1}.

$$\nu^{0-0} = (-1.615 \pm 0.021)SP + (27.662 \pm 0.015) \quad (5)$$

A_1 Transition in C_{60}

The slight solvatochromism exhibited by C_{60} has aroused much interest, partly because it is a bulky spherical nonpolar molecule consisting solely of carbon atoms; C_{60} exhibits marked color changes in different solvents.[25,26]

Based on the claims by Renge[19] that the 0−0 component in the gas phase for electronic transitions of the chromophore in *n*-alkanes can be estimated using the Lorenz−Lorentz $f(n^2)$ function, in 1994 Catalán[20] predicted the position of the most salient spectral peaks for C_{60} in the gas phase.

In 1995, Renge[27] reexamined the behaviour of these transitions in *n*-alkanes. Also, Gallagher and co-workers[28] analysed the transitions of C_{60} in 15 different solvents by using a multi-parameter treatment involving the refractive index, various polarizability functions [viz. $(n^2 - 1)/(n^2 + 2)$ and $(n^2 - 1)/(2n^2 + 1)$], polarity functions [$(\varepsilon^2 - 1)/(2\varepsilon^2 + 1)$], dielectric functions [$(\varepsilon - 1)/(\varepsilon + 2)$], the molecular volume (V), Hildebrand's solubility parameter (δ_H) and the polarity−polarizability parameter (π*) as corrected for polarizability. The authors of such a complex treatment concluded that "the general theory that the energy shifts should be mainly dependent on the polarizability of the solvents is not obeyed". Catalán[29] reported the position of the peaks in the spectrum for C_{60} in 51 different solvents and the gas phase, and examined them in the light of the solvent polarity−polarizability (SPP) scale. He concluded that the solvatochromism of C_{60} was 2−3 times less sensitive than that of anthracene and that, except for a few deviations observed in acid media potentially suggesting that the compound is slightly basic, there were no significant shifts in the positions of the spectral peaks for this compound in such a wide variety of solvents.

Figure 6 shows the variation of peak A_1 for C_{60} as a function of the solvent polarizability parameter (SP). As can be seen, there are no significant deviations suggestive of specific interactions with aromatic solvents, nor − that with methanol excepted − suggesting that C_{60} is basic.

Solvent Shift and Rate Constants for the $^1\Delta_g \rightarrow {}^3\Delta_g^-$ Phosphorescence of O_2

Wessel and Rodgers[30] reported the solvent shifts in the $^1\Delta_g \rightarrow {}^3\Sigma_g^-$ phosphorescence of O_2 in 49 different solvents and found it to be proportional to the value of the polarizability function $\alpha = (n^2 - 1)/(n^2 + 2)$ (see Figure 2 in their paper) except in water, methanol, acetonitrile, acetone, dioxane and tetrahydrofuran, which departed clearly from the

Table 2. Solvent polarity/polarizability (SPP), wavenumber for the 0−0 component of the ^1L_a transition of anthracene (in kK), energy for the A_1 peak of C_{60}, energy for the 0−0 component (in kK) and radiative constant of the singlet-oxygen phosphorescence (kK = 1000 cm^{-1})

Solvent	SPP	^1L_a(anthracene)	A_1 (C_{60})	$\nu(0-0)$ $^1\Delta_g$ (O_2)	$k_{a\text{-}X}$ (O_2)
Saturated hydrocarbon solvents and gas phase:					
gas	0	27.643	25.132	7918.1	
perfluoro-*n*-hexane	0.214	27.140			
2-methylbutane	0.479		24.765		
petroleum ether	0.493				
n-pentane	0.507	26.721	24.765	7859.8	0.47
n-hexane	0.519	26.681	24.728	7858.2	0.60
n-heptane	0.526	26.648	24.740	7856.8	0.66
n-octane	0.542	26.633	24.728	7858.0	
n-nonane	0.552	26.608	24.728	7855.0	
cyclohexane	0.557	26.613	24.710	7853.8	
n-decane	0.562	26.603		7854.2	
n-undecane	0.563	26.588			
methylcyclohexane	0.563		24.710		
n-dodecane	0.571		24.704	7853.1	
decalin	0.574		24.667		
n-tetradecane		26.564			
n-pentadecane	0.578		24.704		
n-hexadecane	0.578	26.527		7851.3	
cis-decalin	0.601		24.661		
Aromatic solvents:					
mesitylene	0.576				
hexafluorobenzene	0.629		24.808		0.51
o-xylene	0.641			7848.6	
toluene	0.655		24.558	7839.9	
benzene	0.667	26.392	24.540	7839.5	1.51
tetralin	0.668				
1-methylnaphthalene	0.726			7825.5	2.96
cineole	0.750				
phenetole	0.769				
fluorobenzene	0.769			7844.4	1.28
dibenzyl ether	0.819				2.00
anisole	0.823		24.552		1.80
chlorobenzene	0.824		24.570	7839.6	1.44
bromobenzene	0.824	26.272	24.546	7832.8	1.97
methyl benzoate	0.836				
veratrol	0.854				
(trifluoromethyl)benzene	0.857		24.697	7856.2	1.14
acetophenone	0.904	26.272			
1,2-dichlorobenzene	0.911				
benzonitrile	0.960	26.278	24.600	7836.3	1.80
aniline	0.962				
nitrobenzene	0.968				
pyridine	0.970				
1-methyl-pyrrolidin-2-one	0.970				
1,4-difluorobenzene			24.667		
1-bromonaphthalene		26.109		7824.1	3.11
Solvents with acidic groups:					
1-undecanol	0.748		24.691		
1-decanol	0.765		24.685	7850.2	
1-nonanol	0.770		24.685	7850.4	
acetic acid	0.781				
1-octanol	0.785		24.691	7851.2	
1-heptanol	0.795		24.697		
1-hexanol	0.810		24.703	7851.7	
1-pentanol	0.817	26.553	24.716	7852.3	
1-butanol	0.837	26.567	24.728	7853.8	0.465
cycloheptanol	0.841				
1-propanol	0.847	26.594	24.728	7855.6	0.63
2-propanol	0.848	26.638			0.47
ethanol	0.853	26.620	24.752	7856.8	0.55
methanol	0.857	26.656	24.820	7853.2	0.39
allyl alcohol	0.875	26.504			

Table 2. *(continued)*

Solvent	SPP	^1L_a(anthracene)	A_1 (C_{60})	ν(0−0) $^1\Delta_g$ (O_2)	$k_{a\text{-}X}$ (O_2)
benzyl alcohol	0.886	26.272		7832.5	
1,1,1-trifluoroethanol	0.908			7869.2	0.331
Other solvents:					
triethylamine	0.617				
tributylamine	0.624		24.759		
tetrachloromethane	0.632	26.389	24.588	7850.1	1.17
diethyl ether	0.694	26.664			0.615
butyl-methyl ether	0.695		24.734		
dioxan	0.701	26.469	24.624	7841.6	0.56
dimethyl carbonate	0.711				
2-methyl-tetrahydrofuran	0.717				
tetramethylguanidine	0.734				
methyl acetate	0.782				
trichloromethane	0.786	26.399	24.661	7847.6	0.962
ethyl acetate	0.795	26.602	24.752		
ethyl formate	0.812				
tetrahydrofuran	0.838			7848.1	0.62
1-chlorobutane	0.837	26.563	24.710		
1,1,1-trichloroethane	0.850	26.492			
propionitrile	0.875				
dichloromethane	0.876	26.445	24.673		0.75
acetone	0.881	26.579	24.783	7852.6	0.543
2-pentanone	0.883	26.568			
3-pentanone	0.883	26.548			
1,2-dichloroethane	0.890	26.407			0.75
nitroethane	0.894	26.501			
acetonitrile	0.895	26.589		7851.5	0.45
nitromethane	0.907	26.483			
butyronitrile	0.915				
acetic anhydride	0.920				0.53
propylene carbonate	0.930				
dimethylformamide	0.954	26.403			
N,*N*-dimethylacetamide	0.970		24.623		
dimethyl sulfoxide	1.0		24.588		
propionaldehyde		26.536			
carbon disulfide			24.378	7829.1	3.14

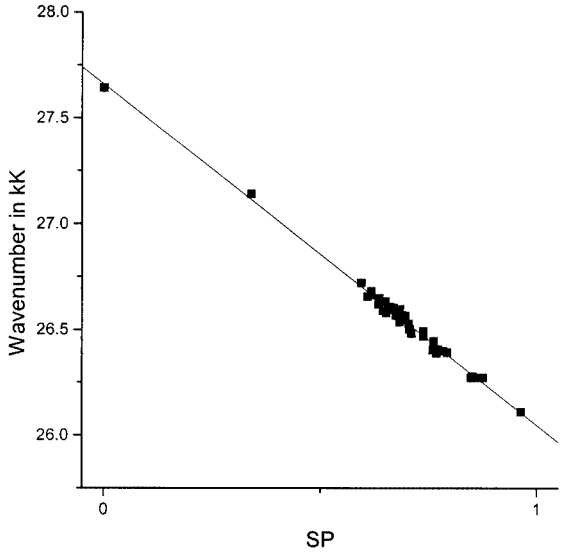


Figure 5. Correlation of the 0−0 component of the ^1L_a transition of anthracene in 42 solvents vs. their corresponding polarizability value.

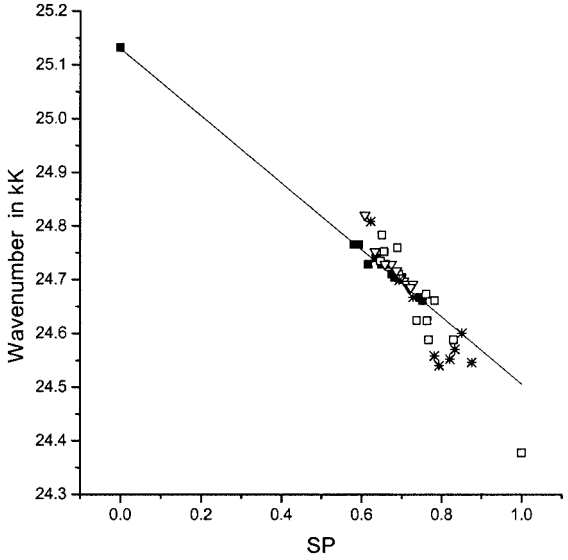


Figure 6. Frequency of the A_1 peak of C_{60} vs. the SP value of the solvent (filled squares: gas phase, perfluorohexane, and saturated hydrocarbons; *: aromatic solvents; filled triangles: solvents with acidic groups: open squares: other solvents)

general trend and were thus assumed to involve not only dispersive, but also inductive and orientational contributions. However, the inclusion of a dielectric constant function in a more complex function such as $v = C[(\varepsilon - 1)/(2\varepsilon + 1) - (n^2 - 1)/(n^2 + 2)][(2n^2 + 1)/(n^2 + 2)] + P(n^2 - 1)/(n^2 + 2)$, where C is related to properties of the solute molecule and P depends mainly on the change of the polarizability of the solute after electronic excitation, failed to improve the results obtained by these authors using a pure polarizability function.

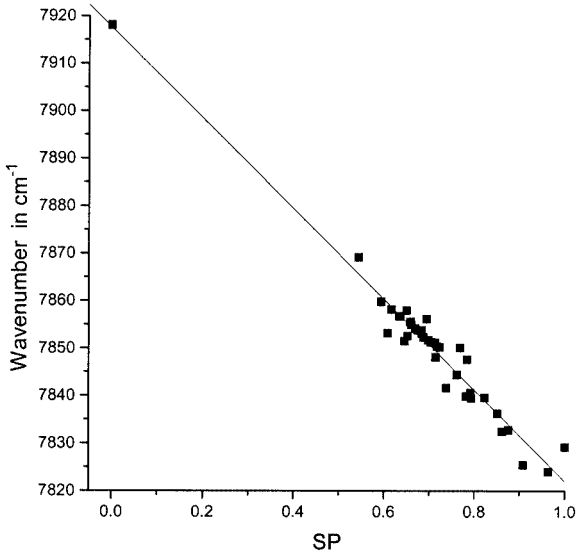


Figure 7. Correlation of the 0−0 component for the phosphorescence of singlet oxygen $^1\Delta_g$ vs. the correspondig SP value of the solvent

Figure 7 illustrates the behaviour of the solvatochromism of O_2 in the 38 solvents for which an SP value was available. With $r = 0.981$ and sd = 2.9 cm^{-1} there is acceptable consistency. Note that the solvents included acetone, acetonitrile, tetrahydrofuran, dioxane and methanol; water was excluded because it cannot dissolve ttbP9.

Hild and Schmidt[31] compiled the rate constants for the $^1\Delta_g \rightarrow {}^3\Sigma_g^-$ process in a wide range of solvents 33 of which we had reported the SP value of (this list does not include the solvent CS_2 in accordance with Schmidt et al.[32]). As can be seen from Figure 8, and as proposed by Schmidt and Bodesheim[33] the ratio of a rate constant divided by the solvent molar volume clearly increases with increasing the squared polarizability of the medium.

Conclusions

The polyolefin ttbP9 is an ideal probe for the empirical determination of the polarizability of a wide variety of media. The development of a pure polarizability scale provides an entry to the empirical assessment of the general solvent effect.

The proposed SP scale should provide an accurate description of the solvatochromism of any nonpolar solute, thereby filling the gap in the empirical treatment of the solvent effect noted by Abe 14 years ago.

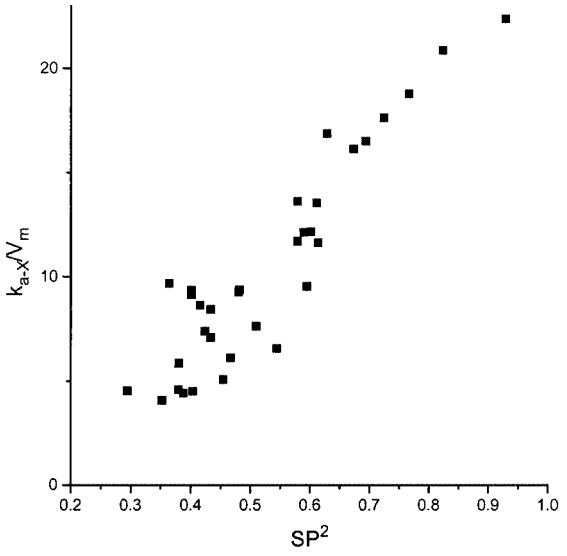
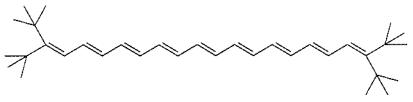


Figure 8. Correlation of the radiative constant, $K_{a\text{-}X}$, for the phosphorescence of the singlet oxygen $^1\Delta_g$ divided by the solvent molar volume vs. the squared polarizability of the solvent

Experimental Section

3,20-Di-*tert*-butyl-2,2,21,21-tetramethyl-3,5,7,9,11,13,15,17,19-docosanonaene (ttbP9, see Scheme 1) was prepared as described elsewhere.[34] All solvents used were purchased in the highest available grade from Aldrich, Fluka or Merck. UV/Vis measurements were performed with a newly calibrated Cary 5 spectrophotometer with a reproducibility better than 0.05 nm and a precision better than ± 0.1 nm in wavelength. The instrument was routinely checked for wavelength accuracy using holmium oxide and didymium filters. All spectral measurements were carried out at 20 °C, using a matched pair of quartz cells of 1-cm path length. The maximum absorption wavelength for the 0−0 component of the first electronic transition in each compound was determined from the derivative function. The results reported here are the means of two spectra the maxima of which differed not more than 0.1 nm. Also, the tabulated wavenumbers are direct conversions of λ(0−0) values.



ttbP9

Scheme 1

Acknowledgments

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