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Additivity of substituent effects on the visible absorption spectra of some heteroarylazo compounds: the influence of solvent

Michael G. Hutchings [a,*,1], Andrew Mills [b]

[a] *BASF plc, Earl Road, Cheadle Hulme, Cheshire SK8 6QG, UK*
[b] *Department of Pure and Applied Chemistry, University of Strathclyde, Thomas Graham Building, 295 Cathedral Street, Glasgow G1 1XL, UK*

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Dedicated to Dr A.T. Peters on the occasion of his retirement as editor of *Dyes and Pigments*

Abstract

Pronounced solvatochromic shifts are observed in the visible spectra of two series of heteroarylazobenzene derivatives based on *m*-acetylamino- and *m*-methyl-*N,N*-diethylaniline, measured in various solvents. The heteroaryl azo component of these dyes can be viewed as a thiophene ring substituted by cyano, nitro, alkoxycarbonyl, or ring aza (to give thiazole and isothiazole derivatives). Free–Wilson analysis has shown that the influence of each of the substituents is constant across all molecules within the two series for a given solvent. However, the substituent increments vary between different solvents and correlate with the Kamlet–Taft dipolarity/polarisability parameter π^* of the solvents. There appears to be no intuitive explanation for the relative solvent variation of different substituents, but Onsager theory suggests sensitivity to the relative size and shape of the dyes. Visible absorption maxima are predicted for unknown heteroarylazo compounds related to those studied. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Heteroarylazo; Solvatochromism; Substituent additivity; Kamlet–Taft; Onsager theory

1. Introduction

A recent study of the solvatochromism of several arylazo derivatives based on the two azo-coupling components *m*-acetylamino- and *m*-methyl-*N,N*-diethylaniline has generated extensive visible absorption data in 22 solvents [1]. Specifically, these dyes included azobenzenes **1A** and **1T**, azothiophenes **2A–5A** and **2T–5T**, and related heterocyclic analogues, including **6A–8A** and **6T–8T**. Detailed analysis of the visible transition energies via linear solvation energy relationships has resolved the questions of when and why, contrary to conventional belief, the toluidine (**T**) derivative is sometimes more bathochromic than its anilide (**A**) analogue [1]. However, beyond this study the availability of these data opens the possibility for further investigations concerning the additivity of substituent effects. A substituent effect may be called additive if it is the same in more than one system, irrespective of other molecular variations. A

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* Corresponding author. Tel.: +44-161-488-5920.
E-mail address: michael.hutchings@basf-plc.co.uk or hutchings.michael@dystar.com (M.G. Hutchings).

[1] Present address: DyStar UK Ltd, Earl Road, Cheadle Hulme, Cheshire SK8 6QG, UK.

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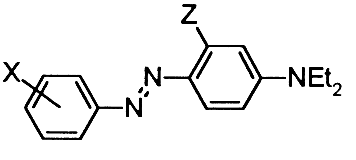
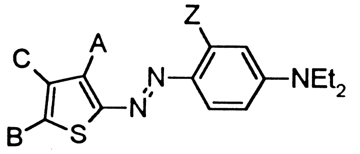
central question of colour–structure relationships is how appending substituents to a chromophore influences its basic colour. Although additivity is not inevitable, in fact it has been demonstrated that such substituent effects can be constant and additive: tables of substituent increments have been published for azobenzene chromophores [2]. Detailed study of such effects can lead to elucidation of subtle interactions such as the conformational change — torsion of just 30° — induced in a sulphonate group by an ortho-related chloro substituent, in several series of azobenzenes and heteroarylazo-benzenes **9** [3]. In the current case, the data are analysed not just from the aspect of additivity, but we also have the novel opportunity for determining how solvent variation affects substituent increments. This paper reports the result of this study.



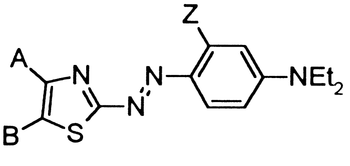
1A Z = NHAc
1T Z = Me



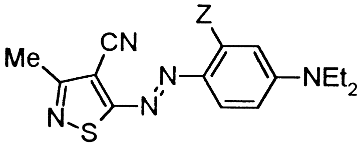
2A A = CO_2Me B = NO_2 C = H Z = NHAc
2T A = CO_2Me B = NO_2 C = H Z = Me
3A A = B = NO_2 C = H Z = NHAc
3T A = B = NO_2 C = H Z = Me
4A A = CN B = NO_2 C = H Z = NHAc
4T A = CN B = NO_2 C = H Z = Me
5A A = B = CO_2Et C = Me Z = NHAc
5T A = B = CO_2Et C = Z = Me

2. Method

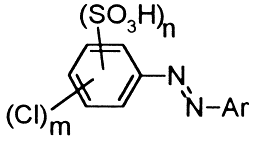
The 14 azothiophenes, azothiazoles and azoisothiazoles of interest, **2A–8A** and **2T–8T**, can be generalised by the generic formulae **10A** and **10T**, although two assumptions are necessary: that the methoxycarbonyl and ethoxycarbonyl groups have the same effect on visible spectra; and that the effect of the ring-methyl group sometimes present in the thiaheterocycle can be ignored. Thus, X and Y in **10A/T** are taken to represent the substituents $C(CO_2R)$, C(CN), $C(NO_2)$ and N.



6A A = H B = NO_2 Z = NHAc
6T A = H B = NO_2 Z = Me
7A A = Me B = CO_2Et Z = NHAc
7T A = Z = Me B = CO_2Et



8A Z = NHAc
8T Z = Me



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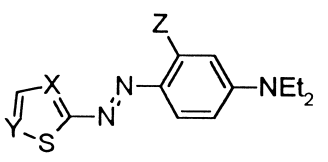


10A Z = NHAc
10T Z = Me

The method used to determine whether substituent effects are additive or not is based on a modified version of the statistical approach of

Free and Wilson [4,5]. In this, the least squares solution to the series of Eq. (1)

$$y_i = c_0 + \sum_{i,j} c_j x_{ij} \qquad (1)$$

is derived where y_i is the transition energy for molecule i, c_0 is the transition energy in the absence of any substituent, c_j are the energy increments for a given substituent in a given position j on the chromophore, and x_{ij} are the number of substituents in position j for molecule i (= 0 or 1). Failure to derive a statistically satisfactory solution to this series of equations for all molecules i means that substituent additivity does not apply within this series. In order to allow the solution of these equations, it is necessary to define from within the experimental data a reference molecule (combination of substituents). Normally this is chosen to be that where the reference substituent is hydrogen (i.e. unsubstituted). However, in this study, data for an unsubstituted azothiophene (**10A/T** where X = Y = CH) are not available. Nitro has, therefore, been arbitrarily selected as a reference substituent (**3A/T**), and all further discussion of substituent effects must, therefore, refer to a comparison with nitro, not hydrogen, as the baseline.

Visible absorption data for **2A–8A** and **2T–8T** in 22 solvents have already been published [1], so for the sake of brevity only the data for the solvents at opposite extremes of the dipolarity range, cyclohexane and dimethyl sulfoxide (DMSO), are reproduced in Table 1, alongside the corresponding transition energies. The x_{ij} values for each of the molecules of interest are also given in Table 1. The substituent increments c_0 and c_j and corresponding statistics were derived by multilinear regression using the STATISTICA/w package [6]. Results for all solvents for all molecules are given in Table 2. In this Table, the intercept values correspond to the calculated transition energy c_0 for the dinitrothiophene reference, while the other values correspond to the respective increments induced by the substituent indicated. All energy terms are given in units of $10^3 \times \mathrm{cm}^{-1}$ (kK). The statistics quoted are R^2, the square of the multilinear correlation coefficient, and σ, the standard deviation for the model, in kK. The former indicates how well substituent additivity applies across the series of molecules **2A–8A** and **2T–8T**, values closer to unity corresponding to better additivity of substituent effects.

3. Results and discussion

The major conclusion repesented by the results of Table 2 is that, in general, additivity is observed for all substituents in all solvents for the azoanilide series **2A–8A**. The standard deviation of the

Table 1

Selected absorption maxima (nm) and transition energies ($1000 \times \mathrm{cm}^{-1}$) for dyes **2A–8A** and **2T–8T**, and substituent data input x_{ij} to Free–Wilson multilinear regression analyses

	Acetanilide series (**A**)				Toluidine series (**T**)								
	DMSO		Cyclohexane		DMSO		Cyclohexane		Substituents x_{ij}				
Dye	λ_{max}	Transition energy	λ_{max}	Transition energy	λ_{max}	Transition energy	λ_{max}	Transition energy	3-CCN	3-CCO2R	5-CCO2R	3-N	5-N
2	632.3	15.8153	578.9	17.2741	642.7	15.5594	563.2	17.7557	0	1	0	0	0
3	651.3	15.3539	607.9	16.4501	686.1	14.5751	597.8	16.7280	0	0	0	0	0
4	639	15.6495	592.8	16.8691	658.6	15.1837	587.2	17.0300	1	0	0	0	0
5	570.8	17.5193	542.7	18.4264	569.4	17.5623	503.8	19.8491	0	1	1	0	0
6	615	16.2602	555	18.0180	612.7	16.3212	541.9	18.4536	0	0	0	1	0
7	554.2	18.0440	512.9	19.4970	554.1	18.0473	495.1	20.1979	0	0	1	1	0
8	563.2	17.7557	533.8	18.7336	568.5	17.5901	515.7	19.3911	1	0	0	0	1

Table 2
Results of MLRA: substituent contributions to transition energies relative to dyes **3A/T** (1000×cm^{-1}) (lactone = butyrolactone; TMU = tetramethylurea; TFE = trifluoroethanol)

	DMSO	DMF	Lactone	TMU	Acetone	THF	EtOAc	Et$_2$O	Et$_3$N	c-Hx	Pyridine	Toluene	CH$_2$Cl$_2$	CHCl$_3$	MeCCl$_3$	CCl$_4$	MeOH	EtOH	*n*-PrOH	*i*-PrOH	HOAc	TFE
***A** series*																						
R^2	0.99979	0.99949	0.99994	0.99902	0.99918	0.99885	0.99882	0.99897	0.99916	0.99624	0.99877	0.99903	0.99999	0.99988	0.99888	0.99895	0.99996	0.99986	0.99947	0.99931	0.99999	0.99734
σ	0.040	0.061	0.022	0.087	0.079	0.092	0.095	0.088	0.078	0.163	0.097	0.083	0.008	0.029	0.094	0.085	0.015	0.029	0.059	0.067	0.008	0.122
c_0	15.354	15.470	15.477	15.494	15.736	15.758	15.873	16.147	16.234	16.450	15.456	15.921	15.647	15.691	15.878	16.171	15.803	15.820	15.818	15.855	15.873	15.863
3-CCN	0.296	0.418	0.335	0.384	0.417	0.507	0.504	0.514	0.658	0.419	0.417	0.480	0.472	0.511	0.502	0.446	0.561	0.552	0.605	0.573	0.574	0.290
3-CCO2R	0.441	0.584	0.542	0.568	0.721	0.698	0.716	0.743	0.804	0.742	0.624	0.727	0.718	0.746	0.728	0.799	0.809	0.793	0.770	0.791	0.853	0.427
5-CCO2R	1.744	1.644	1.709	1.702	1.591	1.531	1.565	1.432	1.363	1.316	1.667	1.392	1.523	1.498	1.511	1.294	1.420	1.364	1.421	1.411	1.287	1.490
3-N	0.926	1.119	1.054	1.133	1.236	1.370	1.386	1.593	1.688	1.650	1.176	1.463	1.170	1.238	1.503	1.602	1.189	1.265	1.306	1.325	1.159	0.781
5-N	2.106	2.085	2.163	2.059	2.102	2.006	2.029	1.957	1.782	1.865	2.113	2.015	2.136	1.993	2.080	1.902	1.851	1.870	1.838	1.890	1.768	1.895
***T** series*																						
R^2	0.99826	0.99845	0.99922	0.99995	0.99971	0.99991	0.99999	0.99997	0.99934	0.99732	0.99981	0.99958	0.99838	0.99607	0.99986	0.99775	0.98692	0.99048	0.99231	0.99410	0.99107	0.98418
σ	0.138	0.131	0.092	0.023	0.055	0.030	0.009	0.016	0.081	0.175	0.045	0.064	0.137	0.212	0.039	0.155	0.340	0.287	0.262	0.227	0.256	0.404
c_0	14.575	14.784	14.808	14.848	15.223	15.518	15.659	16.145	16.515	16.728	14.925	15.992	15.200	15.396	15.738	16.399	15.321	15.521	15.501	15.654	15.649	15.038
3-CCN	0.609	0.591	0.617	0.656	0.726	0.572	0.532	0.508	0.414	0.302	0.603	0.463	0.653	0.604	0.480	0.293	0.782	0.634	0.695	0.585	0.584	0.644
3-CCO2R	1.053	1.149	1.041	1.037	1.083	1.020	1.075	1.057	1.078	1.115	1.123	0.989	1.105	1.133	1.083	1.112	1.207	1.067	1.158	1.065	1.117	0.902
5-CCO2R	1.865	1.804	1.883	1.904	1.838	1.859	1.700	1.809	1.787	1.919	1.850	1.763	2.063	2.081	1.953	1.867	1.590	1.634	1.666	1.662	1.522	2.180
3-N	1.677	1.762	1.666	1.697	1.690	1.579	1.746	1.666	1.639	1.638	1.663	1.581	1.507	1.412	1.585	1.532	1.621	1.503	1.547	1.503	1.172	1.074
5-N	2.406	2.415	2.347	2.249	2.200	2.188	2.313	2.155	2.151	2.361	2.266	2.166	2.362	2.345	2.380	2.349	2.046	2.073	2.041	2.079	2.014	1.946

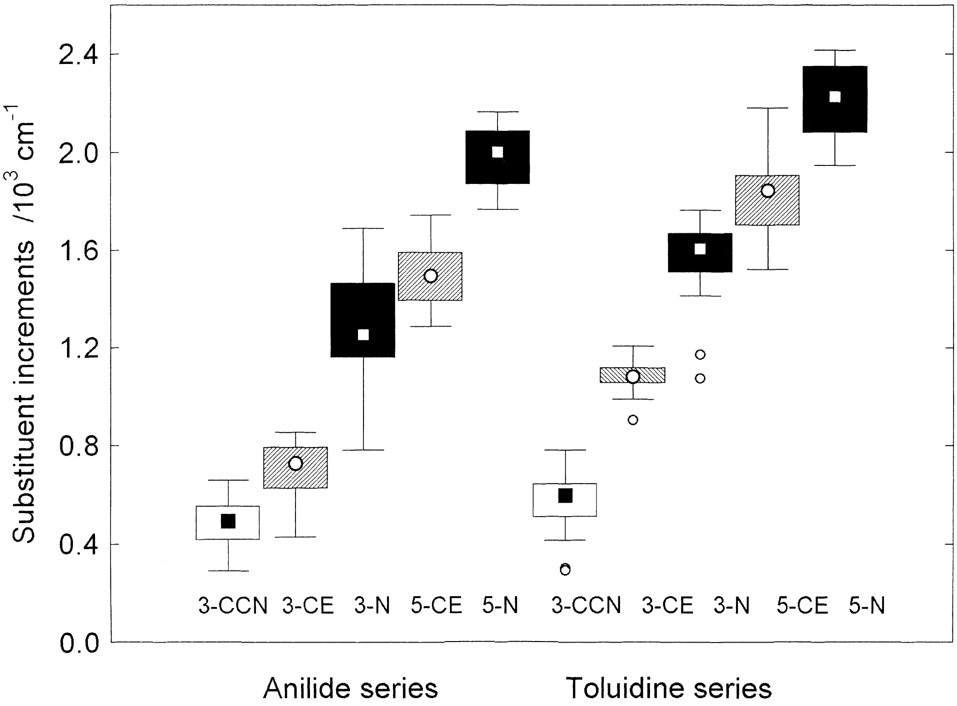
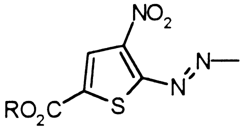
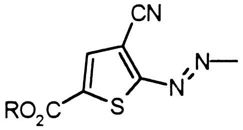
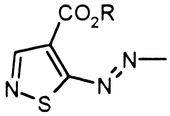
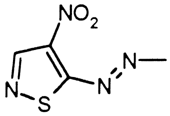
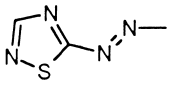
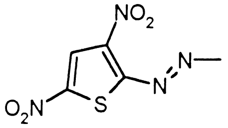


Fig. 1. Plots of substituent increment contributions to the solvatochromism of heteroarylazo compounds **2A/T–8A/T**, relative to nitro as substituent. For convenience the ester substituents, $C(CO_2R)$ are abbreviated to CE.

linear model is in most cases low and does not exceed anticipated experimental error for the measured transition energies. While additivity is also observed for the azotoluidine series **2T–8T**, in the cases of the spectra measured in hydroxylic solvents additivity is less good and the standard deviations are somewhat high. Nevertheless, in only two solvents does R^2 fall below 0.99 (methanol and trifluoroethanol). The increments for each of the five substituents are different, not only with respect to one another, but also from solvent to solvent. In all cases the increments are positive, consistent with a hypsochromic effect for each relative to nitro. The ranges of substituent increments are plotted in Fig. 1, initially ignoring the subtleties of the solvent variations. (For convenience a common heterocycle numbering scheme is used, where the heterocyclic S atom is 1, C-azo is 2, and so on.) The relative order $C(NO_2)$ < 3-C(CN) < 3-$C(CO_2R)$ < 5-$C(CO_2R)$ < 3-N < 5-N is the same for the anilide and toluidine series, although the increments for the toluidine series are greater than for the anilide. This order conforms with experience of substituent effects in azobenzene series. If the 3-$C(NO_2)$ substituent is twisted out of plane because of steric effects its bathochromic effect would be relatively less than in the 5-position. Consequently the difference betweeen nitro and other substituents would be less in the 3-position than the 5-position, where nitro exerts its full effect, as observed.

Knowledge of the substituent increments allows prediction of visible transition energies, and thus absorption maxima, for 10 unknown heterocyclic **A/T** derivatives **11–15**, in the various solvents, as listed in Table 3. Also shown are the solvatochromic shifts between cyclohexane and DMSO for each species. Inevitably, none is as bathochromic or solvatochromic as the dinitrothiophene derivatives **3A/T**. The toluidine series **T** is appreciably more solvatochromic than the anilides **A**, as expected. Disperse dyes such as these are frequently used for the coloration of polyester textiles, and to model this medium we have chosen data predicted in

Table 3
Estimated absorption maxima (nm) and estimated solvatochromic shifts (Δ = difference between absorption maxima in DMSO and cyclohexane, nm) by interpolation from substituent increments for speculative dyes **10A–14A** and **10T–14T**, and corresponding experimental data for **3A** and **3T**

		Acetanilide **A**				Toluidine **T**			
		Cyclohexane	EtOAc	DMSO	Δ	Cyclohexane	EtOAc	DMSO	Δ
11		563	573	585	22	536	576	608	72
12		550	557	575	25	528	559	587	59
13		525	537	559	34	495	525	555	60
14		546	559	573	27	524	556	589	65
15		501	518	544	33	482	507	536	54
3		608	630	651	43	598	639	686	88

ethyl acetate solvent, also given in Table 3. For the more red dyes **13A/T** and **15A/T**, the toluidine derivatives are more hypsochromic than the anilides. Each member of the other three pairs **11A/T, 12A/T**, and **14A/T** has about the same absorption maxima in ethyl acetate, and would thus be expected to give the same colour on polyester. Verification of these predictions must await synthesis of these species.

The relationship between substituent effect and solvent has not previously been investigated. We chose to probe this by examining plots of the former against the Kamlet–Taft solvent parameter π^*, which quantifies the dipolarity/polarisability of a solvent, and for which values have been compiled for many solvents [7,8]. For example, nonpolar cyclohexane is given a value of $\pi^* = 0$, while that for the highly dipolar DMSO is 1. Plots are shown for the dipolar aprotic solvents in Fig. 2, where the straight lines are the least squares fits. In only a few cases does any aprotic solvent deviate from the trend defined by other solvents; cyclohexane for 3-C(CN) is particularly notable and has been omitted from the plots. In any case, all deviations are less than the statistical errors associated with each increment estimate — about the same as the standard deviation σ of the regression (Table 2). Increments for all five substituents derived in the protic solvents deviate from the regression lines of

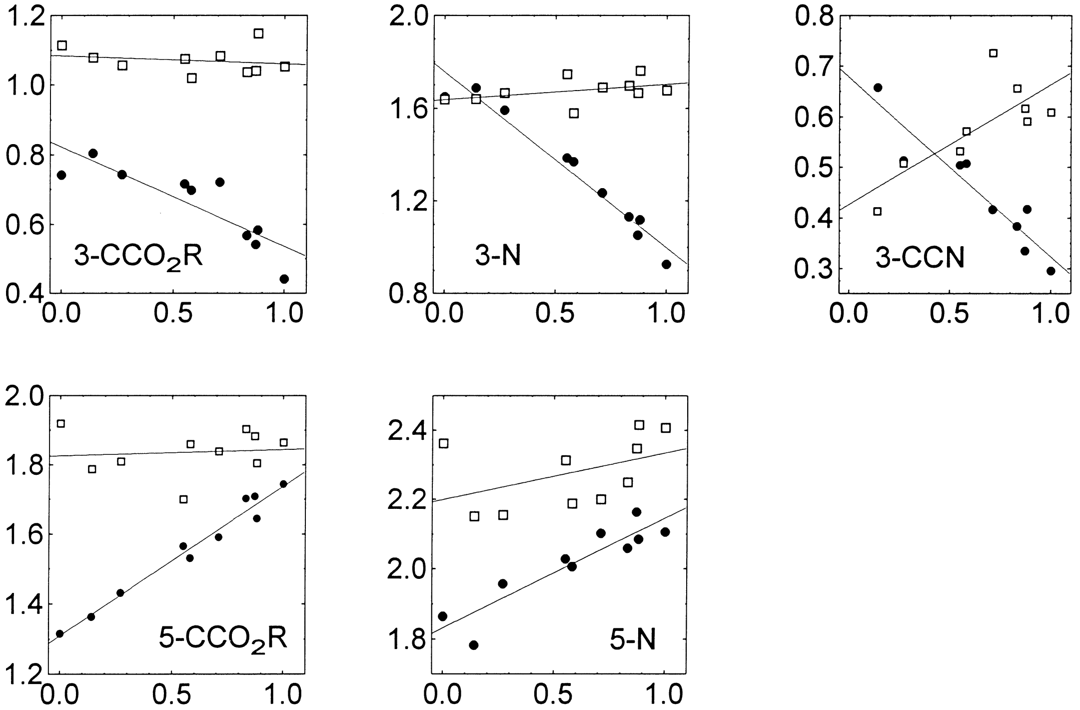


Fig. 2. Plots of substituent contributions against the Kamlet–Taft solvent dipolarity/polarisability parameter π^*. In all cases the x-axis is π^*, while the y-axis is transition energy increment in $1000 \times \mathrm{cm}^{-1}$. The azoanilide series of dyes **A** are represented by ● while the azotoluidine dyes **T** are represented by □. The straight lines are the least squares fit to the points shown.

Fig. 2 to varying degrees, but in most cases by no more than the error of their estimate. However, these are not shown and not discussed further.

The most marked feature for the anilide series (filled circles in the plots of Fig. 2) is that in the case of the substituents in the 3-position of the heterocyclic ring the slope is negative, while for the 5-substituents the slope is positive. This means as solvent polarity increases the difference between the effect in the 3-position for nitro and ester, cyano or ring aza becomes less. Thus, these substituents induce a less hypsochromic effect in DMSO than in cyclohexane. The opposite is the case for ester and ring-aza in the 5-position. In the toluidine series, there is very little variation in substituent increment as solvent polarity changes for 3- or 5-ester or 3-ring aza. There is a more marked solvent effect for 5-aza and 3-C(CN) (Fig. 2). There appears to be no simple intuitive explanation for this observed behaviour. However, we can attempt to take the story further by resorting to theory. Onsager theory relates solvent shifts to ground and excited state electronic properties (dipole moments) and, in its simplest form, to a size parameter, as well as to the solvent properties dielectric constant and refractive index [9–11]. Simplifying assumptions (see Appendix) lead to Eq. (2)

$$\Delta\nu^A/\Delta\nu^B = (a^B/a^A)^3(\mu_0\Delta\mu_{01})^A/(\mu_0\Delta\mu_{01})^B \qquad (2)$$

where $\Delta\nu$ is the difference in transition energies for 2 solvents, μ_0 is the ground state dipole moment, $\Delta\mu_{01}$ is the difference between the ground state and first excited state dipole moments, a is a size parameter, and the suffixes A and B refer to two species under comparison.

To demonstrate the possible application of Eq. (2), we consider the two pairs of dyes **3A/T** and **4A/T**. Calculated dipole moment values and solvatochromic shifts for these dyes are given in Table 4. Substitution of the appropriate values into Eq. (2) leads to the expressions

Table 4
Calculated ground (μ_0) and excited state (μ_1) dipole moments (Debye), their differences ($\Delta\mu_{01}$), and solvatochromic shifts ($1000\times cm^{-1}$) between cyclohexane and DMSO for dyes **3A/T** and **4A/T**. For details of calculations see Ref. 1

Dye	μ_0	μ_1	$\Delta\mu_{01}$	Solvatochromic shift
3A	15.4	22.3	6.9	−1.081
3T	17.2	29.4	12.2	−2.239
4A	13.2	20.4	7.2	−1.293
4T	15.3	27.4	12.1	−1.815

$(a^{NO_2}/a^{CN})^3 = 1.337$ or $(a^{NO_2}/a^{CN}) \approx 1.10$ for the **A** pair of dyes, and $(a^{NO_2}/a^{CN})^3 = 0.919$ or $(a^{NO_2}/a^{CN}) \approx 0.97$ for the **T** pair of dyes.

This result implies that the nitro-substituted dye is "bigger" than the analogue substituted by cyano in the azoacetanilide pair of dyes, **A**, and "smaller" in the azotoluidines, **T**. Such behaviour could be traced, for example, to conformational differences about the azo linkage, nonplanarity of substituents (e.g. nitro), different intramolecular H-bonding options, etc. We choose not to speculate further.

This simple model is far from exact, but serves to demonstrate that substantial differences in solvatochromic behaviour for the anilide and toluidine pairs can be traced to small geometric and/or conformational changes of the order of a few per cent between otherwise comparable molecules. Moreover, the evident sensitivity of the solvatochromic effect of individual increments to small geometric changes, coupled with the approximations applied to the already idealised Onsager theory, deters us from applying the model further to the even less marked differences for the other **A/T** pairs (Fig. 2).

4. Conclusions

Within the two series of heteroarylazo dyes under consideration, substituent increments relative to nitro are constant and transferable between different chromophores. The increments derived have been applied to the prediction of visible absorption maxima and solvatochromic shifts for unknown but related heteroarylazo dyes. The observed increments vary linearly with the solvent dipolarity parameter π^*. However, these cannot be explained intuitively, although they are possibly derived from geometric and/or conformational changes.

Appendix

Onsager theory [9–11] relates the energy of a chromophore's solvatochromic shift $\Delta\nu$ to solvent polarity functions $f(\Delta\epsilon)$ and $f(\Delta n^2)$, chromophore ground and excited state dipole moments, μ_0 and μ_1, and their difference $\Delta\mu_{01}$, and a chromophore geometry parameter, a, according to Eq. (3):

$$\Delta\nu = \mu_0\Delta\mu_{01}f(\Delta\varepsilon)/4\pi\varepsilon_0 hc_0 a^3 + (\Delta\mu_{01})^2 f(\Delta n^2)/8\pi\varepsilon_0 hc_0 a^3 \tag{3}$$

Since the refractive index, n, of most common solvents is approximately constant, then $f(\Delta n^2)\approx 0$, and so for two chromophores A and B being compared in any two solvents we can immediately write Eq. (2):

$$\Delta\nu^A/\Delta\nu^B = (a^B/a^A)^3(\mu_0\Delta\mu_{01})^A/(\mu_0\Delta\mu_{01})^B \tag{4}$$

since all other terms cancel.

Approximations which may lead to the inaccuracy of this expression include the assumption of spherical chromophore geometry in the Onsager equation itself; the assumption of constant refractive index for different solvents; the source of dipole moment estimates [1]; and the assumption that ground state and excited state dipole moment vectors are coincident (discussed briefly previously [1], and discounted).

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