The Comparative Solvatochromism of Arylazo and Heteroarylazo Compounds Based on *N*,*N*-Diethyl-*m*-acetylaminoaniline and *N*,*N*-Diethyl-*m*-toluidine

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Abstract: Azobenzene dyes derived from various anilines and aminothiaheterocycles azo-coupled with commercially important *N*,*N*-diethyl-*m*-toluidine (**T** series) and *N*,*N*-diethyl-*m*-acetylaminoaniline (**A** series) are positively solvatochromic. The visible spectra of 16 pairs of derivatives have been measured in up to 22 solvents, and the transition energies related to Kamlet–Taft solvent polarity parameters. In general, **A**-series dyes are more bathochromic than their **T**-series counterparts in nonpolar solvents, consistent with colour chemistry tradition. However, in more dipolar solvents the more bathochromic T-series representatives unexpectedly become more bathochromic than their **A**-series partners. The relative solvatochromic shifts of the **A** and **T** series are related to their respective dipole moments. These in turn are distinguished by the effect of the anilide carbonyl group dipole moment, which is antiparallel to, and thus reduces, the dipole moment of the chromogen.

Keywords
azo compounds · dyes · heterocycles · correlation analysis · solvatochromism

Introduction

Much of organic chemistry is underpinned by rules of thumb derived over many years of empirical observation. As one of the oldest and best-established branches of organic chemistry, colour chemistry is particularly rich in such lore. Any new observation running counter to an accepted "rule" invites further scrutiny, not least to help define the limits of its applicability. Just such an observation led to the study reported in this paper. The accepted effect on colour of the acetylamino group in arylazobenzenes and their heteroaryl analogues (**1**; **A** series; Figure 1) is to induce a bathochromic shift (red shift; lower transition energy) relative to the corresponding toluidine derivative (**2**; **T** series).[1] In contrast to this generalisation, it was unexpectedly observed for some azothiophene derivatives in certain solvents that the visible absorption maximum in the electronic spectra of the anilide derivative is *less* bathochromic than the corresponding toluidine. The effect is illustrated by the spectra shown in Figure 2. This anomalous inverse bathochromic effect can have consequences of significance in the technical application of these colouring matters, where their visible appearance

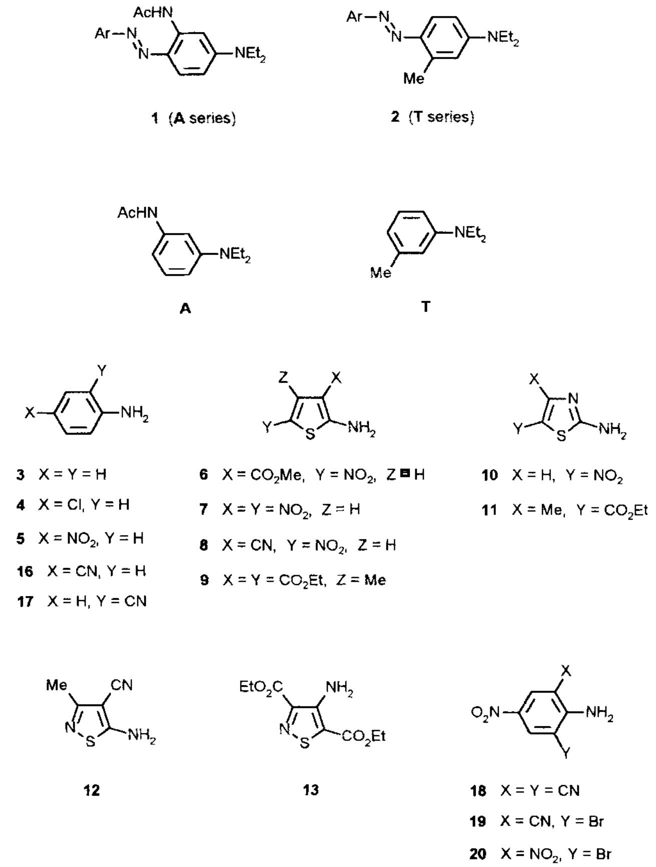

Figure 1. Structures of diazo components (**3**–**13**, **16**–**20**), coupling components (**A**, **T**) and general structures of the **A** and **T** series of azo dyes.

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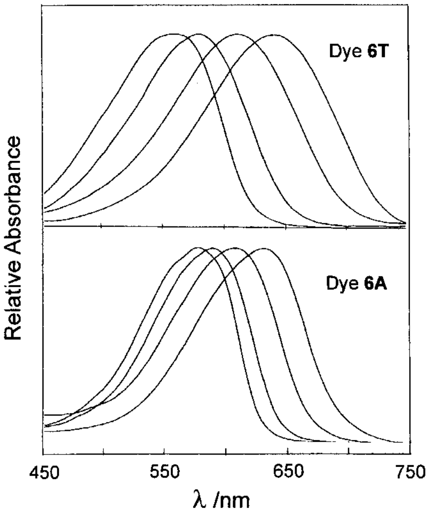


Figure 2. Visible spectra of azothiophenes **6A** and **6T** each recorded in cyclohexane, diethyl ether, acetone, DMSO (left to right). No attempt was made to allow for the high-energy shoulder on the absorption envelope of **6A** in cyclohexane (and possibly other solvents).

and other optical properties could be affected by solvent, host polymer matrix, textile substrate, and so on. As no immediate explanation for this unexpected observation came to mind, and since furthermore many azo dyes derived from **A** and **T** are of commercial importance, a more detailed study has been undertaken, the results of which comprise this paper.

Azobenzene dyes derived from three different anilines (**3**–**5**) were selected for study to define baseline behaviour. Since it appeared from the initial observation that a sulfur atom in the heterocycle, especially as a thiophene, might be significant in inducing the anomalous behaviour, azo compounds based on four 2-aminothiophenes (**6**–**9**) were also included. These were augmented by derivatives of two 2-aminothiazoles (**10**, **11**), and two aminoisothiazoles (**12**, **13**) to give a wider variety of sulfur-based heterocycle. The structures of all these aryl and heteroaryl diazo precursor residues are shown in Figure 1. In each of these cases, the pairs of anilide- and toluidine-based azo compounds derived from the corresponding anilines **A** and **T** (Figure 1) were studied in detail. The azo dyes themselves are labelled **3A**, **3T**, etc., depending on the diazo and coupling components used. Most data are from compounds available from the ICI/Zeneca specimen collection, apart from **3T** and **12T** which were prepared specially for this study.

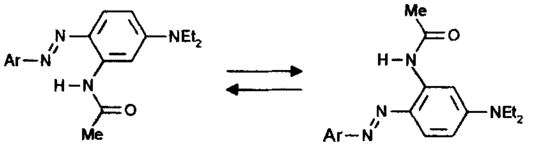
Since the nature of the solvent is evidently significant in determining whether the anomalous inverse bathochromic effect applies or not, and since furthermore it is known that many azobenzenes exhibit marked positive solvatochromism,[2] as further evidenced by the spectra shown in Figure 2, visible spectra for all compounds of interest were measured in a range of solvents of differing polarity and H-bonding characteristics. The goal was then to undertake correlation analyses of the measured data to yield quantitative relationships between transition energies and measures of solvent polarity. Such models would then be used to address two fundamental questions: when and why are some toluidine-derived azo dyes more bathochromic than their anilide counterparts?

Results and Discussion

Absorption maxima of visible spectra of the 22 azo dyes **3A**–**13A** and **3T**–**13T** measured in up to 22 solvents are recorded in Table 1. Because of duplicated measurements, a total of over 1500 spectra were recorded in this study. In most cases, the visible spectra comprised a single featureless absorption. However, in some cases, particularly for the **A** series, a more or less ill-resolved blue-shifted shoulder was apparent. The origin of this is not known, but vibrational fine structure of *N*,*N*-diethylaniline derivatives has been noted.[3] A second possibility is the presence of two conformers in solution. In support of this, a recent NMR study[4] has shown that an azobenzene closely related to **5A** adopts two planar conformations in solution as well as in the solid phase. In the first (**14**) the anilide substituent

Table 1. Visible absorption maxima (nm) and solvent polarity parameters for 22 solvents.

Solvent	Kamlet–Taft parameters							Absorption										
	π^*	α	β	δ	π^*_{azo}	$E_T(30)$	S'	**3A**	**3T**	**4A**	**4T**	**5A**	**5T**	**6A**	**6T**	**7A**	**7T**	**8A**
DMSO	1	0	0.76	0	1	45.1	3.00	463.4	438.3	474.5	456.3	529.6	520.8	632.3	642.7	651.3	686.1	639.0
DMF	0.88	0	0.69	0	0.86	43.8	2.78	458.3	429.7	471.1	443.9	521.6	513.8	621.7	630.2	646.4	676.4	629.4
butyrolactone	0.87	0	0.49	0		44.3	2.80	462.5	431.8	472.8	445.6	523.2	515.2	623.8	632.8	646.1	675.3	632.4
TMU	0.83	0	0.80	0		41.0		458.2	428.2	470.9	440.1	523.1	512.5	620.9	630.0	645.4	673.5	629.8
acetone	0.71	0.08	0.43	0	0.53	42.2	2.47	453.5	424.8	466.4	441.3	513.0	501.1	606.2	614.3	635.5	656.9	619.1
THF	0.58	0	0.55	0		37.4	1.69	454.8	422.3	466.9	436.1	516.0	498.8	606.0	604.1	634.6	644.4	614.8
EtOAc	0.55	0	0.45	0	0.37	38.1	1.80	452.2	420.5	464.2	433.5	509.4	490.6	601.1	597.4	630.0	638.6	610.6
Et_2O	0.27	0	0.47	0	0.16	34.5	1.21	447.8	416.2	460.1	425.6	503.2	476.0	590.5	581.6	619.3	619.4	600.2
Et_3N	0.14	0	0.71	0		32.1	0.40	441.3	414.4	457.0	424.4	504.7	468.5	585.6	569.7	616.0	605.5	592
c-hexane	0	0	0	0	0	30.9	0.15	440.9	414.7	453.3	422.9	507.5	465.9	578.9	563.2	607.9	597.8	592.8
pyridine	0.87	0	0.64	1	0.80	40.5	2.16							620	624	647	670	630
toluene	0.54	0	0.11	1	0.38	33.9	1.11	453.1		469.9	430.5	512.9	487.4	599.2	590.0	628.1	625.3	609.7
CH_2Cl_2	0.82	0.13	0.10	0.5	0.62	40.7	2.08	460.5	426.6	469.9	434.3	518.3	506.8	611.2	615.9	639.1	657.9	620.4
$CHCl_3$	0.58	0.20	0.10	0.5	0.62	39.1	1.74	459.3	423.1	469.8	432.3	518.3	504.0	608.9	608.9	637.3	649.5	617.2
$MeCCl_3$	0.49	0	0	0.5		36.2		451.8	420.1	466.4	431.1	512.7	497.8	600.5	595.2	629.8	635.4	610.5
CCl_4	0.28	0	0.10	0.5		32.4	0.87	448.8	417.7	468.9	425.9	513.2	478.2	587.8	573.6	618.4	609.8	601.8
MeOH	0.60	1.09	0.73	0	0.89	55.4	2.87	449.9	421.7	463.4	431.3	509.3	498.9	601.7	611.3	632.8	652.7	611.1
EtOH	0.55	0.88	0.80	0	0.86	51.9	2.80	449.8	420.2	463.2	429.8	507.8	496.9	601.4	608.1	632.1	644.3	610.8
1-PrOH	0.53	0.79	0.85	0	0.85	50.7	2.68	450.0	419.5	463.5	429.1	509.6	497.2	601.8	605.0	632.2	645.1	608.9
2-PrOH	0.48	0.68	0.93	0		49.2	2.66	449.3	417.7	463.2	427.7	507.1	494.4	599.5	602.2	630.7	638.8	608.7
HOAc	0.64	1.12		0			2.39							598	601	630	639	608
CF_3CH_2OH	0.73	1.51	0	0		59.8	3.55	463.1	464.9	469.3	471.3	515.2	520.9	616.2	635.4	630.4	665.0	619.1



14 **15**

H-bonds to the more remote of the two azo nitrogen atoms in a six-membered ring, while in the second the anilide group lies *anti* to this arrangement, implying H-bonding, or more probably electrostatic attraction, to the nearer of the azo nitrogen atoms in a five-membered ring (**15**). The situation becomes further complicated once it is recognised that some of the unsymmetrically substituted diazo components in **6A/T**–**13A/T** can adopt different, but still planar, conformations, again implying multiple absorption bands. Whatever the reason for the more complicated spectra observed in some cases, no attempt has been made to resolve the absorption envelope into its component bands, but rather the analysis has concentrated on the absorption maximum alone. As will become evident, this approach has led to a consistent result.

Plots of the transition energies corresponding to these wavelength maxima against single-parameter descriptions of solvent polarity, such as the well-known $E_T(30)$ scale,[5] proved unsatisfactory. In particular, H-bond donor (HBD) solvents such as alcohols deviated from the trend described by other solvents. However, even for these other, non-HBD, solvents, the plot was far from linear. Instead we turned to the Kamlet–Taft (K–T) multiparameter scale of solvent polarity.[6] This includes three main parameters: π^*, which quantifies solvent dipolarity/polarisability, and α and β, which quantify solvent HBD (Lewis acidity) and H-bond acceptor (HBA; Lewis basicity) strengths, respectively. Additionally, a correction factor δ, ascribed to polarisability, is sometimes necessary for aromatic and/or chlorinated solvents.[7] Values for all these parameters[8, 9] are included in Table 1. The K–T formalism describes an observable quantitative property in terms of a linear solvation–energy relationship (LSER),[6] as in Equation (1).

$$E = E_0 + s\pi^* + a\alpha + b\beta + d\delta \qquad (1)$$

In the present case, E corresponds to the observed transition energies ($E\,[\mathrm{cm}^{-1}] = 10^7/\lambda\,[\mathrm{nm}]$), and the coefficients s, a, b and d quantify the significances of the relevant K–T solvent parameters. E_0 is a constant term which corresponds to the transition energy in a solvent where $\pi^* = \alpha = \beta = \delta = 0$ (e.g. cyclohexane). Values for the coefficients and E_0 may be determined by (multilinear) regression analysis (MLRA).

Solvents can be conveniently classified depending on their K–T parameter values. In this study, we distinguish between the following. a) Dipolar aprotic solvents (non-HBD; $\alpha = \delta = 0$). This class includes both HBA and non-HBA solvents. Although acetone is a weak HBD solvent according to the K–T formalism ($\alpha = 0.08$), it is nevertheless included in this class. b) Aromatic solvents, in this case only toluene and pyridine ($\alpha = 0$, $\delta = 1$). c) Hydroxylic solvents (HBD; $\alpha > 0$) including alcohols and acetic acid, from amongst which we distinguish the particularly strong H-bond donor trifluoroethanol (TFE, which unlike the other alcohols is classified as a non-HBA solvent, $\beta = 0$). d) Chlorinated non-HBD solvents (CCl_4, $MeCCl_3$) ($\alpha = 0$, $\delta = 0.5$). e) Chlorinated HBD solvents ($CHCl_3$, CH_2Cl_2) ($\alpha > 0$, $\delta = 0.5$).

Solvatochromism in nonhalogenated, nonaromatic, nonhydroxylic solvents: In order to simplify an understanding of the solvatochromism of **3A/T**–**13A/T**, initial analysis was restricted to the ten dipolar aprotic solvents of class a. In principle, for these the LSER model of Equation (1) should depend only on the K–T π^* and β parameters, since $\alpha = \delta = 0$. However, for all the 22 dyes studied (**3A/T**–**13A/T**), the b coefficient of β was found to be essentially equal to zero in all cases, reflecting the fact that the solutes contain either no acidic HBD site (**T** series), or acidic/electrophilic sites such as the anilide NH (**A** series) that

maxima (nm)																				
8T	**9A**	**9T**	**10A**	**10T**	**11A**	**11T**	**12A**	**12T**	**13A**	**13T**	**16A**	**16T**	**17A**	**17T**	**18A**	**18T**	**19A**	**19T**	**20A**	**20T**
658.6	570.8	569.4	615.0	612.7	554.2	554.1	563.2	568.5	502.3	488.5	498	488	500	488	603	614	603.5	580	569	574
650.4	566.0	561.7	603.9	602.0	547.5	546.9	556.4	562.1	500.0	481.8										
648.3	564.4	562.5	605.3	605.3	547.9	546.1	556.3	562.7	497.6	484.3										
645.0	564.3	561.8	603.0	604.0	544.3	542.4	557.5	563.3	500.0	483.7										
627.0	555.3	550.3	590.6	590.3	537.6	534.1	547.8	551.0	492.8	469.9										
621.5	557.4	544.0	585.4	585.4	534.6	527.1	547.3	547.1	493.7	466.3										
617.6	552.3	542.6	581.0	574.7	529.9	523.3	543.3	540.4	492.2	461.5	487	457	487	458	590	591	586.5	554	557	552
600.5	547.1	525.8	565.1	561.2	520.4	509.9	537.1	531.7	489.3	451.4	484	449	484	449	588.5	583	581	543	552	531
590.7	544.6	514.9	559.2	549.6	517.5	502.5	535.5	524.1	487.0	444.5										
587.2	542.7	503.8	555.0	541.9	512.9	495.1	533.8	515.7	485.2	439.1	(486)	444	474	445	583.5	580	581.5	528	547	525
644	565	558	603	602	545	543	556	562	502	482										
607.7	555.6	532.6	576.6	568.0	531.4	518	543.0	537.0	494.7	456.3										
630.8	558.9	542.4	594.5	596.1	545.4	534.7	547.8	549.0	496.9	471.9										
625.0	557.1	534.3	590.2	591.2	543.1	532.4	549.6	545.1	494.6	462.6										
616.6	553.4	532.1	576.9	576.6	528	519.3	541.7	537.7	490.9	457.5										
599.1	548.8	514.0	564.0	555.3	523.3	507.1	540.0	525.2	489.2	444.4										
621.0	554.8	546.8	588.8	584.4	542.9	544.6	549.0	551.0	494.8	475.8										
619.0	556.7	544.5	585.8	582.5	541.6	540.1	548.2	548.6	494.0	469.9										
617.4	556.2	541.8	585.0	582.1	538.4	538.1	547.6	548.3	495.1	468.4										
615.8	554.8	540.7	583.2	579.0	536.9	534.6	545.9	545.9	494.1	466.6										
616	555	543	587	590	546	549	549	548	493	471										
637.7	560.5	545.8	598.6	613.0	553.3	552.8	554.1	567.3	498.5	491.8										

evidently leave the spectral shifts unaffected even if they take part in intermolecular interaction with basic/nucleophilic solvents rather than intramolecular H-bonding.[4] Thus, LSER in the class a solvents can be simplified to Equation (2), as evidenced by generally good linear plots of transition energy E against π^* values for most solutes.

$$E = E_0 + s\pi^* \qquad (2)$$

Deviations were few. The solvatochromic behaviour of each azobenzene solute is therefore characterised by two terms: E_0, which is an intercept energy at $\pi^* = 0$ and which thus has a value close to the experimental value for cyclohexane, and s, which corresponds to the slope of the plot. The larger the magnitude of s, the more solvatochromic is the solute (bigger shift between nonpolar cyclohexane, $\pi^* = 0$, and highly dipolar DMSO, $\pi^* = 1$). The E_0 and s values for each azo derivative are given in Table 2, alongside relevant statistics. The negative sign of s reflects the positive solvatochromism of all these solutes, corresponding to a more dipolar excited state and less dipolar ground state.[10] From a review of the results in Table 2, two significant general observations are immediately apparent. Firstly, for each **A**/**T** pair, the E_0 value of the **A** partner is lower than that of its **T** counterpart, that is, azo dye derived from **A** is more bathochromic than that from **T** in solvents as nonpolar as cyclohexane. Secondly, the solvatochromism as reflected by s is higher for the **T** member of each pair than for its **A** counterpart. A conclusion from this is that for all azo compounds studied there will be a characteristic value of $\pi^* > 0$ above which the **T** derivative will become more bathochromic than **A**. These values are easily derived and are recorded in Table 2 as $\pi^*_{\mathrm{A=T}}$. As far as we are aware, no π^* value greater than 1.2 has been reported for a pure solvent in the literature (e.g. $\pi^* = 1.2$, 1.12 and 1.0 for 2-cyanopyridine, $HCONH_2$ and DMSO respectively).[8] Thus, for some of the azo compounds with $\pi^*_{\mathrm{A=T}}$ appreciably above 1, the **A** derivative in all known solvents will always be observed to be more bathochromic than the **T** derivative, as shown graphically in Figure 3 for **13A**/**T**. However, for other arylazo solutes, the $\pi^*_{\mathrm{A=T}}$ values are less than 1.2, reflecting the observation that there are more polar solvents where the **T** derivative becomes more bathochromic than **A**. The most extreme case of those under study is **8A**/**T** (Figure 3), where $\pi^*_{\mathrm{A=T}} = 0.24$, corresponding to a crossover which occurs in solvents of such low dipolarity as Et_2O ($\pi^* = 0.27$).[11]

Table 2. Results of correlation analysis and derived $\pi^*_{\mathrm{A=T}}$ values; absorption energies (cm^{-1}) recorded in nonaromatic, nonchlorinated, nonhydroxylic solvents only.

	Regression constants		Statistics			
Dye	E_0	s	N	r^2	σ (cm^{-1})	$\pi^*_{\mathrm{A-T}}$
3A	22713	−1108.3	10	0.952	90.3	1.92
3T	25363	−2488.8	5	0.928	83.8	1.92
4A	22029	−947.4	10	0.981	48.5	1.95
4T	24207	−2063.3	7	0.838	99	1.95
5A	20106	−1111.5	9	0.894	119	1.13
5T	21594	−2427.7	10	0.987	101.7	1.13
6A	17311	−1432.7	9	0.99	56.7	0.63
6T	17834	−2258.6	10	0.992	75.7	0.63
7A	16430	−1081.1	10	0.99	40.4	0.31
7T	16786	−2238.8	10	0.995	59.3	0.31
8A	16998	−1292.6	10	0.975	75.6	0.24
8T	17121	−1814.8	10	0.969	117.9	0.24
9A	18497	−896.2	10	0.946	77.8	0.91
9T	19731	−2246.6	10	0.996	75.6	0.91
10A	*18122*	*−1796.1*	10	0.995	59.3	0.89
10T	18459	−2176.5	10	0.989	82.7	0.89
11A	19561	−1814.8	10	0.969	117.9	0.93
11T	20214	−2151.6	10	0.998	37	0.93
12A	18831	−978.6	10	0.948	83.3	0.65
12T	19360	−1798.8	10	0.987	74.7	0.65
13A	20634	−693.6	9	0.971	45.8	1.3
13T	22827	−2385.4	10	0.985	106.8	1.3
16A	20920	−815.6	3	0.968	77.3	1.46
16T	22724	−2048.6	4	0.933	287.6	1.46
17A	21048	−1042.9	4	0.972	92.3	1.68
17T	22684	−2014.8	4	0.933	283.3	1.68
18A	17184	−546.2	4	0.943	70.2	0.51
18T	17519	−1207.2	3	0.984	80.9	0.51
19A	17321	−666.5	4	0.874	132.4	1.6
19T	18921	−1668.3	4	0.996	53.1	1.6
20A	18302	−704.9	4	0.991	35.1	0.83
20T	19132	−1708.2	4	0.976	139.8	0.83

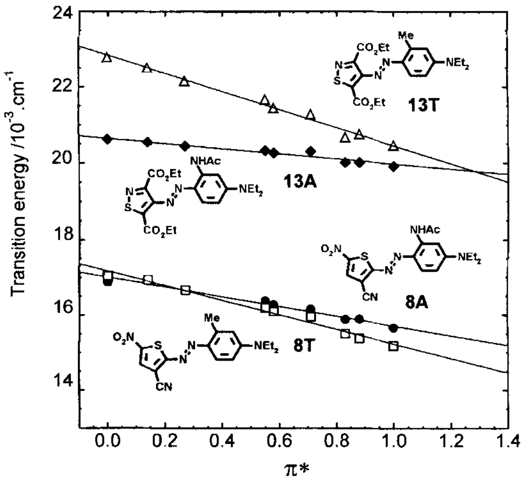


Figure 3. Plots of transition energies versus π^* for the **8A** (●), **8T** (□) and **13A** (◆), **13T** (△) pairs of azo dyes in some aprotic solvents, demonstrating $\pi^*_{\mathrm{A=T}} = 0.24$ for the former and $\pi^*_{\mathrm{A=T}} = 1.3$ for the latter.

Inspection of the series of $\pi^*_{\mathrm{A=T}}$ values suggests a correlation with measures of diazo component electronegativity, and this is borne out by acceptably linear plots against other empirical parameters which reflect the electronegativity of the diazo components, such as $\lambda_{\max}$ values in cyclohexane or E_0 (Figure 4). This relationship is significant in that it includes the

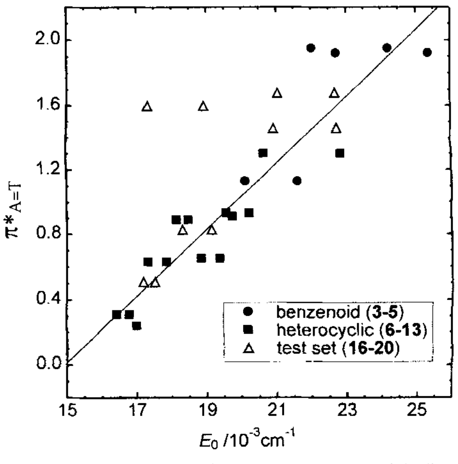


Figure 4. Plot of $\pi^*_{\mathrm{A-T}}$ versus correlation equation intercept, E_0. The straight line shown was defined by the behaviour of three pairs of benzenoid (●) and eight pairs of heterocyclic (■) azo dyes. The remaining points (△) correspond to a test set of five pairs of benzenoid azo dyes.

benzenoid and heterocyclic derivatives on the same line, indicating that the heterocyclic sulfur atom is *not* having a special effect on the solvatochromic properties. Nor are specific solvent HBD effects responsible, since none of the solvents so far discussed is an H-bond donor.

In order to provide confirmation for the above conclusion, a test set comprising further pairs of arylazo compounds based on anilines **16**–**20** (Figure 1) were studied in a restricted number of solvents. These dyes include examples of substituent patterns where the bathochromicity switch is predicted to occur in the accessible solvent dipolarity range. Measurement of a few critical absorption maxima (Table 1) allowed estimation of E_0 and s and thus $\pi^*_{\mathrm{A=T}}$ values (Table 2). When these data are included in the plot defined by the previous series of molecules (Figure 4), with one exception they behave as predicted and fall on the correlation line. The exception (**19A/T**) possibly derives from the highly nonlinear E versus π^* plot for **19A** ($r^2 = 0.87$; cf. $r^2 > 0.93$ for most other dyes considered), leading to imprecise $\pi^*_{\mathrm{A=T}}$ estimation. Significantly, the benzenoid species **18A/T** and **20A/T** show bathochromicity inversion just as for the comparably bathochromic heterocyclic derivatives already discussed. Clearly there is no need to invoke special behaviour on the part of thiaheterocyclic derivatives.

Although this relationship answers one of the key questions underlying this study and allows prediction of *whether* and *when* the toluidine-based arylazo derivative will become more bathochromic than the corresponding anilide, it does not explain *why* different arylazo derivatives behave in the way they do. Since the $\pi^*_{\mathrm{A=T}}$ crossover points of the LSER of the **A** and **T** series are determined both by the slope of the line s and the intercepts E_0, we looked for underlying physical properties which influenced their values. To aid this, a series of SCF-MO CI calculations was undertaken at the PPP level using a model which allows for the effects of sigma-framework polarisation.[12] Further details of the calculation are given in the Experimental Procedure, and results are given in Table 3. The calculated absorption maxima correlate equally well both with experiment (cyclohexane and DMSO data) and wavelengths corresponding to E_0 for azo dyes **3A/T**–**13A/T** (Figure 5). However, the slope of the correlation is not unity and the intercept is not zero, so that while the experimental trend is reproduced satisfactorily, absolute values are not. But, more importantly, because of this good correlation it was concluded that other computed parameters were also likely to be reliable. In particular, further analysis is based on calculated ground- and excited-state dipole moments, and their difference (i.e., μ_0, μ_1, and $\Delta\mu_{01}$, respectively, Table 3).

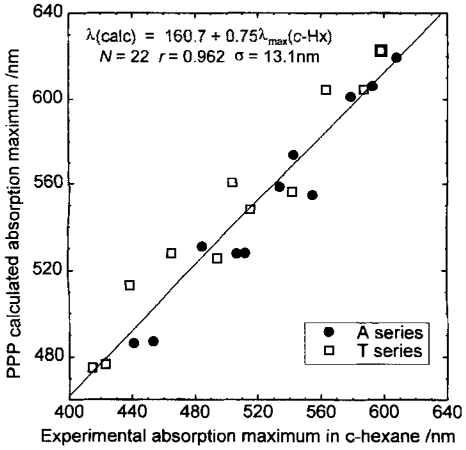


Figure 5 Plot of PPP-calculated absorption maxima versus experimental values for azo dyes **3A/T**–**13A/T**.

Table 3. Results of PPP calculations.

Dye	PPP calculation μ_0	μ_1	λ	Experimental $\lambda_{\max}$ (nm) *c*-hexane	DMSO
3A	2.9	10.9	486.2	440.9	463.4
3T	4.6	16.4	474.9	414.7	438.3
4A	4.2	12.8	487.0	453.3	474.5
4T	6.7	18.4	476.5	422.9	456.3
5A	10.1	25.3	527.6	507.5	529.6
5T	13.1	30.9	527.8	465.9	520.8
6A	11.8	20.7	601.0	578.9	632.3
6T	13.8	27.9	604.2	563.2	642.7
7A	15.4	22.3	619.3	607.9	651.3
7T	17.2	29.4	622.5	597.8	686.1
8A	13.2	20.4	605.9	592.8	639.0
8T	15.3	27.4	604.4	587.2	658.6
9A	4.4	11.3	573.7	542.7	570.8
9T	7.1	18.9	560.5	503.8	569.4
10A	14.6	21.5	554.7	555.0	615.0
10T	16.7	27.8	556.3	541.9	612.7
11A	10.4	15.5	527.8	512.9	554.2
11T	13.1	22.4	525.6	495.1	554.1
12A	5.4	11.3	558.5	533.8	563.2
12T	7.3	18.1	548.1	515.7	568.5
13A	3.7	20.4	531.0	485.2	502.3
13T	6.8	24.1	513.0	439.1	488.5

We have just seen that the trend in E_0 term of Equation (2) for different azo dye structures can be modelled quantum-mechanically, and therefore relies on conventional substituent effects such as electronegativity. Somewhat more surprising is the observation, in the case of the *relative* behaviour of **A/T** pairs, that the relationship between transition energy and electronegativity, or overall charge distribution, can be reduced to a simple correlation between $E_0^{\mathrm{T}}/E_0^{\mathrm{A}}$ and the ground-state dipole moment ratio $\mu_0^{\mathrm{T}}/\mu_0^{\mathrm{A}}$. Figure 6a demonstrates a reasonable, if inexact, relationship.

We turn now to the parameter s, the π^* coefficient in Equation (2) which quantifies the experimentally observed solvatochromism, again concentrating initially on the relative behaviour. Significantly, the PPP-calculated ground-state dipole moment of the **A** member of each pair is in every case less than that of its **T** partner (Table 3). Excited-state dipole moments follow the same pattern, except that the difference between the **T** and **A** molecules is even greater: $\Delta\mu_1^{\mathrm{TA}} > \Delta\mu_0^{\mathrm{TA}}$. Since relative stabilisation is dependent on dipole moment, it follows qualitatively that $|s^{\mathrm{T}}| > |s^{\mathrm{A}}|$, as is observed experimentally for all the series under study (Table 2).

Attempts to derive a more quantitative relationship have revealed that $s^{\mathrm{T}}/s^{\mathrm{A}}$ correlates reasonably with the ground-state dipole moment ratio $\mu_0^{\mathrm{T}}/\mu_0^{\mathrm{A}}$ as shown in Figure 6b. Interestingly, both the relationships of Figures 6a and 6b pass near to the points $E_0^{\mathrm{T}}/E_0^{\mathrm{A}} = \mu_0^{\mathrm{T}}/\mu_0^{\mathrm{A}} = 1$ and $s^{\mathrm{T}}/s^{\mathrm{A}} = \mu_0^{\mathrm{T}}/\mu_0^{\mathrm{A}} = 1$, respectively. This suggests that a hypothetical **A/T** pair will have identical absorbance maxima behaviour if their ground-state dipole moments are equal.

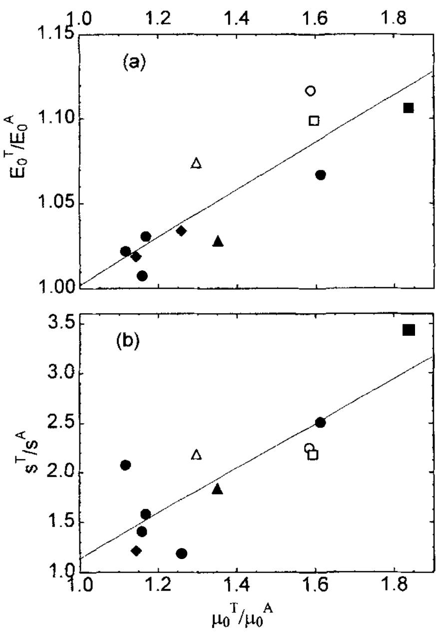


Figure 6. a) Plot of E_0^T/E_0^A versus μ_0^T/μ_0^A for dye pairs **3A/T** (○), **4A/T** (□), **5A/T** (△), azothiophenes **6A/T**–**9A/T** (●), azothiazoles **10A/T**, **11A/T** (◆), 5-azoisothiazoles **12A/T** (▲), and 4-azoisothiazoles **13A/T** (■) ($N = 11$, $r = 0.87$). b) Plot of s^T/s^A versus μ_0^T/μ_0^A; the symbols represent the same dye pairs as in (a) ($N = 11$, $r = 0.86$).

In fact, a full study of the problem should entail application of the well-established modified Onsager equation [Eq. (3)].[13]

$$E(\text{solvent}) = E(\text{gas}) - \mu_0 \cdot \Delta\mu_{01} f/(hc_0)(1 - Rf) - (\Delta\mu_{01})^2 f'/(2hc_0)(1 - Rf') \qquad (3)$$

This equation relates transition energy quantitatively both to molecular structure in terms of size, polarisability (R) and dipole moments, and to solvent properties: the functions f and f' are dependent on solvent dielectric constant and refractive index, respectively, as well as on solute dimensions. This formulation makes the common assumption that disperse interactions are small enough to be ignored.

In a recent application to the case of a donor–acceptor substituted bithiophene, allowance for all other variables in Equation (3) has led to an estimate of the excited state dipole moment in excellent agreement with a value determined by a totally different method.[14] However, in view of the complexity of Equation (3) due to its multiparameter dependence, coupled with the variations in polarisabilities and molecular dimensions of **3A/T**–**14A/T**, we have chosen not to attempt to derive all the terms necessary to apply it. However, given a series of crude but not unreasonable approximations, it can be shown that Equation (3) can be reduced to the empirical relationship of Figure 6b. Thus, if the refractive indices of the solvents under consideration are roughly equal, the solvatochromism of a general dye can be related to the dielectric constant function, f, alone since the right-hand term of Equation (3) dependent on the refractive index function f' cancels, so that we obtain Equation (4), where k_4 is a constant accounting for all the non-dipole terms in Equation (4).

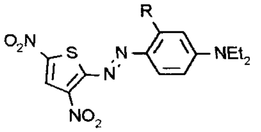
$$s = E(\text{DMSO}) - E(c\text{-Hx}) \approx -\mu_0 \cdot \Delta\mu_{01}[f^{\text{DMSO}}/(1 - Rf^{\text{DMSO}}) - f^{c\text{-Hx}}/(1 - Rf^{c\text{-Hx}})]/hc_0 \approx k_4\mu_0\Delta\mu_{01} \qquad (4)$$

Thus, for an **A/T** pair based on diazo component **x**, Equation (5) applies, where $k_5 = k_4^{xT}/k_4^{xA}$.

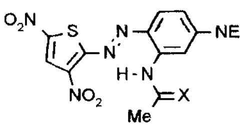
$$s^{xT}/s^{xA} \approx k_5\mu_0^{xT}\Delta\mu_{01}^{xT}/\mu_0^{xA}\Delta\mu_{01}^{xA} \qquad (5)$$

This applies for a single **xA/T** pair. If the geometries and polarisabilities of the series of azo dyes based on **3**–**14** can be considered roughly equal, then k_5 can be considered constant for all **x** (= anilines and aminoheterocycles **3**–**14**).[15] Furthermore, from the data in Table 3, $\Delta\mu_{01}^{xT}/\Delta\mu_{01}^{xA} \approx$ constant ≈ 1.7, and so Equation (6) holds, corresponding to the experimentally based correlation of Figure 6b.

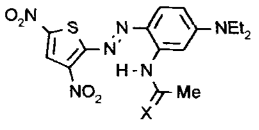
$$s^T/s^A \approx k\mu_0^T/\mu_0^A \qquad (6)$$



21 (R = H, Me, OMe, NH$_2$)



s-cis



s-trans

	μ_0		μ_0	$\Delta\mu_0$
22 X = O	15.4	**23** X = O	17.9	2.5
24 X = NH	15.9	**26** X = NH	17.7	1.8
25 X = CH$_2$	17.5	**27** X = CH$_2$	17.8	0.3

Figure 7. Azo derivatives of thiophene **7** for which PPP calculations were carried out, and resultant GS dipole moment values and differences (Debye) for alternative conformations of anilide and analogous substituents.

Given the evident significance of dipole moment in determining relative solvatochromic shift as implied both by the relationships of Figure 6 and the theoretical Onsager equation, we further investigated its connection with molecular structure by means of PPP calculations on other azo derivatives based on azothiophene **7**, shown as **21**–**27** in Figure 7. These were selected to include variations in the chemical nature of the substituent *ortho* to azo in the coupling component, as well as conformational variations where appropriate. When constrained in the *s-cis* conformation (N–H *trans* to C=O; **22**) commonly adopted by acyclic amides,[16] the calculated dipole moment of the anilide was uniquely less than that of all other derivatives (**21**; R = H, Me, OMe, NH$_2$). The dipole moment of the anilide dye increased when the carbonyl group was oriented *cis* with respect to the NH bond (**23**). When the carbonyl oxygen was substituted by successively less-electronegative atoms in amidine **24** and enamine **25**, the difference between *s-cis* and *s-trans* became less for the former, and was near zero for the latter (Figure 7). This behaviour was the same in the excited state. We therefore believe that the underlying physical reason for the decreased dipole moments of the **A** series of azo derivatives compared with those of **T**, and thus eventually their relative solvatochromic behaviour, is simply the contribution of the highly dipolar carbonyl group of the anilide pointing essentially antiparallel to the dipole moment of the remainder of the chromogen.

The relationships and the derived conclusion so far discussed concern only *relative* behaviour of **A**/**T** pairs. Attempts to include all *absolute* data from the present study in a single empirical relationship by correlation analysis have been unsuccessful. A common view is that solvatochromic shift tends to increase with substitution of electron acceptor groups into the diazo component.[2h] However, for the series of azo compounds included in this study this is far from the truth: there is no correlation between *s*, quantifying the solvatochromic shift, and the transition energies in either cyclohexane or DMSO, as measures of electron acceptor strength in the diazo component. Other workers[2f] have identified a nonlinear relationship between *s* values determined for the solvatochromism of nine azobenzenes, and the PPP-calculated $\Delta\mu_{01}$ parameter, implying increased solvatochromism for species with higher calculated dipole moment differences. However, when these quantities are plotted for the current data, no such relationship is observed ($r = 0.4$), as Equation (3) would in any case predict. At best, the **A** and the **T** series of data fall into two roughly differentiated clusters, of no quantitative predictive value. Rather reluctantly we currently accept that in the case of wide-ranging structural types, a successful unified model for solvatochromism derived from correlation analysis is likely to remain elusive.

Solvatochromism in all solvents: Inclusion of all solvent data in plots such as that shown for dye **12T** in Figure 8 reveals how other solvents relate to the LSER defined by the class a "ideal" dipolar aprotic solvents already discussed. Several more or less general observations became apparent which are addressed before more detailed analysis of the full LSER.

First, in almost all dyes studied, the experimental difference between transition energies in dichloromethane and chloroform was less than implied by their K–T π* values,[8] and further preliminary analysis indicated that allowance for specific effects via the K–T α, β, and δ parameters gave no satisfactory improvement. Data measured in these two solvents were omitted from the detailed LSER, and are considered again below. Secondly, it was generally found that glacial acetic acid data fell on the *E* versus π* lines and required no allowance for an HBD effect. This is not uncommon for acetic acid, where the strength of the acetic acid cyclic dimer H-bonds is sufficiently high to prevent H-bonding to weaker acceptor sites in solutes.[17] In effect, acetic acid is behaving as a non-HBD dipolar solvent, and was not included in further LSER analyses. Thirdly, it became apparent in some cases that particular solvents, frequently trifluoroethanol, were outliers. In the case of TFE this is possibly because, being a much stronger HBD solvent, it can H-bond to solute sites where such bonding is not possible by weaker HBD alcohols. In any case, such data were omitted from LSER development.

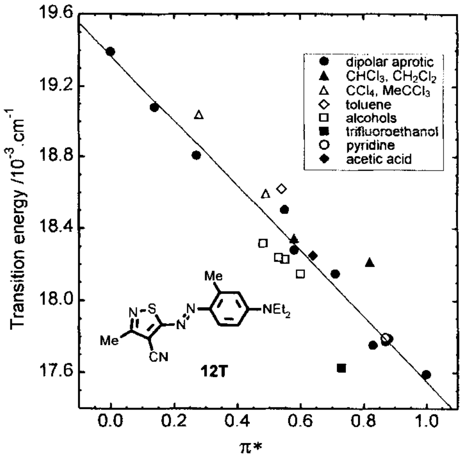


Figure 8. Plot of transition energies of azoisothiazole **12T** versus π* recorded in 22 solvents.

LSERs based on the full K–T Equation (1) were explored by multilinear regression analysis. The most acceptable models derived and their corresponding statistics are recorded in Table 4. Also included are comments which list particular sol-

Table 4. LSER derived from full data set.

	Regression coefficients				Statistics				
Dye	E_0	$s\,\pi^*$	$a\,\alpha$	$d\,\delta$	N	r^2	σ	F	Comment
3A	22678	−1077.4	166.7		17	0.948	73.9	127.9	py not measured; TFE bad outlier omitted
3T	24758	−1778.8			14	0.935	83.2	173.6	also omitted cHx, Et_3N, CCl_4, TFE; not good correlation
4A	22049	−955.3			15	0.962	55	329.7	all chlorinated omitted, plus toluene; α may be significant
4T	23958	−1727.5	301.8	301.4	15	0.883	156.5	27.6	also omitted *c*-Hx, Et_3N, CCl_4, TFE; not good correlation
5A	20123	−1143.8	134.8		15	0.903	97.4	55.6	poor correlation; omitted all chlorinated solvents plus *c*-Hx
5T	21550	−2388.6	−139.2		17	0.964	138.5	116.7	*d* coefficient of δ ca. zero
6A	17362	−1436.3			19	0.961	79.2	419.8	
6T	17877	−2317.4	−216.1	248.3	19	0.986	83.8	347.2	
7A	16435	−1093.6			18	0.982	41.2	879.5	TFE omitted as outlier
7T	16821	−2301.3	−81.8	261.2	19	0.986	81.6	346.7	tol and py worst deviants
8A	17008	−1296.7	87.5		19	0.973	61.1	286.6	note +ve α
8T	17180	−1970.8	26.3	173.9	19	0.973	95.9	179.3	tol, py worst; positive *a* coefficient of α
9A	18487	−888.9			19	0.945	58.8	292.1	
9T	19783	−2320.6	−140	255	18	0.984	88.8	287.4	TFE omitted as bad outlier
10A	18141	−1829.2			19	0.97	87.4	558.5	thiazole
10T	18505	−2241.7	−224.2	160.8	19	0.97	119.3	159.9	TFE, tol, py deviants
11A	19556	−1426.8	−296.7		19	0.983	57.9	459.5	negative *a* coefficient of α (thiazole)
11T	20198	−2142.5	−478.6	185.0	19	0.986	83.3	348.4	negative *a* coefficient of α (thiazole)
12A	18830	−981.8			19	0.929	74.5	221.6	ROH well within s.d.
12T	19410	−1868.9	−223.1	143.5	19	0.979	84.1	228.2	*d* coefficient of δ hardly statistically significant
13A	20635	−708.5			19	0.896	63.9	156.8	acetone is outlier
13T	22929	−2521.8	−408.1	233.3	19	0.973	130.3	182.3	tol, py worst

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vents that have been omitted from each study. In most cases the models fit the experimental data well, although those for **3T** and **4T** in particular are not good.

In none of the series of azo compounds studied has the solvatochromism of the thiophene or other heterocyclic derivatives shown greater (or less) dependence on H-bonding solvents compared with the benzenoid analogues. Thus H-bonding to sulfur has no role in influencing solvatochromism. Indeed, a search of the Cambridge Structure Database[18] for thiophenes with potentially H-bonding hydrogen atoms near sulfur has revealed *no* definitive example of H-bonding to thiophene in the crystal. We therefore conclude that solvent H-bonding to the sulfur atom of derivatives in this study is unlikely. Furthermore, the LSER derived for the full solvent data set indicate that the observed solvatochromism is dominated by nonspecific dipolar and polarisability effects. Specific effects due to H-bonding, as reflected by α, can be viewed as perturbations of this trait.

The availability of the series of LSER given in Table 4 opens the possibility of calculating π^* K–T parameters for solvents not included in the model development. Rearrangement of Equation (1) leads to Equation (7) which, after substitution of measured excitation energies recorded in $CHCl_3$ and CH_2Cl_2 and data from Table 4, can be solved by MLRA. The **A** and **T** series were treated separately. i) In the former, input LSER were restricted to the seven data sets in Table 4 for which the a coefficient of α was found to be negligible, thus giving a value for π^* alone. ii) In the latter series, solution for all 11 data sets gave both π^* and α values.[19]

$$E(solvent) - E_0 - d\delta = s\pi^* + a\alpha \qquad (7)$$

The results from the two sets of data are consistent: $\pi^*(CHCl_3) = 0.66 \pm 0.02$ (i), 0.63 ± 0.03 (ii); $\pi^*(CH_2Cl_2) = 0.71 \pm 0.02$ (i), 0.725 ± 0.02 (ii). These estimates of π^* differ appreciably from older literature values:[8] $\pi^*(CHCl_3) = 0.58$; $\pi^*(CH_2Cl_2) = 0.82$. On the other hand, they are close to the more recent values:[3] $\pi^*(CHCl_3) = 0.69$; $\pi^*(CH_2Cl_2) = 0.73$.

Correlation of solvatochromism data with other solvent polarity schemes: Buncel and Rajagopal have introduced alternative π^* values for solvents based on the solvatochromism of a series of diazahemicyanines, and labelled the new values π^*_{azo} (Table 1).[20] It was claimed that these were superior to the conventional K–T π^* values in many correlations of solvatochromism and other data, and we anticipated that in view of their derivation from azo-like molecules they should be more appropriate in the current study. However, for the dipolar aprotic class a solvents alone, the K–T π^* parameter proved superior to π^*_{azo} in 12 of 22 correlations (ten data points in the former case; six in the latter). We therefore see no compelling reason to favour the newer π^*_{azo} parameters over π^*.

Also recently introduced is Drago's multiparameter so-called "Unified Solvation Model".[21] We restrict attention to the dipolarity/polarisability parameter S' (Table 1) which comes closest to reflecting the same properties as π^*. While correlation of solvatochromic shifts for all 22 solutes, again restricted to class a solvents, with S' was satisfactory (nine measurements, Table 1), π^* (ten measurements) gave superior correlations as reflected by the correlation coefficient, r, in every case. Notwithstanding Drago's critique of the K–T scale,[21] there appears to be no reason to abandon π^*, at least in solvatochromism studies of azo derivatives.

Conclusions

The mass of data reported in this paper comprise a four-dimensional solvatochromism matrix—transition energy as a function of solvent polarity, diazo component electronegativity and coupling component substituent. We contend that only by studying the problem in this degree of detail has it been possible to derive answers to the two questions posed in the Introduction. Correlation analysis has shown that "anomalous" bathochromicity crossover is a function of the relative electronegativity of the substituents in the molecule, and it will occur more readily for more bathochromic species, whatever their constitution. The effect of the conformation of the acetanilide carbonyl group is central to the decrease of the overall dipole moment of arylazo chromophores compared with the relatively apolar methyl group, and results in the differing solvatochromic behaviour of the two species. Cross-over behaviour of this type has been noted qualitatively in a previous study for the methylsulfonamide analogue of **5A**, in comparison with the unsubstituted and appreciably more solvatochromic parent azo dye.[1] The substituent structure and conformational options suggest that the same explanation could apply to this pair of dyes as to the anilide/toluidine series. It is planned to examine these and other substituent combinations, and explore the significance of the crossover π^* values alongside those discussed here.

Alternative analyses of the data could reveal other properties of interest. For example, diazo component substituent additivity can be demonstrated for a subset of the heterocyclic azo compounds.[22] The relationship between the derived empirical substituent increments and solvent will be the subject of a later report.

Experimental Procedure

Materials: Solvents, which were the highest-quality, driest ones commercially available, were used immediately after opening. All azo dyes apart from **3T** and **12T** were available from the Zeneca Specialties Fine Chemicals Collection. All had been prepared by conventional diazotisation and coupling, either in aqueous acid or in concentrated sulfuric acid. The procedures described for dyes **3T** and **12T** are typical.

***N*,*N*-Diethyl-3-methyl-4-[(phenyl)azo]benzeneamine** (**3T**): To aniline (2.28 g, 2.45×10^{-2} mol) in water (56 mL) containing 3 equiv of hydrochloric acid (7.16×10^{-2} mol) at 0–5(°C was added dropwise a cold aqueous solution (13 mL) of sodium nitrite (1.71 g, 2.48×10^{-2} mol). After 10 min, excess nitrite was destroyed by addition of 10% aqueous sulfamic acid solution, and the diazonium salt solution was added to *N*,*N*-diethyl-*m*-toluidine (4 g, 2.45×10^{-2} mol) in acetone while the the temperature was held below 5(°C. Aqueous sodium carbonate solution (20%) was added to bring the pH to 8.3 and after a further 4 h at 5(°C the temperature was allowed to warm to ambient. The suspension was filtered, washed with water and dried to give crude product (5.63 g, 86%) which was crystallised from ethanol; m.p. 55(°C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.21$ (6H, t, $J = 7.1$ Hz), 2.70 (3H, s), 3.42 (4H, q, $J = 7.1$ Hz), 6.53 (1H, d, $J = 2.9$ Hz), 6.54 (1H, dd, $J = 8.7$ Hz, 2.9 Hz), 7.34 (1H, t, $J = 7.3$ Hz), 7.45 (2H, dd, $J = 7.3$ Hz, 8.4 Hz), 7.75 (1H, d, $J = 8.7$ Hz), 7.83 (2H, d, $J = 8.4$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 12.77$ (CH_3), 18.31 (CH_3), 44.57 (CH_2), 108.57 (CH), 111.97 (CH), 117.17 (CH), 122.26 (CH), 128.86 (CH), 128.89 (CH), 141.36 (Cq), 141.42 (Cq), 150.08 (Cq), 153.72 (Cq); m/z (EI^+) 268 (70.8%, M^+).

***N,N*-Diethyl-3-methyl-4-[(5-carboxyethyl-4-methyl-2-thiazolyl)azo]-benzeneamine (12T)**: Nitrosylsulfuric acid (2.53 g, 1.99×10^{-2} mol) in sulfuric acid (10.10 g) was poured into 40 mL of a mixture of acetic and propionic acids (50:50, v/v) and cooled to 0–5 °C. The aminothiazole **12** (3.7 g, 1.99×10^{-2} mol) was added and the mixture stirred for 90 min at this temperature, then added to *N,N*-diethyl-*m*-toluidine (3.8 g, 2.33×10^{-2} mol) in acetone (25 mL) containing 2 mL of 1 M sulfamic acid. The pH was raised until the dye precipitated. This was filtered, washed with water and dried to give crude product (3.78 g, 53 %) which was chromatographed on silica gel using ethyl acetate and dichloromethane (5:95, v/v) as eluent to give pure product as violet crystals; m.p. 145 °C; IR (KBr)(cm^{-1}): $\tilde{\nu}_{\max} = 1690, 1685$; ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$): $\delta = 1.17$ (6H, t, $J = 7.2$ Hz), 1.30 (3H, t, $J = 7.2$ Hz), 2.56 (3H, s), 2.70 (3H, s), 3.40 (4H, q, $J = 7.2$ Hz), 4.27 (2H, q, $J = 7.2$ Hz), 6.44 (1H, d, $J = 2.5$ Hz), 6.49 (1H, dd, $J = 9.4$ Hz, 2.5 Hz), 7.89 (1H, d, $J = 9.4$ Hz); ^{13}C NMR (100 MHz, $\mathrm{CDCl_3}$): $\delta = 12.80$ ($\mathrm{CH_3}$), 14.36 ($\mathrm{CH_3}$), 17.83 ($\mathrm{CH_3}$), 18.32 ($\mathrm{CH_3}$), 44.96 ($\mathrm{CH_2}$), 61.04 ($\mathrm{CH_2}$), 110.50 (CH), 111.85 (CH), 119.75 (CH), 120.16 (Cq), 141.02 (Cq), 145.05 (Cq), 152.63 (Cq), 159.92 (Cq), 162.90 (Cq), 179.70 (Cq); m/z ($\mathrm{EI^+}$) 361 (0.1 %, M^+).

Spectroscopy: Spectra were recorded at room temperature in dilute solutions under slow scan on Perkin–Elmer Lambda 2 and Lambda 9 spectrophotometers operating under PECSS control. Absorption maxima recorded in Table 1 are the average of at least three scans and are believed to be accurate to within ±2 nm. In some cases, particularly in the nonpolar solvents cyclohexane and triethylamine, spectra clearly deviated from the trend defined by other solvents, and aggregation was suspected even at the low dilutions studied. These data were therefore omitted from subsequent analyses. A typical treatment of other solvents is summarised in Table 4. Any shoulders on the major absorption peaks were ignored. However, in the case of dyes **18 A** and **19 A** in the test set, twin maxima of roughly equal intensity were clearly observed, and for these the higher-energy peaks were taken.

Computations: Correlation analyses were carried out in the Statistica/w package,[23] taking advantage of (multi)collinearity diagnostics present in the routines for multilinear regression analyses. Statistics recorded are: N, the number of data points; r^2, the square of the (multi)linear regression coefficient; σ, the standard deviation of the model in cm^{-1}, and F, Fisher's statistic. Ground- and excited-state properties were calculated in the PPP MO program PISYSTEM for Windows[12] with the program's default parameters, which are taken from the literature.[24] Input molecular geometries assumed the acetylamino group in **A**-series dyes H-bonds to the more remote of the azo nitrogen atoms, as represented in **1** and **14**. The same assumption was made for **21** (R = $\mathrm{NH_2}$). In contrast, the toluidine methyl group of all **T**-series dyes plus **21** (R = H, OMe) was oriented *anti* to the same nitrogen, as in **2** and **21**, to minimise steric clash. In general, diazo component conformation was such that the smaller substituent, usually either a C–H unit or a ring heteroatom, was *syn* to the more remote azo nitrogen, as implied by the conformations shown for structures **21**–**27**. In this way, planar conformations appeared to be quite realistic for most azo dyes, and geometry minimisation within a planar conformation was carried out prior to submission for SCF MO calculation. The main questionable case is that of **13 A/T**, where steric interaction of one ester group with azo nitrogen is likely to lead to bond torsion somewhere in the molecule. However, even here we have assumed planarity, our main justification being the good agreement between calculated and experimental $\lambda_{\max}$ values (Table 3). Geometry optimisation of input molecular sketches was carried out automatically by PISYSTEM with a two-dimensional force field routine, yielding realistic bond lengths and angles.

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[1] P. Gregory, D. Thorp, *J. Chem. Soc. Perkin Trans. 1* **1979**, 1990.
[2] a) B. Marcandalli, I. R. Bellobono, E. Selli, A. Polissi, *Dyes and Pigments* **1987**, *19*, 239; b) D.-M. Shin, D. G. Whitten, *J. Am. Chem. Soc.* **1988**, *110*, 5206; c) D.-M. Shin, K. S. Schanze, D. G. Whitten, *J. Am. Chem. Soc.* **1989**, *111*, 8494; d) N. Nishimura, T. Tanaka, M. Asano, Y. Sueishi, *J. Chem. Soc. Perkin Trans. 2* **1986**, 1839; e) S. Kobayashi, H. Yokoyama, H. Kamei, *Chem. Phys. Lett.* **1987**, *138*, 333; f) H. Mustroph, J. Epperlein, *J. Prakt. Chem.* **1980**, *322*, 305; g) B. Marcandalli, E. Dubina-Paglia, L. Pelliciari-Di Liddo, *Gazz. Chim. Ital.* **1981**, *111*, 187; h) A. T. Peters, A. Gbadamosi, *J. Chem. Technol. Biotechnol.* **1992**, *53*, 301–308.
[3] C. Laurence, P. Nicolet, M. T. Dalati, J.-L. M. Abboud, R. Notario, *J. Phys. Chem.* **1994**, *98*, 5807.
[4] G. McGeorge, R. K. Harris, A. M. Chippendale, J. F. Bullock, *J. Chem. Soc. Perkin Trans. 2* **1996**, 1733.
[5] C. Reichardt, *Solvents and Solvent Effects in Organic Chemistry*, VCH, Weinheim, **1988**.
[6] M. J. Kamlet, J.-L. M. Abboud, R. W. Taft, *Prog. Phys. Org. Chem.* **1981**, *13*, 485.
[7] R. W. Taft, J.-L. M. Abboud, M. J. Kamlet, *J. Am. Chem. Soc.* **1981**, *103*, 1080; R. W. Taft, M. J. Kamlet, *Inorg. Chem.* **1983**, *22*, 250.
[8] Y. Marcus, *Chem. Soc. Rev.* **1993**, *22*, 409.
[9] We are aware of a more recent compilation of π^* values (ref. [3]). However, we have chosen not to rely on these since no comparable values are given for hydroxylic solvents, and nor is it clear that older α and β values are consistent with these newer π^* values. See, however, ref. [11].
[10] J. Griffiths, *Colour and Constitution of Organic Molecules*, Academic Press, London, **1976**, p. 76.
[11] The correlations of Table 2 have been repeated with the more recent π^* values (ref. [3]), with very little difference in regression coefficients, statistics or derived $\pi^*_{\mathrm{A=T}}$ values.
[12] PISYSTEM for Windows, v 3.1 (**1994**), R. Naef, Im Budler 6, CH-4419 Lupsingen, Switzerland. This program has been reviewed in: M. G. Hutchings, *Dyes & Pigments* **1995**, *29*, 95.
[13] E. G. McRae, *J. Phys. Chem.* **1957**, *61*, 562; W. Liptay, *Angew. Chem. Int. Ed. Engl.* **1969**, *8*, 177; W. Liptay in *Modern Quantum Chemistry, Part 2* (Ed.: O. Sinanoglu), Academic Press, New York, **1965**, p. 173.
[14] F. Effenberger, F. Würthner, *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 719; F. Effenberger, F. Würthner, F. Steybe, *J. Org. Chem.* **1995**, *60*, 2082.
[15] This discussion has been implicitly simplified by neglecting the fact that the $\mu_0 \cdot \Delta\mu_{01}$ term is a vector dot product and therefore dependent on the angle between the dipole vectors. In fact, the PPP-calculated ground-state and first excited-state dipole vectors are essentially in the same direction, so the scalar assumption is valid, at least to the same extent as the other approximations which have been made.
[16] W. E. Stewart, T. H. Siddall III, *Chem. Rev.* **1970**, *70*, 517; V. P. Manea, K. J. Wilson, J. R. Cable, *J. Am. Chem. Soc.* **1997**, *119*, 2033.
[17] R. W. Taft, M. J. Kamlet, *J. Chem. Soc. Perkin Trans. 2* **1979**, 1723.
[18] F. H. Allen, J. E. Davies, O. J. Johnson, O. Kennard, C. F. Macrae, E. M. Mitchell, G. F. Mitchell, J. M. Smith, D. Watson, *J. Chem. Inf. Comput. Sci.* **1991**, *31*, 187.
[19] The new α values determined from Equation (7) have large associated errors: $\alpha(\mathrm{CHCl_3}) = 0.17 \pm 0.34$, $\alpha(\mathrm{CH_2Cl_2}) = 0.21 \pm 0.14$; cf. literature values 0.44, 0.30, respectively (ref. [8]). Thus these new α values are not recommended.
[20] E. Buncel, S. Rajagopal, *J. Org. Chem.* **1989**, *54*, 798; E. Buncel, S. Rajagopal, *Acc. Chem. Res.* **1990**, *23*, 226.
[21] a) R. S. Drago, *J. Chem. Soc. Perkin Trans. 2* **1992**, 1827; b) R. S. Drago, *J. Org. Chem.* **1992**, *57*, 6547; c) R. S. Drago, M. S. Hirsch, D. C. Ferris, C. W. Chronister, *J. Chem. Soc. Perkin Trans. 2* **1994**, 219; d) R. S. Drago, *Applications of Electrostatic–Covalent Models in Chemistry*, Surfside Scientific Publishers, Gainesville, **1994**.
[22] M. G. Hutchings, unpublished results.
[23] Statistica/w, from StatSoft, Inc., 2325 East 13th Street, Tulsa, OK 74104 (USA).
[24] J. Pancir, I. Matoušek, R. Zahradnik, *Coll. Czech. Chem. Commun.* **1973**, *38*, 3039.