The Influence of Chlorine and Sulphonate Substituents on the Visible Absorption Maxima of Some Azo Dyes

David Greenwood, Michael G. Hutchings,* and Brian Lamble
Imperial Chemical Industries plc, Organics Division, P.O. Box 42, Hexagon House, Blackley, Manchester M9 3DA

A total of 110 arylazo dyes have been prepared, based on five benzenoid and heterocyclic coupling components, and containing combinations of chlorine and sulphonate (sulpho) substituents in the diazo components. Their visible absorption maxima have been analysed in order to determine the degree to which chloro and sulpho substituent influences are constant and transferable, both within a series, and between series. Additivity is found to pertain, if allowances are made for steric effects. A 2-sulpho group alone can induce nonplanarity, depending on the nature of the coupling component. The 2-sulpho-3-chloro combination is particularly responsible for hypsochromic shifts unexpected on the basis of strict additivity. Computer-aided molecular modelling studies have clarified the steric interactions present. Di-*ortho*-substitution also induces nonplanarity and hypsochromic effects. There is some evidence for non-equivalence of a substituent in the two distinct *meta*-orientations, although MO calculations do not reproduce this behaviour.

A general objective in colour chemistry is the prediction of the effect of a substituent in a given position on the colour properties of a chromogen. There has been continuing interest in azobenzene dyes in this context, not least because of their commercial importance. It has become accepted that within the azobenzene series, the effect of substituents is largely additive, and may be transferred from one series to another. Compilations of such substituent effects have been published.[1] However, the extent to which transferability pertains between less closely related chromogens is less well documented.

In this paper, we discuss comprehensive results for the technically important, mildly electron-withdrawing chlorine and sulphonic acid (sulpho) groups in five series of azo dyes (**1**). These are derived from the diazo components aniline, the three chloroanilines, the three sulphoanilines, all ten possible chlorosulphoanilines, and selected dichlorosulphoanilines, numbered as in Table 1. The five series are characterised by the coupling components (**A**)—(**E**), corresponding to Ar in (**1**). These include both 5- and 6-membered-ring heterocycles, as well as benzenoid species. The position of attachment of the azo group is arrowed in (**A**)—(**E**). The azo compounds derived from (**A**) are referred to as series A, and so on. Individual azo dyes can then be labelled according to the two components from which they derive [*e.g.* (**2A**)].

Visible absorption spectra have been measured for a total of 110 azo compounds, and analysed with a view to answering the following questions:

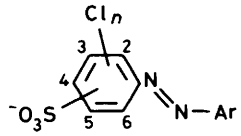
(1) Is the effect of a substituent in a particular orientation constant for all isomeric arrangements of other substituents?

(2) Is the value transferable to related molecules based on different coupling components [Ar in (**1**)]?

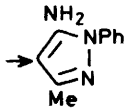
(3) How can exceptions to any trends be related to the structures of the compounds?

The approach described in this paper *assumes* additivity of substituent effects in the development of quantitative models for absorption maxima. If, however, the models ultimately reflect *non*additivity, further analysis is attempted in order to rationalise the deviations. In fact, nonadditivity was anticipated in some cases and allowed for in advance, as the following discussion explains.

Method.—The method used is based on the statistical approach of Free and Wilson,[2] which finds the least-squares solution to the equations



(**1**)



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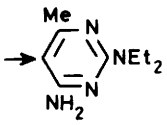

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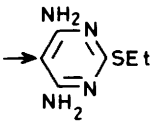
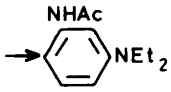
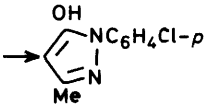


(**C**)



(**D**)



(**E**)

$$y_i = c_0 + \sum_j c_j x_{ij}$$

Here, the y_is are the observed absorption data for molecule i. The c_js are substituent increments for a given substituent in a given position, j. The x_{ij}s are the number of substituents in position j for molecule i (usually 0 or 1, but see below). c_0 Is a base value which is equal to y_i when there are no substituents present. In statistical terms, the solution to these equations is derived by regressing the experimental values, y_i, against the x_{ij} data. The regression coefficients calculated by the procedure are equal to the c_j terms, and represent the substituent increments of interest.

Table 1 includes all the relevant input data. The y-block contains experimental values of absorption wavelength maxima, in nm. In fact, it would be more correct to consider an energy scale rather than wavelength. However, the difference between the two is only considered sufficiently important when comparing series of molecules from fundamentally different

Table 1. Absorption maxima in nm (*y*-block) for azo compounds derived from anilines (**2**)—(**25**), and coupling components (**A**)—(**E**). The *x*-block data describe the substitution patterns of the anilines. See text for clarification

		y-block					*x*-block											
		A	B	C	D	E	2CL	2S	3CL	3S	4CL	4S	5CL	5S	6CL	35CL	35S	2S3CL
(**2**)	ANILINE	366	385	384	464	392	0	0	0.0	0.0	0	0	0.0	0.0	0	0	0	0
(**3**)	2CL	378	403	400	472	394	1	0	0.0	0.0	0	0	0.0	0.0	0	0	0	0
(**4**)	3CL	369	396	390	472	389	0	0	0.5	0.0	0	0	0.5	0.0	0	1	0	0
(**5**)	4CL	374	394	391	472	396	0	0	0.0	0.0	1	0	0.0	0.0	0	0	0	0
(**6**)	2S	383	399	395	453	391	0	1	0.0	0.0	0	0	0.0	0.0	0	0	0	0
(**7**)	3S	370	391	388	470	389	0	0	0.0	0.5	0	0	0.0	0.5	0	0	1	0
(**8**)	4S	377	397	393	477	394	0	0	0.0	0.0	0	1	0.0	0.0	0	0	0	0
(**9**)	2CL-3S	385	405	400	475	395	1	0	0.0	1.0	0	0	0.0	0.0	0	0	1	0
(**10**)	2CL-4S	392	411	406	487	398	1	0	0.0	0.0	0	1	0.0	0.0	0	0	0	0
(**11**)	2CL-5S	386	405	402	481	394	1	0	0.0	0.0	0	0	0.0	1.0	0	0	1	0
(**12**)	3CL-2S	386	398	395	446	390	0	1	1.0	0.0	0	0	0.0	0.0	0	1	0	1
(**13**)	3CL-4S	382	402	395	488	392	0	0	0.5	0.0	0	1	0.5	0.0	0	1	0	0
(**14**)	3CL-5S	378	400	391	482	387	0	0	0.5	0.5	0	0	0.5	0.5	0	1	1	0
(**15**)	4CL-2S	392	407	400	467	394	0	1	0.0	0.0	1	0	0.0	0.0	0	0	0	0
(**16**)	4CL-3S	378	398	391	478	395	0	0	0.0	0.5	1	0	0.0	0.5	0	0	1	0
(**17**)	5CL-2S	392	407	400	468	388	0	1	0.0	0.0	0	0	1.0	0.0	0	1	0	0
(**18**)	23CL2-4S	398	415	413	492		1	0	1.0	0.0	0	1	0.0	0.0	0	1	0	0
(**19**)	24CL2-5S	392	412	410	490		1	0	0.0	0.0	1	0	0.0	1.0	0	0	1	0
(**20**)	25CL2-4S	400	418	412	499		1	0	0.0	0.0	0	1	1.0	0.0	0	1	0	0
(**21**)	34CL2-2S	398	405	402	454		0	1	1.0	0.0	1	0	0.0	0.0	0	1	0	1
(**22**)	34CL2-5S		405				0	0	0.5	0.5	1	0	0.5	0.5	0	1	1	0
(**23**)	45CL2-2S	402	413	411	480		0	1	0.0	0.0	1	0	1.0	0.0	0	1	0	0
(**24**)	6CL-2S	364	378	378	440	345	0	1	0.0	0.0	0	0	0.0	0.0	1	0	0	0
(**25**)	26CL2-4S	355	382	378	456		1	0	0.0	0.0	0	1	0.0	0.0	1	0	0	0

absorption maxima ranges, or colours (in this case, series D, which is red, compared with all the others which are yellow). The wavelength data have been converted into energies relative to the unsubstituted aniline derivative, but for clarity the data are not given here.

The *x*-block of data describes the structure of the azo molecules in terms of the presence, or absence, of a particular substituent. If a substituent is present, it is recorded by 1, otherwise 0. Several points relevant to the way in which the *x*-matrix is put together are significant. The fact that the azo linkage in the azobenzene skeleton is nonlinear introduces inequivalences into the positions 2 and 6 in (**1**). Thus, the molecule can in principle be *ortho*-substituted in either of these two positions, to give two non-equivalent structures. However, steric considerations, backed up by *X*-ray structural information on suitable analogues,[3] make it clear that a mono-*ortho* substituent can only occupy position 2, to the exclusion of 6. When the molecule is di-*ortho*-substituted, precedent leads us to anticipate anomalies in the colour–structure relationships due to sterically-induced nonplanarity.[3] Molecules of this type were not included in the Free–Wilson analyses, and are discussed in detail separately, below.

The two *meta*-positions, 3 and 5 in (**1**), are also non-equivalent. However, in the case of mono-*meta* substitution, the two possibilities are considered to be equally likely, since neither interacts directly with the azo group. If two substituents are present, one *ortho* and one *meta*, the fixed orientation of the former dictates which position the latter must adopt. Thus, it is again possible in such cases to distinguish between 3- and 5-substitution. For this reason, several series of Free–Wilson analyses have been performed. In one series, no distinction has been made between the 3- and 5-orientation, and relevant *x*-block data are recorded in Table 1 under the labels 35CL and 35S.

Parallel analyses have been made where the corresponding *x*-block data have been split (3CL, 5CL, and 3S, 5S in Table 1). In the case of *meta*-substitution in the absence of an *ortho*-group, the entries in Table 1 for both positions 3 and 5 are given values of 0.5.

The next refinement after simple additivity is to assume constant pairwise interactions between all possible substituents in all possible combinations. A prohibitive drawback to the inclusion of all such terms in an analysis is that the number of unknown variables now becomes higher than the number of observations. However, important cross-terms *can* be included if there are not too many. As is described in the next section, a special effect seems to be present for 2-sulpho-3-chloro derivatives. Table 1 reflects the presence of these combinations by a positive entry in the *x*-block, under 2S3CL.

Results

Synthesis.—The ten chlorosulphoanilines were either readily available, or have recently been prepared by unambiguous routes.[4] Of the dichlorosulphoanilines, only two are novel and these are described in the Experimental section. One preparation is of note, where a recently discovered intramolecular redox reaction allowed direct conversion of an *o*-nitrothiophenol derivative into the desired *o*-aminobenzenesulphonic acid (**21**) (Scheme).[5] The five coupling components (**A**)—(**E**) were either available materials or were prepared by well documented methods. The azo dyes were prepared in a conventional manner by diazotisation of the anilines in aqueous acid at 0—5 °C. Coupling with (**A**)—(**E**) was unexceptional, buffering to pH 8 aiding otherwise sluggish reactions. Dyes were isolated as sodium sulponate salts rather than the free sulphonic acids.

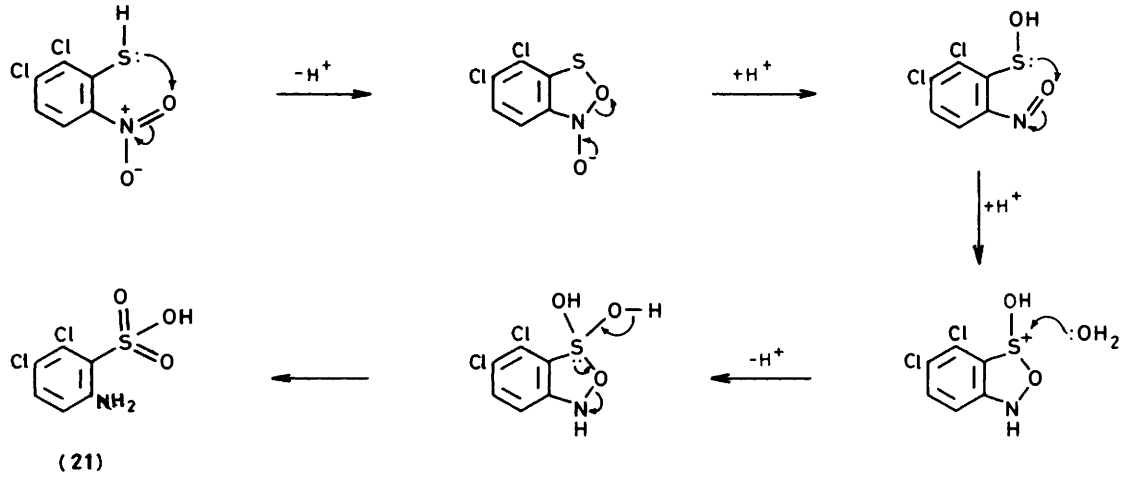
Results of Free–Wilson Analyses.—Analyses of the data for series A—D are considered together, and series E separately, for the simple reason that all the former exist as azo tautomers (**1**), whereas the dyes in the latter series are exclusively hydrazo (**26**).

For series A—D, the first set of analyses, (i), did not distinguish between the two possible *meta*-positions, and made

Table 2. Substituent increments (nm) for the azo dyes based on the coupling components (A)—(E), and relevant statistics from the Free–Wilson analyses.[a] The two sets of results for each series are explained in the text

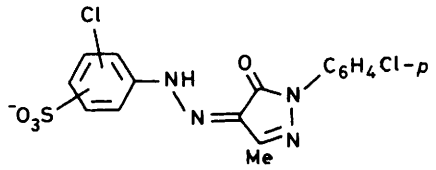
	A		B		C		D		E	
	(ii)	(iii)	(ii)	(iii)	(ii)	(iii)	(ii)	(iii)	(ii)	(iii)
Base[b]	363.9	364.0	387.5	387.5	384.1	384.2	462.3	462.9	391.3	391.3
2CL	15.0	14.9	14.2	14.1	15.8	15.5	9.0	8.4	3.8	3.8
2S	20.1	19.5	12.1	11.6	10.9	10.8	−6.2	−7.7	−1.0	−1.0
35CL	7.2		7.2		5.9		11.3		−2.5	
3CL		5.2		6.0		5.3		6.7		−2.8
5CL		8.4		8.0		6.2		13.9		−2.3
35S	5.9		3.8		1.7		7.2		−1.2	
3S		6.2		3.9		0.3		4.1		−0.7
5S		5.6		3.8		2.8		9.6		−1.7
4CL	9.1	9.1	6.7	6.7	7.1	6.9	10.4	9.7	4.4	4.4
4S	12.6	12.7	8.3	8.4	6.8	6.8	14.1	14.5	2.9	2.9
2S3CL	−3.9	−1.3	−8.6	−7.0	−5.9	−5.2	−22.7	−16.8	2.1	2.6
n	21	21	22	22	21	21	21	21	16	16
R^2	0.985	0.988	0.984	0.986	0.974	0.978	0.978	0.993	0.959	0.963
s	1.59	1.54	1.27	1.29	1.67	1.69	2.48	1.53	0.87	0.95
F	124	104	119	90.6	70.0	53.2	81.4	168	27.0	17.4

[a] n number of compounds in the series; R^2 square of multiple correlation coefficient; s standard deviation in nm; F Fisher's F-statistic. [b] Calculated absorption maxima of unsubstituted derivatives *i.e.* derived from aniline, *cf.* Table 1.



Scheme.*

no allowance for 2,3-interactions. Full results of this analysis are not recorded here, but can be summarised as follows. With this set of molecular descriptors, additivity of substituent effects was approximately reflected for series A—C. However, the calculated absorption maxima for series D diverged appreciably



(26)

from the experimental, reflecting a lack of substituent addivitity. Furthermore, the standard errors for the calculated increments were all unacceptably high. Inspection of the differences between calculated and experimental maxima revealed the biggest discrepancies (*ca.* 12 nm) to be for those dyes, (**12D**) and (**21D**), where both 2-sulpho and 3-chloro groups were present in the same molecule. Closer scrutiny of the results revealed that analogous molecules in series A—C were the most deviant in their respective series.

For this reason the next set of analyses, (ii), also included

* In the Scheme, water can be replaced by other nucleophiles. The presence of an attractive interaction between S^{II} (or Se^{II}) and adjacent nitro groups is revealed by the unexpected near-planarity of such systems in the solid phase, where S···O or Se···O nonbonded separations are much less than the van der Waals contact distances. (For structural data, see: J. D. Korp, I. Bernal, and G. E. Martin, *J. Cryst. Mol. Struct.*, 1981, **11**, 11; J. S. Ricci and I. Bernal, *J. Chem. Soc. B*, 1970, 806; S. P. N. van der Heijden, W. D. Chandler, and B. E. Robertson, *Can. J. Chem.*, 1975, **53**, 2102; W. C. Hamilton and S. J. La Placa, *J. Am. Chem. Soc.*, 1964, **86**, 2289; R. Eriksen and S. Hauge, *Acta Chem. Scand., Ser. A*, 1972, **26**, 3153; R. Eriksen, *ibid.*, 1975, **29**, 517.) This observation is relevant to the first and third steps of the mechanism proposed in the Scheme. It is equally feasible that nucleophilic attack at sulphur by water takes place earlier in the pathway than shown, and/or that some of the reaction steps should be drawn as reversible.

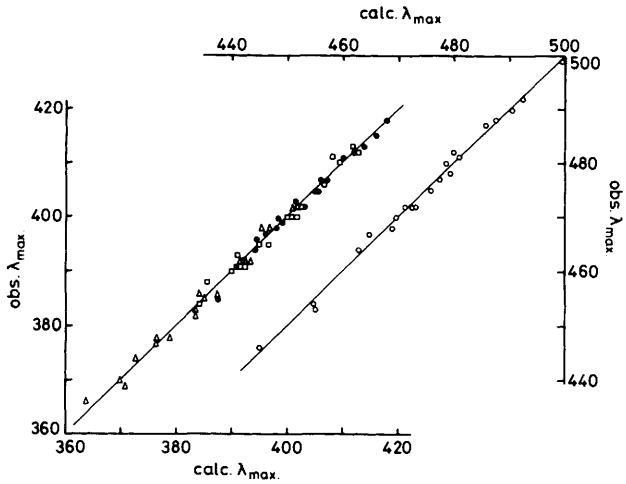


Figure. Plot of observed visible absorption maxima against values calculated by the additivity models using increments recorded in Table 2. △ series A; ● series B; □ series C; ○ series D. The left and bottom axes refer to the first three series; the right and top axes refer to series D. Some points overlap.

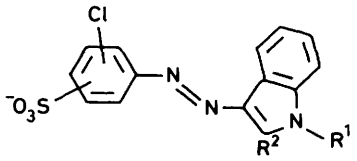
the 2S3CL parameter in order to account empirically for such a substituent combination where appropriate. The calculated substituent increments are recorded in Table 2, along with relevant statistics, under (ii). The deviations between calculated and experimental absorption maxima were now less, particularly for series D. The standard errors of the parameter estimates were less than, or about, 1 nm for series A—C, and about 1.5 nm for series D. The absorption maxima calculated by these increments were close to the experimental values. The *maximum* residuals were 2.1 nm in series A, 2.5 nm in series B, 3.0 nm in series C, and 2.1 nm in series D (*cf.* also the standard deviation of the estimates, statistic *s* in Table 2).

The final set of analyses, (iii), drew a distinction between the two possible *meta* orientations, 3 and 5 in (**1**), as well as including the interaction term as just discussed. The calculated substituent increments are again recorded in Table 2, under (iii), alongside the previous set of analyses. The overall predictions for series D now improve appreciably. However, there is no statistical improvement in the other three series. The Figure shows the agreement between absorption maxima and those calculated from the increments recorded in Table 2.

Discussion

meta- *and* para-*Substitution.*—The substituent increments for both chloro and sulpho in series D are about twice as big in the 5-position as in the 3-position, and in both cases the effects are bathochromic. A similar trend applies to chloro in series A—C, although the differences of 3 nm or less are much less statistically significant. The increments for the sulpho group in series A—C in the two *meta* positions are almost constant. Overall then, it appears that the 5-position, *syn* to the azo group (**1**), is more sensitive to substituent influences than the 3-position, *anti* to azo.

In order to check whether there is an intrinsic difference between the two *meta* positions, MO calculations were run for analogues of compounds (**2D**) and both conformers of (**4D**) (Table 1). The methods used were the π-electron-only PPP-model,[6] and three different parametrisations of the CNDO/S approximation[7] which take account of all valence electrons. A configuration interaction treatment was used in all excited-state calculations. The results of the calculations on (**2D**) show that



(**27**)

there is insignificantly little change in electron density at positions 3 and 5 on single-electron excitation, indicating the essential equivalence of the two positions to substitution. Furthermore, all the calculations for the two possible *meta*-substituted conformers of (**4D**) gave essentially the same absorption maxima for each. Inherent molecular effects are therefore not responsible for the observed differences in the 3- and 5-position.

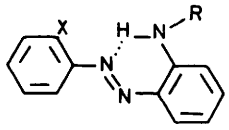
An alternative explanation for the different substituent effects observed for 3- and 5-substitution is that solvation of either side of the molecule need not be the same, because of the inequivalence induced by the nonlinear azo group. Absorption spectra could be affected accordingly.

With only one exception, the 3- and 5-chloro substituents induce more bathochromic shifts than sulpho groups in the same positions, for all four azo series A—D. The opposite is true for substituents in the *para* position [site 4 in (**1**)] of three of the series (A, B, D) (Table 2). In series C the 4-chloro and 4-sulpho substituents are about the same. It is by no means clear why the relative magnitudes of chloro and sulpho reverse on going from *meta* to *para*. However, it is tempting to distinguish the two by their relative abilities to π-conjugate with the azo group, and *via* this with the amino donor groups in the coupling components. Since the *para*-position is π-conjugated, and the sulpho group can, at least formally, act as a π-acceptor group, it might be anticipated that it would demonstrate a relatively greater effect than the non-π-conjugating chloro group.

It is also apparent from Table 2 that the substituent effects are *not* constant across the different series. (It is here that energies should be compared, rather than wavelengths. However, a series of analyses using energy data rather than absorption maxima wavelengths led to the same conclusion.) While the differences are small, they are statistically and experimentally real. No ready explanation springs to mind, although it should be noted that there is no *a priori* reason to expect transferability between different chromogens.

Free–Wilson analysis has also been applied to the visible absorption spectra reported in the literature for some azoindoles (**27**).[8] The trend observed from *meta*-sulpho and *para*-sulpho, bathochromic by 8 nm and 13 nm, respectively, is the same as that recorded in Table 2, and the magnitudes are about the same as for the aminopyrazoles (series A) and acetylaminoanilines (series D). The *meta*-chloro increment, 6.7 nm, is in line with the data for series A—C (Table 2).

The effects of chloro substitution in several other azobenzene types have been extracted from a literature compilation of data.[1] *meta*-Chloro in a variety of five azobenzenes has a bathochromic effect of 7—13 nm (mean 10 nm). This compares with 11 nm for the nearest analogue, (series D). The effect of *para*-chloro in 8 similar azobenzenes ranged between 7—10 nm (mean 8.75 nm) (*cf.* 10 nm in series D, and somewhat less in the other series). However, in other azobenzenes where the donor amino groups are constrained to be more planar, the chloro effect is higher: 10—19 nm for 4 molecules (mean 16 nm). Thus, in comparable systems, the corresponding values are very similar, although as within the series A—E, the values are not transferable to markedly different chromogens.



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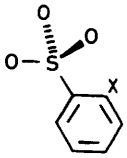

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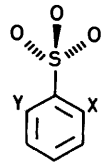


(30)

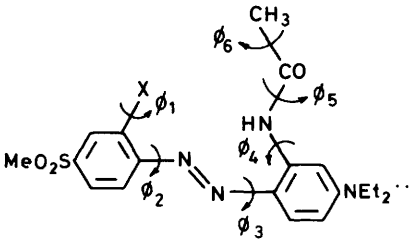
ortho-*Substitution*.—Discussion of the *meta*- and *para*-substituents has been relatively straightforward, in that there have been no confusing steric effects present. Steric influences for *ortho*-substituents have already been alluded to, and for this reason the relevant results are considered separately, beginning with a consideration of the likely conformations of these molecules.

In the absence of hydrogen-bonding interactions, a substituent *ortho* to an azo group occupies position 2 in (**1**), so that nonbonded interaction with the more remote azo nitrogen atom is minimised (**28**).[3] In all four of the series A—D, a substituent is present in the *coupling* component which *can* H-bond to its more remote azo nitrogen atom (**28**). This gross conformational assignment is supported by *X*-ray diffraction studies of close analogues of the D-series azo compounds, where it is found that in the solid phase, derivatives with 2-chloro substituents are essentially planar.[3] It is assumed that the same situation pertains in the 2-chlorinated dyes based on (**A**)—(**C**).

The situation for the 2-sulpho group is more complicated, in that the sulpho group itself is able to alter its conformation, depending on what other substituents are adjacent to it. A survey of solid-state conformations of *ortho*-substituted arylsulphonates and sulphonic acids recorded in the Cambridge crystal structure database revealed two distinct situations. In the presence of one *ortho*-substituent, the sulpho group adopts conformation (**29**), where one S–O bond essentially eclipses the plane of the benzene ring.[9] The other two S–O bonds are equidistant from the *ortho*-substituent, as minimisation of nonbonded contact would intuitively suggest. In the presence of two *ortho*-substituents, steric interaction is minimised by the sulpho group adopting the conformation shown in (**30**), characterised by one S–O bond now being orthogonal to the ring plane.[10]

Thus, for azo dyes containing a 2-sulpho group and no 3-substituent, the conformation approximates to (**29**; X = N=NAr). However, as soon as a 3-chloro group is introduced, the conformation is expected to change to (**30**; X = N=NAr, Y = Cl). The degree to which this alteration in sulpho conformation affects the colour properties of the molecule will depend on the rest of the molecule [*i.e.* the exact nature of X in (**30**)].

In the azopyrazole series A, the extra 3-chloro group has essentially no influence on the spectra (2S3CL $\simeq$ 0; Table 2). Whatever conformational changes are occurring for sulpho, they are not influencing the measured absorption maxima. However, in going from the 5-ring pyrazole, (**A**), to the 6-ring pyrimidines (**B**) and (**C**), the amino group of the coupling component is brought closer both to the azo group, and to any nearby 2-substituent in the diazo component, due to the exocyclic valence angles closing up (5-ring *ca.* 126°; 6-ring *ca.* 120°). In order to compensate for any induced nonbonded interaction, torsion about an aryl–azo C–N bond leads to decreased planarity. It is usually this behaviour which is accepted to result in a hypsochromic shift.[11] This is in fact reflected by the decreased inherent sulpho substituent effects in series B and C compared with A (Table 2). Introduction of a 3-chloro group tends to force an oxygen atom of the sulpho group even closer to the H-bonding NH_2 group [conformation (**30**)]. The molecule compensates by further relaxation, probably by similar out-of-plane aryl group torsion, thus leading to an additional hypsochromic shift, as reflected by the increased 2S3CL values recorded in Table 2.



(31) a; X = Cl
b; X = SO_3^-

This overall type of behaviour is magnified in series D. Here, an additional steric influence is introduced by the methyl group of the acetylamino substituent present in the coupling component. Direct interaction with 2-substituents, and especially with sulpho, is possible. The bathrochromic effect of 2-chloro is now even less, and an overall *hypsochromic* shift is now induced by 2-sulpho (Table 2). Introduction of 3-chloro exacerbates the steric clashing appreciably, as reflected by the value of the 2S3CL increment.

Computer-based molecular modelling techniques have been applied to this problem, and lead to estimates of the degree of nonplanarity of the *ortho*-substituted series of dyes based on (**D**). There are five degrees of torsional freedom for the groups involved in the interaction for the *o*-chloro-substituted derivative (**31a**), with an additional degree of freedom when chloro is replaced by sulpho (**31b**). The structure used for (**31a**) is that found in the crystalline phase.[12] The model of (**31b**) was derived from (**31a**) by using standard bond lengths and angles for the sulpho group. In both cases, because of the complexities of the structures, no attempt was made to minimise the energy of the structures. Instead, it has been assumed that the main relaxation mode is by group rotation (torsion) about single bonds. Structures have been generated automatically by rotating various groups in 5° increments. For each of these, chosen nonbonded interatomic separations have been simultaneously calculated, and these have been monitored with respect to theoretical van der Waals' contact distances.[13]

A minimum Cl ••• H contact distance of 3.0 Å is assumed. In a wholly planar conformation, the Cl ••• H distance in (**31a**) is 3.1 Å. However, only slight torsion (φ_2) is needed to *shorten* this separation. In the absence of crystal-packing forces, it is easy to imagine that the Cl ••• H distance could be sufficiently short to necessitate further torsion to relieve nonbonded strain. Whereas molecular modelling does little to shed light on this hypothetical situation, it is of direct help in resolving the situation in (**31b**).

In (**31b**), the O ••• H separations are less than van der Waals' contact distance (2.6 Å) in the planar conformation, with sulpho adopting conformation (**29**). In fact, no combination of φ_1 and φ_6 values sufficed to bring this separation to an acceptable value. The conclusion is that further relaxation elsewhere in the molecule is necessary to increase this distance. It has been assumed, primarily on the basis of solid-state conformation precedent, that increase of torsion angle φ_2 is the most likely relaxation mode. It is found that φ_2 has to assume a value of 35°, with φ_1 and φ_6 optimally relaxed, before the O ••• H separation

reaches the van der Waals' contact value of 2.6 Å. If now the SO_3 group is constrained by a 3-chloro substituent to conformation (**30**), much greater torsion about φ_2 is required before the shortest O···H distance again becomes acceptable. The molecular modelling study therefore adds further quantitative support to the stereochemical assertions from above: a 2-sulpho group does indeed clash with other substituents to enforce nonplanarity on the molecule, with consequent effects on the electronic absorption spectrum.

2,6-*Di*-ortho-*substitution*.—2,6-Dichloro-substituted azobenzenes are known from *X*-ray structure determinations to be nonplanar due to the extreme nonbonded interaction of the 6-chloro atom with azo nitrogen.[14] The plane of the diazo component is forced orthogonal to the plane of the remainder of the molecule. If it is assumed that sulpho is at least as big as chloro (and the results discussed above suggest that in the current context it is), the same geometric modification would be expected in the 2,6-chlorosulpho dyes. A consequence is that the mode of interaction of *meta*- and *para*-substituents, whatever it may be in the planar azobenzenes, would not necessarily be the same in nonplanar 2,6-disubstituted derivatives (*e.g.* through lack of π-conjugation). For this reason, they were not included in the Free–Wilson analyses. Instead, the combined effect of such pairs of substituents has been calculated for the 8 compounds based on diazo components (**24**) and (**25**).

In the aminopyrazole series, A, the 2,6-chlorosulpho combination has little effect compared with the unsubstituted azobenzene (**2A**). That is, it is about −34 nm hypsochromic relative to the value anticipated if the 2-sulpho and 2-chloro effects were transferable and additive. The 2,6-chlorosulpho combination in the two pyrimidine series, B and C, is overall hypsochromic relative to unsubstituted aniline [−9.5 nm for (**2B**); −6.2 nm for (**2C**)]. It is interesting, though, that the differences from additivity based on the sum of the mono increments for 2-sulpho and 2-chloro are very similar to the aminopyrazoles, at −36.5 nm and −33.5 nm, respectively. Finally, in series D, which is already suspected to be nonplanar for simple 2-substituted derivatives, the shift for 2,6-chlorosulpho is −22.9 nm compared with aniline (**2D**), but only −23.6 nm compared with additivity based on the values in Table 2. It appears that since the mono-substituted derivatives are already somewhat nonplanar, there is less geometric difference to be made by introducing a 6-substituent, reflected in lower hypsochromic shift.

The 2,6-dichloro combination induces hypsochromic shifts for the 4 series A—D, ranging between −11.4 nm and −23.7 nm.

Overall, the effect of di-*ortho* substitution is in line with expectations based on previous studies of azo dyes, which bear different combinations of substituents.[3a]

Azopyrazolones (*Series E*).—The compounds derived by azo coupling with pyrazolone (**E**) exist as hydrazone tautomers (**26**), and thus substituent effects are not comparable with azo tautomers in series A—D. Free–Wilson analysis shows that the substituent effects for this series are internally additive (Table 2). They are notable for their small magnitudes compared with the corresponding azo tautomers, and in fact they do not differ appreciably from zero in most cases. Only for the 2,6-disubstituted compound (**24E**) is there an appreciable hypsochromic effect (−47 nm), again no doubt due to disruption of the planarity of the chromogen resulting from steric interactions.

The visible energy absorption of (**26**) is accompanied by a transfer of electron density from the hydrazo NH unit to the adjacent, bonded N of the N=C unit.[14] The π-electron availability of the NH group is not sufficiently affected by the weak electron-withdrawing groups, sulpho and chloro, to influence the visible absorption spectrum. It is only when conjugation with the bonded aryl group is reduced or eliminated, as in (**24E**), that the picture changes and a marked hypsochromic shift is observed.

Normally, the absolute magnitude of substituent effects in hydrazo tautomers are about the same as observed for azo compounds.[11b] The series E values are markedly *less* than azo tautomer increments, in series A—D (Table 2).

Conclusion

In conclusion, we return to the questions posed in the Introduction. A substituent in a particular orientation is indeed constant for a particular chromogen (*i.e.* within a series), but only if special steric factors are not present. In the latter eventuality, further allowance for such factors, as in the case of 2-sulpho-3-chloro compounds, allows wider generalisation. Transfer of values from one series to another is less warranted, as the results of Table 2 show. However, trends within series are constant, again as long as account is taken of the steric factors. Finally, it has been shown how the nonadditive situations can be explained by consideration of the actual nonbonded interactions within the molecules. In this context, the picture constructed should allow extrapolation to other chlorosulphoazobenzenes where extra purely steric factors are built into the molecule (*e.g.* by methyl).

One of the aims of a treatment such as that described in this paper is to allow prediction of properties for molecules yet to be prepared. Other dichlorosulpho derivatives are an example. In fact, when this study was begun, data derived solely from the monochlorosulphoazobenzenes were available, and these were used to make predictions for dichlorinated species. On the basis of these predictions, various dichloroanilines were synthesised and the azobenzenes recorded in Table 1 prepared therefrom. When measured, the observed visible absorption maxima were in good agreement with the predictions, as the largely additive nature of the substituents demonstrated in this paper would lead one to expect.

Experimental

U.v. visible spectra were recorded on Unicam SP8000 or Perkin-Elmer 554 instruments in ethanol, and were calibrated with a holmium filter. ^{1}H N.m.r. spectra were recorded at 100 MHz on a Varian HA100 spectrometer with 3-(trimethylsilyl)propanesulphonic acid as internal standard, and ^{13}C n.m.r. spectra were recorded at 22.62 MHz on a Bruker WH90 instrument in $(CD_3)_2SO$ solution. I.r. spectra were taken as Nujol mulls on a Perkin-Elmer 297 instrument. Unless otherwise described below, starting materials were either commercially available or were obtained from the I.C.I. specimen collection. If necessary they were recrystallised or distilled prior to use, and satisfied normal purity criteria. M.p.s are not generally feasible for sulphoanilines, and none are recorded below.

2,3-*Dichloro*-6-*nitrothiophenol*.—Sodium sulphide crystals ($Na_2S{\cdot}9H_2O$, 10 g, 40 mmol) were stirred as a suspension in DMSO (4 ml) at room temperature for 0.25 h. 2,3,4-Trichloronitrobenzene (9.06 g, 40 mmol) dissolved in DMSO (12 ml) at 30 °C was added to the above suspension over 1.5 h at 25—30 °C. The deep red mixture was stirred for a further 0.5 h and then poured into ice–water (100 ml). A small amount of insoluble material was filtered off and the remaining solution added to ice–water (50 ml) containing 36% hydrochloric acid (8 ml). The fawn coloured precipitate was filtered off, washed acid-free with water, and dried *in vacuo* at room temperature (8.35 g, 93% crude yield). This was not further purified, but was used in the next stage.

3,4-*Dichloro*-2-*sulphoaniline* (**21**).—2,3-Dichloro-6-nitrothiophenol (6.72 g, 30 mmol) was refluxed for 2 h in 1,4-dioxane (peroxide-free, 75 ml) containing a little water (3.6 ml). The white precipitate was filtered from the hot reaction mixture, washed with hot dioxane until the washings were colourless, and then washed with acetone. The *aniline* was dried at 55 °C (5.2 g, 72%) (Found: C, 29.7; H, 1.9; Cl, 29.4; N, 5.4; S, 12.8. $C_6H_5Cl_2NO_3S$ requires C, 29.8; H, 2.1; Cl, 29.3; N, 5.8; S, 13.2%); $\nu_{max.}$ 3 100br (NH), 1 100—1 210, 1 030 (SO_3), 810, 780, and 640 cm^{-1}; δ_H (K^+ salt) 7.1 (d, *J* 9 Hz, 1 H, 5-H), 6.6 (d, *J* 9 Hz, 1 H, 6-H), and 6.5 (s, exch. D_2O, 2 H, NH_2).

2,3-*Dichloro*-4-*nitroaniline*.—The formyl derivative of 2,3-dichloroaniline (190 g, 1.0 mol) was dissolved in 98% sulphuric acid at 25—30 °C, cooled to 0 °C, and mixed nitric acid–sulphuric acid (104 ml containing 1 mol HNO_3) was added over 1.5 h at 0—5 °C. The mixture was added to water (1.2 l), allowing the temperature to rise to 75—80 °C. The suspension was held at this temperature for 1.5 h to effect deacylation. After cooling to room temperature the product was filtered off, washed acid-free with water, and dried at 70 °C (198 g, 96% of isomer mixture). This was extracted for 24 h with light petroleum (b.p. 60—80 °C), the extract containing unwanted 2,3-dichloro-6-nitroaniline (m.p. 167—168 °C). The residue of 2,3-*dichloro*-4-*nitroaniline* was recrystallised from ethanol (81.1 g, 39%), m.p. 180—181 °C (Found: C, 35.2; H, 1.8; Cl, 33.8; N, 13.4. $C_6H_4Cl_2N_2O_2$ requires C, 34.8; H, 1.9; Cl, 34.3; N, 13.5%); $\nu_{max.}$ 3 480, 3 370 (NH), 1 630, 1 560, 1 300, 950, 825, and 750 cm^{-1}. The structures of the two isomers were unequivocally assigned by reference to their respective ^{13}C n.m.r. spectra, in comparison with shift values calculated from base values measured for 2,3-dichloroaniline; δ observed (calculated) for C-1 to C-6 of 2,3-dichloro-4-nitroaniline: 151.0 (152.4), 116.3 (116.3), 127.5 (127.2), 136.1 (137.3), 126.7 (123.1), and 111.8 (114.7); C-1 to C-6 of 2,3-dichloro-6-nitroaniline: 143.0 (141.8), 119.1 (116.3), 139.9 (137.8), 115.9 (118.2), 125.5 (123.1), and 130.7 (133.8).

2,3-*Dichloro*-4-*nitrobenzenesulphonic Acid*.—2,3-Dichloro-4-nitroaniline (41.2 g, 200 mmol) was stirred in 36% hydrochloric acid (160 ml) for 2 h at 30—40 °C, and then cooled to < 5 °C. Sodium nitrite (14.4 g) dissolved in water was added to the cream suspension over 0.5 h at this temperature. The reaction mixture was stirred for a further 0.5 h, filtered, and the insoluble material washed with 36% hydrochloric acid (15 ml). The diazonium salt solution was then added simultaneously with sodium sulphite solution ($Na_2SO_3 \cdot 7H_2O$, 50.4 g, in water, 80 ml) at < 5 °C over 0.25 h to a mixture of 36% hydrochloric acid (360 ml), copper sulphate ($CuSO_4 \cdot 5H_2O$, 4 g), sodium sulphite (50.4 g), and water (80 ml). The addition of the two solutions was made below the liquid surface. The thick pale green suspension was stirred for 1 h, filtered, and the collected solid washed with water until only slightly acid to Congo Red. The resulting sulphonyl chloride was then added to water (500 ml) and concentrated sodium hydroxide solution (32 ml) and the suspension stirred at room temperature for 18 h. The dark brown insoluble material was filtered off, and the solution was adjusted to pH 5 with hydrochloric acid. The solution of the nitrosulphonic acid was reduced without isolation.

2,3-*Dichloro*-4-*sulphoaniline* (**18**).—Iron powder (24 g) and ferrous sulphate crystals (2.4 g) were added to water (80 ml) and the mixture was heated to 90—95 °C for 0.25 h. The solution of 2,3-dichloro-4-nitrobenzene sulphonic acid was added over 0.75 h at this temperature and held for a further 4 h, when reduction was judged to be complete by t.l.c. Sodium carbonate was added until the mixture was alkaline, and the suspension was filtered. The solution was then acidified with 36% hydrochloric acid (75 ml) and cooled to 5 °C. The white precipitate was filtered off, washed with ice-cold water (3 × 50 ml) and acetone, and dried at 55 °C (27 g, 56%) (Found: C, 29.8; H, 2.1; Cl, 28.7; N, 5.7; S, 13.4. $C_6H_5Cl_2NO_3S$ requires C, 29.8; H, 2.1; Cl, 29.3; N, 5.8; S, 13.2%); $\nu_{max.}$ 3 020br, 1 210—1 090, 1 040, 900, 820, and 700 cm^{-1}; δ_H (K^+ salt) 7.6 (d, *J* 9 Hz, 1 H, 5-H), 6.7 (d, *J* 9 Hz, 1 H, 6-H), and 5.7 (s, exch. D_2O, 2 H, NH_2).

Preparation of Azo Compounds.—All dyes were obtained in an unexceptional manner by standard diazotisation and coupling methods. Sulpho-containing dyes were isolated as salts and purified by precipitation from a water or water–solvent solution. Other dyes were recrystallised from a suitable organic solvent. The dyes were shown to be pure by t.l.c., elemental analysis, and estimation of water content by the Karl Fischer technique. The absorption maxima were the same for the salt and the free acid (which is presumably fully dissociated under the hydroxylic conditions used).

Computations.—Free–Wilson analyses were done using the commercial SAS statistical analysis package.[15] Molecular orbital calculations used standard programs. Input was by means of graphically drawn structures, constructed from templates using standard geometries. The same graphics facility (Digital VT-11 graphics terminal plus PDP-11, running commercial software modified in-house) was used for the molecular modelling.

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