Dyes and Pigments **10** (1989) 123–140

An Approach to the Prediction of Absorption Bandwidths of Dyes using the PPP–MO Procedure

Cheng Lubai, Chen Xing, Hou Yufen

Department of Chemical Engineering, Dalian Institute of Technology, Dalian, People's Republic of China

&

John Griffiths

Department of Colour Chemistry and Dyeing, The University, Leeds LS2 9JT, UK

(Received 8 July 1988; accepted 26 July 1988)

ABSTRACT

A possible method for predicting absorption bandwidths of dyes using PPP–MO theory has been devised and investigated. The method is based on the empirical linear relationship between the fluorescence Stoke's shift of a dye and the absorption half-bandwidth (the Pestemer rule). Thus theoretical Stoke's shifts are computed by the PPP–MO method and so related to bandwidths. The requisite MO parameters for various types of bonds commonly encountered in dyes have been developed for Stoke's shift calculations and these are presented. The predictive value of the method has been tested for 31 dye structures, representing the azo, hydrazone, methine, anthraquinone, naphthoquinone, di- and tri-phenylmethane, squarylium and fulvene classes, with experimental half-bandwidths ranging from 116 nm to 30 nm. A reasonable correlation between calculated and experimental half-bandwidths was found, suggesting that the method has practical potential for predicting not only the colour of a dye but also its brightness.

1 INTRODUCTION

The PPP–MO method has proved to be valuable for the prediction and interpretation of the visible absorption spectra of complex dyes,[1-4] and is now within the reach of anyone with access to a reasonably powerful personal computer.[5] The method is used principally for predicting the hue of a dye, i.e. its λ_{max} value, and at least one set of MO parameters has been developed empirically specifically for the calculation of this quantity.[3] The method will also give an indication of absorption intensities, although less satisfactorily, and has been used to calculate other colour-related properties, notably transition moment directions (of value in designing dyes for liquid-crystal applications[6]) and fluorescence Stoke's shifts.[7-9] One important colour property of a dye that does not appear to have been examined within the framework of PPP–MO theory is the width of the visible absorption band. This can vary widely from one type of chromophore to another, even within a particular chromophoric class, and has an important influence on the brightness of a dye. In qualitative terms, the absorption bandwidth can be seen to be dependent on the overall equilibrium geometry difference between the ground state and the first excited singlet state of the dye. Thus it is well known that the cyanine dyes, which have very uniform bond orders in the ground state and show very little change in bond orders in the excited state, have characteristically narrow absorption bands and afford very bright colours. In contrast, the carotenoid colours have strongly alternating single–double bond orders in the ground state and show a large change in bond orders after light absorption. Thus they have broad absorption bands and give relatively dull colours. Another factor in a dye molecule which determines bandwidth is the presence of steric crowding, which distorts the ground state from the ideal fully planar geometry. Insofar as the PPP–MO method can calculate ground-state and excited-state π-bond orders, there does appear to be the possibility that the method could give a quantitative estimation of bandwidths. Another factor that influences the brightness of a dye is its ability to fluoresce. However, this would appear to fall outside the scope of the PPP–MO method, since although the latter can be used to predict fluorescence wavelength maxima,[7-9] it cannot as yet be used to predict the probability of fluorescence. Thus in the present investigation we have confined our attention to bandwidths as the controlling factor in determining the brightness of a dye.

The clue as to how the PPP–MO method might be used to estimate bandwidths came from the work of Pestemer on fluorescent brighteners.[10] He demonstrated that for a wide range of fluorescent brightening agents there existed a simple relationship between the width of the absorption band and the frequency difference between the absorption and fluorescence

maxima (the Stoke's shift). Thus the bandwidth was defined as the width of the band at half-height, measured from the absorption maximum to the lower-frequency edge of the band. In this way the width of the unsymmetrical bands could be more precisely defined. This quantity, which approximates to one-half of the more commonly used half-bandwidth, in frequency units, was then linearly related to the Stoke's shift, also in frequency units. In practice, for dyes which absorb in approximately the same region of the spectrum, one can replace frequency units by wavelength values.

It is perhaps not surprising that there exists, to a first approximation, a simple relationship between bandwidth and Stoke's shift, since both properties are dependent on the equilibrium geometry difference between the ground and first excited singlet states.

To exploit the conclusions of Pestemer, it is necessary that one can predict the Stoke's shift (real or imaginary) of a dye, and here the groundwork had already been laid by Fratev *et al.*,[7] and by subsequent work by Mehlhorn and co-workers,[8] and by Fabian,[9] who had applied PPP–MO theory to the problem of calculating the fluorescence maxima of dyes. The method lacks rigorous theoretical justification, but results are good and it appears to be a reasonable semi-empirical approach to the prediction of Stoke's shifts. A conventional PPP calculation is carried out for the molecule in question, using standard bond lengths R^0_{mn} and resonance integrals β^0_{mn}, thus giving the absorption λ_{max} value, and also the π-bond orders, P_{mn}, for the excited state. It is then necessary to calculate a new λ_{max} value which can be equated to the fluorescence maximum. This is done by first using the excited-state bond orders to calculate excited-state bond lengths, R_{mn}, according to the equation

$$R_{mn} = a + bP_{mn} \tag{1}$$

The terms a and b are constants, where a can be regarded as the maximum value ($P_{mn} = 0$) for bond mn, and b is an empirical quantity, the generally accepted value being $-0{\cdot}18$. With the excited-state bond lengths one can then calculate the resonance integrals, β_{mn}, corresponding to these bond lengths from eqn (2):[8]

$$\beta_{mn} = \beta^0_{mn} \exp\left[-2{\cdot}3(R_{mn} - R^0_{mn})\right] \tag{2}$$

Thus one can now carry out another PPP calculation for the molecule with the geometry and β_{mn} values of the excited state. The resultant λ_{max} value will be greater than that of the first calculation, and is assumed to approximate the emission wavelength. A further improvement of this value is obtained by readjusting the bond lengths and the β_{mn} values with eqns (1) and (2) and repeating the calculation iteratively until convergence of the

transition energies or bond lengths is achieved. The difference between the original calculated λ_{max} value and the converged value from the second set of calculations is the Stoke's shift.

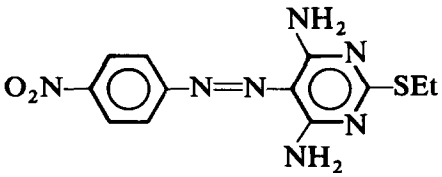
In the basic eqn (1), it is important that the parameters a and b be given due consideration, so that they are appropriate to the various bond types found in typical dye structures. Thus it was necessary to examine these parameters, and to establish empirically their optimum values. Having done this, the PPP–MO method was then used to predict the Stoke's shifts, and hence bandwidths, of a wide range of dyes. The dyes chosen for this study provide a very wide range of bandwidths, and thus constitute a good test of the viability of the method.

2 RESULTS AND DISCUSSION

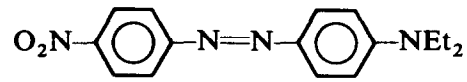
2.1 Parameter optimisation

The usual PPP parameters (valence state ionisation potential, electron affinity and core charges of each atom; bond resonance integrals; bond lengths and bond angles) that have been evolved as a generalised set for dyes were retained for calculating the absorption λ_{max} of the selected model compounds.[3] In calculating the theoretical fluorescence λ_{max} of these compounds, additional parameters that require specific consideration are a and b in eqn (1). The widely accepted value for parameter b is $-0{\cdot}18$, and it was decided that this should in the first instance be retained in order to examine the sensitivity of the calculations to the parameter a. In the event, it was found that small modifications to a were all that were required to give reasonable calculated results, and thus modifications of parameter b were not pursued.

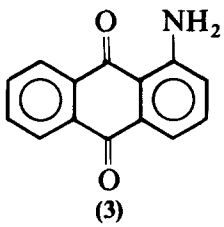
It was found that the calculated Stoke's shift (or bandwidth) was very dependent on the choice of parameter a, and in fact a reasonably linear relationship existed between the Stoke's shift and the a value for a particular bond in a dye molecule. This is exemplified for the two azo dyes **1** and **2**, where the value of a was varied from 1·351 to 1·420 Å, and the resultant Stoke's shifts ranged from 32 to 60 nm (Fig. 1a). The shift decreased towards zero as a approached the normal ground-state bond length for the azo group (1·23 Å). This effect is general for all bond types; for example, the anthraquinone dye (**3**) showed a variation in calculated Stoke's shift from 19 to 40 nm when parameter a was varied from 1·371 to 1·610 Å for the carbonyl group (Fig. 1b). It is clear from Fig. 1 that the sensitivity of Stoke's shift to a depends on the bond type, and the correct choice of a is much more critical for the azo group than for the carbonyl group.



(1)



(2)



(3)

Using representative examples of each dye type it was possible to carry out calculations of Stoke's shifts and to relate these to experimental bandwidths. Then by a process of empirical modification of *a* values for each bond type, optimum *a* values could be derived. This results in a generalised set of bond parameters, and the resultant values for 23 different types of bond are summarised in Table 1. The test of the predictive validity of these values then lay in calculating the bandwidths of a wider range of dye structures which incorporate these bond types.

2.2 Calculation of bandwidths

The width of the visible absorption band of a dye is most conveniently expressed by the half-band width, $\Delta\lambda_{1/2}$ (in wavelength units), or $\Delta\nu_{1/2}$ (in frequency units). This is the width of the absorption band in the appropriate units at one-half of the total height of the band, the height being measured in units of absorbance. This is a constant whatever the height of the peak. For the 31 dye examples listed in Table 2, the half-bandwidths, in nm and in cm^{-1}, measured in a solvent of as low a polarity as solubility will permit, are presented. It can be seen that values of $\Delta\lambda_{1/2}$, range from the relatively broad values of *ca.* 116 nm for azo dye **22**, to the exceptionally narrow bands of the squarylium dyes, e.g. **21**, with $\Delta\lambda_{1/2} = 30$ nm.

The results for the calculation of absorption λ_{max} values and Stoke's shifts for the 31 examples are summarised in Table 2. It was clear from the calculated Stoke's shifts that these values were significantly smaller than would normally be expected (few of the dyes showed any significant fluorescence, and thus a systematic measurement of experimental Stoke's shifts could not be undertaken). However, as the purpose of the investigation was to predict bandwidths, this was not regarded as important. What was most important was that the *relative* Stoke's shift values should reflect the

TABLE 1

PPP-MO Parameters for the Calculation of Absorption Maxima and Half-bandwidths of Dyes

Bond X—Y	r_{X-Y}[a] (Å)	β_{X-Y}[b] (*eV*)	$VSIP_Y$[c] (*eV*)	A_Y[d] (*eV*)	Z_Y[e]	a_{X-Y}[f] (Å)
C=C (aromatic)	1·40	−2·39	11·16	0·03	1	1·52
C=C (olefinic)	1·35	−2·60	11·16	0·03	1	1·55
=C—C	1·45	−2·30	11·16	0·03	1	1·52
C=N	1·40	−2·48	14·70	2·30	1	1·48
N=N (azo)	1·23	−2·90	14·70	2·30	1	1·385
N—O (nitro)	1·21	−3·05	21·00	2·50	1	1·33
C—N (nitro)	1·49	−2·00	24·80	12·53	2	1·54
C=O (free)	1·22	−2·46	15·00	0·71	1	1·41
C=O (H-bonded)	1·22	−2·46	17·70	2·47	1	1·61
C≡N (cyano)	1·15	−2·67	14·18	3·50	1	1·31
C—CN (cyano)	1·40	−2·30	11·19	0·10	1	1·52
NH—C= (hydrazone)	1·38	−2·65	11·16	0·03	1	1·455
=N—NH (hydrazone)	1·35	−2·62	21·00	9·26	2	1·44
C=N— (hydrazone)	1·26	−2·90	15·00	0·97	1	1·405
C=N (heterocyclic)	1·40	−2·50	16·00	2·50	1	1·50
X—N (heterocyclic)	1·35	−2·40	21·00	10·00	2	1·43
C—S	1·71	−1·20	22·20	9·16	2	1·77
C—NH_2	1·38	−2·75	21·00	9·26	2	1·49
C—NHMe	1·38	−2·75	20·00	8·63	2	1·48
C—NMe_2	1·38	−2·75	19·00	8·00	2	1·46
C—NEt_2	1·38	−2·75	18·00	7·50	2	1·42
C—O^-	1·22	−2·46	18·00	3·80	1	1·71
C=NEt_2^+ (squaraine)	1·38	−2·75	18·00	7·50	2	1·38
C—NHMe (H-bonded)	1·38	−2·75	15·00	8·60	2	1·45
C—$NHBu^n$ (H-bonded)	1·38	−2·75	15·00	8·60	2	1·65
C—OH (H-bonded)	1·36	−2·60	28·60	10·30	2	1·40
C—OMe	1·36	−2·60	32·90	11·43	2	1·45
C—NMe_2 (arylmethane)	1·40	−2·75	13·20	7·12	2	1·55
C—NH (heterocyclic)	1·35	−2·40	21·00	10·00	2	1·42
C=N (heterocyclic)	1·33	−2·60	16·00	2·50	1	1·50
C—N= (heterocyclic)	1·38	−2·40	16·00	2·50	1	1·50
C—CCl	1·40	−2·39	12·00	0·03	1	1·56

[a] Bond length.
[b] Resonance integral.
[c] Valence state ionisation potential.
[d] Electron affinity.
[e] Core charge.
[f] Bond parameter used in eqn (1).

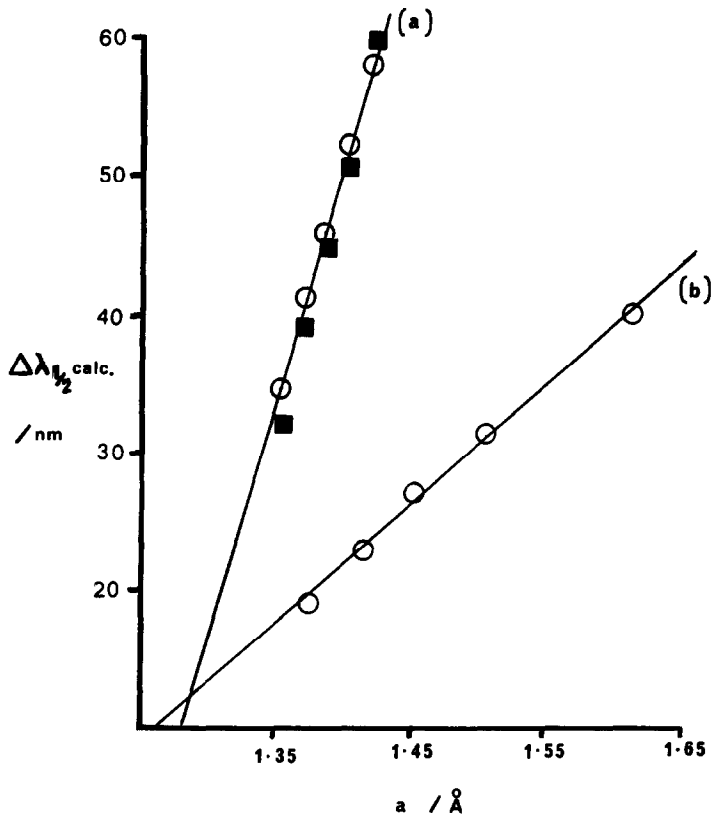


Fig. 1. Variation of $\Delta\lambda_{1/2}$ calc. with the parameter a [eqn (1)] for (a) the azo group in dye 1 (■) and dye **2** (○), and (b) the carbonyl group in dye **3**.

true situation accurately. It was then assumed that a linear relationship might exist between the calculated Stoke's shift [S(calc.)] and the experimental half-bandwidth [$\Delta\lambda_{1/2}$], and this was examined graphically, as shown in Fig. 2. A similar plot of S(calc.) against experimental $\Delta\nu_{1/2}$ is shown in Fig. 3.

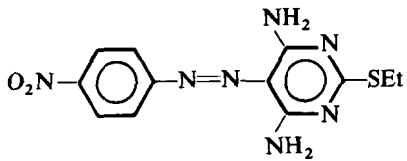
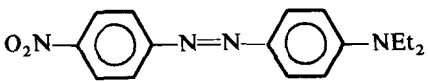
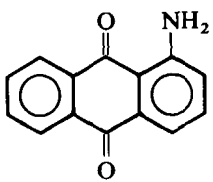
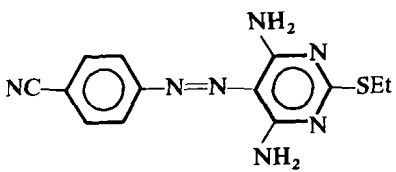
It is evident that a reasonably linear correlation exists in both cases, and regression analysis leads to the relationships (3) and (4).

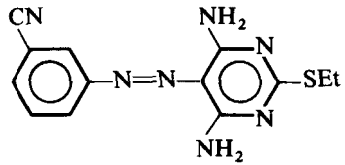
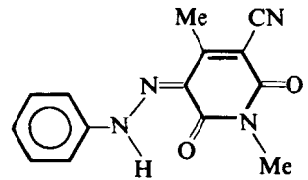
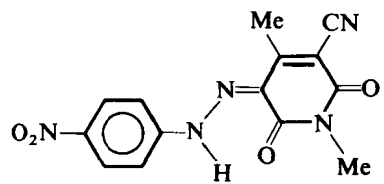
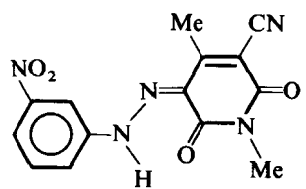
$$\Delta\lambda_{1/2} = 12{\cdot}26 + 1{\cdot}92S(\text{calc.}) \quad (\text{nm}) \tag{3}$$

$$\Delta\nu_{1/2} = 0{\cdot}727 + 1{\cdot}937S(\text{calc.}) \quad (\text{cm}^{-1}) \tag{4}$$

For eqn (3) the correlation coefficient was 0·936, and for eqn (4) a slightly higher value of $r = 0{\cdot}945$ was obtained. In view of the very wide range of structural types used in this analysis, and the various uncertainties due to solvent effects, possible non-planarity, and the many approximations in the method, the agreement between theory and experiment is surprisingly good.

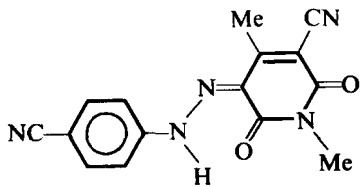
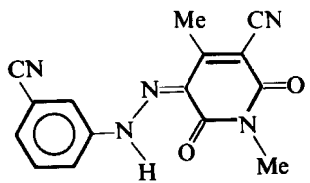
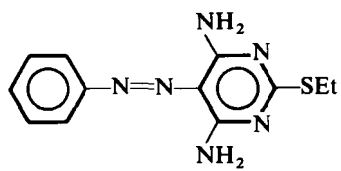
TABLE 2
Experimental and Calculated Electronic Absorption Spectral Data for Dyes **1–31**

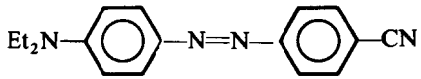
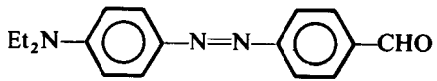
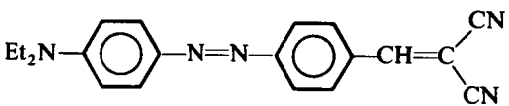
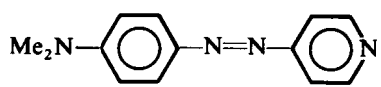
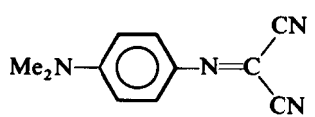
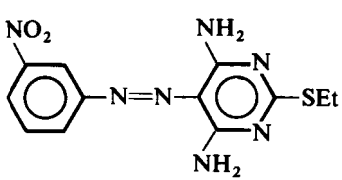
Dye	*Structure*	*Experimental values*[a]			*Calculated values*			
		λ_{max} (*nm*)	$\Delta\lambda_{1/2}$[b] (*nm*)	$\Delta\nu_{1/2}$[c] ($10^3\ cm^{-1}$)	λ_{max} (*nm*)	S[d] (*nm*)	$\Delta\lambda_{1/2}$[e] (*nm*)	$\Delta\nu_{1/2}$[f] ($10^3\ cm^{-1}$)
1		423	97	5·35	421	45	98	5·16
2		486	106	4·64	449	46	101	4·73
3		466	86	4·05	451	40	89	4·23
4		409	89	5·29	458	45	98	5·31

5		397	80	5·00	438	42	93	5·41
6		433	68	3·70	460	27	64	3·36
7		435	64	3·43	477	29	68	3·36
8		423	66	3·76	451	23	56	3·03

(continued)

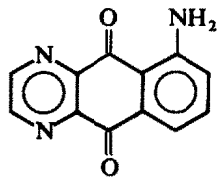
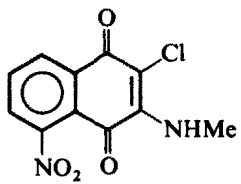
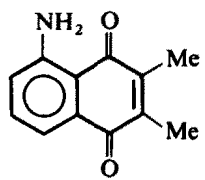
TABLE 2—*contd.*

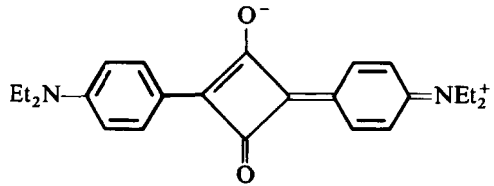
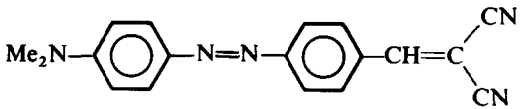
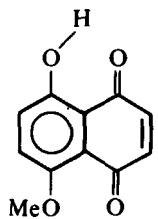
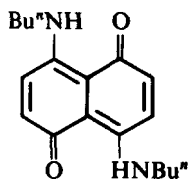
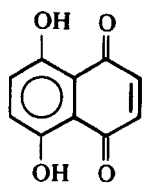
Dye	*Structure*	*Experimental values*[a]			*Calculated values*			
		λ_{max} (*nm*)	$\Delta\lambda_{1/2}$[b] (*nm*)	$\Delta\nu_{1/2}$[c] ($10^3\ cm^{-1}$)	λ_{max} (*nm*)	S[d] (*nm*)	$\Delta\lambda_{1/2}$[e] (*nm*)	$\Delta\nu_{1/2}$[f] ($10^3\ cm^{-1}$)
9		429	66	3·64	474	28	66	3·28
10		423	66	3·77	429	25	60	3·21
11		389	82	5·39	396	44	96	5·60

12		468	97	4·61	478	40	89	4·43	
13		473	96	4·39	472	43	95	4·83	
14		535	114	4·12	542	51	110	4·44	
15		442	94	4·80	446	43	95	5·35	
16		463	43	2·05	476	20	51	2·51	
17		400	86	5·36	437	39	87	5·07	

(continued)

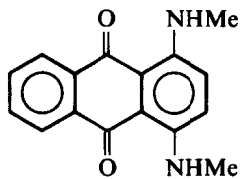
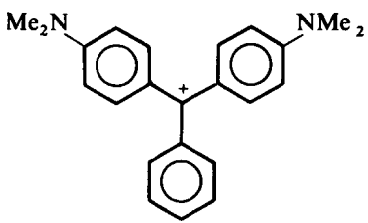
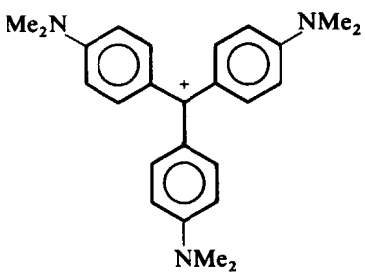
TABLE 2—*contd.*

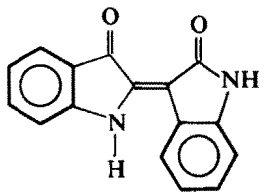
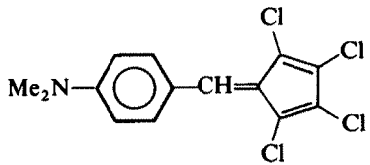
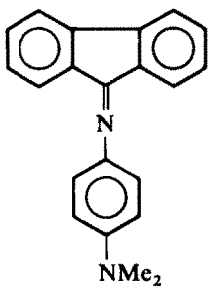
Dye	*Structure*	*Experimental values*[a]			*Calculated values*			
		λ_{max} (*nm*)	$\Delta\lambda_{1/2}$[b] (*nm*)	$\Delta\nu_{1/2}$[c] ($10^3\ cm^{-1}$)	λ^{m}_{ax} (*nm*)	S[d] (*nm*)	$\Delta\lambda_{1/2}$[e] (*nm*)	$\Delta\nu_{1/2}$[f] ($10^3\ cm^{-1}$)
18		490	101	4·28	462	41	91	4·13
19		477	106	4·74	478	58	123	5·10
20		472	90	4·17	498	39	87	3·55

21		638	30	0·71	637	14	39	1·36
22		519	116	4·46	476	52	112	4·74
23		487	106	4·62	473	47	102	4·43
24		654	80	2·00	647	37	83	2·35
25		520	111	4·28	503	41	91	3·63

(continued)

TABLE 2—*contd.*

Dye	*Structure*	*Experimental values*[a]			*Calculated values*			
		λ_{max} (*nm*)	$\Delta\lambda_{1/2}$[b] (*nm*)	$\Delta\nu_{1/2}$[c] ($10^3\ cm^{-1}$)	λ_{max} (*nm*)	S[d] (*nm*)	$\Delta\lambda_{1/2}$[e] (*nm*)	$\Delta\nu_{1/2}$[f] ($10^3\ cm^{-1}$)
26		620	103	2·87	607	45	98	2·93
27		617	44	1·16	626	19	48	1·63
28		582	66	2·05	580	27	62	2·16

29		527	92	3·38	521	41	91	3·44
30		462	56	2·76	463	24	58	2·78
31		476	106	4·78	500	46	101	3·98

[a] Spectra recorded in the following solvents: **1**, **3–10** and **17** in toluene; **16**, **19**, **20**, **24**, **29–31** in cyclohexane; **12–14**, **21–23**, **25**, **26**, **28** in CH_2Cl_2; **2**, **15**, **18** and **27** in ethanol.

[b] Width of absorption band, on wavelength scale, at one-half of peak height.

[c] Width of absorption band, on frequency scale, at one-half of peak height.

[d] Calculated Stoke's shift. $S = \lambda_{max}^{fluor}(calc.) - \lambda_{max}^{abs}(calc.)$.

[e] Half-width (nm) calculated from eqn (3).

[f] Halfwidth (cm^{-1}) calculated from eqn (4).

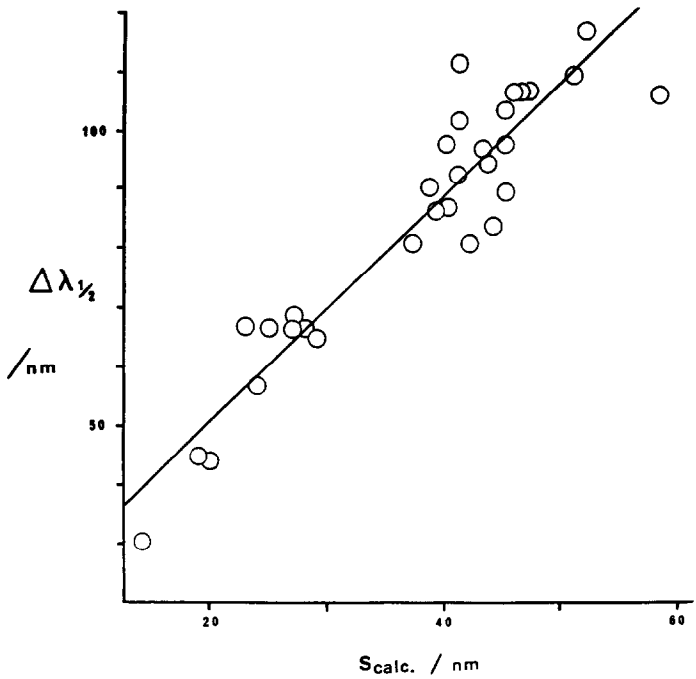


Fig. 2. Relationship between experimental half-bandwidth $\Delta\lambda_{1/2}$ and calculated Stoke's shift $S_{calc.}$ for dyes **1**–**31**.

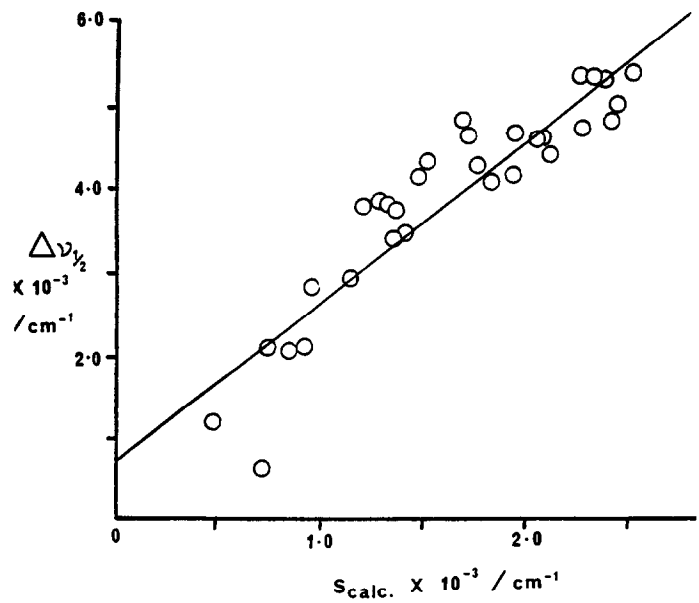


Fig. 3. Relationship between experimental half-bandwidth $\Delta\nu_{1/2}$ and calculated Stoke's shift for dyes **1**–**31**.

Thus it would seem that any dye chromophore which has reasonable planarity can be handled by this method to give a realistic estimate of the absorption bandwidth, and hence the probable brightness of the dye can be predicted.

Certain features of the data in Table 2 are worthy of comment. For example, it is interesting to note that the azobenzene dyes, e.g. **2** and **12–15**, have somewhat broader bands than the intramolecularly hydrogen bonded hydrazone dyes **6–10**. This can be attributed to the greater extent of bond-order changes in the former after light absorption compared with the latter. This effect is well reproduced by the MO procedure, and leads to the correct prediction of a narrowing of the absorption band in the hydrazones. The dyes **6–10** are noted for their outstanding brightness.

Another successful prediction by the MO method is the significant band narrowing found in the 1,5-naphthoquinone (**24**) relative to the similarly coloured anthraquinone (**26**), and relative to other 1,4-naphthoquinones, such as **23** and **25**. This is a particularly striking feature of the 1,5-naphthoquinones when compared with other 1,4-quinone dyes. Finally, it is interesting to note that the very bright triarylmethane cationic dyes, such as Malachite Green (**27**) and Crystal Violet (**28**), and the even narrower-band squarylium dye (**21**) are predicted correctly to have narrower bands than any of the other dye classes.

3 EXPERIMENTAL

3.1 MO calculations

These were carried out using a conventional PPP SCF-CI program[5] for calculating absorption maxima, and a modified FORTRAN program for calculating Stoke's shifts. Relevant parameters are listed in Table 1. The program CHNPRN is suitable for use on a personal computer;[11] for example, with an STM-PC minicomputer, Stoke's shifts could be calculated in 15–40 min, depending on the number of π-centres in the dye molecule, for the dyes **1–31**.

3.2 Dyes

The dyes **1–31** were samples available from previous work of the authors, and were analytically pure materials. Solvents used for determining bandwidths are indicated in Table 2. Where dyes presented structured absorption bands due to discrete vibronic transitions, the half-bandwidth was measured for

the complete band envelope (e.g. in the case of 1,4-disubstituted quinones, such as **25** and **26**).

4 SUMMARY

It has been demonstrated that the PPP–MO method can be adapted to the prediction of the bandwidths of the visible absorption bands of a wide range of dye types, using a generalised, empirically derived set of bond parameters. The method depends on the calculation of the absorption and (hypothetical) fluorescence maxima of a dye, and then relating the difference between these (i.e. the Stoke's shift) to the half-bandwidth. Equations (3) and (4) can be used to calculate half-bandwidth from the Stoke's shift. Although the method is dependent on empirically derived parameters and needs more extensive testing on other dye systems, it does appear to offer considerable promise as a practical means of predicting the potential brightness of new dye chromophores.

REFERENCES

1. Griffiths, J., *Colour and Constitution of Organic Molecules.* Academic Press, London, 1976.
2. Fabian, J. & Hartmann, H., *Light Absorption of Organic Colorants.* Springer, Berlin, 1980.
3. Griffiths, J., *Rev. Prog. Coloration*, **11** (1981) 37.
4. Griffiths, J., *Chemistry in Britain*, **22** (1986) 997.
5. Griffiths, J., Lasch, J. G. & Schermaier, A. J., *Quantum Chemistry Program Exchange Bulletin*, **8** (in press). (Program QCMP054.)
6. Blackburn, C. & Griffiths, J., *Mol. Cryst. Liq. Cryst.*, **101** (1983) 341.
7. Fratev, F., Hiebaum, G. & Gochev, A., *J. Mol. Struct.*, **23** (1974) 437.
8. Mehlhorn, A., Schwenzer, B. & Schwetlick, K., *Tetrahedron*, **33** (1977) 1483.
9. Fabian, W., *Dyes and Pigments*, **6** (1985) 341.
10. Pestemer, M., Berger, A. & Wagner, A., *Textilveredlung*, **19** (1964) 420.
11. L. Cheng, unpublished results (1987).