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PRACTICAL ASPECTS OF COLOUR PREDICTION OF ORGANIC DYE MOLECULES

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SUMMARY

The colour of a dye is determined largely by the position of its absorption band in the visible spectrum, but other electronic absorption spectroscopic properties are also of practical interest, namely intensities, band shapes, and band polarisation directions. Chemical interactions between a dye molecule and its environment are also important, e.g. solvatochromic and aggregation effects. Although no single theoretical treatment is yet available for predicting all these quantities from a knowledge of the structure of the dye molecule, the well-established Pariser–Parr–Pople molecular orbital (PPP-MO) method goes a long way towards providing such a method, and is adaptable to routine use. Applications of the PPP-MO method to colour prediction within the main dye classes are reviewed, with particular emphasis on the 'generalised parameter' approach favoured by the author. Practical aspects of the method and its predictive limitations are discussed. Unanswered questions which might prove amenable to treatment by the PPP-MO method are considered, and some possible approaches to solving these problems are suggested.

1. INTRODUCTION

Prediction of the colour of organic dyes has concerned chemists for more than a hundred years, and the potential fruits of such investigations are considerable, not only intellectually, but also from the less altruistic (though equally justifiable) commercial point of view. It was not until the advent of quantum theory that a true understanding of the light absorption process itself was obtained, and from that point on, rapid progress in colour and constitution studies was made. The subsequent development of molecular orbital theory in turn greatly facilitated quantitative prediction of light absorption properties, and we are now in the

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position of being able to predict with reasonable reliability the colour of any dye molecule. Needless to say, the recent rapid advances in computer technology are doing much to encourage the exploitation of such molecular orbital methods in industry.

It is the intention in this paper that only one such molecular orbital approach to colour prediction will be considered, namely the Pariser–Parr–Pople (PPP) MO method, which was first introduced in 1953.[1] The reason for this restriction is that, in the author's opinion, this method at the present time is the best for combining predictive reliability and generality with ease of use. No doubt this situation will be subject to change, and one can envisage more sophisticated all-valence electron methods, with their incumbent problems of parameter evaluation and heavy demand on computer capacity, receiving wider usage in the near future. However, for the present, the PPP-MO method has no rival for the industrial research chemist, and there is a need to generate a greater awareness of the value of the technique.

Before considering applications of the PPP method in detail, we should consider first what we mean by 'colour prediction'. From the purely practical viewpoint, colour prediction should embrace any aspect of light absorption by a dye molecule that is of technological relevance. Thus we can recognise the following properties as falling within our sphere of interest:

(*a*) *The wavelength of maximum absorption* (λ_{max}) *of the visible band*
This is a convenient means of specifying the position of the absorption band, and thus gives an approximate indication of the hue of the dye.

(*b*) *The absorption band intensity*
Whilst not affecting the hue of the dye, this quantity (generally measured at the position of λ_{max}) is of considerable commercial significance, in that it indicates the effectiveness of a dye as a colouring agent.

(*c*) *The polarisation direction of the absorption band*
Formerly of academic interest only, this vector property has assumed technical significance in recent years in connection with coloured liquid crystal display devices.

Other important colour-influencing properties that cannot as yet be calculated directly by the PPP method include:

(*d*) *The shape of the absorption band*
Band width and band asymmetry have a significant effect on colour, since these control brightness and spectral purity.

(*e*) *Solvatochromism*
Interaction of a dye molecule with its environment (solvent molecules, polymer substrate etc.) can cause colour modification by displacement of the absorption band. Such interactions are likely to be found in any practical situation using a dye as a colorant.

(*f*) *Aggregation*
Interactions between several dye molecules, or an effectively infinite number in the case of pigment crystals, induces important spectroscopic shifts which can result in pronounced colour modification. This phenomenon is important technically with pigments and with photographic sensitising dyes.

Routine prediction of these various colour-determining properties has only achieved any measure of success with (*a*)–(*c*), although useful predictions in connection with (*f*) have been made in the case of some sensitising dyes. Thus the bulk of this discussion will be concerned with the prediction of λ_{max} values, absorption intensities, and band polarisation directions by the PPP-MO method. The other factors will be considered briefly.

2. PRACTICAL ASPECTS OF THE PPP-MO METHOD

The mathematical formalism of the PPP method[1] is essentially the same as that of the Hückel MO method,[2] and need not concern us here. Suffice it to say that computer programmes are readily available, and whilst they may differ in minor details, all depend on the same input parameters, and give the same basic information. A *configuration interaction* treatment is normally an integral part of such programmes, and this is used to improve the reliability of calculated λ_{max} values.

To calculate the absorption spectrum of a particular dye, firstly the structure must be known, and secondly a range of parameters is required. This is best exemplified with the simple dye molecule shown in Fig. 1. We first recognise the fact that the PPP method deals with the π-electron part of the molecule only, and to simplify data input all atoms contributing to the π-system are numbered in any convenient sequence. Thus in Fig. 1 the 15 atoms shown are numbered. The structure of the molecule is defined by indicating all bond angles and all bond lengths involving these 15 atoms. In most cases a dye molecule will be assumed planar, but non-planar molecules can also be handled by including out-of-plane bond angles if desired.

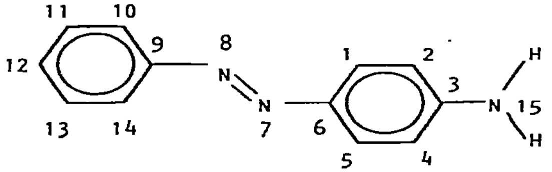

Fig. 1. Atomic centres of 4-aminoazobenzene for a PPP-MO calculation.

The parameters that are next required are essentially of two types:

(1) *Electronic*. Each numbered atom is given a *core charge* value, which is the charge on that atom after all the π-electrons have been removed. In this case (Fig. 1) atoms 1–14 have a value of 1, whereas the nitrogen atom 15 has a value of 2. The total number of π-electrons must also be indicated, since the PPP method directly calculates interelectronic repulsions. The dye in Fig. 1 has 16 π-electrons.

(2) *Energy*. The energy parameters are also referred to as 'integrals'. For each of the 15 atoms in the present case one must specify the *valence state ionisation potential* (VSIP) of that atom, and the repulsion energy between two electrons if they were residing on that atom (γ_{nn}). These values are obtainable from tables in most cases. Similarly for each pair of bonded atoms (there are 16 in this case) the *resonance integral* (β_{nm}) is indicated.

A fourth energy term used by the program is the electron repulsion energy between two electrons when these reside on different atoms (γ_{nm}). However, these are evaluated by the computer from the appropriate γ_{nn} and γ_{mm} values, and require no specific input.

With these data, the computer will carry out a simple Hückel-type calculation, ignoring electron repulsion effects. This enables a rough picture of the electron density distribution to be built up, which can be used as a starting point for calculating electron repulsion effects. Calculations are then repeated successively, each one being an improvement on the preceding calculation, until eventually self-consistency is reached, i.e. additional calculations give no further improvement. At this stage the molecular orbital wave functions are given, together with their energies, and consequently ground and excited state energies can be computed. To improve the calculated transition energies (i.e. λ_{max} values), a configuration interaction treatment is carried out, and one can specify the extent of this. With the larger computers now available, the calculations take only a few seconds, and in fact the major time-consuming exercise is compilation of the input data, which can take of the order of 30 min per molecule.

The advantages of the PPP method over the simpler Hückel approach are numerous. Thus predictive accuracy is greatly improved because of the inclusion of electron interaction effects, and the method has a geometry sensitivity, permitting geometrical isomerism and non-planarity effects to be computed. The self-consistency of the method means that heteroatomic systems are handled just as well as hydrocarbons. Although the PPP method cannot include σ-electron effects directly (unlike the all-valence electron methods), one can generally allow for these empirically, thus avoiding the greater parameter and computational complexities of the latter.

The major problem encountered with the PPP method stems, in part, from the need to absorb in the various energy parameters uncertainties such as σ-electron effects, and thus parameter selection becomes an empirical exercise in many cases.

There are three different approaches to this problem. In the first, parameters are largely standardised and are based on experimental data. The effect of σ-electrons on these parameters is then calculated by suitably designed equations.[3] For example, the nitrogen atom in an amino group would not have the same VSIP value if the atom were progressively substituted with methyl groups, and the effect of the latter can be calculated. This approach does increase the amount of computation required for each new dye structure, and has not been extended to a wide range of complex chromogens. The second approach is adopted for colour prediction in a series of very closely related dyes (e.g. colour photographic dyes). Thus, using model compounds, parameters are refined to give maximum agreement between calculated and observed λ_{max} values, adjustments being of a purely empirical nature. Whilst providing valuable data of a specialised nature, parameters obtained in this way are unlikely to prove satisfactory in a completely unrelated type of chromogen. Thus if this approach were adopted for all dye classes the number of available parameters to suit all eventualities would rapidly become unmanageable. The third approach is also empirical, but here the emphasis is placed on obtaining a generalised set of parameters, limited in number but applicable to all known dye types. Thus to some extent predictive accuracy is sacrificed in order to maintain generality.

The third approach is that favoured by the author, and we shall discuss the predictive limitations of the general approach by consideration of the main dye classes. One set of parameters that has proved very successful is summarised in Table 1, and at this stage it is worth considering general strategy for determining such quantities.

Experience has shown that not all parameter types exert the same influence on calculated λ_{max} values for the longest wavelength band of an organic dye. With few exceptions it is found that parameter sensitivity follows the general order:

$$\mathrm{VSIP}_n \simeq \gamma_{nn} > \beta_{mn} > \text{bond lengths, bond angles}$$

Exceptions are occasionally encountered, however, and it should be stressed that this observation relates to the λ_{max} value of the *first* absorption band. A different parameter dependence may be found for other computed quantities, such as second or third absorption bands, or absorption intensities. This parameter sequence suggests that when optimising such parameters, attention should be directed mainly to the VSIP_n and γ_{nn} values. Thus it will be noted that in Table 1 there is a much greater variation in these quantities than in β_{mn} or geometry parameters. The empirical sequence also suggests that the modified PPP method referred to as the 'variable β approach', which lays much emphasis on refining β_{mn} values so that they are consistent with calculated bond orders, may have only a small advantage over the normal method for predicting λ_{max} values.

Parameter derivation is basically a trial-and-error exercise, using suitable model dyes, and attempting to obtain the best possible fit between calculated and observed

TABLE 1
GENERALISED PPP-MO PARAMETERS FOR THE CALCULATION OF VISIBLE ABSORPTION SPECTRA OF DYES

Bond X—Y	$r_{X\text{-}Y}$[a] (*nm*)	$\beta_{X\text{-}Y}$[b] (*eV*)	*VSIP*$_Y$[c] (*eV*)	γ_Y[d] (*eV*)	Z_Y[e]
C=C (aromatic)	0·140	−2·39	11·16	11·13	1
C=C (alkene)	0·135	−2·60	11·16	11·13	1
=C—C	0·145	−2·30	11·16	11·13	1
C=N	0·126	−2·80	15·00	14·00	1
C≡N (cyano)	0·115	−2·67	14·18	10·70	1
N≡C (cyano)	0·115	−2·67	11·19	11·09	1
N=N	0·123	−2·90	14·70	12·40	1
N=O (nitro)	0·121	−3·05	16·30	14·50	1
C—NO$_2$ (nitro)	0·149	−2·00	24·80	12·27	2
C=O (free)	0·122	−2·46	15·00	14·30	1
C=O (H-bonded)	0·122	−2·46	17·70	15·20	1
C=O[f]	0·122	−2·50	18·00	15·50	1
N=C—N[g]	0·135	−2·40	21·00	11·00	2
N=N —N[g]	0·135	−2·45	21·00	11·00	2
C=N—N[g]	0·135	−2·40	21·00	11·00	2
N=C—O[g]	0·135	−2·40	40·00	25·50	2
N—C=N[g]	0·133	−2·60	16·00	13·50	1
O—C=N[g]	0·133	−2·60	16·00	13·50	1
N—N=N[g]	0·133	−2·70	16·00	13·50	1
C—N=N[g]	0·133	−2·70	16·00	13·50	1
C—NH$_2$	0·138	−2·75	21·00	11·74	2
C—NMe$_2$	0·138	−2·75	19·00	11·00	2
C—NEt$_2$	0·138	−2·75	18·00	10·50	2
C—OH C—OMe	0·136	−2·60	32·90	21·47	2
C—NH$_2$ (H-bonded)	0·138	−2·75	18·80	10·10	2
C—NHMe (H-bonded)	0·138	−2·75	15·00	6·40	2
C—OH (H-bonded)	0·136	−2·60	28·60	18·30	2
C—NMe$_2$[h]	0·140	−2·75	12·7	6·08	2
C—NMe$_2$[i]	0·140	−2·75	13·2	6·08	2

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[a] Bond length.

[b] Bond resonance integral.

[c] Valence state ionisation potential.

[d] One-centre electron repulsion integral for atom Y.

[e] Core charge of atom Y.

[f] Averaged carbonyl parameters suitable for use with hydrogen-bonded —NH$_2$, —NHMe, and —OH parameters in quinone dyes, e.g. series (**12**).

[g] Five-membered ring aromatic heterocycles.

[h] For diarylmethane cationic systems, e.g. (**13**).

[i] For triarylmethane cationic systems, e.g. (**14**) and (**15**).

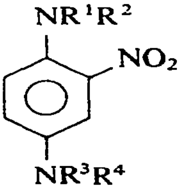
λ_{max} values. It is important to note, however, that solvent effects must be minimised when determining the absorption maximum of the model compound. Thus such spectra are measured in non-polar solvents (e.g. cyclohexane), and the derived parameters will then give predicted λ_{max} values relating to such solvents.

Little has been said about configuration interaction, and the extent to which this is used depends very much on the computer capacity and economic considerations. It is common in the literature for complete configuration interaction treatments to be carried out, but for large molecules this becomes very time-consuming. Experience has shown that in the majority of cases a very limited treatment is satisfactory if one is interested only in the first absorption band of the chromogen, e.g. involving the first nine singly excited states. The parameters listed in Table 1, and all calculations referred to in this paper, have been based on such a limited treatment.

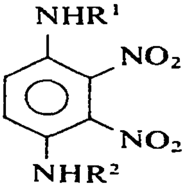
3. A SURVEY OF ABSORPTION WAVELENGTH PREDICTIONS BY THE PPP METHOD FOR VARIOUS DYE CLASSES

3.1. *Nitrophenylenediamines*

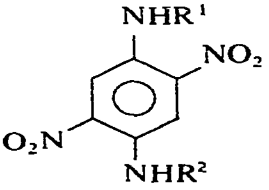
The nitrophenylenediamines (**1**)–(**4**) have been chosen for discussion first because they are the simplest chromogens that have been exploited commercially. Their colour and constitution properties have been investigated in detail recently.[4] The colours range from orange to blue, depending on the degree of alkylation of the amino groups and the number and position of nitro groups. In a study of these chromogens by the PPP method, the generalised parameter approach was used, and thus no attempt was made to include secondary effects such as hydrogen bonding, or *ortho* steric interactions. Even so, a good correlation between observed and calculated λ_{max} values was obtained (Fig. 2) with the exception of three compounds. Thus for (**1**; $R^1 = R^2 =$ Me, $R^3 = R^4 =$ H), (**1**; $R^1 = R^2 = R^3 =$ Me, $R^4 =$ H) and (**1**; $R^1 = R^2 = R^3 = R^4 =$ Me) the calculated values are higher than the observed values. This can readily be attributed to pronounced steric crowding in these dyes, where interaction between the dimethylamino group and the *ortho* nitro group causes the former to rotate out of conjugation with the benzene ring. This is confirmed



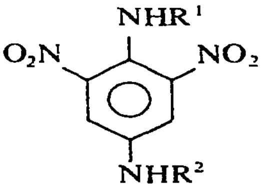
(1)



(2)



(3)



(4)

$R^1, R^2, R^3, R^4 =$ Me or H

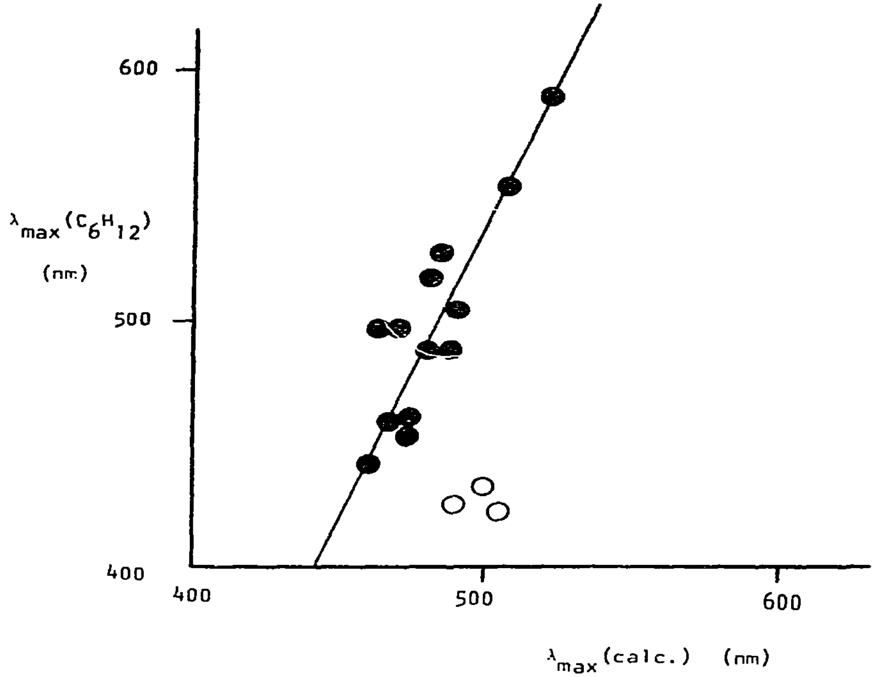


Fig. 2. Comparison of calculated and experimental λ_{max} values for the nitro-*p*-phenylenediamine dyes (1)–(4): ● planar; ○ non-planar dyes.

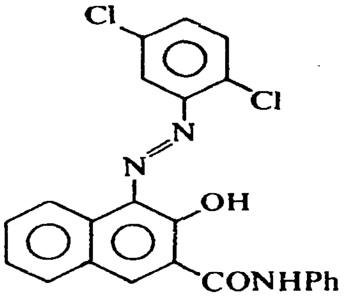
experimentally by the low extinction coefficients for the three anomalous derivatives.[4]

The curve shown in Fig. 2 does not pass through the origin, which indicates that the parameters used are not ideal for this particular system. However, it is clear that the PPP method can adequately predict such effects as the relative orientation of two nitro groups on λ_{max}, or that in the mono-nitro series the stronger electron-releasing amino group should be *ortho* to the nitro group for maximum bathochromic effect. It is this sort of structural problem that can be handled most elegantly by the PPP method.

3.2. The azo dyes

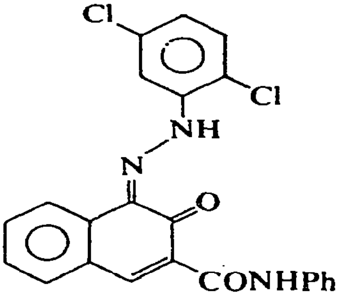
The azo dyes are the most important class of commercial dyes, and thus colour computations for these should be of particular interest. It is somewhat surprising therefore to find that very few applications of SCF-MO theory to the azo dyes have been reported.[5,6] Kogo and Kikuchi have achieved some success with aminoazobenzene dyes using the variable β approach.[6] However, equally good results can be obtained with the basic PPP method, using the parameters of Table 1.[5]

The hydroxyazo dyes are often complicated by azo–hydrazone tautomerism, and it is important to consider the correct tautomer when computing the colour of such compounds. The well known spectroscopic differences between the azo and hydrazone tautomeric forms can be well predicted by the PPP method, as exemplified by (5) and (6).



(5)

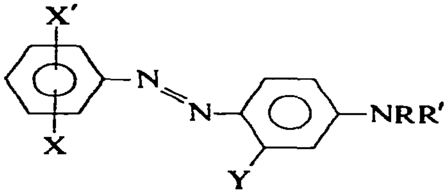
$\lambda_{max}(C_6H_{12}) = 425$ nm
λ_{max} (calc.) = 409 nm



(6)

λ_{max} $(C_6H_{12}) = 503$ nm
λ_{max} (calc.) = 506 nm

For the 'normal' azo dyes which have no such tautomerism problems, in particular the aminoazo compounds, application of the PPP method is quite straightforward, provided steric effects are minimal and the molecule is reasonably planar. The *trans* configuration is of course always assumed for the dye under normal conditions of application. The predictive value of the technique for dyes of this type can be seen from Fig. 3, which shows the correlation between calculated and observed λ_{max} values for dyes of general structure (7).



(7)

X, X' = H, NO_2, CN, MeO, CH_3CO, OH
Y = H, MeO, HO
R, R' = H, Me, Et

It will be noted from Fig. 3, however, that certain dyes, namely (8a–c), give a very poor agreement between theory and experiment. These all contain a hydroxy group *ortho* to the azo group and are thus strongly intramolecularly hydrogen bonded (cf. structure (8)). This hydrogen bond will exert a bathochromic shift on the absorption band that is not accounted for by the PPP method, since the parameters employed

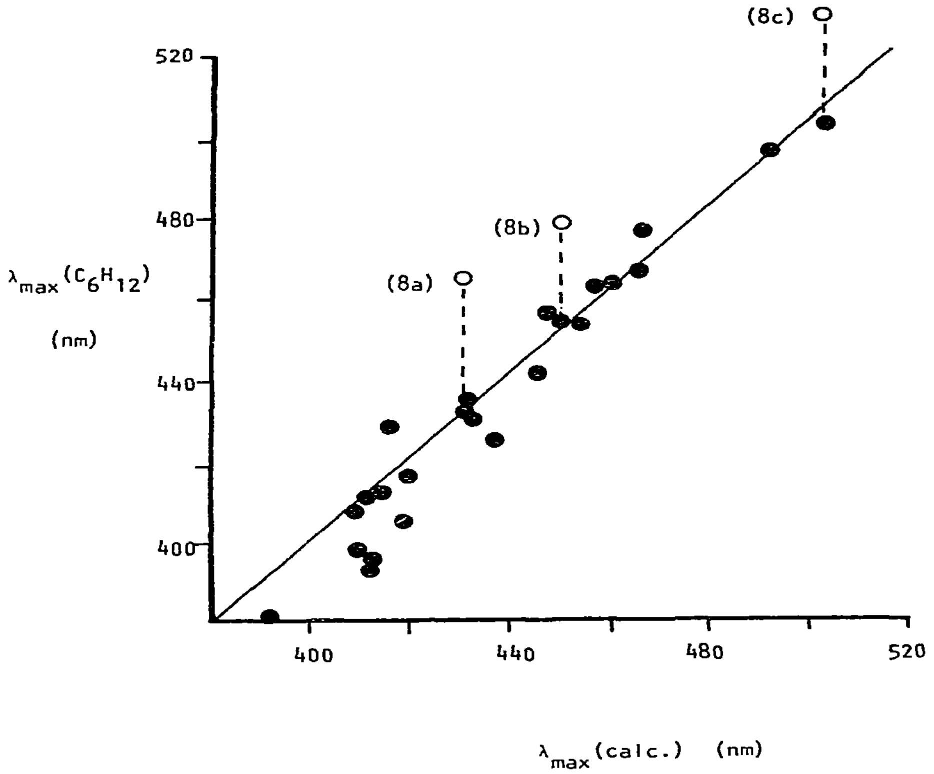
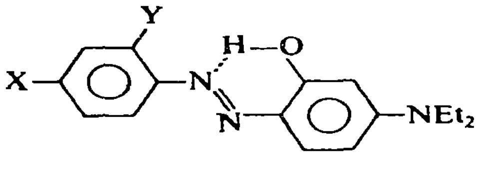
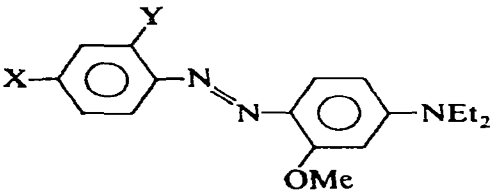


Fig. 3. Comparison of calculated and experimental λ_{max} values for the azo dyes (7)–(9). Broken lines indicate related pairs of hydrogen bonded dyes (8) and corresponding methylated dyes (9).

for the hydroxyl oxygen atom and the azo nitrogen atom take no cognisance of the hydrogen bond. The corresponding methoxy dyes (9a–c) do lie on the curve in Fig. 3, however. The correct λ_{max} values for (8a–c) can be calculated by suitable choice of parameters.



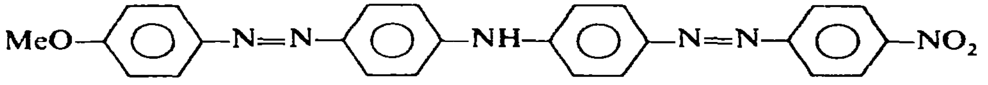
(8)



(9)

a; X = Ac, Y = H
b: X = NO_2, Y = H
c: X = Y = NO_2

Little work has been carried out on disazo dyes and it is difficult to comment on the usefulness of the PPP method for such chromogens. However, we have examined recently disazo dyes of the type (**10**), and excellent predictions of both λ_{max} and intensities have been obtained.



(**10**)

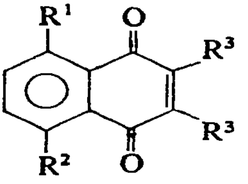
λ_{max} (C_6H_{12}) = 452 nm
λ_{max} (calc.) = 449 nm

As noted with the nitrophenylenediamine dyes, the spectroscopic effects of positional isomerism in the azo dyes, i.e. the variation of λ_{max} with the relative positioning of electron-donating and -withdrawing substituents in the azo chromogen, can be well accounted for by the PPP method, as shown, for example, by the dicyano-4-diethylaminobenzenes.[7] It would seem, therefore, that the method has much to offer in the search for new azo dyes with improved spectroscopic properties.

3.3. Quinone dyes

Dyes based on anthraquinone are second in commercial importance to the azo dyes, and in a wider context, research into naphthoquinone and heterocyclic quinone dyes has intensified in recent years. Applications of the PPP method in this field have been somewhat more in evidence than was the case with azo dyes. For example, Kogo and co-workers have computed the λ_{max} values of a wide range of donor substituted anthraquinone dyes,[8] and also of a series of benzannelated analogues,[9] using the variable β modification, with notable success. Thus for 40 9,10-anthraquinone derivatives an excellent correlation between theory and experiment was obtained, although absolute agreement between the λ_{max} values was poor. The latter observation could be attributed to inadequate parameter selection, some of those used differing widely from those given in Table 1.

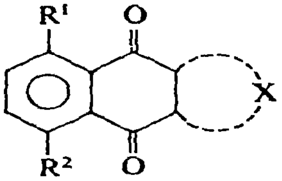
The 1-amino- and 1-hydroxy-anthraquinones provide further examples of chromogens containing strong intramolecular hydrogen bonding, and as with the azo dyes, this can be allowed for by slight modification of the parameters of the two atoms involved in the hydrogen bond (cf. Table 1). Very good absolute agreement between theoretical and experimental λ_{max} values has been obtained for the naphthoquinone series (**11**),[1] although in more complex dyes with donor groups in



(**11**)

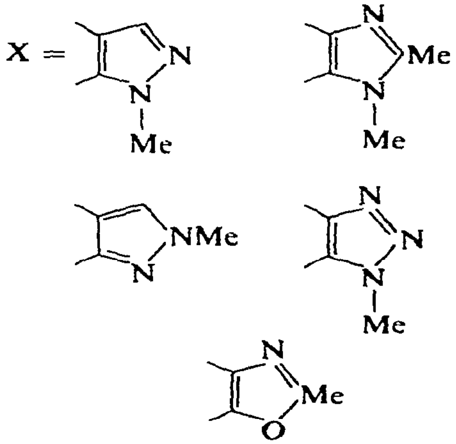
R^1, R^2 = H, NH_2, NHMe, OH, OMe
R^3 = H, Cl, CN

both rings, and consequently having two separate absorption bands, agreement tended to be less satisfactory.[11] Many heteroannelated analogues of the type (12) have been studied,[12,13] and it was found that hydrogen bonding effects could be ignored if simplified parameters for the carbonyl groups were used (Table 1), without causing a very great loss of predictive accuracy. Thus it can be seen from Fig. 4 that a good linear correlation holds for some 55 dyes, spanning the whole of the visible spectrum.



(12)

$R^1, R^2 = H, NH_2, NHMe, OH, OMe$



3.4. Cyanine-type dyes

Because of the importance of cyanine dyes in silver halide photography, and of merocyanine-types in colour photography, colour and constitution studies in these fields have been extensive. Many applications of the PPP method, and even all-valence electron methods, have been made to these dyes, but because of the commercial interest in such studies, few have been reported in the literature. One notable exception is the study of acetylenic cyanines by Mee and Sturmer, who used both the PPP and CNDO methods.[14] On a more basic level, it was considered of interest to examine the application of the PPP method to the di- and triarylmethane cyanine-type dyes, to establish the feasibility of the 'generalised

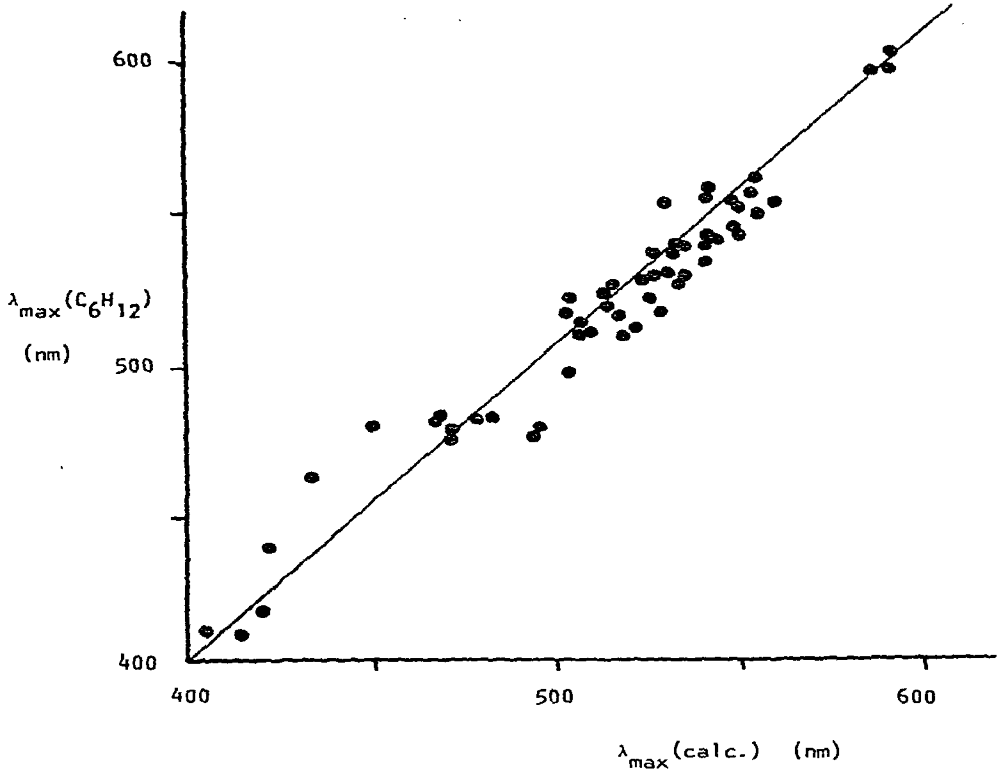
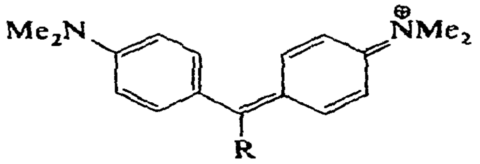


Fig. 4. Comparison of calculated and experimental λ_{max} values for heterocyclic quinone dyes (12).

parameter' approach in such systems.[15] The three basic systems (**13**) (Michler's Hydrol Blue), (**14**) (Malachite Green), and (**15**) (Crystal Violet) were chosen as model compounds, and assuming a planar geometry in all three cases it was found



(**13**); R = H
(**14**); R = Ph
(**15**); R = p-$Me_2N.C_6H_4$

that the 'normal' nitrogen parameters for the Me_2N group (Table 1) were unsatisfactory, giving lower λ_{max} values than observed. This can be attributed to (a) the approximations involved in assuming a planar geometry (particularly in the case of (**14**) and (**15**), (b) the high degree of positive charge on the Me_2N groups, and their closer adoption of sp^2 hybridisation than that found in neutral dyes, and (c) the uncertainties arising from solvent effects, since the spectra of (**13**)–(**15**) could not be measured in non-polar solvents.

Empirical adjustment of the nitrogen parameters led to the values indicated in Table 1. It was found judicial to use different parameters for the diarylmethanes and for the triarylmethanes, possible because the former are planar and the latter are not. The resultant parameter changes are physically reasonable in terms of the increased sp^2 hybridisation of the nitrogen atom. With these parameter values, the absorption spectra of a range of substituted derivatives of (**13**)–(**15**) could be predicted remarkably well. This was true for the two (x and y) visible absorption bands peculiar to dyes of the series based on (**14**). Agreement between theory and experiment with more extensively conjugated analogues of these compounds was less satisfactory however, and this may be due in large part to the increased deviation from molecular coplanarity in these crowded cationic systems.[15]

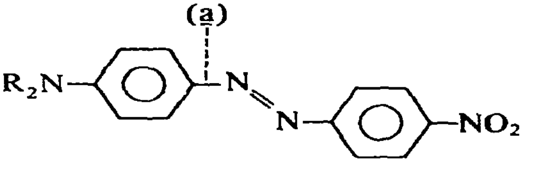
3.5. Miscellaneous dye systems

Numerous other dye systems have been examined by the PPP method, although in the majority of cases attention has been directed towards a general interpretation of light absorption properties, rather than practical colour prediction.[16] However, where λ_{max} prediction has been the prime consideration, results have been consistently good, as exemplified by studies on fluorescent brightening agents,[17] indigoids,[18–20] carotenoids,[21] fulvenes,[22] and cyanovinyl dyes.[23] The last two studies were based on the parameters of Table 1.

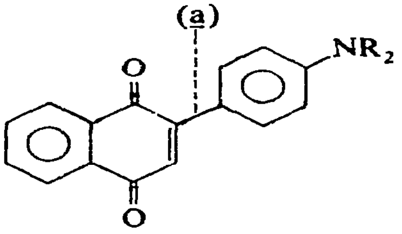
The wide success enjoyed by the PPP method when applied to chromogens as disparate as indigoids and triarylmethane cations suggests that colour predictions for completely new and as yet unsynthesised chromogens can be treated with some confidence, and thus the method could prove valuable in the search for new chromogens. However, it is important to recognise that the method may have limitations, and it is up to the research worker to test the method as fully as possible in order to establish what these limitations are.

3.6. Limitations of the PPP method

During the course of study of a large number of dyes of widely differing structure some apparent limitations of the PPP method were uncovered, which apply particularly to λ_{max} predictions. Two examples which highlight these anomalies are (**16**) and (**17**). It has been established experimentally that bulky substituents in (**16**) and (**17**) which cause loss of planarity by twisting the molecule about bond (a) cause hypsochromic shifts of the visible band. However, when the PPP method is applied to these compounds, and bond rotation is allowed for by the usual decrease in β value for bond (a) (e.g. according to the expression $\beta = \beta_0 \cos \theta$ where θ is the angle of twist), a bathochromic shift is always predicted. An exhaustive survey of all possible parameter effects failed to indicate the cause of this anomaly.



(16)



(17)

One parameter that is not altered in a typical PPP calculation for a non-planar molecule in three dimensions is the two-centre electron repulsion integral, γ_{mn}, for the bond rotated. Since orbital overlap is decreased by bond rotation, it is reasonable to assume that γ_{mn} might decrease, as does β_{mn}, when such rotation occurs. It was found that inclusion of such a reduction in γ_{mn} in the calculations for (16) and (17), assuming a non-planar structure, gave the correct hypsochromic shift. No attempt has been made to derive an optimum relationship between γ_{mn} and the angle of twist θ, but the arbitrary expression (eqn. 1) gave satisfactory results.

$$\gamma^{\theta}_{mn} = \gamma^{0}_{mn} \cos^2 \theta \tag{1}$$

It would thus appear that inclusion of the modification indicated by eqn. 1 in a non-planar PPP calculation can overcome one serious limitation of the method. However, much more experimental evidence is required before it can be assumed that all eventualities can be accomodated by this method.

4. THE PREDICTION OF ABSORPTION INTENSITIES

It could be argued convincingly that prediction of the absorption intensity of a dye is of greater practical value than prediction of its colour. This is certainly the case where the economics of the application and exploitation of a dye are overriding factors. It is surprising therefore that no studies of intensity prediction by the PPP or any other method appear to have been undertaken. Conventional PPP calculations of λ_{max} values do, of course, automatically give calculated intensity values, and these have been related on occasions to experimental values. However, no studies of the influence of geometry or other parameters on the validity of predicted intensity values have been made at the present time. It is therefore interesting to make a very general comparison between calculated and experimental intensities for a wide range of dye types, the former being obtained with the aid of the generalised parameters of Table 1. It should be noted that the PPP method gives intensities as oscillator strengths (f values), which experimentally are related to the area of the absorption band. Since the normally measured ε_{max} value is related to the height (absorbance) of the band, the two quantities are linearly related only if in a given

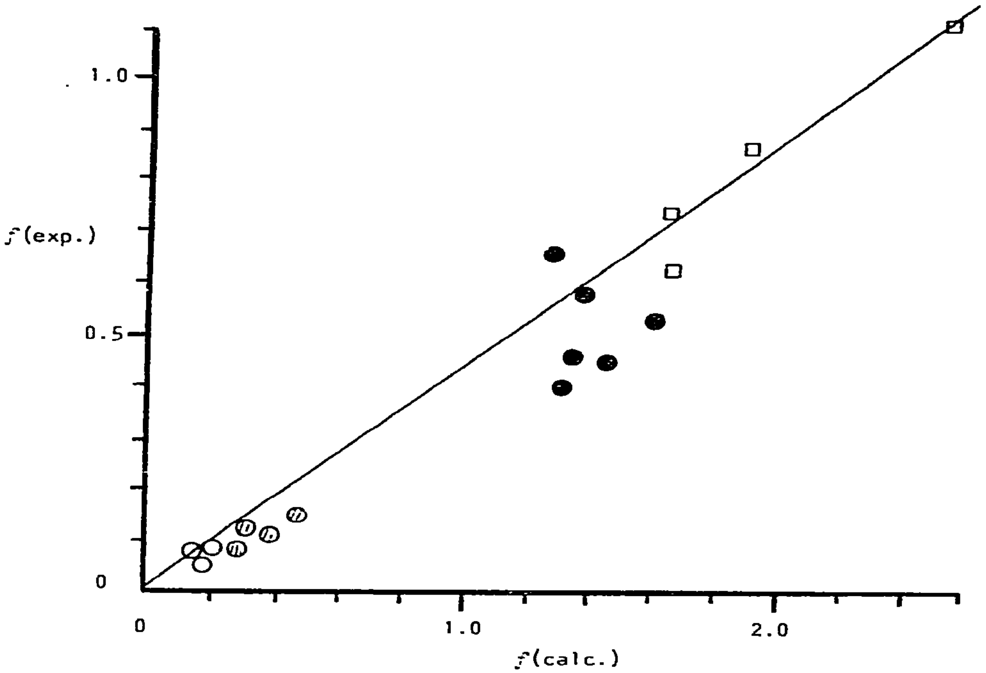


Fig. 5. Relationship between calculated and experimental absorption intensities (oscillator strengths, f) for representative dye classes: ○ nitro-p-phenylenediamines; ⊘ quinone dyes; ● aminoazo dyes; ☐ di- and tri-arylmethane cationic dyes.

series of dyes the band widths are the same, and if the bands are reasonably symmetrical. In general, theoretical f values are about twice the experimental value.

In Fig. 5 the calculated and experimental intensities of dyes ranging from the weakly absorbing nitrophenylenediamines to the extremely intense triarylmethanes are compared. A reasonable correlation is found for broad classes of dyes, but within a particular class correlations are poor and often misleading. This is particularly noticeable for the azo dyes. Thus it appears that the basic theory for evaluating intensities is reasonable, but, at least using the parameters developed for λ_{max} calculations, the method is not suitable for predicting more subtle structural effects on absorption intensity. It would thus be of interest to examine the role of input parameters in intensity prediction, and this would be a most worthwhile area for future study.

5. POLARISATION OF ABSORPTION BANDS

The oscillator strength of an absorption band is in fact derived from the *transition dipole moment*, the latter being directly calculable from the geometry of the molecule and the form of the molecular orbital wave functions. In addition to magnitude, this dipole moment has directional properties, i.e. for a given chromogen the transition moment has a well defined axis relative to the long axis of the molecule. The significance of this is that for light absorption to occur, the electric vector of the incident light wave must oscillate in the same direction as the transition moment. Of course, under normal conditions light is not polarised, and dye molecules are randomly orientated with respect to the incident light, and thus light absorption always occurs. It is possible, however, to orient dye molecules in a regular manner, as in crystals or in stretched polymer films, and by using polarised light one can then detect a variation in the absorption intensity as the plane of polarisation of the light is rotated relative to the direction of alignment of the dye molecules. This phenomenon is often referred to as *polarisation of absorption*.

For many years this effect was of academic interest only, but with the recent interest in coloured liquid crystal displays, which depend on polarisation of dye absorption bands, the phenomenon has taken on a more technologically relevant role. In such displays, a dye molecule dissolved in the host liquid crystal must align as closely as possible with the liquid crystal molecules, so that as the latter are switched from one orientation to another by application of an electric field, the orientation of the dye molecules follows suit. In normal light the cell appears coloured, but when the voltage is applied, the dye molecules are aligned with their long axis parallel to the direction of the light wave, i.e. perpendicular to the electric vector of the wave, and thus light absorption does not occur, and the cell appears colourless. For a dye to exhibit a very high contrast ratio (order parameter) in such cells, three requirements must be met:

(a) The liquid crystal itself should have a high degree of orientation in the switched-on state.

(b) The dye molecule must align as closely as possible with the liquid crystal molecules. It can be seen from Fig. 6 that if a molecule A—B aligns imperfectly, such that the dye axis falls anywhere in the cone described, there will be a component of the transition moment M in the electric vector direction, E, and thus some light absorption will occur. This of course assumes for simplicity that M coincides with the A—B axis of the dye molecule.

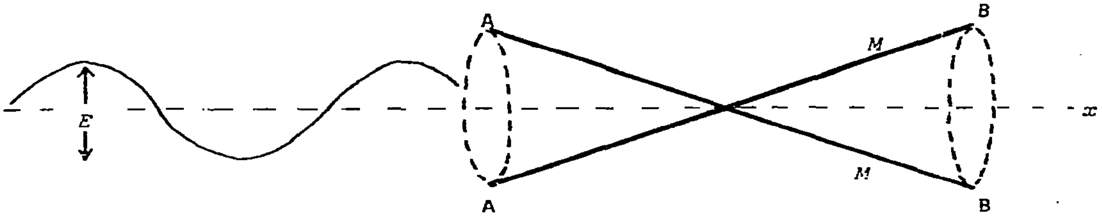


Fig. 6. Incomplete alignment of dye molecule A—B with the liquid crystal orientation axis, x.

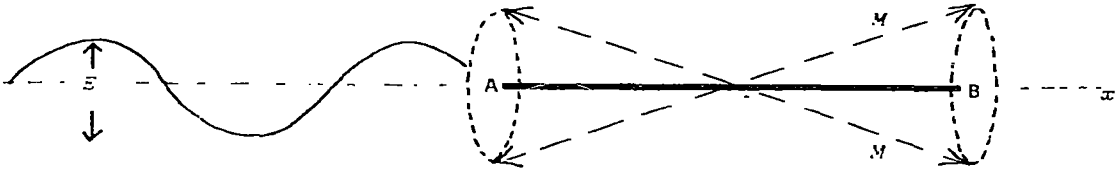


Fig. 7. Effect of non-parallel transition moment (M) and dye orientation axis (AB) for a perfectly aligned dye in a liquid crystal host.

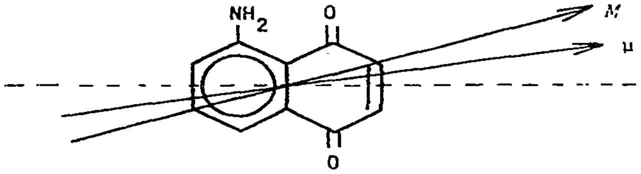
(c) Even if a dye aligns perfectly with the liquid crystal, light absorption can still occur in the switched-on state if M does not lie in the same direction as the orientation axis of the dye molecule. This can be seen from Fig. 7. Thus although A—B lies at all times perpendicular to the electric vector E, the transition moment M can lie along any of the directions described by the cone. Consequently, M again has a finite component in the E direction, and some light absorption can occur.

At the present time, obtaining dyes for liquid displays with high order parameters is an empirical exercise. It is interesting therefore to see if molecular orbital methods such as the PPP method can make any contribution to this field, perhaps permitting some prediction of possible chromogens having high order parameters.

Requirement (a) is independent of the dye molecule and need not be considered here. Requirement (b) may be predictable once a better understanding of those factors influencing dye alignment are better understood. However, a simple approach to the problem may be made if one assumes that two major factors are molecular geometry and ground state dipole moment of the dye. The former is difficult to quantify, but qualitatively one can reason that long planar molecules, e.g. azo dyes, should orientate preferentially with their long axis parallel to the long axes of the host molecules. This may be the dominant factor in many cases. Given the overall preferred orientation direction based on geometrical considerations, dipole moments may then determine how close the alignment is, particularly as most liquid crystal components are highly polar. The permanent dipole moment of a molecule may be dissected approximately into a σ-electron component, which is readily calculable from bond moments, and a π-electron component, which is readily given by the PPP method. Thus it is possible in a series of closely related chromogens to obtain relative dipole moments (absolute values may not be reliable), which in turn may give a measure of dye alignment properties. This is speculative at this stage, but is amenable to experimental test.

Requirement (c) is predicted by the PPP method, since this gives directly the transition moment direction. Provided the dye orientation axis is reasonably well defined, then the larger the angle between this axis and M, the lower should be the order parameter.

Although application of the PPP method to these problems is still in its infancy,



(18)

Fig.8. Ground state π-electron dipole moment (μ) and visible band transition moment (M) for 5-amino-1,4-naphthoquinone.

some promising results have been obtained. For example, the red dye 5-amino-1,4-naphthoquinone (**18**) (Fig. 8) appears to have no features to commend it as a liquid crystal dye. It is a compact molecule, and the electron donor amino group is perpendicular to the long axis of the molecule (cf. aminoazo dyes). However, it demonstrates a reasonable order parameter in liquid crystal media. The reasons for this can be seen from the PPP data of Fig. 8. Thus the π-electron dipole moment (which is much larger than the σ component) lies reasonably close to the molecular long axis, and in addition has a large value. Thus good dye orientation is favoured. Furthermore, the transition moment *M* lies reasonably close to the ground state dipole moment direction. The combination of the two effects helps explain the dichroic behaviour of (**18**). This approach has also been useful in accounting for certain dyes with unexpectedly poor order parameters.

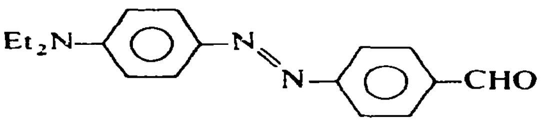
6. OTHER COLOUR-DETERMINING PROPERTIES

In addition to the various aspects of colour so far discussed, there are other factors that can influence the colour of a chromogen, and these can also be of considerable practical significance. In general, attempts to reduce these effects to a form that is amenable to quantitative prediction are sadly lacking. However, it is to be expected that future research into applications of molecular orbital theory will remedy the situation.

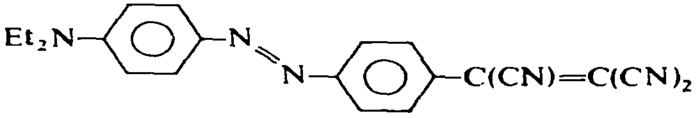
One well-known effect of this type is the phenomenon of *solvatochromism*, or the ability of many chromogens to exhibit shifts in $\lambda_{\max}$ in solvents of differing polarity. Such effects are complicated by hydrogen bonding between certain solvents and discrete parts of the chromogen, but if hydrogen bonding solvents are deliberately excluded, solvatochromism should be more amenable to quantitative prediction. If the chromogen is regarded as a dipole in a uniform dielectric (the solvent), then theory suggests that the solvatochromic shift between solvents A and B will be given by eqn. 2.[24]

$$\Delta\lambda_{\mathrm{A,B}} = \frac{k_{\mathrm{A,B}}}{r^3} \cdot \mu^0(\mu^* - \mu^0) \qquad (2)$$

where $k_{A,B}$ is a measure of the polarity difference between A and B, r is the effective radius of the molecule, μ^0 and μ^* are the dipole moments of the chromogen in the ground state and the excited state respectively. The difference between the ground and excited state dipole moments can be calculated readily by the PPP method, and the other terms can be obtained experimentally or estimated in various ways. Thus it should be possible to predict solvent shifts by the PPP method using eqn. 2. This has been examined with some success for simple u.v. absorbing molecules,[25] but we have found that when applied to large chromogens, e.g. azo, disazo and quinone dyes, eqn. 2 is notoriously unreliable. For example, with the two reasonably related dyes (**19**) and (**20**), the solvatochromic shifts between cyclohexane and nitromethane as solvents are 31 and 5 nm respectively. The products $\mu_\pi^0(\mu^* - \mu^0)$ given by the PPP method are in the ratio (**19**):(**20**) = 1:3·3, which even allowing for differences in σ dipole contribution and in r for the two dyes is clearly contradictory to the observed shifts.



(**19**)

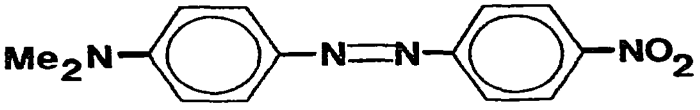


(**20**)

One possible cause of the failure of eqn. 2 when applied to dyes is the assumption that solvent interactions can be regarded as uniform for the whole of the dye molecule. This approximation may be valid for small molecules, but with a large dye molecule there is the likelihood of strong solvent interactions with specific sites in the chromogen. Such interactions could cause bathochromic or hypsochromic shifts, depending on the position and nature of the interaction, and the observed solvatochromism will be the net result of all these effects. The problem thus becomes extremely complicated, and possibly intractable. If the magnitude of the solvent interaction at every atom in the chromogen were known, this could be reflected in small changes in the PPP input parameters for each atom. (cf. intramolecular hydrogen bonding, section 3.2), and a complete calculation could be carried out for the λ_{max} of the dye in that particular solvent. However, such an approach is probably impracticable.

We have examined one grossly simplified approach to see if any improvement of eqn. 2 can be achieved. Here it is assumed that only solvent interactions with discrete high or low electron density sites in the chromogen need be considered, such sites consisting of one atom or several closely grouped atoms. Thus, for example, in the azo dye of Fig. 9, only the amino, azo and nitro groups are considered.

How intimately the solvent molecule dipoles will associate with these sites will be determined in part by the electron density at that site, and this is obtained by the PPP method, summing the appropriate atom values if more than one atom is involved. This quantity we can call Q, and if Q corresponds to a positive charge it can be assumed that solvent dipoles will orient with their negative ends adjacent to that site, and the reverse will occur if Q indicates a net negative charge. Both solvent interactions will stabilise the ground state of the molecule. Light absorption will cause a change in Q at these various sites, but the solvent molecules will not alter their position during this process. Following the same reasoning used in deriving eqn. 2, and assuming that solvent effects at each site can be considered separately, the shift in λ_{max} (change in energy between ground and excited states due to the solvent) due to a particular site will be proportional to $Q.\Delta Q$, where ΔQ is the change in charge density at that site after light absorption, and is also calculated by the PPP method. Summation of all the $Q.\Delta Q$ values for the various sites will give a parameter that may be related in some way to the total solvatochromic shift of the dye.



Q	+0.327	-0.206	-0.131
ΔQ	-0.339	+0.124	+0.450
Q.ΔQ	-0.111	-0.025	-0.059

$\Sigma Q.\Delta Q = -0.195$

Fig. 9. Group charge densities (Q) and charge density charges (ΔQ) for the visible absorption band of 4-dimethylamino-4'-nitroazobenzene.

In Fig. 9 the individual $Q.\Delta Q$ values for the three sites considered are given, and the total value is $-0{\cdot}195$, indicating a large bathochromic shift if solvent polarity is increased. Experimentally a shift of 38 nm is found for this dye between the solvent cyclohexane and nitromethane. Application of this approach to several other azo dyes has given mixed results, but a definite improvement relative to eqn. 2 has been found. In its present form the method is far from satisfactory, but it does suggest a different sort of approach to solvent effects that might be worthy of further elaboration.

Akin to solvent effects are aggregation effects, where interaction between associated dye molecules leads to significant spectroscopic perturbations. The theoretical principles of such interactions are well understood,[26] but few direct calculations have been carried out because of the severe demands on computer capacity if aggregates of more than about four dye molecules are considered. Approximation approaches have thus been used successfully, and integration of the PPP method into these could be most fruitful. In particular, it would be highly desirable to be able to predict the colour of a pigment from a knowledge of the structure of each individual pigment molecule and from the molecular packing arrangement in the crystal lattice.

Band widths and band shapes are also very important parameters for determining the colour characteristics of a chromogen, but as yet no attempts to calculate such difficult quantities have been made. It should be noted, however, that band widths may be correlated in some way with changes in molecular geometry in the excited state, and such changes can in theory be obtained by MO methods. This type of approach has been used to predict the Stokes shift for a chromogen and hence the position of its fluorescence maximum.[27]

7. CONCLUSIONS

The PPP method was introduced in 1953, but exploitation in the field of dye research was very slow to develop, and has only really made any significant advance during the last ten years. The current situation is reasonably satisfactory, in that the colour of any dye molecule can be predicted with some reliability, in a short time and without specialist knowledge, using available parameters. The search for new chromogens need not now depend on serendipity or massive synthetic attack. A pen, paper, an inventive mind and a modest computer can achieve much more, with far greater economy.

The situation is less satisfactory at the present time with regard to predicting absorption intensities, and a lot more work is needed in this area. Secondary colour factors, such as solvatochromism and aggregation effects, are very much in their infancy as far as molecular orbital prediction is concerned, as are those other factors discussed previously. Hopefully if the need for further research into these areas is stressed often enough, theoreticians may turn their attentions to these intriguing yet very practical problems.

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