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Interpretation of the Absorption Spectra of Dicyanovinyl-substituted Dimethoxybenzenes

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SUMMARY

The applicability of configuration analysis of the results of PPP calculations, combined with a simplified molecules-in-molecule model, for the interpretation and rationalization of changes in the absorption spectra brought about by structural modifications of a basic chromophore is demonstrated with reference to a series of dicyanovinyl-substituted dimethoxybenzenes. It is shown that the proposed procedure can be utilized to bridge the gap between accurate numerical colour predictions and more qualitative structure–colour relationships.

1 INTRODUCTION

Molecular orbital theory is now very widely used in dye chemistry and the semiempirical method of Pariser, Parr and Pople (PPP method)[1-3] is still the principal method used with respect to economy and accuracy for the prediction of the light absorption properties of any class of dye molecules.[4] Due to the demand for dyes for new applications, e.g. highly fluorescent laser dyes,[5] electro-optic display systems[6] and nonlinear optics,[7] an increasing use of the PPP method can be expected in the future. A review of the usefulness of this theoretical method for a wide variety of aspects in modern dye chemistry has been given recently by Griffiths.[8]

In addition to an accurate-as-possible prediction of the wavelength of the colour band, another main objective in the current applications of theoretical methods in dye chemistry is the interpretation of the observed trends in the absorption properties within a series of structurally related dyes. Most frequently, perturbational molecular orbital (PMO) arguments

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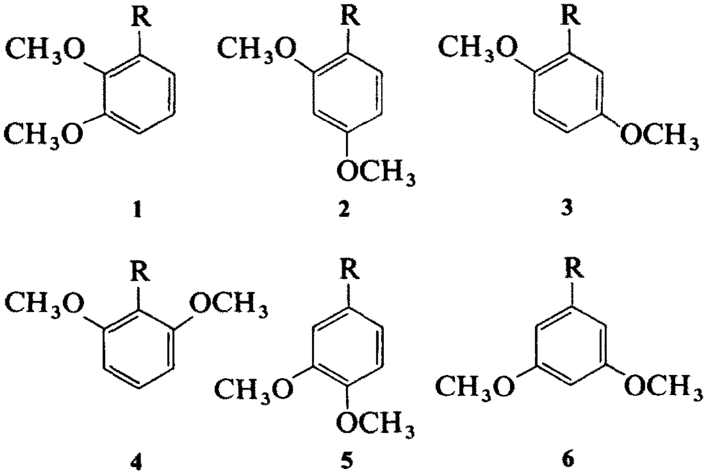
are used to explain both the effects of the nature of substituents (i.e. donor or acceptor properties) or heteroatoms and of their orientation on the long-wavelength absorption band.[9,10] However, this approach is limited to cases where the first excited state is nearly completely described by one single electronic configuration.[9] To overcome these difficulties two largely complementary methods have been suggested:

(1) The molecules-in-molecule (MIM) method of Longuet-Higgins and Murrell[11] in which the wavefunctions of appropriate molecular subunits are used to construct the wavefunctions of the molecule under consideration.

(2) The configuration analysis (CA) method of Baba *et al.*[12] Here the results of PPP calculations on a complex molecule are analysed in terms of suitable model systems.

In attempts to rationalize empirical structure–colour relationships these methods have proved very useful.[13–23] However, the MIM model suffers from some serious difficulties,[24] the most important being the choice of appropriate reference configurations. As is outlined below, the CA method allows, in addition to the analysis of the PPP results in terms of model systems, an assessment of the appropriateness of the chosen model.

In this present paper we discuss the usefulness of this approach in dye chemistry. After a brief description of the method, results are presented on some simple but practically important chromophoric systems[25] (see Fig. 1) selected to illustrate the applicability as well as the limitations of the configuration analysis.



R = —CH=C(CN)$_2$

Fig. 1. Structures of the dyes investigated.

2 OUTLINE OF THE METHOD

By the usual method, both the molecular orbitals ψ and ψ^0 of the molecule and the reference system, respectively, are constructed by a linear combination of atomic orbitals χ [LCAO approximation, eqns (1a) and (1b)]:

$$\psi = \chi \mathbf{C} \tag{1a}$$

$$\psi^0 = \chi \mathbf{C}^0 \tag{1b}$$

where $\mathbf{C}$ ($\mathbf{C}^0$) is the matrix of the linear combination coefficients of the molecule (reference system). Alternatively, the MOs of the molecule can be constructed by a linear combination of the MOs ψ^0 of the reference system (LCMO approximation), since combination of eqns (1a) and (1b) leads to

$$\psi = \psi^0 \mathbf{C}^{0+} \mathbf{C} = \psi^0 \mathbf{B} \tag{2}$$

Now, if configuration interaction is included (as is the case with the PPP method), each electronic state function Ψ (Ψ^0 for the reference system) is expressed as a linear combination of electronic configurations (Slater determinants) Φ (Φ^0):

$$\Psi = \Phi \mathbf{U} \tag{3a}$$

$$\Psi^0 = \Phi^0 \mathbf{U}^0 \tag{3b}$$

where $\mathbf{U}$ ($\mathbf{U}^0$) is the matrix of CI-eigenvectors of the molecule (reference system). Baba *et al.*[12] have shown that in the spirit of eqn (2) it is possible to express also the configurations Φ of the molecule in terms of the reference configurations Φ^0:

$$\Phi = \Phi^0 \mathbf{L} \tag{4}$$

where the various elements of the matrix $\mathbf{L}$ are given by appropriate minor determinants of the matrix $\mathbf{B}$. The detailed formulae for calculating these matrix elements can be found in ref. 12. Combining eqns (3a), (3b) and (4) finally yields

$$\Psi = \Psi^0 \mathbf{U}^{0+} \mathbf{L} \mathbf{U} = \Psi^0 \mathbf{M} \tag{5}$$

This means that the electronic states of the molecule are now expressed in terms of the electronic states of the reference system. Thus, an analysis of the PPP wavefunctions in terms of the MIM model has been accomplished whilst retaining the advantages of the PPP method and avoiding the shortcomings of the MIM model.

It should be noted that the main calculational efforts to perform such an analysis consist in the evaluation of determinants (i.e. elements of $\mathbf{L}$) and, according to eqn (5), simple matrix multiplications. Since for the practical implementation of this method at least two PPP calculations are necessary (one for the molecule and one for the reference system) one could argue against the usefulness of this method. However, in view of the economy and low costs of the PPP method this additional calculation should not be too serious an obstacle for using this procedure. The configuration analysis itself [i.e. evaluation of eqn (5)] takes only a few seconds of computer time.

In the language of the MIM model one can distinguish between three types of reference states:

(1) The no-bond (NB) configuration which describes the various molecular subunits in their respective ground states.
(2) Locally excited (LE) states corresponding to an electronically excited state within one subunit.
(3) Charge transfer (CT) configurations which describe the excitation of an electron from an occupied MO of one subunit to a virtual MO of another subunit.

The weights of these reference states in a particular electronic state of the molecule are given by the squared elements of the matrix **M** [eqn (5)]. Furthermore, it is a rather unique feature of the CA method (for a discussion of some other methods designed to analyse the results of PPP calculations in terms of molecular model systems, compare ref. 26) that in addition an assessment of the appropriateness of the chosen reference system is possible; in practice one always uses a truncated configuration interaction treatment. Thus, the expansion according to eqn (5) is incomplete, and consequently the sum over the squared elements of **M** for a given electronic state will be lower than unity. The actual value of this sum, denoted by $r_M(I)$,

$$r_M(I) = \sum_j \mathbf{M}_{ij}^2 \tag{6}$$

thus indicates the appropriateness of the description of the electronic states of the molecule by the reference system. For such a description to be meaningful as a rule of thumb, r_M should be $\geq 0{\cdot}95$ for ground and $\geq 0{\cdot}80$ for excited states.[26] Since generally quite a number of intuitively meaningful reference systems are conceivable, the CA method offers a quantitative index to choose the most appropriate one.

3 RESULTS

The results of our PPP calculations (the parameters used were those tabulated by Griffiths[4]) on compounds **1**–**6** are compared with the experimental results as well as with previous PPP computations[25] in Table 1.

TABLE 1
Experimental and Calculated (PPP) Absorption Maxima (nm) for Compounds **1**–**6**

Compound	λ_{max}*(exp.)*[a]	λ_{max}*(PPP)*[a]	λ_{max}*(PPP)*[b]
1	312	340	348
	348s	377	365
2	364	370	374
3	404	401	394
4	326	359	349
	349s	405	410
5	364	372	378
	382		
6	320	337	340
	331		
	360s	376	370

[a] Experimental values in C_6H_{12}, ref. 25.
[b] This work.

Generally, the agreement with experiment and both sets of calculations is very satisfactory (the minor deviations in the calculated absorption maxima are most probably due to a different evaluation of the two-centre electron repulsion integrals $\gamma_{\mu\nu}$).

In order to apply the method outlined in the previous section an appropriate reference system must be selected. From Fig. 1 it can be seen that compounds **1**–**4** have in common the *ortho*-methoxydicyanovinylbenzene fragment, differing only in the position of the second methoxy group. Thus a reasonable reference system to interpret the observed trend of the first absorption band in these compounds would be *o*-methoxydicyanovinylbenzene + isolated methoxy group (**F1**). Similarly, for compounds **1**, **3**, **5** and **6** the fragmentation *meta*-methoxydicyanovinylbenzene + methoxy group (**F2**) and for **2**, **4** and **6** *m*-dimethoxybenzene + dicyanovinyl group (**F3**) are considered. Based on these reference systems, the results of the configuration analysis (index r_M, percentage contribution of the reference states to the ground and first two excited molecular states) are collated in Table 2.

As can be seen from the data in Table 2, in most cases more than two reference states significantly contribute to the respective molecular excited states. Therefore, in these cases one cannot expect that PMO theory works properly. It is precisely the different extent of interaction between these reference states which causes the variation in the transition energies. So, on the basis of the results of the CA analysis, a simplified MIM model is used and only those reference states are included which, according to the CA

TABLE 2
Results of the Configuration Analysis

Model	*State*	r_M (%)	*Contribution of reference states* (%)
1/F1	S_0	99·6	89·3 NB
	S_1	90·1	66·3 LE$_1$, 23·5 LE$_2$, 8·2 CT$_1$
	S_2	89·8	31·6 LE$_1$, 59·5 LE$_2$, 6·8 CT$_1$
2/F1	S_0	99·5	86·7 NB
	S_1	87·6	90·4 LE$_1$, 4·7 CT$_1$
	S_2	89·0	91·8 LE$_2$
3/F1	S_0	99·6	88·4 NB
	S_1	89·6	69·2 LE$_1$, 15·6 LE$_2$, 12·4 CT$_1$
	S_2	88·7	25·6 LE$_1$, 66·1 LE$_2$, 6·8 CT$_1$
4/F1	S_0	99·1	83·4 NB
	S_1	85·2	18·7 LE$_1$, 45·7 LE$_2$, 21·4 CT$_1$
	S_2	86·5	77·0 LE$_1$, 16·2 LE$_2$
1/F2	S_0	99·5	87·7 NB
	S_1	89·3	77·9 LE$_2$, 17·2 CT$_1$
	S_2	89·4	99·2 LE$_1$
3/F2	S_0	99·5	87·3 NB
	S_1	88·8	77·3 LE$_1$, 14·1 CT$_1$
	S_2	88·8	93·0 LE$_2$
5/F2	S_0	99·5	87·9 NB
	S_1	89·0	85·7 LE$_1$, 7·0 CT$_1$
	S_2	89·9	89·7 LE$_2$
6/F2	S_0	99·5	87·8 NB
	S_1	88·8	63·8 LE$_1$, 23·0 LE$_2$, 9·5 CT$_1$
	S_2	88·0	33·1 LE$_1$, 58·7 LE$_2$, 5·1 CT$_1$
2/F3	S_0	97·6	82·3 NB
	S_1	82·6	28·5 LE,[a] 34·4 CT$_1$
	S_2	85·3	43·7 LE$_1$, 36·0 CT$_2$
4/F3	S_0	96·6	79·1 NB, 15·5 CT$_2$
	S_1	80·2	—[b]
	S_2	83·3	17·5 LE$_1$, 12·0 LE$_2$, 41·1 CT$_1$, 11·2 CT$_2$
6/F3	S_0	98·1	86·6 NB
	S_1	88·7	27·5 LE$_1$, 54·5 CT$_1$
	S_2	88·3	30·1 LE$_2$, 26·3 CT$_2$

[a] First locally excited state of the dicyanovinyl group.

[b] Rather complicated mixture of a number of reference states with none dominating.

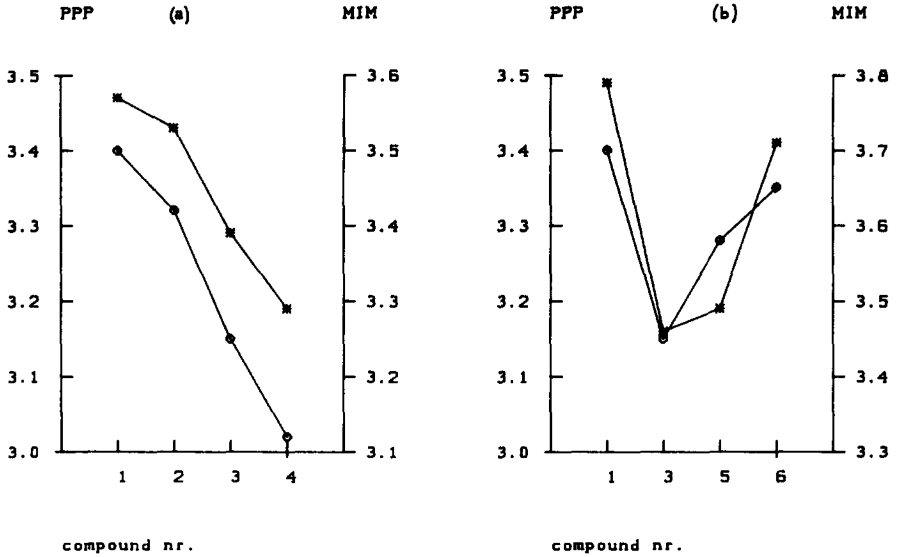


Fig. 2. Variation of the first transition energy (eV) as calculated by the PPP (○) and the simplified MIM model (★) for fragmentation modes **F1** (a) and **F2** (b).

analysis, contribute significantly to the excited molecular states to evaluate these interaction energies. It was not anticipated that such a crude model would yield accurate transition energies (in fact, for the MIM model to achieve the accuracy of PPP calculations, a rather large number of reference states have to be included), but the essential features of the absorption properties should be correctly reproduced.[16–23] It should be noted that in cases where only one LE and one CT state are involved in the description of the molecular excited state (e.g. **2/F1**, **1/F2**, **3/F2**, **5/F2**) this simple model becomes equivalent to a PMO treatment. However, the whole series of molecules studied here cannot be described properly by the latter model. For fragmentation modes **F1** and **F2** the results obtained by the simplified MIM model are displayed in Fig. 2, together with the corresponding PPP results. Figure 2 demonstrates that the marked influence of the position of the second methoxy group on the first transition energy is quite satisfactorily described by this approach.

Especially instructive is a discussion of the reference system **F3**. For the first excited state of compound **4** a rather low value of r_M is obtained. In addition, S_1 of this molecule is composed of a rather complicated mixture of various reference states. Thus, this seemingly quite reasonable fragmentation mode **F3** is judged to be not appropriate on the basis of the CA results. Almost no other method could have led to this important conclusion, thus clearly demonstrating the usefulness of the CA method for interpretative purposes.

4 CONCLUSIONS

From the above discussion it seems clear that the combined use of the configuration analysis method for the selection of the most appropriate molecular model, as well as the most important reference states, and a simplified MIM model to calculate the effect on transition energies of mixing of the previously selected reference states, presents a powerful tool for the rationalization and interpretation of observed trends in the absorption properties caused by structural modifications of a basic chromophore. In attempts to bridge the gap between accurate numerical colour predictions (which is the domain of the PPP method) and necessarily more qualitative structure–colour relationships, this approach is not only of interest from a theoretical point of view but should also be useful for the practising dye chemist.

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