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THE ORIGIN OF THE COLOUR OF INDIGO DYES

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SUMMARY

The π electron system of the basic indigo chromophore can formally be obtained by joining two identical fragments; the coupling of two radical centres thus affords one bonding and one antibonding π MO, which form the HOMO and the LUMO of the system. A small HOMO–LUMO splitting and thus a long-wavelength absorption result from a pronounced delocalization of the unpaired electron in the radical fragments due to the captodative radical stabilization. Results of SCF calculations within the π electron approximation confirm these ideas.

1. INTRODUCTION

Indigo is one of the oldest dyes and has been known for thousands of years; nevertheless, it still is much in use. Although indigo was the object of a great many experimental and theoretical investigations, the deep colour of this dye is still not well understood. In fact, the explanation of the colour of indigo in terms of its molecular structure is one of the most intriguing problems which has been occupying dye chemists for the last hundred years or so.

From theoretical arguments[1] as well as from experimental data[2] it follows that neither the benzene rings nor the double bonds in the five-membered rings are essential for the characteristic indigo spectrum. Thus, the basic chromophore of the indigo dyes is the partial structure **1** consisting of just one CC double bond substituted by two donor groups —$\ddot{X}$ and two acceptor groups —C=Y.

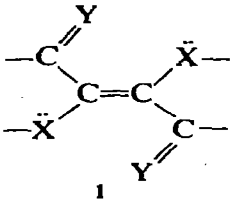

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TABLE I

CLASSIFICATION OF ORGANIC DYES AND THE COLOUR OF INDIGO

Author	*Classes*	*Colour of indigo*
Griffiths (1976)[3]	n–π^* chromogens donor–acceptor chromogens acyclic and cyclic polyene chromogens cyanine-type chromogens	donor-acceptor-chromogen
Dähne (1970)[4]	polymethine compounds aromatic compounds polyene-like compounds	crossed trimethine-merocyanine units
Fabian (1980)[6]	parent chromophores interacting subchromophores	parent chromophore consisting of π system + donor/acceptor
Klessinger (1978)[8]	linear chromophores branched chromophores cyclic chromophores	branched chromophore, cf. text

It is thus quite logical to follow Griffiths,[3] who distinguishes four main classes of chromogens as indicated in Table I, and to consider indigo as a typical donor–acceptor chromogen. But whereas, in general, dyes of this type with a long-wavelength absorption comparable to that of indigo consist of rather extended π systems substituted by donor and acceptor groups, indigo contains just one CC double bond, which is the smallest possible π system.

Another way of looking at organic dyes was proposed by Dähne,[4] who divides the various π systems into three classes: polyene-like, aromatic and polymethine compounds (Table I). Colour is associated with the polymethine state characterized by equal bond lengths and alternating charges. According to Dähne,[5] the basic indigo chromophore should be formulated as consisting of two trimethinemerocyanine units crossed via the central CC bond. But as a consequence of this crossing, the charge alternation typical for the polymethine state is completely destroyed at the common crossing atoms.

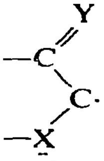
Fabian[6] recently classified organic dyes according to whether the molecule as a whole is responsible for the colour, or whether one may talk of more or less strongly interacting subchromophores (Table I). A theoretical analysis[7] showed that the indigo molecule can be subdivided in several ways, but only the subdivision into the structural unit **1** and the benzene rings allows for a simple and clear-cut interpretation of the lowest excited state, as in this case the configuration contributing predominantly to the colour-determining lowest-energy state is just the locally excited state of the basic indigo chromophore.

From these considerations it is apparent that indigo does not fit naturally into any of the schemes proposed to explain the colour of organic dyes. In fact, there seem to have been as many different explanations of the colour of indigo as there have been attempts to establish colour–structure relations. For this reason we propose to consider the indigo dyes as the main representatives of the class of dyes with branched chromophores, this being a class on its own[8] (Table 1). This of course does not explain the colour of indigo, but merely emphasizes the exceptional properties of this class of compounds.

As the basic indigo chromophore[11] exhibits all these properties, including the strong dependence of the colour on the configuration and conformation of the various groups of the chromophore[9] and the unexpected hypsochromic shift which is observed if the π system of indigo is extended by replacing the central ethylene unit by a butadiene unit,[10] in what follows we will concentrate on the π system of the partial structure **1**, and show how its light absorption depends on the nature of the various constituent groups of this system and their mutual arrangement.

2. APPLICATION OF THE PMO METHOD

The π electron system of the basic indigo chromophore **1** may formally be divided into two identical subsystems **2** each with an odd number of π electrons. Reuniting these subsystems by coupling the two radical centres affords one bonding and one antibonding πMO of the central CC double bond which is substituted by two donor as well as two acceptor groups. If the energetic splitting of these two MOs is sufficiently small they form the HOMO and the LUMO of the combined system, and the difference $\Delta\varepsilon$ of their orbital energies is responsible for the long-wavelength absorption, i.e. for the colour of the basic indigo chromophore. Therefore, if it is possible to find the reasons for a particularly small HOMO–LUMO splitting, this gives an explanation for the deep colour of the indigo dyes.



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Within the framework of the HMO approximation, the union of two odd electron systems with degenerate singly occupied MOs ϕ^R and ϕ^S yields one doubly occupied and one unoccupied MO, the energy difference of which is according to first order perturbation theory[12] given by

$$\Delta\varepsilon = 2c_\rho^R c_\sigma^S \beta_{\rho\sigma}$$

Given the value of the resonance integral $\beta_{\rho\sigma}$, the splitting $\Delta\varepsilon$ is smaller, the smaller are the absolute values of the LCAO–MO coefficients c_ρ^R and c_σ^R of the singly occupied MOs ϕ^R and ϕ^S at the coupling sites ρ and σ. Thus finding the conditions for a small HOMO–LUMO splitting $\Delta\varepsilon$ is equivalent to finding the conditions for small absolute values of c_ρ^R and c_σ^S for which $c_\rho^R = c_\sigma^S$ holds, as the system **1** is obtained by uniting two identical subsystems.

The main variables in the subsystems from which the indigo chromophore may be obtained are the donor and the acceptor groups or the heteroatoms X and Y respectively. In order to obtain the values of the coefficients c_ρ^R and c_σ^S as a function of the nature of the atoms X and Y, first-order perturbation theory may again be applied. From the relation[13]

$$c'_{\mu i} = c_{\mu i} + \sum_{j \neq i} \frac{c_{\kappa i} c_{\kappa j} \delta\alpha_\kappa}{\varepsilon_i - \varepsilon_j} c_{\mu j}$$

which describes the variation of the coefficient $c_{\mu i}$ under the influence of a change $\delta\alpha_\kappa$ of the Coulomb integral at position κ, and starting from the butadiene ion as the hydrocarbon isoelectronic with the subsystems, one obtains

$$c_\rho^R = c_\sigma^S = -0{\cdot}372 - 0{\cdot}304 h_X + 0{\cdot}184 h_Y$$

where h_X and h_Y are the Hueckel parameters describing the heteroatoms X and Y characterized by the Coulomb integrals

$$\alpha_X = \alpha + h_X\beta \text{ and } \alpha_Y = \alpha + h_Y\beta$$

From this relation it is seen that c_ρ^R is small if h_X is small and h_Y is large, i.e. if the electronegativity of X is low so that —$\ddot{X}$ is a good donor group, and the electronegativity of Y is high so that —C═Y is an effective acceptor group. These are exactly the conditions corresponding to a pronounced delocalization of the unpaired electron. It may be shown[14] that the intuitive condition of maximum delocalization of the radical electron agrees with the energetic criteria for an optimum captodative radical stabilization.[15]

The results of these considerations based on simple perturbation (PMO) theory may be summarized as follows:

The long-wavelength absorption of the indigo chromophore may be explained by the fact that uniting two identical odd electron fragments via centres of very low density of the unpaired electron results in an exceptionally low HOMO–LUMO splitting, whereas the low density of the radical electron is due to effective delocalization through captodative stabilization.

This simple model even allows rationalization of finer details of the typical properties of the indigo chromophore. If, for example, the group —$\ddot{X}$ is —SR instead of —NR$_2$, a hyposochromic shift is to be expected due to the fact that the sulphide group is not as good a donor as the amino group, in agreement with the findings for compounds of the indigo and the thioindigo series. If, on the other hand, the central double bond is replaced by two linearly conjugated double bonds, dividing the system into odd-electron fragments leads to non-identical subsystems and the first-order perturbation theory is no longer applicable. This makes comprehensible why the extension of the π systems results in a hypsochromic shift.

3. RESULTS OF PPP CALCULATIONS

As electron interaction which is not included in the PMO treatment is very important in discussing electronically excited states, SCF calculations of the PPP type[16] were performed in order to verify the results of the PMO analysis given above. A slightly modified version of the method[17] was used which was based on the self-consistent group function approach[18] in order to be able to calculate the spectrum of the basic indigo chromophore as a function of the donor and acceptor properties of the groups —Ẍ and —C═Y.

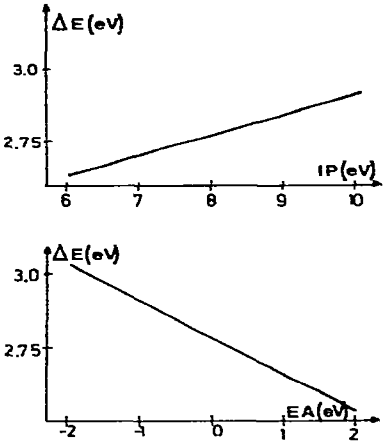
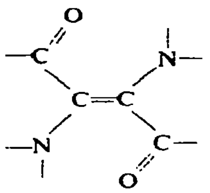
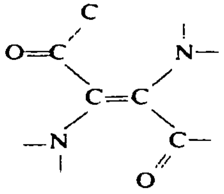
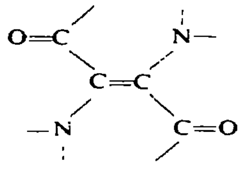


Fig. 1.

The results are given in Fig. 1, where the excitation energy ΔE is plotted against the ionization potential (IP) of the donor and the electron affinity (EA) of the acceptor respectively. It is seen that ΔE increases with decreasing IP values and increasing EA values, i.e. the lower ΔE, the better are the donor properties of —Ẍ (low IP) and the acceptor properties of —C═Y (high EA), in very good agreement with the PMO results given above. The values IP = 8·5 eV and EA = 1·0 eV, which correspond to standard values of the PPP parameters,[19] reproduce the experimental excitation energy of the basic indigo chromophore.[9]

Finally, in Table 2 excitation energies ΔE as well as the orbital energy differences $\Delta\varepsilon$ and the electron interaction terms $J-2K$ are collected for different conformations of the E-configurated indigo chromophore. From these data it is seen that $\Delta\varepsilon$ is more-or-less independent of the geometrical arrangement of the donor and acceptor groups, whereas the repulsion term $J-2K$ is larger the smaller the distance between the acceptor group of one subsystem and the donor group of the other. Thus, the conformation dependence of the light absorption of the basic

TABLE 2
CONFORMATION DEPENDENCE OF THE LONG-WAVELENGTH TRANSITION OF THE E-CONFIGURATED BASIC CHROMOPHORE

	$\Delta\varepsilon$ (eV)	$J-2K$ (eV)	ΔE (eV)
	5·57	2·85	2·72
	5·53	2·71	2·83
	5·47	2·54	2·94

indigo chromophore is seen to be due to electron interaction. In the case of the Z-configurated chromophore the results are more complicated, as with standard geometries a planar *s-cis-s-cis*-conformation is no longer possible without strong interference of the two acceptor groups.

4. CONCLUSIONS

In conclusion it may be said that electron interaction, although important for a quantitative description of the indigo spectrum and in particular of its conformational dependence, does not change the general results from PMO considerations. Thus, the main contribution to the HOMO and the LUMO of the indigo dyes comes from the bonding and the antibonding π MOs of the central CC double bond, and their exceptionally small energetic splitting is a consequence of an effective delocalization of π electrons due to the captodative substitution of the double bond with two donor and two acceptor groups.

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