

## Steric Effects in Light Absorption of Violanthrone Derivatives\*

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Steric effects in conjugated systems were first classified by BRAUDE and coworkers<sup>1,2</sup> into two groups: *Type 1* in which steric hindrance gives rise to changes in intensities only, with relatively little effect on the wavelength of absorption, and *Type 2* where both the in-

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<sup>1</sup> E.A. BRAUDE, F. SONDHEIMER and W.F. FORBES, *Nature* 173 (1954) 117.

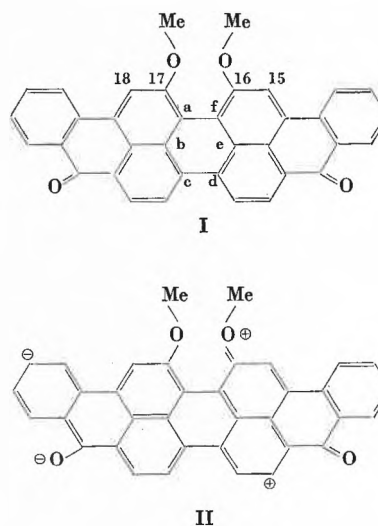
<sup>2</sup> E.A. BRAUDE, E.R.H. JONES, H.P. KOCH, R.W. RICHARDSON, F. SONDHEIMER and J.B. TOOGOOD, *J. Chem. Soc.* 1949, 1890.

tensity and the wavelength are affected. *Type 1* effects were associated with weak steric effects which cause only minor deviation from planarity in the chromophore, while *Type 2* effects were attributed to strong steric interaction. Wavelength shifts in *Type 2* effects can be either hypsochromic or bathochromic. Since resonance involving high energy structures is characteristic of excited states and since resonance is dependent on planarity, the hypsochromic shifts arising from steric interaction were readily accounted for. The explanation of the bathochromic *Type 2* effect, first observed by BRUNINGS and CORWIN<sup>3</sup> in some cyanine dyes, in terms of resonance was not equally facile. BROOKER and co-workers,<sup>4</sup> who made detailed studies on cyanine dyes, rationalized this effect on the basis of the theory of FORSTER.<sup>5</sup> Ground and excited states were regarded as two hybrids arising from resonance of two classical structures that may be written for a cyanine, the positive charge being on one or the other of the two nitrogen atoms of the molecule. It was suggested that when the interacting classical structures are identical, their energy will determine the energy difference between the hybrids, the higher energy structures leading to smaller differences of energy for the hybrids. Since steric interaction raises the energy of these systems, bathochromic shifts are predicted for the symmetrical cyanines. On the other hand, if the interacting classical structures are of different energies, as in the case of an unsymmetrical cyanine, the energy separation between the hybrids would be determined by the energy difference for the two structures, a pair of structures having a larger energy difference than another giving a pair of hybrids with the larger energy separation. In this case hypsochromic effects are expected from steric hindrance. This theory is based on a set of assumptions that have no theoretical basis.

The confusion of these early notions disappears when the problem is considered from the molecular orbital point of view. Two treatments of this type have been given, both using the perturbation approach. In the treatment of COULSON,<sup>6</sup> DEWAR,<sup>7</sup> and HEILBRONNER and GERDIL,<sup>8</sup> the spectral shifts are rationalized in terms of the decrease in resonance integrals of the various bonds resulting from steric interaction and the changes in bond orders associated with the transition from the highest occupied to the lowest unoccupied molecular

orbital. The approach of LONGUET-HIGGINS and MURRELL<sup>9</sup> is quite different. They treat the conjugated system in terms of the component parts. For a molecule AB, the transitions can be either to locally excited states (L.E.) like A\*B or AB\* in which the  $\pi$ -electrons of A and B remain associated with them, or to electron transfer states (E.T.) like A<sup>-</sup>B<sup>+</sup> or A<sup>+</sup>B<sup>-</sup> in which a  $\pi$ -electron is transferred from A to B or *vice versa*. The treatment comes to the conclusion that while steric effects on a transition to an E.T. state give rise to a decrease in absorption intensity with little or no bathochromic shift, transitions to L.E. states give large hypsochromic shifts.

The absorption spectrum of 16,17-dimethoxyviolanthrone, one of the most important of vat dyes, has been discussed in terms of steric hindrance in a couple of early studies. We have recently re-examined<sup>10</sup> the question of steric effects in 16,17-disubstituted violanthrones. The bathochromic shift shown by the 16,17-dimethoxy derivative (*Jade Green*) as compared with the parent quinone was explained earlier by PADHYE *et al.*<sup>11</sup> on the basis of the co-planarity of the methoxy groups with the aromatic framework. DURIE and SHANNON<sup>12</sup> regarded this to be unlikely and suggested that the two benzanthrone moieties of the molecule (I) are twisted with respect to each other about the C<sub>b</sub>-C<sub>e</sub> axis. The bathochromic shift was rationalized in terms of the contribution of structures like II to the resonance



of the excited state, thus permitting the central bonds C<sub>a</sub>-C<sub>f</sub> and C<sub>c</sub>-C<sub>d</sub> to remain single. It has been shown that these earlier interpretations are unsatisfactory. Pointing

<sup>3</sup> K. J. BRUNINGS and A. H. CORWIN, *J. Amer. Chem. Soc.* 64 (1942) 593.

<sup>4</sup> L. G. S. BROOKER, F. L. WHITE, G. VAN ZANDT, S. J. DENT and R. H. SPRAGUE, *Chem. Rev.* 41 (1947) 325.

<sup>5</sup> T. FORSTER, *Z. Electrochem.* 45 (1939) 548.

<sup>6</sup> C. A. COULSON in *Steric Effects in Conjugated Systems*, Ed. G. W. GRAY, Butterworths Scientific Publications, London (1958), p. 8; C. A. COULSON and H. C. LONGUET-HIGGINS, *Proc. Roy. Soc. A* 191 (1947) 39.

<sup>7</sup> M. J. S. DEWAR in *Steric Effects in Conjugated Systems*, Ed. G. W. GRAY, Butterworths Scientific Publications, London (1958), p. 46; *J. Amer. Chem. Soc.* 74 (1952) 3341, 3345.

<sup>8</sup> E. HEILBRONNER and R. GERDIL, *Helv. Chim. Acta* 39 (1956) 1996.

<sup>9</sup> a) H. C. LONGUET-HIGGINS, and J. N. MURRELL, *Proc. Physic. Soc.* 68A (1955) 601.

b) J. N. MURRELL, *J. Chem. Soc.* (1956) 3779.

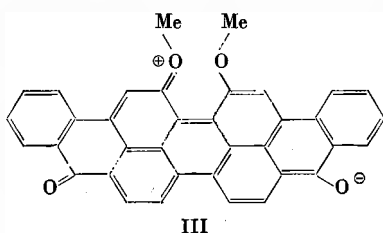
<sup>10</sup> P. MADHAVAN NAIR, C. J. SANCHORAWALA, M. K. UNNI and K. VENKATARAMAN, *Indian J. Chem.* (in Press).

<sup>11</sup> M. R. PADHYE, N. R. RAO and K. VENKATARAMAN, *Proc. Ind. Acad. Sci.* 38A (1953) 307.

<sup>12</sup> R. A. DURIE and J. S. SHANNON, *Aust. J. Chem.* 11 (1958) 168.

out that the first transition of the dye involves intramolecular charge transfer and using the perturbation approach employed by COULSON,<sup>6</sup> DEWAR<sup>7</sup> and by HEILBRONNER and GERDIL,<sup>8</sup> it was deduced that steric effects of substitution at the 16- and 17-positions can lead only to hypsochromic shifts. In agreement with expectation, a substantial blue shift (25 m $\mu$ ) was observed for 16,17-dimethylviolanthrone. Considering the problem in the light of the theory of LONGUET-HIGGINS and MURRELL<sup>9</sup> does not give such a clear cut answer. There can hardly be any doubt that the first transitions of these dyes are to electron transfer (E.T) states. Although the low intensity for 16,17-dimethylviolanthrone as compared with that for the parent quinone is in agreement with the prediction for the steric effect on a transition to an E.T. state, the wavelength shift is not. However, the prediction of wavelength shifts in this approach is not quite certain. Moreover, the system we are concerned with here is very much more complicated than the simple cases discussed by MURRELL.<sup>9b</sup>

In 16,17-dimethoxyviolanthrone there is, undoubtedly, strong steric repulsion between the oxygen atoms which are presumably pushed out to either side of the mean molecular plane as a consequence. There are two situations that have to be considered in this case, one where the deformation is transmitted to the carbon atoms at the 16- and 17-positions of the aromatic framework, and another where the deformation is restricted to the oxygen atoms. Both situations have been analysed and it has been shown that the bathochromic shift displayed by the compound cannot be related to any steric effect. Introduction of a 16-methoxy group has little effect on the long wavelength absorption of violanthrone. It is only with the introduction of the second OMe group at the 17-position that the bathochromic shift is induced. It has been suggested that this shift should be attributed to electronic repulsion in the ground state and 'internal solvation' in the excited state. These interactions result in a raising of the ground state energy and a lowering of the energy of the excited state. An E.T. state as represented by III, in terms of which the excited state is described, is stabilized by the interaction of the positive charge with the ether dipole in its vicinity.



It was also noted that the 7,8-dimethoxy derivative, in which the methoxyls are similarly situated, shows an equally strong bathochromic shift. It could further be

deduced from the considerations which account for the colour of *Jade Green* that only a monomeric structure for 16,17-ethylenedioxyviolanthrone (*Indanthrene Navy Blue G*) would be consistent with its absorption spectrum which does not show any large shift. The conformation of the ether bridge is such that the oxygen lone pairs cannot participate in the resonance of the aromatic system. This conformation can not be expected to be present in the dimeric structure that has been considered for the molecule.

We may now consider how far the spectra of 16-amino and 16,17-diaminoviolantrones are in agreement with the picture that has thus emerged. The data for these compounds in dimethylformamide solution are presented in Table 1 along with those for the corresponding methoxy derivatives and the parent quinone.

Table 1. Absorption Spectra of violanthrone derivatives

No.	Substituents	$\lambda_{max}/m\mu$	$\epsilon_{max}$
1	None	600	60,000
		555	43,950
2	16-Methoxy	598	38,670
		680	13,780
3	16-Amino	620	14,720
		570 (s)	6,680
		636	41,250
4	16,17-Dimethoxy	700	6,540
		640	10,040
		585 (s)	5,260

In order to be able to speak meaningfully about the shifts of the long wavelength band in question, it is necessary to pay some attention to the vibrational fine structure that is observed. An examination of the absorption peaks of the Table show that the  $\lambda_{max}$  values of the centre peaks for the compounds listed are respectively 600, 598, 620, 636 and 640 m $\mu$  and they form a comparable set of values representing the bands. It appears that the peaks corresponding to those at 680 and 700 m $\mu$  in the amino derivatives have become unobservable in the methoxy derivatives and the parent quinone because of their low intensities as compared with the other peaks. Unlike 16-methoxyviolanthrone the 16-amino derivative shows an appreciable bathochromic shift (20 m $\mu$ ). This is in agreement with the stronger electron donor action of the amino group which will lower the energy of the electron transfer state to which the transition takes place. For the 16,17-diamino derivative, if the distortion of the aromatic framework is negligible, we should expect, on the basis of the behaviour of the methoxy derivatives, a stronger bathochromic shift than observed. The decreased bathochromic shift is indicative of a steric effect that is superposed. It is natural that the steric effect of an amino group is larger than that of a methoxy group

since the nitrogen is trivalent. The increased steric interaction has apparently deformed the aromatic skeleton to some extent and the corresponding hypsochromic effect is superposed on the bathochromic shift expected from electronic repulsion in the ground state and internal solvation in the excited state. The pro-

nounced hypochromic effects of substitution at the 16- and 17-positions are probably associated with steric effects, although it does not seem possible to account for the observed intensity variation solely in steric terms.

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