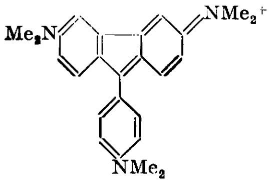
Fluorene Analogues of Triphenylmethane Dyes; Calculation of their Light Absorption by the Molecular-orbital Method.

By D. A. Brown and M. J. S. Dewar.

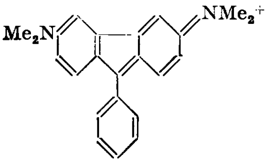
[Reprint Order No. 4889.]

Barker and Barker (*J.*, 1954, 1307) observed remarkable bathochromic shifts in typical triphenylmethane dyes on ring-closure to fluorene derivatives. Calculation of the light absorption of these compounds by the L.C.A.O. molecular-orbital method shows that these shifts can be ascribed quantitatively to the effect of forming the additional C–C bonds. There is no need to postulate non-planarity in the fluorene ring.

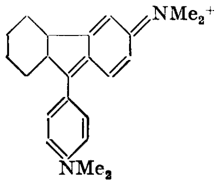
Barker and Barker (*J.*, 1954, 1307) recently prepared the fluorene analogue (I) of crystal-violet, and the two fluorene analogues (II and III) of malachite-green; in each case the fluorene analogue absorbs at much lower frequencies than does the parent triphenylmethane dye. These bathochromic shifts seem at first sight too large to be due merely to the formation of one additional C–C bond, and might therefore be taken as evidence that the fluorene ring is non-coplanar, an idea which has been put forward recently by various workers on other grounds. An alternative—and opposite—explanation would be that the fluorene ring *is* coplanar, and consequently that in the fluorene dyes a coplanar diphenylmethane system is present; whereas examination of models shows that the benzene rings in crystal-violet must be twisted well out of the general plane of the molecule, the angle of twist probably being at least 40°. Conjugation of the rings with the central carbon atom would then be more efficient in the fluorene analogue, and this might have a bathochromic effect.



(I)



(II)



(III)

To distinguish between these possibilities we calculated the light absorption of planar forms of the dyes (I), (II), and (III), and of their triphenylmethane analogues, and so obtained a quantitative estimate of the effects of the additional bonds.

It has been shown that the light absorption of basic dyes can be treated quite satisfactorily by the simple L.C.A.O. M.O. Method (Dewar, *J.*, 1950, 2329), even some of the excited levels being predicted quite accurately. In the case of the fluorene analogues of (I), (II), and (III), which are the non-alternant analogues of their parent alternant compounds, the same simplifying factors should be present: a small singlet–triplet separation, and a tendency for the π-electrons to accumulate on the terminal hetero-atoms.

The previous calculations of the absorption bands of the parent compounds crystal-violet and malachite-green were repeated and fair agreement was obtained with the previous results. However, in Table 1 the absorption previously calculated for 3680 Å has been omitted since this arises from a forbidden transition with the electric vector perpendicular to the plane of the rings; the absence of such a band in the observed spectrum is therefore not surprising. For malachite-green the calculated direction of the electric vector agrees with the experimental value for the first absorption band only if it is assumed that configurational interaction occurs between the symmetrical and the anti-symmetrical bonding orbitals at $-0{\cdot}5043$ and $-0{\cdot}5378\beta$ respectively, and this assumption seems probable in view of the closeness of these levels. The predicted directions of the electric vectors for the two observed transitions are mutually perpendicular. This agrees with the experimental determination by Lewis and Bigeleisen (*J. Amer. Chem. Soc.*, **1943**, **65**, 2102) based on a direct study of the polarised fluorescence of malachite-green. Such experiments do not provide a unique assignment of the electric vector to a given band. They can only establish the mutual perpendicularity of two bands. Consequently the disagreement in Table 1 may be incorrect.

TABLE 1.

Compound	$\lambda_{max.}$ (calc.)	$\lambda_{max.}$ (obs.)	Compound	$\lambda_{max.}$ (calc.)	$\lambda_{max.}$ (obs.)
Crystal-violet	5660 (x, y)	5910 (x, y)	Malachite-green ...	6220 (y)	6200 (x)
	3300 ,,	5450 ,,		5900 (x)	—
	2600 ,,	3050 ,,		3470 (x)	4200 (y
		2500 ,,			

TABLE 2.

Compound	$\lambda_{max.}$ (calc.)	$\lambda_{max.}$ (expt.)	Compound	$\lambda_{max.}$ (calc.)	$\lambda_{max.}$ (expt.)
Fluorene analogue of crystal-violet (I) ...	* 8380 (y)	8500	Fluorene analogue of malachite-green (II)	8070 (x)	8500
	* 6060 (x)	6500		—	9540
				5590 (y)	5070

* The calculated $\lambda_{max.}$ have been corrected for the difference between experiment and calculation of the F.F.A.B. of crystal-violet.

For the fluorene analogues (I) and (II), any strain present in the additional bond was ignored, and it was treated simply as a normal aromatic bond. A number of experimental facts seem to support this assumption, as will be noted later. The results of these calculations are compared with experiment in Table 2. The agreement is satisfactory and suggests that the whole difference between the triphenylmethane and fluorene dyes can be ascribed to the extra C–C bonds in the latter. The effect of these is evidently far greater than intuition might have suggested, and affords ample explanation of the observed shifts.

The fine structure of these bands is worthy of comment. For compound (II) the first absorption band exhibits a well-defined fine structure with a frequency separation of 1280 cm.$^{-1}$. Such a fine structure is common in the para- or L_b-bands of polyacenes, which show a regular vibrational structure with spacing in the region 1100—1500 cm.$^{-1}$. This may be attributed, in the absence of a complete vibrational analysis, to the fundamental and the overtones of a single vibration in each case. For the fluorene analogue the vibration responsible for the vibrational fine structure is probably the symmetric C–C vibration of the extra bond. Consequently, the spacing of 1280 cm.$^{-1}$, which is intermediate between that of the single and the double bond, lends further support to the assumption that this bond is largely aromatic in character. The fluorene analogue of crystal-violet (I) possesses a very wide band at approximately 8500 Å, indicating that the vibrational fine structure is obscured by solvent interaction.

It appears at first sight from the experimental absorption curves (Barker and Barker, *loc. cit.*) that the fluorene compounds absorb more weakly than do the triphenylmethane analogues. However, it is the oscillator strength or the integrated band intensity which is the correct measure of the intensity of absorption (Mulliken, *J. Chem. Phys.*, 1939, **7**, 14) and in this case the lower values of $\varepsilon_{\max.}$ for the fluorenes are compensated by the greater width of the maxima. The integrated band intensities are actually similar in both the parent dyes and their fluorene analogues.

It has been assumed so far that all the C–C resonance integrals have the same value; this is equivalent to neglecting any possible effects of non-coplanarity in the triphenylmethane derivatives. However it has been shown both theoretically and experimentally (Dewar, unpublished work) that the effect of non-coplanarity on the light absorption of such dyes is in fact small. It is very much smaller than the effects that are being considered here. In any case these effects could not possibly be due to such non-coplanarity for the effect of non-coplanarity is *bathochromic*; increasing the coplanarity of a triphenylmethane dye actually has a hypsochromic effect.

We also tried to calculate the differences in light absorption between the analogous diphenylmethane and fluorene derivatives by a perturbation method, regarding the formation of the extra bond in the latter as the perturbation. Although the calculated spectral shifts were in the right direction they were very much smaller than those observed. This is surprising since analogous perturbation methods have proved very successful in other cases; and it suggests that the large bathochromic displacements are not directly due to the formation of the extra bond. It seems likely that the main effect is due to the radical change in charge distribution that occurs when the alternant conjugated system of the diphenylmethane is converted into a non-alternant fluorene structure (cf. Coulson and Rushbrook, *Proc. Camb. Phil. Soc.*, 1940, **36**, 193). This factor was neglected in our first-order perturbation treatment.

Method.—This was quite standard. The L.C.M.O. method (Dewar, *ibid.*, 1949, **45**, 639) was employed for the parent compounds since these can be treated very simply by it and much labour is thereby saved.

Overlap was neglected since the aim of the calculations was comparative; likewise no allowance was made for the inductive effect of the hetero-atoms.

The following values were assigned to the Coulomb term (α) of an atom relative to carbon and to the resonance integrals (β) : α_N (in NR_3) $= \beta_{CC}$; $\beta_{CN} = \beta_{CC}$; $\beta_{CC} = 73{\cdot}2$ kcals.

QUEEN MARY COLLEGE, MILE END ROAD, LONDON, E.1. [*Received, December 15th*, 1953.]