735. *Steric Effects in Electronic Spectra.*

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The importance of steric effects in determining the electronic spectrum of a composite molecule is related to the interaction between locally excited and electron-transfer states of the separated fragments. The intensity of a transition to a typical electron-transfer state is in general more sensitive to steric factors than a transition to a typical locally excited state, but the latter is usually more sensitive in its frequency. The electronic spectra of the diphenyls, dimethylanilines, acetophenones, and cyanine dyes are briefly discussed, and the nature of their electronic bands determined from the effect of *ortho*-substituents on their spectra.

IT is well known that when two conjugated fragments R and S are joined by a single bond the electronic spectrum of the molecule depends sensitively on the degree of coplanarity between the two fragments. If R and S lie in mutually perpendicular planes, the spectrum of the molecule RS strongly resembles the superimposed spectra of RH and SH.

In such a molecule, the intensity of an absorption band usually decreases on steric distortion from the coplanar configuration, although in some cases the intensity remains relatively unchanged: in principle it is possible for the intensity to increase, but examples of this are difficult to find. There are many cases, however, in which the frequency of a band either increases or decreases or remains unchanged as the molecule is distorted. The relevant experimental work has been reviewed by Braude and Waight.[1]

Longuet-Higgins and Murrell[2] have shown that the electronic spectrum of a composite molecule can be conveniently described in terms of wave functions for the separated fragments. These functions fall into two classes: those which describe excited states of the individual fragments (locally excited states; denoted L.E. below); and those

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[1] Braude and Waight, " Progress in Stereochemistry," Butterworths, London, 1954.

[2] Longuet-Higgins and Murrell, *Proc. Phys. Soc.*, 1955, **68**, *A*, 601.

which describe a state in which an electron has been transferred from one fragment to another (electron-transfer states; denoted E.T. below). Transitions from the ground state to the L.E. states give rise to the band spectra of the individual fragments; transitions to the E.T. states are forbidden when the fragments are separated, and so are not observed.

The effect of conjugation between the fragments will be to mix the E.T. states both with the ground state and with the L.E. states. The L.E. states do not mix either with each other or with the ground state to any large extent, since there is no direct interaction element between them. Now, if the perturbation is small, the wave functions for the separated fragments will retain their general character even in the composite molecule. An exception will be if an L.E. and an E.T. state of the unperturbed system happen to be nearly degenerate: the resulting wave functions of the composite molecule will then be an intimate mixture of the two species.

The electronic bands of RS can therefore be described as having the features of a transition either to an L.E. state or to an E.T. state, or to a mixture of the two. In this paper we shall consider the effect of steric distortion on a transition to a typical L.E. or E.T. state and hence predict the behaviours of a band of intermediate character. By observing the sensitivity of a particular band to steric effects, we should therefore be able to throw light on the nature of the electronic transition involved.

Theory.—Suppose the self-consistent molecular orbitals of R are written $\theta_1 \ldots . \theta_p$, and those of S are $\omega_1 \ldots . \omega_q$, then the ground-state wave function for the system R–S, in which the two fragments are separated by a large distance, can be written as a single antisymmetric function in which the electrons are assigned to the lowest orbitals with paired spins. We are assuming that the molecule has a stable closed-shell ground state.

The L.E. states of R will be some linear combination of singlet configurations of the type, $\theta_k^{-1}\theta_l$, in which an electron has been raised from θ_k to θ_l: the L.E. states of S will be combinations of the configurations $\omega_m^{-1}\omega_n$. The E.T. states will be made up either of configurations $\theta_k^{-1}\omega_n$ (R→S), or of configurations of the type $\omega_m^{-1}\theta_l$ (S→R).

Now when R and S come together to form the composite molecule, there will be a change in the Hamiltonian, and the states of the unperturbed system will be mixed together. There are three important interactions to be considered: (i) The L.E. states on different fragments will mix under the influence of electron repulsion.[2] (ii) The field or inductive effect of one fragment will mix together the L.E. states on the other fragments;[3] although these interactions lead to significant differences between the spectrum of RS and the spectra of the separated fragments, they are for the most part independent of the degree of planarity in the molecule, and need not be considered further. (iii) Conjugation between the two fragments will mix the E.T. states with the L.E. states and with the ground state. This interaction, since it depends on the resonance integral between $2p\pi$-atomic orbitals on R and on S, will be sensitive to the geometry of the molecule.

By perturbation theory, the first-order approximation to the wave function of a state Ψ_a is given by

$$\Psi_a' = \Psi_a + \sum_r \frac{H_{ar}'}{E_a - E_r}\Psi_r \quad \ldots \ldots \quad (1)$$

where H_{ar}' is the matrix element of the perturbation between the states Ψ_a and Ψ_r. The second-order approximation to the energy of this state is:

$$E_a' = E_a + \sum_r \frac{(H_{ar}')^2}{E_a - E_r} \quad \ldots \ldots \quad (2)$$

there being no first-order change in energy under the particular perturbation we are considering. Now if Ψ_a is an E.T. state and Ψ_r an L.E. state, the matrix element H_{ar}', being determined by a resonance integral between the two fragments, will be proportional to cos α, where α is the angle between the planes of the two fragments.

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[3] Murrell and Longuet-Higgins, *Proc. Phys. Soc.*, 1955, **68** *A*, 329.

The intensity of a transition $\Psi_0' \longrightarrow \Psi_a'$ is given by .

$$M_{0a}' = \int\left(\Psi_0 + \sum_r \frac{H_{0r}'}{E_0 - E_r}\Psi_r\right)^* \varepsilon r \left(\Psi_a + \sum_s \frac{H_{as}'}{E_a - E_s}\Psi_s\right) d\tau \quad . \quad . \quad (3)$$

$$= M_{0a} + \sum_{s \neq a} \frac{H_{as}'}{E_a - E_s} M_{0s} + \sum_{r \neq 0} \frac{H_{0r}'}{E_o - E_r} M_{ra} \quad . \quad . \quad . \quad . \quad . \quad (4)$$

to the first order in the perturbation. If Ψ_a is the configuration $\theta_p^{-1}\omega_q$, the dipole moment M_{0a} can be reduced to the one-electron integral

$$M_{0a} = \sqrt{2}\int \theta_p \varepsilon r \omega_q d\tau \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

and this is small if there is only a small overlap between the orbitals θ_p and ω_q on the two fragments. M_{0s} will be large if Ψ_s is an L.E. state, which gives rise to a strong band in the separated fragments. M_{ra} can be non-zero if Ψ_r is an E.T. state in which the electrons are transferred in the same direction as in Ψ_a. For a non-zero transition dipole moment between $\theta_p^{-1}\omega_q$ and $\theta_r^{-1}\omega_s$ it is necessary either that $p = r$ or that $q = s$. There are therefore two main contributions to the intensity of the transition $\Psi_0' \longrightarrow \Psi_a'$. One is due to the presence of L.E. wave functions in the upper state, and the other is due to E.T. wave functions in the ground state. The latter gives rise to an increase in the total intensity of absorption by the molecule. All the terms in eqn. (4) go to zero when the two fragments occupy mutually perpendicular planes; it is therefore evident that transitions to the E.T. states have intensities which are extremely sensitive to steric distortion of the molecule.

FIG. 1.

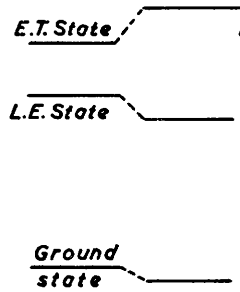
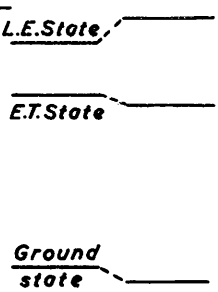


FIG. 2.



If Ψ_a is an L.E. state, then for H_{as}' and H_{0r}' to be non-zero both Ψ_r and Ψ_s must be E.T. states. In this case both M_{0s} and M_{ra} will be small terms, depending on the overlap between molecular orbitals on the two fragments. The main contribution to the intensity of the transition $\Psi_0' \longrightarrow \Psi_a'$ will therefore in general arise from the term M_{0a} in eqn. (4). We therefore expect that transitions to a perturbed L.E. state should have intensities which are relatively insensitive to steric distortion of the molecule. An exception to this will be if the transition $\Psi_0 \longrightarrow \Psi_a$ is symmetry-forbidden. In this case one would expect the second and third terms in eqn. (4) to contribute significantly to the intensity of the band, and this contribution will become zero when the fragments are mutually perpendicular. Second-order terms in the wave functions of the perturbed molecule may also be important in determining the intensity of a weak band.

In general, the more sensitive is the intensity of a band to steric factors, the greater will be the amount of E.T. character in the upper electronic state.

The change in energy of a band due to conjugation between two fragments is more difficult to predict. Consider the cases represented in Figs. 1 and 2. The E.T. state and the ground state repel one another, and so do the E.T. state and the L.E. state. The point which is worth noting is that if the E.T. state lies between the ground state and the

L.E. state, then its energy relative to the ground state might be little changed by conjugation between the two systems (see Fig. 2). If the E.T. state lies very close to the ground state the energy of the E.T. band might in fact be raised. However, if the E.T. state lies above the L.E. state, then the energy of the L.E. band will be lowered by conjugation, since there is no interaction between the L.E. state and the ground state (see Fig. 1). This is a considerable simplification of the problem, but may be a useful guide in deciding the nature of the band.

To summarize : a large hyposochromic shift, on steric distortion of the fully conjugated molecule, suggests that the band arises from a transition to an L.E. state, whilst no shift or a small bathochromic shift suggests that an E.T. state is involved.

If an E.T. state and an L.E. state are degenerate, or nearly degenerate, in the unperturbed system, and if these interact under the influence of the perturbation, then two bands will occur in the spectrum, their separation being of the first order in the resonance integral between the two fragments (proportional to cos α).

APPLICATIONS

ortho-*Substituted Diphenyls.*—The most fully studied example of the effect of *ortho*-substituents on the spectrum of a benzenoid system is found in the diphenyl series. The interest in these molecules arose from the work of Pickett, Walter, and France [4] on dimesityl and hexachlorodiphenyl. They showed that the spectra of these molecules differed in character from those of diphenyls not substituted in the *ortho*-positions. A selection of the relevant data is shown in Table 1.

Both the bands in the near-ultraviolet spectrum of diphenyl move to shorter wavelengths on *ortho*-substitution; this is particularly noticeable on comparing the frequency of the more intense band in 2 : 2′ and 3 : 3′-dimethyldiphenyl. We therefore deduce that the bands arise from transitions to L.E. states, which interact with E.T. states of higher energy. The intensity of the lower band is uncertain, but it cannot be very great since it does not give a noticeable inflexion to the more intense band. The intensity of the band at 4·98 ev falls appreciably on *ortho*-substitution. This is not to be expected if a transition to an L.E. state is involved. If this interpretation is assumed to be correct, however, then the band would correspond to the 2000 Å band of benzene, which arises from a symmetry-forbidden transition, and has an intensity ε 7000. Its intensity is therefore expected to be more sensitive to steric effects than that of a band which arises from an allowed transition in the separate fragments.

We therefore suggest that the bands at 4·98 and 4·59 ev in diphenyl arise from transitions to L.E. states. This conclusion is arrived at by other authors, and is borne out by an approximate calculation on the energy of the lowest E.T. configuration. It is found to be about 7·0 ev.

ortho-*Substituted Anilines.*—Substituents in the *ortho*-position to an amino-group are expected to reduce the conjugation between the nitrogen $2p\pi$-orbital and the aromatic ring, since the hydrogen atoms joined to the nitrogen will have difficulty in lying in the plane of the molecule. Klevens and Platt's data [5] for some dimethylanilines are given in Table 2.

They show that amino-substituents introduce a new band into the spectrum; this is to be expected if there is a low-energy E.T. state. We infer that this state gives rise to the band at 4·96 ev, since one *ortho*-substituent does not change the energy of this band appreciably, yet

TABLE 1. *The near-ultraviolet absorption of diphenyls.*

Derivative	Energy (ev)	$\varepsilon_{max.}$	Energy (ev)	$\varepsilon_{max.}$
Unsubst.	(4·59) [d]	—	4·98 [a]	17,000
2-Me [a]	—	—	5·27	10,500
2-Bu^n [a]	—	—	5·32	10,500
2 : 2′-Me$_2$ [b]	4·70	800	5·46 *	(6800)
3 : 3′-Me$_2$ [c]	—	—	4·86	16,500
2 : 4 : 6 : 2′ : 4′ : 6′-Me$_6$ [4]	4·69	500	>5·46	—

* Inflection. [a] Braude and Forbes, *J.*, 1955, 3776. [b] Beavan, Hall, Lesslie, Turner, and Bird, *J.*, 1954, 131. [c] Williamson and Rodebush, *J. Amer. Chem. Soc.*, 1941, **63**, 3018. [d] The lowest band in diphenyl is masked by the more intense band at 4·98 ev; its energy has been estimated by Wenzel (*J. Chem. Phys.*, 1953, **21**. 403) by comparison with related molecules.

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[4] Pickett, Walter, and France, *J. Amer. Chem. Soc.*, 1936, **58**, 2296.

[5] Klevens and Platt, *ibid.*, 1949, **71**, 1714.

its intensity is halved. Two *ortho*-substituents remove the band from the spectrum altogether. The band at 6·2 ev has an intensity which behaves in a similar way to that of the intense band of diphenyl. In this case, however, *ortho*-substituents produce a shift to longer wavelengths. This is to be expected if there is an E.T. state at lower energies. The bands at 7·04 and 4·09 ev both show the characteristics of transitions to L.E. states; they are repelled by E.T. states which lie between them. A simple calculation[6] shows that there are two low-energy E.T. states at 6·2 and 5·0 ev. The former will give rise to a rather weak band which would be masked by other transitions in this region.

TABLE 2. *The effect of* ortho-*substituents on the spectrum of dimethylaniline* (f = oscillator strength).

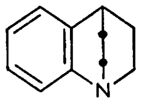
	NN-Dimethylaniline					2 : 6 : *N* : *N*-Tetramethylaniline		
ν (ev)	7·04	6·21	4·96	4·09	ν (ev)	6·76	5·88	4·79
f	0·79	0·54	0·28	0·04	f	0·66	0·15	0·05
	NN-Dimethyl-*o*-toluidine					Benzene		
ν (ev)	6·70	5·95	5·01	—	ν (ev)	6·74	6·14	4·88
f	0·69	0·23	0·12	0·02	f	0·69	0·10	0·0014

TABLE 3. *Ultraviolet absorption of alkylated acetophenones.*

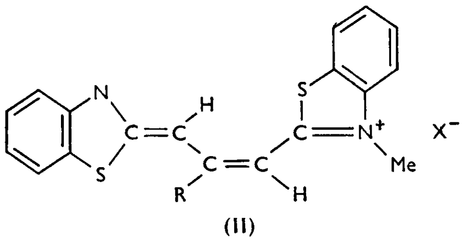
	K-Band		*B*-Band		*R*-Band	
Derivative	ν (ev)	$\varepsilon_{max.}$	ν (ev)	$\varepsilon_{max.}$	ν (ev)	$\varepsilon_{max.}$
Unsubst.	5·10	13,200	4·44	1200	3·94	55
2-Me	5·12	8700	—	—	—	—
	5·06	8300	4·41	1200	3·75	50
4-Me	4·92	15,100	—	—	—	—
2 : 6-Me$_2$	4·94	5600	4·41	890	—	—
	4·84	5200	4·28	740	—	—

An interesting example of hindered mesomerism in an aromatic amine is found in " benzoquinuclidine " (I), whose spectrum[7] closely resembles that of benzene.

Alkylated Acetophenones.—Unlike benzaldehyde, the spectrum of acetophenone shows noticeable changes when *ortho*-substituents are introduced, evidently owing to steric repulsion between the methyl group of the ketone and the *ortho*-substituent. Table 3 contains some results given by Braude and Sondheimer.[8] There appears to be a balance between the bathochromic shift due to a methyl substituent, and the steric effect. This is best seen by comparing the spectra of 2- and 4-methylacetophenone. The *B*-band resembles the weak band in benzene, and the R-band presumably arises from a $\sigma \longrightarrow \pi$ transition of the carbonyl group; both are little affected by conjugation between the fragments. The *K*-band, however, is considerably reduced in intensity by *ortho*-substituents whilst remaining at about the same frequency. It is therefore assigned to a transition to an E.T. state in which an electron would be transferred from the phenyl to the carbonyl group.



(I)



(II)

Cyanine Dyes.—The cyanine dyes are typical of a large class in which there are two conjugated fragments joined by a polyene chain of one, three, or five carbon atoms. As an example of steric effects on the spectra of these molecules, we shall briefly consider the cyanine dye (II). The intense band around 5500 Å is assigned to a transition to an E.T. state. When a substituent R is introduced into the molecule which might be expected to influence its geometry, the

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[6] Murrell, *Proc. Phys. Soc.*, 1955, **68**, *A*, 969.
[7] Wepster, *Rec. Trav. chim.*, 1952, **71**, 1159.
[8] Braude and Sondheimer, *J.*, 1955, 3754.

intensity of this band falls considerably. At the same time, however, there is a considerable shift to longer wavelengths. The latter fact can be explained by a strong interaction between the E.T. state and the ground state, which occurs when the two fragments are conjugated together. These two states will repel one another and give rise to a band at shorter wavelengths than that found when there is no conjugation (see Table 4).

TABLE 4. *The absorption spectra of cyanine dyes.*[9]

R	H	Me	Et	Pr^i	Bu^n
λ	5550	5380	5425	5450	5875
$10^3\varepsilon$	149	122	118	94	21

DISCUSSION

We have attempted to elucidate the nature of the electronic transitions in the spectra of some composite molecules, from the effects of *ortho*-substitution. Although we have tended to assign a band to a transition either to an E.T. state or to an L.E. state, it must be remembered that this only describes the most important contribution to the wave function of the upper state. In particular, the bands at 4·98 ev in diphenyl and at 6·21 ev in dimethylaniline, although assigned to L.E. transitions, almost certainly have a significant amount of E.T. character. In the same way the band at 4·96 ev in dimethylaniline although predominantly arising from a transition to an E.T. state will perhaps have up to 20% of L.E. character.

There are obviously a great many systems in which *ortho*-substitution will give valuable information about the electronic structure of the molecule, *e.g.*, of nitro-compounds, aromatic acids, and azo-dyes.

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[9] Brooker, White, Heseltine, Keyes, Dent, and van Lare, *J. Phot. Sci.*, 1953, **1**, 173.