

Interaction between the Aromatic Chromophores in Polyphenyl Hydrocarbons.

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It is shown that electron interaction between the chromophores in the linear *m*- and *p*-polyphenyls can account for the main features of their electronic spectra. In the *para*-series the first intense absorption is due to an in-phase combination of γ - and β' -transitions in the individual chromophores, whilst in the *meta*-series it is the β -states which in the main give rise to the strong absorption. In both series the transition moment is in the longitudinal direction.

Conjugation between the chromophores has been ignored though this probably occurs to some extent in both series. It has previously been suggested that the different characteristics of the spectra of the two series are due to the presence of conjugation in the *para*- but not in the *meta*-series. It is demonstrated that this is probably a secondary effect and that the difference can be interpreted without reference to conjugation between the aromatic rings.

It is interesting to investigate the interaction between individual chromophores of linear *m*- and *p*-polyphenyls, $C_6H_5 \cdot [C_6H_4]_{n-2} \cdot C_6H_5$, because the two series show marked differences in their electronic spectra (Gillam and Hey, *J.*, 1939, 1170). The frequency of the first intense band in the *para*-series decreases steadily as the number of aromatic rings is increased, no limit having been reached with the first six members, which have been studied experimentally. On the other hand, in the *meta*-series there is virtually no change in the frequency of this band after diphenyl: it has been examined up to *m*-sedeciphenyl ($n = 16$). For both the *m*- and the *p*-polyphenyls the intensity of absorption increases as the series is ascended, being roughly proportional to the number of chromophores in the molecule.

These phenomena have been discussed in terms of the Hückel L.C.A.O. molecular-orbital theory (Dewar, *J.*, 1952, 3532). This theory relies for its simplicity on the assumption that the Hamiltonian for the system can be written as a sum of one-electron operators. Although the theory sometimes appears to be confirmed by experiment, it fails in general to account satisfactorily for any but the broadest features of molecular electronic spectra. In particular the Hückel theory predicts that the electronic states of a molecule R-S in which there is no conjugation between R and S, are equal in energy to the states of RH and SH. Any shift in the bands of the chromophores R and S when they are joined together has been taken to indicate conjugation between R and S, and hence a certain degree of coplanarity between adjacent rings.

Longuet-Higgins and Murrell (*Proc. Phys. Soc.*, in the press) have however shown that, when terms are included in the Hamiltonian which allow for the repulsion between electrons,

there can be appreciable interaction between the chromophores in a molecule even when there is no conjugation between them.

In this paper it will be shown how the main features of the spectra of the polyphenyls can be interpreted as due to repulsion between the π -electrons of adjacent rings without invoking significant conjugation between the aromatic rings.

Method.—It has been shown by Pople (*Proc. Roy. Soc.*, in the press) that, for a molecule having two or more chromophoric groups which are not conjugated together, the self-consistent molecular orbitals of the molecule are just those of the individual chromophores considered separately. The electronic states of such a molecule are of two kinds. There are those states which involve the excitation of an electron between two orbitals belonging to the same chromophoric group, and those which involve the transfer of an electron between molecular orbitals localized on different groups. The former are described as “locally excited” states, and the latter as “electron transfer” states.

Electron interaction has the effect of mixing the locally excited states of one chromophore with the locally excited states of all the others. There will be no mixing with any electron transfer states if there is no conjugation between the chromophores.

For the polyphenyls the locally excited states will correspond to the excited states of a benzene molecule. If the π -orbitals of benzene are written in their real forms, as follows :

$$\begin{aligned}\psi_6 &= \sqrt{\frac{1}{6}}\{\phi_1 - \phi_2 + \phi_3 - \phi_4 + \phi_5 - \phi_6\} \\ \psi_5 &= \sqrt{\frac{1}{12}}\{2\phi_1 - \phi_2 - \phi_3 + 2\phi_4 - \phi_5 - \phi_6\} \\ \psi_4 &= \frac{1}{2}\{-\phi_2 + \phi_3 - \phi_5 + \phi_6\} \\ \psi_3 &= \frac{1}{2}\{\phi_2 + \phi_3 - \phi_5 - \phi_6\} \\ \psi_2 &= \sqrt{\frac{1}{12}}\{2\phi_1 + \phi_2 - \phi_3 - 2\phi_4 - \phi_5 + \phi_6\} \\ \psi_1 &= \sqrt{\frac{1}{6}}\{\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6\}\end{aligned}$$

where ϕ_r are a set of orthogonal atomic-orbital functions, then the singly excited states of lowest energy are :

	Excitation energy (ev)
$\Psi_{\beta'} = \sqrt{\frac{1}{2}}(\chi_3^4 - \chi_2^5)$	6.74
$\Psi_{\beta} = \sqrt{\frac{1}{2}}(\chi_3^5 + \chi_2^4)$	6.74
$\Psi_{\gamma} = \sqrt{\frac{1}{2}}(\chi_3^4 + \chi_2^5)$	6.14
$\Psi_{\alpha} = \sqrt{\frac{1}{2}}(\chi_3^5 - \chi_2^4)$	4.88

where χ_k^l represents a configuration in which one electron has been excited from ψ_k to ψ_l .

The matrix element of the interaction between two configurations χ_k^l and χ_m^n obtained by exciting electrons within different chromophores is given by

$$\iint \chi_k^l H \chi_m^n d\tau = 2 \iint \psi_k(i) \psi_l(i) \frac{1}{r_{ij}} \psi_m(j) \psi_n(j) d\tau_{ij}$$

According to Pariser and Parr (*J. Chem. Phys.*, 1953, **21**, 767) and Pople (*Trans. Faraday Soc.*, 1953, **49**, 1375), an approximation to this integral can be obtained by expanding the molecular orbitals in terms of atomic-orbital functions, neglecting all integrals except those of the form

$$\iint \phi_{\mu}^2(i) \frac{1}{r_{ij}} \phi_{\nu}^2(j) d\tau_{ij}$$

Pople replaces these integrals by the interaction energy of point charges at the nuclei. The evaluation of the matrix elements of the interaction between the locally excited states therefore reduces to the evaluation of the interaction energy of point-charge distributions on the aromatic rings. These charge distributions for the four lowest energy states of

benzene are as shown. It is evident that the locally excited α -states will remain unaffected by electron interaction. In any case they give rise to weak transitions since in benzene the α -band is symmetry-forbidden.



It will now be shown how these locally excited states interact in the m - and the p -polyphenyl series.

p-Polyphenyls.—Since the γ - and the β' -state can be represented by charge distributions symmetrical about the longitudinal axis of the molecule, whilst the β states have a charge distribution antisymmetrical about this axis, there will be no mixing of the γ - and the β' -states with the β -states. Moreover, since we are interested in the lowest allowed transition, we can confine our attention to the γ - and the β' -states, since the β -states interact only weakly.

The locally excited γ - and β' -states will interact to give states of the form

$$\Psi = \sum_r a_r \Psi_\gamma + \sum_r b_r \Psi_{\beta' r}$$

the summations being over all the chromophores in the molecule. When all but nearest neighbour interactions are neglected, the coefficients a_r and b_r are obtained by solving the secular equations:

$$\left. \begin{aligned} (E_\gamma - E)a_r + H_{\gamma\gamma}(a_{r-1} + a_{r+1}) + H_{\gamma\beta'}(b_{r-1} + b_{r+1}) &= 0 \\ (E_{\beta'} - E)b_r + H_{\beta'\beta'}(b_{r-1} + b_{r+1}) + H_{\beta'\gamma}(a_{r-1} + a_{r+1}) &= 0 \end{aligned} \right\} \quad (1)$$

where H_{xy} is the interaction between the state Ψ_x of r and Ψ_y of $(r+1)$. For the *para*-series $H_{xy} = H_{yx}$. Equations (1) can be solved by taking the coefficients in periodic form, namely:

$$a_r = A \sin r\theta$$

$$b_r = B \sin r\theta$$

where $\theta = p\pi/(n+1)$. The secular equations then become:

$$\left. \begin{aligned} \{(E_\gamma - E)A + 2H_{\gamma\gamma}A \cos \theta + 2H_{\gamma\beta'}B \cos \theta\} \sin r\theta &= 0 \\ \{(E_{\beta'} - E)B + 2H_{\beta'\beta'}B \cos \theta + 2H_{\beta'\gamma}A \cos \theta\} \sin r\theta &= 0 \end{aligned} \right\} \quad (2)$$

and these are consistent if

$$\begin{vmatrix} (E_\gamma - E) + 2H_{\gamma\gamma} \cos \theta & 2H_{\gamma\beta'} \cos \theta \\ 2H_{\gamma\beta'} \cos \theta & (E_{\beta'} - E) + 2H_{\beta'\beta'} \cos \theta \end{vmatrix} = 0 \quad (3)$$

There will be a set of such determinants arising from the n distinct non-zero values of $\sin [p\pi/(n+1)]$. Of the $2n$ roots of these equations, that of lowest energy corresponds to $p=1$, and is given by

$$E = \frac{E_\gamma + E_{\beta'}}{2} + (H_{\gamma\gamma} + H_{\beta'\beta'}) \cos \frac{\pi}{n+1} - \frac{1}{2} \left\{ \left(E_\gamma - E_{\beta'} + 2(H_{\gamma\gamma} - H_{\beta'\beta'}) \cos \frac{\pi}{n+1} \right)^2 + 16H_{\gamma\beta'}^2 \cos^2 \frac{\pi}{n+1} \right\}^{\frac{1}{2}} \quad (4)$$

If all the aromatic rings are taken to have the geometry of benzene, with a bond length 1.39 Å, and the connecting bonds to be of length 1.46 Å, the matrix elements of the interaction have the values:

$$H_{\gamma\gamma} = -0.20 \text{ eV}$$

$$H_{\beta'\beta'} = -0.93 \text{ eV}$$

$$H_{\gamma\beta'} = 0.28 \text{ eV}$$

The aromatic rings are assumed to lie in the same plane, but it was shown by Longuet-Higgins and Murrell (*loc. cit.*) that these matrix elements are almost independent of this assumption.

Table I gives the energies of the lowest allowed transitions calculated from equation (4), and compares them with the observed results. If second-neighbour interaction is included

TABLE I. *Comparison of the observed and calculated energies of the lowest allowed transition in the p-polyphenyls* (Gillam and Hey, *J.*, 1939, 1170).

<i>n</i>	Energy (ev)		Observed intensity (10 ⁻³ ε _{max.})	<i>n</i>	Energy (ev)		Observed intensity (10 ⁻³ ε _{max.})
	obs.	calc.			obs.	calc.	
2	4.93	5.58	18.3	5	4.00	4.86	62.5
3	4.43	5.18	25	6	3.90	4.79	>56
4	4.13	4.97	39	∞	—	4.62	—

the energy of *p*-terphenyl is lowered by 0.2 ev. Also it was shown by Longuet-Higgins and Murrell (*loc. cit.*) that, if conjugation is allowed for between the chromophores, the energy of the band in diphenyl is reduced by 0.36 ev. Both these effects explain why our calculated energies are consistently too high.

The lowest-energy band corresponds to an in-phase excitation of the γ- and the β'-state of each chromophore, and as such will be strongly allowed.

m-Polyphenyls.—The β-state of each ring may be taken to have a nodal plane perpendicular to the length of the molecule, and the transition dipoles of these states to be in the same direction. It is then found that the interaction elements between the β-states and the γ- and β'-states obey the relations :

$$H_{\gamma\beta} = -H_{\beta\gamma}; H_{\beta'\beta} = -H_{\beta\beta'}$$

The excited states for the molecule must be expressed in the form :

$$\Psi = \sum_r a_r \Psi_{\gamma r} + \sum_r b_r \Psi_{\beta' r} + \sum_r c_r \Psi_{\beta r}$$

since there is interaction between all three types of state. If all interactions except those between nearest neighbours are again ignored, the coefficients *a_r*, *b_r*, and *c_r* are obtained by solving the following secular equations :

$$\left. \begin{aligned} (E_\gamma - E)a_r + H_{\gamma\gamma}(a_{r+1} + a_{r-1}) + H_{\gamma\beta'}(b_{r+1} + b_{r-1}) + H_{\gamma\beta}(c_{r+1} - c_{r-1}) &= 0 \\ (E_{\beta'} - E)b_r + H_{\beta'\beta'}(b_{r+1} + b_{r-1}) + H_{\gamma\beta'}(a_{r+1} + a_{r-1}) + H_{\beta'\beta}(c_{r+1} - c_{r-1}) &= 0 \\ (E_\beta - E)c_r + H_{\beta\beta}(c_{r+1} + c_{r-1}) + H_{\beta\gamma}(a_{r+1} - a_{r-1}) + H_{\beta\beta'}(b_{r+1} - b_{r-1}) &= 0 \end{aligned} \right\} \quad (5)$$

It is not possible to find an explicit general solution of equations (5) but a solution can be obtained for the infinite chain. In this case we can ignore end effects, and write :

$$\begin{aligned} a_r &= A \sin r\theta, \\ b_r &= B \sin r\theta, \\ c_r &= C \cos r\theta \end{aligned}$$

where $\theta = p\pi/(n + 1)$. We find, as in the *para*-series, that for consistency it is necessary that

$$\begin{vmatrix} (E_\gamma - E) + 2H_{\gamma\gamma} \cos \theta & 2H_{\gamma\beta'} \cos \theta & -2H_{\gamma\beta} \sin \theta \\ 2H_{\gamma\beta'} \cos \theta & (E_{\beta'} - E) + 2H_{\beta'\beta'} \cos \theta & -2H_{\beta'\beta} \sin \theta \\ -2H_{\gamma\beta} \sin \theta & -2H_{\beta'\beta} \sin \theta & (E_\beta - E) + 2H_{\beta\beta} \cos \theta \end{vmatrix} = 0$$

The interaction elements are as follows :

$$\begin{aligned} H_{\gamma\gamma} &= 0.20 \text{ ev} & H_{\beta\beta} &= -0.61 \text{ ev} \\ H_{\beta'\beta'} &= -0.05 \text{ ev} & H_{\gamma\beta} &= -0.25 \text{ ev} \\ H_{\gamma\beta'} &= 0.14 \text{ ev} & H_{\beta'\beta} &= -0.58 \text{ ev} \end{aligned}$$

The root of lowest energy will arise from $p = 1$, in which case $\cos \theta = 1$, $\sin \theta = 0$. The lowest-energy band for the infinite chain should therefore have an energy $E_\beta - 2H_{\beta\beta} = 5.52$ ev. This band is seen to arise from an in-phase excitation of the β -bands of the aromatic chromophores. The energy of the strong absorption band of *m*-terphenyl has been calculated separately by considering only the effect of electron interaction between adjacent rings. It is found to be 5.46 ev.

These results are compared in Table 2 with the experimental values obtained by Gillam and Hey.

TABLE 2. Comparison of the observed and the calculated energies of the lowest allowed transition in the *m*-polyphenyls.

<i>n</i>	Energy (eV)		Intensity ($10^{-3} \epsilon_{\max}$)	<i>n</i>	Energy (eV)		Intensity ($10^{-3} \epsilon_{\max}$)
	obs.	calc.			obs.	calc.	
2	4.93	5.58	18.3	13	4.90	—	252
3	4.93	5.46	44	14	4.90	—	283
9	4.90	—	184	15	4.88	—	309
10	4.90	—	213	16	4.86	—	320
11	4.90	—	215	∞	—	5.52	—
12	4.90	—	233				

Discussion.—We have shown above how electron interaction between the chromophores in the polyphenyls can account for the main features of their electronic spectra. In the *para*-series the lowest allowed transition arises from an in-phase excitation of the γ - and the β' -bands of the individual chromophores, whilst in the *meta*-series it is an in-phase excitation to the β -states which contributes the largest part of the absorption. In the *para*-series interaction between the chromophores is such as to give a slow convergence for the frequency of the band towards the limit reached by the infinite chain. In the *meta*-series, however, our calculations explain why there is little change in frequency after diphenyl. In both series the transition which gives rise to the strong absorption band has a moment in the longitudinal direction, which is why the intensity of the band increases as either series is ascended.

Our calculated energies are consistently greater than those observed both for the *meta*- and the *para*-series, but this is to be expected since we have neglected the effect both of electron interaction between non-nearest neighbours and of conjugation between the chromophores. These effects appear to be of secondary importance since the general features of the spectra are obtained without considering them.