392. *Steric Effects on the Spectra of Aromatic Hydrocarbons.*

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It is shown how the sign of a sterically induced frequency shift of the *p*-band of an alternant hydrocarbon can be predicted theoretically. The predictions are in agreement with experimental findings for the cases examined.

STERIC distortion of an aromatic hydrocarbon can give rise to either a hyposchromic or a bathochromic shift in the absorption bands. In this paper we show how the sign of this shift can be predicted in a simple way for the so-called *p*-band (Clar) (Platt's L_b band). In all cases which we have examined, where the method of relieving the steric strain has been established or can be inferred from the examination of molecular models, our predictions agree with the experimental results.

The *p*-band arises from the excitation of an electron from the highest occupied molecular orbital of the ground state to the lowest unoccupied orbital. It occurs with moderate intensity as either the first or the second band in the spectrum. It has been shown that the energy of this band in a series of aromatic hydrocarbons is well correlated with the difference in energy between the highest occupied and lowest unoccupied orbital, as calculated by the Hückel L.C.A.O. theory with zero-overlap approximation.[1] In this theory the orbitals of the so-called alternant hydrocarbons (those with no odd-membered rings) occur in pairs with energies $\alpha \pm E_r$, the energy E_r being given by $\sum_{\mu}^{*} \sum_{\nu}^{\circ} C_{r\mu}C_{r\nu}\beta_{\mu\nu}$. $C_{r\mu}$ is the coefficient of the μth atomic orbital in the rth molecular orbital, and $\beta_{\mu\nu}$, the resonance integral between orbitals μ and ν, which is taken to be zero unless atoms μ and ν are bonded together. The summation $\sum^{*}$ is over starred atoms and $\sum^{\circ}$ over unstarred, so that no two atoms of the same set are bonded together.

Now $\beta_{\mu\nu}$ is a negative quantity; hence if $C_{r\mu}$ and $C_{r\nu}$ are both positive, the term $C_{r\mu}C_{r\nu}\beta_{\mu\nu}$ contributes negatively to E_r, that is stabilises orbital ψ_r. Reducing the value of β in this case, by straining the molecule in some way, will therefore destabilise this orbital. However, if the coefficients $C_{r\mu}$ and $C_{r\nu}$ have opposite signs, then reducing the value of β will stabilise orbital ψ_r. The pair of orbitals which have energies $\alpha \pm E_r$ also have related coefficients, so that if the occupied orbital is written

$$\psi_r = \sum_{\mu}^{*} C_{r\mu}\phi_\mu + \sum_{\nu}^{\circ} C_{r\nu}\phi_\nu$$

then the corresponding unoccupied orbital is

$$\psi_{-r} = \sum^{*} C_{r\mu}\phi_\mu - \sum_{\nu}^{\circ} C_{r\nu}\phi_\nu$$

This means that if the bonding orbital ψ_r is lowered in energy, the corresponding antibonding

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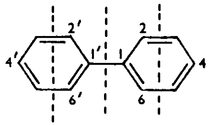
[1] Dewar, *J.*, 1952, 3532.

orbital ψ_r is raised in energy. The result is a hypsochromic shift in the absorption band associated with the excitation $\psi_r \longrightarrow \psi_{-r}$. From this result we predict: (*a*) if the highest occupied orbital has a node through the bond across which the steric strain is being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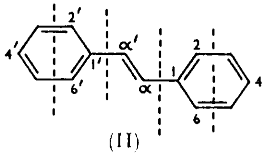
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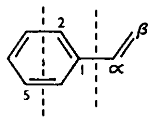
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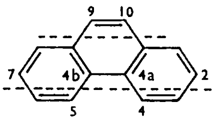
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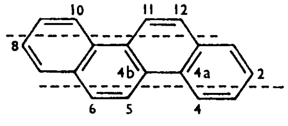
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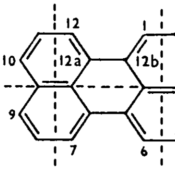
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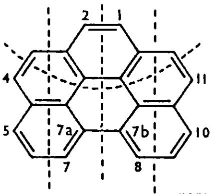
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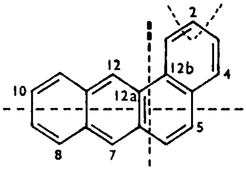
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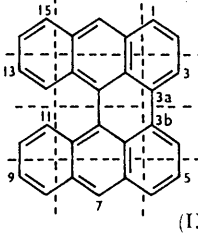
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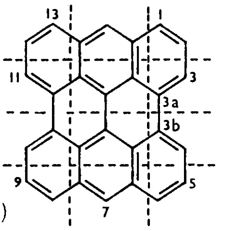
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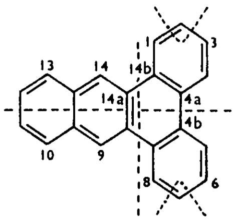
(XI)

Aromatic system	Substituent	Bonds principally twisted	Predicted frequency shift	Exptl. (cm.$^{-1}$)
Biphenyl (I)	2,4,6,2′,4′,6′-hexamethyl	1,1′	+	+5000[g]
trans-Stilbene (II)	2,4,6,2′,4′,6′-hexamethyl	α,1 and α′,1′	+	+4100[a]
Styrene (III)	α-methyl	α,1	+	+800[b]
Phenanthrene (IV)	4,5-dimethyl	4a,4b	—	−2300[g]
Chrysene (V)	4,5-dimethyl	4a,4b	—	−2300[g]
Perylene (VI)	1,12-diacetoxy	12a,12b	+	+610
Benzo[*ghi*]perylene (VII)	7,8-di(hydroxymethyl)	7a,7b	+	+1110[c]
Benz[*a*]anthracene (VIII) (tetraphene)	1,12-dimethyl	12a,12b	+	0[d]
Dibenzo[*a*,*o*]perylene (IX) (helianthrene)	3,4-dimethyl	3a,3b	+	+850[e] †
Phenanthro[1,10,9,8-*opqra*]perylene (*meso*-Naphthodianthrene) (X)	3,4-dimethyl	3a,3b	+	+800[f] ‡
Dibenz[*a*,*c*]anthracene (XI)	4,5-dimethyl	4a,4b	+	
	1,14-dimethyl	14a,14b	+	

† The orbitals for this molecule were calculated for us by Dr. T. Farrar on the EDSAC computer at the Mathematical Laboratory, Cambridge.

‡ The form of the highest orbital was obtained from the orbitals of helianthrene by perturbation theory.

[a] Beale and Roe, *J. Amer. Chem. Soc.*, 1952, **74**, 2302. [b] Gillam and Stern, " Electronic Absorption Spectroscopy," Arnold, London, 1958. [c] Baykut and Cromartie, unpublished work. [d] Cason and Phillips, *J. Org. Chem.*, 1952, **17**, 298. [e] Brockmann, von Falkenhausen, Neeff, Dorlars, and Budde, *Chem. Ber.*, 1951, **84**, 865. [f] Brockmann and Randebrock, *Chem. Ber.*, 1951, **84**, 533. [g] Friedel and Orchin, ref. 3.

relieved, the *p*-band (L_b) will be hypsochromically shifted by the steric effect; (*b*) if there is no node the band will be bathochromically shifted.†

The Table gives the predicted and observed direction of the steric effect for a number of condensed aromatic hydrocarbons, as deduced from the form of the highest occupied molecular orbital. Broken lines indicate the nodes in these orbitals, which have been taken from the published tables [2] except where indicated. In some cases the geometry of the strained molecule has not been determined by *X*-ray analysis; but the probable mode of distortion has been inferred from the examination of Dreiding molecular models, and also from the fact that twisting a bond of low bond-order leads to less destabilization of the π-electron system than twisting one with a high bond-order. Thus in stilbene and styrene it is assumed that the twisting takes place mainly about the single bonds of the classical structure.

The *p*-band of 4,5-dimethylphenanthrene shows a considerably greater bathochromic shift ($\Delta\nu = -2300$ cm.$^{-1}$) than those of the other isomers, *e.g.*, for 2,5-dimethylphenanthrene $\Delta\nu = -570$ cm.$^{-1}$.[3] The overcrowding in molecules of this type is known from Newman's work to be relieved by displacement of the substituents out of plane of the aromatic system with concomitant distortion of the latter.[4] Examination of models shows that the 4a,4b-bond would be the most twisted, and this bond also has a low bond-order. Similar considerations apply to the case of 4,5-dimethylchrysene.

No 1,12-dialkylperylene has yet been made, but 1,12-diacetoxyperylene, which was prepared by the method of Zinke, Penecke, and Hanus,[5] showed a hypsochromic shift; this agrees with the theory if the strain is relieved by twisting the two central bonds joining the two naphthalene units. These bonds have low bond-order and are known to be of mostly single-bond length from the *X*-ray analysis of perylene.[6] A similar type of distortion is assumed for derivatives of benzo[*ghi*]perylene, *meso*-naphthodianthrene and helianthrene bearing substituents in corresponding positions, and hypsochromic shifts are observed in all these cases.

The benz[*a*]anthracene system is a more subtle case. This molecule can be compared with phenanthrene but unlike it the highest occupied molecular orbital has a node across the 12a,12b bond. The product of the coefficient across this bond is, however, rather small (0·0016) and it is therefore predicted that if the resonance integral across this bond were decreased a small hypsochromic shift would be observed. Experimentally it is observed that substitution of a single 12-methyl group brings about a bathochromic shift ($\Delta\nu = 920$ cm.$^{-1}$) but that the 1-methyl derivative and the sterically hindered 1,12-dimethyl derivative absorb at very nearly the same frequency as the unsubstituted hydrocarbon.[7] It is therefore concluded that the hypsochromic shift due to steric distortion cancels out the normal bathochromic effect of methylation. Another interesting case would be dibenz[*a,c*]anthracene in which a hypsochromic shift would be predicted for substitution in the 4,5- or 1,14-positions; but no compounds of this type are known.

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† This approach is similar to that used by Heilbronner and Gerdil (*Helv. Chim. Acta*, 1956, **39**, 1996) and by Dewar (" Steric Effects in Conjugated Systems," ed. Gray, Butterworths, London, 1958, p. 46).

[2] Coulson and Daudel, " Dictionary of Molecular Constants," Centre National de la Recherche Scientifique, Paris.

[3] Friedel and Orchin, " Ultra-violet Spectra of Aromatic Compounds," John Wiley and Sons Inc., New York, 1951.

[4] Newman, *J. Amer. Chem. Soc.*, 1940, **62**, 2295; Newman and Hussey, *ibid.*, 1947, **69**, 3023; Newman and Whitehouse, *ibid.*, 1949, **71**, 3664.

[5] Zinke, Penecke, and Hanus, *Ber.*, 1936, **69**, 624.

[6] Robertson and White, *Proc. Roy. Soc.*, 1953, *A*, **220**, 311.

[7] Jones, *J. Amer. Chem. Soc.*, 1940, **62**, 148; Cason and Phillips, *J. Org. Chem.*, 1952, **17**, 298.