130. *Colour and Constitution. Part I. The Effect of Methyl Substitution on the Ultraviolet Spectra of Alternant Hydrocarbons.*

By David Peters.

The Hückel L.C.A.O. molecular-orbital theory is shown to provide a satisfactory quantitative account of the bathochromic shifts observed in the ultraviolet spectrum when a methyl group is introduced into alternant hydrocarbons. The effect on the ultraviolet spectrum of steric hindrance to coplanarity of the methyl group and the aromatic ring system is discussed.

While the introduction of a methyl group into an alternant * hydrocarbon results in a bathochromic shift in the ultraviolet spectrum,[1] its introduction into a non-alternant hydrocarbon results in either a bathochromic or a hypsochromic shift, depending on the position of substitution.[2] This disparity in the behaviour of the two classes of hydrocarbons stimulated theoretical analysis and the question was examined by Longuet-Higgins and Sowden,[3] by Coulson,[4] and by Pullman, Mayot, and Berthier,[5] using the Hückel L.C.A.O. molecular-orbital (M.O.) method. These authors demonstrated that, in non-alternant hydrocarbons, both the inductive and the conjugative effect of the methyl group must be considered, whereas in alternant hydrocarbons only the conjugative effect is important. The latter effect is the origin of the observed bathochromic shifts. Since the publication of these papers, many data have been accumulated on the magnitude of the bathochromic shifts which occur in the ultraviolet spectra of alternant hydrocarbons on methylation and it is now shown that an extension of the method used by Longuet-Higgins and Sowden [3] gives a satisfactory quantitative account of these results.

Method.—Excellent surveys of the L.C.A.O. (linear combination of atomic orbitals) method are available [6] and no general account will be given here. In the ground state of an alternant hydrocarbon, the π electrons occupy the bonding molecular orbitals in pairs. When electron interaction is neglected, the excitation of lowest energy is from the highest bonding molecular orbital to the lowest antibonding one. When electron interaction is included, it is believed that this particular transition (the p band) retains its identity and there is no mixing of its upper state with other excited states.[7] It is to this transition that the present calculations are applied. The unimportance of the inductive effect in the case of alternant hydrocarbons has been demonstrated [3,4] † and only the conjugative effect will be considered. Mulliken, Rieke, and Brown's suggestion [8] that the methyl group may be regarded as a modified vinyl group is accepted, and the introduction of the methyl group is regarded as resulting in a perturbation of the molecular orbitals of the hydrocarbon.

The expression for the energy of the conjugative shift ($\delta\varepsilon_{ab}$) which follows from these assumptions has been given [3] as

$$\delta\varepsilon_{ab} = \beta_{rs}^2 \, . \, c_{ar}^2 \, . \left\{c_{1s}^2\left(\frac{1}{\varepsilon_b - \varepsilon_1} - \frac{1}{\varepsilon_a - \varepsilon_1}\right) + c_{2s}^2\left(\frac{1}{\varepsilon_b - \varepsilon_2} - \frac{1}{\varepsilon_a - \varepsilon_2}\right)\right\} \quad . \quad (1)$$

---

* An alternant hydrocarbon may be defined for present purposes as an aromatic hydrocarbon containing no odd-numbered rings. A non-alternant contains one or more odd-numbered rings.

† As Crawford [9] has commented, even with as powerful an inductive substituent as the ammonium ion, the change in the ultraviolet spectrum is not large (for other examples, see ref. 19).

[1] Jones, *Chem. Rev.*, 1943, **32**, 1.

[2] Plattner and Heilbronner, *Helv. Chim. Acta*, 1947, **30**, 910, and reference therein.

[3] Longuet-Higgins and Sowden, *J.*, 1952, 1404.

[4] Coulson, *Proc. Phys. Soc.*, 1952, *A*, **65**, 933.

[5] Pullman, Mayot, and Berthier, *J. Chem. Phys.*, 1950, **18**, 257.

[6] (*a*) Dewar, "Progress in Organic Chemistry," Butterworths Scientific Publications, London, 1953, Vol. 2, p. 1; (*b*) Pullman and Pullman, "Les Theories Electroniques de la Chimie Organique," Masson et Cie, Paris, 1952, Chapter 4.

[7] Dewar and Longuet-Higgins, *Proc. Phys. Soc.*, 1954, *A*, **67**, 795.

[8] Mulliken, Rieke, and Brown, *J. Amer. Chem. Soc.*, 1941, **63**, 41; Mulliken and Rieke, *ibid.*, p. 1770.

[9] Crawford, *J.*, 1953, 2065.

where β_{rs} is the resonance integral of the bond between the carbon atom (s) of the methyl group and the ring carbon atom (r), ε_1 and ε_2 are the energies of the bonding and antibonding molecular orbitals of the methyl group, ε_a and ε_b are the energies of the highest bonding and lowest antibonding molecular orbitals of the hydrocarbon, and the *c*'s are atomic orbital coefficients of obvious nomenclature.

In alternant hydrocarbons, $\varepsilon_a = -\varepsilon_b$, and if we assume that the coulomb integral of the pseudo-atom H_3 is equal to that of a carbon atom, then $\varepsilon_1 = -\varepsilon_2$ and $c_{1s}{}^2 = c_{2s}{}^2 = 0{\cdot}5$, and equation (1) reduces to

$$\delta\varepsilon_{ab} = 2\beta_{rs}{}^2 \,.\, c_{ar}{}^2 \left\{\frac{\varepsilon_a}{\varepsilon_1{}^2 - \varepsilon_a{}^2}\right\} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

As Longuet-Higgins and Sowden [3] show, this is a negative quantity and the shift is bathochromic.

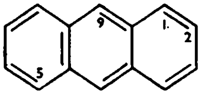
Inserting the usual values of the constants and expressing the energies of the molecular orbitals in units of β, we find the bathochromic shift ($\delta\lambda$) to be

$$\delta\lambda = -475 \,.\, c_{ar}{}^2 \,.\, \left(\frac{\beta_{rs}}{\beta}\right)^2 . \frac{1}{\varepsilon_a(\varepsilon_1{}^2 - \varepsilon_a{}^2)}\,\mathrm{m}\mu \quad . \; . \; . \; . \; . \; . \quad (3)$$

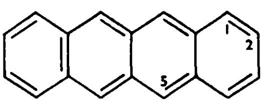
A value of 30,000 cal. per mole has been used for β.[10] The value of the quantity β_{rs}/β remains to be assigned. Previous authors [11] have used a value of 0·7 for it, and it is now found that if a value of 0·51 is used, the data are reproduced well. Hence

$$\delta\lambda = -123{\cdot}4 \,.\, c_{ar}{}^2 \,.\, \frac{1}{\varepsilon_a(\varepsilon_1{}^2 - \varepsilon_a{}^2)}\,\mathrm{m}\mu \quad . \; . \; . \; . \; . \quad (4)$$

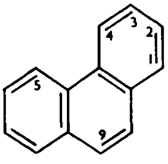
From equation (4), it is clear that, in a given hydrocarbon, the bathochromic shifts are determined by the atomic orbital coefficients of the top bonding molecular orbital. Equation (4) has been used to calculate the bathochromic shifts for those hydrocarbons for which data are available and the results are presented in the Table. A value of 2·5β has been chosen for ε_1.[11] Parentheses indicate that the shift has been estimated from the data for the dimethyl derivatives. In the case of chrysene, 3 : 4-benzophenanthrene, and 1 : 2-benzanthracene, the atomic-orbital coefficients were calculated from the values of the energy of the molecular orbitals given by Pullman and Pullman.[6b]



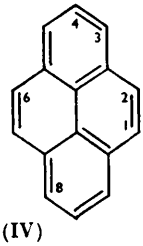
(I)



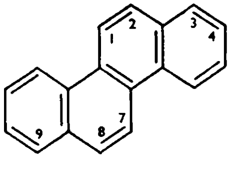
(II)



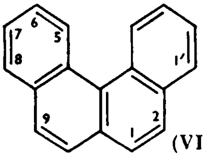
(III)



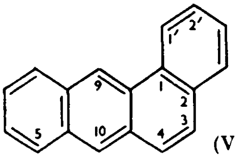
(IV)



(V)



(VI)



(VII).

---

[10] Coulson and Altman, *Trans. Faraday Soc.*, 1952, **48**, 293.

[11] Coulson and Crawford, *J.*, 1953, 2052.

Bathochromic shifts, resulting from methyl substitution, in the p *band of the ultraviolet spectrum of alternant hydrocarbons.*

Hydrocarbon	Position of CH$_3$ group	λ(mμ) of parent	Shift (mμ) Calc.	Shift (mμ) Obs.	Ref.
Benzene *	—	204	8	7	12, 13
Naphthalene	1	276	6	6	14, 15
	2	—	2	0	14, 15
Anthracene (I)	1	374	5	3	16
	2	—	2	(3)	17
	9	—	10	12	17
Naphthacene (II)	1	441	4	(5)	18, 19
	2	—	2	—	—
	5	—	10	8	20
Phenanthrene (III)	1	293	4	(6)	21
	2	—	0	(0—1)	21
	3	—	3	(4)	21
	4	—	2	(4—5)	21
	9	—	6	5	19
Pyrene (IV)	1	334	4	3	19
	3	—	6	8	22
	4	—	0	2	22
Chrysene (V)	1	319	2	5	23
	2	—	6	4	23
	3	—	3	4	23
	4	—	1	1	23
	5	—	2	1	23
	6	—	2	8	23
3 : 4-Benzophenanthrene (VI)	1	314·5	1	1·5	24
	2	—	4	3	24
	5	—	4	6·5	24
	6	—	1	1·5	24
	7	—	2	1·5	24
	8	—	3	3·5	24
1 : 2-Benzanthracene (VII)	1′	341	0	0	25
	2′	—	2	1·5	26
	3′	—	1	2·5	26
	4′	—	1	3·5	26
	3	—	4	0	26
	4	—	4	1	25
	5	—	5	5	25
	6	—	2	2·5	26
	7	—	3	0	26
	8	—	4	5	25
	9	—	7	10·5	25
	10	—	9	13·5	25

* The high symmetry of the benzene molecule leads to degeneracy between the excited states, and the observed agreement may be fortuitous.

Discussion

With regard to the choice of band from the experimental data, the *p* band is the longest-wave intense band.[27, 28] The α band may occur at longer wavelength, but is much less intense and there is rarely any difficulty in identification. The bathochromic shifts have been estimated from the most intense or the best-defined vibrational peaks.

An inspection of the experimental data in the Table shows that there are certain regularities in the bathochromic shifts. The largest shifts occur in the *meso*-positions of anthracene and similar molecules. The α-positions of naphthalene and analogous positions show moderate shifts, while small shifts are found in the β-positions of naphthalene and similar molecules. This situation is exactly that required by the calculations, and the agreement between the calculated and experimental values is very satisfactory when the magnitude of the effect under discussion and the simplicity of the theoretical method are considered. The observed and calculated values appear to differ significantly in certain positions where steric hindrance to coplanarity of the methyl group and the ring is to be expected, and this effect is discussed in detail later.

The bathochromic shifts observed in naphthalene are correctly predicted to be large in

---

[12] Klevens and Platt, *Chem. Rev.*, 1947, **41**, 305.

[13] Klevens and Zimring, *J. Chim. phys.*, 1951—2, **49**, 377.

[14] Morton and de Gouveia, *J.*, 1934, **927**.

[15] de Laszlo, *Compt. rend.*, 1925, **180**, 203.

[16] Mosby, *J. Org. Chem.*, 1953, **18**, 965.

[17] Jones, *Chem. Rev.*, 1947, **41**, 366.

[18] Pogangeanu, *Bull. sect. sci. Acad. roumaine*, 1938, 20, nos. 8—10, 24—8; cf. *Chem. Abs.*, 1940, **34**, 3590^{8}.

[19] Friedel and Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley and Sons, New York, 1951.

[20] Clar, *Ber.*, 1949, **82**, 510.

[21] Askew, *J.*, 1935, 509.

[22] Förster and Wagner, *Z. phys. Chem.*, 1937, *B*, **37**, 353.

[23] Brode and Patterson, *J. Amer. Chem. Soc.*, 1941, **63**, 3254.

[24] Badger and Walker, *J.*, 1954, 3238.

[25] Jones, *J. Amer. Chem. Soc.*, 1940, **62**, 148.

[26] Badger, Pearce, and Pettit, *J.*, 1952, 1112.

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

[28] Platt, *J. Chem. Phys.*, 1949, **17**, 484; 1950, **18**, 1168.

the α- and small in the β-position. Of the three monomethylanthracenes, the ultraviolet spectra of two have been recorded. The 9-methyl derivative shows a large shift and the 1-methyl compound a moderate shift, in agreement with the calculations. The ultraviolet spectrum of 2-methylanthracene is not available, but that of the 1 : 3-dimethyl derivative is known. The shifts being assumed to be additive,* the 2-methyl compound will show a small shift, as required by the theoretical analysis. In the case of naphthacene, the spectrum of the 5-methyl derivative has been recorded and here the calculated and experimental values are in agreement. The bathochromic shift for the 1-position has been estimated from the available data for the 1 : 6-compound to be of the calculated size.

The available data on the ultraviolet spectra of the monomethylphenanthrenes is restricted to that of the 9-methyl compound. The bathochromic shifts for the other four positions have been estimated from data on the dimethyl compounds. The largest shifts occur in the 1-, 3-, and 9-position, while the 2-position shows no shift. These findings agree with the calculations, but in the 4-position, the experimental value is substantially greater than the calculated. This effect may arise from the fact that the 4-position is subject to steric hindrance, the methyl group being forced out of the plane of the ring. The point is discussed later. In view of the possible inaccuracies in the assumption of additivity of the bathochromic shifts, too much emphasis should not be placed on the case of phenanthrene.

The monomethylpyrenes are free from steric effects and the calculated and experimental values are in good agreement. The same result has been reported by Masse,[29] using the L.C.A.O. method. In chrysene, the 2- and the 3-position are calculated to show moderate shifts and the remaining positions to show small shifts. These expectations are fulfilled in four of the six cases, the two exceptions being the 1- and the 6-position where the experimental values are very much larger than the calculated. These are just the positions which must suffer the same steric hindrance to coplanarity of the methyl group and the ring, as does the 4-position of phenanthrene.

The spectra of all of the monomethyl-3 : 4-benzophenanthrenes have been reported in detail by Badger and Walker.[24] They find that the 2-, 5-, and 8-position exhibit larger shifts than do the other three positions, and this is exactly the situation predicted from the calculations. In the 5-position, there is an indication of a steric bathochromic shift. Jones [25] and Badger, Pearce, and Pettit [26] have reported the spectra of all of the monomethyl-1 : 2-benzanthracenes. Their experimental findings are that the 9- and the 10-position show very large shifts, the 5- and the 8-position show moderate shifts, and the remaining positions show small shifts. The results of the present calculations agree thus far with experiment, but there is a measure of disagreement among the positions which show small shifts, with respect to both magnitude and order. This discrepancy is particularly striking in the cases of the 3- and the 4-derivative. If 1 : 2-benzanthracene is regarded as 2 : 3-benzophenanthrene, these positions are seen to be derived from the 9- and the 10-position of phenanthrene, which show moderate shifts. It might be expected that these shifts would persist in the benz-annelated molecule to some degree, and this is the position suggested by the calculations. Nevertheless, the experimental results are that there is no shift in the 3-position and only a 1 mμ shift in the 4-position. The case of 1′-methyl-1 : 2-benzanthracene is also of particular interest since there is no detectable bathochromic shift. This result is completely borne out by the present calculations. Pullman, Berthier, and Pullman [30] have used the L.C.A.O. method to demonstrate the large bathochromic shifts which occur in the 5-, 8-, 9-, and 10-position of 1 : 2-benzanthracene and the absence of a bathochromic shift in the 1′-position.

---

* A survey of the available data [19] for the mono- and di-methylnaphthalenes shows this assumption to be reasonable for present purposes.

[29] Masse, *Compt. rend.*, 1954, **238**, 1226.

[30] Pullman, Berthier, and Pullman, *Acta Intern. Cancer*, 1950, **7**, 140, quoted by Pullman and Pullman, ref. 6*b*, p. 515.

Apart from the complete theoretical treatments mentioned earlier, it has been suggested that the magnitude of the bathochromic shift in alternant hydrocarbons is to be related to the self-polarisability of the methylated carbon atom.[26] Such a correlation does seem to exist but is inferior to the present treatment. In particular, the absence of a bathochromic shift in the 1′-position of 1 : 2-benzanthracene does not follow from the self-polarisability method.

Steric Effects.—One example of the effect of steric crowding within the molecule on the ultraviolet spectrum is well known, that of steric inhibition of coplanarity of two chromophores.[31, 32] The usual example is the case of styrene and α-methylstyrene, where the presence of the methyl group results in a hypsochromic shift of the long-wave band. The accepted explanation of this result is that the methyl group is interfering with the coplanarity of the phenyl and vinyl chromophores, reducing their interaction and producing the observed hypsochromic shift. There is some indication that another example of steric hindrance and its effect on the ultraviolet spectrum is now at hand. The result is, however, a bathochromic shift. As noted earlier, 4-methylphenanthrene, 1- and 6-methylchrysene, and 5-methyl-3 : 4-benzophenanthrene all have substantially larger bathochromic shifts than predicted and in all of them the methyl group occupies a similar position in the molecule, in which steric hindrance to the group's coplanarity with the ring should be greatest. The excess of shift is not large but seems nevertheless to be real. Badger and Walker [24] have commented on this point but were led to doubt the general conclusion that steric hindrance to coplanarity results in a bathochromic shift by the fact that no bathochromic shift occurs in the similar case of 1′-methyl-1 : 2-benzanthracene. It is now shown that such a steric bathochromic shift is to be expected in the general case but that 1′-methyl-1 : 2-benzanthracene should indeed show no such shift.

When a methyl group is situated in the 4-position of the phenanthrene ring or in a similar position, some distortion of the bond lengths or bond angles must occur. No information is available as to the exact outcome, but it seems on general grounds that one of most favourable processes will be the twisting of the methyl group out of the plane of the ring system. Such a distortion will be accompanied by a change in the hybridisation at the ring carbon atom in such a way as to minimise the energy of the resulting system. The sp^2 bond between the ring and the carbon atom of the methyl group will acquire an increased measure of p character and the $2p$ atomic orbital of the ring carbon atom will acquire a measure of s character. The latter orbital will then no longer be parallel with the adjacent pure $2p$ orbitals. The result will be a reduction in the resonance integral between the methylated carbon atom and the adjacent carbon atoms. Such a reduction is readily dealt with by perturbation theory.

Let the methylated carbon atom (p) be flanked by carbon atoms q and r. Then the change in the energy of the ith molecular orbital ($\delta\varepsilon_i$) resulting from a small change in the resonance integral β_{pq} is given [6] by

$$\delta\varepsilon_i = 2c_{ip} \,.\, c_{iq} \,.\, \delta\beta_{pq} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where c_{ip} and c_{iq} are the atomic orbital coefficients of the ith molecular orbital at atoms p and q. The total energy change ($\Delta\varepsilon_i$) of the ith molecular orbital resulting from an equal change ($\delta\beta$) in both β_{pq} and β_{pr} is given to a first approximation by

$$\Delta\varepsilon_i = 2 \,.\, c_{ip}(c_{iq} + c_{ir}) \,.\, \delta\beta . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

From the secular equations,

$$-\varepsilon_i \,.\, c_{ip} + \beta(c_{iq} + c_{ir}) = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

and

$$\Delta\varepsilon_i = 2 \,.\, c^2_{ip} \,.\, \varepsilon_i \,.\, \delta\beta/\beta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

[31] Braude and Sondheimer, *J.*, 1955, 3773, and references therein.
[32] Pullman and Pullman, ref. 6*b*, chapter 8.

In equation (8), $\delta\beta$ is a positive quantity, β is a negative quantity, and, since, for bonding molecular orbitals ϵ_i is negative, the expression on the right-hand side of equation (8) is positive. That is, the bonding molecular orbital is raised by such changes in the resonance integrals. Equally, ϵ_i is positive for antibonding molecular orbitals so that such orbitals are lowered at the same time. The net result is a decrease in the energy of the ultraviolet transition, a bathochromic shift.

At the same time, it is clear from equation (8) that no such shift is to be expected in the case of 1′-methyl-1 : 2-benzanthracene since the magnitude of the bathochromic shift is proportional to the square of the atomic orbital coefficients of the top bonding molecular orbital and this quantity, in the 1′ position of 1 : 2-benzanthracene, is extremely small.

It is encouraging to find that a treatment of this simplicity is capable of giving a quantitative account of the small effects discussed here. The method is also of value in the event of the preparation of methyl derivatives of unknown orientation. While complete discrimination between all positions of a complex hydrocarbon is unattainable, an inspection of the ultraviolet spectrum of the parent hydrocarbon and of the methyl derivative and the calculation of the expected shift will substantially reduce the possibilities.

The author thanks Professor M. J. S. Dewar for reading the manuscript and for helpful advice.

" BRENTWOOD," PLASKYNASTON LANE, RUABON,
DENBIGHSHIRE, WALES.

[*Received, September 5th,* 1956.]