839. *Colour and Constitution. Part III.*† *The Effect of Methyl Substitution on the* α- *and* β-*Bands of the Ultraviolet Spectrum of Alternant Hydrocarbons.*

By DAVID PETERS.

The effect of the methyl group on the α- and β-bands of the ultraviolet spectrum of alternant hydrocarbons is discussed in terms of the Hückel L.C.A.O. molecular-orbital theory. Substantial progress is possible from a purely theoretical analysis but, in order to obtain results as general as those for the *p*-band, the inclusion of an empirical element is essential.

IN general, either three or four bands (α, *p*, β, and β_1 in Clar's nomenclature[1] ‡) are observed in the ultraviolet spectrum of the condensed, six-membered ring, benzenoid hydrocarbons. They are believed to be of the π–π * type, and a molecular-orbital interpretation of these bands, due to Dewar and Longuet-Higgins,[2] will be followed here and is shown diagrammatically in Fig. 1.

It has been shown (Parts I and II) that the effects of the common substituents on the *p*-band of the ultraviolet spectrum of these hydrocarbons may be quantitatively interpreted in terms of this model, the simple Hückel L.C.A.O. molecular-orbital theory. The *p*-band is, however, only one of the three or four bands appearing in these spectra, and the

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† Parts I and II, *J.*, 1957, 646, 1993.

‡ Clar's actual nomenclature is α, *p*, β, and β′ but as the prime is used elsewhere in this paper with a different significance, Clar's β′ is written β_1.

[1] Clar, " Aromatische Kohlenwasserstoffe," Springer-Verlag, Berlin, 1941.

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

next step is clearly to examine how far these methods are applicable to the other bands. It is now shown that, as with the α- and β-bands of the parent hydrocarbons, difficulties arising from first-order configurational interaction [2,3] prevent a complete formal treatment, but if the inclusion of an empirical element is allowed a complete discussion of the methyl substituent is possible.

FIG. 1.

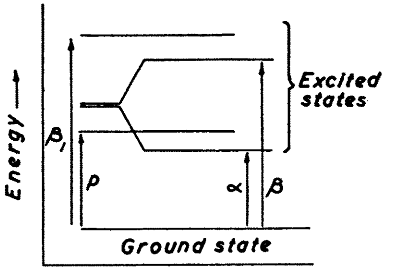
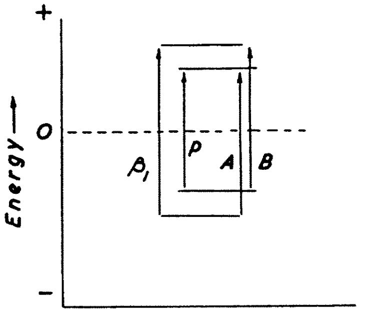


FIG. 2. *Hückel molecular orbitals.*



In the interpretation chosen, then, the *p*-band was derived in a simple manner from the highest bonding and lowest antibonding molecular orbitals, and the β_1-band similarly from the next highest and lowest molecular orbitals. The bathochromic effect of substituents on the *p*-band has been discussed: the bathochromic shifts ($\delta\lambda_{\beta_1}$) of the β_1-band are then given (in mμ) by the same expression as those of the *p*-band (Part I), *viz.*,

$$\delta\lambda_{\beta_1} = -123{\cdot}4c^2_{br}\frac{1}{e_b(e_1^2 - e_b^2)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where e_b is the energy of the second-highest bonding molecular orbital of the hydrocarbon, c_{br} is the coefficient of this molecular orbital at the methylated carbon atom (r), and e_1 is the energy of the bonding molecular orbital of the methyl group. Since $e_b > e_a$, and the term $(e_1^2 - e_b^2)$ is relatively insensitive to small changes in e_b, the β_1-shifts will tend to be smaller than those of the *p*-band. 'For the smaller and more fully investigated benzenoid hydrocarbons, however, the β_1-band falls outside the range of the conventional spectrometers and there is little information by which the accuracy of equation (1) can be examined.

This simple derivation of the *p*- and β_1-bands does not carry over to the α- and β-bands. The latter are derived from the transitions marked *A* and *B* in Fig. 2 in the following way. The molecular orbitals of alternant hydrocarbons are symmetrically distributed about the arbitrary zero of energy (Fig. 2) and this symmetry leads to equal energy for transitions *A* and *B* (Fig. 1) and thus, within the approximations of the Hückel method, to a first-order configurational interaction between their excited states.[2, 3] These excited states are then split by an interaction element γ:

$$\gamma = \sum_{i<j}\int \chi_A \frac{e^2}{r_{ij}} \chi_B \mathrm{d}t \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where χ_A and χ_B are the antisymmetrised wave functions of the excited states of the *A* and *B* transitions.

This completes the description of the origins of the π–π* bands of the ultraviolet spectrum of the alternant hydrocarbons.

Method.—The effect of the methyl substituent is now examined by the method which proved of value for the *p*-band. As in the latter case, the inductive and mesomeric effects are discussed separately.[4]

[3] Moffitt, *J. Chem. Phys.*, 1954, **22**, 1820.
[4] Longuet-Higgins and Sowden, *J.*, 1952, 1404.

Inductive effect. This is defined as the effect arising from the change in coulomb integral ($\delta\alpha_r$) of the carbon atom (r) to which the substituent is attached. The well-known equation [5]

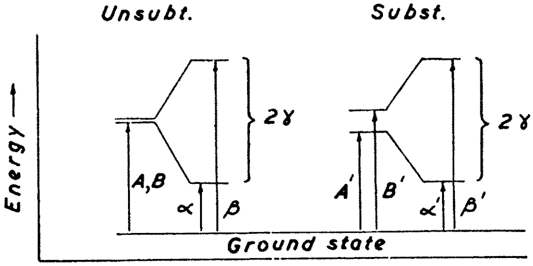
$$\delta e_i = c^2_{ir} \, . \, \delta\alpha_r \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

(where δe_i is the change in energy of the ith molecular orbital, c_{ir} is the atomic orbital coefficient of this orbital at the rth carbon atom) is applied to the A and B transitions with the result

$$\delta E_A = -\delta E_B = (c^2_{ar} - c^2_{br})\delta\alpha_r \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where δE_A and δE_B are the changes in the energy of the A and B transitions and c_{ar} and c_{br} are the atomic orbital coefficients at the rth carbon atom of the highest and second-highest bonding molecular orbitals respectively. The shifts δE_A and δE_B are equal in magnitude and opposite in sign, but, as c_{ar} and c_{br} are only accidentally equal, there is only trivial restriction on the magnitude of δE_A and δE_B. The resulting situation, shown diagrammatically in Fig. 3, is a symmetrical arrangement of the A and B levels about the original level of the A and B configurations. The sum of the A and B (and of the α and β) shifts is zero. The α′ and β′ levels are now separated by $2\gamma'$, where γ' is an interaction element analogous to γ.

FIG. 3.†



† Throughout this paper, primes denote the substituted molecule.

At this point, further progress depends on an evaluation of γ and γ' or their difference, $\delta\gamma$. Unfortunately, it is not easy to evaluate these interaction elements quantitatively, nor does it seem possible to show that $\delta\gamma$ vanishes absolutely. We are faced with the same difficulties as those encountered when the α and β bands of the hydrocarbons themselves are examined by the molecular-orbital method.[2] If we are to confine ourselves to a purely theoretical treatment, we can only discuss the sum of the α- and β-shifts, since, although methods are available for the evaluation of the two electron integrals involved in γ,[6, 7] they are rather too complex and uncertain for the present simple approach. If we are prepared to admit a purely empirical element into the discussion, further progress is possible. In Table 1 is gathered the available information on the shifts which result from the introduction of the purely inductive, ammonium ion group into alternant hydrocarbons.

When it is realised that these small shifts are the result of a substituent whose inductive power is many times greater than that of the methyl group,† it is clear that the inductive effect of the latter group on the ultraviolet spectrum is very small indeed. This conclusion constitutes a practical demonstration that, for the methyl group, $\delta\gamma$ is effectively zero. The expedient of introducing an empirical element into the discussion is unsatisfactory

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† It has been estimated that the inductive effect of the ammonium ion is some ten times greater than that of the methyl group (Peters, *J.*, 1957, 2654).

[5] Coulson and Longuet-Higgins, *Proc. Roy. Soc.*, 1947, *A*, **191**, 39.

[6] Pariser and Parr, *J. Chem. Phys.*, 1953, **21**, 466.

[7] Pople, *Trans. Faraday Soc.*, 1953, **49**, 1375.

from a formal viewpoint but, if it is rejected, the even less attractive alternative of discussing the sum of the α- and β-shifts remains. The difficulty originates in a well-known shortcoming of the Hückel method.[3]

TABLE 1.

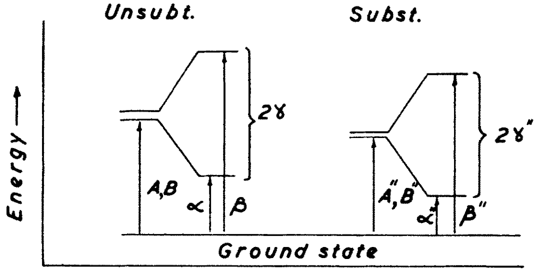
Hydrocarbon	Position of substituent	Shift *p*	Shift α	Shift β	Ref.
Naphthalene	2	0	0	+1	*a*
Anthracene	2	0—2	—	0	*b*
Phenanthrene	2	0	*	Small	*c*
	3	0	*	0	*c*
	9	0	*	Small	*c*
Pyrene	3	+5	+2	+2	*a*
1 : 2-Benzanthracene	3	+2—3	—	+2	*d*
	8	+6	+2	+2	*a*

* These α-band shifts are anomalous, there being a 20—30 mμ hypsochromic shift.

[a] Jones, *J. Amer. Chem. Soc.*, 1945, **67**, 2127. [b] *Idem, Chem. Rev.*, 1947, **41**, 353. [c] Epsztein. *Mem. Services chim. État*, 1951, **36**, 245. [d] Jones, *J. Amer. Chem. Soc.*, 1941, **63**, 151.

Mesomeric effect. The model used for the conjugative action of the methyl group in the discussion of the *p*-band is applied to the α- and β-bands, the group being treated as a modified vinyl group with molecular orbitals of energy ± e_1. The energy change (δe_i) of the *i*th molecular orbital of energy e_i resulting from the formation of the bond of resonance integral β_{rs} from the carbon atom (*r*) of the ring to the carbon atom (*s*) of the methyl group is:[4, 8]

FIG. 4.



$$\delta e_i = \sum_K \frac{c_{ir}^2 c_{ks}^2}{e_i - e_K} \beta_{rs}^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where the *c*'s are atomic orbital coefficients of nomenclature derived from the other quantities. The summation is over the two molecular orbitals of the methyl group ($K = \pm 1$). Applying equation (5) to the *A* and *B* transitions, we have

$$-\delta E_B = -\delta E_B = \left\{ \frac{e_a c_{ar}^2 \beta_{rs}^2}{e_a^2 - e_b^2} + \frac{e_b c_{br}^2 \beta_{rs}^2}{e_b^2 - e_1^2} \right\} \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Substituting the values of the universal constants and expressing the energy quantities in units of β, we have for the shifts $\delta\lambda_A$ and $\delta\lambda_B$ (in mμ)

$$\delta\lambda_A = \delta\lambda_B = \frac{247}{(e_a + e_b)^2} \left\{ \frac{e_b c_{br}^2}{e_b^2 - e_1^2} + \frac{e_a c_{ar}^2}{e_a^2 - e_1^2} \right\} \quad . \quad . \quad . \quad . \quad (7)$$

β_{rs} is taken as 0·51β (Part I), and a value of 30 kcal. per mole is used for β. Since $e_1 > e_a, e_b$, and e_a and e_b are negative energy quantities, it is clear that both the *A* and the *B*

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[8] Dewar, *J. Amer. Chem. Soc.*, 1952, **74**, 3341.

transitions are shifted bathochromically by the same amount. If $e_a = e_b$, then $c_{ar} = c_{br}$ and the expression reverts to that for the *p*-band. The situation before and after the introduction of the methyl group may be represented as in Fig. 4.

TABLE 2.

		λ of parent (mμ)		Shift (mμ)			
				calc.	obs.		
Hydrocarbon	Position of substituent	α	β		α	β	Ref.
Naphthalene	1	311	217	2	3	4	*a, b*
	2			4	8	4	*a, b*
Anthracene	1	—	252	5	—	1	*d*
	2			1	—	—	
	9			2	—	3—4	*c*
Phenanthrene	1	346	252	3	—	—	
	2			3	—	—	
	3			1	—	—	
	4			3	—	—	
	9			3	3	3—4	*b*
Chrysene	1	360	267	4	7	2	*e*
	2			2	2	2	*e*
	3			1	2	2	*e*
	4			5	1	2	*e*
	5			2	2	2	*e*
	6			2	6	4	*e*
Pyrene	1	372	272	1	2	2	*b*
	3			2	4	2	*f*
	4			4	3	3	*f*
3 : 4-Benzophenanthrene	1	354	281	3	5	3	*g*
	2			3	2	2	*g*
	5			2	8	5	*g*
	6			2	2	2	*g*
	7			1	1·5	1·5	*g*
	8			2	3	4	*g*
1 : 2-Benzanthracene	1′	384	287	4	3	0·5	*h*
	2′			2	3·5	3·5	*i*
	3′			2	1	1·5	*i*
	4′			4	3·5	5·5	*i*
	3			3	3·5	3·5	*i*
	4			2	0·5	1·5	*h*
	5			2	1·5	2	*h*
	6			2	0·5	1·5	*i*
	7			1	3	1	*i*
	8			2	2	3	*h*
	9			3	8·5	3·5	*h*
	10			3	5	4	*h*

[a] Morton and de Gouveia, *J.*, 1934, 916. [b] Friedel and Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley & Sons, New York, 1951. [c] Ref. *b* of Table 1. [d] Mosby, *J. Org. Chem.*, 1953, **18**, 964. [e] Brode and Patterson, *J. Amer. Chem. Soc.*, 1941, **63**, 3252. [f] Förster and Wagner, *Z. phys. Chem.*, 1937, **37**, *B*, 352. [g] Badger and Walker, *J.*, 1954, 3238. [h] Jones, *J. Amer. Chem. Soc.*, 1940, **62**, 148. [i] Badger, Pearce, and Pettit, *J.*, 1952, 1112.

Having determined the behaviour of the *A* and *B* transitions, we must consider the derived α- and β-transitions. The situation is similar to that which arose when the inductive effect was examined, differing only in that the excited states of the *A* and the *B* transition are now of equal energy, but are bathochromically shifted. The interaction element γ'' differs from γ and we are again in the position of either retaining the purely theoretical approach and discussing only the sum of the α- and β-shifts or incorporating an empirical element and discussing the shifts separately. Adopting the latter course, we examine the data collected in Table 2 and find that again $\delta\gamma$ is zero to a reasonable approximation. Serious deviations from this generalisation are sometimes apparent in the positions where steric hindrance to coplanarity of the methyl group and the ring is known (Part I) to occur. As with the inductive effect, this appeal to experiment is not the most satisfactory solution but is the best available at present. It should be made clear that we cannot show on theoretical grounds alone that the α- and β-shifts are both bathochromic.

This situation is rather disappointing, for, experimentally, the α- and β-shifts seem to present no more complex a pattern than do those of the *p*-band. The experimental and calculated shifts are gathered in Table 2; e_1 is taken as 2·5β.

Discussion.—With regard to the experimental data, the β-band is usually an intense, well-developed single peak, sometimes with ill-defined shoulders or subsidiary peaks. The weak α-band is usually rather poorly developed, having an irregular fine structure, and difficulties sometimes arise in the estimation of the shift or in the identification of the vibrational peaks in the derivative. In anthracene and naphthacene, the α-band is completely hidden beneath the strong *p*-band.

One quite general conclusion from the experimental data collected in Table 2 is that, when positions subject to steric effects are excluded, the α- and β-shifts of all the monomethyl-substituted derivatives of any one of the parent molecules scatter less about their mean than is the case in the corresponding *p*-shifts. This may be seen from Table 3.

TABLE 3. *Range between minimum and maximum experimental shifts of monomethyl derivatives.*

Me deriv. of:	*p*	α	β	Me deriv. of:	*p*	α	β
Naphthalene	6	5	0	Pyrene	6	2	1
Anthracene	9	—	2—3	3 : 4-Benzanthracene	2	3	2
Chrysene	3	1	2	1 : 2-Benzanthracene	13·5	5	5

This close grouping of the α- and β-shifts is a consequence of equation (7), as the following argument shows. Consider a position in a given hydrocarbon at which $\delta\lambda_p$ is large. For this to be so, it is sufficient that c_{ar} be large; for $\delta\lambda_\alpha$ and $\delta\lambda_\beta$ to be large, however, both c_{ar} and c_{br} must be large at the same atom. Clearly, the latter situation is much less probable than that c_{ar} or c_{br} alone is large, and, in fact, the two atomic orbital coefficients tend to balance each other owing to the relation $2\sum_{a} c_{ar}^2 = 1$ (ref. 9). The same reasoning shows that a zero shift of the α- and β-bands is equally unlikely. This levelling of the α- and β-shifts is brought out quite clearly by the experimental data and has the practical result that the *p*-band is of greater value for diagnostic work.

For present purposes, the close grouping of the α- and β-shifts, together with the inaccuracies in the assumption that the α- and β-shifts are equal, make it difficult to compare the calculated and experimental shifts critically. On occasion, the range covered by these shifts is comparable with the probable error in the method. Since we now have three bands to discuss, however, conclusions of a broader kind are possible.

The methylnaphthalenes are well documented. De Laszlo [10] has commented that the *p*-band shows the larger bathochromic shift when the methylation is in the 1-position, while the α-band is affected to a greater extent by methylation in the 2-position. The results presented in Part I and in this paper explain this situation precisely.

In anthracene, *meso*-methylation causes a marked bathochromic shift of the *p*-band but a much smaller shift in the β-band. This qualitative conclusion is correctly predicted by the calculation, but there is some discrepancy between the magnitudes of the calculated and experimental shifts.

In phenanthrene, only the 9-methyl compound has a recorded spectrum. The agreement between the calculated and the observed values of the α- and β-shifts is good, and it may be predicted that the other positions will show quite small α- and β-shifts. This consideration alone will probably prove to be inadequate for the 4-position, steric hindrance to coplanarity of the methyl group and the ring causing a further, perhaps quite large, bathochromic shift.

Steric bathochromic shifts of the α- and β-bands are apparent in the 1- and the 6-position in chrysene. This is also the case with the *p*-band. These steric shifts are large compared with the mesomeric shifts, and are not equal for the α- and β-bands. In pyrene,

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[9] Coulson and Rushbrooke, *Proc. Camb. Phil. Soc.*, 1940, **36**, 193.

[10] De Laszlo, *Compt. rend.*, 1925, **180**, 203; *Proc. Roy. Soc.*, 1926, *A*, **111**, 377.

the α- and β-shifts show the usual close grouping but it may be noticed that the zero shift of the *p*-band in the 4-position—owing to a zero value of the atomic orbital coefficient of the top bonding molecular orbital—does not occur in the α- and β-bands.

The most prominent feature of the α- and β-shifts of 3 : 4-benzophenanthrene is the marked steric bathochromic shift in the 5-position. The 9-position of 1 : 2-benzanthracene shows the same effect; in this hydrocarbon, the close grouping of the α- and β-shifts compared with the wide range of the *p*-shifts, is brought out very clearly.

This paper and Part I deal explicitly only with the methyl substituent, but there is no doubt that the larger alkyl groups behave similarly. Anderson and Smith's data [11] on the alkylnaphthalenes exemplify this generalisation. There is a possible complication in that the steric requirements of the larger alkyl groups may affect the magnitude of the steric bathochromic shifts which occur in certain positions with the methyl group, and also may cause such shifts in positions where the methyl group is not sufficiently bulky to do so. For this reason, caution is required in applying the present method to very bulky alkyl groups, such as the *tert.*-butyl radical.

Application of this method to simple olefins and polyenes is straightforward, as the success of Woodward's rules [12] shows. The latter are a particular case of this method.

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" Brentwood," Plaskynaston Lane, Cefn Mawr, Wrexham, Denbighshire.
[Present address: Royal Holloway College,
Englefield Green, Surrey.]

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[11] Anderson and Smith, *J. Inst. Petroleum*, 1952, **38**, 426.

[12] Woodward, *J. Amer. Chem. Soc.*, 1941, **63**, 1123; 1942, **64**, 72, 76.