676. *Colour and Constitution. Part II.* Aromatic Hydrocarbons.*

By M. J. S. Dewar.

An extension of the treatment, applied in Part I * to basic dyes, is described by which the first absorption maxima of aromatic hydrocarbons can be predicted with very little labour. The absorption spectra of such compounds are discussed, and reasons given for identifying the first transition with the first absorption maximum with log ε not appreciably less than 4. The agreement between the predicted and observed wave-lengths of such bands is remarkably good, much better than the agreement with the values predicted by LCAO MO theory (to which the present treatment is a first approximation). A possible explanation of this apparent anomaly is given. Agreement is bad for the peropyrenes; reasons are given for ascribing this failure to an unusually large " fixation " of certain double bonds in them. Agreement also appears to be bad for the compound to which Clar ascribed the structure (I); it is suggested that it may in fact have been the isomer (III), in the event that it proves not to have a band in the infra-red as predicted for (I).

In Part I * a set of rules was derived theoretically for the relation between colour and constitution in odd alternant † ions such as the ions of basic dyes. These rules were obtained by a modification ‡ of the usual LCAO MO method in which perturbation theory was used to estimate approximately the effects of structural changes on the light absorption of such compounds. Such a treatment cannot be applied directly to even alternant systems, like those present in aromatic hydrocarbons and polyenes; but a variation of it will now be described whereby the frequency of the first absorption band (FFAB) of an even alternant hydrocarbon can be calculated with a minimum of labour and with surprising accuracy.

In the PMO (perturbation molecular orbital) method the energy levels of a conjugated molecule RS are calculated from those of R and of S by regarding their combination to RS as a perturbation and applying the familiar methods of perturbation theory. This technique has been used to develop a general semiquantitative theory of chemical reactivity, full details of which are in course of publication (*J. Amer. Chem. Soc.*); here the same procedure will be used to investigate the light absorption of even alternant hydrocarbons.

Method.—In general, the energy difference between RS and (R + S) is a second- and higher-order perturbation energy, the first-order perturbation vanishing. An exception arises in the case where R and S are both odd alternant hydrocarbons; *e.g.*, when R = S = benzyl, RS = stilbene. An odd alternant hydrocarbon has a non-bonding § MO (NBMO) of zero energy in LCAO MO approximation, *i.e.*, an MO of energy identical with that of a carbon $2p$ AO. The degeneracy of the two NBMO's in (R + S) leads to a first-order perturbational splitting of the level in forming RS [if RS is to be a normal even alternant hydrocarbon, the two NBMO's in (R + S) must have contained just two electrons between them; in RS these can be accommodated in the lower of the two MO's corresponding to the original zero-energy NBMO's, and consequently there is a first-order perturbation energy difference between (R + S) and RS].

Suppose the linkages in RS are between atom number m in R and atom number m in S,

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* Part I, *J.*, 1950, 2329.

† In an alternant compound the conjugated atoms can be divided into two sets, " starred " and " unstarred," such that no two atoms of the same set are directly linked. Compounds are excluded from this category only if they contain odd-numbered mesomeric rings (*e.g.*, azulene, fulvene). The special properties of alternant hydrocarbons were first indicated by Coulson and Rushbrooke (*Proc. Camb. Phil. Soc.*, 1940, **36**, 193).

‡ Similar methods have been used by Matsen (*J. Amer. Chem. Soc.*, 1950, **72**, 5243) in a study of the light absorption of benzene derivatives.

§ The term " non-bonding MO " in this connection is due to Longuet-Higgins (*J. Chem. Phys.*, 1950, **18**, 265), who has discussed the properties of such orbitals in detail. See also Coulson and Rushbrooke, *loc. cit.*

atom *n* in R and atom *n* in S, etc.; then it can be shown * that, to the approximation of first-order perturbation theory, the NBMO's (of zero energy) of R, S, are replaced in RS by two MO's of energy $\pm E$ with

$$E = \beta(a_m b_m + a_n b_n + \ldots .) \qquad (1)$$

where a_m is the coefficient of the AO of atom *m* in the NBMO of R, and b_n the corresponding coefficient in the NBMO of S, and β is the C–C resonance integral.† It follows that the difference in total π-electron energy between RS and (R + S) is given to this approximation by $2E$, since the two odd electrons in the NBMO's of (R + S) can both occupy the corresponding bonding perturbed MO in RS of energy $-E$.

Now as a general rule ‡ the union of R and S to form RS alters the energies of the MO's but does not alter their order; so that the highest occupied and lowest unoccupied MO's of RS correspond to the highest occupied and lowest unoccupied MO's in (R + S). In the case we are considering these are the NBMO's of R and of S; hence, to the approximation of first-order perturbation theory, the highest occupied and lowest unoccupied MO's of RS have energies $\pm E$, with E given by equation (1). The FFAB ν_0 of RS should then be given by

$$h\nu_0 = 2E = 2\beta\sum_m a_m b_m \qquad (2)$$

or equivalently, the wave-length λ_0 of the first absorption bond by

$$\lambda_0 = \frac{c}{\nu_0} = \frac{hc}{2\beta}\Big(\sum_m a_m b_m\Big)^{-1} = C\Big(\sum_m a_m b_m\Big)^{-1} \qquad (3)$$

where C is an empirical constant, since in the simple LCAO method the resonance integral β is determined empirically. (In this argument it is implicitly assumed that the FFAB corresponds to a transition between two π-orbitals, *i.e.*, a π–π transition; this point will be discussed later.)

An ambiguity arises in applying equation (3), since the energy difference E depends on the mode of partition of the even hydrocarbon RS into two odd radicals. That this should be so can be seen clearly from the fact that the difference in π-electron energy between RS and (R + S) will be less, the more stable the radicals R and S, and this energy difference is also given in the present approximation by $2E$.

This ambiguity can be resolved by the following argument. It can be shown that the effect of the second-order perturbations is to reduce the splitting of the two levels in question. If then, as seems reasonable, higher perturbations can be neglected, the value for λ_0 estimated from (3) will necessarily be too small. The best estimate of λ_0 will then be given by that mode of partition of RS which minimises E and so maximises λ_0. A proviso should be added that if any of the R–S bonds in RS link inactive § atoms in R or S, so that the corresponding products $a_m b_m$ vanish, these bonds will not contribute to the first-order perturbation energy E, but they will contribute to the higher-order perturbations which are being neglected. The mode of partition of RS should therefore

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* Full details will be found in the forthcoming papers referred to above.

† The usual simplifying assumptions are made that all C–C resonance integrals between adjacent atoms are similar, and that resonance integrals between non-adjacent atoms, and also overlap integrals, can be neglected.

‡ This non-crossing rule holds rigorously if no level of RS is the same as one of R or of S, since it can then be shown (Dewar, *Proc. Camb. Phil. Soc.*, 1949, **45**, 639) that the levels of RS interlace with those of (R + S). The only cases where this condition is not fulfilled are those where a level in R or S is degenerate, or where an MO of R or S has vanishing coefficients at the points of union with S or R respectively in RS. The latter condition seldom arises, and in the cases under consideration here the relevant orbitals of R and of S are non-degenerate.

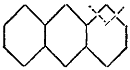
§ If the coefficient of an AO in the NBMO of an odd alternant hydrocarbon vanishes, that atom is called "inactive" (see Longuet-Higgins, *loc. cit.*).

be one in which none of the terms in the summation vanishes, *i.e.*, one in which the uniting bonds are all between pairs of active atoms in R and S.

No general rules can be given for finding this optimum mode of partition; but two guiding principles limit the choice. First, minimising E implies, as we have seen, that the radicals R and S should be the most stable pair into which RS can be dissected; and secondly, the number of terms in the sum, and so the number of bonds broken, should be as small as possible. In all the cases studied, with two exceptions, the optimum partition has involved the breaking of just two bonds.

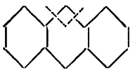
The NBMO coefficients can be found extremely simply by the method discovered by Longuet-Higgins (*loc. cit.*), and even in the most complex hydrocarbons their calculation can be effected in a few minutes. The labour involved in calculating λ_0 for all the reasonable modes of partition of a given AH (alternant hydrocarbon) is therefore very small.

Example.—The method can be illustrated by an example, *viz.*, anthracene. One would expect the optimum pair of radicals to be one in which two of the three aromatic rings remained intact, other pairs of radicals being less stable; calculation shows in fact that the sum in equations (1)—(3) is appreciably greater for partitions of the latter type. Values of the sum are given below for the remaining five modes; * clearly the optimum mode is that involving partition into two benzyl radicals. Since the corresponding value for benzene is unity, the FFAB's of benzene and anthracene should be in the ratio 7 : 4 (for comparison with observation, see Table 1).

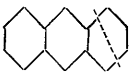


$E = 4/\sqrt{26}$

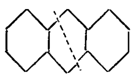
$E = 4/\sqrt{18}$



$E = 4/\sqrt{40}$



$E = 4/\sqrt{37}$



$E = 4/\sqrt{49} = 4/7$

Results.—In this way the FFAB's of the normal fused-ring aromatic hydrocarbons with up to six rings have been calculated together with those of a few hydrocarbons of greater complexity. The corresponding wave-lengths are given (in mμ) in Tables 1 and 2. The constant C in equation (3) was fixed by equating λ_0 for benzene to 208 mμ.† In Table 1 are also given some values for λ_0 found by solving the LCAO MO secular equations, for comparison with the values given by the present approximate treatment and with experiment (these calculations are taken from Pullman and Pullman, "Les Théories Electroniques de la Chimie Organique," Masson, Paris, 1952).

Experimental Values.—The quantities that have been predicted are the wave-lengths of the absorption bands corresponding to the first π–π transitions. As several authors have pointed out (see Pullman and Pullman, *op. cit.*, for references), the simple MO method does not distinguish between singlet and triplet excited states, and consequently the predictions should properly be compared with the means of the transition energies for the first singlet–singlet and singlet–triplet transitions.

Unfortunately, the singlet–triplet separations are known only in a few cases, and so some method is necessary for deriving such means from the observed singlet–singlet transitions. Some authors (see Pullman and Pullman, *op. cit.*) have assumed that the separations of the first excited singlet and triplet levels are constant, but an alternative assumption would be that the singlet–singlet and singlet–triplet transition energies are proportional to one another. The latter assumption seems to be supported by the values quoted in Table 3 (the singlet–triplet transitions were measured by McClure, *J. Chem. Phys.*, 1951, **19**, 670; the values for the singlet–singlet transitions are discussed below. Note that the singlet–triplet separations are not constant).

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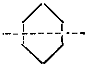
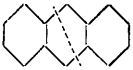
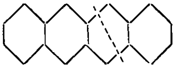
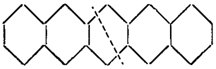
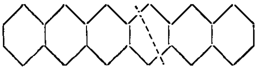
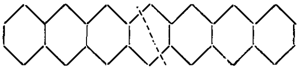
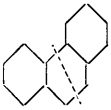
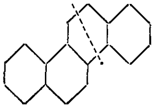
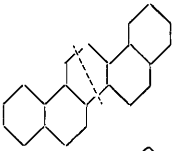
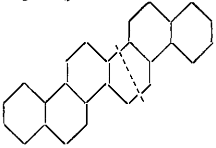
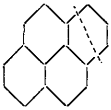
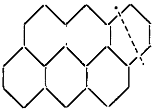
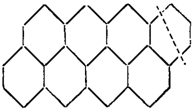
* Note that in (*a*)—(*c*) single atoms are detached (formally R or S = methyl). This is legitimate since the 2*p* AO of a methyl radical has the same energy, in this approximation, as a NBMO. The corresponding coefficient in equations (1)—(3) is of course unity.

† In the simple LCAO MO treatment, the first transition in benzene is four-fold degenerate. Inclusion of electron spin removes this degeneracy; so in comparing the calculated and observed values for benzene, the observed value taken should be the mean (208 mμ) of the four corresponding singlet–singlet transitions. This argument is due to Platt (*J. Chem. Phys.*, 1950, **18**, 1168). It so happens that the first intense transition in benzene lies at about the same wave-length.

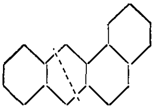
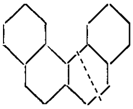
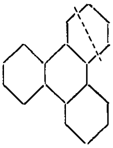
TABLE 1. *Light absorption of condensed aromatic hydrocarbons.*

Compound *	λ_0, calc.: (*a*) PMO	λ_0, calc.: (*b*) Secular equation	λ_0, obs.
	(208)	(208)	208
	259	337	275
	364	503	375
	454	618	474
	589	950	581
	714	—	693[a]
	883	—	—
	328	343	293

Compound *	λ_0, calc.: (*a*) PMO	λ_0, calc.: (*b*) Secular equation	λ_0, obs.
	308	304	319
	320	439	329
	326	—	340[b]
	360	467	364
	406	—	433
	588	—	589[c]

[a] Clar, *Ber.*, 1948, **81**, 63. [b] Private communication from Dr. E. Clar. [c] Clar, *Ber.*, 1943, **76**, 332.
* Kekulé double bonds are omitted.

TABLE 2. *Light absorption of condensed aromatic hydrocarbons.*

Compound *	λ_0, calc. (PMO)	λ_0, obs.
	351	359
	284	317
	245	257

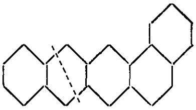
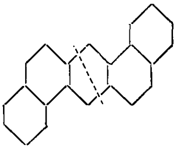
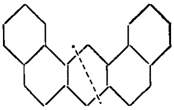
Compound *	λ_0, calc. (PMO)	λ_0, obs.
	482	453
	346	351
	319	338

TABLE 2—*continued.*

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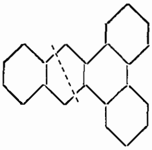
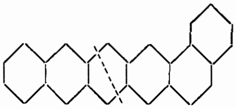
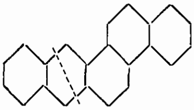
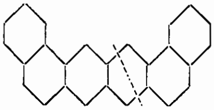
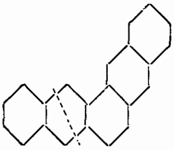
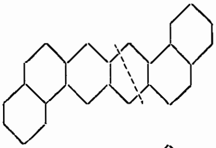
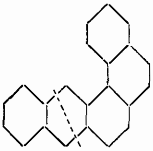
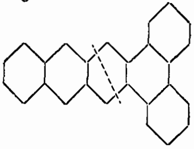
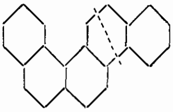
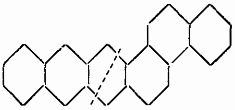
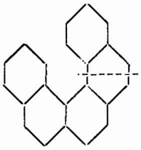
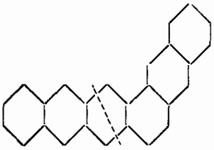
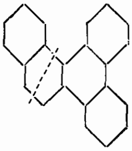
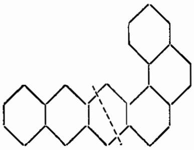
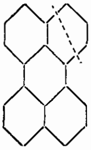
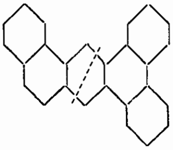
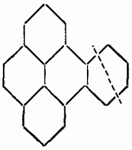
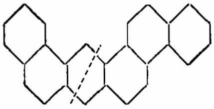
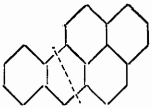
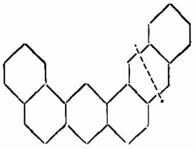
	317	336		546	551 [c]
	368	367		394	438 [d]
	357	348		407	438, 411 [d]
	357	—		378	441, 414 [e]
	302	—		450	—
	296	330 [a]		427	443
	294	—		435	—
	395	434		302	345
	323	331 [b]		332	—
	449	385		355	—

TABLE 2—*continued.*

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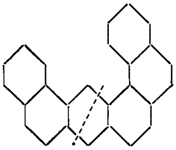
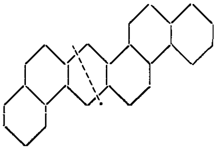
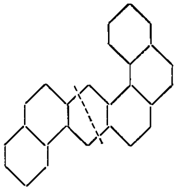
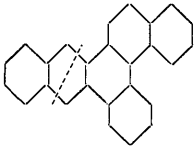
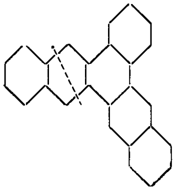
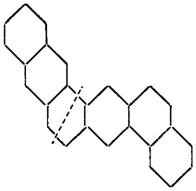
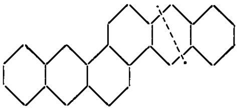
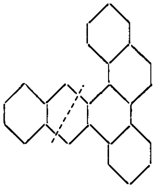
	342	—
	360	371 [d]
	350	—
	330	—
	317	—
	354	368
	380	420
	344	—

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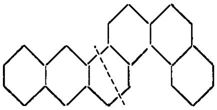
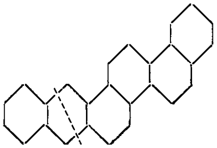
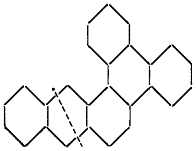
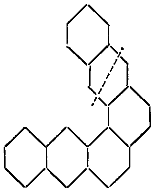
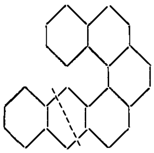
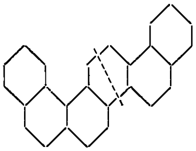
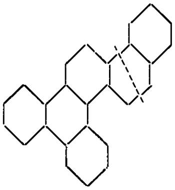
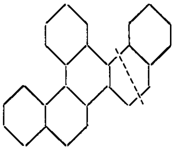
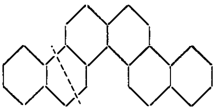
	340	—
	366	—
	369	—
	367	—
	359	—
	317	—
	305	—
	296	—
	292	—

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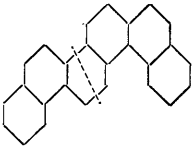
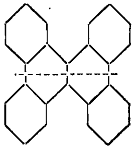
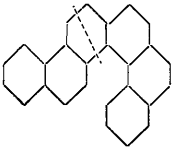
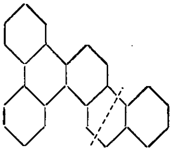
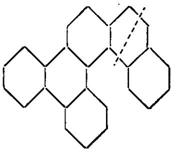
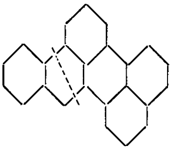
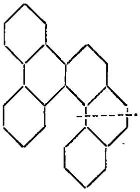
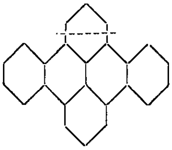
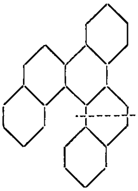
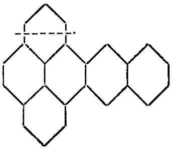
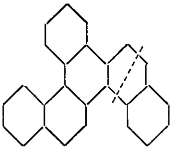
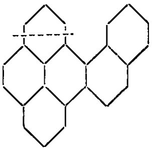
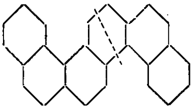
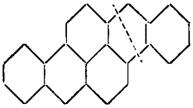
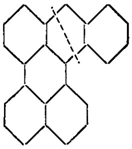
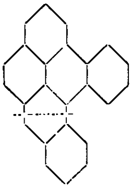
	317	—		347	—
	310	—		305	—
	296	—		444	—
	296	—		299	377, 329[c]
	312	—		321	—
	300	—		349	—
	292	—		512	451
	554	—		416	402[c]

TABLE 2—*continued.*

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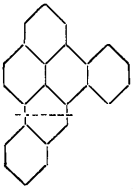
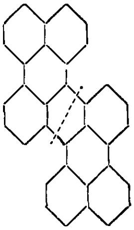
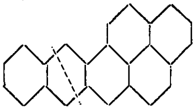
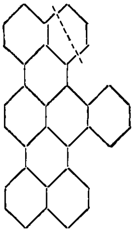
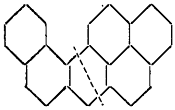
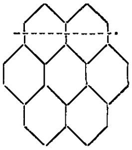
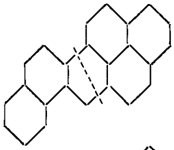
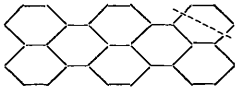
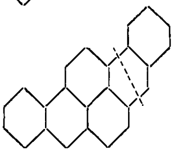
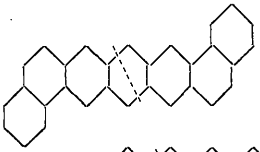
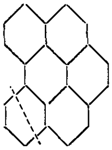
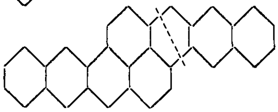
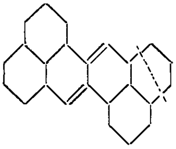
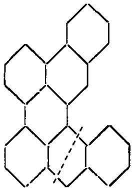
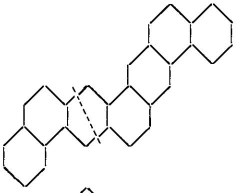
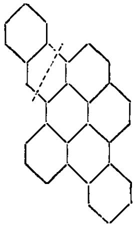
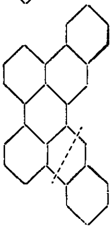
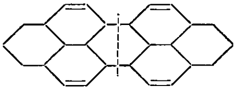
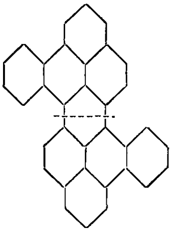
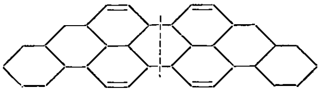
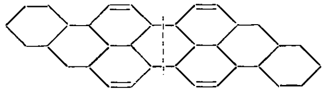
	392	378 [c]		843	643 (?) [f]
	456	458		641	643 (?) [f]
	420	—		293	341
	456	—		505	516 [g]
	474	433		509	529 [h]
	342	388		680	582 [i]
	660 (527)	—		549	503 [j]
	355	368		402	402 [j]
	439	433			

TABLE 2—*continued.*

Compound *	λ_0, calc. (PMO)	λ_0, obs.	Compound *	λ_0, calc. (PMO)	λ_0, obs. [k]
	624 (457)	458 [k]		506	445 [k]
	740 (479)	498 [k]			
	759 (493)	523 [k]			

[a] Bergmann and Szmuszkovicz, *J. Amer. Chem. Soc.*, 1951, **73**, 5150. [b] Clar, *Ber.*, 1943, **76**, 609. *Idem, Ber.*, 1948, **81**, 63. [d] *Idem, Ber.*, 1943, **76**, 151. [e] *Idem, Ber.*, 1948, **81**, 68. [f] Clar and Guzzi, *loc. cit.* [g] Clar and Sandke, *Ber.*, 1949, **82**, 52. [h] Clar, *Ber.*, 1948, **81**, 261. [i] *Idem, J.*, 1949, 2013. [j] *Idem, Ber.*, 1949, **82**, 46. [k] *Idem, Ber.*, 1943, **76**, 458.

If this is true in general, then the first singlet–singlet (E_{11}) and singlet–triplet (E_{13}) transition energies will be related by:

$$E_{13} = kE_{11} \qquad (4)$$

where k is a constant. The mean, $\bar{E}$, of the two transition energies is then given by

$$E = \tfrac{1}{2}(E_{11} + E_{13}) = \tfrac{1}{2}(1 + k)E_{11} \qquad (5)$$

The predicted value for E is of the form $x\beta$ [cf. equation (2)] where β is the empirical resonance integral; it follows that the calculated values can be referred directly to singlet–singlet transitions by using a different value β' for the resonance integral with

$$\beta' = 2\beta(1 + k)^{-1} \qquad (6)$$

This has been done implicitly in Tables 1 and 2, the adjustable parameter in equation (3) being chosen to give agreement between the calculated and observed values of λ_0 for the first singlet–singlet transition of benzene.

TABLE 3. *Comparison of first singlet–singlet and singlet–triplet transition energies.*

Compound.	E_{11} (cm.$^{-1}$)	E_{13} (cm.$^{-1}$)	($E_{11} - E_{13}$) (cm.$^{-1}$)	E_{13}/E_{11}
Benzene	51,900	29,400 [a]	22,500	0·61
Naphthalene	36,400	21,300	15,100	0·59
Anthracene	26,700	14,700	12,000	0·55
Phenanthrene	34,100	21,600	12,500	0·63
1 : 2-Benzanthracene	32,200	16,500	15,700	0·59
Chrysene	31,400	19,800	11,600	0·63
Triphenylene	38,900	23,800	15,100	0·61
1 : 2-5 : 6-Dibenzanthracene	31,500	18,300	13,200	0·64

[a] Values for E_{13} are those reported by McClure, *J. Chem. Phys.*, 1951, **19**, 670.

The identification of the first singlet–singlet transition presents difficulties, since the study of the spectra of aromatic hydrocarbons is still in its infancy. No ambiguity arises in the polyacenes, where the first absorption bands are invariably intense; but in other cases there are often several weak bands (log ε <3) to the long-wave side of the first intense band (log $\varepsilon \sim 4$). It is necessary to decide which of these regions of absorption corresponds to the first π–π singlet–singlet transition.

It seems natural on general grounds to identify this with the first intense maximum, since the MO method predicts a large transition moment for the first π–π band (except in the rare cases where the transition is forbidden through symmetry). This assumption is also supported by analogy from a consideration of the vibrational fine structure of the bands. In the polyacenes the first transitions show a regular vibrational structure, apparently corresponding to the fundamental and overtones of a single vibration in each case, and the spacing is invariably in the range 1100—1500 cm.$^{-1}$. The first intense absorption bands of other aromatic hydrocarbons have a similar fine structure in all cases where it is resolved. The weaker bands at lower frequencies usually show a more complex structure with other vibrations appearing. Since bands of the former type almost certainly correspond to the first normal π–π transitions in the case of polyacenes, where there is no ambiguity, it seems natural to identify the analogous bands of other hydrocarbons with similar transitions.

The origin of the weaker bands would then remain to be elucidated. Possibly an explanation may be found in terms of σ–π interactions of the kind considered by Altmann (*Proc. Roy. Soc.*, 1951, *A*, **210**, 343) and shown by him to provide a possible explanation of the analogous weak band in ethylene near 200 mμ.

There is no reason why in a vibrational band system the zero–zero transition should be the most intense. It is so in the polyacenes, but in 1 : 2-benzanthracene, for instance, the first excited vibrational peak is the highest. The transition energies calculated by MO theory are electronic transition energies, and they should therefore be compared with those observed for zero–zero transitions. This implies, for example, that the "observed" first absorption band of 1 : 2-benzanthracene must be taken to be the first peak at 359 mμ, not the more intense vibrational level at 341 mμ. Since, however, the absorption maxima quoted in the literature commonly correspond to the maxima of the first band systems and not of the first peaks in them, it is important to have the actual absorption spectrum for reference to avoid this ambiguity. The experimental results given in Tables 1 and 2 correspond to the first peak in the first absorption band with log ε not appreciably less than 4; and they are given only for compounds whose absorption spectra have been published. In one or two cases, where there is still ambiguity, values for both peaks are given.

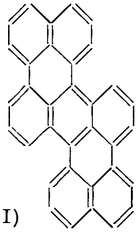
One further complication is the fact that the absorption maxima of hydrocarbons show appreciable solvent effects. Ideally, absorption spectra of the vapours should be used for comparison, but since these are seldom available the data in Tables 1 and 2 refer to solutions (usually in alcohol). The variations due to solvent effects are unlikely to exceed 10 mμ, or at most 20 mμ, and errors of this magnitude are negligible in the present connexion.

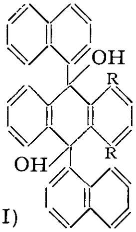
Except where explicitly stated the data are taken from Clar ("Aromatische Kohlenwasserstoffe," Berlin, 1941).

Discussion.—The general agreement between theory and experiment shown in Tables 1 and 2 is astonishingly close, considering the crudity and simplicity of the theoretical methods used. In one respect the agreement is almost embarrassing since the LCAO MO method, to which the present treatment is a first approximation, is unsatisfactory (cf. Table 1). A possible explanation for this curious situation may be suggested. It is known that the failure of the LCAO MO method (in its simple form) is due mainly to its neglect of electron spin and to the resulting lack of antisymmetry in the corresponding molecular wave-functions, and possibly also to its neglect of configurational interaction. Now, it seems likely that in the most complete MO treatment of an odd alternant hydrocarbon radical, when all these factors have been taken into account, it will still appear that the odd unpaired electron occupies something analogous to the NBMO of the simple theory. If then the present perturbation treatment were applied to the formation of RS from (R + S), but with use of the best possible anti-symmetrised MO wave-functions for R and S, instead of simple product wave-functions, the results might not differ significantly from those given by the present simple treatment. In other words, the effects of electron spin, etc., on RS and (R + S) may well be similar so that in the present treatment their effects cancel, and the results obtained are in effect first approximations, not to the simplified MO treatment, but to the antisymmetrised molecular orbital method with configurational interaction.

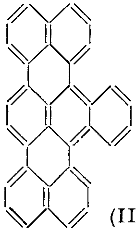
The general success of the present treatment focuses attention on the few cases where it fails badly. The most interesting of these is the compound formulated by Clar and Guzzi (*Ber.*, 1932, **65**, 1521) as (I). This was obtained by treating (II; R = H) with aluminium chloride, and as the authors themselves pointed out, the chemical evidence that the resulting compound was (I), although suggestive, by no means excluded the isomeric structure (III).* The predicted first absorption for (III) (641 mμ) agrees almost exactly with that observed (643 mμ) by Clar and Guzzi for their product. On the other hand, they did not study the absorption spectrum beyond 700 mμ, at which point the extinction coefficient was still very high ($\log \varepsilon = 3$); and it is possible that there may be an additional band, as predicted for (I), at about 840 mμ. Evidently, the structure and absorption spectrum of Clar's hydrocarbon should be reinvestigated.

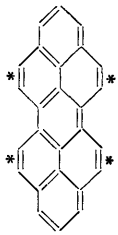
Large discrepancies are also observed in the peropyrene series—both in peropyrene itself (IV) and in the two dibenzo-derivatives (V) and (VI). Reasonable agreement is found, however, for the third dibenzo-derivative (VII). Now, the bond orders in (IV) should alternate more than the bond orders in most aromatic hydrocarbons, since each of the lateral bonds [asterisked in (IV)] is double, and each adjacent bond single, in all but one principal resonance form.† The corresponding variations in bond length will alter the C–C resonance integrals. Numerous authors have, of course, considered this effect and devised methods to allow for it (see, *e.g.*, Lennard-Jones, *Proc. Roy. Soc.*, 1937, *A*, **158**, 280). No attempt will be made to apply any such refined treatment here; but it may be noted that if allowance is made in a crude manner by ascribing values ‡ of 1·09β and 0·91β, respectively, to the " strong " and " weak " bonds in (IV), the calculated value for λ_0 falls to 457 mμ in exact agreement with experiment, and similar calculations for (V) and (VI) give values for λ_0 of 479 and 493 mμ, respectively, which are also close to those actually observed. This variation in the C–C resonance integral seems of a very reasonable order of magnitude in view of the magnitude of the alternation in bond order that would be expected in these compounds [the bond orders in (IV) are being calculated by standard methods to test this prediction]. It seems very likely, therefore, that the bond-order effect is real, the more so since a similar explanation will be shown in the following paper to account satisfactorily for the light absorption of the polyenes where the effect becomes very large.


(I)

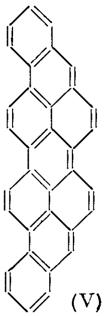


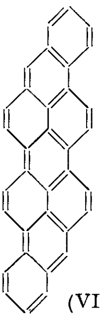
(II)

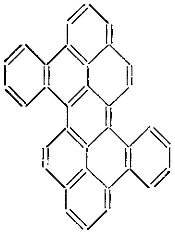

(III)



(IV)


(V)


(VI)


(VII)

Hence, it might appear that the present method could be improved by calculating (by

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* The only evidence adduced was that the 1 : 4-dimethyl derivative (R = Me) of (II), which cannot cyclise to a compound analogous to (I), gave no similar product; and that the hydrocarbon gave an adduct reversibly with maleic anhydride. Both (I) and (III) could add maleic anhydride across the *meso*-positions without stereochemical difficulties arising, and both should react with comparable ease; while the failure of the reaction of (II; R = Me) with aluminium chloride is scarcely significant since (II; R = H) itself reacted to give (I) [or (III)] only under carefully controlled conditions.

† This use of resonance theory can be justified by an argument based on the PMO treatment (Dewar and Longuet-Higgins, *Proc. Roy. Soc.*, in the press), but the same conclusion could in any case be reached by calculating approximately the relevant bond orders, making use of the PMO techniques to which reference was made above.

‡ The values ascribed were actually $\beta \,.\, 2^{\frac{1}{8}}$ and $\beta \,.\, 2^{-\frac{1}{8}}$ respectively, being chosen by analogy with the values found appropriate for polyenes (see following paper).

the PMO method) approximate bond orders in each hydrocarbon, assuming constancy of the C–C resonance integrals, and then allowing for the changes in those resonance integrals due to the variations in the orders, and so the lengths, of the various bonds in calculating the FFAB by the method indicated here. In view of the crudity of the whole treatment, and of the fact that in the majority of aromatic hydrocarbons the bond orders vary little, such a refinement would be somewhat gratuitous.* It is interesting that even in the case of (V) and (VI), the simple treatment does correctly predict the relative values of the FFAB's and could have been used to distinguish between the isomers if their identities were not already known. Such calculations may therefore be useful in establishing the structures of isomers obtained by ambiguous methods of synthesis [cf. (I) and (III) above].

APPENDIX

Validity of the Present Use of Perturbation Theory.—This paper forms one of a series in which perturbation methods are being used to build up a general theory of organic chemistry. The mathematical validity of this procedure is not immediately apparent, since it amounts to an expansion of certain energy quantities in powers of resonance integrals which are not small, and there is no guarantee that the leading terms will be dominant. Although the use of perturbation theory in much less satisfactory connections is commonplace (cf. radiation theory, where the higher perturbations are actually known to diverge !), the following partial justification of the present treatment seems of interest since it reduces the empirical element in it.

Consider first the calculation of excitation energies developed in this paper. By using the notation of Part I (*loc. cit.*), and including the second-order perturbation, the excitation energy $2E$ of RS becomes

$$\begin{aligned} 2E &= 2a_{or}b_{os}\beta + \sum_{n \neq 0} \frac{a_{or}{}^2 b_{ns}{}^2 \beta^2}{a_{or}b_{os}\beta - F_n} + \sum_{m \neq 0} \frac{a_{mr}{}^2 b_{os}{}^2 \beta^2}{a_{or}b_{os}\beta - F_n} \\ &= 2a_{or}b_{os}\beta \left\{ 1 - \sum_{n \neq 0}^{\text{occ}} \frac{a_{or}{}^2 b_{ns}\beta^2}{a_{or}{}^2 b_{os}{}^2 \beta^2 - F_n{}^2} - \sum_{m \neq 0}^{\text{occ}} \frac{a_{mr}{}^2 \mathrm{b}^2{}_{os}\beta^2}{a_{or}{}^2 \mathrm{b}_{os}{}^2 \beta^2 - E_m{}^2} \right\} \quad . \quad . \quad (7) \end{aligned}$$

(The second line follows from the first when use is made of the fact that R and S are both AH's; cf. Part I). Now the mean values of $a_{mr}{}^2$ and $b_{ns}{}^2$ are approximately $1/n_{\mathrm{R}}$ and $1/n_{\mathrm{S}}$, respectively, where n_{R} and n_{S} are the numbers of conjugated atoms in R and S, respectively. The numbers of terms in the sums in (7) are $\frac{1}{2}n_{\mathrm{R}}$ and $\frac{1}{2}n_{\mathrm{S}}$, respectively. As a first approximation, replace the denominators of the terms in (7) by their mean values; then

$$2E \simeq 2a_{or}b_{os}\beta \left\{ 1 - \frac{a_{or}{}^2\beta^2}{2(a_{or}{}^2 b_{os}{}^2 \beta^2 - \bar{F}_n{}^2)} - \frac{b_{os}{}^2\beta^2}{2(a_{or}{}^2 b_{os}{}^2 \beta^2 - \bar{E}_m{}^2} \right\} \quad . \quad . \quad (8)$$

where $\bar{E}_m$ and $\bar{F}_n$ are the mean values of E_m and F_n, respectively. Now $a_{or}{}^2$ and $b_{os}{}^2$ are of the order of $2/n_{\mathrm{R}}$ and $2/n_{\mathrm{S}}$, respectively, while the mean values of $E_m{}^2$ and $F_n{}^2$ are necessarily $>\beta^2$, and in practice are invariably close to $2\beta^2$. Hence, the ratio of the first- to second-order perturbations is approximately $2n_{\mathrm{R}}n_{\mathrm{S}}/(n_{\mathrm{R}} + n_{\mathrm{S}})$, which is always much greater than unity, thus justifying neglect of the latter as a first approximation. Also, the ratio of the first- to second-order perturbations should be greatest, and the first-order perturbation consequently the most accurate, when $(a_{or}{}^2 + b_{os}{}^2)$ is a minimum; minimising this expression will normally be equivalent to minimising the first-order perturbation $2a_{or}b_{os}\beta$ as was done in the main body of the paper.

The argument can be extended to cover the use of similar perturbation methods for calculating differences in total π-electron energy. The difference R_{RS} in π-electron energy between RS and (R + S), R and S being even AH's, is given by second-order perturbation theory (Dewar, *loc. cit.*) as

$$R_{\mathrm{RS}} = 4 \sum_{m}^{\text{unocc}} \sum_{n}^{\text{occ}} \frac{a_{mr}{}^2 b_{ns}{}^2 \beta^2}{E_m - F_n} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

where $\overset{\text{occ}}{\Sigma}$ and $\overset{\text{unocc}}{\Sigma}$ imply summation over MO's double occupied, or unoccupied, respectively,

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* Except in the rare cases where bond fixation is abnormally large; some examples are indicated in Table 2, the wave-lengths calculated with allowance for bond fixation (by the crude method indicated above) being given in parentheses.

in R or S. Now, the mean values of E_m for unoccupied MO's, and of F_n for occupied MO's, are given by

$$\begin{aligned}\overline{E}_m\,(\text{unocc}) &= \beta + R_{\mathrm{R}}/n_{\mathrm{R}} \quad \ldots \ldots \quad (10)\\ F_n\,(\text{occ}) &= -\beta - R_{\mathrm{S}}/n_{\mathrm{S}}\end{aligned}$$

where R_{R} and R_{S} are the resonance energies of R and S, respectively, relative to classical structures. The second terms in (10) are the less important, so the mean value of the denominators in (9) is greater than, but not much greater than, 2β. On substitution of mean values for a_{mr}^2 and b_{ns}^2 as before, (9) becomes

$$R_{\mathrm{RS}} \simeq \tfrac{1}{2}\beta\ (<\tfrac{1}{2}\beta) \quad \ldots \ldots \quad (11)$$

In practice the resonance energies of even AH's RS relative to pairs of even parts R and S (*e.g.*, of diphenyl relative to benzene + benzene) are closely similar, and somewhat less than $\frac{1}{2}\beta$, in cases where, as assumed in the above analysis, R is singly linked to S in RS (the analysis can be shown to apply also to cases of multiple attachment provided that no additional aromatic rings are formed in the process). The constancy of these energy differences has been noted by Coulson and Longuet-Higgins (*Proc. Roy. Soc.*, 1949, *A*, **195**, 188), who correlate it with the small range of self-polarisibility in even AH's. Note that, owing to the form of the expression in (9), none of the denominators is small, and the total variation in the denominators is never likely to be large; it is therefore not surprising that the denominators can be replaced by mean values without serious error.

If R and S are both odd AH's, there is now a first-order energy difference between RS and (R + S). It can be shown that the total second-order perturbation energy should again be approximately constant, this time slightly less than in the previous case since one relatively important term in the sum necessarily vanishes. Since the first-order perturbations are usually considerably greater than $\frac{1}{2}\beta$, this suggests that the higher perturbations converge and can in any case be replaced, like the second-order perturbations, by mean values. If so, then

$$R_{\mathrm{RS}} \simeq C + 2a_{or}b_{os}\beta \quad \ldots \ldots \quad (12)$$

This relation holds quite accurately for a number of cases that have been studied, with $C = 0{\cdot}3\beta$ (Dewar, *J. Amer. Chem. Soc.*, 1952, **74**, 3349).

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