677. *Colour and Constitution. Part III.* Polyphenyls, Polyenes, and Phenylpolyenes; and the Significance of Cross-conjugation.*

By M. J. S. Dewar.

The methods of Part II * are extended to a study of light absorption in polyphenyls, polyenes, and phenylpolyenes. It is found, as suggested in Part II, that allowance must be made for changes in C–C resonance integrals with bond length in hydrocarbons where the bond orders vary greatly. When such allowance is made in a very simple manner, the observed and calculated wave-lengths (λ_0) of the first absorption bands agree remarkably well. An expression is derived for λ_0 in polyenes in terms of the number (N) of conjugated double bonds which agrees much better with experiment than does the currently accepted square-root relationship. The significance of cross-conjugation is analysed, and the currently accepted rule for the light absorption of cross-conjugated alternant hydrocarbons is thereby derived.

A method was described in Part II* whereby the frequency of the first absorption band (FFAB) of an even alternant hydrocarbon (even AH) could be calculated in a simple manner; and the predictions so made for a wide range of condensed aromatic hydrocarbons were shown to agree well with experiment. Here the method is extended to the polyphenyls, polyenes, and phenylpolyenes.

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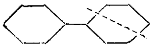
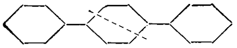
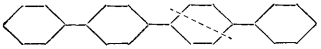
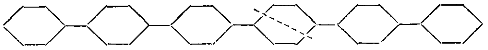
* Part II, preceding paper.

(a) p-*Polyphenyls.*—The method of Part II can be applied directly to the *p*-polyphenyls, and in Table 1 values for λ_0 (the wave-lengths of the first absorption band, in mμ) so calculated [col. (*a*)] are compared with experiment. The constant *C* of equation (3) in Part II was assumed to have the value found appropriate for condensed aromatic hydrocarbons. The optimum modes of bisection of the *p*-polyphenyls are also indicated.

TABLE 1.

	λ_0, calc.:		
Compound * and mode of bisection	(*a*)	(*b*)	λ_0, obs.†
	244	257	252
	286	296	280
	296	302	300
	306	310	310
	308	311	318

* Kekulé double bonds are omitted.
† Experimental data from Braude, *Ann. Reports*, 1945, **42**, 111.

The agreement with experiment is remarkably good. At the same time the use of a single value for β (the C–C resonance integral) is suspect, since the bonds between the phenyl groups must be longer than the intra-annular bonds. However, if allowance is made for this effect [see Section (b)], and the constant *C* adjusted slightly, the values of col. (*b*) in Table 1 are obtained; these are still in excellent agreement with experiment.

(b) *Unbranched Polyenes.*—The same method can be applied very simply to a linear polyene with $2N$ conjugated carbon atoms (*i.e.*, *N* double bonds in the classical formulation). Suppose the dissection be into odd AH radicals with $(2m - 1)$ and $(2n - 1)$ conjugated atoms, so that

$$m + n = N + 1 \qquad (1)$$

It is easily shown that the terminal NBMO coefficients in the radicals are $m^{-\frac{1}{2}}$ and $n^{-\frac{1}{2}}$, respectively; hence from equation (3) of Part II,

$$\lambda_0 = C(mn)^{\frac{1}{2}} \qquad (2)$$

when *m* and *n* have been chosen to maximize $(mn)^{\frac{1}{2}}$. The maximum value is given when *m* and *n* are equal (*N* odd), or $m - n = \pm 1$ (*N* even). With *N* odd, we then have

$$\lambda_0 = \tfrac{1}{2}C(N + 1) \qquad (3)$$

and the same expression holds to a good approximation with *N* even. Thus λ_0 should vary linearly as *N*. A similar linear dependence has been deduced by an alternative approximate MO treatment by Herzfeld and Sklar (*Rev. Mod. Phys.*, 1942, **14**, 294), and it also follows from Kuhn's simple uniform potential model (cf. *J. Chem. Phys.*, 1949, **17**, 1198); but in actual fact λ_0 varies much less rapidly with *N*.

Kuhn (*loc. cit.*) has ascribed this discrepancy to the large alternation in bond order of alternate bonds in a polyene, the corresponding variation in length being much greater than for bonds in typical aromatic hydrocarbons or in the odd alternant systems of typical basic dyes. By segregating the "single" and "double" bonds and allowing for the differences between them, he has been able to derive the square-root relationship (4) from the uniform potential model:

$$\lambda_0 = kN^{\frac{1}{2}} \qquad (4)$$

The same expression has been deduced by Lewis and Calvin (*Chem. Reviews*, 1939, **25**, 237) by a classical argument of little theoretical significance. Equation (4) holds accurately for the lower polyenes, but it fails progressively with increasing chain length.

In view of the close connexion between the uniform potential model and the LCAO MO method (Simpson, *J. Chem. Phys.*, 1948, **16**, 1124), it seems natural to ascribe the derivation of the incorrect relation (3) to the over-simplified assumption that all C–C resonance integrals in a polyene are similar; the more so since it was found in Part II that a similar discrepancy arose in the case of certain aromatic hydrocarbons (peropyrene and its derivatives), where the bond orders were predicted to show unusually large variations, and where by ascribing slightly modified resonance integrals to the "fixed" single and double bonds, agreement between observation and theory could be restored.

Assume, then, as a first approximation that all the "double" bonds in a polyene are equivalent, and also all the "single" bonds; but that different values must be ascribed to the resonance integrals of bonds of the two dissimilar types.* Let these values be $a\beta$ and $a^{-1}\beta$, respectively, with $a > 1$. Here a is to be regarded as an additional parameter to be determined empirically. Consider the odd AH with $(2m - 1)$ conjugated atoms obtained by bisection of the $2N$-atom polyene. It is, of course, assumed that the bonds in this radical have the same resonance integrals as corresponding bonds in the parent polyene. The general rule for calculating the NBMO coefficients is given by equation (5) (Longuet-Higgins, *J. Chem. Phys.*, 1950, **18**, 265)

$$a_r\beta_{i\,r} + a_s\beta_{ps} + a_t\beta_{pt} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where a_n is the NBMO coefficient of atom n, and β_{pq} the resonance integral of the bond between atoms p and q. On application of (5) to the odd AH with $(2m - 1)$ conjugated atoms, in which alternate bonds have resonance integrals $a\beta$ and $a^{-1}\beta$, the NBMO coefficients are seen to be :

$$\begin{array}{ccccccccc} A & & -Aa^2 & & Aa^4 & & & A(-a^2)^{m-1} & \\ \mathrm{C} & = & \mathrm{C}-\mathrm{C} & = & \mathrm{C}-\mathrm{C} & = & = & \mathrm{C} & -\mathrm{C} \end{array} \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where the normalizing factor A is given by

$$A = (\sum_{r=0}^{m-1} a^{4r})^{-\frac{1}{2}} = (a^4 - 1)^{\frac{1}{2}}(a^{4m} - 1)^{-\frac{1}{2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Similar expressions are obtained for the NBMO coefficients of the odd AH with $(2n - 1)$ atoms, n replacing m in (6) and (7). Substitution of the values for the terminal coefficients into equation (3) of Part II gives

$$\lambda_0 = C(a^{4m} - 1)^{\frac{1}{2}}(a^{4n} - 1)^{\frac{1}{2}}(a_4 - 1)^{-1}a^{1-2N} \quad . \quad . \quad . \quad . \quad . \quad (8)$$

The optimum mode of bisection of the polyene is again that which makes $(m - n)$ zero or unity. If N is odd, equation (8) then becomes :

$$\begin{aligned} \lambda_0 &= C(a^{2N+2} - 1)(a^4 - 1)^{-1}a^{1-2N} \\ &= D(1 - a^{-2N-2}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9) \end{aligned}$$

where the constant D is defined by

$$D = a^3C(a^4 - 1)^{-1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

If N is even, equation (9) still holds to a good approximation. The parameter a was assumed † to be given by

$$a = 2^{\frac{1}{8}} \simeq 1{\cdot}09 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

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* Calculations by the MO method imply that the alternation in bond lengths in a long polyene should decrease rapidly towards the middle of the chain (see Coulson, *Proc. Roy. Soc.*, 1939, *A*, **169**, 413). The quantitative reliability of these calculations is, however, uncertain, since the empirical method used to estimate the variation in the C–C resonance integral with bond length is open to criticism and since no experimental data are available for comparison with theory except for short polyenes where the alternations in bond length are in any case large. The success of the MO method in the case of polycyclic aromatic hydrocarbons is irrelevant in the present connection in view of the dissimilarity of such compounds to polyenes and the small alternations in the lengths of bonds in them. The available chemical and physical evidence seems to suggest that the alternation in bond length in polyenes will prove greater than that predicted by the MO method in the investigation referred to above. The present treatment implies that the mean difference in length between "double" and "single" bonds should be about 0·05 Å, if reliance can be placed in the empirical method for estimating the variation in β with bond length (see Mulliken, Rieke, and Brown, *J. Amer. Chem. Soc.*, 1941, **63**. 48).

† The parameters a and D are of course to be determined empirically, as is β in the usual LCAO treatment.

and the parameter D of equation (9) was chosen to give agreement between theory and experiment for butadiene. The values so calculated are given in col. 3 of Table 2. Experimental values for λ_0 are given in the col. 4. These require some comment since the values are maxima of the first strong system of bands, no account being taken of fine structure (cf. Part II). In the lower members of the series the fine structure is not resolved, and in any case its origin is by no means certain; so this procedure seems the best available. The values for λ_0 refer to solutions in alcohol or paraffin hydrocarbons, the absorption maxima of polyenes being similar in these solvents, and are taken from Karrer and Eugster (*Helv. Chim. Acta*, 1951, **34**, 1805) and Braude (*loç. cit.*). In the last column of Table 2 are given values of λ_0 calculated from the square-root relationship (4) the constant being also adjusted to give agreement for butadiene.

TABLE 2.

		λ		
N	Polyene	From (9)	Obs.	From (4)
1	Ethylene	157	163	154
2	Butadiene	(217)	217	(217)
3	Octatrienol	268	265	266
4	*iso*Axerophthene	310	308	307
5	Axerophthene	345	346	343
6	Anhydro-vitamin A	376	371	376
7	—	402	—	406
8	Dihydro-β-carotene	422	420	434
9	ε_1-Carotene	441	439	460
10	α-Carotene	456	445	485
11	γ-Carotene	469	462	509
12	Dehydro-β-carotene	480	475	532
13	Decapreno-ϵ_1-carotene	489	495	553
14	Anhydroeschscholtzxanthin	497	500	574
15	Dehydro-β-lycopene	503	504	594
16	—	508	—	614
17	—	513	—	632
18	—	517	—	650
19	Dodecapreno-β-carotene	520	531	668
20	—	522	—	686
∞	—	536	—	∞

(c) *Discussion of Sections* (a) *and* (b).—The agreement between the experimental values for λ_0 and those calculated from equation (9) is remarkable; it is well within the limits of variation of λ_0 due to the effects of alkyl substituents or changes in solvent (cf. Part II), neither of which was considered in the calculation. Note once again that the full MO treatment (neglecting electron spin) breaks down completely in the calculation of excitation energies both in the polyphenyls and in the polyenes; a possible explanation of this curious situation was given in Part II. Note also that no satisfactory relation has previously been found between N and λ_0, even empirically.

The values for λ_0 for the lower polyenes calculated from (9) agree very closely with those calculated from the square-root expression (4); but the two expressions diverge progressively when $N > 7$. Equation (9) predicts that λ_0 should tend to a limit as $N \rightarrow \infty$. The experimental evidence evidently favours (9), particularly when it is realized that the only known examples of higher polyenes are those with numerous alkyl substituents, and the bathochromic effect of these has been ignored in comparing observed and predicted values of λ_0.

The empirical value for the ratio of " double " and " single " bond resonance integrals is comparable to that assumed in Part II for peropyrene; this supports the explanation given there for the discrepancy between the observed and predicted FFAB's. The ratio also seems reasonable from theoretical estimates of the variation of β with bond length.

The value assumed for D in equation (9) is nearly 20% less than that calculated from equation (10) by using the value of C found appropriate for aromatic hydrocarbons and *p*-polyphenyls. This discrepancy is disappointing but not surprising; apart from the dissimilarity between aromatic and aliphatic C–C π-bonds, Frank–Condon effects must be much greater in polyenes than in aromatic systems and these should reduce λ_0 and so also D in equation (9). It should be added that agreement between theory and experiment even to within $\pm 20\%$ would have been highly gratifying in view of the much greater discrepancies given by the usual MO method; disappointment arises only because the predictions from equation (9) are so extraordinarily successful when D is suitably chosen.

(d) *Phenyl- and Diphenyl-polyenes.*—The same methods can be used for phenyl- and diphenyl-polyenes, by accepting the values β, $a^{-1}\beta$, and $a\beta$ respectively for resonance integrals between ring carbons and between " singly " bound and " doubly " bound polyene is by fission of the polyene chain at or near its mid-point (cf. the polyenes), and of the first three phenylpolyenes into (benzyl + methyl), (benzyl + allyl), and (phenylallyl + allyl) respectively. The choice of C in calculating from equation (3) of Part II is ambiguous, since different values have been found appropriate for aromatic compounds on the one hand, and polyenes on the other. Values for λ_0 corresponding to both values of C are compared with experiment in Table 3 (the experimental values are from Braude, *loc. cit.*).

TABLE 3

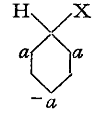
Compound	λ_0, calc. with : aromatic C	polyene C	λ_0, obs.
Styrene	244	201	250
1-Phenylbutadiene	318	261	299
1-Phenylhexatriene	366	301	—
Stilbene	311	256	295
Ph·[CH:CH]$_n$·Ph; $n = 2$	357	294	328
,, $n = 3$	412	339	349
,, $n = 4$	445	366	375
,, $n = 5$	480	395	403
,, $n = 6$	505	416	420
,, $n = 7$	532	438	435

On intuitive grounds one might have expected the polyene value for C to be appropriate in the limiting case when the polyene chain forms the greater part of the molecule, and intermediate values to hold for the lower polyenes where the molecule is largely aromatic. The results in Table 3 are in good agreement with this idea: the observed values for λ_0 agree closely with those calculated from " polyene C " for the higher diphenylpolyenes, but show a progressive divergence as the polyene chain diminishes in length. carbons, with a given by (11). The optimum mode of dissection of the diphenylpolyenes In styrene and stilbene, the " aromatic C " values for λ_0 agree quite well with experiment, and the agreement is excellent for diphenyl itself (Table 1).

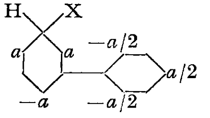
(e) *Cross-conjugation.*—Before discussing the light absorption of hydrocarbons commonly described as cross-conjugated, it is first necessary to examine the definition and significance of cross-conjugation.

Consider, first, the case of an odd AH. It has been shown elsewhere (Dewar, *J. Amer. Chem. Soc.*, 1952, **74**, 3340) that the chemistry of such compounds is dominated by the properties of their NBMO's. Suppose such a compound to be " starred " (Coulson and Rushbrooke, *Proc. Camb. Phil. Soc.*, 1940, **36**, 193) so that the AO's in the NBMO belong to the starred set; and suppose further that not all the starred atoms are active (an active atom being one the coefficient of whose AO in the NBMO differs from zero). Then removal of the inactive segment of the molecule, *i.e.*, the part containing only inactive starred atoms, will not affect the NBMO, and so will not affect the chemical behaviour of the parent odd AH.

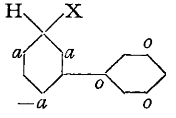
Consider, for example, the transition states for substitution in benzene, and in the *o*-, *m*-, and *p*-positions of diphenyl; according to Wheland (*J. Amer. Chem. Soc.*, 1942, **64**, 900) these are odd AH's, and the relative rates of substitution by a given reagent should run parallel to the differences in total π-electron energy between them and the parent hydrocarbons. These energy differences can be related (Dewar, *loc. cit.*) to the coefficients of AO's in their NBMO's, the coefficients being given below :



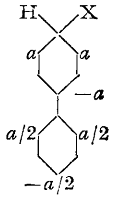
$a = 1/\sqrt{3}$



$a = 1/\sqrt{3{\cdot}75}$



$a = 1/\sqrt{3}$



$a = 1/\sqrt{3{\cdot}75}$

NBMO Coefficients in transition states for substitution in benzene and diphenyl.

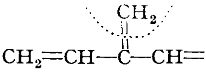
In the transition state for *m*-substitution in diphenyl, the phenyl group is inactive; it should consequently have no effect on the rate of substitution. In the isomeric transition states the phenyl group is active, and can be shown to accelerate the reaction.

This phenomenom, the redundance of part of a mesomeric system, is usually described as cross-conjugation; the present discussion leads to the definition : * *An odd AH is cross-conjugated if not all the starred atoms in it are active.*

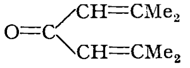
It can be shown that this definition is equivalent in effect to that given by resonance theory, from a correspondence that has been found to exist (Dewar and Longuet-Higgins, *Proc. Roy. Soc.*, in the press) between the resonance theory and the MO method.

In chemical applications, cross-conjugation is important only in odd alternant systems; its apparent influence on the chemistry of even systems is due to the fact that the reactions of such compounds commonly proceed through odd transition states, and in such cases it is the odd transition states that are directly affected (cf. substitution in diphenyl, discussed above). The same is true in the present treatment of the light absorption of even AH's, since it has been related to the properties of pairs of odd AH's into which the even AH's can in principle be divided. It is, however, clear that if an even AH cannot in any way be divided into a pair of non-cross-conjugated odd AH's, then it will be predicted to have the same FFAB as some analogous even AH with fewer conjugated atoms. It is convenient then to define such even AH's as being themselves cross-conjugated : *An even AH is cross-conjugated if it cannot be divided into two non-cross-conjugated odd AH's.*

This definition differs somewhat from those given by current theories; thus the hydrocarbon (III) is not cross-conjugated by the present definition since it can be divided as indicated into two non-cross-conjugated odd AH's. The analogous ketone (IV) does, in fact, absorb at appreciably lower frequencies than its lower analogue (V), implying that (IV) is not cross-conjugated; whereas the light absorption of derivatives of 2 : 3-diphenylbutadiene, which is cross-conjugated by the present definition also, closely resembles that of analogous styrene derivatives (Braude, *J.*, 1949, 1902).

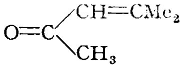

$\mathrm{CH_2{=}CH{-}\overset{\overset{\displaystyle CH_2}{\|}}{C}{-}CH{=}CH_2}$

(III)


$\mathrm{O{=}C}\begin{array}{l}\diagup \mathrm{CH{=}CMe_2}\\ \diagdown \mathrm{CH{=}CMe_2}\end{array}$

$\lambda_0 = 259$

(IV)


$\mathrm{O{=}C}\begin{array}{l}\diagup \mathrm{CH{=}CMe_2}\\ \diagdown \mathrm{CH_3}\end{array}$

$\lambda_0 = 230$

(V)

From these arguments a general principle may be derived. Division of a cross-conjugated even AH R gives two odd AH's, one or both of which contain *inactive segments* (i.e., segments containing no active atoms). Removal of these inactive segments would leave two non-cross-conjugated odd AH's which could combine to an even non-cross-conjugated AH R′. It is evident that the values of λ_0 calculated from equation (3) of Part II with this particular mode of bisection of R and R′ will be identical, since the inactive segments in no way affect the NBMO coefficients. The best approximation to the FFAB of R will then be given by the mode of bisection which maximises λ_0 for R′; hence follows the rule : *The FFAB of a cross-conjugated even AH is the same as the least FFAB of any non-cross-conjugated even AH contained in it.*

This rule again corresponds closely to current intuition, except that the definition of cross-conjugation is slightly different.

(f) *Even Cross-conjugated AH's : the* m-*Diphenylyls.*—The *m*-diphenylyls are cross-conjugated according to the present definition, and the largest non-cross-conjugated unit present in them is diphenyl. All should have FFAB's similar to diphenyl itself, and it is well known that they do, up to the highest member of the series yet prepared in which there are no less than 16 benzene rings (Braude, *loc. cit.*).

Conclusions.—These results consolidate the conclusion reached in Part II (*loc. cit.*), *viz.*, that quite satisfactory estimates of FFAB's and AH's can be obtained by the PMO

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* A system containing hetero-atoms is cross-conjugated if the equivalent, or isoconjugate, AH is cross-conjugated.

method in spite of its crudity and simplicity. In certain cases such calculations may prove of some practical value since they can be carried out with no effort and in a very short time. The success of the method also raises some interesting theoretical problems, the solution of which may throw a new light on the significance of the molecular orbital approximation.

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