Theoret. chim. Acta (Berl.) 2, 75—83 (1964)

Chemistry Department, University of Glasgow

A Simple Molecular-Orbital Study of the β-, α-, and p-Bands in Triphenylenes

By

T. H. Goodwin and **D. A. Morton-Blake**

Clar has observed that the spectra of annellated derivatives of triphenylene such as II, III, IV below show remarkable resemblance to those of the phenes defined by the central ring of the triphenylene and its two longest acene limbs, II resembling tetraphene I, and III and IV pentaphene V. We show that this observation can be explained in terms of a simple modification of the Hückel molecular-orbital method.

Eine Beobachtung von Clar hat gezeigt, daß die Spektren der Benzologen des Triphenylens, wie z. B. II, III, IV außerordentlich ähnlich sind denen der Phene, die ausgehend vom zentralen Ring und den beiden längsten Armen der obigen Systeme gebildet werden. Daher ähnelt das Spektrum von II stark dem des Tetraphens I und die von III und IV dem des Pentaphens V. Es wird gezeigt, daß dieser Beobachtung durch eine einfache Modifikation der Hückelschen MO-Theorie Rechnung getragen werden kann.

Clar a observé que les spectres d'absorption des dérivés annelés du triphénylène tels que, II, III et IV montrent une ressemblance extraordinaire à ceux des phènes définis par l'anneau central du triphénylène et ses deux armes les plus longues. Ainsi le spectre de II ressemble à celui du tétraphène et ceux de III et de IV à celui du pentaphène V. Nous avons démontré qu'on peut expliquer cette observation par une modification simple de la méthode des orbitales moléculaires d'Hückel.

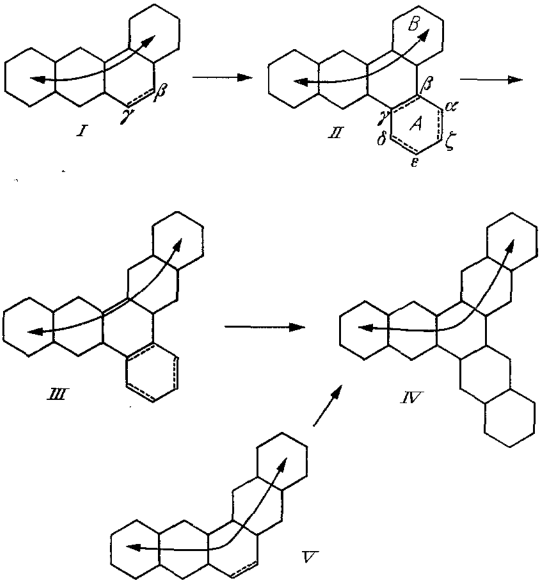
1. Energy levels in Triphenylenes

In this paper we discuss the positions of the absorption bands in a large number of annellated derivatives of triphenylene, but since the systematic names of these compounds are often decidedly cumbrous we have used the following simple scheme for referring to them. The molecules consist of benzenoid rings annellated at three alternate bonds in benzene; we therefore describe them as $s\mathrm{B}ml$ where s, m, l are the numbers of rings in the three limbs. s is separated from the other two indices and refers to the shortest limb; l is the longest; $s \leq m \leq l$. Triphenylenes with the same m and l are said to form a class. Thus I to V (below) are described as 0B 1,2; 1B 1,2; 1B 2,2; 2B 2,2; 0B 2,2 and the first two and the last three belong to different classes.

Clar and his colleagues [2] have observed only very small shifts in the positions of the β ultra-violet absorption bands when an aromatic system is annellated to a bond of high π-electron density. In tetraphene, I, (0B 1,2), molecular-orbital calculations show that the bond $\beta\gamma$ has a high double bond character corresponding to its chemical properties; for these reasons, and in accordance with Clar's ideas concerning these molecules we represent this bond as a formal double bond. The addition of a butadiene system at $\beta\gamma$ of I to give the triphenylene II, (1B 1,2) is accompanied by a zero spectral shift of the β-band and this leads Clar to conclude that the phene system I is present in II and is unaffected by the presence of the newly formed benzenoid ring A.

The high order of the bond $\beta\gamma$ in I is apparently maintained in II with the consequence that the bonds $\delta\varepsilon$, $\zeta\alpha$ are also of higher order and $\alpha\beta$, $\gamma\delta$, $\varepsilon\zeta$ of lower order than the average.

However, if a further ring is annellated to II at B (or A) to give III it is found that the β-band of longest wavelength now occurs 240 Å away at 3140 Å. This is almost exactly the position of the corresponding band, 3170 Å, in pentaphene V, and further extension of the shortest limb of III by a second ring to give IV is accompanied only by a very small (violet) shift to 3120 Å. Thus III, IV and V all give rise to the same β-band and presumably have, at the moment of producing the spectrum, the same aromatic conjugation, that of pentaphene. Clar therefore concludes that, as far as the origin of the first β-band is concerned, the aromatic conjugation of any triphenylene extends only over the two longest limbs and is unaffected by the benzenoid rings of the shortest limb. This is clearly demonstrated in Tab. 1 where all the absorption spectra recorded for phenes and triphenylenes are summarised. 14 spectra are noted including pairs of spectra for the five classes *s*B 1,1, *s*B 1,2, *s*B 1,3, *s*B 1,4, *s*B 3,3 and three spectra for the class *s*B 2,2. In no class is the spread of β-band heads greater than 60 Å. Similar though less close agreement is observed in the α- and p-bands.



We must emphasise here that this paper is not concerned with the β'-bands which, according to Clar, originate from one of the two aromatic conjugation schemes which involve the shortest limb.

We have applied the method of molecular-orbitals to a large number of triphenylenes not strictly to calculate the positions of the β-, α- and p-bands but to determine in units of β_0*, the energy levels of the molecular orbitals, transitions between which are responsible for those bands.

With alternant hydrocarbons having $2n$ carbon atoms in the π-electron system it is well recognised that the p-bands (of intermediate intensity, $\log \varepsilon \approx 4$) arise from transitions between the nth and $(n+1)$th electronic levels (counting the lowest as the first level) while the α- and β-bands (of low and high intensity $\log \varepsilon \approx 2.5$ and 5 resp.) both arise from transitions between the nth and $(n+2)$th

---

* Confusion is unlikely to arise between this β and that labelling the most intense absorption band.

Table 1

		Absorption Bands				Hückel			
s B m l	n	p	α	β	Δ	k_n	k_{n-1}	$k_n + k_{n-1}$	Δ
011	7	2925 A	3450 A	2510 A	60 A	0.605	0.769	1.374	0.006
111	9	2840	3400	2570		0.684*d*		1.368	
012	9	3590	3850	2900	0	0.453	0.715	1.168	0.005
112	11	3490	3750	2900		0.499	0.714	1.213	
013	11	4525		3190	10	0.327	0.688	1.015	
113	13	4415		3180					
014	13	5510		3480	50				
114	15	5385		3430					
022	11	3590	4230	3170	30	0.437	0.521	0.958	
122	13	3390	3940	3140					
222	15	3400	3890	3150					
023	13	4400	4670	3580					
123	15								
223	17								
033	15	4230	5190	3910	60				
133	17	4380	4850	3850					

d doubly degenerate level

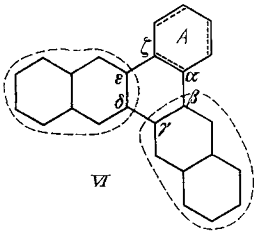
Table 1 (continuation)

		Series I				Series II			
s B m l	n	k_n	k_{n-1}	$k_n + k_{n-1}$	Δ	k_n	k_{n-1}	$k_n + k_{n-1}$	Δ
011	7	0.741	0.816	1.556	0.058	0.741	0.816	1.556	0.058
111	9	0.749*d*		1.498		0.749*d*		1.498	
012	9	0.502	0.814	1.316	0.006	0.569	0.719	1.288	0.042
112	11	0.516	0.794	1.310		0.604	0.726	1.330	
013	11	0.357	0.782	1.139	0.004	0.460	0.728	1.188	0.020
113	13	0.366	0.777	1.143		0.481	0.727	1.208	
014	13	0.262	0.668	0.930	0.012	0.419	0.678	1.097	0.002
114	15	0.268	0.674	0.942		0.397	0.702	1.099	
022	11	0.510	0.545	1.056	0.041	0.560	0.620	1.180	0.050
122	13	0.531	0.545	1.076		0.605	0.620	1.225	
222	15	0.531	0.566*d*	1.097		0.615*d*		1.230	
023	13	0.371	0.531	0.902	0.028	0.468	0.597	1.065	0.046
123	15	0.378	0.541	0.918		0.488	0.617	1.105	
223	17	0.384	0.546	0.930		0.491	0.620	1.111	

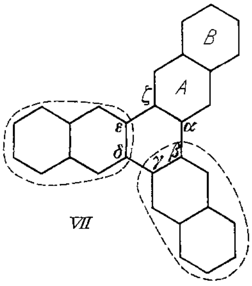
d doubly degenerate level

and between the $(n-1)$th and $(n+1)$th levels, these being degenerate in the simple forms of the molecular-orbital theory in which overlap is neglected. We have not here attempted to break this degeneracy (see e. g. ref. [8] for one method of doing this) being more interested to see whether Clar's observations are explicable in terms of a simple molecular-orbital approach to the electronic structures of molecules. Thus we have required the energies of the highest and penultimate levels of the ground states of the molecules since $2k_n$ should be related to the p-band wavelengths and $k_n + k_{n-1}$ to those of the α- and β-bands, where k is the (positive) Hückel number *i.e.*, the coefficient of β in the energy expression $\varepsilon_i = \alpha + k_i\beta$, and $k_{2n+1-i} = - k_i$.

Two series of calculations have been carried out. In the first the β-values of the bonds were assumed equal except for the extreme single and double bonds. In VI, for example, the β's within the dotted islands were put equal to β_0, the interaction integral between atomic $2p_z$-orbitals on neighbouring carbon atoms separated by the standard C-C distance in benzene, and since the formulae written by Clar [2] for these triphenylenes show the bonds $\alpha\beta$, $\gamma\delta$, $\varepsilon\zeta$ as of low order we have allotted them the β-values of $0.8\,\beta_0$. In the benzo-ring A we have supposed the β's to be alternately $0.8\,\beta_0$ and $1.1\,\beta_0$ $\alpha\zeta$ having, of course, the higher value.



VI



VII

In VII and in molecules having a shortest limb of two or more rings ($s \geqslant 2$) we have, however, put all β's equal to β_0. Again the β's for $\alpha\beta$, $\gamma\delta$, $\varepsilon\zeta$ have been taken to be $0.8\,\beta_0$.

We have felt justified in this approach by the results of Ahmed and Trotter [1] who have made a three-dimensional examination of the crystal structure of triphenylene and report a mean bond length of 1.446 Å for the interphenylene bonds corresponding to $\alpha\beta$ etc. of VI and mean lengths of 1.415 (for the bond corresponding to $\alpha\zeta$), 1.416, 1.377, 1.402, 1.377 and 1.416 Å round the peripheral rings. β_{ij} must depend on the distance between atoms i and j and these lengths imply [6, 7] β-values of $0.81\,\beta_0$ for $\alpha\beta$, $0.91\,\beta_0$ (for $\alpha\zeta$), $0.91\,\beta_0$, $1.04\,\beta_0$, $0.95\,\beta_0$, $1.04\,\beta_0$, $0.91\,\beta_0$. Our calculations were complete before the work of Ahmed and Trotter became available and in any case the X-ray results given above are not only the average values over all similar bonds in the crystal but represent averages over many minutes or hours whereas spectroscopy presents the situation over an enormously shorter interval of time. It is therefore of considerable significance that the length reported for the interphenylene bonds corresponds with the β-value we have allocated to them and that the pattern of lengths in the peripheral rings corresponds (apart from $\alpha\zeta$) with the β's we have assumed for bonds in rings such as A of VI. We do not compare our selected β for the bonds between the rings with values appropriate to lengths such as the 1.50 Å found by Hargreaves and Hasan Rizvi [5] for the central bond in diphenyl because we believe this bond to be elongated by repulsions between the 2:2′ and 6:6′ pairs of hydrogen atoms [4].

In the second series of calculations Clar's scheme was not invoked. The triphenylene *s*B*m*, *l* was regarded as formed from *s*-, *m*- and *l* ring acenes joined by low order bonds $\alpha\beta$, $\gamma\delta$, $\varepsilon\zeta$. The β-values for the bonds of the various limbs were derived from the bond orders calculated for these acenes. In VI, for example, the β's for ring A were β_0, as in benzene, and those for the naphthalene systems were interred from the calculated bond orders in naphthalene; those for $\alpha\beta$, $\gamma\delta$, and $\varepsilon\zeta$ were again $0.8\,\beta_0$. In this way it was hoped that the two series of calculations would provide some evidence for or against the Clar theory of aromaticity. The results are shown in Tab. 1 and 2. These differ only in that Tab. 1 includes all the spectra of triphenylenes known to us and such Hückel molecular-orbital levels as have been published, either in Coulson and Daudel's "Dictionary of Values of Molecular Constants" [3] or Streitwieser's "Molecular Orbital Theory for Organic Chemists" [9]. These Hückel molecular orbitals are based, as is well known, on the assumption of an interaction integral $\beta = \beta_0$ between all neighbouring orbitals. We have not ourselves made such calculations for all the many compounds which have been the subjects of our study here because they seemed less likely to yield the desired explanation of Clar's observations.

Table 2

		Series I				Series II			
*s*B*ml*	n	k_n	k_{n-1}	$k_n + k_{n-1}$	Δ	k_n	k_{n-1}	$k_n + k_{n-1}$	Δ
024	15	0.271	0.531	0.802	0.022	0.390	0.592	0.981	0.043
124	17	0.275	0.542	0.817		0.402	0.617	1.019	
224	19	0.279	0.545	0.824		0.404	0.620	1.024	
034	17	0.273	0.374	0.647	0.021	0.394	0.478	0.872	0.048
134	19	0.276	0.381	0.657		0.403	0.494	0.897	
234	21	0.278	0.390	0.668		0.392	0.498	0.890	
334	23	0.277	0.377	0.654		0.401	0.520	0.921	
044	19	0.271	0.276	0.547	0.016	0.394	0.398	0.792	0.023
144	21	0.269	0.285	0.554		0.394	0.417	0.811	
244	23	0.266	0.297	0.563		0.390	0.425	0.815	
344	25	0.262	0.299	0.561		0.385	0.429	0.814	
444	27	0.251	0.300*d*	0.551		0.372	0.431*d*	0.803	
055	23	0.205	0.210	0.415	0.009	0.321	0.324	0.645	0.013
155	25	0.203	0.217	0.420		0.318	0.338	0.656	
255	27					0.315	0.343	0.658	
355	29	0.198	0.226	0.424		0.313	0.346	0.658	
455	31	0.196	0.226	0.422					

Inspection of Tab. 1 and 2 shows that our Series I calculations do lead to fairly constant values of $k_n + k_{n-1}$ in any class of triphenylenes. The series II calculations are not generally quite so constant though the superiority of the series I results over those of series II and of the Hückel method is not so great as to compel out-of-hand rejection of the others or to constitute unequivocal theoretical justification of Clar's conclusions. A more satisfactory comparison is to plot the frequencies of the β-bands against $k_n + k_{n-1}$, because CLAR's conclusion is not accurate to an Å unit and the slight variations in β-band wavelengths correspond to the variations in $k_n + k_{n-1}$. Graphical representation of these results is shown in Fig. 1 where it is seen that there is little to choose between our series I and series II results but that both are better than the Hückel values which show a much greater spread although, there being fewer of them, the comparison is not so extensive as one could desire.

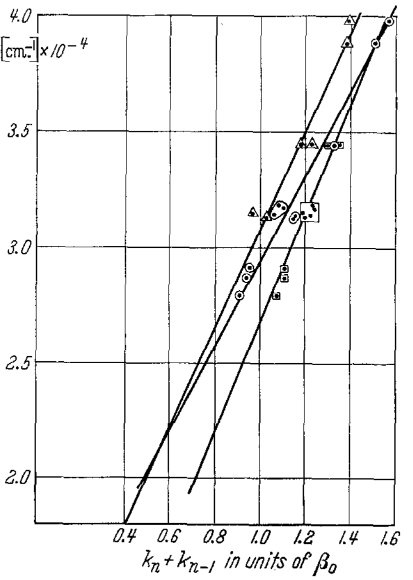


Fig. 1. β-Band frequencies against $k_n + k_{n-1}$.
⊙ Series I, ⊡ Series II, △ Hückel

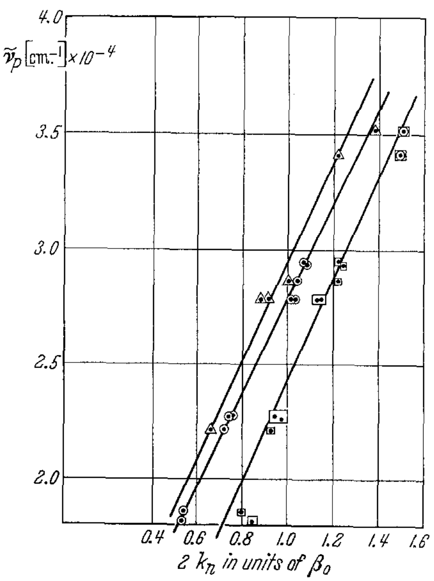


Fig. 2. p-Band frequencies against 2 k_n.
⊙ Series I, ⊡ Series II, △ Hückel

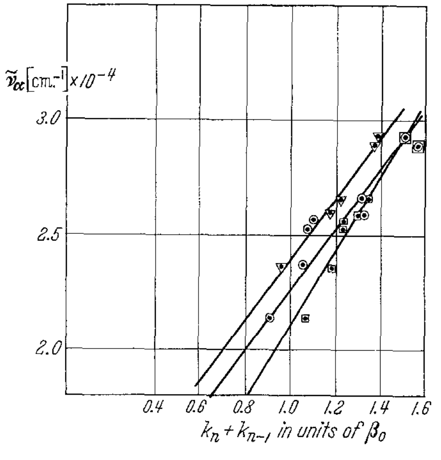


Fig. 3. α-Band frequencies against $k_n + k_{n-1}$.
⊙ Series I, ⊡ Series II, △ Hückel

Generally similar conclusions result from inspection of the values of k_n and Fig. 2 (p-band frequencies against 2 k_n) and of Fig. 3 (α-band frequencies against $k_n + k_{n-1}$).

A particularly important point is however that just as the spectra (p, α- and β-bands as a whole) of pentaphene (0B 2,2) and *iso*-pentaphene* (0B 1,3) are distinctly different so do the values of 2 k_n and $k_n + k_{n-1}$ while agreeing within the classes sB 2,2 and sB 1,3 differ between the classes. So far this is in accordance with observation, but pentaphene and *iso*-pentaphene* have their β-bands at almost exactly the same wavelength. Our series I calculations suggest ($k_n + k_{n-1}$ different) that the β-bands should differ appreciably, but the series II calculations do make them almost equal. This

---

* 1.2-benztetracene

suggests that the series II results are superior. Unfortunately no other similar comparison can be made for lack of experimental data on triphenylenes with $m_1 + l_1 = m_2 + l_2$ but with $m_1 \neq m_2$.

2. Bond Length Alternation in a Benzenoid Ring

Consider a benzene molecule consisting of two kinds of C-C bonds alternating round the ring, with β-values equal to β_1 and β_2. The molecule would, therefore, have D_{3h} symmetry and the one-electron molecular orbitals C_{3v}. This leads to the following linearly independent molecular orbitals of the A_1, the A_2 and the doubly degenerate E classes:

$$\Phi\,(A_1) = \frac{1}{\sqrt{6}}(\varphi_1 + \varphi_2 + \varphi_3 + \varphi_4 + \varphi_5 + \varphi_6)$$

$$\Phi\,(A_2) = \frac{1}{\sqrt{6}}(\varphi_1 - \varphi_2 + \varphi_3 - \varphi_4 + \varphi_5 - \varphi_6)$$

$$\Phi'\,(E) = \frac{1}{2\sqrt{3}}(2\,\varphi_1 + 2\,\varphi_2 - \varphi_3 - \varphi_4 - \varphi_5 - \varphi_6)$$

$$\Phi''\,(E) = \frac{1}{2}(\varphi_3 - \varphi_4 - \varphi_5 + \varphi_6).$$

Expressing the energies $\mathscr{E}$ of these in terms of the interaction integrals $\int \varphi_{i-1}^{*} \mathscr{H} \varphi_i \, d\tau = \beta_1$, $\int \varphi_i^{*} \mathscr{H} \varphi_{i+1} \, d\tau = \beta_2$ and the coulomb integrals $\int \varphi_i^{*} \mathscr{H} \varphi_i \, d\tau = \alpha$ (the subscripts to φ being expressed in modulus 6) we have

$$\mathscr{E}\,(A_1) = \alpha + \beta_1 + \beta_2$$

$$\mathscr{E}\,(A_2) = \alpha - \beta_1 - \beta_2$$

$$\mathscr{E}^{\pm}\,(E) = \alpha \pm (\beta_1^2 + \beta_2^2 - \beta_1 \beta_2)^{\frac{1}{2}}.$$

The doubly occupied molecular orbitals of the ground state are $\Phi\,(A_1)$, $\Phi'\,(E)$ and $\Phi''\,(E)$ leading then to the total ground state π-electron energy

$$E\,(3v) = 2\,\mathscr{E}\,(A_1) + 4\,\mathscr{E}^{+}\,(E) = 6\,\alpha + 2\,[\beta_1 + \beta_2 + 2\,(\beta_1^2 + \beta_2^2 - \beta_1 \beta_2)^{\frac{1}{2}}]. \quad (1)$$

The π-electron energy of the ground state if all C-C bonds are equivalent (molecular orbital symmetry C_{6v}) is

$$E\,(6v) = 6\,\alpha + 8\beta_0 \quad (2)$$

where β_0 is the interaction integral for the observed benzene C-C bond length.

Equating (1) and (2) we obtain a relationship showing how β_1 and β_2 must change relative to each other, in order to preserve in the C_{3v} model the same total π-electron energy obtained with the C_{6v} model. Since we are concerned with the relative rather than the actual magnitudes of β_0, β_1 and β_2 we shall work in terms of β_1' and β_2' the ratios of β_1 and β_2 to β_0. The required relationship is then

$$\beta_1' = \beta_2' - \frac{4}{3}\left[1 - (4 - 3\,\beta_2')^{\frac{1}{2}}\right]. \quad (3)$$

This is plotted out in Fig. 4, which is really a single energy contour line (with the energy value $6\,\alpha + 8\,\beta_0$) in β'-space. For an extended range a family of such contours would be required.

We may now observe the effect of changing the β' values of adjacent bonds in an annellated benzene ring subject to the requirement that the total π-electron energy of the annellated benzene ring remains constant. Thus, accepting the validity of Clar's explanation of the origin of the β-bands in the spectra of the triphenylenes, we may regard one of the three outer rings of VIII, say ring A, as having bonds of alternately high and low order, while the other rings constitute a phenanthrene system. We may, therefore, vary the β' values for the bonds in this ring iso-energetically according to (3) and, for simplicity, assume that the β' values for bonds $\alpha\beta$, and $\gamma\delta$ are the same as those of the low order bonds in ring A. In phenanthrene IX although the bond $\beta\gamma$ is not shared with another ring we may still suppose, for purposes of comparison, that the β' values of bonds $\alpha\beta$, $\beta\gamma$, $\gamma\delta$ are again given by (3).

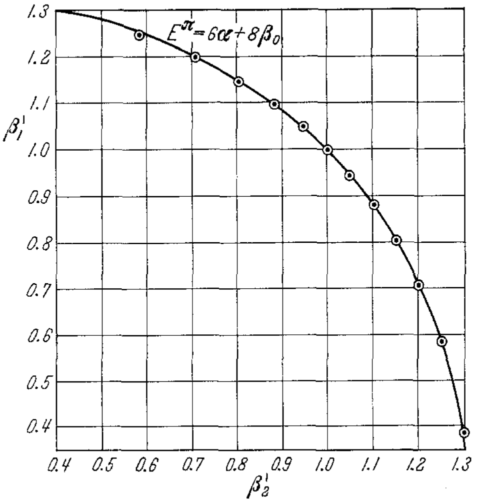
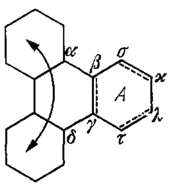
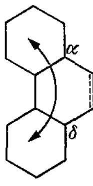


Fig. 4. Relationship between β_1' and β_2'



VIII



IX

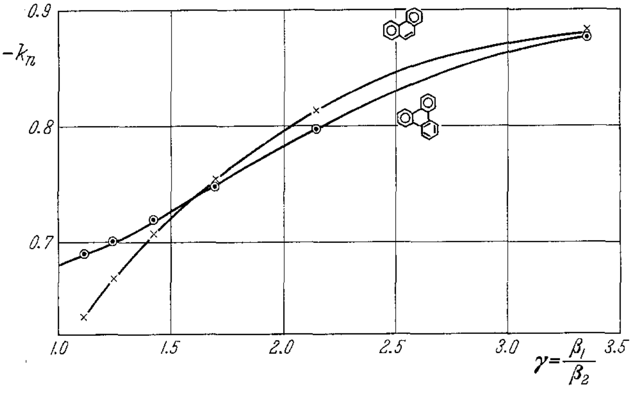


Fig. 5
Highest occupied molecular orbital energy k_n as a function of $\gamma = \beta_2/\beta_1$

The results of these calculations are illustrated in Fig. 5 where the highest occupied molecular orbital energies have been plotted in units of $-\beta_0$ against $\gamma = \beta_2/\beta_1$. The curves cross at $\gamma = 1.61$ and, using this with (3) we find that $\beta_1 = 0.737$ and $\beta_2 = 1.187$. Substitution of these values into a new Hückel molecular orbital calculation on phenanthrene and triphenylene leads to k_n equal to 0.7407 β_0 and 0.7403 β_0 respectively and so confirms the technique described.

Discussion

We do not claim that the calculations described here yet furnish unassailable proof of Clar's theories of aromaticity. They are in general agreement with the relevant spectra of the known triphenylenes and to this extent corroborate the predictions made on the basis of Clar's models. However, the fact that we are using Hückel molecular-orbitals as bases precludes the acceptance of localised electron-pair models. These can have no meaning in the Hückel theory unless some of the β_{rs} values are assumed to be zero even when r and s are neighbours. For example, if in triphenylene VIII we put the β values for bonds $\beta\sigma$ and $\gamma\tau$ equal to zero, as would be necessary if these were considered to be pure σ-bonds, we should obviously find the secular determinant factorising to give the π-levels of phenanthrene from the conjugated system to the left of and including $\beta\gamma$ and those of butadiene (or of ethylene if $\varkappa\lambda$ also has $\beta = 0$) from the rest of the molecule. In either case the lowest electronic transition energies would therefore be those of phenanthrene. However, there is ample evidence to support the view that between sp^2-hybridised carbon atoms β is a function of bond length and cannot be zero in aromatic hydrocarbons. Further β' appears always to be between 0.7 and 1.2. Our calculations indicate that the relative spectral measurements are predictable by using β-values lying within this range.

Conclusion

We conclude that the observations of Clar and his colleagues on the spectra of the triphenylenes are explicable on the basis of molecular orbital calculations such as our series I and II the latter being probably the better. We certainly do not assert that we can explain the spectra in detail or that we are confident that the interaction integrals β are unequivocally determined, indeed we show that it is possible to vary these in a benzene ring without altering the highest occupied levels k_n. We hope to report in a subsequent publication on the result of assuming in the Bm, l portion of the molecule sBm, l that the β's are those of the phene 0Bm, l.

We gratefully acknowledge many helpful discussions with Dr. E. Clar and Dr. J.-F. Guye-Vuillème and the award of a D. S. I. R. Maintenance Grant to one of us (D. A. M.-B.).

Chemistry Department, University of Glasgow.

References

[1] Ahmed, F. R., and J. Trotter: Acta cryst. **16**, 503 (1963).
[2] Clar, E., A. McCallum, and R. A. Robertson: Tetrahedron **18**, 1471 (1962).
[3] Coulson, C. A., and R. Daudel: "Dictionary of Values of Molecular Constants", Volume II, 1955.
[4] Goodwin, T. H., and D. A. Morton-Blake: Theoret. chim. Acta **1**, 458 (1963).
[5] Hargreaves, A., and S. Hasan Rizvi: Acta cryst. **15**, 365 (1962).
[6] Lennard-Jones, J. E.: Proc. Roy. Soc. **A**, **158**, 280 (1937).
[7] Mulliken, R. S., C. Rieke, and W. G. Brown: J. Amer. chem. Soc. **63**, 48 (1941).
[8] Pariser, R.: J. chem. Physics **24**, 250 (1956).
[9] Streitwieser, A., Jr.: "Molecular Orbital Theory for Organic Chemists", p. 218. New York: Wiley 1961.

(Received December 9, 1963)