659. *Molecular-orbital Calculations for a New Class of Aromatic Hydrocarbon.*

By R. Pauncz and A. Cohen.

Molecular-orbital calculations are reported for a class of aromatic hydrocarbons investigated by Clar and his co-workers; the results agree with the regularities found by them. The bond lengths of the quasi-single bonds connecting the benzenoid rings are predicted to be longer than those of other bonds. The maximum free valences are smaller than those of isomeric aromatic hydrocarbons, explaining the relative inertness of the compounds. Predicted spectral trends agree with experimental findings.

RECENTLY Clar and his co-workers [1] investigated a new class of condensed aromatic hydrocarbons which have the common property that they are built up from benzenoid rings interlinked by quasi-single bonds. They have a low reactivity, do not dissolve in cold concentrated sulphuric acid, and show strong phosphorescence of very long life at low temperature, and their absorption spectra are shifted towards the violet region as compared with the corresponding aromatic hydrocarbons (except for the polyphenyls) possessing the same number of benzenoid rings. Clar and his co-workers interpreted the spectra and the chemical behaviour by the use of Kekulé structures.

It seemed of interest to investigate the molecules belonging to this class on the basis of the L.C.A.O.–M.O. method. We carried out standard L.C.A.O.–M.O. calculations (neglecting overlap) for a number of these molecules and for some other polynuclear hydrocarbons which were needed for comparison purposes. In the Figures we give the bond orders and free valences, and in the Table the energies of the two highest filled orbitals of the molecules.

Molecule	I	II	III	IV	V	VI	VII	VIII
k values of the two highest filled orbitals	0·87939	0·67329	0·61731	0·60523	0·51581	0·61803	0·6375	0·65479
	0·68404	0·55496	0·50290	0·57740	0·50710	0·46477	0·4114	0·42473

Orbital energies: $E = \alpha + k\beta$

Bond Orders.—We have calculated the Coulson bond orders, defined as

$$p^c(rs) = \sum_i n_i c_{ri} c_{si} \qquad \qquad (1)$$

where n_i is the number of the electrons and c_{ri} the coefficient of the r-th atomic orbital in the i-th molecular orbital; r and s are indices of neighbouring atoms. For a discussion of various mobile bond orders and their interrelation we refer to Ham and Ruedenberg.[2] We also evaluate the Pauling bond orders [3] based on a description of the molecules in terms of equally weighted Kekulé structures (K.S.) only:

$$p^p(rs) = \frac{\text{No. of K.S. having } rs \text{ as double bond}}{\text{Total no. of K.S.}} \qquad \cdots \qquad (2)$$

The latter were computed by using Ham's theorem.[4] By the use of these quantities the qualitative arguments of Clar *et al.* were put on a quantitative basis.

Inspection of the Coulson bond orders of the relevant molecules shows that we can divide the bonds into two groups. The first contains those corresponding to the benzenoid units (marked in the Figures by the inscription Bz); the bond orders vary between 0·550 and 0·700. (The bond order in benzene is 0·667.) The second group contains the bonds connecting the benzenoid units; these have smaller bond orders, which correspond to

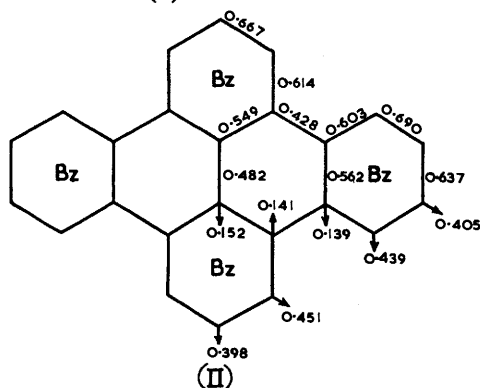[1] Clar and Zander, *J.*, 1958, 1861; Clar, Ironside, and Zander, *J.*, 1959, 142.
[2] Ham and Ruedenberg, *J. Chem. Phys.*, 1958, **29**, 1215.
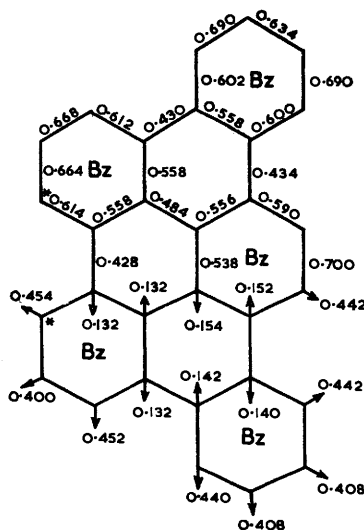[3] Pauling, " The Nature of the Chemical Bond," Cornell University Press, Ithaca, 1940, p. 142.
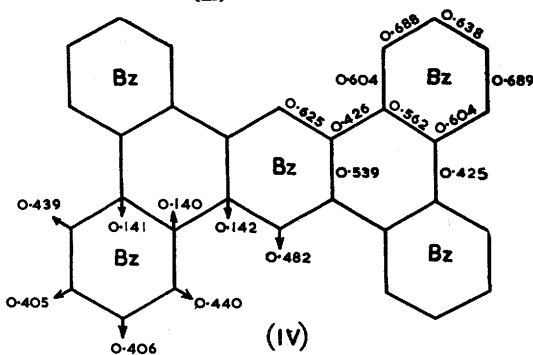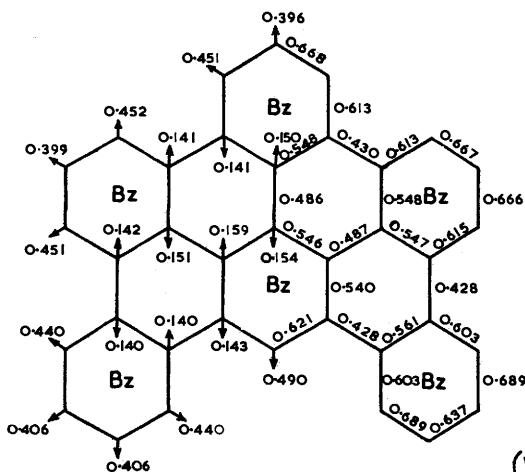[4] Ham, *J. Chem. Phys.*, 1958, **29**, 1229.
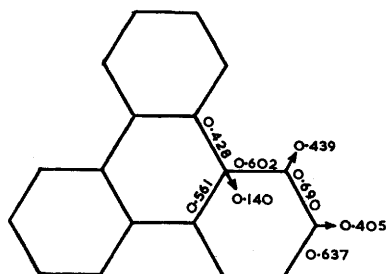
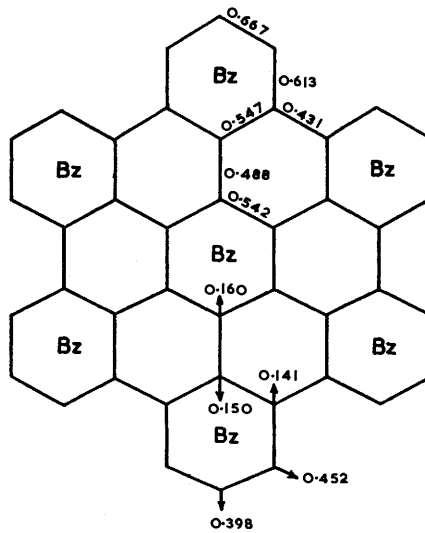Fig. 1. (I) *Triphenylene.*[a] (II) 1,2:6,7-*Dibenzo-pyrene.* (III) 1,12:2,3:10,11-*Tribenzoperylene.* (IV) 1,2:3,4:5,6:7,8-*Tetrabenzanthracene.* (V) 1,2:3,4:5,6:10,11-*Tetrabenzanthanthrene.* (VI) 2,3:4,5:6,7:8,9:10,11:12,1-*Hexabenzocoronene.*

[a] Berthier, Coulson, Greenwood, and Pullman, A., *Compt. rend.*, 1948, **226**, 1906.

longer bond length and weaker bond.   In all of the molecules we have a value of about 0·43 for bonds in the periphery and of about 0·48 for bonds in the inner part of the molecule.

These results can be compared with those based on the Pauling bond orders using Kekulé structures exclusively.   The latter give bond orders between 0·35 and 0·55 for the benzenoid rings and 0·1 for the quasi-single bond in the periphery, 0·2 in the inner part. This emphasises even more the difference between the bonds occurring in the benzenoid units and the quasi-single bonds connecting them.

Hall,[5] in computing the bond orders of a number of aromatic molecules, notes that these are only first approximations and more reliable results can be obtained by using a self-consistent treatment.   He performed the calculations for a few molecules and observed the tendency for the larger bond orders to be increased and the smaller ones to be decreased. If we extrapolate this result to our molecules, it follows that the bond orders of the quasi-single bonds will be further decreased and a greater separation would be obtained between

FIG. 2.

A   B
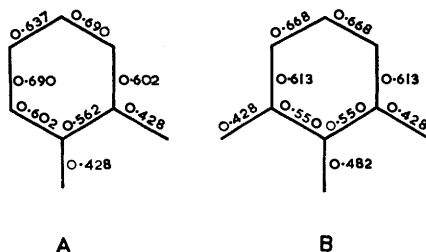
these and the bonds occurring in the benzenoid rings.   Thus the attractive view put forward by Clar *et al.*[1] that we can regard these molecules as built up from benzene units, which are more or less independent, is supported on the basis of the molecular-orbital treatment.

We note, furthermore, the great constancy of the shape of the corresponding benzenoid units.   We can classify them according to the number of the benzene rings to which they are linked.   There are enough data available in order to compare the rings A and B in the various molecules, which are linked to two and three benzene units, respectively.   The corresponding bond orders given in Fig. 2 are remarkably constant within a few units in the third decimal place throughout the molecules.

Reactivity.—Clar *et al.*[1] observe that these molecules are relatively inert and do not dissolve even in cold concentrated sulphuric acid.

We have not evaluated all the quantities necessary for a more or less complete characterisation of the reactivity of the molecules from the M.O.-theoretical point of view (localisation energies, self-polarisabilities, etc.).   We give in Fig. 1 only the free valences which are obtained from the bond orders by the relation

$$F_r = N_m - \sum p_{rs} \ (s \text{ neighbour to } r) \quad . \quad . \quad . \quad . \quad . \quad (3)$$

For N_m we used the same value ($\sqrt{3}$) for secondary and tertiary carbon atoms.   The free valences are characteristic of the reactivity in radical reactions; on the other hand, for the alternant aromatic hydrocarbons (all the molecules discussed here belong to this class) a close correlation exists between the free valences and the other quantities characterising the reactivity.[6]   This correlation is not always complete,[7] but generally the most reactive positions are predicted in the same way when either the free valences or the localisation energies are used.

[5] Hall, *Trans. Faraday Soc.*, 1957, **53**, 573.
[6] Pullman, B., and Pullman, A., *Progr. Org. Chem.*, 1958, **4**, 31.
[7] Coulson, Moser, and Barnett, *J.*, 1954, 3108;   Fukui, Yonezawa, and Nagata, *J. Chem. Phys.*, 1957, **26**, 831.

Let us consider the free valences of the secondary atoms. The corresponding free valences of most of the benzenoid polynuclear hydrocarbons cluster into three distinct groups:

(i) 0·400—0·410   (ii) 0·440—0·460   (iii) 0·500—0·540

For example, the free valences of the anthracene β, α, and μ positions fall into these groups, respectively.

Inspection of the free valences of the molecules belonging to the class under investigation, shows that (I), (II), (III), and (VI) do not have any from the third group, *i.e.*, the maximal reactivity is about the same as in the anthracene (or naphthalene) α-position; (IV) and (V) do contain two positions with the free valence 0·482 and 0·490, respectively, which are close to the third group. But these are also decreased if we compare them with the corresponding anthracene value (0·520). Generally we can state that the free valences are decreased as compared with those of closely related hydrocarbons.

The same statement can be made with respect to the sum of the free valences corresponding to a pair of positions where a condensation can be expected. For example,

FIG. 3.   (VII) 1,12:4,5:10,11-*Tribenzoperylene.*   (VIII) 1,2:3,4:7,8:9,10-*Tetrabenzo-naphthacene.*
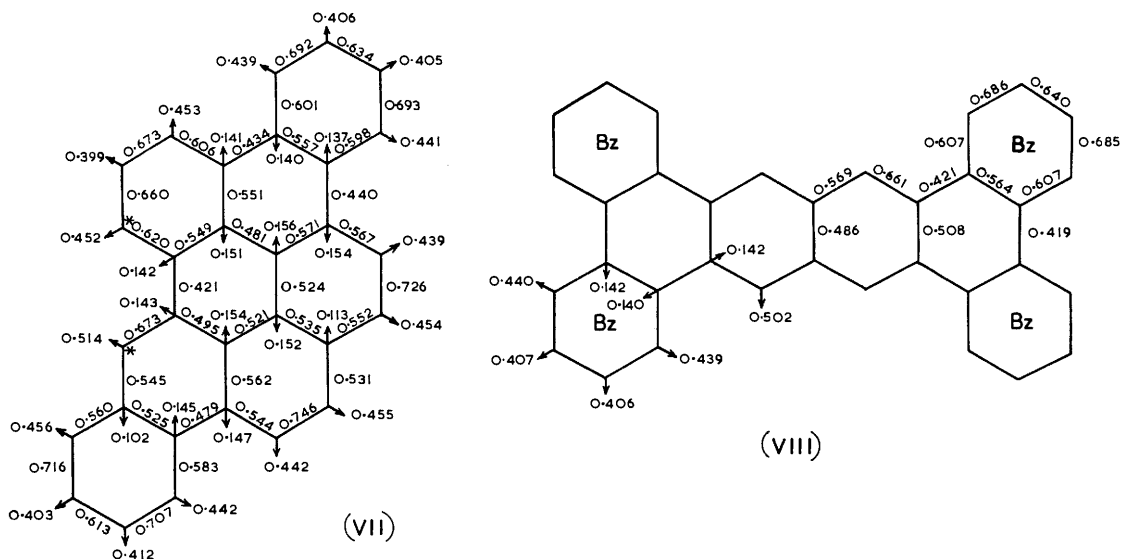
Clar *et al.*,[1] comparing the Diels–Alder activity of (III) with that of the isomeric (VII), observe that the first does not react with maleic anhydride whereas the second does. This is explained by the fact that in (III) the sum of the corresponding free valences (0·908) is decreased as compared with the corresponding quantity in (VII) (0·966). (The positions are marked by asterisks in both compounds.) A more careful investigation is needed in the case of (IV) where the free valences are relatively high. Here we computed the *para*-localisation energy relating to the μ-positions. The value obtained ($-3\cdot65\beta$) as compared with that of the anthracene ($-3\cdot31\beta$) indicates that the rate of the Diels–Alder reaction must be slower by a factor of 10^{-7} (cf. ref. 7) in compound (IV) than in anthracene, thus confirming the relative inertness of the molecule.

Moreover, we note the absence of bonds with very high bond orders (0·720—0·740) which indicates a relative inertness towards addition reactions.

The general decrease of free valences may give an explanation for the fact that these molecules do not dissolve in strong acids to form a protonated compound. According to

the model described by Gold and Tye[8] the proton is localised on the carbon atom which is the most reactive. Thus the ease of the formation of the protonated compound, *i.e.*, the solubility of the molecule in acids, is related to the maximum free valence and this is generally decreased in this class of compound.

Further, as we shall see in the next section, the highest filled orbital lies generally lower than in other hydrocarbons with the same number of benzene rings. This may be also a cause of the relative inertness of the molecules belonging to the class, in certain reaction mechanisms.[9]

Finally, it is interesting to investigate one further compound, (VIII), which strictly does not belong to the class but has many properties in common with it: it does not dissolve in concentrated sulphuric acid, it has the lowest reactivity of all benzologues of tetracene, and it shows a strong phosphorescence at $-170°$ in solid solution.[10]

The molecular diagram shows that the bond orders of the four benzene rings are very close to those of the benzenoid rings of the class (type *A*). Again we see the small bond orders (0·420) in the periphery corresponding to the bonds which connect the benzenoid rings with each other and with the central part of the molecule. Here are some positions with high free valence (0·502) but these are still low compared with the free valences of the corresponding positions in naphthacene (0·529). Clar observes that this molecule reacts very slowly with boiling maleic anhydride. We computed the *para*-localisation energy for the most plausible positions (with the free valence 0·502). The value obtained $(-3·48\beta)$ is smaller than that in compound (IV) $(-3·65\beta)$ thus explaining why (VIII) is more reactive than (IV); on the other hand, it is considerably greater than the corresponding one for the naphthacene 5,12-positions $(-3·25\beta)$,[11] *i.e.*, it corresponds to a slower reaction rate by a factor of 10^{-6}.

Spectrum.—The simple treatment that we used is less reliable for optical transitions, but generally the trends are predicted quite well.

If we compare the energies of the highest filled orbitals with those of other aromatic compounds possessing the same number of rings, we see that the absolute values of these are greatest, *i.e.*, the relevant transitions from the highest filled to the lowest empty orbital (pairing theorem) have the shortest wavelength among the transitions of the corresponding compounds. This is exactly what the comparison of the absorption spectra reveals.

We did not attempt to interpret the strong phosphorescence shown by the compounds at low temperature. The peculiar position of aromatic molecules with regard to phosphorescence is more or less understood on the basis of the model calculations relating to benzene,[12] but these are not easy to extend to large aromatic systems. On the other hand, more quantitative experimental data are needed (*e.g.*, measurement of life-times) before, in our opinion, it is worthwhile to formulate a more sophisticated theoretical treatment.

Diamagnetic Anisotropy.—Triphenylene (I), which is the simplest compound of the group, has the smallest diamagnetic anisotropy[13] of any condensed aromatic compound with four benzene rings. This is related to the mobility of the π-electrons around the whole molecule being decreased on account of the smaller conjugation of the benzene units.[14] Tentatively, we can extrapolate this result to the other members of the group and expect smaller diamagnetic anisotropy as compared with the corresponding isomers.

Conclusion.—The molecular-orbital treatment supports the explanation of Clar *et al.*, that we can regard the benzene units of the molecules belonging to this class of compound

[8] Gold and Tye, *J.*, 1952, 2173, 2181, 2184.
[9] Pullman, B., and Effinger, " Calcul de Fonctions d'Onde Moleculaire," Centre National de la Recherche Scientifique, Paris, 1958, p. 329.
[10] Clar, *Tetrahedron*, 1959, **6**, 355.
[11] Brown, *J.*, 1950, 691.
[12] Hameka and Oosterhoff, *J. Mol. Phys.*, 1958, **1**, 358.
[13] Pauncz and Berencz, *Acta Phys. Acad. Sci. Hung.*, 1952, **2**, 183.
[14] McWeeny, *Proc. Phys. Soc.*, 1951, **64**, 921.

as being more or less independent and that there are quasi-single bonds connecting the benzenoid units. The relative inertness of the compounds is explained by the decrease of maximum free valence and the absence of bonds with high bond order. The spectral behaviour is reflected by the lower positions of the energies of the highest filled orbitals. The treatment indicates also that we cannot draw a sharp line between the members of the class and some molecules which are closely related to it.

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