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ON THE STABILITY OF SUBSTITUTED DIPHENYLENES

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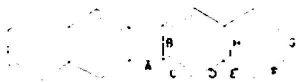
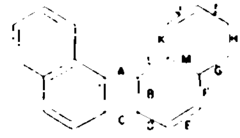
Abstract—Simple molecular-orbital calculations of the π electron energies and bond orders in the linear dibenzodiphenylene (I) and the *cis*-dibenzodiphenylene (II) are sufficient to show that the resonance energy of I exceeds that of II by about 4·3 kcal/mole. Similar conclusions follow from the bond orders in the central cyclobutadiene-like ring.

A number of derivatives of diphenylene(III) have been synthesized:[1,2] of these, 2:3,6:7 dibenzodiphenylene(I) and 1:2,7:8 dibenzodiphenylene(II) are of considerable interest because of the great difference they exhibit in their properties, as emphasized in a recent note by Curtiss.[3] I is very highmelting and exceedingly stable (unchanged on sublimation at 350°) whereas II decomposes easily and behaves as a highly unsaturated compound.



I



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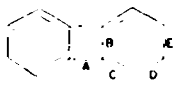

III

Both of these molecules are derived from diphenylene(III) by benzenoid annellation, but they may equally be regarded as derived from the hypothetical cyclobutadiene by annellation of naphthalene systems in the 2:3- and 1:2-positions respectively. The greater stability of I as compared with II must be related to the electron distribution in the region of this central cyclobutadiene-like ring. For cyclobutadiene[4] is not stable in a totally aromatic (i.e. square) configuration, and tends to distort in such a way as to favour a Kekule structure such as  or . It would follow from this that if the naphthalene regions in I and II took up the predominant Kekule bond diagrams, as shown in the figure, then in II we should have a situation in which the bonds labelled A and C would inevitably be weak, and where we might expect a lower stability than in I where none of the π-electron influences

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[1] R. F. Curtiss and G. Viswanath, *J. Chem. Soc.* 1670 (1959).
[2] M. P. Cava and J. F. Stucker, *J. Amer. Chem. Soc.* 77, 6022 (1955).
[3] R. F. Curtiss, *J. Chem. Soc.* 3650 (1959).
[4] C. A. Coulson, *Chemical Society Symposia.* Special Publication No. 12, p. 85. Bristol (1958).

responsible for the instability of cyclobutadiene would arise. We might even argue that II had a locally pseudo-aromatic structure, using the terminology introduced by Craig,[5] and would therefore be expected to be unstable and unconjugated by analogy. Recently, Baker *et al.*[6] have shown that the chemical reactivity of diphenylene can be well understood in conjunction with simple molecular-orbital theory, if it is assumed that the most important contributing structure in diphenylene is that shown in III. Now the bond structures drawn in I and II are extreme, and no one suggests that the double-bonds are strictly localized in this way. But it should be possible to calculate the bond orders in I and II, and see whether the explanation which we have suggested for the difference between these molecules, is correct.

We have used the standard simple molecular-orbital theory, of Hückel type, with no inclusion of overlap integrals and with the assumption that all Coulomb (i.e. electronegativity) terms have the same value α. Since, however, our concern is with the differences in bond order, it is important to allow for variable resonance integrals β_{rs}. Without including some sort of dependence of β_{rs} on bond length, no self-consistence is possible. Lennard-Jones[7] used a Hooke-law potential function. But, partly through an inadequate knowledge of the way in which the radius of a carbon atom depends on the type of σ-hybridization, his predicted bond lengths were not entirely satisfactory. We have therefore preferred to use the functional form suggested by Longuet-Higgins and Salem[8] in their discussion of long cyclic and straight polyenes;

$$\beta(l) = -\mathrm{B}e^{-l/a} \tag{1}$$

where $a = 0{\cdot}3106$ Å, and $\beta(1{\cdot}40 \text{ Å}) = \beta_0 = -25{\cdot}56$ kcal/mole. Similarly, for the dependence of bond length l on π-bond order p, we used the linear relation

$$l = (1{\cdot}50 - 0{\cdot}15p) \text{ Å}. \tag{2}$$

though recent studies on ethylene, where $p = 1$, suggest that the factor $0{\cdot}15p$ could more properly be replaced by $0{\cdot}16p$, and 1·51 is probably closer to the truth than 1·50. However, these are small points, which will not materially affect our conclusions. The forms (1) and (2) are such that the correct bond length and breathing-frequency are predicted for the case of benzene. Bond orders p are calculated according to the standard formula of Coulson.[9]

In order to obtain self-consistency, we want the calculated bond orders to lead, via (2) and (1), to molecular orbitals from which the original bond orders are now retrieved. This is achieved by an iterative procedure. First, we set all $\beta_{rs} = \beta_0$ and compute the molecular orbitals and bond orders p_{rs}. These lead to new β-values which must now be used to obtain improved bond orders, etc. The process is continued until further iterations make effectively no difference in computed bond orders and bond lengths. For I and III the starting values were available from the calculations of Crawford[10] and the Dictionary of Molecular Constants compiled by Coulson and Daudel. As might be expected, the effect of the various iterations is to

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[5] D. P. Craig, *J. Chem. Soc.* 3175 (1951).

[6] W. Baker, J. F. W. McOmie, D. R. Preston and V. Rogers, *J. Chem. Soc.* 414 (1960).

[7] J. E. Lennard-Jones, *Proc. Roy. Soc.* A **158**, 280 (1937).

[8] H. C. Longuet-Higgins and L. Salem, *Proc. Roy. Soc.* A **251**, 172 (1959).

[9] C. A. Coulson, *Proc. Roy. Soc.* A **169**, 413 (1939).

[10] V. A. Crawford, *Canad. J. Chem.* 47 (1952); See also M. A. Silva and B. Pullman, *C. R. Acad. Sci., Paris* **242**, 1888 (1956).

increase the bond order of those bonds which are already fairly high, and to decrease those which are low. It is known, from much work on butadiene, that this improves the agreement with experiment.

Bond orders obtained for I, II and III by this self-consistent scheme are given in Table 1. The labelling of the bonds is as in the diagrams. Table 2 shows the total energies of I and II.

TABLE 1. FINAL BOND ORDERS AND LENGTHS (Å)

Bond	Molecule I		Molecule II		Molecule III	
	π-Bond order	Length	π-Bond order	Length	π-Bond order	Length
A	0·273	1·459	0·205	1·469	0·219	1·467
B	0·472	1·429	0·655	1·402	0·572	1·414
C	0·757	1·387	0·171	1·474	0·701	1·395
D	0·506	1·424	0·631	1·405	0·612	1·408
E	0·557	1·416	0·688	1·397	0·705	1·394
F	0·733	1·390	0·581	1·413		
G	0·587	1·412	0·520	1·422		
H	0·548	1·418	0·763	1·386		
I			0·551	1·417		
J			0·764	1·385		
K			0·518	1·422		
L			0·579	1·413		
M			0·511	1·423		

TABLE 2. TOTAL π-ELECTRON ENERGIES

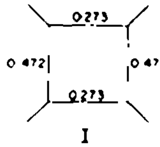
Molecule I	$20\alpha - 27{\cdot}307\beta_0$
Molecule II	$20\alpha - 27{\cdot}138\beta_0$
Difference	$0{\cdot}169\beta_0$

An indication of the rate of convergence of the calculated bond orders may be obtained by considering the highest and lowest bond orders in molecule I. These are bonds C and A respectively. Here successive integrations yield:

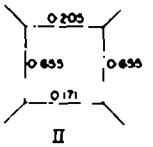
Bond C: 0·722, 0·750, 0·755, 0·757

Bond A: 0·316, 0·279, 0·274, 0·273

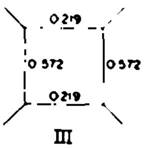
A glance at the tables shows that the central ring is described by the diagrams below:



I



II



III

Thus the degree of double-bond fixation increases in the sequence

Molecule I < Molecule III < Molecule II.

But this corresponds exactly with the sequence of stability of these molecules, the greater the degree of bond fixation, the less the extent of conjugation and the lower the stability. Another way of putting this is to notice that the extra benzenoid annelation of diphenylene lowers the bond orders of the two connecting bonds in II, but increases them in I. It is not surprising that the resonance energy of I exceeds that of II by $0{\cdot}169\beta_0 = 4{\cdot}3$ kcal/mole.

It is possible that the difference in stability may be greater than that arising from this difference in resonance energy. For, although the products of decomposition of II have not been described and we cannot therefore discuss any probable transition state, it seems very plausible that II would tend to split across bond C to give a di-α-naphthyl system, or across both A and C to give two separate naphthalenes. Now if we use the simple perturbation theory as developed by Coulson and Longuet-Higgins,[11] the energy required to break bond C in II is $0{\cdot}171 \times 2 \times$ corresponding resonance integral ($0{\cdot}788\ \beta_0$)

$$= 0{\cdot}269\beta_0.$$

The corresponding energy in I is $0{\cdot}237 \times 2 \times 0{\cdot}827\beta_0$

$$= 0{\cdot}451\beta_0.$$

The difference between these two is $0{\cdot}182\beta_0 = 4{\cdot}7$ kcal/mole. Alternatively, if we break both A and C in II and the corresponding bonds in I, the difference is $0{\cdot}903\beta_0 - 0{\cdot}598\beta_0 = 7{\cdot}8$ kcal/mole. Either of these values, in addition to the larger resonance energy of 4·3 kcal/mole possessed by I, is sufficient to account for the much greater observed stability of I as compared with II.

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[11] C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc.* A **191**, 39 (1947).