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ON THE STABILITY OF SOME POLYCYCLIC BIPHENYLENE DERIVATIVES

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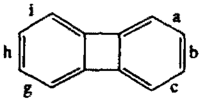
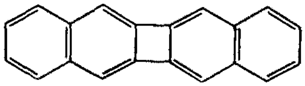
Abstract—MO calculations on the recently-prepared dibenzo[a,c]biphenylene (III) show that its stability should be intermediate between those of dibenzo[b,h]biphenylene (I)[1] and dibenzo[a,i]biphenylene (II),[2] previously studied by Ali and Coulson.[3] Similar work on the as yet unprepared sesquibiphenylenes IV and V shows that V should have a higher resonance energy and be less reactive than IV.





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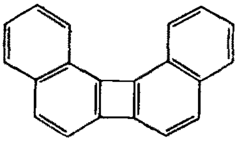

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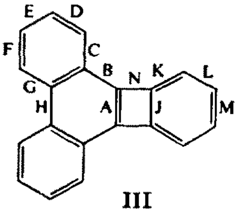
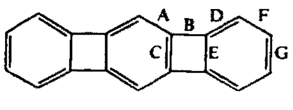


III



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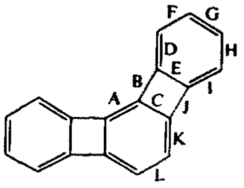

V

INTRODUCTION

The calculations reported in this paper are based on the Hückel MO model of Coulson and Poole.[4] In this model all overlap integrals vanish and all Coulomb integrals have the same value α, but the resonance integrals β_{rs} depend on bond-length l and hence on π-bond order p according to the relations:[5]

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[1] R. F. Curtis and G. Viswanath, *J. Chem. Soc.* 1670 (1959).

[2] M. P. Cava and J. F. Stucker, *J. Amer. Chem. Soc.* **77**, 6022 (1955).

[3] M. A. Ali and C. A. Coulson, *Tetrahedron* **10**, 41 (1960).

[4] C. A. Coulson and M. D. Poole, *Tetrahedron* **20**, 1859 (1964).

[5] C. A. Coulson and A. Golebiewski, *Proc. Phys. Soc.* **78**, 1310 (1961).

$$\beta(l) = \beta_0 \exp[-2{\cdot}683\,(l - 1{\cdot}397)], \quad (1)$$

$$l = 1{\cdot}517 - 0{\cdot}18\,p; \quad (2)$$

here l is measured in Å and β_0 is the resonance integral at the bond-length of benzene. A self-consistent set of molecular orbitals, resonance integrals and bond-lengths can be obtained by iteration.

The model is remarkably successful in accounting for the bond-lengths of hydrocarbons with undistorted sp_2 hybridization, and there is some evidence from NMR studies[6] that its predictions may be at least qualitatively correct even for molecules containing 4-membered rings. It has been suggested by Dewar and Gleicher[7] that such molecules are better treated by taking electron–electron interaction into account with a self-consistent field approximation, but the bond-lengths they calculate in this way agree with those calculated by the Hückel method[3,4,8] to within 0·01 Å. The most recent measurements[9,10] of bond-lengths in biphenylene differ from these calculated values by more than this, and it thus appears that a more radical treatment of the distortion of the sp_2 hybridization is needed. In the absence of a wholly adequate theory, however, the simpler approach of Coulson and his colleagues is used in the present paper.

Dibenzobiphenylenes

The first molecule investigated, dibenzo[a,c]biphenylene (III), has recently been prepared.[11] Self-consistent field calculations have been carried out concurrently by Dewar and Gleicher,[7] and it thus provides another comparison of the two methods.

TABLE 1. π-BOND ORDERS AND LENGTHS (Å) FOR III

	This work			Dewar and Gleicher[7] (PPP)
	π-Bond order			
Bond	zero-order	iterated	Final bond length	Final bond length
A	0·672	0·727	1·386	1·374
B	0·527	0·500	1·427	1·435
C	0·562	0·557	1·417	1·416
D	0·714	0·731	1·385	1·383
E	0·613	0·593	1·410	1·412
F	0·704	0·723	1·387	1·384
G	0·587	0·577	1·413	1·415
H	0·473	0·453	1·436	1·440
I	0·522	0·552	1·418	1·405
J	0·562	0·561	1·416	1·415
K	0·699	0·722	1·387	1·384
L	0·598	0·586	1·412	1·412
M	0·707	0·726	1·386	1·384
N	0·244	0·195	1·482	1·483

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[6] A. R. Katritzky and R. E. Reavill, *Rec. Trav. Chim.* **83**, 1230 (1964).

[7] M. J. S. Dewar and G. J. Gleicher, *Tetrahedron* **21**, 1817 (1965).

[8] M. A. Ali, J. G. Carey, D. Cohen, A. J. Jones, I. T. Millar and K. V. Wilson, *J. Chem. Soc.* 387 (1964).

[9] J. Waser and V. Schomaker, *J. Amer. Chem. Soc.* **65**, 1451 (1943).

[10] T. C. W. Mak and J. Trotter, *J. Chem. Soc.* 1 (1962).

[11] J. W. Barton, A. M. Rogers and M. E. Barney, *J. Chem. Soc.* 5537 (1965).

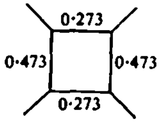
TABLE 2. TOTAL ITERATED π-ELECTRON ENERGIES

Molecule III	$20\alpha + 27{\cdot}248\,\beta_0$
(zero order)	$(20\alpha + 27{\cdot}908\,\beta_0)$
Molecule I	$20\alpha + 27{\cdot}307\,\beta_0$
Difference (I–III)	$0{\cdot}059\,\beta_0$
Molecule II	$20\alpha + 27{\cdot}138\,\beta_0$
(Difference II–III)	$-0{\cdot}110\,\beta_0$

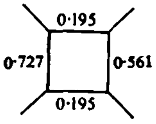
Table 1 gives the bond-orders and bond-lengths for the model of Coulson and Poole. Five iterations were found sufficient to ensure consistency with both Eqns. (1) and (2) to within the quoted accuracy. The rate of convergence can be illustrated by the successive bond-orders for bonds N(0·244, 0·202, 0·196, 0·195, 0·195) and D(0·714, 0·727, 0·730, 0·731, 0·731). Table 1 gives also the bond-lengths calculated by Dewar and Gleicher, which agree with the present calculations to within ±0·01 Å.

Table 2 gives the total π-electron energies, together with those calculated by Ali and Coulson[1] for the [b, h] and [a, i] isomers I and II;[12] the resonance stability of III should therefore lie between those of I and II; if we take[8] $\beta_0 = -25{\cdot}6$ kcal mole^{-1}, then III lies 2·8 kcal mole^{-1} above I and 1·5 kcal mole^{-1} below II. This is borne out by a preliminary examination of its properties.[11]

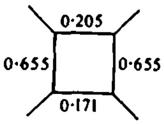
We show below the bond orders in the central rings of the three molecules, in order of decreasing stability:



I



III



II

It should be noted that, although III is more stable than II, the total π-bond order in the central ring of III is hardly less than in II. This is due to the very high order of bond A in III, brought about by the angular annellation of two benzene rings on one side of the biphenylene system. This high bond order is confirmed experimentally by the compound's facile reaction to give a dibromide by addition of bromine at bond A.[11]

Ali and Coulson (Ref. 1, p. 44) have suggested that the energy required to break a bridge bond in I and II can be estimated by evaluating the π-electron energy. For bond N of III this is given by

$$2 \times p_N \times \beta_N = 2 \times 0{\cdot}195 \times 0{\cdot}796\,\beta_0 = 0{\cdot}31\,\beta_0,$$

as compared with $0{\cdot}45\,\beta_0$ for I and $0{\cdot}27\,\beta_0$ for the weaker bond of II. Thus although the resonance stability of III lies nearer to that of I than to that of II, its reactivity with respect to cleavage of a bridge bond should be closer to that of II. Unfortunately there is at present no means of testing this prediction. All the dibenzobiphenylenes can readily be hydrogenated with rupture of the four-membered ring, but precise data

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[12] Since Ali and Coulson used slightly different numerical constants in Eqns (1) and (2), it was necessary to ensure that these energies are strictly comparable. This was done by recalculating the energy for III using Ali and Coulson's model, which was found to give an identical value within the quoted accuracy.

on the relative ease of hydrogenation is not available and would be difficult to obtain. Moreover, this reaction takes place only in the presence of a metal catalyst, which may well introduce factors not considered in the theoretical argument. This may explain why both dibenzo[a,i]biphenylene (II)[2] and dibenzo[a,h]biphenylene[13] give only 2,2′-binaphthyl on hydrogenation, although this requires cleavage of the stronger and more sterically hindered bond in II.

Sesquibiphenylenes

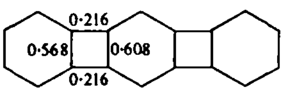
Calculations for the two sesquibiphenylenes (IV and V) have been carried out in advance of current attempts to synthesize them in these laboratories. The results are given in Tables 3 and 4. Convergence of successive iterations is similar to that of the examples already quoted for the dibenzobiphenylenes.

TABLE 3. π-BOND ORDERS AND LENGTHS (Å) FOR IV AND V

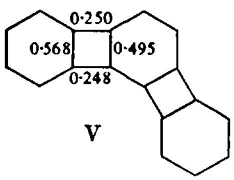
Bond	Molecule IV			Molecule V		
	Bond order		Final bond length	Bond order		Final bond length
	zero	iterated		zero	iterated	
A	0·642	0·652	1·400	0·701	0·734	1·385
B	0·264	0·216	1·478	0·301	0·248	1·472
C	0·584	0·608	1·408	0·492	0·495	1·428
D	0·685	0·706	1·390	0·666	0·686	1·394
E	0·562	0·568	1·415	0·549	0·568	1·415
F	0·614	0·605	1·408	0·635	0·626	1·404
G	0·695	0·711	1·389	0·676	0·692	1·393
H				0·637	0·626	1·404
I				0·664	0·685	1·394
J				0·303	0·250	1·472
K				0·703	0·738	1·384
L				0·587	0·558	1·417

A simple Kekulé picture suggests that IV should have the lower resonance energy, since all its canonical forms possess at least one double bond in one of the four-membered rings; whereas V has one form which does not. This is consistent with the iterated π-electron energies, although these predict that the difference in energy is quite small (~1 kcal mole^{-1}).

We show below the bond orders in the four-membered rings:



IV



V

According to the theory of Ali and Coulson, cleavage of bond B in IV requires a π-electron energy fission of

$$2 \times p_B \times \beta_B = 2 \times 2\cdot16 \times 0\cdot804\, \beta_0 = 0\cdot35\, \beta_0;$$

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[13] J. W. Barton and S. A. Jones, unpublished observations.

TABLE 4. TOTAL π-ELECTRON ENERGIES

	zero-order	iterated
Molecule IV	$18\alpha + 25{\cdot}010\,\beta_0$	$18\alpha + 24{\cdot}448\,\beta_0$
Molecule V	$18\alpha + 25{\cdot}082\,\beta_0$	$18\alpha + 24{\cdot}492\,\beta_0$
Difference (V–IV)	$0{\cdot}072\,\beta_0$	$0{\cdot}044\,\beta_0$

in V, cleavage of bond B (or bond J) requires $0{\cdot}41\ \beta_0$, about 1·5 kcal mole^{-1} more than in IV. Hence rupture of the four-membered ring in V should be slightly more difficult than in IV. Since the bond orders of B and J are almost identical, steric and other factors not taken into account by the theory will determine the bonds where cleavage occurs. As with the dibenzobiphenylenes, it would probably be difficult to determine the relative ease of breaking bonds B and J; furthermore, the 1- or 2-phenylbiphenylenes produced would undergo further ring fission.

Acknowledgments—We thank the University of Bristol Computer Unit for their advice and co-operation, and the Science Research Council for a Maintenance grant (J. D. J.).