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THE STABILITY OF NAPHTHOCYCLOBUTADIENES

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Abstract—A molecular-orbital study of the recently synthesized naphthocyclobutadiene IV shows that, although there is a very large degree of double-bond fixation in the four-membered ring, and the molecule should be very reactive, it should nevertheless be more stable and less reactive than the hypothetical molecules V and VI. Bond localization energies and free valences support this view, and provide guidance in interpreting the chemistry of IV.

CAVA *et al.*[1] have recently reported the synthesis of IV. This is the first compound to be recorded in which a cyclobutadiene nucleus is neither stabilized as a transition metal complex nor fused on both sides, as in diphenylene III, to aromatic rings. Several problems are raised by this synthesis:

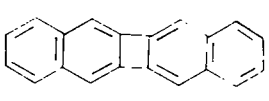
(i) What is the difference in stability between the 2:3 compound which has been found, the hypothetical 1:2 compound V, and the known diphenylene III, all three molecules being isomers? (In considering IV we neglect the phenyl groups and replace them by hydrogen.)

(ii) Can we compare the reactivities of IV, V and the even simpler benzo-compound VI as dienophiles?

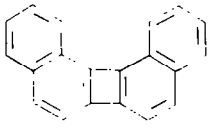
(iii) What can be said about the positions of long-wave UV absorption in the molecules III–VI?

(iv) What relation is there between the degree of bond-fixation in the unsymmetrical molecules IV–VI and the corresponding symmetrical ones I–III?

In order to answer these questions and throw some light on the chemistry of IV we have studied III–VI using the Hückel molecular-orbital method. Molecules I–III



I



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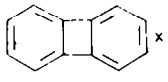
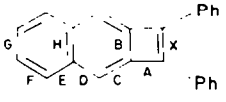
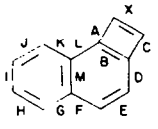


III



IV



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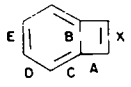
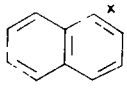


VI



VII

[1] M. P. Cava, B. Hwang and J. Van Meter, *J. Amer. Chem. Soc.* **85**, 4032 (1963).

have already been studied by Ali and Coulson,[2] whose methods have been adopted in the present work. The numbering of the three molecules I–III is the same as that used by Ali and Coulson.

First, however, a simple qualitative argument, similar to that in Ref. 2, would suggest that IV should be more stable than V. We start by drawing the dominant double-bond distribution, based on a Kekulé structure for naphthalene VII with a double bond at the 1:2 position X. This shows (see diagrams) that the four-membered ring in V may be expected to have some of the stability characteristics of cyclobutadiene, whereas in IV it will not. Cyclobutadiene itself[3] is calculated not to be stable in a totally aromatic (i.e. square) configuration, and tends to distort in such a way as to favour one of the two possible (rectangular) Kekulé structures. In V if the bond B were really fixed as a double bond, we should expect instability, by analogy with the known instability of cyclobutadiene, possibly leading to fission of the bonds A and C. On the other hand, in IV and VI where the bonds B tend to be single, we expect, by similar arguments, a relatively greater stability.

For most of the present calculations we have been content with the simplest form of the Hückel theory, putting all the resonance integrals (β) equal. But, since the degree of bond fixation might depend upon differences in the resonance integrals, we have also made some calculations in which each β is taken to vary with bond length l as in Ref. 2, but using the numerical values of Coulson and Gołębiewski[4]

$$\beta(l) = \beta_0 \exp(-(l - l_0)/a) \qquad (1)$$

where $\beta(1{\cdot}397\ \text{Å}) = \beta_0$, $l_0 = 1{\cdot}397\ \text{Å}$ = bond length in benzene, and $a = 0{\cdot}3727\ \text{Å}$. In these calculations which we refer to as 'iterated' we have made three iterations, starting with the zero-order (simple Hückel) values. An adequate degree of self-consistency is achieved by this process.

TABLE 1. COMPARISON OF VARIOUS MOLECULAR QUANTITIES (uniterated)

Molecule	III[a]	IV[b]	V[b]	VI[a]	VII[a]
Total π-energy	$16{\cdot}506\beta_0$	$16{\cdot}200\beta_0$	$15{\cdot}996\beta_0$	$10{\cdot}381\beta_0$	$13{\cdot}683\beta_0$
Delocalization energy	$4{\cdot}506\beta_0$	$4{\cdot}200\beta_0$	$3{\cdot}966\beta_0$	$2{\cdot}381\beta_0$	$3{\cdot}683\beta_0$
Localization energy of bond X	$1{\cdot}35\beta_0$	$0{\cdot}52\beta_0$	$0{\cdot}32\beta_0$	$0{\cdot}38\beta_0$	$1{\cdot}26\beta_0$
Mean free valence of atoms joined by X	0·421	0·598	0·637	0·620	0·428
Lowest electronic transition energy	$0{\cdot}890\beta_0$	$0{\cdot}679\beta_0$	$0{\cdot}295\beta_0$	$0{\cdot}525\beta_0$	$1{\cdot}236\beta_0$

[a] These systems (uniterated) have been dealt with by Streitwieser, *Molecular Orbital Theory for Organic Chemists* Chap 10. J. Wiley, New York and London (1961); and some numerical results are given by Roberts, Streitwieser and Regan, *J. Amer. Chem. Soc.* **74**, 4579 (1952).

[b] New calculations.

Some of our results are shown in Table 1. The first two rows of the table show that neither IV nor V is as stable as the isomeric diphenylene III, but that IV is considerably more stable than V. The corresponding total π-energies after iteration are $16{\cdot}044\beta_0$ for IV, and $15{\cdot}915\beta_0$ for V, so that this extra stability of IV is not critically dependent upon the degree of self-consistency.

The third row of the table gives the energy required to localize two electrons in the bond marked X in each of the diagrams. This is the most reactive bond. The

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

[3] C. A. Coulson, *Chemical Society Symposium Special Publication* No. 12, p. 85. Bristol (1958).

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

localization energy is calculated by subtracting from the total π-energy (i) the π-energy of the 'residual molecule' which is left when the atoms comprising bond X are removed, and (ii) a further $2\beta_0$ for the two electrons localized in X. Even small differences in such localization energies are known to be good measures of dienophile reactivity in the bonds. The figures in this row of Table 1 show that V is highly unstable, perhaps even more so than the smaller molecule VI. This makes it seem unlikely that V will be prepared experimentally; for Cava *et al.*[1] report that even IV is highly reactive as a dienophile. A comparison with naphthalene VII shows that the high reactivity of IV is to be expected. Another way of illustrating the greater reactivity of IV, V and VI as compared with the others is to compare the free valences for the atoms at the ends of the reactive bonds X, which are given in the fourth row of the Table. It is clear from these figures that diphenylene and naphthalene are in a different class from the cyclobutadiene derivatives IV–VI. Among these latter molecules V has the greatest mean free valence, followed by VI and then IV. Free valences of the order of 0·64 are more nearly typical of almost non-conjugated double bonds, as with the end atom of butadiene, which has a free valence of 0·84, than of aromatic systems such as benzene, where it is 0·40. The free valences in IV and V are hardly changed on iteration, the iterated values being 0·597 and 0·653 respectively.

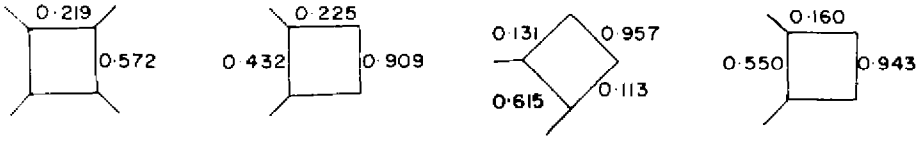
The final row of Table 1 appears to show that IV would absorb at slightly longer wavelengths than diphenylene and at considerably longer wavelengths than naphthalene. The preliminary measurements of Cava *et al.*[1] do not support this, for the absorption in IV occurs near that of naphthalene. However, in systems such as IV, where the olefinic region implies that the resonance integrals are far from being equal, it appears that the energies of the top occupied and bottom unoccupied orbitals are very sensitive to the β-values. In successive iterations on molecule IV the predicted energy transition increases in the sequence $0{\cdot}679\beta_0$, $0{\cdot}970\beta_0$, $1{\cdot}035\beta_0$, $1{\cdot}045\beta_0$; and for molecule V it is $0{\cdot}295\beta_0$, $0{\cdot}678\beta_0$, $0{\cdot}730\beta_0$, $0{\cdot}739\beta_0$. It looks therefore as if a more refined theory would lead to closer agreement with experiment.

The numerical values in this row of the Table, corrected where possible by iteration, may also be taken to measure the relative ease of formation of a dianion or a dication.

In Table 2 we give the π-bond orders found for the various bonds of molecules IV–VI. We also give 'iterated' values. The corresponding bond lengths may be derived from the orders by using the formula[4]

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

We show, below, the bond orders in the cyclobutadiene region of molecules III–VI. Those for III are from Ali and Coulson,[2] whereas for IV to VI they are 'iterated' values.



III IV V VI

TABLE 2. π-BOND ORDERS

Bond	Molecule IV		Molecule V		Molecule VI	
	zero-order	iterated	zero-order	iterated	zero-order	iterated
X	0·842	0·908	0·913	0·957	0·897	0·943
A	0·292	0·227	0·194	0·131	0·215	0·160
B	0·449	0·432	0·615	0·650	0·550	0·550
C	0·768	0·806	0·169	0·113	0·728	0·747
D	0·475	0·450	0·686	0·664	0·563	0·561
E	0·597	0·590	0·616	0·657	0·732	0·746
F	0·685	0·705	0·612	0·607		
G	0·637	0·619	0·533	0·507		
H	0·538	0·562	0·741	0·772		
I			0·574	0·537		
J			0·744	0·776		
K			0·527	0·500		
L			0·613	0·615		
M			0·462	0·493		

Table 2 shows that the outer bond X of the four-membered ring is almost a pure double bond, indicating relatively little conjugation between it and the rest of the molecule. As expected, iteration towards self-consistency enhances the degree of bond fixation. This is entirely in keeping with the NMR observations of Cava *et al.*[1] who interpret their measurements on IV in terms of a "remarkable degree" of double-bond character in the cyclobutadiene region of the molecule.

Our conclusions from this study are quite simple:

(i) From a comparison of delocalization energies, free valences and bond-localization energies all three molecules IV, V and VI are shown to be much less stable and more reactive than III or VII.

(ii) In all these criteria the sequence of reactivity is IV $<$ VI $<$ V.

(iii) It is not expected therefore that VI will easily be synthesized.

(iv) The extent of double-bond fixation is quite abnormally high. In this respect these molecules, in which a cyclobutadiene nucleus is stabilized by fusion of an aromatic ring system on one side only, differ markedly from those (I, II, III) previously studied by Ali and Coulson[2] in which aromatic rings are fused on both sides. The simplest description of these latter is that we have two aromatic regions in the molecule, with only a little cross-conjugation in the ground state. The corresponding description of the former is that there is one aromatic region and one olefinic double bond with only a little mutual conjugation. In neither case does it seem chemically appropriate to speak of a genuinely cyclobutadiene-like system.

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