STABILITY OF MOLECULES CONTAINING (4n)-RINGS

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Over the last two decades it has become increasingly clear that the rules of "resonance theory", at least as applied to alternant hydrocarbons, are more readily understood in terms of Hückel molecular orbital (HMO) theory than in terms of valence bond (VB) theory (1). On the one hand, Pullman and Pullman showed (2) that for napthacene the Kekule resonance structures (unexcited structures) make a negligible contribution to the VB description of the ground state. On the other hand Coulson and Rushbrooke (3a) and Longuet-Higgins (3b) showed that for odd alternate systems the predictions based on Kekule structures are identical with those based on HMO theory. Moreover, by application of the Dewar N.B.M.O. perturbation method (4) Dewar and Longuet-Higgins (5) demonstrated brilliantly that the simple structure counting rules of resonance have quantitative significance when applied to <u>even</u> alternant systems constructed from rings of (4n + 2) atoms and chains. They showed that these same simple rules would not apply generally to systems containing (4n)-rings.

The purpose of this paper is to present modified resonance rules of structure counting that extend the Dewar and Longuet-Higgins approach to include alternate systems containing either simple or fused (4n)-rings. Although these modified rules, like their parent, provide no information not available by solution of the appropriate secular determinant, they do offer the obvious advantage of making it possible to predict stability from an inspection of Kekule structures alone and thus they provide a formalism for thinking about the molecules symbolically as well as numerically. To understand the presentation that follows it is essential that the reader be aware of the parity rules (5) of Dewar and Longuet-Higgins and to appreciate that resonance structures as used here have an associated algebraic sign.

Consider the case of an alternant hydrocarbon containing any number of (4n + 2)-rings but only a single four-membered ring (6). Such a molecule can be considered as arising from the joining of two alternant hydrocarbon molecules containing no four-membered rings. The possible

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Kekule structures for the fragments will have one or more of the following arrangements of double bonds at the site of the potential four-membered ring. By definition (5) these structures are all

(a)   (b)   (c)   (d)
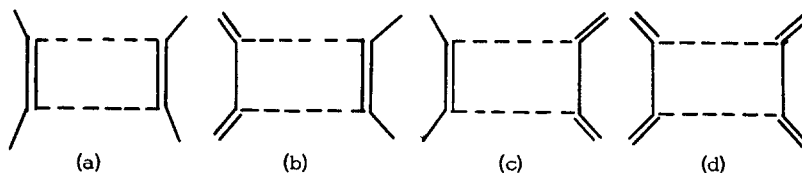
of the same sign. If the four-membered ring is now formed the only additional class of structure possible is (e). There are as many members of the (e) class as members of the (a) class.


(e)
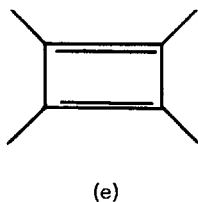
Since these two classes have opposite sign, the algebraic number of structures for molecules containing one four-membered ring can be obtained by counting all Kekule structures remaining after those containing formal cyclobutadiene structures have been deleted.

This rule has already been invoked empirically in discussions (7) of the relative stability of the hydrocarbons I and II. The observed instability of II relative to I was ascribed to the

I   II
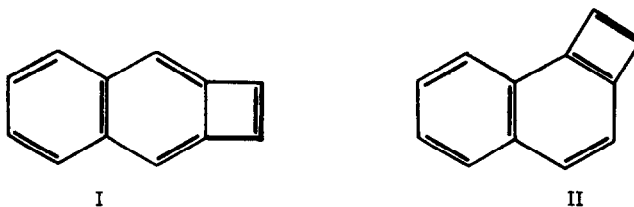
"known instability of cyclobutadiene" and hence by extrapolation the instability of any Kekule structure containing a cyclobutadiene structure. From the previous discussion it can be seen that a more general principle is involved, namely that such cyclobutadiene structures are excluded because they are of opposite parity and make no net contribution to the algebraic structure count (ASC). The same is true of cyclobutadiene itself except that since it has zero

contributing structures it is accordingly predicted to have a triplet ground state. This rule can be

generalized in the same fashion to include molecules containing a single linearly substituted

(4n)-ring of any size. An example is III (note linear substitution).
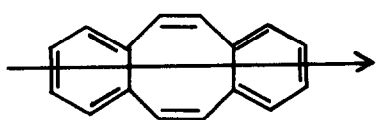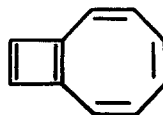
III   IV

If a molecule contains two (4n)-rings that are not fused [i.e., molecules like IV contain

fused (4n)-rings], the algebraic number of structures is given by deleting from the count all

structures possessing one or more (4n)-membered rings that contain 2n double bonds. This rule

follows because for non-fused (4n)-membered rings containing 2n double bonds it is possible to

draw for each ring pairs of Kekule structures of opposite sign. By mathematical induction this

rule can be extended to any number of non-fused (4n)-rings leading to the general rule: the

algebraic number of structures of a molecule containing any number of non-fused 4n-membered

rings is the number of structures remaining after all structures having 2n cyclic double bonds

within any of the (4n)-membered rings have been deleted.

As an example of this more general rule for counting resonance structures the relative

stabilities of hydrocarbons V and VI might be considered. Hydrocarbon V has an algebraic

structure count of ± 1 and is predicted to be polyolefinic but stable. Hydrocarbon VI has an

algebraic structure count of zero and has an expected triplet ground state by an HMO calcula-

tion. Such is found (8).
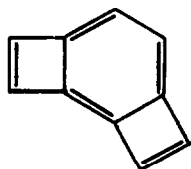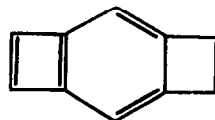

V   VI
|ASC| = 1 |ASC| = 0
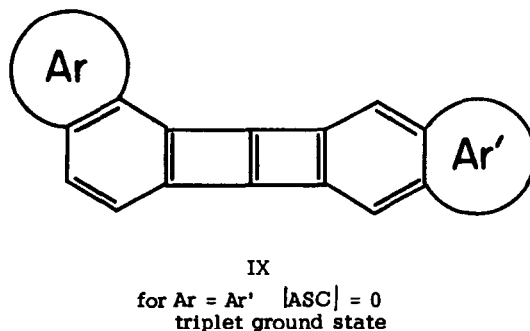singlet ground state   triplet ground state

Molecules containing fused (4n)-membered rings can be treated in a fairly general fashion. For the case of two fused 4-membered rings, arguments of the type given above lead to the generalization that the algebraic number of structures is the difference in the number of structures of type (f) minus the number of type (g) with all other structures ignored. In these structures the Ar


(f)   (g)
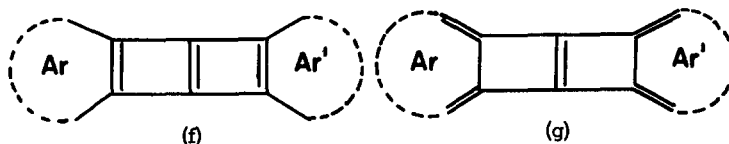
and Ar' residues refer to aromatic systems. For fused systems containing (4n)-rings with n $\neq$ 1 Ar and Ar' must be linearly disposed. Application of this rule to butylene, VII, leads to the correct prediction that it has an algebraic structure count of one and a consequent HMO singlet ground state (8). On the other hand one can see from the same rule that the algebraic structure count for dibenzobutylene, VIII, is zero and that it has an HMO triplet ground state (9).


VII   VIII
$|ASC| = 1$ $|ASC| = 0$
singlet ground state   triplet ground state
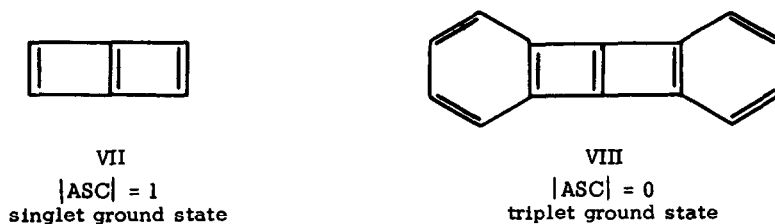
Results for several members of this bicyclic class are shown below. It is interesting that all examples of type IX in which Ar = Ar' are predicted to have triplet ground states (including the case Ar = Ar' = H_2). Compounds X and XI illustrate that butylene derivatives can have singlet ground states
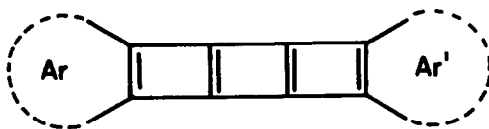

IX
for Ar = Ar' $|ASC| = 0$
triplet ground state
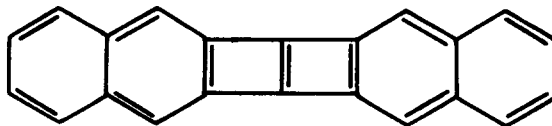
X

$\left|\text{ASC}\right| = 3$

singlet ground state
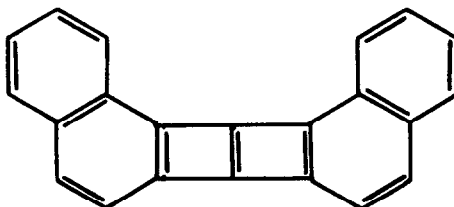
XI

$\left|\text{ASC}\right| = 3$
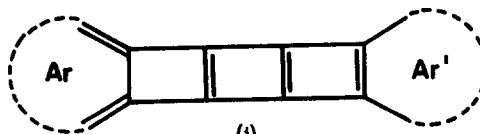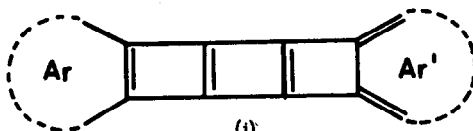
singlet ground state

The rules can be extended easily by the method used above to the case of three linearly fused (4n)-rings. The resulting rule is to count all resonance structures having the part structures shown in (h), (i), and (j). Any other resonance structures are ignored in the count.
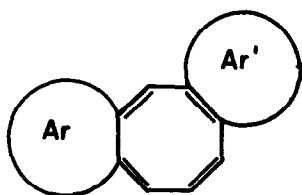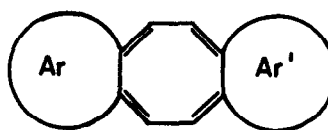

(h)

(i)

(j)

The interesting property of this system, as can be seen from the rule, is that a zero structure count can <u>not</u> occur and that all possible members will have <u>singlet ground states</u>.

In the preceding discussion the formulas were restricted to linearly fused (4n)-rings. With inclusion of cyclooctatetraene as a building block _angular_ systems become possible. These can be analyzed in the same fashion as above. Some of these give interesting contrasts to the linearly substituted analogs. For example, in the angularly substituted system symbolized in XII it is predicted that all cases with Ar = Ar' will have triplet ground states regardless of the structure of Ar (as long as it is not Ar = H_2). With the linearly substituted analog XIII the opposite conclusion is reached and all structures should have a singlet ground state.

XII
for Ar = Ar' $|A \Sigma C| = 0$
triplet ground state

XIII
for Ar = Ar' $|ASC| \neq 0$
singlet ground state

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4. M. J. S. Dewar, _J. Am. Chem. Soc._, 74, 3341, 3345, 3353, 3355, 3357 (1952).

5. M. J. S. Dewar and H. C. Longuet-Higgins, _Proc. Roy. Soc._, A214, 482 (1952).

6. The alternant hydrocarbons being joined must not themselves contain (4n)-rings.

7. M. P. Cava, B. Hwang and J. P. Van Meter, _J. Am. Chem. Soc._, 85, 4032 (1963). See also T. C. W. Mak and J. Trotter, _J. Chem. Soc._, 1, (1962).

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