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MOLECULAR ORBITAL CALCULATIONS ON SOME NON-CLASSICAL AROMATICS

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Abstract—Calculations by the Hückel Molecular Orbital method have been made on ten non-classical aromatics, most of them non-alternant. Considerable resonance stabilization is predicted for all the systems studied. Except for charge distribution in the non-alternants, the calculated properties are mostly similar to those of normal benzenoid aromatics. The application to our systems of Craig's rules for predicting aromaticity is discussed.

The simple Hückel Molecular Orbital Theory[2] has been used to calculate the properties of some non-benzenoid aromatic systems. In this procedure overlap is neglected, all coulomb integrals are considered equal, and all resonance integrals between adjacent carbons are considered equal. Calculations were carried out on an I.B.M. 650 computer, using a standard matrix-diagonalization program.[3]

The compounds considered are shown in Fig. 1, which also gives bond orders, free valences and charge densities (in parentheses following the free valences).[4] The charge densities of the alternant hydrocarbons II and V are unity at all positions. The values for the odd system I refer to the cation. Delocalization energies for I–X are given in Table 1.

For purposes of discussion, the results fall logically into three groups: (1) I, (2) II, V and (3) III, IV, VI–X. Of these substances, only III and IV are known.[5]

The cation I has the same number of π-electron centers as the tropylium ion and a slightly lower delocalization energy.[6] Unlike tropylium ion, I has a lowest unoccupied molecular orbital which is non-bonding, so the radical and anion from I should have the same delocalization energy as the cation (neglecting interelectronic repulsion). The electron deficiency of the cation is much greater in the four- than in the five-membered ring.

The cyclo-octatetraene derivatives II and V show no particularly unusual features. Delocalization energies per π-electron run somewhat less than those of benzenoid aromatics of comparable size (naphthalene is $0{\cdot}37\beta$ per π-electron). Our calculations do not, of course, consider bond-angle strains which could counterbalance the resonance stabilization of the planar system. II, at least, might be better than cyclo-octatetraene in this respect, since the fused four-member ring should help to flatten out the eight-member ring.

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[1] To whom requests for reprints should be directed.

[2] [a] E. Hückel, *Z. Physik.* **70**, 240 (1931); [b] C. A. Coulson, *Valence* Chap. IX. Oxford University Press, London (1952); [c] H. Eyring, J. Walter and G. E. Kimball, *Quantum Chemistry* Chap. XIII. John Wiley, New York (1944).

[3] We thank the University of Rochester Computing Center for donating the time on the computer.

[4] These quantities were calculated from the coefficients of the atomic orbitals as described.[2b]

[5] K. Hafner and J. Schneider, *Liebigs Ann.* **624**, 37 (1959) have prepared dimethyl-substituted derivatives of III and IV, but not the parent hydrocarbons.

[6] J. D. Roberts, A. Streitwieser, Jr. and C. M. Regan, *J. Amer. Chem. Soc.* **74**, 4579 (1952) report $2{\cdot}99\,\beta$ for tropylium ion.

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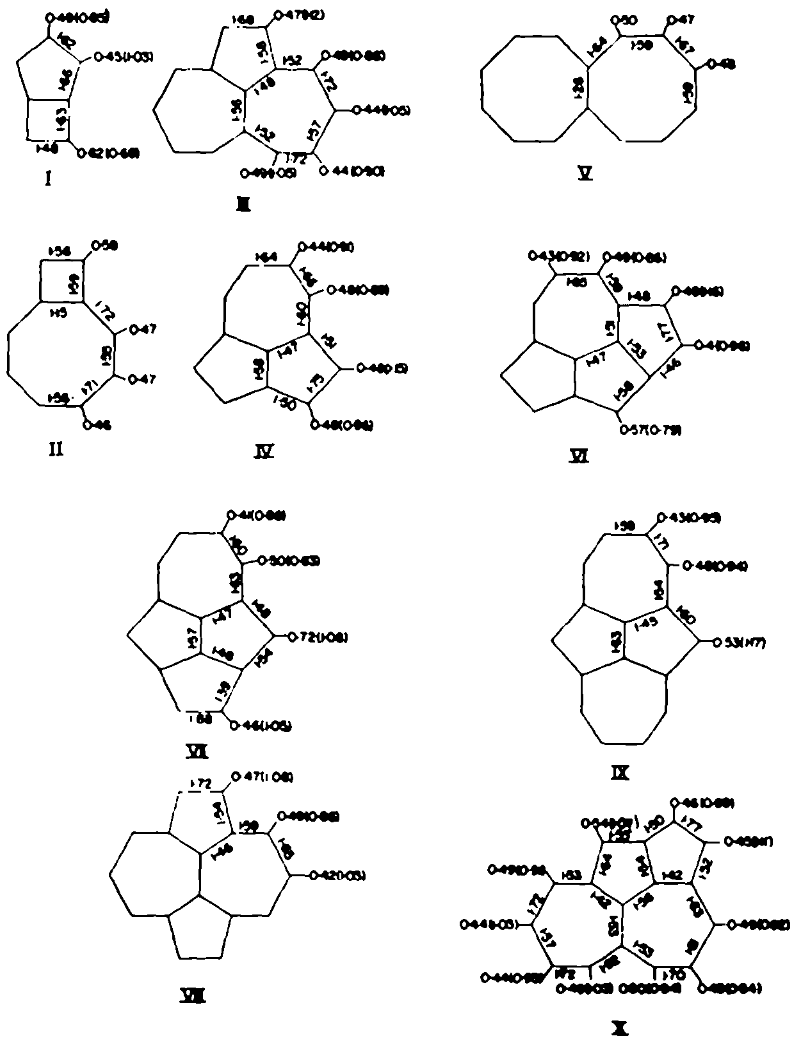

Fig. 1. Properties of some non-classical aromatics as calculated by the molecular orbital method. Numbers along the bonds are bond orders. Numbers at lines to ring positions are free valences. The numbers in parenthesis following free valences are charge densities.

Of the remaining compounds none is known, but Hafner[5] has prepared the dimethyl derivatives XI and XII, of III and IV, respectively. Within the limitations of our approximations, the methyl groups should not significantly affect our conclusions. Both III and IV have delocalization energies comparable to those of the benzenoid aromatics and none of the other calculated properties (including the distribution of energy levels),[7] leads one to expect any pronounced differences between the two. Hafner[5], however, reports that XI behaves as a normal aromatic, forming a trinitrobenzene complex and giving electrophilic substitution reactions (though the Vilsmeier formylation with dimethyl formamide and $POCl_3$ in benzene is the only one actually

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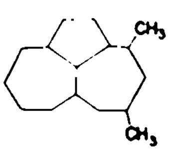
[7] After completion of our work we learned that Professor A. Streitwieser, Jr. has performed more complete calculations on III and IV, including localization energies for substitution reactions. His results will be published separately.

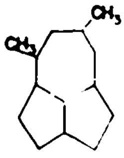
TABLE 1. DELOCALIZATION ENERGIES OF SOME NON-CLASSICAL AROMATICS

Compound[a]	Total DE[b]	DE per π-electron[b]
I	2·91	0·42
II	2·84	0·28
III	4·91	0·35
IV	4·37	0·36
V	4·10	0·29
VI	5·28	0·38
VII	5·13	0·37
VIII	6·04	0·38
IX	6·03	0·38
X	5·94	0·37

[a] See Fig. 1 for structures.
[b] In units of the resonance integral β (ca. 18 kcal/mole).



XI



XII

described). It also is recoverable from a solution in 50 per cent sulfuric acid. In contrast, XII gave no trinitrobenzene adduct and polymerized with acids and on heating so that no electrophilic substitutions could be performed. In defense of the theory one might point out that these differences are not necessarily consequences of differences in the π-electron systems of the isolated molecules and may arise from other factors such as bond-angle strain.

The remaining molecules, VI–X, are derived from III and IV by fusion of additional rings and mostly resemble III and IV in calculated properties. The delocalization energies per π-electron are also similar to those of benzenoid aromatics (compare with 0·37β for naphthalene, 0·38β for anthracene and 0·41β for pyrene). Highest bond orders in most cases are in five-member rings, but the bonds that are common to five- and seven-member rings tend to have low bond orders. A point of particular interest is that the lowest unoccupied orbital of VII is non-bonding, while for the other compounds of this group it is antibonding ($-0·20\beta$ to $-0·44\beta$). One would thus expect VII to reduce to the radical-anion with unusual ease.

The charge densities follow the same patterns as in azulene. Negative charge concentrates in the 5-member rings and is highest on positions adjacent to a 7-member ring. The 7-member rings are electron deficient, usually having their lowest charge densities in positions next to a 5-member ring. One would expect considerable regularity in the substitution reactions of III–IV and VI–X, since electrophilic attack should occur at the position of highest and nucleophilic attack at the position of lowest charge density. Calculation of localization energies[8] would provide a check of these predictions, but the extra labor was not considered worthwhile in a preliminary survey dealing with mostly unknown molecules.

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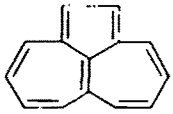
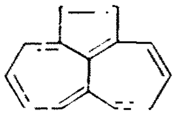
[8] G. W. Wheland, *J. Amer. Chem. Soc.* 64, 900 (1942); R. D. Brown, *Quart. Rev.* 6, 63 (1952).

The free valences, usually taken as measures of reactivity toward radicals, show considerably less consistency than the charge densities. In two compounds, VII and IX, the maximum free valence is at the same position as the maximum charge density. In all except VIII and X, the maximum free valence is in a 5-member ring. Free valences of one or more other positions of III, IV and X are quite close to the figure for the maximum position. For comparison, most normal benzenoid aromatics have free valences of 0·40–0·45, though the 9-position of anthracene has a free valence of 0·52. Overall, the predictions on radical attack are more ambiguous and probably less reliable than the predictions on electrophilic attack.

Whether more sophisticated approaches than simple molecular orbital theory would predict aromaticity for the compounds examined here is a point of some interest. An approach that is particularly easy to apply has been developed by Craig[9]. His arguments are based on the symmetry properties of the valence-bond ground states. Of our molecules, I, II and X do not possess sufficient symmetry for the method to be used. V is clearly aromatic. The remaining (and most interesting) cases, III, IV, VI, VII, VIII and IX, present problems of application.



XIII



XIV

These problems can be illustrated with III. The valence-bond structure XIII fits Craig's symmetry criterion for aromaticity, but the structure XIV does not. Dr. Craig believes that this indicates little stabilization by interaction of XIII and XIV, and consequently little aromaticity.[10] It is clear that from the valence-bond viewpoint all of these molecules are in some sense abnormal.[10] There is not yet adequate experimental evidence on this interesting extension of Craig's rules. Syntheses of VI–IX would certainly provide valuable information on the reliability of these symmetry arguments as well as the suitability of simple molecular orbital theory for treating non-alternant systems.

[9] D. P. Craig, *J. Chem. Soc.* 3175 (1951).
[10] D. P. Craig. Private communication.