Tetrahedron Vol 23, pp. 4257 to 4263 Pergamon Press Ltd. 1967 Printed in Great Britain

CALCULATIONS ON THE CORANNULENE SYSTEM

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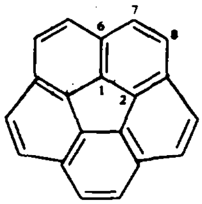
(*Received in USA 2 February 1967; accepted for publication 20 March 1967*)

Abstract—Self-Consistent Field MO calculations and strain energy calculations were applied to the recently prepared corrannulene system. The system is believed to exist in a non-planar configuration but should show appreciable aromatic character. Properties related to the π system have been determined

BARTH and Lawton have recently synthesized the dibenz(ghi, mno)flouranthene or corannulene system, I.[1] As these authors have suggested, the strain which is present in the underlying σ-bonded core of the molecule might be sufficient to cause extreme deviation from planarity even to the point of complete loss of aromatic character. An investigation is herein described in which both the σ and π-portions of the compound are examined. It is hoped that insight may be gained as to the most probable structure of the system.



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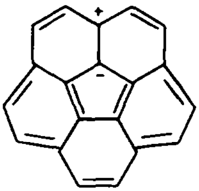

II

The π-electron system encountered was treated using an iterative SCF-MO-LCAO approach.[2] Calculations were carried out based on standard Pople–Pariser–Parr two-center electron repulsion integrals (ii, jj) and a resonance integral β derived from ground state constants. The π-binding energy was determined for this molecule in two extreme geometries. The first was a simple planar system. In the second a "basket-like" structure was presumed with each planar benzene ring pitched 38·75° from the plane defined by the 5-member ring. In the latter geometry, the p-orbitals on each carbon atom can no longer be mutually parallel. Minimal deviation in this respect is maintained when the p-orbitals on adjacent, bonded carbon atoms are treated as being essentially coplanar but tipped toward one another. As has been pointed out,[3] any such tipping will introduce a decrease in the effective π-overlap and a corresponding increase in the σ-overlap between the two atoms involved.

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[1] W. E. Barth and R. G. Lawton, *J. Am. Chem. Soc.* **88**, 380 (1966).

[2] M. J. S. Dewar and G. J. Gleicher, *J. Chem. Phys.* **44**, 759 (1966).

[3] J. D. Roberts, *Notes on Molecular Orbital Calculations* p. 83. Benjamin, New York (1961).

The effective value for the resonance integral between such atoms may be given by:

$$\beta = \beta_0 \sin \varphi_1 \sin \varphi_2 \tag{1}$$

where the φ's represent the angles of the p-orbitals on atoms 1 and 2 with the line connecting the atoms. The two center electron repulsion integrals were assumed to be independent of any geometrical factors other than internuclear separation.[4] All determinations of the π-binding energy were carried out using a fixed C—C distance of 1·40 Å. Table 1 presents the calculated energy terms.

TABLE 1. CALCULATED ENERGY TERMS (EV)

Molecule	π-Binding energy[a]	Strain energy	Total energy
Planar corannulene	28·924	−8·171	20·753
Non-planar corannulene	26·306	−2·479	23·827

[a] Based on a value for β_0 of −1·7515 ev (Ref. 2).

As can be seen the non-planar form of the compound has over 90% of the π-binding energy found in the planar structure. In terms of loss of π-energy, deformation of the planar form of the molecule should be readily accomplishable.

In order to pursue this line of reasoning, it is necessary to examine the possible strain which might be present in the systems. The general approach is that which was originated by Westheimer[5] and further developed by Hendrickson[6] and Wiberg.[7] Calculations of this type have been used in conjunction with MO calculations by Allinger *et al.*[8] Recently Gleicher and Schleyer have extended the principles involved to a correlation of chemical reactivity with gratifying results.[9] The general method involves summation over all possible strain producing interactions in the σ-system. For saturated molecules this is usually given as:

$$E_{\text{Strain}} = E_{\substack{\text{Bond}\\\text{Stretching}}} + E_{\substack{\text{Bond}\\\text{Bending}}} + E_{\text{Torsional}} + E_{\substack{\text{Non-bonded}\\\text{Interactions}}} \tag{2}$$

In extending this formalism to aromatic molecules, one must carefully assess whether the above dissection of terms fully describes all possible strain without redundancies, as well as examine all new parameters chosen.

An iterative approach can be utilized to calculate a geometry leading to an energy minimum for the σ-bonded network. This procedure, however, was not carried out because of the lack of certainty in the bond stretching terms. As has been mentioned, a portion of the overlap of tipped p-orbitals will modify the σ-bonds causing this problem. Recourse is therefore taken to a more straightforward approach in which

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[4] M. J. S. Dewar, G. J. Gleicher and C. C. Thompson, Jr., *J. Am. Chem. Soc.* **88**, 1349 (1966).

[5] F. H. Westheimer in *Steric Effects in Organic Chemistry* (Edited by M. S. Newman). Wiley, New York (1955).

[6] J. B. Hendrickson, *J. Am. Chem. Soc.* **86**, 4854 (1964) and Refs. cited therein.

[7] K. B. Wiberg, *J. Am. Chem. Soc.* **87**, 1070 (1965).

[8] [a] N. L. Allinger, M. A. Miller, L. W. Chow, R. A. Ford and J. C. Graham, *J. Am. Chem. Soc.* **87**, 3430 (1965); [b] N. L. Allinger, *Tetrahedron* **22**, 1367 (1966).

[9] G. J. Gleicher and P. von R. Schleyer, *J. Am. Chem. Soc.* **89**, 582 (1967).

the strain for various fixed conformations is evaluated.[5,6] This is not too drastic an assumption as bond length is generally invariant within a small range. It also allows for direct comparison with the π-binding energy determined for fixed geometries.

The energies associated with bond stretching and bond bending (angle strain) are given by simple harmonic potentials of the form:

$$E = k(\tau - f)^2 \tag{3}$$

where τ and f are the equilibrium and true values respectively of some bond length or valence angle and k is the appropriate force constant. The values of k and τ, based on Cyvin's analysis of benzene,[10] are given in Table 2.[11] It must also be pointed out that in a system built up from sp^2 hybridized carbon atoms a second type of bond bending is possible. This is bending out of the plane defined by these atoms. The values of the force constants for out of plane bending are respectively 20·8 kcal/mole radian^2 and 5·97 kcal/mole radian^2 for removal of carbon atoms and hydrogen atoms from the plane.[12] This particular set of constants was chosen because of the author's claim that they reproduced the experimental data in a satisfactory manner without the inclusion of interaction constants.[12]

TABLE 2. FORCE CONSTANTS AND EQUILIBRIUM VALUES

Interaction	τ	k
C—C stretch	1·40 Å	460·8 kcals/mole Å
C—H stretch	1·075 Å	360·0 kcals/mole Å
C—C—C bend (in plane)	120°[a]	104·1 kcal/mole radian^2
C—C—H bend (in plane)	120°	94·8 kcal/mole radian^2

[a] Based on ana analysis of benzene.[10]

The question of inclusion of terms for torsional and non-bonded interactions is a worrisome one. As interest in this study is primarily focussed on determining the aromatic character of corannulene, care must be taken not to explicitly include strain considerations which may be implicitly included in some other function. As will be seen, an empirical parameter based on the heat of hydrogenation of benzene is used to assess resonance energy. As no separate consideration of torsion is made in obtaining this parameter it must be implicitly included. The following argument must also be considered. The rotational barrier in an aromatic molecule is fourfold and in a perfectly planar system torsional energy should be small and not have a minimum.[9] The only way a differential value for the torsional energy can be obtained is if a group at one or both of the sp^2 hybridized carbons is removed from the planarity defined by the other three atoms. Since this interaction has already been treated by out of plane bending, its inclusion here would be redundant.

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[10] S. Cyvin, *Acta Chem. Scand.* **11**, 1499 (1957).

[11] C. A. Coulson and C. W. Haigh, *Tetrahedron* **19**, 527 (1963).

[12] C. A. Coulson and A. Golebiewski, *J. Chem. Soc.* 4948 (1960).

Some of the same objections can be raised as regards non-bonded interactions in this system. There are 399 non-bonded interactions in corannulene. Unlike those encountered in certain polynuclear hydrocarbons[13] or the lower annulenes[14] they are not so severe as to produce in themselves a driving force for deformation from planarity. On the other hand non-bonded interactions have not been considered in benzene; the molecule relative to which the calculated resonance energy will be compared. Use of the non-bonded functions developed by Bartell[15] lead to approximately 3·2 kcals/mole of strain energy in benzene. This non-bonded strain is principally caused by 1–4 C—C interactions. The interactions in corannulene are comparable in magnitude to those found in benzene. As this non-bonded strain is implicitly included in the constant derived from the heat of hydrogenation of benzene, direct inclusion of similar interactions in corannulene should be avoided. Let it be pointed out, however, that neglect of this factor is justified only by the specific molecule examined. General neglect of this term is not advisable.

For this study, therefore, the strain energy may be given by:

$$E_{\text{Strain}} = E_{\substack{\text{Bond}\\ \text{Stretching}}} + E_{\substack{\text{In-plane}\\ \text{Bond}\\ \text{Bending}}} + E_{\substack{\text{Out-of-plane}\\ \text{Bond}\\ \text{Bending}}} \qquad (4)$$

The strain energy of the geometries previously outlined were calculated from the above Eq. (4). The values, and those of the summing of the π-binding energy and strain energy, are given in Table 1. A large driving force toward adoption of a non-planar structure can be seen. Approximately 70% of the strain present in the planar geometry is lost in the basket-shaped molecule. Of the strain which remains over one-third is due to unavoidable in-plane bending in the 5-member ring. Although some refinement of the parameters utilized is possible, it seems safe to say that the non-planar structure should represent the true geometry of the system.

The resonance energy of many conjugated systems has been determined from the π-binding energy by applying the following equation:[16]

$$E_R = N_{cc}\left[A - \frac{N' - N'')}{2N_{cc}}(E'' - E')\right] - E\pi_b \qquad (5)$$

N_{cc}, N' and N'' are the total number of C—C bonds, single bonds, and double bonds respectively. E'' and E' refer to the dissociation energies of the double and single bonds. A is the empirical parameter previously described. Because of the appreciable strain present, the total energy rather than the π-binding energy, $E\pi_b$, is used. For the non-planar structure a resonance energy of 0·526 ev is obtained. This is a very low value when compared to those for aromatic systems of similar size. Thus, perylene ($C_{20}H_{12}$) has a resonance energy of 5·120 ev and triphenylene ($C_{18}H_{12}$) one of 4·792 ev.[16] It appears, however, that this may be a sufficiently large enough resonance energy to bestow aromatic character upon the system. Two causes also may be immediately given for the seemingly low value obtained: this first lies in the use of an A value determined from a planar system. Of even more importance is a

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[13] C. A. Coulson and S. Senent, *J. Chem. Soc.* 1813 (1955).

[14] K. Mislow, *J. Chem. Phys.* **20**, 1489 (1952).

[15] L. S. Bartell, *J. Chem. Phys.* **32**, 831 (1960).

[16] M. J. S. Dewar and G. J. Gleicher, *J. Am. Chem. Soc.* **87**, 685 (1965).

possible overestimation of strain in the non-planar structure. Most of the strain in that geometry is caused by five severe (33°) out of plane bends. As has been pointed out,[9] deformations of such magnitude may fall well outside of the harmonic portion of the potential and necessitate the use of a smaller force constant. It may be concluded that the resonance energy reported above may represent no more than a probable lower limit.

The heat of formation of this system may be determined in a similar manner.[16] The same problems encountered in evaluation of the resonance energy are present here. There is possible overemphasis of strain and a small error inherent in using a value for the bond energy of an aromatic sp^1–sp^2 C—C bond obtained from a study on planar systems. The heat of formation is calculated as 163·627 ev.

Calculations on the π-system may also be carried out using a procedure in which all two center integrals are allowed to vary in accord with a self-consistent relationship based on π-bond order. The π-binding energies thus obtained are approximately equal to those previously given. This method also allows, moreover, for a prediction of self-consistent bond lengths. The bond lengths so calculated are presented in Table 3. Despite the generally good agreement found between these calculated values and experiment,[16] there is a reluctance to put too much reliance on them in this case. The difficulty arises because of the non-equivalence of all the σ bonds present. Corannulene suffers from the double disadvantage of being both non-planar and non-alternate and few if any comparable precedents are known. Recent calculations by Murrell and Hinchliff show that perhaps correlation of bond lengths with some property of the σ network may provide better agreement in certain systems.[17] It should also be pointed out that an iterative calculation of the strain in the σ system does not yield results compatible with those in Table 3. Planar corannulene could achieve a strain of only 5·560 ev in a geometry with the following bond lengths: 1–2 = 1·354 Å, 1–6 = 1·341 Å, 6–7 = 1·442 Å, and 7–8 = 1·470 Å. Of these results, the only length approximately equal to those calculated via a bond order-bond length relationship is for the 6–7 bond. These results are also opposed to chemical intuition which would predict alternation of length. While it is incorrect to equate an SCF calculation on the σ system with the more classical approach used here, the uncertainty in regard to calculated bond lengths is made manifest. Because of this, a partial justification for not carrying out such an iterative calculation of the strain

TABLE 3. CALCULATED BOND LENGTHS (Å)

Bond[a]	Planar corannulene	Non-planar corannulene
1–2	1·437	1·430
1–6	1·399	1·408
6–7	1·433	1·430
7–8	1·371	1·374

[a] Atoms numbered in accordance with structure I.

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[17] J. N. Murrell and A. Hinchliff, *Trans. Faraday Soc.* **62**, 2011 (1966).

in the σ-system can be made. Obviously the ideal solution is to devise an approach completely self-consistent in all terms. The problems here are insurmountable, however, and recourse to the approximate methods used is the only possibility.

Corannulene may be a resonance hybrid with a fairly large contribution being made by the canonical form shown in II. Such a form has some attractiveness as it may be considered as being two concentric monocyclic rings each of which contains 4n + 2 electrons. The SCF-MO calculated charge densities are given in Table 4 for both the planar and non-planar structures. In the latter case a net dipole should result. This has been calculated as 0·609 D. A Hückel calculation has also been carried out. As might be expected by analogy with previous work, this value of the dipole is appreciably larger than that obtained via the SCF approach. Although small, a dipole of this magnitude is capable of experimental verification.

TABLE 4. CALCULATED CHARGE DENSITIES AND DIPOLES

System	q_1	q_6	q_7	μ(D)
Planar corannulene (SCF)	1·019	0·987	0·996	—
Non-planar corannulene (SCF)	1·027	0·979	0·997	0·609
Non-planar corannulene (Hückel)	1·067	0·971	0·981	1·909

The reactivity of corannulene is also worthy of comment. There is only one site for substitution and the localization energies have been calculated for the non-planar structure. These values are given in Table 5. The SCF calculated localization energies have been shown by Dewar and Thompson to yield excellent correlations of the partial rate factors.[18] All substitutions in corannulene are predicted to procede at a faster rate than the corresponding reaction of benzene. The reactivity of corannulene towards electrophilic attack should be equivalent to that of the 1-position of phenanthrene. It is interesting to note, therefore, that to date attempts to introduce such a group have been unsuccessful.[19] A partial explanation could lie in unfavorable

TABLE 5. RELATIVE LOCALIZATION ENERGIES (EV)[a]

Localization	Energy (ev)
Electrophilic	−1·191
Radical	−0·449
Nucleophilic	−1·541

[a] Taken relative to benzene having zero localization energy.

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[18] M. J. S. Dewar and C. C. Thompson, Jr., *J. Am. Chem. Soc.* **87**, 4414.

[19] R. G. Lawton, private communication.

steric factors, however, the possible *peri* hydrogen interaction should not be much worse than that encountered in substitution at the α-position of naphthalene.

Work is currently underway to examine the properties of corannulene radical ions.[20] The oxidation and reduction potentials calculated to date are in no more than fair agreement with the experimental results.[19] Appreciably more data must be obtained before it can be ascertained whether a relative correlation exists.

In summary, corannulene appears to have sufficient resonance energy to exhibit aromatic character if a non-planar structure may be assumed. It is hoped that the many calculated values presented in this report may act as encouragement toward obtaining their experimental counterparts.

Acknowledgements—Thanks are extended to the Computer Center of Oregon State University which generously supplied the facilities for carrying out these calculations. Deepest thanks must also be given to Professor Richard G. Lawton of the University of Michigan who has graciously provided new information on corannulene chemistry as it continually arose.

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[20] G. J. Gleicher and M. K. Gleicher, work in preparation.