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THE QUESTION OF TRANSANNULAR BONDING IN CYCLOBUTANONE, BORETANE AND THE CYCLOBUTYL CATION[1]

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Abstract—The EHT quantum mechanical method has been applied to cyclobutanone, boretane, and the cyclobutyl cation. Calculations have been made for all of these molecules in various deformed states to permit assignment of the most stable structures. *The EHT method successfully predicts the correct structural parameters and properties of cyclobutanone.* By analogy, the computed properties of cyclobutyl cation and boretane monomer are assumed to be very reasonable.

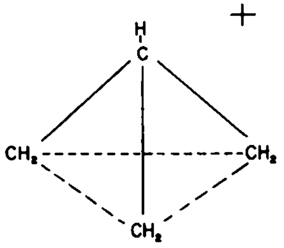
The bond population density of the transannular interaction has been calculated to be negative (about −0·14) in each molecule. The results of the calculations indicate that no transannular bonding is present in any of these systems. It is concluded that the cyclobutyl cation must be completely classical on the basis of EHT theory.

Calculations reveal that formulation as the *tricyclobutonium ion must be rejected even as a transition state* since an ion of such high symmetry is *orbitally degenerate*; the tricyclocation would be a *carbonium ion triplet.*

It has been observed that the $\overset{+}{C}H$ and the C═O groups are very easily deformed in the out-of-the-plane deformation. A suggestion is made that concentration on the out-of-the-plane deformations might bring increasing order in the carbonium ion problem.

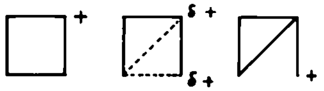
INTRODUCTION

IT WAS originally suggested that the rapid interconversion of cyclobutyl and cyclopropylcarbinyl derivatives in carbonium ion reactions[3] is due to the high stability of the nonclassical tricyclobutonium ion.[4] More recently[5] it has been suggested that these reactions involve a set of bicyclobutonium ions in rapid equilibration. The bicyclobutonium ion involves considerable bonding between the 1,3 carbon atoms in the cyclobutyl cation. This bicyclo ion would appear to require transannular bridging in (or from) the classical cyclobutyl cation for greater stabilization.



C_{3v} symmetry
A carbonium ion triplet

Thus it would be postulated that the nonclassical bicyclo ion would be more stable than the classical cyclobutyl ion.

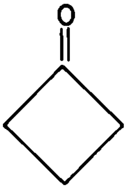


Recent theoretical developments now allow a more serious examination of the magnitude of transannular (1,3) bridging. In the present paper, the amount of bridging has been computed in cyclobutanone, boretane, and the cation.

The status of the nonclassical carbonium ion discussion has been reviewed in Bartlett's reprint and running commentary book.[6] Bartlett has given a somewhat limited but useful definition of a "nonclassical ion". An ion is "nonclassical" if its ground state has delocalized bonding σ electrons.[6a] Since σ electrons are involved, the application of the usually useful Hückel theory with its sole concentration on the π electron network has only enhanced the controversy. However, Hoffmann[7] has continued the development of a very useful extension of this theory called the Extended Hückel Theory (EHT), which uses all the valence electrons. An analysis of the success of this method has been provided by Lipscomb.[8] In that paper these authors consider EHT theory as a method of simulating Hartree–Fock (H–F) calculations by guessing the matrix elements of the H–F Hamiltonian using the Wolfsberg–Helmholz approximation. In EHT theory cancellation of the direction of approximation is also important. EHT theory works well with molecules containing hydrogen and carbon and/or boron atoms on which accurate H_{ii} values and parameters are well known.

THE PRESENT STUDY

EHT theory has been applied to cyclobutanone (**1**), boretane (**2**), and the cyclobutyl cation (**3**).



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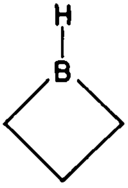

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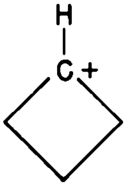

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In a later paper of this series, the normal coordinate analysis of the ketone will be discussed, since it has been used as a model for the carbonium ion. The EHT method of calculation has been discussed.[1,7,9].

The coordinates and the definitions of the variables of these systems are listed in Fig. 1. The atoms A and D were varied to obtain the results on the ketone (A—D being O═C), the borane (H—B), and the carbonium ion (H—C$^+$). The known bond distances and geometry of cyclobutanone[10] were used as the starting point for the calculations. Angle 123 was set equal to angle 143 in most calculations. Thus, initially the more symmetric deformations were considered. Enough different geometries were treated to obtain the most stable configuration.

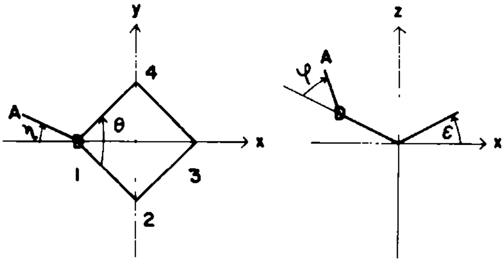


FIG. 1 Coordinate system for the calculations on the four-membered rings. The six hydrogens on positions 2, 3, and 4 are not shown in this diagram but are included in the calculations.

Cyclobutanone. The angle θ in the ground state of the ketone was found[10] to be 90°. This value can be compared with the estimates obtained by using an approximate relationship between the position of the CO IR stretching frequency[11] and the CCC angle at the CO. One estimate using this approximate equation[12] is 82°; another estimate[13] is 83°.

In Table 1 the computed total orbital energy in electron volts (eV) of the ketone is reported as a function of the CO angles, θ and φ, while η and ε are equal to zero. In agreement with the structural data, *the EHT results show that the ketone is most stable with* $\theta = 90°$ *and* $\varphi = 0°$. The MO parameters of charge densities and the bond population densities[14] are listed in Fig. 2. The total overlap population can be obtained by the method suggested by Mulliken. If the total overlap population between two atoms is positive, they are bonded: if negative, they are antibonded.

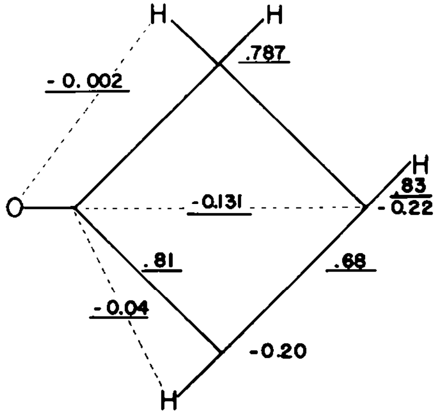


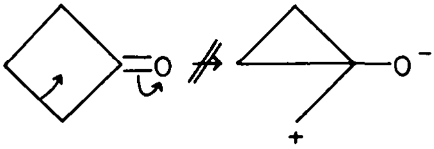
FIG. 2 EHT molecular orbital values of the charge densities and the overlap population densities (underlined) of the ground state of cyclobutanone.

Table 1. Computed total orbital energies of cyclobutanone in eV.

φ	$\theta = 60°$	70°	80°	90°	100°	110°	120°
0°	−527·371	−529·998	−532·193	−533·275[a]	−532·999	−531·589	−529·722
10°	−527·345	−529·969	−532·164	−533·249	−532·990	−532·615	−529·798
20°	−527·263	−529·879	−532·072	−533·172	−532·958	−531·685	−529·998
30°	−527·114	−529·715	−531·907	−533·035	−532·894	−531·772	−530·252
40°	−527·424	−529·457	−531·649	−532·811	−532·777	−531·838	−530·483
50°	−528·861	−529·069	−531·481	−532·481	−532·576	−531·828	−530·616
60°	−528·106	−528·773	−530·707	−531·999	−532·242	−531·676	−530·570
70°	−528·012	−528·610	−529·903	−531·300	−531·704	−531·292	−530·245
80°	−527·374	−527·938	−528·759	−530·292	−530·852	−530·550	−525·499
90°	−525·888	−526·506	−527·169	−528·840	−529·518	−529·260	−528·108

[a] Minimum in energy (most negative value). Calculations between $\theta = 80$ to 100° were performed at close intervals. The angle φ was varied from 0 to 10° with much closer intervals also.

It is of interest to note that the CO carbon bears a large amount of positive charge. The C_1 charge value is positive. This electron deficient carbon affects the adjacent C_1—O, C_1—C_2 and C_1—C_4 bonds (as observed in the overlap population densities). The C_1—O bond has a good π-density value; the C_1—C_2 and C_1—C_4 bonds each have a density of 0·81. The most important point is that electron deficient carbon (C_1) *does not take electrons* from the C_2—C_3 or C_3—C_4 bonds. The transannular interaction (C_1—C_3) has a population density of −0·131. Thus, there is a large amount of repulsion between the C_1 and C_3 atoms. A negative value means a nonbonded pair of atoms.[14] Thus, the calculations reveal that the nonclassical resonance form (4) has *no significance* in the ground state of the cyclobutanone molecule.



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The ketone is completely classical. Note that the charge density on carbon C_4 is −0·20 (Fig. 2) rather than positive as required in the resonance form (4).

In Fig. 3 the energy of the puckered four membered ring is computed as a function of the pucker (angle ε) and with the CCC angle at the carbonyl, θ. In Fig. 4 the carbonyl oxygen has been deformed in an out-of-phase plane motion by changing angle φ and in a planar bending motion by changing angle η. The angle θ was kept constant for the calculations reported in Fig. 4.

The energy surfaces (while static) are related to the surfaces on which the ketone would vibrate in its perpendicular, out-of-the-plane normal mode. We have previously[1] discussed this motion of the ketone as being more closely related to the motion of cyclobutyl tosylate being converted into its carbonium ion.

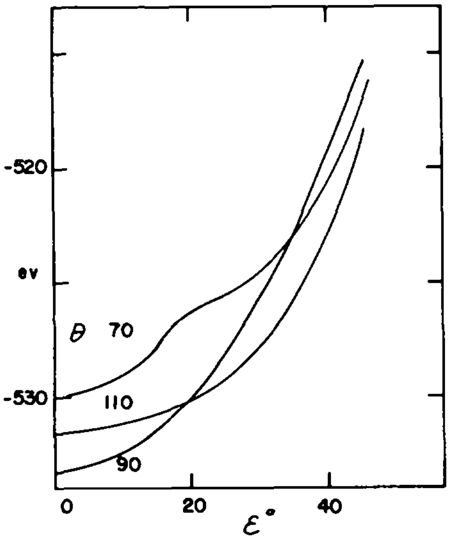


FIG. 3 Cyclobutanone. A plot of the energy in eV versus the ring-pucker angle ε as a function of the carbonyl CCC angle, θ.

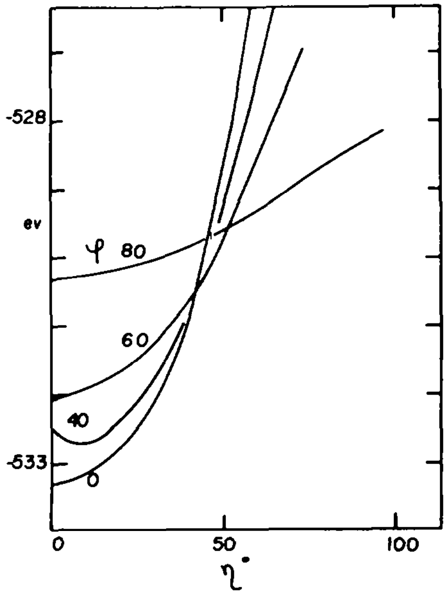


FIG. 4 Cyclobutanone. A plot of the energy in eV as the angle η, the CO in-plane bend, and the angle φ, the out-of-plane bend, are varied.

Examination of Table 1 and Fig. 4 should show that the CO group is easily deformed in the out-of-the-plane vibration.

Foote[15] estimated the rate of acetolysis of cyclobutyl tosylate using an empirical equation relating the rate constants to the CO frequencies. The estimate of rate was in error by 10^{10} fold. Our critique of this equation (and also of the equivalent term in the Schleyer equation):[16]

$$\log k/k_0 = \tfrac{1}{8}(1715 - \nu_{CO}) \qquad (1)$$

k first order rate constant of R_2CHOTs (HOAc 25°)
k_0 first order rate constant of cyclohexyl tosylate
ν_{CO} carbonyl stretching frequency in R_2CO
1715 carbonyl frequency of the standard ketone

was based on a normal coordinate analysis of a CO system and the computed energy of the corresponding carbonium ion. While we could verify the slope of $\frac{1}{8}$, we observed that this slope was constant only over a very narrow range of angles at the CO. *The energy of the carbonium ion was definitely not linear in the* CO *frequency of the* CO *model compound.* We also concluded that the *carbonyl force constants* of the two ketones must be the same for even an approximate agreement with Eq. (1).

In more simple terms, the R_2CO model is too stiff (it has a double bond) to deform in an isosteric[9] manner with the R_2CH^+ ion.

Boretane. Another useful calculational model for the cyclobutyl carbonium ion would be the corresponding monomeric borane. Since this borane has no charge, the EHT calculations are much more self-consistent.[9] The angles are defined as in Fig. 1. The results are reported in Fig. 5 on the energy as a function of the CBC angle, θ, and the HB plane angle, φ. The most stable form of boretane has a CBC angle of 90°.

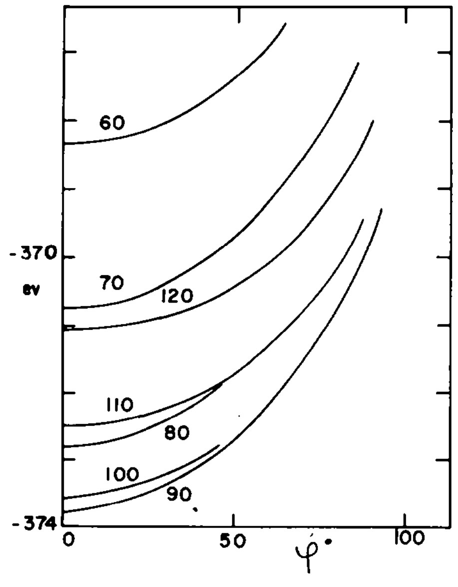


FIG. 5 Boretane. A plot of the energy in eV versus the CBC angle θ as the angle φ is varied.

In Fig. 6 the charge densities and bond overlap populations of the ground state are reported. The overlap population between the boron atom and the carbon atom across the ring is also shown. This is a measure of the amount of electron delocalization caused by the extremely electron deficient boron atom. In valence bond terms, the B—C_3 overlap population is a measure of the amount of resonance:

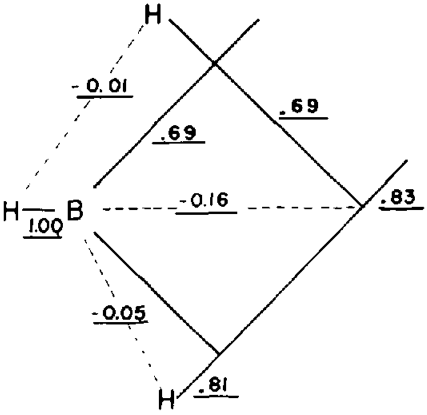
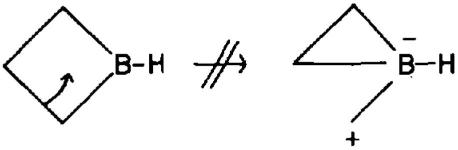


FIG. 6 Boretane. The EHT molecular orbital values of the overlap population densities (underlined) for the ground state of this molecule. Compare with Fig. 2.



We conclude that the nonclassical resonance form does not contribute to the resonance forms of boretane. The boretane is also a classical molecule.

Calculations were performed on geometries which could be labelled as "nonclassical bicycloboretane" structures. All were of much higher energy. Even though the boron is very electron deficient, the molecule prefers to remain classical.

THE CYCLOBUTYL CATION

Bearing in mind that the EHT calculations are being performed on an ionic species, the results might well have an absolute error of perhaps as much as 4 eV. However, since we are comparing different geometries, the errors in the differences between sets of calculations should largely cancel. Evidence that these errors do cancel was presented in the earlier paper[9] on the computed properties of CH_3^+. Since so many geometries of the ion have been suggested in the literature, the coördinates were varied greatly.

The tricyclo ion. This ion was suggested[4] to account for the extreme reactivity of cyclobutyl tosylate in solvolysis reactions. Hoffmann[7] has computed the orbital energies of this ion using the EHT method. We have verified his conclusion.[17] It turns out that the ground state has a set of *degenerate orbitals for the highest filled state* for which there are two electrons. Thus, this ion would be a carbonium ion triplet. In fact, one only needs to examine the character table for a C_{3v} system to arrive at the conclusion of orbital degeneracy.

The tricyclo ion has been ruled out by reexamination and repetition of the labeling data.[5, 18]

Since the extremely symmetric ion (the most nonclassical ion) has orbital degeneracy problems, its intervention even as a transition state in the interconversion of various electronic singlet states of other cyclobutyl, bicyclobutonium or cyclopropyl carbinyl ions must be ruled out.

The bicyclobutonium ion and the classical ion. Starting with the ion (classical structure 3) numerous calculations were performed on variations of the distances, the CCC angle, the ring pucker angle, the HCC in plane angle, and the HCC out-of-plane angle.

In Fig. 7 the computed energy is presented as a function of θ of the CCC angle at the carbonium center and as a function of the angle φ, the out-of-plane $H\overset{+}{C}C$ bend.

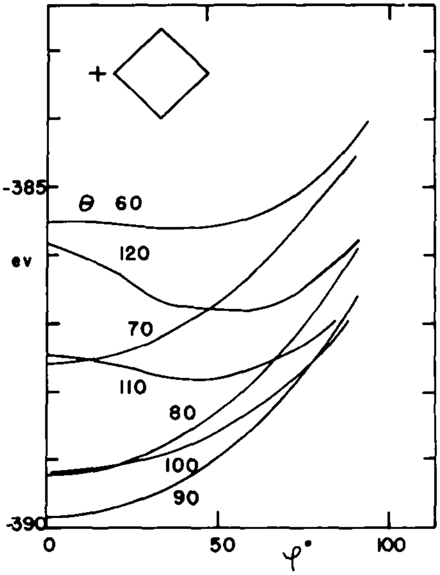
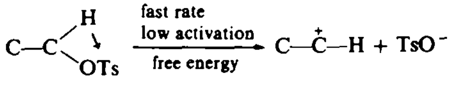


FIG. 7 Cyclo C_4H_7 cation. A plot of the energy of this ion as the angle θ is varied as a function of the out-of-plane bending angle φ.

The most stable form has the $H—\overset{+}{C}$ in the plane of the other three C-atoms. Our calculations indicate that this H-atom is easily moved out of the plane. Note that in Fig. 7 the energy of the cation increases very slowly as angle φ is increased. Careful comparison of the data of Table 1, Fig. 4, and Fig. 7 also substantiates the conclusion of our earlier study:[9] a CO compound can be used as a model for a carbonium ion, *but* the carbonyl compound is much stiffer than the carbonium ion.

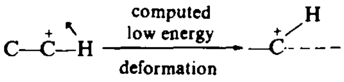
Because of the ease of the out-of-the-plane deformation of the H—$\overset{+}{C}$ of the cation, it is not surprising that cyclobutyl tosylate is a very reactive compound.



cyclobutyl tosylate

side view of cyclobutyl cation

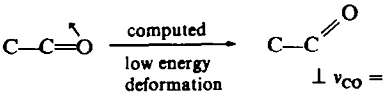
H moves into plane



see Fig. 7

cyclobutyl cation side view of the ring

angle φ



$\perp \nu_{CO} = 393\ cm^{-1}$ experimental value see Ref. 10

cyclobutanone side view of the ring

In Fig. 8 a plot is presented on how the computed energy varies with θ and ε. In Fig. 9 a plot is made of the ring pucker angle φ as a function of η. Similar plots of φ versus ε and η versus ε show that the *most stable form is the classical ion* **3** with bond angles of 90°.[19]

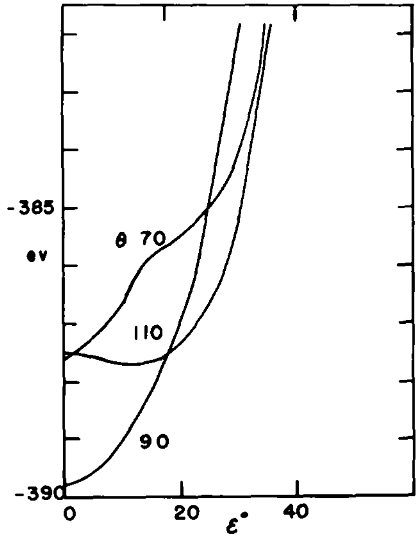


FIG. 8 Cycle C_4H_7 cation. A plot of energy in eV as the angle θ and ε are varied.

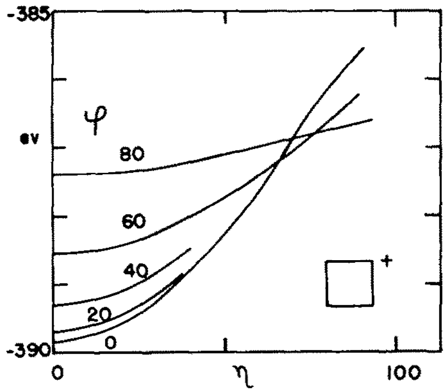


FIG. 9 Cyclo C_4H_7 cation. A plot of the energy in eV as the angle φ is varied as a function of angle η.

The molecular orbital diagram of the ground state is presented in Fig. 10. The most significant point of Fig. 10 is the fact that the C_1—C_3 (across the ring) overlap population is $-0{\cdot}145$ in the most stable form of the ion. We must conclude that EHT theory predicts that the *ground state of the cation is classical.* Another point is that carbons C_2 and C_4 have a negative charge of $-0{\cdot}14$. There is no positive charge placed on these centers. The entire CH_2 group only carries a net charge of $+0{\cdot}18$.

In Paper I, we concluded[9] that generally the properties of a carbonium ion (as CH_3^+) will lie between the properties of the CO model (as H_2CO) and the borane (as BH_3). In the present study it is to be noted that the D_1—C_3 overlap increases in the series ($-0{\cdot}16$ to $-0{\cdot}131$). This order places the carbonium ion ($-0{\cdot}145$) in between the properties of the ketone and the borane. See Fig. 1; $D_1 = C_1$ or B.

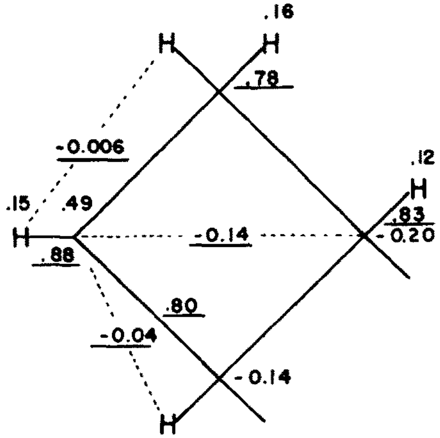
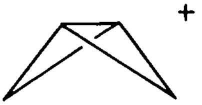


FIG. 10 EHT molecular orbital values of the charge densities and the overlap population densities (underlined) of the ground state (most stable form) of the cyclobutyl cation.

An important question can be asked. When does the C_1—C_3 interaction (as estimated by the population density) indicate that significant bonding occurs across the ring? The "bicyclobutonium ion", while not the minimum in energy of these ions, has the maximum amount of C_1—C_3 bonding when the angle of pucker is 35°.



The populations are reported in Table 2. However, as the angle ε is increased, the population very quickly becomes negative and no binding is observed between these transannular atoms. In agreement with the bicyclobutonium formula, as the C_1—C_3 bonding increases, the C_2—C_3 bonding decreases. Charge is also slowly placed on C_2 as the deformation is continued. However, the calculations indicate that the energy is higher in these deformed ions than in the classical undeformed structure.

TABLE 2. OVERLAP POPULATION ON CYCLOBUTYL CATIONS AS A FUNCTION OF THE PUCKER ANGLE

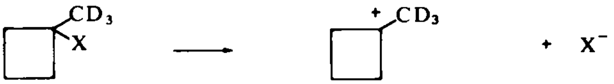
ε°	C_1—C_3	C_1—C_2	C_2—C_3	C_1—H_7	C_2—H_1	C_3—H_3	Energy (eV)
0	−0·145	0·802	0·687	0·935	0·776	0·820	−389·81
5	−0·129	0·703	0·678	0·935	0·781	0·820	−389·62
10	−0·109	0·783	0·660	0·938	0·786	0·828	−389·06
15	−0·075	0·764	0·633	0·941	0·793	0·835	−388·12
20	−0·023	0·737	0·600	0·944	0·801	0·845	−386·84
25	0·044	0·700	0·564	0·947	0·806	0·843	−385·19
30	0·123	0·650	0·520	0·951	0·809	0·828	−383·14
35	0·215	0·581	0·461	0·956	0·812	0·802	−380·57
40	−0·126	0·402	0·474	0·974	0·589	0·897	−377·66
45	−0·099	0·318	0·380	0·996	0·552	0·911	−373·93

Numbering C_1 as the C with the positive charge and single-hydrogen. C_2 and C_4 are adjacent to C_1 and C_3 is transannular from C_1. Hydrogens H_1 and H_2 are on C_2, H_3 and H_4 are on C_3, H_5 and H_6 are on C_4. The hydrogen H_7 is on C_1. Note that the C_1—C_3 population becomes positive near 25°. The C_1—C_3 population suddenly becomes negative near 38°. Note also that 4·6 eV must be added to the cation to deform it so that the C_1—C_3 population even becomes a bit positive. It requires 9·3 eV to reach the maximum amount of C_1—C_3 bonding, which only represents about 30% of a real stable C—C bond which usually has a value of 0·6 to 0·8.

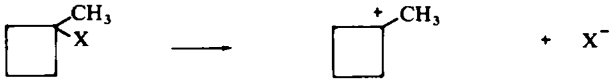
Discussion of certain experimental evidence (Added in Press). The literature to 1966 has been reviewed[20] on the cyclopropylcarbinyl and cyclobutyl cations. The authors concluded that "the cyclobutyl cation may be in equilibrium with the cyclopropylcarbinyl cation" and that "the cyclobutyl cation may have an energy comparable to that of the cyclopropylcarbinyl cation." Brown[21] has suggested that the cyclopropylcarbinyl cation is in equilibrium with the classical cyclobutyl cation and that both react with solvent to give products.

Using secondary deuterium isotope effects and the effect of Me substitution, Borcić and Sunko[22] have suggested that the bicyclobutonium ion is an intermediate. The secondary deuterium isotope effects are small and since the theory of these effects is so poorly understood, we doubt that these effects demand formulation of a nonclassical bicyclobutonium ion.

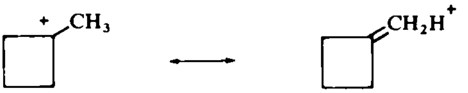
The small CD_3 isotope effects are easily explained using a classical ion:



$k_H/k_D = 1{\cdot}068 \pm 0{\cdot}045$



which *does not* put charge into the Me group. Placing charge into the CH_3 (or CD_3) group would require the formation of an *unfavorable exo*-double bond.



In this regard, we find that Me substitution stabilizes a carbonium center by 1·1 eV in an aliphatic system.[23] Methyl substitution causes a rate acceleration of 10^4 to 10^6 fold in these systems. However, the 1-Me group in cyclobutyl cation stabilizes the ion by only 0·6 eV, *about one-half* of the *effect in the aliphatic series.* Interestingly, 1-methylcyclobutyl chloride reacts only $10^{2\cdot1}$ times faster than cyclobutyl chloride. Using the decrease from 1·1 to 0·6 eV, *we would predict using classical ions* that 1-methylcyclobutyl chloride ought be in the range of $10^{2\cdot1}$ to $10^{3\cdot2}$ fold faster than the unsubstituted compound.

Thus the small isotope effects and the small acceleration caused by a Me group are explicable using classical ions.

CONCLUSION

Application of EHT theory to the cyclobutyl system indicates that transannular 1–3 sigma bonding is not an important factor in cyclobutanone, boretane, or the cyclobutyl cation.

It has been observed from these calculations that the C=O in the ketone, the B—H group in the borane, and the $\overset{+}{C}$—H group are all easily deformed in motions that resemble a reaction path from cyclobutyl tosylate to its cation.

Delocalization of sigma electrons is not supported by these theoretical studies. The ease of the out-of-plane deformation of the CO in the ketone (**1**), and the ease of the carbonium ion reaction will be subjected to further investigation.[24]

EXPERIMENTAL

The computer programs used in this study have been described in earlier papers.[1] Calculations were performed at close intervals of bond distance changes and of bond angle changes.[25]

An analysis of the EHT method and a discussion of the approximations and assumptions can be found in our earlier papers. (See the long footnote 9 of paper I as well as footnote 9 of this paper). The parameters used were $K = 1{\cdot}75$; $H_{ii} = -13{\cdot}60$ eV for hydrogen; H_{ii} (C2s) $= -21{\cdot}43$ eV; H_{ii} (C2p) $= -11{\cdot}42$ eV; H_{ii} (B2s) $= -15{\cdot}20$; (B2p) $= -8{\cdot}53$; H_{ii} (O2s) $= -35{\cdot}30$; and H_{ii} (O2p) $= -17{\cdot}76$ eV.

The program was obtained from the QCPE at Indiana University and revised a bit to fit our IBM 7094 computer.

Acknowledgement—We wish to acknowledge the Dean's Fund of Purdue for covering the computing costs.

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[1] Paper III in this series on Vibrational Effects in Carbonium Ions. Paper II. R. E. Davis, D. Grosse and A. Ohno, *Tetrahedron*, 23, 1029 (1967).

[2] Alfred P. Sloan Fellow, 1962–1966.

[3] J. D. Roberts and R. H. Mazur, *J. Am. Chem. Soc.* 73, 2509 (1951).

[4] J. D. Roberts and R. H. Mazur, *Ibid.* 73, 3542 (1951).

[5] R. H. Mazur, W. N. White, D. A. Semenow, C. C. Ler, M. S. Silver and J. D. Roberts, *Ibid.* **81**, 4390 (1959).

[6] P. D. Bartlett, *Nonclassical Ions*, Page *v* of the Preface. Benjamin, New York, N.Y. (1965); See also G. D. Sargent, *Quart. Rev.* **20**, 301 (1966).

[7] R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.* **36**, 2179 (1962), and *Ibid.* **37**, 2872 (1962); R. Hoffmann, *J. Chem. Phys.* **39**, 1397 (1963); *Ibid.* **40**, 2745 (1964); *Ibid.* **40**, 2474 (1964) and *Ibid.* **40**, 2480 (1964).

[8] F. B. Boer, M. D. Newton and W. N. Lipscomb, *Proc. Nat. Acad. Sci.* **52**, 890 (1964).

[9] [a] R. E. Davis and A. Ohno, *Tetrahedron* **23**, 1015 (1967). Paper I. In this paper the computed properties of methanal, borane, and methyl cation were compared. Both theoretical and experimental arguments were presented. The conclusion was that methanal, H_2CO, is too stiff and borane, BH_3, too plastic to serve as accurate model compounds for CH_3^+. The stiffness of the carbonyl model, when carried to its logical conclusion, precludes the use of the Foote and Schleyer equations (Refs. 15 and 16) as a measure of nonclassical anchimeric assistance. See Paper II, Ref. 1.

[b] A measure of the reliability of the EHT method can be obtained from Paper I. Bond distances and force constants were computed and then compared with the experimental results. The agreement was to within 2–3%. The success of EHT theory is due to several factors. The Slater orbitals and their coefficients are calibrated with the experimental values on hydrogen atoms. The H_{ii} matrix elements are obtained from experimental values for hydrogen, carbon, boron, and oxygen. Lastly, the constant, K, has been chosen so that "charge distributions ... are insensitive to K" and "... as a reasonable compromise between the desire to match the experimental barrier in ethane ... and ... where (charge) populations are stable". See R. Hoffmann, *J. Chem. Phys.* **39**, quoted from p. 1412 (1963). Therefore, the EHT method is well based upon experimentally determined values. There is a mixture of some *ab initio* features with some experimental information.

[c] The real question is whether the EHT method can work on an ion like CH_3^+. Our EHT results[9a] on CH_3^+ can be compared with the *ab initio* LCAO MO SCF calculations on CH_3^+ by R. E. Kari and L. G. Csizmadia, *J. Chem. Phys.* **46**, 1817 (1967)—(KC results) and with the similar work of S. D. Peyerimhoff, R. J. Buenker and L. C. Allen, *Ibid.* **45**, 734 (1966)—(PBA results).

The charge density on the hydrogen was $+0{\cdot}17$ (EHT) or $+0{\cdot}29$ (KC). The energy to deform CH_3^+ out of the plane 10° was computed to $0{\cdot}25$ eV (EHT) or $+0{\cdot}36$ eV (KC). The energy to deform the HCH angle the same amount in the planar molecule was $0{\cdot}35$ eV (EHT) or $0{\cdot}68$ eV (PBA).

Using the PBA results and IR data of Paper II, the limitations made by theory on the Schleyer–Foote relationship is even more severe. We did suggest[1] that our EHT results put a lower limit on the relationship.

The differences between the EHT results on CH_3^+ and those of the LCAO MO SCF *ab initio* calculations are not that much. The manner in which the orbital energies and charge density change with deformations are rather similar.

We have used the EHT theory *not* to obtain *absolute* energies, but energy differences for slightly distorted molecules and ions. In this way a much better cancellation of terms is made.

$$E_{T_1} = 2\sum_{i,1} \varepsilon_i - \sum_{i,j,1} P_{ij} + \sum_{\alpha,\beta,1} Z_\alpha Z_\beta / r_{\alpha\beta} \tag{i}$$

$$E_{T_2} = 2\sum_{i,2} \varepsilon_i - \sum_{i,j,2} P_{ij} + \sum_{\alpha,\beta,2} Z_\alpha Z_\beta / r_{\alpha\beta} \tag{ii}$$

E_T is the total energy (see PBA); $2\sum \varepsilon_i$ is the sum of the orbital energies. $\sum P_{ij}$ is an electron term and the last term is the nuclear term.

While the P_{ij} term may not cancel out the nuclear term in (i), it is a better approximation:

$$\Delta E_{1,2} \approx 2\sum_i \varepsilon_{i,1} - 2\sum_i \varepsilon_{i,2} \tag{iii}$$

to suggest that $\mathbf{P}_{ij,1}$ cancels with $\mathbf{P}_{ij,2}$ and two nuclear terms cancel.

Peyerimhoff[9c] presents a table of ΔE_T and $\Delta \sum_{ii} \varepsilon$ and the difference between these two terms for CH_3^+ as the HCH angle is deformed from 120° to θ°. The difference between the total energy and the sum of the orbital energies is only −0·065 eV at a ∠HCH of 115°, and only +0·57 eV at a ∠HCH of 85° compared to 120°. Thus we feel that the approximations of the EHT are made under very reasonable conditions on ions. Comparison with these data[9c] indicate that the error of applying the EHT theory to an ions as CH_3^+ is *less than* 10% when *we take differences as (iii).*

[*] Another critique of one-electron methods (as the EHT theory) has been made by J. A. Pople, D. P. Santry and G. A. Segal, *J. Chem. Phys.* **43**, S 129 (1965). (See our footnote[9c] in Paper I.) The elements of $\mathbf{H}_{ij} = KS_{ij}(H_{jj})/2$ transform differently in changes of the coordinate system. The magnitude of this error has been estimated to be about 0·6% in H_2O by Newton, *Ibid.* **45**, 2716 (1966) in his debate with L. C. Cusachs, *Ibid.* **45**, 2717 (1966). (See also L. C. Cusachs and B. B. Cusachs, *J. Phys. Chem.* **71**, 1060 (1967). Although the magnitude of the error is small, it might have an effect on obtaining the correct geometry for the ground state.

We are starting a program using Segal's program (QCPE #91). *Cyclobutyl ion appears to be most stable as the classical ion* in this method as well. Charge densities are a bit different, perhaps more reasonable to chemical intuition.

[10] A. Bauder, T. Gaumann and F. Tank, as reported by K. Frei and H. H. Gunthard, *J. Mol. Spectro.* **5**, 218 (1960).

[11] J. O. Halford, *J. Chem. Phys.* **24**, 830 (1956). Based upon a *tetratomic* model, X_2CO, the Halford approximation must be used with *extreme* caution. See ref. 1 for our critique of this relationship.

[12] R. Zbiden and H. K. Hall, Jr., *J. Am. Chem. Soc.* **82**, 1215 (1960).

[13] P. von R. Schleyer and R. D. Nicholas, *Ibid.* **82**, 182 (1961). We estimate an angle change, θ, of 7° would require about 0·8 eV of energy in the ketone.

[14] R. S. Mulliken, *J. Chem. Phys.* **23**, 1833, 1841, 2338 and 2343 (1955). See ref. 7.

[15] C. S. Foote, *J. Am. Chem. Soc.* **86**, 1583 (1964). His equation is $\log k/k_0 = 0{\cdot}132\,(1720 - \nu_{CO})$.

[16] P. von R. Schleyer, *J. Am. Chem. Soc.* **86**, 1854, 1856 (1964). Equation (1) is the first term in the equation suggested by Schleyer.

In Paper I of this series, Eq. (1) is derived using quantum mechanics and normal coordinate analysis. See Refs. 1 and 9.

[17] Hoffmann (*J. Chem. Phys.* **40**, 2480 (1964)) performed some calculations on the tricyclo ion in a geometry of a C—H^+ sitting at various distances on the threefold axis of the ring. "No minimum (in energy) at all was found for this form." See page 2485. He also reports that he did not study the bicyclo ion.

[18] The tricyclo ion was retained[5] as a possible conformation through which the system passes from one bicyclo ion to another. This would involve a very unlikely single-triplet transition. Therefore, no cation can have any greater symmetry than C_{2v} (nondegenerate) in the carbonium ion rearrangements. More recently Howden and Roberts (See M. E. H. Howden and J. D. Roberts, *Tetrahedron* **Supp. 19**, 403 (1963)) commented that the tricyclobutonium is "an electronically unfavorable system" since the energy levels of the π-system are "inverted relative to cyclopropenium ion". In other words, the tricyclo ion is a triplet. We wish to acknowledge fruitful correspondence with J. D. Roberts.

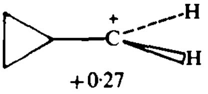
[19] The planar classical cyclobutyl cation with a CCC angle of 90° has not been considered a favored species because of the preferred 120° bond angle of the sp^2 hybridized carbon atom. See Ref. 6, page 273. Referring to Table 2, and our computed wave functions, it is seen that the carbon orbitals are very highly hybridized at the $\overset{+}{C}$—H center.

It is a triumph of EHT theory to correctly predict a 90° C(CO)C bond angle in cyclobutanone. The angle in the cation is probably also 90°.

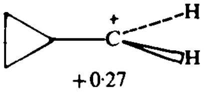
[20] K. B. Wiberg, B. A. Hess, Jr. and A. J. Ashe, article in press. We wish to thank R. Hoffmann for informing us of this article on 8 June 1967 and H. C. Brown for providing us a copy on 9 June and K. Wiberg for a stimulating phone conversation on 9 June 1967.

Interestingly, Wiberg has applied the Pople Complete Neglect of Differential Overlap (CNDO) method to cyclobutyl cation and cyclopropylcarbinyl cation. He finds that cyclobutyl cation is classical with no (1,3) transannular bonding. The cation must be deformed to 35° to obtain any 1,3 bonding (see Table 2 for the EHT results).

Cyclopropyl carbinyl cation in the bisected form has charge distributions of

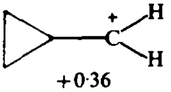


CNDO

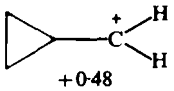


EHT

while the planar form (cyclopropyl ring and the $\overset{+}{C}H_2$ in the same plane) has:



CNDO

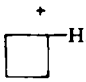


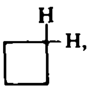
EHT

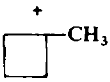
Interestingly the energy to convert the more stable forms to the planar forms in 8 kcal/mole for CNDO or 8·7 kcal/mole for the EHT. The CNDO is another semi-empirical method that makes different types of approximations than the EHT. Qualitatively and semi-quantitatively the results of CNDO and EHT are very similar. These data show that the EHT method *can be used with caution on cations!*

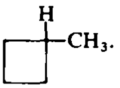
[21] H. C. Brown, *The Transition State*, Spec. Publ. No. 16, pp. 2–24. The Chemistry Society, London (1962).

[22] M. Nikoletić, S. Borcić and D. E. Sunko, *Tetrahedron* 23, 649 (1967); Z. Majerski, M. Nikoletić, S. Borcić and D. E. Sunko, *Ibid.* 23, 661 (1967).

[23] Unpublished calculations on CH_3^+, CH_4, $CH_3CH_2^+$, CH_3CH_3, 







Article in preparation, R. E. Davis, A. Murthy and A. Ohno.

[24] For example, the CH_3^+ system with a HCH bond angle of 90° has been studied in good detail as the other hydrogen has been deformed out of the plane of the remaining CH_2 group. These results along with other studies will be reported in following papers. Unpublished results of Miss A. J. McElheny.

[25] In all cases, the calculations have been made on single molecules or ions in the gas phase. There is no satisfactory way to do calculations on solvated ions using any serious quantum mechanical theory at present. Solvation effects on the neutral molecules as boretane and cyclobutanone ought be small compared to change in solvation of the cation. *However, a polar solvent will stabilize a classical carbonium ion more than a nonclassical ion.* A classical ion would be expected to have a smaller radius than the nonclassical structure which has a more delocalized charge with an effectively large radius. This can be best seen in the Bohr equation of solvation: $\Delta G = (e^2Z^2)(1 - 1/D)/2r$. As r, the radius, increases; the free energy of solvation drops. Thus theory predicts that an ion ought be more stable in solution as the classical ion.