Tetrahedron, 1967, Vol. 23, pp. 1015 to 1028. Pergamon Press Ltd. Printed in Northern Ireland

METHYL CATION AND MODEL SYSTEMS FOR CARBONIUM IONS[1]

R. E. DAVIS[2] and A. OHNO[3]
Department of Chemistry, Purdue University West Lafayette, Indiana, U.S.A.

(*Received in U.S.A.* 1 *March* 1966; *accepted for publication* 15 *June* 1966)

Abstract—Two molecules are used as models for the properties of methyl cation, CH_3^+, namely methanal and borane. The properties of these systems have been computed by the Extended Huckel Theory as each molecule is deformed. The charge densities and energies are presented in graphic manner. It is concluded from the calculations that methanal is much stiffer than methyl cation and that borane is much more plastic than methyl cation. Neither model system undergoes isosteric deformation, the same increase in energy for the same amount of deformation.

INTRODUCTION

A PRESSING chemical problem is that of the nature of the activated complex in a reaction. By definition the Eyring complex has only an unimolecular mode of decomposition to reactants or products. Thus the chemistry of a particular activated complex can only be probed by kinetics (giving the gross element composition of the complex), by isotope effects (giving one number at one temperature that is a small function of the geometry (G matrix) and a major function of the force fields (F matrix)), or by model systems. The use of model systems, is, at best, only based on chemical analogy and inference. In the present paper the computed properties of methyl cation are examined and compared with the computed and known properties of various model systems: namely methanal and borane. Methane has been used as a starting point to estimate the success of EHT theory.

Method

The use is made of the Extended Huckel Theory (EHT) as developed by Hoffmann.[4–7] In this LCAO-MO calculation all valence electrons are considered in both σ and π frameworks. The H_{pp} matrix elements are estimated from ionization potentials of the atoms. The H_{pq} elements are estimated by

$$H_{pq} = 0{\cdot}50\ K[H_{pp} + H_{qq}]S_{pq} \tag{1a}$$

for hydrocarbons, or by

$$H_{pq} = K'S_{pq} \tag{1b}$$

for resonance integrals involving boron or nitrogen. No off-diagonal matrix elements are set equal to zero. The molecular geometry (or symmetry) is entered as the x, y, z

---

[1] Paper I. Vibrational Effects.

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

[3] Postdoctoral Research Associate.

[4] R. Hoffmann, *J. Chem. Phys.* **39**, 1397 (1963).

[5] R. Hoffmann, *J. Chem. Phys.* **40**, 2745 (1964).

[6] R. Hoffmann, *J. Chem. Phys.* **40**, 2474 (1965).

[7] R. Hoffmann, *J. Chem. Phys.* **40**, 2480 (1964).

coordinates of each atom and is used to compute H_{pq} from Slater orbitals. The constant, K, is chosen to fit the known properties of ethane. Coulson and Dewar[8] have presented a critique of the use of the Huckel method on ionic species. More recently the statement has been made that the use of HT or EHT for carbonium ions (as non-classical ions) is "so grossly incorrect that no such justification can be accepted in this case."[9]

In the present work three models for CH_3^+ have been examined: namely methane, methanal and borane. While EHT calculations have been performed on methyl cation, the present authors recognized the error *in computed energy* to be of the order of 4 ev of added repulsion since $|E_{ee}| \neq |E_{nn}|$.

Calculations on BH_3 circumvent this difficulty which only could be overcome for CH_3^+ by using a full Self Consistent Field Molecular Orbital treatment.[10] At present methyl cation can be handled but an ion as 2-norbornyl cation would be impracticable in such a full treatment.

RESULTS

Methane. Numerous calculations have been performed on methane using LCAO-MO-SCF with Slater-base sets,[11,12] MO-one center methods,[13–16] and LCAO-MO-SCF

---

[8] C. A. Coulson and M. J. S. Dewar, *Disc. Faraday Soc.* **2**, 54 (1947); Also see the preceding paper, **2**, 50 (1947).

[9a] M. J. S. Dewar and A. P. Marchand, *Annual Review of Phys. Chem.* **16**, 321–346 (1965). Quoted from p. 344. The authors of this review plead for a return of sanity in carbonium ion chemistry. However, this critique of the EHT method is much too severe. For example, we have calculated using EHT theory the CH valence force constant of CH_3^+ to be 4·47. A model is provided by H_2CO which has a force constant of 4·35 mdynes/A; [b] See F. B. Boer, M. D. Newton and W. N. Lipscomb, *Proc. Nat. Acad. Sci.* **52**, 890 (1964); [c] J. A. Pople, D. P. Santry and G. A. Segal, *J. Chem. Phys.* **43**, S 129 (1965). In this paper the authors point out that the off-diagonal martix elements in EHT theory are not invariant under certain orthogonal transformations. Such invariance is required for a self-consistent one-electron Huckel operator. It is an aesthetic criticism to have a theory which gives *slightly* different results depending on the choice of coordinate system. However the magnitude of this difference is not really that large. Defining our coordinates with the (0, 0, 0) at C for methanal and methyl cation and at B for borane, *does not* introduce a fatal flaw into the semi-empirical calculations reported in this paper.

The real problem with our work (and all most all other) is the mixture of some *ab initio* elements with some empirical elements. For example the Slater orbitals are "calibrated" from experimental atomic spectral data. *K* is calibrated.

At present all quantum calculations on complex molecules are semirigorous. None have apostolic purity. [d] D. G. Carroll and S. P. McGlynn have communicated to us the results of their work on the EHT theory. They find that replacing the *K* of 1·75 in

$$H_{ij} = K(H_{ii} + H_{jj})S_{ij}/2$$

with

$$K = (2 - |S_{ij}|)$$

leads to a much better representation of the electronic energy. Also see D. G. Carroll, A. T. Armstrong and S. P. McGlynn, *J. Chem. Phys.* in press.

[10] B. M. Gimarc and R. G. Parr, *Annual Review of Phys. Chem.* **16**, 451–480 (1965). A good review of the quantum theory and valence.

[11] B. J. Woznick, *J. Chem. Phys.* **40**, 2860 (1964).

[12] J. J. Sinai, *J. Chem. Phys.* **39**, 1575 (1963).

[13] A. F. Saturno and R. G. Pan, *J. Chem. Phys.* **33**, 22 (1960).

[14] D. M. Bishop, *Mol. Phys.* **6**, 305 (1964).

[15] R. Moccia, *J. Chem. Phys.* **40**, 2164 (1964).

[16] E. L. Albasiny and J. R. A. Cooper, *Proc. Phys. Soc.* **82**, 289, 801 (1963).

with Gaussian sets.[17,18] Hoffmann[4] has used the EHT method on methane using only T_d symmmetry. He performed a rough calculation on the C—H stretching force constant (about 5·5 mdynes/Å) near the minimum of the potential curve (about 1·0 Å).

Our calculations of methane (T_d symmetry) were made using the IBM 7094 at 0·05 Å intervals from 0·80 to 1·50 Å for the C—H distance and then from 1·0150 to 1·0250 Å using 0·0005 Å intervals. The calculated total energy in electron volts (ev) are plotted in Fig. 1. The minimum occurred at 1·0230 Å with E = −139·7919 ev. The data are reported in Table 1.

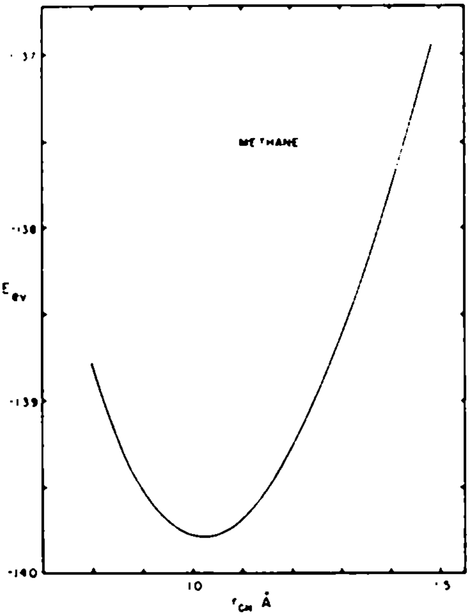


FIG. 1. Computed total energy of methane as a function of C—H distance for the ν_1A_1 deformation.

The second derivative of the energy curve was obtained from these data and was determined to be 5·57 mdynes/Å at the calculated minimum. The C—H distance[19] in methane is known to be 1·091 Å and the normal coordinate force constant[20] is 5·45 mdynes/Å. Since the deformation of T_d methane (only along the valence bonds) is the normal mode ($\nu_1(A_1)$), we have used the $F_r^{A_1}$ force constant which comes from the A block of the FG matrix calculation on methane.[21] The agreement of EHT theory with both of the experimental values is good. This certainly enforces Hoffmann's arguments as to the usefulness of the EHT method and encourages the success of the following calculations.

[17] R. K. Nesbet, *J. Chem. Phys.* 32, 1114 (1960).

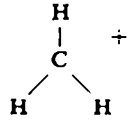
[18] M. Krauss, *J. Chem. Phys.* 38, 546 (1963) and *J. Res. Natl. Bur. Std.* 68 (A), 635 (1964).

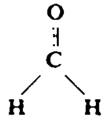
[19] Y. Morino, *Interatomic Distances and Bond Angles, A Chapter of Constants of Organic Compounds* (Edited by M. Kotake) p. 510. Asakura, Tokyo, Japan (1963).

[20] L. H. Jones and M. Goldblatt, *J. Mol. Spectrosc.* 2, 103 (1958).

[21] In particular, $\lambda_1 = \dfrac{1}{M_1} F_r^{A_1}$.

Methanal. The ketone (or aldehyde) has often been suggested as a model for the carbonium ion.





Both systems are planar. Both systems have the same type of hybridization at the carbon. Both systems have positive charge density on the carbon.

TABLE 1. EHT PARAMETERS FOR CH_4 WITH C—H DISTANCE 1·0230 Å

WAVE FUNCTIONS

	1[a]	2	3	4	5	6	7	8
1 H(1)[b]	0·7020	0·7638	0·0029	−1·0801	0·4041	0·0043	−0·2855	0·1586
2 H(2)	0·7020	0·7637	−0·0031	1·0801	−0·4039	−0·0040	−0·2859	0·1586
3 H(3)	0·7020	−0·7639	−1·0800	−0·0030	0·0040	−0·4041	0·2855	0·1586
4 H(4)	0·7020	−0·7639	1·0802	0·0030	−0·0043	0·4039	0·2859	0·1586
5 C(s)	−1·9239	0	0	0	0	0	0	0·5906
6 C(2x)	0	0	0·0034	−1·1949	−0·6207	−0·0063	−0·0003	0
7 C(2y)	0	1·1949	−0·0001	0	−0.0003	−0·0003	0·6207	0
8 C(2z)	0	0·0001	1·1949	0·0034	0·0063	−0·6207	−0·0003	0

Energy Levels ev

E(1)	49·929
E(2)	13·825
E(3)	13·824
E(4)	13·824
E(5)	−14·952
E(6)	−14·952
E(7)	−14·953
E(8)	−25·039

[a] MO across the top. Coefficients in the column.

[b] Atomic orbital. The atomic orbitals are directed along the x, y, z axes as 2x (2px).

Several calculations on H_2CO have been performed[22] using a SCF variational method[23] and the SCF-LCAO method.[24] Duncan's calculations[24] were in good agreement (within 1%) with the experimental value of the molecular energy. The dissociation energy was computed to be 0·440 (e^2/a_0) compared to the experimental value of 0·586. A Mulliken overlap population analysis[25] was also reported.

However, in these calculations[24,25] the electronic structure was computed using formaldehyde in its normal group state of C_{2v} symmetry with the known bond distances determined by microwave data.[26] In the present work the molecule has been greatly deformed starting with the normal molecule with a C—O distance of 1·206 Å and

---

[22] See the Tables of Ref. 10.

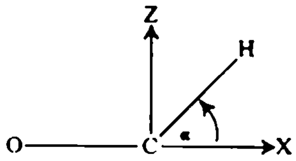
[23] J. M. Foster and S. F. Boys, *Rev. Mod. Phys.* 32, 303 (1960); also see *ibid.* 32, 300 (1960).

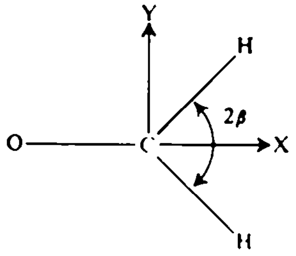
[24] P. L. Goodfriend, F. W. Birss and A. B. F. Duncan, *Rev. Mod. Phys.* 32, 307 (1960). All the basic atomic orbitals on C and O were used in this calculation (1s, 2s and 2p). In the EHT method only the 2s and 2p set are used on O and C.

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

[26] R. B. Lawrence and M. W. P. Strandberg, *Phys. Rev.* 83, 363 (1951).

C—H of 1·117 Å. The angles have been defined starting with the four atoms in the x, y plane as follows:





Keeping the valence bond distances constant, calculations were performed with α from 0 to 90° at 10° intervals and with variation of β from 30 to 100° at 10° intervals. In Fig. 2 the plots have been constructed.

The HCH bond angle (2β when α = 0) in methanal is 115°50′. The EHT method, which does over emphasize hydrogen-hydrogen repulsion,[4–7] leads to a minimum at 130°30′. It is much easier to deform an angle than lengthen a bond. In fact the

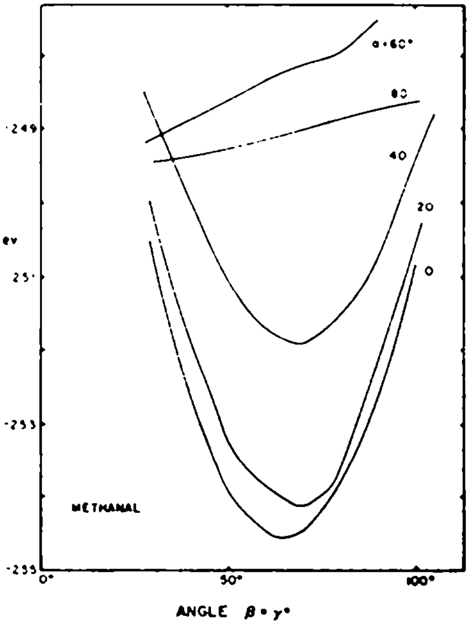


FIG. 2. Deformation of H_2CO. Total energy versus structure as the angle α (related to the OCH angle) and β (related to the HCH angle) are varied.

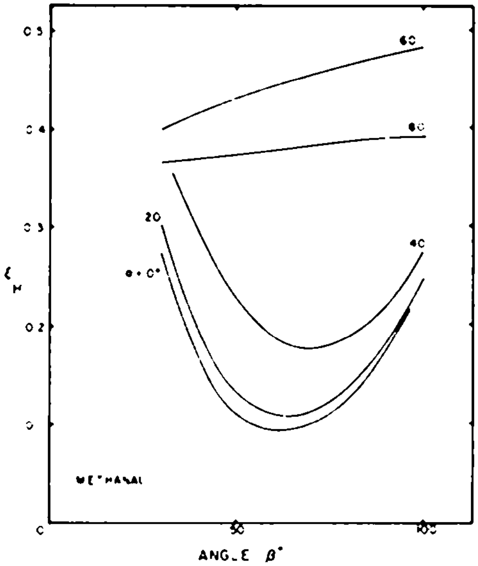


FIG. 3. Charge density on the hydrogen of methanal as a function of the deformation.

calculated total energy of methanal with the experimental bond angle of 116° is only 0·03 ev higher than the computed minimum at 130·5°.

The data of Fig. 2 do indicate that as methanal is deformed by variation of the α angle out of the original x, y plane, the HCH angle opens up. During the severe deformation the computed charge density on the hydrogen and on carbon change as shown in Figs. 3 and 4. In agreement with chemical intuition, the charge density on the carbon decreases as the angle α increases.

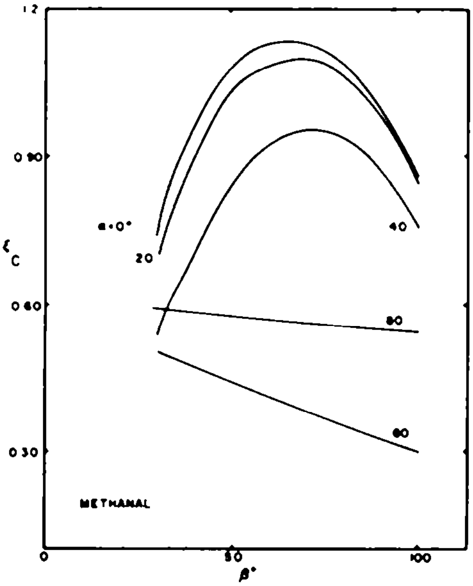


FIG. 4. Charge density on the carbon of methanal as a function of the deformation.

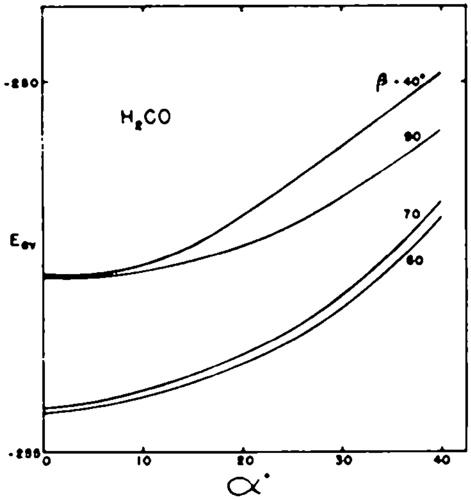
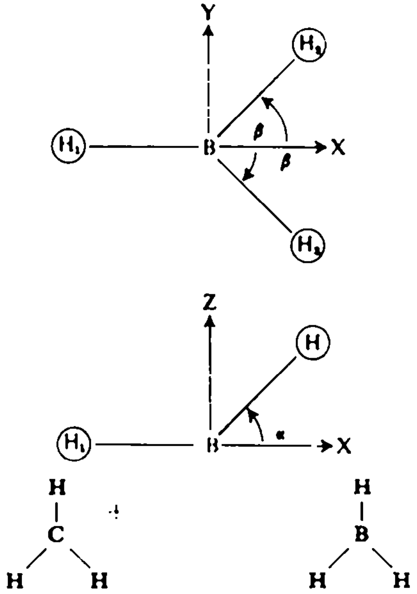


FIG. 5. Total energy of methanal in ev as a function of angle β with variation in the angle α.

Figure 5 presents the data on energy of methanal versus the deformation of angle β as a function of α.

Borane. The borane[27] should represent a very good model for a carbonium ion. The boron atom is electron deficient and the electronegativity of boron and carbon are close enough together to allow an accurate assessment of the amount of electron delocalization from the carbon and/or hydrogen framework.



---

[27] W. L. Clinton and B. Rice, *J. Chem. Phys.* **29**, 445 (1958). LCAO-MO-SCF with Slater Orbital Bases. The B—H distance was calculated to be 1·2325 Å.

Calculations were performed on borane using Coulomb integrals H_{ii} (2s) = $-15{\cdot}20$ ev and H_{ii} (2p) = $-8{\cdot}50$ ev. The Slater exponent used for boron was 1·30. The choice of resonance integrals (Eq. 1) is, at best, semiempirical. Therefore, calculations were performed using both (1b) with the planar D_{3h} molecule using bond distance intervals of 0·0005 Å. Using $H_{ij} = KS_{ij}$ (Eq. 1b), the minimum occurs at 1·14 Å and the force constant for the A_1 symmetric stretch is 3·50 mdynes/Å. Using (Eq. 1a), the most stable, computed form of borane has a boron-hydrogen distance of 1·19 Å and a force constant of 3·29 mdynes/Å. The boron-hydrogen force constant has been estimated[28] to be 3·38 mdynes/Å and the best estimate of the distance[29] is 1·19 Å. The better calculation results from the use of 1a. The best data are reported in Table 2.

TABLE 2. EHT PARAMETERS FOR BH_3 WITH B—H DISTANCE 1·190 Å

	1[a]	2	3	4	5	6	7
H(1)[b] 1	0·8978	1·2021	0·0004	0	−0·0009	−0·5664	−0·2725
H(2) 2	0·8978	−0·6014	1·0408	0	0·4910	0·2825	−0·2725
H(3) 3	0·8978	−0·6007	−1·0412	0	−0·4901	0·2840	−0·2725
B(2s) 4	1·8658	0	0	0	0	0	−0·4787
B(2x) 5	0	1·3804	0·0004	0	0.0007	0·4550	0
B(2y) 6	0	0·0004	−1·3804	0	0·4550	−0·0007	0
B(2z) 7	0	0	0	1·0000	0	0	0

Energy Levels ev.	
E(1)	39·032
E(2)	15·718
E(3)	15·718
E(4)	−8·530
E(5)	−13·914
E(6)	−13·914
E(7)	−20·198

[a] MO. See Table 1.
[b] Atomic orbital.

Calculations on borane were made at two boron-hydrogen bond distances. The BH distance of 1·19 Å is quite long and the borane deforms rather easily. Therefore a second distance of 0·955 Å was used. This is the C—H distance computed for methyl cation. It tends to make borane a little harder to deform (Fig. 6).

Deformation of borane was made defining the angles in the same manner as with methanal. In Figs. 6 and 7 the data using Eq. (1a) are reported.

In Fig. 8 the charge density on the boron atom is given as a function of the angles α and β. In Figs. 9 and 10 the charge density on the hydrogen atoms in borane are illustrated. Our method of calculation uses one of the hydrogens (H_1) and the boron as the anchor points for the deformation. In this manner the deformation of borane can be more easily compared with the deformation of methanal and methyl cation. Similar calculations as reported in Figs. 6–10 were made using (1b). Qualitatively the results are similar.

---

[28] S. H. Bauer, *J. Amer. Chem. Soc.* **78**, 265 (1954).

[29] W. H. Lipscomb, *Boron Hydrides* pp. 2–3. Benjamin, New York, N.Y. (1963).

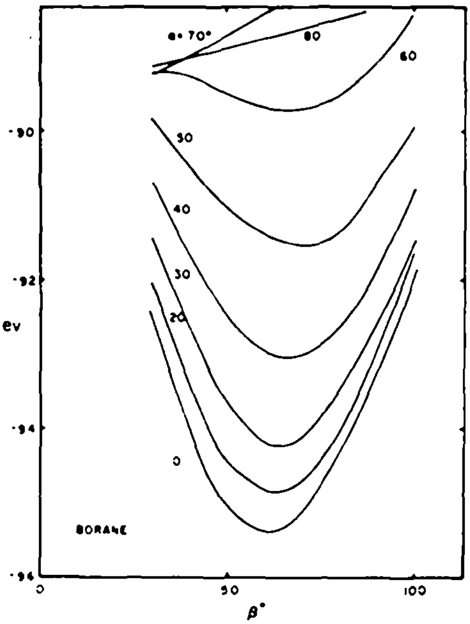


FIG. 6. Deformations of borane. Total energy in ev as a function of angle α as a function of angle β. Computed using a BH distance of 0·955 Å.

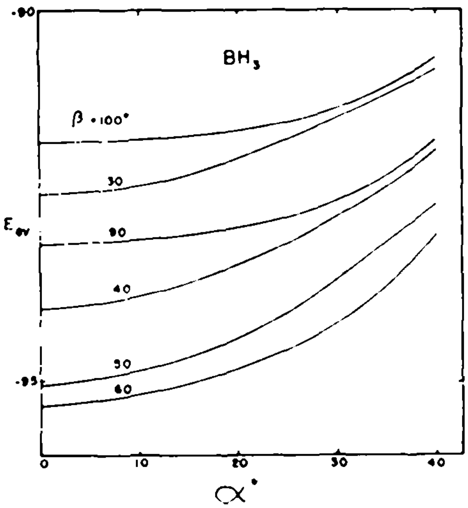


FIG. 7. Deformations of Borane. Total energy in ev as a function of angle β as a function of angle α.

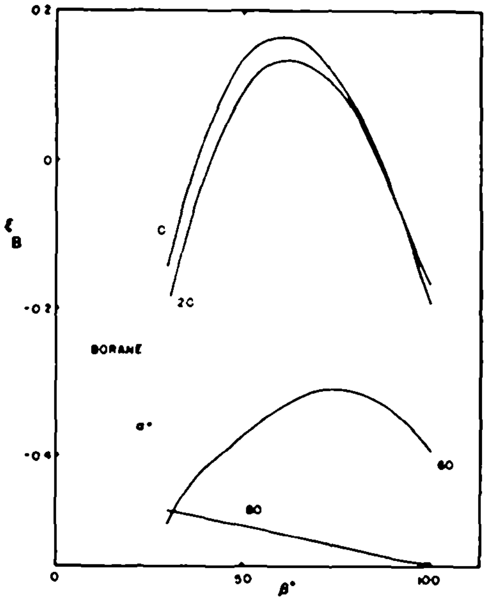


FIG. 8. Computed charge density on the boron atom in borane as a function of the deformation.

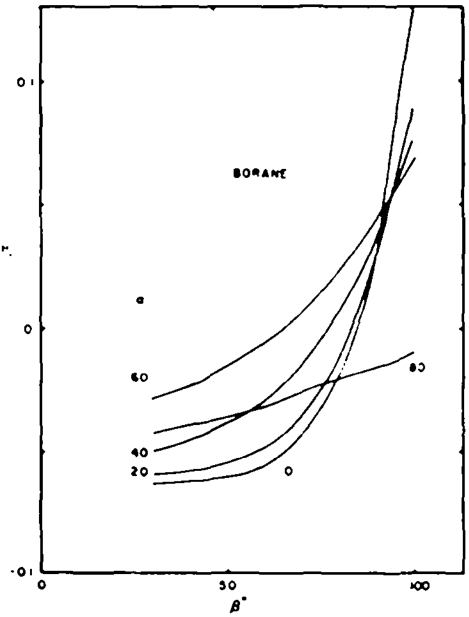


FIG. 9. Computed charge density on hydrogen in borane as a function of the deformation.

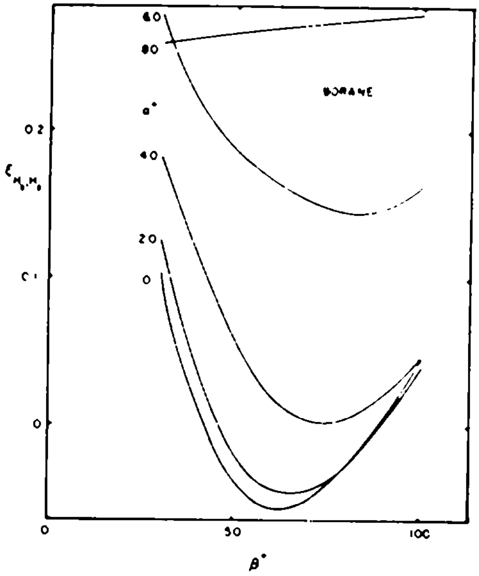


Fig. 10. Computed charge density on the hydrogens of borane as a function of the deformation.

Methyl cation. All of the preceding calculations have been made on neutral molecules using the EHT method. The following calculations were performed on CH_3^+. The angles were defined in the same manner as with methanal and borane.

The variation of carbon-hydrogen distance in the planar D_{3h} ion leads to a minimum at 0·955 Å and an energy of $-110{\cdot}3356$ ev. The computed force constant was 4·47 mdynes/Å. The data are presented in Fig. 11. The wave functions are presented in Table 3.

In Fig. 12 the energy of methyl ion has been illustrated as a function of the angles

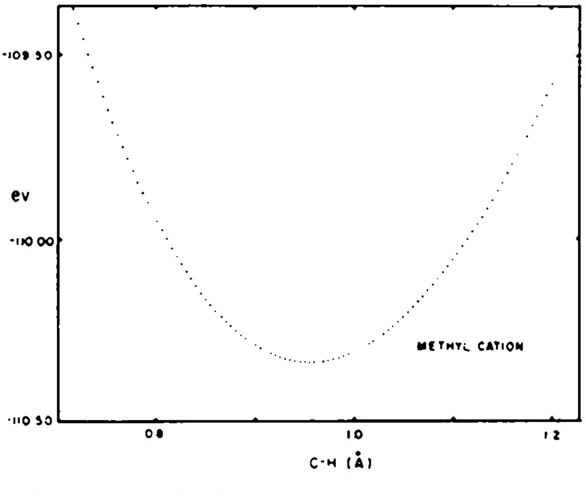


Fig. 11. Energy in ev versus carbon-hydrogen distance in planar CH_3^+ of point group D_{3h}.

TABLE 3. EHT PARAMETERS FOR CH_3^+ WITH C—H DISTANCE 0·955 Å

	1[a]	2	3	4	5	6	7
H(1) 1[b]	0·8877	−0·6617	−1·2034	0	0·3659	−0·2805	−0·1898
H(2) 2	0·8877	1·3731	0·0286	0	−0·4259	−0·1767	−0·1899
H(3) 3	0·8877	−0·7113	1·1748	0	0·0600	0·4572	−0·1899
C(2s) 4	−1·9240	0	0	0	0	0	−0·6111
C(2x) 5	0	−0·6384	−1·1611	0	−0·4841	0·3711	0
C(2y) 6	0	1·1611	−0·6384	0	0·3711	0·4841	0
C(2z) 7	0	0	0	1·0000	0	0	0

Energy Levels ev

E(1)	54·235
E(2)	21·705
E(3)	21·705
E(4)	−11·420
E(5)	−15·154
E(6)	−15·154
E(7)	−24·860

[a] Molecular orbitals.

[b] Atomic orbitals.

of deformation. Comparison of Fig. 12 with Fig. 2 for methanal shows that methyl ion deforms more easily than the aldehyde. Examination of the data of Fig. 6 demonstrates that the computed angular deformation of the borane compares very favourably with that of methyl ion.

In Fig. 13 the parametric plot is presented of energy versus deformation of methyl

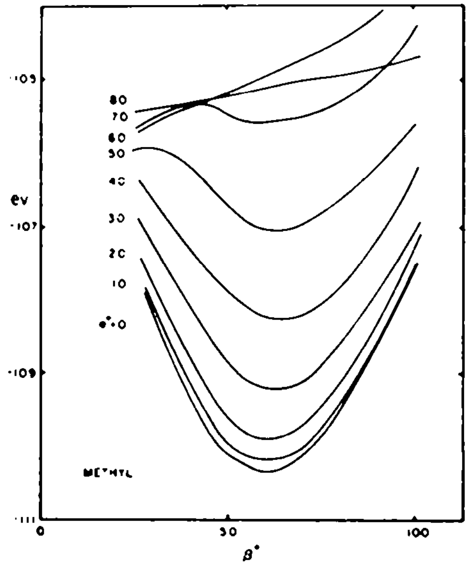


FIG. 12. Computed total energy in ev of methyl cation as a function of angle α as a function of angle β.

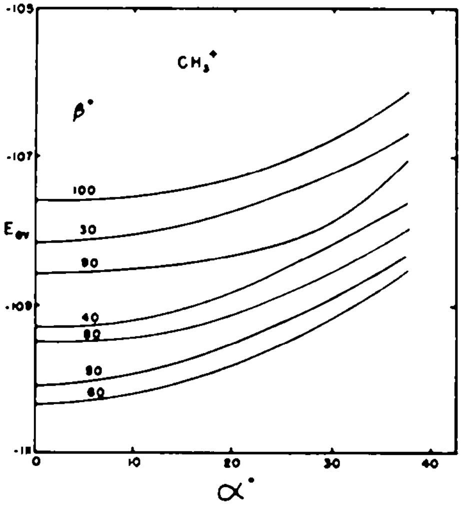


FIG. 13. Computed total energy in ev of methyl cation as a function of β as a function of angle α.

ion as a function of angle α. In Fig. 5 the corresponding plot of methanal has been shown. Again the results indicate that methanal is a good model for methyl provided that the deformation does not become too severe. In Fig. 7 borane is deformed and the energy computed as a function of angle β with variation in angle α. The borane deforms a little more easily than the methyl ion. The boron-hydrogen bond is longer than the carbon-hydrogen bond and the force constants of borane are lower than the corresponding constants in methyl cation.

In Figs. 14 and 15 the computed charge density on the hydrogen and carbon of methyl cation are illustrated. The charge density on the hydrogen in methanal is 0·09

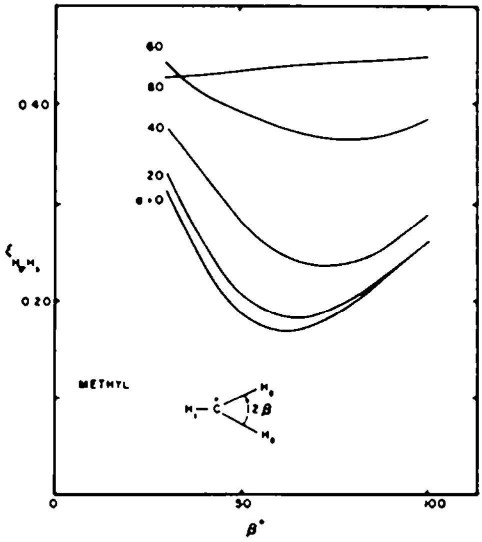


FIG. 14. Computed charge density on the two hydrogens (H_2 and H_3) of methyl cation as a function of β as a function of α.

and in methyl ion 0·17 in the ground state. The charge increases faster with deformation of the aldehyde than in the cation. The charge on the carbon in methanal and in methyl cation again demonstrates that the aldehyde is a stiffer system to deform. The boron in borane is much less positive (Fig. 8) than the carbon in methyl ion. Of course, the hydrogens of borane are more hydridic than the hydrogens of methyl cation. The data of Figs. 9 and 15 show this fact.

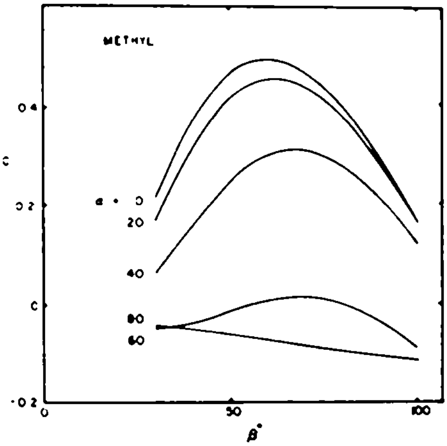
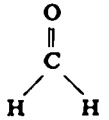
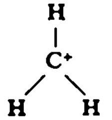


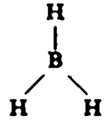
FIG. 15. Computed charge density on the carbon in methyl cation as a function of the deformation.

CONCLUSION

The main conclusion to be reached from these calculations is that the property of methyl cation can be estimated using model systems. However, methanal tends to be







much too stiff to undergo isosteric deformation[30] with methyl cation. The borane, on the other hand, represents a rather plastic system compared to the methyl cation even if the B—H distance is the same as the C—H distance in methyl cation. It is concluded that the chemical properties of the carbonium ion ought lie in between those of the aldehyde (or ketone) and the corresponding borane.

Bearing in mind the approximations of the EHT method, we conclude that at present it is about the best method to compute the properties of molecules of interest to the organic chemist. Since the method is so well calibrated by using experimental values of the ionization potentials for H_{ii} values and the choice of K to fit the properties of ethane, the EHT is a method to extrapolate experimental data into another system.[31]

[30] An isosteric deformation will be defined as a distortion which results in the same increase in energy of each system for the same amount of distortion, either by bond length or bond angle change.

[31] Following the lead by McGlynn (D. S. Carroll and S. P. McGlynn, paper in press), we have started to use $K = (2 - |S_{ij}|)$. It has been shown that the results are even closer to the HF-SCF values computed by more detailed methods.[illegible] It does not change the arguments presented in this paper.

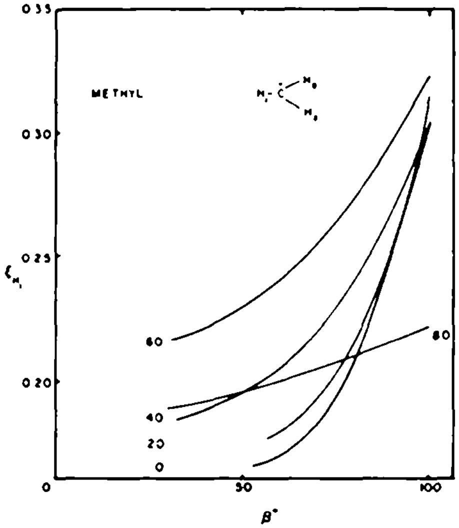


FIG. 16. Computed charge density on hydrogen H_1 of the methyl cation as a function of the deformation.

EXPERIMENTAL

Most of the x, y, z coordinates of each atom in the molecules were computed using a program written in FORTRAN II and using values from the Naval Trig Tables. The EHT program in FORTAN II was also run on an IBM 7094. The program was obtained from the QCPE at Indiana University.

Calculations were performed at 0·0005 Å intervals for bond lengths and at 10° intervals or less for the angles.

Acknowledgement—The authors wish to thank the Petroleum Research Fund, the National Institutes of Health and the Fulbright Grant (for A. O.) for assistance.