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MINDO-Forces Calculation of Molecular Geometries and Reaction Paths*

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A new method for the minimization of molecular energies is described, based on the Murtagh–Sargent procedure and the MINDO/2(3) semiempirical MO method. The derivative of energy is calculated according to the Pulay's Force method. This method was applied to the calculation of heats of formation and geometries of different organic molecules. The results agree well with the experimental and theoretical values known in the literature. The MINDO/2-Forces method was applied to the calculation of the internal rotation barrier of the benzyl carbonium ion. The calculated value 18.79 kcal/mol agrees well with the theoretical values known in the literature. The MINDO/3-Forces method was applied to the calculation of the internal rotation barrier of cyclopropyl carbinyl cation. The calculated rotation barrier, 21.28 kcal/mol is in agreement with the known theoretical values and with the expectation based on the NMR measurement of the barrier height in cyclopropyl dimethyl-carbinyl cation.

Key words: MINDO/2-Forces method

1. Introduction

Quantum mechanical calculations of molecular hypersurfaces included the application of both *ab initio* and semiempirical MO methods. *Ab initio* calculations, reported by different groups [1,2], proved to be rather time consuming and were mostly used within a "restricted minimization" frame. The advantage of semiempirical methods [3–7] falls in the limited computation time and the inclusion of the biggest part of the correlation energy in the parametrization process. Procedures for minimization are well known [8] and fall into two groups. In the first (e.g.

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Simplex [9]) only values of the function being minimized are needed whereas in the second (e.g. Murtagh–Sargent [10] or Davidon–Fletcher–Powell [11]), derivatives of the function with respect to the variables are required. The latter procedures need far fewer function evaluations. This advantage is quite important since each function evaluation requires a complete SCF-MO calculation.

McIver and Komornicki [12] developed a procedure for calculating energy minimized molecular geometries according to the Murtagh–Sargent method using the MINDO-MO method [13]. They evaluated the derivatives analytically by the direct differentiation of the MINDO expression for the total energy. Dewar *et al.* used the Simplex procedure with the MINDO method for the same purpose [9]. This was found to be slow. An alternative procedure was also developed by Dewar *et al.* using the Davidon–Fletcher–Powell [11] method with MINDO/3 and applying internal coordinates. In this procedure the derivatives were found by finite difference [16].

The aim of the present work is to study the possibility of energy minimization with respect to all geometrical parameters, using the Murtagh–Sargent [10] procedure and evaluating the derivative of the energy according to the Pulay's force method [14]. For this purpose a FORTRAN IV program (MINDO-Forces) was written and applied to the energy, geometry and reaction path calculations of various organic molecules.

2. Choice of the Molecular Orbital Method

The MINDO semiempirical MO method of Dewar *et al.* [6] was found suitable for our purposes. The method was constructed in such a way as to obtain molecular energy values that agree well with the experimental results. The MINDO calculation of the $\boldsymbol{H}^c$ and $\boldsymbol{F}$ matrix elements has been fully described by the authors [6, 15, 16]. In the 2nd version of the method (MINDO/2) the core–core repulsion energy between two atoms A and B was evaluated as follows:

$$CR_{\mathrm{AB}} = ER_{\mathrm{AB}} + (Z_{\mathrm{A}} Z_{\mathrm{B}} e^2 / r_{\mathrm{AB}} - ER_{\mathrm{AB}}) f(r_{\mathrm{AB}}) \tag{1}$$

where ER_{AB} is the sum of the interatomic electron repulsion energies of the two neutral atoms A and B.

The MINDO/2 method [15] was applied to molecules containing C, H, N and O atoms. The calculated ΔH_f values of the molecules agreed well with the experimental heats of formation. The method however overestimates the CH and NH bondlengths by 0.1 Å and the OH bondlength by 0.15 Å and underestimates the strain energies of small rings. Recently, a new version (MINDO/3) [16] was developed. The major difference between MINDO/3 and MINDO/2 [15] was in the way of evaluating the core–core repulsion energy (Eq. (1)). In the MINDO/2 method the $f(r_{\mathrm{AB}})$ term was expressed as:

$$f = e^{-(\alpha_{\mathrm{AB}} R_{\mathrm{AB}})} \tag{2}$$

for all types of bonds, whereas in the MINDO/3 method the same term was used for all types of bonds except the NH and OH bonds where it was expressed as:

$$f = \alpha_{\mathrm{HX}}\, e^{-R_{\mathrm{AB}}} \quad (\mathrm{X} = \mathrm{N} \text{ or } \mathrm{O}). \tag{3}$$

Other differences were in the way of evaluating the one center atomic integrals and in the exponents of the AOs. For further details refer to the original work of Dewar *et al.* [16].

3. Minimization of Energy as a Function of Geometry

3.1. The Pulay's Force method

The total energy of a molecule is given by the expectation value:

$$E = \langle \varphi | H | \varphi \rangle \tag{4}$$

where $|\varphi\rangle$ is a real normalized wave function. To obtain a Cartesian force (first derivative of energy over coordinate) the energy is differentiated analytically over the nuclear coordinate, i.e. the force (f_i) acting in the direction of a nuclear coordinate q_i is calculated as:

$$f_i = -\frac{dE}{dq_i} = -\frac{1}{2}\sum_i \sum_j \left(P'_{ij}(H_{ij} + F_{ij}) + P_{ij}(H'_{ij} + F'_{ij})\right) + \sum_{\mathrm{A}} \sum_{\mathrm{B}} C_{\mathrm{A}} C_{\mathrm{B}} CR'_{\mathrm{AB}}. \tag{5}$$

The derivatives in the above equation (5) are expressed as:

$$P'_{ij} = -P_{ij} S'_{ij} P_{ij} = -P^2_{ij} S'_{ij}. \tag{6}$$

$$H^{\mathrm{A,A}'}_{ij} = -\sum_{\mathrm{B}} C_{\mathrm{B}} \gamma'_{\mathrm{AB}}. \tag{7}$$

$$H^{\mathrm{A,B}'}_{ij} = H^{c'}_{ij} = S'_{ij}(I_i + I_j)\beta_{ij}. \tag{8}$$

$$F^{\mathrm{A,A}'}_{ij} = P'_{ij}\left(\tfrac{3}{2}(ij, ij) - \tfrac{1}{2}(ii, jj)\right). \tag{9}$$

$$\begin{aligned} F^{\mathrm{A,B}'} &= H^{c'}_{ij} - \tfrac{1}{2}(P'_{ij}\gamma_{\mathrm{AB}} + P_{ij}\gamma'_{\mathrm{AB}}) \\ &= S'_{ij}(I_i + I_j)\beta_{ij} - \tfrac{1}{2}(P'_{ij}\gamma_{\mathrm{AB}} + P_{ij}\gamma'_{\mathrm{AB}}). \end{aligned} \tag{10}$$

The derivative of the core–core repulsion for the OH and NH bonds in MINDO/3 is expressed as:

$$CR'_{\mathrm{AB}} = -\gamma^3_{\mathrm{AB}} - \alpha\, e^{-R}\left(14.399/R^3 - \gamma^3_{\mathrm{AB}} + \frac{1}{R}(14.399/R - \gamma_{\mathrm{AB}})\right). \tag{11}$$

The derivative of the core–core repulsion function for all other bonds in MINDO/2(3) is expressed as:

$$CR'_{\mathrm{AB}} = -\gamma^3_{\mathrm{AB}} - e^{-\alpha R}\left(14.399/R - \gamma^3_{\mathrm{AB}} + \frac{\alpha}{R}(14.399/R - \gamma_{\mathrm{AB}})\right). \tag{12}$$

The force (f_i) is calculated using Cartesian coordinate of the atom.

This way of calculating the forces differs from that of McIver and Komornicki [12] in that the derivative of the bond order is considered by the calculation (Eqs. (5) and

(6)). McIver and Komornicki however assumed P_{ij} to be constant when evaluating the derivative of E over the coordinate q according to the following equation:

$$\frac{dE}{dq}=\frac{1}{2}\sum_i\sum_j P_{ij}(H'_{ij}+F'_{ij})+\sum\sum_{A<B} C_A C_B R'_{AB}. \tag{13}$$

3.2. *The Minimization Procedure*

The force f (a.u.) obtained from Eq. (5) is substituted in the following recursion equation:

$$Q^{n+1}=Q^n-\alpha_n A^n F^n \tag{14}$$

to generate improved coordinates from the old coordinates Q^n using the Murtagh and Sargent method [10] in a similar manner to that of Ref. [12]. α_n is an arbitrary constant. For rapid geometry optimization α_n is chosen to be 1.6. For slow optimization or near the equilibrium, α_n is chosen to be unity or half, depending on how slow the convergence is needed. The matrix A^n is initially set to be equal to the identity matrix ($AO=1$) and then calculated by the recursion:

$$A^n=A^{n-1}+Z^n Z^{n\dagger}/C^n \tag{15}$$

where

$$Z^n=-A^{n-1}(F^n-(1-\alpha_{n-1})F^{n-1}) \tag{16}$$

and

$$C^n=(F^n-F^{n-1})^\dagger Z^n. \tag{17}$$

The Cartesian forces (a.u.) form a $3N$ dimensional column vector F. They are calculated from the SCF energies after each generation of an improved set of Cartesian coordinates.

The minimum energy is obtained if the largest (in magnitude) component of F is less than (10^{-3}) atomic units. In a few cases the limit $2\cdot10^{-2}$ a.u. is accepted due to convergency problems. In these cases however the resulting energy values are not expected to deviate largely from those of the actual minima. In cases where the forces are found to fluctuate (increase and decrease) during the iterations due to an indefinite matrix A^n, this matrix is reset to identity.

The present method combines for the first time the molecular forces calculation, according to Pulay, with the Murtagh–Sargent minimization technique. It is believed to require less iterative calculation than the other methods where either the energy differences for each parameter variation had to be considered [18] or the Hellman–Feynman forces are used [12].

4. Results and Discussion

4.1. *Application of the* MINDO/2-*Forces Method*

Equilibrium energies and geometries of various organic molecules were calculated with the above mentioned method. Table 1 shows the calculated heats of formation of nine molecules, using the C, H, O parameters of MINDO/2 [16]. Table 2 shows the calculated geometries of the molecules. Both calculated energies and geometries agree well with the experimental values and those of Dewar *et al.* [15]. In most cases slight improvements in the calculated heats of formation are observed. In all the reported calculations complete geometric optimization was considered, except in the case of NH_3 where the HNH bond angle was maintained constant (110°).

Tables 3 and 4 show the calculated heats of formation and geometries of ten molecules respectively, using the C, H, N, O parameters of MINDO/2. The calculated results are generally in agreement with the experimental and calculated results of Dewar *et al.* [15], although these authors used pointwise and restricted minimization to calculate their values. This difference in the minimization procedure is obviously the reason for the two differently obtained ΔH_f values of H_2O (Table 1). The bond angle was kept constant (109.4) by Dewar *et al.* and varied to yield 116° by us during the minimization process. Also, the ΔH_f value of NH_3 (−12.74 kcal/mol) is improved due to similar reasons. The comparison of the

Table 1. MINDO/2-Forces calculated heats of formation (ΔH_f, kcal/mol) using C, H, O parameters

		ΔH_f			
Compd.	I[h]	Calcd.	Obsd.	Dewar *et al.*	F[i]
H_2O	5	−59.31	−57.80[a]	−54.13	10^{-3}
C_2H_2	10	53.55	54.30[c]	53.50[b]	10^{-3}
CH_4	4	−11.87	−17.90[c]	−11.90[b]	10^{-3}
C_2H_4	20	13.71	12.40[c]	16.20[b] (C–H)	10^{-3}
				16.70[b] (C–C)	
C_3O_2	2	−41.36	−23.38[d]	−41.89	10^{-3}
			or −47.40[e]		
HCOOH	2	−90.84[k]	−90.69[g]	−91.10	10^{-2}
HCHO	4	−19.48[k]	−27.70[a]	−19.62	10^{-2}
C_2H_6 (stag.)	2	−22.09	−20.20[c]	−21.70[b]	$4 \cdot 10^{3}$
C_2H_6 (eclip.)	3	−21.30	−17.30[f]	−20.20[b]	$4 \cdot 10^{-3}$

[a] JANAF Thermodynamic Tables, D. R. Stull, Ed., The Dow Chemical Co., Midland, Mich., 1965.

[b] Calculated using the C, H parameters, Ref. [13].

[c] Bartell, L. S., Higginbotham, H. K.: J. Chem. Phys. **42**, 851 (1965).

[d] Keybett, B. D., Johnson, G. K., Barker, C. K., Margrave, J. L.: J. Phys. Chem. **69**, 3603 (1965).

[e] Glemser, O.: Handbook of preparative inorganic chemistry, Vol. 1, G. Brauer, Ed. New York: Academic Press 1963.

[f] Ride, D. L.: J. Chem. Phys. **29**, 1426 (1958).

[g] Green, L. H. S.: Quart. Rev. (London) **15**, 125 (1961).

[h] Number of geometric iterations.

[i] Maximum forces (a.u.).

[j] See Ref. [15].

[k] Due to the succeeding divergence of the geometry iteration, the calculations were stopped at this value of $F(10^{-2})$. The calculated energy values are thus slightly larger than the actual minimal values.

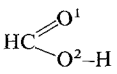
calculated heats of formation and maximum forces in Tables 1 and 3 indicates that the C, H, N, O parameter set is more suitable for MINDO/2 calculations than the C, H, O set.

Since the present calculated results agree well with the reported results of Dewar *et al.* and the experimental results, there was reason for confidence in using this energy minimization procedure to calculate molecular structures and reaction paths. Consequently it was applied to the calculation of the internal rotation barrier of the relatively large benzyl carbonium ion. The details of this calculation are discussed in the following paragraphs.

4.2. The Internal Rotation Barrier of the Benzyl Carbonium Ion

No experimental value for the rotation barrier of the benzyl carbonium ion has been reported, although it is important for the discussion of the reactivity of this ion. Using the MINDO/2 method Shanshal calculated a rotation barrier of 16.29 kcal/mol for this ion [17]. According to his calculation the heat of formation of the planar ground state was 219.56 kcal/mol with a Ph–CH_2^+ distance of 1.390 Å and that of the perpendicular conformation was 235.85 kcal/mol (with a Ph–CH_2^+ bond

Table 2. Calculated molecular geometries using the MINDO/2-Forces method with C, H, O parameters

Compd.	Ref.	Geometries, Calcd.[a] (Obsd.) (Dewar *et al.*) [15]
H_2O	[b]	OH, 0.969 (0.957) ((0.967)); HOH, 116.8 (104.5)
C_2H_2	[d]	CH, 1.068 (1.058) ((1.070)); CC, 1.197 (1.204) ((1.200))
CH_4	[d]	CH, 1.095 (1.093) ((1.096)); HCH, 109.6 (109.5)
C_2H_4	[d]	CH, 1.099 (1.086) ((1.101)); CC, 1.319 (1.337) ((1.335)); HCH, 110.8; HCC, 124.5 (121.6)
C_3O_2	[f]	CO, 1.179 (1.168) ((1.187)); CC, 1.281 (1.294) ((1.278))
	[d]	CH, 1.031; CO^1, 1.241 (1.245) ((1.241); CO^2, 1.340 (1.312) ((1.345)); HCO^1, 120.0; OH, 0.980 (0.960) ((0.981)); HO^2C, 109.4 (107.8); OCO, 120
HCHO	[c]	CH, 1.122 (1.120) ((1.125)); CO, 1.217 (1.210) ((1.224)); HCO, 121.2 (121.0); HCH, 118.0
C_2H_6 (stag.)	[d]	CH, 1.106 (1.093) ((1.109)); CC, 1.520 (1.534) ((1.524)); HCC, 109.4 (111.1)
C_2H_6 (eclip.)		CH, 1.115 ((1.103)); CC, 1.491 ((1.524)); HCC, 110.1

[a] Calculated values for CH bond reduced by 0.1 Å, for OH bonds by 0.15 Å; bond lengths in Å and bond angles in deg.

[b] Benedict, W. S., Gailer, N., Plyler, E. K.: J. Chem. Phys. **24**, 1139 (1956).

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

[d] Sutton, L. E.: Tables of inter-atomic distances. Chem. Soc. Spec. Publ. No. 11 (1958), No. 18 (1965).

[e] Bartell, L. S., Roth, E. A., Hollowell, C. D., Kuchitsu, K., Young Jr., J. E.: J. Chem. Phys. **42**, 2683 (1965).

[f] Almenningen, A., Arnesen, S. P., Bastiansen, O., Seip, H. M., Seip, R.: J. Chem. Phys. Letters **1**, 569 (1968).

Table 3. MINDO/2-Forces calculated heats of formation (kcal/mol) using C, H, N, O parameters

Compd.	I^j	ΔH_f Calcd.	Obsd.	Dewar *et al.*[i]	F^h
CH_4	2	−16.12	−17.90[a]	−16.20	$<10^{-3}$
NO_3^-	2	−96.95	-89 ± 5[b]	−95.80	10^{-3}
NH_3	3	−12.76[j]	−11.00[c]	−11.20	$<10^{-3}$
HCOOH	2	−91.21	−90.50[d]	−89.90	10^{-3}
HCHO	2	−21.99	−27.70[d,c]	−22.40	10^{-2}
C_2H_6 (eclip.)	5	−20.99	−17.30[f]	−20.40	$2\cdot10^{-3}$
C_2H_6 (stag.)	2	−22.80	−20.20[a]	−22.80	$2\cdot10^{-3}$
C_2H_2	2	57.71	54.30[a]	57.70	10^{-3}
CO_2	2	−92.87	−94,00[c]	−92.90	$<10^{-3}$
NH_4^+	21	156.21	150.00[e]	155.90	$<10^{-3}$

[a] See Ref. [c] of Table 1.

[b] Cordes, H. F., Fetter, W. R.: J. Phys. Chem. **62**, 1340 (1958).

[c] See Ref. [a] of Table 1.

[d] Green, L. H. S.: Quart. Rev. **15**, 125 (1961).

[e] Selected values of chemical thermodynamic properties. National Bureau of Standards, Circular 500, U.S. Government Printing Office, Washington, D.C. 1952.

[f] See Ref. [f] of Table 1.

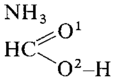
[g] Number of geometric iterations.

[h] Maximum forces (a.u.).

[i] See Ref. [15].

[j] The HNH bond angle was maintained constant during the calculation, (∢HNH = 110°).

Table 4. Calculated molecular geometries using the MINDO/2-Forces method with C, H, N, O parameters

Compd.	Ref.	Geometries, Calcd.[a] (Obsd.) (Dewar *et al.*)
CH_4	c	CH, 1.099 (1.094) ((1.100)); HCH, 109.5
NO_3^-	b	NO, 1.240 (1.241) ((1.239)); ONO, 120.1
NH_3	c	NH, 1.016 (0.912) ((0.918)); HNH, 110.5
 $HC(=O^1)-O^2-H$	c	CH, 1.114; CO^1, 1.172 (1.245) ((1.235)); CO^2, 1.311 (1.12) ((1.338)); OH, 0.959; HO^{2}C, 113.4 (107.8); HCO^1, 118.6; HCO^2, 115.1
HCHO	c	CH, 1.119 (1.121) ((1.120)); CO, 1.210 (1.210) ((1.211)); HCH, 119.0; HCO, 120.5 (121.0)
C_2H_6 (stag.)	c	CH, 1.115 (1.093) ((1.116)); CC, 1.468 (1.534) ((1.506)); HCC, 110.7 (111.1)
C_2H_6 (eclip.)		CH, 1.111 ((1.114)); CC, 1.488 ((1.517))
C_2H_2	c	CC, 1.187 (1.204) ((1.186)); CH, 1.066 (1.058) ((1.061))
CO_2	c	CO, 1.175 (1.162) ((1.179))
NH_4^+	c	NH, 1.034 (1.032) ((1.036)); HNH, 110.3

[a] Calculated values for CH and NH bonds reduced by 0.1 Å for OH bonds by 0.15 Å; bondlengths in Å, and bond angles in degs.

[b] Jonathan, N. B. H.: J. Mol. Spectry. **4**, 75 (1960).

[c] L. E. Sutton, Ed.: Table of interatomic distances, Special Publications No. 11 and 18. London: The Chemical Society, 1958 and 1965.

length of 1.410 Å). However the energy was not minimized with respect to all geometric parameters. Recently, using MINDO/3, the internal rotation barrier of 22.3 kcal/mol was calculated by Dewar *et al.* [18]. In their calculation the energy was minimized with respect to all geometric parameters using the Davidon–Fletcher–Powell method [11].

Applying the minimization program (MINDO/2-Forces) discussed in the recent paragraphs and the C, H parameter values [13], we calculated the heats of formation of this ion with different rotation angles (ϕ) of the CH_2^+ group out of the molecular plane. In these calculations the energy is minimized with respect to all geometric parameters. The numbering of the atoms is as in Fig. 1.

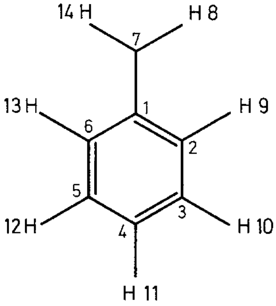


Fig. 1. Numbering of the atoms in the benzyl carbonium ion

The calculated heat of formation for the most stable planar conformation of the ion is 218.40 kcal/mol. It agrees better with the experimental value ($\Delta H_{f,\text{exp.}} = 216$ kcal/mol) than the values reported by Shanshal [17] and Dewar *et al.* (220.4 kcal/mol) [18]. The reaction path for the rotation of the CH_2^+ group is shown in Fig. 2. It shows that the rotation of the methylene group goes through a perpendicular transition state ($\phi = 90°$) and requires an activation energy of 18.79 kcal/mol. This value is intermediate to that reported by Shanshal [17] (16.29 kcal/mol, MINDO/2) and that of Dewar *et al.* (22.3 kcal/mol, MINDO/3) [18].

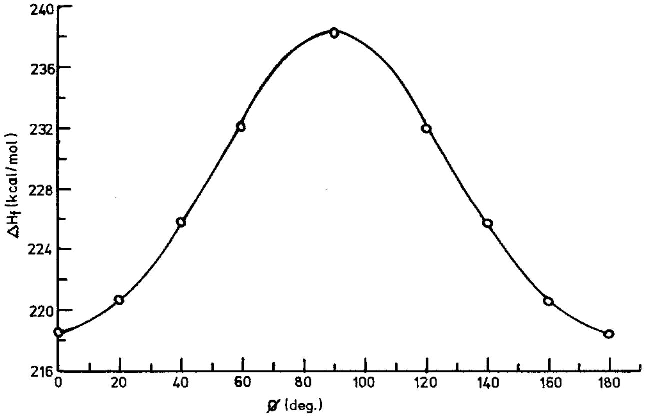


Fig. 2. Calculated heat of formation (ΔH_f) of benzyl carbonium ion as a function of the dihedral angle (ϕ)

The calculated geometry of the planar ground state exhibits a quinone type bond alternation. It appears that the hexagonal symmetry of the six-membered ring is removed by the perturbation of the adjacent CH_2^+ group. The resulting bond alternation is similar to that reported for the benzyl radical on the basis of π-SCF-MO calculations [20]. The bonds C^1–C^7 (1.367 Å) and C^2–C^3 (1.382 Å) may be classified as essential double bonds; the C^1–C^2 (1.444 Å) and C^3–C^4 (1.410 Å) as essential single bonds. Compared with the C–C bond distance of benzene (1.397 Å), the C^1–C^2 bond shows a greater elongation than the C^3–C^4 bond, a result which agrees with the fact that the former bond undergoes a bigger perturbation by the CH_2^+ group than the latter. The rotation of the CH_2^+ group out of the molecular plane causes the following changes in the geometry of the ion:

a) an increase in the C^1–C^7 and C^2–C^3 bond lengths,
b) a decrease in the C^7–H^8, C^1–C^2 and C^3–C^4 bond lengths,
c) an increase in the H^{14}–C^7–H^8 bond angle of the methylene group (115.7° $\rightarrow$ 117.1°).

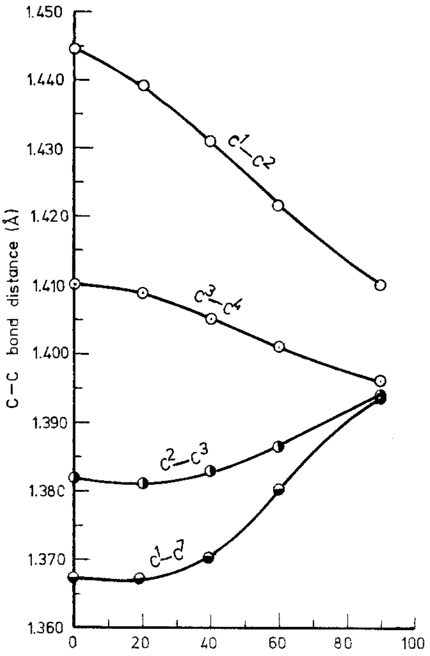
The changes in the other bond distances of the ion are negligible. Figs. 3 and 4 show the changes in the C–C bond distances and the changes in the bond angles of the ion respectively, as a function of the dihedral angle (ϕ).

In the rotation transition state ($\phi = 90°$) the C^1–C^7 bond (1.393 Å) shows a slight increase in its length over its value in the planar ground state (1.367 Å). The C–C bonds in the six-membered ring are almost equivalent in length except for the two bonds adjacent to the CH_2^+ group. This may be explained as a result of a strong hyperconjugative interaction of the CH_2^+ group with the adjacent C–C bonds. This situation is similar to that of the rotation transition state of ethylene [13].

The calculated electrodensities of the atoms in the ion, with different ϕ values are plotted in Fig. 5. The densities in the planar ground state ($\phi = 0°$) correspond to the following distribution of the positive charge; $C^7 > C_{para} > C_{ortho} > C_{meta} > C^1$. On rotating the CH_2^+ group towards the perpendicular transition state, the electron density on the meta position decreases whereas the densities on the ortho and para positions increase. In the transition state both meta and para positions show similar electron densities which are greater in magnitude than the density on the ortho position. This is also due to the hyperconjugation in the transition state.

4.3. Application of the MINDO/3-*Forces Method*

We have carried out calculations for different organic molecules using the minimization program (MINDO-Forces) with MINDO/3 [16] as a semi-empirical method. Tables 5 and 6 show the calculated heats of formation and molecular geometries respectively. The results agree well with the experimental and the calculated results of Dewar *et al.* [18]. The agreement confirms the adequacy of the minimization procedure and suggests its utilization for the calculation of the structures and reaction paths of other molecular systems. We have applied it for the calculation of the internal rotation barrier and the geometry change during this rotation in cyclopropyl carbinyl carbonium ion.



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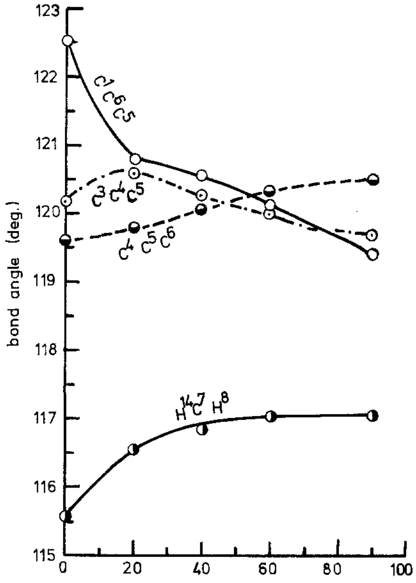

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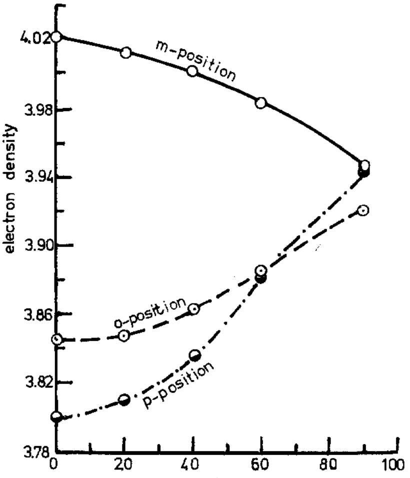

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Fig. 3. Changes in the C–C bond distances as functions of the dihedral angle (ϕ) for $PhCH_2^+$

Fig. 4. Changes in the bond angles as functions of the dihedral angle (ϕ) for $PhCH_2^+$

Fig. 5. Plot of the electron densities vs. ϕ for $PhCH_2^+$

4.4. The Rotation Barrier of the Cyclopropyl Carbinyl Cation

The structure of the cyclopropyl carbinyl cation and its methyl-derivatives was subject to a number of experimental [21–29] and theoretical [30–35] studies for many years. Two conformations are suggested for the cation (Fig. 6), bisected and planar, the former being more stable according to the available experimental and theoretical studies.

Table 5. MINDO/3-Forces calculated heats of formation (ΔH_f)

	ΔH_f (kcal/mol)				
Compd.	Calcd.	Obsd.[a]	Dewar *et al.*[h]	*I*[i]	*F*[j]
H_2	0.16	0.00	0.10	4	$<10^{-3}$
$HC\equiv CH$	57.93	54.30	57.80	3	$<10^{-3}$
$HC\equiv C-C\equiv CH$	91.59	113.00	91.10	2	$7\cdot10^{-3}$
C_2H_4	19.54	12.40	19.20	2	$4\cdot10^{-3}$
C_2H_6 (eclip.)	−18.35	−17.30[g]		3	$<10^{-3}$
CO_2	−95.25	−94.00[b]	−95.70[e]	2	$<10^{-3}$
C_2H_6 (stag.)	−19.29	−20.20	−19.80	3	$<10^{-3}$
c–C_3H_6	9.53	12.70	8.70	4	$<10^{-3}$
$^1CH_2$	100.32	101.00[d]	100.20[f]	6	$<10^{-3}$
CH_4	−6.13	−17.90	−6.30	6	$<10^{-3}$
CH_3^+	260.41	260.00[c]	260.30	2	$3\cdot10^{-3}$
CH_3	43.54	33.20[c]	42.30	2	$4\cdot10^{-3}$

[a] Unless otherwise indicated the observed values are taken from Cox, J. D., Pilcher, G.: Thermochemistry of organic and organo-metallic compounds. New York: Academic Press 1970.

[b] JANAF thermochemical tables, D. R. Stull, Ed. Midland, Mich.: The Dow Chemical Co. 1965.

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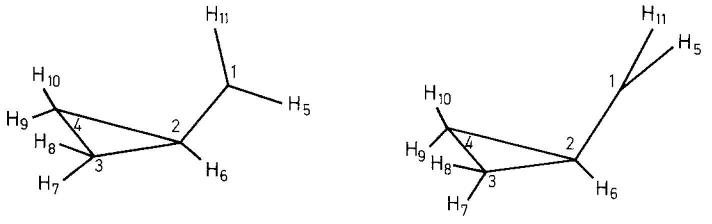
[h] See Ref. [18].

[i] Number of geometric iterations.

[j] Maximum forces (a.u.).



bisected

planar

Fig. 6. Possible structures of the cyclopropyl carbinyl cation

We have calculated the rotation barrier of the methylene group in the cation, varying all its geometric parameters and using the MINDO/3-Forces method. Values of its heat of formation are obtained as a function of the dihedral angle (ϕ) described by the CH_2^+ plane and a plane perpendicular to the three membered ring. Fig. 7 shows the calculated path of the rotation.

Table 6. MINDO/3-Forces calculated molecular geometries

Compd.	Ref.	Calcd. (Obsd.) ((Dewar *et al.*)) geometries[a]
H_2	[b]	H–H, 0.746 (0.742)
HC≡CH	[c]	C–C, 1.196 (1.205) ((1.191)); C–H, 1.071 (1.059) ((1.076))
H–C≡C^1–C^2≡C^3–H	[d]	C^1C^2, 1.396 (1.376) ((1.397)); C^2C^3, 1.210 (1.217) ((1.206)); C–H, 1.073 (1.064) ((1.077))
$H_2C{=}CH_2$	[e]	C–C, 1.316 (1.336) ((1.308)); C–H, 1.096 (1.103) ((1.098)); CCH, 124.6 (121.6) ((124.8)); HCH, 110.7
C_2H_6 (eclip.)		CC, 1.478; CH, 1.11; CCH, 112.9
C_2H_6 (stag.)	[f]	CC, 1.477 (1.532) ((1.486)); CH, 1.110 (1.107) ((1.108)); CCH, 112.1 (111.1) ((112.8))
O=C=O	[g]	CO, 1.178 (1.162) ((1.180))
c–C_3H_6	[h]	CC, 1.496 (1.510) ((1.504)); CH, 1.105 (1.089) ((1.103)); HCH, 108.8 (115.1) ((108.7))
CH_4	[i]	CH, 1.101 (1.106) ((1.102)); HCH, 109.6 (109.5)
$^1CH_2$	[j]	CH, 1.120 (1.110) ((1.121)); HCH, 102.0 (102.4) ((102.0))
CH_3^+		CH, 1.102; HCH, 119.99
CH_3		CH, 1.097; HCH, 119.99

[a] Bond lengths in Å, and bond angles in deg.

[b] Baird, N. C., Dewar, M. J. S.: J. Chem. Phys. **50**, 1262 (1969), see Ref. therein.

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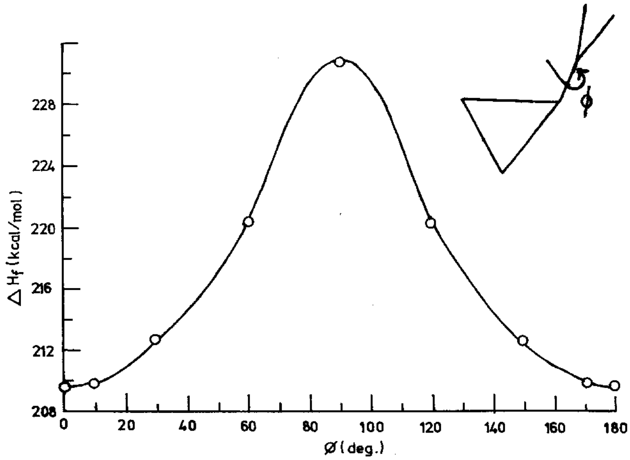

Fig. 7. MINDO/3-Forces calculated heats of formation (ΔH_f) of cyclopropyl carbinyl cation with different dihedral angles (ϕ)

The calculated rotation barrier of 21.28 kcal/mol is greater than the recent theoretical (10.0 kcal/mol) [18] and the experimental (13.7 kcal/mol) [24] values for the dimethyl, cyclopropyl carbinyl cation. This comparatively high rotation barrier of the nonmethylated cation may be attributed to the absence of hyperconjugative difference between the bisected ground state and the planar transition state. The calculated rotation barrier is to be compared with other theoretical values, 25 kcal/mol [30] (CNDO), 9 kcal/mol (EHT) [31], 19 kcal/mol (AS-MO-SCF) [32] and 9.5 kcal/mol (MINDO/2) [33] for the nonmethylated cation.

The rotation of the CH_2^+ group from the stable bisected conformation causes an increase in C^1–C^2 and C^3–C^4 bond distances, and an increase and then decrease in the lengths of the other two C–C bonds of the ring (Fig. 8). As expected both planar and bisected conformations show C_s symmetry relative to a plane which includes the C^1–C^2 bond and bisects the C^3–C^4 bond. This symmetry is removed on departing from the two conformations.

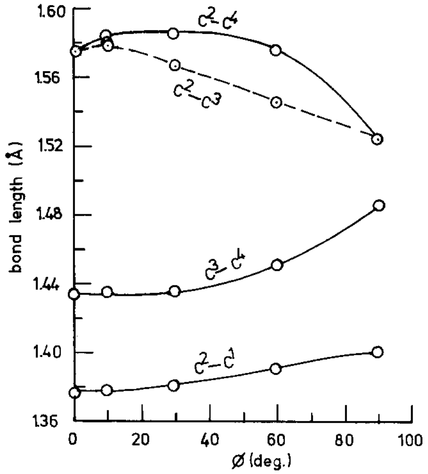

Fig. 8. Changes in the C–C bond lengths with different dihedral angles (ϕ) in the cyclopropylcarbinyl cation

The $H^5C^1H^{11}$ bond angle decreases, then fluctuates in value and increases finally (110.8–112.9°) as a result of this rotation (Fig. 9). Angle $C^1C^2H^6$ decreases (110.4–107.3°) continuously, and the internal angles of the cyclopropyl ring vary during this rotation (Fig. 9). Angle $C^2C^4C^3$ decreases to a minimum (62.9–60.8°) while $C^4C^2C^3$ increases (54.2–58.4°) on going from the bissected to the planar conformation. In the planar conformation, the geometry of the ring approaches almost that of the cyclopropane molecule (C–C$\approx$1.5 Å, $\sphericalangle \approx 60^\circ$). The slight difference in geometry indicates a weaker, but nonnegligible interaction with the Walsh orbitals of the ring than that of the bisected conformation. It represents a second-order perturbative interaction of the methylene group with the internal Walsh MOs as was shown by one of us [36].

No significant change in the C–H bond distances of the cation can be concluded from the calculations. The distances in the bisected ground state correspond to the following values: 1.102 Å (C^1–H^5), 1.104 Å (C^1–H^{11}), 1.111 Å (C^2–H^6), 1.102 Å (C^3–H^7), 1.105 Å (C^3–H^8), 1.102 Å (C^4–H^9), 1.105 Å (C^4–H^{10}).

The calculated electron densities of the cyclopropylcarbinyl cation with different dihedral angles (ϕ) are listed in Table 7. The electron density on C^2(C^1) increases (decreases) on going from the bisected to the planar conformation.

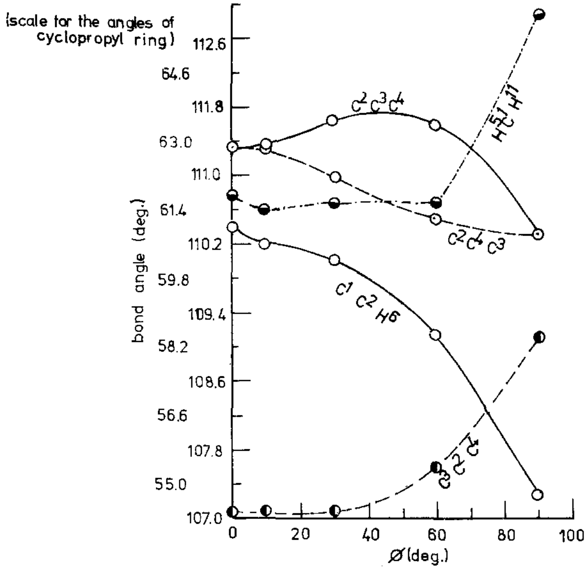

Fig. 9. Changes in the bond angles with different dihedral angles (ϕ) in the cyclopropyl carbinyl cation

Table 7. MINDO/3-Forces calculated electron densities of the cyclopropyl carbinyl cation as functions of the dihedral angle ϕ (deg.)

Atom No.	Electron Density				
	$\phi=0°$	$\phi=10°$	$\phi=30°$	$\phi=60°$	$\phi=90°$
1	3.702	3.701	3.677	3.604	3.456
2	4.049	4.053	4.066	4.105	4.167
3	3.861	3.871	3.899	3.928	3.912
4	3.861	3.844	3.823	3.819	3.912
5	0.924	0.924	0.928	0.928	0.956
6	0.924	0.923	0.915	0.889	0.836
7	0.920	0.919	0.918	0.922	0.938
8	0.945	0.943	0.944	0.950	0.964
9	0.920	0.922	0.926	0.934	0.938
10	0.945	0.945	0.949	0.957	0.964
11	0.954	0.954	0.954	0.954	0.956

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