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The Rotation Barrier of the Cyclopropylcarbinylcation

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The rotation barrier of the cyclopropylcarbinyl-cation has been calculated by the MINDO/2 method.

The structure of the cyclopropylcarbinylcation (1) and its methylderivatives has been the subject of various experimental and theoretical studies [1–4]. With the bisected form being the more stable conformation of the cation, a rotation about the bond between the single- and the ring-carbonatom is expected. A kinetic NMR measurement [4] gave a value of 13.7 kcal/mole for the rotation barrier. We here report a preliminary SCF-MO study for the calculation of rotation barriers in carboniumions. Two sets of calculations are reported. Firstly those carried out with the MINDO/1 SCF-MO-method are considered [5]. Previous efforts failed to calculate rotations barriers of acidamides quantitatively with this procedure [6], obviously because of underestimating the two-center repulsion-energy between the two neighboured nonbonded atomic orbitals, due to the neglect of differential overlap adopted by this procedure. In the cyclopropylcarbinylcation (1) no such repulsion is found, and the change in energy due to rotation should therefore be treated sufficiently.

Secondly, calculations carried out using the same MINDO/1 method with different core-core-repulsion- and one-electron core-resonance-function are reported. The new function used for the core-core repulsion is the following Ohno-Klopman expression [5a]:

$$E_{\text{core-core}} = E_{\text{rep. A,B}} + [Z_{\text{A}} Z_{\text{B}} e^2/R_{\text{A,B}} - E_{\text{rep. A,B}}]\, e^{-\alpha R_{\text{A,B}}} . \tag{1}$$

$E_{\text{rep. A,B}}$ = total electronrepulsion between the two atoms A and B.
$R_{\text{A,B}}$ = distance between atoms A and B.
α = a correction parameter.

The one-electron core-resonance expression was $\beta_{i,j}$

$$\beta_{i,j} = \beta S_{i,j} (I_i + I_j). \tag{2}$$

β = parameter.
$S_{i,j}$ = overlapp between atomic orbitals i and j.
I_i, I_j = valance-state ionizationpotentials of the atoms containing i and j.

The values of the α and β parameters are those previously used by Dewar *et al.* [7] (Table 1).

The second procedure being termed the MINDO/2 method was found to be suitable for the calculation of the heats of formation and forceconstants of electron deficient molecules [8] and the discussion of their reactions [9].

Table 1. *Applied values for the parameters used by* (MINDO/2) *calculations*

	C–C bond	C–H bond	H–H bond
α	1.6343	1.1843	0.6653
β	0.36862	0.34104	0.48328

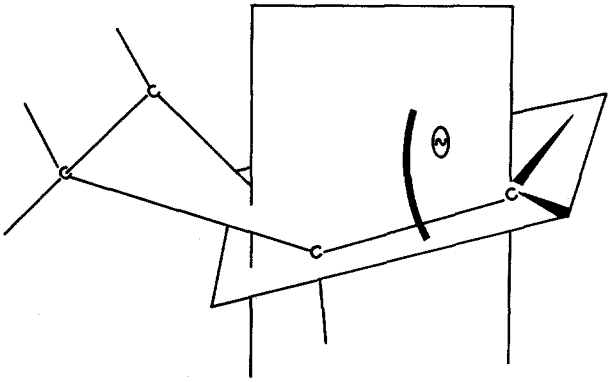

Fig. 1. The rotation of the CH_2^+ plane in the cyclopropylcarbinyl cation (1)

The first set of calculations was carried out using the MINDO/1 standard geometry for the cyclopropylring ($C-C = 1.514$ Å, $C-H = 1.093$ Å). The bondlength between the single carbonatom and the nearest ringcarbonatom was taken to be 1.425 Å. This is the value to be obtained by the addition of the covalent radii of $C_{sp}2$ (1.337/2 Å) and the $C_{cyclopropyl}$ (1.514/2 Å).

The energy (heat of formation) of the carboniumion (1) was calculated as a function of the dihedral angle between the CH_2^+ plane and a plane perpendicular to the threemembered ring (angle Θ) Fig. 1.

The bisected form is predicted to be the most stable conformation of the molecule and the rotationbarrier, 9.5 kcal/mole, is in good agreement with the measured barrier for dimethyl-cyclo-propyl-carbinyl-cation (2) [4] (13.7 kcal/mole).

A continious increase in the charge of the single carbonatom is noticed by the transition from the stable bisected form to the nonstable planar conformation. Obviously the conjugation between the single carbon-atom's free orbital and the bent σ-orbitals of the ring is greater in the first case.

Table 2 gives the change in the electrondensity on the single carbonatom as a function of the dihedral angle Θ.

The second set of calculations was started by minimizing the bonddistance between the single carbonatom and the nearest ring-carbonatom in the plane form. The equilibrium distance was determined through graphical interpolation. The so found bond distance (1.426 Å) was in good agreement with the previously used value by the MINDO/1 calculation. The applied $C-C$ and $C-H$ bond-

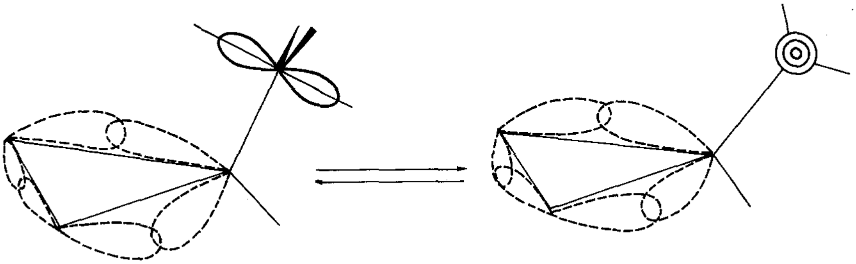

Fig. 2. Position of the nonbonded atomorbital of the single carbonatom relative to the σ bentorbitals of the ring in both bisected and planar conformations

Table 2. *Calculated electrondensities of the single carbonatom in (1), and their corresponding dihedral angles*

Dihedral angle Θ	Electrondensity	
	MINDO/1	MINDO/2
90 (plane)	3.540	3.594
100	3.546	3.603
110	3.561	3.624
120	3.580	3.650
130	3.599	3.674
140	3.616	3.695
150	3.629	3.710
160	3.639	3.720
170	3.644	3.726
180 (bisected)	3.646	3.728

lengths in the cyclopropylring were 1.514 Å and 1.203 Å respectively [7]. The dihedral angle was then varied toward a bisected conformation (Fig. 1). According to these calculations the bisected form was the most stable conformation too. The energy required for the complete rotation is 16.0 kcal/mole. The change of the charge density on the single carbon-atom is of the same pattern as in the first calculations (Table 2).

The calculated force constant for the stretching vibration of the bond between the single carbonatom and the nearest ringcarbonatom was 8.28×10^4 dyn/cm.

Compared with the results for the rotation-barrier in cyclopropylcarbinylcation (1) obtained through other MO-procedures both MINDO/1 and MINDO/2 results show the better agreement with the experimental value. Thus previously obtained values are 25 kcal/mole (CNDO) [11], 9 kcal/mole (EHT) [12], 19 kcal/mole (AS-MO-SCF) [13] and 22 kcal/mole (NDDO) [14].

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