Internal Rotation Barriers of Carbonium Ions

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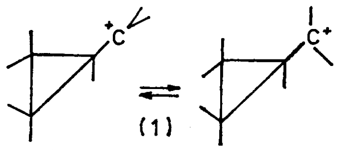
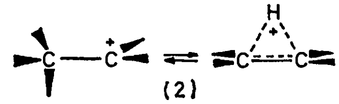
The rotation barriers of allyl-, benzyl-, ethyl-, n-propyl-, and isobutyl-ium ions have been calculated by use of the MINDO/2 SCF–MO method. Barrier heights of 14—17 kcal mol^{-1} for the conjugated ions were obtained. For the ethylium ion a negligible barrier was calculated. The n-propylium ion shows a relatively high barrier (7·64 kcal mol^{-1}) compared with recent *ab initio* calculations. For the non-classical phenylethylium ion estimation has been made for the rotation barrier of the phenyl ring (or the ethylene residue) around the principal axis of the molecule.

RECENTLY we pointed out that, when applying the MINDO/2 SCF–MO method to the calculation of the internal rotation barrier in cyclopropylmethyl cation (1) a good estimate of its height was obtained.[1] The agreement with the experimental value was so encouraging that we proceeded with the treatment of the barrier heights for other carbonium ions. Experimental data for the barrier heights which could allow their correlation with the calculated results do not exist for all ions treated here, yet the theoretical treatment of the dynamic properties of carbonium ions is very important for organic chemistry, since these species are intermediates in many reactions and their behaviour determines the progress of reaction. An increasing number of spectroscopic data support the information acquired by theoretical methods.[2-7]



(1)

Whereas the results obtained by the *ab initio* calculations depend mainly on the nature and size of the basis set applied, they depend in the semiempirical calculations merely on the kind of approximation itself. Thus the calculated relative stability of the non-classical ethylium ion (2) was different when different sets of Gaussian orbitals were used in *ab initio* calculations.[8-10] Further, the utility of the acquired values for the barrier height in cyclopropylmethyl cation (1) varied according to the type of approximation used for the energy calculation by the semiempirical methods.[1] The MINDO/2 SCF–MO method, giving good barrier heights for the cation (1), is expected to give just as good values for the rotation barriers of other carbonium ions.



(2)

The high rotation barrier in cyclopropylmethyl cation (1) suggests strong conjugation between the three-membered ring and the methylene group. Similar conjugation is to be expected for the allylium ion (3). The total energy of this molecule was minimized through variation of the C–C bond lengths and rotation of a methylene group out of the plane of the molecule. For all bond angles the value 120° was applied. The variation of the C–C bond lengths covered the region 1·300—1·500 Å gradually. It was found that the ground state

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[1] M. Shanshal, *Theor. Chim. Acta*, 1971, **20**, 405.

[2] G. A. Olah, J. R. DeMember, A. Commeyras, and J. L. Bribes, *J. Amer. Chem. Soc.*, 1971, **93**, 459.

[3] D. S. Kabakoff and E. Namanworth, *J. Amer. Chem. Soc.*, 1970, **92**, 3234.

[4] N. C. Deno, R. C. Haddon, and E. N. Nowak, *J. Amer. Chem. Soc.*, 1970, **92**, 6691.

[5] J. N. Bollinger, J. M. Brinich, and G. A. Olah, *J. Amer. Chem. Soc.*, 1970, **92**, 4025.

[6] P. v. R. Schleyer, T. M. Su, M. Saunders, and J. C. Rosenfeld, *J. Amer. Chem. Soc.*, 1969, **91**, 5174.

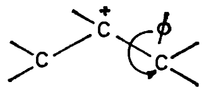
[7] G. A. Olah and J. M. Bollinger, *J. Amer. Chem. Soc.*, 1968, **90**, 6085.

[8] R. Janoscheck, H. Preuss, F. Fratev, *Arb. Ber. Gruppe Quantenchemie, München*, 1968, **10**, 140.

[9] J. E. Williams, jun., V. Buss, L. C. Allen, P. v. R. Schleyer, W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, 1970, **92**, 2143.

[10] G. V. Pfeiffer and J. G. Jewett, *J. Amer. Chem. Soc.*, 1970, **92**, 2144.

of the molecule has completely planar geometry with C–C bond lengths of 1·384 Å. The corresponding calculated heat of formation was 226·24 kcal mol^{-1}. On rotating a CH_2 group out of the plane of the molecule the expected increase in the length of the neighbouring C–C bond (transition to an essentially single bond) and decrease in the remote C–C bond length were noticed. The geometry of the transition state corresponded to an orthogonal conformation of both CH_2 planes. The C–C bond lengths amounted to 1·415 Å for the adjacent essentially single bond, and 1·345 Å for the remote double bond (Figure 1). The corresponding heat of formation was 240·39 kcal mol^{-1}. The difference between the heats of formation of both conformations was 14·15 kcal mol^{-1}, resembling the rotation barrier. This value agrees fairly well with the experimentally measured [5] rotation barrier (15·7 kcal mol^{-1}). Figures 2 and 3 show the change in C–C bond lengths and heat of formation due to the rotation of the CH_2 group out of the molecule's plane.



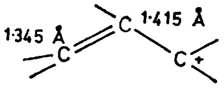


FIGURE 1 Geometry of the rotation transition state of allylium ion (3) calculated by MINDO/2

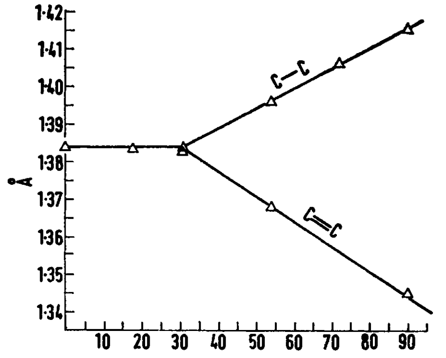


FIGURE 2 Values for the C–C and C=C bond lengths as functions of the dihedral angle (φ) of (3) calculated by MINDO/2

Another carbonium ion which exerts similar conjugation and was considered in these calculations is the benzylium ion (4). Applying to the C–C and C–H bond lengths in the phenyl ring the values 1·407 and 1·084 Å and for the C–H bond length in the methylene group the value 1·083 Å, we calculated the heat of formation of (4) with variation of the Ph–CH_2^+ bond length and the corresponding dihedral angle (φ) (Figure 3). The resulting heat of formation for the planar ground state was 219·56 kcal mol^{-1} with a Ph–CH_2^+ distance of 1·390 Å. An increase in the dihedral angle (rotation of the CH_2 plant) caused an increase in the Ph–CH_2^+ bond length. The transition state showed a perpendicular constellation of the methylene group to the phenyl ring, a Ph–CH_2^+ bond length of 1·410 Å, and a heat of formation 235·85 kcal mol^{-1}. The last value corresponds to a rotation barrier of 16·29 kcal mol^{-1}. So far no experimental or accurately calculated value for this barrier has been reported.

On going to the non-conjugated aliphatic carbonium ions we expect smaller values for the rotation barriers.

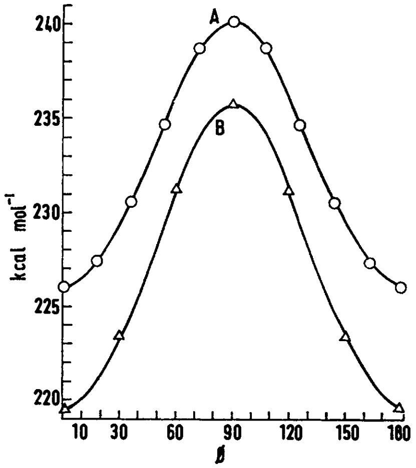


FIGURE 3 Calculated values for the heat of formation of A, allylium ion and B, benzylium ion (4) as a function of the dihedral angle (φ)

(4)

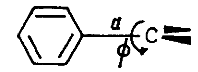


FIGURE 4 Parameters varied in the calculation of the heat of formation of benzylium ion (4); *a*, bond length, φ, dihedral angle

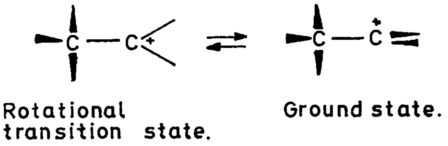
There has been a series of MO calculations concerning these systems with different results.[9-12] No calculation was done for problems, such as the classical or non-classical nature of these cations, by us, since we were mainly interested in the rotation barriers and it has been proved spectroscopically [2] as well as by SCF-MO calculations [9,10] that the classical structure of such cations is the more stable.

In the following calculations for the ethyl-, propyl-, and isobutyl-ium ions the C_{sp^3}–C_{sp^3} and C_{sp^3}–H bond lengths 1·534 and 1·093 Å were applied. The $\geqslant$C–CH_2^+ bond lengths were varied by rotation of the CH_2^+ plane around the C–C bond, over the range 1·400—1·540 Å. The ethylium ion (2) showed a negligible rotation barrier (0·02 kcal mol^{-1}) in accordance with recent *ab initio* calculations.[9,10] The calculated $\geqslant$C–CH_2^+ bond length was 1·410 Å in both ground and rotation transition states. For the ground state the eclipsed structure was found to be the most stable and a heat of formation of 206·37 kcal mol^{-1} was calculated. A 30° rotation of the

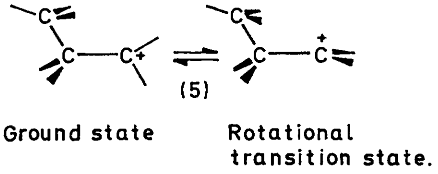
[11] R. Hoffman, *J. Chem. Phys.*, 1964, **40**, 2480.

[12] H. Kollmar and H. O. Smith, *Angew. Chem.*, 1970, **82**, 444.

CH_2^+ plane out of its equilibrium position yielded the rotational transition state.

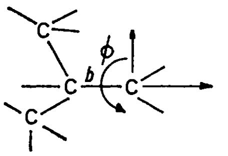


Similar variation of the $\geqslant\mathrm{C{-}CH_2}^+$ bond length and its corresponding dihedral angle (ϕ) in propylium ion (5) yielded the value 199·53 kcal mol^{-1} for the heat of formation of this molecule. The ground state has accordingly an eclipsed conformation of the CH_2^+ group relative to the β-C–C bond. The calculated $\geqslant\mathrm{C{-}CH_2}^+$ bond length was 1·440 Å. The rotational transition state was found to have a perpendicular conformation of the CH_2^+ plane to the C_β–C_γ bond and a $\geqslant\mathrm{C{-}CH_2}^+$ bond length 1·420 Å. Its calculated heat of formation was 207·17 kcal mol^{-1}. The difference between the two values for the heat of formation (7·64 kcal mol^{-1}) resembles the rotation barrier. This value is too high when compared with that calculated by Pople *et al.*[13] using the 3G-STO *ab initio* method. Further, these authors found that, according to their calculations, the ground state should have a perpendicular conformation of the CH_2^+ plane to the C_β–C_γ bond. However, no variation of the $\geqslant\mathrm{C{-}CH_2}^+$ bond length was considered in their treatment and the applied constant bond length (1·48 Å) is larger than our calculated distance of 1·440 Å. Further, the magnitude of the barrier is so small that it may fall within the limits of error of the correlation energy inherent in such calculations.



According to the results obtained from the MINDO/2 calculation the increase in the core–core repulsion energy by the rotation from the eclipsed to the perpendicular conformation is 1·24 eV. The corresponding decrease in the total electronic energy is 0·9 eV. The last entity includes any hyperconjugative effect which might have contributed to the stabilization of the perpendicular form.[14] The determining factor for the rotation barrier is the core–core repulsion which is smaller in the eclipsed conformation owing to the elongation by 0·02 Å of the $\geqslant\mathrm{C{-}CH_2}^+$ bond length.*

In the course of the determination of the conformations of both the ground and rotational transition state for isobutylium ion (6) both the $\geqslant\mathrm{C{-}CH_2}^+$ distance and the dihedral angle (ϕ) were varied over the ranges 1·400—1·460 Å and 60—180° respectively (Figure 5). It was found that the ground state of the molecule is represented by the dihedral angle $\phi = 60°$ and the $\geqslant\mathrm{C{-}CH_2}^+$ bond length 1·433 Å, such that a C–H bond of the methylene group is parallel to the C–H bond of the tertiary proton. The calculated value for its heat of formation was 200·73 kcal mol^{-1}. On rotation, C–CH_2^+ was elongated to 1·450 Å in the transition state (ϕ = 150°). The calculated heat of formation of the transition state was 204·55 kcal mol^{-1}, corresponding to a barrier value of 3·82 kcal mol^{-1}. Figure 6 shows the energy curve for the internal rotation barrier of n-propyl- (5) and isobutyl-ium (6) ion.†



(6)

FIGURE 5 Parameters varied in the MINDO/2 calculation for isobutylium ion (6)

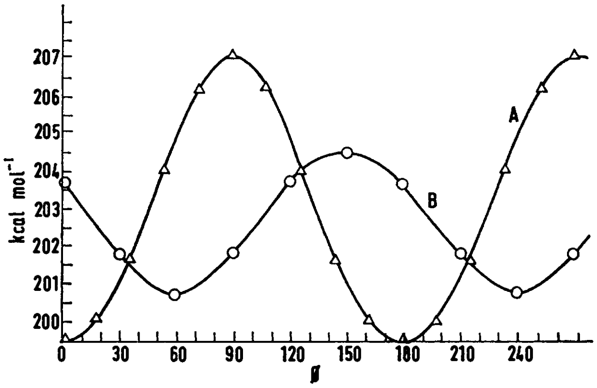


FIGURE 6 Rotation barrier of A, n-propyl- and B, isobutylium ion calculated by MINDO/2

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* Since no energy hypersurface was calculated, no conclusion can be drawn from our calculations about the cyclic forms of the propylium ion. SCF–MO studies of this kind are in progress in our laboratory.

† It was pointed out by M. J. S. Dewar and E. Haselbach (*J. Amer. Chem. Soc.*, 1970, **92**, 590) that on comparing its results with those obtained from the additivity of molecular properties, the MINDO/2 method does overestimate the stability of carbonium ions. The same applies for the ethyl- and n-propyl

$$\Delta H_f(R^+) = \Delta H_f(R{-}H) + D.E.(R{-}H) + I.P.(R\cdot)\cdot - \tfrac{1}{2}D.E.(H_2) \quad (1)$$

cations. From equation (1), where D.E. = dissociation energy and I.P. = ionization potential, one obtains the values shown in the annexed Table calculated by a Referee whom we thank, compared with the MINDO/2 results.

R^+	Estimated	MINDO/2
Et	228·7	206·4
Pr^n	220·0	199·5
$PhCH_2$	221·3	219·6
$CH_2{:}CH{\cdot}CH_2$	225·2	226·24

However similar overestimation of stability is expected for the rotational transition state. The difference between both deviations should be negligible. This was indicated by the calculated rotation barrier of cyclopropylmethyl cation,[1] which showed very good agreement with the experimental value.

[13] J. A. Pople, P. v. R. Schleyer, V. Buss, and L. Random, *J. Amer. Chem. Soc.*, 1970, **92**, 6380.

[14] See M. J. S. Dewar, ' Hyperconjugation,' The Roland Press Co., New York, 1962.

Variation of the Charge Distribution.—For all the carbonium ions for which the MINDO/2 calculations were carried out a decrease in the charge delocalization accompanied the rotation of the CH_2^+ plane from its equilibrium position. Ions with bigger barriers exhibited the bigger difference between the electron densities on the charge centre ($-\overset{+}{C}\!<$) for the ground and rotation transition states. On plotting the difference in electron densities on the charge centre for the ground and rotational transition state against the rotation barrier a nearly linear relationship between both quantities was obtained (Figure 7). Yet no linear relationship could be obtained by considering the charge variation for the whole CH_2^+ group by such a correlation.

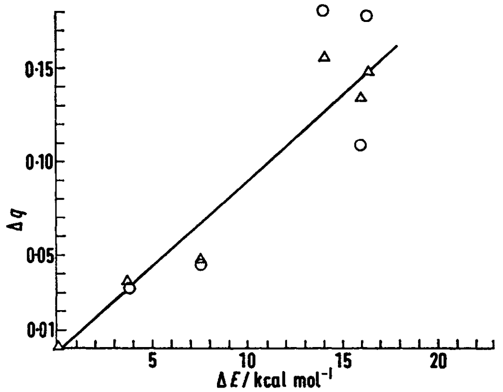

FIGURE 7 Correlation curve of the charge difference ($q = q_{rot} - q_{ground}$) on the charge centre to the corresponding rotation barrier. △, q for the C^+ atom alone; ○, q for the CH_2^+ group

TABLE 1

	Ground state		Transition state	
Carbonium ion	q_{C^+}	$q_{CH_2^+}$	q_{C^+}	$q_{CH_2^+}$
Cyclopropylmethylium (1)	0·272	0·549	0·406	0·594
Ethylium (2)	0·395	0·604	0·395	0·605
Allylium (3)	0·306	0·478	0·461	0·663
Benzylium (4)	0·261	0·397	0·408	0·574
n-Propylium (5)	0·351	0·549	0·398	0·594
Isobutylium (6)	0·374	0·531	0·382	0·564

Table 1 gives the values of the charge densities on the ion centre of the calculated carbonium ions in both ground and rotational transition states.

Phenylethylcarbonium Ion.—The non-classical structure of this ion (7) was established on the bases of kinetic studies,[15] n.m.r. spectral analysis,[16] and a CNDO-SCF-MO treatment.[17] It was a symmetrical π-complex in which the apical phenyl carbon atom enters a three-centre bond with the ethylene residue (Figure 8). The three-centre bond may be considered, within a localized bond model, as the interaction between the empty σ-orbital of the phenyl ring and the occupied bonding π-MO of ethylene, as well as the back-co-ordination between the occupied π-MOs of benzene and the antibonding MO of ethylene.[18]

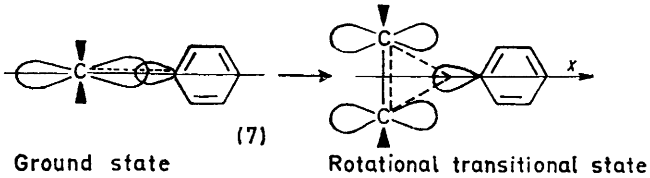

FIGURE 8 Ground and rotational transition states of phenylethylium ion (7)

On rotation of the phenyl ring (or the ethylene residue) around the *X*-axis, the σ-orbital interaction should be maintained while the back-co-ordination decreases to nil in the coplanar rotational transition state, in which the two π-systems are orthogonal. We have calculated both the ground and transition states using the bond lengths 1·407 (C=C) and 1·084 Å (C–H) for the phenyl ring and varying the C=C and phenyl–C=C(π) bonds in the three-membered ring. The spiro-conformation was considered for the geometry of the ground state and the completely coplanar one for the rotational transition state. Table 2 gives the calculated results for the two conformations, which show that the rotation is accompanied by a considerable change of geometry in the three-membered ring, *e.g.*, elongation of the $H_2C \overset{...}{=} CH_2$ and phenyl–C=C(π) bonds, a fact which caused a considerable change in the core–core repulsion and the total electronic energies.

TABLE 2

Calculated results for the ground state and rotational transition state of phenylethylium ion (7)

	Ground state	Rotational transition state
Phenyl–C=C(π) distance	1·484 Å	1·570 Å
$H_2C \overset{...}{=} CH_2$ distance	1·444 Å	1·400 Å
Core–core repulsion	4012·25 eV	4000·74 eV
Total valence electronic energy	−5172·51 eV	−5160·15 eV
Heat of formation	206·47 kcal mol⁻¹	225·52 kcal mol⁻¹

For the ethylene C_{sp^2}–C_{sp^2} bond in the ground state a distance of 1·444 Å was calculated (the C_{sp^2}–C_{sp^2} single bond length in butadiene is 1·47 Å [19]). The corresponding calculated distance between the adjacent phenyl carbon atom and the centre of this bond was 1·474 Å. Both distances changed on rotation (Table 2). The calculated rotation barrier was 19·12 kcal mol⁻¹. A

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[15] D. J. Cram, *J. Amer. Chem. Soc.*, 1952, **74**, 2129; A. Streitwieser, jun., ' Solvolytic Displacement Reactions,' McGraw-Hill, New York, 1962; L. Eberson, J. P. Petrovich, R. Baird, D. Dyckes, and S. Winstein, *J. Amer. Chem. Soc.*, 1965, **87**, 3504; C. J. Lancelot, J. J. Harper, and P. v. R. Schleyer, *ibid.*, 1969, **91**, 4294; C. J. Lancelot and P. v. R. Schleyer, *ibid.*, p. 4296; M. D. Bentley and M. J. S. Dewar, *ibid.*, 1970, **92**, 3996.

[16] G. A. Olah and R. D. Porter, *J. Amer. Chem. Soc.*, 1970, **92**, 7627.

[17] E. I. Snyder, *J. Amer. Chem. Soc.*, 1970, **92**, 7529.

[18] M. J. S. Dewar, ' The Molecular Orbital Theory of Organic Chemistry,' McGraw-Hill, New York, 1969.

[19] See L. E. Sutton, ' Tables of Interatomic Distances,' *Chem. Soc. Special Publ.*, 1958, No. 11.

study of the charge distribution on both the phenyl and ethylene portions showed only a minor charge shift between the two portions caused by the rotation. In the ground state 53% of the positive charge was located on the ethylene residue. In the rotational transition state 59% of the charge is located on the same residue. The difference of 6% is mainly due to the elimination of the back-co-ordination in the transition state.

Despite the formal tetraco-ordination of the planar apical carbon atom in the rotational transition state, it still possesses sp^2 hybridization. For, as pointed out before, the π-complex bonding is being formed by the unoccupied sp^2 orbital of this atom with the π-orbitals of the ethylene residue. The other sp^2 orbitals and the p_z-orbital of this atom contribute as usual to the formation of the benzene system.

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