An SCF MO Treatment of the Conformations of the 1,3,Dimethyl Allyl Carbonium Ion

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The geometry and heat of formation are calculated by means of the MINDO/2 method for the following six conformations of the 1,3,dimethyl allyl carbonium ion: the cis,cis conformation (I), the perpendicular, endo conformation (II), the cis,trans conformation (III), the perpendicular, exo conformation (IV), the trans,trans conformation (V), and the coplanar cis,cis,conformation (VI). Conformation I is predicted to be a stable intermediate, having both CH_3 groups 20° oppositely twisted out of the molecular plane. The order of stability of the planar conformations is V>III>I ≫VI. Utilizing the MINDO/2 calculated geometry, ab Initio calculations were done for all the six conformations. The ab Initio predicted order of stability is similar to that obtained with the MINDO/2 method. It is found that the ab Initio calculations yield rotation barriers that are too high, the MINDO/2 method yields values that are too low, compared with the experimentally determined barriers.

Introduction

Recent MINDO/2 calculations for the allyl carbonium ion yielded an internal rotation barrier of 14.5 kcal/mol [1]. This value agreed well with the experimentally determined barrier of polymethyl substituted allyl carbonium ions [2, 3]. Yet, no measurement exists for the internal rotation barrier of

the allyl carbonium ion itself. To study the influence of the methyl substituent on the stability and geometry of the ground and rotation transition states of the ion, it was found necessary to carry out similar SCF-MO calculations for all possible conformations of the 1,3, dimethyl allyl carbonium ion, minimizing their energies as functions of their corresponding geometric parameters. If the hyperconjugative stabilization of the rotation transition states is bigger than that of the planar ground sates [3], then a smaller rotation barrier as that of the allyl carbonium ion should result from such a theoretical treatment. We applied both MINDO/2 and ab-Initio methods for the study of the following conformations of this ion: the cis, cis conformation (I), the cis, trans conformation (III), the trans, trans conformation (V), the transition state (II) corresponding to the I — III rotative isomerization; the

transition state (IV) of the III — V rotation, and the completely planar conformation (VI).
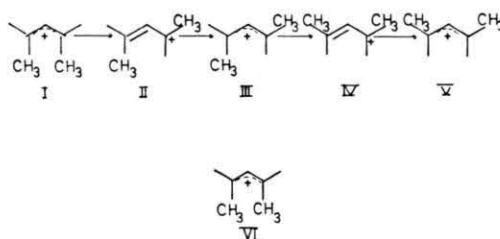

Fig. 1. Ground and rotation transition states of 1,3,dimethyl allyl carbonium ion, for which SCF-MO calculations were carried out.

MINDO/2 Calculations

We applied the MINDO/2 α and β parameters for the C, H, N, O molecules [4]. Accordingly, the $C_{sp}2 - H$ and $C_{sp}3 - H$ bond lengths were increased by 0.1 Å and kept constant (1.183 Å and 1.193 Å) during the calculations. Unless stated in this paper, all the bond angles were varied to obtain their equilibrium values. Bonds that are expected to have the same lengths in two different conformations were transferred from the calculation of one to that of the other. This helped us in reducing the computation time for some conformations.

The Allyl Carbonium Ion

Recalculating the energies of this ion and applying the optimized geometries of Ref. [1], we ob-

tained 227.72 kcal/mol and 239.49 kcal/mol for the heats of formation of the planar and rotation transition states respectively. They correspond to a calculated rotation barrier of 11.7 kcal/mol, compared with 14.5 kcal/mol [1] obtained from the application of the recent C, H, O α and β parameters [5].

The cis.cis.1,3,Dimethyl Allyl Carbonium Ion (I)

The calculation for this ion included the minimization of the total energy as a function of the following parameters; a – the $\overset{+}{C} = C$ and b – $C - CH_3$ bond distances; c – the $C = \overset{+}{C} = C$ bond angle; d – the $C - \overset{\frown}{C} - CH_3$ bond angle; e – the $C - C\overset{H}{\underset{CH_3}{}}$ bond angle; and f – the dihedral angle described by the $H_3C - \overset{+}{C} = C$ and $C = \overset{+}{C} = C$ planes. The C_2 symmetry was retained through out the minimization procedure. Totally we calculated 124 points of the molecular hypersurface to find the minimum of energy.
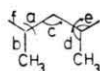

Fig. 2. By the MINDO/2 calculation varied geometric parameters of the cis,cis,1,3,dimethyl allyl carbonium ion (I).

The calculated geometry of this conformation corresponded to the following values: 1.390 Å $(C = C)$, 1.460 Å $(\overset{+}{C} \cdots CH_3)$, 140 $(C\overset{C}{\underset{C}{\overset{+}{\frown}}}$ bond angle), 115° $(C - C\overset{H}{\underset{CH_3}{\frown}}$ bond angle) and 20° for the two $H_3C - C = \overset{+}{C} = C$ dihedral angles, such that the CH_3 groups are oppositely twisted out of the molecular plane $(C_2$ symmetry). The calculated heat of formation was 189.98 kcal/mol.

Chemically interesting is the knowledge of the rotation barrier of one $H - \overset{+}{C} - CH_3$ plane out of its equilibrium position, towards the cis, trans confor-

mation (III), and the behaviour of the molecular geometry during the rotation. We simulated this process by the calculation of the heat of formation of the ion with different rotation angles. Table 1 shows the calculated $C_1 = \overset{+}{C_2} = C_3$ bondlengths, $C\overset{C}{\underset{C}{\overset{+}{\frown}}}$ bondangles and the $H_3C - C = \overset{+}{C} = C$ dihedral angles of ion (I) with different rotation angles of the first $H - \overset{+}{C} - CH_3$ plane

The Perpendicular,endo,1,3,Dimethyl Allyl Carbonium Ion (II)

The total energy of this conformation was minimized as a function of all $C - C$ distances, the $C\overset{C}{\underset{C}{\overset{+}{\frown}}}$ and $C - C\overset{H}{\underset{C}{\searrow}}$ bond angles and the $H_3C - C = C - C$ dihedral angle of the, in plane, methyl group (Figure 3).
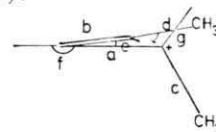

Fig. 3. By the MINDO/2 calculations varied geometric parameters of the perpendicular, endo,1,3,dimethyl allyl carbonium ion (II).

Both $C\overset{C}{\underset{CH_3}{\diagdown}}$ bond angles were assumed 120°, due to the expected vanishing molecular strain. The calculated geometry of this conformation corresponded to the following values: 1.420 Å $(\overset{+}{C} - C =)$, 1.354 Å $(C = C)$, 1.480 Å $(= C - CH_3)$, 1.450 Å $(C - CH_3)$, 130° $(C\overset{C}{\underset{C}{\overset{+}{\frown}}}$ bond angle), 112.5° $(H - C\overset{C}{\underset{C^+}{\searrow}}$ bond angle) and 5° $(H_3C - C = C - C^+$ dihedral angle). The calculated heat of formation was 195.96 kcal/mol. Totally 58 SCF calculations were carried out to obtain the minimum of energy.

Rotation angle	$H_3CC \cdots C_2$ (Å)	$C_2 \cdots C_3CH_3$ (Å)	$C\overset{C}{\underset{C}{\overset{+}{\diagup}}}$ angle	$C_1 \cdots C_2 \cdots C_3 - CH_3$ dihedral angle
30°	1.390	1.370	140°	10°
40°	1.390	1.370	140°	5°
50°	1.390	1.370	140°	5°
60°	1.390	1.360	135°	5°
70°	1.410	1.358	135°	5°
80°	1.410	1.358	135°	5°

Tab. 1. MINDO/2 calculated values of the geometric parameters for the cis,cis,1,3,dimethyl allyl carbonium ion (I) with different rotation angles of one $H - C - CH_3$ plane.

The cis,trans,1,3,Dimethyl Allyl Carbonium Ion (III)

For this conformation the minimal total energy was calculated as a function of the following 6 geometric parameters (Fig. 4); the $C \doteq C_2 \doteq C_3$ bond distance, the $CH_3 - C_1$ bond length, $H_3C - C_3$ bond length, the $C \diagup{C} \atop \diagdown{C}$ bond angle, the $H_3C - CC$ bond angle and the endo, $H - CC$ bond angle. The calculated values of the last two parameters should indicate any nonbonded repulsion between the endo, CH_3 group and the endo H atom.
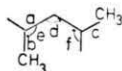
Fig. 4. By the MINDO/2 calculation varied geometric parameters for the cis,trans 1,3,dimethyl allyl carbonium ion (III).

The obtained geometric values were 1.400 Å $(C \doteq C)$, 1.460 Å (for both $H_3C - C$ bonds), 120° $(C \diagup{C} \atop \diagdown{C}$ bond angle), 125° (endo $H_3C - CC$ bond angle) and 120° (endo, $H - CC$ bond angle). The calculated heat of formation was 187.36 kcal/mol. 37 SCF calculations were required to obtain the energy minimum.

The Perpendicular,exo,1,3,Dimethyl Allyl Carbonium Ion (IV)

The rotation of the second $H - \overset{+}{C} - CH_3$ plane towards the cis,cis,conformation (V) should proceed through conformation (IV). Having an alternate propen structure and an unoccupied p_z orbital that is completely orthogonal to the neighboured $C = C$ bond, conformation (IV) is expected to resemble the rotation transition state. The accurate calculation of its energy should provide an estimation of the III – IV – V and V – IV – III rotation barriers. The MINDO/2 calculated geometry corresponded to the following values; 1.440 Å $(\overset{+}{C} - C =)$, 1.350 Å $(\overset{+}{C} = C$ bond length), 1.440 Å $(C - CH_3$ bond length), 1.480 Å $(= C - CH_3$ bond length), 135 Å $(C \diagup{C} \atop \diagdown{C}$ bond angle) and 120° $(C - C \diagup{H} \atop \diagdown{C}$ bond angle. The calculated heat of formation was 191.73 kcal/mol. 48 SCF calculations were carried out to determine the energy minimum.
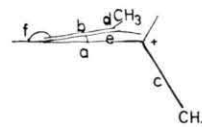
Fig. 5. By the MINDO/2 calculation varied geometric parameters of the perpendicular, exo,1,3,dimethyl allyl carbonium ion (IV).

The trans,trans,1,3,Dimethyl Allyl Carbonium Ion (V)

Since no molecular strain is expected in this ion, we assumed its $C \doteq \overset{+}{C} \doteq C$ bondlengths equal to those of the allyl carbonium ion (1.390 Å)[1]. Further we accepted the $C - CH_3$ bond distance of conformation (III), (1.460 Å). Variation of the $C \doteq \widehat{C} \doteq C$ and $C \doteq C - CH_3$ gave 120° for both. The calculated heat of formation was 181.11 kcal/mol. We carried out 12 SCF calculations with different bond angles to determine the minimum of energy.
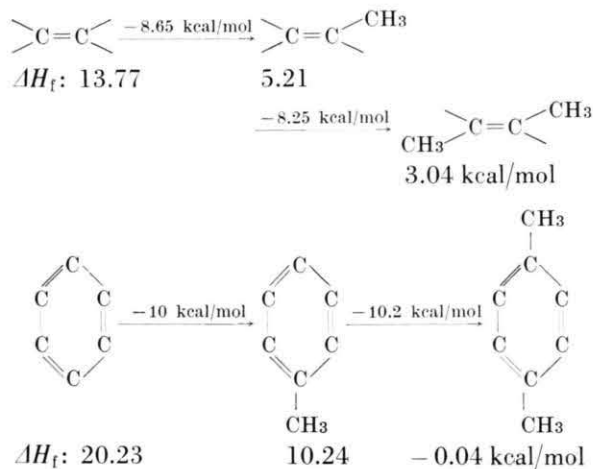
The Coplanar cis,cis,1,3,Dimethyl Allyl Carbonium Ion (VI)

The knowledge of the geometry and energy of this conformation is of a theoretical importance for the conformation analysis of the ion. We carried out MINDO/2 calculations to estimate its heat of formation and geometric values. The C_{2v} symmetry was retained during the calculation. The treatment yielded the following values; 1.500 Å $(C \doteq C)$, 1.460 Å $(C - CH_3)$, 140° $(C \diagup{C} \atop \diagdown{C}$ bond angle), 130° $(H_3C - C \doteq C$ bond angle) and 112.5° $(H - \underset{|}{\overset{+}{C}} \doteq C$ bond angle. The calculated heat of for-
$\;\;\;\;CH_3$
mation was 204.06 kcal/mol. 104 SCF calculations were required to determine the energy minimum.

Discussion of the MINDO/2 Results

According to the reported MINDO/2 calculations the following order of stability is predicted for the three coplanar conformations; V > III > I. The order is parallel to the expected increase of the intramolecular repulsion. The differences in the heats of formation are 5.65 kcal/mol (V – III) and 2.62 kcal/mol (III – I).

A rather interesting result is the difference between the heat of formation of the most stable trans, trans conformation (V) and that of the unsubstituted allyl carbonium ion (46.02 kcal/mol). Considering the C_{2v} symmetry of the ion one calculates 23.01 kcal/mol as the decrease in the heat of formation of the ion due to the introduction of one CH_3 group, compared with 8.45 kcal/mol for the neutral olefinic compounds[6] and 10.1 kcal/mol for the neutral aromatic compounds[6].

$$>C=C< \xrightarrow{-8.65 \text{ kcal/mol}} >C=C<^{CH_3}$$

ΔH_f: 13.77   5.21

$$\xrightarrow{-8.25 \text{ kcal/mol}} \;\; {}_{CH_3}^{}>C=C<^{CH_3}$$

3.04 kcal/mol

$$\xrightarrow{-10 \text{ kcal/mol}} \xrightarrow{-10.2 \text{ kcal/mol}}$$

ΔH_f: 20.23   10.24 -0.04 kcal/mol

It includes an extra hyperconjugative stabilization (10 – 12 kcal/mol) that is caused by the positive charge of the conjugated system. The shortening of the $\overset{+}{C} - CH_3$ bond length (1.460 Å) in (V) relative to 1.480 Å of the in plane $=C-CH_3$ bond in (IV) and (I) confirms the conclusion of the extra hyperconjugative stability in the ground state of the ion. Inspite of the strong hyperconjugation the calculated rotation barrier of the CH_3 group around its bond axis was only 0.64 kcal/mol. Conformation (V) shows no molecular strain, its bond angles are systematically $120°$.

The exo, perpendicular rotation transition state (IV) shows a similar hyperconjugative stabilization as (V). The difference between its heat of formation and that of the allyl carbonium ion's rotation transition state is 47.76 kcal/mol, corresponding to an average of 23.88 kcal/mol for each CH_3 group. Compared with the hyperconjugative difference in (V) (46.02 kcal/mol) it suggests an almost equal effect in both conformations (V) and (IV). Consequently the calculated V – IV – III rotation barrier (10.02 kcal/mol) should be of a similar magnitude as that of the unsubstituted ion (11.7 kcal/mol).

A study of the $=C-CH_3$ (1.480 Å) and $\overset{+}{C}-CH_3$ (1.440 Å) bond lengths suggests a stronger hyperconjugation in the latter, which is obviously due to the bigger positive charge on the neighboured P_z orbital.

Transition state (IV) shows a bond alternation. The $C=\overset{\frown}{C}-\overset{+}{C}$ bond angle ($135°$) is of the same order as that of stilbene ($128°$), calculated by the CNDO method[7]. Our assumption that (IV) resembles the rotation transition state was mainly based on two arguments; a – its symmetric properties cause the removal of conjugation between the formed double bond and the unoccupied lone orbital, b – the MINDO/2 calculation of the similar (I – II) rotation path showed that the perpendicular conformation constitutes the transition state.

The cis, trans conformation (III) is the second stable conformation of the ion. Its calculated ΔH_f is 40.37 kcal/mol less than that of the allyl carbonium ion. (III) is by 5.65 kcal/mol less stable than (V). The decrease in stability is most probably due to the endo, H – endo, CH_3 repulsion as indicated by the calculated value ($125°$) for the endo $C<^C_{CH_3}$ bond angle. The $C=C=C$ bond lengths and angle, as well as the $C-CH_3$ bond lengths (1.460 Å), are similar to those of (V). The calculated $C-CH_3$ bond length (1.460 Å) is intermediate between the $=C-CH_3$ (1.480 Å) and $\overset{+}{C}-CH_3$ (1.440 Å). The comparison indicates the expected order in the hyperconjugative strength of the three types of bond. The MINDO/2 calculation yields only a small difference (4.37 kcal/mol) in the heat of formation between conformations (IV) and (III). The difference is equivalent to the predicted III – IV – V rotation barrier. The experimentally determined barrier of the cation, in a SO_2Cl_2 solvent with SbF_6^- as anion, is 24.0 kcal/mol[8].

Conformation (II) is predicted to have an alternate structure ($C=C = 1.354$ Å and $\overset{+}{C}-C = 1.420$ Å). The out of plane deformation of the second CH_3 group (by $5°$) from its planar structure requires 0.1 kcal/mol. The $C=C-CH_3$ and $C-CH_3$ bondlengths are almost of the same magnitude as those of (IV). The difference in the heat of formation between conformations (II) and (IV), (4.22 kcal/mol) is of a similar magnitude as that between the planar conformations (V) and (III), (5.65 kcal/mol). It suggests that, in the allyl car-

bonium ion an endo CH_3 group is by $4.2 - 5.5$ kcal/ mol less stable than the exo, CH_3 group. According to its calculated heat of formation the cis.cis, conformation (I) with both $H - \overset{+}{C} - CH_3$ planes $20°$ oppositely twisted out of the molecular plane should form a stable intermediate. The bond angles, $140°$ $(C - \overset{+}{C} = C)$ and $130°$ $(C - \overset{+}{C} - CH_3)$ show the tendency of the molecule to avoid intramolecular repulsion. The bondlengths are similar to those of the planar conformations (III) and (V). The difference in the heat of formation between (I) and (V) is 8.27 kcal/mol, corresponding to 4.14 kcal/ mol for each methyl group. This value is in agreement with the recent difference between conformations (II) − (IV) and (III) − (V).

$$\Delta(\Delta H_f): \quad I-V \;=\; 8.27\;\text{kcal/mol} = 2 \times 4.14\;\text{kcal/mol},$$
$$III-V \quad=\quad 5.65\;\text{kcal/mol},$$
$$II-IV \quad=\quad 4.22\;\text{kcal/mol},$$
$$I-III \quad=\quad 2.62\;\text{kcal/mol}.$$

To determine the geometry of the transition state for the I − III rotation, we calculated the heat of formation of (I) as a function of the rotation angle of one $H - \overset{+}{C} - CH_3$ plane in an opposite direction to that of the second $H - \overset{+}{C} - CH_3$ plane. A rotation towards the second plane should lead to a coplanar transition state that is similar to conformation (VI), which was calculated to be energetically high. Table 1 includes the results of the geometry calculation for each conformation. It is seen that the bond alternation begins by the rotation angle $30°$ and increases with its increase. The $C - \overset{+}{C} - C$ bond angle remains constant $(140°)$ till $60°$, where it decreases to $135°$. The $H_3C - C_3 = C_2 - C_1$ dihedral angle decreases to $10°$ by a $30°$ rotation and to $5°$ by a $40°$ rotation and remains by this value till the ion reaches the perpendicular, endo conformation (II). Preliminary calculations for the ion with rotation angles $>90°$ showed a decrease in the heat of formation and indicated that conformation (II) does resemble the transition state. Figure 6 shows the calculated path for the I − III rotation.

According to the calculated results, the coplanar cis, cis, conformation (VI) forms a highly strained and unstable species. Its $C - C$ bonds are much too long $(1.500\,\text{Å})$ compared with those of conformations V, III and I. Its bond angles $(140°$ and $135°)$ indicate its tendency to avoid nonbonded repulsion. The high value of its calculated heat of formation
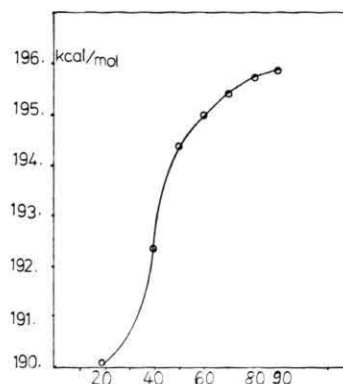

Fig. 6. MINDO/2 calculated heat of formation of cis,cis, 1,3,dimethyl allyl carbonium ion (I) as a function of the rotation angle of one $H - C - CH_3$ plane.

$(204.06\;\text{kcal/mol})$ excludes its existance even as a rotation transition state for the free and uncoordinated 1,3,dimethyl allyl carbonium ion.

Ab Initio Calculations

The MINDO/2 method was parametrized to reproduce experimental geometries and heats of formation of organic molecules. In fact recent applications showed that it did yield good geometries of organic molecules [4, 5, 9]. The ab Initio methods do give equilibrium geometries that agree quite well with the experimental results. It should be more economical then to carry out ab Initio calculations for the molecular energies using MINDO/2 geometries than trying to determine the equilibrium geometry using the ab Initio method alone. To check the energy values calculated by the MINDO/2 method, including the values for the rotation barriers, we carried out such ab Initio calculations for the same ionic conformations. We applied the Mely and Pullman's Gaussian basis [10] which consist of $3 \times s$ Gaussians for the H atom and $4 \times s + 3 \times 2\,p$ Gaussians for the C atom. Totally 107 Gaussians and 34 groups were required for each calculation.

Tab. 2. Ab Initio calculated total energies of the conformations of 1,3,dimethyl allyl carbonium ion relative to the energy of the trans,trans conformation (V).

Conformation	ΔE (kcal mol)
cis,cis (I)	22.53
perpendicular,endo (II)	48.02
cis,trans (III)	1.10
perpendicular,exo (IV)	45.41
trans,trans (V)	0.0

Table 2 shows the calculated energies of all conformations relative to the total energy of the trans, trans conformation (V).

The predicted order of stability of the planar conformations is similar to that of the MINDO/2 treatment. The calculated differences in energy between (I) − (III) and (III) − (V) are 21.43 kcal/mol and 1.10 kcal/mol respectively. The first difference is to high, the second agrees well with the energy differences that are based on the interpolation of kinetic measurements (5.0 kcal/mol and 1.6 kcal/mol respectively) [12]. The calculated rotation barriers, (I − III, 25.49 kcal/mol) and (III − V, 44.31 kcal/mol) are parallel to the experimental NMR values (17.5 kcal/mol and 24.0 kcal/mol resp.), of Schleyer et al.[8]. Obviously no quantitative agreement with the experimental results is achieved. Table 3 shows the values of the rotation barriers as estimated by the three methods.

Tab. 3. Theoretical and experimental values of the rotation barriers of 1,3,dimethyl allyl carbonium ion.

	MINDO/2	ab Initio	NMR [8]
I − III	5.98	25.49	17.5
III − V	4.37	44.31	24.0

The ab Initio calculated III − V rotation barrier is in the order of the recently published and ab Initio calculated rotation barrier of the unsubstituted allyl carbonium ion (42.0 kcal/mol) [11a]. The close agreement indicates that the introduction of the methyl groups is of minor influence on the barrier height, and that the hyperconjugation in the ground state is almost equal to that in the rotation transition state of this ion.

Compared wih the experimental values, the MINDO/2 calculated rotation barriers are too low. Similar calculations for the rotation barrier of ethylene [5] showed an underestimation of its value by 11.1 kcal/mol relative to experimental value too.

Conclusion

The order of stabilities for the five conformations (I − V) of 1,3,dimethyl allyl carbonium ion is correctly predicted by the MINDO/2 and ab Initio calculations. The order of the V − III and III − I rotation barriers is correctly predicted by the ab Initio method (parallel to the NMR measured values). The MINDO/2 method underestimates the rotation barriers, apparently due to its overestimation of the transition states' stability. A comparison of the V − III rotation barrier with that of the unsubstituted allyl carbonium ion suggests an almost equal hyperconjugative stabilization of the ground and rotation transition states.

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