ab initio Study of Positive Charge Stabilization by Silicon in Five-membered Rings

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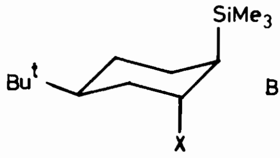
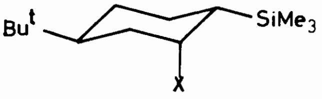
Angular constraints in a five-membered ring prevent the optimal overlap between positive charge on carbon and a β-C–Si bond that is possible in six-membered rings. *ab initio* methods have been used for the first time to study this phenomenon in secondary, common ring systems. Within the most stable conformer of the cyclopentyl cation (the twist form) introduction of a β-pseudo-axial C–Si bond (as SiH_3) stabilizes the system by 15.8 kcal† mol^{-1}, whereas introduction of a β-pseudoequatorial C–Si bond stabilizes it by only 5.6 kcal mol^{-1}. The structure distorts in three ways to optimize the hyperconjugative interaction: by adjusting the dihedral angle between the C–Si bond and the empty p-orbital to as low a value as permissible by angle strain, by lowering the $^{+}C_{\alpha}$–C_{β}–Si valence angle, and by shortening the C_{α}–C_{β} bond length. The calculated dihedral angles are in good agreement with solvolysis results. The maximum hyperconjugative and inductive contributions were calculated to be 15.8 and 0.9 kcal mol^{-1}, respectively.

Although the ability of silicon to stabilize β positive charge (Si–C–C^{+}) has been known for some time,[1] the dihedral dependence of this effect has only recently been explored.[1–3] If the primary mechanism of interaction is hyperconjugation, then its magnitude depends on the square of the cosine of the Si–C–C–X dihedral angle (X is the leaving group). The favourable orbital overlap offered by a six-membered ring when Si and X are disposed *trans* (antiperiplanar) to each other (**1**) results in a much faster reaction than that of the six-membered ring with a *gauche* disposition (**2**).[1] In terms of a rate ratio, the trifluoroacetate of (**1**) reacts 6.0 × 10^7 times faster than (**2**) with the same leaving group in 97% trifluoroethanol at 25 °C (the ratio is 1.7 × 10^5 for the unbiased versions lacking the anchoring t-butyl groups).



(1)



(2)

The *trans*/*cis* ratio for the corresponding five-membered rings is only 75.[3] This much lower value presumably results from the less favourable dihedral angle in the *trans* form (in which the Si–C–C–X fragment has moved away from the maximum at 180 °) and the more favourable dihedral angle in the *cis* form (in which Si–C–C–X has moved toward the maximum at 0°). Calculations from our solvolysis data,[3] based on the theory of hyperconjugation, indicated that the *trans* dihedral angle in the five-membered ring is approximately 147° in the transition state and the *cis* dihedral angle is about 56°. The meaning of these numbers in the context of the mixture of conformations offered by five-membered rings[4] is not at all clear. The conformation of the cyclopentyl cation has been studied under stable ion conditions.[5]

Because individual five-membered ring conformations may not be examined easily by experiment, we have performed *ab initio* calculations on the cyclopentyl cation carrying a β-silyl substituent. Our objectives were the determination of the relative energies of the various conformations, and the subsequent determination of the dihedral dependence of the silyl substituent within these conformers. This study was prompted because there has been no previous theoretical assessment of the relative stabilities of the various conformations that the cyclopentyl cation can adopt, and, furthermore, the effect of the β-silyl substituent on the stability of the cyclopentyl conformers has not been examined. Previous theoretical studies have used β-substituted ethyl, propyl, butyl, and cyclopropyl cations,[2,6] and these simple models have two important differences from the five- and six-membered rings that have been the subject of our experimental studies. First, the secondary carbenium ions of the solvolytic systems have higher intrinsic stability and less demand for stabilization than the primary ethyl systems.[6] Second, the acyclic ethyl, propyl, and butyl systems have no structural constraints (other than torsion) on conformation,[2,6] whereas the dihedral angles in the rings are restricted by considerations of angle strain, eclipsing strain, and non-bonded interactions. Ibrahim and Jorgensen[2] reported calculations on cyclopropyl systems, which, however, do not permit conformational operations. Consequently, the present study was carried out on cyclopentyl and β-silyl substituted cyclopentyl cations in order to understand the effect of the silyl substituent on five-membered ring conformations.

Results

Calculations were performed at the restricted Hartree–Fock level, with a Harris version of the SCF-MO GAUSSIAN 82 program.[7] Because of the size of the systems in this study and the presence of the relatively heavy silicon atom, geometries were optimized with the minimal STO-3G basis set and energies were calculated at the 3-21G* level (3-21G*//STO-3G). Although use of a larger basis set or inclusion of electron correlation can improve geometries and relative energies, for large systems even the minimal basis set gives good geometries.[8] Moreover, the 3-21G* energies yielded no different conclusions from the STO-3G energies. Analytical gradients and multiparameter search were used for geometry optimization.[9] The optimized geometries and the related *Z*-matrices are

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† 1 cal = 4.184 J.

Table 1. Calculated total energies.[a]

Molecule[b]	3-21G*//STO-3G energy/au
CH_4	39.976 88
CH_3^+	39.005 62
SiH_4	289.779 46
SiH_3^+	288.886 96
p-C_5H_{10}	194.080 37
e-C_5H_{10}	194.087 43
t-C_5H_{10}	194.087 35
p-$C_5H_9^+$ (**3**)	193.205 55
e-$C_5H_9^+$ (**4**)	193.205 56
t-$C_5H_9^+$ (**5**)	193.207 87
p-$H_3SiC_5H_9$	482.718 97
e-$H_3SiC_5H_9$	482.727 88
t-$H_3SiC_5H_9$	482.727 87
p-$H_3SiC_5H_8^+$	481.867 80
e, a-$H_3SiC_5H_8^+$ (**6**)	481.870 65
e, e-$H_3SiC_5H_8^+$	481.854 66[c]
t, a-$H_3SiC_5H_8^+$ (**7**)	481.873 51
t, e-$H_3SiC_5H_8^+$	481.857 39[c]

[a] Except as noted, structurally optimized; negative of total energies; 1 au = 627.52 kcal mol^{-1}. [b] p-, e-, and t- refer to planar, envelope, and twist structures; when a second letter is given, it represents axial (a) or equatorial (e) dispositions of the SiH_3 group. [c] Interatomic angles and bond lengths were optimized but dihedral angles determined from the axial isomer were held constant.

Table 2. Calculated stabilization energies for $R\overset{+}{C}HR' + CH_4 \longrightarrow RCH_2R' + CH_3^+$.

Ion[a]	3-21G*//STO-3G stab. energy/ kcal mol^{-1}
CH_3^+	0
p-$C_5H_9^+$ (**3**)	60.5[b]
e-$C_5H_9^+$ (**4**)	56.1
t-$C_5H_9^+$ (**5**)	57.6[b]
p-$H_3SiC_5H_8^+$	75.4[b]
e, a-$H_3SiC_5H_8^+$ (**6**)	71.6
e, e-$H_3SiC_5H_8^+$	61.5
t, a-$H_3SiC_5H_8^+$ (**7**)	73.4
t, e-$H_3SiC_5H_8^+$	63.2

[a] See footnote *b* in Table 1. [b] These comparisons are made between neutral and cation with the same conformation. Comparisons also may be made between the cation and the most stable neutral. Changes result in only three cases: 56.1 kcal mol^{-1} for p-$C_5H_9^+$, 57.5 kcal mol^{-1} for t-$C_5H_9^+$, and 69.8 kcal mol^{-1} for p-$H_3SiC_5H_8^+$.

included as a supplementary publication, SUP 56775 (22 pp).†

Three conformations were considered for each system, *i.e.* the planar, envelope, and twist forms. For the neutral hydrocarbon cyclopentane, symmetry constraints were employed to obtain these forms, respectively D_{5h}, C_s, and C_2. For the cyclopentyl cation, symmetry constraints were similarly employed to produce the analogous C_{2v}, C_s, and C_2 forms. In this case, the envelope form always converged to the planar form during optimization. For the silyl systems, SiH_3 was used instead of $SiMe_3$ in order to reduce computational time. For the neutral silylcyclopentane, symmetry constraints were employed to obtain the planar (C_s) form. Of the various envelope conformations, only the more stable C_s form in which the silyl-substituted carbon is at the flap was examined. The twist form is C_1 and could be obtained without any geometric constraints. Similarly, for the silylcyclopentyl cation, the planar, envelope, and twist forms have only C_1 symmetry. For the envelope, we considered only the form in which the positively charged carbon is at the flap. For this envelope form and the twist form, geometry always converged entirely to the pseudoaxial conformer. In order to calculate the energy for the pseudoequatorial forms, the silyl group was switched from pseudoaxial to its geminal position without altering the remainder of the structure. Interatomic angles and bond lengths were then optimized but dihedral angles were held constant in order to retain the pseudoequatorial structure.

Geometries optimized at the STO-3G level were used to calculate energies at the 3-21G* level.[10] The latter basis set includes d-type polarization functions, which can be important for heavy atoms such as silicon. The calculated total energies are given in Table 1. Stabilization energies of the ions were evaluated from the isodesmic reaction of equation (**1**) and are listed in Table 2.

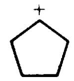
$$R\overset{+}{C}HR' + CH_4 \longrightarrow CH_3^+ + RCH_2R' \qquad (1)$$

Discussion

Neutral Species.—In general, saturated five-membered rings are non-planar, existing as a mixture of two puckered forms, the C_s or envelope form and the C_2 or twist form.[4] A continuous spectrum of geometries between these forms also can exist, so long as the conformation is not overly puckered. The present calculations are in line with previous results. For both cyclopentane and silylcyclopentane, the envelope and twist forms are essentially identical in energy and somewhat more stable than the planar form, by 4.4 kcal mol^{-1} for cyclopentane and by 5.6 kcal mol^{-1} for silylcyclopentane (Table 1).

In the optimized envelope geometry, the flip angle (the dihedral angle between the plane of the four coplanar atoms and the plane of the three atoms of the flap) is 36.6° for cyclopentane and 37.6° for silylcyclopentane. These large angles help to avoid eclipsing interactions.

Ions.—All comparisons between ions were made on the basis of isodesmic reactions of the type given in equation (1). The planar (**3**) and envelope (**4**) forms converge to the same geometry, and the twist form (**5**) is only 1.4 kcal mol^{-1} more stable than (**3**) and (**4**). These results may be explained in terms of hyperconjugative effects between the C–H bonds on the β carbon and the empty p-orbital. Because the C–H bond on the trigonal carbon is approximately normal to those on the adjacent carbons, there is no benefit from reduced eclipsing through bending or twisting. More importantly, the overall stabilization from C–H hyperconjugation does not benefit from twisting, because any gain for one C–H bond is offset by a loss for the geminal C–H bond. As a result, the envelope form converges to planarity (flip angle of 0.02°), and the flip angle of the twist form (the dihedral angle between the C–C$^+$–C plane and the C_β–C_γ bond vector) is only 9.8°.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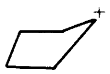
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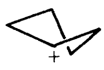
(5)

Introduction of the silyl (SiH_3) group on C_β results in the stabilization of all forms. Comparisons are made with respect to CH_3^+ by the isodesmic equation (1) (Table 2). With the twist cyclopentyl cation (**5**) moved to the point of comparison, the planar silylcyclopentyl cation is stabilized by 17.8 kcal mol^{-1} (or 12.3 kcal mol^{-1} by the comparison in footnote *b* of Table 2). The envelope and twist forms with pseudoaxial silyl groups, (**6**) and (**7**), are more stable by 14.0 and 15.8 kcal mol^{-1}, respectively (the

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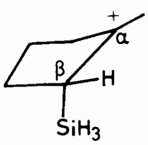
† For details of the Supplementary Publications Scheme, see 'Instructions for Authors (1990),' *J. Chem. Soc., Perkin Trans. 2*, Issue 1 p. *v*.



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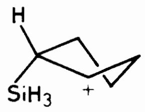

(7)

alternative method of footnote *b* of Table 2 makes no appreciable change for these cases). The C–Si bond in all three forms is closer to eclipsing the empty p-orbital than is the C–H bond in (**3**)–(**5**). Thus the dihedral angle between the C–Si bond and the empty p-orbital is 25.9° in the planar form, 13.4° in the envelope form, and 14.1° in the twist form, compared with 30° in the planar cyclopentyl cation (**3**). As the C–Si bond becomes nearly parallel with the empty orbital, the C_β–H bond becomes less so. Clearly, C–Si hyperconjugation is much more effective than C–H hyperconjugation. The most favourable arrangement of course would be a 0° dihedral angle, which is not possible in these rings because it would lead to prohibitive angle strain.

The silicon atom in the cation also moves closer to the centre of positive charge through distortion of the Si–C_β–C_α valence angle, which is 107.8° in the cyclopentyl cations but 101.4°, 100.3°, and 101.5° respectively in the planar, envelope, and twist silylcyclopentyl cations. This same distortion was noted by Jorgensen and co-workers.[6] Hyperconjugative stabilization is more effective when the silicon atom is closer to the positive centre. Another consequence of hyperconjugation is that the C_α–C_β bond is shortened to 1.42 Å, compared with the normal value of about 1.55 Å.

The calculations in Table 2 also show that the envelope and twist forms with pseudoaxial groups, as shown in (**6**) and (**7**), are more stable than the corresponding forms with pseudoequatorial silyl groups. In fact, the pseudoequatorial form is not an energy minimum, as geometry optimization always converted the pseudoequatorial form into the pseudoaxial form. The pseudoequatorial energies in Table 1 were obtained by placing the SiH_3 in that position and prohibiting dihedral angle changes during subsequent geometry optimization, leading to somewhat artificial but still useful results. The pseudoaxial twist form is 15.8 kcal mol^{-1} more stable than the unsubstituted form, but the pseudoequatorial twist form is only 5.6 kcal mol^{-1} more stable. The pseudoaxial C–Si bond of course has a more favourable dihedral angle for hyperconjugation than does the pseudoequatorial C–Si bond.

The dihedral angle between the C_β–Si bond and the empty p-orbital is calculated to be 14.1° in the pseudoaxial twist form and 57.0° in the pseudoequatorial twist form (the values are similar in the envelope form). These values may be used to separate inductive and hyperconjugative contributions to the stabilization according to equation (2), in which θ is the dihedral angle, the double-delta on the free energy of activation refers to

$$\Delta(\Delta G^{\ddagger})_{\mathrm{Si},\theta} = \cos^2\theta[\Delta(\Delta G^{\ddagger})_{\mathrm{Si},0^\circ}]^V + \Delta(\Delta G^{\ddagger})^I \qquad (2)$$

the difference between the value for the C–Si and C–H compounds, the *V*-term is hyperconjugative, and the *I*-term is inductive. The hyperconjugative term is modulated by the cosine-squared function because of the variation with dihedral angle, whereas the inductive term is independent of stereochemistry and hence additive. This equation represents an adaptation[1] of the Sunko–Hehre equation for secondary deuterium isotope effects.[11] Insertion of the two values of $\Delta(\Delta G^{\ddagger})$ from Table 2 and the two values of θ result in evaluation of the maximum hyperconjugative stabilization as 15.8 kcal mol^{-1} and the inductive stabilization as 0.9 kcal mol^{-1}. Thus the total stabilization provided by a β-silyl group is 16.7 kcal mol^{-1} according to this model. The calculations of Jorgensen and co-workers[6] on their primary system gave a total stabilization of 38 kcal mol^{-1}, divided into 29.1 kcal mol^{-1} for hyperconjugation and 8.9 kcal mol^{-1} for induction. These larger values are expected for a primary system but also may result from Jorgensen's higher level of calculation. In their secondary system ($SiH_3CH_2C^+HCH_3$), Ibrahim and Jorgensen[2] calculated a total stabilization of 14.8 kcal mol^{-1} at 6-31G(d) or 22.1 kcal mol^{-1} at MP2/6-31G(d), in good agreement with our value of 16.7 kcal mol^{-1} in this different system.

As seen from Table 2, these calculations indicate that the twist form of 2-silylcyclopentyl cation is more stable than the planar and envelope forms. Forsyth and co-workers[5] came to the same conclusion for the parent cyclopentyl cation on the basis of deuteriated studies of proton chemical shifts.

Little can be said by way of comparing these calculations with the solvolysis results,[3] although all trends are identical. The solvolysis data indicated that the average dihedral angle between the C–Si bond and the leaving group in *cis*-2-(trimethylsilyl)cyclopentyl trifluoroacetate is about 56°, which compares favourably to the 57° dihedral angle calculated herein between the C–Si bond and the empty p-orbital in pseudoequatorial, twist 2-silylcyclopentyl cation. Similarly, the average solvolytic dihedral angle of about 147° for *trans*-2-(trimethylsilyl)cyclopentyl trifluoroacetate compares with 165.9° (14.1°) calculated for pseudoaxial, twist 2-silylcyclopentyl cation (**7**). Although the trends are parallel, direct comparisons are inappropriate without knowledge of the location of the transition state in the solvolysis reaction.

Conclusions

ab initio Calculations at the 3-21G*//STO-3G level confirm conclusions about the hyperconjugative interaction between positive charge on carbon and a β C–Si bond in five-membered rings, based on solvolysis studies.[3] The twist form of the cyclopentyl cation was found to be slightly more stable than the planar and envelope forms, in agreement with conclusions based on NMR isotope shifts.[5] Introduction of the β-silyl group dramatically increases the stability, up to 15.8 kcal mol^{-1} when the silyl group is pseudoaxial. A smaller increase is imparted by a pseudoequatorial silyl group, because of less favourable overlap between the C–Si bond and the empty p-orbital. The molecule distorts so that the β-C–Si bond is better lined up with the p-orbital than is the geminal β-C–H bond. Other consequences of hyperconjugation include distortion of the $^+C_\alpha$–C_β–Si valence angle so that the Si atom is closer to the positive charge, and shortening of the C_α–C_β bond length. Analysis of the stabilization energies in terms of the Sunko–Hehre equation indicates that the maximum stabilization (*i.e.*, if the C–Si and p-orbitals were parallel) is 16.7 kcal mol^{-1}, of which 15.8 kcal mol^{-1} is hyperconjugative (angular dependent) and 0.9 kcal mol^{-1} is inductive (angular independent).

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