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A combined ab initio and gas-phase electron diffraction investigation of the molecular structure and conformation of (silylmethyl)cyclopropane[☆]

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Abstract

The molecular structure and conformational composition of (silylmethyl)cyclopropane (SMCP), $C_3H_5-CH_2-SiH_3$, with respect to the $C_{ring}-CH_2$ and the CH_2-Si axes have been studied by gas-phase electron diffraction and ab initio calculations using a 6-31G* basis set. The conformational analysis, with respect to the $C_{ring}-C$ bond, has shown that the gauche (skew) form is the predominant conformation (> 98%) in the gas phase. A reasonable explanation for the preference of the gauche conformation is provided by the $\sigma-\pi$ hyperconjugation effect. Repulsive through-space interactions are most probably responsible for the cis conformer, being higher in energy and thus less favorable. The major bond distances (r_a , $Å^{-1}$) and angles (°) for the skew conformer obtained from the least-squares refinements with uncertainties estimated at 3σ are r(C-H) = 1.120(4), $r(C_1-C_2)_{ring} = 1.510(10)$, $r(C_2-C_3)_{ring} = 1.490(12)$, $r(C_{ring}-C) = 1.540(10)$, r(Si-C) = 1.876(2); $\angle HSiC = 111.0(2.0)$, $\angle SiCC = 112.1(1.0)$, $\angle C-C(ring plane) = 122.7(0.5)$, and the dihedral torsional angle $\tau_{SiCCX} = 119.0(2.0)$ (X is the center of the ring).

1. Introduction

For more than two decades, we have been involved in investigating the effects of substituents in novel cyclic systems of small and medium size. The particular sensitivity of the electron density distribution in cyclopropane, and, consequently, the changes in its geometry upon substitution along with its relatively low strain energy within the series of saturated cycloalkanes, has been the focal point of numerous models and chemical investigations. In order to assess more fully the influence of electron donating or electron accepting groups on the exceptional electronic properties of cyclopropane, we have synthesized numerous representatives of the series $c-Pr-XY_3$ (X = Si, Ge and Y = H, F, Cl) [1,2] and investigated the bonding properties within these monosubstituted cyclopropanes utilizing electron diffraction [3–5], spectroscopic methods [6–9], and ab initio calculations [4,5]. In the course of systemization of effects of substituents, and in order to increase our understanding of the predicted ability of the unique cyclopropane system to act as a charge transmitter between attached substituents, we extended our investigations to a new series of cyclopropanes of

 $[\]stackrel{*}{\Rightarrow}$ This paper is dedicated to Professor Ken Hedberg, a most respected colleague, on his 75th birthday.

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the type $c-Pr-CH_2-XY_3$ (X = Si, Ge and Y = H, F).

The main objectives for synthesizing and studying the new series c-Pr-CH₂-XY₃ are to investigate whether electronic interaction between the XY_3 group and the cyclopropyl group occurs through the bonds or through space and to investigate the conformational stability of these molecules which possess two internal rotors. It is particularly interesting to obtain the structural data for all of the representatives of this series in order to elucidate the influence of the XY₃ group on the potential barriers for both internal rotations around the exocyclic C-C and C-X bonds. Moreover, the cyclopropylmethyl group is found to be a basic structural element in a wide range of naturally occuring compounds in plants and micro-organisms, e.g. in the side chain of petrosterol [10], which belongs to the group of marine sterols, or in the narcotic antagonist naltrexone [11]. It is generally accepted that the presence of the cyclopropylmethyl group in these compounds is responsible for their biological activity [12].

In this paper we will report on the first representative of the novel cyclopropylmethyl series, $c-Pr-CH_2-XY_3$, silylmethyl(cyclopropane) (SMCP).

2. Experimental

The sample of SMCP was prepared as follows. Allyl trichlorosilane was converted to the corresponding trimethoxysilane [13] and the cyclopropanation of this compound to cyclopropylmethyltrimethoxysilane (CPMTMS) was then performed using the Simmon-Smith procedure [14]. We, however, modified this reaction by applying the sonication technique (Bronson equipment, 50Hz, 250 W). The application of ultrasound irradiation promoted this reaction and yielded 72% of CPMTMS instead of 43% when the reaction was carried out under usual conditions. The treatment of CPMTMS with LiAlH₄ led to SMCP (b.p. 55-56°C at 715 Torr). Details of the preparation of the series $c-Pr-CH_2-R$ (R = SiH₃, SiF₃, GeH₃, C=C-H) are described elsewhere [15]. The purity of the sample was confirmed by gasphase IR, NMR spectra and mass spectrometry.

The gas-phase electron diffraction photographs were recorded on Kodak electron image plates using a Balzers KD-G2 diffractometer. Two sets of data were obtained at approximate camera distances of 25 and 50 cm, yielding a total intensity range s = 2-35 Å⁻¹. The sample was kept at -25° C and the inlet system and nozzle at 40° C. The accelerating voltage was 60 kV. The electron wavelength ($\lambda_{250} = 0.04882 \pm 0.00010$ Å, $\lambda_{500} =$ 0.04868 ± 0.00005 Å) was determined from ZnO diffraction patterns. Three plates from each camera distance were traced on our computer-controlled and modified ELSCAN, E-2500 (Optronics International, Chelmsford, MA, USA) [16] with data being recorded at intervals of 0.1 mm. Data reduction and least-squares refinements were carried out using our usual procedures which are described elsewhere [17,18]. The atomic scattering amplitudes and phases of Haase [19] were used.

3. Ab initio and vibrational calculations

The important role of the interplay of ab initio calculations and experimental methods with regard to reliable investigations of structure and molecular dynamics has been demonstrated repeatedly in numerous papers. Considering the complexity of the structural and conformational analyses of molecules of the cyclopropylmethyl-XY₃ type, and based upon the positive results gained from previous joint theory-experimental studies, we have utilized the guidance of theoretical calculations for the present investigation. Geometry optimizations and conformational analysis of SMCP were carried out at a 4-21G^{*} level [20] by standard ab initio gradient procedures [21,22] using the program BRABO [23] and at the 6-31G* level [24] using the program GAUSSIAN-86 [25]. Both basis sets have shown that the population of the near-gauche (skew) conformer with respect to the $C_{ring}-C_4$ axis is predominant. At the 4-21G* level of calculation, the skew form is more stable than the syn conformer by 1.97 kcal mol^{-1} and, at the 6-31G^{*} level, by 2.3 kcal mol^{-1} . Although, we consider the results obtained mainly from the 6-31G* basis set, it is nonetheless worth mentioning that the agreement between the predicted structural results provided by both basis sets applied in this study is very good. It is also worth noting that the bond distances for the cis and the gauche conformers produced by ab initio calculations at both $6-31G^*$ and $4-21G^*$ levels are essentially equivalent.

In order to obtain the vibrational mean-square amplitudes, a normal coordinate analysis at the 6-31G^{*} level was performed. For SMCP. 47 internal vibrational coordinates have to be defined. These are 15 bond stretch, 30 valence angle bending and two torsions about the Cring-C₄ and the C-Si bonds. However, this set of internal coordinates implies eight redundancies which must be accounted for. These are three ring redundancies [5] and each for the tetra-coordinated centers C_1 , C_2 , C_3 , C_4 and Si. The cartesian force field was transformed to the corresponding one in molecular symmetry coordinates as described by Zhao and Krimm [26]. In order to reproduce the vibrational frequencies properly, the scaling factors 0.9, 0.8 and 1.0 were used for

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the stretching, bending and torsional coordinates, respectively. The criteria for the selection of the scale factors was the agreement between experimental and calculated vibrational frequencies (deviation about 5%), as well as the values for the potential energy distribution (PED) [26].

4. Structural and conformational analysis

Most of the starting parameters have been adopted from the results provided by the ab initio calculations. In order to facilitate the analysis and limit the variable parameters to a reasonable number, the following constraints concerning the molecular model were introduced (for atomic numbering, see Figs. 1 and 2): (i) ring C_1-C_2 and C_1-C_3 bond lengths are equal; (ii) all C-H bond lengths are equal; (iii) all Si-H bond lengths are equal; (iv) all H-Si-C₄ angles are equal; (v) all ring H-C-H angles are equal; (vi) local C_{3v}



Fig. 1. Experimental (\triangle) and calculated (—) reduced molecular intensity s * M(s).



Fig. 2. Experimental (\triangle) and calculated (—) radial distribution curves for SMCP.

symmetry of the silyl group was assumed. In addition, several similar amplitudes were grouped together. Initially, a mixture of two conformers, the gauche and the cis forms, was used for the analysis and this was assumed to have the same structure except for the torsion angle of the CH₂SiH₃ group, τ_2 . Thus, with the aforementioned constraints and in addition to a composition parameter, the structure of SMCP can be described by a set of 18 geometrical parameters and 34 vibrational amplitudes. Several refinements of the structure were carried out for various assumed populations of gauche and cis conformations by applying a nonlinear least-squares procedure [27] based on the reduced scattering intensities.

The reduced molecular intensities s * M(s) for all plates at two camera distances and the corresponding radial distribution curves obtained from the final least-squares refinement are illustrated in Figs. 1 and 2. A comparison of the radial distribution functions in the region of the non-bonded distances (r > 2.1 Å) and values of the "R-factor" immediately confirmed the predominance of the

gauche (skew) conformer. This was particularly evident from comparison of the regions of the radial distribution function (RDF) where the non-bonded Si $C_{2,3}$ distances in both conformers are expected to occur. While the agreement between the experimental and calculated RDF in the area around 3.6 Å and 4.2 Å in the case of the pure gauche form is excellent, this agreement, however, gets worse when mixtures of gauche and cis conformers are fitted. On the basis of these results, the electron diffraction data cannot provide clear evidence for the presence of a cis conformer in addition to the gauche form. Nevertheless, the occurence up of to 5% of the cis rotamer cannot be excluded for definite.

The results we obtained from the structural and conformational analysis of SMCP are summarized in Table 1. It is interesting to note that a comparison between the experimentally determined and calculated values of the vibrational amplitudes (Table 2) shows that the latter are smaller by about 7-10% in the case of bonded distances, and up to 30% in the case of non-bonded distances.

Table 1 Comparison between optimized (6-31 G*) and experimental structural parameters of (silylmethyl)cyclopropane $(SMCP)^a$

Experimental ^b	Ab initio
1.510 (10)	1.499
1.490 (12)	1.500
1.540 (10)	1.520
1.876 (2)	1.895
1.470 ^c	1.478
1.120 (4)	1.076-1.089
111.0 (2.0)	110.3
112.1 (1.0)	113.5
122.7 (0.5)	126.3
115.7 ^c	114.1
106.7 ^c	106.0
117.0 ^c	114.0
172.0 (2.0)	177.4
119.0 (2.0)	119.9
	Experimental ^b 1.510 (10) 1.490 (12) 1.540 (10) 1.876 (2) 1.470 ^c 1.120 (4) 111.0 (2.0) 112.1 (1.0) 122.7 (0.5) 115.7 ^c 106.7 ^c 117.0 ^c 172.0 (2.0) 119.0 (2.0)

^a Almost exclusively the skew form (> 98%).

^b This work.

^c Not refined.

^d τ_1 , dihedral angel H₁₃-Si-C₄-C₁.

^e τ_2 , dihedral angel Si-C₄-C₁-X (X is the center of the ring). The uncertainty values in parentheses are 3σ .

Table 2

Comparison between a selection of experimental and calculated vibrational amplitudes for (silylmethyl)cyclopropane (skew form)

	Experimental	Ab initio ^a
For bonded distance	es (Å)	
$1(C_1 - C_2)$	0.054 (1)	0.050
$1(C_2 - C_3)$	0.054 (1)	0.050
$1(C_1 - C_4)$	0.056 (3)	0.050
$1(Si-C_4)$	0.060 (2)	0.053
1(Si-H)	0.095 ^b	0.088
1(C-H)	0.080 (2)	0.076
For non-bonded dis	stances (Å)	
$1(\mathbf{Si}\cdots\mathbf{C_1})$	0.089 (4)	0.090
$1(C_4 \cdots C_2)$	0.080 (3)	0.075
$1(\mathbf{Si}\cdots\mathbf{C}_2)$	0.117 (7)	0.080
$1(Si \cdots C_3)$	0.182 (10)	0.103
$1(Si \cdots H_9)$	0.160 (30)	0.120
$1(C_4 \cdots H_6)$	0.172 (50)	0.088
$1(C_1 \cdots H_9)$	0.110 (4)	0.105
$1(Si \cdots H_{11})$	0.293 (90)	0.152-0.177

^a 6-31G* basis set.

^b Assumed.

5. Results

5.1. Geometry of the silyl group

Because of correlation problems, it was necessary to fix the Si-H bond length to be 1.470 Å. The HSiC bond angle, however, was determined to be $111.0(2.0)^{\circ}$. This angle, assuming C_{3v} symmetry for the SiH₃ group, results in a HSiH angle of 108°, which is in good agreement with the corresponding values in methylsilane (108.7° [28]), vinylsilane (108.7° [29]), and cyclopropylsilane (107.9°0 [3]). The plausibility of this value is also supported by ab initio calculations which give a value of 108.4° for this angle. Moreover, the assumption of local C_{3v} symmetry for the silvl group is also supported by the ab initio calculations. There is no evidence either from the experiment or from the theoretical calculations for a tilt of the silyl group. This remarkable result is in contrast to that found in cyclopropylsilane. The experimentally determined Si-C bond distance of 1.876 Å parallels that found in allylsilane (1.875 Å [30,31]) and is slightly longer than in methylsilane (1.867 Å [28]) and ethylsilane (1.866 A [32]). However, this bond length is significantly longer than in the parent molecule cyclopropylsilane (1.840 Å [3]). The well known overestimation of the Si-C bond length by ab initio calculations, is also observable in the case of SMCP for which the value of 1.895 Å is calculated. This tendency, which to we previously alluded [3,5,33], is most likely the result of an underestimation of the contribution of the d-orbitals to bonding on silicon by the theory.

5.2. Geometry of the exocyclic methylene group

As can be seen from Table 1, the experimentally determined value for the HCH angle of the exocyclic methylene group of 107.0° agrees well with the predicted value by ab initio calculations of 106.0° . Similar excellent agreement between experiment and theoretical calculations is also present for the SiCC bond angle. Values of 112.0° and 113.5° were provided by experiment and theory, respectively, for this angle. It is noteworthy that the empirical linear relationship between the $H-C_{\alpha}-H$ and the $C-C_{\alpha}-C$ angles in acyclic methylene groups postulated by Mastryukov et al. [34] of the form $\angle(H-C_{\alpha}-C) = 126.1-0.175 + \angle(C-C_{\alpha}-C)$ is found to also be applicable to H-C-H and Si-C-C angles. Using the value obtained from electron diffraction for the SiCC angle, this equation provides 106.5° for the HCH angle which agrees very well with the experimentally determined value of 107.0°.

It is interesting to note that the structural results we obtained so far from our investigations of the c– $Pr-CH_2-XY_3$ series show the following general feature; the XY₃ group seems to govern the conformational behavior of these molecules but its influence on the geometry of the c- $Pr-CH_2$ moiety appears to be minor. Table 3 illustrates this finding by comparing ethylcyclopropane with SMCP. As can be seen, the structural parameters for the two molecules are very similar. Such a remarkable feature probably once again reflects the inferior role of through-bond interactions and the predominance of steric through-space effects within this type of molecules.

5.3. Geometry of the cyclopropyl ring

By analogy with previously investigated $c-Pr-XY_3$ homologues [3-5], the distal C-C bond is shorter (by 0.02 Å) than the vicinal C-C bonds. Nevertheless, it is likely that while through-bond

Table 3

Comparison between a selection of geometrical parameters (gauche structure) for ethylcyclopropane (ECP) and SMCP as obtained from ab initio calculations at the 4-21G* level

	ECP	SMCP
Bond distances (Å)		
1-2	1.4983	1.4976
2-3	1.4996	1.4996
1-4	1.5163	1.5223
Bond Angles (deg)		
1-4-5	112.47	113.10
4-1-6	114.36	114.40
11-4-12	106.63	106.10
4-(ring plane)	125.60	125.80
τ_2	119.90	118.30

electronic effects are responsible for this kind of disparity of the C-C bond lengths in the c-Pr- XY_3 compounds, steric through-space interactions give rise to this distortion in the case of SMCP.

5.4. Conformational stability of SMCP

SMCP may exist in various conformational forms. However, the predominance of one or the other possible conformer depends on the changes in the attractive and repulsive potential energies associated with the substituent group SiH₃. According to the results we obtained from vibrational [35] and the present electron diffraction studies, (silylmethyl)cyclopropane exists almost exclusively (> 98%) in the skew form. This unexpected finding allows for the conclusion that mainly the steric through-space interactions govern the structural and energetic properties of this molecule.

For a proper description of the internal motion of both the SiH₃ and CH₂SiH₃ rotors, we introduced the dihedral angles τ_1 and τ_2 . τ_1 is defined as the angle H_6SiCC (Fig. 1) and is 180° for H_6 in its staggered position to the ring. τ_2 is defined as the angle SiCCX (X is the center of the ring) and is 0° for the cis structure. The investigation of the conformational composition with respect to the C_{ring}- C_4 axis has revealed that the skew conformer is predominant and hence the most stable form for SMCP. Many attempts to reproduce the experimental intensity function using different conformers and different ratios between them have led to unreasonable results. Basically, from the energetic point of view, the most favorable position for the silvl group is the staggered one. The present study, however, has shown that the dihedral angle τ_1 deviates by about 8° from this position leading to a near-staggered arrangement of the SiH₃ group. Interestingly, ab initio calculations confirm this finding to a large extent (Table 1). The Newman presentation in Fig. 3 visualizes the conformation with respect to the Si–C₄ (τ_1) and $C_{ring}-C_4(\tau_2)$ axis in SMCP.

In order to obtain additional support for the relative stability of the skew-staggered conformation, we analyzed the potential energy surface with



Fig. 3. Newmann projections of possible conformations of SMCP: (a) with respect to the Si–C bond (silvl torsion) and (b) with respect to the C_1-C_4 bond (ring torsion).

respect to both torsional motions of the silvl (τ_1) and $CH_2SiH_3(\tau_2)$ groups using the option SCAN in GAUSSIAN-86. For this purpose, it is necessary to assume C_s local symmetry for the ring and the methylene groups, and C_{3v} symmetry for the SiH₃ group. Keeping these groups symmetrized, the silyl group was rotated between $\tau_1 = 120^\circ$ and -120° in 20° steps and simultaneously the ring torsion angle au_2 was varied between 0° and 180° in 15° intervals. The resulting potential surface from torsional these simultaneous motions is represented in Fig. 4.

From this potential surface, it is apparent that the skew-staggered ($\tau_2 = 120^\circ$ and $\tau_1 = 180^\circ$) conformation is the most stable form for SMCP. From this representation, it can also be derived that the anti conformer ($\tau_2 = 180^\circ$ and $\tau_1 = 180^\circ$) is unstable. It is most likely that the repulsive interactions between the ring hydrogens and those of the exocyclic methylene group are responsible for the unfavorable occurence of the anti conformer. The lower stability of the cis form ($\tau_2 = 0^\circ$ and $\tau_1 = 180^\circ$) may be attributed to the repulsion between silyl hydrogens and the ring hydrogens.



Fig. 4. Potential surface of SMCP with respect to the silyl and ring torsions evaluated from 6-31G* results. Position 2 in the surface represents the favourable gauche conformation and the positions 1 and 3 represent the unfavorable cis and trans forms, respectively.

Nevertheless, based on the ab initio results, a second energy minimum also exists on the potential surface ($\tau_2 = 2.6^\circ$) indicating that a near-syn conformer probably exists in a small proportion (about 5%). However, the determination of such a small population is beyond the resolution limit of the electron diffraction method. Again, it should be emphasized that all these conclusions are based on the symmetry assumptions previously mentioned for analyzing the potential surface. Thus, strictly speaking, it is not meaningful to discuss stabilizing or destabilizing effects of substituents from this potential surface representation and the geometries corresponding to the minima on this surface. Accordingly, the structure corresponding to the gauche position, as well as those at the gauche to gauche transition state (i.e. the anti form) and the cis to gauche transition state, were optimized by relaxation of all the geometric parameters. At the 6-31G* level of calculation, we obtained values of 2.27 and 3.23 kcal mol^{-1} for the cis to gauche and gauche to gauche potential barriers, respectively. It should be noted that our ab initio calculations at the 4-21G* level have revealed that in analogy to SMCP ethylcyclopropane exists almost exclusively (98.4%) in the gauche conformation [36]. This is in agreement with the experimental result provided by vibrational spectroscopy [37]. The barrier to internal rotation of the silvl group in the gauche conformer as obtained from ab initio calculations is 1.75 kcal mol⁻¹ and the energy minimum is at $\tau_1 = 177.4^\circ$. This value for the barrier of the silyl torsion agrees well with that value determined from vibrational spectroscopy [35] of 1.96 kcal mol^{-1} and is very close to the values 2.12 kcal mol⁻¹ [30], 1.98 kcal mol^{-1} [38,33] and 1.98 kcal mol^{-1} [6a] determined for allysilane, ethylsilane and cyclopropylsilane, respectively.

Two possible effects may be invoked for the rationalization of the preference of the gauche (skew) conformer in SMCP. The first is the "gauche effect" [39] which implies that energy minimum is reached when the difference in the changes of the attraction and repulsion terms $(\Delta V_{rep} - \Delta V_{att})$ has reached its maximum value. A second, and probably more reasonable, explanation is provided by the so-called $\sigma - \pi$

hyperconjugation [30,40-42]. This effect refers, in the case of SMCP, to the hyperconjugation between the σ -orbital of the Si–C bond and the 3é orbital of the ring. As demonstrated by Fig. 5, it is obvious that such an interaction is maximum when the σ -orbital of the Si–C bond is parallel to the 3é orbital of cyclopropane, when the bisector of the ring $C_2-C_1-C_3$ angle is perpendicular to the Si–C bond. The deviation of this angle from 90° $(\tau_2 = 119^\circ)$ is the result of steric repulsion between the ring and the silvl hydrogens (Fig. 6). It is noteworthy that no significant evidence (e.g. tilt of the SiH₃ group) has been obtained for a noticeable through-bond substituent interaction between the silyl group and the cyclopropyl system. Moreover, the whole geometry and conformational behavior of SMCP seems to be almost exclusively governed by through-space (i.e. mainly repulsive steric) interactions.

It is worth noting that the conformational behavior of various (halomethyl) cyclopropanes [43-49] and (cyanomethyl) cyclopropane [50,51] has been analyzed using either spectroscopic methods [44-51] or the electron diffraction technique [52]. These studies have revealed that all these molecules show a strong tendency towards the gauche conformation. Such a trend has been rationalized on the basis of increasing steric crowding as a result of the increase of the size of the substituent residing above the ring plane in the



Fig. 5. Illustration of the hyperconjugation effect in SMCP.



Fig. 6. Visualization of (a) the presence of steric conflict when the torsional angle $\tau_2 = 90^\circ$ and (b) the minimization of the repulsive interactions in the case of the gauche conformation, $\tau_2 = 120^\circ$.

case of the cis conformation. This means that there are apparently no electronic interactions in these molecules which would tend to stabilize the cis form. However, we believe that such an explanation for the occurence of the cis form in these conformational equilibria should be considered with some reservation. This is because, depending on the electronic properties of the substituent, steric interactions might be repulsive but attractive as well [53-57]. Therefore, the increase of the steric attractive interactions between the substituent and the surface orbitals of the ring leads consequently to a larger preference for the cis conformation. This type of rationalization is supported to some extent by the increasing stability of the cis rotamer upon moving from iodo- [49] to bromo- [48], chloro- [45], cyano- [50] ethynyl-methylcyclopropane and [58]. The abundance of the cis form within this series is 0, 2, 5, 13 and 26%, respectively. Interestingly, this trend parallels the increase of the electronegativity of the substituents considered in this series. The values for the electronegativity of I, Br, Cl, $C \equiv N$ and $C \equiv CH$ are 2.47 [59], 2.81 [59], 3.07 [59], 3.46 [60] and 3.10 [60], respectively. In the case of the ethynyl group, the contribution attributed to the electronegativity effect is probably superimposed by attractive interactions between the ethynyl hydrogen and the ring surface orbitals leading to an additional stabilization of the cis conformer.

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