ether-linked phospholipids compared to their diacyl phospholipid counterparts.

The differences in the predominant conformational states in each choline glycerophospholipid subclass are further exemplified by analysis of the distribution of conformational states (gauche and antiperiplanar) about the C_3–O_{31} bond (see Figure 1) from the calculated coupling constants of phosphorous and the sn-3 glycerol methylene protons. Although the antiperiplanar conformation is the major conformation in all three choline glycerophospholipid subclasses, differences exist between the relative distribution of gauche and antiperiplanar conformations in each subclass. For example, the fractional percentage of the gauche rotamer in phosphatidylcholine is nearly 50% larger than that present in plasmanylcholine (Table II).

While the distribution of individual conformational states in phospholipids in a micellar aggregation state are likely different from those present in membrane bilayers, the present results clearly indicate that differences in the population distribution of the individual rotamers in each subclass of choline glycerophospholipids are present in at least some organized states. Given the multiplicity of rotameric states in phospholipids (i.e., rotamers of the C_1–C_2 and C_3–O_{31} bonds as well as rotamers of the proximal regions in the aliphatic chains) and the likelihood that specific mosaics of total conformational states selectively and differentially interact with complimentary regions of polypeptides, it is tempting to speculate that alterations in the rotameric distribution of phospholipids in mammalian membranes contribute to the marked subclass selectivity of phospholipases that selectively catalyze hydrolysis of ether-linked phospholipid substrates.[26-29]

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Experimental and Theoretical Investigation of the Molecular Structure of Cyclopropylgermane

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Abstract: In this work the gas-phase molecular structure of cyclopropylgermane (CPG) has been investigated by electron diffraction and ab initio molecular orbital calculations. The geometry optimization has been performed with use of the basis sets 3-21G*, 4-21G*, and STO-3G. The ring parameters (r_a values with 3σ uncertainties) derived from the electron diffraction study are the following: $r(C_1–C_2) = 1.521$ (7) Å, $r(C_2–C_3) = 1.502$ (9) Å, $r(C–H) = 1.091$ (3) Å, and $\angle H–C–H = 118.2$ (2.3)°. Other parameters are $r(Ge–C) = 1.924$ (2) Å, $\angle C_1–Ge–H_6 = 108.8$ (1.2)°, $\angle C_1$–Ge–ring plane = 55.5 (1.6)°, $\angle C_1–H_5$–ring plane = 57.3 (1.9)°. Furthermore, both the experimental and the theoretical studies have revealed that the GeH_3 group is tilted toward the ring plane. The values for this tilt angle obtained from electron diffraction and from calculations are 3.4 (2.0)° and 2.1° (when the 4-21G* basis set is used), respectively. This tilt has been rationalized to be the result of hyperconjugative interaction. The geometric parameters of cyclopropylmonofluorogermane, cyclopropyldifluorogermane, and cyclopropyltrifluorogermane also have been optimized. The progressive shortening of the Ge–F bond with increasing fluorination is interpreted as being the consequence of a fluorine negative hyperconjugation effect. The barrier heights for internal rotation for the GeH_3 and SiH_3 groups and their fluorinated counterparts in various compounds have been calculated. Furthermore, the structural results obtained assess the strong π-donor character of the cyclopropyl system and demonstrate that π-acceptor ability of the germyl group is less pronounced than that of the silyl group.

Introduction

Several complementary concepts[1-6] have been evaluated in order to characterize the versatile bonding behavior and the intrinsic nature of electronic interaction between a vast array of charge-withdrawing or -donating substituents and the strained ring fragment as a pseudo-π system.

Until recently only one representative of the series c-Pr-XH_3 (X = group IV element), methylcyclopropane, had been studied. This was the initial reason for synthesizing the cyclopropane series C_3H_5–XY_3 (X = Si, Ge; Y = H, F, Cl)[7,8] and for starting to explore the bonding properties and stabilizing effects of these monosubstituted ring systems by means of electron diffraction[9] and spectroscopic methods.[10,11] The exceptional electronic

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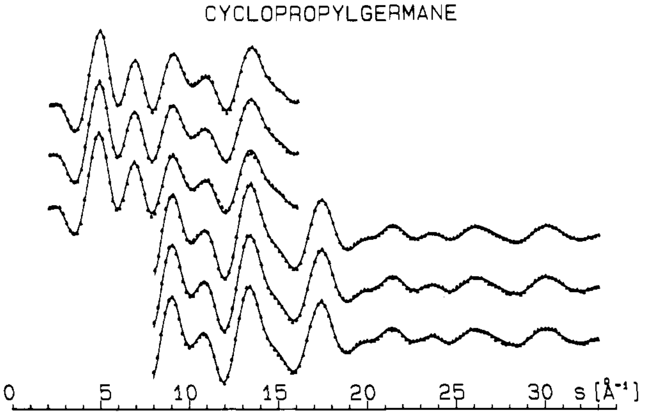

Figure 1. Experimental (▲) and calculated (—) modified molecular intensities, sM (s).

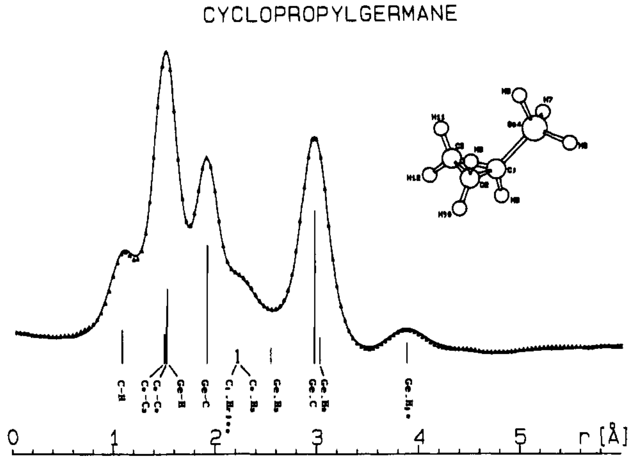

Figure 2. Experimental (▲) and calculated (—) radial distribution curves for CPG.

properties of cyclopropane within the series of cyclic hydrocarbons are based on the particular sensitivity of this molecular system as a "detector" for possible interaction with attached substituents. This distinct peculiarity has drawn our attention and has encouraged us to intensify our previous efforts in order to obtain additional support for the systemization of the type and nature of the effects of substituents on cyclopropane. One further aspect that has stimulated the study of cyclopropylgermane (CPG) has been the investigation of if and to what extent the germyl group in CPG is capable of undergoing a hyperconjugative interaction in a similar manner to that long-recognized in methyl[12] and trifluoromethyl[13] groups.

Experimental Section

The sample of CPG was prepared by the treatment of cyclopropyllithium with $GeCl_4$ to obtain trichloro(cyclopropyl)germane. The intermediate compound was then reduced with $LiAlH_4$ to give cyclopropylgermane (bp 44.0 °C at 760 Torr). The sample was purified by rectification, and the purity was checked by mass and infrared spectroscopy. Details of the preparation and purification are given elsewhere.[8]

The gas electron diffraction intensities of CPG were recorded at the University of Tübingen with use of Balzers KD-G2 diffractometer. The acceleration voltage was 60 keV, and the recording temperature was 20 °C. Kodak electron image plates were used, and the optical density values were recorded on a modified ELSCAN·2500 microdensitometer[14] with use of a step width (Δr) of 0.1 mm. The electron wavelength was calibrated with the ZnO diffraction pattern. Two sets of data were obtained at camera distances of 50 and 25 cm (nominal), yielding molecular intensity values at intervals (Δs) of 0.2 ranging from s = 2 to 16 Å^{-1} and from s = 8 to 33 Å^{-1}, respectively. Our usual data reduction and refinement procedures were applied;[15,16] the atomic scattering amplitudes and phases of Haase[17] were used.

Computational Procedures. The geometry of CPG was optimized following standard procedures.[18,19] In order to check the basis set dependence of the calculated structural parameters the following split-valence basis sets on carbon were used: 4-21G(4-21G*),[20] 3-21G(3-21G*).[21] The split-valence d-polarized 3-21G*[22,23] basis set was used on the germanium atom. One further ab initio geometry refinement was performed by applying the minimal basis set STO-3G.[24]

Table I. Structural Parameters for Cyclopropylgermane Obtained from Electron Diffraction Analysis

(a) Interatomic Distances (r_a Values) and Mean-Square Amplitudes (Å)			
C1–C2	1.521 (7)	0.054 (9)	
C2–C3	1.502 (9)	0.053[a]	
C–Ge	1.924 (2)	0.052 (1)	
Ge–H	1.530[a]	0.097 (4)	
C–H	1.091 (3)	0.086 (3)	
(b) Bond Angles (deg)			
C–Ge–H_6	108.8 (1.2)	Θ[e]	30.0[a]
C–Ge–$H_{7,8}$	113.9[b]	τ[f]	3.4 (2.0)
H–C–H	118.2 (2.3)	R_{500}[g]	0.043
α[c]	55.5 (1.6)	R_{250}[g]	0.058
η[d]	57.3 (1.9)		
(c) Dependent Interatomic Distances (Å) and Mean-Square Amplitudes (Å)			
$C_2 \cdots Ge$	2.983 (21)	0.078 (2)	
$C_2 \cdots H_5$	2.251 (18)		
$C_2 \cdots H_6$	3.193 (22)		
$C_2 \cdots H_7$	4.184 (16)	0.160 (33)	
$C_2 \cdots H_8$	3.706 (20)		
$C_1 \cdots H_9$	2.230 (12)		
$C_1 \cdots H_7$	2.847 (18)	0.073 (46)	
$C_3 \cdots H_9$	2.214 (10)		
$Ge \cdots H_5$	2.553 (12)	0.113 (18)	
$Ge \cdots H_9$	3.033 (26)	0.169 (29)	
$Ge \cdots H_{10}$	3.891 (10)	0.124 (14)	
$H_6 \cdots H_7$	2.508 (18)		
$H_7 \cdots H_9$	4.406 (26)		
$H_7 \cdots H_{10}$	5.054 (24)		
$H_6 \cdots H_{12}$	4.398 (20)		
$H_9 \cdots H_{12}$	3.101 (12)		
$H_9 \cdots H_{11}$	2.472 (12)		

[a] Not refined parameters. [b] Calculated from the angles C–Ge–H_6 and τ. [c] α is the angle between the Ge–C bond and the ring plane. [d] η is the angle between the C_1–H_5 and the ring plane. [e] Θ is the angle between the C_2–C_3 bond and the H_9–C_2–H_{10} plane. [f] τ is the tilt angle of the germyl group. [g] *R* is the agreement factor. Quoted errors (in parentheses) are 3σ values.

Results and Discussion

Electron Diffraction. The preliminary values for the geometric parameters were refined by least-squares analysis based on the molecular intensities shown in Figure 1. Due to resolution problems resulting from contributions of close parameters, the following assumptions were made (for numbering of atoms see Figure 2): (i) all C–H distances are equal; (ii) all Ge–H bond lengths and H–Ge–H bond angles are equal (local C_{3v} symmetry); (iii) because of the expected correlation between the parameters under the peak ranging from 1.2 to 1.6 Å in the radial distribution function, the Ge–H bond distance was fixed at the value indicated

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Table II. Optimized Geometry for Cyclopropylgermane

	4-21G/(3-21G*)[a]	4-21G*/(3-21G*)[a]	STO-3G[b]
	Bond Distances[c]		
1–2	1.5253	1.5059	1.5098
2–3	1.5086	1.4905	1.4982
1–4	1.9227	1.8947	1.8983
4–6	1.5462	1.5466	1.4335
4–7	1.5458	1.5467	1.4342
1–5	1.0734	1.0787	1.0811
2–9	1.0719	1.0781	1.0808
2–10	1.0712	1.0771	1.0811
	Bond Angles[d]		
τ[e]	2.12	2.15	0.2
3–1–2	59.38	59.32	60.2
3–2–1	60.36	60.34	60.2
1–4–6	108.28	108.47	108.96
1–4–7	111.46	111.69	109.59
5–1–4	115.48	115.75	114.63
9–2–10	114.40	114.23	113.30

[a] Basis set for Ge: refs 22 and 23. [b] Using GAUSSIAN 86 (GAUSSIAN, Inc, Pittsburgh, PA). [c] In angstroms. [d] In degrees. [e] Tilt angle of the GeH_3 group (see Table I).

in Table I. It is worth mentioning that several structural refinements were carried out with use of different fixed values for the Ge–H bond length ranging from 1.520 to 1.560 Å. The resulting agreement factors took up the smallest values at a Ge–H bond length of 1.530 Å. It is of particular interest to note that in a very recent MW study[25] the Ge–H_6 and Ge–$H_{7,8}$ bond distances (for numbering of atoms see Figure 2) have been determined to be 1.5380 (6) and 1.5306 (3) Å, respectively. Taking into account that the electron diffraction method is unable to resolve the disparity between these bonds, the unrefined value of 1.530 Å appears to be reasonable. Moreover, as it will be shown later in this work, this value has also been substantiated by ab initio calculations. With these constraints nine geometric parameters and ten vibrational amplitudes were refined simultaneously. A nonlinear least-squares procedure developed by Marquardt[26] was used to perform the refinements of the structural parameters on the basis of the molecular intensities. The radial distribution curves resulting from this analysis are shown in Figure 2.

The final results obtained from the least-squares analysis of the electron diffraction data are listed in Table I. As is apparent, the most intriguing and perhaps most informative structural features are as follows: First we have the observed difference between the C–C bond lengths in CPG as 0.019 Å. This value agrees very well with that obtained from MW spectroscopy (0.017 Å).[25] Second we have the tilt angle τ of the germyl group of 3.4°, which also agrees well with the MW value[25] of 3.67° (this tilt is positive and means that the GeH_3 group is tilted toward the ring plane). Third we have the short C–H bond and the relatively large H–C–H angle compared to the same parameters in other cyclopropanes. These structural features of CPG will be discussed below in more detail in the context of the discussion of the calculated geometry of this molecule.

Ab Initio Calculations. On several occasions[27-29] we have alluded to the advantages of joint theoretical and experimental investigations, particularly in those cases where experimental ambiguities or correlations between observables (e.g. geometric parameters) are expected. This clarifying role of theoretical calculations was also evident in the case of CPG. The most important structural parameters obtained from the ab initio calculations are displayed in Table II. Taking into consideration that the calculated values represent an equilibrium geometry, inspection of the results shown in Table II reveals that the agreement between the calculated bond distances and bond angles produced by the basis set augmented by d-polarization functions, 4-21G*(C)/3-21g*(Ge), and the experimentally determined ones (Table I) is fairly good.

It is worthwhile to mention that the introduction of empirical corrections, termed "offset values", which adjust theoretically optimized geometries to related experimental values has proved to be useful.[30] Since the accurate experimental value for the Ge–H bond length in germane of 1.5253 Å is available,[31] we optimized the geometry of germane using the basis set 3-21G*[22,23] and STO-3G. The values for the Ge–H bond distance produced by these calculations are 1.5392 and 1.4313 Å, respectively. The calculations using the 3-21G* basis set overestimate the Ge–H bond in CPG by about 0.012 Å and in germane by 0.014 Å. The application of minimal basis set STO-3G, however, underestimates this bond by 0.092 and 0.094 Å in CPG and germane, respectively. While this discrepancy is to some extent tolerable in the case of the split-valence basis sets, in the case of the minimal basis set STO-3G this difference is not acceptable. The differences (Δ) between the calculated and experimentally determined values for the Ge–H bond lengths for germane of 0.014 Å in the case of the 3-21G* basis set and of –0.094 Å when the basis set STO-3G is used represent the so-called "systematic correction" or "offset values" for the Ge–H bond distance. These are obviously only related to those basis sets used above.

The incorporation of these systematic corrections for the calculated values for the Ge–H bond distance in cyclopropylgermane yields 1.532 Å for the overestimated value produced by the 3-21G* basis set and 1.527 Å for the underestimated value obtained from the minimal basis set STO-3G. It is worthwhile to mention that the "corrected" value for the Ge–H bond length in the case of the 3-21G* basis set supports the assumption made for this bond distance in the electron diffraction investigation (Table I).

Structural Analysis. It is interesting to note that the influence of the germyl group on the ring C–C bond distances is less pronounced than that produced by the silyl group. Whereas the difference between the distal and the vicinal bond lengths in CPS as obtained from experiment is about 0.038 Å[9] and that from calculations is 0.022 Å,[32] in CPG it is only 0.019 and 0.012 Å, respectively. The remarkably large difference between the C–C bonds in CPS was rationalized[9] in terms of the Hoffmann predictions[2] and is mainly a result of a transfer of electron density from the 3e orbitals of the ring to the 3d orbitals of the silicon atom. It has long been recognized[33] that the cyclopropyl group is a fairly strong π-donor and is stabilized by π-acceptors. On the other hand, it has also been accepted that silyl and germyl groups are σ-electron donors and π-electron acceptors. Inspection of the C–C bond distances in both CPS and CPG reveals that the π-acceptor character is significantly more pronounced in the silyl group than in the germyl group. In this context it can be concluded that the germyl group is mainly a σ-electron donor and a weak π-electron acceptor, if anything. The destabilization of the vicinal ring C–C bonds and the almost nonvariance of the distal bond in comparison to the C–C bond in the parent molecule of 1.509 Å[34] are clearly indicative of this conclusion.

A plausible alternative interpretation of the aforementioned bonding features is provided by the concept of surface or σ-electron delocalization (σ-aromaticity) initiated by Dewar[35] and developed by Cremer and co-workers.[36] According to this model of σ-

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Table III. Mulliken Population Analysis (Charge Distribution on Atoms) in Methylcyclopropane (MCP), Cyclopropylsilane (CPS), and Cyclopropylgermane (CPG)

atom	MCP	CPS[a]	CPS[b]	CPS[c]	CPG[a]
C_1	–0.280	–0.606	–0.418	–0.62	–0.708
$C_{2,3}$	–0.406	–0.410	–0.252	–0.34	–0.401
C, Si, Ge	–0.546	0.793	0.784	1.03	1.042
H_5	0.209	0.228	0.146	0.19	0.232
H_6	0.190	–0.159	–0.190	–0.22	–0.215
$H_{7,8}$	0.197	–0.155	–0.179	–0.22	–0.209
$H_{9,11}$	0.211	0.217	0.136	0.18	0.214
$H_{10,12}$	0.212	0.221	0.134	0.19	0.220

[a] This work, 3-21G* basis set was used. [b] This work, 6-31G** basis set was used. [c] Reference 37.

electron delocalization, atoms of substituents of the type XY_3 (e.g. CH_3, SiH_3, GeH_3, or their fluorinated analogues) residing above the ring plane distort the electron density of the surface orbitals. Most likely, this so called "secondary effect" is also responsible for the disparity of the X–Y bond lengths within the XY_3 substituent groups on cyclopropane. One other probable explanation for the distortion of the C_{3v} symmetry of these groups and simultaneously for their subsequent tilt is the occurrence of hyperconjugation (or negative hyperconjugation in the case of XF_3 substitution). Although the effects of hyperconjugation on the energetic stability of the remainder of the molecule are seemingly much less pronounced in Si and Ge compounds than in the carbon analogues, the observed tilt of the SiH_3 and GeH_3 groups in CPS and CPG, however, may be interpreted as indicating a hyperconjugative interaction in these molecules. Magnusson[13] has pointed out that it is mainly the magnitude of the tilt of the CH_3 or CF_3 axis that is an indicator for the contribution of a hyperconjugative interaction between these groups and groups or atoms with orbitals of the appropriate symmetry.

Mulliken Charge Distribution. The charge distribution on atoms in CPS, CPG, and methylcyclopropane (MCP) is compared in Table III. Taking the values produced by the 3-21G* basis set into account, the net charge of the silyl and germyl groups is 0.32 and 0.40 au, respectively. This indicates in a qualitative manner that the flow of charges from the substituent group into the ring is slightly higher in CPG than in CPS. This, however, appears to be to some extent questionable if we take into consideration that the electronegativities of the germyl and the silyl groups are 2.05[38] and 1.91,[38] respectively. The main criticism directed against the Mulliken population analysis is that the partitioning of overlap population is arbitrary. Therefore, a significant dependence on the basis set used is the result.[39] This tendency is clearly apparent if the charge distribution values obtained for CPS, by applying the basis sets 3-21G*, are compared with those provided by the 6-31G* (Table III). Now if we correlate the Ge–C bond lengths in methylgermane (1.945 Å),[40] vinylgermane (1.926 Å),[41] and CPG (1.924 Å) with the corresponding electronegativities of the methyl (2.56),[38] vinyl (2.78),[42] and cyclopropyl (2.49)[42] groups, we notice that there is no certain systematic behavior between those values. Thus, this emphasizes once more that electronegativity arguments play an inferior role in the explanation of the electronic effect of the substituent group in CPG. Moreover, it is most likely that the shortening of the bond between the ring carbon and the central atom of the substituent group and the changes of the C–C bond lengths of the ring in CPG are attributed to the hyperconjugation effect. This kind of rationalization of bonding properties in CPG is supported by the occurrence of the positive tilt of the substituent group.

Table IV. Calculated[a] and Experimentally Determined Barrier Heights (kcal·mol^{-1}) for Internal Rotation of Methyl, Silyl, and Germyl Groups

	CH_3–MX_3		CH_2=CH–MX_3		c-Pr–MX_3	
MX_3	exp	calc	exp	calc	exp	calc
–CH_3	2.88[b]	3.04[a]	1.99[c]	2.02[a]	3.03[d]	3.02[a]
–SiH_3	1.69[e]	1.56[a]	1.50[f]	1.64[a]	1.98[g]	1.78[a]
–GeH_3	1.24[h]	1.16[a]	1.24[i]	1.44[a]	1.36[j]	1.37[a]

[a] 3-21G* basis set used: this work. [b] Reference 43. [c] Reference 44. [d] Reference 45. [e] Reference 46. [f] Reference 47. [g] Reference 10a. [h] Reference 40. [i] Reference 41. [j] Reference 10b.

Table V. C–Ge Bond Distance (Å) and Barrier Heights (kcal·mol^{-1}) for Internal Rotation in Some Germanes of the Type R–GeH_3

	C–Ge		V_3	
R	exp	calc	exp	calc
CH_3–	1.945[a]	1.935[b]	1.24[a]	1.16[b]
CH_2=CH–	1.926[c]	1.903[b]	1.24[c]	1.44[b]
c-Pr–	1.924[d]	1.894[b]	1.36[e]	1.37[b]

[a] Reference 40. [b] This work, 3-21G* basis set used. [c] Reference 41. [d] This work. [e] Reference 10a.

Table VI. Experimental C–X Bond Distance (Å) and Barrier for Internal Rotation (kcal·mol^{-1}) in Cyclopropanes of the Type C_3H_5–XH_3

–XH_3	C–X	V_3
–CH_3	1.517[a]	3.03[b]
–SiH_3	1.840[c]	1.98[d]
–GeH_3	1.924[e]	1.36[f]

[a] Reference 48. [b] Reference 45. [c] Reference 9. [d] Reference 10a. [e] This work. [f] Reference 10b.

Calculated Potential Barriers. Another interesting feature found in the present study is the variation in the barrier for internal rotation in various methyl, silyl, and germyl compounds (Table IV). The agreement between calculated and experimentally determined values for the barrier heights for the internal rotation of the XY_3 group is in most cases very good (Table IV), particularly for CPG.

It is also to some extent remarkable that the barrier for the internal rotation of the germyl group in CPG is only 0.12 kcal·mol^{-1} higher than the same barrier in vinylgermane. In the case of the silyl counterpart, however, this difference is higher, 0.48 kcal·mol^{-1}.

As might be expected, the rotational barrier decreases constantly as the bond lengths increase due to the reduction of the steric repulsion upon proceeding from methyl to germyl compounds. This trend, as Table IV shows, is well reproduced in both experiment and calculations. In order to understand the origin of these trends, particularly within the germane series, the calculated and experimental values of the bond distances and the rotational barriers of methyl-, vinyl-, and cyclopropylgermane are given in Table V. These values confirm the obvious decrease of the rotational barriers as a consequence of the lengthening of the Ge–C bond. Furthermore, as is evident from Table VI, the experimental values for the C–X bond distances and those for the rotational barriers in the listed cyclopropane series indicate the same tendency. It is noteworthy that the noninclusion of d-functions in the basis sets for the second- and third-row elements (here Si and Ge) often leads to unreasonable barrier heights for rotors; e.g. optimization at the STO-3G level provided a rotational barrier for the methylsilane rotor of 1.3 kcal·mol^{-1}.[49] Even more drastic

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Table VII. Optimized Structural Parameters for Cyclopropyltrifluorogermane (CPTFG) and Cyclopropylgermane (CPG)

atom nos.	CPTFG[a]	CPG[a]
	Bond Distances (Å)	
1-2	1.5064	1.5013
2-3	1.4833	1.4887
1-4	1.8756	1.9070
4-6	1.6305	1.5369
4-7	1.6284	1.5367
1-5	1.0830	1.0852
2-9	1.0831	1.0841
2-10	1.0819	1.0831
	Bond Angles (deg)	
τ^b	4.88	1.79
3-1-2	58.99	59.45
3-2-1	60.50	60.27
1-4-6	107.78	108.48
1-4-7	115.11	111.13
5-1-4	118.04	115.21
9-2-10	115.05	114.28

[a] 3-21G* basis set used. [b] Tilt angle of the substituent group.

Table VIII. Calculated[a] Bond Distances (Å) for Progressively Fluorinated CPG

substituent	C_1–C_2	C_2–C_3	Ge–C	Ge–F
$-GeH_2F$	1.5026	1.4873	1.9008	1.6431
$-GeHF_2$	1.5043	1.4846	1.8877	1.6356
$-GeF_3$	1.5064	1.4833	1.8756	1.6305

[a] For uniformity all of the data are calculated at the 3-21G* level.

is the discrepancy between the calculated[50] values for the barrier height of the SiH_3 rotor in vinylsilane provided by the basis sets 6-31G* and STO-3G* of 1.65 and 0.75 kcal·mol^{-1}, respectively. One further example in this respect is the value for the rotational barrier for the germyl group in vinylgermane. In this case the barrier heights[50] calculated with use of the basis sets 3-21G* and STO-3G* were 1.44 and 0.64 kcal·mol^{-1}, respectively. These examples emphasize the previously recognized dependence of the optimized rotational barriers on the basis set used.[49]

GeF_3 Negative Hyperconjugation. Now let us turn our attention to the optimized geometry of cyclopropyltrifluorogermane (CPTFG) given in Table VII. As can be inferred by inspection of this table, the Ge–C bond in CPTFG decreases in comparison to the same bond in the nonfluorinated counterpart. This contraction of the Ge–C bond as a result of the substitution of the hydrogen atoms for fluorine is in agreement with the long-recognized trend in organogermanium compounds.[51] Either electrostatic arguments, i.e. attractive polar interaction of the type $C^{-\sigma}$–$Ge^{+\sigma}$ or the increase in the s character of the Ge–C bond as a result of isovalent rehybridization,[51-54] may be invoked in order to elucidate the migration of the Ge–C bond upon fluorination of Ge. The comparison between the calculated values for the vicinal and distal ring C–C bond distances reveals that only the latter are slightly affected by the replacement of the GeF_3 for the GeH_3 group. This small effect is somewhat surprising because the electronegativity difference between the cyclopropyl group (2.49 au)[42] and those of the substituents GeH_3 (2.05 au)[55] and GeF_3 (3.20 au)[55] is considerable.

One further interesting finding in the structural results of CPTFG is the short Ge–F bonds as compared to the same bond in cyclopropylmonofluorogermane (Table VIII). Basically, the decrease of the Ge–F bond length may be rationalized by using the aforementioned electrostatic arguments that have been invoked to explain the Ge–C bond shortening. An alternative and perhaps more reliable reasoning for both the Ge–C and Ge–F bond contraction in fluorinated organogermanium hydrides might be a negative (anionic) hyperconjugative interaction released by the GeF_3 group. In order to obtain additional support for such a conclusion we optimized the molecular geometries of cyclopropylmonofluorogermane, cyclopropyldifluorogermane, and CPTFG. The progressive shortening of both the Ge–F and Ge–C bonds upon moving from the monofluorinated to the trifluorinated derivative are clearly indicative of an anionic hyperconjugative interaction of the Ge–F bond. This resulting effect in CPTFG which involves orbital interactions (back-donation of π-type lone pair electrons from fluorine into antibonding σ^*X-F orbital)[56-60] is illustrated in Scheme I.

Scheme I

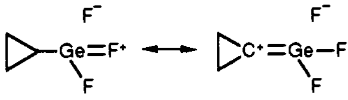

Table IX. Calculated[a] Ge–F and Ge–H Bond Distances (Å) for Progressively Fluorinated Germane

	Ge–F	Ge–H
$FGeH_3$	1.633	1.528
F_2GeH_2	1.628	1.518
F_3GeH	1.622	1.499
F_4Ge	1.614	

[a] 3-21G* basis set was used (refs 22 and 23).

Table X. Calculated[a] C–Ge Bond Distance (Å) and Barrier Heights (kcal·mol^{-1}) for Internal Rotation for Some Germanes and Their Fluorinated Counterparts

	C–Ge	V_3
CH_3–GeH_3	1.935	1.16
CH_3–GeF_3	1.900	0.59
c-Pr–GeH_3	1.907	1.37
c-Pr–GeF_3	1.875	1.18

[a] 3-21G* basis set used.

As is apparent from Table IX this progressive shortening of the Ge–F bond with increasing fluorine substitution for hydrogen as a consequence of negative hyperconjugative effect seems to be rather more pronounced upon going from GeH_3F to GeF_4 (the overall effect here is ca. 0.02 Å). Interestingly, the Ge–H bond in this series indicates the same tendency of bond strengthening with each additional substitution of F for H. It is also worthwhile to mention that the F–Ge–F bond angle in F_2GeH_2 (104.9°) and in F_3GeH (106.5°) deviates significantly from the tetrahedral value. This remarkable feature which parallels the tendency found in the analogous fluorinated methane and silane[56] has been rationalized in terms of angular dependence of negative hyperconjugation.

Replacement of GeF_3 for GeH_3 on the Potential Barrier about the C–Ge Bond. One further, and perhaps most striking, effect resulting from the GeH_3/GeF_3 substitution is the reduction of rotational barrier about the Ge–C axial bond. The calculated barrier heights for internal rotation in methyltrifluorogermane and CPTFG on one side and those of their parent molecules on the other hand in addition to the corresponding axial bond distances are shown in Table X. Inspection of the data presented in this table indicates that the potential barrier decreases upon fluorination of the germyl group and consequently as the axial

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Table XI. Calculated Tilt Angle τ (deg) of the Substituent R and the Electronegativity χ in some Cyclopropanes of the Type C_3H_5-R

R	χ^a	τ^b
$-CH_3$	2.17	0.20
$-SiH_3$	2.04	1.70
$-GeH_3$	2.06	1.77
$-CF_3$	3.46	0.45
$-SiF_3$	3.14	3.75
$-GeF_3$	3.20	4.88

[a] For the purpose of consistency and in order to avoid scaling problems of electronegativity values originating from different methods, all χ values are taken from ref 55. [b] 3-21G* basis set used.

bond distance shortens. It is of particular interest to mention that such a trend of simultaneous reduction of the axial bond length and potential barrier about this bond has been experimentally observed upon proceeding from CH_3–SiH_3 to CH_3–SiH_2F[61] and from CH_3–GeH_3 to CH_3–GeH_2F.[62] This feature, however, is in contrast to the aforementioned obvious increase of the rotational barriers associated about the Ge–C bond in various nonfluorinated species (Table IV) along with the decrease of the axial bond length. Table X also indicates that while the Ge–C bond shortening upon fluorination within the methyl and cyclopropyl systems is almost the same, the reduction of the rotational barrier is less pronounced in the cyclopropane species than in the methyl ones. This might be interpreted as a result of a compensation effect attributed to the through-space interaction (secondary effect) alluded to previously.

Tilt of the XY_3 Group. According to the results obtained in this study it appears that there is a qualitative simple relationship between the tilt angle of the substituent groups in CPG and CPTFG and the electronegativity of these groups. In a subsequent investigation[32] on a variety of monosubstituted cyclopropanes and their fluorinated homologues of the type discussed here (c-Pr-XY_3), additional support was obtained which confirms this correlation. The data given in Table XI indicate that the tilt angle of the substituent group toward the ring increases upon fluorination and thus the higher the electronegativity of this group is. This tendency may be interpreted as a consequence of through-space interaction between the atom Y above the ring plane and the surface orbitals in the ring. The delocalization of σ-electrons in the surface of the cyclopropyl system (σ aromatic) is apparently more affected by the XF_3 moiety than by its nonfluorinated counterpart. The tilt of the XY_3 group within the series shown in Table XI may also be rationalized as the result of hyperconjugative (XH_3) or anionic hyperconjugative (XF_3) interaction. The considerably larger tilt of the fluorinated and nonfluorinated silyl and germyl groups in comparison to the tilt of their methyl counterparts is explicable in terms of appreciably stronger hyperconjugative interactions and hence higher ionic contribution in the former than in the latter groups.

Summary and Conclusions

In summary, the following conclusions may be derived from the present work:

(1) The destabilization of the vicinal C–C bonds (1.521 Å) and the nearly nonvariance of the distal bond (1.502 Å) in CPG in comparison to the C–C bond in cyclopropane (1.509 Å) are most likely the result of the enhanced π-donor ability of cyclopropane and the weak π-electron acceptor property of the germyl group.

(2) The positive tilt of the germyl group in CPG and in a variety of substituted cyclopropanes of the type c-Pr-XY_3 (X = C, Si, Ge; Y = H, F) is accounted for by interactions between atoms residing above the ring and the delocalized σ-electrons in the surface orbitals of cyclopropane. Nevertheless, the tilt of the substituent group XH_3 as well as the bond length changes within the ring may be described adequately by invoking hyperconjugative (XH_3) and negative (anionic) hyperconjugative (XF_3) arguments. While this kind of interaction has been extensively studied in CH_3 and CF_3 groups, this effect has rarely been investigated, if at all, in the silyl or germyl group and their fluorinated species.

(3) It appears that there is a simple correlation between the tilt angle of the XY_3 group on the three-membered ring and the electronegativity of this substituent.

(4) In contrast to the minor changes produced in the ring C–C bonds on substituting XH_3 by XF_3, the C–X bond in both CPTFG and cyclopropyltrifluorosilane (CPTFS), in comparison to the same bond in CPG and CPS, is substantially shortened. This obvious shortening of the C–X bond on proceeding from c-Pr–XH_3 to the fluorinated analogues is most likely the result of the considerable difference between the electronegativities of the substituent groups. This kind of electrostatic interaction is enhanced by the σ-electron delocalization of the cyclopropyl system and the strong σ-acceptor capacity of the XF_3 group.

(5) The calculated values for the barrier heights for the GeH_3 and SiH_3 groups and their fluorinated counterparts in various hydrocarbons are generally in good agreement with the experimental values so far available.

(6) The fluorination of the GeH_3 and SiH_3 groups leads to a significant decrease of the X–C bond length and, surprisingly, to a simultaneous striking reduction of the barrier for internal rotation about the X–C bond. Furthermore, the substitution of the XH_3 group for the XF_3 group leads to an increase of the positive tilt of the substituent group.

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Supplementary Material Available: Tables of data for the total intensities for CPG (3 pages). Ordering information is given on any current masthead page.

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