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Deviation from Tetrahedral Geometry in Me_2GeCl_2: Crystal Structure of a Model Compound and Insight from ab Initio Calculations

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The molecular structure of Me_2GeCl_2, and the value of the C–Ge–C angle in particular, was studied by ab initio quantum calculations to examine the deviation of this molecule from ideal geometry in the gas phase and in the crystalline state. The results show that, in the crystal, intermolecular interactions do have a large influence on the geometry of the molecule. An experimental value of 121.2 ± 0.2° is found for the C–Ge–C angle in the crystal structure of dichlorodi(2-phenethyl)germane, and it provides the first crystallographic evidence for the deviation from tetrahedral geometry. This molecule crystallizes in the monoclinic space group $P2_1/c$, with $a = 9.2079(2)$ Å, $b = 19.5396(4)$ Å, $c = 9.7845(2)$ Å, $\beta = 114.217(1)°$, and $Z = 4$. Calculations show that the conformation of the organic substituents has a sizable effect on the local geometry of the Ge-atom. Analysis of the distribution of the electron density suggests that the larger value of C–Ge–C in Me_2GeCl_2 compared to the equivalent but smaller angle in Me_2CCl_2 is indirectly the result of the higher ionic character of the bonds in the former molecule.

Introduction

Electron diffraction (ED) studies[1] on molecules of the form Me_2GeX_2 where X = F, Cl, and Br show that the value of the C−Ge−C valence angle in these molecules is in excess of 120°, whereas in Me_2CX_2 and Me_2GeH_2 the same angle adopts a much smaller or near-tetrahedral value.[2] This observation can be rationalized in terms of Bent's rule[3] which states that atomic s-character concentrates in orbitals directed toward electropositive substituents, thus opening up the value of C−Ge−C and decreasing ∠X−Ge−X because of the more electronegative halogen atoms. Unfortunately, the experimental error on the value of the valence angles is large (2−4°) because the C···C peak in the radial distribution function is not well resolved from the stronger X···C peak. The analysis of the ED results is also hampered by the existence of multiple sets of parameters that fit the experimental data equally well. In the case of the Me_2GeCl_2 molecule for example, Vajda and Hargittai[1b] favored a model with ∠C−Ge−C equal to 121.7 ± 1.4° above one with a value of 114.5 ± 2.1° for the same angle. A reinvestigation of the same molecule by Drake et al.[1c] combining diffraction data with rotational constants obtained from microwave spectroscopy removed the ambiguity and coined the value of ∠C−Ge−C to 121 ± 4°.

There are only five crystal structures that contain the $C{-}GeX_2{-}C$ (X = halogen) structural unit in the 5.22 version of the Cambridge Structural Database,[4] and this limited amount of data does not confirm that the C−Ge−C angle is significantly larger than the tetrahedral value. In four of these structures, however, the angle is part of a five or six membered ring, thus putting severe geometrical constraints onto its value. In the one remaining open structure which has X = I and two equal, fully chlorinated phenyl rings as the other substituents, the value of ∠C−Ge−C is found to be 108.7°, considerably smaller than that suggested by the ED studies on the dihalodimethylgermane compounds. It may be argued that, being the least electronegative of the halogens, iodine will, in terms of Bent's rule, display the smallest

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(1) Drake, J. E.; Hemmings, R. T.; Hencher J. L.; Mustoe, F. M.; Shen Q. *J. Chem. Soc., Dalton Trans.* **1976**, 394−398. (b) Vajda, E.; Hargittai, I. *Acta Chim. Acad. Sci. Hung.* **1976**, *91*, 185−192. (c) Drake, J. E.; Hencher, J. L.; Shen, Q. *Can. J. Chem.* **1977**, *55*, 1104−1110. (d) Drake, J. E.; Hemmings, R. T.; Hencher J. L.; Mustoe, F. M.; Shen Q. *J. Chem. Soc., Dalton Trans.* **1976**, 811−814.

(2) (a) Takeo, H.; Sugie, M.; Matsumura, C. *J. Mol. Struct.* **1995**, *352/353*, 267−272. (b) Hirota, M.; Iijima, T.; Kimura, M. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 1589. (c) Mack, H. G.; Dakkouri, M.; Oberhammer, H. *J. Phys. Chem.* **1991**, *95*, 3136. (d) Thomas, E. C.; Laurie, V. W. *J. Chem. Phys.* **1969**, *50*, 3512−1315.

(3) Bent, H. A. *Chem. Rev.* **1961**, *61*, 275−311.

(4) Allen, H. H.; Kennard, O. *Chemical Design Automation News* **1993**, *8*, 31−37.

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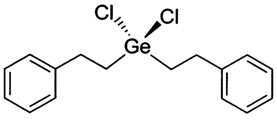
deviation from an idealized geometry, but the discrepancy appears to be rather large.

Hartree−Fock (HF) and second-order Møller−Plesset (MP2) calculations by Frenking et al.[5] on Me_2ACl_2 (A = C, Si, Ge, Sn, Pb) reveal a systematic increase of the C−A−C angle when going from C to Pb, with a value of 118.6° (HF) or 118.3° (MP2) for the germanium compound. Schaeffer et al.[6] calculate a value of 117.6° for Me_2GeCl_2 using a different basis set and the CISD level of theory. In view of the large experimental error, these calculated values are not outside the range obtained with the diffraction experiment, but it is noted that the values are systematically smaller.

We became interested in the geometries of dihalodimethylgermanes during preliminary studies to test the feasibility of a new generic force field for main group elements, where one of the main problems is the parametrization of bending constants. For example, the universal force field (UFF) developed by Rappé et al.[7] uses a bend interaction with an angle parameter that is based on the nature (the atom type) of the central atom only and produces a near-tetrahedral geometry for Me_2GeX_2, regardless of the nature of X. These secondary substituent effects are easily taken care of in a molecular mechanics force field with explicit parametrization for all interactions[8] but are difficult to implement in a generic force field, where parameters are typically atom-based. Because of the relatively large experimental error in the ED studies, the systematically smaller values obtained by ab initio calculations, and the lack of comparable molecules in the Cambridge Structural Database, we wanted to add more experimental and computational substance to the available data. Our aim was to choose a molecule that is representative for Me_2GeCl_2 and to determine the value of ∠C−Ge−C by crystallography. For this, we choose a compound that (i) is solid at room temperature and is easy to crystallize, (ii) has substituents that are flexible enough to prevent sterical influence from affecting the angle of interest, (iii) does not change the immediate electronic environment of the germanium atom compared to Me_2GeCl_2, and (iv) reduces the risk of the formation of secondary bonding as observed in the corresponding tin compounds.[14] As a first attempt, we therefore replaced the methyl group by CH_2CH_2Ph, to study dichlorodi(2-phenethyl)germane, **1**.



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Experimental Section

$GeCl_4$ and $PhCH_2CH_2Cl$ were obtained from Aldrich. First, the Grignard reagent $PhCH_2CH_2MgCl$ was prepared by adding magnesium turnings (1.823 g; 0.075 mol) in 25 mL of dry diethyl ether. To this was added 5 mL of a mixture of 2-phenethyl chloride (6.577 mL; 0.05 mL) and 25 mL of diethyl ether. The solution was warmed slightly to initiate the reaction and stirred throughout. Once the reaction started, as indicated by a slight milkiness, the rest of the 2-phenethyl chloride/ether mixture was added dropwise to the reaction flask, and the solution refluxed for a further 2 h. Phenethylmagnesium chloride from the previous reaction was added dropwise to a solution of tetrachlorogermane (5.360 g; 0.025 mol) in THF (20 mL; 17.78 g; 0.2218 mol), and the reaction mixture stirred at ambient temperature for 16 h. The solvent was then distilled off under vacuum, benzene (75 mL; 65.55 g; 0.7797 mol) was added, and the solution was heated under reflux for a further hour. The product was left to cool and precipitate at room temperature, and the solution was evaporated to dryness. Enough hexane was added to the product of the previous reaction to dissolve it and the resulting solution filtered. The filtered solution was then distilled to half its original volume and left to stand for crystallization. The crystals obtained were evaporated to dryness, dissolved in hexane, separated into three parts, and layered with THF, dichloromethane, and ether for the final recrystallization.

Diffraction data were collected on a Nonius Kappa CCD diffractometer. The structure was solved with SHELXS97[9] and refined with SHELXL97.[10] All hydrogen atoms were constrained to ride upon their associated heavy atoms using standard distances and angles. A perspective drawing of the molecule with numbered atoms is shown in Figure 1. The large anisotropic parameters for carbon atom 5 could not be resolved with a static disordered model of the structure. A summary of the crystal parameters is given in Table 1. Selected bond lengths and angles appear in Table 2.

All quantum mechanical calculations were performed with the Gaussian 98 program[11] at the HF level of theory and the 6-31G(d) basis set, except where stated otherwise in the text. Geometries were optimized using standard convergence criteria and verified to be energy minima by calculation of the vibrational frequencies and normal modes (only positive eigenvalues).

Results

The most important feature in the crystal structure of **1**, at least for the purpose of the current discussion, is the value

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(5) Jonas, V.; Boehme, C.; Frenking, G. *Inorg. Chem.* **1996**, *35*, 2097−2099.

(6) Vacek, G.; Mastryukov, V. S.; Schaefer, H. F., III. *J. Phys. Chem.* **1994**, *98*, 11337−11341.

(7) Rappé, A. K.; Casewit, C. J.; Colwell, K. S.; Goddard, W. A., III.; Skiff, W. M. *J. Am. Chem. Soc.* **1992**, *114*, 10024−10035.

(8) Rohwer, H. The structure and properties of dihalodimethylgermanes and related compounds. M. Sc. Thesis, University of Stellenbosch, Stellenbosch, South Africa, 2002.

(9) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *45*, 467−472.

(10) Sheldrick, G. M. *Shelx97, Version 97.2*; University of Göttingen: Göttingen, Germany, 1997.

(11) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.

(12) Alder, R. W.; Allen, P. R.; Hnyk, D.; Rankin, D. W. H.; Robertson, H. E.; Smart, B. A.; Gillespie, R. J.; Bytheway, I. *J. Org. Chem.* **1999**, *64*, 4226−4232.

(13) Oyamada, T.; Iijima, T.; Kimura, M. *Bull. Chem. Soc. Jpn* **1971**, *44*, 2638−2642.

(14) (a) Davies, A. G.; Milledge, H. J.; Puxley, D. C.; Smith, P. J. *J. Chem. Soc. A* **1970**, 2862−2866. (b) Reuter, H.; Pawlak, R. *Z. Kristallogr.* **2001**, *216*, 56−59.

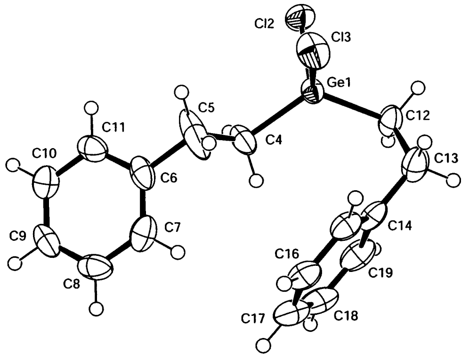

Figure 1. Perspective drawing of dichlorodi(2-phenethyl)germane (**1**) showing atom numbering with thermal ellipsoids at 50%.

Table 1. Crystallographic Data for **1**

empirical formula	$C_{16}H_{18}Cl_2Ge$
fw	353.81 g/mol
space group	$P2_1/c$
a	9.2079(2) Å
b	19.5396(4) Å
c	9.7845(2) Å
β	114.217(1) °
Z	4
V	1605.50(6) Å^3
D_{calcd}	1.4638 g/cm^3
λ(Mo Kα)	0.710 73 Å
μ	22.25 cm^{-1}
T	173 K
$R(F^2)$, $R_w(F^2)$	0.032, 0.077

Table 2. Selected Bonds (Å) and Angles (deg) for **1**

C(4)−C(5)	1.422(7)	C(4)−Ge(1)	1.942(4)
C(5)−C(6)	1.510(6)	C(12)−Ge(1)	1.935(4)
C(12)−C(13)	1.539(5)	Cl(2)−Ge(1)	2.160(1)
C(13)−C(14)	1.504(5)	Cl(3)−Ge(1)	2.167(1)
C(4)−C(5)−C(6)	116.5(5)	C(5)−C(4)−Ge(1)	117.5(3)
C(5)−C(6)−C(7)	121.8(4)	C(13)−C(12)−Ge(1)	113.0(3)
C(5)−C(6)−C(11)	120.1(4)	C(4)−Ge(1)−Cl(2)	107.2(2)
C(12)−C(13)−C(14)	113.9(3)	C(12)−Ge(1)−Cl(2)	107.8(1)
C(13)−C(14)−C(15)	121.0(3)	Cl(2)−Ge(1)−Cl(3)	103.2(1)
C(15)−C(14)−C(19)	117.4(3)	C(4)−Ge(1)−C(12)	121.2(2)
C(13)−C(14)−C(19)	121.6(3)	C(4)−Ge(1)−Cl(3)	108.7(2)
		C(12)−Ge(1)−Cl(3)	107.2(1)

of the C−Ge−C angle, which is found to be 121.2 ± 0.2°. This is comfortably in the region of values as found with ED for the smaller dimethyl analogues and, thus, larger than the calculated ab initio value for these molecules. It is also noteworthy that the molecule is asymmetrical with one side chain having more or less a linear conformation, whereas the other one is *folded* under the germanium atom, with a torsion angle C−Ge−C−C of −73°. In the "linear" substituent, the corresponding torsion angle is 141°, deviating 39° from the ideal trans geometry. Except for the C(4)−C(5) bond which is shortened as a result of the excessive thermal motion of atom C(5), bonds and angles do not adopt unusual values. Although one of the phenyl carbons is only 3.40 Å from the germanium atom, the average distance between the latter and the atoms in the phenyl ring that is folded under the molecule is 4.49 Å, which indicates that there is no stabilizing interaction between the two. Within one molecule, the phenyl rings adopt the common T-shaped conformation.

To investigate the effect of the crystal packing on the internal geometry of the molecule, we minimized the energy of a number of models, summarized in Table 3. An overlay of the molecule as found in the crystal and the calculated 6-31G(d) structure of the same conformation is given in Figure 2. The main difference between experimental and calculated structures is that in the calculations the C−Ge−C−C angle of the "linear" substituent changes from 141° to −177°, which suggests that in the crystal the steric repulsions resulting from the deviation from ideal trans geometry are balanced by a more favorable packing. Calculated bond lengths and the C−Ge−C angle are close to the experimental values. Table 3 also shows that the calculated value of the C−Ge−C angle is strongly dependent on whether polarization functions are included in the basis set or not. This trend is also visible in the calculations of Me_2GeCl_2 performed by Schaefer et al.[6] To test the effect of the observed gauche substituent on the value of the C−Ge−C angle, we performed additional calculations on a limited number of conformations of the parent compound **1**. We also investigated the effect of the presence of the phenyl rings by repeating the calculations on dichlorodiethylgermane, where the phenyl ring is replaced by a hydrogen, the results of which are also summarized in Table 3. We will discuss the results of the latter first.

Table 3. Selected Geometrical Parameters[a] for Some Conformations of Dichlorodi(2-phenethyl)Germane, **1**, and Dichlorodiethylgermane

conformation	basis set	C(4)−Ge	Ge−C(12)	C(4)−Ge−C(12)	ω_1[b]	ω_2
			$PhCH_2CH_2GeCl_2$			
expt		1.942	1.935	121.2	141	−73
	6-31G	1.936	1.942	125.3	178.2	−74.4
	6-31G(d)	1.932	1.939	122.0	−177.3	−75.4
linear	6-31G	1.936	1.936	121.8	179.9	179.9
	6-31G(d)	1.932	1.932	117.3	180.0	180.0
twisted	6-31G	1.941	1.941	128.3	76.9	76.9
	6-31G(d)	1.938	1.938	123.5	80.9	80.9
			Et_2GeCl_2			
tt[c]	6-31G	1.938	1.398	121.8	180.0	180.0
	6-31G(d)	1.933	1.933	117.3	180.0	180.0
tg	6-31G	1.936	1.937	120.3	177.5	52.3
	6-31G(d)	1.934	1.933	118.4	176.0	54.4
gg	6-31G	1.933	1.933	118.1	53.0	53.0
	6-31G(d)	1.933	1.933	119.2	56.3	56.3

[a] Bond lengths in angstroms and angles in degrees. [b] ω_1 = C(5)−C(4)−Ge−C(12), ω_2 = C(4)−Ge−C(12)−C(13), or the equivalent angles in Et_2GeCl_2. [c] t = trans, g = gauche.

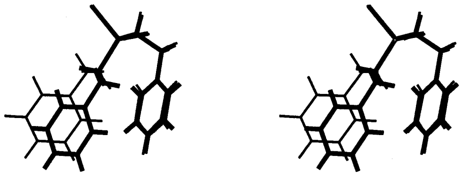

Figure 2. Stereo picture of the overlaid experimental (bold) and calculated 6-31G(d) geometries of **1**.

As expected, the all-trans form of dichlorodiethylgermane is the conformation with the lowest energy. The energy increases marginally by 0.46 kJ/mol (6-31G(d)-value) for the gauche−trans form and to 0.85 kJ/mol for gauche−gauche. The increase in the C−Ge−C angle is about 1° for each additional gauche interaction. In the equivalent carbon compound, 3,3-dichloropentane, the valence angle for the corresponding conformations is calculated to be 110.7°, 113.4°, and 115.8°, respectively, which is a considerably

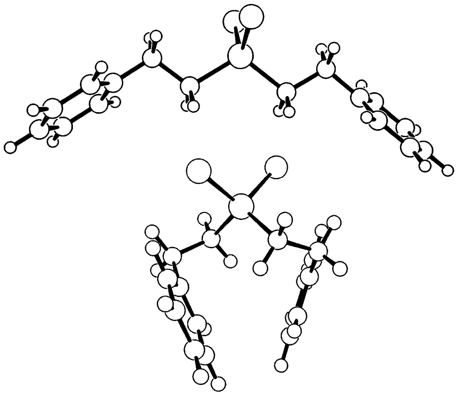

Figure 3. Two alternative conformations of **1**, denoted linear (top) and twisted (bottom).

larger increase compared to that of the germanium compound. Increases of a few degrees in C−C−C angles resulting from gauche interactions are not uncommon, and the values are similar to those found experimentally in the similar 3,3-diethylpentane.[12] This trend is easily rationalized in terms of the longer C−Ge bond length, compared to C−C, and the resulting smaller sterical hindrance between the terminal gauche methyl group and one of the chlorine atoms. However, this result hints that the experimentally found conformation of title compound **1** may indeed have an influence on the value of the central C−Ge−C angle. The presence of phenyl rings also introduces additional degrees of freedom to the system that make the exploration of a full conformational surface by ab initio methods impossible. We therefore limit the discussion to the two symmetrical conformations depicted in Figure 3, the results of which are given in Table 3. These two conformations were chosen because they represent the two extremes in molecular "congestion". They were also identified as low energy conformations during a conformational energy surface scan with the UFF molecular force field.[7] The molecular mechanics geometry, followed by an energy minimization with the modest 3-21G basis set, served as a starting point for further calculations. The linear conformation shown in the top of Figure 3 is found to be 7.25 kJ/mol higher in energy than the optimized form of the crystal structure. A point calculation using MP2 theory on the optimized 6-31G(d) geometries yields an increased energy difference of 20.72 kJ/mol. The C−Ge−C angle of 117.3° is similar to the values obtained for both Me_2GeCl_2 and Et_2GeCl_2, highlighting the large effect of the conformation of the side chain on this angle. In the symmetrical twisted conformation at the bottom of Figure 3, the angle increases by 1.5° to 123.5°. This form is 2.79 kJ/mol *lower* in energy (13.61 kJ/mol with MP2) than the geometry found in the crystal structure, probably because of stabilizing phenyl−phenyl interactions. As for the experimental structure, there are no short germanium−phenyl distances. The fact that this conformation is not observed experimentally obviously means that this conformation results in a more unfavorable packing of molecules.

Finally, we also undertook to investigate whether the formation of secondary bonding could be important in crystalline Me_2GeCl_2. It could be argued that the crystal structure of this compound would univocally determine whether the C−Ge−C angle is substantially larger than tetrahedral or not. Crystal packing alone is indeed unlikely to have a large influence on the geometry of this molecule. Up to this date, the crystal structure of none of the dihalodimethylgermanes is known, but some of the Sn-analogues have been investigated. Dimethyltin dichloride, for example, has been studied both by gas-phase ED[13] and by single-crystal diffraction.[14] In the gas-phase study, the C−Sn−C angle was not determined directly, but it can be calculated from the reported Cl−Sn−Cl and C−Sn−Cl angles if local C_{2v} symmetry is assumed. The value thus found is 100 ± 4°. Note again the large standard deviation. In sharp contrast to this value is the ab initio figure of 122° obtained by Frenking et al.[5] In an early single-crystal diffraction study,[14a] the value for this angle was determined as 123.5 ± 4.5°, in close agreement with Frenking's result. A recent investigation using a diffractometer[14b] redetermined it to be considerably larger: 142.2 ± 0.4°. This figure is in line with the values found in other R_2SnCl_2 compounds.[15] The angle in the crystal is expected to be larger than in the gas phase because of the occurrence of secondary bonding, that is, the presence of strong interactions between the Sn atom and chlorines from neighboring molecules. This results in the formation of (distorted) octahedrally coordinated Sn atoms. These secondary bonds can be very strong as is evident in, for example, Me_2SnF_2, where the tin atom is found to have four equal Sn−F bonds.[16] In Me_2SnCl_2, the Sn−Cl bond is 2.389(2) Å whereas the Sn⋯Cl length is 3.433 Å. Although considerably longer than the primary valence bond, this value is shorter than the sum of the van der Waals radii of Sn (2.2 Å) and Cl (1.8 Å) by about 0.6 Å.

Taking the crystal structure of the tin compound as a starting point for Me_2GeCl_2, we first optimized three molecules arranged as in Figure 4 (top). As a model for a crystal, this is limited, but it reflects the immediate surroundings of one molecule as found experimentally. During the calculations, symmetry was kept to the experimentally observed C_{2v} point group, but the molecules were not forced to be identical. The van der Waals radius of Ge does not seem to have been determined, and we adopt the value of 2.1 Å, being the average between Si (2.0 Å) and Sn (2.2 Å). The geometry-optimized Ge⋯Cl distance of 4.080 Å is slightly longer than the sum of the radii of Ge and Cl. Nevertheless, the effect on the C−Ge−C angle is remarkable, increasing from 118.1° for the isolated molecule to 125.9° for the central molecule in this simple model. In the second model, consisting of five molecules and shown in the middle of Figure 4, the Ge⋯Cl distance shortens to 3.886 Å, shorter than the sum of the van der Waals radii but not very convincingly so. The C−Ge−C increases to 127.7°. Finally, in the bottom model in Figure 4, the central molecule is not only flanked by 2 neighbors but also sandwiched by 2 planes of 6 molecules each, bringing the total number of molecules to 15. In view of the computational effort, we used DFT

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(15) Alcock, N. W.; Sawyer, J. F. *J. Chem. Soc., Dalton Trans.* **1977**, 1090−1095.

(16) Schlemper, E. O.; Hamilton, W. C. *Inorg. Chem.* **1966**, *5*, 995−998.

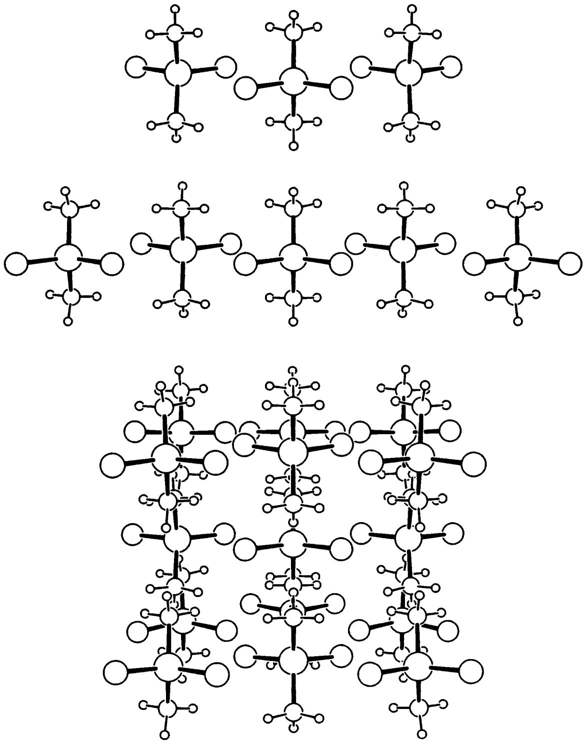

Figure 4. Three different models representing the local environment of Me_2GeCl_2 in the crystalline state having 3 (top), 5 (middle), and 15 molecules (bottom).

with the B3LYP functional rather than Hartree−Fock. We also stopped the energy minimization after 45 cycles because convergence could not be obtained with the standard criteria. The difference in energy between the last two cycles was only 0.044 kJ/mol, however, and rms and maximum force criteria were met. The Ge···Cl distance for the central molecule in this model is 3.859 Å, and the C−Ge−C angle 129.2°. Because only the overall symmetry of the clusters is kept fixed, individual distances and angles are not the same for all molecules in each model. The general trend is a lengthening of the Ge···Cl distance when moving away from the central molecule, and a decrease in the C−Ge−C angle. There are no particularly short Ge···Cl contacts that suggest a substantial degree of secondary bonding as all values are more or less equal to the van der Waals distance, but ∠C−Ge−C is consistently larger than in the isolated molecule.

Discussion

We used crystalline dichlorodi(2-phenethyl)germane (**1**) as a model compound to study the deformation from ideal geometry observed by ED studies on a number of dihalodimethylgermane compounds. The experimental value of the main angle of interest, ∠C−Ge−C, is found to be 121.2 ± 0.2°. This value is in good agreement with Hartree−Fock ab initio calculations on this molecule using a 6-31G(d) basis set. This excellent correspondence is somewhat surprising because the calculated ab initio values on Me_2GeX_2 with X= F, Cl, or Br are systematically smaller than the experimental ED values by a few degrees.[5,6,8] The calculations on **1** and on dichlorodiethylgermane demonstrate that the conformation as found in the crystal of **1** will increase the C−Ge−C angle by a few degrees relative to a form where both substituents are in a trans conformation. This conformation is expected to have a value for ∠C−Ge−C which is close to the parent compound Me_2GeCl_2. However, there is little doubt that the C−Ge−C angle in all these compounds is noticeably larger than the "ideal" value of 109.5°.

The calculations on Me_2GeCl_2 in the solid state do not predict the occurrence of secondary bonding, at least not if the distance between the Ge and Cl atoms is to be taken as a representative criterion. Nevertheless, the C−Ge−C angle increases by more than 10°, which we consider to be a substantial amount. Although it is clear that this increase is caused by intermolecular interactions, the exact nature of these interactions is still obscure. We hope to shed more light on this subject during a later study. However, on the basis of the computational results, it is questionable whether the crystal structure of Me_2GeCl_2 would be a good model for the isolated molecule.

The larger value of the central valence angle in Me_2GeCl_2 relative to Me_2CCl_2 can be explained in terms of the higher ionic character of the C−Ge bond compared to C−C. The calculated charges on the atoms differs dramatically for the two molecules. In Me_2CCl_2, the Mulliken charge on the central carbon atom is −0.203 e, whereas the chlorine atoms bear a modest −0.036 e, and the methyl carbons −0.458 e. The hydrogen atoms all have a positive charge. The germanium atom in Me_2GeCl_2 has a calculated charge of +0.748 e, with −0.290 e on chlorine and −0.710 e on the methyl carbons. The numerical values look very different when charges are calculated in terms of Bader's atoms in molecules (AIM) theory.[17] For Me_2CCl_2, this yields −0.283, +0.218, and +0.123 e for Cl, the central carbon, and the methyl carbon, respectively, and −0.630, +2.068, and −0.594e for Cl, Ge, and methyl carbon in Me_2GeCl_2. Especially, the large positive charge on the germanium atom is noteworthy. The numerical values of the charges vary considerably between both schemes, but either way, a large charge difference exists between the germanium atom and the methyl carbons. The increased ionic character of the bonds in Me_2GeCl_2 compared to Me_2CCl_2 is also visible in the Laplacian (second derivative) of the electron density, $\nabla^2\rho(\mathbf{r})$ (Supporting Information). It is seen that, in Me_2CCl_2, $\nabla^2\rho(\mathbf{r})$ is spread out over the whole bonding region of the molecule, conforming with the picture of the existence of covalent bonds, whereas in Me_2GeCl_2 there is a clear depletion of electron density around the germanium atom. This increased ionic character is also reflected in the numeric values of the electron density, $\rho_b(\mathbf{r})$, itself, and its Laplacian at the bond critical point (BCP). As pointed out by one of the referees, that fact that the Ge−C bond is longer than C−C necessarily affects these properties, but they confirm the stated observations. The electron density at the BCP in C−Ge is 0.134 au, only half of the value of 0.264 found in the C−C bond of Me_2CCl_2. Similarly, a value of 0.093 au

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(17) Bader, R. F. W. *Atoms in Molecules: A Quantum Theory*; Oxford University Press: New York, 1990.

is calculated for the Ge−Cl bond, whereas 0.186 au is found for the equivalent C−Cl bond. The Laplacian of the electron density, $\nabla^2\rho_b(\mathbf{r})$, confirms this picture. A negative value is generally associated with a valence bond, whereas a positive number indicates a closed shell interaction, for example, an ionic or van der Waals bond. The values calculated are 0.123 and −0.735 au for Ge−C and C−C bonds, respectively, and 0.188 and −0.297 au for the Ge−Cl and C−Cl bonds. Hence, the larger value of the C−Ge−C angle in Me_2GeCl_2 compared to the equivalent one in the carbon compound can be attributed to the larger electrostatic interaction between the methyl groups, which is a direct result of the increased ionic character of the Ge−C bond. Extrapolating this result to title compound **1** shows that this increased ionic character will also be responsible for the relatively large dependence of the C−Ge−C angle on the conformation of the organic ligands.

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Supporting Information Available: X-ray crystallographic file in CIF format for the crystal structure of **1**, a text file with the final coordinates of all calculated ab initio structures, a table summarizing key geometric parameters for Me_2GeCl_2 calculated with varying basis sets, and a picture of the Laplacian of the electron density, $\nabla^2\rho(\mathbf{r})$. This material is available free of charge via the Internet at http://pubs.acs.org.

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