Dimethyl-, Disilyl- and Digermylsulfide: Different Intermolecular Contacts in the Solid State

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Z. Naturforsch. **59b,** 635 – 638 (2004); received March 22, 2004

The compounds $(H_3C)_2S$, $(H_3Si)_2S$ and $(H_3Ge)_2S$ have been crystallised *in situ* on a diffractometer and their crystal structures determined by low-temperature X-ray diffraction. The molecules are present as monomers in the crystals. The aggregation of the molecules through secondary intermolecular contacts in the crystal is different: $(H_3C)_2S$ is weakly associated into dimers by S···S contacts, whereas $(H_3Si)_2S$ and $(H_3Ge)_2S$ form Si···S and Ge···S contacts in an ice-analogous aggregation motif. Important geometry parameters are $(H_3C)_2S$: C-S 1.794(av) Å, C-S-C 99.2(1)°; $(H_3Si)_2S$: Si-S 2.143(1) Å, Si-S-Si 98.4°; $(H_3Ge)_2S$ Ge-S 2.223(2) and 2.230(2) Å, Ge-S-Ge 98.2(1)°.

Key words: Silicon, Germanium, Sulphur, Crystal Structure, Secondary Bonds

Of the simplest ethers and thioethers of group 14 only the crystal structure of disiloxane has been determined so far [1]. For dimethyl ether and digermyl ether and the corresponding thioethers only the gas-phase structures have been reported. They have either been determined by microwave spectroscopy $\{(H_3C)_2S$ [2]$\}$ or by gas-phase electron diffraction $\{(CH_3)_2O$ [3], $(H_3Ge)_2O$ [4], $(H_3Si)_2S$ [5 – 7], $(H_3Ge)_2S$ [4, 8]$\}$. As structures of compounds with substantial molecular dipole moments are likely to be dependent on the phase [9], it seemed desirable to get reliable information about the crystal structures of these simple parent systems of sulphur chemistry. The knowledge of the exact structures of these molecules is important for comparison with more complex systems and with Lewis acid adducts in which the structures of these Lewis bases could be markedly distorted.

Here we report on the crystal structures of $(H_3C)_2S$, $(H_3Si)_2S$ and $(H_3Ge)_2S$. $(H_3C)_2S$ was a commercial sample purified by distillation, while $(H_3Si)_2S$ and $(H_3Ge)_2S$ were prepared following literature procedures [10,11] from anhydrous Li_2S with two equivalents of H_3SiBr and H_3GeBr, respectively, in dimethyl ether as solvent. They were purified by low-temperature fractional condensation.

Single crystals of $(H_3C)_2S$, $(H_3Si)_2S$ and $(H_3Ge)_2S$ were grown in sealed capillaries from the melt by establishing a solid-liquid equilibrium close to the melting point of the sample, followed by melting most of the solid by application of heat through a wire and allowing the remaining seed crystals to grow again. This procedure was repeated several times and finally everything was melted except a single well-formed seed crystal selected under microscopic observation. By slowly lowering the temperature (1 K / 10 min for the first 10 K, then more rapidly) single crystals filling the whole capillary were grown and X-ray diffraction experiments were carried out in the usual manner.

The most relevant structural parameters are listed in Table 1 together with data for the gas-phase structures of $(H_3C)_2S$, $(H_3Si)_2S$ and $(H_3Ge)_2S$. For comparison we also calculated the molecular geometries by ab initio methods on various levels up to CCSD/6-311G**. These calculated data are listed in Table 2. Plots of the unit cells and the molecular structures are provided in Figures 1 – 3 for $(H_3C)_2S$, $(H_3Si)_2S$ and $(H_3Ge)_2S$, respectively.

The calculated data show some dependence of the geometry parameters on the level of theory applied. The variations in the bond lengths are to be expected. The C-S-C angle variations are relatively small for $(H_3C)_2S$, where the maximum deviation of 1.5° is found between the lowest (SCF/3-21G*) and highest-level calculation (CCSD/6-311+G**). The deviations of the angle Si-S-Si for $(H_3Si)_2S$ between the same levels of theory is larger at 4.7°, but there are only slight deviations of the medium level calculations from that at the highest level. In contrast the calculations for

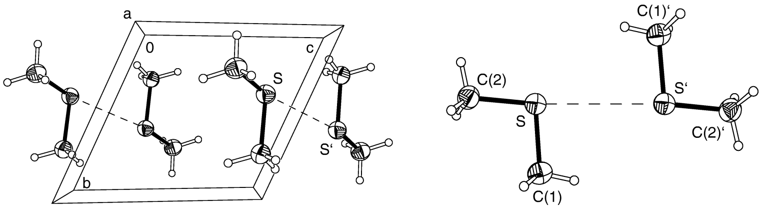

Fig. 1. Unit cell and molecular structure of $(H_3C)_2S$. The dashed lines represent the shortest contacts between two S atoms.

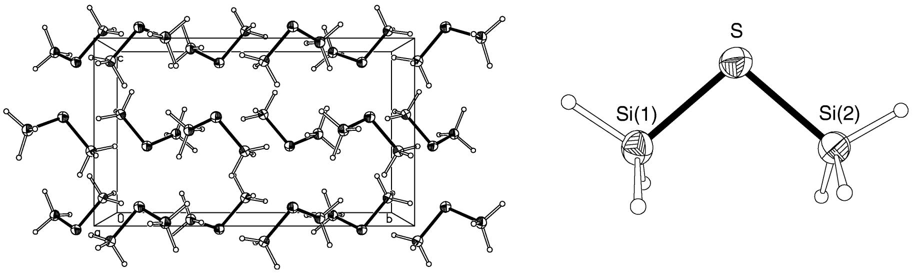

Fig. 2. Unit cell and molecular structure of $(H_3Si)_2S$.

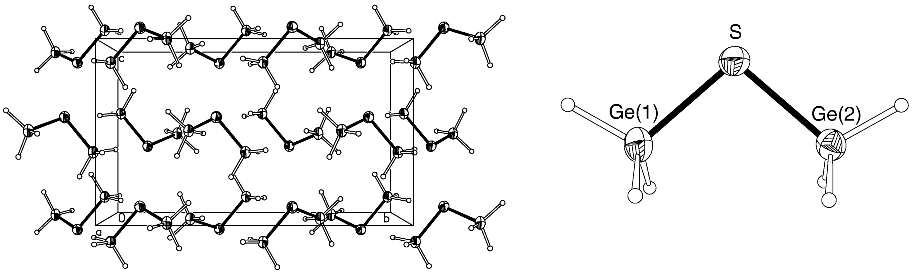

Fig. 3. Unit cell and molecular structure of $(H_3Ge)_2S$.

Table 1. Structural parameters of $(H_3C)_2S$, $(H_3Si)_2S$ and $(H_3Ge)_2S$ as determined by low-temperature single-crystal X-ray diffraction, microwave spectroscopy and by gas phase electron diffraction for comparison.

	$(H_3C)_2S$		$(H_3Si)_2S$		$(H_3Ge)_2S$	
	XRD	MW [2]	XRD	GED [5]	XRD	GED [4]
E(1)-S	1.793(2)	1.802(1)	2.143(1)	2.136(2)	2.223(2)	2.223(2)
E(2)-S	1.795(2)		2.143(1)		2.230(2)	
E(1)-S-E(2)	99.2(1)	98.9(2)	98.4(1)	97.4(7)	98.2(1)	98.9(1)

Table 2. Calculated structural parameters of $(H_3C)_2S$, $(H_3Si)_2S$ and $(H_3Ge)_2S$ at different levels of theory.

Method	Basis set	$(H_3C)_2S$		$(H_3Si)_2S$		$(H_3Ge)_2S$	
		r(C-S)	<CSC	r(Si-S)	<SiSSi	r(Ge-S)	<GeSGe
SCF	3-21G*	1.812	99.4	2.138	104.7	2.235	100.4
	6-31G*	1.808	100.0	2.149	104.0	2.227	98.5
MP2	6-31G*	1.802	98.5	2.141	100.9	2.228	93.6
	6-311G**	1.806	98.2	2.138	99.6	2.232	99.0
	6-311+G**	1.802	98.1	2.139	99.2	2.233	98.8
MP4	6-31G*	1.815	98.5	2.148	100.7	2.238	93.3
CCSD	6-31G*	1.813	98.7	2.147	101.2	2.235	94.2
	6-311G**	1.810	98.5	2.144	100.0	2.239	99.4
	6-311+G**	1.810	98.4				

$(H_3Ge)_2S$ show significant deviations for the Ge-S-Ge angle from the highest level value at 99.4° with deviations up to 6° for the MP4 and MP2 calculations employing the 6-31G* basis set, which shows that small basis sets seem to be unsuitable to account for the details of molecular structure of this compounds.

For all three compounds the experimental geometry parameters obtained from the gas phase and from the solid state are so similar that one can conclude that intermolecular interactions or packing effects do not distort the molecular structures significantly. These parameters agree within about 0.01 Å and 2° for bond lengths and angles with the theoretical values. From an overall view the E-S bond lengths and E-S-E bond angles are typical values for such thioethers.

An interesting detail of the crystal structures of $(H_3C)_2S$, $(H_3Si)_2S$ and $(H_3Ge)_2S$ concerns the packing of the molecules in the solid state. $(H_3C)_2S$ crystallizes in the triclinic space group $P\bar{1}$, while $(H_3Si)_2S$ and $(H_3Ge)_2S$ are isomorphous (orthorhombic space group *Pbcn*). Despite the closely similar structures of the molecules in particular regarding their E-S-E angles, their packing mode is completely different.

In $(H_3C)_2S$ the closest relevant intermolecular contacts are between the sulphur atoms of two molecules.

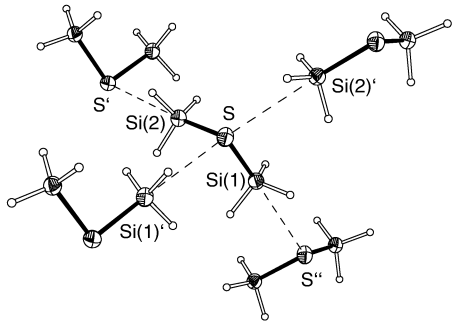

Fig. 4. Intermolecular Si···S contacts in the solid-state structure of $(H_3Si)_2S$ showing the intermolecular connectivity pattern. $(H_3Ge)_2S$ is isostructural.

This leads to the formation of weakly associated dimers in the crystal. The intermolecular S···S distances are 3.475(1) Å, which is markedly smaller than the sum of the van-der-Waals radii of two sulphur atoms at 3.70 Å. The occurrence of S···S interactions of that length in alkylsulfides is a commonly observed structural motif as is obvious from a search of the Cambridge Crystal Structure Database [12]. In $(H_3C)_2S$ the S···S vector is almost parallel to the S-C(2) bonds as indicated by the angle S'···S-C(2) at 167.7(1)°, while the angle S'···S-C(1) measures 85.1(1)°. The whole arrangement of the heavy atoms $C_2S\cdots SC_2$ is almost planar. The density of $(H_3C)_2S$ in the solid state is 1.116 g cm^{-3}, which is substantially larger than that of the liquid at 0.846 g cm^{-3}. Notwithstanding, the crystallographic average heavy-atom volume at 30.8 $Å^3$ is quite large.

Even larger are the average heavy-atom volumes of $(H_3Si)_2S$ and $(H_3Ge)_2S$, which amount to 43.4 and 44.6 $Å^3$. This indicates a less dense packing of molecules in the crystalline state. Despite the higher atomic mass of silicon, the solid-state density of $(H_3Si)_2S$ at 1.202 g cm^{-3} is not much larger than that of $(H_3C)_2S$, but expectedly there is a large difference in the densities between the isostructural silicon compound $(H_3Si)_2S$ and its germanium analogue $(H_3Ge)_2S$ (2.274 g cm^{-3}).

The closest intermolecular contacts between the group 14 and sulphur atoms in $(H_3Si)_2S$ and $(H_3Ge)_2S$ are of the same type. Their lengths are 3.537(2) and 3.564(2) Å for the two different Si···S contacts in the silicon compound and 3.505(1) and 3.533(1) Å for the Ge···S distances in the germanium compound. These values are significantly below the sum of the van-der-Waals radii, which is 3.85 Å for the pair Si/S [13] and is probably similar for the pair Ge/S, for which no literature data are available. The orientation of these contacts is such that an almost linear S-E···S arrangement is achieved, which leads to a weak aggregation of the $(H_3Si)_2S$ and $(H_3Ge)_2S$ molecules into a three-dimensional network as is depicted in Fig. 4. In this way the whole aggregate resembles the structure of ice. However, the coordination geometries of the sulphur atoms in $(H_3Si)_2S$ and $(H_3Ge)_2S$ deviate more from a tetrahedral environment than that of the oxygen atoms in ice as is indicated by the large angles Si(1)'···S···Si(2)' [$(H_3Si)_2S$: 128.8(1)° and $(H_3Ge)_2S$: 128.7(1)°], Si(1)-S···Si(1)' [$(H_3Si)_2S$: 90.9(1)° and $(H_3Ge)_2S$: 90.8(1)°], and Si(2)-S···Si(2)' [$(H_3Si)_2S$: 99.4(1)° and $(H_3Ge)_2S$: 99.7(1)°]. All other Si···S and Ge···S intermolecular distances are much longer than 4 Å and thus do not contribute primarily to the observed aggregation motif. There are also no short S···S interactions as found in $(H_3C)_2S$.

The variations in the aggregation between the simple sulphides $(H_3C)_2S$, $(H_3Si)_2S$ and $(H_3Ge)_2S$ can thus be summarized with respect to the different electronegativities of the methyl, silyl (H_3Si) and germyl (H_3Ge) groups. The relatively electropositve substituents H_3Si and H_3Ge at sulphur have significant Lewis acidic properties to form contacts with the electronegative sulphur atom, while the methyl groups in $(H_3C)_2S$ cannot behave as Lewis acids. The obvious reason for that is the absence of polarity in a C-S bond as the electronegativity of sulphur and carbon are about equal, whereas the polar Si-S and Ge-S bonds favour the described intermolecular interactions.

Experimental Section

Quantumchemical calculations were carried out with the Gaussian 98 [14] suite of programs and the methods and basis sets implemented therein.

Crystal structure determination of $(H_3C)_2S$, $(H_3Si)_2S$ *and* $(H_3Ge)_2S$. Single crystals of $(H_3Si)_2S$ and $(H_3Ge)_2S$ were grown by *in situ* methods as described in the text. Data collection was undertaken with a Nonius Turbo-CAD4 diffractometer.

Crystal data $(H_3C)_2S$, H_6C_2S, $M_r = 63.13$ g mol^{-1}, crystal system triclinic, space group $P\bar{1}$, $Z = 2$, $a = 5.619(2)$, $b = 5.843(3)$, $c = 6.408(2)$ Å, $\alpha = 113.16(2)$, $\beta = 103.87(3)$, $\gamma = 93.58(4)°$, $V = 184.87(13)$ $Å^3$ at 123(2) K, $\mu = 0.604$ mm^{-1}. $2\theta_{max.} = 54°$, ω-scans, 1609 scattering intensities collected of which 806 were unique ($R_{int} = 0.0427$), 52 parameters, $R_1 = 0.0232$ for 772 reflections with $F_o > 4\sigma(F_o)$ and $wR_2 = 0.0581$ for all 806 data, extrema of residual electron densities 0.14 and -0.43 e $Å^{-1}$.

Crystal data $(H_3Si)_2S$, H_6SSi_2, $M_r = 94.29$ g mol^{-1}, crystal system orthorhombic, space group *Pbcn*, $Z = 8$, $a = 8.152(1)$, $b = 14.776(1)$, $c = 8.653(1)$ Å, $V = 1042.3(2)$ Å^3 at 128(2) K, $\mu = 0.887$ mm^{-1}. $2\theta_{\text{max.}} = 54°$, ω-scans, 5404 scattering intensities collected of which 1136 were unique ($R_{\text{int}} = 0.0297$), 52 parameters, $R_1 = 0.0236$ for 1043 reflections with $F_o > 4\ \sigma(F_o)$ and $wR_2 = 0.0841$ for all 1139 data, extrema of residual electron densities 0.424 and -0.311 e Å^{-1}.

Crystal data $(H_3Ge)_2S$, H_6SGe_2, $M_r = 183.29$ g mol^{-1}, crystal system orthorhombic, space group *Pbcn*, $Z = 8$, $a = 8.216(2)$, $b = 14.888(3)$, $c = 8.755(2)$ Å, $V = 1070.9(4)$ Å^3 at 128(2) K, $\mu = 11.426$ mm^{-1}. $2\theta_{\text{max.}} = 54°$, ω-scans, 5404 scattering intensities collected of which 1136 were unique ($R_{\text{int}} = 0.0297$), 52 parameters, $R_1 = 0.0236$ for 823 reflections with $F_o > 4\ \sigma(F_o)$ and $wR_2 = 0.0841$ for all 1139 data, extrema of residual electron densities 0.852 and -1.011 e Å^{-1}.

Structure solutions and refinements were undertaken with the program SHELXTL 5.01 [15]. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-233998 [$(H_3C)_2S$], CCDC-233999 [$(H_3Si)_2S$] and CCDC-233997 [$(H_3Ge)_2S$]. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (e-mail: deposit@ccdc.cam.ac.uk).

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