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Crystal structures of (.mu.-trithio)bis[tricyclohexylgermanium(IV)] and (.mu.-trithio)bis[triphenylgermanium(IV)]

Francois Brisse, Micheline Vanier, Marc J. Olivier, Yves Gareau, and Kosta Steliou

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of the molecule is shown in Figure 2. The structure is similar to that of 4 with the PMe_3 group of 4 now replaced by CO. In this reaction the $Mn_2(CO)_{10}$ no doubt acts as a phosphine "sink" and permits the $Ni_2(\mu\text{-}t\text{-}Bu_2P)_2$ core to be attacked by CO present in solution. As noted above the tetracarbonyl complex $[Ni(\mu\text{-}Ph_2P)(CO)_2]_2$ is a known, stable species. However 6 does not react with further CO and can be recovered unchanged after exposure to CO (5 atm). IR and ^1H and ^{13}C NMR spectra under CO (1 atm) also show no change at room temperature and at −80 °C. However, replacement of one CO in 6 is possible with PMe_3 which yields 4 in high yield. At present we have no rationale to account for the asymmetric substitution patterns observed nor for the failure to form a tetracarbonyl complex by reaction of 6 with CO. Steric factors are probably not a major factor in the latter case since we have recently synthesized and characterized the cobalt complex $[Co(\mu\text{-}t\text{-}Bu_2P)(CO)_2]_2$ which is quite stable and has two pseudotetrahedral Co atoms.[22]

Lastly, it has been noted by several groups of workers that the ^{31}P NMR resonances for bridging $\mu\text{-}PPh_2$ ligands can be correlated with M–P–M bond angles and M–M bond distances. Low-field (50–200 ppm) resonances are associated with short (i.e., bonding) M–M distances and acute M–P–M angles. For the three Ni(I) di-*tert*-butylphosphido dimers which we have structurally characterized **1**, **4**, and **6**, the geometry of the M_2P_2 cores are very similar (Ni–Ni = ca. 2.4 Å, Ni–P–Ni = ca. 66°). However, the $^{31}P\{^1H\}$ NMR chemical shifts for the bridging phosphido phosphorus atoms cover a considerable downfield range ((1) δ 171, (4) δ 269, (6) δ 312.52). The downfield shift increases with increasing numbers of carbonyls on the central $Ni_2(\mu\text{-}t\text{-}Bu_2P)_2$ core. The trend may therefore be due to increased deshielding of the phosphorus nuclei by the CO ligands since they are better π acceptors than PMe_3 ligands. Further studies are in progress.

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Supplementary Material Available: Tables of thermal parameters, complete bond lengths and angles, and structure factors for 4 and 6 (24 pages). Ordering information is given on any current masthead page.

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[23] **Note Added in Proof**: The structure has recently been published, see: Deppisch, Von. B.; Schäfer, H. *Z. Anorg. Allg. Chem.* **1982**, *490*, 129.

Crystal Structures of (μ-Trithio)bis[tricyclohexylgermanium(IV)] and (μ-Trithio)bis[triphenylgermanium(IV)]

François Brisse,* Micheline Vanier, Marc J. Olivier, Yves Gareau, and Kosta Steliou

Département de Chimie, Université de Montréal, C.P. 6210, Succursale A,
Montréal, Québec, H3C 3V1 Canada

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Crystals of (μ-trithio)bis[tricyclohexylgermanium(IV)], $[(C_6H_{11})_3Ge]_2S_3$ (I), belong to the triclinic system of space group $P1$. The unit cell has the following dimensions: a = 9.004 (7) Å, b = 9.808 (4) Å, c = 11.815 (5) Å, α = 83.14 (3)°, β = 84.64 (5)°, γ = 66.92 (5)°, V = 951.8 Å^3, Z = 1, d_{calcd} = 1.291 Mg m^{-3}, $F(000)$ = 394, Cu Kα radiation, μ(Cu Kα) = 3.59 mm^{-1}. The structure, solved by direct methods, was refined by least squares to a final R value of 0.063 for 3185 observed reflections. $[(C_6H_5)_3Ge]_2S_3$ (II), (μ-trithio)bis[triphenylgermanium(IV)], is monoclinic of space group $P2_1/n$. The unit cell has the following dimensions: a = 11.969 (5) Å, b = 17.982 (6) Å, c = 16.741 (9) Å, β = 100.37 (4)°, V = 3543.9 Å^3, d_{calcd} = 1.319 Mg m^{-3}, Z = 4, $F(000)$ = 1432, Mo Kα radiation, μ(Mo Kα) = 1.864 mm^{-1}. The least-squares refinement of the atomic coordinates and temperature factors was concluded when R reached 0.096 for 1435 observed reflections. Both structures consist of a Ge–S–S–S–Ge sequence, in a coiled-type conformation, at the ends of which are bonded three cyclohexyl groups (I) or three phenyl groups (II). The two torsion angles describing the Ge–S–S–S–Ge part are both equal to 100.2 (3)° in I and to −96 (1) and −104 (1)° in II. The S–S, S–Ge, and Ge–C distances respectively have average values of 2.009, 2.282, and 1.976 Å in I and 2.023, 2.260, and 1.90 Å in II. The S–S–S angle is 111.3 (3)° in I and 107.5 (7)° in II while S–S–Ge average 105.0° in I and 103.1° in II. Around Ge, the S–Ge–C and C–Ge–C angles have mean values of 106.7 and 112.1°, respectively, for I and 107.6 and 111.4°, respectively, for II. The substituents on Ge have a propeller-like arrangement. Looking down the Ge–Ge direction they adopt a staggered disposition.

Introduction

As part of our continuing interest in the synthetic utility of group 4 metal-protected mercaptides,[1] we have prepared some phenyl- and cyclohexyl-substituted germanium(IV) polysulfides whose crystal structures have been established by X-ray analysis. This study has led us to some interesting observations concerning the substituent conformation about the sulfur sequence. For example, the dihedral angle between the sulfur substituents in most nonchelated carbon-bonded disulfides is known[2] to have values in the

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Table I. Fractional Atomic Coordinates for $[(C_6H_{11})_3Ge]_2S_3$ and Their Esd's[a] ($\times 10^4$) and U_{eq}[b] ($\times 10^4$ for Ge and $\times 10^3$ for S and C Atoms)

atom[c]	x	y	z	U_{eq}	atom[c]	x	y	z	U_{eq}
Ge2	0	0	0	415 (5)	C35	7430 (18)	−882 (15)	−5784 (13)	62 (6)
Ge1	3879 (2)	2557 (2)	−3946 (1)	408 (5)	C36	5957 (15)	−77 (13)	−5105 (13)	57 (6)
S3	30 (5)	1511 (4)	−1617 (3)	68 (2)	C41	65 (14)	−1856 (13)	−500 (10)	42 (5)
S2	1862 (5)	2199 (4)	−1437 (3)	61 (1)	C42	−926 (19)	−1642 (17)	−1560 (12)	65 (7)
S1	3841 (4)	1053 (4)	−2317 (3)	61 (2)	C43	−870 (20)	−3063 (19)	−1815 (14)	77 (8)
C11	2110 (14)	2913 (12)	−4850 (11)	45 (5)	C44	−1213 (23)	−4055 (19)	−887 (14)	79 (9)
C12	460 (15)	4219 (16)	−4458 (12)	56 (6)	C45	−184 (29)	−4349 (18)	66 (16)	103 (11)
C13	−896 (15)	4429 (19)	−5204 (14)	68 (7)	C46	−331 (19)	−2818 (15)	454 (11)	58 (6)
C14	−570 (17)	4837 (17)	−6460 (13)	64 (6)	C51	−1963 (10)	1164 (10)	828 (7)	22 (3)
C15	1001 (21)	3628 (22)	−6870 (14)	82 (9)	C52	−1909 (20)	2626 (18)	1078 (14)	72 (7)
C16	2466 (15)	3243 (16)	−6094 (11)	57 (6)	C53	−3495 (19)	3590 (18)	1693 (16)	80 (7)
C21	3839 (17)	4439 (14)	−3446 (13)	55 (6)	C54	−4936 (19)	3852 (18)	1021 (16)	79 (7)
C22	4384 (20)	5315 (16)	−4475 (12)	66 (7)	C55	−4968 (16)	2352 (22)	763 (15)	83 (8)
C23	5309 (21)	6582 (19)	−3060 (13)	72 (8)	C56	−3404 (18)	1422 (17)	156 (12)	62 (6)
C24	4343 (23)	6725 (18)	−4094 (16)	84 (9)	C61	1907 (14)	−351 (14)	942 (11)	46 (5)
C25	4663 (21)	5783 (16)	−2029 (10)	65 (7)	C62	1555 (18)	−765 (20)	2219 (11)	69 (7)
C26	4799 (20)	4247 (16)	−2480 (11)	66 (7)	C63	2862 (16)	−904 (19)	2902 (13)	69 (7)
C31	6079 (21)	1366 (17)	−4709 (16)	77 (8)	C64	4316 (19)	−2174 (20)	2540 (15)	76 (8)
C32	7481 (13)	1083 (17)	−4099 (12)	55 (6)	C65	4801 (21)	−1895 (22)	1327 (16)	84 (9)
C33	9054 (18)	169 (17)	−4791 (14)	68 (7)	C66	3402 (16)	−1513 (17)	544 (12)	61 (6)
C34	8967 (18)	−1183 (18)	−5159 (13)	67 (6)					

[a] The numbers in parentheses are the estimated standard deviations in the last significant digit. [b] $U_{eq} = {}^1/_3 \Sigma_i \Sigma_j U_{ij} a^*_i a^*_j a_i a_j$. [c] Atoms are labeled in agreement with Figure 1.

range of 90–100°. Deviation from this angle in the trans (180°) direction requires the substituents to be exceptionally bulky. A torsion angle of 115° has been reported[3] in 3,3,3′,3′-tetramethyl-D-cystine (*D*-penicillamine disulfide) dihydrochloride. In the case of (μ-dithio)bis[tricyclohexylgermanium(IV)] a surprisingly large dihedral angle of 154° has been found[4] for the Ge–S–S–Ge linkage. Although several crystal structures of germanium(IV) monosulfides, for example, those of (μ-thio)bis[tribenzylgermanium(IV)][5] and of (μ-thio)bis[triphenylgermanium(IV)],[6] are known, to our knowledge X-ray structural analyses of higher sulfur homologues have not been reported previously.

Experimental Section

(μ-Trithio)bis[tricyclohexylgermanium(IV)] was prepared in 85% yield by treating $(C_6H_{11})_3GeSH$[7a,b] (mp 86–87 °C) with SCl_2 and 2,4,6-trimethylpyridine in benzene: mp 159.5–161 °C. Anal. Calcd for $C_{36}H_{66}S_3Ge_2$: C, 58.41; H, 8.99; S, 12.99. Found: C, 58.40; H, 9.18; S, 13.08. Similarly, (μ-trithio)bis[triphenylgermanium(IV)] was prepared (75% yield) from $(C_6H_5)_3GeSH$[7b] (mp 197–200 °C). Anal. Calcd for $C_{36}H_{30}S_3Ge_2$: C, 61.45; H, 4.26; S, 13.65. Found: C, 63.36; H, 4.54; S, 13.69. Although crystals suitable for X-ray diffraction could be grown from hexane/CCl_4, both trisulfides undergo significant decomposition and deposit elemental sulfur during recrystallization.

X-ray Data Collection. Precession photographs of I indicate that the crystals belong to the triclinic system with one molecule per unit cell. This led us to the *P*1 space group. Compound II belongs to the monoclinic system of space group $P2_1/n$. The unit-cell dimensions were arrived at by a least-squares refinement of the angular measurements of 25 reflections centered on the Nonius CAD-4 diffractometer using graphite-monochromatized copper radiation (λ (Cu K$\bar{\alpha}$) = 1.54178 Å) for I and molybdenum radiation (λ(Mo K$\bar{\alpha}$) = 0.71069 Å) for II.

Three-dimensional intensity data were collected on the Nonius CAD-4 diffractometer using the $\omega/2\theta$ scan technique. The details of the data collection have been placed with the supplementary material. The reflection intensities were corrected for background and converted to structure factors by applying Lorentz and polarization corrections. In the case of I the absorption correction was applied since μ(Cu Kα) = 3.59 mm^{-1} and the crystal had dimensions 0.40 × 0.40 × 0.07 mm. The value of the transmission factor varied from 0.28 to 0.78. Of the 3395 measured reflections, 3185 were considered observed, as the net count of each was higher than $1.90\sigma(I)$, where $\sigma(I)$ is the standard deviation estimated from counting statistics.[8] Because no good single crystal of II could be grown (the compound decomposes with the deposition of elemental sulfur during recrystallization) a chunk of roughly 0.3–0.4 mm was used for the data collection. Since the crystal was of an ill-defined shape, no absorption correction was applied. In this case, of the 2433 measured reflections only, 1455 were considered observed.

Solution and Refinement of the Structure. The structure of I was solved in space group *P*1 by direct methods using the MULTAN multisolution program.[9] Most atoms were revealed on the *E* map corresponding to the set of phases having the highest combined figure of merit. The remaining atoms were eventually located following a series of least-squares refinements and difference Fourier syntheses. The structure of II was also only partially revealed by direct methods.

The scattering factors for neutral C, O, S, and Ge atoms[10] and for H atoms[11] were used. The real and imaginary parts of the anomalous dispersion for S and Ge[12] were also included in the structure factor calculations. The function minimized was $\sum w||F_o| - |F_c||^2$. All non-hydrogen atoms were given anisotropic temperature factors. The hydrogen atoms whose positions were calculated (C–H = 0.95 Å; C–C–H = 109.46°) were assigned isotropic temperature factors of B = 4.5 Å^2. In the case of I, the R value at the end of the refinement was $R = \sum \Delta F / \sum F_o = 0.063$ for the observed reflections and 0.070 for all measured reflections.

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(9) The programs used in this work are locally adapted versions of NRC-2, data reduction, NRC-3, absorption correction, NRC-10, bond distances and angles, and NRC-22, mean planes (Ahmed, Hall, Pippy, and Huber, 1973), FORDAP, Fourier and Patterson maps (A. Zalkin), NUCLS, least-squares refinement (Doedens and Ibers, 1967), MULTAN, multisolution program (Main, Woolfson, Lessinger, Germain, and Declercq, 1978), and ORTEP stereo drawings (Johnson, 1965).

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Table II. Fractional Atomic Coordinates for $[(C_6H_5)_3Ge]_2S_3$ and Their Esd's[a] ($\times 10^4$) and U_{eq}[b] ($\times 10^4$ for Ge and S and $\times 10^3$ for C)

atom[c]	x	y	z	U_{eq}	atom[c]	x	y	z	U_{eq}
Ge1	8700 (3)	2040 (2)	3191 (3)	514 (16)	C35	10744 (30)	3752 (23)	2442 (26)	70 (19)
Ge2	3500 (3)	1395 (2)	2973 (3)	510 (16)	C36	10292 (29)	3130 (20)	2870 (21)	53 (16)
S3	5323 (8)	1048 (6)	2995 (7)	716 (52)	C41	2750 (28)	1410 (21)	1907 (20)	49 (15)
S2	6240 (9)	1740 (7)	3807 (7)	728 (52)	C42	2859 (29)	907 (24)	1326 (22)	62 (17)
S1	6954 (8)	2516 (6)	3175 (7)	703 (50)	C43	2330 (33)	913 (22)	536 (22)	63 (17)
C11	8729 (30)	1073 (22)	2712 (24)	63 (17)	C44	1592 (33)	1441 (25)	265 (21)	70 (18)
C12	9108 (31)	969 (23)	1965 (22)	60 (17)	C45	1395 (30)	1969 (25)	798 (22)	70 (19)
C13	9134 (33)	334 (22)	1577 (26)	76 (20)	C46	1928 (30)	1957 (25)	1577 (21)	68 (18)
C14	8635 (37)	−264 (26)	1869 (27)	90 (21)	C51	2901 (27)	614 (18)	3540 (22)	42 (15)
C15	8187 (33)	−206 (23)	2606 (26)	75 (19)	C52	3458 (30)	445 (21)	4355 (20)	52 (16)
C16	8213 (30)	484 (22)	2983 (26)	71 (19)	C53	3020 (33)	−146 (23)	4759 (24)	68 (18)
C21	9427 (28)	1932 (21)	4263 (21)	49 (16)	C54	2059 (33)	−543 (23)	4418 (24)	70 (19)
C22	10186 (29)	1395 (24)	4561 (22)	63 (17)	C55	1531 (33)	−355 (24)	3670 (25)	74 (19)
C23	10731 (31)	1293 (27)	5332 (22)	75 (19)	C56	1922 (28)	206 (20)	3232 (24)	55 (16)
C24	10567 (28)	1772 (25)	5892 (25)	73 (19)	C61	3460 (28)	2348 (20)	3466 (22)	52 (16)
C25	9764 (33)	2306 (25)	5684 (23)	74 (20)	C62	3785 (30)	3023 (23)	3162 (23)	62 (17)
C26	9238 (30)	2365 (23)	4865 (23)	67 (18)	C63	3741 (36)	3679 (23)	3562 (29)	88 (21)
C31	9317 (27)	2815 (20)	2573 (25)	58 (17)	C64	3413 (32)	3755 (23)	4268 (26)	75 (19)
C32	8728 (32)	3027 (24)	1816 (24)	72 (18)	C65	3076 (40)	3122 (26)	4614 (25)	99 (23)
C33	9136 (37)	3561 (29)	1369 (25)	91 (22)	C66	3083 (36)	2433 (25)	4270 (24)	78 (20)
C34	10129 (37)	3903 (24)	1676 (25)	79 (20)					

[a] The numbers in parentheses are the estimated standard deviations in the last significant digit. [b] $U_{eq} = \frac{1}{3}\Sigma_i\Sigma_j U_{ij}a^*_i a^*_j a_i a_j$. [c] Atoms are labeled in agreement with Figure 1.

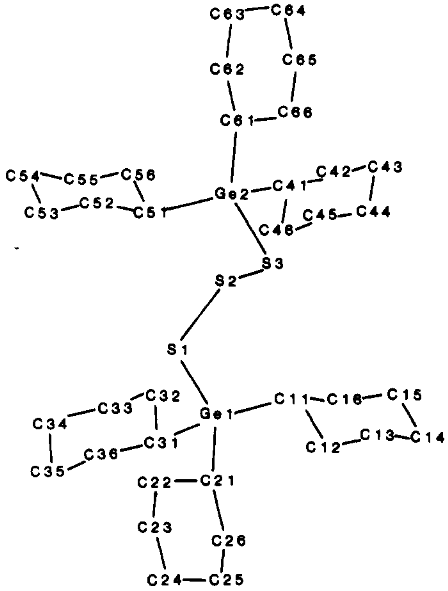

Figure 1. Schematic view of a molecule of $[(C_6H_{11})_3Ge]_2S_3$ (I) and atomic numbering. The same numbering applies to $[(C_6H_5)_3Ge]_2S_3$ (II).

A final difference electron density map revealed a few small peaks. The highest of them (1.2 e Å^{-3}) was in the vicinity of the sulfur atoms, at 1.92, 2.21, and 2.04 Å from the S(1), S(2), and S(3) atoms, respectively. This residual electron density may be related to the slow decomposition of the compound. The final positional parameters and their estimated standard deviations are presented in Table I. For compound II, the anisotropic thermal parameters and the positional parameters of the non-hydrogen atoms were refined by the block-diagonal least-squares approximation while the H atoms were kept at a fixed position relative to the C atoms to which they were bonded (C–H = 0.95 Å; C–C–H = 120°). The refinement converged to $R = 0.096$ for all observed reflections. The lowest and highest peaks in a final Fourier difference map were −0.3 and 0.4 e Å^{-3}. The final atomic coordinates of II are given in Table II. The lists of anisotropic temperature factors and of the observed and calculated structure amplitudes are available.[13]

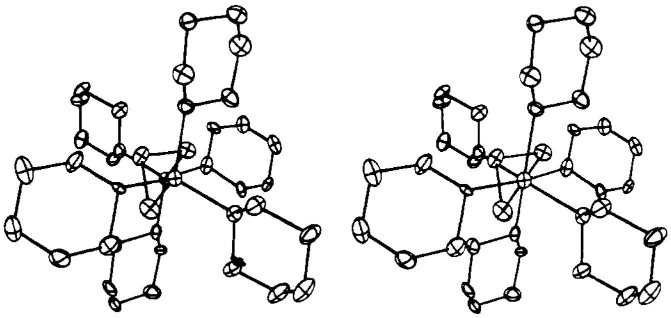

Figure 2. Stereoview showing one molecule of $[(C_6H_{11})_3Ge]_2S_3$ down the Ge–Ge direction.

Results and Discussion

The atomic numbering applying to both molecules is given in Figure 1 while the stereo pairs shown in Figures 2 and 3 represent molecules I and II, respectively. Both molecules consist of a Ge–S–S–S–Ge sequence where each Ge atom is bonded to three cyclohexyl rings (in the chair conformation) for compound I or to three planar benzene rings for compound II.

The Ge–S–S–S–Ge Sequence. Both molecules have the same conformation along the Ge–S–S–S–Ge sequence of atoms. The stereo pair shown in Figure 2 has been prepared so that the viewer may appreciate the coiled or helicoidal-type conformation adopted in the Ge–S–S–S–Ge part of the molecule. The actual values of the torsion angles of interest are given in Table III. Due to the minimization of sulfur lone-pair–lone-pair repulsive interactions,[14,15] the distributions of sulfur-sulfur dihedral angles in compounds containing an S–S–S–X sequence, where X = S, N, or C, are known to be centered around the optimal value of 90°[15,16] (see Figure 4). Both values observed here for the two S–S–S–Ge torsion angles in I are equal to 100.2 (3)° while the corresponding values are −96 (1) and −104 (1)° in II and are in agreement with the generally observed values[16] summarized in Figure 4. The four atoms Ge1, S1, S3, and Ge2 of (I) are coplanar (χ^2 =

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(13) Supplementary material.

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(16) Obtained through the use of the Cambridge data file.

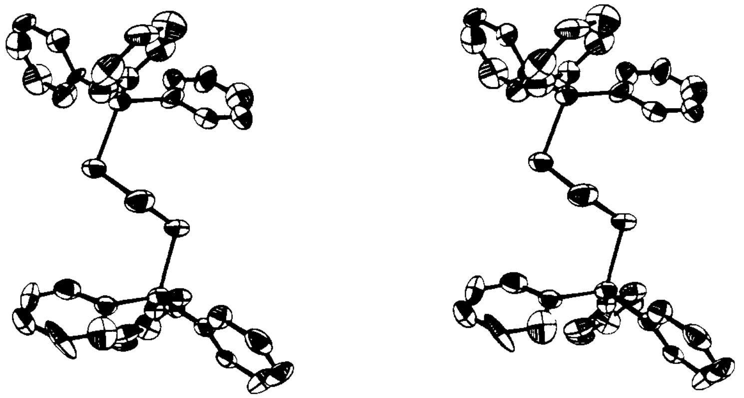

Figure 3. Stereoview of the $[(C_6H_5)_3Ge]_2S_3$ molecule.

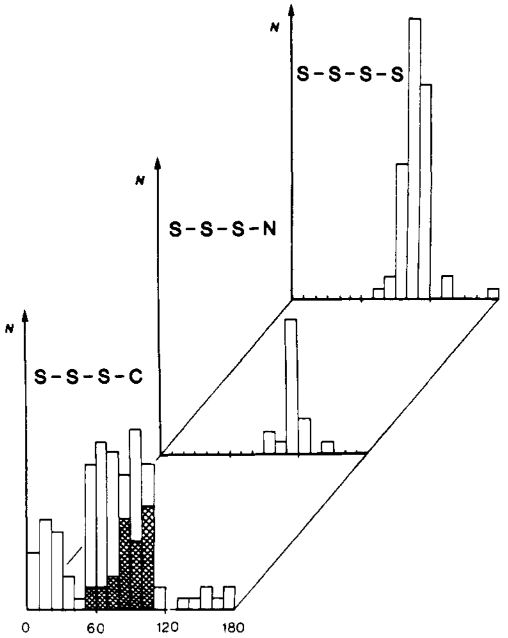

Figure 4. Distribution of the S–S–S–X torsion angles where X = C, N, or S atoms. The hatched area corresponds to compounds in which the S–S–S–C sequence is not part of a cycle. This plot was made possible by the use of the Cambridge data file.

7.1) while S2 is at 1.136 (4) Å from this plane. Similarly in II, only S2 is out of the Ge1, S1, S3, and Ge2 plane (χ^2 = 0.57), at 1.19 (1) Å.

The bond distances and angles for the Ge–S–S–S–Ge part of the molecules are given in Table III. The S–S bonds have lengths of 1.970 (6) and 2.048 (7) Å in I and 2.016 (17) and 2.061 (16) Å in II. These quantities are in good agreement with literature[16] values for which the average, based on 440 reported measurements, is 2.064 Å. It should be noted that only 13 of the 440 distances were shorter than 2.000 Å.

The angles at the S atoms are larger for the S–S–S than for the Ge–S–S angles. The S1–S2–S3 bond angle is 111.3 (3)° in I and 107.5 (7)° in II while the Ge1–S1–S2 and Ge2–S3–S2 bond angles are 105.0 (2) and 104.8 (2)° in I and 104.3 (6) and 102.0 (6)° in II.

The two Ge–S distances have values of 2.278 (5) and 2.286 (5) Å in the case of (μ-trithio)bis[tricyclohexylgermanium(IV)] and 2.254 (11) and 2.263 (11) Å in the triphenyl analogue. These values are slightly longer than usual. For example, a value of 2.233 (4) Å was reported[5] in (μ-thio)bis[tribenzylgermanium(IV)] and in two polymorphs of hexaphenyldigermyl sulfide,[6] the Ge–S distances averaged 2.237 and 2.234 Å, respectively. Another "short" Ge–S distance was reported in tetramethylgermanium hexasulfide[17] where Ge–S = 2.218 (3) Å. It is clear that for compounds having a Ge–S–Ge moiety, the Ge–S distance is shorter than for those where there is a Ge–S–S sequence of atoms.

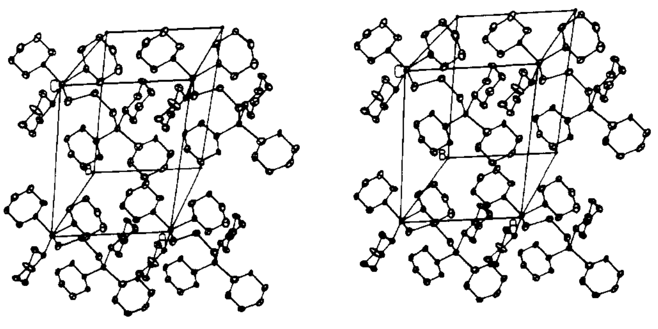

Figure 5. Stereoview of the unit-cell content of $[(C_6H_{11})_3Ge]_2S_3$. The *a* axis is horizontal, and the *c* axis is almost vertical.

The Ge Coordination. Figures 2 and 3 clearly reveal the tetrahedral coordination around the germanium atoms. In both compounds the angles involving the Ge atom are of two types. The C–Ge–C angles average 111.4° (phenyl) and 112.1° (cyclohexyl), and the S–Ge–C angles correspondingly have averages of 107.6° and 106.7°, respectively. The above C–Ge–C values appear, therefore, not to depend on the state of hybridization of the C atoms. However, as expected, the Ge–C bond lengths, on the other hand, do change significantly according to the state of hybridization of the C atom. In the case of Ge–C(sp^3), as in (μ-trithio)bis[tricyclohexylgermanium(IV)] an average distance of 1.976 Å is observed and an average of 1.971 Å is reported for (μ-thio)bis[tribenzylgermanium(IV)].[5] In the two polymorphs of hexaphenyldigermyl sulfide[6] the Ge–C(sp^2) distances average 1.945 (5) and 1.943 (4) Å, respectively. In the structure of triphenylgermanium *p*-tert-butylphenyl mercaptide,[18] the Ge–C(sp^2) distances have an average of 1.938 (8) Å. In the case of II the individual Ge–C(sp^2) bond lengths, ranging in values from 1.86 (3) to 1.96 (4) Å, have an average of only 1.90 Å.

The Cyclohexyl and Phenyl Groups. The interatomic distances and angles as well as the torsion angles calculated from the final refined coordinates for the cyclohexyl groups (I) and the phenyl rings (II) are available.[13] In I the C(sp^3)–C(sp^3) bond distances, ranging from 1.43 (2) to 1.61 (2) Å, average 1.515 Å. The C(sp^3)–C(sp^3)–C(sp^3) angles are, on the average, slightly larger than the value for a tetrahedral angle. The average angle is 111.4°

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Table III. Bond Distances (Å), Bond Angles (deg), Torsion Angles (deg), and Their Estimated Standard Deviations in Parentheses between Atoms in the Ge-S-S-S-Ge Chains in I and II

	I	II		I	II
		Distances			
Ge1-S1	2.278 (5)	2.254 (11)	Ge2-S3	2.286 (5)	2.263 (11)
S1-S2	1.970 (6)	2.031 (16)	S2-S3	2.048 (7)	2.016 (17)
Ge1-C11	1.896 (13)	1.92 (4)	Ge2-C41	1.958 (12)	1.86 (3)
Ge1-C21	1.990 (15)	1.86 (3)	Ge2-C51	1.935 (9)	1.91 (3)
Ge1-C31	2.050 (18)	1.96 (4)	Ge2-C61	2.027 (13)	1.91 (4)
		Angles			
Ge1-S1-S2	104.8 (2)	102.0 (6)	Ge2-S3-S2	105.0 (2)	104.3 (6)
S1-S2-S3	111.3 (3)	107.5 (7)			
S1-Ge1-C11	111.9 (4)	115.2 (12)	S3-Ge2-C41	106.3 (4)	108.6 (11)
S1-Ge1-C21	106.3 (4)	108.9 (11)	S3-Ge2-C51	103.2 (3)	103.7 (11)
S1-Ge1-C31	101.8 (5)	99.2 (11)	S3-Ge2-C61	110.6 (4)	109.8 (11)
C11-Ge1-C21	111.5 (6)	105.6 (16)	C41-Ge2-C51	116.0 (5)	109.4 (15)
C11-Ge1-C31	113.6 (6)	112.8 (16)	C41-Ge2-C61	111.8 (5)	111.0 (15)
C21-Ge1-C31	111.2 (7)	115.4 (15)	C51-Ge2-C61	108.6 (5)	114.0 (15)
		Torsion Angles			
Ge1-S1-S2-S3	100.3 (3)	−96.3 (7)	S2-S1-Ge1-C31	174.3 (5)	179.9 (12)
S1-S2-S3-Ge2	100.2 (3)	−103.9 (7)	S2-S3-Ge2-C41	−128.5 (5)	137.2 (12)
S2-S1-Ge1-C11	−64.1 (6)	59.2 (14)	S2-S3-Ge2-C51	109.0 (5)	−106.6 (12)
S2-S1-Ge1-C21	57.8 (5)	−59.1 (13)	S2-S3-Ge2-C61	−7.0 (5)	15.6 (13)

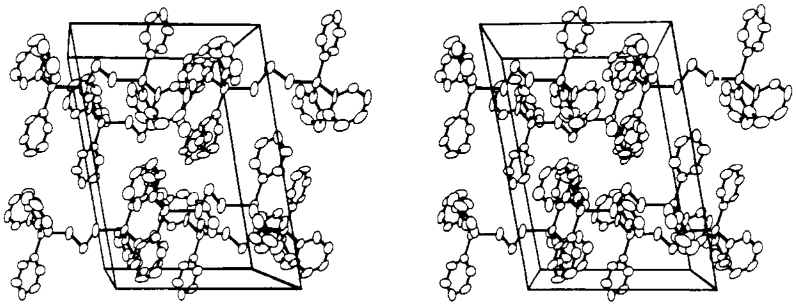

Figure 6. Stereoview showing the disposition of the $[(C_6H_5)_3Ge]_2S_3$ molecules in the unit cell. The vertical axis is *a*, and the horizontal axis is *c*.

while the individual values vary from 108.0 (14) to 119.0 (16)°. All six cyclohexyl groups are in the chair conformation. The torsion angles vary from 47.4 (16) to 64.7 (18)° and average 54.5°. These observed quantities are in good agreement with the values for the valence angles (111.1°) and torsion angles (55°) which have been computed[19] for the minimum energy conformation of cyclohexane. Although the individual angles at the C atoms in the phenyl rings in II have values in the range of 109 (3)–129 (4)°, they average 120° in each of the phenyl rings. Furthermore, the comparison of similar angles in the six different rings reveals that the angles at the carbon atom attached to Ge average 114.0°. Simultaneously, the two angles adjacent to it average 123.9 and 122.4°, while the three remaining angles are not affected since they have averages of 120.6, 119.0, and 119.7° respectively. Such a concomitant effect is a significant phenomenon of the type described[20] earlier. All phenyl rings are planar, and the germanium atoms, although not included in the least-squares plane calculations, are also coplanar.

The three cyclohexyl substituents in I or phenyl groups in II bonded to each Ge atom have a propeller-like arrangement. When seen along the Ge–Ge direction, the cyclohexyl or the phenyl groups adopt a staggered disposition (Figure 2).

Packing of the Molecule. There are only two short contacts between adjacent molecules of I. They are S(2)···C(24), $(0\bar{1}0)$ = 3.721 (8) Å, and S(2)···C(25), $(0\bar{1}0)$ = 3.734 (17) Å. Other longer contacts are between carbon atoms. There are no unusual short contacts in II either.

Consequently, the molecules are held by van der Waals forces only. Stereo pairs of the molecules in their unit cells are shown in Figures 5 and 6 for I and II, respectively.

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Registry No. I, 85185-49-5; II, 85185-50-8.

Supplementary Material Available: The lists of observed and calculated structure amplitudes, anisotropic thermal parameters, and bond distances and angles in the cyclohexyl and phenyl rings as well as the equations of the least-squares planes of the phenyl rings (30 pages). Ordering information is given on any current masthead page.

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