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CRYSTAL AND MOLECULAR STRUCTURE OF $\Delta^{1,7}$2,2,6,6-TETRAMETHYL-4-THIA-8,8,9,9-TETRACHLORO-8,9-DIGERMABICYCLO[5.2.0]NONENE; THE FIRST REPRESENTATIVE OF 1,2-DIGERMACYCLOBUTENES

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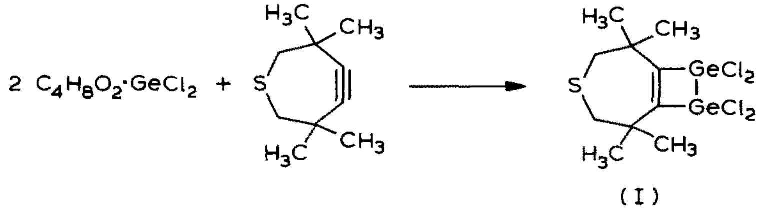
Summary

The first representative of 1,2-digermacyclobutenes, $\Delta^{1,7}$-2,2,6,6-tetramethyl-4-thia-8,8,9,9-tetrachloro-8,9-digermabicyclo[5.2.0]nonene, and its structure by an X-ray crystallographic study.

Results

The reaction of the dioxane complex of $GeCl_2$ [1] with 3,3,6,6-tetramethyl-1-thiacyclohept-4-yne [2] in THF solution under an inert atmosphere was found to give high yields (~ 85%) of a stable crystalline compound, $\Delta^{1,7}$-2,2,6,6-tetramethyl-4-thia-8,8,9,9-tetrachloro-8,9-digermabicyclo[5.2.0]nonene (I), which is the first representative of 1,2-digermacyclobutenes. The structure of this compound was established unequivocally by an X-ray structural study.



(I)

In spite of the presence of a highly strained digermacyclobutene moiety, compound I exhibits surprisingly high thermal stability. In the inert atmosphere crystals of I are stable for indefinite time. Irreversible thermal transformation (probably

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polymerization) occurs only on melting near 200 °C. In CH_2Cl_2 solution compound I survives short-term treatment with gaseous HCl and O_2. In this respect I differs from the much less stable and reactive 1,2-disilacyclobutenes [4–8].

The formation of I can be explained either by successive (cf. [7]) or by simultaneous (cf. [4,6]) addition of $GeCl_2$ molecules to the cyclic acetylene. In the first case the formation of intermediate germirene Ge, should be supposed while the second route presumes the intermediate formation of dichlorogermylene dimer with a double Ge=Ge bond. Both these molecules are of great interest with respect to the studies of small heterocycles and heteroolefines.

Discussion

The digermacyclobutene cycle of molecule I * is planar, the deviations of the C(1) and C(2) atoms from its mean-square plane (A) do not exceed 0.017(5) Å. The C(3) and C(7) atoms are displaced from this plane by 0.030(6) and 0.071(6) Å, respectively. The atoms C(1), C(2), C(3) and C(7) are situated in one plane (B) within 0.008(6) Å. The dihedral angle between planes A and B is equal to 2.8°. The conformation of the 7-membered 4-thiacycloheptene ring is a $S(\alpha)$-chair according to the accepted nomenclature [9]. The dihedral angles between the plane C(3)C(4)C(7)C(8) (the maximum deviation is 0.005(8) Å) and the planes SC(4)C(8) and B are equal to 63.0 and 34.3°, respectively.

The bond lengths Ge–Cl (2.145–2.150(2) Å) and Ge–C (1.998(6) and 2.002(6) Å) have normal values (Ge^{IV}–Cl 2.08–2.15 and Ge^{IV}–$C(sp^2)$ 1.96–2.01 Å) [10–12]. The Ge–Ge bond (2.380(1) Å) is considerably shorter than analogous bonds in gaseous digermane (2.403(3) Å [13]), hexaphenyldigermane (2.437(2) Å [14]) and in germanium metal (2.450(1) Å [15]). The length of the double C(1)=C(2) bond of 1.319(8) Å is close to the standard $C(sp^2)$=$C(sp^2)$ bond length (1.337 Å [16]) and to the value found in cyclobutene (1.33(4) Å [17]).

Experimental

IR spectra were recorded with a Hitachi-Perkin-Elmer 225 spectrometer in KBr pellets. ^1H NMR spectra and ^{13}C (natural abundance) NMR spectra were measured with Tesla BS-467 (60 MHz) and Bruker WH-360 (90.5 MHz) spectrometers, respectively. Mass spectra were recorded either with a Varian MAT CH-6 or a Kratos MS-30 instruments.

Compound I (m.p. 192–194 °C) was purified by sublimation in vacuo and recrystallization from CH_2Cl_2. Found: C, 26.54; H, 3.70; S, 6.99; Cl, 30.52; Ge, 32.00. Calcd. for $C_{10}H_{16}SGe_2Cl_4$: C, 26.38; H, 3.54; S, 7.04; Cl, 30.52; Ge, 31.15%.

^1H NMR spectrum (in CH_2Cl_2, δ, ppm): singlets 1.50 (12 H; CH_3), 2.67 (4 H; CH_2). ^{13}C NMR spectrum (in $CDCl_3$, δ, ppm): 30.6 (CH_3), 31.2 (C_{tert}), 46.6 (CH_2), 170.9 (C=C). Mass spectrum (electron impact), m/z: 456$[M]^+$, 312$[M-GeCl_2]^+$, 297$[M-GeCl_2-CH_3]^+$, 277$[M-GeCl_3]^+$, 168$[M-Ge_2Cl_4]^+$, 153$[M-Ge_2Cl_4-CH_3]^+$. Mass spectrum (chemical ionization), m/z: 457$[M+H]^+$, 277$[M-GeCl_3]^+$, 169$[M-Ge_2Cl_4+H]^+$, 168$[M-Ge_2Cl_4]^+$, 153$[M-Ge_2Cl_4-CH_3]^+$.

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* The numbering of atoms used here differs from that accepted in the IUPAC nomenclature

The m/z values of Ge-containing ions are given for the strongest peak in the group of peaks corresponding to different isotopic combinations of Ge and Cl.

The strong influence of germyl groups on the double C=C bond is exhibited in the absence of ν(C=C) bands in the region 1510–2000 cm^{-1} in the IR and Raman spectra (cf. [3]).

X-Ray diffraction study of I

Crystals of I are monoclinic, at $-50\,^\circ$C $a = 9.301(2)$, $b = 11.059(3)$, $c = 16.031(4)$ Å, $\beta = 99.30(2)^\circ$, $d_x = 1.86$ g cm^{-3}, space group $P2_1/n$.

Unit cell parameters and intensities of 2485 independent reflections with $F^2 \geqslant 4\sigma$ were measured at $-50\,^\circ$C with an automatic four-circle Syntex P2$_1$ diffractometer (λMo-K_α, graphite monochromator, $\theta/2\theta$ scan, $2\theta \leqslant 50^\circ$). Coordinates of both Ge atoms were determined from a Patterson synthesis, all non-hydrogen atoms were

TABLE 1

ATOMIC COORDINATES ($\times 10^4$, for Ge $\times 10^5$) AND EQUIVALENT ISOTROPIC THERMAL PARAMETERS, $B_{eq} = 1/3 \Sigma_i \Sigma_j B_{ij} a_i^* a_j^* (\vec{a}_i \vec{a}_j)$

Atom	x	y	z	B_{eq} (Å^2)
Ge(1)	5523(7)	23567(6)	32597(4)	1.67(2)
Ge(2)	27934(7)	23306(6)	27229(4)	1.65(2)
Cl(1)	134(2)	3824(2)	4067(1)	2.79(5)
Cl(2)	−344(2)	827(2)	3820(1)	3.00(5)
Cl(3)	4208(2)	3856(2)	3023(1)	2.65(4)
Cl(4)	4241(2)	814(2)	2765(1)	3.01(5)
S	−1175(2)	2921(2)	−79(1)	4.06(6)
C(1)	6(6)	2533(5)	2008(4)	1.62(15)
C(2)	1242(6)	2488(5)	1706(4)	1.49(14)
C(3)	−1616(7)	2596(6)	1620(4)	2.07(16)
C(4)	−1907(8)	3406(7)	832(4)	2.83(20)
C(5)	−2142(9)	1296(8)	1402(6)	3.50(23)
C(6)	−2485(9)	3128(9)	2256(5)	3.12(23)
C(7)	1673(7)	2521(5)	820(4)	1.87(15)
C(8)	690(9)	3327(7)	205(5)	2.88(21)
C(9)	1618(9)	1200(7)	486(5)	2.89(21)
C(10)	3222(9)	2978(9)	874(5)	3.34(23)

TABLE 2

BOND LENGTHS (Å) IN MOLECULE I

Bond		Bond	
Ge(1)–Ge(2)	2.380(1)	C(1)–C(2)	1.319(8)
Ge(1)–Cl(1)	2.150(2)	C(1)–C(3)	1.537(9)
Ge(1)–Cl(2)	2.146(2)	C(2)–C(7)	1.536(8)
Ge(2)–Cl(3)	2.146(2)	C(3)–C(4)	1.54(1)
Ge(2)–Cl(4)	2.145(2)	C(7)–C(8)	1.52(1)
Ge(1)–C(1)	1.998(6)	C(3)–C(5)	1.54(1)
Ge(2)–C(2)	2.002(6)	C(3)–C(6)	1.52(1)
S–C(4)	1.790(8)	C(7)–C(9)	1.55(1)
S–C(8)	1.779(8)	C(7)–C(10)	1.52(1)

than located in a subsequent series of Fourier maps. The structure was refined by full-matrix least-squares technique first in isotropic and then in anisotropic approximation. All H atoms were found in the difference Fourier map and included in refinement with fixed thermal parameters $B_{iso} = 4.5$ Å. The final R-value is equal to 0.0428 ($R_w = 0.0479$). All calculations were carried out with an Eclipse S/200 computer using the INEXTL programs [18]. Coordinates of non-hydrogen atoms and equivalent isotropic thermal parameters are given in Table 1, the general view of the molecule is shown in Fig. 1. Bond lengths and bond angles are listed in Tables 2 and 3.

TABLE 3

BOND ANGLES (degrees) IN MOLECULE I

Angle		Angle	
Ge(2)Ge(1)Cl(1)	118.75(6)	Ge(1)Ge(2)Cl(3)	116.71(6)
Ge(2)Ge(1)Cl(2)	124.33(6)	Ge(1)Ge(2)Cl(4)	125 45(6)
Ge(2)Ge(1)C(1)	74.6(2)	Ge(1)Ge(2)C(2)	74.7(2)
Cl(1)Ge(1)Cl(2)	102.84(7)	Cl(3)Ge(2)Cl(4)	104.39(7)
Cl(1)Ge(1)C(1)	119.3(2)	Cl(3)Ge(2)C(2)	116.7(2)
Cl(2)Ge(1)C(1)	116.4(2)	Cl(4)Ge(2)C(2)	117.4(2)
Ge(1)C(1)C(2)	105 7(4)	Ge(2)C(2)C(1)	105.1(4)
Ge(1)C(1)C(3)	119.1(4)	Ge(2)C(2)C(7)	119.6(4)
C(2)C(1)C(3)	135.2(5)	C(1)C(2)C(7)	135 4(5)
C(1)C(3)C(4)	113.0(5)	C(2)C(7)C(8)	113.3(5)
C(1)C(3)C(5)	107.8(5)	C(2)C(7)C(9)	107 3(5)
C(1)C(3)C(6)	109.7(5)	C(2)C(7)C(10)	110 5(5)
C(4)C(3)C(5)	107.7(5)	C(8)C(7)C(9)	110.1(6)
C(4)C(3)C(6)	106.5(5)	C(8)C(7)C(10)	107.9(6)
C(5)C(3)C(6)	109.2(6)	C(9)C(7)C(10)	108.1(6)
C(3)C(4)S	117.1(5)	C(7)C(8)S	118.5(5)
C(3)C(4)SC(8)	101.5(4)		

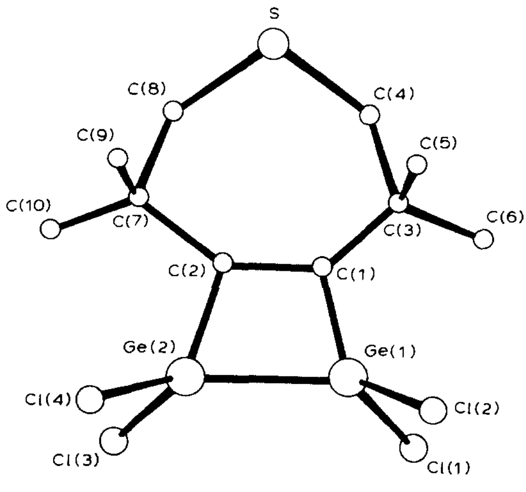

Fig. 1. The structure of I with atomic numbering.

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