

0.08 Å<sup>2</sup>;  $\sum w(|F_o| - |F_c|)^2$  minimized with  $w = [\sigma^2(F_o)]^{-1}$ ; max.  $\Delta/\sigma = 0.063$ , av. = 0.004;  $(\Delta\rho)_{\max} = 0.67$ ,  $(\Delta\rho)_{\min} = -0.50 \text{ e \AA}^{-3}$ ;  $R = 0.067$ ,  $wR = 0.089$ ,  $S = 2.93$ ; expected *S* configuration at chiral C atoms confirmed by refinement on  $\eta$  parameter (Rodgers, 1981) [ $\eta = 1.14$  (36),  $(1 + \eta)/\sigma(\eta) = 5.4$ ]; a solvent molecule of nitromethane was disordered over two sites, with occupancies of each site set at 0.5; atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 71–151) with corrections for anomalous scattering; calculations carried out on a MicroVAX 3600 computer using the Glasgow *GX* suite of programs (Mallinson & Muir, 1985).

**Discussion.** Final positional parameters are given in Table 1, with selected bond distances and angles in Table 2.\* The atomic labelling scheme and molecular structures of the two independent molecules, (*A*) and (*B*), are shown in Figs. 1 and 2. There are only relatively minor differences between the two crystal-

\* Lists of structure factors, anisotropic thermal parameters, calculated H-atom positional parameters, and a complete listing of bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54438 (26 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

lographically independent molecules. The Mo—Mo distances of 2.172 (3) and 2.154 (3) Å [(*A*) and (*B*) respectively] are similar, differing by only  $5\sigma$ , and fall within the range previously tabulated (Agaskar *et al.*, 1986). The torsion angle P—Mo—Mo—P ( $\varphi$ ) defines the degree of twist in the Mo<sub>2</sub> chromophore, and is 25.8 (3)° for (*A*) and 21.9 (3)° for (*B*). The nearly linear SCN ligands [range of angle N—C—S 174 (3)–178 (3)°] are *N*-coordinated to the Mo atoms, as found in [Mo<sub>2</sub>(SCN)<sub>8</sub>]<sup>4-</sup> (Bino, Cotton & Fanwick, 1979), Mo<sub>2</sub>(SCN)<sub>4</sub>(dppm)<sub>2</sub> (Abbott, Bose, Cotton, Hall & Sekutowski, 1978) and Mo<sub>2</sub>(SCN)<sub>4</sub>(Ph<sub>2</sub>Ppy)<sub>2</sub> (Cotton & Matusz, 1989).

#### References

- ABBOTT, E. H., BOSE, K. S., COTTON, F. A., HALL, W. T. & SEKUTOWSKI, J. C. (1978). *Inorg. Chem.* **17**, 3240–3245.  
 AGASKAR, P. A., COTTON, F. A., FRASER, I. F., MANOJLOVIC-MUIR, L. J., MUIR, K. W. & PEACOCK, R. D. (1986). *Inorg. Chem.* **25**, 2511–2519.  
 BINO, A., COTTON, F. A. & FANWICK, P. E. (1979). *Inorg. Chem.* **18**, 3558–3561.  
 COTTON, F. A. & MATUSZ, M. (1989). *Inorg. Chim. Acta*, **157**, 223–225.  
 GILMORE, C. J. (1984). *J. Appl. Cryst.* **17**, 42–46.  
 MALLINSON, P. R. & MUIR, K. W. (1985). *J. Appl. Cryst.* **18**, 51–53.  
 PEACOCK, R. D. (1987). *Polyhedron*, **6**, 715–721.  
 RODGERS, D. (1981). *Acta Cryst.* **A37**, 734–741.  
 WALKER, N. & STUART, D. (1983). *Acta Cryst.* **A39**, 158–166.

*Acta Cryst.* (1991). **C47**, 2558–2561

## Structure of Tetraspiro[1,3,5,7-tetraoxa-2,4,6,8-tetragermacyclooctane-2,1':4,1'':6,1''':8,1''''-tetrakisgerminane]

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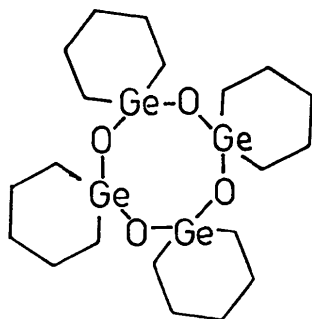
(Received 15 February 1991; accepted 11 April 1991)

**Abstract.** C<sub>20</sub>H<sub>40</sub>Ge<sub>4</sub>O<sub>4</sub>,  $M_r = 634.89$ , monoclinic, *C2/c*,  $a = 13.628$  (4),  $b = 22.562$  (3),  $c = 10.329$  (3) Å,  $\beta = 128.47$  (2)°,  $V = 2486$  (1) Å<sup>3</sup>,  $Z = 4$ ,  $D_m = 1.67$ ,  $D_x = 1.696 \text{ Mg m}^{-3}$ ,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 4.75 \text{ mm}^{-1}$ ,  $F(000) = 1280$ ,  $T = 142 \text{ K}$ ,  $R = 0.037$  for 2515 unique reflections. The germacyclohexane rings adopt chair conformations in which the fold of the ring is smaller in the vicinity of and greater away

from the germanium atom. The tetraoxatetragermacyclooctane ring adopts a skewed-tub conformation.

**Introduction.** Germacyclohexane is a key compound in the stereochemistry of organogermanium compounds. In our previous study, NMR and molecular mechanics calculations revealed that the germacyclohexane ring adopts a chair conformation in

solution (Takeuchi, Shimoda, Tanaka, Tomoda, Ogawa & Suzuki, 1988). To obtain the precise molecular geometry of the germacyclohexane ring, which is not contained in the Cambridge Structural Database files, we carried out an X-ray crystallographic analysis of the title compound (1) at 142 K.



(1)

**Experimental.** The title compound (1) was prepared by the literature method (Mazerolles, 1962) and recrystallized from petroleum ether, m.p. 416 K, crystal size  $0.40 \times 0.30 \times 0.25$  mm.  $D_m$  measured by flotation in aqueous KI solution was  $1.67 \text{ Mg m}^{-3}$  at 298 K. The crystal was coated with collodion, without which a decay of more than 10% per day at 298 K was observed on exposure to X-rays. A Rigaku *AFC5* diffractometer equipped with a graphite monochromator and a Rigaku variable temperature system was used to collect the data. The cell dimensions were obtained from least-squares refinement of 40  $\theta$  values in the range  $25 < 2\theta < 30^\circ$ . The data were collected using the  $\omega$ - $2\theta$  scan technique at an  $\omega$  scan rate of  $3.0^\circ \text{ min}^{-1}$  with a  $2\theta$  range of  $2.0$ – $60.0^\circ$ . Data having  $-19 \leq h \leq 15$ ,  $0 \leq k \leq 31$ ,  $0 \leq l \leq 14$  were measured. Three reflections (200, 040, 004) were measured every 50 reflections to monitor instrument and crystal stability, intensity variation  $\leq 3.1\%$ . Of 2962 reflections with  $|F_o| \geq 3\sigma(F_o)$ , 2515 were unique, with  $R_{\text{int}} = 0.0084$  from averaging symmetry-equivalent reflections. The data were corrected for Lp effects, but not for absorption because  $\mu r \leq 1.0$ , where  $r$  is the maximum radius of the crystal. The structure was solved by direct methods (Sheldrick, 1986) and refined by full-matrix least squares (Sheldrick, 1976). The number of the parameters refined was 207. The non-H atoms were refined with anisotropic displacement parameters. All of the H atoms were initially calculated in idealized positions but were refined under C—H bond length constraint during the final refinement cycles. The function  $\sum w(|F_o| - |F_c|)^2$  was optimized, where  $w = [\sigma^2(F_o) + 0.0002(F_o)^2]^{-1}$ . In the final least-squares refinement,  $R = 0.037$ ,  $wR = 0.042$ ,  $S = 1.684$ , and  $(\Delta/\sigma)_{\text{max}} = 0.001$ . The maximum and minimum heights in the final difference Fourier syn-

Table 1. *Non-H-atom positional and isotropic displacement parameters* ( $\text{\AA}^2$ ), with *e.s.d.*'s in parentheses

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	$U_{\text{eq}}$
Ge1	0.39263 (4)	0.40286 (2)	0.32566 (5)	0.0191 (2)
Ge2	0.34194 (4)	0.34695 (2)	0.00680 (5)	0.0192 (2)
O1	0.3462 (3)	0.3445 (1)	0.1815 (3)	0.023 (2)
O2	0.5580 (3)	0.4057 (1)	0.4616 (3)	0.022 (1)
C11	0.3198 (4)	0.3822 (2)	0.4322 (6)	0.026 (2)
C12	0.1778 (5)	0.3957 (3)	0.3072 (6)	0.035 (3)
C13	0.1483 (5)	0.4597 (3)	0.2445 (6)	0.038 (3)
C14	0.1803 (5)	0.4770 (2)	0.1314 (6)	0.032 (2)
C15	0.3210 (4)	0.4779 (2)	0.2163 (6)	0.028 (2)
C21	0.1773 (4)	0.3634 (2)	-0.1971 (6)	0.027 (2)
C22	0.1785 (5)	0.3514 (3)	-0.3420 (6)	0.033 (2)
C23	0.2255 (5)	0.2903 (3)	-0.3420 (6)	0.037 (3)
C24	0.3632 (5)	0.2782 (2)	-0.2011 (7)	0.034 (3)
C25	0.3923 (5)	0.2732 (2)	-0.0323 (6)	0.028 (3)

Table 2. *Bond distances* ( $\text{\AA}$ ), *bond angles* ( $^\circ$ ) and *torsion angles* ( $^\circ$ )

Ge1—O1	1.784 (3)	Ge2—O2	1.781 (3)
Ge1—O2	1.765 (3)	Ge2—O1	1.770 (4)
Ge1—C11	1.942 (7)	Ge2—C21	1.931 (4)
Ge1—C15	1.929 (5)	Ge2—C25	1.936 (6)
C11—C12	1.548 (6)	C21—C22	1.53 (1)
C12—C13	1.531 (8)	C22—C23	1.519 (9)
C13—C14	1.53 (1)	C23—C24	1.522 (7)
C14—C15	1.535 (8)	C24—C25	1.53 (1)
O2—Ge1—O1	107.8 (2)	O1—Ge2—O2	107.5 (2)
Ge1—O1—Ge2	126.7 (2)	Ge2—O2—Ge1	124.9 (2)
C11—Ge1—C15	107.0 (3)	C21—Ge2—C25	105.1 (2)
Ge1—C11—C12	107.1 (4)	Ge2—C21—C22	108.7 (4)
C11—C12—C13	113.8 (5)	C21—C22—C23	114.9 (5)
C12—C13—C14	116.0 (6)	C22—C23—C24	115.6 (4)
C13—C14—C15	114.5 (4)	C23—C24—C25	113.2 (6)
C14—C15—Ge1	108.7 (4)	C24—C25—Ge2	107.4 (3)
O1—Ge2—O2—Ge1	75.2 (3)	O2—Ge1—O1—Ge2	-78.2 (2)
Ge2—O2—Ge1—O1	-19.1 (3)	Ge1—O1—Ge2—O2	20.5 (2)
Ge1—C11—C12—C13	-55.8 (6)	Ge2—C21—C22—C23	53.3 (5)
C11—C12—C13—C14	69.3 (6)	C21—C22—C23—C24	-66.3 (8)
C12—C13—C14—C15	-67.1 (5)	C22—C23—C24—C25	69.4 (7)
C13—C14—C15—Ge1	52.7 (5)	C23—C24—C25—Ge2	-58.5 (5)
C14—C15—Ge1—C11	-42.3 (4)	C24—C25—Ge2—C21	46.4 (4)
C15—Ge1—C11—C12	43.6 (4)	C25—Ge2—C21—C22	-43.8 (4)

thesis were 0.48 and  $-0.42 e \text{\AA}^{-3}$ , respectively. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). Calculation of the geometrical parameters and *ORTEP* drawings were carried out using *XTAL2.6* and *XTAL3.0* (Hall & Stewart, 1989, 1990).

**Discussion.** Atomic coordinates and selected geometrical parameters are given in Tables 1 and 2, respectively.\* A view of the molecule is given in Fig. 1, which confirms the structure of (1) to be the cyclic tetramer of germacyclohexane oxide, as predicted by Mazerolles (1962).

\* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54157 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Since the center of the molecule lies on the  $C_2$  axis in the crystal, the molecule is  $C_2$  symmetric and has two kinds of germacyclohexane rings, both of which adopt chair conformations, which are slightly different. A perspective view of the germacyclohexane ring with Ge1 is shown in Fig. 2.

All the C—C bond lengths [1.519 (8)–1.548 (6) Å] are normal. The C—Ge bond lengths [1.929 (5)–1.942 (7) Å] are within the range of  $C(sp^3)$ —Ge bond lengths [1.933 (6)–1.967 (3) Å] previously reported for germacyclanes (Faucher, Mazerolles, Jaud & Galy, 1978; Preut, Köcher & Neumann, 1985; Sommes, Cremer, Campbell & Thompson, 1990). All the C—C—C angles [113.2 (6)–116.0 (6)°] are significantly larger than all the Ge—C—C [107.1 (4)–108.7 (4)°] and C—Ge—C angles [105.1 (2),

107.0 (3)°]. The absolute values of the torsion angles in the germacyclohexane rings increase in the order C—Ge—C—C [42.3 (4)–46.4 (4)°] < Ge—C—C—C [52.7 (5)–58.5 (5)°] < C—C—C—C [66.3 (8)–69.4 (7)°], making the fold of the ring smaller in the vicinity of the germanium atom and larger further away. These geometrical features of the germacyclohexane ring are approximately in accordance with the results of molecular mechanics calculations for 1,1-dimethylgermacyclohexane (2). (Takeuchi, Shimoda, Tanaka, Tomoda, Ogawa & Suzuki, 1988), except for the bond angle  $C_{ring}$ —Ge— $C_{ring}$ , for which the calculation gave a significantly smaller value (101.9°). This disagreement seems to be reasonable, because the calculation was not carried out for (1) but for (2). The O atoms directly bonded to the germanium atoms in (1) would increase the  $p$  character of the atomic orbital of the germanium atoms and correspondingly the bond angle  $C_{ring}$ —Ge— $C_{ring}$ .

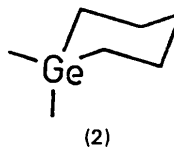


Fig. 3 shows that the tetragermatetraoxacyclooctane ring adopts a skewed-tub conformation as in 1,1,3,3,5,5,7,7-octaphenyl-1,3,5,7-tetragerma-2,4,6,8-tetraoxacyclooctane (3) (Ross & Dräger, 1984). There are, however, significant differences in the ring structure between (1) and (3). While the non-bonding distances Ge1...Ge1 and Ge2...Ge2 in (1) [4.086 (1) and 4.108 (1) Å, respectively] are shorter than the sum of the van der Waals radii of the germanium atoms (2.1 Å; Bondi, 1964), those in (3) [4.434 (7)

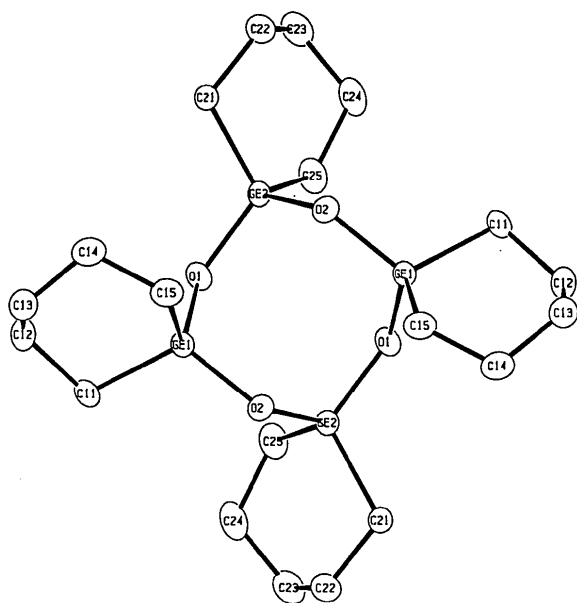


Fig. 1. Drawing of the molecule viewed down the  $b$  axis.

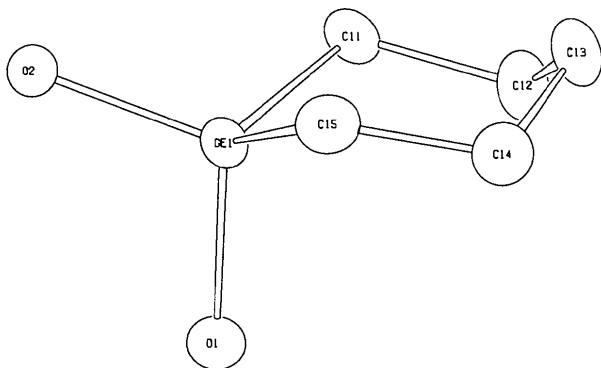


Fig. 2. Perspective view of the germacyclohexane ring with Ge1.

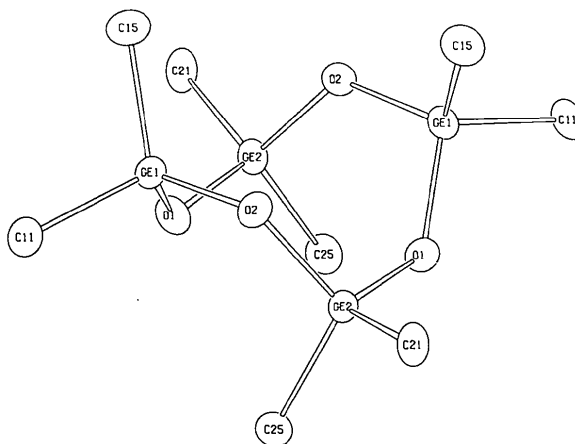
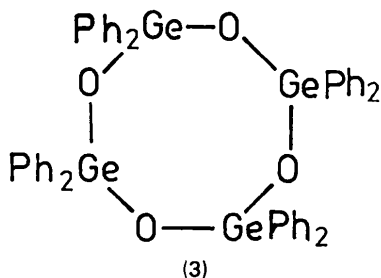


Fig. 3. Perspective view of the 1,3,5,7-tetraoxa-2,4,6,8-tetragermacyclooctane ring.

and 4.433 (7) Å, respectively] are longer. The bond angles of Ge—O—Ge in (1) [124.9 (2), 126.6 (2)°] are significantly smaller than those in (3) [131.4 (5)–136.9 (5)°].



Although there is no intramolecular distance shorter than the sum of the van der Waals radii, except for Ge1...Ge1 and Ge2...Ge2, there is an intermolecular distance that is shorter, *i.e.* H252...H232 [ $-0.5 + x, 0.5 - y, 0.5 + z; 2.15$  (6) Å], where H252 and H232 are the H atoms bonded to C25 and C23, respectively. That is, short intermolecular contacts only occur between the germacyclohexane rings with Ge1, suggesting that the effect of molecular packing on the structure is less in the germacyclohexane ring with Ge1 than in the other germacyclohexane ring.

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#### References

- BONDI, A. (1964). *J. Phys. Chem.* **68**, 441–451.  
 FAUCHER, A. R., MAZEROLLES, P., JAUD, J. & GALY, J. (1978). *Acta Cryst.* **C34**, 442–445.  
 HALL, S. R. & STEWART, J. M. (1989, 1990). Editors. *XTAL2.6, XTAL 3.0 Users Manuals*. Univ. of Western Australia, Australia, and Maryland, USA.  
 MAZEROLLES, P. (1962). *Bull. Soc. Chim. Fr.* pp. 1907–1913.  
 PREUT, H., KÖCHER, J. & NEUMANN, W. P. (1985). *Acta Cryst.* **C41**, 912–915.  
 ROSS, L. & DRÄGER, M. (1984). *Z. Naturforsch. Teil B*, **39**, 868–875.  
 SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.  
 SHELDRICK, G. M. (1986). *SHELXS86*. Program for crystal structure solution. Univ. of Göttingen, Germany.  
 SOMMESE, A. G., CREMER, S. E., CAMPBELL, J. A. & THOMPSON, M. R. (1990). *Organometallics*, **9**, 1784–1792.  
 TAKEUCHI, Y., SHIMODA, M., TANAKA, K., TOMODA, T., OGAWA, K. & SUZUKI, H. (1988). *J. Chem. Soc. Perkin Trans. 2*, pp. 7–13.

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## Structure of 1,2;1,3-Di- $\mu$ -carbonyl-1,1,2,2,3,3,4-heptacarbonyl-2,3- $\mu$ - $\eta^3$ -cyclooctenyl-2,4- $\mu$ -hydrido-4-tricyclohexylphosphine-tetrahedro-trirutheniumplatinum

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**Abstract.** [Ru<sub>3</sub>Pt( $\mu$ - $\eta^3$ -C<sub>8</sub>H<sub>13</sub>)( $\mu$ -CO)<sub>2</sub>(CO)<sub>7</sub>( $\mu$ -H)-{P(C<sub>6</sub>H<sub>11</sub>)<sub>3</sub>}], *M<sub>r</sub>* = 1141.02, triclinic, *P*1̄, *a* = 10.192 (1), *b* = 21.121 (7), *c* = 21.235 (6) Å,  $\alpha$  = 118.83 (3),  $\beta$  = 96.67 (2),  $\gamma$  = 95.56 (2)°, *V* = 3916 (2) Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 1.94 g cm<sup>-3</sup>,  $\lambda$ (Mo *K* $\alpha$ ) = 0.71069 Å,  $\mu$  = 48.0 cm<sup>-1</sup>, *F*(000) = 2216, *T* = 298 K, *R* = 0.035 for 5663 unique observed reflections. The metal atoms adopt a tetrahedral core, with a 58 cluster valence-electron count. A *cyclo*-C<sub>8</sub>H<sub>13</sub> ligand bridges two Ru atoms in a three-electron

donor  $\mu$ -allyl mode, while the other two Ru—Ru edges are bridged by carbonyl ligands.

**Introduction.** A considerable number of triruthenium-platinum clusters have now been structurally characterized (Farrugia, 1990), and these may have either a tetrahedral Os<sub>3</sub>Pt core for cluster valence-electron (CVE) counts of 58 or 60, or a 'butterfly' core with 60 CVE's. The tetrahedral 58 CVE clusters, exemplified by Os<sub>3</sub>Pt( $\mu$ -H)<sub>2</sub>(CO)<sub>10</sub>(PR<sub>3</sub>) (1) (Farrugia, Howard, Mitprachachon, Stone & Woodward, 1981), are chemically unsaturated and highly reac-

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