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Tetrakis(phenylethynyl)germanium(IV)

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The title compound, $(PhC{\equiv}C)_4Ge$ or $[Ge(C_8H_5)_4]$, crystallizes in the space group $I\bar{4}$ with $\bar{4}$ molecular symmetry. The coordination polyhedron of the central atom is a slightly distorted tetrahedron, with C—Ge—C angles in the range 107.95 (17)–110.24 (9)°.

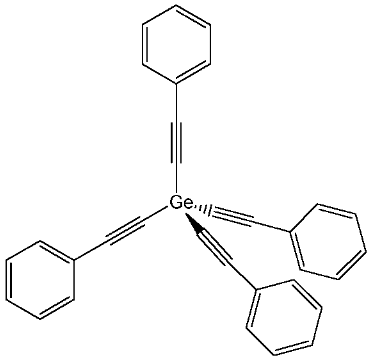
Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.005 Å
R factor = 0.028
wR factor = 0.065
Data-to-parameter ratio = 14.2

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

The title compound, $(PhC{\equiv}C)_4Ge$, (I) (Fig. 1), crystallizes in the space group $I\bar{4}$. The crystal structure comprises isolated molecules, with the Ge atom in a slightly distorted tetrahedral environment. The molecule has $\bar{4}$ symmetry with only one independent $PhC{\equiv}C$ ligand in the asymmetric unit. This supports the proposal of Kitaigorodskii (1955) that the molecules of MA_4-type compounds which possess $\bar{4}$ symmetry in the solid state prefer to crystallize in the space groups $I\bar{4}$, $P4_2/n$ or $P\bar{4}2_1c$. These space groups allow close packing of MA_4 molecules.



(I)

Compound (I) is the third example of a structure with four alkynyl substituents directly bonded to a Ge atom. The structures of $(Me_3SiC{\equiv}C)_4Ge$ [(II); Ovchinnikov *et al.*, 1991; Dallaire *et al.*, 1993] and $[({\equiv}C{-}o{-}C_6H_4{-}C{\equiv}C{-})_2]_2Ge$ [(III); Guo *et al.*, 1999] were reported previously. The Ge—C distance in (I) [1.886 (3) Å] is close to the values previously found for (II) and (III) (average values 1.893 and 1.887 Å, respectively). However, these values are noticeably shorter than those found for analogous germanium derivatives bearing four identical substituents [Ge—Csp^3 bonds: $(PhCH_2)_4Ge$ with 1.946 (6)–1.974 (5) Å (Ferguson & Glidewell, 1996) and $(1\text{-indenyl})_4Ge$ with 1.990 (4)–2.016 (4) Å (Atwood *et al.*, 1984); Ge—C(sp^2) bonds: Ph_4Ge with 1.9537 (5)–1.957 (4) Å (Chieh, 1971; Karipides & Haller, 1972), $(o\text{-tolyl})_4Ge$ with 1.956 (3) Å (Belsky *et al.*, 1984), $(p\text{-tolyl})_4Ge$ with 1.941 (4)–1.958 (4) Å (Charissé *et al.*, 1992), $(C_6F_5)_4Ge$ with 1.957 (4) Å (Karipides *et al.*, 1974),

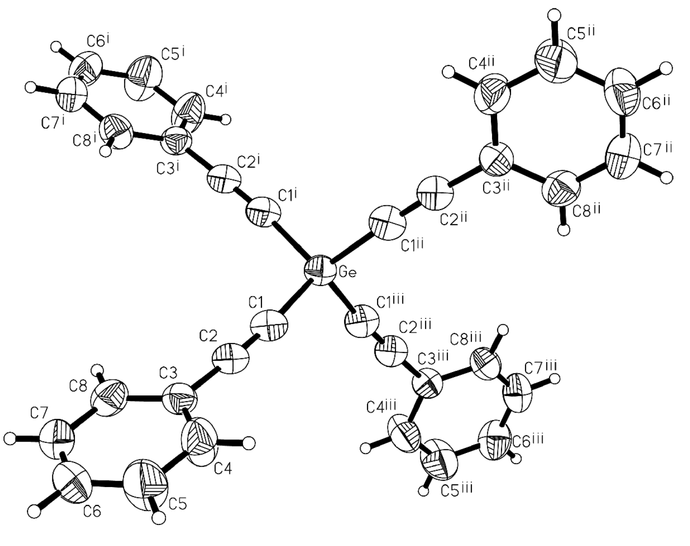


Figure 1

The molecular structure of (I), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $-x, 1-y, z$; (ii) $-\frac{1}{2}+y, \frac{1}{2}-x, \frac{1}{2}-z$; (iii) $\frac{1}{2}-y, \frac{1}{2}+x, \frac{1}{2}-z$.]

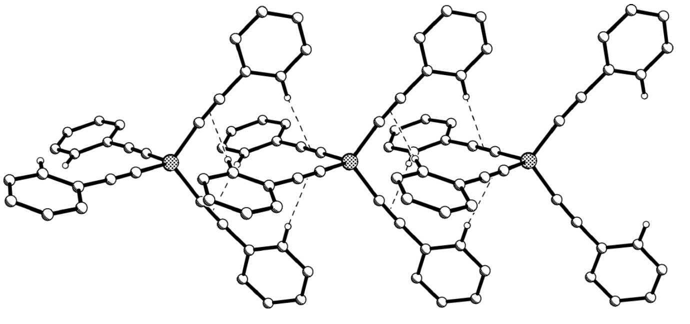


Figure 2

A column of (I), extending along the *c* axis. H atoms (except H8) have been omitted for clarity. $H8\cdots M$ contacts (*M* is the centre of the triple bond) are indicated by dashed lines.

$[(Me_5CpRuPh)^+]_4Ge(CF_3SO_3^-)_4$ with 1.949 (6)–1.968 (5) Å (Fagan *et al.*, 1989) and $(2\text{-thienyl})_4Ge$ with 1.94 (1) Å (Karipides *et al.*, 1977)]. As expected, the Ge—C bond length shortens with increase of *s*-character of the orbital of the C atom attached to the Ge atom. The alkynyl fragment in the structure of (I) is almost linear, with Ge—C—C and C—C—Ph angles equal to 174.6 (2) and 177.4 (3)°, respectively.

In the crystal structure, the molecules of (I) are combined into columns (along the *c* axis) by $C-H\cdots\pi(C\equiv C)$ interactions (Fig. 2). The $H8\cdots M$ separation (*M* denotes the centre of the triple bond) is 2.80 Å and the $C8-H8\cdots M$ angle is 167.3°. The latter values are comparable with those found for $C\equiv C-H\cdots\pi(C\equiv C)$ interactions in the structures of di- and triethynylbenzenes (2.60–2.81 Å and 140.1–174.8°; Weiss *et al.*, 1997).

Experimental

Compound (I) was prepared by the reaction of a diethyl ether solution of $PhC\equiv CLi$ with $MeN(CH_2CH_2O)_2GeBr_2$ (Karlov *et al.*, 2003). Crystals suitable for X-ray analysis were obtained by slow evaporation of a $CHCl_3$/hexane solution. ^{13}C NMR data are consistent with those reported previously (Koester *et al.*, 1993).

Crystal data

$[Ge(C_8H_5)_4]$
$M_r = 477.07$
Tetragonal, $I\overline{4}$
$a = 13.532$ (2) Å
$c = 6.746$ (2) Å
$V = 1235.3$ (4) Å^3
$Z = 2$
$D_x = 1.283$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 12$–$13°$
$\mu = 1.26$ mm^{-1}
$T = 295$ (2) K
Needle, colourless
$0.50 \times 0.10 \times 0.10$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scans
Absorption correction: multi-scan (*SHELXTL-Plus*; Bruker, 2000)
$T_{min} = 0.533$, $T_{max} = 0.879$
4296 measured reflections
1076 independent reflections
1043 reflections with $I > 2\sigma(I)$

$R_{int} = 0.037$
$\theta_{max} = 25.0°$
$h = -16 \rightarrow 16$
$k = -16 \rightarrow 16$
$l = -8 \rightarrow 8$
2 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.065$
$S = 1.15$
1076 reflections
76 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0443P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.32$ e Å^{-3}
$\Delta\rho_{min} = -0.53$ e Å^{-3}
Absolute structure: Flack (1983), 486 Friedel pairs
Flack parameter = 0.370 (16)

Table 1

Selected geometric parameters (Å, °).

Ge—C1	1.886 (3)	C4—C5	1.388 (7)
C1—C2	1.194 (4)	C5—C6	1.369 (8)
C2—C3	1.434 (4)	C6—C7	1.350 (5)
C3—C8	1.382 (4)	C7—C8	1.379 (5)
C3—C4	1.389 (4)		
C1—Ge—C1^{ii}	110.24 (9)	C2—C1—Ge	174.6 (2)
C1—Ge—C1^{i}	107.95 (17)	C1—C2—C3	177.4 (3)

Symmetry codes: (i) $-x, 1-y, z.$; (ii) $y-\frac{1}{2}, \frac{1}{2}-x, \frac{1}{2}-z$.

All H atoms were placed in calculated positions (C—H = 0.93 Å) and refined using a riding model, with $U_{iso}(H) = 1.2U_{eq}(C)$. The structure is an inversion twin, with 0.630 (16):0.370 (16) occupancies of the two components.

Data collection: *CAD*-4 *Diffractometer Program* (Schagen *et al.*, 1988); cell refinement: *CAD*-4 *Diffractometer Program*; data reduction: *XCAD*4 (Harms, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL-Plus* (Bruker, 2000); software used to prepare material for publication: *SHELXL*97.

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