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Derivatives of substituted 3-trichlorogermylpropionic acid

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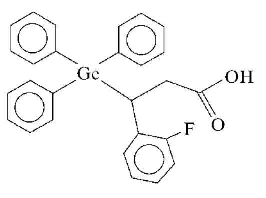
The central Ge atoms in the structures of 3-(2-fluorophenyl)-3-(triphenylgermyl)propionic acid, $[Ge(C_6H_5)_3(C_9H_8FO_2)]$, 3-(2-tolyl)-3-(tri-4-tolylgermyl)propionic acid, $[Ge(C_7H_7)_3(C_{10}H_{11}O_2)]$, and 3-(4-tolyl)-3-(tribenzylgermyl)propionic acid, $[Ge(C_7H_7)_3(C_{10}H_{11}O_2)]$, are four-coordinate with slightly distorted tetrahedral geometry. The Ge—Csp^3 distances [1.970 (3)–1.997 (3) Å] are significantly longer than the Ge—C$_{\text{aromatic}}$ distances [1.940 (3)–1.959 (2) Å]. In all three structures, the molecules form dimeric pairs about inversion centres through strong hydrogen-bonding interactions between carboxylic acid groups.

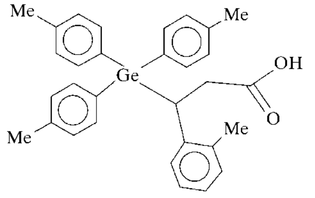
Comment

There has been considerable interest in recent years in the chemistry of germanium compounds, due to their diverse applications in the fields of medicine, electronics and optics, and as radiation detectors. A number of reports have been published regarding the structural chemistry of these compounds and their applications (Mackay, 1995; Westaway & Joly, 1995). In order to develop new kinds of organogermanium compounds with potential therapeutic properties, we have synthesized three derivatives of triorganogermyl propionic acid, namely 3-(2-fluorophenyl)-3-(triphenylgermyl)propionic acid, (I), 3-(2-tolyl)-3-(tri-4-tolylgermyl)propionic acid, (II), and 3-(4-tolyl)-3-(tribenzylgermyl)propionic acid, (III), and characterized them using X-ray diffraction methods. The results are presented in this paper. The crystal structure of 2-methyl-3-phenyl-3-(tri-*p*-tolylgermyl)propionic acid has been reported recently by our group (Imtiaz-ud-Din *et al.*, 2002).

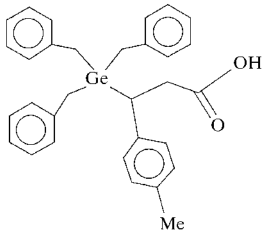
Figs. 1–3 show the structures of (I)–(III), respectively. The central Ge atom in each compound is four-coordinate and the geometry about it is slightly distorted from tetrahedral, with C—Ge—C angles in the range 106.08 (6)–112.29 (7)° in (I), 105.31 (11)–115.63 (11)° in (II) and 106.94 (13)–113.30 (12)° in (III). The Ge—Csp^3 distances (Ge—C3) in (I) and (II) are significantly longer [1.997 (2) and 1.984 (2) Å, respectively] than the Ge—C$_{\text{aromatic}}$ distances, which are identical within 3σ limits in each of the two structures, with mean values of 1.954 (2) and 1.945 (2) Å, respectively. On the other hand, the Ge—C3 distance of 1.981 (3) Å in (III) is barely longer than the Ge—C$_{\text{benzyl}}$ distances, which are also identical, with a mean value of 1.971 (1) Å. These Ge—C$_{\text{aromatic}}$ distances are in agreement with those reported in the related structures $(C_9H_{11})_3GeCN{\cdot}0.5C_4H_8O$, $(C_9H_{11})_3GeNCS$ and $(C_9H_{11})_3GeN_3$ (Hihara *et al.*, 2000), Ph_3GeOH (Ferguson *et al.*, 1992), $(C_7H_7)_4Ge$ (Belsky *et al.*, 1984) and $(C_6H_5)_4Ge$ (Karipides & Haller, 1972).



(I)



(II)



(III)

The propionic acid moiety in (I) (O1/O2/C1/C2/C3) is essentially planar, with atom Ge1 lying 0.380 (2)° out of the plane formed by these atoms, and is inclined at an angle of 88.11 (5)° to the mean plane of the C4–C9 phenyl-ring atoms.

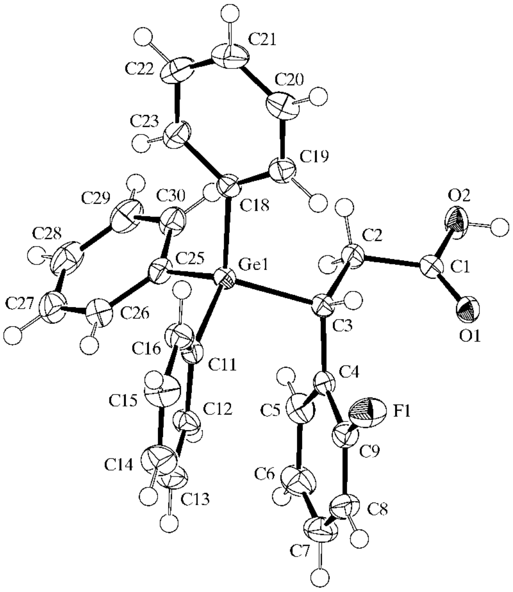


Figure 1
A view of the molecule of (I), with displacement ellipsoids plotted at the 50% probability level. H atoms are shown as small spheres of arbitrary radii.

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The mean planes of phenyl rings C11–C16 (ring 1), C18–C23 (ring 2) and C25–C30 (ring 3) bonded to atom Ge1 are inclined with respect to each other at angles of 69.09 (6), 59.92 (7) and 68.21 (5)° for the pairs of rings 1/2, 1/3 and 2/3, respectively.

The propionic acid moiety in (II) is not planar, in contrast to (I). In this case, only atoms O1, O2, C1 and C2 are planar to within 0.012 (3) Å, while atoms C3 and Ge1 lie 0.679 (5) and 0.086 (7) Å, respectively, out of the plane of these atoms. The mean planes of the phenyl rings [rings 1–3, as defined for (I)] bonded to atom Ge1 are inclined with respect to each other at angles of 80.90 (10), 64.21 (12) and 67.42 (12)° for the pairs of rings 1/2, 1/3 and 2/3, respectively.

The propionic acid moiety in (III) is also non-planar, as observed in (II), whereby only atoms O1, O2, C1 and C2 are planar to within 0.012 (3) Å, while atoms C3 and Ge1 are 0.814 (5) and 0.277 (8) Å, respectively, out of the plane of these atoms. The mean planes of the benzyl rings [rings 1–3, as defined for (I)] bonded to atom Ge1 are inclined with respect to each other at angles of 71.7 (4), 74.3 (3) and 84.7 (1)° for the pairs of rings 1/2, 1/3 and 2/3, respectively. One of the phenyl rings in (III) is disordered over sites C19–C24 and C19′–C24′ with site-occupancy factors of 0.65 (4) and 0.35 (4), respectively, and with the mean planes of these rings lying at 7.0 (5)° with respect to each other.

In all three structures, the molecules form dimeric pairs about inversion centres through strong hydrogen-bonding interactions between carboxylic acid groups. These hydrogen-bonding interactions can be described in terms of graph-set representations of $R_2^2(8)$ (Bernstein *et al.*, 1994). In addition, there are short intermolecular C—H···O interactions (involving atoms C8 and O1) and intramolecular C3—H3···F1 contacts present in (I). The structure of (II) exhibits short intermolecular H8···H8$^{\rm ii}$ interactions involving adjacent molecules [2.08 Å; symmetry code: (ii) $-x$, $1 - y$, $2 - z$], resulting in a phenyl ring of the phenylpropionic acid molecule with C—C distances spanning a wide range; the shortest distance is C7—C8. Intramolecular C3—H3···O1 contacts are also observed in (II) and (III). Details of the hydrogen-bonding geometry for compounds (I)–(III) are given in Tables 2, 4 and 6, respectively.

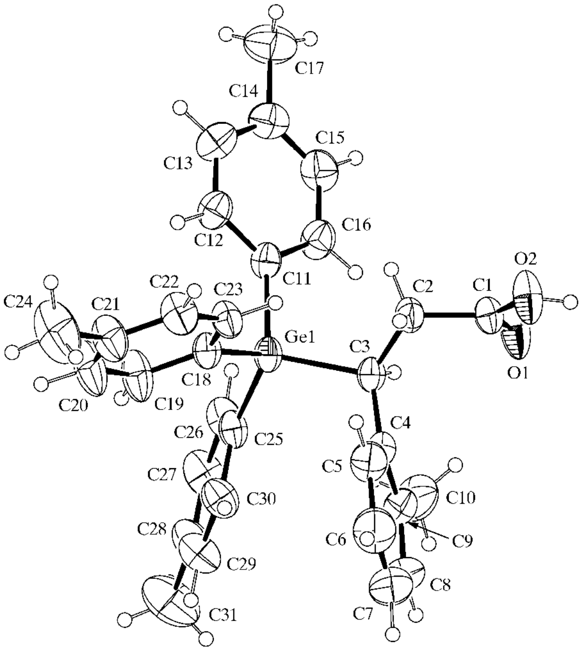

Figure 2
A view of the molecule of (II), with displacement ellipsoids plotted at the 50% probability level. H atoms are shown as small spheres of arbitrary radii.

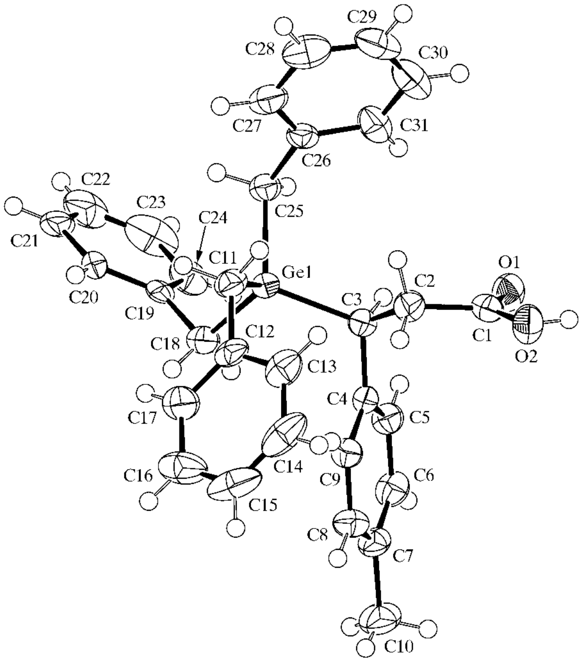

Figure 3
A view of the molecule of (III), with displacement ellipsoids plotted at the 50% probability level. H atoms are shown as small spheres of arbitrary radii. The C19′–C24′ phenyl ring, representing the minor fraction, is not illustrated.

Experimental

Compounds (I)–(III) were prepared following the standard methods described by Choudhary *et al.* (2002). Crystals suitable for X-ray analysis were grown by dissolving the respective compound (0.5 g) in chloroform (5.0 ml), to which a few drops of acetone were added. Slow evaporation of the solvent at room temperature over a period of several days yielded fine crystals which were subsequently washed with acetone.

Compound (I)

Crystal data

$[\mathrm{Ge(C_6H_5)_3(C_9H_8FO_2)}]$
$M_r = 471.04$
Monoclinic, $P2_1/c$
$a = 9.7278$ (10) Å
$b = 17.907$ (3) Å
$c = 13.541$ (2) Å
$\beta = 110.907$ (8)°
$V = 2203.5$ (6) Å^3
$Z = 4$

$D_x = 1.420$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 9816 reflections
$\theta = 1.0$–27.5°
$\mu = 1.42$ mm^{-1}
$T = 170$ (2) K
Block, colourless
0.20 × 0.15 × 0.14 mm

Data collection

Nonius KappaCCD area-detector diffractometer
ω and φ scans
Absorption correction: multi-scan (*SORTAV*; Blessing, 1997)
$T_{\min} = 0.711$, $T_{\max} = 0.820$
9816 measured reflections
5026 independent reflections
4338 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.017$
$\theta_{\max} = 27.5^\circ$
$h = -12 \rightarrow 12$
$k = -23 \rightarrow 23$
$l = -17 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.070$
$S = 1.03$
5026 reflections
281 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0332P)^2 + 0.8526P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 0.30$ e Å^{-3}
$\Delta\rho_{\min} = -0.44$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (I).

Ge1—C11	1.951 (2)	F1—C9	1.367 (2)
Ge1—C25	1.953 (2)	O1—C1	1.217 (2)
Ge1—C18	1.959 (2)	O2—C1	1.316 (2)
Ge1—C3	1.997 (2)		
C11—Ge1—C25	110.55 (7)	C11—Ge1—C3	106.08 (6)
C11—Ge1—C18	110.60 (6)	C25—Ge1—C3	112.29 (7)
C25—Ge1—C18	108.93 (7)	C18—Ge1—C3	108.35 (6)

Table 2
Hydrogen-bonding geometry (Å, °) for (I).

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2···O1$^{\rm i}$	0.84	1.83	2.6689 (16)	178
C8—H8···O1$^{\rm ii}$	0.95	2.57	3.323 (2)	137
C3—H3···F1	1.00	2.34	2.805 (2)	108

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

Compound (II)

Crystal data

$[\mathrm{Ge(C_7H_7)_3(C_{10}H_{11}O_2)}]$
$M_r = 509.16$
Monoclinic, $P2_1/c$
$a = 10.984$ (3) Å
$b = 13.710$ (4) Å
$c = 20.245$ (5) Å
$\beta = 113.857$ (14)°
$V = 2788.3$ (13) Å^3
$Z = 4$
$D_x = 1.213$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 10 731 reflections
$\theta = 1.0$–27.5°
$\mu = 1.12$ mm^{-1}
$T = 293$ (2) K
Prism, colourless
$0.20 \times 0.17 \times 0.13$ mm

Data collection

Nonius KappaCCD area-detector diffractometer
ω and φ scans
Absorption correction: multi-scan (*SORTAV*; Blessing, 1997)
$T_{\min} = 0.749$, $T_{\max} = 0.864$
10 731 measured reflections
6346 independent reflections
4185 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.025$
$\theta_{\max} = 27.5^\circ$
$h = -14 \rightarrow 14$
$k = -16 \rightarrow 17$
$l = -26 \rightarrow 26$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.115$
$S = 1.01$
6346 reflections
308 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.047P)^2 + 0.8585P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 0.38$ e Å^{-3}
$\Delta\rho_{\min} = -0.42$ e Å^{-3}

Table 3
Selected geometric parameters (Å, °) for (II).

Ge1—C25	1.940 (3)	Ge1—C3	1.984 (2)
Ge1—C18	1.946 (3)	O1—C1	1.228 (3)
Ge1—C11	1.948 (3)	O2—C1	1.276 (3)
C25—Ge1—C18	108.93 (11)	C25—Ge1—C3	107.07 (11)
C25—Ge1—C11	111.67 (11)	C18—Ge1—C3	115.63 (11)
C18—Ge1—C11	108.26 (11)	C11—Ge1—C3	105.31 (11)

Table 4
Hydrogen-bonding geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2···O1$^{\rm i}$	0.82	1.83	2.637 (3)	169
C3—H3···O1	0.96	2.41	2.849 (4)	107

Symmetry code: (i) $-x, -y, 2 - z$.

Compound (III)

Crystal data

$[\mathrm{Ge(C_7H_7)_3(C_{10}H_{11}O_2)}]$
$M_r = 509.16$
Monoclinic, $P2_1/n$
$a = 10.476$ (2) Å
$b = 16.337$ (3) Å
$c = 15.119$ (5) Å
$\beta = 92.018$ (8)°
$V = 2586.0$ (11) Å^3
$Z = 4$
$D_x = 1.308$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 16 881 reflections
$\theta = 1.0$–25.0°
$\mu = 1.21$ mm^{-1}
$T = 123$ (2) K
Prism, colourless
$0.12 \times 0.10 \times 0.10$ mm

Data collection

Nonius KappaCCD area-detector diffractometer
ω and φ scans
Absorption correction: multi-scan (*SORTAV*; Blessing, 1997)
$T_{\min} = 0.769$, $T_{\max} = 0.886$
16 881 measured reflections
4533 independent reflections
3586 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.054$
$\theta_{\max} = 25^\circ$
$h = -12 \rightarrow 12$
$k = -19 \rightarrow 19$
$l = -17 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.094$
$S = 1.04$
4533 reflections
339 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.042P)^2 + 1.7P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.64$ e Å^{-3}
$\Delta\rho_{\min} = -0.33$ e Å^{-3}

Table 5
Selected geometric parameters (Å, °) for (III).

Ge1—C18	1.970 (3)	Ge1—C3	1.981 (3)
Ge1—C25	1.971 (3)	O1—C1	1.229 (4)
Ge1—C11	1.973 (3)	O2—C1	1.274 (3)
C18—Ge1—C25	107.26 (11)	C18—Ge1—C3	108.79 (12)
C18—Ge1—C11	111.93 (14)	C25—Ge1—C3	108.38 (12)
C25—Ge1—C11	106.94 (13)	C11—Ge1—C3	113.30 (12)

Table 6
Hydrogen-bonding geometry (Å, °) for (III).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O2—H2$\cdots$O1^{i}	0.84	1.81	2.651 (3)	175
C3—H3$\cdots$O1	1.00	2.42	2.845 (4)	105

Symmetry code: (i) $-x, -y, 1-z$.

For all three structures, the H atoms were located from difference Fourier syntheses and were included in the refinements at idealized positions, with $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(O) or 1.2$U_{\rm eq}$(C). Default C—H and O—H distances were allowed for the various types of H atoms, as set by *SHELXL*97 (Sheldrick, 1997). One of the phenyl rings in (III) is disordered over sites C19–C24 and C19′–C24′, with unequal site-occupancy factors of 0.65 (4) and 0.35 (4), respectively. The final difference maps were free of any chemically significant features for all three structures.

For all compounds, data collection: *COLLECT* (Nonius, 1998); cell refinement: *HKL DENZO* (Otwinowski & Minor, 1997); data reduction: *SCALEPACK* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SAPI*91 (Fan, 1991); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1392). Services for accessing these data are described at the back of the journal.

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