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Azidotriphenylgermane

Ivor Wharf[a]* and Francine Bélanger-Gariépy[b]

[a]Department of Chemistry, Otto Maass Chemistry Building, McGill University, 801 Sherbrooke St. West, Montreal, Quebec, Canada H3A 2K6, and [b]Département de Chimie, Université de Montréal, CP 6128, Succ. Centre-ville, Montréal, Québec, Canada H3C 3J7

Correspondence e-mail: ivor.wharf@mcgill.ca

The title compound, $[\mathrm{Ge}(\mathrm{C}_6\mathrm{H}_5)_3(\mathrm{N}_3)]$, (I), is monomeric with quasi-tetrahedral geometry around germanium. The azide group ($-\mathrm{N}_\alpha-\mathrm{N}_\beta-\mathrm{N}_\gamma$) is disordered. One form has $d(\mathrm{N}_\alpha-\mathrm{N}_\beta) > d(\mathrm{N}_\beta-\mathrm{N}_\gamma)$, the other has $d(\mathrm{N}_\alpha-\mathrm{N}_\beta) < d(\mathrm{N}_\beta-\mathrm{N}_\gamma)$. In contrast, the mesityl analogue, (II), has $d(\mathrm{N}_\alpha-\mathrm{N}_\beta) > d(\mathrm{N}_\beta-\mathrm{N}_\gamma)$. As expected, on going from (I) to (II), angle $(\mathrm{C}-\mathrm{Ge}-\mathrm{C})_{\mathrm{ave}}$ increases while angle $(\mathrm{C}-\mathrm{Ge}-\mathrm{N}_\alpha)_{\mathrm{ave}}$ decreases. However, in contrast to the silicon case, $d(\mathrm{Ge}-\mathrm{N}_\alpha)$ and $d(\mathrm{Ge}-\mathrm{C})_{\mathrm{ave}}$ remain effectively unchanged on going from (I) to (II).

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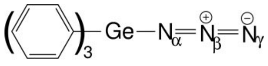
Key indicators

Single-crystal X-ray study
T = 220 K
Mean σ(C–C) = 0.003 Å
Disorder in main residue
R factor = 0.033
wR factor = 0.101
Data-to-parameter ratio = 14.3

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

Comment

A few years ago, we determined the structures of several pseudohalotrimesitylgermanes [$(\mathrm{Mes})_3\mathrm{Ge}X$: Mes = 2,4,6-trimethylphenyl; X = CN, NCS, NCO, N_3 and OH] (Hihara *et al.*, 2000) with the aim of comparing the geometries of these molecules with those of related phenylgermanium systems. However, only the structures of $\mathrm{Ph}_3\mathrm{GeNCO}$ (Tarkhova *et al.*, 1976) and $\mathrm{Ph}_3\mathrm{GeOH}$ (Ferguson *et al.*, 1992) were available for this purpose at the time and only recently has the structure of $\mathrm{Ph}_3\mathrm{GeH}$ (McGrady *et al.*, 2002) become available for comparison with that of $(\mathrm{Mes})_3\mathrm{GeH}$ (Lambert *et al.*, 1998). Thus, to enable a further comparison of this type to be made, we now report the structure of $\mathrm{Ph}_3\mathrm{GeN}_3$, (I).



(I)

Compound (I) is monomeric (Fig. 1) and is isostructural with $\mathrm{Ph}_3\mathrm{SiN}_3$ (Wharf & Belanger-Gariépy, 2004). The average C—Ge—C angle [113.4 (1)°] is greater than the average C—Ge—N angle [105.1 (1)°] (Table 1), with averaged (Ge—C) = 1.936 (2) Å and d(Ge—N1) = 1.8968 (17) Å. A similar geometry has been found for $\mathrm{Ph}_3\mathrm{GeNCO}$ (Tarkhova *et al.*, 1976), although the data are less precise than those given here. For $(\mathrm{Mes})_3\mathrm{GeN}_3$, (II), the corresponding data are 115.6 (4)°, 102.2 (4)°, 1.95 (1) Å and 1.895 (9) Å, respectively. Thus, while on going from (I) to (II), changes in average angles around Ge follow the trends predicted by Andose & Mislow (1974), for $\mathrm{Ph}_3\mathrm{CH}(\mathrm{Mes})_3\mathrm{CH}$, no change in average d(Ge—C) and d(Ge—N1) is apparent. In contrast, when comparing $\mathrm{Ph}_3\mathrm{SiN}_3$ with $(\mathrm{Mes})3\mathrm{SiN}_3$ (Zigler *et al.*, 1989), we found both average d(Si—C) and d(Si—N1) to increase when Ph is replaced by Mes. Presumably, the longer Ge—C and Ge—N1 bonds are able to accommodate the distal o-$\mathrm{CH}_3\cdots\mathrm{N}_1$ interactions in (II) without lengthening. However, the proximal o-$\mathrm{CH}_3\cdots o$-CH_3 interactions increase the average C—Ge—C angle on going

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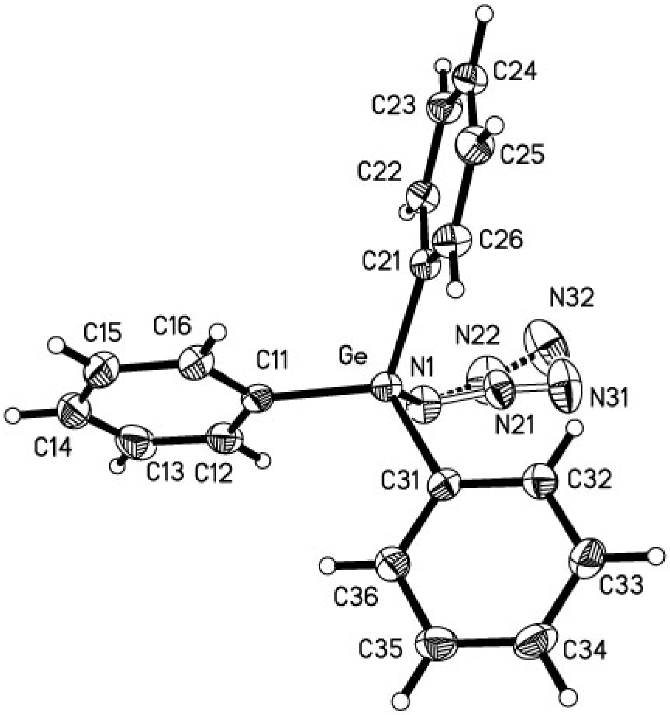

Figure 1
The structure of the title compound. Displacement ellipsoids are drawn at the 30% probability level. Both disorder components are shown.

from (I) to (II) to the same extent as found for the two analogous silicon compounds.

The azide group in (I) is disordered (50/50); one component has d(N1—N21) > d(N21—N31) with Ge—N1—N21 = 118.1 (9)° and N1—N21—N31 = 171.2 (2)°, while the second component has d(N1—N22) < d(N22—N32), Ge—N1—N22 = 121.3 (1)° and N1—N22—N32 = 171 (3)°. This situation is exactly comparable to that found for Ph_3SiN_3 (Wharf & Belanger-Gariépy, 2004) and the same structural interpretation will thus apply. This may also account for the large U_{eq} values noted for atoms N31 and N32.

Experimental

The title compound was prepared by refluxing chlorotriphenylgermane (12.9 mmol, 4.36 g) in dry tetrahydrofuran (300 ml) with dried sodium azide (0.14 mol, 9.4 g) for 4 d. Evaporation of the filtrate under reduced pressure gave crude (I), which was recrystallized from hexane [m.p. 380–381 K; literature 380–380.5 K (Reichle, 1964)]. Analysis calculated for $C_{18}H_{15}GeN_3$: C 62.50, H 4.37%; found: C 62.22, H 4.30%. X-ray quality crystals were obtained by slow evaporation of a hexane solution of (I).

Crystal data

$[Ge(C_6H_5)_3(N_3)]$
$M_r = 345.92$
Monoclinic, $P2_1/n$
$a = 9.7428$ (2) Å
$b = 17.0689$ (3) Å
$c = 10.3630$ (2) Å
$\beta = 110.449$ (1)°
$V = 1614.76$ (5) Å^3
$Z = 4$

$D_x = 1.423$ Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 11289 reflections
$\theta = 4.6$–72.9°
$\mu = 2.56$ mm^{-1}
$T = 220$ (2) K
Block, colourless
0.50 × 0.20 × 0.15 mm

Data collection

Bruker AXS SMART 2K/Platform diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.403$, $T_{max} = 0.681$
13062 measured reflections

3097 independent reflections
2939 reflections with $I > 2\sigma(I)$
$R_{int} = 0.026$
$\theta_{max} = 73.0°$
$h = -12 \rightarrow 11$
$k = -20 \rightarrow 20$
$l = -12 \rightarrow 12$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.101$
$S = 1.05$
3097 reflections
217 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.084P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.29$ e Å^{-3}
$\Delta\rho_{min} = -0.62$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ge—N1	1.8968 (17)	N1—N22	1.14 (2)
Ge—C11	1.9317 (18)	N1—N21	1.24 (2)
Ge—C21	1.9370 (16)	N21—N31	1.10 (2)
Ge—C31	1.9378 (17)	N22—N32	1.20 (3)
N1—Ge—C11	101.69 (9)	C21—Ge—C31	112.91 (7)
N1—Ge—C21	107.51 (7)	N22—N1—Ge	121.3 (1)
C11—Ge—C21	113.31 (7)	N21—N1—Ge	118.1 (9)
N1—Ge—C31	106.27 (7)	N31—N21—N1	171.20 (19)
C11—Ge—C31	114.02 (7)	N1—N22—N32	171 (3)
C11—Ge—N1—N22	158.20 (16)	N1—Ge—C11—C12	18.08 (17)
C21—Ge—N1—N22	38.90 (16)	N1—Ge—C11—C16	−160.86 (15)
C31—Ge—N1—N22	−82.20 (16)	N1—Ge—C21—C22	37.05 (16)
C11—Ge—N1—N21	169.90 (12)	N1—Ge—C21—C26	−147.37 (14)
C21—Ge—N1—N21	50.60 (12)	N1—Ge—C31—C32	75.48 (16)
C31—Ge—N1—N21	−70.60 (12)	N1—Ge—C31—C36	−101.80 (15)

The azide group is found to be disordered with two sets of N atoms. The occupancy factor was originally refined but was then fixed at 0.5 for each atom set in the final cycles. All the H atoms were positioned geometrically (C—H = 0.94 Å) and were included in the refinement in the riding-model approximation, with U_{iso}(H) = $1.2U_{eq}$(parent atom).

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: UdMX (Maris, 2004).

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