

## Two germatranes with bulky substituents

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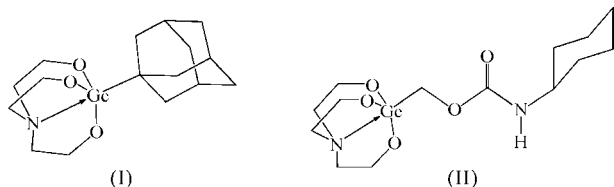
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In 1-adamantyl-2,8,9-trioxa-5-aza-1-germabicyclo[3.3.3]undecane or 1-adamantylgermatrane, [Ge(C<sub>10</sub>H<sub>15</sub>)(C<sub>6</sub>H<sub>12</sub>NO<sub>3</sub>)], (I), and (2,8,9-trioxa-5-aza-1-germabicyclo[3.3.3]undecan-1-yl)methyl *N*-cyclohexylcarbamate or [(germatran-1-yl)methyl]-cyclohexylcarbamate, [Ge(C<sub>6</sub>H<sub>12</sub>NO<sub>3</sub>)(C<sub>8</sub>H<sub>14</sub>NO<sub>2</sub>)], (II), the Ge atoms are characterized by trigonal-bipyramidal configurations. The Ge···N distances [2.266 (3) and 2.206 (3) Å in (I) and (II), respectively] are among the longest observed in germatranes. The significant distortion of the apical N—Ge—C angle in (II) is caused by crystal packing effects.

## Comment

Organogermanic compounds with expanded coordination spheres around the metal, such as substituted germatranes, have been of interest since 1970. Most probably, this is due to their potential use as biologically active substances (Lukevics *et al.*, 1990, 1992). The wide spectrum of pharmacological action of organogermanic compounds, their low toxicity and other useful properties have created favourable conditions



for the development of bioorganogermanic chemistry. Successful progress in this area is impossible without a wide search for the most active substances and discovering the correlation between their structure and biological activity. As a continuation and development of our work in this area (Gurkova *et al.*, 1984; Knyazev *et al.*, 2000; Korlyukov *et al.*, 2003), the crystal and molecular structures of 1-germanyadamantane, (I), and [1-(germatran-1-yl)methyl]cyclohexyl-

carbamate, (II), have been studied by X-ray diffraction and the results are presented here (Figs. 1 and 2).

The coordination around atom Ge1 in (I) and (II) is trigonal-bipyramidal. Atom N1 of the atrane framework and the organic *R* group occupy the axial positions, while three O atoms occupy the equatorial positions. The Ge1 atoms deviate from the plane of the equatorial O atoms towards *R* by 0.28 Å in (I) and 0.24 Å in (II). Analysis of the Cambridge Structural Database (CSD, Version 5.27; Allen, 2002) reveals that the interatomic Ge1···N1 distance in (I) is among the longest observed for this class of compounds. According to the CSD, the Ge1···N1 distance varies in the range 2.01–2.32 Å (for 85 examined structures). The longest Ge1···N1 distances are observed in 1-(1-trimethylsilylcyclopropyl)germatrane (Korlyukov *et al.*, 2003) and 1-(germatran-1-yl)methylgermatrane (Gurkova *et al.*, 1982) (2.300 and 2.315 Å). The presence of the electron-withdrawing carbamate group in (II) leads to a decrease in this interatomic distance by 0.06 Å compared with the corresponding value in (I). The absence of a greater shortening of the Ge1···N1 interatomic distance in (II) can be explained by a significant delocalization of electron density in the N2/C8/O4/O5 carbamate fragment. Indeed, the N2—C8 and C8—O4 bonds are shorter than the respective standard single bonds, but they are noticeably longer than the corresponding double bonds (Allen *et al.*, 1987). Thus, in both (I)

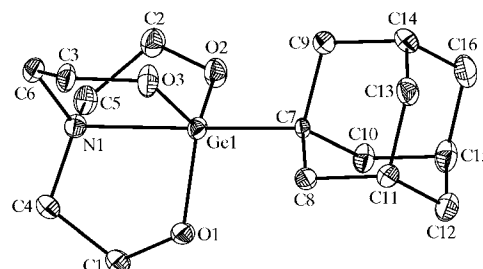


Figure 1

The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity.

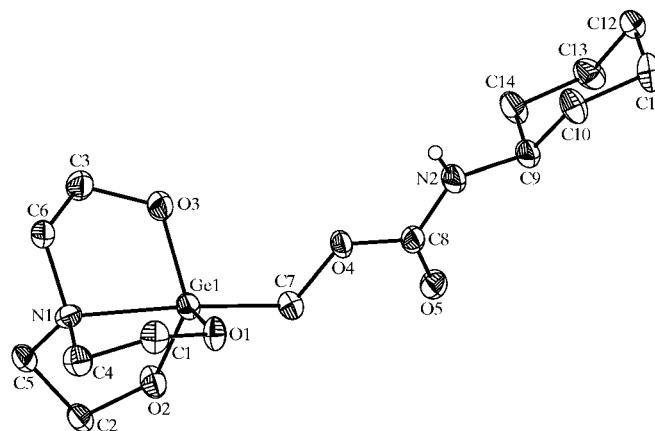


Figure 2

The molecular structure of (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity.

and (II), the interatomic Ge1···N1 distances are typical for germatranes with donor substituents (for instance, in 1-ethylgermatrane, the Ge1···N1 distance is 2.24 Å; Atovmyan *et al.*, 1970).

In the present compounds, the Ge atoms are bonded to bulky carbamate and adamantane substituents. In (II), the N1—Ge1—C7 angle is 173.73 (13)°, while in the majority of germatranes, the relative values are in the range 175–179°. In the case of the adamantane group in (I), the N1—Ge1—C7 angle remains almost undistorted [178.69 (11)°]. It is of interest to study the reason for the decrease in the N1—Ge1—C7 angle in (II).

We have found that the distortion of the N1—Ge1—C7 angle is related to the formation of intra- and intermolecular contacts between the O atoms of the atrane framework and the substituents (Allen *et al.*, 1987). For a more reliable analysis of the intramolecular contacts, we normalize all C—H bonds to 1.08 Å according to single-crystal neutron diffraction data. The germatranes with  $R_1C=CR_2R_3$  substituents ( $R_1 = H, I$  or  $Br, R_2 = H, Br$  or  $Cl$  and  $R_3 = Ph$ ; N1—Ge1—C7 angles in the range 173.5–178.1°; Karlov *et al.*, 2001; Faller & Kultyshev, 2003; Selina, Karlov *et al.*, 2004; Selina, Zhachkina *et al.*, 2004) may serve as examples of the influence of intramolecular contacts on the linearity of the N1—Ge1—C7 angle. In these compounds, short C—H···O contacts between an O atom and a phenyl group are always observed. In addition, the Br and I atoms also form short intermolecular contacts with O atoms of the atrane framework (torsion angle O—Si—C—Hal  $\approx$  22°, where Hal = Br or I).

The influence of the intermolecular contacts can be demonstrated by methyl (germatranyl)trimethylsilylacetate (Zaitseva *et al.*, 1997) and (pentafluorophenyl)germatrane (Kultyshev *et al.*, 2004) (N1—Ge1—C7 = 175.73 and 176.29°, respectively). In the case of the former compound, the acetate group forms four C—H···O contacts (C···O  $\approx$  3.5 Å, H···O  $\approx$  2.6 Å and C—H···O = 107–146°) as well as three H···H and C···H contacts (H···H  $\approx$  2.2 Å and C···H  $\approx$  3.1 Å). In (pentafluorophenyl)germatrane, four C—H···F contacts

(C···F  $\approx$  3.4 Å, H···F  $\approx$  2.5 Å and C—H···F = 138–164°) and one C—H··· $\pi$  contact (H···Cg  $\approx$  2.8 Å and C—H··· $\pi$  = 116°, where Cg is the centroid of the C<sub>6</sub>F<sub>5</sub> ring) are observed. Of course, all the above contacts are weak, but their total energy is sufficient for the distortion of the N1—Ge1—C7 angle. In (II), one may see that the N1—Ge1—C7 angle deviates further from the ideal value of 180° than in other germatranes. Such a deviation is related to the influence of crystal packing. Actually, atom N2 of the carbamate group participates in an N2—H2C···O1 hydrogen bond [H2C···O1 = 2.077 Å, N2···O1 = 2.951 (4) Å and N2—H2C—O1 = 172°; symmetry code:  $x, \frac{3}{2} - y, z - \frac{1}{2}$ ], while atom O5 forms a contact with the atrane framework (Fig. 3). Taking into account the noticeable flexibility of the Ge coordination polyhedron, one may conclude that the formation of the N—H···O interaction leads to distortion of the N1—Ge1—C7 angle.

In (I), the presence of the adamantane fragment does not lead to a significant deviation of N1—Ge1—C7 from ideal linearity. The adamantane hydrocarbon does not afford the O atoms of the atrane cage the opportunity to form intermolecular contacts. In turn, the intramolecular contacts of the methylene groups of the adamantane fragment to the O atoms of the atrane cage are unfavourable, due to large O···H distances (2.7–2.9 Å) and small C—H···O angles (106–110°). So one may therefore conclude that the bulky adamantane group preserves the N1—Ge1—C7 angle from distortion due to crystal packing.

## Experimental

The synthesis of (I) was carried out according to the previously published method of Gar *et al.* (1985). The compound was recrystallized from hexane. Compound (II) was prepared from (trichlorogermyl)methanol (21.0 g, 0.1 mol), isocyanocyclohexane (12.5 g, 0.1 mol) and triethanolamine (14.0 g, 0.9 mol). The reaction mixture was heated until gas evolution ceased. After cooling to room temperature, crystals of (II) appeared (yield 17.6 g, 46.9%; m.p. 421–425 K). <sup>1</sup>H NMR (Bruker AM-360 spectrometer; 360 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  1.53–1.92 (*m*, 11H, C<sub>6</sub>H<sub>11</sub>), 1.96 (*t*, 6H, CH<sub>2</sub>), 3.50 (*t*, 6H, CH<sub>2</sub>O), 4.42 (*s*, 1H, NH), 4.64 (*s*, 2H, OCH<sub>2</sub>Ge); IR (Bruker IFS-113V spectrometer; KBr tablet,  $\nu$ , cm<sup>-1</sup>): 3283 (NH), 1707 (C=O), 1103, 1074, 1045, 1022 [Ge(OCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N].

## Compound (I)

### Crystal data

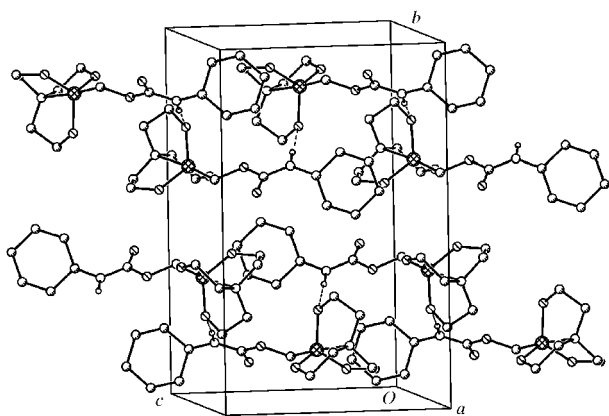
[Ge(C<sub>10</sub>H<sub>15</sub>)(C<sub>6</sub>H<sub>12</sub>NO<sub>3</sub>)]  
 $M_r = 353.98$   
 Monoclinic,  $P2_1/c$   
 $a = 10.641$  (6) Å  
 $b = 7.292$  (4) Å  
 $c = 19.943$  (11) Å  
 $\beta = 90.001$  (12)°  
 $V = 1547.3$  (14) Å<sup>3</sup>

$Z = 4$   
 $D_x = 1.520$  Mg m<sup>-3</sup>  
 Mo K $\alpha$  radiation  
 $\mu = 1.99$  mm<sup>-1</sup>  
 $T = 120$  (2) K  
 Prism, colourless  
 0.30 × 0.10 × 0.10 mm

### Data collection

Bruker SMART 1000 CCD area-detector diffractometer  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: multi-scan (SADABS; Sheldrick, 1998)  
 $T_{\min} = 0.587$ ,  $T_{\max} = 0.826$

15300 measured reflections  
 4396 independent reflections  
 3193 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.059$   
 $\theta_{\text{max}} = 30.0^\circ$



**Figure 3**

The crystal packing of (II). H atoms have been omitted for clarity, with the exception of atom H2C. The N2—H2C···O1 hydrogen bonds are shown as dashed lines.

## Refinement

Refinement on  $F^2$ 

$$R[F^2 > 2\sigma(F^2)] = 0.038$$

$$wR(F^2) = 0.108$$

$$S = 0.97$$

4396 reflections

191 parameters

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0517P)^2]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

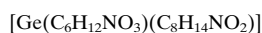
$$(\Delta/\sigma)_{\max} < 0.001$$

$$\Delta\rho_{\max} = 1.02 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.56 \text{ e } \text{\AA}^{-3}$$

## Compound (II)

## Crystal data



$$M_r = 374.96$$

Monoclinic,  $P2_1/c$ 

$$a = 9.4398 \text{ (13) } \text{\AA}$$

$$b = 16.690 \text{ (2) } \text{\AA}$$

$$c = 10.3361 \text{ (16) } \text{\AA}$$

$$\beta = 97.740 \text{ (3)}^\circ$$

$$V = 1613.6 \text{ (4) } \text{\AA}^3$$

$$Z = 4$$

$$D_x = 1.543 \text{ Mg m}^{-3}$$

Mo  $K\alpha$  radiation

$$\mu = 1.92 \text{ mm}^{-1}$$

$$T = 120 \text{ (2) K}$$

Plate, colourless

$$0.20 \times 0.10 \times 0.03 \text{ mm}$$

## Data collection

Bruker SMART CCD 1000 area-detector diffractometer

 $\varphi$  and  $\omega$  scans

Absorption correction: multi-scan (SADABS; Sheldrick, 1998)

$$T_{\min} = 0.700, T_{\max} = 0.945$$

8957 measured reflections

3487 independent reflections

2310 reflections with  $I > 2\sigma(I)$ 

$$R_{\text{int}} = 0.048$$

$$\theta_{\max} = 27.1^\circ$$

## Refinement

Refinement on  $F^2$ 

$$R[F^2 > 2\sigma(F^2)] = 0.047$$

$$wR(F^2) = 0.108$$

$$S = 1.05$$

3487 reflections

199 parameters

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0462P)^2]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} = 0.001$$

$$\Delta\rho_{\max} = 1.53 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.39 \text{ e } \text{\AA}^{-3}$$

Table 1

Selected bond lengths (Å) in (I) and (II).

Bond	(I)	(II)
Ge1...N1	2.206 (3)	2.266 (3)
Ge1—O1	1.817 (2)	1.822 (3)
Ge1—O2	1.794 (2)	1.825 (3)
Ge1—O3	1.791 (2)	1.820 (3)
Ge1—C7	1.957 (4)	1.966 (3)
N—C (mean)	1.471 (4)	1.473 (5)
O—C (mean)	1.415 (4)	1.416 (3)

Table 2

Selected bond angles (°) in (I) and (II).

Angle	(I)	(II)
N1—Ge1—C7	104.5 (2)	104.4 (3)
O—Ge—O (mean)	118.26 (12)	117.65 (14)
C—N—C (mean)	114.0 (3)	114.0 (3)
C7—O4—C8	114.3 (3)	

The H atoms were calculated geometrically and refined using a rigid-body model, with C—H = 0.99–1.00 Å and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ . The crystals of (I) were found to be twinned. The structure was refined in *XL* using the method of Pratt *et al.* (1971) and Jameson

(1982) with a TWIN matrix defined as TWIN 100 0 $\bar{1}$  00 $\bar{1}$ , which is the default for a monoclinic type with  $\beta$  approximately 90°. All calculations were carried out using *SHELXTL* (Version 5.10; Sheldrick, 1998).

For both compounds, data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT-Plus* (Bruker, 1998); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1998); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3019). Services for accessing these data are described at the back of the journal.

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