Three new germaimines have been synthesized and two of them characterized by X-ray diffraction; the Ge=N bond lengths agree well with an \textit{ab initio} prediction for H$_2$Ge-NH.

The Ge=N distance in unsubstituted germaimine (H$_2$Ge-NH) has been predicted to be 169.5 pm by \textit{ab initio} calculation with double-$\zeta$ (DZ) plus polarization basis sets.\textsuperscript{1} Germaimines have been observed as transient species (and trapped by various substrates) since 1978 (see ref. 2 for a recent review). Here we report the synthesis of three new germaimines prepared from highly sterically hindered diazagermylenes\textsuperscript{6} and 2,6-disubstituted phenylazides as shown in Scheme 1.\textsuperscript{1} In the $^{13}$N NMR spectrum of 3 signals with 2:1 intensity ratio at $\delta = -295$ and $-193$ (rel. to MeNO$_2$) have been detected.

Compounds 1-3 crystallized easily from hot THF (tetrahydrofuran) to give well-shaped amber crystals, which change from yellow at $-196 \degree$C to red at 150 $\degree$C. Compound 1 hydrolyses in air to give [2,6-(Pr$_2$)$_2$C$_6$(H$_2$)$_2$(Me)$_2$Ge(OH)$_2$-H$_2$C=2,6(Pr)$_2$]$_2$ (from spectroscopic evidence). Likewise, methanol is added across the (Ge=N) double bond of 3 thus filtering off and dried in vacuo. Satisfactory C, H, N elemental analyses were obtained for 1-3 and 5.

1: Bis[2,6-diisopropylphenyl)(trimethylsilyl)amino]germane (m.p. 195 $\degree$C (decomp.)); yield 11.0 g (74%). C$_{33}$H$_{52}$GeN$_2$Si$_2$ (618.53); MS [m/z (%)]: 763 (5), 73 (100); NMR (in C$_6$D$_6$): $\delta$(H) 0.20 (s, 18H, SiMe$_3$); 1.06, 1.28, 1.32 (3 x d, J$_{HH}$ 6.6 Hz, 3 x H, 6 x CH$_3$); 2.00, 3.80, 4.06 (3 x sept., J$_{HH}$ 3 x 2H, 6 x CH$_3$); 6.70-7.10, 7.24-7.27 (2 x m, 9H, arom.); $\delta$(C) 13.57 (SiMe$_3$); 24.63, 24.73, 25.36, 25.68 (threefold intensity) (ALL CH$_3$); 28.71, 29.06, 29.15 (all CH-Pr); 120.05, 123.25, 124.93, 125.47, 127.08, 139.30, 141.67, 147.15, 147.52, 148.65 (10 signals apparently due to non-equivalence of the 2/6 and 3/5 positions of the imino-bonded aromatic ring) (ALL arom.); $\delta$(Si) 16.2.

2: Bis[2,4,6-trimethylphenyl)(trimethylsilyl)amino]germane (m.p. 177 $\degree$C; yield 8.54 g (69%); C$_{38}$H$_{63}$GeN$_3$O$_2$Si$_2$ (722.70); MS [m/z (%)]: 763 (2), 73 (100); IR (KBr): 3583 (vOH), 3390 (vNH). NMR (in C$_6$D$_6$): $\delta$(H) 0.03 (s, 18H, SiMe$_3$); 1.41 (m, 4H, H-3 and H-5 of THF); 2.54, 2.79, 2.80 (6H, p-CH$_3$); 3.56 (m, 4H, H-2 and H-5 of THF); 3.91 (m, 2H, OMe); 6.60-6.80 (br, 6H, CH$_3$); IR (in Nujol) 3350 (vNH).

Crystal data for 1: C$_{33}$H$_{52}$GeN$_2$Si$_2$, triclinic, space group $\overline{P}$1, $a = 1144.62(2)$, $b = 1178.72(2)$, $c = 1278.63(4)$, $\alpha = 88.84(1)$, $\beta = 98.67(1)$, $\gamma = 86.20(1)$, $U = 2.13$ nm$^3$, $Z = 2$, $D$ = 1.16 g cm$^{-3}$, $\mu = 0.80$ mm$^{-1}$, $F(000) = 504$, crystal dimensions 0.3 x 0.6 x 0.8 mm, 8471 reflections collected with $\theta < 50^\circ$, 7488 unique and 6999 with $F > 3\sigma(F)$ used in the structural analysis. 3: C$_{38}$H$_{63}$GeN$_3$O$_2$Si$_2$, monoclinic, space group $P2_1/n$, $a = 852.3(2)$, $b = 299.1(4)$, $c = 1382.1(2)$, $\beta = 100.30(2)^\circ$, $U = 3.43$ nm$^3$, $Z = 4$, $D$ = 1.20 g cm$^{-3}$, $\mu = 0.39$ mm$^{-1}$, $F(000) = 1320$, crystal dimensions 0.4 x 0.4 x 0.6 mm, 7086 reflections collected with $\theta < 20^\circ$, 5991 unique and 4589 with $F > 3\sigma(F)$ used in the structural analysis. Both data sets were collected on a Siemens-Stoe AED diffractometer using Mo-K$_\alpha$ radiation ($\lambda = 71.073$ pm) at a temperature of 153 K. Semiempirical absorption corrections were applied. The structures were solved by Patterson and Direct methods. All non-hydrogen atoms were refined anisotropically, and a riding model starting from calculated positions was employed for the hydrogen atoms. 437 I and 356 3 parameters were refined with a weighting scheme $w^{-1} = a(F^2)+0.0002 F^2$ and $w^{-1} = a(F) + 0.0001 F^2$. The refinement converged with $R = 0.041$, $R_{w} = 0.037$ and $R_{M} = 0.048$, $R_{w} = 0.040$ and final difference electron density maxima of 0.5(1) and 0.2(3) e A$^{-3}$. Atomic coordinates, bond lengths and angles, and anisotropic displacement parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

The structures of 1 and 3 have been determined by single crystal X-ray diffraction. The structures of 1 and 3 are consistent with a trigonal torsion angle 1.5(5), and 1.5(5) for 1 and 3.

The structures of 1 and 3 have been determined by single crystal X-ray diffraction. In these molecules, which are stable for months under dry nitrogen at room temperature, the Ge=N bond lengths are found to be 170.3(2) pm and 169.1(3) pm, which are in excellent agreement with the calculated value for germanium.\textsuperscript{1} The C-N=Ge torsion angles 1.5(5), 178.4(3)$^\circ$ for 1 and -1.5(5), 178.1(3)$^\circ$ for 2 are consistent with a...
normal π-π double bond. The difference between the mean Ge–N and Ge=–N distances in these compounds is only 12 pm; for most pairs of atoms a double bond is about 20 pm shorter than a single bond. In view of the Ge–N distances reported here, [GeN(2,6-Pr₂C₆H₃)]₃ [mean Ge–N 185.9(2) pm] should be regarded as a Geᴵ derivative without significant multiple bonding.

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References