Reactions of Diazo-compounds with the Electron-rich Germylene $Ge[N(SiMe_3)_2]_2$. Characterisation and Some Addition Reactions of $[(Me_3Si)_2N]_2GeNNC(COOMe)_2$: Crystal and Molecular Structure of $[(Me_3Si)_2N]_2Ge[NHN{=}C(COOMe)_2][C(N_2)COPh]$†

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Two forms of the stable germyleneazine $[(Me_3Si)_2N]_2GeNNC(COOMe)_2$, formed by addition of the diazo-compound $N_2C(COOMe)_2$ to the electron-rich germylene $Ge[N(SiMe_3)_2]_2$ have been characterised in solution by ^1H and ^{13}C n.m.r. spectroscopy. MNDO calculations on the simpler analogue $[(H_3Si)_2N]_2GeNNC(COOMe)_2$ indicate that the two forms have planar transoid and cisoid GeNNC groups respectively, with the cisoid isomer as the more stable: the calculations also indicate that charge-controlled additions of electrophiles will occur at N^1, adjacent to germanium, while all nucleophilic addition will occur at Ge. Some adducts of $[(Me_3Si)_2N]_2GeNNC(COOMe)_2$ with weak acids HX are described; in all cases 1,2-addition of HX occurs across the Ge–N^1 bond to yield $[(Me_3Si)_2N]_2Ge(X)[NHN{=}C(COOMe)_2]$. Crystals of one such adduct $[(Me_3Si)_2N]_2Ge[NHN{=}C(COOMe)_2][C(N_2)COPh]$ are triclinic, space group $P\bar{1}$, with a = 9.627(2), b = 12.672(19), c = 15.702(3) Å, α = 101.66(4), β = 85.02(2), γ = 77.65(5)°, and Z = 2. The structure was refined from diffractometer data (5 173 observed reflections) to an R value of 0.046. The structure determination confirms the 1,2-addition of $HC(N_2)COPh$ across the Ge–N^1 bond of $[(Me_3Si)_2N]_2GeNNC(COOMe)_2$ and reveals a free diazo-group, sterically unconstrained. Reaction of tosyl azide with $Ge[N(SiMe_3)_2]$ follows a different course from the reactions involving diazo-compounds; nitrogen is lost and the product is a polygermazane $\{[(Me_3Si)_2N]_2GeNSO_2C_6H_4Me\text{-}p\}_n$, which is insoluble in aqueous media and all common organic solvents, wholly resistant to hot 50% aqueous alkali, but readily hydrolysed by concentrated hydrochloric acid.

It has recently been demonstrated that the electron-rich germylene $Ge[N(SiMe_3)_2]_2$ reacts with diazo-compounds $N_2C(R^1)R^2$ to yield germyleneazines $[(Me_3Si)_2N]_2GeNNC(R^1)R^2$ which may be trapped, for example, by added ethanol[1] but had not hitherto been characterized: if either of the substituents (R^1,R^2) contains an enolisable group, then the trapping reaction may be intra-molecular.[1,2] The results of the trapping reactions using ethanol in the case of $R^1 = R^2 =$ COOMe indicated[1] that the germyleneazine had appreciable stability in solution. Here we report spectral characterisation of $[(Me_3Si)_2N]_2Ge{=}N{-}N{=}C(COOMe)_2$, dimethyl bis[bis(trimethylsilyl)amino]germylenehydrazonomalonate, further addition reactions with weak acids, and the crystal and molecular structure of one such addition product $[(Me_3Si)_2N]_2Ge[NHN{=}C(COOMe)_2][C(N_2)COPh]$, [benzoyl(diazo)methyl][bis(methoxycarbonyl)methylenehydrazino]bis[bis(trimethylsilyl)amino]germane. The formation, involving loss of nitrogen, of a polygermazane from the reaction of tosyl azide with $Ge[N(SiMe_3)_2]_2$ is also described.

Experimental

The germylene $Ge[N(SiMe_3)_2]_2$ was prepared from $GeCl_2{\cdot}$diox (diox = dioxane)[3] by reaction[4] with $LiN(SiMe_3)_2$. Dimethyl diazomalonate[5] was purified by repeated recrystallisation from diethyl ether at −80 °C.

All solvents were dried and purified by conventional methods; light petroleum had b.p. 40—60 °C. Elemental analyses were by the Microanalytical Laboratory of the Chemistry Department, University of St. Andrews. All solutions containing $Ge[N(SiMe_3)_2]_2$ or $[(Me_3Si)_2N]_2GeNNC(COOMe)_2$ were handled under dry nitrogen.

Spectral Characteristics of $[(Me_3Si)_2N]_2GeNNC(COOMe)_2$.—Equimolar quantities of $Ge[N(SiMe_3)_2]_2$ and $N_2C(COOMe)_2$, each 0.5 mol dm^{-3} in C_6D_6 (wherein their respective ^1H chemical shifts are 0.31 and 3.35 p.p.m., with spectra unchanged over several weeks), were mixed in a n.m.r. tube and sealed under nitrogen. N.m.r.: ^1H, δ 0.24 (36 H, s, $SiMe_3$), 3.39 and 3.72 (2 × 3 H, 2 × s, 2 × $COOCH_3$); ^{13}C, δ 4.9 ($SiMe_3$), 51.1 and 52.2 (2 × $COO\mathit{C}H_3$), 119.6 [$\mathit{C}(COOCH_3)_2$], 157.5 and 165.8 (2 × $\mathit{C}OOCH_3$). During a period of one week this spectrum was slowly replaced by that of a second isomer. N.m.r.: ^1H, δ 0.19 (36 H, s, $SiMe_3$), 3.02 and 3.48 (2 × 3 H, 2 × s, 2 × $COOCH_3$); ^{13}C, δ 4.9 ($SiMe_3$), 43.4 and 52.1 (2 × $COO\mathit{C}H_3$), 123.0 [$\mathit{C}(COOCH_3)_2$]. Two days after mixing the $Ge[N(SiMe_3)_2]_2$ and $N_2C(COOMe)_2$ solutions, the two species were present in approximately equimolar quantities: after 7 d, only the second product was present. Similar solutions, similarly prepared, in which the molar ratios of $Ge[N(SiMe_3)_2]_2$:$N_2C(COOMe)_2$ were 2:1 and 1:2 respectively showed initial ^1H n.m.r. spectra which were a summation of the first spectrum described above and that of the reagent in stoicheiometric excess. When $Ge[N(SiMe_3)_2]_2$ was in molar excess the spectral changes noted for the equimolar solution were complete within 2 d of mixing, whereas when $N_2C(COOMe)_2$ was in molar excess, no spectral change occurred, even in 7 d.

U.v.-visible spectra were measured using an SP–8100

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† [Benzoyl(diazo)methyl][bis(methoxycarbonyl)methylenehydrazino]bis[bis(trimethylsilyl)amino]germane.

Supplementary data available (No. SUP 56681, 6 pp.): Z-matrices and cartesian co-ordinates. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

Table 1. Electronic spectral data

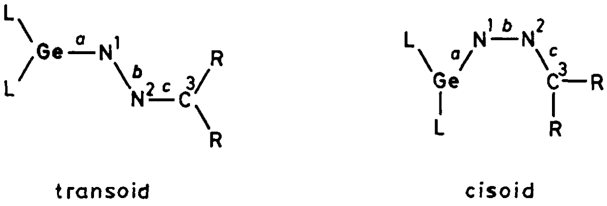
Compound	Solvent	$\lambda_{max.}$/nm	ε/dm^3 mol^{-1} cm^{-1}
Ge[N(SiMe$_3$)$_2$]$_2$	Et$_2$O	224	1 307
		480	2.74
N$_2$C(COOMe)$_2$	Et$_2$O	225	7 453
		255	7 764
		357	22.3
(**1**)	Et$_2$O	502	44.8
	Benzene	504	40.8

spectrophotometer. Solutions of $Ge[N(SiMe_3)_2]_2$ in Et_2O were 1.109×10^{-1} and 5.547×10^{-4} mol dm^{-3}; solutions of $N_2C(COOMe)_2$ in Et_2O were 3.833×10^{-2} and 1.916×10^{-4} mol dm^{-3}; solutions of $[(Me_3Si)_2N]_2GeNNC(COOMe)_2$ were 3.918×10^{-2} mol dm^{-3} in Et_2O and 1.985×10^{-2} mol dm^{-3} in benzene. The values of $\lambda_{max.}$ and the corresponding absorption coefficients are given in Table 1. The spectrum of $Ge[N(SiMe_3)_2]_2$ has been previously reported[4] in n-hexane solution.

Reactions of $[(Me_3Si)_2N]_2GeNNC(COOMe)_2$ *with Weak Acids*.—(*a*) *Water*. To a benzene solution (20 cm^3) of the germyleneazine (5.7 mmol) was added, under nitrogen and with stirring, 0.21 cm^3 (11.7 mmol) of water. After 30 min, the mixture was evaporated to dryness and the residue taken up in CH_2Cl_2 (30 cm^3) and filtered. After evaporation, the solid residue was chromatographed on silica, where elution with ether–light petroleum (1:12 v/v initially, increasing to 1:1) yielded $Ge(OH)_2[N(SiMe_3)_2]_2$ (510 mg, 21%), identical (i.r., ^{1}H n.m.r., m.p.) with an authentic sample,[1] and the hydrazone $H_2NN{=}C(COOMe)_2$ (295 mg, 32%), m.p. (from acetonitrile) 134—136 °C (Found: C, 37.7; H, 5.1; N, 17.5. $C_5H_8N_2O_4$ requires C, 37.5; H, 5.0; N, 17.5%). N.m.r.: ^{1}H ($CDCl_3$), δ 3.82 and 3.86 (2 × 3 H, 2 × s, 2 × OCH_3), 9.3 (2 H, s, br, NH_2). I.r. (ν/cm^{-1}): 3 320 and 3 190 (NH), 1 694 and 1 670 [–C(O)–C=N–]. Mass spectrum: *m/e* 161 $(M + 1)^+$, 160 (M^+), 159 $(M - 1)^+$, 158 $(M - 2)^+$; accurate mass found for M^+ 160.0476, $(C_5H_8N_2O_4)^+$ requires 160.0484. When a deficit of water was added (1 mol equiv.) in an otherwise similar experiment, the products, in addition to $Ge(OH)_2[N(SiMe_3)_2]_2$ (34%) and $H_2NN{=}C(COOMe)_2$ (16%), were the polymeric oxide $\{GeO[N(SiMe_3)_2]_2\}_n$, identical (i.r., ^{1}H, ^{13}C n.m.r.) with an authentic sample,[1] (40%) and the adduct $[(Me_3Si)_2N]_2Ge(OH)[NHN{=}C(COOMe)_2]$ (4.1%), as a labile oil. N.m.r.: ^{1}H ($CDCl_3$), δ 0.28 (36 H, s, $SiMe_3$), 1.9 (1 H, s, br, OH), 3.83 and 3.85 (2 × 3 H, 2 × s, 2 × OCH_3), 9.3 (1 H, s, br, NH). I.r. (ν/cm^{-1}): 3 470br (OH), 3 200 (NH), 1 728, 1 710, and 1 680 (C=O and C=N). Attempts to purify this material, in order to obtain an analytical sample, were frustrated by its spontaneous breakdown to yield a mixture of $H_2NN{=}C(COOMe)_2$ and $\{GeO[N(SiMe_3)_2]_2\}_n$.

(*b*) *Other acids*. The general procedure described[1] for the reaction of $[(Me_3Si)_2N]_2GeNNC(COOMe)_2$ with ethanol was followed. In this manner was obtained, with methanol, $[(Me_3Si)_2N]_2Ge(OMe)[NHN{=}C(COOMe)_2]$ as colourless crystals, m.p. 84—85 °C, from hexane (Found: C, 37.0; H, 8.0; N, 9.5. $C_{18}H_{46}GeN_4O_5Si_4$ requires C, 37.1; H, 8.0; N, 9.6%). N.m.r.: ^{1}H ($CDCl_3$), δ 0.26 (36 H, s, $SiMe_3$), 3.62 (3 H, s, $GeOCH_3$), 3.77 and 3.83 (2 × 3 H, 2 × s, 2 × $COOCH_3$), 11.1 (1 H, s, br, NH). I.r. (ν/cm^{-1}): 3 200 (NH), 1 726, 1 715 (sh), and 1 673 (C=O and C=N). Using $NH(SiMe_3)_2$ in like manner was obtained, as an oil in low yield (typically 5—6%) $[(Me_3Si)_2N]_3GeNHN{=}C(COOMe)_2$. N.m.r.: ^{1}H ($CDCl_3$), δ 0.27 (54 H, s, $SiMe_3$), 3.77 and 3.83 (2 × 3 H, 2 × s, 2 × OCH_3), 11.0 (1 H, s, br, NH). I.r. (ν/cm^{-1}): 3 210 (NH), 1 730, 1 715 (sh), and 1 676 (C=O and C=N).

Table 2. Calculated molecular parameters for $[(H_3Si)_2N]_2GeNNC(COOMe)_2$



	transoid	cisoid
Bond lengths (Å)		
a	1.763	1.915
b	1.284	1.207
c	1.327	1.434
Bond angles (°)		
a—*b*	121.4	129.3
b—*c*	119.0	122.2
Bond orders		
a	1.243	0.738
b	1.276	1.921
c	1.650	1.033
Atomic charges		
Ge	+1.764	+1.864
N^1	−0.757	−0.549
N^2	−0.008	+0.128
C^3	−0.137	−0.375
ΔH_f°/kJ mol^{-1}	−590.2	−775.9

Dehydration of $Ge(OH)_2[N(SiMe_3)_2]_2$.—The diol (0.25 g, 0.58 mmol) was dissolved in mesitylene (5 cm^3) and boiled under reflux over 4 Å molecular sieves for 2 h. After filtration and removal of the solvent, the residue was chromatographed on silica. Elution with ether–light petroleum (1:12 v/v) yielded 130 mg of a colourless oil which was rechromatographed using ether–light petroleum (1:99 v/v) to yield 80 mg (34%) of a colourless solid. The i.r. spectrum showed no ν(OH). N.m.r.: ^{1}H ($CDCl_3$), δ 0.06, 0.14, 0.18, 0.30. T.l.c. confirmed that $Ge(OH)_2[N(SiMe_3)_2]_2$ was absent.

No reaction of the diol was detected under the following reaction conditions: (*a*) toluene reflux, 5 h, Dean-Stark trap; (*b*) xylene reflux, 5 h, 4 Å molecular sieve; (*c*) toluene reflux, 6 h, anhydrous $CaSO_4$: in all cases the diol was recovered unchanged.

Reaction of $Ge[N(SiMe_3)_2]_2$ *with Tosyl Azide*.—A solution of tosyl azide (1.0 g, 5.1 mmol) in benzene (10 cm^3) was added to a solution of the germylene (2.0 g, 5.1 mmol) in benzene (15 cm^3) under nitrogen with stirring. Nitrogen was evolved and the solution became lighter in colour. After stirring for 30 min, the resulting white solid was filtered off and dried, affording $\{[(Me_2Si)_2N]_2GeNSO_2C_6H_4Me\text{-}p\}_n$ (1.25 g, 44%), m.p. 257—258 °C [Found: C, 40.8; H, 7.8; N, 7.4. $(C_{19}H_{43}GeN_3O_2SSi_4)_n$ requires C, 40.6; H, 7.7; N, 7.5%]. The product was insoluble in all common organic solvents. I.r.: no assignable features. Mass spectrum: *m/e* (^{74}Ge) 564 (monomer + H)$^+$, 548 (monomer $-CH_3$)$^+$; accurate mass found for (monomer $-$ CH_3)$^+$, 548.1151; $(C_{18}H_{40}{}^{74}GeN_3O_2SSi_4)^+$ requires 548.1128. In an otherwise identical reaction, using tetrahydrofuran (thf) instead of benzene as solvent, the identical product was obtained (0.94 g, 33%). The polymer (0.5 g) was recovered unchanged and in quantitative yield after reflux during 1 h with

Table 3. Fractional atomic co-ordinates (× 10^4) for $[(Me_3Si)_2N]_2Ge[NHN{=}C(COOMe)_2][C(N_2)COPh]$

Atom	*x*	*y*	*z*
Ge(1)	1 716	2 839	2 179
N(1)	1 031(3)	1 566(2)	2 152(2)
N(2)	348(3)	1 472(2)	2 894(2)
C(3)	155(3)	523(3)	3 018(2)
C(4)	−733(4)	542(3)	3 836(3)
O(5)	−1 187(3)	−220(2)	3 963(2)
O(6)	−1 011(3)	1 512(2)	4 404(2)
C(7)	−1 929(6)	1 623(4)	5 215(3)
C(8)	799(4)	−536(3)	2 383(2)
O(9)	1 026(5)	−613(2)	1 604(2)
O(10)	1 230(3)	−1 375(2)	2 738(2)
C(11)	2 022(5)	−2 413(3)	2 160(3)
C(12)	38(3)	4 021(3)	2 684(2)
N(13)	−1 012(3)	3 863(2)	3 199(2)
N(14)	−1 899(4)	3 724(3)	3 653(2)
C(15)	−162(4)	5 106(3)	2 483(2)
O(16)	874(3)	5 341(2)	2 122(2)
C(17)	−1 578(3)	5 919(3)	2 714(2)
C(18)	−2 874(4)	5 617(3)	2 541(3)
C(19)	−4 125(5)	6 408(4)	2 740(4)
C(20)	−4 171(4)	7 487(3)	3 121(3)
C(21)	−2 916(4)	7 789(3)	3 281(3)
C(22)	−1 626(4)	7 019(3)	3 073(2)
N(3)	2 194(3)	2 827(2)	1 028(2)
Si(30)	3 509(1)	3 474(1)	663(1)
C(31)	2 730(6)	4 692(4)	201(3)
C(32)	4 486(5)	4 025(4)	1 547(3)
C(33)	4 885(5)	2 460(4)	−191(3)
Si(40)	1 174(1)	2 222(1)	259(1)
C(41)	−777(4)	2 599(4)	690(3)
C(42)	1 821(5)	682(3)	−68(3)
C(43)	1 313(6)	2 713(5)	−785(3)
N(4)	3 119(3)	2 745(2)	2 893(2)
Si(50)	2 843(1)	3 669(1)	3 938(1)
C(51)	4 460(5)	3 449(4)	4 525(3)
C(52)	1 340(4)	3 455(4)	4 666(2)
C(53)	2 523(5)	5 142(3)	3 879(3)
Si(60)	4 431(1)	1 502(1)	2 709(1)
C(61)	4 441(5)	566(4)	1 625(3)
C(62)	6 289(4)	1 705(4)	2 676(4)
C(63)	4 093(6)	717(4)	3 551(4)

50% aqueous NaOH solution (10 cm^3). Concentrated hydrochloric acid (6 cm^3) was added to the polymer (1 g) and the whole stirred at room temperature for 20 h. The mixture was poured into water (20 cm^3) and filtered yielding *p*-toluenesulphonamide, and the filtrate was extracted with CH_2Cl_2 (3 × 20 cm^3). The extract was dried over Na_2SO_4 and the solvent was removed to yield further *p*-toluenesulphonamide (combined yield 267 mg, 88%). No further material was recovered from the aqueous solution after basification.

MNDO Calculations.—Calculations[6] were made using the MOPAC system,[7] implemented on a VAX 11/785 computer; atomic parameters used were from published sources.[7–9] All independent geometric variables were simultaneously optimised in the molecular structure calculations, except that local C_{3v} symmetry was imposed on all CH_3 and SiH_3 groups. Calculated values of selected molecular parameters for two isomers of $[(H_3Si)_2N]_2GeNNC(COOMe)_2$ are recorded in Table 2.

Crystal Structure Determination.—Crystals of $[(Me_3Si)_2N]_2$-$Ge[NHN{=}C(COOMe)_2][C(N_2)COPh]$[1] suitable for *X*-ray examination were grown from hexane.

Crystal data. $C_{25}H_{48}GeN_6O_5Si_4$, M = 697.64, triclinic, a = 9.627(2), b = 12.672(19), c = 15.702(3) Å, α = 101.66(4), β = 85.02(2), γ = 77.65(5)°, U = 1 815.6 $Å^3$, space group $P\bar{1}$ (no. 2), Z = 2, D_c = 1.276 g cm^{-3}, $\mu(Mo\text{-}K_\alpha)$ = 9.98 cm^{-1}, λ = 0.710 69 Å, $F(000)$ = 736.

Data collection.[10] CAD4 diffractometer using graphite-monochromated Mo-K_α radiation, $\omega/2\theta$ scan mode, ω scan width = (0.8 + 0.35 tanθ)°, ω scan speed = 1.35—6.77° min^{-1}, $1.5 \leqslant \theta \leqslant 25°$. 6 697 Reflections measured, of which 6 380 unique, and 5 173 with $I \geqslant 3\sigma(I)$.

Structure solution and refinement. Direct methods, followed by SFLS and difference-Fourier cycles. All non-hydrogen atoms refined anisotropically. Hydrogen atoms H(1) and H(18)—H(22) (phenyl) refined isotropically; all other hydrogen atoms were included in the refinement at calculated positions; individual isotropic thermal parameters for the phenyl hydrogens, and two common isotropic thermal parameters for the hydrogen atoms in the COOMe and $SiMe_3$ groups respectively. The weighting scheme $w = 1/[\sigma^2(F_o) + 0.0001 F_o^2]$ gave final R and R' values of 0.046 and 0.040, with 393 refined parameters. Programs and computers used, and sources of scattering factor data, were as given in ref. 10.

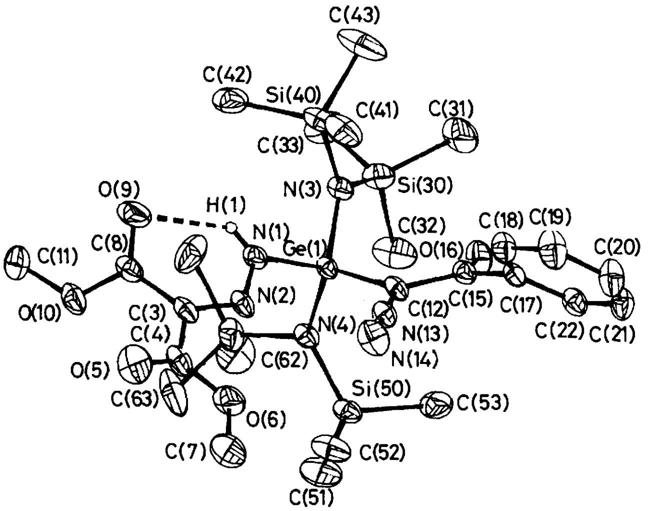
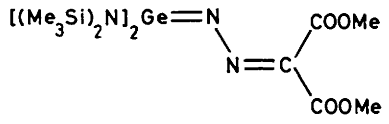


Figure. Perspective view of the molecule $[(Me_3Si)_2N]_2Ge[NHN{=}C(COOMe)_2][C(N_2)COPh]$, showing the atom-numbering scheme

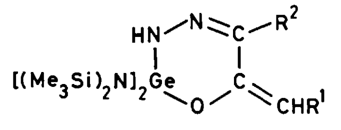
Final refined atom co-ordinates are given in Table 3. Bond lengths and angles are in Tables 4 and 5. A perspective view of the molecule, showing the atom-numbering scheme, is shown in the Figure.

Results and Discussion

Characterisation of $[(Me_3Si)_2N]_2GeNNC(COOMe)_2$.—The reaction of the germylene $Ge[N(SiMe_3)_2]_2$ with an equimolar quantity of $N_2C(COOMe)_2$, in benzene solution, rapidly and quantitatively affords a new species (**1**) containing two non-equivalent COOMe groups which are distinguishable by ^1H and ^{13}C n.m.r., and two $N(SiMe_3)_2$ groups which are identical by n.m.r. spectroscopy. The n.m.r. data, together with the earlier isolation[1] of $[(Me_3Si)_2N]_2Ge(OEt)[NHN{=}C(COOMe)_2]$ from a trapping experiment with ethanol, allow the



(1)

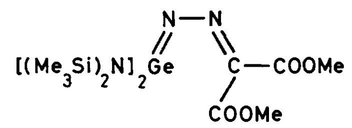


(2a) R^1 = COOEt, R^2 = H

(2b) R^1 = $SO_2C_6H_4Me$-*p*, R^2 = H

(2c) R^1 = COPh, R^2 = H

(2d) R^1, R^2 = $C(O)CH_2CMe_2$



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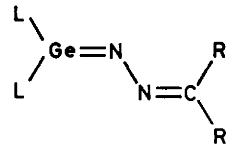
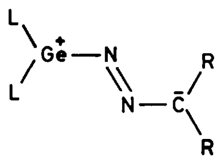


(I)



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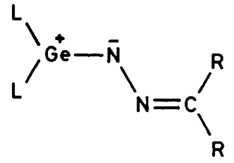
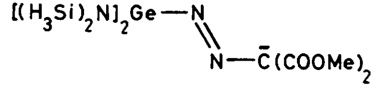


(III)

L = $N(SiMe_3)_2$, R = COOMe



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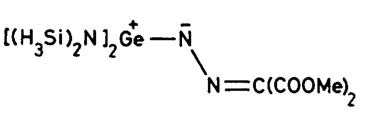

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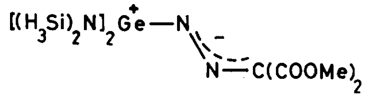

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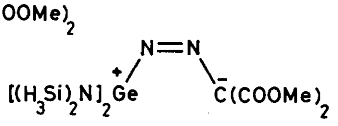


(VII)

identification of this new species (**1**) as $[(Me_3Si)_2N]_2GeNNC(COOMe)_2$; the unique carbon atom has a chemical shift (δ +119.6) to lower frequency than the C=N carbon atom in the cyclic species (**2**).[1]

Compound (**1**) slowly changes over a period of several days into a second species (**3**) in which again the two COOMe groups are distinguishable, but the two $N(SiMe_3)_2$ groups are not. The general similarity of the n.m.r. parameters for (**1**) and (**3**) shows that they are isomeric, most probably cisoid and transoid forms of the germyleneazine $[(Me_3Si)_2N]_2GeNNC(COOMe)_2$; molecular orbital calculations (see below) indicate that (**1**) is the transoid isomer and (**3**) the cisoid.

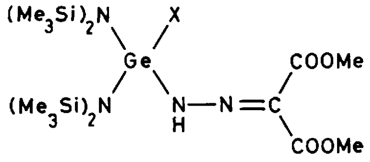
The n.m.r. spectra show that there is slow rotation about the N=C bond, and fast rotation about the Ge=N bond; these facts, and the low-frequency chemical shift of the unique carbon suggest that the true electronic structure of (**1**) and (**3**) should be represented as a hybrid of three forms (**I**)—(**III**) (shown for convenience only in the transoid form). Of these (**III**) is the most important contributor, and (**I**) the least important. Molecular orbital calculations (see below) fully support this interpretation.

The rate of conversion from (**1**) into (**3**) was dependent upon the presence of excess $Ge[N(SiMe_3)_2]_2$. When one molar equivalent of $Ge[N(SiMe_3)_2]_2$ was present together with (**1**), the initial n.m.r. spectrum was a summation of those of (**1**) and the germylene, but the rate of conversion of (**1**) into (**3**) was accelerated, and isomerisation was complete within 2 d, rather than the 7 d required for (**1**) (see above). On the other hand, when 1 mol equiv. of $N_2C(COOMe)_2$ was mixed with (**1**), the n.m.r. spectrum, which was a summation of those of (**1**) and $N_2C(COOMe)_2$, remained unchanged, apart from slight traces of decomposition products, during 7 d; no trace of (**3**) was observed in the presence of excess of $N_2C(COOMe)_2$.

The spectra recorded in the presence of excess $Ge[N(SiMe_3)_2]_2$ or $N_2C(COOMe)_2$ showed that no fast exchange occurred between $[(Me_3Si)_2N]_2GeNNC(COOMe)_2$ (either isomer) and $Ge[N(SiMe_3)_2]_2$ or between the transoid isomer and $N_2C(COOMe)_2$. Further spectral characterisation of the deep orange-red $[(Me_3Si)_2N]_2GeNNC(COOMe)_2$ solution was obtained using u.v.–visible spectroscopy; the resulting electronic spectral data are recorded in Table 1.

The characterisation of $[(Me_3Si)_2N]_2GeNNC(COOMe)_2$ represents the first system containing three-co-ordinate germanium forming a formal double bond, and thermodynamically stable and persistent in solution, which does not rely on the presence of sterically bulky substituents at both ends of the formal double bond to confer kinetic persistence. The system $Ge[CH(SiMe_3)_2]_2$, although forming a Ge–Ge bonded dimer in the crystal,[11] is monomeric in the vapour phase:[12] the Ge–Ge interaction in the dimer $Ge_2[CH(SiMe_3)_2]_4$ is very weak, and the central Ge_2C_4 core is not[11] ethene-like in configuration. The compound $Ge_2(C_6H_3Et_2\text{-}2,6)_4$, although not dissociating in solution,[13] relies on its bulky substituents for its persistence, as does $(2,4,6\text{-}Me_3C_6H_2)_2Ge{=}P(C_6H_2Bu^t_3\text{-}2,4,6)$.[14] Other reported Ge=X species are all transient intermediates, inferred only from the products of trapping experiments.[15–19]

Molecular Orbital Calculations.—Molecular and electronic structure calculations were made on $[(H_3Si)_2N]_2GeNNC(COOMe)_2$, where the $SiMe_3$ groups in (**1**) and (**3**) have been replaced, for the sake of computational economy, by SiH_3 groups. The principal calculated parameters are given in Table 2, and the complete Z-matrices and atomic co-ordinates are in SUP 56681.



(6) X = $C(N_2)COPh$

(7) X = $N(SiMe_3)_2$

(8) X = OMe

(9) X = OEt

(10) X = OH

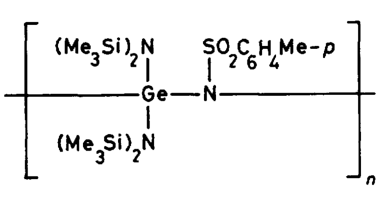
The calculations show that for $[(H_3Si)_2N]_2GeNNC(COOMe)_2$ the cisoid isomer (**4**) is substantially more stable than the transoid (**5**); a similar conclusion was drawn earlier[1] for the simple model compound $(H_2N)_2GeNNC(COMe)COOMe$, derived from the enolisable diazo-compound $MeCOC(N_2)COOMe$. The geometric and electronic structures of the two isomers of $[(H_3Si)_2N]_2GeNNC(COOMe)_2$ show significant differences: in particular the calculated bond orders for the transoid isomer indicate a valence-bond representation which is a mixture of (**IV**) and (**V**) with (**V**) dominant, *i.e.* an allylic system (**VI**). On the other hand the cisoid isomer is represented as (**VII**): this canonical form dominates the structure to the almost complete exclusion of other forms.

On the basis of the ΔH_f° values in Table 2 we assign to the first-formed isomer of $[(Me_3Si)_2N]_2GeNNC(COOMe)_2$, compound (**1**), the transoid conformation, and the cisoid conformation to the second isomer, compound (**3**).

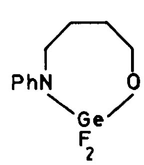
The net atomic charges calculated for the model $[(H_3Si)_2N]_2GeNNC(COOMe)_2$ indicate that in charge-controlled reactions, electrophiles will add preferentially at N^1 (irrespective of isomer) while nucleophiles will add preferentially at germanium. For both transoid and cisoid isomers of $[(H_3Si)_2N]_2GeNNC(COOMe)_2$, the highest occupied molecular orbital is a π-type orbital, concentrated in the central GeNNC fragment, with its largest coefficients at N^1 and C^3 (having almost equal magnitudes), so that orbital-controlled addition of electrophiles is possible at either of these sites: in each isomer the lowest unoccupied molecular orbital is a π-type orbital, again concentrated in the GeNNC fragment, with by far the largest coefficient at germanium, so that orbital-controlled, as well as charge-controlled addition of nucleophiles is expected to occur exclusively at germanium.

Addition of Weak Acids to $[(Me_3Si)_2N]_2GeNNC(COOMe)_2$.—Consistent with net atomic charges calculated for $[(H_3Si)_2N]_2GeNNC(COOMe)_2$, addition of weak acids HX to $[(Me_3Si)_2N]_2GeNNC(COOMe)_2$ (expected to be a charge-controlled process) occurs exclusively in a 1,2-fashion across the GeN bond: no evidence was obtained for any 1,4-addition products. The weak acid HX can be equally a carbon, nitrogen, or oxygen acid, *e.g.* $HC(N_2)COPh$, $HN(SiMe_3)_2$, or HOMe or HOEt, and in each case the corresponding adduct $[(Me_3Si)_2N]_2Ge(X)[NHN{=}C(COOMe)_2]$ was obtained, (**6**)—(**9**) respectively.

When the acid HX represents water the reaction is more complex. With at least two molar equivalents of water the germyleneazine $[(Me_3Si)_2N]_2GeNNC(COOMe)_2$ undergoes complete cleavage of the unique GeN bond to give the previously characterised[1,20] germanediol $Ge(OH)_2[N(SiMe_3)_2]_2$, together with the hydrazone $H_2NN{=}C(COOMe)_2$. Similar hydrolysis to yield $Ge(OH)_2[N(SiMe_3)_2]_2$ and a hydrazone $H_2NN{=}C(COPh)COOEt$ was observed[1] when the 1 : 1 addition product of $Ge[N(SiMe_3)_2]_2$ with $PhCOC(N_2)COOEt$ was chromatographed on silica.



(**11**)



(**12**)

When, however, only one molar equivalent of water was added to $[(Me_3Si)_2N]_2GeNNC(COOMe)_2$, the products included not only $Ge(OH)_2[N(SiMe_3)_2]_2$ and $H_2NN{=}C(COOMe)_2$ as before, but also the very labile $[(Me_3Si)_2N]_2Ge(OH)[NHN{=}C(COOMe)_2]$ (**10**). This hydroxygermane could not be isolated in analytically pure form as it spontaneously decomposes according to equation (1). A similar decomposition of a

$$[(Me_3Si)_2N]_2Ge(OH)[NHN{=}C(COOMe)_2] \longrightarrow \tfrac{1}{n}\{GeO[N(SiMe_3)_2]_2\}_n + H_2NN{=}C(COOMe)_2 \quad (1)$$

hydroxogermane was postulated,[1] although no hydrazone was isolated, in order to explain the formation, in low yield (4%) of the polymeric oxide $\{GeO[N(SiMe_3)_2]_2\}_n$ in the reaction of the germylene $Ge[N(SiMe_3)_2]_2$ with $HC(N_2)COOEt$. In the present example, the oxide was obtained in yields of 40%, and this preparation of the oxide is, at present, the best available. The diol $Ge(OH)_2[N(SiMe_3)_2]_2$ is highly resistant to dehydration, and it is clear that under the reaction conditions employed in the addition of water to $[(Me_3Si)_2N]_2GeNNC(COOMe)_2$ no dehydration of the diol could occur: the oxide must be formed by a route other than dehydration of $Ge(OH)_2[N(SiMe_3)_2]_2$, equation (1).

Attempted Dehydration of $Ge(OH)_2[N(SiMe_3)_2]_2$.—In refluxing hydrocarbon solvents, the diol $Ge(OH)_2[N(SiMe_3)_2]_2$ can be dehydrated only under very forcing conditions. In refluxing mesitylene (b.p. 165 °C), dehydration occurs in the presence of 4 Å molecular sieves, but this reaction does not proceed cleanly, yielding a single product: at least four kinds of $SiMe_3$ groups are present in the solid material isolated after extensive chromatography.

The related diol $Ge(OH)_2(CMe_3)_2$ is fairly readily dehydrated[21] in a clean reaction to yield the cyclic trimeric oxide $[GeO(CMe_3)_2]_3$. The steric crowding around germanium is similar in $Ge(OH)_2[N(SiMe_3)_2]_2$, where N–Ge–N is 121.9°,[20] and in $Ge(OH)_2(CMe_3)_2$, where C–Ge–C is 122.5°.[21] The difficulty in effecting clean dehydration of $Ge(OH)_2[N(SiMe_3)_2]_2$ is therefore presumably a consequence of sterically unfavourable interactions between $N(SiMe_3)_2$ groups bound to different germanium atoms. The $N(SiMe_3)_2$ group is clearly more highly branched than CMe_3 and fills more space.

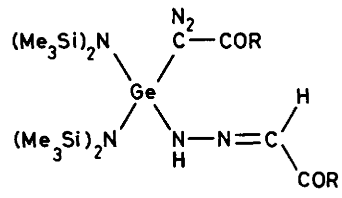
Reaction of $Ge[N(SiMe_3)_2]_2$ *with Tosyl Azide*.—The reactions of $Ge[N(SiMe_3)_2]_2$ with a wide range of diazo-compounds all yielded[1] products in which the nitrogen atoms were all retained, in contrast to the reactions of the simpler germylenes $GePh_2$ and GeF_2[18] where molecular nitrogen was lost. Since diazo-compounds with electron-withdrawing groups react with $Ge[N(SiMe_3)_2]_2$ to yield species containing the $>Ge{=}N{-}N{=}C<$ fragment, the corresponding reaction with tosyl azide was studied to see if the analogous $>Ge{=}N{-}N{=}N{-}SO_2C_6H_4Me\text{-}p$ might be stable. In the event, molecular nitrogen was lost from the reaction of $Ge[N(SiMe_3)_2]_2$ and $N_3SO_2C_6H_4Me\text{-}p$ in benzene, and the product in the absence of trapping agents was

Table 4. Bond distances (Å)

Ge–N(1)	1.864(5)	O(10)–C(11)	1.451(5)	C(20)–C(21)	1.371(7)	Si(30)–C(33)	1.863(6)
N(1)–N(2)	1.327(5)	O(9) ··· H(1)	2.11	C(21)–C(22)	1.372(6)	Si(40)–C(41)	1.865(6)
N(1)–H(1)	0.79(3)	Ge–C(12)	1.935(5)	C(22)–C(17)	1.384(6)	Si(40)–C(42)	1.865(6)
N(2)–C(3)	1.305(6)	C(12)–N(13)	1.313(5)	Ge–N(3)	1.821(5)	Si(40)–C(43)	1.872(7)
C(3)–C(4)	1.472(6)	N(13)–N(14)	1.131(6)	Ge–N(4)	1.829(5)	Si(50)–C(51)	1.876(7)
C(4)–O(5)	1.187(6)	C(12)–C(15)	1.449(6)	N(3)–Si(30)	1.764(5)	Si(50)–C(52)	1.865(6)
C(4)–O(6)	1.324(5)	C(15)–O(16)	1.225(5)	N(3)–Si(40)	1.779(5)	Si(50)–C(53)	1.848(6)
O(6)–C(7)	1.449(6)	C(15)–C(17)	1.488(5)	N(4)–Si(50)	1.774(4)	Si(60)–C(61)	1.865(7)
C(3)–C(8)	1.475(5)	C(17)–C(18)	1.389(6)	N(4)–Si(60)	1.750(5)	Si(60)–C(62)	1.858(7)
C(8)–O(9)	1.203(6)	C(18)–C(19)	1.376(6)	Si(30)–C(31)	1.877(7)	Si(60)–C(63)	1.855(8)
C(8)–O(10)	1.305(6)	C(19)–C(20)	1.367(7)	Si(30)–C(32)	1.848(7)		

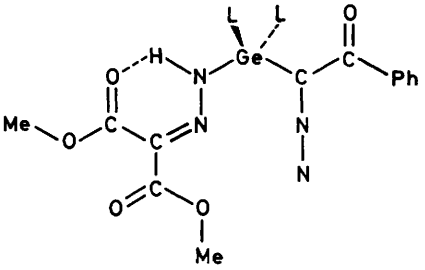
Table 5. Bond angles (°)

N(1)–Ge–C(12)	102.9(2)	C(3)–C(8)–O(9)	123.3(4)	C(20)–C(21)–C(22)	120.8(5)	C(42)–Si(40)–C(43)	105.6(3)
N(1)–Ge–N(3)	104.4(2)	C(3)–C(8)–O(10)	114.4(4)	C(21)–C(22)–C(17)	120.2(5)	C(43)–Si(40)–C(41)	105.8(3)
N(1)–Ge–N(4)	105.3(2)	O(9)–C(8)–O(10)	122.0(4)	N(1)–H(1) ··· O(9)	135(3)	Ge–N(4)–Si(50)	120.1(2)
C(12)–Ge–N(3)	110.1(2)	C(8)–O(10)–C(11)	117.5(4)	H(1) ··· O(9)–C(8)	92.8(3)	Ge–N(4)–Si(60)	118.4(2)
C(12)–Ge–N(4)	113.0(2)	Ge–C(12)–N(13)	121.4(3)	Ge–N(3)–Si(30)	123.2(2)	Si(50)–N(4)–Si(60)	118.3(3)
N(3)–Ge–N(4)	119.2(2)	Ge–C(12)–C(15)	122.1(3)	Ge–N(3)–Si(40)	117.4(3)	N(4)–Si(50)–C(51)	112.1(3)
Ge–N(1)–N(2)	117.3(3)	N(13)–C(12)–C(15)	116.5(4)	Si(30)–N(3)–Si(40)	119.2(2)	N(4)–Si(50)–C(52)	110.9(3)
Ge–N(1)–H(1)	125(3)	C(12)–N(13)–N(14)	178.8(4)	N(3)–Si(30)–C(31)	112.7(3)	N(4)–Si(50)–C(53)	113.2(3)
H(1)–N(1)–N(2)	117(3)	C(12)–C(15)–O(16)	118.2(4)	N(3)–Si(30)–C(32)	113.1(3)	C(51)–Si(50)–C(52)	106.2.3)
N(1)–N(2)–C(3)	122.3(3)	C(12)–C(15)–C(17)	121.2(4)	N(3)–Si(30)–C(33)	110.2(3)	C(52)–Si(50)–C(53)	110.0(3)
N(2)–C(3)–C(4)	117.1(4)	O(16)–C(15)–C(17)	120.7(4)	C(31)–Si(30)–C(32)	105.3(3)	C(53)–Si(50)–C(51)	104.0(3)
N(2)–C(3)–C(8)	122.5(4)	C(15)–C(17)–C(18)	122.0(4)	C(32)–Si(30)–C(33)	106.4(3)	N(4)–Si(60)–C(61)	112.5(3)
C(4)–C(3)–C(8)	120.4(4)	C(15)–C(17)–C(22)	119.0(4)	C(33)–Si(30)–C(31)	108.8(3)	N(4)–Si(60)–C(62)	113.3(3)
C(3)–C(4)–O(5)	123.6(4)	C(18)–C(17)–C(22)	118.9(4)	N(3)–Si(40)–C(41)	111.8(3)	N(4)–Si(60)–C(63)	110.4(3)
C(3)–C(4)–O(6)	113.0(4)	C(17)–C(18)–C(19)	119.8(5)	N(3)–Si(40)–C(42)	111.8(3)	C(61)–Si(60)–C(62)	104.1(3)
O(5)–C(4)–O(6)	123.4(5)	C(18)–C(19)–C(20)	121.0(5)	N(3)–Si(40)–C(43)	111.9(3)	C(62)–Si(60)–C(63)	110.0(4)
C(4)–O(6)–C(7)	116.8(5)	C(19)–C(20)–C(21)	119.2(5)	C(41)–Si(40)–C(42)	109.6(3)	C(63)–Si(60)–C(61)	106.3(3)



(13) R = Ph

(14) R = OEt



(VIII)

the polygermazane $\{[(Me_3Si)_2N]_2GeNSO_2C_6H_4Me\text{-}p\}_n$ (**11**), which was insoluble both in aqueous media and in all common organic solvents. The same polymer was obtained using thf as solvent. The transient germimide $F_2Ge{=}NPh$, from GeF_2 and phenyl azide,[17] was trapped by thf to yield the perhydro-1,3,2-oxazagermepane (**12**), as well as $(F_2GeNPh)_n$, but no evidence for such thf trapping of a monomeric germimide intermediate was obtained in the present example.

The polygermazane (**11**), which has a backbone of alternating germanium and nitrogen atoms, is wholly resistant to refluxing in 50% aqueous alkali, but is readily hydrolysed by concentrated hydrochloric acid giving a near quantitative yield of $NH_2SO_2C_6H_4Me\text{-}p$.

Crystal Structure of $[(Me_3Si)_2N]_2Ge[NHN{=}C(COOMe)_2][C(N_2)COPh]$ (**6**).—The structure consists of isolated molecules whose constitution confirms entirely the deductions made earlier[1] from spectral data, and provides definitive structural proof of the 1,2 addition of a weak acid, here $HC(N_2)COPh$, across the unique GeN bond in $[(Me_3Si)_2N]_2GeNNC(COOMe)_2$.

In this molecule, the $Ge[N(SiMe_3)_2]_2$ group shows the same features that are found in both (**2a**)[2] and $Ge(OH)_2[N(SiMe_3)_2]_2$,[20] namely GeN bonds much shorter than in free $Ge[N(SiMe_3)_2]_2$,[22] and much larger N–Ge–N angles. As the angle N(3)–Ge–N(4) (119.2°) is much bigger than the tetrahedral value, so the corresponding angle N(1)–Ge–C(12) (102.9°) is much smaller. The other bond distances and angles are unexceptional.

The first feature of interest in the structure is the free diazo-group, C(12)–N(13)–N(14). The presence of similar free diazo-groups has been established[1] spectroscopically in the 2:1 adducts (**13**) and (**14**) formed by $Ge[N(SiMe_3)_2]_2$ with $HC(N_2)COPh$ and $HC(N_2)COOEt$ respectively. Each of (**6**), (**13**), and (**14**) shows, in its i.r. spectrum, $\nu(N_2)$ in the range 2 078—2 090 cm^{-1}; $\delta(^{13}C)$ values for the $-C(N_2)-$ carbon atom are 62.3, 62.8, and 53.4 respectively, indicative in each case of the formulation $>\overset{-}{C}-\overset{+}{N}\equiv N$ for the diazo-function, just as for free $HC(N_2)COPh$ and $HC(N_2)COOEt$. However, neither of **(13)** and **(14)** reacts[1] with the free germylene $Ge[N(SiMe_3)_2]_2$; the steric and electronic environment of their diazo-groups in solution must be similar to that in **(6)**. Inspection of the van der Waals' surface of **(6)**, generated by molecular graphics techniques, shows that the diazo-group in the compound is not in any way sterically hindered.

Second, there is a fairly weak hydrogen bond between N(1)–H(1) and O(9). The H(1) ··· O(9) distance is 2.11 Å, well below the sum of the van der Waals' radii[23] for hydrogen and oxygen, and within Hamilton's criterion[24] for hydrogen bonding. This hydrogen bond results in formation of a six-membered ring, comprising H(1), N(1), N(2), C(3), C(8), and O(9): the ring is almost planar, with the internal angle sum of 712.9°; only C(8) is significantly displaced [by 0.17(14) Å] from the mean plane of the ring. The torsion angle N(13)–C(12)–C(15)–O(16) is 168.6(6)°, so that the conformation of the molecule can be represented by **(VIII)** [$L = N(SiMe_3)_2$].

The *X*-ray structure analysis reported here has confirmed the structure of **(6)** deduced from the spectroscopic data.[1] The spectra show that **(6)**—**(10)** clearly form a family of like compounds, and hence we conclude that the combination of spectral data with the *X*-ray data for **(6)** adequately establishes the structures of **(7)**—**(10)** also.

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