Crystal Structure † and Variable-temperature Hydrogen-1 Nuclear Magnetic Resonance Spectrum of (Dimethylnitratosilyl)[methyldiphenylsilyl]bis(trimethylsilyl)methane, $C(SiMe_3)_2(SiMePh_2)(SiMe_2ONO_2)$

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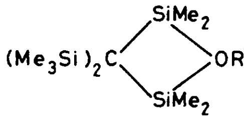
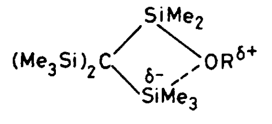
The crystal structure of the title compound has been determined. The silicon-bonded oxygen atom of the nitrate group is adjacent to the silicon atom of the $SiMePh_2$ group, but this does not seem to be the result of significant interaction between these atoms. The structure has no symmetry, so that the nine methyl groups are all non-equivalent, as are the two phenyl groups. In keeping with this, the ^1H n.m.r. resonances from the $SiMe_3$ and $SiMe_2$ protons, which show two singlets at room temperature appear as eight singlets at −90 °C (with no change in the signal from the Si*Me*Ph_2 group), and at the same time the two multiplets from the phenyl protons are replaced by two pairs of similar multiplets.

Unexpectedly high reactivities at Si–X bonds in highly sterically hindered species of the type $C(SiMe_3)_2(SiMe_2OR)(SiMe_2X)$ (*e.g.* R = Me, X = Cl;[1] R = Me, X = Me;[2,3] R = COMe, X = OCOMe[1,4]) have been explained in terms of anchimeric assistance by the OR group to the leaving of the X group, with formation of a bridged cation of type (1). Models reveal that in $C(SiMe_3)_3(SiMe_2OR)$ and related species the oxygen atom tends to be forced close to one of the silicon atoms to which it is not attached, and suggest that there could be some relief of compression between the other groups if a lone pair of the oxygen interacted with the *d* orbitals on silicon, as in (2). To seek evidence for such an interaction we carried out a single-crystal *X*-ray diffraction study on the nitrate $C(SiMe_3)_2(SiMePh_2)(SiMe_2ONO_2)$ (3). The results of the study, and of an investigation of the ^1H n.m.r. spectrum of (3) which it prompted, are described below.


(1)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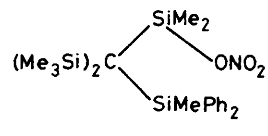
(3)

Results and Discussion

Structure of (3).—The structure of (3) is shown in Figure 1, and bond lengths and angles are listed in Table 1. At first sight the Figure appears to confirm the existence of an interaction of the type sought, the silicon-bound oxygen atom of the nitrate, O(1), lying towards the silicon atom, Si(4), of the $SiMePh_2$ group, but the O(1), Si(1), C(22), and Si(4) atoms are further from coplanarity than they appear, the O(1)–Si(1)–C(22)–Si(4) torsion angle being 44.5°, and the O(1)–Si(4) distance (3.20 Å) is only slightly less than the sum (3.50 Å) of the relevant van der Waals radii. [The C(8)–Si(1) and C(9)–Si(3) distances of 3.37 and 3.42 Å, respectively, are comparably less than the sum of the van der Waals radii.] Nevertheless, although there is no evidence of significant interaction between O(1) and Si(4), the nitrato group would be well placed to start to provide anchimeric assistance to the (notional) departure of the Me group of the $SiMePh_2$ ligand.

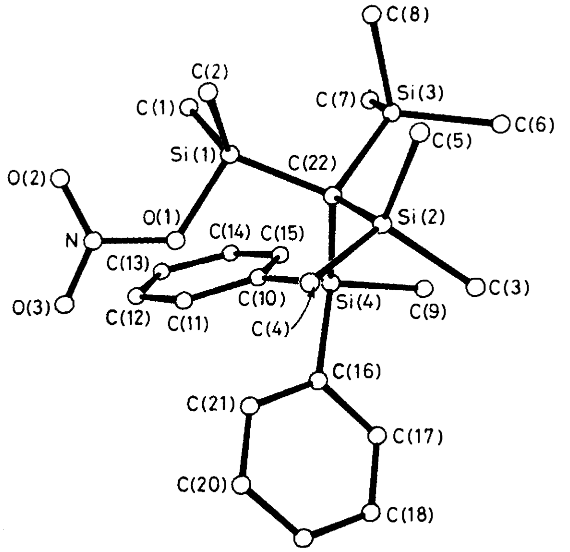

Figure 1. Crystal structure of (3), showing the atom numbering scheme

Interestingly, the C(22)–Si(1)–O(1) angle, 100.2(3)°, is significantly below the tetrahedral value, whereas the mean of all the C(22)–Si–C angles, 113.3°, is distinctively above it. Other aspects of the structure are in line with those of the related species $C(SiMe_3)_3(SiMe_2Ph)$[5] and of the less crowded $CH(SiMe_3)_3$[6] and $CH(SiMe_2Ph)_3$.[7] Thus the strain is relieved mainly by opening of the C(22)–Si–C angles (see above) and closing of the Me–Si–Me, Me–Si–Ph, and Ph–Si–Ph angles [mean of these angles around Si(2), Si(3), and Si(4): 105.2°]. There is also the usual lengthening of the bonds between silicon and the central carbon atom; thus the mean of the C(22)–Si(2), C(22)–Si(3), and C(22)–Si(4) bond lengths is 1.929 Å [though the C(22)–Si(1) bond is significantly shorter, at 1.881 Å], whereas the mean of the Si–Me bond lengths is

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† *Supplementary data available* (No. SUP 23988, 9 pp.): H-atom co-ordinates, thermal parameters, structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

Figure 2. Hydrogen-1 n.m.r. spectrum (360 MHz) of (3) at 35 °C

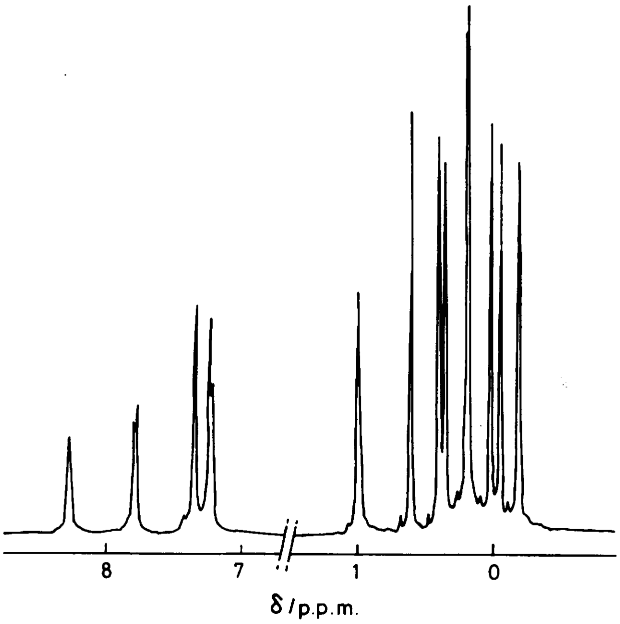

Figure 3. Hydrogen-1 n.m.r. spectrum (360 MHz) of (3) at −90 °C

1.861 Å. The distortion of the aromatic rings [notably the values of 116.6(7) and 116.2(7)° for the C(11)–C(10)–C(15) and C(17)–C(16)–C(21) angles, respectively] again parallels that in related compounds.[5,7]

Table 1. Intramolecular distances (Å) and angles (°) with estimated standard deviations in parentheses

(*a*) Distances

Si(1)–O(1)	1.728(5)	Si(1)–C(1)	1.857(8)
Si(1)–C(2)	1.847(8)	Si(1)–C(22)	1.881(7)
Si(2)–C(3)	1.856(8)	Si(2)–C(4)	1.871(8)
Si(2)–C(5)	1.863(8)	Si(2)–C(22)	1.921(7)
Si(3)–C(6)	1.864(9)	Si(3)–C(7)	1.859(9)
Si(3)–C(8)	1.866(9)	Si(3)–C(22)	1.926(7)
Si(4)–C(9)	1.868(7)	Si(4)–C(10)	1.886(8)
Si(4)–C(16)	1.896(8)	Si(4)–C(22)	1.940(7)
N–O(1)	1.380(9)	N–O(2)	1.197(9)
N–O(3)	1.187(9)	C(10)–C(11)	1.399(10)
C(10)–C(15)	1.386(10)	C(11)–C(12)	1.374(11)
C(12)–C(13)	1.386(11)	C(13)–C(14)	1.351(12)
C(14)–C(15)	1.415(12)	C(16)–C(17)	1.397(10)
C(16)–C(21)	1.386(10)	C(17)–C(18)	1.372(11)
C(18)–C(19)	1.362(12)	C(19)–C(20)	1.381(11)
C(20)–C(21)	1.390(11)		

(*b*) Angles

O(1)–Si(1)–C(1)	107.4(3)	O(1)–Si(1)–C(2)	104.2(3)
O(1)–Si(1)–C(22)	100.2(3)	C(1)–Si(1)–C(2)	109.5(4)
C(1)–Si(1)–C(22)	116.0(4)	C(2)–Si(1)–C(22)	117.9(3)
C(3)–Si(2)–C(4)	106.6(4)	C(3)–Si(2)–C(5)	104.5(4)
C(3)–Si(2)–C(22)	113.2(3)	C(4)–Si(2)–C(5)	104.8(4)
C(4)–Si(2)–C(22)	113.7(3)	C(5)–Si(2)–C(22)	113.1(3)
C(6)–Si(3)–C(7)	105.4(4)	C(6)–Si(3)–C(8)	105.2(4)
C(6)–Si(3)–C(22)	114.1(4)	C(7)–Si(3)–C(8)	103.7(4)
C(7)–Si(3)–C(22)	114.9(3)	C(8)–Si(3)–C(22)	112.5(3)
C(9)–Si(4)–C(10)	104.8(4)	C(9)–Si(4)–C(16)	104.9(4)
C(9)–Si(4)–C(22)	109.6(3)	C(10)–Si(4)–C(16)	106.7(3)
C(10)–Si(4)–C(22)	114.9(3)	C(16)–Si(4)–C(22)	115.0(3)
O(1)–N–O(2)	117(1)	O(1)–N–O(3)	113.9(9)
O(2)–N–O(3)	129(1)	Si(1)–O(1)–N	122.0(6)
Si(4)–C(10)–C(11)	123.2(7)	Si(4)–C(10)–C(15)	120.0(7)
C(11)–C(10)–C(15)	116.6(7)	C(10)–C(11)–C(12)	122.2(8)
C(11)–C(12)–C(13)	120.3(8)	C(12)–C(13)–C(14)	119.1(8)
C(13)–C(14)–C(15)	121.0(8)	C(10)–C(15)–C(14)	120.7(8)
Si(4)–C(16)–C(17)	118.7(6)	Si(4)–C(16)–C(21)	124.9(6)
C(17)–C(16)–C(21)	116.2(7)	C(16)–C(17)–C(18)	122.5(8)
C(17)–C(18)–C(19)	120.5(8)	C(18)–C(19)–C(20)	118.9(8)
C(19)–C(20)–C(21)	120.5(8)	C(16)–C(21)–C(20)	121.4(7)
Si(1)–C(22)–Si(2)	110.2(3)	Si(1)–C(22)–Si(3)	105.1(3)
Si(1)–C(22)–Si(4)	112.1(4)	Si(2)–C(22)–Si(3)	109.3(4)
Si(2)–C(22)–Si(4)	109.6(4)	Si(3)–C(22)–Si(4)	110.5(3)

Variable-temperature Hydrogen-1 *N.M.R. Spectrum of* (3).—The structure shown in Figure 1 has no symmetry, and so all the Me groups are non-equivalent, as are the two phenyl groups, and thus it was of interest to study the ^{1}H n.m.r. spectrum. At 35 °C the spectrum (360 MHz) of a solution in CD_2Cl_2 is as expected for free rotation, showing three singlets in the SiMe region, at δ 0.29 ($SiMe_3$), 0.38 ($SiMe_2ONO_2$), and 1.05 ($SiMePh_2$) (see Figure 2). As the temperature is lowered the position of the Si*Me*Ph_2 signal remains unchanged, but even at −10 °C the peaks at 0.29 and 0.38 have coalesced (spectrum not shown) and a progressive broadening then break-up of the band is followed finally by its resolution at −90 °C into eight distinct peaks, effectively of equal intensity, showing that all eight methyl groups are non-equivalent at that temperature. Analysis of the spectrum shown in Figure 3 suggests that the peaks at δ 0.36 and 0.40_5 come from the $SiMe_2$ protons and those at −0.19, -0.05_5, 0.02, 0.18_5, 0.19_5, and 0.62 from the $SiMe_3$ protons. In the aryl region the two sets of peaks present at room temperature are replaced by four sets at −90 °C, consistent with non-equivalence of the two phenyl groups. The appearance of the spectrum indicates

Table 2. Fractional atomic co-ordinates (× 10^4) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Si(1)	5 280(3)	4 643(3)	2 414(2)	C(8)	5 557(10)	1 577(9)	2 838(6)
Si(2)	7 586(3)	3 796(3)	1 196(2)	C(9)	10 305(8)	6 265(9)	3 542(6)
Si(3)	7 249(3)	3 227(3)	3 135(2)	C(10)	8 058(8)	7 720(8)	4 011(6)
Si(4)	8 645(2)	6 495(2)	3 019(2)	C(11)	7 265(9)	8 630(9)	3 886(6)
N	4 411(8)	6 805(8)	2 033(5)	C(12)	6 858(9)	9 522(9)	4 619(6)
O(1)	5 514(5)	6 207(5)	2 066(4)	C(13)	7 279(10)	9 588(9)	5 522(6)
O(2)	3 234(6)	6 127(8)	2 177(5)	C(14)	8 108(11)	8 778(10)	5 670(6)
O(3)	4 765(7)	7 918(7)	1 825(6)	C(15)	8 504(10)	7 831(10)	4 919(6)
C(1)	4 574(9)	4 963(10)	3 551(6)	C(16)	9 343(8)	7 627(8)	2 202(5)
C(2)	3 851(9)	3 177(10)	1 524(7)	C(17)	10 835(8)	8 057(9)	2 123(6)
C(3)	9 555(8)	4 077(9)	1 117(6)	C(18)	11 447(9)	8 961(10)	1 599(6)
C(4)	6 951(10)	4 599(9)	337(6)	C(19)	10 603(10)	9 486(9)	1 132(6)
C(5)	6 672(9)	1 765(9)	707(6)	C(20)	9 124(9)	9 102(9)	1 200(6)
C(6)	8 785(10)	2 469(10)	2 949(7)	C(21)	8 504(8)	8 181(8)	1 728(6)
C(7)	7 381(10)	4 009(10)	4 413(6)	C(22)	7 197(8)	4 571(8)	2 435(5)

that only one conformation is present in significant amount (>5%) at −90 °C, and it is reasonable to assume that this conformation is the same as that in the crystal. The fact that the position of the signal from the Si*Me*Ph$_2$ protons does not vary significantly with the temperature suggests that this conformation is exclusively or very predominantly present even at room temperature, but with sufficient rotation about Si–C bonds to allow chemically equivalent Me groups to become equivalent on the n.m.r. time-scale.

Experimental

The preparation of compound (3) has been described previously.[8]

The ^{1}H n.m.r. spectra of solutions in CD_2Cl_2 were recorded at 360 MHz on a Bruker WM360 spectrometer.

Structure Determination.—Crystal data. $C_{22}H_{37}NO_3Si_4$, $M = 475.9$, triclinic, $a = 9.693(4)$, $b = 9.962(2)$, $c = 15.094(4)$ Å, $\alpha = 105.64(2)$, $\beta = 92.24(3)$, $\gamma = 107.86(2)°$, $U = 1\,324.1$ Å^3, $Z = 2$, $D_c = 1.19$ g cm^{-3}, $F(000) = 512$, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, $\mu = 2.5$ cm^{-1}, space group $P\bar{1}$ from the successful structure refinement.

Data were measured on an Enraf-Nonius CAD4 diffractometer with a crystal of dimensions *ca.* 0.3 × 0.3 × 0.2 mm. Preliminary cell dimensions were derived by using the SEARCH and INDEX routines of the CAD4 and final values calculated from the setting angles for 16 reflections with $\theta \approx 12°$. Intensities for $h \pm k \pm l$ reflections with $2 < \theta < 20°$ were measured by a θ—2θ scan with a scan width $\Delta\theta = (1.2 + 0.35\tan\theta)°$ and monochromated Mo-K_α radiation. The scan rate for each reflection was estimated from a rapid pre-scan at 10° min^{-1} in θ when any reflection with $I < \sigma(I)$ was coded as unobserved. Otherwise it was rescanned at such a speed as to give $\sigma(I)/I$ of 0.05 subject to a maximum scan time of 120 s. Two standard reflections monitored every hour showed no significant variation. After correction for Lorentz-polarisation (Lp) effects but not for absorption, any equivalent data were averaged, and 1 287 reflections with $|F^2| > \sigma(F^2)$ were used in the structure refinement. The values of $\sigma(F^2)$ were calculated as $[\sigma^2(I) + (0.04I)^2]^{\frac{1}{2}}/\mathrm{Lp}$.

The structure was solved by direct methods using the MULTAN[9] program. Refinement of non-hydrogen atoms with anisotropic thermal parameters was by full-matrix least squares. Hydrogen atoms were placed at calculated positions (C–H 1.08 Å) and held fixed with a common isotropic thermal parameter of $B = 5.0$ Å^2. Continued refinement converged at $R = 0.055$, $R' = 0.058$, where the maximum shift/error was <0.01 and the weighting scheme was $w = 1/\sigma^2(F)$. A final difference map was everywhere < 0.25 e Å^{-3}.

The structure solution and refinement were carried out on a PDP11/34 computer using the Enraf-Nonius Structure Determination Package. Scattering factors for neutral atoms were from ref. 10. Non-hydrogen atomic co-ordinates are listed in Table 2.

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