THE CRYSTAL STRUCTURE OF DIMETHYLVINYLSILOXYGERMATRANE

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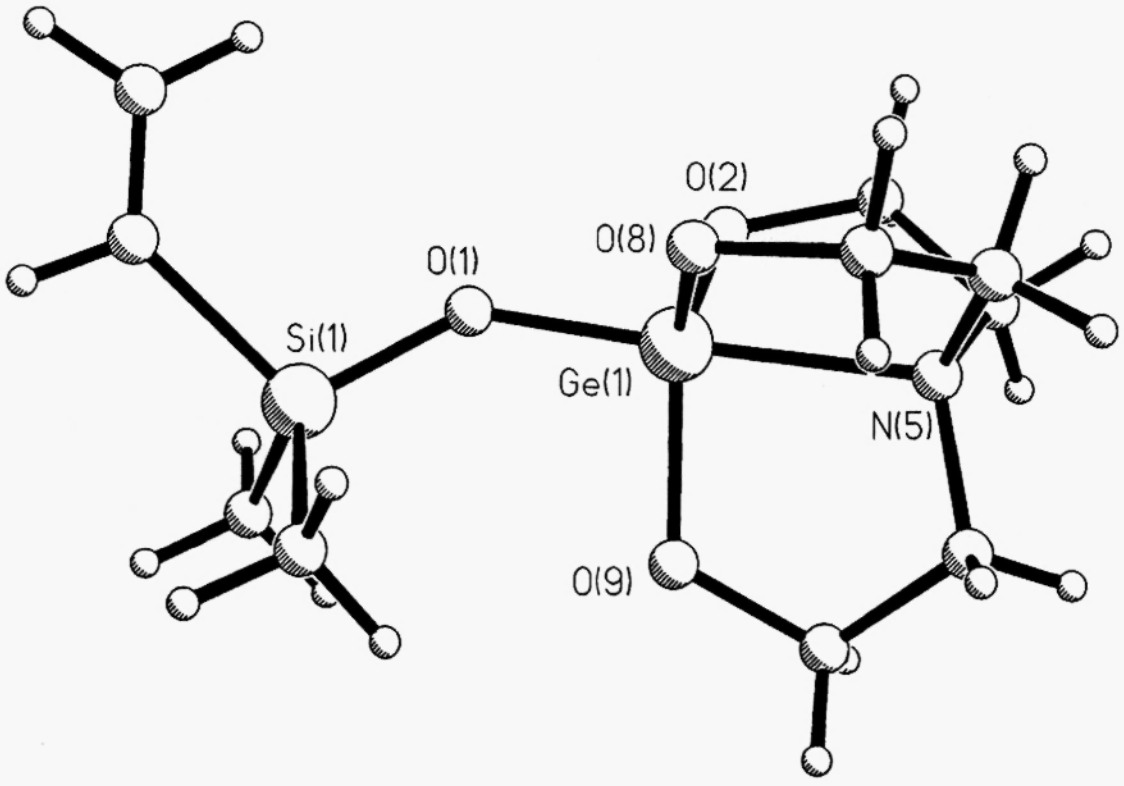

Figure 1. Molecular structure of dimethylvinylsiloxygermatrane

Comment

Over past two decades, germatranes have attracted considerable attention due to their five-coordinated structure. The intramolecular N→Ge bond length in germatranes (2.01 – 2.29 Å) depends on the electronic effects of the substituents bound to the germanium atom [1 – 6]. Previously for the structural analogues of the title compound it was demonstrated that the intramolecular N→Ge bond length of various thienylsiloxygermatranes changes from 2.105(4) Å to 2.156(6) Å [7].

Vinyldimethylethoxysilane reacts with anhydrous hydroxygermatrane in the presence of catalytic amount of sodium hydroxide to give the title compound in 82% yield. Its X-ray crystal structure (Figure 1) reveals that germanium atom is five-coordinated and adopts trigonal bipiramidal geometry as in other known germatranes. Three oxygen atoms are positioned in the equatorial fashion [O(8)-Ge(1)-O(9) 118.7(3)°, O(8)-Ge(1)-O(2) 119.2(3)°, O(9)-Ge(1)-O(2) 119.2(3)°]. The siloxy group and the nitrogen atom occupy apical positions [N(5)-Ge(1)-O(1) 176.9(3)°] with N→Ge transannular bond of 2.132(7) Å. The Si(1)-O(1)-Ge(1) angle equals 136.5(4)°. This value is slightly increased as compared with trimethylsiloxygermatrane [133.0 (4)°] and lies between 134.8(3)° for (2-thienyl)dimethylsiloxygermatrane and 139.6(3)° for di(2-thienyl)methylsiloxygermatrane, being considerably different from 180.° [tri(2-thienyl)siloxygermatrane] [7].

Experimental

The mixture of vinyldimethylethoxysilane (0.02 mol) and hydroxygermatrane (0.02 mol) in dry xylene (40 ml) was refluxed for 5 hours. After cooling to room temperature the title product was filtered off as white solid (Yield 82%). Single crystals were grown from ethanol by slow evaporation of the solvent, mp 144 °C.

^{1}H NMR ($CDCl_3$) _: 0.17 (6H, s, Me_2Si); 2.89 (6H, t, J=6.1 Hz, CH_2N); 3.86 (6H, t, J=6.1 Hz, CH_2O); 5.64-6.36 (3H, m, $CH=CH_2$).

^{29}Si NMR ($CDCl_3$) _: 16.8 (Me_2Si).

Table 1. Crystal data and structure refinement for dimethylvinylsiloxygermatrane

Empirical formula	$C_{10}H_{21}GeNO_4Si$	Index ranges	$0 \le h \le 7$, $0 \le k \le 16$, $-15 \le l \le 15$
Formula weight	319.96		
Temperature	293(2) K		
Diffractometer	Syntex $P2_1$	Independent reflections	1905
Wavelength	0.71069 Å	Observed reflections, I>2_(I)	1491
Crystal system	monoclinic	Refinement method	Full-matrix least-squares on F^2
Space group	$P2_1/c$		
Unit cell dimensions	a = 6.726(2) Å b = 15.276(5) Å c = 14.144(2) Å β = 95.83(2)°	Restraints / parameters	0 / 155
		Goodness-of-fit on F^2	1.063
		Final R factors [I>_(I)]	R = 0.073 [I>2_(I)], R = 0.087 (for all data)
		Weighting R on F^2	wR2 = 0.209
Volume	1445.7(6) Å^3	Weighting scheme	$1/w = \sigma^2(F^2) + (0.1555P)^2 + 0.49P$, where $P = (F_o^2 + 2F_c^2)/3$
Z	4		
Density (calculated)	1.470 g/cm^3		
Absorption coefficient	2.204 mm^{-1}	Extinction coefficient	0.024(5)
F(000)	664	Largest diff. peak and hole	1.09 and –0.91 e Å^{-3}
Crystal size	0.50 x 0.50 x 0.75 mm	Programs used	AREN [8], SHELXL-93 [9] PLUTO [10]
2θ range for data	0 to 45°		
		Deposition number	CCDC 155997

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Received: March 6,2001 – Accepted: March 9,2001
Accepted in publishable format: March 12,2001