CRYSTAL STRUCTURE OF THE STABLE SILYLENE, N, N'-DI-TERT-BUTYL-1,3-DIAZA-2-SILACYCLOPENT-4-EN-2-YLIDENE

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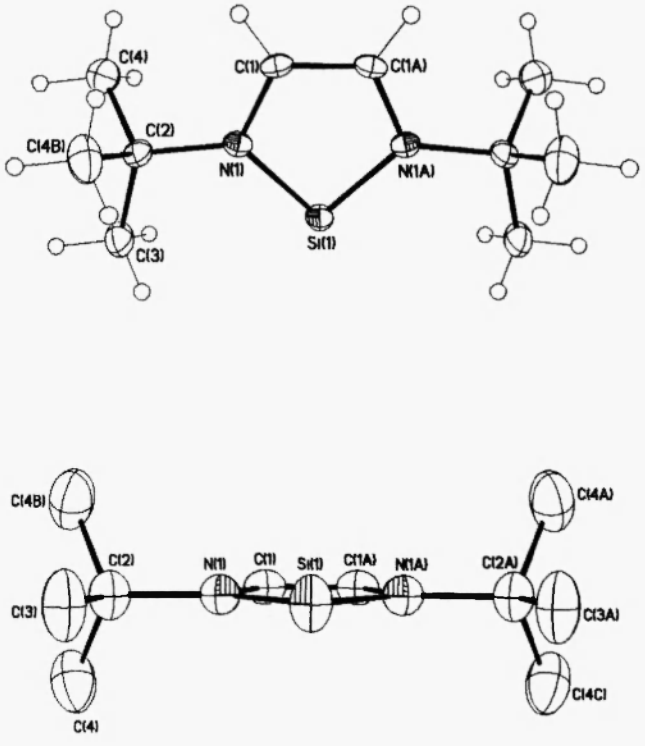

Figure 1. Molecular Structure of $C_{10}H_{20}N_2Si$ (shown in two views). Displacement ellipsoids are plotted at the 50% probability level. Selected bond distances and angles: Si-N(1) 1.747(4), N(1)-C(1) 1.388(5), N(1)-C(2) 1.459(3), C(1)-C(1A), 1.320(8) Å; N(1)-Si-N(1A) 88.1(2), C(1)-N(1)-Si 112.4(3), C(1A)-C(1)-N(1) 113.6(2)°.

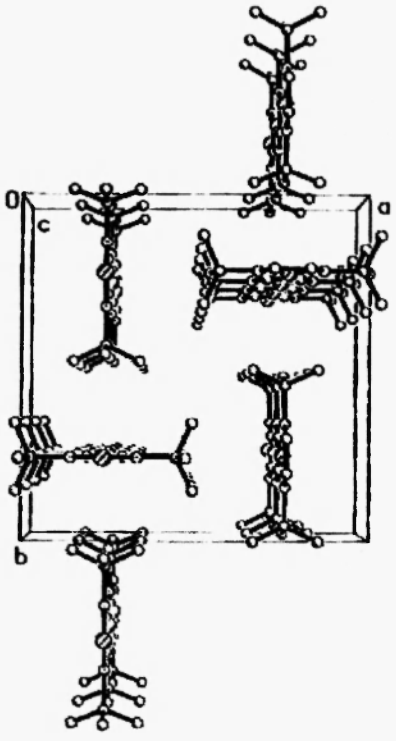

Figure 2. Packing diagram for $C_{10}H_{20}N_2Si$.

Comment

The title compound was isolated in 1994 as the first known room temperature divalent, dicoordinate silicon species [1]. Extensive studies of this silylene indicate that it is stabilized both by electron donation from nitrogen to silicon and by aromatic delocalization in its six π-electron ring [2,3]. In 1994, in spite of several attempts, a single crystal X-ray structure could not be obtained for the silylene. Its structure was instead established by gas phase electron diffraction [1]. The crystal structure for the prototypical silylene (Figure 1) has at last been determined and is

reported here. The compound, isolated from a saturated hexane solution at -20 °C, crystallized with two symmetry independent molecules in the unit cell with each molecule residing on two perpendicular crystallographic mirror planes. Each molecule contains a two-fold axis coinciding with the intersection line of the two mirror planes. The crystal structure is isotypic with its germanium analog [4] and is planar, as can be seen in Figure 1. The packing diagram (Figure 2) shows the perfect alignment of the molecules in columns, stacked head to tail. There is no indication of intermolecular association by hydrogen bonding, such as found for the isostructural carbene [5].

Experimental

The compound was synthesized with some modifications to a previous procedure [1]. To 10.2 g (38.2 mmol) of the dichloro precursor in 200 mL of THF was added 3.44 g (87.9 mmol) of potassium metal. The solution was heated to reflux and monitored by ^{1}H NMR. After 4 h, the reaction was cooled and filtered. The solvent was removed *in vacuo* and the resulting solid was sublimed (0.1 torr, 90 °C) to yield 6.01g (80%) of silylene.

Crystallography:

Table 1. Crystal data for $C_{10}H_{20}N_2Si$

Formula	$C_{10}H_{20}N_2Si$	Formula weight	196.37
Crystal system	Orthorhombic	Crystal size, mm	0.50 × 0.20 × 0.20
Space group	Pmmn	*a*, Å	13.7994(11)
b, Å	13.8201(11)	*c*, Å	6.3814(5)
V, Å^3	1216.99(17)	*Z*	4
Diffractometer	Bruker CCD-1000	Temperature, K	173(2)
μ(Mo-Kα), mm^{-1}	0.157	D_{calcd}, g cm^{-3}	1.07
F(000)	432	θ max, °	26.34
Reflns. Meas.	9163	Reflns unique, R_{int}	1345, 0.069
Reflns with $I \geq 2\sigma(I)$	1345	$R(F^2)$, $R_w(F^2)$ (all data)	0.079, 0.120
ρ, e Å^{-3}	0.31	Programs used	SHELXTL v. 5.1 [6]
Weighting Scheme:	$R(wF^2) = \Sigma[w(F_o^2-F_c^2)]/\Sigma[(wF_o^2)^2]^{1/2}$; $R = \Sigma\Delta/\Sigma(F_o)$, $\Delta = \lvert(F_o-F_c)\rvert$		
Absorption Correction	Empirical by SADABS [7]		
Deposition number	CCDC 169218		

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Received: August 28, 2001 - Accepted: September 21, 2001 – Accepted in publishable format: September 25, 2001