

The Crystal Structure of 2-Trimethylsilyl-1,3,5 λ^4 ,2,4,6-trithiatriazine 1,1-Dioxide

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Abstract

C₃H₉N₃O₂S₃Si, monoclinic, $P2_1/n$, $Z = 8$, $a = 14.349$ (7), $b = 6.327$ (2), $c = 22.516$ (9) Å, $\beta = 98.34$ (3)°, $V = 2023$ (1) Å³, $D_c = 1.599$ Mg m⁻³; single-crystal diffractometer data were used up to $\sin \theta/\lambda = 0.60$ Å⁻¹. Final $R = 0.048$. The S₃N₃ ring has an envelope conformation with the Si-coordinated N atom lying 0.82 Å out of the plane of the ring. The S–N lengths range from 1.539 (3) to 1.689 (2) Å.

Introduction

The title compound was prepared as described by Roesky, Witt, Diehl, Bats & Fuess (1979). An orange coloured needle 0.90 × 0.16 × 0.15 mm was sealed in a glass capillary as the compound is unstable in air.

Data were collected in two quadrants of reciprocal space, up to $\sin \theta/\lambda = 0.60$ Å⁻¹, on a Syntex $P2_1$ diffractometer with Nb-filtered Mo $K\alpha$ radiation. 6905 reflections were obtained of which 3583 were unique.

Background corrections were made by profile analysis (Blessing, Coppens & Becker, 1974). Three standard reflections observed after every 45 reflections showed no significant fluctuations. The data were corrected for absorption ($\mu = 0.792$ mm⁻¹); the transmission factor ranged from 0.858 to 0.905. A weight was assigned to each observation according to $w(I) = [\sigma^2(I)_{\text{counting}} + (0.03I)^2]^{-1}$. After equivalent reflections were weighted-averaged, 3283 reflections had $I > 0$ and were used for the structure refinement.

The structure was determined with *MULTAN* (Main, Woolfson, Lessinger, Germain & Declercq, 1974). The first E map showed all non-hydrogen atoms of both independent formula units. Difference syntheses after refinement with anisotropic thermal parameters yielded the positional parameters of the H atoms. They were included in the refinement with $B = 4.4$ Å².

Scattering factors were from *International Tables for X-ray Crystallography* (1974), except those for H which were from Stewart, Davidson & Simpson (1965). Anomalous-dispersion factors (Cromer & Liberman, 1970) were applied to Si and S. Extinction was found to

be negligible. The refinement resulted in $R(F) = 0.048$, $R_w(F) = 0.039$ and $S = [\sum w(|F_o| - |F_c|)^2 / (\text{NO} - \text{NV})]^{1/2} = 1.23$.

The calculations were carried out with XRAY 72 (Stewart, Kruger, Ammon, Dickinson & Hall, 1972)

Table 1. Fractional atomic coordinates

	<i>x</i>	<i>y</i>	<i>z</i>
Si(1)	0.43740 (5)	0.1052 (1)	0.11686 (3)
Si(2)	0.68786 (5)	0.0170 (1)	0.36503 (3)
S(1)	0.27174 (5)	-0.1686 (1)	0.06332 (3)
S(2)	0.23608 (5)	0.1185 (1)	0.15031 (3)
S(3)	0.24125 (6)	-0.3178 (1)	0.17570 (4)
S(4)	0.51789 (5)	-0.2433 (1)	0.31196 (3)
S(5)	0.49028 (5)	0.0392 (1)	0.40239 (3)
S(6)	0.49894 (5)	-0.3967 (1)	0.42649 (3)
N(1)	0.3132 (1)	0.0340 (4)	0.1055 (1)
N(2)	0.2234 (2)	-0.0875 (4)	0.1940 (1)
N(3)	0.2680 (2)	-0.3595 (4)	0.1117 (1)
N(4)	0.5622 (1)	-0.0424 (3)	0.3540 (1)
N(5)	0.4838 (2)	-0.1684 (4)	0.4467 (1)
N(6)	0.5159 (2)	-0.4357 (4)	0.3605 (1)
O(1)	0.1779 (1)	-0.1267 (4)	0.0359 (1)
O(2)	0.3407 (1)	-0.2217 (4)	0.0266 (1)
O(3)	0.5847 (1)	-0.2969 (3)	0.2739 (1)
O(4)	0.4234 (1)	-0.1970 (3)	0.2862 (1)
C(1)	0.4547 (3)	0.2655 (6)	0.1860 (2)
C(2)	0.4549 (2)	0.2549 (7)	0.0497 (2)
C(3)	0.5110 (2)	-0.1358 (6)	0.1272 (2)
C(4)	0.7090 (3)	0.1767 (7)	0.4336 (2)
C(5)	0.7082 (3)	0.1635 (7)	0.2981 (2)
C(6)	0.7563 (3)	-0.2308 (6)	0.3747 (2)
H(11)	0.416 (2)	0.381 (5)	0.186 (1)
H(12)	0.513 (2)	0.315 (5)	0.193 (1)
H(13)	0.441 (2)	0.187 (5)	0.221 (1)
H(21)	0.417 (2)	0.378 (5)	0.047 (1)
H(22)	0.511 (2)	0.283 (5)	0.049 (1)
H(23)	0.441 (2)	0.174 (5)	0.015 (1)
H(31)	0.510 (2)	-0.215 (5)	0.092 (1)
H(32)	0.574 (2)	-0.098 (5)	0.134 (1)
H(33)	0.505 (2)	-0.208 (5)	0.164 (1)
H(41)	0.679 (2)	0.309 (5)	0.435 (1)
H(42)	0.773 (2)	0.194 (5)	0.441 (1)
H(43)	0.694 (2)	0.112 (5)	0.465 (1)
H(51)	0.677 (2)	0.290 (5)	0.296 (1)
H(52)	0.768 (2)	0.192 (5)	0.298 (1)
H(53)	0.684 (2)	0.088 (5)	0.262 (1)
H(61)	0.819 (2)	-0.192 (5)	0.387 (1)
H(62)	0.760 (2)	-0.310 (5)	0.411 (1)
H(63)	0.754 (2)	-0.306 (5)	0.343 (1)

on the Univac 1108 computer of the University of Frankfurt. The positional parameters are reported in Table 1, bond lengths and angles in Table 2.* A stereoscopic view of the structure is shown in Fig. 1.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34091 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond lengths (Å) and angles (°)

Molecule 1		Molecule 2	
S(1)—O(1)	1.423 (2)	S(4)—O(4)	1.426 (2)
S(1)—O(2)	1.418 (2)	S(4)—O(3)	1.416 (2)
S(1)—N(1)	1.654 (2)	S(4)—N(4)	1.656 (2)
S(1)—N(3)	1.632 (3)	S(4)—N(6)	1.638 (2)
S(2)—N(1)	1.689 (2)	S(5)—N(4)	1.687 (2)
S(2)—N(2)	1.659 (3)	S(5)—N(5)	1.660 (3)
S(3)—N(2)	1.546 (3)	S(6)—N(5)	1.539 (3)
S(3)—N(3)	1.567 (3)	S(6)—N(6)	1.561 (3)
Si(1)—N(1)	1.820 (2)	Si(2)—N(4)	1.823 (2)
Si(1)—C(1)	1.845 (4)	Si(2)—C(4)	1.832 (4)
Si(1)—C(2)	1.832 (4)	Si(2)—C(5)	1.828 (4)
Si(1)—C(3)	1.850 (4)	Si(2)—C(6)	1.846 (4)
C—H _{average}	0.916		
O(1)—S(1)—O(2)	119.1 (1)	O(3)—S(4)—O(4)	119.3 (1)
N(1)—S(1)—O(1)	110.1 (1)	N(4)—S(4)—O(4)	109.8 (1)
N(1)—S(1)—O(2)	107.2 (1)	N(4)—S(4)—O(3)	107.0 (1)
N(3)—S(1)—O(1)	107.9 (1)	N(6)—S(4)—O(4)	108.5 (1)
N(3)—S(1)—O(2)	107.9 (1)	N(6)—S(4)—O(3)	107.7 (1)
N(1)—S(1)—N(3)	103.5 (1)	N(4)—S(4)—N(6)	103.4 (1)
N(1)—S(2)—N(2)	104.1 (1)	N(4)—S(5)—N(5)	103.8 (1)
N(2)—S(3)—N(3)	118.4 (1)	N(5)—S(6)—N(6)	118.6 (1)
S(1)—N(1)—Si(1)	122.4 (1)	S(4)—N(4)—Si(2)	121.8 (1)
S(2)—N(1)—Si(1)	123.4 (1)	S(5)—N(4)—Si(2)	122.3 (1)
S(1)—N(1)—S(2)	112.1 (1)	S(4)—N(4)—S(5)	112.6 (1)
S(2)—N(2)—S(3)	123.1 (2)	S(5)—N(5)—S(6)	122.9 (2)
S(1)—N(3)—S(3)	121.7 (2)	S(4)—N(6)—S(6)	122.5 (1)
N(1)—Si(1)—C(1)	105.3 (1)	N(4)—Si(2)—C(4)	105.6 (1)
N(1)—Si(1)—C(2)	105.1 (1)	N(4)—Si(2)—C(5)	105.4 (1)
N(1)—Si(1)—C(3)	110.1 (1)	N(4)—Si(2)—C(6)	109.8 (1)
C(1)—Si(1)—C(2)	113.3 (2)	C(4)—Si(2)—C(5)	112.8 (2)
C(1)—Si(1)—C(3)	110.0 (2)	C(4)—Si(2)—C(6)	110.4 (2)
C(2)—Si(1)—C(3)	112.7 (2)	C(5)—Si(2)—C(6)	112.4 (2)
Si—C—H _{average}	112.4		
H—C—H _{average}	106.0		

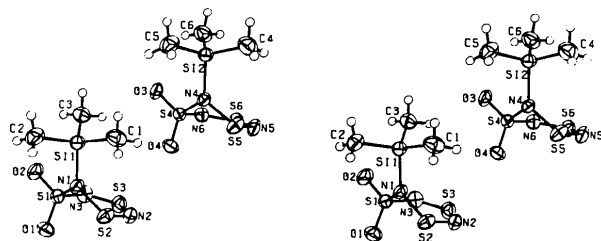


Fig. 1. Stereoscopic view of the two independent molecules. The thermal ellipsoids are the 50% probability surfaces. H atoms are drawn on an arbitrary scale.

Discussion

The two independent molecules are almost identical; corresponding bond lengths agree within 2σ . The two S_3N_3 rings have an envelope conformation with the substituted N atom 0.82 Å out of the plane formed by the other ring atoms (Table 3). The conformation and geometry of the six-membered rings are very similar to those of the corresponding Sn complex (Roesky, Witt, Diehl, Bats & Fuess, 1979). Differences are found in the S—N distances of the substituted N atom which are about 0.023 (3) Å shorter in the Sn than in the Si complex. All other distances and angles in the ring agree within 3σ .

The S—N lengths range from 1.539 (3) to 1.689 (2) Å. The longest distances involve the substituted N atom. The angles at that atom are 112.1 in one and 112.6° in the other molecule, whereas the angles at the two other N atoms are close to 120° (mean 122.6°) which is the most favourable for a planar six-membered ring. The smaller angles at S (mean 103.7°) are at the two atoms bonded to the substituted N atom. The shortest S—N distances involve the S atom with angles of 118.4 (1) and 118.6 (1)°, which are observed for several sulphur diimide structures (Gieren, Dederer, Roesky & Janssen, 1976).

The Si atoms have a slightly distorted tetrahedral configuration with an average N—Si—C angle of 106.9 and an average C—Si—C angle of 111.9°. The Si—N lengths of 1.820 (2) and 1.823 (2) Å are relatively long for a single Si—N bond. A value of 1.808 (3) Å has been reported for bis(trimethylsilyl)diimine (Veith & Bärnighausen, 1974) while values of 1.770 (4) and 1.789 (3) Å were found for tetrakis(trimethylsilyl)-tetrazene (Veith, 1975). Consequently the average Si—C length of 1.839 Å in the title compound is shorter than the 1.853, 1.883 and 1.861 Å in those compounds.

The S—O distances have a mean of 1.421 (3) Å, which is slightly shorter than the mean of 1.434 Å reported by Gieren, Hahn, Dederer, Roesky & Amin (1978) for 16 compounds with an $R-N-SO_2-X$ configuration.

The molecular packing is governed by van der Waals forces. The shortest intermolecular contacts are repor-

Table 3. Deviations (Å) from least-squares planes

Plane 1		Plane 2	
S(1)	-0.037	S(4)	-0.018
S(2)	0.036	S(5)	0.022
S(3)	-0.001	S(6)	0.008
N(2)	-0.037	N(5)	-0.027
N(3)	0.039	N(6)	0.015
N(1)*	0.819	N(4)*	0.819

* Atom not used in the definition of the plane.

Table 4. *Short intermolecular contacts* (Å)

S(2)···O(4)	3.098 (2)	S(3)···S(5)	3.640 (2)
S(6)···O(1)	3.146 (2)	S(5)···S(6)	3.610 (2)
S(2)···S(3)	3.611 (2)	S(6)···S(6)	3.555 (2)
S(2)···S(6)	3.561 (2)		

ted in Table 4. They are about 0.10–0.15 Å shorter than the sum of the van der Waals radii of the constituent atoms and thus can be considered to form weak bonds.

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Conformation Repliée à l'Etat Solide de la *N*-Pivaloyl-*D*-alanyl-*L*-proline-*N*-isopropylamide

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Abstract

Crystals of *N*-pivaloyl-*D*-alanyl-*L*-proline-*N*-isopropylamide (C₁₆H₂₉N₃O₃) grown from ethyl acetate solution crystallize in the orthorhombic system, space group *P*2₁2₁2₁, with the unit-cell constants *a* = 8.963 (1), *b* = 10.433 (1) and *c* = 19.329 (3) Å, *D*_c = 1.10 Mg m⁻³, *Z* = 4. The final reliability index *R* = 0.041. Molecules are folded by a 4 → 1 hydrogen bond stabilizing a β(II') conformation which was shown to be the most populated conformer in CCl₄ solution.

Introduction

Le mode de repliement β couramment observé dans les chaînes peptidiques des protéines (Chou & Fasman, 1977) intéresse une courte séquence de trois unités peptidiques CO–*X*–*Y*–NH dans laquelle *X* et *Y* sont deux résidus α-amino acide. Il est en outre stabilisé par une liaison hydrogène intramoléculaire intéressant les deux sites NH et CO extrêmes et qui ferme un cycle à dix atomes (Lewis, Momany & Scheraga, 1973).

Une étude statistique sur la nature des résidus amino