3. L. Pauling, The Nature of the Chemical Bond, Cornell Univ. Press, Ithaca (1960).
4. N. W. Alcook, Adv. Inorg. Chem. Radiochem., 15, 2 (1972).
5. Yu. V. Zefirov and P. M. Zorkii, Zh. Strukt. Khim., 17, 994 (1976).

CRYSTAL AND MOLECULAR STRUCTURE OF 1,3-DICHLORO-1,1,3,3-TETRAPHENYLDISILAZANE

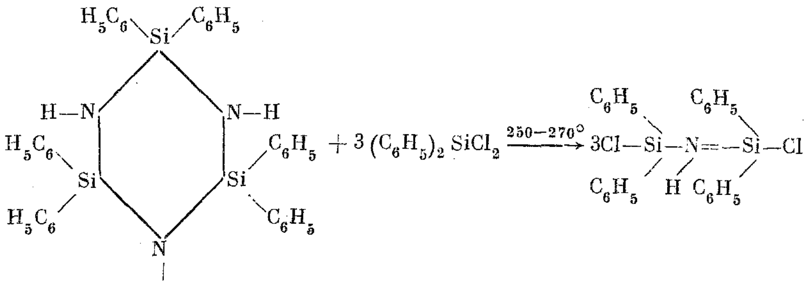
S. N. Gurkova, A. I. Gusev,
N. V. Alekseev, and Yu. M. Varezhkin

UDC 548.737

The aim of the present paper is to study the reaction of formation of 1,3-dichloro-1,1,3,3-tetraphenyldisilazane (I) and to investigate its crystal and molecular structure by x-ray structural analysis.

It is well known that the treatment of two- or threefold metallized hexamethylcyclotrisilazane with excess dimethyldichlorosilazane does not lead to the formation of a di-dimethylchlorosilanized product of the original cyclosilazane, but of 1,3-dichloro-1,1,3,3-tetramethylsilazane (II) and 1,3-bis(dimethylchlorosilyl)-2,2,4,4-tetramethylcyclodisilazane (III); the latter compound crystallizes readily and is obtained in yields of 75% or more, whereas the yield of II does not exceed 25% [1]. 2,2,4,4,6,6-Hexamethylcyclotrisilazane undergoes decomposition by dimethyldichlorosilane at 90-150°C leading to the formation of compound II in a much higher yield (70-80% [2, 3]).

Therefore it seemed interesting to effect the synthesis of compound I by an analogous reaction of telomerization of 2,2,4,4,6,6-hexaphenylcyclotrisilazane and diphenyldichlorosilane, the starting reagents being in the ratio of 1:3, respectively:



I

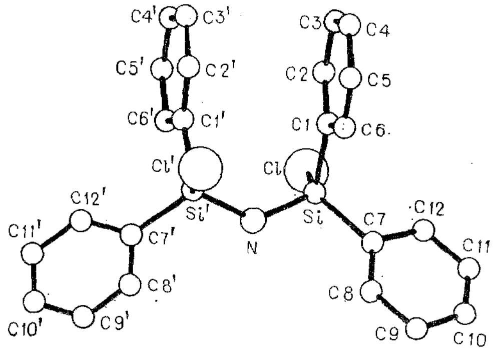


Fig. 1. Structure of the molecule of 1,3-dichloro-1,1,3,3-tetraphenyldisiloxane.

Translated from Zhurnal Strukturnoi Khimii, Vol. 25, No. 4, pp. 153-155, July-August, 1984. Original article submitted December 9, 1982.

TABLE 1. Atomic Coordinates ($\times 10^4$, for H $\times 10^3$)

Atom	x	y	z	Atom	x	y	z
Si	553(1)	1502(1)	1896(1)	C(11)	2203(2)	−104(5)	1527(5)
Cl	129(1)	1920(1)	−153(1)	C(12)	1677(2)	683(4)	1413(4)
N	0	821(1)	2500	H(1)	0	506(3)	250
C(1)	844(2)	3053(3)	2763(3)	H(2)	134(2)	220(4)	457(4)
C(2)	1223(2)	3015(5)	4132(4)	H(3)	334(2)	92(4)	422(5)
C(3)	1428(2)	4134(5)	4871(5)	H(4)	365(2)	104(4)	35(4)
C(4)	1266(2)	5289(5)	4252(6)	H(5)	418(2)	116(4)	248(4)
C(5)	901(2)	5365(5)	2906(6)	H(6)	46(2)	429(3)	122(3)
C(6)	693(2)	4252(4)	2158(4)	H(7)	−393(2)	400(4)	−183(4)
C(7)	1242(2)	391(3)	2061(3)	H(8)	303(2)	274(4)	156(4)
C(8)	1364(2)	−732(4)	2807(4)	H(9)	234(2)	327(4)	263(4)
C(9)	1889(2)	−1516(5)	2925(5)	H(10)	246(2)	13(4)	108(4)
C(10)	2309(2)	−1189(5)	2278(5)	H(11)	163(2)	147(4)	94(4)

This reaction is not terminated by the stage of formation of compound I: With rising temperature the reaction mixture can yield 1,3-bis(diphenylchlorosilyl)-2,2,4,4-tetraphenylcyclodisilazane (IV), the crystal structure of which has been studied elsewhere [4]. Fractional recrystallization of the reaction products of 2,2,4,4,6,6-hexaphenylcyclotrisilazane and diphenyldichlorosilane from benzene yielded colorless transparent crystals of compound I.

To confirm the structure of compound I we carried out an x-ray diffraction structural investigation.

Compound I was obtained by the interaction of 47.36 g (0.08 mole) of 2,2,4,4,6,6-hexaphenylcyclotrisilazane and 60.77 g (0.24 mol. wt.) of diphenyldichlorosilane in inert-gas atmosphere at 250-270°C for 12 h, resulting in a yield of 93% (100.5 g). The substance was then purified by fractional recrystallization from benzene. Melting point 125-126°C. Found, % C 63.83, H 4.68, Cl 15.70, N 3.13, Si 12.50. mol. wt. 450 (mass spectrometry). $C_{24}H_{21}Cl_2N_1Si_2$. Calculated, %: C 63.98, H 4.70, Cl 15.74, N 3.11, Si 12.47. mol. wt. 450.53.

Experimental data for x-ray diffraction analysis were obtained on an automatic R-3m (nicolet) four-circle x-ray diffractometer (λMo, graphite monochromator). The crystals were monoclinic, space group C2/c, a = 21.792(1), b = 10.378(2), c = 10.546(2) Å, β = 110.61(2)°, Z = 8, d_{calc} = 1.34 g/cm³. The structure was determined by the direct method and refined by the least-squares procedure in the anisotropic approximation using 890 reflections with $I \geqslant 3\sigma$ (R = 0.029). A difference series yielded all the H atoms (only their positional parameters were refined). The calculations were performed on a Nova-3 computer using the XTL program set.

The structure of molecule I and numbering of the atoms can be seen in Fig. 1. The atomic coordinates, bond lengths, and valence angles are given in Tables 1 and 2.

The molecule is located on a two-fold axis passing through the N atom and the H atom bound to it. The N atom has a planar bond configuration (the sum of the valence angles is 360°).

The Si—N bond length in I (1.702 Å) is shorter than other Si—N bond lengths found in linear disilazanes (1.718-1.738 Å [5-6]). This seems to be due to the presence of electronegative substituents near the Si atoms. The valence angle Si—N—Si' (131.0°) is close to that found in the lateral chain of 1-methyldiphenylsilyl-3-(1,1,3-trimethyl-3,3-diphenylsilazanyl)-2,2,4,4-tetramethylcyclodisilazane (131.2°) [7]. Whereas in $Ph_3SiNHSiPh_3$, $H_3SiNHSiH_3$, and $Me_3SiNHSiMe_3$ [5] a lengthening of the Si—N bonds (1.718, 1.725, and 1.735 Å, respectively) leads to a decrease in the Si—N—Si valence angle (138.1, 127.7, and 125.5°, respectively), the situation is not the same in molecule I where the Si—N bond length was found to be 1.702 Å, and the Si—N—Si' valence angle 131.0°.

The Si—Cl distance (2.075 Å) is somewhat longer than the standard value 2.01 Å [8], but close to the distances found in III (2.056 Å) and IV (2.072 Å [4]. The Si—C bond lengths (1.850 Å) are typical of phenyl-substituted silanes. The Si atoms have a slightly distorted tetrahedral bond coordination.

TABLE 2. Bond Lengths d (Å) and Valence Angles ω (deg)

Bond	d	Bond	d	Angle	ω	Angle	ω
Si—N	1,702(2)	C(10)—C(11)	1,349(7)	NSiCl	111,2(1)	C(6)C(1)C(2)	117,5(4)
Si—Cl	2,075(1)	C(11)—C(12)	1,377(7)	NSiC(1)	109,9(1)	SiC(7)C(8)	124,5(3)
Si—C(1)	1,850(4)	C(12)—C(7)	1,384(6)	NSiC(7)	111,3(1)	SiC(7)C(12)	119,4(3)
Si—C(7)	1,851(4)	N—H(1)	0,79(4)	ClSiC(1)	106,4(1)	C(8)C(7)C(12)	116,1(4)
C(1)—C(2)	1,389(5)	C(2)—H(2)	0,95(4)	ClSiC(7)	106,1(1)	C(7)C(8)C(9)	122,6(4)
C(2)—C(3)	1,382(7)	C(3)—H(3)	0,91(5)	C(1)SiC(7)	111,7(2)	C(8)C(9)C(10)	119,5(5)
C(3)—C(4)	1,351(8)	C(4)—H(4)	0,87(5)	SiC(1)C(2)	117,7(3)	C(9)C(10)C(11)	119,7(5)
C(4)—C(5)	1,363(8)	C(5)—H(5)	0,91(5)	SiC(1)C(6)	124,8(3)	C(10)C(11)C(12)	120,8(5)
C(5)—C(6)	1,383(7)	C(6)—H(6)	0,94(3)	C(1)C(2)C(3)	121,2(4)	C(11)C(12)C(7)	121,3(4)
C(6)—C(1)	1,384(6)	C(8)—H(7)	0,89(5)	C(2)C(3)C(4)	119,6(5)	SiNSi′	131,0(2)
C(7)—C(8)	1,379(6)	C(9)—H(8)	0,93(4)	C(3)C(4)C(5)	120,8(5)	SiNH(1)	114,5(1,5)
C(8)—C(9)	1,375(7)	C(10)—H(9)	0,92(5)	C(4)C(5)C(6)	119,9(5)		
C(9)—C(10)	1,363(7)	C(11)—H(10)	0,88(5)	C(5)C(6)C(1)	120,8(4)		
		C(12)—H(11)	0,94(4)				

The phenyl rings C(1)—C(6) and C(7)—C(12) are planar and make a dihedral angle of 96.1° between them. The rings C(1)—C(6) and C(1')—C(6'), related by a two-fold axis, are parallel. These rings have a crossed conformation relative to the Si—Si' vector [the torsion angle C(1)—Si—Si'—C(1') is equal to 59.0°], and therefore there is only one contact between the C atoms of the rings which is shortened in comparison with the sum of the van der Waals radii: The C(6)...C(6)' distance is equal to 3.343 Å. The remaining substituents also have a crossed conformation relative to the Si...Si' vector (the torsion angles Cl—Si—Si'—Cl' and C(7)—Si—Si'—C(7') are equal to 154.7 and 18.7°, respectively).

The molecules in the crystal are bound by van der Waals forces.

LITERATURE CITED

1. W. Fink, Helv. Chim. Acta, 51, 1011 (1968).
2. U. Wannagat, Pure Appl. Chem., 13, 263 (1966).
3. P. Geymayer and E. F. Rochow, Angew. Chem., 77, 618 (1965).
4. S. N. Gurkova, A. I. Gusev, N. V. Alekseev, et al., Zh. Strukt. Khim., 19, 182 (1978).
5. C. Glidwell and H. D. Holden, Acta Crystallogr., B37, 754 (1981).
6. A. J. Robiette, J. H. Sheldrick, and W. S. Sheldrick, J. Mol. Struct., 5, 423 (1970).
7. J. Chioccola and J. J. Daly, J. Chem. Soc. A, 568 (1968).
8. N. G. Bokii and Yu. T. Struchkov, Zh. Strukt. Khim., 9, 722 (1968).
9. S. N. Gurkova, A. I. Gusev, N. V. Alekseev, et al., Zh. Strukt. Khim., 22, 173 (1981).

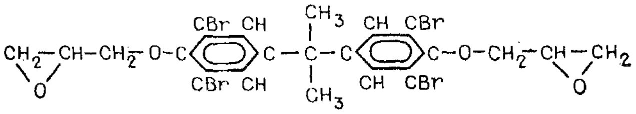
CRYSTAL STRUCTURE OF THE DIGLYCIDYL ETHER OF TETRABROMODIPHENYLPROPANE

Yu. N. Saf'yanova, V. P. **Golovachev**,
and É. A. Kuz'min

UDC 548.737

X-ray diffraction was used to study the crystal structure of the diglycidyl ether of tetrabromodiphenylpropane. Refinement of the structure model was carried out in the full-matrix anisotropic approximation (R = 0.073). The molecule of the above compound (DGETB) has an angular shape with a bending at the central C atom of the propane group.

The diglycidyl ether of tetrabromodiphenylpropane (DGETB), $C_{21}H_{20}O_4Br_4$,



is a monomer which is one of the starting materials for the production of polymers.

The colorless DGETB single crystals are usually obtained in the shape of platelets. For the x-ray structural investigation we chose a small crystal in the shape of a parallelepiped (dimensions 0.1 × 0.17 × 0.5 mm). The parameters of the monoclinic unit cell were determined from x-ray oscillating-crystal photographs and refined on a DRON-1,5 diffractometer: $a = 9.703(7)$, $b = 25.35(2)$, $c = 9.242(7)$ Å, $\gamma = 91.0(1)°$, $Z = 4$, $d_{calc} = 1.92$ g/cm^3, $M = 656$, $V_{cell} = 2273$ Å^3. The space group $P112_1/b$ was unambiguously deduced from extinctions.

Experimental data were obtained on a single-crystal diffractometer based on the DRON-1,5 apparatus using the "fixed counter-rotating crystal" method (813 reflections, MoK_α radiation, max $\sin \vartheta/\lambda \leqslant 0.57$ Å^{-1}, graphite monochromator). Speed of rotation of the crystal 2 deg/min, scanning interval 0.66 and 1.32°.

Physicotechnical Research Institute, Gorki. Translated from Zhurnal Strukturnoi Khimii, Vol. 25, No. 4, pp. 156-157, July-August, 1984. Original article submitted March 9, 1983.

0022-4766/84/2504-0658$08.50