

Table 3. Examples of compounds with species XYX in the space group $C2/c$ with unit-cell dimensions and geometry of the bridging groups, when known

	Ref.	<i>a</i>	<i>b</i>	<i>c</i>	β	X–Y–X	X–Y
$CH_2(SO_3K)_2$	<i>a</i>	12.55	7.75	7.30	90.5	119.7 (7)°	1.770 (7) Å
$CH_2(SO_3NH_4)_2$	<i>b</i>	12.70	7.85	7.65	92.6		
$NH(SO_3K)_2$	<i>c</i>	12.43	7.46	7.18	91.2	124.5 (5)	1.662 (5)
$NH(SO_3NH_4)_2$	<i>b</i>	12.72	7.74	7.49	92.8		
$NH(SO_3Rb)_2$	<i>b</i>	12.80	7.68	7.45	91.9		
$NH(SO_2CH_3)_2 \cdot H_2O$	<i>d</i>	12.71	7.51	8.07	97.2	125.0 (1)	1.645 (1)
$O(SO_3K)_2$	<i>e</i>	12.35	7.31	7.27	93.1	124.2 (3)	1.645 (5)
$O(CrO_3NH_4)_2$	<i>f</i>	13.26	7.54	7.74	93.2	115	1.91 (5)
$S(SO_3TI)_2$	<i>g</i>	13.20	7.45	7.58	91.0		
$CH_2(POCl_2)_2$	<i>h</i>	15.87	5.85	9.16	106.6	116.4 (4)	1.795 (4)

References: (a) Truter (1962). (b) Jones (1955). (c) Cruickshank & Jones (1963). (d) This work. (e) Lynton & Truter (1960). (f) Byström & Wilhelmi (1951). (g) Ketelaar & Sanders (1936). (h) Sheldrick (1975).

eral neutral or anionic species X–Y–X with bridging Y, such as CH_2 , NH, O, S and tetrahedral groups X, with central S, P or Cr (Table 3).

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Octamethylbicyclopentasiloxane

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Abstract. $Si_5O_6C_8H_{24}$, M.W. 365.5, m.p. 115°C, space group $P2_1/m$, monoclinic (from systematic absences and *E* statistics), $a = 8.595$ (5), $b = 14.321$ (5), $c = 8.116$ (4) Å, $\beta = 90.7^\circ$ (from oscillation and Weissenberg photographs), $Z = 2$, $D_x = 1.184$, $D_m = 1.163$ (6) g cm⁻³ (by flotation). The symmetry of the molecule is near to $\bar{6}2m$, the direction connecting Si(1) and Si(3) being the pseudotrigonal axis.

Introduction. Garzó, Székely, Tamás & Ujszászi (1971) isolated and identified several new polycyclic methylpolysiloxane oligomers produced by thermal decompo-

sition of branched-chain polymers. The title compound was chosen first in order to determine its structure by X-ray methods. It will be denoted as T_2D_3 where T stands for the unit $CH_3SiO_{3/2}$ and D for $(CH_3)_2SiO_{2/2}$. Like several cyclic methylpolysiloxanes, T_2D_3 is characterized by high volatility. A crystal of the appropriate size for X-ray investigation volatilized after about 20 min at ambient pressure and temperature. The sample was sealed in a thin-walled glass capillary tube (0.3 mm in diameter). Weissenberg photographs were taken at 20–22°C with unfiltered Cu radiation around [001] (0–5 layers) and $[\bar{1}10]$ (0–9 layers), all with the same

specimen of dimensions about $0.5 \times 0.5 \times 0.2$ mm. 2003 independent reflexions were measured by visual estimation, but only 1032 were classed as observed, owing to the relatively short exposure times. No absorption corrections were made; 34 reflexions were left out of the calculations on account of extinction or the uncertainty of the intensity measurement. The structure was solved by direct methods; the program *MULTAN* (Main,

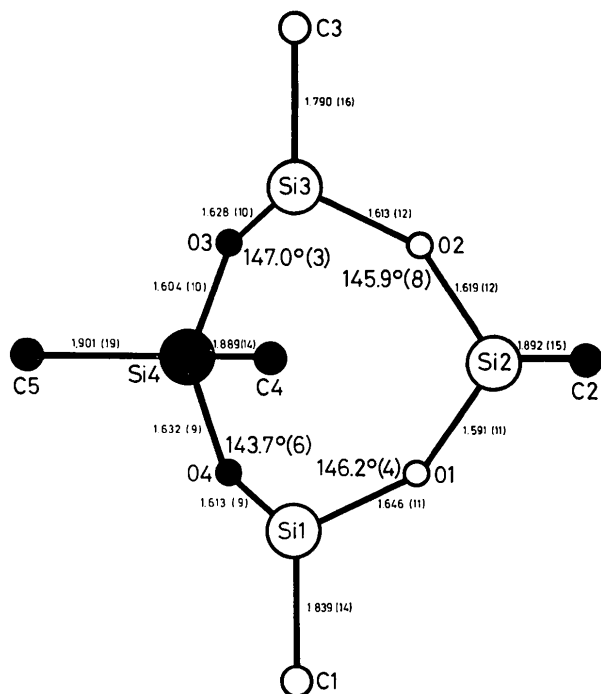


Fig. 1. Projection of the molecule along *b*. Atoms coinciding in projection with their mirror equivalents are marked by full circles.

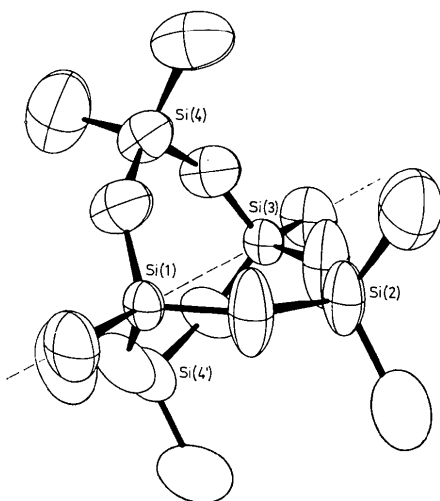
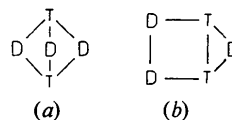


Fig. 2. Perspective view of the molecule (*ORTEP*: Johnson, 1965). Atoms below the mirror plane *P*₁ are indicated by contours only.

Germain & Woolfson, 1970) produced signs for 249 reflexions with $E > 1.5$. An *E* map and a subsequent *F_o* map revealed the positions of all non-hydrogen atoms. The structure-factor calculation, with the rather high overall temperature factor $B = 5.6 \text{ \AA}^2$ given by the Wilson plot, resulted in $R = 0.21$ for the observed data. After three cycles of block-diagonal least-squares refinement with individual isotropic and three with anisotropic thermal parameters R was 0.129 for all reflexions and 0.108 for those observed. A difference map gave uncertain maxima, and H atoms were ignored, but the scattering factor of C (*International Tables for X-ray Crystallography*, 1962) was replaced by that of N (Peyronel, 1954).^{*} Table 1 contains the atomic parameters. Fig. 1 shows the projection of the molecule along [010], with the bond distances and Si-O-Si angles; other angles are listed in Table 2. Fig. 2 gives a perspective view of the molecule.

Discussion. Two possible isomeric structures can be given for T_2D_3 :



The result of the present investigation shows that the actual structure corresponds to (a), confirming the suggestion of Garz3 & Alexander (1971) made on the basis of gas chromatographic analysis. The siloxane skeleton of the molecule consists of three planar five-membered half rings intersecting at the axis through Si(1) and Si(3); two neighbouring half rings form an eight-membered ring. The plane *P*₁ through Si(1),

^{*} A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30823 (37 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Final fractional atomic coordinates* ($\times 10^4$) *and thermal parameters* ($\times 10^4$) *with estimated standard deviations in parentheses*

(a) Fractional coordinates

	<i>x</i>	<i>y</i>	<i>z</i>
Si(1)	4713 (4)	7500	10998 (5)
Si(2)	4216 (5)	7500	7212 (5)
Si(3)	907 (4)	7500	8657 (5)
Si(4)	2111 (4)	8979 (3)	11150 (5)
O(1)	5002 (13)	7500	8997 (13)
O(2)	2343 (13)	7500	7396 (15)
O(3)	1062 (9)	8413 (7)	9842 (12)
O(4)	3730 (9)	8414 (6)	11502 (11)
C(1)	6606 (15)	7500	12080 (16)
C(2)	4864 (16)	8606 (12)	6145 (15)
C(3)	-910 (17)	7500	7559 (21)
C(4)	2616 (14)	10128 (9)	10145 (20)
C(5)	971 (20)	9120 (15)	13127 (21)

Table 1 (*cont.*)(b) Thermal parameters in the form $\exp[-(h^2B_{11} + hkB_{12} + hlB_{13} + k^2B_{22} + kIB_{23} + l^2B_{33})]$

	B_{11}	B_{12}	B_{13}	B_{22}	B_{23}	B_{33}
Si(1)	96 (4)	0	-54 (8)	64 (2)	0	133 (5)
Si(2)	114 (5)	0	-50 (10)	149 (4)	0	129 (6)
Si(3)	84 (4)	0	-75 (8)	74 (2)	0	169 (6)
Si(4)	139 (3)	39 (5)	-117 (9)	84 (2)	-78 (7)	293 (7)
O(1)	143 (15)	0	-40 (28)	196 (13)	0	145 (17)
O(2)	110 (14)	0	-55 (30)	252 (17)	0	194 (21)
O(3)	186 (11)	11 (14)	-253 (23)	84 (6)	-62 (19)	381 (19)
O(4)	185 (11)	44 (13)	-211 (22)	82 (5)	-104 (17)	339 (17)
C(1)	191 (19)	0	-184 (34)	99 (10)	0	222 (23)
C(2)	364 (26)	16 (33)	-49 (43)	144 (11)	-31 (31)	258 (23)
C(3)	138 (18)	0	-203 (40)	142 (13)	0	372 (33)
C(4)	252 (20)	13 (22)	-133 (50)	90 (8)	-61 (30)	569 (35)
C(5)	396 (36)	130 (41)	-84 (63)	228 (19)	-153 (45)	427 (35)

Table 2. Bond angles ($^\circ$)Estimated standard deviations range from 0.3 to 0.7 $^\circ$.

O(1)-Si(1)-O(4)	109.6	O(3)-Si(3)-O(3')	106.9
O(4)-Si(1)-O(4')	108.4	O(2)-Si(3)-C(3)	110.8
O(1)-Si(1)-C(1)	109.1	O(3)-Si(3)-C(3)	111.0
O(4)-Si(1)-C(1)	110.0	O(3)-Si(4)-O(4)	109.7
O(1)-Si(2)-O(2)	109.1	O(3)-Si(4)-C(4)	106.5
O(1)-Si(2)-C(2)	107.0	O(3)-Si(4)-C(5)	108.7
O(2)-Si(2)-C(2)	109.9	O(4)-Si(4)-C(4)	107.9
C(2)-Si(2)-C(2')	113.7	O(4)-Si(4)-C(5)	110.6
O(2)-Si(3)-O(3)	108.5	C(4)-Si(4)-C(5)	113.3

O(1), Si(2), O(2) and Si(3) coincides with the mirror plane of the cell. The least-squares plane $P2$ formed by Si(1), O(4), Si(4), O(3) and Si(3) and $P1$ form an angle of 120.4° . None of the atoms forming $P2$ has a distance from the plane greater than 0.01 Å. The plane $P3$, defined by Si(2), Si(4) and Si(4') (the prime indicates an atom related by mirror symmetry to the atom with the same serial number) is a pseudo-mirror plane of the molecule. The differences in distances of corresponding atoms on opposite sides of $P3$ are not significant; C(2), C(4) and C(5) are close to $P3$ (0.03–0.06 Å). The symmetry of the molecule is therefore near to $\bar{6}2m$; the axis through Si(1) and Si(3) is the pseudo-triad. Si(1)-C(1) and Si(3)-C(3) coincide almost exactly with the pseudo-triad.

Table 3 contains the average bond distances and angles of T_2D_3 and the data of some related compounds measured by X-ray methods. An important characteristic of cyclic siloxanes is the Si-O-Si angle; its value in T_2D_3 corresponds to the data for cyclic polysiloxanes with eight-membered rings. From the Si-C bonds in T_2D_3 , those belonging to the two T units are noticeably shorter than the other six; averages are 1.815 and 1.894 Å respectively. Though the errors of measurements have a large influence on the positional parameters of the methyl groups because of their high temperature factors, one can assume that the large difference (about 5σ) is – at least partly – accounted for by the fact that the Si-C bonds in the T units are more ionic than those in the D units. For the non-bonded intramolecular Si...Si distances Si(1)...Si(3) is 3.763 Å, the other six range from 3.084 to 3.097 Å. The shortest intermolecular distances are those between neighbouring methyl groups ranging from 3.91 to 4.27 Å.

The calculations were performed on the Odra 1304 computer at the Computing Centre of the Faculty of Sciences of the L. Eötvös University; the authors thank the staff of the computing centre. We are indebted to Dr Gy. Argay for producing the ORTEP drawing.

Table 3. Characteristic bond distances (Å) and angles ($^\circ$) of some cyclic polysiloxanes

T_2D_3	Si-O	Si-C	Si-O-Si	O-Si-O	C-Si-C
Octamethylspiro-5,5-pentasiloxane ^a	1.618	1.874	145.6	108.9	113.5
Hexamethylcyclotrisiloxane ^b	1.63	1.88	130	107	106
Octamethylcyclotetrasiloxane ^c	1.61	1.99	136	104	106
Octa(methylsilsequioxane) ^d	1.65	1.92	142.5	105	106
Octa(methylsilsequioxane) ^d	1.612	1.895	145	110	
N-Ethyl-2,2,4,4,6,6-hexaphenyl-3-azacyclotrisiloxane ^e	1.642	1.875	131.9	108.0	108.4
Hexaphenylcyclotrisiloxane ^f	1.64	1.83	131.9	107.7	112.6
2,6-cis-Diphenylhexamethylcyclotetrasiloxane ^g	1.631	1.851	144.2	109.5	112.5
trans-1,2,3-Trimethyl-1,2,3-triphenylcyclotrisiloxane ^h	1.65	1.88	132	107	112

(a) Roth & Harker (1948); (b) Peyronel (1954); (c) Steinfink, Post & Fankuchen (1955); (d) Larsson (1960); (e) Fink & Wheatley (1967); (f) Bokii, Zakharova & Struchkov (1972); (g) Carlström & Falkenberg (1973); (h) Shklover, Bokii, Struchkov, Adrianov, Zavin & Svistunov (1974).

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6-Methyl-5-thioformylpyrrolo[2,1-*b*]thiazole

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Abstract. C₈H₇NS₂, monoclinic, space group *P*2₁/*c*, *a* = 9·350 (3), *b* = 12·130 (3), *c* = 7·216 (3) Å, β = 98·00 (4)°, *Z* = 4, *D*_c = 1·483 g cm⁻³, *R* = 0·032, 662 reflexions. The thioformyl group is in the *syn* configuration. The thioformyl group and the atoms of the pyrrole ring are planar, this plane being inclined at an angle of 1·6° to the plane of the thiazole ring.

Introduction. The crystals were dark red, elongated along *c*. The cell parameters were obtained from the best orientation matrix on a Siemens four-circle diffractometer.

The intensities of 662 independent reflexions were measured on the diffractometer with Mo *K*α radiation and a Zr filter. The five-point measuring cycle was employed and some 592 of the reflexions were measured within a counting statistics accuracy of between 2 and 6%, the remainder being measured to between 6 and 14%. The integrated intensities of three standard reflexions measured every 30 reflexions did not change significantly over the collection period. No absorption corrections were made (*μ* = 5·62 cm⁻¹). An earlier low-accuracy data set had been used to obtain the coordinates of the two S atoms from a Patterson synthesis. A Fourier summation phased on these atoms gave the positions of all the non-hydrogen atoms, but the subsequent least-squares refinement stopped at an *R* of 0·14. From these coordinates and the new data set, three cycles of least-squares refinement with iso-

tropic temperature factors (*R* = 0·089) were followed by three cycles with anisotropic temperature factors (*R* = 0·046). A difference map then clearly showed the positions of all seven H atoms. A final refinement of the non-hydrogen atoms was then carried out with absolute weights (Killean & Lawrence, 1969) with 0·0003 and 0·0012 for *c*² and *k*² respectively. This gave an *R* of 0·032 where

$$R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

and a value

$$\frac{\sum w\Delta^2}{m-n} = 0\cdot94.$$

Three reflexions, 102, 391, and 5,11,1 had large values of $|A|/\sigma$ {4·4, 3·9, and 4·1 respectively} suggesting that these reflexions are affected by some systematic error. Scattering factors were taken from *International Tables for X-ray Crystallography* (1962). The final atomic coordinates and temperature factors are listed in Tables 1 and 2.†

Discussion. The structures of two other pyrrolo[2,1-*b*]thiazoles, 3,6-dimethyl-5-thioformylpyrrolo[2,1-*b*]thiazole (Sharma & Killean, 1974) and 3-methyl-6-*t*-butyl-5-thioformylpyrrolo[2,1-*b*]thiazole (Sharma, Lawrence & Killean, 1975) have been determined to compare the

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† A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30859 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.