Frenz, B. A. (1978). *The Enraf–Nonius CAD-4 – A Real-Time System for Concurrent X-ray Data Collection and Crystal Structure Solution. Computing in Crystallography*, edited by H. Schenk, R. Olthof-Hazekamp, H. van Koningsveld & G. C. Bassi, pp. 64–71. Delft University Press.
Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.
Sheldrick, G. M. (1976). *SHELX76. Program for Crystal Structure Determination*. University of Cambridge, England.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Walker, N. & Stuart, D. (1983). *Acta Cryst.* A**39**, 158–166.

Acta Cryst. (1996). C**52**, 3179-3181

An Optically Active Pentacoordinate Silicate: (+)-Bis(triethylammonium) Bis[(*R*,*R*)-tartrato(4−)]diphenyldisilicate

ZHI-GANG WANG, SHENG-GAO LIU, DONG WANG AND XIU-MEI SUI

Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China. E-mail: huangsl@infoc3.icas.ac.cn

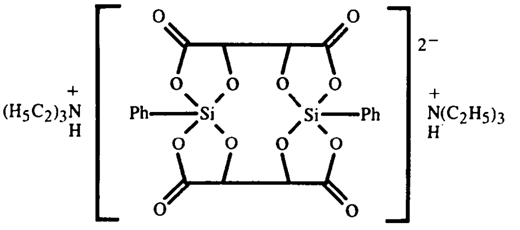
(*Received 19 April 1996; accepted 11 July 1996*)

Abstract

The title compound, $2C_6H_{16}N^+.C_{20}H_{14}O_{12}Si_2^{2-}$, was prepared by the reaction of (*R*,*R*)-(+)-tartaric acid with triethoxyphenylsilane and triethylamine in ethanol. The structure of this optically active pentacoordinate phenylsilicate consists of independent bis[(*R*,*R*)-tartrato]diphenyldisilicate anions and triethylammonium cations. In the crystal, the two Si atoms are five-coordinate and the geometry of each of the Si atoms is distorted from a trigonal bipyramid towards a square pyramid along the Berry pseudorotational coordinate by *ca* 9.8 and 8.9%, respectively.

Comment

The study of hypervalent silicon compounds is currently one of the most interesting areas of research in organosilicon chemistry (Holmes, 1990; Chuit, Corriu, Reye & Young, 1993; Tacke, Becht, Lopez-Mras & Sperlich, 1993). In particular, the five-coordinate silicates have drawn much attention over the past few years, their preparation and structures having been investigated extensively (Frye, 1970; Tacke, Lopez-Mras & Jones, 1994; Holmes, Day, Harland, Sau & Holmes, 1984; Small, McCord, Greaces & Shea, 1995; Tamao *et al.*, 1995; Hosomi, Kohra, Ogata, Yauagi & Tominaga, 1990). Tacke, Mühleisen & Jones (1994) reported the preparation and structure of the first optically active pentacoordinate silicate. However, work on the crystal structures of optically active hypervalent organosilicon compounds is quite rare. We report here the crystal structure of a new optically active pentacoordinate silicate: (+)-bis(triethylammonium) bis[(*R*,*R*)-tartrato(4−)]diphenyldisilicate, (I).



(I)

The disilicate dianion contains two pentacoordinate (formally negatively charged) Si atoms, each of which is coordinated by one phenyl group and four O atoms from two chiral tetradentate (*R*,*R*)-tartrato(4−) ligands which bridge the two Si atoms such that each ligand bonds to each of the Si atoms at the two coordination sites forming a group of four five-membered rings. Charge balance is provided by two triethylammonium cations. The geometry of the two five-coordinate Si atoms, Si(1) and Si(2), is distorted from an ideal trigonal bipyramid towards a square pyramid by *ca* 9.8 and 8.9%, respectively, as calculated by the dihedral-angle method (Holmes & Deiters, 1977). The axial Si—O bond lengths are Si(1)—O(1) 1.838 (4), Si(1)—O(3) 1.799 (4), Si(2)—O(5) 1.848 (4) and Si(2)—O(8) 1.801 (4) Å. The equatorial Si—O bond lengths are Si(1)—O(2) 1.671 (4), Si(1)—O(4) 1.668 (4), Si(2)—O(6) 1.671 (4) and Si(2)—O(7) 1.665 (4) Å.

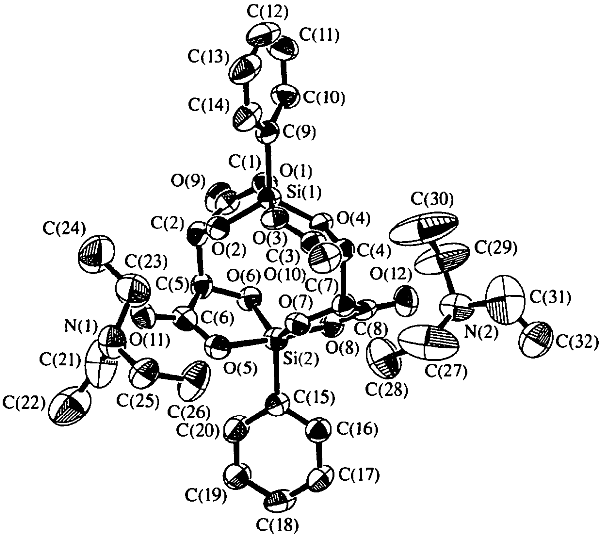


Fig. 1. *ORTEP* (Johnson, 1965) view of (I) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

© 1996 International Union of Crystallography
Printed in Great Britain – all rights reserved

In the dianion, the dihedral angle between the two phenyl groups is 74.4°. All the atoms in each of the four tartrato planes (planes 3–6; Table 3) are nearly coplanar, with mean deviations of 0.024, 0.030, 0.029 and 0.033 Å for planes 3, 4, 5 and 6, respectively. The dihedral angles between the tartrato planes are around 120°, and those between plane 1 and planes 5 and 6, and plane 2 and planes 3 and 4 range from 61.8 to 69.5° (see Table 3).

Thermal motion in the triethylammonium cations is significant and the derived molecular geometry exhibits higher uncertainties than for the dianion.

Experimental

Compound (I) was prepared by the dissolution of (*R*,*R*)-(+)-tartaric acid and triethoxyphenylsilane in ethanol in the presence of triethylamine. Crystals were grown by slow evaporation of the solvent from a dilute ethanolic solution over a period of three weeks.

Crystal data

$2C_6H_{16}N^+.C_{20}H_{14}O_{12}Si_2^{2-}$	Mo $K\alpha$ radiation
$M_r = 706.89$	$\lambda = 0.71073$ Å
Orthorhombic	Cell parameters from 20 reflections
$P2_12_12_1$	$\theta = 11.73–13.21°$
$a = 9.625 (3)$ Å	$\mu = 0.162$ mm^{-1}
$b = 20.989 (3)$ Å	$T = 293$ K
$c = 17.653 (2)$ Å	Prismatic
$V = 3566 (1)$ Å^3	0.30 × 0.20 × 0.20 mm
$Z = 4$	Colourless
$D_x = 1.316$ Mg m^{-3}	
D_m not measured	

Data collection

AFC-7*R* diffractometer	$h = 0 \rightarrow 11$
ω–2θ scans	$k = 0 \rightarrow 15$
Absorption correction: none	$l = 0 \rightarrow 12$
3555 measured reflections	3 standard reflections monitored every 200 reflections
2813 observed reflections $[I > 3\sigma(I)]$	intensity decay: 0.49%
$\theta_{max} = 25°$	

Refinement

Refinement on F	$(\Delta/\sigma)_{max} = 0.151$
$R = 0.049$	$\Delta\rho_{max} = 0.464$ e Å^{-3}
$wR = 0.064$	$\Delta\rho_{min} = -0.366$ e Å^{-3}
$S = 2.11$	Extinction correction: none
2813 reflections	Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C)
433 parameters	
H atoms placed in calculated positions but not refined	
$w = 1/\sigma^2(F_{obs})$	

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Si(1)	0.7409 (2)	0.20443 (6)	0.76936 (7)	0.0402 (3)
Si(2)	0.7356 (2)	0.01098 (6)	0.78357 (7)	0.0411 (3)
O(1)	0.8143 (4)	0.2027 (2)	0.8655 (2)	0.0462 (10)
O(2)	0.8826 (3)	0.1655 (2)	0.7401 (2)	0.0422 (9)
O(3)	0.6691 (4)	0.1968 (2)	0.6757 (2)	0.048 (1)
O(4)	0.6023 (4)	0.1667 (2)	0.8040 (2)	0.0429 (9)
O(5)	0.8687 (4)	0.0114 (2)	0.7081 (2)	0.0482 (10)
O(6)	0.8471 (4)	0.0520 (2)	0.8374 (2)	0.0435 (9)
O(7)	0.6298 (4)	0.0466 (2)	0.7221 (2)	0.0454 (9)
O(8)	0.6037 (4)	0.0189 (2)	0.8553 (2)	0.0463 (9)
O(9)	0.9963 (4)	0.1668 (2)	0.9304 (2)	0.056 (1)
O(10)	0.4793 (4)	0.1605 (2)	0.6165 (2)	0.066 (1)
O(11)	1.0739 (4)	0.0545 (2)	0.6806 (2)	0.055 (1)
O(12)	0.3866 (4)	0.0547 (2)	0.8707 (2)	0.069 (1)
N(1)	0.7780 (5)	0.1534 (3)	0.0381 (2)	0.064 (2)
N(2)	0.0379 (6)	0.1196 (2)	0.5473 (3)	0.065 (2)
C(1)	0.9315 (5)	0.1732 (2)	0.8709 (3)	0.045 (1)
C(2)	0.9773 (5)	0.1447 (2)	0.7962 (3)	0.041 (1)
C(3)	0.5483 (6)	0.1672 (2)	0.6733 (3)	0.047 (1)
C(4)	0.5046 (5)	0.1439 (2)	0.7513 (3)	0.044 (1)
C(5)	0.9721 (5)	0.0724 (2)	0.8035 (3)	0.043 (1)
C(6)	0.9764 (6)	0.0444 (3)	0.7237 (3)	0.045 (1)
C(7)	0.5038 (6)	0.0702 (2)	0.7513 (3)	0.044 (1)
C(8)	0.4904 (6)	0.0479 (2)	0.8328 (3)	0.048 (1)
C(9)	0.7447 (5)	0.2934 (2)	0.7671 (3)	0.050 (1)
C(10)	0.7281 (7)	0.3298 (3)	0.8328 (4)	0.069 (2)
C(11)	0.7334 (8)	0.3968 (3)	0.8289 (5)	0.088 (3)
C(12)	0.7534 (7)	0.4267 (3)	0.7624 (6)	0.092 (3)
C(13)	0.7695 (7)	0.3924 (3)	0.6977 (5)	0.083 (2)
C(14)	0.7649 (6)	0.3269 (3)	0.6986 (4)	0.065 (2)
C(15)	0.7363 (5)	−0.0788 (2)	0.7897 (3)	0.042 (1)
C(16)	0.6159 (6)	−0.1128 (2)	0.8000 (3)	0.050 (2)
C(17)	0.6141 (6)	−0.1795 (3)	0.8031 (3)	0.057 (2)
C(18)	0.7379 (7)	−0.2126 (3)	0.7977 (4)	0.063 (2)
C(19)	0.8603 (6)	−0.1793 (3)	0.7867 (4)	0.070 (2)
C(20)	0.8594 (6)	−0.1141 (3)	0.7824 (4)	0.059 (2)
C(21)	0.8449 (8)	0.1124 (6)	0.0959 (4)	0.110 (3)
C(22)	0.921 (1)	0.0566 (4)	0.0648 (7)	0.126 (4)
C(23)	0.7327 (9)	0.2182 (4)	0.0681 (4)	0.098 (3)
C(24)	0.8469 (9)	0.2617 (5)	0.0812 (5)	0.123 (4)
C(25)	0.6603 (7)	0.1218 (3)	−0.0023 (3)	0.067 (2)
C(26)	0.5412 (8)	0.1048 (4)	0.0482 (4)	0.101 (3)
C(27)	0.086 (2)	0.0825 (4)	0.4859 (4)	0.151 (4)
C(28)	0.2385 (10)	0.0517 (4)	0.5129 (4)	0.103 (3)
C(29)	0.098 (1)	0.1779 (4)	0.5756 (4)	0.135 (4)
C(30)	0.117 (2)	0.2293 (5)	0.5161 (5)	0.201 (6)
C(31)	−0.118 (1)	0.1367 (6)	0.5276 (5)	0.130 (4)
C(32)	−0.2115 (9)	0.0867 (4)	0.5244 (5)	0.099 (3)

Table 2. *Selected geometric parameters (Å, °)*

Si(1)—O(1)	1.838 (4)	Si(2)—O(5)	1.848 (4)
Si(1)—O(2)	1.671 (4)	Si(2)—O(6)	1.671 (4)
Si(1)—O(3)	1.799 (4)	Si(2)—O(7)	1.665 (4)
Si(1)—O(4)	1.668 (4)	Si(2)—O(8)	1.801 (4)
Si(1)—C(9)	1.868 (5)	Si(2)—C(15)	1.887 (5)
O(1)—Si(1)—O(2)	87.9 (2)	O(5)—Si(2)—O(6)	87.8 (2)
O(1)—Si(1)—O(3)	173.8 (2)	O(5)—Si(2)—O(7)	87.2 (2)
O(1)—Si(1)—O(4)	87.6 (2)	O(5)—Si(2)—O(8)	174.3 (2)
O(1)—Si(1)—C(9)	91.8 (2)	O(5)—Si(2)—C(15)	92.5 (2)
O(2)—Si(1)—O(3)	89.2 (2)	O(6)—Si(2)—O(7)	122.1 (2)
O(2)—Si(1)—O(4)	122.3 (2)	O(6)—Si(2)—O(8)	90.3 (2)
O(2)—Si(1)—C(9)	117.8 (2)	O(6)—Si(2)—C(15)	118.6 (2)
O(3)—Si(1)—O(4)	89.3 (2)	O(7)—Si(2)—O(8)	89.2 (2)
O(3)—Si(1)—C(9)	94.4 (2)	O(7)—Si(2)—C(15)	119.2 (2)
O(4)—Si(1)—C(9)	119.9 (2)	O(8)—Si(2)—C(15)	93.2 (2)

Table 3. *Dihedral angles between planes 1–6 (°)*

Plane	1	2	3	4	5
2	74.4				
3	93.9	64.8			
4	96.2	61.8	120.1		
5	69.5	61.0	125.7	27.3	
6	68.7	66.8	26.5	128.6	119.4

Plane 1: ring C(15)–C(20); plane 2: ring C(9)–C(14); plane 3: Si(1), O(1), C(1), C(2), O(2); plane 4: Si(1), O(3), C(3), C(4), O(4); plane 5: Si(2), O(5), C(5), C(6), O(6); plane 6: Si(2), O(7), C(7), C(8), O(8).

The crystal was mounted on a glass fibre. Data were collected at a scan speed of 16.0° $\min^{-1}$ in ω; ω scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.33° with a take-off angle of 6.0°. The weak reflections $[I < 15\sigma(I)]$ were rescanned to a maximum of five scans and the counts were accumulated to ensure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak to background counting time was 2:1.

The structure was solved by direct methods (Fan, 1991) and expanded using Fourier techniques (Beurskens *et al.*, 1992). The non-H atoms were refined anisotropically.

Anomalous dispersion effects were included in F_c (Ibers & Hamilton, 1964). The values for $\Delta f'$ and $\Delta f''$ were those of Creagh & McAuley (1992). The values for the mass attenuation coefficients were those of Creagh & Hubbell (1992). All calculations were performed using *TEXSAN* (Molecular Structure Corporation, 1985, 1992).

This work was supported by the NNSFC. The authors are grateful to Dr J. Sun at the Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China, for helpful discussions.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BM1085). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Beurskens, P. T., Admiraal, G., Beurskens, G., Bosman, W. P., Garcia-Granda, S., Gould, R. O., Smits, J. M. M. & Smykalla, C. (1992). *The DIRDIF Program System*. Technical Report. Crystallography Laboratory, University of Nijmegen, The Netherlands.

Chuit, C., Corriu, R. J. P., Reye, C. & Young, J. C. (1993). *Chem. Rev.* **93**, 1371–1448.

Creagh, D. C. & Hubbell, J. H. (1992). *International Tables for Crystallography*, Vol. C, pp. 200–206. Dordrecht: Kluwer Academic Publishers.

Creagh, D. C. & McAuley, W. J. (1992). *International Tables for Crystallography*, Vol. C, pp. 219–222. Dordrecht: Kluwer Academic Publishers.

Fan, H. F. (1991). *Structure Analysis Programs with Intelligent Control*. Rigaku Corporation, Tokyo, Japan.

Frye, C. L. (1970). *J. Am. Chem. Soc.* **92**, 1205–1210.

Holmes, R. R. (1990). *Chem. Rev.* **90**, 7–31.

Holmes, R. R., Day, R. O., Harland, J. J., Sau, A. C. & Holmes, J. M. (1984). *Organometallics*, **3**, 341–353.

Holmes, R. R. & Deiters, J. A. (1977). *J. Am. Chem. Soc.* **99**, 3318–3326.

Hosomi, A., Kohra, S., Ogata, K., Yauagi, T. & Tominaga, Y. (1990). *J. Org. Chem.* **55**, 2415–2420.

Ibers, J. A. & Hamilton, W. C. (1964). *Acta Cryst.* **17**, 781.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794, Oak Ridge national Laboratory, Tennessee, USA.

Molecular Structure Corporation (1985, 1992). *TEXSAN. TEXRAY Structure Analysis Package*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Small, J. H., McCord, D. J., Greaces, J. & Shea, K. J. (1995). *J. Am. Chem. Soc.* **117**, 11588–11589.

Tacke, R., Becht, J., Lopez-Mras, A. & Sperlich, J. (1993). *J. Organomet. Chem.* **446**, 1–8.

Tacke, R., Lopez-Mras, A. & Jones, P. G. (1994). *Organometallics*, **13**, 1617–1623.

Tacke, R., Mühleisen, M. & Jones, P. G. (1994). *Angew. Chem. Int. Ed. Engl.* **33**, 1186–1188.

Tamao, K., Nagata, K., Asahara, M., Kawachi, A., Ito, Y. & Shiro, M. (1995). *J. Am. Chem. Soc.* **117**, 11592–11593.

Acta Cryst. (1996). C**52**, 3181–3183

Oxopregnenyl 4-Allyloxybenzoate

DAVID W. TOMLIN,[a] TIMOTHY J. BUNNING,[b]* COLIN M. MCHUGH[c] AND W. WADE ADAMS[c]

[a]*Technical Management Concepts Inc., PO Box 340345, Beavercreek, OH 45434, USA,* [b]*Science Applications International Corporation, 101 Woodman Drive, Suite 103, Dayton, OH 45431, USA, and* [c]*Wright Laboratory, Materials Directorate, Wright–Patterson AFB, OH 45433, USA. E-mail: bunnintj@ml.wpafb.af.mil*

(*Received 11 March 1996; accepted 30 April 1996*)

Abstract

The molecule of 20-oxo-5-pregnen-3-yl 4-allyloxybenzoate, $C_{31}H_{40}O_4$, is extended, with the benzoate moiety twisted by 34.0 (1)° from the least-squares plane through the tetracyclic core. The extended molecules pack in a parallel manner with respect to one another.

Comment

Polysiloxane backbones with pendant cholesterol ester groups are well known to produce liquid-crystalline behavior (Shibaev & Freidzon, 1989). The phase behavior of macromolecules based on liquid-crystalline cyclosiloxane backbones and cholesterol-based mesogens has also been examined extensively (Bunning & Kreuzer, 1995; Kreuzer *et al.*, 1991; Gresham *et al.*, 1994). These structures can be quenched into glassy transparent films which show promise for filter and storage applications. X-ray analysis of these materials has shown that a complex molecular architecture is present wherein two types of layered packing domains occur, each exhibiting characteristic X-ray diffraction features (Bunning, Klei, Samulski, Crane & Linville, 1991; Bunning, Klei, Samulski, Adams & Crane, 1993; Bunning, Socci, Farmer, Campbell & Adams, 1996). In systems with long spacer groups (the unit used to link the backbone to the tetracyclic core of the lath-shaped cholesterol molecule), a reflection corresponding approximately to the length of the extended mesogen is observed. In short spacer group compounds, a second reflection indicative of partial interdigitation of mesogens is also observed. Both reflections, corresponding to

© 1996 International Union of Crystallography
Printed in Great Britain – all rights reserved