References

Beurskens, P. T. (1984). *DIRDIF. Direct Methods for Difference Structures - an Automatic Procedure for Phase Extension and Refinement of Difference Structure Factors.* Technical Report 1984/1. Crystallography Laboratory, Toernooiveld, 6525 ED Nijmegen, The Netherlands.

Kozukue, E. & Mizuno, S. (1989). *J. Jpn Soc. Hortic. Sci.* **58**, 719–722.

Martin, D. M., Mayes, P. A. & Rodwell, V. W. (1983). *Harper's Review of Biochemistry*, 19th ed., pp. 288–292. Tokyo: Marzen Asia.

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

Ponzoni, M., Casalaro, A., Lanciotti, M., Montaldo, P. G. & Cornaglia-Ferraris, P. (1992). *Cancer Res.* **52**, 931–939.

Rigaku Corporation (1988). *MSC/AFC Data Collection and Refinement Software.* Rigaku Corporation, Tokyo, Japan.

Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures.* Univ. of Göttingen, Germany.

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3,3'-(1,1,3,3-Tetramethyldisiloxane-1,3-diyl)bis(N-ethyl-N,N-dimethyl-1-propanaminium) Diperchlorate at 163 K and Room Temperature

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## Abstract

In the title compound, $C_{18}H_{46}N_2OSi_2^{2+}.2ClO_4^-$, the cations lie in special positions on the crystallographic twofold axis. The contacts between N^+ and ClO_4^- build up a three-dimensional net. The Si—O—Si angle is relatively small [between 141.8 (3) and 144.4 (5)°] and depends on the measuring temperature.

Comment

This article is part of an ongoing series of crystal structure investigations of siloxane amphiphilic compounds (Ramm, Schulz, Sonnek & Schmaucks, 1990; Ramm, Schmaucks, Rudert & Schulz, 1993; Rudert & Schmaucks, 1994a,b). The comparison of crystal structure data of siloxane surfactants with data determined from the adsorption isotherm at

interfaces should give information about the possible arrangement of molecules at the interface. Recently published results show good agreement of the surface area per molecule of N-alkyl-N,N-dimethyl-3-(1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)-1-propanaminium bromides determined from their X-ray crystal structures with those calculated from the Frumkin adsorption isotherm (Schmaucks, Sonnek, Wüstneck, Herbst & Ramm, 1992). The investigation of additional siloxane surfactants with different structures should reveal possible principle connections. Here we report the crystal structure of the title compound, (I), at 163 K and room temperature.

(I)
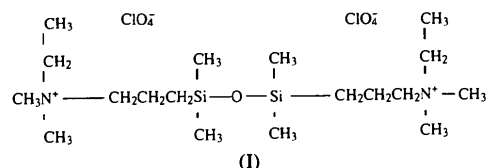
The atomic numbering scheme is shown in Fig. 1. Fig. 2 shows a perspective projection of the crystal structure. The cation has C_2 symmetry with a twofold axis through O1. One interesting feature is the Si—O—Si angle. In other crystal structures, in which this angle is not part of a ring, it ranges from 137 to 180° [for a theoretical discussion, see Newton (1981) and Gibbs (1982)]. The Si—O—Si angle of the title compound, being 141.8 (3)° at low temperature, is one of the lowest ever found in this class of compounds. As predicted by Gibbs (1982) and confirmed by X-ray crystal structure determination by Rudert & Schmaucks (1994a), the temperature may have a rather large effect on the Si—O—Si angle. In this study, this angle is only 2.6° larger at room temperature than at 163 K, but nevertheless concurs with the prediction of Gibbs (1982).

The displacement parameters of the ethyl group are remarkably high. This leads to an apparent shortening of the C5—C6 bond, especially at room temperature. The ethyl group may be disordered at room temperature, but it was impossible to resolve separate positions for C6. The position of C6 is different from the corresponding positions of this atom in dialkyldimethylammonium bromides (Taga, Machida, Kimura, Hayashi, Umemura & Takenaka, 1986, 1987; Taga, Miwa, Machida, Kimura, Hayashi, Umemura & Takenaka, 1990), in N-alkyl-N,N-dimethyl-3-(heptamethyltrisiloxan-3-yl)-1-propanaminium bromide (Ramm, Schulz, Sonnek & Schmaucks, 1990) and in N-butyl-N,N-dimethyl-3-(1,1,3,5,5,5-heptamethyltrisiloxan-1-yl)-1-propanaminium bromide (Rudert & Schmaucks, 1994a). The title compound has a C3—N4—C5—C6 torsion angle of 178.0 (4)°, whereas the above cited compounds have corresponding torsion angles between 50.2 and 57.3° (absolute values). The Si—C—C—C—N chains have *trans*-planar conformations. The maximum deviation from the least-squares plane is 0.04 (2) Å. The
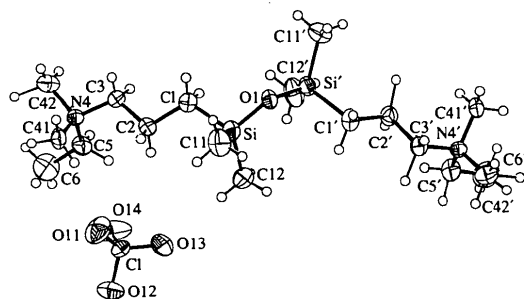
Fig. 1. Drawing (*PLUTON*92; Spek, 1992) of the compound with displacement ellipsoids at the 50% level (low-temperature measurement). Only one of the two symmetry-related ClO_4^- ions is shown.
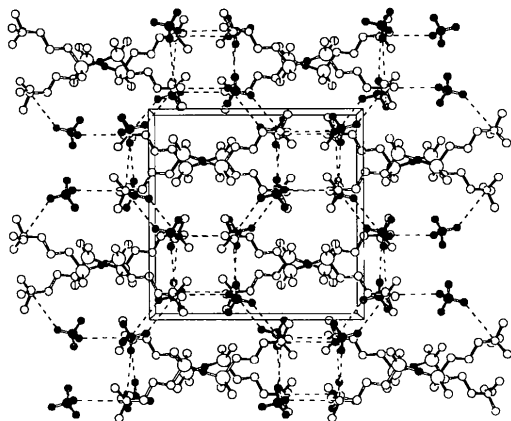

Fig. 2. Crystal packing (*SCHAKAL*92; Keller, 1992) viewed in the [001] direction. The *b* axis is in the horizontal direction. Short O···N contacts are shown by dotted lines. Cl and O atoms are symbolized by filled circles.

distances of O1 and C42 from this plane are 0.21 (3) and 0.22 (1) Å. The angle between the planes of each half of the molecule is 128.2 (6)° (all values are from the low-temperature analysis).

Each ammonium group is surrounded by four perchlorate molecules at the corners of a distorted tetrahedron. The N···O contacts in the crystal form a three-dimensional net (see Table 3 and Fig. 2). In contrast to most other crystal structures of amphiphilic compounds, no layer structure can be observed. The long stretched form of the molecule may not be responsible for this; a similar compound with a bent shape, 3,3'-[1,2-ethanediylbis(dimethylsilylene)]-bis(*N,N',N'*-trimethyl-1-propanaminium) diiodide (Tacke, Niedner, Frohnecke, Ernst & Sheldrick, 1980), also does not crystallize in layers. The hydrophilic parts and the hydrophobic parts are almost in a line [the distance between both N atoms is 12.143 (7) Å]; therefore, the surface activity of this conformer may be very low. The conformation may easily change at the water surface, however, by rotation of one or both propylene spacers around the C—Si bond.

Experimental

From a 0.01 molar solution of *N*-ethyl-*N,N*-dimethyl-3-(pentamethyldisiloxanyl)-1-propanaminium bromide in 0.5 mol l^{-1} of sodium perchlorate in the presence of a phosphate buffer to keep the pH value at 7, white needles spontaneously began to crystallize. These white needles were isolated and recrystallized from acetone.

Compound at 293 K
Crystal data

$C_{18}H_{46}N_2OSi_2^{2+}.2ClO_4^-$	Mo $K\alpha$ radiation
$M_r = 561.6$	$\lambda = 0.71069$ Å
Orthorhombic	Cell parameters from 59
Pccn	reflections
$a = 16.154$ (3) Å	$\theta = 5-20°$
$b = 16.483$ (6) Å	$\mu = 0.329$ mm^{-1}
$c = 11.454$ (6) Å	$T = 293$ (2) K
$V = 3050$ (2) Å^3	Needle
$Z = 4$	$0.33 \times 0.10 \times 0.08$ mm
$D_x = 1.223$ Mg m^{-3}	Colourless

Data collection

Huber four-circle diffractometer	$R_{int} = 0.004$
	$\theta_{max} = 23.5°$
2θ–ω scans	$h = 0 \rightarrow 16$
Absorption correction:	$k = 0 \rightarrow 18$
none	$l = 0 \rightarrow 12$
2319 measured reflections	2 standard reflections
2291 independent reflections	frequency: 90 min
928 observed reflections	intensity decay: 4.0%
$[I > \sigma(I)]$	

Refinement

Refinement on F	$(\Delta/\sigma)_{max} = 0.27$
$R = 0.082$	$\Delta\rho_{max} = 0.30$ e Å^{-3}
$wR = 0.062$	$\Delta\rho_{min} = -0.34$ e Å^{-3}
$S = 4.02$	Extinction correction: none
928 reflections	Atomic scattering factors
150 parameters	from *International Tables*
H-atom parameters not	*for Crystallography* (1992,
refined	Vol. C)
Weighting scheme based	
on measured e.s.d.'s	

Compound at 163 K
Crystal data

$C_{18}H_{46}N_2OSi_2^{2+}.2ClO_4^-$	Cu $K\alpha$ radiation
$M_r = 561.6$	$\lambda = 1.54178$ Å
Orthorhombic	Cell parameters from 25
Pccn	reflections
$a = 15.676$ (3) Å	$\theta = 18-21°$
$b = 16.433$ (5) Å	$\mu = 3.22$ mm^{-1}
$c = 11.316$ (3) Å	$T = 163$ (2) K
$V = 2915$ (1) Å^3	Needle
$Z = 4$	$0.33 \times 0.10 \times 0.08$ mm
$D_x = 1.280$ Mg m^{-3}	Colourless

Data collection

CAD-4 diffractometer	$R_{int} = 0.027$
2θ–ω scans	$\theta_{max} = 54°$

Absorption correction:
refined from ΔF
(*DIFABS*; Walker &
Stuart, 1983)
1905 measured reflections
1754 independent reflections
1384 observed reflections
$[I > \sigma(I)]$

Refinement

Refinement on F
$R = 0.060$
$wR = 0.045$
$S = 2.69$
1384 reflections
206 parameters
All H-atom parameters
refined
Weighting scheme based
on measured e.s.d.'s

$h = 0 \rightarrow 15$
$k = -1 \rightarrow 17$
$l = 0 \rightarrow 11$
2 standard reflections
frequency: 30 min
intensity decay: 9.0%

$(\Delta/\sigma)_{max} = 0.17$
$\Delta\rho_{max} = 0.45$ e Å^{-3}
$\Delta\rho_{min} = -0.32$ e Å^{-3}
Extinction correction: none
Atomic scattering factors
from *International Tables
for Crystallography* (1992,
Vol. C)

Table 1. *Fractional atomic coordinates and equivalent
isotropic displacement parameters* (Å^2)

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

	x	y	z	U_{eq}
293 K				
Si	0.2807 (2)	0.16140 (17)	0.4637 (3)	0.0885 (10)
O1	1/4	1/4	0.5069 (6)	0.081 (3)
N4	0.1088 (5)	−0.1146 (4)	0.3481 (6)	0.086 (3)
C1	0.1849 (6)	0.0981 (5)	0.4517 (9)	0.102 (4)
C2	0.1946 (6)	0.0124 (5)	0.4036 (9)	0.099 (5)
C3	0.1135 (6)	−0.0318 (6)	0.4011 (8)	0.085 (4)
C5	0.1231 (7)	−0.1061 (9)	0.2193 (8)	0.165 (6)
C6	0.1062 (11)	−0.1491 (12)	0.1453 (10)	0.308 (12)
C11	0.3507 (7)	0.1188 (7)	0.5740 (10)	0.143 (6)
C12	0.3328 (7)	0.1712 (7)	0.3198 (9)	0.126 (5)
C41	0.1705 (7)	−0.1673 (6)	0.4047 (10)	0.112 (5)
C42	0.0245 (6)	−0.1501 (7)	0.3728 (9)	0.118 (5)
Cl	0.09239 (16)	0.59656 (15)	0.2538 (2)	0.0919 (9)
O11	0.1111 (6)	0.6317 (6)	0.3508 (7)	0.212 (5)
O12	0.0307 (5)	0.6343 (6)	0.1932 (7)	0.185 (5)
O13	0.0735 (7)	0.5229 (5)	0.2675 (13)	0.297 (7)
O14	0.1580 (6)	0.5982 (9)	0.1931 (7)	0.291 (7)
163 K				
Si	0.28358 (10)	0.16194 (9)	0.48136 (14)	0.0395 (5)
O1	1/4	1/4	0.5285 (4)	0.0370 (16)
N4	0.1098 (3)	−0.1132 (2)	0.3475 (4)	0.0313 (16)
C1	0.1857 (3)	0.0972 (3)	0.4661 (5)	0.046 (2)
C2	0.1990 (3)	0.0120 (3)	0.4124 (5)	0.039 (2)
C3	0.1127 (3)	−0.0293 (3)	0.4059 (5)	0.0367 (19)
C5	0.1231 (3)	−0.1016 (3)	0.2169 (4)	0.0430 (19)
C6	0.1251 (4)	−0.1765 (4)	0.1476 (5)	0.072 (3)
C11	0.3567 (4)	0.1177 (3)	0.5924 (6)	0.066 (3)
C12	0.3399 (4)	0.1736 (3)	0.3371 (6)	0.065 (3)
C41	0.1768 (3)	−0.1667 (3)	0.4026 (5)	0.044 (2)
C42	0.0241 (3)	−0.1492 (3)	0.3710 (5)	0.047 (2)
Cl	0.09065 (8)	0.59475 (8)	0.25081 (12)	0.0374 (4)
O11	0.10327	0.64153	0.35620	0.0823 (19)
O12	0.02468	0.63184	0.17896	0.0643 (17)
O13	0.06576	0.51342	0.27803	0.105 (2)
O14	0.17051	0.59501	0.18613	0.104 (2)

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

273 K			
Si—O1	1.620 (4)	N4—C5	1.500 (12)
Si—C1	1.871 (10)	N4—C41	1.472 (13)
Si—C11	1.835 (12)	N4—C42	1.509 (13)
Si—C12	1.858 (11)	C1—C2	1.524 (12)
N4—C3	1.496 (12)	C5—C6	1.14 (2)

O1—Si—C1	105.8 (3)	C3—N4—C41	109.0 (7)
O1—Si—C11	108.9 (4)	C3—N4—C42	108.9 (7)
O1—Si—C12	109.4 (4)	C5—N4—C41	112.5 (8)
C1—Si—C11	110.3 (5)	C5—N4—C42	111.1 (8)
C1—Si—C12	111.0 (5)	C41—N4—C42	107.4 (7)
C11—Si—C12	111.4 (5)	Si—C1—C2	117.3 (7)
Si—O1—Si^i	144.4 (5)	C1—C2—C3	111.6 (8)
C3—N4—C5	107.8 (8)	N4—C3—C2	119.7 (8)

163 K			
Si—O1	1.633 (2)	N4—C5	1.505 (6)
Si—C1	1.878 (5)	N4—C41	1.507 (7)
Si—C11	1.851 (7)	N4—C42	1.494 (7)
Si—C12	1.867 (7)	C1—C2	1.542 (7)
N4—C3	1.532 (6)	C2—C3	1.518 (7)

O1—Si—C1	105.68 (17)	C3—N4—C42	107.9 (4)
O1—Si—C11	109.1 (2)	C5—N4—C41	112.6 (4)
O1—Si—C12	110.3 (2)	C5—N4—C42	110.5 (4)
C1—Si—C11	110.3 (2)	C41—N4—C42	108.8 (4)
C1—Si—C12	111.4 (3)	Si—C1—C2	116.2 (3)
C11—Si—C12	109.9 (3)	C1—C2—C3	107.8 (4)
Si—O1—Si^i	141.8 (3)	N4—C3—C2	116.9 (4)
C3—N4—C5	107.8 (4)	N4—C5—C6	115.0 (4)
C3—N4—C41	109.1 (4)		

Symmetry code: (i) $\frac{1}{2} - x, \frac{1}{2} - y, z$.

Table 3. *Contact distances* (Å) *at* 163 K

O-atom positions have been corrected by thermal-motion analysis of
low-temperature data (Schomaker & Trueblood, 1968).

N4···O11^i	4.033	N4···O13^{iv}	3.731
N4···O11^{ii}	4.523	N4···O14^{iii}	3.960
N4···O12^{iii}	3.993	N4···O14^{ii}	3.909
N4···O12^{iv}	4.555	Si···O13^{ii}	4.379

Symmetry codes: (i) $x, y - 1, z$; (ii) $\frac{1}{2} - x, \frac{1}{2} - y, z$; (iii) $x, \frac{1}{2} - y, \frac{1}{2} + z$;
(iv) $-x, y - \frac{1}{2}, \frac{1}{2} - z$.

Data collection: CAD-4 diffractometer software (Enraf–
Nonius, 1977). Cell refinement: CAD-4 diffractometer soft-
ware. Data reduction: *MolEN* (Fair, 1990). Program(s) used
to solve structures: *GENEV, GENSIN* and *GENTAN* of the
Xtal2.2 program system (Hall & Stewart, 1987). Program(s)
used to refine structures: *MolEN*. Molecular graphics: *PLA-
TON92* (Spek, 1992) and *SCHAKAL92* (Keller, 1992). Soft-
ware used to prepare material for publication: *PLATON92*.

References

Enraf–Nonius (1977). *CAD-4 Operations Manual*. Enraf–Nonius,
Delft, The Netherlands.
Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for
Crystal Structure Analysis*. Enraf–Nonius, Delft, The Netherlands.
Gibbs, G. V. (1982). *Am. Mineral.* **67**, 421–450.
Hall, S. R. & Stewart, J. M. (1987). Editors. *Xtal2.2 Users Manual*.
Univs. of Western Australia, Australia, and Maryland, USA.
Keller, E. (1992). *SCHAKAL92. A Fortran Program for the Graphic
Representation of Molecular and Crystallographic Models*. Univ. of
Freiburg, Germany.

Newton, M. D. (1981). *Structure and Bonding in Crystals*, Vol. I, edited by M. O'Keefe & A. Narotsky, pp. 175–193. New York: Academic Press.

Ramm, M., Schmaucks, G., Rudert, R. & Schulz, B. (1993). *Acta Cryst.* C49, 2145–2147.

Ramm, M., Schulz, B., Sonnek, G. & Schmaucks, G. (1990). *Cryst. Res. Technol.* 25, 763–769.

Rudert, R. & Schmaucks, G. (1994a). *Acta Cryst.* C50, 631–635.

Rudert, R. & Schmaucks, G. (1994b). *J. Organomet. Chem.* 474, 59–62.

Schmaucks, G., Sonnek, G., Wüstneck, R., Herbst, M. & Ramm, M. (1992). *Langmuir*, 8, 1724–1730.

Schomaker, V. & Trueblood, K. N. (1968). *Acta Cryst.* B24, 63–76.

Spek, A. L. (1992). *PLATON92. Molecular Graphics Program.* Univ. of Utrecht, The Netherlands.

Tacke, R., Niedner, R., Frohnecke, J., Ernst, L. & Sheldrick, W. S. (1980). *Liebigs Ann. Chem.* pp. 1859–1876.

Taga, T., Machida, K., Kimura, N., Hayashi, S., Umemura, J. & Takenaka, T. (1986). *Acta Cryst.* C42, 608–610.

Taga, T., Machida, K., Kimura, N., Hayashi, S., Umemura, J. & Takenaka, T. (1987). *Acta Cryst.* C43, 1204–1206.

Taga, T., Miwa, Y., Machida, K., Kimura, N., Hayashi, S., Umemura, J. & Takenaka, T. (1990). *Acta Cryst.* C46, 293–295.

Walker, N. & Stuart, D. (1983). *Acta Cryst.* A39, 158–166.

(Carboxymethyl)dimethyloctylammonium Bromide

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Abstract

The title compound, $C_{12}H_{26}NO_2^+.Br^-$, forms monolayers and crystallizes in a head-to-tail arrangement stabilized by $Br^-\cdots H$—O hydrogen bonds and $Br^-\cdots N^+$ contacts.

Comment

Surface-active carboxybetaines have a wide field of applications, particularly in cosmetic formulations. The adsorption ability of a carboxybetaine is important in determining its surface-active properties.

Alkylbetaines can exist in aqueous solution in zwitterionic and protonated forms depending on the pH. The homologous hydrobromides can be purified easily, in contrast to the corresponding betaines. The series of N-n-alkyl-N,N-dimethylammonio acetic acid hydrobromides of the formula R—$N^+(CH_3)_2$—CH_2—COOH Br^- are good candidates for adsorption studies in aqueous solutions as they show good solubility up to an alkyl-chain length of 18 C atoms. The interest in analogies between the three-dimensional crystal structures and the two-dimensional monolayers formed by these compounds results from comparable intermolecular interactions in the layer planes.

The zigzag octyl chain in the title compound, (I), is nearly planar. The atoms C2 to C8 have a maximum deviation from the least-squares plane of 0.05 (4) Å. C1, N1 and C31 deviate from the plane by 0.41 (4), 0.49 (4) and 0.46 (5) Å, respectively. O1, O2, C31 and C32 are coplanar with a maximum deviation of 0.006 (2) Å. The conformation of the head region of the title molecule is comparable with that of the B form of octadecanoic acid, the atoms C31, C32, N1 and C1 in the former corresponding to the atoms C1 to C4 in the latter (Kaneko, Sakashita, Kobayashi, Kitagawa, Matsuura & Suzuki, 1994). The average C—C bond distance in the octyl chain is 1.511 Å. The C—C bond distances are alternately short and long, the average of the short distances being 1.498 (4) Å and the average of the long distances being 1.520 (4) Å.

(I)
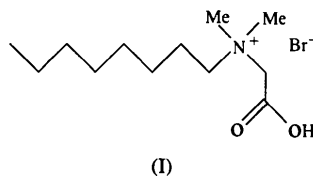
The molecules form monolayers parallel to the (001) plane and are packed in a head-to-tail arrangement. All planes defined by the alkyl chains are parallel to each other. In the polar region, each Br^- ion is coordinated by three N atoms at distances of 4.211 (3), 4.260 (3) and 4.535 (3) Å (see Fig. 2). Shorter contacts are prevented by the steric hindrance afforded by the four C atoms bonded to each N atom [compare, for example, with the results of Okuyama, Mizuguchi, Xu & Shimomura (1989) or Taga, Machida, Kimura, Hayashi, Umemura & Takenaka (1986)]. One of the three $Br\cdots N$ contacts connects two different monolayers; the other two are intralayer contacts. This threefold coordination may be the reason why the N atom has the smallest displacement parameter of all of the atoms in the molecule. One intralayer hydrogen bond, $Br\cdots H2$—O2, with a $Br\cdots O$ distance of 3.121 (3) Å, is formed.

All $C\cdots C$ distances between neighbouring alkyl chains are longer than 4 Å. There are six $C\cdots C$ contacts below 4.2 Å. The displacement parameters of the