

C5—C6	1,400 (5)	C35—C36	1,403 (5)	Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1982). <i>MULTAN11/82. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data</i> . Univs. de York, Angleterre, et de Louvain, Belgique.
C6—C7	1,439 (5)	C36—C37	1,434 (5)	Ruccia, M., Vivona, N., Piozzi, F. & Aversa, M. C. (1969). <i>Gazz. Chim. Ital.</i> 99 , 588–599.
C7—C8	1,388 (5)	C37—C38	1,372 (5)	Soufiaoui, M., Laude, B. & Arriau, J. (1977). <i>J. Heterocycl. Chem.</i> 14 , 1183–1192.
C7—C9	1,468 (5)	C39—C40	1,480 (5)	
C9—C10	1,476 (5)	C40—C41	1,397 (6)	
C10—C11	1,386 (6)	C40—C45	1,381 (5)	
C10—C15	1,368 (5)	C41—C42	1,388 (5)	
C11—C12	1,379 (6)	C42—C43	1,399 (6)	
C12—C13	1,368 (6)	C43—C44	1,366 (6)	
C13—C14	1,369 (6)	C44—C45	1,394 (6)	
C14—C15	1,390 (6)	C46—C47	1,388 (6)	
C16—C17	1,374 (6)	C46—C51	1,387 (6)	
C16—C21	1,388 (5)	C47—C48	1,385 (6)	
C17—C18	1,394 (6)	C48—C49	1,390 (6)	
C18—C19	1,367 (6)	C49—C50	1,377 (6)	
C19—C20	1,381 (6)	C50—C51	1,354 (6)	
C20—C21	1,378 (6)			
C1—N1—C8	110,0 (3)	C31—C32—C33	116,9 (4)	<i>Acta Cryst.</i> (1993). C49 , 2145–2147
C1—N1—C22	123,6 (3)	C32—C33—C34	122,0 (4)	
C8—N1—C22	126,3 (3)	C33—C34—C35	120,7 (4)	
N3—N2—C9	117,8 (3)	C34—C35—C36	118,0 (4)	Structure of 1-Ethyl-3-(heptamethyltri-siloxan-3-yl)pyrroline Hydrochloride, C₁₃H₃₂NO₂Si₃⁺Cl⁻
N2—N3—C16	117,6 (3)	C31—C36—C35	119,6 (3)	
N1—C1—C2	130,8 (4)	C31—C36—C37	107,8 (3)	MATTHIAS RAMM
N1—C1—C6	107,1 (3)	C35—C36—C37	132,5 (4)	<i>Zentrum für Selektive Organische Synthese, Rudower Chaussee 5, 12489 Berlin, Germany</i>
C2—C1—C6	122,0 (4)	C36—C37—C38	106,0 (4)	
C1—C2—C3	117,1 (4)	C36—C37—C39	124,4 (4)	
C2—C3—C4	121,4 (4)	C38—C37—C39	129,5 (4)	
C3—C4—C5	122,3 (4)	N31—C38—C37	110,2 (4)	
C4—C5—C6	118,0 (4)	N32—C39—C37	124,4 (4)	
C1—C6—C5	119,2 (3)	N32—C39—C40	116,1 (3)	
C1—C6—C7	107,1 (4)	C37—C39—C40	119,4 (3)	
C5—C6—C7	133,6 (4)	C39—C40—C41	120,6 (4)	
C6—C7—C8	106,0 (3)	C39—C40—C45	119,7 (4)	
C6—C7—C9	124,4 (4)	C41—C40—C45	119,7 (3)	
C8—C7—C9	129,6 (4)	C40—C41—C42	121,0 (4)	
N1—C8—C7	109,8 (3)	C41—C42—C43	118,0 (4)	
N2—C9—C7	126,4 (4)	C42—C43—C44	121,6 (4)	
N2—C9—C10	115,0 (4)	C43—C44—C45	119,9 (5)	
C7—C9—C10	118,6 (4)	C40—C45—C44	119,8 (4)	
C9—C10—C11	121,1 (4)	N3—C16—C17	121,6 (4)	
C9—C10—C15	121,4 (4)	N3—C16—C21	118,2 (4)	
C11—C10—C15	117,5 (4)	C17—C16—C21	120,1 (4)	
C10—C11—C12	120,9 (5)	C16—C17—C18	119,6 (4)	
C11—C12—C13	120,2 (5)	C17—C18—C19	121,6 (5)	
C12—C13—C14	120,3 (4)	C18—C19—C20	117,4 (4)	
C13—C14—C15	118,6 (5)	C19—C20—C21	122,9 (5)	
C10—C15—C14	122,4 (4)	C16—C21—C20	118,5 (4)	
C31—N31—C38	108,1 (3)	N33—C46—C47	122,5 (4)	
C31—N31—C52	124,7 (4)	N33—C46—C51	118,6 (4)	
C38—N31—C52	127,3 (4)	C47—C46—C51	118,9 (4)	
N33—N32—C39	118,9 (3)	C46—C47—C48	120,9 (4)	
N32—N33—C46	118,5 (3)	C47—C48—C49	119,3 (4)	
N31—C31—C32	129,3 (4)	C48—C49—C50	118,9 (4)	
N31—C31—C36	107,9 (3)	C49—C50—C51	122,1 (5)	
C32—C31—C36	122,8 (4)	C46—C51—C50	119,9 (4)	

Les listes des facteurs de structure, des facteurs d'agitation thermique anisotrope, des coordonnées des atomes d'hydrogène, des distances et angles des atomes d'hydrogène, ont été déposées au dépôt d'archives de la British Library Document Supply Centre (Supplementary Publication No. SUP 71352: 15 pp.). On peut en obtenir des copies en s'adressant à: The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, Angleterre. [Référence de CIF: PA1035]

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Abstract

The structure consists of double layers with a head-to-head arrangement of the polar parts of the molecules. The chloride ions interact with the polar parts within the same and neighbouring layers. The polar regions are held together by electrostatic interactions and the nonpolar regions by weak van der Waals forces.

Comment

The question about the nature of structures formed by surfactants in absorption layers has been discussed in an increasing number of publications in the last few years (Charvolin, 1990; Heusch, 1991; Egorov, Zaitsev, Klyamkin, Ksenofontova & Zubov, 1990). A possible conclusion is that there is a relationship between the three-dimensional arrangement of the surfactant molecules in the crystal lattice and their two-dimensional mono- or bilayers at the interfaces. The arrangement of the molecules may be

influenced by comparable intermolecular interactions. Another interesting point is the Si—O—Si angle which, as many earlier publications have shown, has a large variability (140–180°). The reason for this is not yet fully understood.

The investigation of the crystal structures of amphiphiles should give information about their possible arrangement at the interface (Lehmann, Buschmann, Luger, Demoulin, Fuhrhop & Eichhorn, 1990; Abrahamsson, Dahlen, Löfgren & Pascher, 1978; Schmaucks, Sonnek, Wüstneck, Herbst & Ramm, 1992). So far, only a few structures of trisiloxanes have been published, but this paper is part of a series which investigates the X-ray structures of some selected siloxane surfactants. A comparison of all crystal structures with the data from the adsorption isotherms will appear elsewhere.

The final positional parameters with equivalent isotropic temperature factors of the non-H atoms are given in Table 1. A drawing of the molecule with the atomic numbering scheme is shown in Fig. 1. Table 2 contains bond lengths and angles and some intermolecular distances are compiled in Table 3. As a result of high thermal movement, especially of the terminal atoms, some bond lengths were found to be too short. For comparison, calculations with the semiempirical method MNDO (*MOPAC*; Stewart, 1987) were carried out and resulted in theoretical Si—O bond lengths of 1.63 Å and Si—C bond lengths of 1.82 Å.

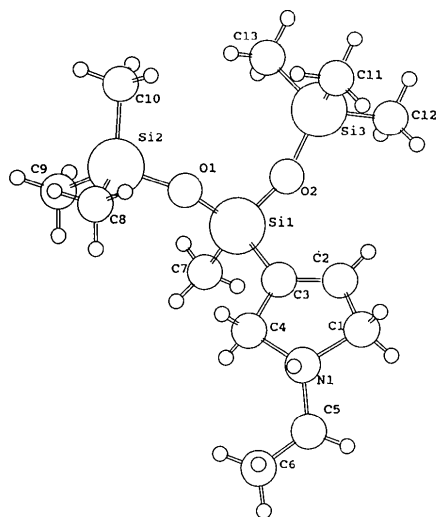


Fig. 1. *PLUTO* (Motherwell & Clegg, 1976) drawing of the molecular structure with crystallographic numbering scheme.

Of special interest is the packing of the molecules, shown in Fig. 2. The structure consists of double layers parallel to the (100) plane with a head-to-head arrangement of the polar parts. The molecules in

every layer are packed in the two-dimensional space group P_g . The area per molecule is 62.52 (4) Å², which is comparable with other siloxane-containing ammonium compounds (Ramm, Schulz, Sonnek & Schmaucks, 1990) and much larger than the cross section normally required by a hydrocarbon chain in the solid state, which amounts to 20 Å² (Abrahamsson, Ställberg-Stenhagen & Stenhagen, 1963; Sundell, 1977). The non-polar regions are held together by weak van der Waals interactions between the methyl groups, the intermolecular C...C distances being larger than 4 Å. Favourable electrostatic interactions within the polar regions are possible as chloride ions are distributed between the head groups, as shown in Fig. 2. Each chloride ion is surrounded by four head groups. The nitrogen atom N(1) and the chloride ion form a hydrogen bond characterized by the distance N(1)...Cl(1)(-x + 1, -y + 1, -z + 1) = 2.997 (5) Å. Distances to the N atoms of the other three head groups are comparable, as shown in Table 3. The chloride ions interact with the polar part of the molecules within the same layer and in the neighbouring layer. The electrostatic interactions in the polar region dominate the molecular arrangement probably to such an extent that the non-polar parts cannot adopt arrangements with optimum van der Waals interactions.

The pyrrole ring is nearly planar with an average deviation of the atoms from the least-squares plane of 0.02 (5) Å. The Si—O—Si angles lie within the range found in other trisiloxanes (Mooney, Choy, Knox & Kenney, 1975; Graalman, Klingebiel, Clegg, Haase & Sheldrick, 1984; Schmidt-Bäse & Klingebiel, 1989; Ramm, Schulz, Sonnek, Schmaucks, 1990).

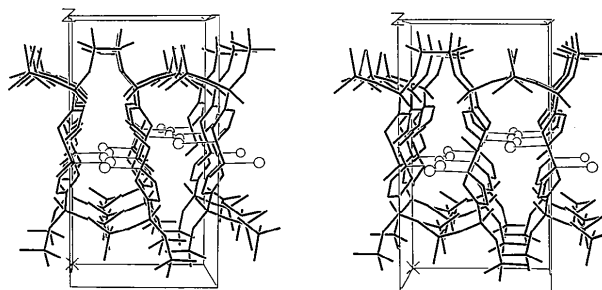


Fig. 2. *CELLGRAF* (Reck & Kretschmer, 1991) drawing of the molecules in the unit cell. Hydrogen bonds are shown by thin lines.

Experimental

Crystal data

$C_{13}H_{32}NO_2Si_3 \cdot Cl^-$

$M_r = 354.11$

Monoclinic

$D_x = 1.0578 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71069 \text{ \AA}$

$P2_1/c$	Cell parameters from 25 reflections
$a = 17.794$ (5) Å	$\theta = 11-17^\circ$
$b = 10.002$ (3) Å	$\mu = 0.331$ mm ⁻¹
$c = 12.502$ (4) Å	$T = 293$ K
$\beta = 92.16$ (3)°	Plate
$V = 2223.5$ (5) Å ³	$0.4 \times 0.3 \times 0.3$ mm
$Z = 4$	Colourless
Data collection	
Enraf-Nonius CAD-4 diffractometer	2328 observed reflections
$\omega/2\theta$ scans	$[I > \sigma(I)]$
Absorption correction: empirical	$\theta_{\max} = 22^\circ$
$T_{\min} = 0.577$, $T_{\max} = 0.958$	$h = -18 \rightarrow 18$
3081 measured reflections	$k = -10 \rightarrow 0$
2919 independent reflections	$l = 0 \rightarrow 13$
	2 standard reflections
	frequency: 120 min
	intensity variation: -33% over 41.6 h

Refinement

Refinement on F	$(\Delta/\sigma)_{\max} = 0.02$
$R = 0.062$	$\Delta\rho_{\max} = 0.276$ e Å ⁻³
$wR = 0.072$	$\Delta\rho_{\min} = -0.187$ e Å ⁻³
$S = 2.927$	Atomic scattering factors from Enraf-Nonius <i>SDP-Plus</i> (Frenz, 1982)
1675 reflections	
181 parameters	
$w = 1/\sigma(F)^2$	

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

	x	y	z	B_{eq}
Cl(1)	0.4623 (1)	0.7280 (2)	0.0398 (1)	6.84 (4)
Si(1)	0.73455 (9)	-0.0393 (2)	0.6347 (1)	5.39 (4)
Si(2)	0.7924 (1)	0.2363 (2)	0.5468 (2)	6.60 (5)
Si(3)	0.8792 (1)	-0.1730 (2)	0.7332 (2)	7.55 (6)
O(1)	0.7691 (2)	0.1040 (5)	0.6123 (3)	7.0 (1)
O(2)	0.7979 (2)	-0.1348 (5)	0.6836 (4)	9.1 (1)
N(1)	0.5475 (2)	0.0323 (5)	0.8176 (4)	5.3 (1)
C(1)	0.5924 (4)	-0.0630 (7)	0.8873 (5)	6.8 (2)
C(2)	0.6586 (3)	-0.0902 (6)	0.8246 (5)	5.8 (2)
C(3)	0.6611 (3)	-0.0228 (5)	0.7354 (4)	4.2 (1)
C(4)	0.5934 (4)	0.0641 (7)	0.7217 (5)	7.5 (2)
C(5)	0.4710 (5)	-0.0216 (8)	0.7929 (6)	9.0 (2)
C(6)	0.4218 (4)	0.0771 (9)	0.7466 (7)	10.7 (2)
C(7)	0.6932 (4)	-0.1118 (9)	0.5141 (6)	10.8 (2)
C(8)	0.7346 (5)	0.3741 (9)	0.5886 (7)	10.4 (3)
C(9)	0.7765 (7)	0.210 (1)	0.4032 (7)	12.8 (3)
C(10)	0.8907 (5)	0.272 (1)	0.5832 (8)	11.9 (3)
C(11)	0.9029 (7)	-0.066 (1)	0.842 (1)	19.2 (5)
C(12)	0.8770 (7)	-0.340 (1)	0.781 (1)	17.8 (5)
C(13)	0.9488 (5)	-0.153 (1)	0.6371 (9)	17.0 (4)

Table 2. Geometric parameters (Å, °)

Si(1)—O(1)	1.589 (5)	Si(3)—C(12)	1.775 (11)
Si(1)—O(2)	1.583 (5)	Si(3)—C(13)	1.769 (10)
Si(1)—C(3)	1.856 (5)	N(1)—C(1)	1.501 (8)
Si(1)—C(7)	1.805 (8)	N(1)—C(4)	1.510 (8)
Si(2)—O(1)	1.618 (5)	N(1)—C(5)	1.486 (9)
Si(2)—C(8)	1.809 (9)	C(1)—C(2)	1.465 (9)
Si(2)—C(9)	1.826 (9)	C(2)—C(3)	1.305 (8)
Si(2)—C(10)	1.826 (9)	C(3)—C(4)	1.490 (9)
Si(3)—O(2)	1.599 (4)	C(5)—C(6)	1.428 (12)
Si(3)—C(11)	1.769 (12)		

O(1)—Si(1)—O(2)	109.7 (2)	C(11)—Si(3)—C(12)	108.5 (5)
O(1)—Si(1)—C(3)	109.0 (2)	C(11)—Si(3)—C(13)	107.4 (4)
O(1)—Si(1)—C(7)	111.3 (2)	C(12)—Si(3)—C(13)	111.2 (4)
O(2)—Si(1)—C(3)	107.5 (2)	Si(1)—O(1)—Si(2)	159.2 (2)
O(2)—Si(1)—C(7)	110.0 (2)	Si(1)—O(2)—Si(3)	156.2 (2)
C(3)—Si(1)—C(7)	109.1 (2)	C(1)—N(1)—C(4)	107.6 (3)
O(1)—Si(2)—C(8)	108.5 (2)	C(1)—N(1)—C(5)	110.7 (3)
O(1)—Si(2)—C(9)	110.4 (2)	C(4)—N(1)—C(5)	115.5 (3)
O(1)—Si(2)—C(10)	107.1 (2)	N(1)—C(1)—C(2)	103.2 (3)
C(8)—Si(2)—C(9)	109.0 (3)	C(1)—C(2)—C(3)	114.5 (4)
C(8)—Si(2)—C(10)	109.2 (3)	Si(1)—C(3)—C(2)	125.5 (3)
C(9)—Si(2)—C(10)	112.6 (3)	Si(1)—C(3)—C(4)	124.1 (3)
O(2)—Si(3)—C(11)	109.9 (3)	C(2)—C(3)—C(4)	110.3 (3)
O(2)—Si(3)—C(12)	109.0 (3)	N(1)—C(4)—C(3)	104.2 (3)
O(2)—Si(3)—C(13)	110.8 (3)	N(1)—C(5)—C(6)	112.1 (4)

Table 3. Selected contact distances (Å)

Cl(1)···N(1 ⁱ)	2.997 (5)	Cl(1)···N(1 ⁱⁱⁱ)	4.554 (5)
Cl(1)···N(1 ⁱⁱ)	4.427 (5)	Cl(1)···N(1 ^{iv})	4.875 (5)

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

The crystals were obtained by treating liquid 3-heptamethyltri-siloxypropylpyrrolidine with dry gaseous hydrogen chloride. The positions of the H atoms were calculated.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71373 (36 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SE1021]

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