C3′B	0.4001 (12)	−0.1273 (5)	0.4095 (3)	0.049 (4)
C2′B	0.3740 (12)	−0.0729 (6)	0.4481 (3)	0.054 (4)
C1′B	0.3371 (11)	0.0123 (5)	0.4384 (3)	0.045 (3)
C6′B	0.3143 (12)	0.0417 (6)	0.3904 (3)	0.058 (4)
C5′B	0.3404 (13)	−0.0133 (5)	0.3517 (3)	0.056 (4)
C10B	0.2256 (15)	0.1960 (5)	0.5422 (4)	0.080 (5)
C2B	0.3339 (16)	0.1159 (5)	0.5562 (3)	0.057 (4)
C3B	0.5383 (17)	0.1362 (6)	0.5730 (4)	0.063 (4)
C4B	0.5502 (16)	0.1235 (6)	0.6278 (4)	0.057 (4)
C9B	0.3807 (16)	0.0851 (5)	0.6427 (3)	0.049 (4)
C1B	0.2466 (16)	0.0735 (7)	0.6008 (4)	0.064 (4)
C8B	0.3442 (15)	0.0629 (6)	0.6922 (3)	0.067 (4)
C7B	0.4990 (18)	0.0805 (7)	0.7236 (4)	0.082 (4)
C6B	0.6672 (17)	0.1174 (7)	0.7094 (4)	0.089 (5)
C5B	0.7008 (14)	0.1371 (6)	0.6602 (4)	0.084 (5)

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

O1A—C3A	1.18 (1)	O1B—C3B	1.23 (1)
O2A—C1A	1.20 (1)	O2B—C1B	1.23 (1)
O3A—N3A	1.24 (1)	O3B—N3B	1.18 (1)
O4A—N3A	1.20 (1)	O4B—N3B	1.19 (1)
N1A—N2A	1.25 (1)	N1B—N2B	1.23 (1)
N1A—C1′A	1.46 (1)	N1B—C1′B	1.44 (1)
N2A—C2A	1.49 (1)	N2B—C2B	1.49 (1)
N3A—C4′A	1.47 (1)	N3B—C4′B	1.47 (1)
C4′A—C3′A	1.39 (1)	C4′B—C3′B	1.39 (1)
C4′A—C5′A	1.41 (1)	C4′B—C5′B	1.37 (1)
C3′A—C2′A	1.37 (1)	C3′B—C2′B	1.37 (1)
C2′A—C1′A	1.39 (1)	C2′B—C1′B	1.40 (1)
C1′A—C6′A	1.39 (1)	C1′B—C6′B	1.40 (1)
C6′A—C5′A	1.36 (1)	C6′B—C5′B	1.38 (1)
C10A—C2A	1.56 (1)	C10B—C2B	1.52 (1)
C2A—C3A	1.53 (1)	C2B—C3B	1.52 (1)
C2A—C1A	1.54 (2)	C2B—C1B	1.51 (1)
C3A—C4A	1.48 (1)	C3B—C4B	1.51 (1)
C4A—C9A	1.40 (2)	C4B—C9B	1.38 (2)
C4A—C5A	1.40 (1)	C4B—C5B	1.38 (2)
C9A—C1A	1.49 (1)	C9B—C1B	1.48 (1)
C9A—C8A	1.40 (2)	C9B—C8B	1.41 (1)
C8A—C7A	1.38 (2)	C8B—C7B	1.39 (2)
C7A—C6A	1.39 (2)	C7B—C6B	1.35 (2)
C6A—C5A	1.37 (2)	C6B—C5B	1.39 (2)
N2A—N1A—C1′A	112.6 (6)	N2B—N1B—C1′B	112.8 (6)
N1A—N2A—C2A	113.4 (6)	N1B—N2B—C2B	113.6 (6)
O3A—N3A—O4A	123.4 (9)	O3B—N3B—O4B	122.0 (9)
O4A—N3A—C4′A	119.6 (9)	O4B—N3B—C4′B	117.7 (8)
O3A—N3A—C4′A	117.0 (8)	O3B—N3B—C4′B	120.0 (9)
N3A—C4′A—C5′A	119.2 (8)	N3B—C4′B—C5′B	118.6 (7)
N3A—C4′A—C3′A	119.5 (7)	N3B—C4′B—C3′B	118.5 (8)
C3′A—C4′A—C5′A	121.3 (8)	C3′B—C4′B—C5′B	122.8 (8)
C4′A—C3′A—C2′A	118.4 (8)	C4′B—C3′B—C2′B	118.8 (7)
C3′A—C2′A—C1′A	120.1 (8)	C3′B—C2′B—C1′B	119.0 (7)
N1A—C1′A—C2′A	115.1 (7)	N1B—C1′B—C2′B	123.9 (7)
C2′A—C1′A—C6′A	121.4 (8)	C2′B—C1′B—C6′B	121.2 (7)
N1A—C1′A—C6′A	123.5 (7)	N1B—C1′B—C6′B	114.7 (7)
C1′A—C6′A—C5′A	119.3 (8)	C1′B—C6′B—C5′B	119.4 (8)
C4′A—C5′A—C6′A	119.4 (8)	C4′B—C5′B—C6′B	118.5 (8)
N2A—C2A—C10A	114.6 (7)	N2B—C2B—C10B	116.6 (7)
C10A—C2A—C1A	110.9 (7)	C10B—C2B—C1B	112.0 (8)
C10A—C2A—C3A	111.5 (7)	C10B—C2B—C3B	110.9 (8)
N2A—C2A—C1A	105.7 (7)	N2B—C2B—C1B	107.5 (7)
N2A—C2A—C3A	107.9 (7)	N2B—C2B—C3B	106.0 (8)
C3A—C2A—C1A	105.8 (7)	C3B—C2B—C1B	102.8 (7)
O1A—C3A—C2A	126.5 (8)	O1B—C3B—C2B	128.0 (9)
C2A—C3A—C4A	105.5 (7)	C2B—C3B—C4B	108.7 (8)
O1A—C3A—C4A	127.9 (8)	O1B—C3B—C4B	123.3 (9)
C3A—C4A—C5A	128.7 (9)	C3B—C4B—C5B	130.8 (9)
C3A—C4A—C9A	112.2 (7)	C3B—C4B—C9B	107.7 (9)
C9A—C4A—C5A	118.9 (9)	C9B—C4B—C5B	121.3 (8)
C4A—C9A—C8A	122.8 (8)	C4B—C9B—C8B	122.7 (8)
C4A—C9A—C1A	109.1 (9)	C4B—C9B—C1B	111.0 (8)
C1A—C9A—C8A	127.8 (9)	C1B—C9B—C8B	126.3 (9)
C2A—C1A—C9A	106.5 (9)	C2B—C1B—C9B	108.4 (8)
O2A—C1A—C9A	127.1 (10)	O2B—C1B—C9B	127.1 (8)
O2A—C1A—C2A	126.3 (9)	O2B—C1B—C2B	124.5 (8)
C9A—C8A—C7A	115.8 (9)	C9B—C8B—C7B	113.4 (9)
C8A—C7A—C6A	122.3 (11)	C8B—C7B—C6B	124.4 (10)
C7A—C6A—C5A	121.4 (11)	C7B—C6B—C5B	120.8 (11)
C4A—C5A—C6A	118.6 (10)	C4B—C5B—C6B	117.0 (10)

Empirical absorption corrections based on an ellipsoidal fit to ψ-scan data were applied (Kopfmann & Huber, 1968). The H atoms of the benzene rings were refined riding on the parent C atoms at a distance of 1.08 Å. Each Me group was refined as a rigid group. The H atoms had fixed isotropic temperature factors. Refinement was by blocked full-matrix least-squares methods. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985); *SIR*88 (Burla *et al.*, 1989). Program(s) used to refine structure: *SHELX*76 (Sheldrick, 1976). Software used to prepare material for publication: *PARST* (Nardelli, 1983). Molecular graphics: *ORTEP*II (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, bond angles involving H atoms and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71644 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: NA1042]

References

Burla, M. C., Camalli, M., Cascarano, G., Giacovazzo, C., Polidori, G., Spagna, R. & Viterbo, D. (1989). *J. Appl. Cryst.* **22**, 389–393.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Kopfmann, G. & Huber, R. (1968). *Acta Cryst.* A**24**, 348–351.

Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.

Sheldrick, G. M. (1976). *SHELX76. Program for Crystal Structure Determination.* Univ. of Cambridge, England.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Acta Cryst. (1994). C**50**, 631–635

Butyl[3-(1,1,3,3,5,5,5-heptamethyltrisiloxan-1-yl)propyl]dimethylammonium Bromide, $C_{16}H_{42}NO_2Si_3^+.Br^-$, at 173 and 301 K

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Abstract

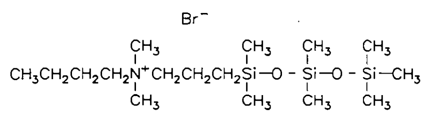
The molecules form double layers in head–head arrangements. The non-polar regions of the layers are held together by weak van der Waals interactions and the polar regions mainly by electrostatic interactions. One of the Si—O—Si bond angles is much

smaller at low temperature (173 K) than at room temperature (301 K).

Comment

This article is part of a series which describes the structure investigations of some selected siloxane surfactants. The extraordinary interfacial activity of siloxane surfactants in comparison to structurally similar hydrocarbon compounds can be explained in several different ways. Neumann & Renzow (1969) suggested that the siloxane groups of the amphiphiles form an absorption layer consisting exclusively of methyl groups, comparable to an idealized paraffin, and that there is remarkable flexibility of the siloxanyl groups. In more recent publications (Charvolin, 1990; Egorov, Zaitsev, Klyamkin, Ksenofontova & Zubov, 1990; Heusch, 1991) the existence of a long-range crystalline order of amphiphiles in aqueous solution is discussed.

The aim of our investigation is to show the relationship between the crystal structure of siloxane surfactants in the solid state and their arrangement at interfaces by comparing the required surface areas per molecule. The surface area per molecule of butyl[3-(1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)propyl]dimethylammonium bromide, an isomer of the title compound, determined using the X-ray crystal-structure analysis, is 59.8 Å^2, which is in good agreement with the 62.8 Å^2 determined at the water/air interface (Schmaucks, Sonnek, Wüstneck, Herbst & Ramm, 1992). In this article we report the crystal structure of *N*-butyl-3-(1,1,3,3,5,5,5-heptamethyltrisiloxan-1-yl)propyl-*N*,*N*-dimethylammonium bromide (I) determined from two separate measurements at temperatures of 173 (low) and 301 K (room).



(I)

A drawing of the molecule with the atomic numbering scheme is shown in Fig. 1. The molecules form double layers with a head–head arrangement. The packing of the molecules is shown in Fig. 2. The N atom carries a formal positive charge. There are two intra-layer Br···N(4) contacts and one inter-layer contact which form a two-dimensional network (Table 2). They are larger than the sum of van der Waals radii (3.4 Å) because the methyl groups at N(4) do not allow a Br···N(4) distance of less than 3.8 Å (see, for example, Taga, Machida, Kimura, Hayashi, Umemura & Takenaka, 1986). The interactions between the hydrophobic parts of neighbouring double layers consist mainly of weak van der Waals

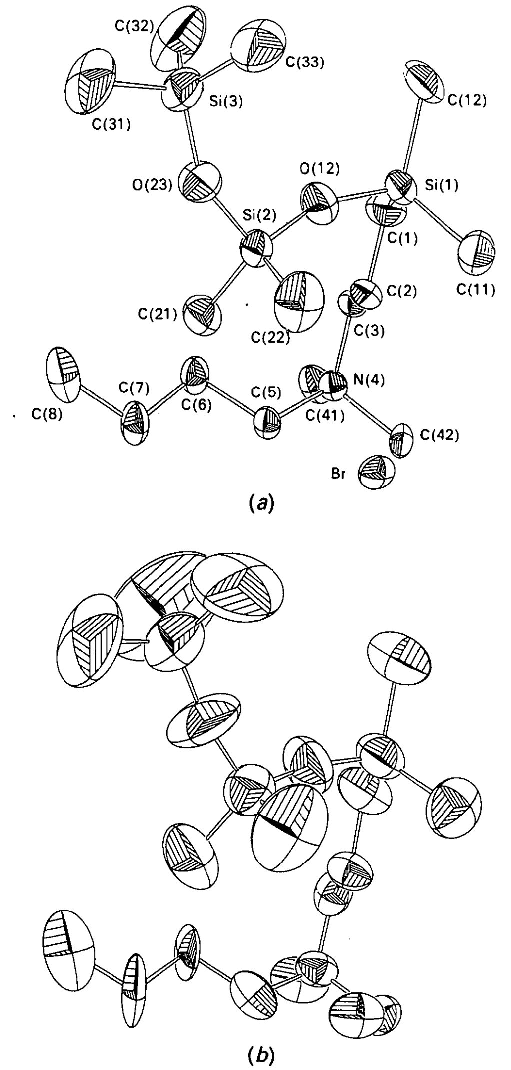


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of the molecular structure with crystallographic numbering scheme. (*a*) 173 K and (*b*) 301 K.

interactions, the C···C distances being larger than 3.9 Å. Despite the different molecular structures the packing symmetry is the same as in two other amphiphilic trisiloxanes (Ramm, Schulz, Sonnek & Schmaucks, 1990). This is surprising because the molecules of title compound have a greater flexibility than the other two trisiloxanes, which would allow a denser packing of the molecules within each layer. The area occupied per molecule is $(b \times c)/2 = 58.8$ (1) (173 K) and 60.46 (3) Å^2 (301 K). Measurements at the water/air interface suggested an area of 45 Å^2 per molecule.

Most bond lengths in the siloxane and butyl parts of the molecules were shorter at 301 K compared with those measured at 273 K. This is certainly due to the large thermal motion of these parts of the

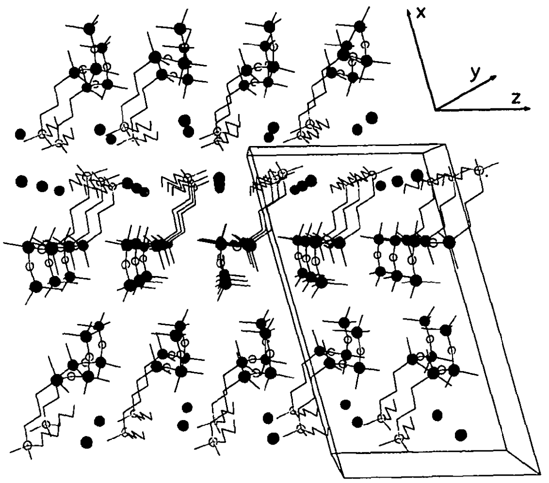


Fig. 2. Packing of the title compound viewed along the *b* axis. O and N atoms are symbolized by open circles, Br^- ions and Si atoms by filled circles.

molecule. Cooling the crystal to 173 K reduces the displacement parameters by a factor of two or three. In both measurements the part of the molecule next to the N atom, which has the strongest interactions with the Br ions, has the smallest thermal motion.

The most striking difference between the data measured at different temperatures is the Si(2)—O(23)—Si(3) bond angle, which is much larger at 301 K [163.1 (7)°] than at 173 K [147.0 (4)°]. This is consistent with the quantum-chemical calculations of Gibbs (1982), who found that only a little energy is needed to stretch an Si—O—Si angle in disiloxane from its optimum of 140° to 180°, but much more energy to reduce the angle. Therefore, if other influences can be neglected, thermal motion should increase the Si—O—Si angle. To the authors' knowledge this is the first time the influence of temperature on the Si—O—Si angle of an organic siloxane compound has been shown by crystallographic methods.

Experimental

Structure at 173K

Crystal data

$C_{16}H_{42}NO_2Si_3^+.Br^-$
M_r = 444.68
Monoclinic
$P2_1/c$
a = 22.723 (7) Å
b = 8.908 (3) Å
c = 13.20 (2) Å
β = 104.34 (6)°
V = 2588 (4) Å^3
Z = 4
D_x = 1.141 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 9–13°
μ = 1.71 mm^{-1}
T = 173 K
Rhombic
0.4 × 0.25 × 0.03 mm
Colourless
Crystal source: acetone solution

Data collection

CAD-4 diffractometer
ω-2θ scans
Absorption correction: refined from ΔF
T_{min} = 0.87, T_{max} = 1.12
3261 measured reflections
3071 independent reflections
2217 observed reflections [$F_o > 2\sigma(F_o)$]
R_{int} = 0.029

θ_{max} = 22°
h = 0 → 23
k = 0 → 9
l = −13 → 13
2 standard reflections (73$\bar{2}$, 10,2,$\bar{1}$)
frequency: 60 min
intensity variation: −4.8% over 48 h exposure

Refinement

Refinement on F
R = 0.049
wR = 0.032
S = 2.0
2175 reflections
208 parameters
H-atom parameters not refined

$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{max}$ = 0.06
$\Delta\rho_{max}$ = 0.5 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *MolEN* (Fair, 1990)

Structure at 301 K

Crystal data

$C_{16}H_{42}NO_2Si_3^+.Br^-$
M_r = 444.68
Monoclinic
$P2_1/c$
a = 23.128 (6) Å
b = 9.031 (2) Å
c = 13.389 (4) Å
β = 105.11 (3)°
V = 2699.9 (13) Å^3
Z = 4
D_x = 1.094 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 7–10°
μ = 1.645 mm^{-1}
T = 301 K
Rhombic
0.4 × 0.25 × 0.03 mm
Colourless
Crystal source: acetone solution

Data collection

CAD-4 diffractometer
ω-2θ scans
Absorption correction: empirical ψ-scans
T_{min} = 0.89, T_{max} = 1.00
4577 measured reflections
4337 independent reflections
1574 observed reflections [$F_o > 2\sigma(F_o)$]
R_{int} = 0.024

θ_{max} = 22°
h = 0 → 21
k = 0 → 10
l = −15 → 15
2 standard reflections ($\bar{5}\bar{3}\bar{2}$, 10,0,0)
frequency: 60 min
intensity variation: −8.5% over 85 h exposure

Refinement

Refinement on F
R = 0.062
wR = 0.033
S = 1.9
1403 reflections
208 parameters
H-atom parameters not refined

$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{max}$ = 0.01
$\Delta\rho_{max}$ = 0.5 e Å^{-3}
$\Delta\rho_{min}$ = −0.18 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *MolEN* (Fair, 1990)

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

First line 173 K data; second line 301 K data.

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

	x	y	z	U_{eq}
Br	0.09769 (3)	0.90247 (9)	0.20092 (5)	0.0369 (2)
	0.09594 (5)	0.90295 (14)	0.20283 (8)	0.0829 (4)
Si1	0.29787 (9)	0.8515 (2)	0.13550 (16)	0.0411 (7)
	0.29417 (13)	0.8499 (3)	0.1422 (2)	0.0886 (14)
Si2	0.28727 (9)	1.1340 (2)	0.27796 (15)	0.0437 (7)
	0.28981 (14)	1.1228 (4)	0.2865 (2)	0.1009 (14)
Si3	0.41296 (10)	1.2789 (3)	0.30307 (19)	0.0589 (8)
	0.41289 (18)	1.2754 (4)	0.3213 (3)	0.1467 (19)
O12	0.3018 (2)	1.0098 (5)	0.2001 (3)	0.0556 (17)
	0.2967 (3)	1.0009 (7)	0.2066 (5)	0.116 (3)
O23	0.3440 (2)	1.2459 (6)	0.3074 (4)	0.069 (2)
	0.3492 (3)	1.2147 (9)	0.3159 (6)	0.168 (4)
N4	0.0821 (2)	0.9851 (5)	−0.1338 (3)	0.0235 (17)
	0.0828 (3)	0.9850 (7)	−0.1312 (5)	0.058 (3)
C1	0.2494 (3)	0.8832 (8)	0.0019 (4)	0.045 (3)
	0.2473 (3)	0.8834 (11)	0.0070 (6)	0.091 (4)
C2	0.1836 (2)	0.9198 (7)	−0.0049 (4)	0.032 (2)
	0.1818 (3)	0.9166 (10)	−0.0017 (5)	0.066 (4)
C3	0.1492 (2)	0.9477 (7)	−0.1168 (4)	0.029 (2)
	0.1476 (3)	0.9488 (9)	−0.1133 (5)	0.066 (4)
C5	0.0710 (3)	1.1146 (7)	−0.0676 (4)	0.032 (2)
	0.0710 (3)	1.1116 (9)	−0.0650 (5)	0.067 (4)
C6	0.1045 (3)	1.2576 (6)	−0.0749 (4)	0.034 (2)
	0.1037 (4)	1.2515 (9)	−0.0722 (6)	0.079 (4)
C7	0.0854 (3)	1.3756 (7)	−0.0041 (4)	0.042 (3)
	0.0845 (4)	1.3668 (9)	−0.0038 (6)	0.111 (5)
C8	0.1249 (3)	1.5145 (7)	0.0077 (5)	0.064 (3)
	0.1180 (5)	1.5008 (10)	0.0082 (7)	0.167 (7)
C11	0.2658 (3)	0.7017 (7)	0.2029 (5)	0.057 (3)
	0.2619 (4)	0.7005 (11)	0.2032 (6)	0.123 (5)
C12	0.3763 (3)	0.8052 (8)	0.1282 (5)	0.071 (3)
	0.3714 (4)	0.8101 (12)	0.1391 (7)	0.133 (6)
C21	0.2205 (3)	1.2405 (8)	0.2094 (5)	0.060 (3)
	0.2272 (4)	1.2452 (11)	0.2275 (8)	0.167 (7)
C22	0.2752 (3)	1.0495 (9)	0.3968 (5)	0.093 (4)
	0.2769 (5)	1.0412 (14)	0.4007 (7)	0.219 (8)
C31	0.4359 (3)	1.4583 (8)	0.3702 (6)	0.104 (4)
	0.4229 (6)	1.4503 (14)	0.3835 (10)	0.285 (10)
C32	0.4178 (4)	1.2871 (10)	0.1682 (6)	0.127 (4)
	0.4221 (7)	1.296 (2)	0.1925 (9)	0.378 (13)
C33	0.4613 (3)	1.1261 (10)	0.3698 (6)	0.119 (5)
	0.4657 (5)	1.1442 (16)	0.3877 (11)	0.345 (13)
C41	0.0569 (3)	1.0176 (7)	−0.2471 (4)	0.042 (2)
	0.0586 (4)	1.0200 (10)	−0.2442 (5)	0.097 (5)
C42	0.0475 (3)	0.8542 (6)	−0.1086 (4)	0.035 (2)
	0.0492 (3)	0.8555 (8)	−0.1069 (5)	0.071 (4)

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

	173K		301K
Si1—O12	1.639 (5)	Si1—O12	1.606 (7)
Si1—C1	1.855 (6)	Si1—C1	1.876 (8)
Si1—C11	1.850 (7)	Si1—C11	1.834 (10)
Si1—C12	1.855 (8)	Si1—C12	1.833 (10)
Si2—O12	1.599 (5)	Si2—O12	1.572 (7)
Si2—O23	1.599 (6)	Si2—O23	1.565 (8)
Si2—C21	1.828 (8)	Si2—C21	1.829 (10)
Si2—C22	1.821 (8)	Si2—C22	1.791 (11)
Si3—O23	1.609 (6)	Si3—O23	1.556 (9)
Si3—C31	1.839 (8)	Si3—C31	1.772 (13)
Si3—C32	1.812 (9)	Si3—C32	1.802 (13)
Si3—C33	1.832 (9)	Si3—C33	1.766 (14)
N4—C3	1.522 (7)	N4—C3	1.491 (10)
N4—C5	1.506 (8)	N4—C5	1.514 (10)
N4—C41	1.491 (7)	N4—C41	1.504 (9)
N4—C42	1.489 (8)	N4—C42	1.486 (10)
C1—C2	1.511 (9)	C1—C2	1.519 (10)
C2—C3	1.511 (8)	C2—C3	1.525 (9)
C5—C6	1.499 (9)	C5—C6	1.488 (12)
C6—C7	1.539 (9)	C6—C7	1.527 (12)
C7—C8	1.514 (9)	C7—C8	1.423 (13)
Br···N(4)	4.406 (8)	Br···N(4)	4.465 (7)
Br···N(4[i])	4.085 (8)	Br···N(4[i])	4.119 (7)
Br···N(4[ii])	4.146 (8)	Br···N(4[ii])	4.202 (7)
O12—Si1—C1	107.9 (3)	O12—Si1—C1	108.2 (4)
O12—Si1—C11	110.4 (3)	O12—Si1—C11	110.3 (4)
O12—Si1—C12	106.8 (3)	O12—Si1—C12	106.2 (4)
C1—Si1—C11	110.8 (3)	C1—Si1—C11	110.4 (4)
C1—Si1—C12	109.7 (3)	C1—Si1—C12	109.3 (4)
C11—Si1—C12	111.2 (3)	C11—Si1—C12	112.2 (5)
O12—Si2—O23	107.7 (3)	O12—Si2—O23	107.7 (4)
O12—Si2—C21	108.6 (3)	O12—Si2—C21	109.8 (4)
O12—Si2—C22	111.5 (3)	O12—Si2—C22	111.2 (5)
O23—Si2—C21	108.5 (3)	O23—Si2—C21	109.4 (5)
O23—Si2—C22	109.5 (3)	O23—Si2—C22	109.5 (5)
C21—Si2—C22	110.9 (3)	C21—Si2—C22	109.1 (5)
O23—Si3—C31	107.7 (3)	O23—Si3—C31	110.0 (6)
O23—Si3—C32	109.8 (4)	O23—Si3—C32	109.8 (6)
O23—Si3—C33	108.7 (3)	O23—Si3—C33	108.0 (6)
C31—Si3—C32	111.1 (4)	C31—Si3—C32	108.9 (7)
C31—Si3—C33	110.4 (4)	C31—Si3—C33	111.9 (7)
C32—Si3—C33	109.1 (4)	C32—Si3—C33	108.2 (7)
Si1—O12—Si2	159.4 (3)	Si1—O12—Si2	164.6 (5)
Si2—O23—Si3	147.0 (4)	Si2—O23—Si3	163.1 (6)
C3—N4—C5	112.8 (4)	C3—N4—C5	113.5 (6)
C3—N4—C41	108.2 (4)	C3—N4—C41	107.6 (6)
C3—N4—C42	111.1 (4)	C3—N4—C42	110.7 (6)
C5—N4—C41	110.8 (4)	C5—N4—C41	110.7 (6)
C5—N4—C42	107.3 (4)	C5—N4—C42	106.4 (6)
C41—N4—C42	106.4 (4)	C41—N4—C42	107.8 (6)
Si1—C1—C2	115.8 (4)	Si1—C1—C2	114.8 (5)
C1—C2—C3	111.0 (4)	C1—C2—C3	111.4 (6)
N4—C3—C2	115.9 (4)	N4—C3—C2	116.2 (6)
N4—C5—C6	116.9 (5)	N4—C5—C6	115.5 (6)
C5—C6—C7	108.5 (5)	C5—C6—C7	107.9 (7)
C6—C7—C8	111.8 (5)	C6—C7—C8	114.4 (8)

Symmetry codes: (i) $-x, 2-y, -z$; (ii) $x, \frac{3}{2}-y, \frac{1}{2}+z$.

The crystal used for cell determination was fixed inside a glass capillary, using high-vacuum grease, in an arbitrary orientation. Intensity data were corrected for Lorentz and polarization effects. For the 173 K measurements, the sample was cooled using an Enraf-Nonius FR558SH nitrogen cryostat. The structures were solved by using part of the isomorphous structure of butyl[3-(1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)propyl]dimethylammonium bromide (Ramm, Schulz, Sonnek & Schmaucks, 1990) and Fourier methods. H-atom positions were calculated at C—H 0.95 Å and kept fixed. *MolEN* (Fair, 1990) was used for computations. *PLATON*92 (Spek, 1992) was used to prepare material for publication.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71599 (47 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SE1028]

References

Charvolin, J. (1990). *Prog. Colloid Polym. Sci.* **81**, 6–8.
Egorov, V. V., Zaitsev, S. Yu., Klyamkin, A. A., Ksenofontova, O. B. & Zubov, V. P. (1990). *Kolloid Z.* **52**, 770–774.
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.

Heusch, R. (1991). *Tenside Surfactants Deterg.* **28**, 38–46.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Neumann, A. W. & Renzow, D. (1969). *Z. Phys. Chem.* **68**, 11–18.
Ramm, M., Schulz, B., Sonnek, G. & Schmaucks, G. (1990). *Cryst. Res. Technol.* **25**, 763–769.
Schmauks, G., Sonnek, G., Wüstneck, R., Herbst, M. & Ramm, M. (1992). *Langmuir*, **8**, 1724–1730.
Spek, A. L. (1992). *PLATON*92. Univ. of Utrecht, The Netherlands.
Taga, T., Machida, K., Kimura, N., Hayashi, S., Umemura, J. & Takenaka, T. (1986). *Acta Cryst.* C**42**, 608–610.

Acta Cryst. (1994). C**50**, 635–638

Cyclohexanone Semicarbazone and 4-*tert*-Butylcyclohexanone Semicarbazone

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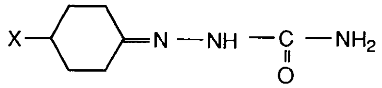
Abstract

Cyclohexanone semicarbazone (CSC), $C_7H_{13}N_3O$, and 4-*tert*-butyl-cyclohexanone (BCSC), $C_{11}H_{21}N_3O$, each adopt a slightly distorted chair conformation, with an increase of the total puckering of the six-membered ring for BCSC. The two crystal structures are very similar, with the $NHCONH_2$ groups connected in infinite ribbons through O···H—N hydrogen bonds, with distances in the range 2.84–3.12 Å. The conformation adopted by the C=O bond with respect to the N—N bond is *trans* in both crystals.

Comment

It is usually found in the crystal structures of uncomplexed thiosemicarbazones that the C=S bond is *trans* to the N—N bond, and this *trans* conformation is retained in semicarbazones, the only exception being acetone semicarbazone (Naik & Palenik, 1974). Since it has not been established what factors determine the *cis*/*trans* conformation of the semicarbazide fragment in semicarbazones, the title compounds were chosen for an X-ray investigation to provide more structural information on this class of compounds.



X = H (CSC)
= $C(CH_3)_3$ (BCSC)

The ring conformation of each compound can be described as a slightly distorted chair flattened at the C=N apex (Figs. 1 and 2), allowing the C(2)—C(1)—C(6) bond angle to increase to 115.7 (2)° for

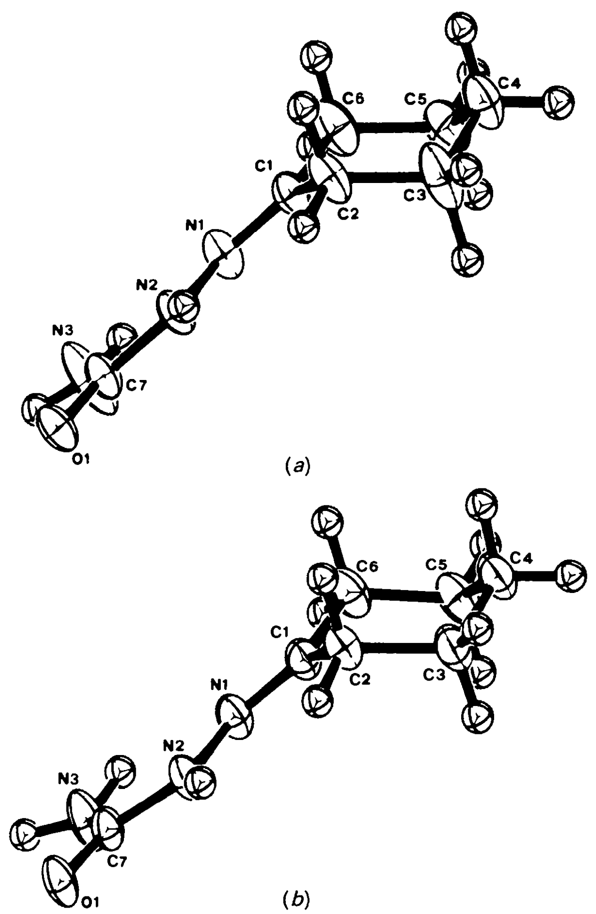


Fig. 1. Drawings of (*a*) molecule *A* and (*b*) molecule *B* in the crystal of cyclohexanone semicarbazone (CSC) showing the anisotropy of the thermal motion. The displacement ellipsoids of the non-H atoms have been scaled to the 30% probability level. The drawing is based on the atomic parameters from the final refinement.

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