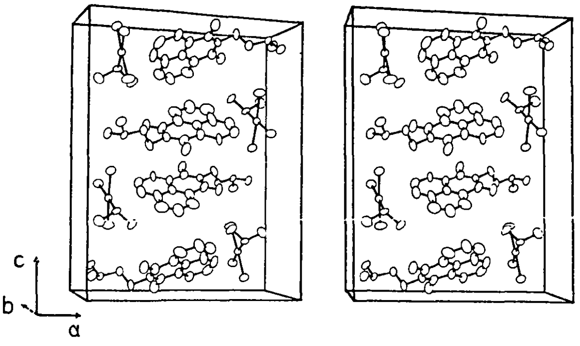

Fig. 5. Unit-cell packing for (4).

(Sobolev, Chetkina, Gol'der, Federov & Zavodnik, 1973; Grigor'eva, Chetkina, Neigauz & Gol'der, 1975; Grigor'eva & Chetkina, 1977).

The imide ring *C* consists of three consecutive aromatic carbons, two carbonyl carbons, and a tertiary N. In each structure the observed C(1*b*')—N(1)—C(8*b*') angle at N(1) deviates from the tetrahedral angle (the angles average 125·6° in the four compounds) indicating considerable electron withdrawal by the adjacent imide carbonyls. The cations in each structure are essentially planar.

The unit-cell packing arrangements for compounds (1) to (4) are illustrated in Figs. 2 to 5.

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1,3,3,5,5,7,9,9,11,11-Decamethyl-2,4,6,8,10,12-hexaoxa-1,3,5,7,9,11-hexasilabicyclo[5.5.2]tetradecane

By Yu. E. Ovchinnikov, V. E. Shklover,* Yu. T. Struchkov, T. V. Astapova, I. A. Zamaev and A. A. Zhdanov

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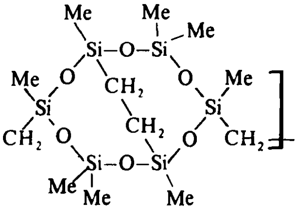
Abstract. $C_{12}H_{34}O_6Si_6$, $M_r = 442{\cdot}9$, orthorhombic, *Pcan*, $a = 12{\cdot}083\ (1)$, $b = 12{\cdot}083\ (1)$, $c = 17{\cdot}702\ (1)$ Å, $V = 2584{\cdot}3\ (3)$ Å^3, $Z = 4$, $D_x = 1{\cdot}138$ Mg m^{-3}, $\lambda(\text{Mo}\ K\alpha) = 0{\cdot}71069$ Å, $\mu = 0{\cdot}34$ mm^{-1}, $F(000) = 952$, $T = 297$ K, $R = 0{\cdot}047$ for 969 observed reflections. The molecule has a twofold symmetry axis; the conformation of the hexasiloxane ring is a twisted saddle, the dihedral angle between the wings being 98·4 (3)°. The SiCCSi bridge has a synclinal conformation with a torsion angle of 67·3 (5)°. The crystal structure is loose with molecules forming layers coplanar to the *ab* and *bc* planes.

Introduction. Earlier we determined the crystal structure of a cyclotetrasiloxane with an intracyclic $-CH_2CH_2-$ bridge (I) (Ovchinnikov, Shklover, Struchkov, Astapova & Zhdanov, 1986). In this work the molecular and crystal structure of the cyclohexasiloxane analogue (II) is reported. Like (I), molecule (II) represents a single unit of the carbocyclosiloxane polymer (see below), a structural study of which is proposed in the future.



Experimental. Irregular-shaped single crystal 0·8 × 0·6 × 0·4 mm used for measurements of unit-cell parameters (12 reflections with $28 \leq 2\theta \leq 32°$) and

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intensities of 1334 reflections ($0 \le h \le 12$, $0 \le k \le 12$, $0 \le l \le 19$). Hilger & Watts diffractometer (graphite monochromator, $\theta/2\theta$ scan, $2\theta_{\max} = 56°$). Despite the coincidence of two parameters of the orthorhombic cell, the intensities in *hkl, k$\bar{h}$l, $\bar{h}\bar{k}$l,* and *$\bar{k}$hl* groups differed greatly, *i.e.* a fourfold symmetry axis was absent. Space group *Pcan* determined from systematic absences. In the course of data collection intensities of two standard reflections measured after every 100 reflections were reduced by *ca* five times because of surface melting ($T_m = 321$ K), so intensities of all reflections were corrected according to the drift of the standard reflections with a special program. No absorption or secondary-extinction corrections. Structure solved by direct methods (*MULTAN* program; Germain, Main & Woolfson, 1971) and refined by block-diagonal least squares with anisotropic thermal parameters for non-H atoms using 969 unique reflections with $F > 5\sigma(F)$ and minimizing $\sum w(|F_o| - |F_c|)^2$; $w = [\sigma^2(F_o) + 0{\cdot}01F_o^2]^{-1}$. Scattering factors from *International Tables for X-ray Crystallography* (1974). H atoms located by a difference synthesis and refined isotropically. Final $R = 0{\cdot}047$, $wR = 0{\cdot}049$, $S = 2{\cdot}68$, max. $\Delta/\sigma = 0{\cdot}3$, final electron density fluctuations $\pm 0{\cdot}4$ e Å^{-3}. All calculations carried out with an Eclipse S/200 computer using the *INEXTL* programs (Gerr, Yanovsky & Struchkov, 1983).

Discussion. Atomic coordinates are given in Table 1,* relevant bond lengths and bond angles in Table 2. A perspective view of molecule (II) with the atom numbering is shown in Fig. 1.

Table 1. *Atomic coordinates* (× 10^5 *for* Si, × 10^4 *for* O *and* C) *and equivalent isotropic temperature factors* (Å^2)

$$B_{\rm eq} = \tfrac{4}{3}\textstyle\sum_i\sum_j B_{ij}a_i^*a_j^*(\mathbf{a}_i.\mathbf{a}_j).$$

	x	y	z	$B_{\rm eq}$
Si(1)	20929 (18)	48597 (11)	14453 (8)	5·19 (5)
Si(2)	33503 (18)	26649 (12)	16813 (7)	5·47 (5)
Si(3)	39905 (16)	33802 (12)	33194 (8)	5·18 (5)
O(1)	2381 (4)	3562 (3)	1543 (2)	6·0 (1)
O(2)	3906 (4)	2866 (3)	2491 (2)	9·5 (2)
O(3)	3197 (4)	4447 (3)	3380 (2)	6·3 (1)
C(1)	979 (5)	5249 (4)	2107 (3)	6·9 (2)
C(2)	1667 (8)	5114 (5)	451 (3)	10·5 (3)
C(3)	4408 (7)	2825 (5)	953 (4)	9·9 (3)
C(4)	2727 (7)	1283 (4)	1683 (3)	9·1 (3)
C(5)	5422 (6)	3813 (5)	3491 (4)	9·6 (3)
C(6)	3582 (7)	2327 (5)	4014 (3)	9·4 (3)

Table 2. *Relevant bond lengths* (Å) *and bond angles* (°)

Si(1)—O(1)	1·615 (3)	Si(1)—C(2)	1·860 (6)
Si(1)—O(3$^{\rm i}$)	1·605 (5)	Si(2)—C(3)	1·826 (8)
Si(2)—O(1)	1·615 (4)	Si(2)—C(4)	1·832 (6)
Si(2)—O(2)	1·602 (4)	Si(3)—C(5)	1·833 (8)
Si(3)—O(2)	1·595 (4)	Si(3)—C(6)	1·836 (6)
Si(3)—O(3)	1·610 (4)	C(1)—C(1$^{\rm i}$)	1·514 (7)
Si(1)—C(1)	1·845 (6)		

O(3$^{\rm i}$)Si(1)O(1)	107·9 (2)	Si(3)O(3)Si(1$^{\rm i}$)	157·8 (3)
O(1)Si(2)O(2)	109·8 (2)	Si(1)C(1)C(1$^{\rm i}$)	118·8 (4)
O(2)Si(3)O(3)	109·6 (2)	C(1)Si(1)C(2)	110·9 (3)
Si(1)O(1)Si(2)	145·5 (3)	C(3)Si(2)C(4)	112·7 (3)
Si(2)O(2)Si(3)	155·3 (3)	C(5)Si(3)C(6)*	109·9 (3)

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

* The OSiC angles are 108·0–110·5°, e.s.d.'s 0·2–0·3°.

The presence of the $-CH_2CH_2-$ bridge distorting the 'normal' geometry of siloxane rings determines the similarity of the molecular structures (I) and (II). As in (I), the siloxane ring in (II) has a 'saddle' conformation, the SiCCSi bridge has a synclinal conformation, the SiCC bond angles of 118·8 (4)° are much greater than the tetrahedral value, and the molecule also has crystallographic C_2 symmetry (twofold axis passing through the middle of the C—C bond). However, as the increase of a ring dimension enhances the ring's flexibility, significant differences between (I) and (II) result. The dihedral angle between the mean planes of the 'wings' Si(1)O(1)Si(2)O(2)Si(3)O(3)Si(1′) and Si(1′)O(1′)Si(2′)O(2′)Si(3′)O(3′)Si(1) in (II) is 98·4 (3) *vs* 115·0 (6)° in (I). Nonplanarity of the wings is somewhat greater; the maximum deviation of the atoms from the mean wing plane in (II) is 0·445 (4) *vs* 0·210 (6) Å in (I). The greater flexibility of the ring allows molecule (II) to adopt a less strained conformation, which is displayed, in particular, in the increase of the non-bonded Si(1)···Si(1′) distance up to 3·750 (2) Å [3·442 (4) Å in (I)], a considerably 'untwisted' conformation of the bridge [SiCCSi torsion angle of 67·3 (5) in (II) *vs* 39·1° in (I)], and shortening of the C—C bond to 1·514 (7) Å, which is less than the standard C(sp^3)—C(sp^3) bond [1·563 (5) Å in (I)]. It is interesting that even the SiCC bond angle of 118·8 (4)° in (II) exceeds the corresponding angle of 117·1 (2)° in (I). Apparently, an energy gain in other parameters

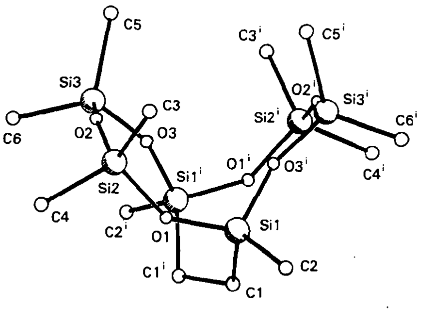

Fig. 1. Perspective view of molecule (II). H atoms are omitted. For symmetry code see Table 2.

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51087 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

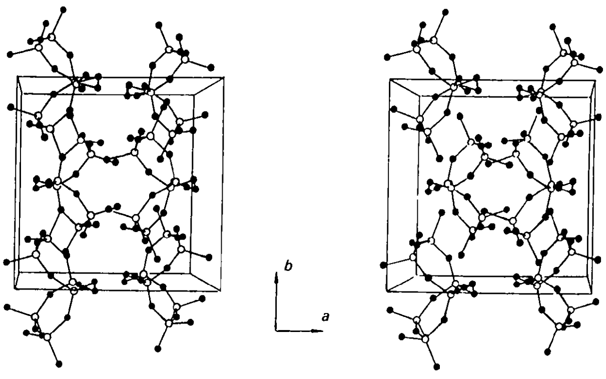

Fig. 2. Stereopair showing the molecular packing in (II).

compensates the increase of conformational energy caused by this enlargement of the angle.

The mean Si—O bond length of 1·608 (3) Å in (II) is somewhat smaller than the value of 1·625 Å which is usual for sterically non-overloaded tetrasiloxanes with nearly the same values of the SiOSi bond angles (Shklover & Struchkov, 1980). It emphasizes the absence of significant strain in the siloxane ring in (II); on the contrary, in molecule (I) a small lengthening of the Si—O bonds and a noticeable decrease of the bond angles at the O atoms are observed in comparison with the usual angles in tetrasiloxanes. Other bond lengths and bond angles in (II) are ordinary.

The crystal structure of (II) is very loose; there is only one intermolecular contact less than 4 Å: C(6)···C(2)($\frac{1}{2}-x$, $\frac{1}{2}-y$, $\frac{1}{2}+z$) of 3·907 (7) Å. The layers of molecules, which are coplanar to the crystallographic *ab* and *bc* planes, are clearly distinguished (Fig. 2). It is possible that the mobility of these layers is the cause for crystals of (II) becoming shapeless without a decrease of rigidity in 2–3 days at room temperature.

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Structure of a Planar Organic Compound: 2,1,3-Benzoselenadiazole (Piaselenole)

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Abstract. $C_6H_4N_2Se$, $M_r = 183·11$, orthorhombic, $Pna2_1$, $a = 12·553$ (4), $b = 12·414$ (3), $c = 3·941$ (1) Å, $V = 614·2$ Å^3, $Z = 4$, $D_x = 1·98$ g cm^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 6·46$ cm^{-1}, $F(000) = 352$, $T = 288$ K. Final $R = 0·044$ for 747 observed reflections. The molecule is planar within experimental error. The mean N—Se distance is 1·784 (5) Å, and a pseudo C_{2v} axis is observed in the molecule.

Introduction. The structure determination of the title compound (received through the courtesy of Dr Wirz of Universität Basel, Switzerland) was undertaken as part of a series of studies of carcinogenic heterocyclic planar chromophoric organic compounds, seeking structure–function correlations because these compounds are important for their selective intercalation in DNA and for chemotherapeutic uses. Structural elucidation of these series of compounds may also explain physical properties, such as cleavage and melting point, and may clarify salient features of the effect of intermolecular binding forces.

The primary synthesis and chemical characterization reports concerning piaselenole and others were published by Hinsberg (1889) and Zincke & Schwartz (1899); the 2D structure was reported by Luzzati (1951) and subsequently further NMR studies and molecular orbital calculations have been undertaken (Rettig & Wirz, 1976). This paper presents a complete

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