

Fig. 3. Stereoscopic diagram of the packing of the molecules in the crystal structure of compound (I) viewed along the *c* axis (*a* axis horizontal, *b* axis vertical).

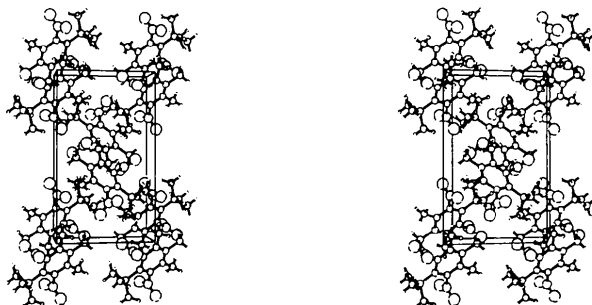


Fig. 4. Stereoscopic diagram of the packing of the molecules in the crystal structure of compound (II) viewed along the *c* axis (*a* axis horizontal, *b* axis vertical).

The packing arrangements of the molecules in compounds (I) and (II) are illustrated in Figs. 3 and 4 respectively. The crystal structures are solely stabilized by van der Waals interactions. There are only two intermolecular contacts in the range 3.30–3.33 Å for compound (II), whereas there are 13 contacts in the range 3.02–3.48 Å for compound (I). This is consistent

with the lower value of the density of the crystals of (II) (1.267 g cm<sup>-3</sup>) compared with that of (I) (1.384 g cm<sup>-3</sup>).

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## The Structures of Clathrates of Bis(triphenylsilane) Oxide with Benzene and Piperidine

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**Abstract.** Hexaphenyldisiloxane–benzene (1/2), C<sub>36</sub>H<sub>30</sub>OSi<sub>2</sub>·2C<sub>6</sub>H<sub>6</sub>, *M<sub>r</sub>* = 691.0, hexagonal, *R* $\bar{3}$ , *a* =

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11.196 (4), *c* = 26.515 (15) Å, *V* = 2878 (2) Å<sup>3</sup>, *Z* = 3, *D<sub>x</sub>* = 1.20 g cm<sup>-3</sup>, Mo *K*α, λ = 0.71069 Å, μ = 1.228 cm<sup>-1</sup>, *F*(000) = 1098, *T* = 150 K, *R* = 0.056 for 856 unique observed reflections. Hexaphenyldisiloxane–piperidine (1/2), C<sub>36</sub>H<sub>30</sub>OSi<sub>2</sub>·2C<sub>5</sub>H<sub>11</sub>N, *M<sub>r</sub>* = 705.1, hexagonal, *R* $\bar{3}$ , *a* = 11.197 (3), *c* =

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27.670 (12) Å,  $V = 3004 (2) \text{ \AA}^3$ ,  $Z = 3$ ,  $D_x = 1.17 \text{ g cm}^{-3}$ , Mo  $K\alpha$ ,  $\lambda = 0.71069 \text{ \AA}$ ,  $\mu = 1.198 \text{ cm}^{-1}$ ,  $F(000) = 1134$ ,  $T = 150 \text{ K}$ ,  $R = 0.074$  for 781 unique observed reflections. The molecules lie in special positions on the crystallographic threefold axes. A cavity-type packing of bis(triphenylsilane) oxide (BTPSO) molecules occurs. The guest molecules occupy cavities between the host molecules. In the clathrate with piperidine (BTPSO/PP) disorder of the guest was observed. A crystal-packing-energy analysis was performed to establish the orientation of the piperidine molecule.

**Introduction.** The present work is part of an investigation of the geometrical relationship existing between organic host lattices and guest molecules in clathrate compounds. Clathrates formed by triphenylmethane (TPM) have been reported previously (Allemand & Gerdil, 1975) and were found to be fairly unstable. Because of the particular head-to-head pairing of TPM molecules ( $\text{Ph}_3\text{-CH}\cdots\text{HC-Ph}_3$ ), it was interesting to find out whether isostructural stable clathrates could be formed by the larger molecule bis(triphenylsilane) oxide (BTPSO) which has approximately the same shape and dimensions as two paired TPM molecules. Two clathrates, with benzene (BTPSO/BZ) and piperidine (BTPSO/PP) as guest molecules, are discussed in this paper. It must be noted that the structure of BTPSO/BZ has already been solved by Russian investigators (Dubchak, Shklovskiy & Struchkov, 1983) but the present structure has been refined to a lower  $R$  and is reported along with the structure of BTPSO/PP.

**Experimental.** Details of the structure refinement are summarized in Table 1. Philips PW1100 diffractometer, graphite-monochromated Mo  $K\alpha$ ;  $\omega$ - $2\theta$  scan mode; Lorentz-polarization correction; no absorption correction; structures solved using approximate coordinates for Si and O atoms deduced from molecular packing in isostructural triphenylmethane clathrates (Allemand & Gerdil, 1975); geometry of piperidine in BTPSO/PP clathrate calculated by force-field method (*MM2*: Allinger, 1977) and included as rigid body (with overall thermal parameter for whole molecule) in crystallographic model. The two possible positions of N atom with respect to  $z$ -axis orientation (Fig. 1*b*) were tested. Atomic scattering factors for non-hydrogen atoms taken from Cromer & Mann (1968), those for H atoms from Stewart, Davidson & Simpson (1965), and anomalous-dispersion terms from *International Tables for X-ray Crystallography* (1974); no secondary-extinction correction made. All calculations performed with local version of *XRAY76* (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976), *PARST* (Nardelli, 1983) and *ORTEPII* (Johnson, 1976).

Table 1. Summary of intensity measurement and structure refinement

	BTPSO/BZ	BTPSO/PP
Crystal dimensions (mm)	0.30 × 0.30 × 0.37	0.22 × 0.28 × 0.36
Unit-cell determination	LS 24 reflections ( $5 \leq \theta \leq 12^\circ$ )	LS 25 reflections ( $6 \leq \theta \leq 11^\circ$ )
( $\sin \theta / \lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )	0.59	0.59
$h, k, l$ range	0/13, 0/10, -31/31	0/11, 0/11, -32/32 (and all anti-reflections of these)
Number of standard reflections	2 (328, 538)	3 (328, 538, 258)
$R_{\text{int}}$	0.030	0.020
Number of reflections measured	3514	3516
Number of observed reflections	2744	1743
Number of unique observed reflections	856	781
Criterion for observed reflections	$ F  \geq 2\sigma(F)$	$ F  \geq 2\sigma(F)$
Refinement (on $F$ )	Full matrix	Full matrix (see text)
Number of parameters	98	125
Weighting scheme	$1/\sigma(F)$	$1/\sigma(F)$
H atoms	Refined for host, calculated for guest	Refined for host, calculated for guest
Av. shift to e.s.d. ratio	0.30	4.06*
Max. and min. $\Delta\rho$ (e Å <sup>-3</sup> )	0.35, -0.29	0.82, -0.69*
$S$	3.99	3.66*
$R, wR$	0.056, 0.044	0.074, 0.054*

\* The model with the lowest packing energy has been considered as the final model (see Table 7).

**Discussion.** The final atomic parameters are given in Tables 2 and 3.\*

#### Host molecule

Bond lengths and angles are given in Tables 4 and 5, respectively, and torsion angles in Table 6. The numbering scheme is shown in Fig. 1. In both clathrates the host molecules adopt  $S_6$  symmetry with the O atom situated at a centre of symmetry. The Si—O—Si fragment is constrained to be linear in accordance with its being coincident with a crystallographic threefold axis. The same observation was made earlier by Glidewell & Liles (1978) for the unsolvated form of BTPSO and by Dubchak, Shklovskiy & Struchkov (1983) for BTPSO/BZ. Values for the Si—O—Si valence angles found in disiloxane derivatives are:  $156^\circ$  for  $\text{O}(\text{SiF}_3)_2$  (Airey, Glidewell, Rankin, Robiette, Sheldrick & Cruickshank, 1970),  $146^\circ$  for  $\text{O}(\text{SiCl}_3)_2$  (Airey, Glidewell, Robiette & Sheldrick, 1971),  $142.2^\circ$  for  $\text{O}(\text{SiH}_3)_2$  (Barrow, Ebsworth & Harding, 1979),  $148.8^\circ$  for  $\text{O}[\text{Si}(\text{CH}_3)_3]_2$  (Barrow, Ebsworth & Harding, 1979). We report Si—O bond lengths of 1.617 (3)

\* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42665 (50 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Fractional atomic coordinates for BTPSO/BZ ( $\times 10^4$ ) and equivalent isotropic thermal parameters ( $\text{\AA}^2 \times 10^4$ )

E.s.d.'s are given in parentheses.  
 $U_{\text{eq}} = 1/3(\text{trace of orthogonalized } U_{ij} \text{ matrix}).$

	x	y	z	$U_{\text{eq}}$
Si	0	0	610 (1)	210
O	0	0	0	254
C(1)	542 (4)	1784 (4)	832 (1)	255
C(2)	84 (4)	2025 (4)	1291 (1)	274
C(3)	467 (4)	3353 (4)	1441 (2)	317
C(4)	1324 (4)	4454 (5)	1140 (1)	332
C(5)	1807 (4)	4251 (5)	695 (2)	368
C(6)	1431 (4)	2920 (4)	538 (1)	304
Benzene molecule				
C(7)	-1041 (7)	313 (9)	2697 (2)	714
C(8)	305 (10)	1322 (7)	2701 (2)	803

Table 3. Fractional atomic coordinates for BTPSO/PP ( $\times 10^4$ ) and equivalent isotropic thermal parameters ( $\text{\AA}^2 \times 10^4$ )

E.s.d.'s are given in parentheses.  
 $U_{\text{eq}} = 1/3(\text{trace of orthogonalized } U_{ij} \text{ matrix}).$

	x	y	z	$U_{\text{eq}}$
Si	0	0	584 (5)	209
O	0	0	0	276
C(1)	494 (3)	1773 (3)	803 (1)	227
C(2)	-1 (3)	1979 (3)	1243 (1)	295
C(3)	407 (3)	3309 (3)	1413 (1)	316
C(4)	1312 (3)	4461 (4)	1147 (1)	352
C(5)	1822 (3)	4286 (3)	713 (1)	388
C(6)	1425 (3)	2960 (3)	544 (1)	313

Piperidine molecule\*  
 Orientation (1), H(N) equatorial

N	1183	1627	2922	677 (34)†
C(71)	-1329	-122	2873	
C(72)	464	-854	2795	
C(8)	1551	670	2691	
C(81)	-182	1378	2768	
C(82)	-984	-1160	2634	

Orientation (1), H(N) axial

N	1292	1582	2890	698 (30)†
C(71)	-1249	-75	2875	
C(72)	444	-943	2809	
C(8)	1573	543	2676	
C(81)	-61	1379	2741	
C(82)	-995	-1199	2656	

Orientation (2), H(N) equatorial

N	1612	535	2733	715 (35)†
C(7)	1306	1563	2942	
C(71)	-1262	-65	2818	
C(72)	483	-888	2813	
C(81)	-41	1416	2738	
C(82)	-899	-1119	2605	

Orientation (2), H(N) axial

N	1492	549	2676	603 (29)†
C(7)	1252	1600	2903	
C(71)	-1338	-50	2886	
C(72)	405	-862	2800	
C(81)	-166	1421	2706	
C(82)	-1043	-1131	2654	

\* S.o.f. 0.33, rigid-body refinement of 'ideal' molecule obtained from force-field calculations.

† Overall temperature factor for rigid body.

and 1.616 (2) Å for BTPSO/BZ and BTPSO/PP, respectively. These values are very close to those reported previously for BTPSO/BZ (1.618 Å) and for unsolvated BTPSO (1.616 Å). A slight lengthening of the Si—O bond is brought about by a decrease of the electron-withdrawing power of the substituent linked to Si as revealed by the following Si—O bond distances

Table 4. Bond distances (Å) for BTPSO/BZ and BTPSO/PP clathrates

E.s.d.'s are given in parentheses.

	BTPSO/BZ	BTPSO/PP
Si—O	1.617 (3)	1.616 (2)
Si—C(1)	1.868 (4)	1.875 (3)
C(1)—C(2)	1.398 (5)	1.404 (3)
C(1)—C(6)	1.397 (4)	1.408 (4)
C(2)—C(3)	1.384 (6)	1.403 (5)
C(3)—C(4)	1.376 (5)	1.388 (4)
C(4)—C(5)	1.363 (7)	1.385 (5)
C(5)—C(6)	1.394 (7)	1.400 (5)
Benzene molecule		
C(7)—C(8)	1.358 (10)	
C(7)—C(8')	1.359 (13)	
Piperidine molecule*		
N—C(8)		1.472
N—C(81)		1.473
C(8)—C(72)		1.549
C(71)—C(81)		1.548
C(71)—C(82)		1.545
C(82)—C(72)		1.545

Equivalent position: (i)  $-y, x - y, z$

\* Rigid-body refinement of 'ideal' molecule obtained from force-field calculations.

Table 5. Bond angles ( $^\circ$ ) for BTPSO/BZ and BTPSO/PP clathrates

E.s.d.'s are given in parentheses.

	BTPSO/BZ	BTPSO/PP
C(1)—Si—C(1')	110.5 (2)	110.1 (1)
O—Si—C(1)	108.4 (1)	108.8 (1)
Si—O—Si <sup>ii</sup>	180.0 (1)	180.0 (1)
Si—C(1)—C(6)	120.1 (2)	121.5 (2)
Si—C(1)—C(2)	121.8 (3)	121.5 (2)
C(2)—C(1)—C(6)	118.2 (3)	116.9 (3)
C(1)—C(2)—C(3)	120.8 (3)	121.3 (3)
C(2)—C(3)—C(4)	119.9 (4)	120.5 (3)
C(3)—C(4)—C(5)	120.6 (4)	119.3 (3)
C(4)—C(5)—C(6)	120.2 (4)	120.3 (3)
C(1)—C(6)—C(5)	120.3 (3)	121.6 (3)
Benzene molecule		
C(8)—C(7)—C(8')	117.6 (9)	
C(7)—C(8)—C(7 <sup>iii</sup> )	122.3 (7)	
Piperidine molecule*		
C(8)—N—C(81)		112.2
N—C(8)—C(72)		111.7
C(81)—C(71)—C(82)		110.6
N—C(81)—C(71)		111.7
C(71)—C(82)—C(72)		109.8
C(8)—C(72)—C(82)		110.5

Equivalent positions: (i)  $-y, x - y, z$ ; (ii)  $-x, -y, -z$ ; (iii)  $y - x, -x, z$

\* Rigid-body refinement of 'ideal' molecule obtained from force-field calculations.

Table 6. *Torsion angles* ( $^\circ$ ) for *BTPSO/BZ* and *BTPSO/PP* clathrates

E.s.d.'s are given in parentheses.

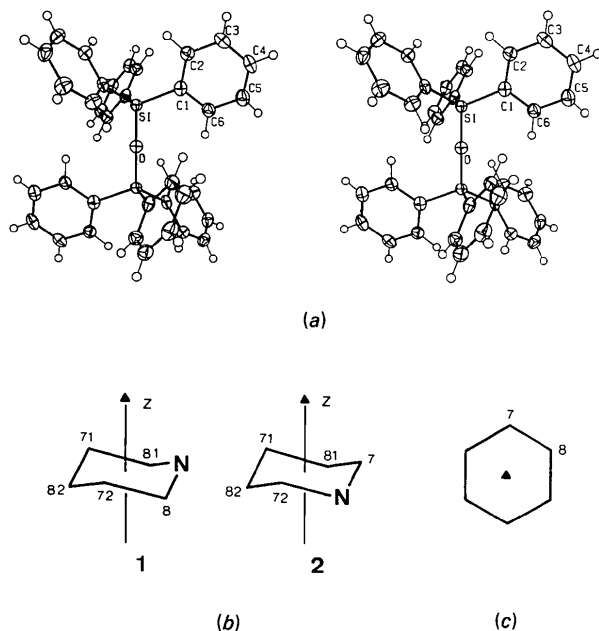
	BTPSO/BZ	BTPSO/PP
O—Si—C(1)—C(2)	150.8 (3)	149.9 (2)
O—Si—C(1)—C(6)	-29.4 (4)	-32.8 (3)
C(1 <sup>i</sup> )—Si—C(1)—C(6)	-148.0 (3)	-152.1 (3)
C(1 <sup>i</sup> )—Si—C(1)—C(2)	32.1 (4)	30.7 (3)
Si—C(1)—C(6)—C(5)	178.1 (3)	-178.4 (2)
Si—C(1)—C(2)—C(3)	-177.1 (3)	177.9 (2)
C(2)—C(1)—C(6)—C(5)	-2.0 (6)	-1.1 (5)
C(6)—C(1)—C(2)—C(3)	2.1 (6)	0.6 (5)
C(1)—C(2)—C(3)—C(4)	-0.9 (7)	0.3 (5)
C(2)—C(3)—C(4)—C(5)	-0.3 (7)	-0.7 (5)
C(3)—C(4)—C(5)—C(6)	0.3 (7)	0.2 (5)
C(4)—C(5)—C(6)—C(1)	0.9 (7)	0.7 (5)

**Benzene molecule**C(8<sup>i</sup>)—C(7)—C(8)—C(7<sup>ii</sup>) 1.5 (1.3)**Piperidine molecule\***

C(8)—N—C(81)—C(71)	57.2
C(81)—N—C(8)—C(72)	-57.4
N—C(8)—C(72)—C(82)	56.0
C(82)—C(71)—C(81)—N	-55.7
C(81)—C(71)—C(82)—C(72)	54.2
C(71)—C(82)—C(72)—C(8)	-54.3

Equivalent positions: (i)  $-y, x - y, z$ ; (ii)  $y - x, -x, z$ 

\* Rigid-body refinement of 'ideal' molecule obtained from force-field calculations.

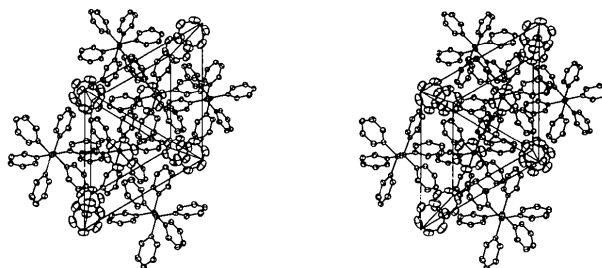
Fig. 1. (a) Stereoview and atom-numbering scheme of the host molecule (the vibrational ellipsoids of the non-H atoms are plotted at 50% probability level; the H atoms were arbitrarily chosen as spheres with 0.1 Å radius); (b) atom-numbering scheme and two possible orientations of piperidine in BTPSO/PP with respect to the crystallographic *c* axis; (c) atom-numbering scheme for the benzene molecule in BTPSO/BZ.

together with the preceding values: 1.58 Å for  $O(SiF_3)_2$  (Airey, Glidewell, Rankin, Robiette, Sheldrick & Cruickshank, 1970), 1.593 Å for  $O(SiCl_3)_2$  (Airey, Glidewell, Robiette & Sheldrick, 1971), 1.631 Å for  $O(SiH_3)_2$  (Barrow, Ebsworth & Harding, 1979) and 1.626 Å for  $O[Si(CH_3)_3]_2$  (Barrow, Ebsworth & Harding, 1979). The Si—C(1) distances, 1.868 (4) and 1.875 (3) Å for BTPSO/BZ and BTPSO/PP, respectively, are also very close to the values found earlier [average 1.864 Å (Glidewell & Liles, 1978) and 1.88 Å (Dubchak, Shklover & Struchkov, 1983)]. The average C—C bond distance in the phenyl rings is 1.385 (12) for BTPSO/BZ and 1.392 (8) Å for BTPSO/PP. The reason for the difference in geometry between  $O(SiPh_3)_2$  and other disiloxanes is still not well understood (Glidewell & Liles, 1978). For BTPSO/BZ and BTPSO/PP the O—Si—C(1) valence angles are 108.4 (1) and 108.8 (1) $^\circ$ , whereas the C(1)—Si—C(1<sup>i</sup>) angles [*i* denotes the symmetry-related position  $-y, x - y, z$ ] are 110.5 (2) and 110.1 (1) $^\circ$ , respectively. The average values for endocyclic bond angles in phenyl substituents are 120.0 $^\circ$  for both structures but, at the 3 $\sigma$  level, the angle at C(1) is significantly smaller than average in both BTPSO/BZ [118.2 (3) $^\circ$ ] and BTPSO/PP [116.9 (3) $^\circ$ ].

The dihedral angle between the phenyl mean planes and the plane through O—Si—C(1) is 29.3 (1) $^\circ$  in BTPSO/BZ and 31.4 (1) $^\circ$  in BTPSO/PP. It is worth noting that for the unsolvated BTPBO molecule the corresponding angles are 58.1, 43.8, 35.0 $^\circ$  (Glidewell & Liles, 1978). A similar phenomenon was observed in triphenylmethane and its benzene clathrate. For TPM/BZ the phenyl torsion angles were 29.9 $^\circ$  (Allemand & Gerdil, 1975), whereas in unsolvated TPM the values are 53, 34 and 30 $^\circ$  for the first and 47, 38 and 21 $^\circ$  for the second independent molecule (Riche & Pascard-Billy, 1974). These structural modifications of the host point to a noticeable flattening of the propeller-shaped moiety when it forms part of the unsolvated lattice.

**Benzene as guest molecule**

The benzene molecule is centered in a trigonal cage with the ring sixfold axis coincident with a crystal-

Fig. 2. Stereoview of the cavity of the BTPSO/BZ clathrate down the *c* axis. The vibrational ellipsoids of the non-hydrogen atoms are plotted at the 50% probability level.

lographic threefold axis. The enclosed guest is loosely held by four surrounding BTPSO molecules as shown in Fig. 2. A strong anisotropic thermal motion of the guest imparts a significant apparent shortening of the C—C bond to 1.36 Å. A large displacement component [0.33 Å for C(7) and 0.36 Å for C(8)] is observed along the bond directions (Fig. 2).

#### Piperidine as guest molecule

The piperidine molecule lacks threefold symmetry but fills the same cavity as the benzene guest molecule. Consequently, piperidine can occupy three symmetry-related positions by rotation about a threefold axis, each with an occupancy factor of 1/3. The likely position of the N atom with respect to the  $z$  axis (Fig. 1b) was established as follows. The difference synthesis calculated within the cavity (Fig. 3) reveals slightly higher electron-density maxima within the cross section at  $z \approx 0.29$  as compared to those at  $z \approx 0.27$ ; however, the position of hydrogen attached to nitrogen is still unknown. An ideal geometry for the guest was calculated using the force-field method (*MM2*: Allinger, 1977) and included as a rigid component in the X-ray structure model. Four different orientations of the piperidine molecule with different N—H bond orientations have been considered but there were no significant differences between the  $R$  factors for different models (Table 7). As a consequence a minimization of the crystal lattice energy with respect to the lattice constants, translations and rotations of the guest molecule was performed by means of the *PCK6* program (Williams, 1972*b*, 1974). The electrostatic interactions were neglected as well as the thermal effects. The function  $E(r) = -Ar^{-6} + B\exp(-Cr)$  representing the non-bonded interatomic potential energy was applied. The coefficients  $A$ ,  $B$  and  $C$  for C...C, C...H and H...H interactions were taken from Williams (1972*a*); those for O...O, O...H and O...C from Gavezzotti & Simonetta (1975); those for N...N,

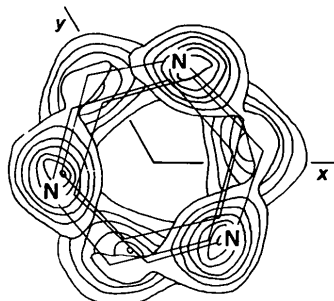


Fig. 3. Compound view of two difference maps plotted on planes perpendicular to  $c$ ; lower cross section at  $z \approx 0.27$ , upper at  $z \approx 0.29$ ; lowest contour at  $60 \text{ e } \text{Å}^{-3}$ , contour interval  $40 \text{ e } \text{Å}^{-3}$ . The final orientation of the piperidine molecule is also shown as the projection of three symmetry-related rigid bodies each with s.o.f. equal to 1/3.

Table 7. Packing-energy analysis for BTPSO/PP

Orientation of guest molecule*	Orientation of N—H bond	$R$ factors (refinement)	Final cell parameters (Å)	Packing energy ( $\text{kJ mol}^{-1}$ )
Orientation (1)	Axial	$R = 7.2$ $wR = 4.9$	$a = 11.198$ $c = 27.670$	-421.9
Orientation (1)	Equatorial	$R = 7.4$ $wR = 5.4$	$a = 11.018$ $c = 27.620$	-437.4
Orientation (2)	Axial	$R = 7.3$ $wR = 5.3$	$a = 11.197$ $c = 27.671$	-408.9
Orientation (2)	Equatorial	$R = 7.2$ $wR = 5.7$	$a = 11.197$ $c = 27.671$	-409.4

\* See Fig. 1.

N...H and N...C were calculated by approximations derived by Govers (1975) using the method of Williams (1967); the Si...C, Si...H, O...N, Si...O and Si...N interactions were calculated as geometrical means for  $A$  and  $B$  and as arithmetical means for  $C$ ; finally, the Si...Si interaction was taken from Ahmed, Kitaigorodsky & Mirskaya (1971). The results of the minimizations are reported in Table 7. The packing energy with N at  $z \approx 0.29$  is lower by 10–20  $\text{kJ mol}^{-1}$  than that for N at  $z \approx 0.27$ . This is consistent with the results obtained from the difference synthesis illustrated in Fig. 3 and suggests the most probable position of the nitrogen atom to be at  $z \approx 0.29$ . The minimum crystal lattice energy ( $-437 \text{ kJ mol}^{-1}$ ) was found for piperidine in orientation (1) with an equatorial N—H bond, in agreement with the prohibitively short contact engendered by the bond in axial orientation (see below).

#### Crystal packing

A drawing of the cavity for the BTPSO/BZ clathrate as viewed down the  $c$  axis is shown in Fig. 2. In BTPSO/BZ there are no significant differences between intermolecular distances and the corresponding sums of van der Waals radii. In BTPSO/PP [orientation (1)] there is one short contact, 1.96 Å, between H(5) of the host and H(72a) of the guest molecule positioned at  $1/3 - y$ ,  $2/3 + x - y$ ,  $-1/3 + z$ . For the same piperidine orientation and axial N—H bond there appears to be another short contact of 1.977 Å between H(5) and H(N). In conclusion, orientation (1) for piperidine with an equatorial N—H bond is considered as prevalent within the clathrate lattice.

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## Structure of DL-Lanthionine Monohydrate: Hydrogen-Bonding Patterns in Amino Acid Crystal Structures

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**Abstract.** C<sub>6</sub>H<sub>12</sub>N<sub>2</sub>O<sub>4</sub>S.H<sub>2</sub>O, *M<sub>r</sub>* = 226.1, monoclinic, *P*2<sub>1</sub>/*n*, *a* = 13.645 (2), *b* = 8.099 (1), *c* = 8.441 (1) Å, β = 91.64 (1)°, *V* = 932.4 (4) Å<sup>3</sup>, *Z* = 4, *D<sub>m</sub>* = 1.6, *D<sub>x</sub>* = 1.61 g cm<sup>-3</sup>, λ(Cu Kα) = 1.5418 Å, μ = 30.8 cm<sup>-1</sup>, *F*(000) = 512, *T* = 294 K. Final *R* = 0.029 for 1580 reflections >3σ. The S atom is synclinal to the N atom and the two carboxyl groups have slightly different twists about the Cα–C bond. A carboxyl O has a contact with S of 3.238 (1) Å and it approaches Sγ as a nucleophile, nearly in the sulfide plane and at the back of the Cβ(2)–Sγ bond. The hydrogen-bonding patterns of amino acids are compared to the pattern for DL-lanthionine. This structure exhibits two bifurcated hydrogen bonds involving the two amino groups.

**Introduction.** Lanthionine (3,3'-thiodialanine) is a rare, naturally occurring amino acid, the sulfide analog of cystine. We have determined earlier the crystal structure of *meso*-lanthionine dihydrochloride (Rosenfield & Parthasarathy, 1974) and found an interesting intermolecular S...S contact of 3.251 (2) Å that prompted us to carry out our studies on non-bonded atomic contacts with divalent sulfur (Rosenfield, Parthasarathy & Dunitz, 1977; Guru Row & Parthasarathy, 1981). This study forms part of our program on non-bonded atomic contacts with divalent sulfur. In this study, we have crystallized lanthionine in the zwitterionic form and find that this crystal structure contains an interesting intermolecular S...O interaction that follows

the pattern of the direction of approach of nucleophile to sulfide.

**Experimental.** A mixture of DL- and *meso*-lanthionine (Sigma) crystallized from water to yield needle-like crystals and also, on further evaporation, several badly shaped and significantly smaller crystals. One needle-like crystal of dimensions 0.1 × 0.17 × 0.30 mm was chosen for study; needle-like crystals turned out to correspond to DL-lanthionine; density measured using bromoform/benzene; three-dimensional data on a CAD-4 diffractometer to the limit 2θ = 154° for Cu Kα; 4128 reflections collected and averaged to yield a unique set of data of 1967 reflections (*R*<sub>int</sub> = 0.02) with 1580 >3σ; range of *hkl*: -17 to 17, 0 to 10 and -10 to 10; ω/2θ scan widths calculated using expression (0.50 + 0.15 tanθ)°, aperture widths using equation (4.0 + 1.2 tanθ) mm; maximum time spent on any reflection measurement 100s, faster scan used for strong reflections. Unit-cell constants from 25 reflections with 8 < θ < 25°. Intensities of three reflections ( $\bar{4}10$ , 424 and  $\bar{2}23$ ) monitored after every hour of exposure, variation in intensity <2% during data collection; orientation matrix checked every 100 reflections. Lorentz and polarization corrections applied; intensities of three reflections at χ ~ 90° measured for all values of φ from 0 to 360° and resultant curve of transmission as a function of φ used to calculate the anisotropy of absorption for all reflections, average transmission factor 0.95. Structure solved by direct methods using *MULTAN* (Germain Main & Woolfson, 1971). H atoms located from

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