

# Binding Neutral Guests to Concave Surfaces of Molecular Hosts. Rigid Structural Model for Complexation Between Two Lipophilic Entities

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**Abstract.** The 1:2 compound formed between a new cavitand  $C_{40}H_{48}Si_4O_8$  [chemical name: 5,10;12,17;19,24;26,3-tetrakis(dimethylsiladioxa)-1,8,15,22-tetramethyl[1<sub>4</sub>]metacyclophane] and  $CS_2$  ( $M_r = 921.42$ ) provided a suitable structural model for a rigid inclusion complex between uncharged lipophilic molecules. The detailed structure of this compound has been determined by single crystal X-ray diffraction at 128 K (Crystal data:  $a = 11.233$ ,  $b = 20.018$ ,  $c = 10.069$  Å,  $\beta = 90.84^\circ$ ,  $Z = 2$ , space group  $P2_1/m$ ). Anisotropic refinement converged at  $R = 0.040$  for 3768 reflections above the intensity threshold, leading to positional and thermal parameters of a relatively high precision. The cavitand has an enforced cavity appropriately sized to include only slim linear guests. The crystallographic analysis revealed a 1:1 molecular inclusion complex with  $CS_2$ , the guest species being almost entirely encapsulated within the 'basket'-shaped cavity of the host. The complex is stabilized by dispersion forces. All the guest atoms lie within van der Waals distances from the surrounding sections of the host and are well ordered. The second  $CS_2$  molecule is located in the crystal lattice between molecules of the complex and is slightly disordered. Mirror plane symmetry characterizes the entire structure.

**Key words:** Molecular inclusion, host-guest van der Waals complex, cavitands.

**Supplementary Data** relating to this article are deposited with the British Library as Supplementary Publication No. SUP 82032 (22 pages).

## 1. Introduction

The selective molecular inclusion of small guests by larger host species has been, for many years, a challenging target for the synthetic chemist in his continuous efforts to produce suitably designed models of natural receptor systems. At first, remarkable progress was made in the preparation, analysis and application of host-guest complexes involving charged or polar species, where association between the interacting components is determined by relatively strong electrostatic forces. Suitable examples include the complexation of metal ions and amino acid derivatives by crown ethers and cryptates [1].

Recently, and as a further and natural development of the molecular inclusion concept, an increasing interest has been shown in the study of the separation and storage of uncharged molecules with hydrophobic surfaces within similarly neutral and apolar synthetic host species. It appears that such complexes, although stabilized only by rather weak binding forces, can be achieved in both the crystal and solution states [2]. They can, thus, also be useful in studies of transport phenomena. So far, only a relatively small number of structures of synthetic inclusion complexes between apolar hosts and guests have been published [2]. Most of them involve calixarene, cyclophane, oligolactone and oligolactam derivatives as

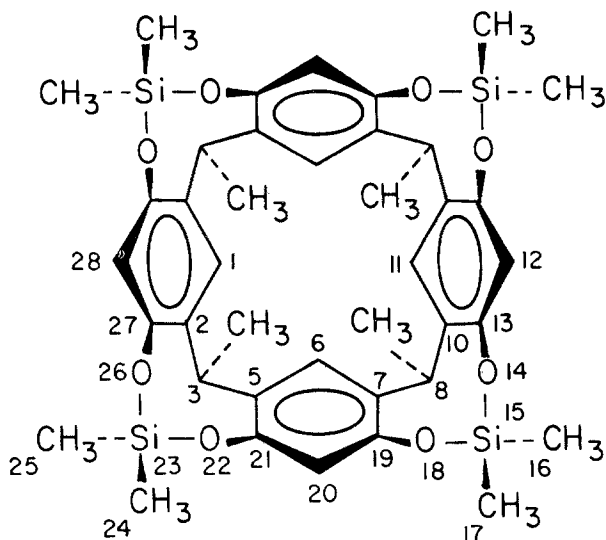


Fig. 1. Molecular scheme of the host cavitaand, showing the crystallographic numbering used. The corresponding chemical name, derived from that of the parent octol derivative [10], is 5,10,12,17;19,24;26,3-tetrakis(dimethylsilyloxa)-1,8,15,22-tetramethyl[ $l_4$ ]metacyclophane.

hosts and a small number of guests such as acetone, acetonitrile, chloroform, dichloromethane, dioxane and toluene. The question of selectivity in complexation has also been referred to in some of the publications.

In a recent communication, Cram *et al.* [3] reported the synthesis of a new series of cavitaands containing *enforced* cavities (based on the framework shown in Figure 1) capable of complexing nonpolar partners in  $CDCl_3$  and  $C_6D_6$  solutions. The host cavity is in the form of a cylindrical well of a limited diameter, and can accommodate only slim linear guests such as  $CS_2$ ,  $CH_3C\equiv CH$  and  $O_2$ . The free energy for the complex formation between the host shown and  $CS_2$  is  $-0.4$  kcal/mol at 212 K and about  $+1.0$  kcal/mol at 300 K. It should be kept in mind, however, that the free energy for the cavity formation has already been supplied during the host synthesis.

Crystallographic analysis of the above complex was needed to confirm the encapsulated-type structure and to provide structural details of the host conformation, shape of the binding site and the geometry of inclusion. The latter are particularly useful for the analysis of host-guest interactions within the complexed system.

## 2. Experimental

Single crystals of the inclusion complex suitable for crystallographic study were obtained by a slow evaporation of the solution of the cavitaand in  $CS_2$ . To prevent possible deterioration during the experiment, the crystal (size  $0.3 \times 0.3 \times 0.2$  mm) was enclosed within a thin glass capillary. Diffraction data were measured at *ca.* 128 K on an upgraded Picker diffractometer [4] equipped with a graphite monochromator, using  $MoK\alpha$  ( $\lambda = 0.7107 \text{ \AA}$ ) radiation, the  $\omega - 2\theta$  scan technique, and a constant scan rate of  $3^\circ \text{ min}^{-1}$ .

*Crystal Data:*  $C_{40}H_{48}Si_4O_8 \cdot 2CS_2$ ,  $M_r = 921.42$ , monoclinic,  $P2_1/m$ ,  $a = 11.233(1)$ ,  $b = 20.018(2)$ ,  $c = 10.069(1) \text{ \AA}$ ,  $\beta = 90.84(2)^\circ$ ,  $V = 2263.9(4) \text{ \AA}^3$ ,  $Z = 2$ ,  $D_x = 1.352 \text{ gcm}^{-3}$ ,  $\mu(MoK\alpha) = 3.53 \text{ cm}^{-1}$ ,  $F(000) = 968$ .

Out of the 4814 reflections collected to  $2\theta_{\max} = 54^\circ$ , 4254 were unique ( $R_{\text{int}} = 0.027$ ). The crystal was stable during the measurements. The intensity data were corrected for Lorentz and polarization effects but not for absorption or secondary extinction. Final refinement calculations were based on 3768 reflections with  $F_0 > 6\sigma(F_0)$ .

The crystal structure was solved by a combination of direct methods (MULTAN80 [5]) and Fourier techniques. The refinement was carried out by the full-matrix least-squares method (SHELX76 [6]), including the positional and anisotropic thermal parameters of all the nonhydrogen atoms of the asymmetric unit. The hydrogens were introduced in calculated positions, their coordinates being partially adjusted with low-order data below  $\sin \theta/\lambda = 0.50 \text{ \AA}^{-1}$ . During this refinement the methyls were treated as rigid groups. Least-squares calculations were based on the experimental weights,  $w = 1/\sigma^2(F_0)$ . At convergence no parameter shift was greater than 0.3 e.s.d. The final discrepancy factors are  $R = 0.040$

Table I. Atomic coordinates and isotropic thermal parameters.  $U_{\text{eq}}$  is one third of the trace of the orthogonalized  $U^{ij}$  tensor

Atom	$x/a$	$y/b$	$z/c$	$U_{\text{eq}}$
C(1)	0.2888(3)	0.2500	0.9296(3)	0.0176(9)
C(2)	0.2679(2)	0.1886(1)	0.8678(2)	0.0173(6)
C(3)	0.2935(2)	0.1226(1)	0.9398(2)	0.0179(6)
C(4)	0.2550(2)	0.1243(1)	1.0849(2)	0.0222(7)
C(5)	0.4231(2)	0.1034(1)	0.9224(2)	0.0169(6)
C(6)	0.5124(2)	0.1209(1)	1.0152(2)	0.0164(6)
C(7)	0.6314(2)	0.1039(1)	1.0021(2)	0.0158(6)
C(8)	0.7270(2)	0.1227(1)	1.1043(2)	0.0164(6)
C(9)	0.6779(2)	0.1236(1)	1.2457(2)	0.0218(7)
C(10)	0.7857(2)	0.1887(1)	1.0668(2)	0.0149(7)
C(11)	0.7361(3)	0.2500	1.0988(3)	0.0156(8)
C(12)	0.9458(3)	0.2500	0.9631(3)	0.0161(9)
C(13)	0.8924(2)	0.1899(1)	0.9963(2)	0.0168(6)
O(14)	0.9478(1)	0.1306(1)	0.9613(1)	0.0178(5)
Si(15)	0.9022(1)	0.0843(1)	0.8345(1)	0.0172(2)
C(16)	1.0088(2)	0.0149(1)	0.8153(2)	0.0242(7)
C(17)	0.8814(2)	0.1387(1)	0.6878(2)	0.0287(8)
O(18)	0.7773(1)	0.0453(1)	0.8702(2)	0.0212(5)
C(19)	0.6628(2)	0.0677(1)	0.8883(2)	0.0187(6)
C(20)	0.5762(2)	0.0487(1)	0.7943(2)	0.0206(7)
C(21)	0.4591(2)	0.0667(1)	0.8119(2)	0.0198(6)
O(22)	0.3757(2)	0.0439(1)	0.7188(2)	0.0239(5)
Si(23)	0.3009(1)	0.0835(1)	0.6021(1)	0.0222(2)
C(24)	0.4011(3)	0.1343(2)	0.5000(3)	0.0419(10)
C(25)	0.2188(2)	0.0179(1)	0.5096(3)	0.0309(8)
O(26)	0.1988(2)	0.1315(1)	0.6696(2)	0.0226(5)
C(27)	0.2232(2)	0.1900(1)	0.7373(2)	0.0204(7)
C(28)	0.2014(3)	0.2500	0.6732(3)	0.0220(10)
C(29)	0.6282(3)	0.2500	0.6380(3)	0.0269(11)
S(30)	0.5793(1)	0.2500	0.7806(1)	0.0380(3)
S(31)	0.6775(1)	0.2500	0.4953(1)	0.0339(3)
C(32)	0.0198(4)	0.2500	0.3389(4)	0.0542(19)
S(33)	0.0197(1)	0.1727(1)	0.3401(1)	0.0730(5)

Atoms of the cavitant-included guest are C(29), S(30) and S(31); those of the lattice-included solvent are C(32) and S(33).

Table II. Bond distances (Å) and bond angles (deg) with e.s.d.'s in parentheses

C(1)–C(2)	1.396(2)	Si(15)–C(16)	1.846(2)
C(2)–C(3)	1.532(2)	Si(15)–C(17)	1.847(2)
C(2)–C(27)	1.401(3)	Si(15)–O(18)	1.649(1)
C(3)–C(4)	1.530(3)	O(18)–C(19)	1.376(2)
C(3)–C(5)	1.518(3)	C(19)–C(20)	1.400(3)
C(5)–C(6)	1.405(3)	C(20)–C(21)	1.378(3)
C(5)–C(21)	1.398(2)	C(21)–O(22)	1.392(2)
C(6)–C(7)	1.388(3)	O(22)–Si(23)	1.639(1)
C(7)–C(8)	1.523(2)	Si(23)–C(24)	1.842(3)
C(7)–C(19)	1.405(2)	Si(23)–C(25)	1.848(2)
C(8)–C(9)	1.535(2)	Si(23)–O(26)	1.651(1)
C(8)–C(10)	1.526(2)	O(26)–C(27)	1.379(2)
C(10)–C(11)	1.388(2)	C(27)–C(28)	1.384(2)
C(10)–C(13)	1.402(3)	C(29)–S(30)	1.544(3)
C(12)–C(13)	1.388(2)	C(29)–S(31)	1.548(3)
C(13)–O(14)	1.388(2)	C(32)–S(33)	1.547(1)
O(14)–Si(15)	1.652(1)		
C(2)–C(1)–C(2)*	123.4(1)	O(14)–Si(15)–C(17)	108.7(1)
C(1)–C(2)–C(27)	117.2(2)	O(14)–Si(15)–C(16)	108.0(1)
C(1)–C(2)–C(3)	121.3(2)	C(17)–Si(15)–O(18)	110.8(1)
C(3)–C(2)–C(27)	121.5(2)	C(16)–Si(15)–O(18)	102.9(1)
C(2)–C(3)–C(5)	109.8(2)	C(16)–Si(15)–C(17)	115.7(1)
C(2)–C(3)–C(4)	112.2(2)	Si(15)–O(18)–C(19)	132.5(1)
C(4)–C(3)–C(5)	113.6(2)	C(7)–C(19)–O(18)	121.5(2)
C(3)–C(5)–C(21)	120.9(2)	O(18)–C(19)–C(20)	117.6(2)
C(3)–C(5)–C(6)	122.4(2)	C(7)–C(19)–C(20)	120.8(2)
C(6)–C(5)–C(21)	116.7(2)	C(19)–C(20)–C(21)	119.8(2)
C(5)–C(6)–C(7)	123.7(2)	C(5)–C(21)–C(20)	121.8(2)
C(6)–C(7)–C(19)	117.2(2)	C(20)–C(21)–O(22)	117.5(2)
C(6)–C(7)–C(8)	123.1(2)	C(5)–C(21)–O(22)	120.6(2)
C(8)–C(7)–C(19)	119.7(2)	C(21)–O(22)–Si(23)	131.1(1)
C(7)–C(8)–C(10)	110.5(2)	O(22)–Si(23)–O(26)	109.8(1)
C(7)–C(8)–C(9)	111.7(2)	O(22)–Si(23)–C(25)	105.4(1)
C(9)–C(8)–C(10)	112.4(2)	O(22)–Si(23)–C(24)	110.8(1)
C(8)–C(10)–C(13)	121.0(2)	C(25)–Si(23)–O(26)	106.1(1)
C(8)–C(10)–C(11)	122.1(2)	C(24)–Si(23)–O(26)	110.0(1)
C(11)–C(10)–C(13)	116.8(2)	C(24)–Si(23)–C(25)	114.5(1)
C(10)–C(11)–C(10)*	124.4(1)	Si(23)–O(26)–C(27)	124.3(2)
C(13)–C(12)–C(13)*	120.3(1)	C(2)–C(27)–O(26)	120.9(2)
C(10)–C(13)–C(12)	120.8(2)	O(26)–C(27)–C(28)	118.3(2)
C(12)–C(13)–O(14)	118.9(2)	C(2)–C(27)–C(28)	120.8(2)
C(10)–C(13)–O(14)	120.2(2)	C(27)–C(28)–C(27)*	120.5(1)
C(13)–O(14)–Si(15)	122.8(1)	S(30)–C(29)–S(31)	179.8(3)
O(14)–Si(15)–O(18)	110.6(1)	S(33)–C(32)–S(33)*	179.1(3)

\* The asterisks denotes equivalent atoms in the mirror-related half of the molecule.

for 3768 reflections above the intensity threshold and  $R = 0.046$  for all 4254 observations. Final difference Fourier maps confirmed the correctness of the structural model:  $\Delta\rho_{\max}$  and  $\Delta\rho_{\min}$  0.25 and  $-0.17 \text{ e } \text{Å}^{-3}$  respectively.

The final atomic coordinates of the nonhydrogen atoms are given in Table I. Table II shows the intramolecular bond distances and angles within this new system. Lists of anisotropic thermal parameters, coordinates of the H atoms and structure factors have been deposited with the British Library Lending Division under SUP 82032.

### 3. Discussion of Results

The stoichiometric ratio between host and guest within the crystal structure is 1 : 2. However, only one molecule of carbon disulphide is embedded within the host ('molecular inclusion'), the second  $\text{CS}_2$  lying between neighboring units of the complex ('lattice inclusion'). All three components are located on crystallographic mirror planes. Figures 2 and 3 illustrate the structure of the inclusion complex and the crystal packing arrangement, respectively.

The host structure is characterized by a closed surface on one side and an open surface on the other side of the molecule. The cavity has a form of a rectangular well (see below), its walls being lined with four phenyl rings. The bottom of the well can be best defined by the lowest parts of these rings (Table III). The four axial  $\text{CH}_3$ 's form the upper rim of the cavity whose size is determined by the inward-turning hydrogens. The side and diagonal dimensions of the rim are then given by the respective  $\text{H}\cdots\text{H}$  distances: 3.1–3.3 Å ( $\perp$  to the mirror plane), 4.6 Å ( $\parallel$  to the mirror plane) and 5.6 Å. The related  $\text{C}\cdots\text{C}$  distances between the methyls are 4.46–4.63, 5.69 and 7.28 Å. Owing to the high rigidity of the molecular framework, the above data confirm, therefore, that only linear guest molecules with a limited van der Waals diameter ( $<ca. 3.5$  Å) can penetrate significantly into this cavity.

In the present structure the molecular axis of the accommodated  $\text{CS}_2$  guest is nearly perpendicular to the cross-section of the cavity, forming an angle of about  $50^\circ$  with the planes

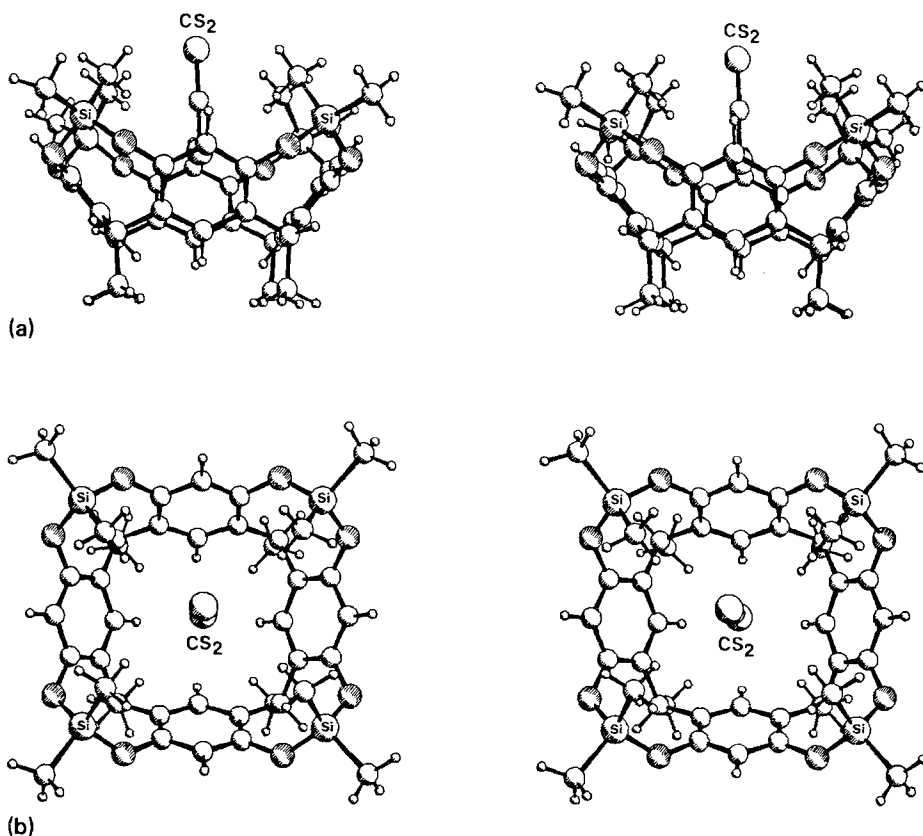


Fig. 2. Stereoviews of the molecular inclusion complex with  $\text{CS}_2$  parallel (a) and perpendicular (b) to the cavity surface.

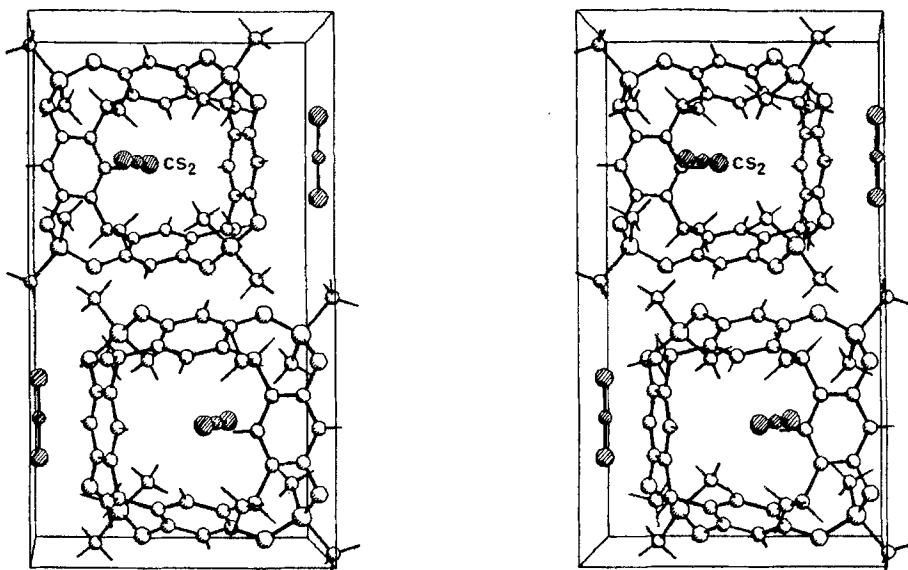


Fig. 3. Stereographic projection of the crystal structure approximately down  $c$ .

of the four phenyls. The depth of the guest penetration into the well of the host is measured by the relative location of the  $\text{CS}_2$  atoms with respect to different sections through the cavity. Relevant data are given in Table III. They show that the inserted sulphur S(30) is located deep

Table III. Relevant structural parameters within the molecular complex

(a) *Dimensions of the host cavity* (Å)

<i>Bottom</i>		<i>Center</i>		<i>Upper rim</i>	
C(1)···C(6)	3.697	C(12)···C(20)	6.013	C(17)···C(24)	5.692
C(6)···C(11)	3.694	C(20)···C(28)	5.942	C(17)···C(17)*	4.458
C(1)···C(11)	5.282	C(12)···C(28)	8.816	C(24)···C(24)*	4.633
C(6)···C(6)*	5.169	C(20)···C(20)*	8.061	C(17)···C(24)*	7.283

(b) *Relative dislocation of the guest atoms from different cross-sections of the host cavity* (in Å)

	<i>Plane 1</i>	<i>Plane 2</i>	<i>Plane 3</i>	<i>Plane 4</i>
S(30)	2.486	0.230	-2.013	-1.520
C(29)	4.029	1.774	-0.470	0.022
S(31)	5.575	3.321	1.077	1.568

The plane sections are through atoms:

Plane 1: C(1), C(6), C(11), C(6)\*;

Plane 2: C(12), C(20), C(28), C(20)\*;

Plane 3: C(17), C(24), C(17)\*, C(24)\*;

Plane 4: H(17c), H(24b), H(17c)\*, H(24b)\*

(c) *Shortest intermolecular distances* (Å) *between guest and host atoms*

S(30)···C(1)	3.612;	S(30)···C(6)	3.589;	S(30)···C(11)	3.633;
C(29)···C(17)	3.643;	C(29)···C(24)	3.701;	C(29)···H(17c)	2.73;
S(31)···C(17)	3.721;	S(31)···C(24)	3.875;	S(31)···H(17c)	3.09;
				S(31)···H(24b)	3.29

The average e.s.d. of distances involving C atoms only is 0.003 Å; that involving S and C atoms is 0.001 Å.

\* An asterisks denotes equivalent atoms in the other half of the molecule.

below the plane defined by the C atoms of the four axial methyls, while the outer sulphur S(31) is only about 1 Å above it. This clearly indicates that the guest CS<sub>2</sub> molecule is almost entirely encapsulated within the cavitand. The nonbonding distances of the guest atoms from their immediate surroundings reflect on the steric fit and type of interaction between the complexing partners. Thus, the inner sulphur S(30) lies 2.5 Å above the bottom of the cavity and 3.6 Å from the phenyl carbons. The central carbon C(29) is closest to the upper rim, within 2.7–2.8 Å from the hydrogens and 3.6–3.7 Å from the carbons of the axial methyl groups (Table III). These values represent typical van der Waals contacts, indicating a perfect fit between the two components and suggesting an effective contribution of the dispersion forces to the stability of the complex.

The molecular framework of the host is rigid to a considerable extent. In a ‘rigid-body’ analysis of the refined parameters of thermal motion in terms of translation, libration and screw tensors [7] the discrepancy between the observed and calculated parameters is  $\langle (\Delta U^{ij})^2 \rangle^{1/2} = 0.0036 \text{ Å}^2$  for the entire host and  $\langle (\Delta U^{ij})^2 \rangle^{1/2} = 0.0020 \text{ Å}^2$  when the peripheral methyl groups were excluded. The latter value is less than twice the average value of  $\sigma(U_0^{ij}) = 0.0012 \text{ Å}^2$ , indicating that the assumption of the rigid-body model is valid. The encapsulated guest molecule of CS<sub>2</sub> is perfectly ordered within the cavity, as is reflected in the relatively low amplitudes of the atomic thermal vibrations for C and S, which are comparable to those of the host (Table I; in fact, the principal components of the  $U^{ij}$  tensors show some but not extreme anisotropy for C(29), S(30) and S(31):  $U^{11} = 0.026, 0.045, 0.037$ ;  $U^{22} = 0.025, 0.043, 0.043$ ;  $U^{33} = 0.029, 0.027, 0.022$ , respectively). This feature is rather outstanding, as in most of the previously published structures of van der Waals complexes, the guest species were found either disordered or exhibiting very broad thermal motions (at least at room temperature) [2].

In the crystal structure, units of the complex are stacked one on top of the other along the *c* axis, with the convex part of one moiety in close contact with the opposite face of its neighbour along the stack. Thus, the outer sulphur of one complex is approached by the methyl ‘legs’ of another complex; the shortest nonbonding distances are S(31)...C(9) 3.57 Å and S(31)...H(9a) 3.1 Å. The entire guest molecule is therefore enclosed in this structure by a lipophilic environment composed of phenyl groups within the cavity and methyl groups on and above its surface.

The deviation of the molecular structure from a square symmetry can possibly be explained by the different *side* packing of the molecular complex in the other directions. Adjacent molecules along the long *b* axis of the crystal are related to each other by the twofold screw axis. They pack efficiently, with the equatorial methyl groups of one molecule interspersing the equatorial methyls of another moiety. Packing of molecules related by translation along *a* is less efficient. In fact, voids are created between neighbouring entities which are filled in the crystal by the second CS<sub>2</sub> molecule. The refined thermal parameters of the latter are relatively large [the largest values are  $U^{22} = 0.10$  and  $0.11 \text{ Å}^2$  for atoms C(32) and S(33), respectively], indicating either a slight dynamic disorder of this molecule or an incomplete occupancy of all sites in the crystal, or both. Such an observation is characteristic of many other structures of the lattice-inclusion type [8]. All intermolecular distances are equal to or greater than the sums of the corresponding van der Waals radii.

The above described structure is a perfect example of a purely van der Waals molecular inclusion complex between apolar guest and host species. The stability of this complex both in solution as well as in the crystal should be mainly attributed to two factors: (1) the fact that the host framework was specially designed to contain a rigid cavity that would not collapse in solution, and (2) the steric complementarity between the interacting components [9]. The

cavitands containing concave surfaces of varying depths and diameters [3] provide particularly useful models for the study of molecular inclusion phenomena.

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