

A new triol host framework and the remarkable crystal structure of its DMSO inclusion complex

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Abstract A new trigonal host molecule **1** featuring three 4-(9-hydroxy-9-fluorenyl)phenyl units symmetrically attached to a benzene core was synthesized and is shown to yield a 1:3 (host:guest) crystalline inclusion compound with DMSO (**1a**). The crystal structure of **1a** is distinguished by a rare case of piedfort arrangement of host molecules and a unique hexameric cluster formation of DMSO.

Keywords Hydroxy host · DMSO guest · Crystalline inclusion compound · X-ray crystal structure · Supramolecular interactions

Introduction

Symmetry, shape and functionality are important parameters in the design of crystal inclusion host compounds [1–5]. Using these parameters provided a great variety of molecular structures, many of them being efficient clathrate formers [6]. Twofold rotational symmetry of the host compound has been realized a keynote in this design strategy [1, 2]. Bulky linear [7, 8] or roof-shaped [2, 3, 9] and scissor like [2, 3, 10] geometries proved particular successful guiding principles regarding the shape selection of the host molecules. Aside from carboxylic units [3, 11, 12], hydroxyl groups [2, 7, 13, 14] demonstrated highest effectiveness from the point of functionality. Compared with the host molecules of this specific design, i.e. having a C_2 symmetry as a structural feature, corresponding host compounds involving C_3 symmetry are not just as frequent

and have not been so broadly varied in the past [1, 15, 16] though the structure type of trisubstituted triazines is currently very promising [17–20].

Here, we report the synthesis of a new trigonal host compound **1** (Scheme 1) having three 9-hydroxy-9-fluorenyl units laterally attached to a central 1,3,5-triphenyl benzene moiety. We describe preparation of a DMSO inclusion complex of **1**, i.e. **1a** (Scheme 1), and discuss the special features of this remarkable crystal structure.

Results and discussion

Synthesis

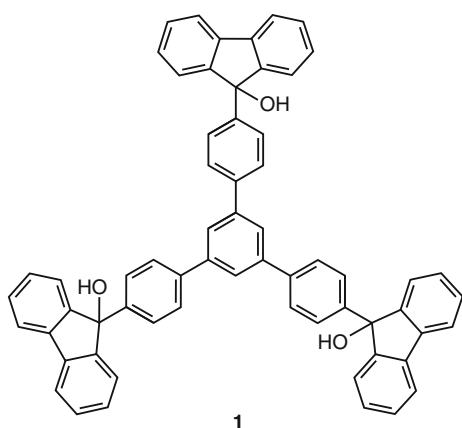
The host compound **1** was synthesized from 1,3,5-tris(4-bromophenyl)benzene via lithiation with *n*-BuLi and subsequent reaction with fluoren-9-one. The starting compound 1,3,5-tris(4-bromophenyl)benzene [16] was prepared through $SiCl_4$ mediated triple condensation of 4-bromoacetophenone [21]. The inclusion compound **1a** was obtained from crystallization of **1** from DMSO.

X-ray structural study

The X-ray crystal structure of the inclusion compound **1a** [**1**·DMSO (1:3)] has been determined. Crystal data, details of the data collection and refinement calculations of the structure are summarized in Table 1. Information regarding non-covalent interactions is given in Table 2. A perspective view of the molecular structure including atom labeling and ring specification is shown in Fig. 1. Details of the packing structure are illustrated in Figs. 2, 3, 4, and 5.

The crystals of **1a** belong to the rhombohedral space group $R\bar{3}$. Since the threefold molecular symmetry

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1a 1 · DMSO (1:3)

Scheme 1 Compounds studied in this paper

coincides with the threefold crystallographic symmetry, the asymmetric part of the unit cell consists of one-third of the 1:3 host–guest aggregate (Fig. 1). Bond lengths and angles conform to expected values. The fluorenyl moieties of **1** deviate slightly from planarity and show maximum atomic distances of 0.073(3) [C(3)] and $-0.056(2)$ Å [C(5)] from the least squares plane of this unit. The twist angle between the phenylene rings (B) and the central aromatic ring (A) is $35.2(1)^\circ$, while the dihedral angle given by the best plane of a fluorenyl moiety and the ring plane of A is $73.8(1)^\circ$. The hydroxy hydrogens of the triol host form strong hydrogen bonds to DMSO molecules [O(1)–H(1)···O(1G) 1.89 Å, 161.7°], while the hydroxy oxygens participate in weaker C–H···O contacts [22] to one of the acidic hydrogens of neighbouring solvent molecules [C(2G)–H(2G3)···O(1) 2.76 Å, 114.9°]. According to its threefold symmetry, the host molecule adopts a bowl-like shape, which prevents a columnar packing of molecules in the solid-state structure. Instead, pairs of centrosymmetrically related host molecules form so-called ‘piedfort aggregates’ [1, 23] being stabilized by multiple C–H··· π contacts [24] between the aromatic units of the 9-phenylfluorene arms [C(10)–H(10)···C(2) 2.77 Å, 144.5° , C(16)–H(16)···C(17) 2.86 Å, 144.6°] as illustrated in Fig. 2. In this self-assembled dimer, which represents the basic supramolecular entity of the crystal structure, the central aromatic rings are accurately superposed and adopt a distance of 3.60 Å. On closer inspection of the geometry property of the present piedfort unit, a C_{3i} symmetry can be identified. As demonstrated in Scheme 2a, this is a symmetry for a benzene type piedfort aggregate known from previous structures described in the literature [23, 25, 26].

The symmetry relationships between molecules must also be fulfilled for a second crystal species [25]. In this way, the solvent molecules are assembled to hexameric

Table 1 Crystallographic and structure refinement data of compound **1a**

Compound	1a
Empirical formula	C ₆₃ H ₄₂ O ₃ ·3C ₂ H ₆ SO
Formula weight	1081.35
Crystal system	Rhombohedral
Space group	<i>R</i> -3
<i>a</i> (Å)	22.7618(4)
<i>b</i> (Å)	22.7618(4)
<i>c</i> (Å)	18.3872(9)
α (°)	90.0
β (°)	90.0
γ (°)	120.0
<i>V</i> (Å ³)	8250.1(5)
<i>Z</i>	6
<i>F</i> (000)	3420
<i>D</i> _c (Mg m ⁻³)	1.306
μ (mm ⁻¹)	0.191
Temperature (K)	153(2)
No. of collected reflections	53219
Within the ϕ -limit (°)	1.8–27.4
Index ranges $\pm h, \pm k, \pm l$	–29/29, –29/29, –23/23
No. of unique reflections	4158
<i>R</i> _{int}	0.0698
Refinement calculations: full-matrix least-squares on all <i>F</i> ² values	
Weighting expression <i>w</i> ^a	$\sigma^2(F_o^2) + (0.0873P)^2 + (0.0000P)^{-1}$
No. of refined parameters	238
No. of <i>F</i> values used	2860
[<i>I</i> > 2 σ (<i>I</i>)]	
<i>R</i> (=Σ Δ <i>F</i> /Σ <i>F</i> _o)	0.0581
<i>wR</i> on <i>F</i> ²	0.2006
<i>S</i> (=Goodness of fit on <i>F</i> ²)	1.088
Final $\Delta\rho_{\max}/\Delta\rho_{\min}$ (e Å ⁻³)	0.73/–0.57

$$^a P = (F_o^2 + 2F_c^2)/3$$

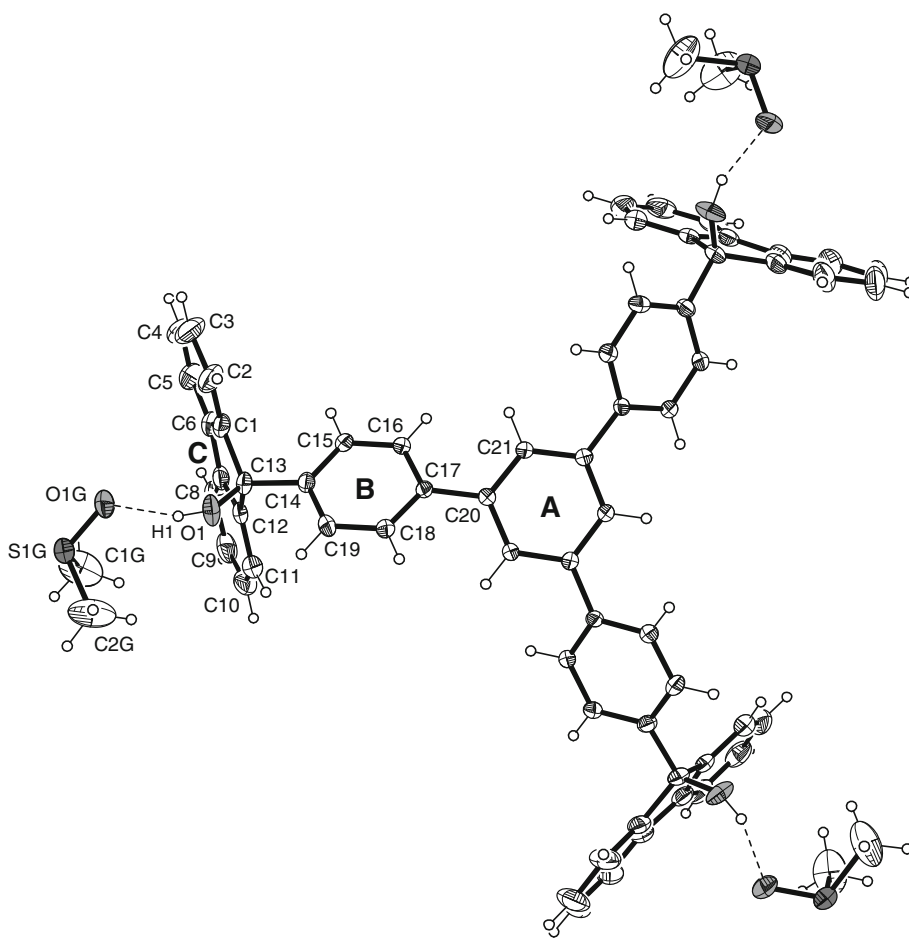
clusters (Fig. 3) held together by relatively strong hydrogen bonds of the C–H···O type [22] [C(2)–H(2G2)···O(1G) 2.60 Å, 138.9°]. The distance between the sulphur atoms of the trimeric elements of a cluster is 3.548(3) Å, which is less than twice of the van der Waals radius of sulphur (1.80 Å) thus indicating close S···S contact [27]. As apparent from the packing excerpt in Fig. 4, each of the hexamers of solvent molecules is occupied in a closed cavity formed by the fluorenyl parts of six host molecules, the hydroxy groups of which protrude out of the cavity wall. The occurrence of this particular kind of a solvent cluster is perhaps the most remarkable feature of the structure of **1a**. As far as we know, similar behaviour of DMSO as a component of crystalline solvent inclusion has

Table 2 Distances and angles of hydrogen bond type interactions observed for compound **1a**

Atoms involved D–H···A	Symmetry	Distance (Å)		Angle (°) D–H···A
		D···A	H···A	
O(1)–H(1)···O(1G)	x, y, z	2.696(3)	1.89	161.7
C(2G)–H(2G3)···O(1G)	$0.333 + y, 0.667 - x + y, -0.333 - z$	3.404(3)	2.60	138.9
C(2G)–H(2G3)···O(1)	$0.333 + y, 0.667 - x + y, -0.333 - z$	3.299(3)	2.76	114.9
C(8)–H(8)···C(16) ^a	$0.667 - x + y, 0.333 - x, 0.333 + z$	3.808(4)	2.87	170.6
C(9)–H(9)···C(15) ^a	$0.667 - x, 0.333 - y, 2.333 - z$	3.836(4)	2.93	159.3
C(10)–H(10)···C(2) ^a	$+x - y, x, 2 - z$	3.585(4)	2.77	144.5
C(16)–H(16)···C(17) ^a	$y, -x + y, 2 - z$	3.681(4)	2.86	144.9
C(18)–H(18)···C(9) ^a	$0.333 - x + y, 0.667 - x, -0.333 + z$	3.495(4)	2.71	140.2

^a To achieve a reasonable hydrogen bond geometry, an individual carbon atom instead of the ring centroid was chosen as an acceptor for CH/π interaction

Fig. 1 ORTEP plot of the 1·DMSO inclusion compound **1a**. Broken lines represent hydrogen bond interactions. Thermal ellipsoids are drawn at 40% probability level



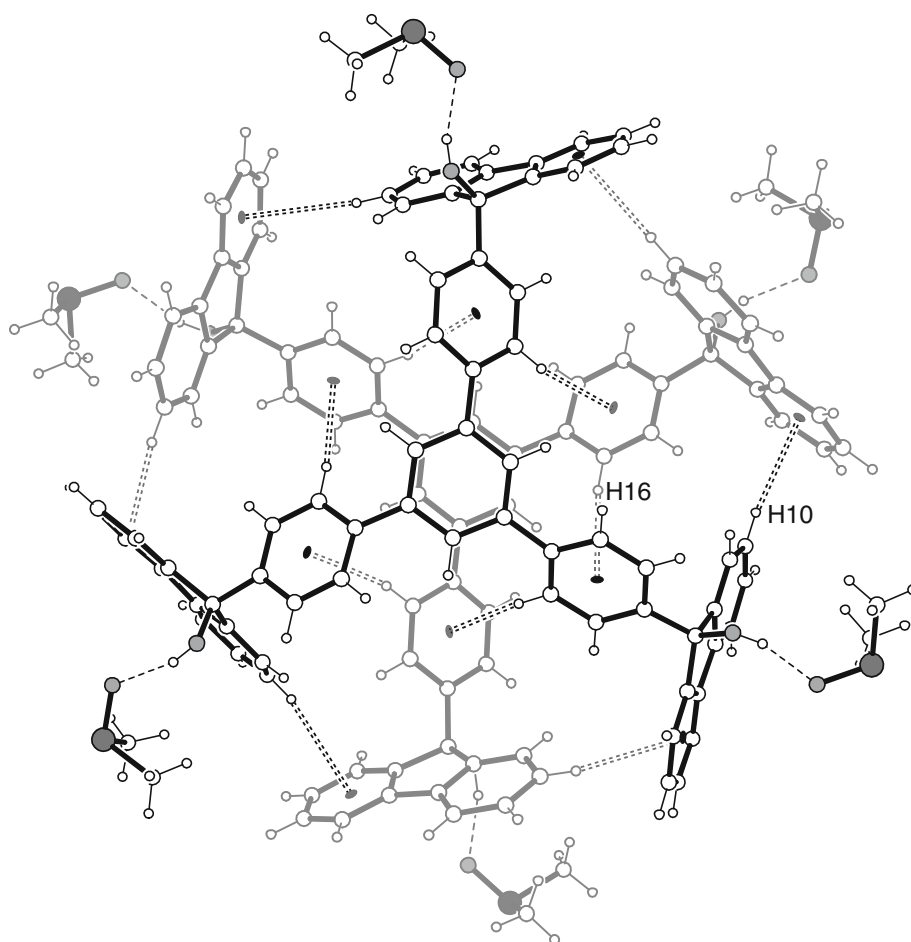
not been observed till now. Usually in the solid complexes of hydroxy hosts and others with DMSO, the solvent molecules are included as separate species [8, 28–30] or occasionally as dimers [31] and infinite chains [32].

A view of the crystal structure along the *a*-axis reveals a layered packing of molecules (Fig. 5). Within a given layer, the piedfort units of the triol are hydrogen bonded by

trimers of solvent molecules. The offset of consecutive molecular layers allows a variety of C–H···π (2.71–2.93 Å) and face-to-face interactions [33] with a distance of 3.2 Å between interacting aromatic residues.

Besides the above mentioned examples of benzene involved piedfort aggregates [23, 25, 26], a number of similar structures are reported [1], in particular referring to the

Fig. 2 Presentation of the piedfort unit existing in **1a**, viewed along the crystallographic *c*-axis. *Broken lines* represent hydrogen bond interactions, *broken double lines* CH/ π contacts



symmetrically trisubstituted 1,3,5-triazines [23, 26, 34, 35] instead of trisubstituted benzenes. Among them, 2,4,6-tris(4-bromophenoxy)-1,3,5-triazine shows a remarkable behaviour in their crystalline complexes [35]. Different from **1a**, here the C_3 -symmetric piedfort aggregates of the triazine (Scheme 2b) are directly interlinked via $\text{Br}\cdots\text{Br}$ interactions [36] resulting in the formation of a porous host lattice structure, which includes tri- or hexa-substituted aromatic guest molecules. On the other hand, in the *i*-PrOH complex of a related arylphenoxy substituted 2,4,6-triazine [26] which, however, lacks coordinating terminal groups, three different types of piedfort units following the symmetries C_3 , C_{3i} and D_3 (Scheme 2) coexist in the crystal structure, with the guests included in two crystallographically independent trigonal cages. Another specific mode of piedfort structure has been demonstrated with a trigonal compound possessing ethynylborneol side arms attached to a benzene unit, which gave rise to the formation of interlocked chiral piedfort pairs [37].

Conclusion

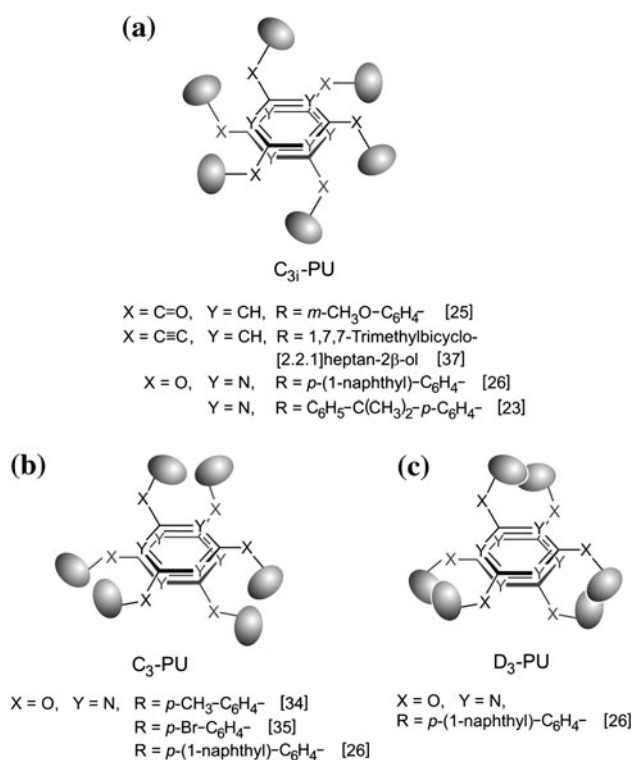
Following the broad use of the 9-hydroxy-9-fluorenyl residue as a bulky construction element for linear inclusion hosts

[2, 8, 38–40], this particular structural unit, now in the frame of compound **1**, proved also favourable for designing an analogous host molecule of trigonal geometry such as documented with the present 1:3 DMSO inclusion compound **1a**. The crystal structure of **1a** is a remarkable one showing a particular case of piedfort arrangement of host molecules. While the reported piedfort structures are mostly formed of trigonal host molecules possessing apolar side arms [23, 25, 26, 34, 35], the present host molecule is a functional derivative featuring hydroxy groups. They should have given rise to the realization of the uncommon hexameric cluster of DMSO molecules, being another characteristic of the structure of **1a**. Future studies involving compound **1** will show whether this host molecule is capable of enclathrating other solvent molecules in cluster mode in the crystal lattice, which would be a point of theoretical interest.

Experimental

General

The melting point (uncorrected) was determined on a microscope heating stage PHMK Rapido (Wägetechnik



Scheme 2 Symmetry types of piedfort units (PU) in the crystal structures of known compounds featuring a piedfort arrangement

Dresden). The IR spectrum was measured on a Nicolet FT-IR 510 as KBr pellet. ¹H and ¹³C NMR spectra were recorded on a Bruker Avance DPX 400 at 400 and 100 MHz, respectively, using TMS as reference. The MS spectrum was obtained from a Micromass Zabspec (FAB MS) instrument. The TLC analysis was performed with aluminium sheets precoated with silica gel 60 F₂₅₄ (Merck). Solvents were purified by standard procedures [41]. Fluoren-9-one was used as purchased (Acros). 1,3,5-Tris(4-bromophenyl)benzene was prepared according to the literature procedure [21].

Synthesis of the host compound 1

To a stirred suspension of 1,3,5-tris(4-bromophenyl)benzene (5.43 g, 10 mmol) in dry diethylether (60 mL) was slowly added via syringe *n*-BuLi (1.6 N in *n*-hexane, 23.8 mL, 38.0 mmol) at 0 °C under argon. The mixture was stirred for 3 h at the same temperature. A solution of fluoren-9-one (6.31 g, 35.0 mmol) in dry diethylether (50 mL) was added dropwise. Stirring was continued for 2 h at room temperature. The mixture was then heated to reflux until completeness of the reaction (tested by TLC), cooled to room temperature and quenched with a saturated aqueous solution of ammonium chloride. The solid was separated and washed with diethylether. The crude product

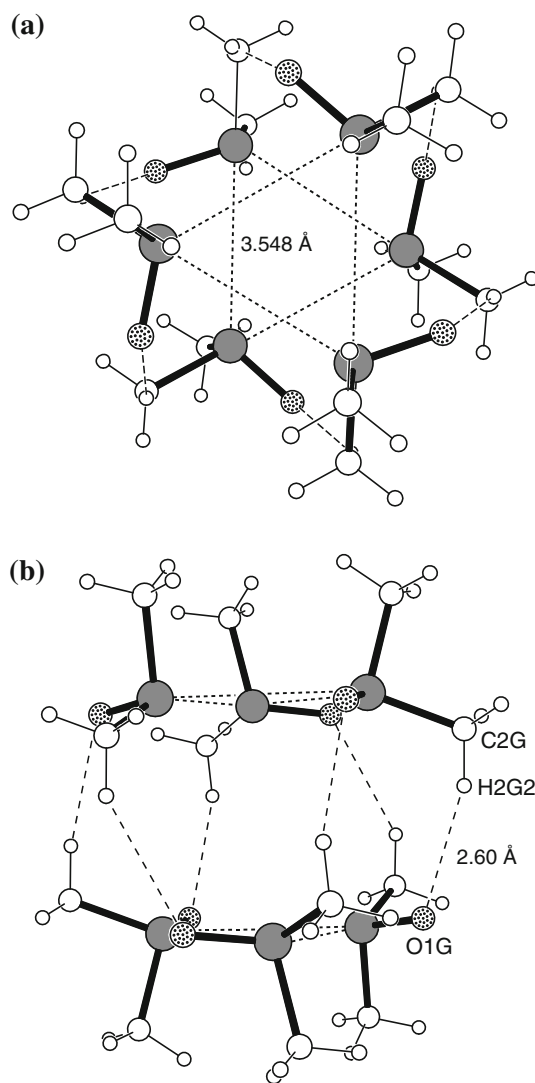


Fig. 3 **a** Top view and **b** side view of the hexameric cluster of DMSO solvent molecules in the crystal structure of **1a**. The sulfur atoms are displayed as *dark grey* and oxygen atoms as *dotted circles*. *Broken lines* represent hydrogen bond type contacts

was treated with refluxing dichloromethane, separated by filtration while hot and washed with additional dichloromethane to yield 2.4 g (29%) of a colourless powder. mp: 195–200 °C.

IR (KBr) $\tilde{\nu}$, cm⁻¹: 3416 (O–H), 3064, 3038 (Ar–H), 1631, 1605, 1590, 1564 (C=C), 1455, 1393, 1031 (C–O), 829, 772, 757, 741 (Ar–H). ¹H NMR (CDCl₃/[D₆-DMSO]) δ , ppm: 2.59 (s, 3 H, OH), 7.23–7.27, 7.34–7.39, 7.44–7.52, 7.64–7.69 (m, 39 H, Ar–H). ¹³C NMR (CDCl₃/[D₆-DMSO]) δ , ppm: 82.5 (C–OH), 119.3, 125.5, 127.7 (Ar–CH), 124.0, 124.4, 126.3, 128.1 (Fluorenyl–CH), 138.9, 139.1, 143.5 (Ar–C), 141.3, 150.8 (Fluorenyl–C). MS (FAB) *m/z*: 839 (M⁺). Anal calcd. for C₆₃H₃₄O₃: C 90.19, H 4.08; found C 89.87, H 3.94.

Fig. 4 Packing excerpt of the inclusion structure of **1a**. The sulfur atoms are displayed as *dark grey* and oxygen atoms as *light grey circles*. *Broken lines* represent hydrogen bond interactions

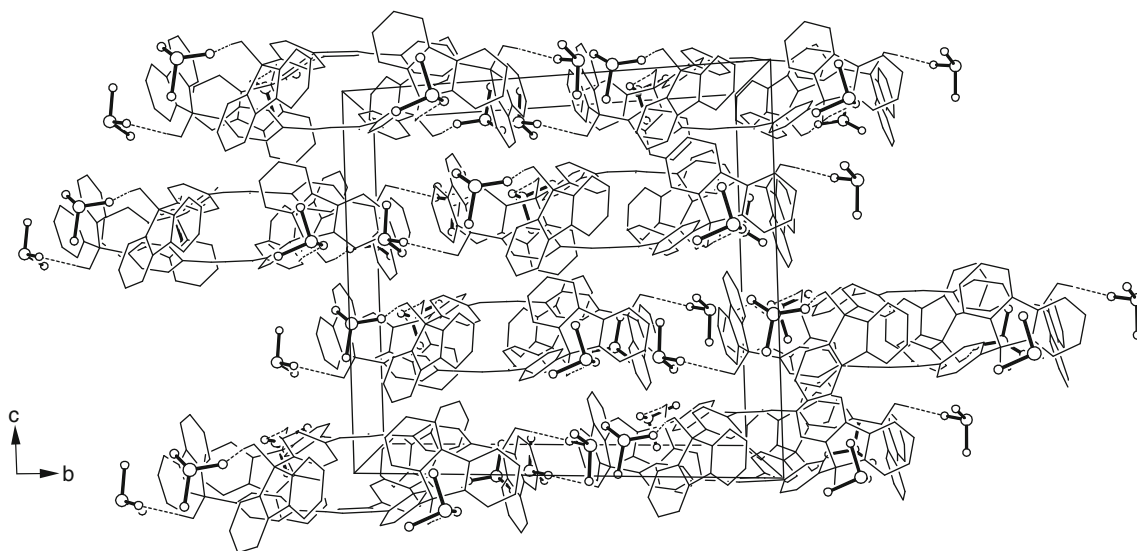
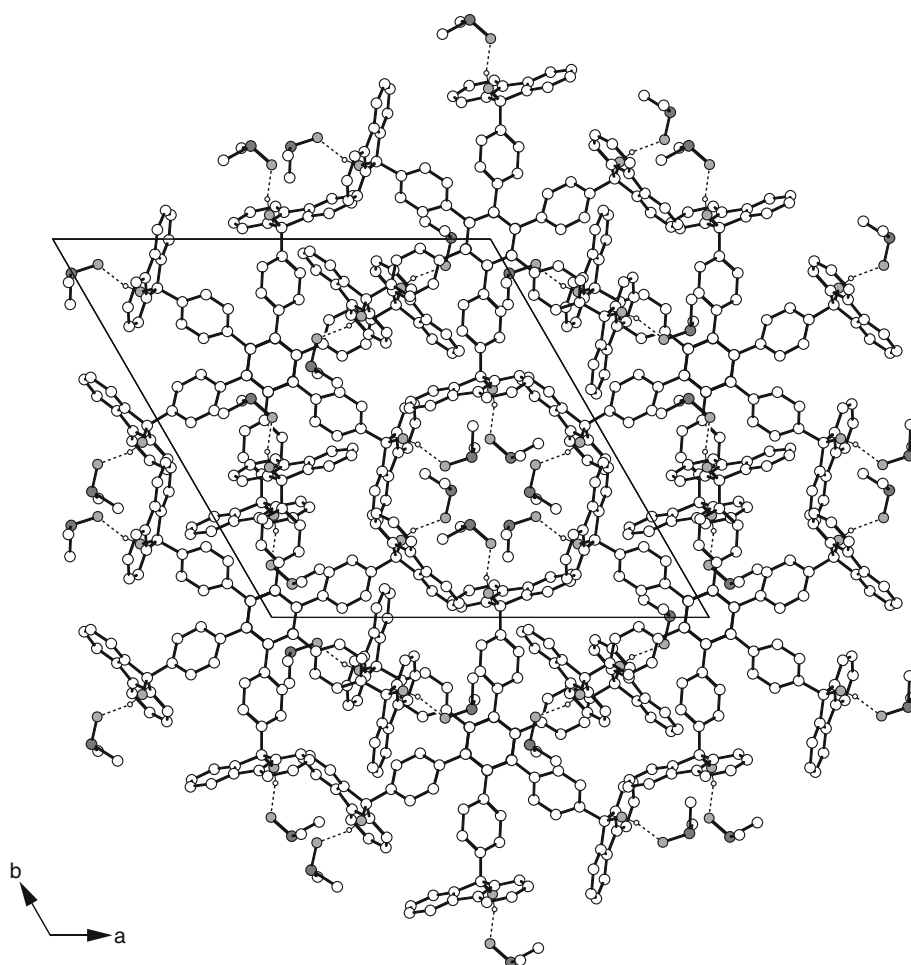


Fig. 5 Packing diagram of **1a** viewed along the crystallographic *a*-axis. Molecules of the host lattice are displayed as a wire model, DMSO molecules as a ball-and-stick model. *Broken lines* represent hydrogen bond interactions

X-ray crystallography

Single crystals of the inclusion compound **1a** suitable for data collection were obtained from slow crystallization of **1** from DMSO. A Bruker APEX II diffractometer ($\lambda_{\text{MoK}\alpha} = 0.71073 \text{ \AA}$, graphite monochromator) was employed for data collection using ω - and ϕ -scans. Reflections were corrected for background, Lorentz and polarisation effects. Preliminary structure models were derived by application of direct methods [42] and were refined by full-matrix least-squares calculation based on F^2 for all reflections [42]. All hydrogen atoms were included in the models in calculated positions and were refined as constrained to bonding atoms. Crystallographic data for the structure have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC-782503. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2, 1EZ, UK (fax: +44-1223-336033, e-mail: deposit@ccdc.cam.ac.uk).

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