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Synthesis and Structural Studies of Cyclotriveratrylene Derivatives

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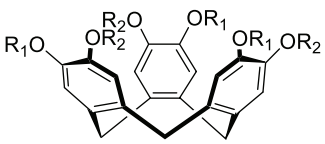
Cyclotriveratrylene (CTV) derived host molecules with ethyl, propyl, allyl or propargyl functional groups have been synthesised using standard or solventless reaction methodologies. The known structural and clathrate chemistry of cyclotriveratrylene (CTV) and these analogues has been extended. Crystal structures of the hexa(ethyl), tri(ethyl), tri(propargyl) analogues have been determined, and show either intra-cavity host-guest binding or self-stacking motifs. Two new clathrates of CTV have also been structurally characterised, namely CTV.$(DMSO)_2$.$(H_2O)_2$ with intra-cavity complexation of DMSO, and CTV.$(EtOH)_{0.25}$ which has a γ-phase CTV structure.

Keywords: Cyclotriveratrylene; Host molecules; Clathrate complexes; Crystal structures

INTRODUCTION

Cyclotriveratrylene (CTV **1**) is a cyclic trimer of veratrole with a relatively rigid bowl-shape [1]. It is an excellent host molecule for fullerene-C_{60} [2–4], and forms intra-cavity host-guest complexes with it and other large guest molecules or ions including *o*-carborane [5], organometallic sandwich complexes [6], {Na[2.2.2]cryptate}$^+$[7], and $[Ag(NCCH_3)_4]^+$[8]. CTV can be incorporated into infinite network structures through hydrogen bonding interactions to the dimethoxy groups [9–11] and/or through coordinate interactions with Group 1 metal cations [12–18]. In such network structures the intra-cavity guest molecule can be a small organic solvent molecule [10–16], or larger *o*-carborane, fullerene-C_{70} [9] or dimeric $(C70)_2^-$ [17,18].



$R_1 = R_2 = CH_3$ CTV **1**

With small organic guest molecules as potential guests, CTV alone does not usually form intra-cavity host-guest complexes, rather forming clathrate inclusion complexes in the majority of cases. Two main phases have been identified, α and β-phase CTV [19–23], where the CTV molecules stack into misaligned columns and guest molecules are contained within channels created by the packing of these columns. The self-stacking columns of CTV do not generally show π-π stacking interactions. The α-phase structure is characterised by a unit cell length, usually that of *b*, of around 9.60–9.80 Å and occurs for unsolvated CTV [20], and clathrate complexes with guests H_2O [21], benzene and water, toluene and water, bromobenzene and water [22], chlorobenzene [23], chloroform [22] and carbon tetrachloride [24]. The β-phase CTV clathrates show a rotation of one methoxy group of the CTV [22], which is characterised by a shorter *b* unit cell length of around 8.00–8.40Å. This occurs with guests acetone, dimethoxyethane [22], carbon disulfide and butirric acid [23]. There is one known example of γ-phase CTV clathrate that occurs in a 4:1 CTV:acetone complex where two types of inclusion behaviour are observed; a misaligned self-stacking similar to that of α-phase CTV and a molecular

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capsule arrangement where two CTV molecules form a head-to-head association around guest acetone molecules [25]. Recently two further examples of intra-cavity complexation within CTV inclusion complexes have been reported with guests 1,1,2-trichloroethane, and a mixture of 1,1,2-trichloroethane and 1,1,
1-trichloropropane [24].

The CTV framework can be covalently modified to give cryptophanes [1] and extended arm hosts [1,26–35]. While there are many examples of extended arm hosts, there have been few structural studies of their inclusion chemistry [30–35]. There is only one reported example of a crystal structure of a hexa-substituted CTV analogue, in which the host molecules show a perfectly aligned self-stacking motif [30]. Tri-substituted analogues fall into one of three categories; a mis-aligned self-stacking motif similar to that of β-phase CTV [31,32]; a self-clasping motif where an arm of one host acts as the guest for another host and vice versa [30,33,34]; and a head-to-head dimerisation around guest molecules to give a molecular capsule [35], similar to that seen in γ-phase CTV.

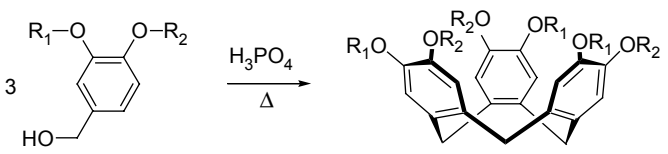
We report herein the crystal structures of new CTV clathrate complexes, including the second example of γ-phase CTV; a number of new structures and clathrates of extended arm CTV analogues, along with the synthesis of various extended arm CTV analogues. The traditional synthesis of CTV and some hexa-substituted derivatives has involved strongly acidic conditions, such as glacial acetic acid/H_2SO_4 mixtures [36]. Tri-substituted analogues can be synthesised either from direct condensation of a benzyl alcohol using $HClO_4$ [37–39], or via a preformed CTV analogue with $R_1 = CH_3$ and $R_2 = H$ [26–29]. Considerably faster, simpler and greener routes to CTV and a tri-allyl substituted host were reported in 2000 by Raston and coworkers [31], who reported excellent yields by reacting the appropriate benzyl alcohol in an ionic liquid with only a catalytic amount of H_3PO_4. Smaller but still respectable yields could be obtained in the absence of any solvent by simply heating the benzyl alcohol with catalytic amounts of H_3PO_4. Notably, these methods did not give any traces of higher oligomers such as the tetrameric cyclotetraveratrylene. We have adopted the latter methodology and have been exploring its generality for synthesising various hexa and tri substituted CTV analogues.

RESULTS AND DISCUSSION

Synthesis of Host Compounds

The synthesis of hexa-substituted CTV analogues with extended alkyl and unsaturated groups was attempted using the solvent-less approach according to Scheme 1. This involved heating the appropriately substituted benzyl alcohol with small amounts of pure H_3PO_4. For the hexa-ethyl and hexa-propyl substituted hosts, **2** and **3**, the benzyl alcohol starting materials were synthesised from the corresponding aldehyde, which were generated by reaction of the appropriate RBr species with 3,4-dihydroxybenzaldehyde, all according to established procedures [40,41]. These were then cyclised according to Scheme 1, but only 2,3,7,8,12,13-hexa-ethoxy-10,15-dihydro-5*H*-tribenzo-[*a*,*d*,*g*]cyclononene or hexakis(ethyl)CTV **2** was successfully synthesised in any appreciable yield. This compound has been previously reported in better yields from the condensation of diethoxybenzene with formaldehyde in glacial acetic acid/H_2SO_4 [36]. Synthesis of the hexa-substituted CTV analogues with allyl and propargyl groups, compounds **4** and **5** respectively, was not attempted by the method shown in Scheme 1 due to difficulties in synthesising the aldehyde intermediates. Instead compounds **4** and **5** were synthesised by the commonly employed alternative route shown in Scheme 2 which involves reaction of allyl bromide or propargyl bromide with cyclotricatechylene ($R_1 = R_2 = H$, CTC). 2,3,7,8,12,13-hexa-prop-2-enyloxy-10,15-dihydro-5*H*-tribenzo-[*a*,*d*,*g*]cyclononene, **4** and 2,3,7,8,12,13-hexa-prop-2-ynyloxy-10,15-dihydro-5*H*-tribenzo-[*a*,*d*,*g*]cyclononene, **5** have not been previously reported.

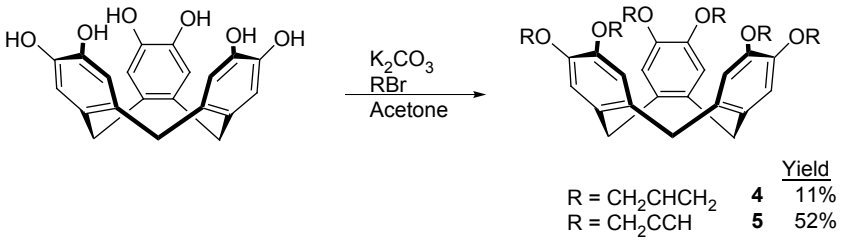
The analogous tri-substituted compounds **6** to **8** were also synthesised by the solvent-less method shown in Scheme 1, noting that the synthesis of the allyl derivative, 2,2,12-tris-alloxy-3,8,13-trimethoxy-10,



		Yield
$R_1=R_2=CH_2CH_3$	**2**	46%
$R_1=R_2=CH_2CH_2CH_3$	**3**	0%
$R_1=R_2=CH_2CHCH_2$	**4**	-
$R_1=R_2=CH_2CCH$	**5**	-

		Yield
$R_1=CH_3;R_2=CH_2CH_3$	**6**	59%
$R_1=CH_3;R_2=CH_2CH_2CH_3$	**7**	13%
$R_1=CH_3;R_2=CH_2CCH$	**8**	18%

SCHEME 1



SCHEME 2

15-dihydro-*5H*-tribenzo[*a,g,d*]cyclononene has already been reported by this method [31]. The benzyl alcohol precursor for **8**, 4-(prop-2-ynyloxy)-3-methoxybenzylalcohol (or 4-propargyl-3-methoxybenzylalcohol) has not been previously reported and was synthesised in good yields from reaction of 4-hydroxy-3-methoxybenzylalcohol and propargyl bromide in the presence of base. Of compounds **6** to **8** only 2,7,12-tri-methoxy-3,8,13-tri-ethoxy-10,15-dihydro-5*H*-tribenzo-[*a,d,g*]cyclononene **6** has been previously reported, in lower yields than found here, from the acid catalysed condensation of 4-ethoxy-3-methoxybenzyl alcohol with large amounts of perchloric acid [37].

Structural Studies of CTV Analogues

The hexa- and tri-substituted hosts molecules **2** and **3–8** were recrystallised from solvents dimethylsulfoxide (DMSO), acetontrile and/or dichloromethane. Crystals of a quality suitable for single crystal studies were isolated for the hexakis-ethyl derivative **2**, for the tri-ethyl derivative **6**, and for the tri-propargyl derivative **8**.

Unsolvated single crystals of **2** were obtained by recrystallisation of **2** from DMSO, while a clathrate complex of **2**, **2**.$(CH_3CN)_3$, was obtained by recrystallisation from acetonitrile. The unsolvated host **2** crystallises in a monoclinic cell with a *b* unit cell length of 9.5645(2)Å. This is within the range found for α-phase CTV clathrates as well as unsolvated CTV, and the structure of **2** is closely related to that of α-phase CTV. There are two molecules in the asymmetric unit, and they differ in the orientation of their ethyl groups. In one molecule, shown on the left of Fig. 1, all torsion angles between the H_3C-CH_2 and O-C_{aryl} bonds of each group are reasonably close to 180°, while in the second molecule, shown to the right of Fig. 1, there is one ethyl group twisted out of plane with a torsion angle of 72° between the H_3C-CH_2 and O-C_{aryl} bonds. Crystallographically equivalent molecules stack into columns along the *b* axis, Fig. 2a. Molecules within each column are related by a 2_1 screw axis giving two molecular orientations within each column, although both have the bowl of the molecular host pointing in approximately the same direction. This is essentially the same as the misaligned columns found in α-phase CTV. These columns pack in the crystal lattice such that columns adjacent to one another along the *c* axis have alternating up-down orientations, but have the same up-up or down-down orientation along the *a* axis. This arrangement effectively fills space, Fig. 2b, and there are no enclathrated guest molecules.

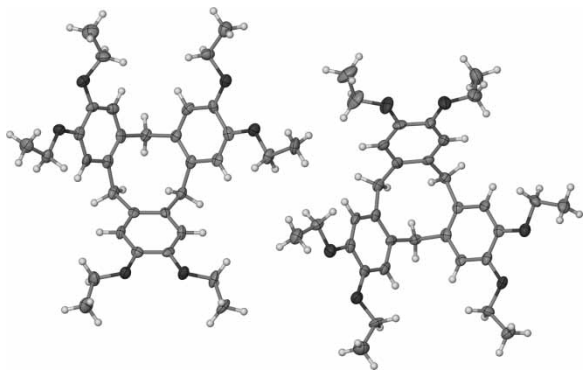


FIGURE 1 Asymmetric unit of the crystal structure of **2**. The hexakis(ethyl)CTV shown on the right has one ethyl group bent out of plane. Ellipsoids are shown at 50% probability level.

The 1:3 host:guest complex **2**.$(CH_3CN)_3$ has an entirely different structure to the unsolvated crystals of **2**. The complex crystallises in an orthorhombic unit cell and there is half a host molecule and one and a half CH_3CN molecules in the asymmetric unit. A mirror plane runs through the host, and all of the ethyl arms have similar conformations. There are two crystallographically distinct acetonitrile guest molecules, one of which is an intra-cavity guest for the hexakis(ethyl)CTV host, Fig. 3. As would be anticipated from the hydrophobic effect, the methyl end of the CH_3CN points into the hydrophobic host cavity, at a distance of 3.996Å from the CH_3CN methyl carbon atom to the centre the plane formed by three bridging methylene groups of the host.

Packing of the host molecules is such that the nearest neighbour host molecules have an inverted orientation with their extended ethyl arms encroaching into the molecular cavity, Fig. 4a. Host-guest assemblies show an aligned stacking along the *b* axis, although these assemblies are well separated at the *b* unit cell length of 9.1395(2)Å, Fig. 4a. The overall packing diagram viewed down the *b* axis is shown in Fig. 4b, which shows formation of square channels throughout the structure, which are occupied by additional acetonitrile guest molecules.

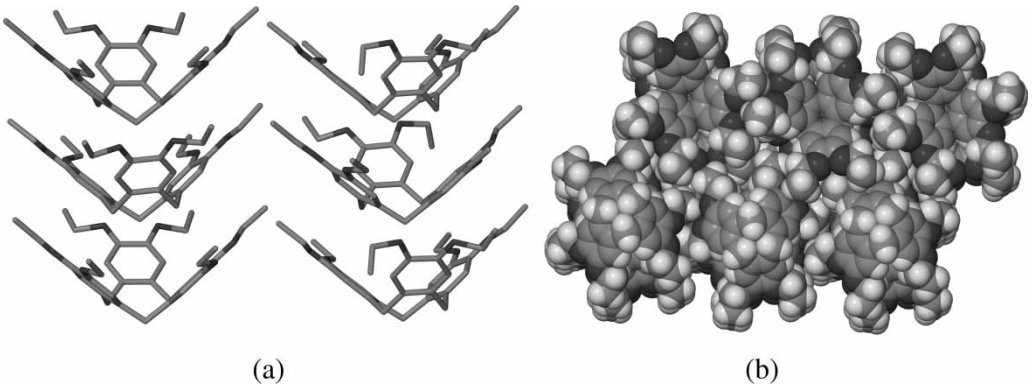


FIGURE 2 Packing of host molecules in the crystal structure of **2**. (a) Side views of misaligned columns of **2**; (b) top-view showing packing of columns.

The tri-ethyl substituted CTV analogue, compound **6**, also forms a 1:3 host-guest clathrate complex with acetonitrile, complex **6**.$(CH_3CN)_3$. This has a high symmetry structure, crystallising in a trigonal space group, with one third of the host and an acetonitrile molecule in the asymmetric unit. Unlike complex **2**.$(CH_3CN)_3$, this structure does not show intra-cavity inclusion of the acetonitrile guest by the host, which instead forms a self-stacking motif. The tri-ethyl substituted hosts pack into columns with perfect alignment of the $[(C_6H_4)CH_2]_3$ cores of the host molecules, at a separation of 4.69Å, half the *c* unit cell length, Fig. 5. Tri-substituted CTV derivatives are chiral and adjacent molecules of **6** within each self-stacking column have the opposite chirality, hence the ethyl and methyl arms are not perfectly aligned within the columns, but have alternating identities.

The columns of self-stacking host molecules pack in the crystal lattice such that multiple channels are created along the *c* axis, Fig. 6. Channels occur in a hexagonal arrangement, with six channels surrounding each column of host molecules, and these channels are occupied by acetonitrile molecules. The orientation of the acetonitrile molecules is the same within each channel and alternates around the host column, with the methyl end of a CH_3CN molecule pointing towards each methoxy/ethoxy region of the host, and a nitrile end pointing towards each aryl-CH_2-aryl region of the host. The acetonitrile approaches the methoxy group of the host sufficiently closely to indicate formation of a weak C-H···OMe hydrogen bond, with C-H···O distance 2.447Å and corresponding C···O distance 3.204Å. The nitrile group of the CH_3CN shows a closest contact with an aryl C-H of the host at CN···H-C distance 2.766Å and N···C distance 3.675Å.

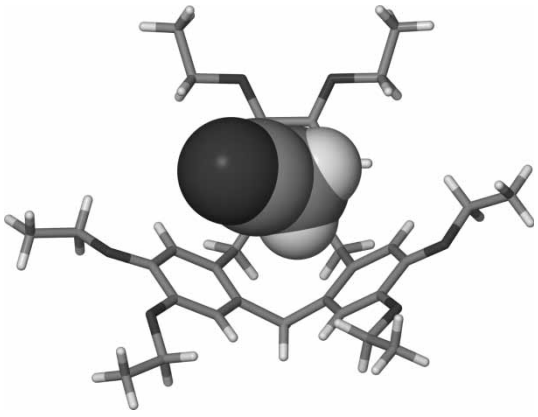


FIGURE 3 Host-guest assembly from the crystal structure of complex **2**.$(CH_3CN)_3$, showing intra-cavity complexation of the CH_3CN guest.

Recrystallisation of the tri(propargyl) derivative **8** from DMSO solution gives unsolvated single crystals after several weeks of standing. Compound **8** crystallises with a monoclinic cell and the asymmetric unit of the structure comprises a molecule of **8**. The arrangement of the OCH_2CCH arms in the crystal structure of **8** is not symmetric, with two propargyl arms extending away from the molecular bowl, while the third is bent away from the molecular bowl with a torsion angle of 52.2° between the C≡C and O-C_{aryl} bonds, Fig. 7a. The *b* unit cell length is 9.3976(3)Å, which is slightly less than the typical stacking length of α-phase CTV, and host **8** does show a misaligned self-stacking motif very similar to that of α-phase CTV, Fig. 7b. Each molecule of **8** within a misaligned column is the same enantiomer, unlike in the stacking pattern seen in **6**.3(CH_3CN).

The misaligned columns of **8** pack together such that the adjacent columns have alternating orientations of the molecular cavities of the host molecules, Fig. 8a. This arrangement effectively fills space and there are no included guest molecules. The packing together of the columns seems influences by weak interactions of the extended propargyl extended arms, Fig. 8b. The bent propargyl arm is directed towards an aryl ring of a neighbouring host, which in turn has its bent propargyl arm pointing towards the aryl ring in a pairwise motif at long C-H···π distance 3.023Å (C···π distance 3.815Å). One of the straight

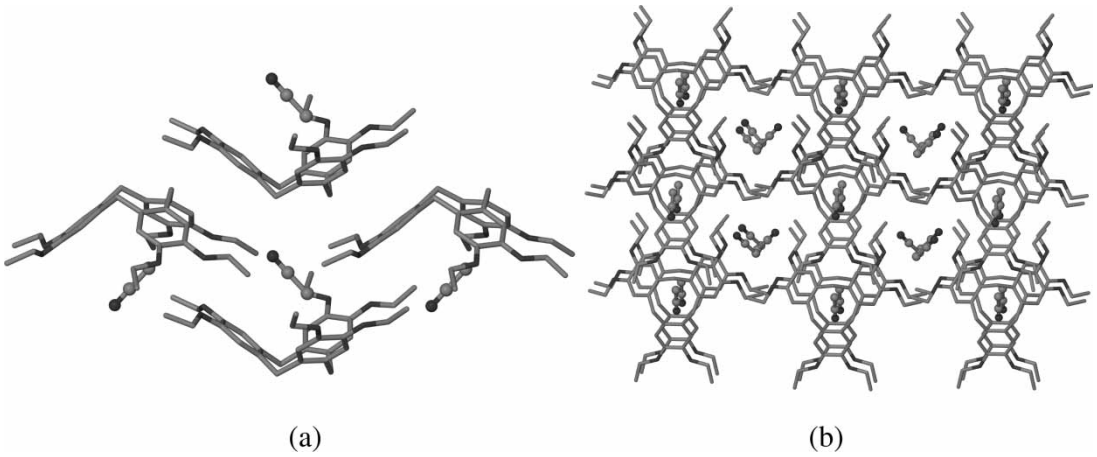


FIGURE 4 Crystal packing in complex **2**.(CH-CN)$_3$. (a) Detail showing close approach of host-guest assemblies; (b) view down the *b* axis illustrating formation of square channels containing additional CH_3CN molecules.

propargyl groups forms a weak C-H···OMe hydrogen bond to a neighbouring host at C-H···O distance 2.125Å (C···O distance 3.113Å), while the other straight propargyl arm hydrogen bonds in a pairwise ring motif, again through C-H···OMe interactions (C-H···O distance 2.323Å, C···O distance 3.243Å). This final hydrogen bonding interaction has the propargyl groups in a parallel but slipped arrangement with a 3.539Å separation between the alkyne centroids, indicating additional π-π stacking interactions.

New Clathrates of CTV

CTV dissolved in DMSO and the solution left to slowly evaporate for several weeks gives clathrate crystals of composition **1**.$(DMSO)_2$.$(H_2O)_2$. The complex crystallises with a monoclinic cell and the asymmetric unit of the structure is comprised of one CTV molecule, two DMSO and two water molecules. The two DMSO molecules show different behaviour with one acting as an intra-cavity guest for the CTV. This DMSO has its S atom disordered over two positions, and one of the methyl groups is directed into the cavity of the CTV at a distance of 3.944Å from the DMSO methyl carbon atom to the centre the plane formed by three bridging methylene groups of the host. The C=O of this guest DMSO is a hydrogen bond acceptor for both water molecules at O···O separations 2.854 and 2.603Å. The water molecules also hydrogen bond to the crystallographically distinct DMSO molecule at O···O distances 2.858 and 3.173Å, Fig. 9.

The crystal packing in complex **1**.$(DMSO)_2(H_2O)_2$ is shown in Fig. 10. The host-guest assemblies are well separated from one another and do not form π-π stacking interactions between the CTV hosts; aryl rings that appear aligned for such interactions are separated by over 4.5Å. Host-guest assemblies are aligned with the same orientation through slices

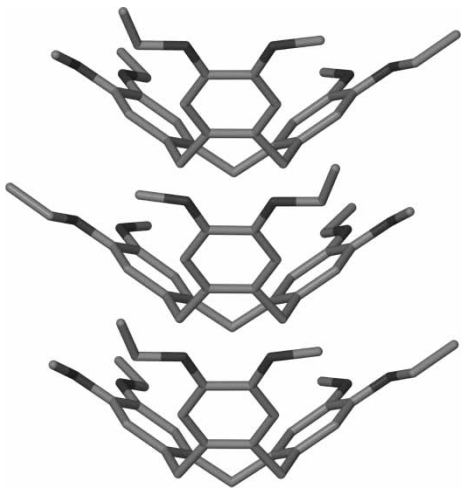


FIGURE 5 Column of stacked host molecules in the crystal structure of complex **6**.$(CH_3CN)_3$. Note that alternating host molecules in the column have opposite chiralities.

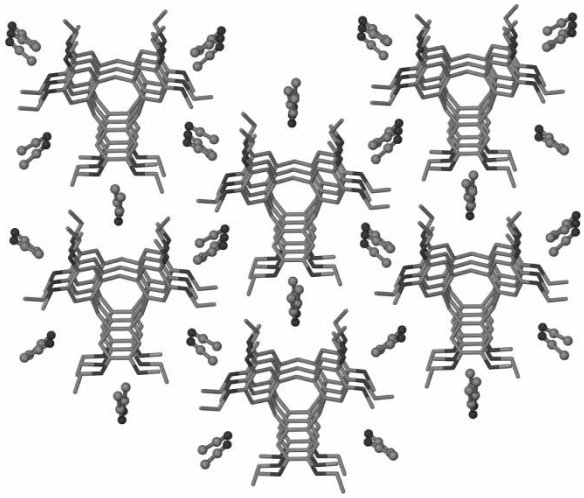


FIGURE 6 Crystal structure of complex **6**.$(CH_3CN)_3$ viewed down the *c* axis. Each column of self-stacking host molecules is surrounded by acetonitrile-containing channels in a hexagonal arrangement.

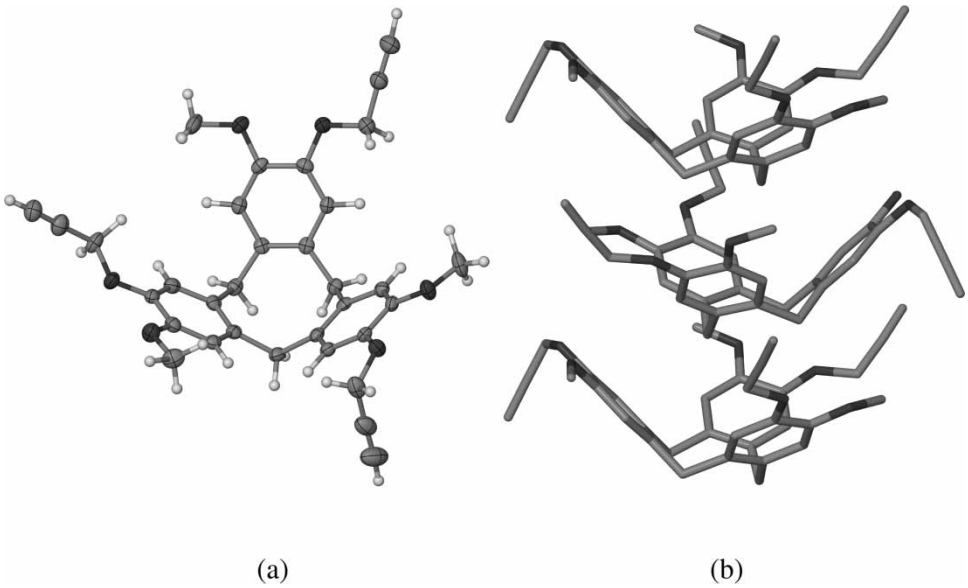


FIGURE 7 Crystal structure of **8**. (a) Asymmetric unit with ellipsoids shown at 50% probability level; (b) stacking of host molecules into a misaligned column.

of the *bc* plane, and the orientation of the CTV bowl alternates along the *a* axis. This crystal packing is quite distinct from packing of the host-guest assemblies of other known examples of intra-cavity complexation with CTV hosts and small organic guests [24].

Attempts to recrystallise the related host cyclotetraveratrylene (CTTV) from ethanol gave minor amounts of a CTV clathrate, presumably from a slight contamination of CTTV with CTV. Although only a contaminant, the clathrate isolated, **1**$(CH_3CH_2OH)_{0.25}$, is worth reporting as it is only the second example of γ-phase CTV. The structure of **1**.$(CH_3CH_2OH)_{0.25}$ is isostructural with the previously reported γ-phase CTV with acetone.[17] There are two types of CTV host with one forming a self-stacking motif typical of α-phase CTV, while the other forms a head-to-head capsule arrangement around the disordered ethanol guest, Fig. 11.

In summary, the solventless methodology for the synthesis of CTV derivatives has been shown to be effective for a variety of tri-substituted CTV analogues with both alkyl and unsaturated functional groups. The approach was less successful for hexa-substituted derivatives with 3,4-diethylbenzylalcohol successfully cyclising, but the bulkier 3,4-dipropylbenzylalcohol did not react to any appreciable extent. New crystal structures and clathrate complexes of extended arm CTV-type hosts have been characterised and these show a distinct preference for forming self-stacking columns of host molecules, usually with stacking

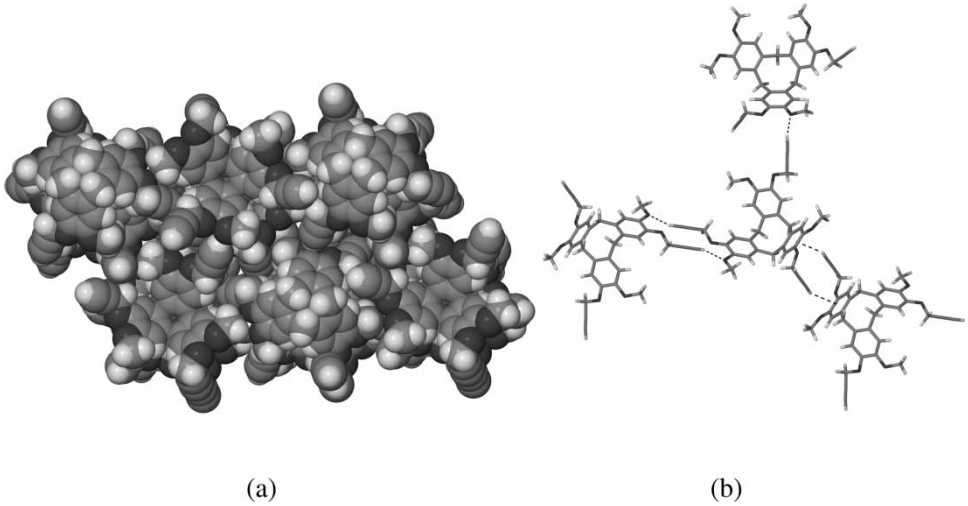


FIGURE 8 Crystal packing of **8**. (a) Space-filling diagram showing orientations of neighbouring columns of host molecules; (b) detail of intermolecular interactions with dashed lines indicating weak hydrogen bonds or long C-H···π contacts.

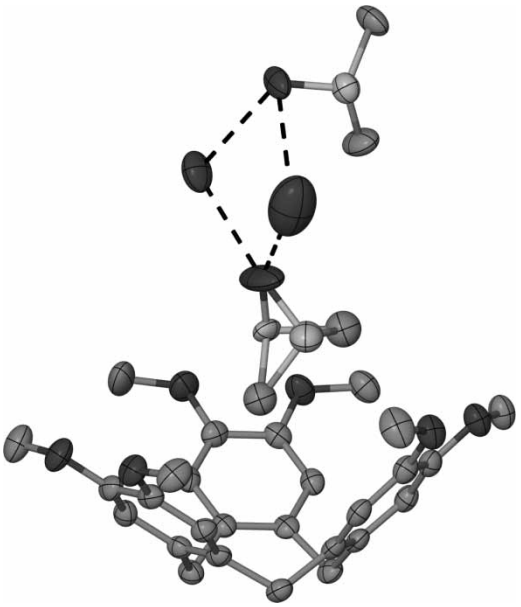


FIGURE 9 Intra-cavity host-guest assembly of complex **1**.$(DMSO)_2$.$(H_2O)_2$. Guest DMSO has S atom disordered across two positions. Dashed lines indicate hydrogen bonding. Ellipsoids shown at 50% probability levels and hydrogen atoms excluded for clarity.

patterns closely related to those shown by α-phase CTV clathrates.

EXPERIMENTAL

Melting points were recorded on a Bibby melting point apparatus and are uncorrected. The University of Leeds microanalytical laboratory performed elemental analyses. NMR spectra were recorded on a Bruker 250 MHz or Bruker 300 MHz spectrometer. Solvents were pre-dried over the appropriate drying agent and then distilled under an inert atmosphere.

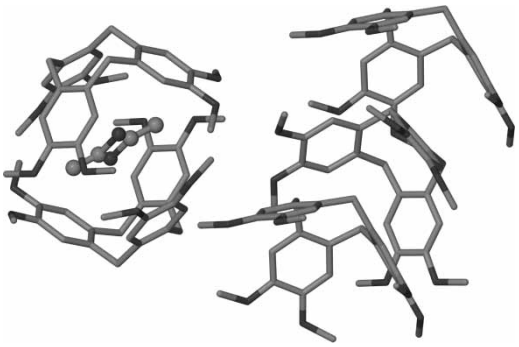


FIGURE 11 Partial packing diagram from the crystal structure of **1**.$(EtOH)_{0.25}$, showing misaligned self-stacking of CTV molecules on right, and formation of a capsule-like assembly around guest EtOH on left. The EtOH molecule is disordered across the two positions shown.

Cyclotricatechylene was prepared from CTV by the literature procedure [36].

2,3,7,8,12,13-Hexa-ethoxy-10,15-dihydro-5*H*-tribenzo-[*a*,*d*,*g*]cyclononene, 2

3,4-Diethoxybenzylalcohol (0.81 g, 4.1 mmol) was heated to approximately 80–90°C in a round bottom flask. A spatula tip of phosphoric acid crystals were then added with stirring. Once the mixture became solid the reaction mixture was cooled, methanol was added and it was left to stir for 1 hour. The resulting off-white product, **2**, was filtered off. Yield: 0.34 g: 46%. ^{1}H NMR: (500.23 MHz, $CDCl_3$, 300.0 K) δ 1.39 (t, 18H, OCH_2CH_3), 3.50 (d, 3H, -CH_2-link, ^{2}J (^{1}H-^{1}H) = 13.80 Hz), 4.04 (q, 12H, OCH_2CH_3), 4.72 (d, 3H, -CH_2-link, ^{2}J (^{1}H-^{1}H) = 13.70 Hz), 6.83 (s, 6H, aryl ring C*H*). ^{13}C-{^{1}H} NMR: (125.79 MHz, $CDCl_3$, 300.0 K) δ 14.92 (OCH_2CH_3), 36.35 (-CH_2-link), 64.88 (OCH_2CH_3), 113.53 (aryl ring *C*H). IR (KBr, ν cm^{-1}): 2980s, 2928s,

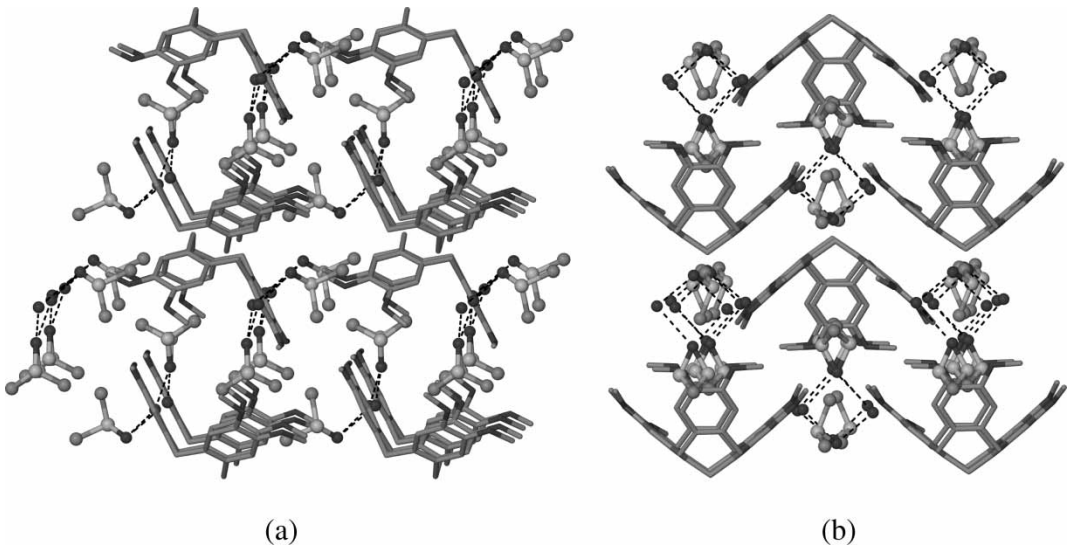


FIGURE 10 Crystal packing of complex **1**.$(DMSO)_2$.$(H_2O)_2$. (a) View down *b* axis; (b) view down *c* axis.

2901s, 2872s, 2737m, 2612m, 2440w, 1945m, 1607s, 1512s, 1478s, 1443s, 1368s, 1337s, 1262s, 1217s, 1196s, 1148s, 1090s, 1042s. Microanalysis calculated for $C_{33}H_{42}O_6.{}^1/_2H_2O$: C, 72.89; H, 7.99%. Found: C, 73.30; H, 7.70%. MS (ES): 535.3 [M^+], 552.3 ([M^+] + 17). Mp: 152-153°C.

2,3,7,8,12,13-Hexa-prop-2-enyloxy-10,15-dihydro-*5H*-tribenzo-[*a,d,g*]cyclononene, 4

Cyclotricatechylene (1.12 g, 3.07 mmol) was dissolved in 100 cm^3 of acetone under N_2, together with an excess of K_2CO_3 (4.01 g, 0.04 mol) and heated to reflux. A slight excess beyond six equivalents of allyl bromide (1.76 cm^3, 0.021 mol) was then added and the reaction mixture was then stirred under reflux conditions for approximately 12 hours. The reaction mixture was cooled and acetone removed under reduced pressure. Water (30 cm^3) was added to the residue and then extracted with dichloromethane (3×50 cm^3). The extracts were combined, dried over anhydrous magnesium sulfate, filtered and solvent removed under reduced pressure to give the off-white precipitate **4**. Yield: 0.21 g: 11%. ^{1}H NMR: (500.23 MHz, $CDCl_3$, 300.0 K) δ 3.48 (d, 3H, -CH_2-link, ^{2}J (^{1}H-^{1}H) = 13.79 Hz), 4.56 (m, 12H, OCH_2 CHCH_2), 4.70 (d, 3H, -CH_2-link, ^{2}J (^{1}H-^{1}H) = 13.72 Hz), 5.25 (d, 6H, OCH_2CHCH_2), ^{2}J (^{1}H-^{1}H) = 10.47 Hz), 5.39 (d, 6H, OCH_2CHCH_2), ^{2}J (^{1}H-^{1}H) = 17.28 Hz), 6.06 (m, 6H, OCH_2CHCH_2), 6.83 (s, 6H, aryl ring C*H*). ^{13}C-{^{1}H} NMR: (125.78 MHz, $CDCl_3$, 300.0 K) δ 35.47 (-CH_2-link), 69.38 (OCH_2CHCH_2), 115.32 (aryl ring C H), 116.30 (OCH_2CHCH_2), 131.41 (C_q), 132.83 (OCH_2CHCH_2), 146.35 (C_q). IR (solid phase, ν cm^{-1}): 2997s, 2948s, 2909s, 2882s, 2694s, 2656m, 2604s, 2018s, 1645s, 1605s, 1505s, 1415s, 1337s, 1256s, 1147s, 1084s, 1002s. Microanalysis calculated for $C_{39}H_{42}O_6.H_2O$: C, 74.97; H, 7.11%. Found: C, 74.95; H, 7.00%. MS (ES): 607.3 [M^+], 623.3 ([M^+] + 16.0). Mp: 92-93 °C.

2,3,7,8,12,13-Hexa-prop-2-ynyloxy-10,15-dihydro-*5H*-tribenzo-[*a,d,g*]cyclononene, 5

Cyclotricatechylene (1.03 g, 2.82 mmol), K_2CO_3 (2.01 g, 0.02 mol) and propargyl bromide (1.59 cm^3, 0.02 mol) were treated as for **4**, to give the off-white solid **5**. Yield: 0.87 g: 52%. ^{1}H NMR: (500.23 MHz, $CDCl_3$, 300.0 K) δ 2.48 (s, 6H, OCH_2CCH), 3.51 (d, 3H, -CH_2-link, ^{2}J (^{1}H-^{1}H) = 13.78 Hz), 4.65 (s, 12H, OCH_2CCH), 4.68 (d, 3H, -CH_2-link, one peak is masked by the singlet at 4.65), 6.98 (s, 6H, aryl ring C*H*). ^{13}C-{^{1}H} NMR: (125.79 MHz, $CDCl_3$, 300.0 K) δ 35.38 (-CH_2-link), 56.36 (OCH_2CCH), 74.96 (OCH_2-CC H), 77.85 (OCH_2CCH), 116.36 (aryl ring C H), 132.26, 145.38 (C_q). IR (KBr, ν cm^{-1}): 3284s, 3250s, 2965s, 2924m, 2869m, 2126s, 2024w, 1946w, 1686w, 1609s, 1512s, 1480s, 1449s, 1406s, 1366s, 1337s, 1262s, 1196s, 1140s, 1019s. Microanalysis calculated for $C_{39}H_{42}O_6.H_2O$: C, 78.77; H, 5.10%. Found: C, 78.80; H, 5.55%. MS (ES): 595.2 [M^+], 612.2 ([M^+] + 17.0). Mp: 158-160°C.

2,7,12-Tri-methoxy-3,8,13-tri-ethoxy-10,15-dihydro-*5H*-tribenzo-[*a,d,g*]cyclononene, 6

4-Ethoxy-3-methoxybenzylalcohol (3.44 g, 0.019 mol) was placed in a round bottomed flask and heated to approximately 80–90°C. A spatula tip of phosphoric acid crystals was then added with stirring. Once the mixture solidified the reaction mixture was cooled, methanol added and it was left to stir for 1 hour. The off-white solid **6** was filtered off. Yield: 1.83 g: 59%. ^{1}H NMR: (500.23 MHz, $CDCl_3$, 300.0 K) δ 1.41 (t, 9H, OCH_2CH_3), 3.53 (d, 3H, -CH_2-link, ^{2}J (^{1}H-^{1}H) = 13.81 Hz), 3.82 (s, 9H, OCH_3), 4.06 (m, 6H, OCH_2CH_3), 4.75 (d, 3H, -CH_2-link, ^{2}J (^{1}H-^{1}H) = 13.73 Hz), 6.81, 6.84 (s, 1H aryl C*H*). ^{13}C-{^{1}H} NMR: (125.79 MHz, $CDCl_3$, 300.0 K) δ 14.88 (OCH_2CH_3), 36.55 (-C H-link), 56.14 (OC H_3), 64.50 (OC H_2CH_3), 113.51, 114.91 (aryl ring C H), 131.86, 146.91, 148.11 (C_q). IR (KBr, ν cm^{-1}): 3434w, 3042m, 2982s, 2932s, 2901s, 2872m, 2850m, 2828s, 2737m, 2612m, 1609s, 1514s, 1478s, 1466s, 1445s, 1399s, 1345s, 1262s, 1219s, 1194s, 1090s, 1048s, 1017s. Microanalysis calculated for $C_{30}H_{36}O_6.{}^1/_2H_2O$: C, 71.83; H, 7.65%. Found: C, 72.95; H, 7.55%. MS (ES): 535.3 [M^+], 551.3 ([M^+] + 16.0). Mp: 170-171°C.

2,7,12-Tri-methoxy-3,8,13-tri-propoxy-10,15-dihydro-*5H*-tribenzo-[*a,d,g*]cyclononene, 7

4-Propoxy-3-methoxybenzylalcohol (3.52 g, 0.018 mol) was treated as for the synthesis of **6** to give the off-white product, **7**. Yield: 1.27 g: 13%. ^{1}H NMR: (500.23 MHz, $CDCl_3$, 300.0 K) δ 0.99 (t, 9H, $OCH_2CH_2CH_3$), 1.81 (m, 6H, $OCH_2CH_2CH_3$), 3.53 (d, 3H, -CH_2-link, ^{2}J (^{1}H-^{1}H) = 13.79 Hz), 3.82 (s, 9H, OCH_3), 3.93 (t, 6H, $OCH_2CH_2CH_3$), 4.75 (d, 3H, -CH_2-link, ^{2}J (^{1}H-^{1}H) = 13.72 Hz), 6.82 (s, 3H, aryl ring C*H*), 6.84 (s, 3H, aryl ring C*H*). ^{13}C-{^{1}H} NMR: (125.79 MHz, $CDCl_3$, 300.0 K) δ 10.44 ($OCH_2CH_2CH_3$), 22.51 ($OCH_2CH_2CH_3$), 36.50 (-C H-link), 56.11 (OC H_3), 70.74 (OC $H_2CH_2CH_3$), 113.11, 115.23 (aryl ring C H), 131.99, 147.25, 148.24. (C_q). IR (solid phase, ν cm^{-1}): 3305s, 2979s, 2874s, 2624s, 2017s, 1837s, 1760s, 1608s, 1593s, 1513s, 1472s, 1395s, 1324s, 1260s, 1222s, 1212s, 1136s, 1109s, 1024s. Microanalysis calculated for $C_{33}H_{42}O_6.{}^1/_2H_2O$: C, 72.89; H, 7.99%. Found: C, 73.25; H, 7.95%. MS (ES): 535.3 [M^+], 552.3 ([M^+] + 17). Mp: 143–145°C.

4-(Prop-2-ynyloxy)-3-methoxybenzylalcohol

4-Hydroxy-3-methoxybenzylalcohol (10.23 g, 0.066 mol), potassium carbonate (18.24 g, 0.132 mol) and propargyl bromide (5.60 cm^3, 0.070 mol) were treated as for the synthesis of **4**, to give 4-(prop-2-ynyloxy)-3-methoxybenzylalcohol as a liquid. Yield: 11.01 g: 86%.

^{1}H NMR: (500.23 MHz, $CDCl_3$, 300.0 K) δ 2.40 (s, 1H, OCH_2CCH), 2.93 (s, 1H, CH_2OH), 3.82 (s, 3H, OCH_3), 4.53 (s, 2H, OCH_2CCH), 4.70 (s, 2H, CH_2OH), 6.83 (d, 1H, aryl ring C*H*, ^{2}J (^{1}H-^{1}H) = 8.17 Hz), 6.89 (s, 1H, aryl ring C*H*), 6.95 (d, 1H, aryl ring C*H*, ^{2}J (^{1}H-^{1}H) = 8.15 Hz). ^{13}C-{^{1}H} NMR: (125.79 MHz, $CDCl_3$, 300.0 K) δ 56.23 (OCH_3), 57.22 (OCH_2CCH), 65.17 (CH_2OH), 76.33 (OCH_2CCH), 79.06 (OCH_2CCH), 111.30, 114.80, 119.50 (aryl ring *C*H), 135.67, 146.46, 150.11 (C_q). IR: (Nujol, ν cm^{-1}): 3285s, 3073s, 3006s, 2940s, 2877s, 2595w, 2452w, 2120s, 2033w, 1699s, 1595s, 1514s, 1464s, 1372s, 1266s, 1138s, 1024s.

2,7,12-Tri-methoxy-3,8,13-tri-(prop-2-ynyloxy)-10,15-dihydro-5H-tribenzo-[*a*,*d*,*g*]cyclononene, 8

4-(Prop-2-ynyloxy)-3-methoxybenzylalcohol (11.01 g, 0.019) was treated as for the synthesis of **6** to give **8** as

TABLE I Details of data collection and structure refinements

	2	**2**.$(CH_3CN)_3$	**6**.$(CH_3CN)_3$
Formula	$C_{33}H_{42}O_6$	$C_{39}H_{51}N_3O_6$	$C_{36}H_{45}O_6N_3$
M_r	534.67	657.82	615.75
Crystal colour/shape	Colourless, prismatic	Colourless, prismatic	Colourless, prismatic
Crystal size(mm)	0.37 × 0.33 × 0.26	0.49 × 0.33 × 0.31	0.42 × 0.30 × 0.28
Crystal system	Monoclinic	Orthorhombic	Trigonal
Space group	$P2_1/c$	$Cmc2_1$	$R3c$
T(K)	150(2)	150(2)	150(2)
a(Å)	25.4082(3)	25.1606(7)	24.6607(5)
b(Å)	9.5645(2)	9.1395(2)	24.6607(5)
c(Å)	27.0639(5)	16.2276(5)	9.3760(2)
α(°)	90	90	90
β(°)	117.243(6)	90	90
γ(°)	90	90	120
V(Å^3)	5847.41(18)	3731.62(18)	4938.09(18)
Z	8	4	6
F(000)	2304	1416	1980
ρ_{calc}(g cm^{-3})	1.215	1.171	1.242
μ(cm^{-1})	0.082	0.079	0.085
$\theta_{min,max}$(°)	1.51, 22.50	2.99, 28.28	2.86, 28.39
Data collected	45011	10067	21420
Unique data	7525	4228	2731
R_{int}	0.1250	0.0523	0.1026
Obs data ($I > 2\sigma(I)$)	6056	3102	1753
Parameters	716	234	142
Restraints	0	1	1
R_1 (observed data)	0.1484	0.0503	0.0449
wR_2 (all data)	0.4060	0.1379	0.1186
S	1.113	0.867	1.028
Max/min residual e density (eÅ^{-3})	0.500, −0.538	0.198, −0.236	0.241, −0.301
	8	**1**.$(DMSO)_2(H_2O)_2$	**1**.$(EtOH)_{0.25}$
Formula	$C_{33}H_{30}O_6$	$C_{31}H_{46}O_{10}S_2$	$C_{27.5}H_{31}O_{6.25}$
M_r	522.57	642.80	461.53
Crystal colour/shape	Colourless, prismatic	Colourless, prismatic	Colourless, prismatic
Crystal size(mm)	0.27 × 0.23 × 0.21	0.51 × 0.44 × 0.40	0.22 × 0.10 × 0.03
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/c$
T(K)	150(2)	150(2)	150(2)
a(Å)	12.9352(4)	11.4351(2)	18.681(4)
b(Å)	9.3876(3)	13.2548(2)	24.406(5)
c(Å)	22.4384(6)	21.4210(4)	10.430(2)
α(°)	90	90	90
β(°)	90.755(1)	89.27(3)	90.70(3)
γ(°)	90	90	90
V(Å^3)	2724.47(14)	3246.80(10)	4755.1(16)
Z	4	4	8
F(000)	1104	1376	1968
ρ_{calc}(g cm^{-3})	1.274	1.315	1.289
μ(cm^{-1})	0.087	0.219	0.091
$\theta_{min,max}$(°)	2.68, 28.30	2.35, 26.00	2.78, 27.50
Data collected	25998	45220	33560
Unique data	6633	6346	10754
R_{int}	0.1165	0.1255	0.1129
Obs data ($I > 2\sigma(I)$)	3613	4422	5548
Parameters	472	399	844
Restraints	0	0	0
R_1 (observed data)	0.0731	0.0830	0.0682
wR_2 (all data)	0.2043	0.2580	0.1881
S	1.093	1.015	1.0013
Max/min residual e density (eÅ^{-3})	0.499, −0.284	0.812, −0.592	0.671, −0.433

an off-white solid. Yield: 1.85 g: 18%. ^{1}H NMR: (500.23 MHz, $CDCl_3$, 300.0 K) δ 3.49 (s, 3H, OCH_2CCH), 3.52 (d, 3H, -CH_2-link, ^{2}J (^{1}H-^{1}H) = 13.83 Hz), 3.86 (s, 9H, OCH_3), 4.71 (s, 6H, OCH_2CCH), 4.77 (d, 3H, -CH_2-link, ^{2}J (^{1}H-^{1}H) = 13.75 Hz), 6.88, 7.02 (s, 3H, aryl ring C*H*). ^{13}C-{^{1}H} NMR: (125.79 MHz, $CDCl_3$, 300.0 K) δ 36.53 (-CH_2-link), 56.18 (OCH_3), 57.01 (OCH_2CCH), 75.72 (OCH_2CCH), 79.03 (OCH_2CCH), 113.90, 116.56 (aryl ring CH), 148.44 (C_q). IR (KBr, ν cm^{-1}): 3426w, 3278s, 3235s, 2973s, 2940m, 2913m, 2865m, 2834m, 2126s, 1607s, 1514s, 1482s, 1466s, 1456s, 1381s, 1376s, 1365s, 1262s, 1213s, 1194s, 1148s, 1086s, 1032s. Microanalysis calculated for $C_{33}H_{30}O_6.\frac{1}{2}H_2O$: C, 74.62; H, 5.80%. Found: C, 74.95; H, 6.20%. MS (ES): 523.2 [M^+], 540.2 ([M^+] + 17.0). Mp: 214–216°C.

X-ray Crystallography

Crystals were mounted on a glass fibre under oil and data were collected at 150(1) K on a Nonius Kappa CCD diffractometer with graphite-filtered Mo-K α radiation ($\lambda = 0.71073$Å). Data were corrected for Lorentzian and polarization effects, and for absorption effects using multi-scan methods. Structures were solved by direct methods using SHELXS-97 [38] and refined with full-matrix least squares on F^2 using SHELXL-97 [39]. All non-hydrogen atoms were refined anisotropically, unless otherwise specified. Hydrogen atoms were included at geometrically estimated positions and refined with a riding model, unless otherwise indicated. Details of data collections and structure refinements are given in Table I, and any additional details are given below. Supplementary data is available in CIF format from the Cambridge Crystallographic Data Centre, deposition numbers CCDC 279715-279720.

Crystals of **2** were of poor quality as indicated by their high R_{int} value, and were weakly diffracting, with observed data to a 2θ of around 45°, hence the structure shows high residuals. Some acetonitrile hydrogens for **2**.(CH_3CN), all hydrogen atoms for compound **8**, and the host hydrogens for complex (**1**)$_2$.$(EtOH)_{0.5}$ were fully refined. One DMSO molecule for complex **1**.$(DMSO)_2$.(H_2O) was disordered with the S atom across two positions at 50% occupancy at each position. The water O-H hydrogen atoms were not located in the difference map hence have not been included in the refinement. All hydrogen atoms aside from those of the EtOH were fully refined in complex **1**.$(EtOH)_{0.25}$, and the EtOH was disordered across an inversion centre with two molecular positions at 50% occupancy each.

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