

Clathrate Design for Dioxane Inclusion Involving Singly Bridged Triarylmethanol Hosts. Synthesis, X-Ray Crystal Structures and Thermal Stabilities of Five Inclusion Compounds†

Ingeborg Csöreg,*,^a Edwin Weber,*,^b Luigi R. Nassimbeni,*,^c Olga Gallardo,^a
Norbert Dörpinghaus,^b Anne Ertan^a and Susan A. Bourne^c

^a Department of Structural Chemistry, Arrhenius Laboratory, Stockholm University, S-106 91 Stockholm, Sweden

^b Institut für Organische Chemie der Technischen Universität Bergakademie Freiberg, Leipziger Strasse 29, D-09596 Freiberg/Sachsen, Germany

^c Department of Chemistry, University of Cape Town, Rondebosch 7700, South Africa

A series of singly bridged triarylmethanols, with different substituents and modified bridging units, form crystalline inclusion compounds with dioxane. X-ray diffraction studies revealed hydrogen bonds between host and guest in all these structures, and in one case also a host-to-host hydrogen bond. Most crystals contain either 1:1 or 2:1 hydrogen-bonded host-dioxane complexes, dependent on the structural parameters of the host molecule. With both host-guest and host-host hydrogen bonds present, 4:1 host-dioxane units are formed. Some structures accommodate additional dioxane guests which are held by van der Waals forces. The stabilities of the different dioxane clathrates were studied by thermal analysis.

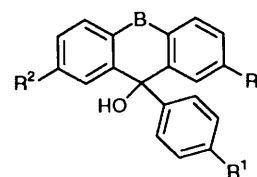
Dioxane has very efficient solvent properties² and is thus widely used. However, dioxane is also a dangerous compound causing health problems.³ Because safe handling and storage or sensing of this solvent is difficult, we wanted to design relevant receptors or sequestering agents based on crystalline inclusion (clathrate)⁴ formation. Previous results^{5,6} showed the singly bridged triarylmethanols to be promising, because many examples of this compound class are hosts that form inclusion compounds with dioxane. Interestingly, the stoichiometric ratio (host: dioxane) of these clathrates was found to vary (between 2:3 and 4:1) depending on the structural parameters of the host molecule, involving substitution of the aryl groups and/or modification of the bridging unit. It is probable that clathrate stabilities also vary significantly.

In order to learn the features in dioxane recognition, enclathration and binding as well as packing principles of this particular clathrate family, a systematic structural study including compounds **1a**–**7a** was undertaken. Here we present the X-ray crystal structures of **2a**–**6a**, where **2** in **2a** refers to a newly synthesized host compound. We compare these new structures with those of the previously reported **1a**⁶ and **7a**,⁵ and give thermal analysis data (TG, DSC) for all these clathrates. The objective of carrying out thermal analysis on these compounds was to reconcile thermodynamics with structure.

Results and Discussion

Synthesis.—The synthesis of host compounds **1** and **3**–**7** is described in a previous paper.⁶ Host molecule **2** was prepared analogously from fluorenone and 4-bromo(trifluoromethyl)benzene with BuLi. Clathrates **1a**–**7a** were obtained by recrystallization of the respective host compound from dioxane.

X-Ray Diffraction Analysis.—Crystal data of compounds **2a**–**6a** are given in Table 1. Selected conformational features are shown in Table 2. Distances and angles in hydrogen bonds



	R ¹	R ²	B
1	H	H	—
2	CF ₃	H	—
3	CMe ₃	H	—
4	H	Br	—
5	H	CMe ₃	—
6	H	H	O
7	H	H	CH ₂ CH ₂

1a = **1**·Dioxane (4:3) **4a** = **4**·Dioxane (2:1)
2a = **2**·Dioxane (2:1) **5a** = **5**·Dioxane (4:1)
3a = **3**·Dioxane (1:1) **6a** = **6**·Dioxane (2:3)
7a = **7**·Dioxane (2:1)

and possible C–H···O interactions are given in Table 3. Perspective views of the stoichiometric units of the inclusion compounds **2a**–**6a**, are depicted in Figs. 1(a)–(e), respectively, whereas Figs. 2(a)–(e) give stereo packing illustrations of the inclusion compounds **2a**–**6a**, respectively. Complete lists of covalent bond lengths, bond angles, fractional atomic coordinates and isotropic vibrational parameters of the hydrogen atoms as well as fractional atomic coordinates and anisotropic displacement parameters of the non-hydrogen atoms have been deposited.

Molecular Structures.—The geometries of the semi-rigid 9-phenyl-fluoren-9-ol moieties of the hosts **2**–**5** are very similar [cf. Figs. 1(a)–(d)], and resemble also those of the parent 9-phenylfluoren-9-ol molecule **1**⁶ and related 9-substituted fluoren-9-ol hosts,¹ previously studied by us. The corresponding bond lengths and bond angles in molecules **2**–**5** are comparable with each other within experimental errors, and together with those of the phenyl substituted xanthenol host, **6** [Fig. 1(e)], generally conform to expected values (cf. Supplementary Data). The units of three condensed rings, fluorene or xanthen, are

† Triarylmethanol Hosts and Analogues. Part 8. For Part 7 of this series see ref. 1.

Table 1 Crystal data and selected details of the data reduction and structure refinement calculations^a

	2a	3a	4a	5a	6a
Formula unit					
host	C ₂₀ H ₁₃ OF ₃	C ₃₂ H ₂₂ O	C ₁₉ H ₁₂ OBr ₂	C ₂₇ H ₃₀ O	C ₁₉ H ₁₄ O ₂
guest	C ₄ H ₈ O ₂	C ₄ H ₈ O ₂	C ₄ H ₈ O ₂	C ₄ H ₈ O ₂	C ₄ H ₈ O ₂
Host: guest stoichiometry	2:1	1:1	2:1	4:1	2:3
Formula weight	740.74	402.53	920.32	1570.24	812.96
Crystal system	monoclinic	monoclinic	triclinic	triclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> /Å	12.192(1)	7.961(1)	9.832(3)	11.346(3)	8.996(1)
<i>b</i> /Å	22.634(2)	10.636(1)	10.140(3)	14.282(4)	14.371(2)
<i>c</i> /Å	13.758(1)	26.349(2)	10.977(4)	15.888(4)	16.795(1)
α /°	90.0	90.0	92.76(2)	114.78(2)	90.0
β /°	96.847(6)	94.460(8)	97.12(2)	93.14(1)	97.02(1)
γ /°	90.0	90.0	118.72(2)	93.17(1)	90.0
<i>V</i> _c /Å ³	3769.5(5)	2224.3(4)	945.0(6)	2325(1)	2155.0(4)
Refinement of the unit cell dimensions					
No. of reflections used	70	30	32	48	40
2 θ -range/°	30–54	19–36	32–40	11–22	36–52
<i>Z</i>	4	4	1	1	2
<i>D</i> _c /g cm ⁻³	1.3052(2)	1.2020(2)	1.617(1)	1.1213(5)	1.2528(2)
<i>F</i> (000)	1536	864	456	848	864
<i>T</i> /K	291 ± 1	193 ± 1	291 ± 1	233 ± 1	291 ± 1
Radiation	CuK α	MoK α	MoK α	MoK α	CuK α
μ /cm ⁻¹	8.40	0.72	42.57	0.63	6.66
Range of 2 θ /°	3–140	3–60	3–70	3–50	3–140
No. of collected reflections	7401	6808	8792	8355	4377
No. of standard reflections	5	4	4	5	4
Time interval between the standards/min	90	90	90	90	90
Intensity instability	< 1%	< 1%	< 1%	< 2%	< 5%
No. of unique non-zero reflections	6143	4952	5977	6717	3302
No. of significantly observed reflections	3727	1672	1938	2912	1686
Criterion of significance	<i>I</i> / σ (<i>I</i>) < 3	<i>I</i> / σ (<i>I</i>) < 3	<i>I</i> / σ (<i>I</i>) < 3	<i>I</i> / σ (<i>I</i>) < 3	<i>I</i> / σ (<i>I</i>) < 3
No. of refined parameters	538 ^b	301	223	279	273
Final agreement factors					
<i>R</i> [= $\sum \Delta F /\sum F_o $]	0.075	0.041	0.041	0.047	0.061
<i>wR</i> [= $(\sum w \Delta F ^2/\sum w F_o ^2)^{1/2}$]	0.093	0.048	0.053	0.058	0.083
Weighting: <i>w</i> = [$\sigma^2(F) + gF^2$] ⁻¹					
<i>g</i> =	0.000 10	0.000 60	0.000 78	0.000 40	0.000 55
Final $\Delta\rho_{\max}/\Delta\rho_{\min}$ [e Å ⁻³]	0.36/–0.29	0.14/–0.23	0.98/–0.38	0.37/–0.27	0.26/–0.21

^a Esds are in parentheses. ^b In the refinement of compound **2a** the 'blocked full-matrix least-squares' refinement techniques^{15,16} had to be used because of the large number of variables. Accordingly, two blocks with 438 and 100 variables, respectively, were refined in consecutive cycles.

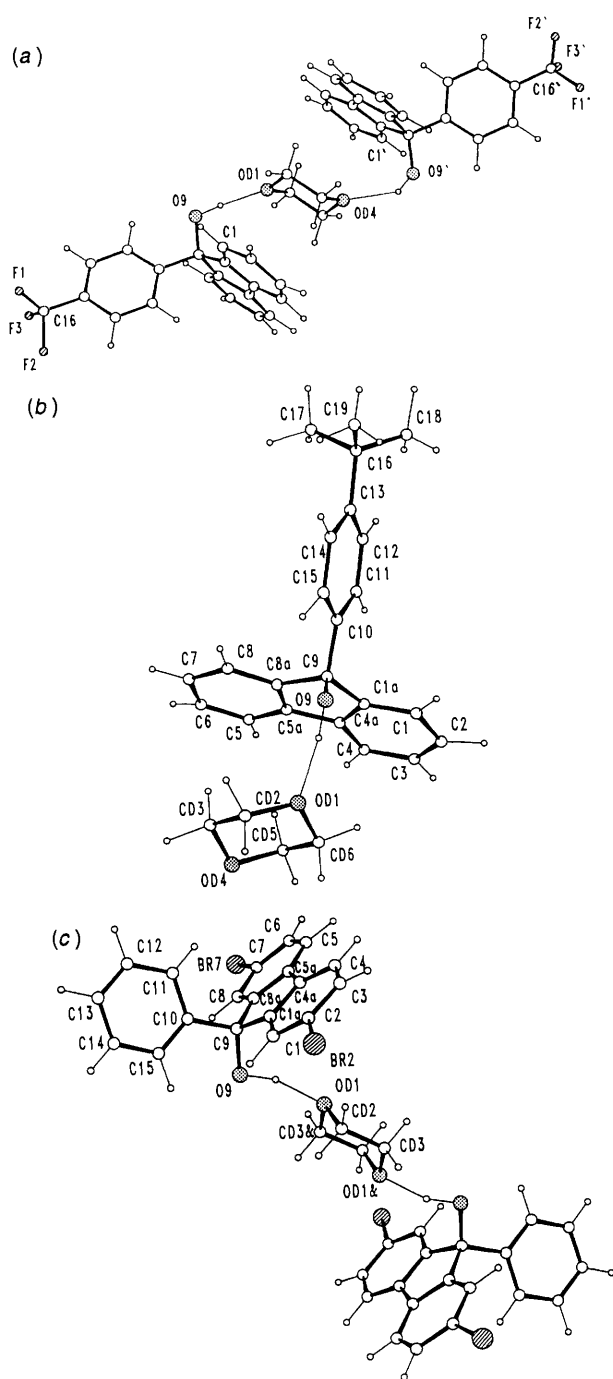
Table 2 Selected conformational features of the singly bridged triarylmethanol hosts **1–6** in their inclusion compounds with dioxane (**1a–6a**), studied by X-ray diffraction^a

	1 ^{b,c}	2 ^c	3	4	5 ^c	6 ^d
The ring atoms of the fused ring system ^d (fluorene/xanthene) are co-planar within/Å	0.10 0.06	0.12 0.15	0.13	0.10	0.28 0.09	0.16
Dihedral angle ^e between the LS planes of the phenyl rings of the fused ring system ^d (fluorene/xanthene)/°	3.7(1) 1.8(2)	4.2(2) 5.3(2)	5.3(1)	3.0(2)	11.3(2) 3.4(1)	4.9(2)
The ring atoms of the phenyl substituent are co-planar within/Å	0.015 0.023	0.018 0.011	0.006	0.005	0.012 0.020	0.003
Dihedral angle ^e between the LS planes of the fused ring system ^d (fluorene/xanthene) and the phenyl substituent/°	95.7(1) 95.8(1)	80.7(1) 89.5(1)	97.5(1)	81.3(1)	85.9(1) 85.4(1)	93.6(1)

^a Esds are in parentheses. ^b According to ref. 5. ^c The crystals of **1a**, **2a** and **5a** contain two crystallographically independent host molecules (the unprimed and the primed one). ^d The bridged diaryl moiety in hosts **1–5** is a fluorene moiety with 13 ring atoms, whereas host molecule **6** contains a xanthene group with 14 ring atoms. ^e Following Nardelli.¹⁷

approximately flat (*cf.* Table 2). Remarkably, the unprimed molecule of **5** differs somewhat from the other related molecules by having a dihedral angle as large as 11.3(2)° between the two phenyl rings in its fluorene moiety. The mean value of the corresponding dihedral angle, calculated for the other eight independent molecules, listed in Table 2, is 4[1]° (with the measure of dispersion around the arithmetic average given in

square brackets). The deviations of the bromo substituents from the fluorene plane in host **4** are 0.018(1) and 0.083(1) Å for Br(2) and Br(7), respectively. Furthermore, the phenyl substituent is roughly perpendicular to the least-squares (LS) plane of the respective fluorene or xanthene moiety, in agreement with our earlier experience with related molecules.^{1,6} The mean deviation of this dihedral angle from 90° in compounds **1–6** is 5[3]°.



The 1,4-dioxane guests show the usual chair conformation. No anomalous bond distances and bond angles were observed for them.

Packing Relations and Host-Guest Interactions.—All the host molecules 1–7 comprise an alcoholic –OH group, which gives them both good proton donor and acceptor ability in hydrogen bonding. The dioxane guest, on the other hand, can accept a hydrogen bond through its ring oxygen atoms, and thus can be hydrogen-bonded by the hydroxy function of the present host molecules (Table 3). The host molecules 1–6 are very similar to each other, but their inclusion compounds with the dioxane guest show a wide and interesting variation of host:guest stoichiometries, indicating different modes of host-guest interactions [Figs. 1(a)–(e) and 2(a)–(e)]. If both oxygens of the dioxane guest are hydrogen-bonded, 2:1 host:guest associates are formed, such as in compounds 1a,⁶ 2a and 4a. Nevertheless,

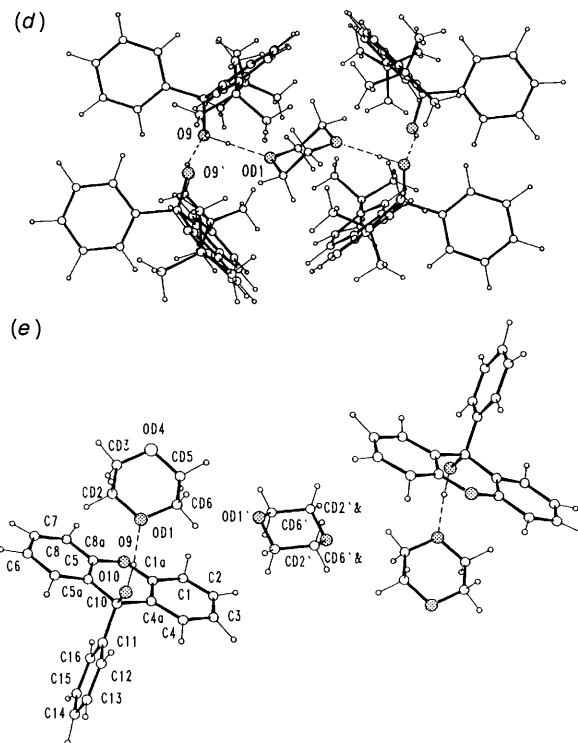


Fig. 1 Perspective view of the stoichiometric units of compounds 2a (a), 3a (b), 4a (c), 5a (d) and 6a (e), indicating also the crystallographic labelling of the atoms. The carbon atoms of the 9-phenylfluoren-9-ol moieties of 2a and 5a are labelled identically with those of 3a and 4a. Solid and dashed lines represent covalent and hydrogen bonds, respectively. Heteroatoms are shaded.

the crystals of 2a [Fig. 2(a)] and 4a [Fig. 2(c)] are built up by the hydrogen-bonded 2:1 units, linked together by ordinary van der Waals forces, whereas those of 1a contain additional dioxane guests, filling up the voids between the 2:1 complexes, thus resulting in 4:3 stoichiometry for that compound.

Furthermore, in the complexes 3a [Fig. 2(b)] and 6a [Fig. 2(e)] only one oxygen of each dioxane guest is joined to the host by a hydrogen bond, thus giving rise to a hydrogen-bonded unit of one host and one guest molecule. Nevertheless, the host:guest stoichiometries of these two latter compounds are different. In the case of 3a, the 1:1 host-guest associates can pack so as to form a stable crystalline architecture. In 6a, however, further dioxane guests are included [Figs. 1(e) and 2(e)], probably to increase the packing density and thus to lower the potential energy. Similarly to the crystals of 1a,⁶ the additional dioxane molecules in 6a seem to have nothing but weak van der Waals interactions with the hydrogen-bonded host-guest associates. Besides the ordinary van der Waals forces, the crystal structure of 6a seems to be stabilized also by an electrostatically favourable molecular packing (*cf.* Table 4).

It should be mentioned that the present hosts 1–6 have the potential capability for intermolecular hydrogen bond interaction not only with the guests, but also with each other. We have found previously, that both 9-methyl- and 9-phenylfluoren-9-ol can form hydrogen-bonded tetramer aggregates.^{1,6} The tendency of substituted 9-fluorenols to join each other by hydrogen bonding, however, seems to decrease with increasing size of the 9-substituent,¹ which is reasonable from the steric point of view. Concerning the present dioxane inclusions, only in one case, in compound 5a [Fig. 1(d)], was hydrogen bonding observed also between host molecules. This inter-host hydrogen bond links the unprimed and the primed molecules of 5 into a dimer, in which there is a relatively short intermolecular distance also between C(8) and O(9') [C(8)⋯O(9') = 3.171(5) Å, *cf.* Table 3]. This latter approach is probably a

Table 3 Bond distances (Å) and angles (°) in possible O–H...O hydrogen bonds and C–H...O interactions in compounds **2a–6a** (standard deviations, where given,^a are in parentheses)

Atoms involved	Symmetry	Distance/Å			Angle/°
		Donor...Acceptor	D–H	H...O	<D–H...O
2a					
O(9)–H(O9)...O(D1)	<i>x, y, z</i>	2.727(5)	0.97	1.76	173
O(9')–H(O9')...O(D4)	<i>x, y, z</i>	2.743(5)	0.96	2.02	130
3a					
O(9)–H(O9)...O(D1)	<i>x, y, z</i>	2.746(4)	0.99	1.77	167
C(5)–H(5)...O(D4)	$-x + 1, -y + 1, -z$	3.277(5)	1.03	2.59	124
4a					
O(9)–H(O9)...O(D1)	<i>x, y, z</i>	2.731(6)	1.08	1.69	160
C(8)–H(8)...O(9)	$-x, -y, -z + 1$	3.313(5)	1.08	2.30	156
5a					
O(9)–H(O9)...O(D1)	<i>x, y, z</i>	2.729(4)	0.99	1.74	180
O(9')–H(O9')...O(9)	<i>x, y, z</i>	2.849(5)	1.04	1.90	149
O(9)–H(9)...O(D'1)	$-x + 1, -y + 1, -z + 1$	2.729(4)	0.99	1.74	180
C(8)–H(8)...O(9')	<i>x, y, z</i>	3.171(5)	1.00	2.47	127
6a					
O(10)–H(O10)...O(D1)	<i>x, y, z</i>	2.752(5)	1.06	1.70	173
C(D6)–H(D61)...O(D'1)	<i>x, y, z</i>	3.181(8)	1.08	2.45	124
C(6)–H(6)...O(10)	$-x, -y, -z + 1$	3.455(6)	1.10	2.71	125
C(D'6)–H(D64)...O(D4)	$-x, -y, -z + 2$	3.495(9)	1.08	2.64	136

^a The H atom positions are not refined (*cf.* the text).

packing effect [Fig. 2(d)], but the possibility of a slightly attractive C–H...O interaction, which might be responsible for the unusual bending of the fluorene moiety of the unprimed **5** molecule, cannot be completely ruled out. The dimers, related by the inversion symmetry, are arranged so as to form a well shaped cavity around the centre of symmetry, suitable for a guest such as dioxane. Inclusion of the dioxane guest is also supported by hydrogen bonds from each of the coordinating host dimers, thus yielding a beautiful example of coordination-assisted clathrate formation.⁷ Accordingly, the unprimed host **5** is hydrogen-bonded to both the guest and the other host, whereas the primed one is hydrogen-bonded only to the unprimed host molecule. In this way 4:1 host–guest associates are formed.

Thermal Analysis.—Fig. 3 shows the differential scanning calorimetry (DSC) and thermogravimetry (TG) traces for compounds **1a–6a**, the results of which are summarized in Table 4, together with the known data for **7a**.⁵ There is good agreement between the calculated and observed weight losses in the TG for all compounds, thus confirming their host:guest ratios.

The decomposition patterns of the compounds vary considerably. Compound **1a** [Fig. 3(a)] shows a single step decomposition in the TG, whereas the DSC displays a first peak corresponding to the loss of the guest, followed by the host melting endotherm. This is a decomposition pattern similar to that observed for **7a**.⁵ Compounds **2a** [Fig. 3(b)] and **3a** [Fig. 3(c)] show comparable behaviour in that the TG curves show a single-step decomposition, but the DSC curves yield a single endotherm, which might be interpreted as the release of the guest with concomitant dissolution of the host compound. We have reported the same phenomenon for the decomposition of the inclusion compound formed by the host 1,1,6,6-tetraphenylhexa-2,4-diyne-1,6-diol with dioxane.⁸ We confirmed this interpretation by observing the decomposition of **2a** on a Linkam TH600 hot stage set on a Nikon SMZ-10 stereo microscope. At 60 °C we noted small bubbles appearing on the surface of the crystal and decomposition started at 86 °C, when liquid was seen exuding from the crystals. Melting occurred

over a range 95–107 °C. This is also reflected in the shape of the endotherm in **2a**, which is not sharp but has a leading tail. This makes it difficult to report sensible onset temperatures, and we report therefore peak temperatures for the peaks in this study. Compound **4a** [Fig. 3(d)] exhibits the most complex decomposition pattern, displaying a two-step decomposition in TG, and the DSC curve correspondingly yielding two distinct guest-release endotherms which are followed by the melting of the host. Compound **5a** [Fig. 3(e)] has a single-step decomposition, but the endotherms owing to the guest loss and the host melting could not be completely resolved, even at slower heating rates. Compound **6a** displays a single-step decomposition in the TG, but the DSC curve is complicated, and we again interpreted it with the aid of visual observation. The leading tail of the first endotherm, starting at 50 °C, corresponded to the crystal becoming opaque, and between 66 and 76 °C it developed surface cracks, caused by the loss of guest. Between 93 and 114 °C, we observed sharp outgrowths from the crystals, which we interpret as a phase change. This was followed by the break-up of the crystal, between 148 and 157 °C, into distinct crystallites, which corresponds to the exotherm peaking at 150 °C in the DSC. This is immediately followed by the final melting endotherm.

In a previous study⁸ of a series of hydroxy hosts with dioxane, we calculated the energy of the structures as manifested by host–guest interactions. Following the methods outlined previously⁸ we selected the compounds **2a**, **4a** and **7a** for this study, because they have the same host:guest ratio and similar molecular structures with the dioxane guest bonded to two host molecules *via* O–H...O hydrogen bonds (see above). We obtained U_{\min} values of -17.2 , -14.8 and -16.5 kJ mol⁻¹ for **2a**, **4a** and **7a**, respectively. These values are similar but, because the decomposition patterns are very different, we are unable to correlate the energies with the thermal data.

Summary and Conclusions.—Singly bridged triarylmethanols **1–7** have proved to be useful hosts for the inclusion of dioxane. Apparently, the host efficiency essentially depends on structural features.

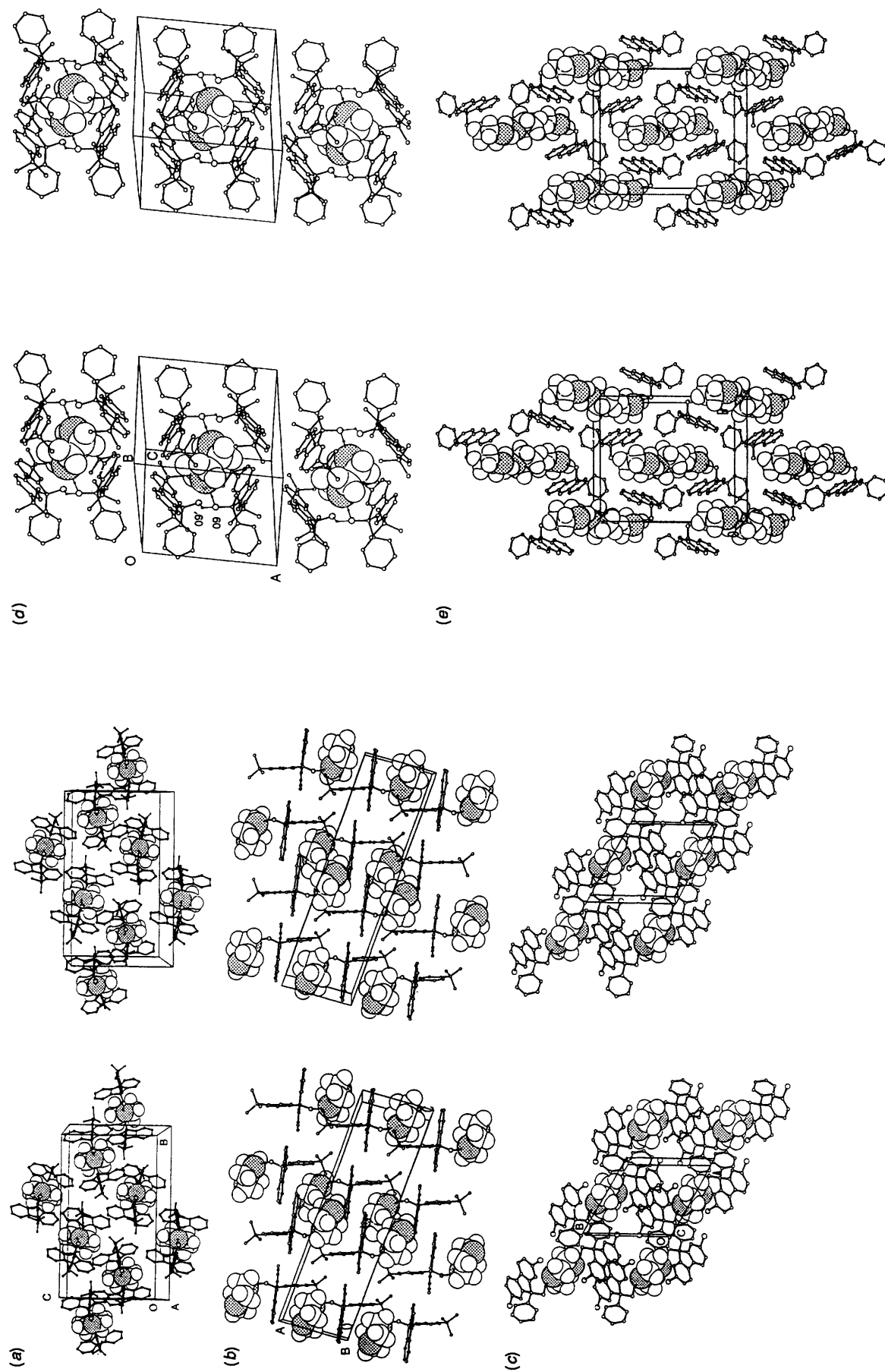
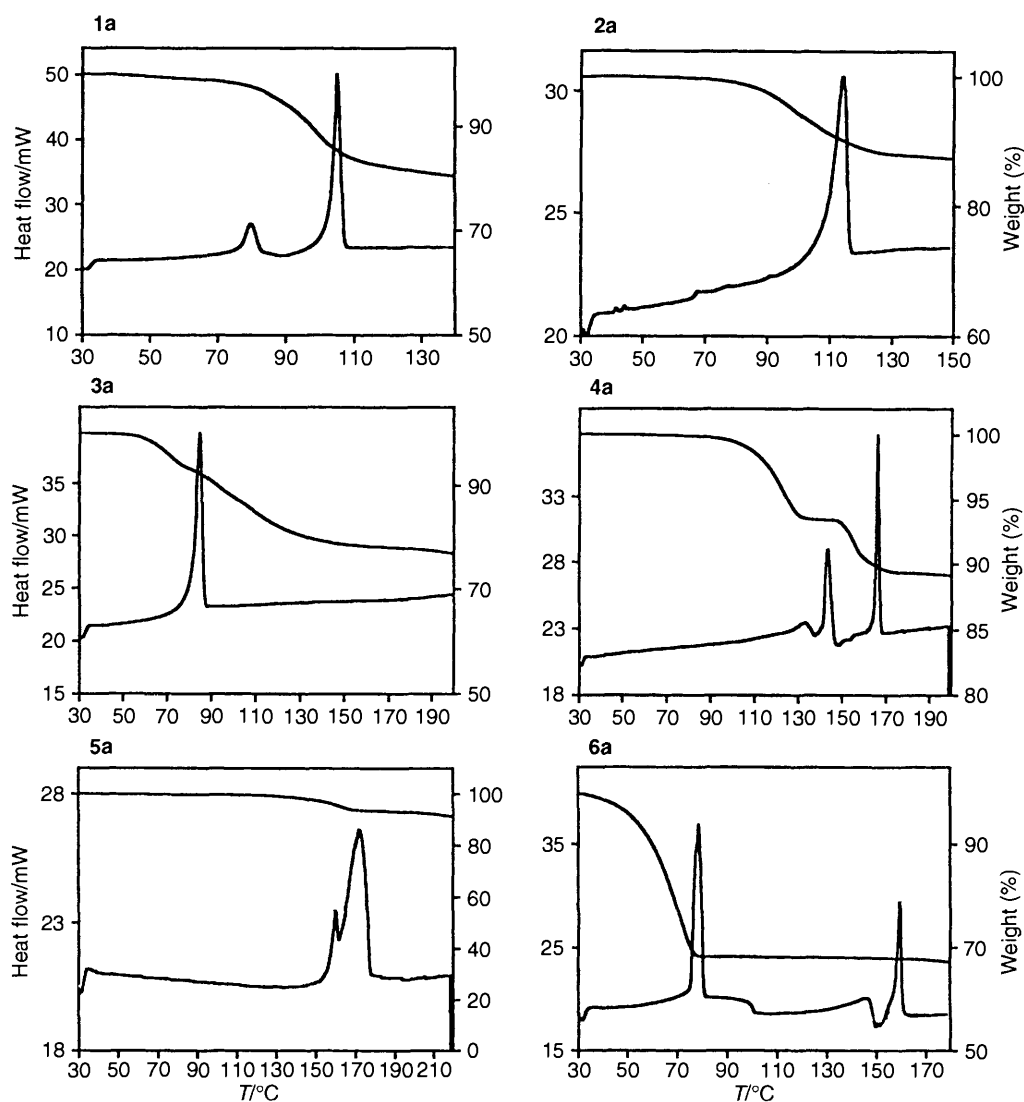


Fig. 2 Stereo packing illustrations of the compounds **2a** (a), **3a** (b), **4a** (c), **5a** (d) and **6a** (e). The host molecules are drawn in stick and ball style, whereas the dioxane guests are represented by their space filling models. The carbon-bonded H atoms of the hosts are omitted for clarity; the oxygens of the dioxane guests are shaded. Hydrogen bonds are represented by thin lines.

Table 4 Thermal analysis

Compd.	Stoichiometric ratio (host:guest)	TG weight loss (%)		Guest loss endotherm Peak temp./°C	Host melt endotherm Peak temp./°C
		Calc.	Obs.		
1a	4:3	20.4	19.0	80	105
2a	2:1	11.9	11.7	114	—
3a	1:1	21.9	21.4	85	—
4a	2:1	9.6	10.3	132, 143	166
5a	4:1	5.6	6.0	161	172
6a	2:3	32.5	31.6	79	150(exo), 159(endo)
7a^a	2:1	13.3	12.0	128	156

^a According to ref. 5.**Fig. 3** DSC and TG traces for compounds **1a** (a), **2a** (b), **3a** (c), **4a** (d), **5a** (e) and **6a** (f)

Host **6** has favourable (2:3 host:dioxane) stoichiometry in **6a**, unlike **5** (4:1 stoichiometry in **5a**). However, as regards the thermal stability **5a** (peak temperature of guest loss is 161 °C) is superior to **6a** (79 °C). The other host compounds **1–4** and **7** are between these two extremes, yielding host:guest stoichiometric ratios of 2:1 (**2a**, **4a**), 4:3 (**1a**) and 1:1 (**3a**) for their dioxane inclusions of moderate thermal stability (see Table 4).

From the crystal packings, different modes of interaction between host and dioxane are obvious, which may be related to structural parameters. On the one hand, we see 2:1 host-guest hydrogen-bonded aggregates corresponding to the two-fold hydrogen bond acceptorship of dioxane and the single

hydrogen bond donorship of the hosts. This particular mode of interaction is found for the parent **1** and the less bulky substituted derivatives **2** and **4**. On the other hand, there are also cases of 1:1 host-guest associates with dioxane in single hydrogen acceptor state, leaving one dioxane oxygen free of hydrogen bonds. These are formed of the more bulky substituted hosts **3** and **6**. Irrespective of this behaviour, if these complexed moieties cannot pack closely in the crystal, as in **1a** and **6a**, additional dioxane molecules with nothing but weak van der Waals interaction are included. Moreover, but only in the case of **5a**, host-to-host hydrogen bonds are seen, as in unsolvated host structures.¹

In comparison, triphenylmethanol, the unbridged analogue of **1**, also yields an inclusion compound with dioxane,⁸ which consists of 1:1 hydrogen bonded host–dioxane units. Inter-host hydrogen bonding, such as in **5a**, was found also in the dioxane inclusion of the triphenylsilanol host.⁸

It should be noted that neither the requirement for maximum saturation of the hydrogen bonds, nor the 'maximum acceptor rule', postulated a few years ago,^{9,10} is fulfilled in these dioxane inclusions. The necessity of close packing in organic crystal structures may be a possible reason for that: hydrogen bonds will arise only if the hydrogen-bonded associates can achieve a packing with acceptable density. Common organic crystals usually show a packing coefficient (*i.e.* the ratio between the space occupied by a molecule to the space allotted for it in the unit cell, calculated according to Kitaigorodsky) between 0.65 and 0.77, and no crystals can exist with a packing coefficient below 0.6.¹¹ If the requirements of close packing and hydrogen bonding cannot be satisfied simultaneously, because of the inconvenient shape of the hydrogen-bonded associates, the hydrogen bonding will be prevented, either partly or completely, and the crystal will be built up of smaller units. This conclusion is supported also by our recent experience concerning the packing relations in the guest-free 9-substituted 9-fluorenols.¹ Accordingly, the overall shape of the hydrogen-bonded host–guest associate, and its ability to pack with acceptable density, seems to determine the crystalline architecture, and also the molecular composition (host:guest stoichiometry) of the presented dioxane inclusions.

Summing up, it may be said, that in view of the objectives mentioned at the beginning, we see possibilities to use these hosts for stabilization, storage and sensing¹² of dioxane.

Experimental

Synthesis.—Compounds **2–6** were synthesized from the respective tricyclic ketones and corresponding Grignard or lithium reagents according to the general procedures (i or ii) given in literature.⁶

9-[4-(Trifluoromethyl)phenyl]fluoren-9-ol **2** (not reported in lit.⁶). From fluoren-9-one and 4-bromo(trifluoromethyl)benzene with BuLi (hexane) in Et₂O; recrystallization from dioxane gave the clathrate **2a**. The solvent free compound was obtained by heating the clathrate to 100 °C at 15 Torr (1 Torr = 133.322 Pa) for 18 h. White powder (65%) m.p. 86–88 °C (lit.,¹³ 64–66 °C).

Inclusion compounds **2a–6a** were obtained by recrystallization of the respective host compound from dioxane.⁶

Crystal Structure Determination.—**Sample preparation.** Crystals of **2a–6a**, suitable for X-ray analysis, were grown by slow evaporation. In order to prevent possible solvent evaporation during the data collection, the selected single crystals of **4a** and **6a** were put in a glass capillary, whereas those of **2a**, **3a** and **5a** were coated by epoxy glue.

Data collection and processing. The intensity data were collected on a STOE/AED2 diffractometer with either MoK α ($\lambda = 0.71069 \text{ \AA}$) or CuK α radiation ($\lambda = 1.54183 \text{ \AA}$), and using ω - 2θ scan technique. Single crystals with the following approximate dimensions (mm) were used: $0.45 \times 0.55 \times 0.65$ for **2a**, $0.40 \times 0.36 \times 0.17$ for **3a**, $0.24 \times 0.30 \times 0.23$ for **4a**, $0.38 \times 0.21 \times 0.40$ for **5a** and $0.55 \times 0.50 \times 0.35$ for **6a**. Data reductions included corrections for background, decay, Lorentz and polarization effects, and in the case of **4a** also for absorption effects. The empirical absorption correction was based on ψ scans of five reflections with high χ ($\chi > 70^\circ$) and different 2θ values. The transmission factors varied between 0.168 and 0.297. Crystal data and further details of the data reduction and structure refinement calculations are shown in Table 1.

Structure analysis and refinements. The structures were solved by application of direct methods¹⁴ and refined by full-matrix least-squares refinements based on $|F|$ (SHELX).^{15,16} The hydrogen atoms were either located from difference electron density ($\Delta\rho$) maps and were kept riding on their 'mother' atoms during the subsequent calculations, or were assumed to be in geometrically idealized positions, recalculated after each cycle of the refinement. In the last stage of the refinements the non-hydrogen atoms (with full site occupancies) were allowed to vibrate anisotropically, whereas isotropic displacement parameters were refined for the fluoride disorder sites and for the hydrogen positions. The two trifluoromethyl groups of host **2** show rotational disorder. Fourteen and ten disorder sites, with the sum of site occupancies of 2.97 [at C(16)] and 2.95 [at C(16')], respectively, were taken into account in the structural model. Possible disorder sites with site occupancies refined to less than 10% were excluded. In the refinement calculations, the site occupation factors and the isotropic vibrational parameters of the fluoro disorder sites were refined in consecutive cycles, but no other constraints were applied to them. A few reflections (20 for **2a**, 2 for **4a**, 12 for **5a** and 14 for **6a**), with considerably lower F_{obs} than F_{calc} , most likely due to extinction, have been omitted from the final refinement calculations, which yielded the reliability indexes shown in Table 1. Refined fractional atomic coordinates of the non-hydrogen atoms and of the hydroxy H atoms (located from $\Delta\rho$ maps) have been deposited as supplementary data.*

Thermal Analysis.—Differential scanning calorimetry (DSC) and thermogravimetry (TG) were performed on a Perkin-Elmer PC7 Series system. Crystals were removed from their mother liquor, blotted dry on filter paper and crushed before analysis. Sample weight in each case *ca.* 5 mg. The temperature ranged from ambient to approximately 50 °C beyond the melting point of the host compounds at a heating rate of 10 °C min⁻¹.

Supplementary Data.—Lists of fractional atomic coordinates, bond lengths and bond angles have been deposited as supplementary data at the Cambridge Crystallographic Data Centre.* Lists of anisotropic displacement parameters of the C, O and Br atoms, and of the observed and calculated structure factors are available directly from the authors (I. C.).

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* For details of the CCDC deposition scheme, see 'Instructions for Authors,' *J. Chem. Soc., Perkin Trans. 2*, 1993, issue 1.

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