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SUPRAMOLECULAR CRYSTALLINE COMPLEXES INVOLVING BULKY HYDROXY HOSTS: X-RAY STRUCTURE ANALYSIS OF INCLUSION COMPOUNDS WITH ACETONE AND TOLUENE

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The structures of two solid inclusion compounds formed between roof-shaped diarylmethanol-substituted 9,10-dihydro-9,10-ethanoanthracene hosts, 1 and 2, and acetone or toluene, 1 · acetone (2 : 1) and 2 · toluene (1 : 1), were investigated by single-crystal x-ray analysis. Both compounds crystallize in the monoclinic system, although in different space groups [$C2/c$ for 1 · acetone (2 : 1) and $P2_1/n$ for 2 · toluene (1 : 1)]. The crystal data are as follows: 1 · acetone (2 : 1), $a = 19{\cdot}314(1)$, $b = 8{\cdot}451(1)$, $c = 28{\cdot}533(1)$, $\beta = 103.38(1)°$; 2 · toluene (1 : 1), $a = 9{\cdot}715(5)$, $b = 29{\cdot}51(2)$, $c = 9{\cdot}858(6)$, $\beta = 104{\cdot}98(4)°$. Conclusions are drawn concerning the rigidity of the molecules, the nature and degree of internal molecular motions and the type of disorder present in the crystals. Both hosts 1 and 2 reveal weak intramolecular interactions between the OH group and the π-face of the adjacent benzo ring of the ethanoanthracene moiety. The packing arrangement of 1 · acetone (2 : 1) is governed by weak C–H · · · O host–guest interactions, whereas the somewhat controversial C–H · · · F interactions seem to stabilize the host framework in the fluoro-containing 2 · toluene (1 : 1) compound. © 1997 by John Wiley & Sons, Ltd.

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INTRODUCTION

Rigidity, bulkiness and functionality have proved to be important design features of crystalline host molecules.[1] Following these basic ideas, a variety of so-called ‘clathrands’ (lattice inclusion host compounds[2]) have been developed. They include molecules of different shapes and geometries,[3] those with roof-type structure belonging to the most efficient frameworks.[4] On the other hand, there are relatively simple but still bulky molecular constitutions that are also suitable host compounds.[1a, 3b] Prominent examples of this latter compound type are the triarylmethanol[5] and singly bridged triarylmethanol hosts.[6] Recently we have shown that an amalgamation of both these strategies gives rise to the development of a new host family featuring a roof-shaped carbinol structure.[7]

Here we report the building principle of two of these crystalline inclusion compounds, involving aprotic polar and apolar guest molecules, and discuss the crystal structures of α,α-diphenyl-9,10-dihydro-9,10-ethanoanthracene-11-methanol with acetone [**1** · acetone (2:1)] and α,α-bis-(4-fluorophenyl)-9,10-dihydro-9,10-ethanoanthracene-11-methanol with toluene [**2** · toluene (1:1)], referring to monofunctional analogies of this host family.

RESULTS AND DISCUSSION

Perspective views of the compounds **1** · acetone (2:1) and **2** · toluene (1:1) with the crystallographic numbering scheme are shown in Figures 1(a) and (b). Stereoscopic illustrations of the packing modes are shown in Figures 2 and 3. Crystal data and selected experimental details are given in Table 1, and fractional atomic coordinates of the non-hydrogen atom with equivalent isotropic displacement parameters are given in Table 2.

Molecular structures

The OH groups of the host molecules in both compounds are engaged in possible intramolecular hydrogen bonding,

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involving the π-face of the adjacent benzo ring of the ethanoanthracene moiety (Table 3). Interest in this type of interaction has been growing in recent years, and some common features of these contacts to monosubstituted phenyl rings have been described.[8] The alcoholic hydrogen atoms in both hosts **1** and **2** lie above the periphery of the π-cloud of the phenyl ring C(1a) · · ·C(4a): the distance from H(13) to the nearest carbon C(1a) is 2·32(3) Å in host **1** and 2·10 Å in host **2**. The angles formed by the H(13) · · ·centroid vector and the normal to the least-squares plane of the ring C(1a) · · ·C(4a) are 39·3(5)° and 27°, respectively.

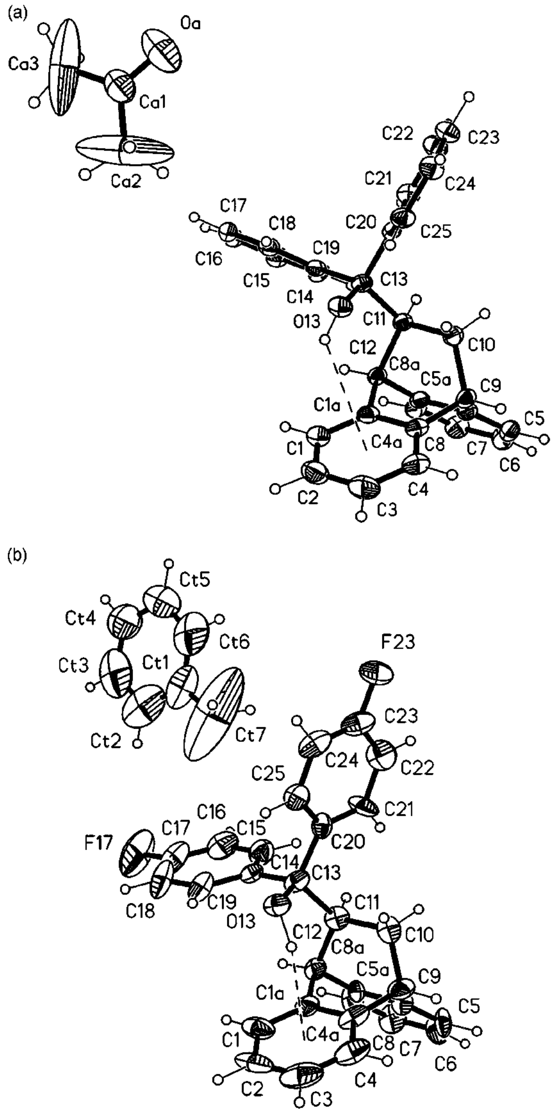

Figure 1. Perspective views of host and guest in the compound **1** · acetone (2:1) (a) and the asymmetric unit of compound **2** · toluene (1:1) (b) with the crystallographic numbering scheme. The displacement ellipsoids for non-hydrogen atoms are drawn at the 50% probability level and the H atoms are shown as spheres of arbitrary radius. The OH · · ·π(aryl) interaction is indicated by a dashed line

A noteworthy feature of these structures is the relative flexibility of the phenyl ring orientations in the diarylmethanol moieties. The conformational transformation from host **1** to host **2** can be seen as a 42·6° anti-clockwise rotation of the C(14) · · ·C(19) phenyl ring around the C(13)—C(14) bond and a 35° clockwise rotation of the C(20) · · ·C(25) phenyl ring about the C(13)—C(20) bond. Selected torsion angles are given in Table 4.

The anisotropic displacement parameters (ADPs), U_{ij}, were analyzed in order to obtain further information about possible internal molecular motions and, possibly, the nature of the disorder present in the crystals. Such information is of relevance in many areas of chemistry, physics and biology but is not easily attainable. It is often possible to reproduce the observed ADPs and their temperature dependence, and also to suggest appropriate corrections to apparently foreshortened covalent distances.[9, 10]

The least-squares fitting of T, L and S tensors[11] to the observed atomic U_{ij} tensors of all non-hydrogen atoms in the host molecule **1** led to a rather high discrepancy index, $R\{=[\Sigma(\Delta U)^2/\Sigma(U_{\mathrm{obs.}})^2]^{1/2}\}=0{\cdot}146$, where $\Delta U = U_{\mathrm{obs}} - U_{\mathrm{calc}}$, suggesting that the molecule cannot be considered as entirely rigid. The values $\Delta_{\mathrm{A,\,B}} = \langle u^2\rangle_{\mathrm{A}} - \langle u^2\rangle_{\mathrm{B}}$ for every pair of atoms A and B, where $\langle u^2\rangle$ is the mean-square displacement amplitude (MSDA) of an atom along the interatomic direction of the molecular fragment, were also calculated for host **1** (Table 10, Supplementary material). The root mean square (r.m.s.) value of Δ for 35 bonded pairs of atoms is 0·0014 Å^2 and thus satisfies the rigid-bond criterion proposed by Hirshfeld.[12] Analysis of the Δ distribution indicates that, as expected, non-bonded interactions within the individual phenyl rings are not significantly less rigid than the bonds themselves, but the rings exhibit considerable relative motions.[13] The Dunitz–White treatment[14] of host **1** suggests that the motion of each ring is more complicated than a simple predominant libration in one direction.

The interatomic distances between the non-hydrogen atoms in host **1**, as derived from the refinements (Table 5), are not significantly different from the expected values.[4, 7, 15] Nevertheless, interatomic separations within the acetone molecule (Table 5) are shorter than the expected values.[15] As is known,[16–19] the apparent contraction of intramolecular distances can be the result of internal molecular motion or disorder in crystals. In the case of internal motions, reasonable corrections can be applied. Indeed, inspection of Figure 1(a) makes it probable that the acetone molecule undergoes high-amplitude librations. However, the high r.m.s. Δ value[12] for the atomic pairs (0·048 Å^2) indicates that static disorder mimicking librational motions about the crystallographic axes might be present, rather than intramolecular motions. The principal axes of inertia of the guest molecule ($I_1 > I_2 > I_3$) run along the [001], [010] and [100] directions, respectively.

The observed vibrational ellipsoids for the aromatic carbons of host **2** are correlated because of the bond length constraints imposed during the refinement. Consequently, the TLS analysis was used only to estimate the effects of intramolecular motions on the unconstrained interatomic separations. Except for the interatomic distances to the fluoro atoms, which are significantly shorter than the expected value of C_{ar}—F (mono) = 1·363 Å,[15] all other unconstrained bond lengths were found to be consistent with the literature.[4, 7, 15] (Table 5). Inspection of Fig. 1(b) and of the corresponding ADP values (Table 2 here and Table 11 in the Supplementary material) indicates that both F atoms, especially F(17), oscillate appreciably. The different ADPs of the two fluoro substitutions are in all probability the result of the differences in their engagement in intermolecular interactions (see below). Estimates from a simple riding model[16–19] suggest that the bond distances should be considerably longer (by more than 0·02 Å).

The vibrational ellipsoids of the carbon atoms in the toluene molecule are extremely anisotropic, which probably indicates unresolved, positionally disordered sites [Figure 1(b)]. The calculated principal axes of inertia ($I_1 > I_2 > I_3$)[20] are roughly orientated along the crystallographic *a*, *c* and *b* axes, respectively. The major displacement, representing an in-plane librational displacement about the centre of the benzo ring, is consistent with the packing arrangement (Figure 3) and suggests that there relative freedom of libration about the crystallographic *a* axis might exist.

Packing relationships

The space groups in which these two compounds crystallize, namely, *C*2/*c* [**1** · acetone (2 : 1)] and $P2_1/n$ [**2** · toluene (1 : 1)], allow efficient ‘closest packing’[21, 22] for molecular organic compounds. The values of the packing coefficients, using parameters supplied with the program PLATON,[20] are 0·685 for **1** · acetone (2 : 1) and 0·680 for **2** · toluene (1 : 1), and lie within the limits usually observed in molecular crystals.[21] The packing coefficients, estimated for the hypothetical solvent-free structures of **1** and **2**, are 0·631 and 0·541, respectively, thus well illustrating the effect of solvent inclusion in enhancing close packing.

The host molecule in both structures contains a hydroxy group capable of intermolecular host–host hydrogen bonding or hydrogen bonding with suitable guest molecules, but the possibility is not realized in either of these substances. This cannot be attributed to the bulkiness of the host molecule only, since H-bonds have been observed between related *α*,*α*-bis-*p*-chlorophenyl-9,10-dihydro-9,10-ethanoanthracene-11-methanol hosts and cyclohexylamime

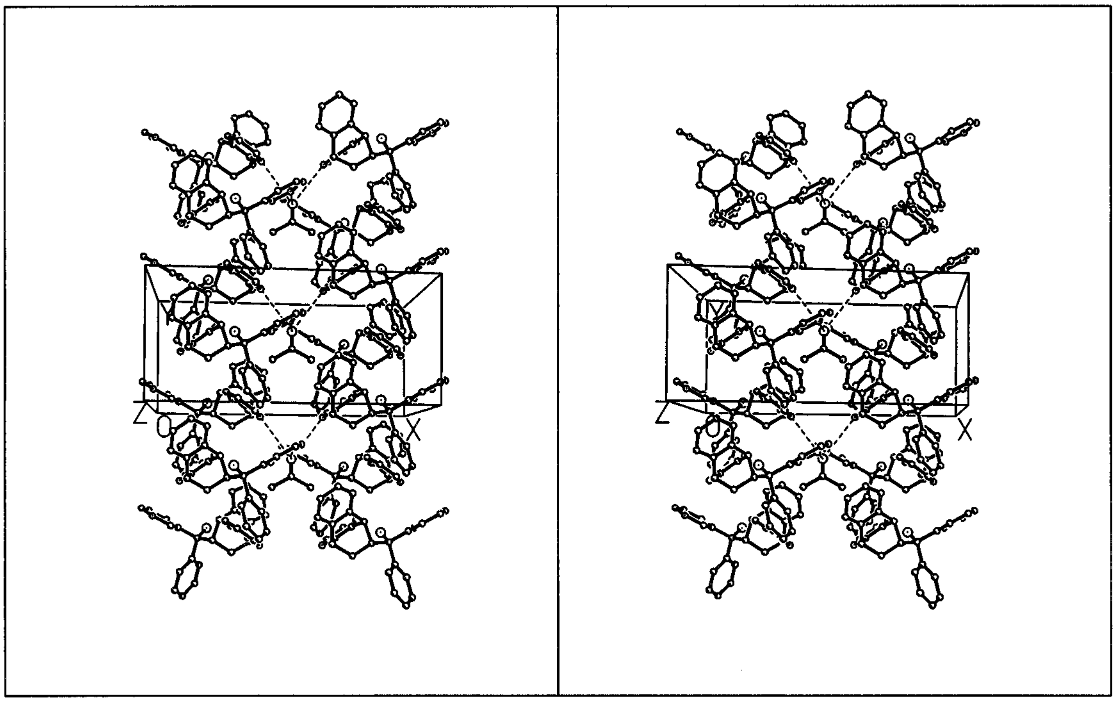

Figure 2. Molecular packing in the compound **1** · acetone (2 : 1). All hydrogen atoms are omitted for clarity. The O atoms are indicated as dotted circles with larger diameter. Dashed lines indicate C—H · · · O interactions between O atoms of the guest and C atoms of the host molecules

guests.[23] In the absence of O—H · · · O hydrogen bonds, the present crystal structures seem to be stabilized mainly by weaker intermolecular forces: host–guest C—H · · · O bonds[24–28] in **1** · acetone (2:1) and host–host C—H · · · F interactions[29] in **2** · toluene (1:1) (Table 3). Despite the different polarities of both the guests and the hosts, the packing patterns show some similarities in these two inclusion compounds: both have layer arrangements with the oxygen atoms of the host hydroxy groups pointing towards the layer surface.

The crystal architecture of **1** · acetone (2:1) is in the form of alternating layers stacked along the *c* axis, each consisting of homochiral host molecules. In every layer, the carbonyl oxygen of the guest acetone molecule forms four possible C—H · · · O contacts with aromatic hydrogens of four neighbouring host molecules related either by C-centering or by a twofold axis (Figure 2 and Table 3). The ∠H(5)—O(a)—H(5) and ∠H(16)—O(a)—H(16) angles are 64·4(1°) and 157·5(1)°, respectively. The neighbouring layers are held together by ordinary van der Waals forces. The angles of elevation of H(5) · · ·O(a) and H(16) · · ·O(a) vectors above the lone pair of the carbonyl oxygen, which is assumed to be in the plane of the O(a), C(a1), C(a2) and C(a3) atoms, are 10·8(1)° for H(5) and 78·6(1)° for H(16). The angles H(5) · · ·O(a)=C(a1) and H(16) · · ·O(a)=C(a1) are 147·7(1)° and 101·2(1)°, respectively.

In the toluene complex of the fluoro-containing host **2**, the layers are stacked along the *a* axis and contain both enantiomers of the host molecule. The pairs of oppositely handed host molecules within each layer are linked together by possible C—H · · · F interactions (Table 3) involving only one [F(23)] of the two fluoro substituents. The F(17) atom, on the other hand, seems to have only ordinary van der Waals contacts with the minimum intermolecular H · · · F distances of 2·85 Å to $H(8)_{(-x,\ -y+1,\ -z+1)}$ and 2·86 Å to $H(t6)_{(x,\ y,\ z+1)}$. The differences in the crystallographic environment around the two fluoro substituents might be the reason for the observed difference in the C—F distances (Table 5). Hence, unequal C—F bonds together with the significantly different atomic displacement parameters (Table 2 here and Table 11 in the Supplementary material) in all probability indicate the varying nature of the intermolecular interactions involving the two fluorine atoms. The host molecules, linked together by the C—H · · · F interactions, form a kind of a ribbon structure, running along the *c* axis (Figure 3). The toluene guests reside in the voids in between the parallel host ribbons and exhibit rather high mobility (see above), indicating weak fixation.

An earlier study (1983) of the C—F · · · H—X (X = O, N, C) interactions[29] showed that the C—F bond acting as a proton acceptor is neither very common nor

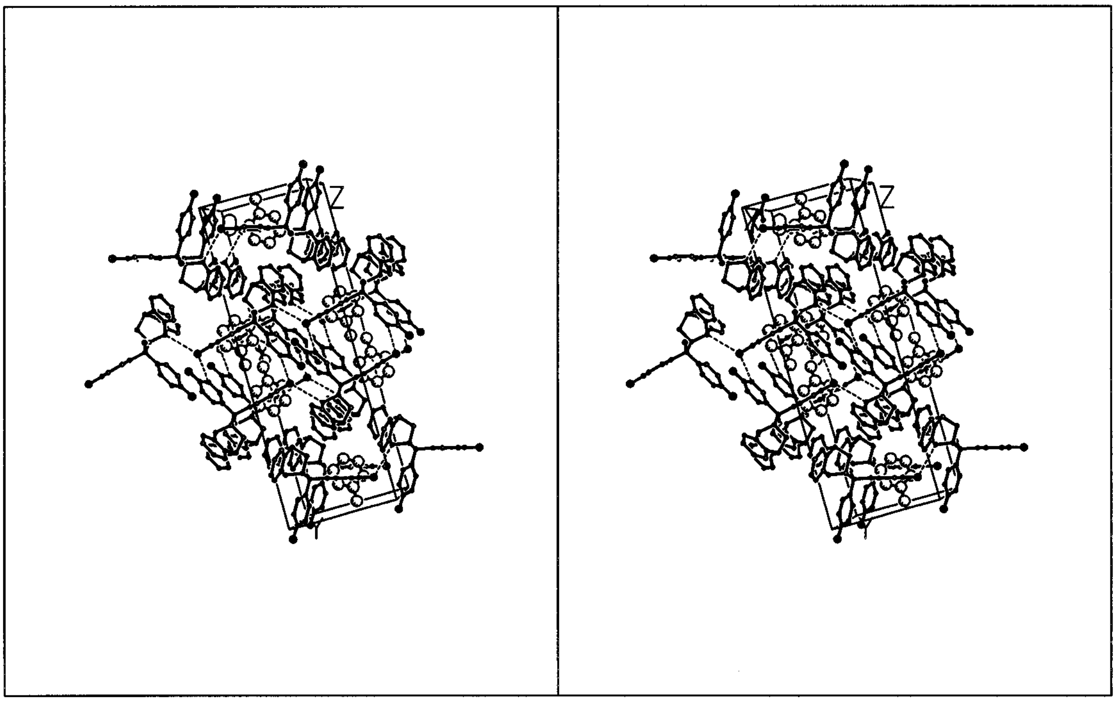

Figure 3. Molecular packing in the compound **2** · toluene (1:1). All hydrogen atoms are omitted for clarity. The host molecules are shown in ball-and-stick style. The F atoms are indicated as cross-hatched circles. The carbons of the guest molecules are drawn as circles with larger diameter, for clarity. Dashed lines indicate C—H · · · F interactions between the host molecules

crystal structure determining. A recent quick search for C—H · · ·F—C fragments in organic crystals in the April 1996 version of the Cambridge Structural Database[30] yielded 388 structures containing 498 fragments with $C\cdots F<3{\cdot}5$ Å and $H\cdots F<2{\cdot}5$ Å.The calculated mean values for the 498 connection are 2·409(3) Å for H · · · F, 3·336(6) Å for C · · · Fand 145·5(7)° for the angle C—H · · · F, indicating relatively weak interactions. We may assume that some connections may be due to the fortuitous proximity of the H and F atoms, owing to the exposed position of the fluoro substituents in many molecules and the requirement of dense packing in organic crystals. At the same time, the ability of the C-bonded fluorine to act as a proton acceptor seems to be unclear.[29] Nevertheless, the packing arrangement in the present toluene complex of the fluoro-containing host **2** gives evidence that in the absence of other, stronger intermolecular interactions, C—H · · · F(—C) connections may play a crucial role in molecular crystals.

CONCLUSIONS

Novel host molecules with the rigid 9,10-dihydro-9,10-ethanoanthracene building block and appended diarylmethanol clathratogenic[3, 31] groups have proved to exhibit some conformational flexibility that can be interpreted as a response to the requirements of compact packing. They form crystalline inclusion compounds with guests of different characteristics (polar acetone and non-polar toluene), stabilized by weak intermolecular interactions of basically electrostatic nature: C—H · · · O bonds between hosts and the acetone oxygen in **1** · acetone (2 : 1), and by

Table 1. Crystal data, experimental parameters and selected refinement details for the compounds **1** · acetone (2 : 1) and **2** · toluene (1 : 1)

Compound	**1** · acetone (2 : 1)	**2** · toluene (1 : 1)
Crystal data:		
Formula	$C_{29}H_{24}O \cdot 0.5C_3H_6O$	$C_{29}H_{22}OF_2 \cdot C_7H_8$
Formula weight	417·55	516·63
$F(000)$	1776	1088
Space group	$C2/c$	$P2_1/n$
a (Å)	19·314(1)	9·715(5)
b (Å)	8·451(1)	29·51(2)
c (Å)	28·533(2)	9·858(6)
α (°)	90·00	90·00
β (°)	103·38(1)	104·98(4)
γ (°)	90·00	90·00
V (Å^3)	4530·8(7)	2730·3(4)
Z	8	4
D_c (g cm^{-3})	1·224	1·257
μ (cm^{-1})	0·735	0·833
Approximate crystal size (mm)	0·40×0·34×0·46	0·35×0·14×0·30
Intensity measurements:		
Radiation, λ	Mo Kα (0·71069 Å)	Mo $K\alpha$ (0·71073 Å)
Temperature (K)	173±1	298±1
Scan type	$\omega-2\theta$	$\omega-2\theta$
Range of 2θ (°)	3—60	2—60
Range of hkl	−27/26 0/11 0/40	−1/11 −1/35 −11/11
No. of collected reflections: total/non-zero	7032/5689	6099/4808
No. of standard reflections	4	3
Interval between the standards	90 min	200 reflections
Intensity instability	3·5%	3·5%
Structure refinement:		
No. of reflections included	3037 with $I>3\sigma$	1653 with $I>2\sigma$
Total No. of refined parameters	297	293
Linear agreement factor $R=\sum\|\Delta F\|/\sum\|F_o\|$	0·042	0·094
Weighted agreement factor $wR=[\sum w\|\Delta F\|^2/\sum w\|F_o\|^2]^{1/2}$	0·053	0·088
Weighting: $w=1/[\sigma^2(F)+g\|F\|^2]$ with g	0·0006	0·00044
Soof (goodness of fit)	1·78	1·88
Weighted agreement factor including all unique non-zero reflections wR_{tot}	0·063	0·114
Final $\Delta\rho_{max}/\Delta\rho_{min}/(e^-$ Å$^{-3})$	0·24/−0·20	0·42/−0·33

C—H · · · F interhost interactions in the fluoro-containing **2** · toluene (1:1) complex.

Table 2. Fractional atomic coordinates and equivalent isotropic displacement parameters U_{eq} of the non-hydrogen atoms in the compounds **1** · acetone (2:1) and **2** · toluene (1:1), with esds, where given[a], in parentheses

Atom	*x*	*y*	*z*	U_{eq} (Å^2)
***1* · acetone (2:1):**				
C(1)	0·2944(1)	0·3293(3)	0·6112(1)	0·0342(7)
C(1a)	0·3020(1)	0·1848(2)	0·6351(1)	0·0258(6)
C(2)	0·3471(1)	0·3804(3)	0·5886(1)	0·0415(8)
C(3)	0·4074(1)	0·2882(3)	0·5905(1)	0·0414(9)
C(4)	0·4152(1)	0·1435(3)	0·6143(1)	0·0333(7)
C(4a)	0·3626(1)	0·0917(3)	0·6367(1)	0·0260(6)
C(5)	0·3892(1)	−0·0840(3)	0·7553(1)	0·0306(7)
C(5a)	0·3485(1)	−0·0296(2)	0·7118(1)	0·0249(6)
C(6)	0·3700(1)	−0·0428(3)	0·7981(1)	0·0362(8)
C(7)	0·3110(1)	0·0525(3)	0·7968(1)	0·0356(7)
C(8)	0·2699(1)	0·1076(3)	0·7532(1)	0·0295(7)
C(8a)	0·2889(1)	0·0662(2)	0·7108(1)	0·0246(6)
C(9)	0·3604(1)	−0·0644(2)	0·6621(1)	0·0252(6)
C(10)	0·2924(1)	−0·1509(2)	0·6331(1)	0·0253(6)
C(11)	0·2246(1)	−0·0556(2)	0·6359(1)	0·0222(6)
C(12)	0·2491(1)	0·1090(2)	0·6601(1)	0·0237(6)
C(13)	0·1709(1)	−0·0426(2)	0·5864(1)	0·0223(6)
O(13)	0·2029(1)	0·0356(2)	0·5519(1)	0·0278(4)
C(14)	0·1018(1)	0·0431(2)	0·5892(1)	0·0226(6)
C(15)	0·0772(1)	0·0602(3)	0·6313(1)	0·0273(6)
C(16)	0·0127(1)	0·1374(3)	0·6304(1)	0·0305(7)
C(17)	−0·0273(1)	0·1971(3)	0·5877(1)	0·0287(6)
C(18)	−0·0037(1)	0·1790(2)	0·5457(1)	0·0296(7)
C(19)	0·0598(1)	0·1027(2)	0·5464(1)	0·0259(6)
C(20)	0·1519(1)	−0·2095(2)	0·5662(1)	0·0224(6)
C(21)	0·1085(1)	−0·3097(3)	0·5857(1)	0·0274(7)
C(22)	0·0915(1)	−0·4595(3)	0·5669(1)	0·0315(7)
C(23)	0·1176(1)	−0·5126(3)	0·5280(1)	0·0309(7)
C(24)	0·1606(1)	−0·4146(3)	0·5085(1)	0·0303(7)
C(25)	0·1772(1)	−0·2633(3)	0·5272(1)	0·0283(7)
O(a)	0·00	0·0906(4)	0·75	0·080(2)
C(a1)	0·00	−0·0461(5)	0·75	0·049(2)
C(a2)	−0·0679(3)	−0·1308(8)	0·7394(2)	0·206(4)
***2* · toluene (1:1):**				
C(1)	0·2854	0·3070	0·5731	0·054(5)
C(1a)	0·1616	0·3032	0·4642	0·036(4)
C(2)	0·3786	0·2703	0·6070	0·065(5)
C(3)	0·3479	0·2299	0·5320	0·071(6)
C(4)	0·2240(9)	0·2261(2)	0·4230(8)	0·056(6)
C(4a)	0·1309	0·2628	0·3891	0·037(4)
C(5)	−0·2520	0·2605	0·3288	0·045(5)
C(5a)	−0·1202	0·2809	0·3389	0·035(4)
C(6)	−0·3498	0·2809	0·3912	0·053(5)
C(7)	−0·3157	0·3217	0·4637	0·056(6)
C(8)	−0·1839(7)	0·3421(2)	0·4738(6)	0·051(4)
C(8a)	−0·0861	0·3217	0·4114	0·030(4)
C(9)	−0·0040(10)	0·2647(3)	0·2745(10)	0·041(5)
C(10)	0·0188(10)	0·3023(3)	0·1759(9)	0·037(4)
C(11)	0·0498(9)	0·3483(3)	0·2578(9)	0·031(4)
C(12)	0·0560(9)	0·3396(3)	0·4118(9)	0·033(4)
C(13)	0·1787(10)	0·3743(3)	0·2321(10)	0·037(4)
O(13)	0·3056(6)	0·3486(2)	0·2787(6)	0·037(3)
C(14)	0·1990(8)	0·4181(2)	0·3132(7)	0·033(4)
C(15)	0·0879	0·4495	0·2866	0·050(5)
C(16)	0·1033	0·4901	0·3613	0·063(6)
C(17)	0·2298	0·4994	0·4625	0·076(7)
F(17)	0·2488(9)	0·5374(2)	0·5399(9)	0·124(4)
C(18)	0·3408	0·4679	0·4891	0·070(6)
C(19)	0·3254	0·4273	0·4144	0·052(5)
C(20)	0·1604(7)	0·3845(2)	0·0756(5)	0·032(4)
C(21)	0·0276	0·3893	−0·0202	0·048(5)
C(22)	0·0190	0·4012	−0·1590	0·054(5)
C(23)	0·1432	0·4084	−0·2021	0·048(5)
F(23)	0·1336(6)	0·4201(2)	−0·3353(6)	0·061(3)
C(24)	0·2760	0·4037	−0·1063	0·046(5)
C(25)	0·2846	0·3917	0·0325	0·042(5)
C(t1)	0·3301	0·5554	0·0486	0·087(8)
C(t2)	0·3490(9)	0·5815(6)	0·1699(13)	0·120(12)
C(t3)	0·3620	0·6285	0·1628	0·111(10)
C(t4)	0·3562	0·6493	0·0345	0·093(8)
C(t5)	0·3374	0·6232	−0·0869	0·095(9)
C(t6)	0·3243	0·5762	−0·0798	0·106(10)
C(t7)	0·312(2)	0·5104(6)	0·042(3)	0·31(2)

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[a] In the fixed groups in **2**·toluene (1:1) the positional parameters were refined only for the pivot atoms. Those are C(4), C(8), C(14), C(20) and C(t2) for the hexagons C(1a) · · ·C(4a), C(5a) · · ·C(8a), C(14) · · ·C(19), C(20) · · ·C(25) and C(t1) · · ·C(t6), respectively.

EXPERIMENTAL

Preparation of crystalline inclusion compounds. Both crystalline inclusion compounds were prepared by dissolving the host compound in the respective guest solvent and subsequent crystallization from the slowly cooled solution. The host:guest stoichiometric ratios were determined by ^{1}H NMR integration.[32]

Structure analysis and refinement. Low-temperature (173±1 K) intensity data sets for both compounds were collected with a STOE/AED2 diffractometer, using graphite-monochromatized Mo $K\alpha$ radiation. However, in the case of **2** · toluene (1:1), all the tested crystals diffracted poorly. For the best sample only 26% of the reflections with $\Theta_{max}=30°$ were observed, according to the criterion $I \geq 2\sigma(I)$. Therefore, a second data set was collected with a Siemens P4/RA diffractometer equipped with a high-intensity rotating molybdenum anode, although at room temperature. This time, 36% of the collected reflections were observed with $\Theta_{max}=30°$ and $I \geq 2\sigma(I)$. The structure analysis presented here is based on the latter data set. The crystals used for data collection for both compounds were colourless, transparent and irregularly shaped. Lattice constants were determined by least-squares fitting of the setting angles of carefully centred reflections: 36 reflections in the range $35 < 2\theta < 42°$ for **1** · acetone (2:1) and, because

Table 3. Geometry of possible donor—H · · ·acceptor interactions for **1** · acetone (2:1) and **2** · toluene (1:1), with esds, where given, in parentheses[a]

Atoms involved	Symmetry	Distance (Å)			Angle (°)
		Donor · · ·acceptor	Donor—H	H · · ·acceptor	Donor—H · · ·acceptor
***1** · acetone (2:1):*					
O(13)—H(13) · · ·centroid(1)[b]	*x, y, z*	3·484(2)	0·92(3)	2·81(3)	131(3)
C(5)—H(5) · · ·O(a)	$x+1/2, y-1/2, z$	3·509(3)	1·00	2·57	157
C(5)—H(5) · · ·O(a)	$-x+1/2, y-1/2, -z+1/2+1$	3·509(3)	1·00	2·57	157
C(16)—H(16) · · ·O(a)	*x, y, z*	3·500(2)	1·00	2·58	154
C(16)—H(16) · · ·O(a)	$-x, y, -z+1/2+1$	3·500(2)	1·00	2·58	154
***2a** · toluene (1:1):*					
O(13)—H(13) · · ·centroid(1)[b]	*x, y, z*	3·360(10)	1·07	2·32	164
C(12)—H(12) · · ·F(23)	$x, y, z+1$	3·386(11)	1·00	2·42	163
C(16)—H(16) · · ·F(23)	$-x, -y+1, -z$	3·475(9)	1·00	2·42	166

[a] The only refined H atom position is H(13) in **1** · acetone (2:1).

[b] Centroid (1) means the geometrical centre of the benzo ring C(1a) · · ·C(4a).

of the poor crystal quality, only 12 reflections in the range $10<2\theta<13°$ for **2** · toluene (1:1). Background, crystal decay, Lorentz and polarization corrections were applied, but no allowance was made for the small effects of absorption.

The space group $P2_1/n$ (a special setting of $P2_1/c$, No. 14) for **1** · acetone (2:1) was uniquely established by the observed systematic absences and the Laue symmetry. In the case of **2** · toluene (1:1), the observed systematic absences are consistent with space groups *Cc* (No. 9) or *C*2/*c* (No. 15). The latter was assumed from intensity statistics and further verified by the successful solution and refinement of the structure. Both structures were solved with the automatic direct methods routine of the *SHELXS86*[33] program. The coordinates of all non-hydrogen atoms were derived from the E-maps with the best figures of merit.

In the acetone inclusion compound the guest molecule was found to contain a space-group symmetry element, namely a two-fold axis. Thus, the asymmetric unit contains one host and half a guest molecule. The initial structural models were completed and refined by difference electron density calculations ($\Delta\rho$) and full-matrix least-squares calculations based on $|F|$, by means of the software packages *SHELX76*[34] [**1** · acetone (2:1)] and *SHELXTL/*

Table 4. Selected torsion angles for the host molecules in **1** · acetone (2:1) and **2** · toluene (1:1), with esds in parentheses

Sequence of atoms	Angle (°)	
	Host **1**	Host **2**
C(10)—C(11)—C(13)—O(13)	− 60·0(2)	− 61(1)
C(10)—C(11)—C(13)—C(14)	176·7(2)	180(1)
C(10)—C(11)—C(13)—C(20)	55·8(2)	58(1)
O(13)—C(13)—C(14)—C(15)	− 145·0(2)	− 180(1)
O(13)—C(13)—C(20)—C(21)	− 168·4(2)	149(1)

Table 5. Bond distances between the non-hydrogen atoms in compounds **1** · acetone (2:1) and **2** · toluene (1:1), with esds in parentheses[a, b]

Atoms	Distance (Å)	Atoms	Distance (Å)
***1** · acetone (2:1):*			
C(1)—C(1a)	1·390(3)	C(11)—C(13)	1·553(3)
C(1)—C(2)	1·395(4)	O(13)—C(13)	1·437(3)
C(1a)—C(4a)	1·402(3)	C(13)—C(14)	1·536(3)
C(1a)—C(12)	1·518(3)	C(13)—C(20)	1·536(3)
C(2)—C(3)	1·391(4)	C(14)—C(15)	1·399(3)
C(3)—C(4)	1·391(3)	C(14)—C(19)	1·394(3)
C(4)—C(4a)	1·389(3)	C(15)—C(16)	1·401(3)
C(4a)—C(9)	1·511(3)	C(16)—C(17)	1·379(3)
C(5)—C(5a)	1·386(3)	C(17)—C(18)	1·386(3)
C(5)—C(6)	1·399(3)	C(18)—C(19)	1·382(3)
C(5a)—C(8a)	1·402(3)	C(20)—C(21)	1·395(3)
C(5a)—C(9)	1·517(3)	C(20)—C(25)	1·389(3)
C(6)—C(7)	1·389(3)	C(21)—C(22)	1·384(3)
C(7)—C(8)	1·393(3)	C(22)—C(23)	1·396(4)
C(8)—C(8a)	1·389(3)	C(23)—C(24)	1·378(3)
C(8a)—C(12)	1·516(3)	C(24)—C(25)	1·394(3)
C(9)—C(10)	1·563(3)	O(a)—C(a1)	1·156(5)
C(10)—C(11)	1·554(3)	C(a1)—C(a2)	1·464(7)
C(11)—C(12)	1·575(3)		
***2** · toluene (1:1):*			
C(1a)—C(12)	1·482(11)	C(11)—C(13)	1·544(14)
C(4a)—C(9)	1·494(12)	O(13)—C(13)	1·419(11)
C(5a)—C(9)	1·508(13)	C(13)—C(14)	1·505(11)
C(8a)—C(12)	1·477(11)	C(13)—C(20)	1·536(11)
C(9)—C(10)	1·528(14)	F(17)—C(17)	1·344(9)
C(10)—C(11)	1·570(13)	F(23)—C(23)	1·338(8)
C(11)—C(12)	1·525(13)	C(t1)—C(t7)	1·338(26)

[a] The intramolecular distances within the phenyl rings in **2** · toluene (1:1) are not given. The respective rings were treated as regular hexagons with C—C = 1·39 Å (see text).

[b] Distances given here are not corrected for atomic motions.

PC[35] [**2** · toluene (1:1)]. The non-hydrogen atoms were treated anisotropically in both compounds. However, the phenyl rings in **2** · toluene (1:1) were fitted to regular hexagons with C—C = 1·39 Å in order to increase the observation to parameter ratio for that compound. Thus, for each of five hexagons three positional, three angular and 36 displacement parameters were refined.

The hydrogen atoms of the host **1** were located from $\Delta\rho$ maps and were held riding on their carrier atoms during the subsequent calculations. For the hydroxy H atom, however, the positional and isotropic displacement parameters (IDP) were refined in order to geometrically characterize the O—H · · ·aryl interaction.[8] The hydrogens of the acetone guest molecule were calculated assuming ideal geometry with C—H = 1·00 Å. In all, three group IDPs were refined for the hydrogen atoms of **1** · acetone (2:1), one for all aromatic, another for all aliphatic hydrogens in the host, and the third for the hydrogens of the guest molecule (Table 8, Supplementary material). The hydroxy H atom of host **2** was located from $\Delta\rho$ maps, and its position was held riding on its carrier atom O(13) during the subsequent calculations, but its IDP was refined.[8] All the other hydrogens in the **2** · toluene (1:1) complex were introduced at calculated positions and were held riding on their carrier C atoms with ideal geometry and C—H = 1·00 Å. Their IDPs were fixed at a value of 1·2 times the value of the U_{eq} of the respective carrier carbon atom. Further crystal data and selected experimental details are given in Table 1.

The program packages *PLATON*,[20] *PARST*[36] and Mathcad PLUS 6·0[37] were used for geometrical calculations and for preparing material for publication. The molecular motions were analysed with the computer program *THMA14*.[38] Molecular graphics were prepared using the XP routine of the software package *SHELXTL/PC*.[35]

Supplementary data. The tables of final fractional atomic coordinates, bond lengths and angles involving all the non-hydrogen and hydrogen atoms are deposited as supplementary data at the Cambridge Crystallographic Data Centre. All these tables together with the details of the calculations of the weighted least-squares planes, anisotropic displacement parameters for the non-hydrogen atoms, the table of mean square displacement amplitudes for atoms in various specified directions in the *TLS* analysis for host **1** and lists of the observed and calculated structure factors may be obtained directly from the authors (O.H.) on request.

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