Supramolecular Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713649759

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To cite this Article Csöregh, Ingeborg , Gallardo, Olga , Weber, Edwin and Dörpinghaus, Norbert(1995) 'Supramolecular complexation of DMF and acetone involving singly bridged triarylmethanol and analogous hosts', Supramolecular Chemistry, 5: 2, 159 — 165

To link to this Article: DOI: 10.1080/10610279508029489
URL: http://dx.doi.org/10.1080/10610279508029489

SUPRAMOLECULAR CHEMISTRY, Vol. 5, pp. 159–165
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Supramolecular complexation of DMF and acetone involving singly bridged triarylmethanol and analogous hosts.[#] X-ray crystal structures of four inclusion compounds

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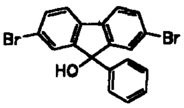
(Received June 20, 1994)

DMF and acetone inclusions with the 2,7-dibromo-9-phenylfluoren-9-ol host (1) and the DMF complexes of the 13-phenyl- (2) and 13-(phenyl-ethynyl)- (3) derivatives of the 1,3,5-tribenzocycloheptatriene-13-ol hosts have been studied by X-ray diffraction. All four complexes contain hydrogen bonded (1:1) host-guest associates, which build up the crystal structures by ordinary van der Waals forces, occasionally supported by weak C-H···O interactions. The host-guest aggregates in the 1•DMF (1:1) and the 1•acetone (1:1) compounds show very similar geometry, possibly enforced by the packing forces. The host 2 molecules in the 2•DMF (1:1) complex are arranged so as to form endless tunnels in which the disordered DMF guests reside. The DMF complex of the slightly helical 3 [3•DMF 1:1)] crystallizes with a chiral space group symmetry ($P2_1$).

INTRODUCTION

Triarylmethanols and analogues having a bridge between two of the aryl groups have proved to be efficient clathrate hosts.[1] Inclusion selectivity depends on the structural features of the host molecule and involves particular modes of host-guest interaction. We have studied the packing relations of inclusion compounds with various apolar and aprotic guest molecules, including benzene[1] and dioxane,[2,3] and we have based a host molecule design *via* lattice considerations on these results.[4] We have also determined the interaction modes between singly bridged triarylmethanols and alcoholic guest molecules, which together form defined supramolecular networks.[5] Now we present the results of structural investigations concerning the inclusion compounds formed between the hosts **1–3** and DMF (**4**,**6** and **7**), and between **1** and acetone (**5**), *i.e.* inclusion compounds of the respective host type with carbonyl containing hydrogen acceptor guests.



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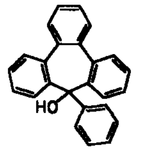

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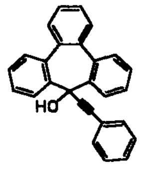

3

4 = **1** • DMF (1:1)
5 = **1** • Acetone (1:1)
6 = **2** • DMF (1:1)
7 = **3** • DMF (1:1)

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[#] Triarylmethanol Hosts and Analogues. Part 10. For Part 9 of this series see ref. 5.

EXPERIMENTAL

Sample preparation

The host compounds **1–3**, synthesized as described previously,[1] were dissolved in a minimum amount of the respective guest solvent. Suitable crystals for X-ray analysis were grown by slow evaporation. The selected single crystals were coated with epoxy glue in order to prevent possible solvent evaporation during the data collection.

X-ray data collection and processing

Intensity data were collected on a STOE/AED2 diffractometer, equipped with graphite monochromator delivering MoK_α (λ = 0.71069 Å) radiation, using the ω-2θ scan technique. Four (**4**) or five reference reflections (**5**, **6** and **7**) were measured approximately every 90 minutes during the data collection. No systematic variation was detected. The data reduction included correction for Lorentz and polarization effects, and in the case of compounds **4** and **5** also for absorption effects. The empirical absorption correction, used for **4**, was based on ψ scans of three reflections with $80 < \chi < 86^\circ$ and $13 < 2\theta < 22^\circ$. The transmission factors varied between 0.17 and 0.30. The data from **5**, however, were corrected using the numerical absorption correction program of the SHELX system.[6] The maximum and minimum transmission factors in the latter case were 0.42 and 0.24, respectively. Crystal data are listed in Table 1.

Structure analysis and refinement

Application of direct methods (**4**, **6** and **7**) (SHELXS[7]), or a combination of heavy atom and direct methods (**5**) (SHELXS[7]), yielded reasonable starting models comprising almost all the non-hydrogen atoms, and also the carbon disorder sites of the DMF guest in **6** [*cf.* Fig. 1(c)]. Conventional difference Fourier ($\Delta\rho$) syntheses were used to find the missing C atoms in **4** and **5**. The hydroxy H atoms of the hosts in all four structures and also some carbon-bonded hydrogens in **6** and **7** were located from $\Delta\rho$ maps and were held riding on their parent atoms during the subsequent calculations. The remaining hydrogens were assumed to be in idealized positions with C-H = 1.00 Å, which were recalculated after each refining cycle using geometric evidence. In the full-matrix least-squares refinements, based on $|F|$ (SHELX),[6,8] the non-hydrogen atoms, and also the disordered C atoms in **6**, were handled anisotropically, whereas isotropic vibrational parameters were refined for the H

Table 1 Crystal data and selected details of the data reduction and structure refinement calculations (Esd's, where given, in parentheses)

Compound	**4** *1·DMF* *(1:1)*	**5** *1·acetone* *(1:1)*	**6** *2·DMF* *(1:1)*	**7** *3·DMF* *(1:1)*
Formula unit	$C_{19}H_{12}OBr_2\cdot C_3H_7NO$	$C_{19}H_{12}OBr_2\cdot C_3H_6O$	$C_{25}H_{18}O\cdot C_3H_7NO$	$C_{27}H_{18}O\cdot C_3H_7NO$
Formula weight	489.21	474.19	407.51	431.53
Crystal system	triclinic	triclinic	triclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1$
Cell dimensions				
a,Å	14.912(2)	8.370(1)	8.256(1)	9.326(1)
b,Å	14.012(3)	9.007(1)	8.930(1)	8.498(1)
c,Å	10.617(2)	14.187(1)	15.714(1)	14.489(2)
α,deg.	86.04(1)	87.340(6)	88.455(5)	90.0
β,deg.	70.58(2)	83.592(7)	78.382(5)	97.351(8)
γ,deg.	82.30(1)	67.951(6)	74.058(5)	90.0
V_c,Å^3	2072.6(7)	985.1(2)	1090.7(2)	1138.8(2)
Refinement of the unit cell dimensions:				
No. of reflections used	50	36	44	38
2θ-range,deg.	22–40	30–43	27–51	10–27
Z	4	2	2	2
D_c,g cm^{-3}	1.5678(6)	1.5986(3)	1.2409(3)	1.2584(3)
$F(000)$	976	472	432	456
Temperature,K	291(1)	173(1)	173(1)	173(1)
Radiation	MoK_α	MoK_α	MoK_α	MoK_α
μ,cm^{-1}	38.91	40.86	0.72	0.73
θ limit,deg.	25	30	30	30
No. of collected reflections	7762	5740	6357	3529
No. of unique non-zero reflections	6181	4980	5523	3314
No. of reflections with $I > 3\sigma(I)$	3364	2953	3143	2329
No. of refined parameters	509[a]	253	326	307
Final agreement factors R [$=\Sigma\|\Delta F\|/\Sigma\|F_o\|$	0.036	0.052	0.041	0.040
wR [$=(\Sigma w\|\Delta F\|^2/\Sigma w\|F_o\|^2)^{1/2}$	0.045	0.067	0.053	0.053
wR_{tot}	0.050	0.092	0.058	0.057
Weighting: $w=[\sigma^2(F) + g\cdot F^2]^{-1}$ with g=	0.00020	0.00400	0.00058	0.00140

[a] In the refinement of **4** 'blocked full matrix' refinement technique[8] had to be used because of the large number of variables. Accordingly, the two crystallographically independent host-guest associates were refined in consecutive cycles.

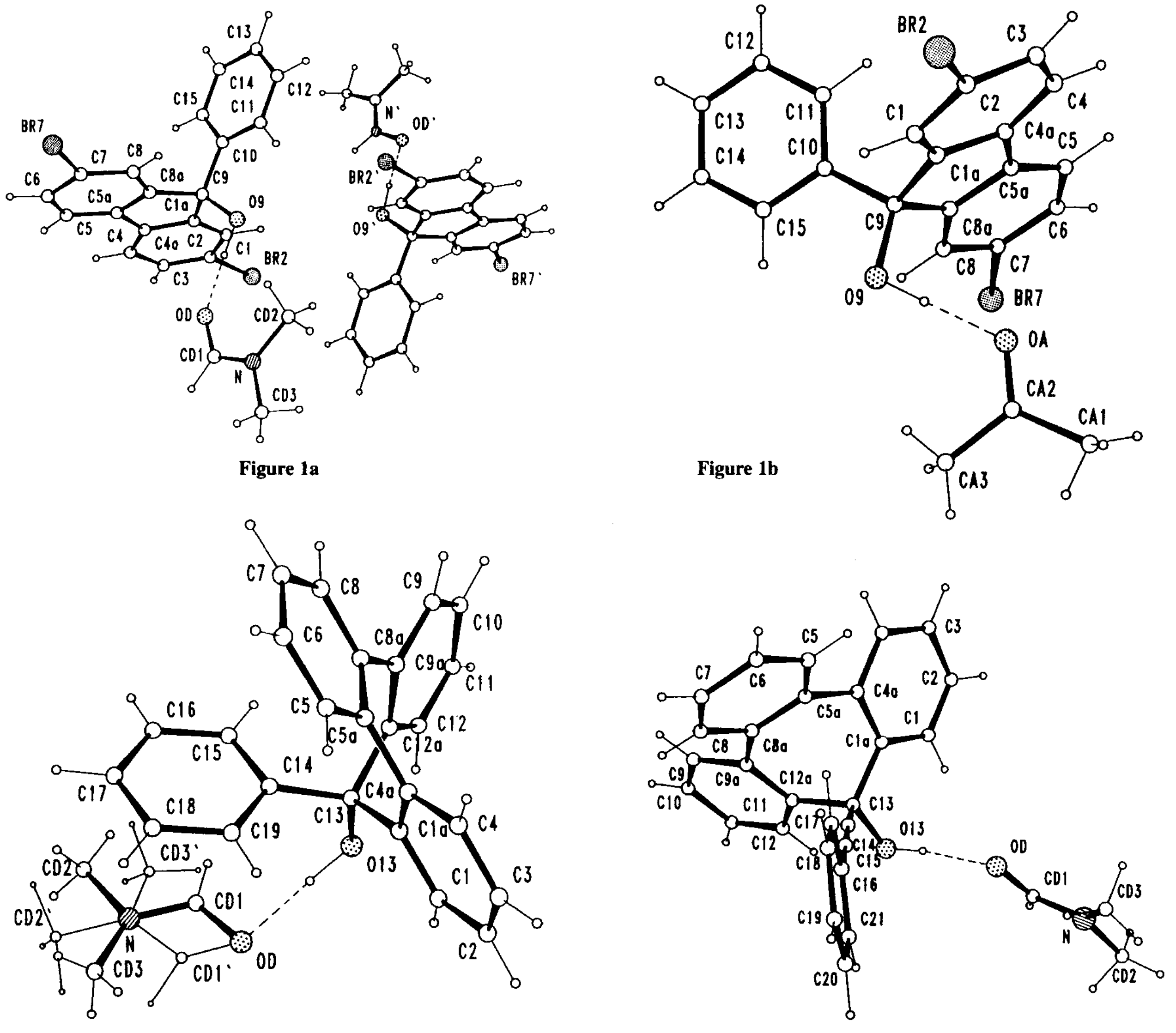

Figure 1a

Figure 1b

Figure 1c

Figure 1d

Figure 1 Perspective views of the asymmetric units, with atomic numbering, for compounds: (a) **4** [**1**•DMF (1:1)], (b) **5** [**1**•acetone (1:1)], (c) **6** [**2**•DMF (1:1)], and (d) **7** [**3**•DMF (1:1)]. The DMF guest in **6** is partially disordered. The C(D') disorder sites, with the lower probability (*cf.* the text), are drawn with smaller atomic radii in Figure 1(c). Solid and dashes lines represent covalent and hydrogen bonds, respectively; O atoms are dotted, N atoms are hatched.

atoms. The methyl groups were treated as rigid. 10 and 6 low-θ reflections, with considerably lower observed than calculated F, in all probability due to extinction effects, were excluded from the final refinements of **4** and **5**, respectively. Details of the refinement calculations together with the final R values are shown in Table 1. The wR_{tot} values were calculated for the final structural models, using all unique, non-zero reflections.

The DMF guest in **6** is partially disordered, having two major disorder sites (unprimed and primed) for each C atom, and also for the hydrogens bonded to them [Fig. 1(c)]. In the least-squares calculations all partially occupied positions, belonging to the same disorder model, were assumed to have the same probability, and the sum of each unprimed/primed pair of site occupation factors (sof) was put equal to 1.0. Accordingly, the sof for the unprimed C(D) and H(D) sites refined to 0.64(6), while that of the primed positions became 0.34(6).

The final atomic coordinates and the equivalent isotropic displacement parameters (B_{eq}) of the non-hydrogen atoms are listed in Table 2.

RESULTS AND DISCUSSION

The crystallographic asymmetric units with atomic numbering of compounds **4**–**7** are depicted in Figs. 1(a)–(d), respectively. Selected conformational features of the

Table 2 Fractional atomic coordinates and equivalent isotropic displacement parameters[a], B_{eq} (Å^2), for the non-hydrogen atoms of compounds **4–7**

Atom	*x/a*	*y/b*	*z/c*	B_{eq}[a]
4[**1**•DMF(1:1)]				
C(1a)	0.6401(4)	1.6013(4)	-0.3659(5)	3.6(2)
C(1)	0.5902(4)	1.5294(4)	-0.2946(5)	4.4(2)
C(2)	0.4915(4)	1.5425(4)	-0.2580(6)	5.0(2)
Br(2)	0.42099(5)	1.44500(5)	-0.15542(8)	7.82(3)
C(3)	0.4434(4)	1.6265(4)	-0.2938(6)	5.3(2)
C(4)	0.4942(4)	1.6998(4)	-0.3642(6)	4.6(2)
C(4a)	0.5934(4)	1.6875(4)	-0.4003(5)	3.8(2)
C(5a)	0.6652(4)	1.7518(4)	-0.4690(5)	3.4(2)
C(5)	0.6561(4)	1.8463(4)	-0.5182(5)	4.0(2)
C(6)	0.7372(4)	1.8917(4)	-0.5761(5)	4.0(2)
C(7)	0.8254(4)	1.8435(4)	-0.5839(5)	3.6(2)
Br(7)	0.93559(4)	1.90839(4)	-0.66370(6)	5.30(2)
C(8)	0.8366(4)	1.7500(4)	-0.5350(5)	3.4(2)
C(8a)	0.7552(4)	1.7054(3)	-0.4782(5)	3.3(2)
C(9)	0.7484(3)	1.6039(4)	-0.4168(5)	3.5(2)
O(9)	0.7902(2)	1.5870(3)	-0.3136(4)	4.3(1)
C(10)	0.7992(4)	1.5289(3)	-0.5234(5)	3.5(2)
C(11)	0.8840(4)	1.4759(4)	-0.5240(6)	4.9(2)
C(12)	0.9312(4)	1.4102(5)	-0.6242(7)	6.2(3)
C(13)	0.8944(5)	1.3974(5)	-0.7217(7)	6.4(3)
C(14)	0.8093(5)	1.4495(5)	-0.7233(6)	5.7(2)
C(15)	0.7626(4)	1.5156(4)	-0.6237(6)	4.9(2)
O(D)	0.7032(3)	1.7129(3)	-0.1182(5)	7.4(2)
C(D1)	0.7157(5)	1.7425(5)	-0.0184(8)	7.2(3)
N	0.7816(4)	1.7068(4)	0.0316(5)	4.9(2)
C(D2)	0.8488(5)	1.6270(6)	-0.0311(7)	8.7(3)
C(D3)	0.7906(7)	1.7463(5)	0.1485(7)	9.4(4)
C(1a′)	0.3440(4)	0.9212(4)	-0.0986(5)	3.4(2)
C(1′)	0.3954(4)	0.9929(4)	-0.1677(5)	4.3(2)
C(2′)	0.4939(4)	0.9773(4)	-0.2014(6)	4.6(2)
Br(2′)	0.56643(5)	1.07598(5)	-0.30205(8)	7.08(3)
C(3′)	0.5407(4)	0.8938(4)	-0.1653(6)	4.9(2)
C(4′)	0.4885(4)	0.8224(4)	-0.0971(6)	4.8(2)
C(4a′)	0.3892(3)	0.8355(4)	-0.0634(5)	3.6(2)
C(5a′)	0.3171(3)	0.7700(4)	0.0025(5)	3.4(2)
C(5′)	0.3258(4)	0.6755(4)	0.0489(5)	4.3(2)
C(6′)	0.2438(4)	0.6290(4)	0.1030(5)	4.4(2)
C(7′)	0.1560(4)	0.6774(4)	0.1065(5)	4.0(2)
Br(7′)	0.04523(4)	0.61327(5)	0.18097(7)	5.97(2)
C(8′)	0.1460(4)	0.7724(4)	0.0603(5)	3.8(2)
C(8a′)	0.2281(4)	0.8181(4)	0.0079(5)	3.3(2)
C(9′)	0.2358(3)	0.9200(3)	-0.0519(5)	3.5(2)
O(9′)	0.1966(2)	0.9370(2)	-0.1566(3)	4.2(1)
C(10′)	0.1835(4)	0.9950(4)	0.0540(5)	3.5(2)
C(11′)	0.0992(4)	1.0473(4)	0.0543(6)	4.6(2)
C(12′)	0.0516(4)	1.1120(5)	0.1551(7)	6.2(3)
C(13′)	0.0880(5)	1.1260(5)	0.2536(7)	6.3(3)
C(14′)	0.1716(5)	1.0746(5)	0.2546(6)	6.3(3)
C(15′)	0.2189(4)	1.0091(4)	0.1548(6)	4.9(2)
O(D′)	0.2782(3)	0.8157(4)	-0.3592(5)	7.3(2)
C(D1′)	0.2217(5)	0.8320(5)	-0.4260(7)	6.6(3)
N′	0.2311(4)	0.7858(3)	-0.5321(5)	4.8(2)
C(D2′)	0.1607(6)	0.8039(6)	-0.6012(8)	9.9(4)
C(D3′)	0.3095(6)	0.7106(5)	-0.5824(7)	8.8(3)
5[**1**•acetone(1:1)]				
C(1a)	0.3903(6)	0.2889(6)	0.6533(3)	1.6(1)
C(1)	0.2685(6)	0.2730(6)	0.6003(4)	1.8(1)
C(2)	0.3027(7)	0.2730(7)	0.5018(4)	2.1(1)
Br(2)	0.13157(7)	0.26165(8)	0.42772(4)	2.98(2)
C(3)	0.4543(7)	0.2860(7)	0.4563(4)	2.4(2)
C(4)	0.5736(7)	0.3055(6)	0.5108(4)	2.0(1)
C(4a)	0.5388(6)	0.3095(6)	0.6092(3)	1.6(1)
C(5a)	0.6342(6)	0.3378(6)	0.6842(3)	1.6(1)
C(5)	0.7805(6)	0.3754(6)	0.6787(4)	1.9(1)
C(6)	0.8373(6)	0.4064(6)	0.7624(4)	1.9(1)
C(7)	0.7445(6)	0.3977(6)	0.8487(3)	1.7(1)
Br(7)	0.81569(7)	0.44840(7)	0.96184(4)	2.59(2)
C(8)	0.5970(6)	0.3601(6)	0.8559(3)	1.8(1)
C(8a)	0.5429(6)	0.3309(5)	0.7720(3)	1.4(1)
C(9)	0.3820(6)	0.2934(6)	0.7613(3)	1.6(1)
O(9)	0.2282(4)	0.4134(4)	0.8028(3)	1.8(1)
C(10)	0.3965(6)	0.1322(6)	0.8068(3)	1.6(1)
C(11)	0.5084(7)	-0.0102(6)	0.7640(4)	2.3(2)
C(12)	0.5213(8)	-0.1548(7)	0.8055(4)	2.7(2)
C(13)	0.4244(9)	-0.1631(7)	0.8884(4)	3.0(2)
C(14)	0.3117(9)	-0.0214(7)	0.9326(5)	3.5(2)
C(15)	0.2968(8)	0.1272(7)	0.8909(4)	2.7(2)
O(A)	0.1937(6)	0.6963(5)	0.7095(3)	3.4(1)
C(A1)	0.0932(1)	0.9760(8)	0.6915(7)	4.9(3)
C(A2)	0.0975(8)	0.8234(7)	0.7422(4)	2.8(2)
C(A3)	-0.0203(10)	0.8352(1)	0.8294(6)	4.7(3)
6 [**2**·DMF (1:1)]				
C(1a)	0.5023(2)	0.9162(2)	0.6989(1)	1.98(4)
C(1)	0.5367(2)	0.9848(2)	0.6194(1)	2.40(5)
C(2)	0.6887(3)	1.0264(2)	0.5916(1)	2.79(5)
C(3)	0.8099(2)	0.9984(2)	0.6436(1)	2.78(5)
C(4)	0.7776(2)	0.9300(2)	0.7232(1)	2.42(5)
C(4a)	0.6245(2)	0.8882(2)	0.7528(1)	1.99(4)
C(5a)	0.6000(2)	0.8117(2)	0.8376(1)	2.03(4)
C(5)	0.7379(2)	0.6944(2)	0.8578(1)	2.44(4)
C(6)	0.7242(3)	0.6199(2)	0.9361(1)	2.88(5)
C(7)	0.5728(3)	0.6628(2)	0.9971(1)	2.87(5)
C(8)	0.4355(2)	0.7791(2)	0.9789(1)	2.59(5)
C(8a)	0.4451(2)	0.8540(2)	0.8993(1)	2.04(4)
C(9a)	0.2905(2)	0.9768(2)	0.8847(1)	2.07(4)
C(9)	0.1959(2)	1.0816(2)	0.9532(1)	2.53(5)
C(10)	0.0469(2)	1.1936(2)	0.9450(1)	2.82(5)
C(11)	-0.0118(2)	1.2027(2)	0.8682(1)	2.78(5)
C(12)	0.0803(2)	1.0998(2)	0.7992(1)	2.39(5)
C(12a)	0.2308(2)	0.9862(2)	0.8063(1)	2.00(4)
C(13)	0.3304(2)	0.8766(2)	0.7288(1)	1.99(4)
O(13)	0.2315(2)	0.9119(1)	0.6619(1)	2.63(4)
C(14)	0.3513(2)	0.7039(2)	0.7493(1)	2.17(4)
C(15)	0.2209(2)	0.6588(2)	0.8048(1)	2.68(5)
C(16)	0.2306(3)	0.5018(2)	0.8161(1)	3.45(6)
C(17)	0.3689(3)	0.3887(2)	0.7718(2)	3.81(7)
C(18)	0.4998(3)	0.4320(2)	0.7166(2)	4.09(7)
C(19)	0.4908(3)	0.5892(2)	0.7055(1)	3.25(6)
O(D)	0.2504(3)	0.6750(2)	0.5505(1)	6.02(7)
C(D1)	0.1359(5)	0.6112(4)	0.5910(2)	3.40(10)
C(D1′)	0.2913(11)	0.5391(8)	0.5386(4)	4.65(24)
N	0.1501(3)	0.4645(2)	0.5773(1)	4.18(6)
C(D2)	0.0059(9)	0.4015(8)	0.6296(3)	8.30(27)
C(D2′)	0.2197(19)	0.2931(10)	0.5660(8)	7.23(40)
C(D3)	0.2833(10)	0.3585(8)	0.5265(5)	9.09(28)
C(D3′)	0.0091(12)	0.5442(14)	0.6229(6)	7.52(38)
7 [**3**•DMF (1:1)]				
C(1a)	0.3603(3)	0.3648	0.6645(2)	1.56(5)
C(1)	0.4622(3)	0.3789(5)	0.6019(2)	1.98(6)
C(2)	0.5129(3)	0.5269(5)	0.5795(2)	2.30(6)
C(3)	0.4626(3)	0.6610(5)	0.6189(2)	2.26(6)
C(4)	0.3616(3)	0.6472(5)	0.6817(2)	1.87(6)
C(4a)	0.3102(3)	0.5003(4)	0.7054(2)	1.55(5)
C(5a)	0.2056(3)	0.4924(4)	0.7747(2)	1.54(5)
C(5)	0.2325(3)	0.5841(5)	0.8550(2)	1.92(6)
C(6)	0.1367(3)	0.5874(5)	0.9210(2)	2.23(6)
C(7)	0.0114(3)	0.4985(5)	0.9065(2)	2.25(6)
C(8)	-0.0170(3)	0.4063(5)	0.8275(2)	1.89(5)
C(8a)	0.0788(3)	0.4018(4)	0.7601(2)	1.51(5)
C(9a)	0.0406(3)	0.3032(5)	0.6759(2)	1.55(5)
C(9)	-0.1022(3)	0.3092(5)	0.6302(2)	2.07(6)
C(10)	-0.1430(3)	0.2211(5)	0.5515(2)	2.64(7)
C(11)	-0.0445(3)	0.1226(5)	0.5167(2)	2.75(7)
C(12)	0.0968(3)	0.1152(5)	0.5600(2)	2.27(6)
C(12a)	0.1408(3)	0.2044(4)	0.6391(2)	1.58(5)
C(13)	0.2993(3)	0.2020(5)	0.6836(2)	1.57(5)

Atom	*x/a*	*y/b*	*z/c*	B_{eq}[a]
O(13)	0.3712(2)	0.0799(4)	0.6406(1)	2.18(5)
C(14)	0.3106(3)	0.1669(5)	0.7850(2)	1.76(5)
C(15)	0.3240(3)	0.1318(5)	0.8655(2)	1.85(6)
C(16)	0.3390(3)	0.0950(5)	0.9632(2)	1.68(5)
C(17)	0.3310(3)	0.2135(5)	1.0288(2)	2.29(6)
C(18)	0.3479(3)	0.1768(5)	1.1231(2)	2.55(7)
C(19)	0.3701(3)	0.0234(5)	1.1526(2)	2.46(7)
C(20)	0.3787(3)	-0.0950(5)	1.0880(2)	2.42(6)
C(21)	0.3634(3)	-0.0600(5)	0.9939(2)	2.13(6)
N	0.1376(3)	0.4218(4)	0.2625(2)	2.58(6)
O(D)	0.3496(3)	0.5536(5)	0.2722(2)	4.08(7)
C(D1)	0.2644(4)	0.4699(5)	0.3058(2)	2.98(8)
C(D2)	0.0455(5)	0.3139(6)	0.3070(3)	4.99(12)
C(D3)	0.0847(4)	0.4716(6)	0.1676(3)	4.00(10)

[a] $B_{eq} = 1/3\Sigma a_i^* a_j^* B_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$

Table 3 Selected conformational features of host **1** in its complexes with DMF (**4**) and acetone guests (**5**)

Host 1 in	*1•DMF (1:1)*[a]		*1•acetone (1:1)*
	unprimed	*primed*	
The thirteen ring atoms of the fluorene moiety are co-planar within (Å)	0.122	0.150	0.190
The deviations (Å) of the Br(2) and Br(7) substituents, respectively, from the plane of the fluorene moiety	0.214(1) 0.104(1)	0.242(1) 0.133(1)	0.3632(8) 0.2532(7)
Dihedral angle[b] (deg) between the LS planes of the bridged phenyl rings of the fluorene moiety	4.2(2)	2.8(2)	7.1(1)
The ring atoms of the single 9-phenyl substituent are co-planar within (Å)	0.008	0.011	0.009
Dihedral angle[b] (deg) between the LS planes of the fluorene moiety and the 9-phenyl *substituent*	84.6(1)	83.5(1)	80.7(2)

[a] There are two crystallographically independent host molecules in **4**, the unprimed and the primed ones.
[b] Following Nardelli[12] and the references therein.

Table 4 Selected conformational features[a] of hosts **2** and **3** in their inclusion compounds with DMF guest

	2	*3*
The six ring atoms of each benzene ring are co-planar within (Å)		
ring 1: C(1a)-C(1)-C(2)-C(3)-C(4)-C(4a)	0.006	0.010
ring 2: C(5a)-C(5)-C(6)-C(7)-C(8)-C(8a)	0.016	0.006
ring 3: C(9a)-C(9)-C(10)-C(11)-C(12)-C(12a)	0.004	0.015
Dihedral angles (deg) between the benzene rings		
rings 1 and 2	44.88(5)	46.0(1)
rings 1 and 3	69.08(5)	74.3(1)
rings 2 and 3	43.22(6)	44.8(1)
Selected torsion angles (deg)		
C(13)-C(1a)-C(4a)-C(5a)	3.7(3)	5.0(4)
C(1a)-C(4a)-C(5a)-C(8a)	-46.4(3)	-48.0(4)
C(4a)-C(5a)-C(8a)-C(9a)	1.3(3)	1.7(5)
C(5a)-C(8a)-C(9a)-C(12a)	45.3(3)	45.0(4)
C(8a)-C(9a)-C(12a)-C(13)	-4.5(3)	-3.2(4)
C(9a)-C(12a)-C(13)-C(1a)	-65.3(2)	-67.1(3)
C(12a)-C(13)-C(1a)-C(4a)	66.2(2)	66.7(3)
C(4a)-C(1a)-C(13)-O(13)	-178.5(2)	-176.1(2)
C(9a)-C(12a)-C(13)-O(13)	177.4(2)	173.0(3)
C(4a)-C(1a)-C(13)-C(14)	-58.7(2)	-54.5(3)
C(9a)-C(12a)-C(13)-C(14)	59.8(2)	54.9(4)
Ring puckering parameters[b] of the cycloheptatriene ring		
ϕ_2,deg.	-76.2(1)	-77.2(2)
ϕ_3,deg.	-26.3(4)	-29.2(7)
Q_T (total puckering amplitude), Å	0.926(2)	0.944(3)
θ (spherical polar angle), deg.	77.6(1)	77.4(2)
Conformation of the cycloheptatriene ring	*'boat'*	*'boat'*
Asymmetry parameter[c] with low (< 0.01) value (deg)		
ΔC_s[C(13)]	0.0072(7)	0.006(1)
The atoms C(1a), C(4a), C(9a) and C(12a), forming the base plane of the boat, (plane-1), are co-planar within (Å)	0.011	0.011
Selected atomic deviations (Å) from plane-1		
C(5a)	-0.778(2)	-0.788(3)
C(8a)	-0.762(2)	-0.776(3)
C(13)	-0.732(2)	-0.749(3)
The phenyl ring atoms of the single aryl substituent are co-planar within (Å)	0.009	0.012
The dihedral angle (deg) between plane-1 and the phenyl ring plane in the single aryl substituent	95.45(8)	83.8(1)

[a] Following Nardelli[12] and references therein.
[b] According to Cremer and Pople.[12,13]
[c] According to Duax, Weeks and Rohrer.[12,14]

host molecules are shown in Tables 3 and 4, whereas Table 5 lists the distances and angles in hydrogen bonds and in possible C-H···O interactions. The molecular packings in crystals **4–7** are illustrated in Figs. 2(a)–(d), respectively.

Molecular structures

The semi-rigid dibromophenylfluorene-9-ol host (**1**) in **4** and **5** shows the expected geometry. Accordingly, the tricyclic fluorene moiety is approximately flat and forms a nearly right angle with the 9-phenyl substituent, in agreement with our earlier observations in the inclusion compounds of **1** with methanol[5] and isopropanol[5] as guest. Only the deviations of the bromine substituents from the least-squares (LS) plane through the fluorene moiety are slightly larger in the present study than in those mentioned above.

Instead of the tricyclic fluorene moiety in **1**, hosts **2** and **3** comprise a tetracyclic tribenzocycloheptatriene unit, which has similar geometry in these two molecules (*cf.* Figs. 1(c) and (d), and Table 4). The central cycloheptatriene ring has boat conformation with an approximate mirror plane through the C(13) atom, and with the OH group in equatorial and the single aryl substituent in axial position in both cases. The only important difference between hosts **2** and **3** is in the single aryl substituent, which is a phenyl in **2** and an phenylacetylene group in **3**, with the phenyl ring planes slightly differently oriented with respect to the tropylidene ring.

Table 5 Distances (Å) and angles (deg) in hydrogen bonds and in possible C-H··· O interactions[a] in compounds **4–7**

Atoms involved	*Symmetry*	*Distances*			*Angle*
		Donor••Acceptor	*D-H*	*H••A*	*<D-H••A*
4 [**1**•DMF (1:1)]					
O(9)-H(O9)···O(D)	*x, y, z*	2.684(6)	1.01	1.68	169
O(9')-H(O9')••O(D')	*x, y, z*	2.685(6)	1.06	1.63	173
C(4)-H(4)···O(D')	*x, 1+y, z*	3.393(7)	1.00	2.64	132
C(4')-H(4')••O(D)	*x, -1+y, z*	3.304(7)	1.00	2.61	127
5 [**1**•acetone (1:1)]					
O(9)-H(O9)···O(AC)	*x, y, z*	2.747(6)	1.03	1.72	180
C(4)-H(4)···O(AC)	*1-x, 1-y, 1-z*	3.491(7)	1.00	2.77	130
C(6)-H(6)···O(9)	*1+x, y, z*	3.408(7)	1.00	2.47	157
6 [**2**•DMF (1:1)]					
O(13)-H(O13)···O(D)	*x, y, z*	2.734(2)	1.02	1.71	179
C(3)-H(3)···O(13)	*1+x, y, z*	3.422(2)	1.00	2.68	132
7 [**3**•DMF (1:1)]					
O(13)-H(O13)···O(D)	*x, y, z*	2.754(3)	0.91	1.85	172

[a]The H atom positions were not refined (*cf.* the text).

The DMF molecules in **4**, **6** and **7**, as well as the acetone guest in **5** have an approximately plane skeleton with the non-hydrogen atoms co-planar to within 0.008(unprimed)/0.048(primed) (**4**), 0.052(unprimed)/ 0.140(primed) (**6**), 0.042 (**7**), and 0.013 Å (**5**). The unprimed and primed DMF skeletons in **6** refer to the two disorder models involving the partially occupied unprimed and primed C(D) positions, respectively. The molecular planes of these two disorder models form a dihedral angle of 9.8(2)°.

Packing relations and host-guest interactions

There is a hydrogen bond from the host to the guest in all four structures yielding 1:1 host-guest associates [Figs. 1(a)–(d)] which build up the crystal structures [Figs. 2(a)–(d)] with ordinary Van der Waals' forces, occasionally supported by weak electrostatic interactions of C-H···O type (*cf.* Table 5).

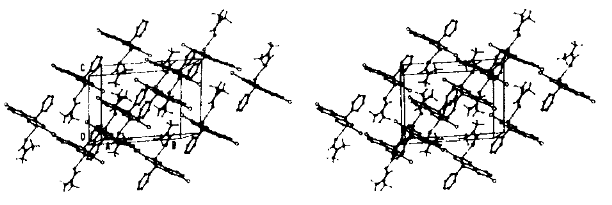

Figure 2a

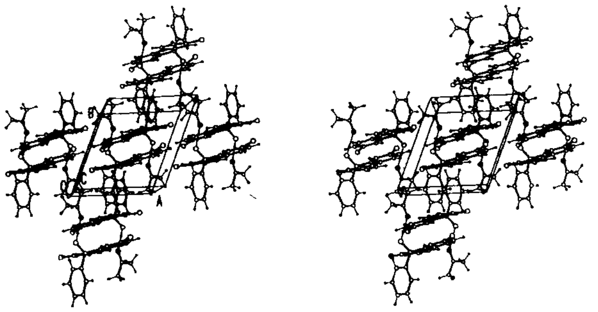

Figure 2b

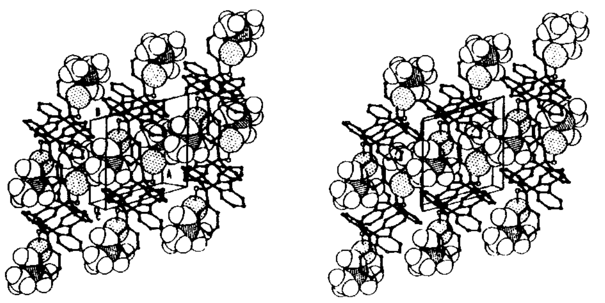

Figure 2c

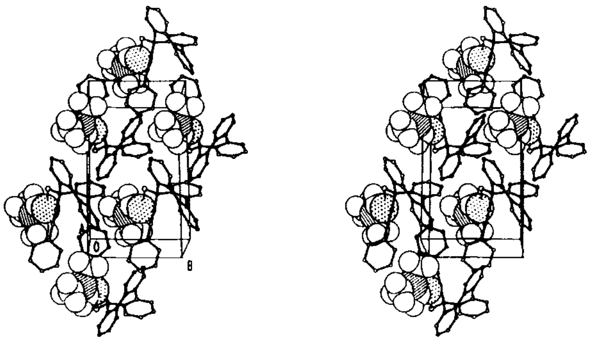

Figure 2d

Figure 2 Stereo packing illustrations of the inclusion compounds: (a) **4** [**1**•DMF (1:1)], (b) **5** [**1**•acetone (1:1)], (c) **6** [**2**•DMF (1:1)], and (d) **7** [**3**•DMF (1:1)]. The host molecules and the guests in Figures 2(a) and (b) are drawn as ball-and-stick models, whereas the guests in Figures 2(c) and (d) are represented by space filling models. The carbon-bonded H atoms of the hosts are omitted for clarity. Thin lines represent hydrogen bonds. In (a) and (b) the carbonyl oxygen of DMF is filled; in (c) and (d) O and N atoms of DMF are dotted and hatched, respectively.

It is noteworthy that despite the single point contact between host and guest, the hydrogen bonded (1:1) host-guest aggregates show very similar geometry in the DMF and acetone complexes of **1**. Accordingly, both crystallographically independent DMF guests in **4** and the acetone molecule in **5** are aligned roughly perpendicular to the fluorene moiety. They are thus nearly parallel to the ring plane of the 9-phenyl substituent. The observed dihedral angles between the planes of the tricyclic fluorene group and the guest skeleton are 83.1(2)[unprimed]/82.6(2)°[primed] in **4** and 81.3(3)° in **5**, and the dihedral angle formed by the planes of the guest and the respective phenyl ring are 7.2(2)/2.9(2)° for the unprimed/primed associates of **4** and 1.80(2)° for **5**. It seems likely that this uniformity in the overall shape of the hydrogen bonded host-guest associates is enforced by the packing requirements. As a consequence, complexes **4** and **5** show closely related packing relations [*cf.* Figs. **2**(a) and (b)] despite the fact that the triclinic ($P\bar{1}$) unit cell of **4** contains four host-guest aggregates whereas that of **5** includes only two.

In **6** [Fig. 2(c)] the host molecules are arranged so as to form endless tunnels in the crystallographic *a* direction, in which the hydrogen bonded DMF molecules are located. The DMF guest has two partially occupied locations in this structure, which partly overlap each other and which are only slightly inclined to the 13-phenyl ring plane. The dihedral angles between the planes of the DMF and phenyl skeletons are 12.5(2) and 11.9(2)°, calculated for guest models involving the C(D) and the C(D') positions, respectively.

The remarkable feature with the **3**•DMF (1:1) inclusion (**7**) [Fig. 2(d)] is that it crystallizes in a chiral space group ($P2_1$). Host **3** is a small helicene. Chiral crystals are important in the design of non-linear optical materials[9] and also for enantiomer separation purposes.[10] The question is if the spontaneous resolution[11] is mainly effected by the host or by the presence of the guest. This question stimulates studies of more compounds of this type. Possibly, solvent interaction is a new tool to produce enantiomorphous crystals via conglomerate crystallization.

ACKNOWLEDGEMENTS

I. C. thanks the Swedish Natural Science Research Council (NFR) and E. W. the Deutsche Forschungsgemeinschaft (SFB 334) and the Fonds der Chemischen Industrie for financial support.

REFERENCES

1 Weber, E.; Dörpinghaus, N.; Csöregh, I.; *J. Chem. Soc., Perkin Trans. 2* **1990**, 2167.

2 Caira, M.R.; Nassimbeni, L.R.; Niven, M L.; Schubert, W.-D.; Weber, E.; Dörpinghaus, N.; *J. Chem. Soc., Perkin Trans. 2* **1990**, 2129.

3 Csöregh, I.; Weber, E.; Nassimbeni, L.R.; Gallardo, O.; Dörpinghaus, N.; Ertan, A.; Bourne, S.A.; *J. Chem. Soc., Perkin Trans. 2* **1993**, 1775.

4 Csöregh, I.; Weber, E.; Dörpinghaus, N.; *J. Chem. Soc., Chem. Commun.* **1992**, 110.

5 Csöregh, I.; Gallardo, O., Weber, E.; Dörpinghaus, N.; *J. Chem. Soc., Perkin Trans. 2* **1994**, 302.

6 Sheldrick, G.M. *SHELX 76,; Program for Crystal Structure Determination*, University of Cambridge, England **1976**.

7 Sheldrick, G.M.; *Acta Crystallogr.* **1990**, *A46*, 467.

8 Sheldrick, G.M.; *SHELX 400 ATOM VERSION*, updated by D. Rabinovich and K. Reich, Department of Structural Chemistry, Weizman Institute of Science, Rehovot, Israel; and subsequently modified by G.M. Sheldrick, University of Göttingen, FRG, **1979**.

9 Etter, M.C.; Frankenbach, G.M.; *Materials* **1989**, *1*, 10.

10 Weber, E.; Wimmer, C.; Llamas-Saiz, A.L.; Foces-Foces, C.; *J. Chem. Soc., Chem. Commun.* **1992**, 733. NEWS; *Chem. Ind. (London)* **1992**, 364.

11 Jacques, J.; Collet, A.; Wilen, S.H.; *Enantiomers, Racemates and Resolutions*, Wiley, New York, **1981**.

12 M. Nardelli, M.; *Acta Crystallogr.* **1983**, *C39*, 1141.

13 Cremer, D.; Pople, J.A.; *J. Am. Chem. Soc.* **1975**, *97*, 1354.

14 Duax, W., L.; Weeks, C.M.; Rohrer, D.C.; *Conformational Analysis*, in: Topics in Stereochemistry **1976**, Vol. 9, (Allinger, N.L.; Eliel, E. L., eds.) Wiley, London, pp. 279–289.