Journal of Inclusion Phenomena and Molecular Recognition in Chemistry **28:** 163–179, 1997.

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Triarylmethanol Host Compounds. Synthesis, Crystalline Complex Formation and X-Ray Crystal Structures of Three Inclusion Species

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(Received: 19 July 1996; in final form: 26 September 1996)

Abstract. A variety of triarylmethanol compounds including benzo condensed and laterally substituted derivatives **1–10** have been prepared and shown to act as crystalline hosts for the inclusion of organic solvents involving protic polar, aprotic dipolar and apolar molecules. The inclusion ability is rather high for aprotic dipolar solvents while protic polar compounds are only rarely enclathrated. Host **9** is an exception, being also efficient with alcohols and amines. Compound **3** displays no inclusion formation under the experimental conditions. X-ray crystal structures of the inclusion compound **1**·acetone (2 : 1) and of two amine inclusion compounds of host **9** [**9**·n-propylamine (1 : 1), **9**·di-n-propylamine (1 : 1)] are reported showing the formation of H-bonded host-guest associates as the common feature of supramolecular association.

Key words: Crystalline complex formation, X-ray structure analysis, triarylmethanol hosts, acetone and amine guests, hydrogen bonding.

Supplementary Data relating to this article have been deposited with the British Library, No. SUP 82226 (10 pages).

1. Introduction

Singly bridged triarylmethanols have demonstrated convenience and versatility in the formation of lattice inclusion compounds [1]. Hundreds of different inclusion species based on this host type have been isolated and a number of their structures reported [2]. On the other hand, the unbridged, extremely simple host compound triphenylmethanol (**1**) is much less broad in its inclusion behaviour, thus revealing amazing specificity in the entrapment of methanol and dimethyl sulfoxide [3]. We know from many other cases that the introduction of substituents onto a given host frame may strongly interfere with the original inclusion behaviour [4]. In order to investigate this effect, we focused our attention on substituted derivatives of the

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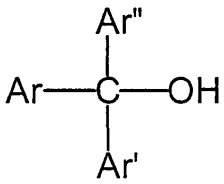

	Ar	Ar′	Ar′′
1	Ph	Ph	Ph
2	2-MeC_6H_4	2-MeC_6H_4	2-MeC_6H_4
3	3-MeC_6H_4	3-MeC_6H_4	3-MeC_6H_4
4	4-MeC_6H_4	4-MeC_6H_4	4-MeC_6H_4
5	4-$(CMe_3)C_6H_4$	4-$(CMe_3)C_6H_4$	4-$(CMe_3)C_6H_4$
6	4-PhC_6H_4	4-PhC_6H_4	4-PhC_6H_4
7	1-Naphthyl	Ph	Ph
8	2-Naphthyl	Ph	Ph
9	1-Naphthyl	1-Naphthyl	Ph
10	1-Naphthyl	1-Naphthyl	1-Naphthyl

Scheme

parent molecule **1**. They are represented by the compounds **2–10** having lateral alkyl or extra phenyl substituents in different positions at each of the phenyl groups or a certain number of naphthyl units as a substituent.

We describe syntheses of **2–10**, report comparative inclusion behaviour of these hosts including parent molecule **1** and present X-ray crystal structures of inclusion compounds **1**·acetone (2 : 1), **9**·n-propylamine (1 : 1) and **9**·di-n-propylamine (1 : 1).

2. Experimental

2.1. SYNTHESIS

2.1.1. *General*

Melting points were taken on a Reichert hot-stage apparatus. Solvents were dried by standard procedures. Starting compounds (bromobenzene, 2-bromotoluene,

3-bromotoluene, 4-bromotoluene, 4-bromobiphenyl, 1-bromonaphthalene, benzophenone, 4,4′-dimethylbenzophenone, benzoyl chloride, diethyl carbonate and granulated Li) as well as triphenylmethanol (**1**) were purchased from Janssen.

2.1.2. *Synthesis of Host Compounds*

4-Bromo-t-butylbenzene [5], *4,4′-Di-t-butylbenzophenone* [5], *Methyl 2-Naphthoate* [6], and *1-Naphthoyl Chloride* [7] were prepared according to literature procedures.

2.1.3. *Triarylmethanols* **4**, **5**, **7–10** *(General Procedure)*

A solution of the corresponding ketone or ester in dry Et_2O was dropped into a Grignard solution prepared in the usual way [8] from the respective aryl halide and Mg turnings in dry Et_2O. The mixture was refluxed for 2 h, cooled and quenched with sat. aqueous NH_4Cl solution. The organic layer was separated, washed with water, dried ($MgSO_4$), and evaporated to yield the products which were purified by recrystallization. Specific details of the individual compounds are given below.

Tri-p-tolylmethanol (**4**). From 4-bromotoluene and 4,4′-dimethylbenzophenone; recrystallization from acetic acid gave the 1 : 1 inclusion compound with acetic acid. Treatment of the inclusion crystals under 15 Torr at 80 °C for 3 h yielded 82% of pure **4** as a colourless solid; m.p. 95 °C (lit. [9] m.p. 96.5 °C).

Tris(p-t-butylphenyl)methanol (**5**). From 4-bromo-*t*-butylbenzene and 4,4′-di-*t*-butylbenzophenone; recrystallization from MeOH yielded 65% colourless powder; m.p. 208–210 °C (lit. [10] m.p. 212–213 °C).

(1-Naphthyl)diphenylmethanol (**7**). From 1-bromonaphthalene and benzophenone; the oil obtained after evaporation of the solvent was digested with petroleum ether (40–60 °C); recrystallization from Et_2O yielded 79.5% colourless powder; m.p. 132–134 °C (lit. [11] m.p. 134–135 °C).

(2-Naphthyl)diphenylmethanol (**8**). From bromobenzene and methyl 2-naphthoate; recrystallization from Et_2O–petroleum ether (40–60 °C) (40 : 60, v/v) yielded 69% colourless solid; m.p. 114–115 °C (lit. [12] m.p. 115.5 °C).

Di(1-naphthyl)phenylmethanol (**9**). From 1-bromonaphthalene and benzoyl chloride; recrystallization from EtOH gave the 1 : 1 inclusion compound with EtOH. Treatment of the inclusion crystals under 15 Torr at 100 °C for 2 h yielded 59% of pure **9** as a colourless solid; m.p. 165 °C (lit. [13] m.p. 166–167 °C).

Tri(1-naphthyl)methanol (**10**). From 1-bromonaphthalene and 1-naphthoyl chloride; on quenching, the 1 : 1 inclusion compound with Et_2O precipitated which was

collected and treated under 15 Torr at 140–150 °C for 4 h to yield 50% of pure **10** as a colourless solid; m.p. 161–163 °C (lit [14] m.p. 165–l66 °C).

2.1.4. *Triarylmethanols* **2**, **3**, *and* **6** *(General Procedure)*

To a suspension of granulated Li (0.3 mol) in dry THF (50 mL) under an atmosphere of argon was dropped the respective aryl halide in dry THF in such a way as to keep the Et_2O at gentle reflux. Refluxing was continued until reaction of the Li was complete. Then diethyl carbonate (37 mmol) in dry THF (20 mL) was dropped in and the mixture was refluxed for 6 h. After addition of Et_2O (100 mL) and quenching with sat. aqueous NH_4Cl solution, the aqueous and organic layers were separated. The aqueous phase was extracted with Et_2O. The combined organic layers were dried ($MgSO_4$), and evaporated under reduced pressure. Specific details of the individual compounds are given below.

Tri-o-tolylmethanol (**2**). 2-Bromotoluene was used as reagent; the oil obtained on evaporation of the organic layer was stirred with dioxane to precipitate the 2 : 1 inclusion compound with dioxane. Treatment of the inclusion crystals under 15 Torr at 70 °C for 2 h yielded 47% of pure **2** as a colourless solid; m.p. 98–99 °C (lit. [15] m.p. 102–103 °C).

Tri-m-tolylmethanol (**3**). 3-Bromotoluene was used as reagent; the oil obtained on evaporation of the organic layer resists crystallization although a number of solvents were tried [16].

Tri(biphenyl)methanol (**6**). 4-Bromobiphenyl was used as reagent; on quenching the product precipitated as a solid which was collected and dried; 55% colourless solid; m.p. 203–204 °C (lit. [17] m.p. 207–208 °C).

2.1.5. *Crystalline Inclusion Compounds*

The host compound was dissolved under heating in a minimum amount of the respective guest solvent. The solution was allowed to cool slowly. After storage for 12 h at room temperature, the crystals which formed were collected by suction filtration and dried (1 h, 15 Torr, room temperature). The host : guest stoichiometric ratios were determined by ^{1}H-NMR integration. Data for each compound are given in Table I.

2.2. CRYSTALLOGRAPHY

2.2.1. *Sample Preparation*

Microcrystals obtained as described in Section 2.1.3 were redissolved in their guest solvent mother liquor. Upon slow evaporation of the solvents suitable single crystals for X-ray analyses were obtained directly.

Table I. Crystalline inclusion compounds (hosts : guest stoichiometric ratios).[a]

Guest solvent[b]	Host compound									
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
MeOH	1 : l	–	–	–	–	–	–	–	1 : 1	–
EtOH	–	–	–	–	–	–	–	–	1 : 1	–
t-BuOH	–	–	–	–	1 : 2	–	–	–	–	–
n-PrNH$_2$	–	–	–	–	–	–	–	–	1 : 1	–
(*n*-Pr)$_2$NH	–	–	–	–	–	–	–	[c]	1 : 1	–
t-BuNH$_2$	–	[c]	–	–	1 : 2	–	[c]	–	–	–
Acetone	2 : 1	–	–	–	–	–	–	–	–	–
THF	–	–	–	[c]	–	–	[c]	–	1 : 2	1 : 4
MeCN	–	–	–	–	–	–	–	–	1 : 1	1 : 1
Et$_2$O	–	–	–	–	–	–	–	–	1 : 1	–
DMF	2 : 1	1 : 1	–	–	2 : 1	–	1 : 1	–	–	–
DMSO	2 : 1	1 : 1	–	1 : 1	1 : 1	1 : 2	2 : 3	3 : 1	2 : 3	1 : 2
Dioxane	1 : 1	1 : 1	–	2 : 1	1 : 1	–	–	–	2 : 1	[c]
Morpholine	1 : 1	–	–	–	–	–	–			
Piperidine	1 : 1	[c]	–	[c]	1 : 1	l : 4	[c]	[c]	–	[c]
Benzene	–	–	–	[c]	–	–	2 : 1	1 : 1	1 : 1	[c]

[a]See. Experimental Section for methods of preparation, drying standard and characterization.
[b]The following solvents yielded no inclusion compounds: *n*-PrOH, *n*-BuOH, *s*-BuOH, *i*-BuOH, *c*-HexOH, *s*-BuNH$_2$, (*i*-Pr)$_2$NH, (*i*-Pr)$_3$N, propionitrile, benzonitrile, nitromethane, nitroethane, *N*-methylpiperidine, 2-methylpiperidine, pyridine, toluene, *o*-, *m*-, *p*-xylene, mesitylene, cyclohexane.
[c]Difficult to crystallize.

2.2.2. *X-Ray Data Collection and Processing*

All X-ray diffraction measurements were carried out at room temperature (ca. 298 K) on automated Picker [for **1**·acetone (2 : 1)] or CAD4 diffractometers [for **9**·*n*-propylamine (1 : 1) and **9**·di-*n*-propylamine (1 : 1)]. Both instruments were equipped with graphite monochromators, using MoK_α (λ = 0.7107 Å) radiation. Intensity data were collected by the $\omega - 2\theta$ scan mode with a constant scan speed of 4.5 deg/min, 4 deg/min and 4 deg/min for the three crystals, respectively. Possible deterioration of the analyzed crystals were tested by detecting periodically the intensities of three standard reflections from different zones of the reciprocal space, and were found to be negligible during the experiments. No corrections for absorption or secondary extinction effects were applied. Relevant crystal and experimental data are given in Table II.

Table II. Crystal data and structure refinement for the **1**·acetone (2 : 1), **9**·*n*-propylamine (1 : 1) and **9**·di-*n*-propylamine (1 : 1) inclusion compounds.

Compound	**1**·acetone (2 : 1)	**9**·*n*-PrNH$_2$ (1 : 1)	**9**·(*n*-Pr)$_2$N (1 : 1)
Formula	$C_{19}H_{16}O \cdot 1/2(C_3H_6O)$	$C_{27}H_{20}O \cdot C_3H_9N$	$C_{27}H_{20}O \cdot C_6H_{15}N$
Formula weight	289.4	419.6	461.6
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$C2/c$	$P2_1/c$	$P2_1/n$
Unit cell dimensions			
a, Å	8.652(1)	8.699(3)	7.755(5)
b, Å	16.164(2)	16.646(2)	39.154(7)
c, Å	23.076(2)	16.658(2)	8.905(1)
β, deg.	97.41(1)	91.38(2)	99.77(3)
V, Å^3	3200.2(3)	411.4(3)	2664.7(9)
Refinement of the cell dimensions			
No. of θ values used	15	25	25
2θ-range, deg.	8.1–12.5	7.0–11.3	7.9–11.0
Z	8	4	4
$F(000)$	1232	896	992
D_c, g cm^{-3}	1.201	1.156	1.151
μ, cm^{-1}	0.69	0.64	0.64
Radiation/λ, Å	0.7107	0.7107	0.7107
Temperature, K	298(2)	298(2)	298(2)
Crystal size, mm	0.25 × 0.30 × 0.50	0.45 × 0.25 × 0.20	0.35 × 0.25 × 0.20
θ-limit, deg.	25.00	23.00	25.00
No. of unique non-zero reflections	2301	2846	3760
No. of reflections with $F_o > 6\sigma(F_o)$	1390	1801 [$F_o > 4\sigma(F_o)$]	1841
No. of refined variables	223	274	328
$R = \Sigma\|\Delta F\|/\Sigma\|F_o\|$	0.066	0.094	0.063
Final $\Delta\rho_{max}/\Delta\rho_{min}$, e Å^{-3}	0.25/−0.26	0.54/−0.38	0.22/−0.21

2.2.3. *Structure Analysis and Refinement*

Initial structure models were invariably obtained for each crystal structure by direct methods (SHELXS-86) [18]. The structure model was refined by full matrix least-squares (SHELX-76) [19] for the **1**·acetone (2 : 1) inclusion complex, including the positional and anisotropic thermal parameters of the non-hydrogen atoms. The acetone guest molecule was found to be located on the crystallographic twofold rotation axes. Consequently, it was assumed to be disordered in the crystal lattice adopting one of two possible orientations with respect to the rotation axis at the different guest sites in the bulk. The two orientations of acetone could clearly be resolved in the refinement calculations, and no constraint of the positional or

thermal parameters was required. The final refinement converged at R = 0.066 for 1390 observations having $F_o > 6\sigma(F_o)$. All hydrogen atoms attached to carbon were introduced in calculated positions; the methyl group being treated as rigid. A possible site for the hydrogen atom attached to O was found in a difference-Fourier map. All guest atoms were assigned an occupancy factor of 0.5 to account for the disorder. It is difficult to determine unequivocally whether the guest, and consequently H-bonding disorder is a genuine feature of this structure or if it has been imposed by assigning the $C2/c$ space symmetry to the lattice. The number of significant data did not allow us to check the possible correctness of an alternative ordered model of the structure in space group Cc which does not contain the twofold axes of symmetry (the asymmetric unit in the latter would consist of a 2 : 1 host–guest entity of the complex). However, since the observed centric distribution of the measured intensity data strongly favors $C2/c$ over Cc, and the refinement converged reasonably well, we believe that the present description of the crystal structure is essentially correct.

The structure model of the **9**·n-propylamine (1 : 1) inclusion compound was refined by full-matrix least-squares (SHELXL-93) [20], including the positional parameters of all non-hydrogen atoms, anisotropic thermal parameters of the host atoms, and isotropic thermal parameters of the guest atoms (see below). All hydrogen atoms attached to carbon and nitrogen were introduced in calculated positions; the guest methyl being treated as a rigid group. The hydrogen atom attached to O was located directly in a difference-Fourier map. Due to the large atomic displacement parameters of the alkyl residue of the n-$PrNH_2$ guest the corresponding C atoms were assigned isotropic thermal parameters only. The final refinement, based on F^2, converged at R = 0.094 for 1801 observations having $F_o > 4\sigma(F_o)$. The relatively poor convergence should be attributed to the apparent partial disorder of the alkyl residue of the guest component, which could not be properly modelled in the calculations.

The structure of the **9**·di-n-propylamine (1 : 1) inclusion compound was refined smoothly by full-matrix least-squares (SHELX-76) [19], including the positional and anisotropic thermal parameters of the non-hydrogen atoms. The final refinement converged at R = 0.063 for 1841 observations having $F_o > 6\sigma(F_o)$. All hydrogen atoms attached to carbon were introduced in calculated positions, those of the guest methyl groups being treated as rigid groups. The hydrogens attached to O and N were located directly in difference-Fourier maps.

Final fractional coordinates of the non-hydrogen atoms for all structures reported herein are listed in Tables III–V.

3. Results and Discussion

3.1. SYNTHESIS

Compounds **2–10** were obtained using aryl Grignard (**4**, **5** and **7–10**) or aryl lithium (**2**, **3** and **6**) addition reactions to a corresponding diaryl ketone or aromatic ester

Table III. Atomic coordinates and U_{eq} values of non-hydrogen atoms and of the —OH hydrogen atom for the **1**·acetone (2 : 1) crystalline complex.

Atom	x/a	y/b	z/c	U_{eq}
O(1)	0.5753(4)	0.1661(2)	0.6995(1)	0.0535(8)
C(2)	0.4890(5)	0.1604(3)	0.6418(2)	0.0442(9)
C(3)	0.3805(5)	0.0855(3)	0.6406(2)	0.0451(8)
C(4)	0.2292(5)	0.0866(3)	0.6123(2)	0.0547(9)
C(5)	0.1347(6)	0.0167(3)	0.6108(2)	0.0661(10)
C(6)	0.1912(6)	−0.0550(3)	0.6377(3)	0.0692(10)
C(7)	0.3407(6)	−0.0568(3)	0.6663(3)	0.0699(10)
C(8)	0.4349(5)	0.0126(3)	0.6678(2)	0.0584(10)
C(9)	0.6074(5)	0.1514(3)	6.5987(2)	0.0452(10)
C(10)	0.5866(5)	0.0979(3)	0.5515(2)	0.0553(10)
C(11)	0.6950(6)	0.0931(3)	0.5124(2)	0.0696(9)
C(12)	0.8260(6)	0.1419(4)	0.5199(2)	0.0723(10)
C(13)	0.8482(6)	0.1963(3)	0.5663(3)	0.0691(10)
C(14)	0.7391(5)	0.2012(3)	0.6052(2)	0.0540(9)
C(15)	0.3988(5)	0.2410(3)	0.6302(2)	0.0459(9)
C(16)	0.3675(6)	0.2743(3)	0.5748(2)	0.0560(9)
C(17)	0.2848(6)	0.3475(3)	0.5651(2)	0.0672(10)
C(18)	0.2310(7)	0.3880(3)	0.6100(3)	0.0806(10)
C(19)	0.2610(8)	0.3563(4)	0.6649(3)	0.0949(10)
C(20)	0.3431(7)	0.2829(3)	0.6752(2)	0.0725(10)
O(21)*	0.1760(8)	0.0683(5)	0.7753(4)	0.0819(9)
C(22)*	0.0492(9)	0.0941(6)	0.7538(5)	0.0672(11)
C(23)*	0.0123(17)	0.1839(5)	0.7477(13)	0.1148(11)
C(24)*	−0.0816(10)	0.0373(8)	0.7345(5)	0.0896(11)
H(2)	0.6810	0.1524	0.7043	0.050

U_{eq} is one third of the trace of the orthoganalized U_{ij} tensor.
*Occupancy is 0.5 for these atoms.

component in yields between 57 and 82%. Inclusion compounds were prepared by the common recrystallization procedure [1].

3.2. INCLUSION PROPERTIES

In order to show the inclusion properties clearly and to learn specificity features, all potential host compounds **1–10** were tested with the same range of solvents (Table I). These include alcohols and amines of different molecular sizes and shapes, dipolar aprotic compounds of different polarities, heterocycles of different ring sizes and with different numbers and types of heteroatoms, as well as aromatic

Table IV. Atomic coordinates and U_{eq} values of non-hydrogen atoms for the **9**·*n*-propylamine (1 : 1) crystalline complex.

Atom	x/a	y/b	z/c	U_{eq}
O(1)	0.1885(4)	0.1854(2)	0.3108(2)	0.0632(14)
C(2)	0.1232(6)	0.1324(3)	0.3684(3)	0.0548(19)
C(3)	0.2154(6)	0.0547(3)	0.3684(3)	0.0565(19)
C(4)	0.2460(7)	0.0131(3)	0.2956(4)	0.0625(22)
C(5)	0.1984(8)	0.0401(4)	0.2189(4)	0.0760(26)
C(6)	0.2351(10)	−0.0009(5)	0.1516(4)	0.1052(35)
C(7)	0.3150(13)	−0.0716(6)	0.1555(6)	0.1266(45)
C(8)	0.3616(10)	−0.1010(4)	0.2279(7)	0.1107(39)
C(9)	0.3284(8)	−0.0610(4)	0.2995(5)	0.0806(31)
C(10)	0.3777(8)	−0.0907(4)	0.3749(6)	0.0906(36)
C(11)	0.3460(8)	−0.0518(4)	0.4421(5)	0.0845(28)
C(12)	0.2647(7)	0.0210(4)	0.4395(4)	0.0719(26)
C(13)	0.1267(7)	0.1741(3)	0.4520(3)	0.0615(22)
C(14)	0.2650(7)	0.2113(3)	0.4821(3)	0.0602(22)
C(15)	0.4059(8)	0.2107(3)	0.4424(4)	0.0672(23)
C(16)	0.5323(8)	0.2476(4)	0.4744(4)	0.0789(26)
C(17)	0.5277(11)	0.2878(4)	0.5473(6)	0.0965(35)
C(18)	0.3961(11)	0.2889(4)	0.5878(4)	0.0936(32)
C(19)	0.2624(9)	0.2494(4)	0.5592(4)	0.0737(26)
C(20)	0.1259(11)	0.2491(5)	0.6026(4)	0.0948(33)
C(21)	0.0007(9)	0.2127(5)	0.5728(4)	0.1005(31)
C(22)	−0.0016(8)	0.1760(4)	0.4983(4)	0.0806(27)
C(23)	−0.0446(7)	0.1149(4)	0.3414(3)	0.0591(21)
C(24)	−0.1138(7)	0.0425(4)	0.3600(3)	0.0719(26)
C(25)	−0.2645(9)	0.0269(5)	0.3378(5)	0.0946(33)
C(26)	−0.3482(9)	0.0833(7)	0.2964(5)	0.1045(41)
C(27)	−0.2839(9)	0.1530(6)	0.2781(4)	0.0986(36)
C(28)	−0.1326(8)	0.1699(4)	0.3003(4)	0.0788(27)
N(29)	0.1136(17)	0.3500(9)	0.3277(8)	0.2348(55)
C(30)	0.2200(26)	0.3916(14)	0.3523(12)	0.2817(92)
C(31)	0.1730(27)	0.4638(17)	0.3967(15)	0.3335(116)
C(32)	0.2944(20)	0.5072(13)	0.4234(11)	0.2470(71)

U_{eq} is one third of the trace of the orthogonalized U_{ij} tensor.

and alicyclic hydrocarbons. The ability of **1–10** to form inclusion compounds is evident from Table I, which specifies 38 different inclusion compounds.

Considering the rather large number of hosts and solvents tested, relatively few inclusion compounds were prepared. They are distributed among the individual host molecules, with hosts **1**, **5** and **9** being somewhat better hosts than the other compounds. Noticeably, dimethyl sulfoxide is accommodated by almost all of the

Table V. Atomic coordinates and U_{eq} values of non-hydrogen atoms for the **9**·di-*n*-propylamine (1 : 1) crystalline complex.

Atom	x/a	y/b	z/c	U_{eq}
O(1)	0.3134(5)	0.1419(1)	0.5981(4)	0.0413(13)
C(2)	0.4809(7)	0.1417(1)	0.6949(6)	0.0400(21)
C(3)	0.6025(8)	0.1669(1)	0.6275(5)	0.0401(20)
C(4)	0.5407(8)	0.1995(1)	0.5679(6)	0.0423(21)
C(5)	0.3740(8)	0.2130(1)	0.5728(7)	0.0578(26)
C(6)	0.3185(10)	0.2432(2)	0.5062(9)	0.0838(33)
C(7)	0.4308(13)	0.2621(2)	0.4330(9)	0.0947(38)
C(8)	0.5947(11)	0.2513(2)	0.4302(8)	0.0785(34)
C(9)	0.6554(9)	0.2204(2)	0.4988(6)	0.0544(28)
C(10)	0.8275(9)	0.2093(2)	0.4969(7)	0.0657(33)
C(11)	0.8869(8)	0.1794(2)	0.5634(7)	0.0647(27)
C(12)	0.7730(8)	0.1582(1)	0.6260(6)	0.0509(26)
C(13)	0.5537(7)	0.1050(1)	0.6950(6)	0.0397(21)
C(14)	0.5618(7)	0.0880(1)	0.5518(6)	0.0429(22)
C(15)	0.5140(7)	0.1041(1)	0.4073(6)	0.0500(24)
C(16)	0.5205(8)	0.0864(2)	0.2761(6)	0.0643(28)
C(17)	0.5747(10)	0.0524(2)	0.2805(8)	0.0787(34)
C(18)	0.6237(8)	0.0363(2)	0.4155(9)	0.9672(28)
C(19)	0.6189(8)	0.0536(1)	0.5540(7)	0.0519(24)
C(20)	0.6687(8)	0.0369(2)	0.6949(8)	0.0610(27)
C(21)	0.6604(8)	0.0533(2)	0.8285(7)	0.0575(23)
C(22)	0.6008(7)	0.0873(1)	0.8264(6)	0.0487(24)
C(23)	0.4615(9)	0.1540(1)	0.8552(6)	0.0461(23)
C(24)	0.3024(9)	0.1546(1)	0.9009(7)	0.0601(28)
C(25)	0.2835(11)	0.1665(2)	1.0438(9)	0.0852(36)
C(26)	0.4259(15)	0.1778(2)	1.1418(8)	0.0898(45)
C(27)	0.5875(12)	0.1769(2)	1.1006(8)	0.0908(40)
C(28)	0.6045(9)	0.1653(2)	0.9575(7)	0.0696(29)
N(29)	0.0967(6)	0.0823(1)	0.5762(5)	0.0552(20)
C(30)	0.1514(8)	0.0523(2)	0.6671(8)	0.0604(27)
C(31)	0.1507(8)	0.0583(2)	0.8337(8)	0.0684(30)
C(32)	0.2017(14)	0.0266(2)	0.9272(10)	0.1024(45)
C(33)	0.0765(8)	0.0752(2)	0.4121(7)	0.0650(30)
C(34)	0.0102(9)	0.1058(2)	0.3182(7)	0.0750(29)
C(35)	−0.0194(14)	0.0992(3)	0.1484(?)	0.1145(49)

U_{eq} is one third of the trace of the orthogonalized U_{ij} tensor.

hosts, while most of the other guest solvents are singular. Thus, the substituted derivatives and analogues **2–10** are hosts that have specificity behaviour similar to the parent compound **1** [3, 21] but, more importantly, they show different selectivity

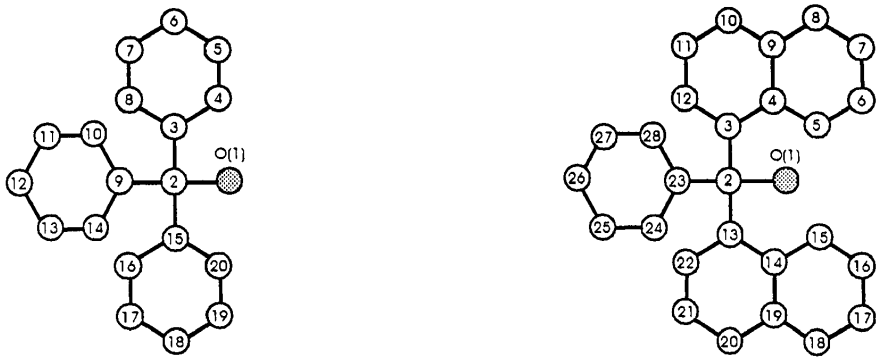

Figure 1. Crystallographic atom labeling scheme of the host frameworks. Open circles represent C atoms, filled circles O atoms. Consecutively numbered labels in the corresponding structures refer to atoms of the guest moieties.

with reference to the individual solvents. For instance, as already mentioned, host **1** is highly selective for the inclusion of methanol [3] considering the whole range of dipolar protic solvents (alcohols and amines), whereas **5** and **9** are selective for t-butanol or ethanol. The amines are only included into the lattices of **5** and **9** with the interesting observation that **5**, which has three t-butyl substituents, seems to prefer guests that also bear a t-butyl group (t-BuOH, t-BuNH$_2$). Acetone is only accommodated into the lattice of **1**, diethyl ether into **9**, and so on (Table I), showing the remarkable selectivity behaviour of this simple host type. With reference to the host : guest stoichiometric ratios, it is generally noticed from Table I that high host quotas are rather rare, which is in contrast with the singly bridged analogues described previously [1].

In view of the features discussed above, crystal structures of three relevant inclusion species were studied: **1**·acetone (2 : 1), **9**·n-propylamine (1 : 1) and **9**·di-n-propylamine (1 : 1) which all represent selective co-crystallizations of the corresponding guest molecules with the triarylmethanol host species of this series.

3.3. STRUCTURE DESCRIPTION

A numbering scheme of the atoms is given in Figure 1. As an example, a perspective view of the molecular structure of **9**·di-n-propylamine (1 : 1) is shown in Figure 2. Views of the molecular organizations and intermolecular H-bond associations in the structures of **1**·acetone (2 : 1), **9**·n-propylamine (1 : 1) and **9**·di-n-propylamine (1 : 1) are presented in Figures 3–5.

3.3.1. *Molecular Structures*

The bond lengths and angles in the present host molecules show good agreement with those found in previous structures [3, 21, 22]. As an eminent feature one has

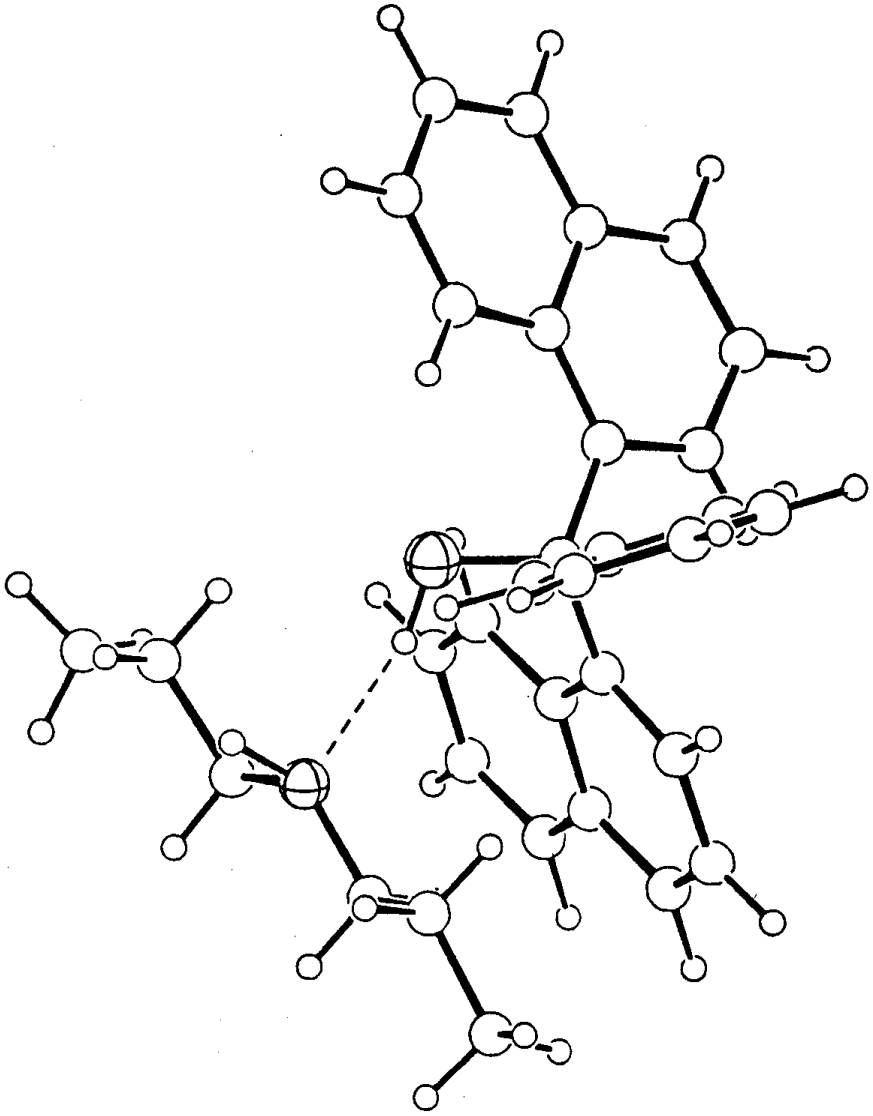

Figure 2. Perspective view of the hydrogen bonded host-guest association in the **9**·di-*n*-propylamine (1 : 1) crystalline complex. In Figures (2–5), the heteroatoms are marked by cross circles, and solid and dashed lines represent covalent and hydrogen bonds, respectively.

to mention the high-angle tilted propeller conformation of the host frameworks (Figure 2), which also corresponds to previous findings [3, 21–23].

In more detail, dihedral angles of the three aromatic planes of the host molecules indicate a nearly perpendicular arrangement in the **1**·acetone and **9**·*n*-propylamine cases (94.3, 95.2 and 94.3°, and 88.5, 98.1 and 76.6°, respectively). The host

molecule in the **9**·di-n-propylamine inclusion compound also has a propeller shape with dihedral angles between the aryl rings of 70.7, 85.0 and 79.0°. The acetone guest in the first structure is placed nearly parallel to the neighbouring phenyl group (dihedral angle 16.6°). The n-propylamine guest in the inclusion compound of **9** is tilted out of the plane of the most parallel naphthyl group by $-33.8°$, while the same group is nearly parallel to the di-n-propylamine least-squares plane (4.4°) in its **9** inclusion complex, a possible buffering effect of the compromise between H-bonding, spatial fitting and propeller shape.

The alkyl residues of the amine guests in the **9**·n-propylamine (1 : 1) and **9**·di-n-propylamine (1 : 1) inclusion complexes are quite loosely packed in the lattice (Figures 4 and 5) and their covalent parameters could not be described with a high precision [24] due to large-amplitude wagging motion or structural disorder.

3.3.2. *Packing Relations and Host–Guest Interactions*

Somewhat surprisingly, the 2 : 1 inclusion complex of **1** with acetone did not form an isomorphous structure to that of the **1**·DMSO adduct (2 : 1) reported previously [3]. Only the host lattice appears to be nearly the same (Figure 3). However, while the size of the unit-cell translations in both complexes are rather similar, the orientation of the monoclinic axis of twofold symmetry is different. Furthermore, in the DMSO complex the S—O bond is roughly parallel to this axis, while in the present structure the corresponding C—O bond of the acetone guest is oriented approximately perpendicularly to the twofold rotation axis. In the latter the guest molecule is also disordered around the C_2 axis, at least in the assigned space group $C2/c$. At each site the acetone guest is hydrogen bonded only to one host if the disorder is static, or 'half-bonded' to two hosts related by the crystallographic symmetry if the disorder is dynamic. The relevant geometry is: O···O 2.673 Å, H···O 1.86 Å, O—H···O 144°, indicating a nonlinear arrangement. The two orientations of the disordered guest could clearly be resolved in the refinement calculations (see Experimental Section). Thus the packing in the **1**·acetone (2 : 1) inclusion complex (Figure 3) reveals intermolecular H-bonding association along the a-axis of the unit cell, and van der Waals interaction of the bulky lipophilic triphenylmethyl fragments along the b and c directions. In a sense, this crystal structure can be viewed as a reversed role mate of the triphenylphosphine oxide (TPPO) complexes reported by Etter [25]. Here the bulky host plays the opposite role and the acetone guest is in a 'stopper' mode thus inhibiting development of continuous H-bonding pattern in the crystal [26].

In the **9**·n-propylamine (1 : 1) crystalline complex the n-$PrNH_2$ guest is found to be hydrogen bonded to the host component via an OH···N interaction (O—H = 0.93 Å, O···N = 2.832 Å, H··· = 1.93 Å, O—H···N = 165°; Figure 4) forming a pseudodimeric building block of the crystal like the acetone associate. Its alkyl residue, however, is quite loosely packed in the lattice, exhibiting large-amplitude wagging motion or structural disorder.

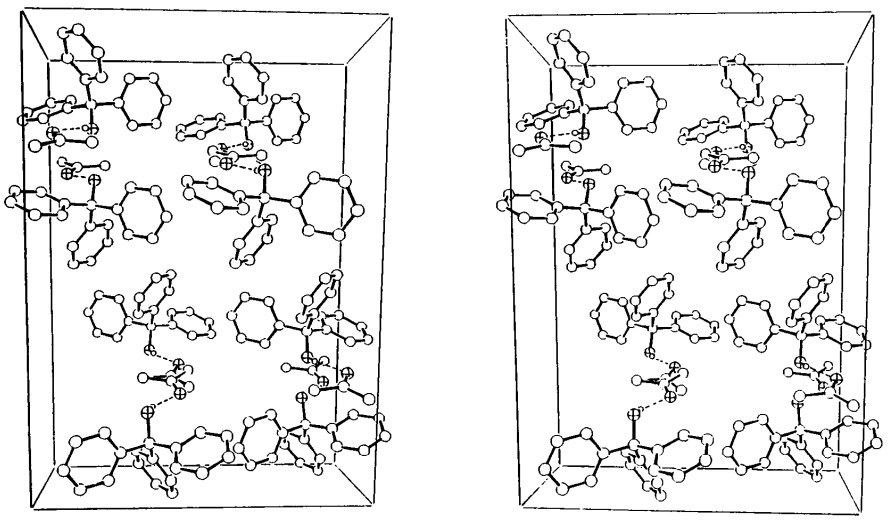

Figure 3. Crystal packing of **1**·acetone (2 : 1), stereoviewed down the a axis (b is horizontal). Two orientations of the acetone and a possible orientation of the host hydroxyl group are shown. The remaining H-atoms are omitted for clarity.

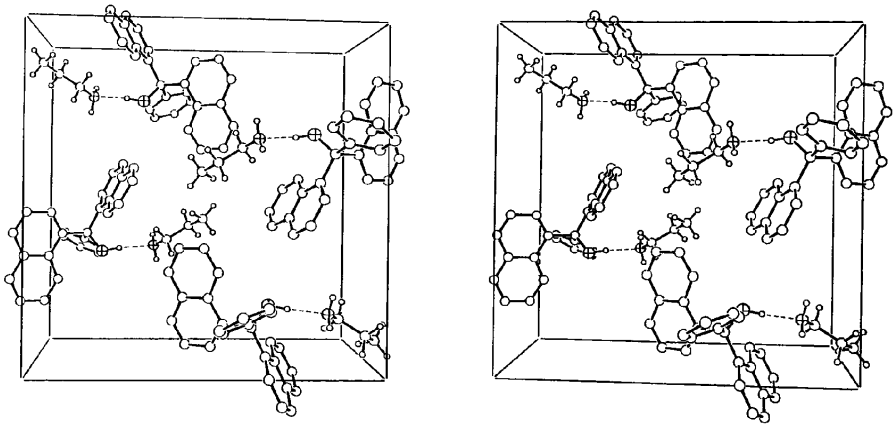

Figure 4. Crystal packing of **9**·n-propylamine (1 : 1), stereoviewed down the a axis (b is horizontal). The carbon bonded H-atoms of the host molecule are omitted for clarity.

The packing of the **9**·di-n-propylamine (1 : 1) inclusion complex (Figure 5) shows that the host and guest species associate via a single localized hydrogen bond (OH$\cdots$N = 2.86 Å). The formation of host–guest associates thus prevails in this structure as well. In the crystal, the guest molecules are accommodated in 'channels' extending along the c-axis of the unit cell, lying between and being aligned parallel to, the naphthyl rings. The channel zones center at y = 0, 1/2 and 1 in the packing diagram. Along the a-direction (horizontal) one channel is separated from another by 'walls' which consist of the naphthyl rings, showing an

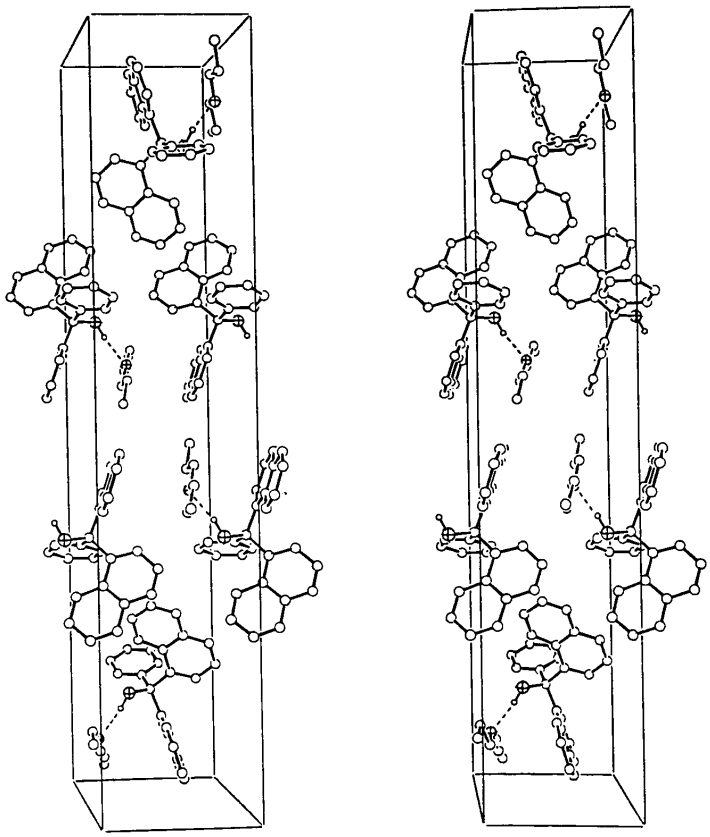

Figure 5. Crystal packing of **9**·di-n-propylamine (1 : 1), stereoviewed down the c axis (b is horizontal). All but the hydroxyl H-atoms are omitted for clarity.

alternating arrangement of the guest molecules and the naphthyl rings. Packing in these channels is relatively loose, the peripheral methyl groups again exhibiting large-amplitude thermal motion. Correspondingly, the calculated density of the material is somewhat low (1.15 g cm^{-3}). The remaining aryl fragments constitute the bulk of the other zone of the crystal structure, layered perpendicular to the long b-axis at y = 0.25 and 0.75.

4. Conclusions

Substituted derivatives of triphenylmethanol (**1**) involving lateral alkyl (**2–5**) or extra phenyl groups (**6**) in different positions at each of the phenyl rings or naphthyl unit substitutes (**7–10**) have been shown to be an efficient source of both highly specific and rather universal clathrate hosts, depending on the nature of the substituent or the aromatic moiety. Moreover, these hosts are very simple in con-

stitution and can easily be synthesized which makes their use in lattice inclusion chemistry favourable.

An apparent common feature of all three crystal structures is the associate formation of 1 : 1 host–guest building blocks. Although the amine guests (n-$PrNH_2$, n-Pr_2NH), like the alcoholic host (**9**), possess both proton donor and acceptor ability, there is only a one-way O—H···N hydrogen bond from the host to the guest in the present inclusion complexes. This yields discrete 1 : 1 host–guest adducts rather than extended H-bonded chain patterns. These associates are then assembled together by ordinary van der Waals forces in the crystal so as to form a channel-like arrangement in which the aryl parts of the host construct the channel around the H-bonded amine guests.

Moreover, it is not obvious why the complexes between **1** and DMSO or acetone assume crystallographically different structures. A reasonable explanation could be provided as follows. The DMSO and acetone guests contain only proton acceptor sites but not proton donor sites. An optimal organization of host molecules **1**, suited to effectively accommodate these guests in the lattice leaves some 'empty' space along the a- and the c-axes of the unit cell between the two hosts related to one another by the twofold axis. This space can be filled in one way by a nonplanar species such as DMSO, and in a different way by an inherently planar molecule such as acetone. Evidently, the original orientation of the host molecules is determined first by the need to optimize the hydrogen-bonding interactions. The weaker host–guest association in the acetone complex can be attributed to the somewhat strained 'one-to-one' H-bonding; as compared to the stronger 'two-to-one' interaction in the structure of the DMSO complex and to the higher basicity of the S=O function. In a way, parallel behaviour is observed in the n-propylamine complexes of **9** considering optimization of H-bonding, propeller conformation and packing requirements.

In summary, the mode of action of the host molecules in these crystals represent just the hydrogen bonding break-up rule seen in TPPO [25, 26], but in an opposite sense. Here hosts **1** and **9** are obvious H-bond donors but never acceptors which obviously relates concomitant actions of space filling via bulky aromatic spacers and anchoring H-bonds between complementary functional sites.

Acknowledgements

E. W. gratefully acknowledges financial support from the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. He also thanks Dr. M. Czugler for helpful discussions.

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