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New Hosts Bearing Two Triphenylcarbinol Groups and Crystal Structures of Their Acetone Inclusion Compounds

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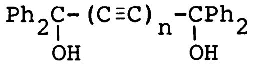
New hosts, *m*- and *p*-bis(diphenylhydroxymethyl)benzene and 2,2'-bis(diphenylhydroxymethyl)-1,1'-diphenyl, were found to exhibit high and selective inclusion tendencies toward a wide variety of guest compounds. Crystal structures of two representative acetone complexes were determined.

Although host compounds **1a**-**1c** which possess two diphenylcarbinol groups show high inclusion ability toward a wide variety of guest molecules,[1-3] host **2** which has only one triphenylcabinol group is much less effective.[3,4] In order to ascertain whether inclusion behavior is critically dependent on the number and disposition of such carbinol functionalities, we have designed new hosts, *o*- (**3a**), *m*- (**3b**), and *p*-bis(diphenylhydroxymethyl)benzene (**3c**) and 2,2'-bis-(diphenylhydroxymethyl)-1,1'-diphenyl (**4**), and studied their guest-inclusion properties.

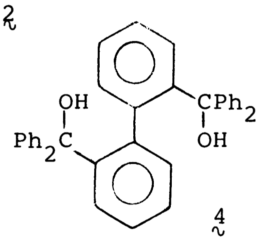


$Ph_2C(OH)-(C\equiv C)_n-C(OH)Ph_2$

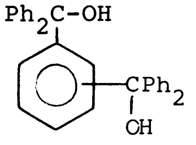
1 **a**: n = 2
b: n = 1
c: n = 0

Ph_3C-OH

2



4



3 **a**: ortho
b: meta
c: para

Each host was prepared by reacting the ethyl ester of the corresponding dioic acid with PhMgBr. Although **3a** exhibited very poor inclusion ability, **3b** and **3c** turned out to be very good hosts, and **4** was particularly effective. The affinities of **3b**, **3c**, and **4** toward some typical guests and the host:guest ratios of the resulting inclusion compounds are summarized in Table 1.

Selective inclusion by these hosts made it possible to separate isomeric guests. For example, when **3c** (1.2 g, 2.7 mmol) was dissolved by heating in a 1:1 mixture of β- and γ-picoline (1.0 g, 10.8 mmol) and the solution was kept at room temperature for 24 h, a 1:2 complex of **3c** with γ-picoline was obtained as colorless prisms (0.79 g, mp 108-110 °C). The resulting complex gave γ-picoline of 82.3% purity in 36.8% yield by distillation in vacuo. When a solution of **4** (1.0 g, 1.93 mmol) and a 1:1 mixture of α- and β-methylnaphthalene (0.28 g, 1.93 mmol) in diethyl ether (5 ml) was kept at room temperature for 6 h, a 2:1 complex of **4** with β-methylnaphthalene was obtained as colorless prisms (1.03 g, mp 200-230 °C). The complex gave β-methylnaphthalene of 84% purity in 79% yield by distillation in vacuo. Treatment of a 1:1 mixture of cyclohexanone and cyclohexanol with **4** by a similar procedure gave cyclohexanone of 89.5% purity in 42% yield.

Table 1. Inclusion compounds formed by the new hosts and their host:guest molar ratios

Guest \ Host	**3b**	**3c**	**4**
MeOH			1:1
EtOH			1:1
Acetone	2:1 (**5**)	2:1	2:1 (**6**)
Cyclopentanone	2:1	1:2	2:1
γ-Butyrolactone	2:1	1:2	2:1
Benzaldehyde		1:2	2:1
THF			1:1
Dioxan	2:1	1:2	2:1
CCl_4			1:1
DMF	1:1	1:2	1:1
DMSO	2:1	1:2	1:1
CH_3CN	1:1	2:1	1:1
Benzene			2:1
Pyridine	2:1	1:2	1:1

In order to understand the cause of high and selective inclusion capabilities exerted by **3** and **4**, crystal strcutures of the complexes of **3b** and **4** with acetone in 2:1 molar ratio, **5** and **6**, respectively, were determined.

Complexes **5** and **6** gradually turned milky upon exposure to air, but fresh samples remained stable for weeks when they were sealed inside Lindemann glass capillaries. X-Ray intensity measurements were made on a Nicolet R3m diffractometer using Mo-*K*α radiation (λ = 0.71073 Å). The structures were solved by direct methods, and computations were performed on a DEC MicroVAX-II system with the SHELXTL PLUS package.[5,6]

Crystal data. $2C_{32}H_{26}O_2 \cdot C_3H_6O$ (**5**), FW = 943.19, triclinic, space group $P\bar{1}$, a = 8.825(2), b = 11.672(1), c = 13.399(3) Å, α = 80.71(1), β = 73.55(2), γ = 84.54(1)°, V = 1304.5(4) Å^3, Z = 1, $F(000)$ = 500, D_c = 1.201 g cm^{-3}, μ(Mo-$K\alpha$) = 0.69 cm^{-1}, crystal size 0.46 x 0.36 x 0.26 mm^3, μr = 0.012, transmission factors 0.921-1.000, $2\theta_{max}$ = 50°, 4635 unique data, R refined to 0.081 for 1741 observed reflections on 334 variables; $2C_{38}H_{30}O_2 \cdot C_3H_6O$ (**6**), FW = 1095.4, rhombohedral (hexagonal unit cell, obverse setting), space group $R\bar{3}$, a = 35.502(6), c =

12.631(1) Å, V = 13787(5) Å^3, Z = 9, F(000) = 5220, D_c = 1.187 g cm^{-3}, μ(Mo-$K\alpha$) = 0.72 cm^{-1}, crystal size 0.40 x 0.40 x 0.30 mm^3, μr = 0.013, transmission factors 0.934-0.999, 2θ$_{max}$ = 50°, 5102 unique data, R refined to 0.094 for 1757 observed reflections on 214 parameters.[7)]

The acetone guest molecule in complex 5 exhibited two-fold disorder about the inversion center at (00½) such that the corresponding methyl C atoms overlapped with each other. All C and O atoms were refined anisotropically, and all H atoms except those of the disordered acetone molecule were included in structure-factor calculations.

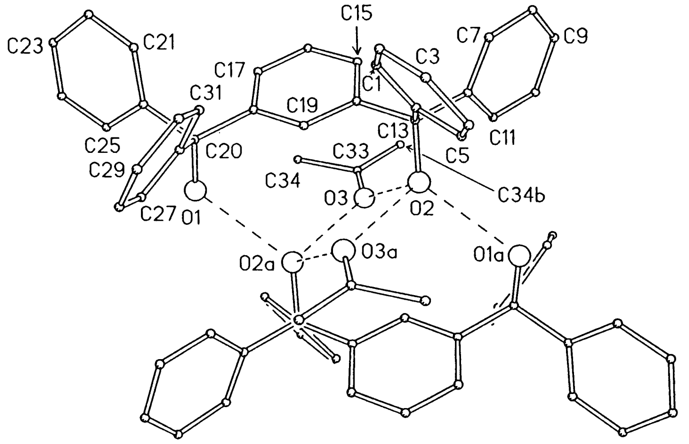


Fig. 1. Perspective view of the molecular arrangements of 5 with atom numbering. Symmetry code: *a* 1-*x*, -*y*, 1-*z*; *b* -*x*, -*y*, 1-*z*. Geometry of hydrogen bonding: O1...O2*a* 2.86, O2 ...O3 2.93, O3...O2 3.09 Å; O1...O2 ...O3 96, O3...O2...O1*a* 106, O3...O2...O3*a* 106°. The e.s.d.'s of bond lengths and angles are 0.02 Å and 1°, respectively.

As regards the crystal structure of 5, two centrosymmetrically-related host molecules are linked by a pair of intermolecular hydrogen bonds between their hydroxyl groups. The resulting dimer is further consolidated by hydrogen bonding involving the disordered acetone guest molecule in a central bridge (Fig. 1).

The acetone molecule in 6 was also found to be disordered with half site occupancy. The phenyl groups were treated as rigid groups, and all other C and O

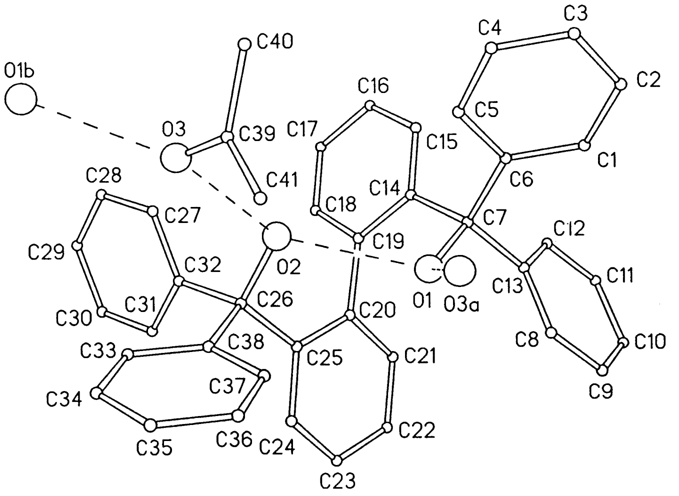


Fig. 2. Perspective view of the molecular arrangements of 6 with atom numbering. Symmetry code: *a* *x*-*y*, -1+*x*, 1-*z*; *b* 1+*y*, 1-*x*+*y*, 1-*z*. Geometry of hydrogen bonding: O1...O2 2.76, O2...O3 2.86, O3...O1*b* 2.86 Å; O3*a*...O1...O2 125, O1...O2...O3 125, O2...O3...O1*b* 127°. The e.s.d.'s of bond lengths and angles are 0.02 A and 1°, respectively.

atoms were refined anisotropically. All H atoms except those of the disordered acetone molecule were included in strcuture-factor calculations.

As for the crystal structure of **6**, the host molecule has an intramolecular hydrogen bond (Fig. 2). Six hosts arranged around a $\bar{3}$ center are alternately bridged by the disordered guest molecules to form a hydrogen-bonded cluster, in which the O atoms are linked together in a star-like pattern (Fig. 3).

Both acetone complexes share a common tendency for the ordered hosts and disordered guests to associate into larger discrete units: the dimeric aggregate in **5** has a hydrogen-bonded central portion bounded by phenyl groups on both sides, whereas the hexameric system in **6** features a hydrogen-bonded toroidal core with hydrophobic phenyl rings and methyl groups lining its surface.

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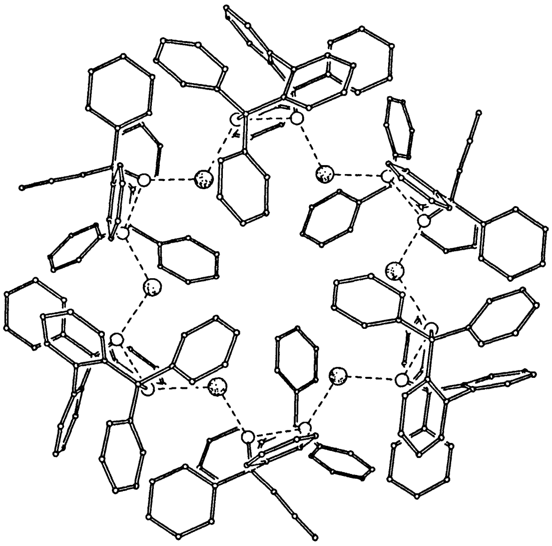

Fig. 3. The hydrogen-bonded cluster of $\bar{3}$ symmetry in **6**. For clarity the O atoms of the disordered acetone molecules are represented by larger dotted circles, and their C atoms are omitted.

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7) The atomic parameters have been deposited with the Cambridge Crystallographic Data Centre. Structure factor tables are available upon request from the last author.

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