Inclusion Compounds of Diol Hosts Featuring Two 9-Hydroxy-9-fluorenyl or Analogous Groups Attached to Linear Spacer Units

Edwin Weber,*[a] Silke Nitsche,[a] Andreas Wierig,[a] and Ingeborg Csöregh*[b]

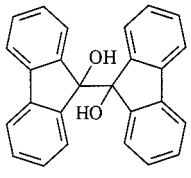
Keywords: Clathrates / Host-guest chemistry / Inclusion compounds / Supramolecular chemistry

A series of new clathrate host molecules **1**–**15**, each containing two 9-hydroxy-9-fluorenyl or analogous terminal groups attached to linear central units of different lengths and structural compositions, has been synthesized. Their crystalline inclusion compounds with a variety of organic guests – including amines, alcohols, ketones, and other dipolar aprotic compounds or aromatic hydrocarbons – are reported (229 examples of clathrates) and their properties are compared. The crystal structures of a free host compound and of six selected clathrates of different compound classes have been determined by X-ray diffraction, showing varied modes of supramolecular interaction.

Introduction

Crystalline inclusion compounds (clathrates) and similar co-crystalline systems are important topics in supramolecular chemistry,[1−3] owing to their great promise in a variety of fundamental and practical issues. These include future technologies[4,5] such as the potential to accommodate guest molecules with desirable optical properties,[6,7] the separation of small molecules on the basis of size exclusion or chemical affinity,[8,9] the provision of tailored reaction environments for included molecules[10,11] to be used in chemical sensor development,[12−14] chiral separation,[15−17] and the construction of new solid materials.[18−20] This interest has stimulated the discovery of new strategies for crystalline inclusion formation and motivated the design of novel host types.[8,9,21,22] In many cases, a rigid and bulkily substituted organic molecule displaying distinct hydrogen-bonding functionality is involved.[23,24] Characteristic examples are the "dog-bone" or "wheel-and-axle" type of diol host molecules, featuring a linear oligoethynylene/-phenylene central unit and two bulky diarylmethanol terminal groups.[23,25−27] On the other hand, molecules incorporating the 9-hydroxy-functionalized fluorene moiety,[28−32] substituted derivatives of it,[33,34] or analogously bridged aromatic groups,[35] even those with very simple molecular structures,[36−39] have also proven to be successful clathrate hosts. A promising approach along these lines would be the preparation of molecules uniting the two known effective strategies: the amalgamation of a central axis with two 9-hydroxy-9-fluorenyl or analogous terminal groups to yield a new structural type of diol host compounds.

With this in mind, we developed an interest in such a series of compounds, differing in the length and composition of the molecular axis as well as in the structure of the terminal groups. Compounds **1**−**15** (Schemes 1−3) either have no central building element (parent compound **1**, Scheme 1),[40] or incorporate ethynylene (**2**), phenylene (**3**−**8**), or a combination of both subunits (**9**−**11**) as the central axis (Scheme 2). The characteristic terminal groups are 9-hydroxy-9-fluorenyl (**2**−**4, 8**−**10**), 2,7-disubstituted 9-hydroxy-9-fluorenyl (**5**−**7**, **11**) (Scheme 2), 9-hydroxy-9-xanthenyl (**12**), 9-hydroxy-9-thioxanthenyl (**13**), dibenzosuberol (**14**), and dibenzosuberenol (**15**) (Scheme 3). Here we report on the synthesis of compounds **1**−**15**, describe their crystal inclusion (clathrate formation) properties in detail, and present crystal structures of a free host compound (**8**) and of six selected clathrate compounds including different hosts (**1**, **2**, **8**, and **10**) and guests of different compound classes.

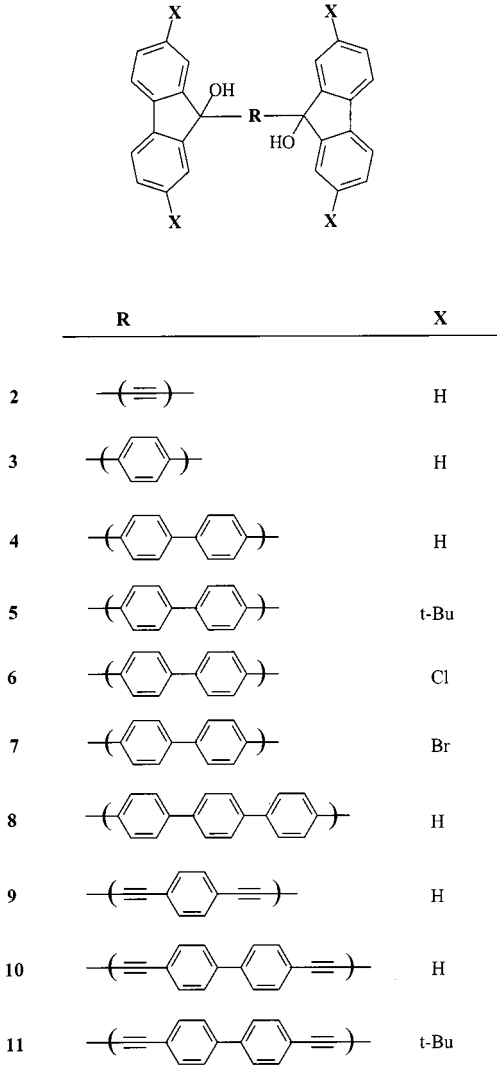


1

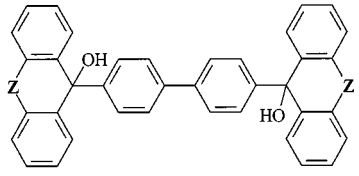
Scheme 1. Parent host compound

[a] Institut für Organische Chemie, Technische Universität Bergakademie Freiberg,
Leipziger Straße 29, 09596 Freiberg/Sachsen, Germany
Fax: (internat.) + 49-(0)3731/393170
E-mail: edwin.weber@chemie.tu-freiberg.de
[b] Department of Structural Chemistry, Arrhenius Laboratory, Stockholm University,
10691 Stockholm, Sweden
Fax: (internat.) + 46-8/163118
E-mail: ics@struc.su.se

  1434−193X/02/0305−0856 $ 17.50+.50/0 *Eur. J. Org. Chem.* **2002**, 856−872



Scheme 2. Bis(fluorenol) host compounds

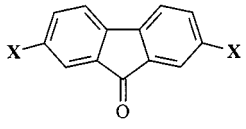


	Z
12	O
13	S
14	CH_2CH_2
15	CH=CH

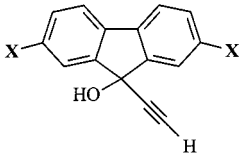
Scheme 3. Analogous diol hosts

Synthesis

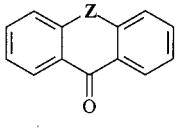
Compound **1** was prepared by reductive coupling of fluorenone (**16a**, Scheme 4), by use of iodine and magnesium.[41] Compound **2** was obtained as a by-product of the synthesis of **17a**, while **3** was synthesized from *p*-dibromobenzene and fluorenone (**16a**) by a Grignard reaction.[42] The bis(fluorenols) **4**−**8** were synthesized by treatment of the respective ketones (**16a**−**16d**) with the corresponding aryllithium reagents. These were prepared by treatment of the appropriate aryl dibromides with *n*BuLi under the usual conditions.[43] The acetylenic bis(fluorenols) **9**−**11** were synthesized by treatment of the corresponding aryl dibromide and the respective ethynyl-substituted fluorenol (**17a**, **17b**) under Hagihara conditions.[44] The diols **12**−**15** were prepared analogously to **4**−**8**, from ketones **18a**−**d** and the respective aryllithium reagents. Because most of the host compounds persistently retained traces of solvent it was difficult to obtain reliable elemental analytical data.



		X
16	a	H
	b	t-Bu
	c	Cl
	d	Br



		X
17	a	H
	b	t-Bu



		Z
18	a	O
	b	S
	c	CH_2CH_2
	d	CH=CH

Scheme 4. Terminal group starting compounds

The starting ketones **16b** and **16d** (Scheme 4) were obtained by oxidation of the corresponding fluorenones with O_2,[36,45] and **16c** by chlorination of fluorenone with NCS.[46] The ethynyl-substituted fluorenols **17a** and **17b** were prepared from fluorenones **16a** and **16b**, with ethylmagnesium bromide and ethyne in dry THF[47,48] to yield compound **2** as a by-product of **17a**.

The inclusion compounds were obtained by recrystallization of the host compound from the respective guest solvent. The drying conditions specified in the Exp. Sect. (1 h, 15 Torr, room temperature) refer to what we consider a "stable clathrate".[49]

Inclusion Properties

Thanks to their structural design, pronounced inclusion behavior is to be expected for potential host compounds

1−**15**, and so a wide variety of solvents (see Tables 1 and 2) was used to test their inclusion properties. These solvents included amines, alcohols, ketones, and other dipolar aprotic solvents, heterocycles, and aromatic hydrocarbons of different constitutions. Fulfilling the expectations, a total of 229 different crystalline inclusions of compounds **1**−**15** was obtained (Tables 1 and 2), which shows the general efficiency of the new host design. Nevertheless, as can be seen from the tables, the individual compounds **1**−**15** are rather different in their inclusion capabilities and demonstrate characteristic individual levels of selectivity.

The greatest numbers of inclusion compounds were formed by **15** (25) and **14** (24), molecules comprising a central axis of medium length and dibenzosuberol or dibenzosuberenol terminal groups, and also by **1** (20) and **2** (19), which are the most closely connected bis(fluorenols). The fewest inclusions were formed by the di-*tert*-butyl-substituted host compound **5** (6) and the xanthenol and thioxanthenol derivatives **12** (8) and **13** (9).

As well as the different number of inclusion compounds formed by an individual host, there are also entrapment preferences induced by the nature and constitution of the solvents. Only DMF and DMSO yield crystalline inclusion complexes with virtually all of the hosts (an exception is **5**), followed by piperidine, morpholine, 1,4-dioxane, and THF, which are also almost uniformly enclathrated by the hosts in question. In contrast, acetonitrile is a special case, since it is only an efficient guest with compound **7**. From a general point of view, the guest compounds most consistently included are to be found among the amine and alcohol classes of compounds, with the amines slightly predominating. This general behavior is a reasonable consequence of the polar hydroxy groups present in the host compounds, making hydrogen bonding to the guest molecules very likely. It follows that apolar hydrocarbons are very rarely enclathrated by these hosts, indicating that "true clathrates"[25] are not favored among these compounds. More specific inclusion behavior associated with the structure of

Table 1. Crystalline inclusion compounds (host/guest stoichiometric ratios)[a]

	Host Compound										
Guest Solvent [b]	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**
*n*PrNH$_2$	-	1:1	-	1:2	-	1:1	1:1	1:1	-	-	-
*n*OctNH$_2$	-	1:2	c	1:2	c	c	c	c	1:1	1:2	1:1
BenzylNH$_2$	c	1:1	-	-	1:1	c	c	c	-	1:1	1:3
CyclopentylNH$_2$	1:2	1:1	c	1:2	-	c	c	-	1:1	c	-
*n*Pr$_2$NH	1:1	-	-	1:1	1:2	1:3	-	2:3	1:1	c	1:2
*n*Pr$_3$N	2:1	c	c	1:1	1:2	1:4	1:4	2:1	1:1	1:2	1:1
Piperidine	1:1	1:2	1:2	1:4	-	1:2	1:2	1:2	2:3	1:2	1:3
Morpholine	1:2	1:2	1:2	1:3	1:1	c	c	c	1:4	1:2	1:4
Pyridine	1:1	1:2	2:1	2:1	-	1:2	1:2	1:2	1:1	c	1:2
MeOH	2:1	1:1	2:1	-	-	-	-	-	2:3	-	1:1
EtOH	2:1	1:1	2:1	-	-	-	-	-	1:2	-	1:1
1-PrOH	1:2	1:2	1:2	-	-	-	1:1	-	1:2	-	c
1-BuOH	2:1	-	1:1	-	-	-	1:2	-	-	1:1	1:2
*t*BuOH	1:2	1:2	1:2	-	-	-	1:2	1.1	1:1	1:1	-
CyclohexylOH	1:2	1:4	1:2	-	-	-	1:2	-	-	-	-
1,2-Propanediol	c	2:1	-	2:1	-	c	c	c	c	1:3	1:4
Acetone	2:1	-	1:1	-	-	1:1	1:1	1:4	c	-	-
Cyclohexanone	1:1	1:2	-	1:3	-	-	-	-	-	c	-
DMF	1:1	1:2	1:1	1:2	c	1:3	1:3	1:3	c	1:2	1:1
DMSO	1:1	1:3	1:1	1:4	-	1:2	1:2	1:4	1:1	1:3	1:2
Acetonitrile	-	-	-	-	-	-	2:1	-	-	-	-
THF	1:1	1:2	1:2	-	2:1	1:2	1:2	1:3	1:1	1:4	1:1
1,4-Dioxane	1:1	1:1	1:2	1:2	4:1	1:1	2:1	2:3	3:2	1:4	1:4
Benzene	1:1	1:2	-	c	c	c	c	1:1	-	1:3	-
Toluene	3:1	-	-	-	-	-	-	-	-	1:1	1:1

[a] See the Exp. Sect. for methods of preparation, drying standard, and characterization. [b] Crystalline inclusion compounds (host/guest stoichiometric ratios) are also formed between: **3** and 2-PrOH (1:2) and 2,4-, 3,5-, 2,6-lutidines (1:2); **4** and cycloheptanone (1:1), β-butyrolactone (1:1); **8** and *p*-xylene (1:1); **9** and cycloheptanone (1:1), diethyl ether (2:1), dichloromethane (1:3); **10** and β-butyrolactone (1:2), while nitromethane and cyclohexane, which were also tested as guest solvents, yielded no inclusion compounds with any of these hosts. [c] Difficult to crystallize.

Table 2. Crystalline inclusion compounds (host/guest stoichiometric ratios)

Guest solvent[b]	Host compound[a] 12	13	14	15
nPrNH$_2$	–	1:1	1:2	1:3
iBuNH$_2$	2:1	–	1:2	1:2
CyclohexylNH$_2$	[c]	[c]	1:2	1:3
Et$_2$NH	1:2	2:1	1:2	1:3
nPr$_2$NH	–	1:1	1:2	1:3
nBu$_2$NH	–	[c]	1:2	1:3
Et$_3$N	1:2	2:1	1:1	1:2
nPr$_3$N	–	2:1	1:1	1:2
nBu$_3$N	3:1	2:1	[c]	2:3
Piperidine	1:2	[c]	1:3	[c]
Morpholine	[c]	[c]	1:3	[c]
MeOH	–	–	–	1:1
EtOH	–	–	–	1:1
1-PrOH	–	–	1:1	1:1
2-PrOH	–	–	1:1	1:1
1-BuOH	–	–	1:1	1:2
iBuOH	–	–	1:1	1:1
2-BuOH	–	–	1:1	1:1
CyclohexylOH	–	–	1:1	[c]
Acetone	–	–	1:2	1:1
Cyclopentanone	1:2	[c]	1:2	1:3
Cyclopenanone	–	1:1	1:1	1:1
DMF	1:2	1:2	1:2	1:2
DMSO	1:2	1:2	1:2	1:2
Acetonitrile	–	–	–	1:1
Propionitrile	–	–	1:2	1:2
1,4-Dioxane	–	–	1:3	1:2
Toluene	–	–	2:1	1:1

[a] See Exp. Sect. for methods of preparation, drying standard, and characterization. [b] tBuOH, cyclohexanone and o-, m-, p-xylene, which were also tested as guest solvents, yielded no inclusion compounds. [c] Difficult to crystallize.

the host compounds is difficult to discern, although the length of the central spacer unit (cf. **1** and **8**) and the bulk of the terminal groups of the host molecules (cf. **4** and **5**) are clearly parameters affecting the mode of inclusion formation. Furthermore, additional heteroatoms at the periphery of the terminal groups are obstructive (cf. **12**, **13**).

Another remarkable point is the host/guest stoichiometric ratios of 1:3 and 1:4, which are exceptionally high with reference to the guest component. They are found in a number of inclusion compounds, indicating high efficiency of guest accommodation.

X-ray Structural Studies

In order to investigate the building principles of the new clathrate design and to determine which modes of interaction the new host type used for enclathration of different guests (proton donors and proton acceptors) – in particular in the cases of inclusion compounds with the unusual 1:4 host/guest ratio – no fewer than six crystal structures of inclusion compounds were studied in this work: **1**·DMSO (1:1), **2**·1-PrOH (1:2), **2**·cyclohexylOH (1:4), **2**·THF (1:2), **8**·acetone (1:4), and **10**·THF (1:4). For comparison, a structural study of the unsolvated host compound **8** is also covered here, and reference is made to previously reported structures of crystalline inclusion complexes involving host compounds **1**[40] and **3**.[51,52]

Crystallographic data and details of structure refinement calculations of the inclusion compounds are given in Table 3. Figures 1–4, prepared by use of the XP molecular graphics program,[53] show perspective views of the stoichiometric host–guest units of the inclusion compounds and of the unsolvated compound **8**. Stereo packing illustrations[53] are presented in Figures 5–9. Conformational features of the host molecules and geometric parameters of selected intermolecular interactions, calculated with the PARST program,[54,55] are listed in Tables 4 and 5.

Molecular Structures

Although each of the studied diol host molecules may have inversion symmetry, and although all studied compounds (Figures 1–4) crystallize with centrosymmetric space group symmetries (Table 3), the host molecules **1** in **1**·DMSO (1:1), **2** in **2**·1-PrOH (1:2), and **8** in its solvent-free crystal exhibit no crystallographic symmetry at all. Nevertheless, the presence or absence of molecular inversion symmetry seems to be crucial for the solid-state conformations of these hosts. Accordingly, in host molecules exhibiting crystallographic symmetry, the two OH functions of each molecule are exactly *trans* oriented {τ [O(1)–C(9)–···–(C9′)–O(1′)] = 180°} and the two flat fluorene moieties are parallel with each other (Table 4). In contrast, in the host molecules without crystallographic symmetry, both the orientation of the OH groups and the dihedral angle between the planes of the fluorene moieties seem to be soft parameters, which may take widely varying values, mostly depending on intermolecular H bond interactions and/or crystal packing forces (cf. below). However, no *cis* configuration, as exhibited by host **3** in its inclusion crystal with 2,6-lutidine as guest,[51] was observed in the diol molecules in this study. Furthermore, the two fluorenyl groups in host **8** are connected through a linear triphenylene unit, in which each ring may rotate freely around the single bonds linking them together. Hence, the phenyl planes of the spacer unit in **8** form the dihedral angles 33.54(6) [rings 1 and 2], 147.23(5) [rings 2 and 3], and 113.94(6)° [rings 1 and 3] in the unsolvated compound [Figure 3 (a)], whereas the same three angles in host **8** in its acetone inclusion crystal have the values 146.69(7), 146.69(7), and 0.0° [Figure 3 (b)], in this latter case satisfying the inversion symmetry of the molecule. The symmetry requirement also forces the two phenyl rings of the central diphenylene moiety of host **10** [in **10**·THF (1:4), Figure 4] to be coplanar.

The small guest molecules, on the other hand, generally conform to expected geometries, although the calculated parameters for the guests are often somewhat more uncertain than those of the hosts, depending on possible static/dynamic disorder in the guest entities.

The DMSO molecule in **1**·DMSO (1:1) has a pyramidal shape (Figure 1) with the sum of the bond angles around

Table 3. Crystal data and details of the final refinement calculations for compounds studied

Compound	**1**·DMSO (1:1)	**2**·1-PrOH (1:2)	**2**·cyclohexylOH (1:4)	
CCDC deposition number	161455	161456	161457	
Chemical formula: host	$C_{26}H_{18}O_2$	$C_{28}H_{18}O_2$	$C_{28}H_{18}O_2$	
guest	C_2H_6OS	C_3H_8O	$C_6H_{12}O$	
Stoichiometry: host:guest	1:1	1:2	1:4	
Molecular mass	440.556	506.640	787.090	
Temperature, K	193(2)	193(2)	193(2)	
Radiation/λ, Å	Mo-K_α/0.71073	Mo-K_α/0.71073	Mo-K_α/0.71073	
Crystal system/space group	monoclinic/$P2_1/n$	triclinic/$P\bar{1}$	triclinic/$P\bar{1}$	
Unit cell dimensions				
a, Å	11.486(1)	8.888(1)	9.843(1)	
b, Å	14.283(2)	12.750(2)	9.852(1)	
c, Å	13.335(1)	13.323(2)	13.132(2)	
α, deg	90.0	89.08(2)	71.17(2)	
β, deg	90.22(1)	79.09(2)	69.42(1)	
γ, deg	90.0	73.52(2)	78.53(1)	
V, Å^3	2187.6(4)	1420.5(4)	1123.1(3)	
Z	4	2	1	
D_c, Mg m^{-3}	1.3376(2)	1.1845(3)	1.1637(3)	
μ, mm^{-1}	0.177	0.076	0.079	
F(000)	928	540	426	
Approx. crystal size, mm	0.30 × 0.27 × 0.11	0.11 × 0.12 × 0.30	0.09 × 0.15 × 0.34	
θ_{max} for collected data, deg	26.08	26.18	26.01	
Index ranges min./max. h,k,l	–14/14, 0/17, 0/16	–10/10, –15/15, –16/16	–11/11, –11/12, –16/16	
Reflections collected	20396	11293	8884	
Independent reflections	4198	5244	4092	
R_{int}	0.0428	0.0740	0.0671	
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2	
Data[a]/parameters refined	4198/379	5234/344	3880/297	
$R(F)$ [$I > 2\sigma(I)$]	0.033	0.061	0.052	
No. of reflections with $I > 2\sigma(I)$	2678	1776	2226	
wR[b] (all F^2)	0.074	0.199	0.136	
Goodness-of-fit on F^2	0.842	0.829	0.866	
Largest diff. peak and hole, e$^-$Å^{-3}	0.21 and –0.29	0.52 and –0.31	0.21 and –0.27	

Compound	**2**·THF (1:2)	**8**·acetone (1:4)	**10**·THF (1:4)	**8** (guest free)
CCDC deposition number	161458	161459	161460	161461
Chemical formula: host	$C_{28}H_{18}O_2$	$C_{44}H_{30}O_2$	$C_{42}H_{26}O_2$	$C_{44}H_{30}O_2$
guest	C_4H_8O	C_3H_6O	C_4H_8O	–
Stoichiometry: host:guest	1:2	1:4	1:4	–
Molecular mass	530.662	823.038	851.092	590.720
Temperature, K	293(2)	170(2)	293(2)	193(2)
Radiation/λ, Å	Mo-K_α/0.71073	Mo-K_α/0.71073	Mo-K_α/0.71073	Mo-K_α / 0.71073
Crystal system/space group	triclinic/$P\bar{1}$	monoclinic/$P2_1/n$	monoclinic/$P2_1/c$	orthorhombic/$Pbca$
Unit cell dimensions				
a, Å	8.317(1)	9.527(1)	9.229(1)	14.261(1)
b, Å	12.298(2)	13.113(1)	17.744(2)	16.550(1)
c, Å	16.322(2)	18.641(3)	15.085(1)	26.590(3)
α, deg	82.91(2)	90.	90.0	90.0
β, deg	75.28(2)	97.43(2)	99.39(1)	90.0
γ, deg	70.23(2)	90.0	90.0	90.0
V, Å^3	1518.2(4)	2309.2(5)	2437.2(4)	6275.8(9)
Z	2	2	2	8
D_c, Mg m^{-3}	1.1608(3)	1.1837(2)	1.1597(3)	1.2504(2)
μ, mm^{-1}	0.074	0.076	0.074	0.0753
F(000)	564	876	908	2480
Approx. crystal size, mm	0.13 × 0.26 × 0.28	0.30 × 0.30 × 0.11	0.06 × 0.11 × 0.18	0.15 × 0.15 × 0.17
θ_{max} for collected data, deg	26.11	26.23	25.96	26.12
Index ranges min./max. h,k,l	–10/10, –15/15, –20/17	–11/11, 0/16, 0/23	–10/10, –21/21, –18/18	0/17, 0/20, 0/32
Reflections collected	8989	18009	19360	58458
Independent reflections	5502	4559	4617	6206
R_{int}	0.0437	0.119	0.080	0.1002
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
Data[a]/parameters refined	5500 / 435	4554 / 311	4607 / 307	6205/446
$R(F)$ [$I > 2\sigma(I)$]	0.069	0.044	0.060	0.036
No. of reflections with $I > 2\sigma(I)$	2484	1927	1501	2266
wR[b] (all F^2)	0.215	0.092	0.177	0.067
Goodness-of-fit on F^2	0.906	0.757	0.792	0.524
Largest diff. peak and hole, e$^-$Å^{-3}	0.35 and –0.24	0.23 and –0.23	0.31 and –0.13	0.18 and –0.19

[a] A few reflections [10 for **2**·1-PrOH (1:2), 1 for **2**·THF (1:2), 5 for **8**·acetone (1:4), 10 for **10**·THF (1:4), and 1 for compound **8**] were excluded from the final refinement calculations due to possible extinction effects or potential systematic errors. [b] The weights of the F^2 values were assumed to be $w = [\sigma^2 (F^2) + (c_1 \cdot P)^2]^{-1}$, where $P = (F_o^2 + 2F_c^2)/3$; and the constant c_1 had the values 0.035 for **1**·DMSO (1:1), 0.095 for **2**·1-PrOH (1:2), 0.075 for **2**·cyclohexylOH (1:4), 0.125 for **2**·THF (1:2), 0.021 for **8**·acetone (1:4), 0.082 for **10**·THF (1:4), and 0.0 for compound **8**.

Table 4. Selected conformational features[a] of the diol molecules **1**, **2**, **8**, and **10**

Host with Guest host:guest stoichiometry	**1** DMSO (1:1)	**2** 1-PrOH (1:2)	**2** cyclohexylOH (1:4)	**2** THF (1:2) mol. A	mol.B	**8** acetone (1:4)	**8** (guest free)	**10** THF (1:4)
The thirteen C atoms of the fluorene moieties are co-planar within, Å	0.165(2) 0.174(2)	0.085(5) 0.114(5)	0.091(3)	0.056(5) 0.049(5)		0.034(2)	0.114(3) 0.071(2)	0.098(5)
Dihedral angles formed by the two fluorene planes, deg	128.81(2)	123.28(6)	180.0	180.0	180.0	180.0	16.68(3)	180.0
Length of the spacer unit (Å) between the fluorene moieties	1.581(2)	4.14(1)	4.14(1)	4.14(1)	4.14(1)	14.45(2)	14.45(2)	15.31(2)
Selected torsion angles, deg.								
C(1)-C(1a)-C(9)-O(1)	-60.8(2)	-63.4(5)	65.2(3)	61.9(4)	62.0(4)	61.0(3)	64.0(3)	-59.7(5)
C(8)-C(8a)-C(9)-O(1)	51.8(2)	58.3(5)	-66.4(3)	-62.6(4)	-61.8(4)	-59.8(3)	-65.2(3)	57.7(5)
C(1)-C(1a)-C(9)-C(spacer)	63.1(2)	62.3(5)	-56.5(3)	-61.9(4)	-61.8(4)	-60.3(3)	-56.3(3)	60.8(4)
C(8)-C(8a)-C(9)-C(spacer)	-69.2(2)	-62.3(5)	57.3(3)	61.1(4)	61.2(4)	60.8(3)	54.3(3)	-63.5(5)
O(1')-C(9')-C(1a')-C(1')	53.2(2)	63.3(6)					59.6(3)	
O(1')-C(9') C(8a')-C(8')	-52.2(2)	-58.4(5)					-59.3(3)	
C(spacer)-C(9')-C(1a')-C(1')	-65.3(2)	-59.8(6)					-61.2(3)	
C(spacer)-C(9')-C(8a')-C(8')	67.0(2)	63.6(6)					59.1(3)	
O(1)-C(9)-···-C(9')-O(1')	-58.7(1)	-95.6(3)	180.0	180.0	180.0	180.0	149.1(2)	180.0

[a] Calculated by using the PARST program.[54]

the central sulfur atom being 308.2(1)°. The **2**·cyclohexylOH (1:4) crystal contains two crystallographically independent cyclohexanol molecules, both exhibiting the usual chair conformation with equatorially attached OH groups [Figure 2 (b)]. The conformation of a puckered six-membered ring may be described by, for example, a spherical polar set of parameters, such as the total puckering amplitude Q (Å), phase angle ϕ (°), and polar angle θ (°).[55] For the ideal chair conformation, θ is equal to either 0 or 180°.[55] The calculated ring-puckering parameters for the cyclohexanol C1/C2 guests are Q = 0.575(4)/0.560(3) Å, ϕ = 62(11)/−26(20)°, and θ = 178.1(4)/1.0(4)°, and the torsion angles for the attached OH functions − τ_1 [for O(1)−C(1)-(C2)−C(3)] and τ_2 [for O(1)−C(1)-(C5)−C(6)] − have the values 176.1(3)/−178.0(2) and −178.9(2)/177.2(2)°, respectively. There are also two independent guest molecules in the **8**·acetone (1:4) crystal [Figure 3 (b)]. The skeletons of the acetone A1/A2 molecules are flat to within 0.006(5)/0.022(5) Å, and are tilted by 40.6(1)° relative to each other. Although A1 is H-bonded to the host and A2 is not, they form nearly the same dihedral angles with the nearest fluorene plane [74.4(1) and 73.9(1)°, respectively].

Interestingly enough, each of the hydrogen-bonded 1:2 host−guest supramolecular units in **2**·THF (1:2) is located on a crystallographic inversion center, but the crystal contains two crystallographically independent host−guest associates. Hence, the unique part of the structure consists of two halves of hosts **2**A and **2**B, respectively, and two guest molecules. Both THF molecules are disordered, but in different ways. The guest linked to host molecule A occupies two distinct disorder sites, designated T1 and T′ [Figure 2 (c)], with 55(1) and 45(1)% probabilities, respectively. The O(1A)−H vector of host A is also disordered, pointing in the direction either of O(1T1) or of O(1T′), thus making hydrogen bond connection to both guest disorder sites possible (Table 5). The other guest, bonded to host B, occurs in two partially overlapping locations [rotated around the axis through the common C(2T2) and C(4T2) atom sites, Figure 2 (d)] with nearly equal probabilities [the refined site occupation factors are 52(1)% for T2 and 48(1) % for T′′]. In this latter case, only O(1T2) is hydrogen-bonded to host B, whereas O(1T′′) is not. The conformation of a puckered five-membered ring may be characterized by a ring-puckering amplitude Q (Å) and a phase coordinate (°).[55,56] The angle ϕ = 0° ± n·36° (n = 1, 2, 3 ... n) corresponds to an ideal envelope conformation [with mirror plane (C_S) symmetry], while ϕ = 18° ± n·36° relates to the half-chair form [with twofold rotational (C_2) symmetry]. The Q(Å)/ϕ(°) values, calculated for each five-membered ring in all four partially occupied guest sites [0.17(2)/−135(6) for T1, 0.18(2)/113(6) for T′, 0.28(1)/−151(3) for T2, and 0.40(1)/−171(2) for T′′],[55,56] indicate conformations intermediate between envelope and half-chair forms for all four disorder models of THF.

There are also two crystallographically independent THF guests (T1 and T2, Figure 4) in **10**·THF (1:4), of which only one is hydrogen-bonded to the host. The calculated ring-puckering parameters [Q(Å)/ϕ(°) are 0.222(8)/120(2) for T1, and 0.43(2)/41(2) for T2][55,56] also reveal intermediate con-

Table 5. Distances and angles of O−H···O intermolecular hydrogen bonds and O−H···π(aryl) intermolecular interactions

Atoms involved	Symmetry	O···O/π Distance, Å	O–H Distance, Å	H···O/π Distance, Å	O–H···O/π Angle, deg
1·DMSO (1:1)					
O(1')-H(1O')···O(1D)	*x, y, z*	2.697(2)	0.92	1.79	170
O(1)-H(1O)···O(1')	*-x,-y+2,-z+1*	2.871(2)	0.90	2.07	148
2·PrOH (1:2)					
O(1)-H(1O)···O(1P)	*x, y, z*	2.674(4)	0.94	2.30	178
O(1')-H(1O')···O(2P)	*x, y, z*	2.643(4)	1.04	1.71	147
O(2P)-H(2OP)···O(1)	*-x+1,-y+1,-z+1*	2.778(4)	1.07	1.71	175
O(1P)-H(1OP)···O(1')	*x-1, y, z*	2.727(5)	0.96	1.93	139
2·cyclohexylOH (1:4)					
O(1)-H(1O)···O(1C2)	*x, y, z*	2.692(2)	0.97	1.73	168
O(1C1)-H(1O1)···O(1)	*x, y, z*	2.729(3)	0.92	1.82	169
O(1C1)-H(1O1)···O(1')	*-x+2, -y, -z*	2.729(2)	0.92	1.82	168
O(1C2)-H(1O2)··O (1C1)	*-x+1, -y, -z*	2.743(3)	1.01	1.75	166
2·THF (1:2)					
O(1A)-H(1OA)···O(1T1)	*x, y, z*	2.669(8)	0.81	1.91	155
O(1A)-H(1O')···O(1T')	*x, y, z*	2.604(9)	0.90	1.70	180
O(1B)-H(1OB)···O(1T2)	*x, y, z*	2.626(7)	1.07	1.71	140
8·acetone (1:4)					
O(1)-H(1O)···O(1A1)	*x, y, z*	2.792(2)	0.90	1.93	161
10·THF (1:4)					
O(1)-H(1O)···O(1T1)	*x, y, z*	2.766(4)	1.05	1.71	176
8 (guest free)					
O(1)-H(1O)···π[a]	*-x+0.5,y+0.5,z -*	3.106(2)	0.90	2.26	155
O(1')-H(1O')···π[a]	*x+1,5,y-0.5,z*	3.238(2)	0.88	2.39	157

[a] π means the centroid of the C(17)−C(16)−C(18)−C(18′)−C(16′)−C(17′) phenyl ring [see Figure 3 (a)].

formations for both THF rings in this structure. Hence, our observations are in accordance with the view that, if the intermolecular force field is unsymmetrical with respect to both C_S and C_2 conformations (e.g., anisotropic packing forces in crystals), an intermediate between envelope and half-chair forms will be the most probable and also the most stable conformation for a puckered five-membered ring.

Host-guest Interactions and Packing Relationships

The structures of these six inclusion crystals provide an excellent demonstration of directed lattice inclusion of small molecular guests: "*coordination-assisted clathrate formation*".[8,9,21] Besides matching sizes and shapes, the diol host molecules make extensive use of functional group interactions between host and guest. Because of the eminent H-bonding efficiency of the host hydroxy functions, and the significant, although variable, proton donor and/or acceptor ability of the guests, the ordinary (O−H···O) hydrogen bond would be expected to play an important role in the molecular recognition modes as well as in the packing relations seen in the inclusion crystals.

The **1**·DMSO (1:1) compound consists of H-bonded 2:2 host−guest supramolecular building blocks (Figure 5), held together by weaker van-der-Waals-type forces. Each guest is an acceptor for a relatively strong hydrogen bond from a host (Table 5), and the 1:1 host−guest units, related by a center of symmetry, are linked together two by two through inter-host hydrogen bonds. Through these latter bonds a closed loop is created, and can be described by the graph set notation $\boldsymbol{R_2^2(10)}$.[56,57] The two OH functions of molecule **1** are gauche, forming the torsion angle τ [for O(1)−C(9)−C(9′)−O(1′)] = −58.7(1)°. As a possible reason for this less common gauche conformation, we have noted that the intramolecular O···O distance, 2.781(1) Å, is typical of an ordinary O(H)···O hydrogen bond connection. However, the unequivocally located and refined hydrogen positions do not suggest an H bond within the molecule. The gauche conformation might also be a necessary condition for loop formation between the centrosymmetrically related host molecules. Nevertheless, three more inclusion

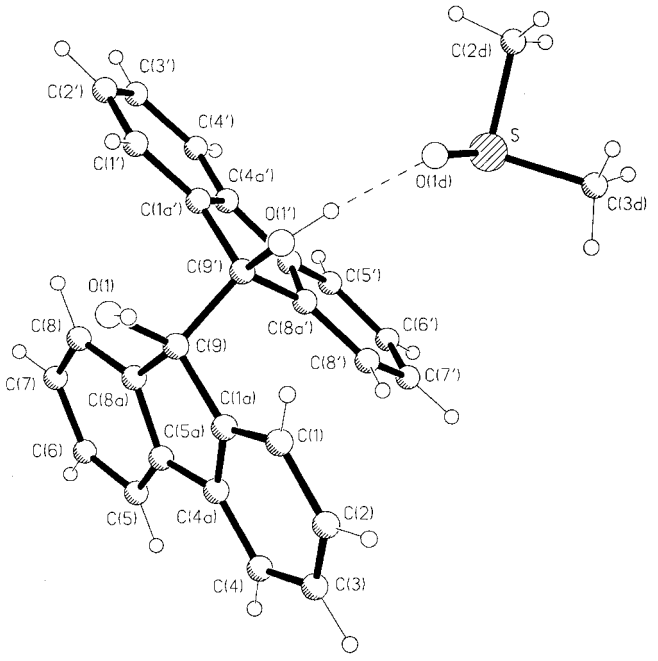


Figure 1. Perspective view of the stoichiometric host−guest unit in compound **1**·DMSO (1:1); the non-hydrogen atoms are labeled as in the text; solid and dashed lines represent covalent and hydrogen bonds, respectively

compounds of host **1,** containing ethanol [**1**·EtOH (2:1)], 1-butyl alcohol [**1**·*n*BuOH (2:1)], and pyridine [**1**·Py (1:1)] as guests, have previously been investigated by X-ray diffraction,[40] and molecule **1** was found to have very similar conformations in all three compounds [the τ angles for O(1)−C(9)−C(9′)−O(1′) ranging between 59 and 65°]. The organization of the **1**·Py (1:1) crystal is very similar to that in the present DMSO-containing one [**1**·DMSO (1:1)], based on similar H-bonded 2:2 host−guest units in which the hosts are connected through a closed H-bonded loop of the $R_2^2(10)$-type. Similar H-bonded loops, linking together neighboring centrosymmetrically related host molecules, have also been observed in the **1**·*n*BuOH (2:1) compound, but host **1** exhibits rather different recognition modes and packing relations in its inclusion crystals with alcoholic guests, cited above. Despite these differences, the conformations of molecule **1** in these three crystals agree remarkably well with each other, and also with that observed in the present DMSO inclusion crystal. This supports the suggestion[40] that the gauche conformation of the OH groups in **1** is more likely to be a consequence of intramolecular steric constraints, imposed by the closeness of the two bulky fluorenyl groups, than of intermolecular packing forces.

Inclusion of guests with OH groups by alcoholic host molecules is usually characterized by coupled systems of hydrogen bonds with full H-bond saturation, such as in the form of closed loops.[36,38,39,58−60] This is the case when the diol host **2** crystallizes with inclusion of 1-propanol [**2**·1-PrOH (1:2)] or cyclohexanol guests [**2**·cyclohexylOH (1:4)], or when host **3** forms an inclusion crystal with 2-propanol [**3**·2-PrOH (1:1)].[52] These three alcoholic inclusion crystals are similar, but show distinct differences as well. They differ in host−guest composition and have different hydrogen-bond loop sizes. Accordingly, eight OH groups of four host and four guest molecules create the [$R_8^8(16)$] loop in the propanol inclusion compound of **2** [Figure 6 (a)], six OH groups, belonging to two hosts and four guests, close a roughly chair-shaped [$R_6^6(12)$] ring in the cyclohexanol complex [Figure 6 (b)], while only four OH groups of two host and two guest molecules create the [$R_4^4(8)$] ring in the 2-propanol inclusion compound of **3**.[52] As molecules **2** and **3** are bifunctional, and because the two diol functions of each host are involved in at least two different loops in all three cases, endless ribbons are formed in these alcoholic inclusion crystals. The organizations of the ribbons are, however, somewhat different. Not only the guest alcohols, but also the host molecules, have different shapes, even in the two crystal structures of host **2**, depending in this last case on the presence or absence of crystallographic molecular inversion symmetry (Table 4). Hence, the asymmetric host **2** in the propanol inclusion compound links the $R_8^8(16)$ loops so as to give rise to a larger ring [$R_4^4(18)$] between them [Figure 6 (a)]. The eighteen-membered ring involves six OH groups of two host molecules and two guests, forming four hydrogen bonds, and also the ethynylene bridges that connect the OH functions in each of the two participating host molecules. On the other hand, the diol molecules with crystallographic inversion symmetry, and hence with perfectly *trans*-oriented OH functions, such as **2** in its cyclohexanol complex [Figure 6 (b)] and **3** in its 2-propanol inclusion complex,[52] interlink the respective loops of hydrogen bonds without giving rise to additional ring formation.

THF, a relatively good proton acceptor, is readily enclathrated by most of these diol molecules (Table 1). Two THF inclusion crystals, **2**·THF (1:2) [Figure 7 (a)] and **10**·THF (1:4) [Figure 7 (b)], with different hosts and stoichiometries, were selected for X-ray diffraction analysis. The host molecules **2** and **10** show similar *trans* conformations in their THF inclusion crystals, due to coincidence of crystallographic and molecular inversion symmetry [cf. Figure 2 (c), (d) and Figure 4], although molecule **10** has a longer spacer unit between its fluorenol moieties (Table 4). Both hosts form 1:2 host−guest associates through hydrogen bonds, but the overall shapes of the 1:2 host−guest entities and the attachment of the H-bonded THF guests to the host are different. In the **2**·THF (1:2) complex, the torsion angles through the C(10)−C(9)−O(1)···O(THF guest) atoms are 51.4(4)° to both O(1T1) and O(1T′) in molecule A, and 51.0(3)° to O(1T2) in molecule B, indicating a *cis* arrangement, whereas the same torsion angle in **10**·THF (1:4) has the value 179.4(2)°, thus indicating a *trans* attachment of the H-bonded guest with relation to the linear spacer unit of the host. Furthermore, the best plane through the THF rings is nearly perpendicular to the nearest fluorene plane in **2**·THF (1:2), but closer to parallel in **10**·THF (1:4). The corresponding dihedral angles are 73.7(4) for T1, 95.8(5) for T′, 84.4(3) for T2, and 82.0(3)° for the non-H-bonded T′′ guest site in **2**·THF (1:2), whereas the same angles in **10**·THF (1:4) are 19.6(2) for the

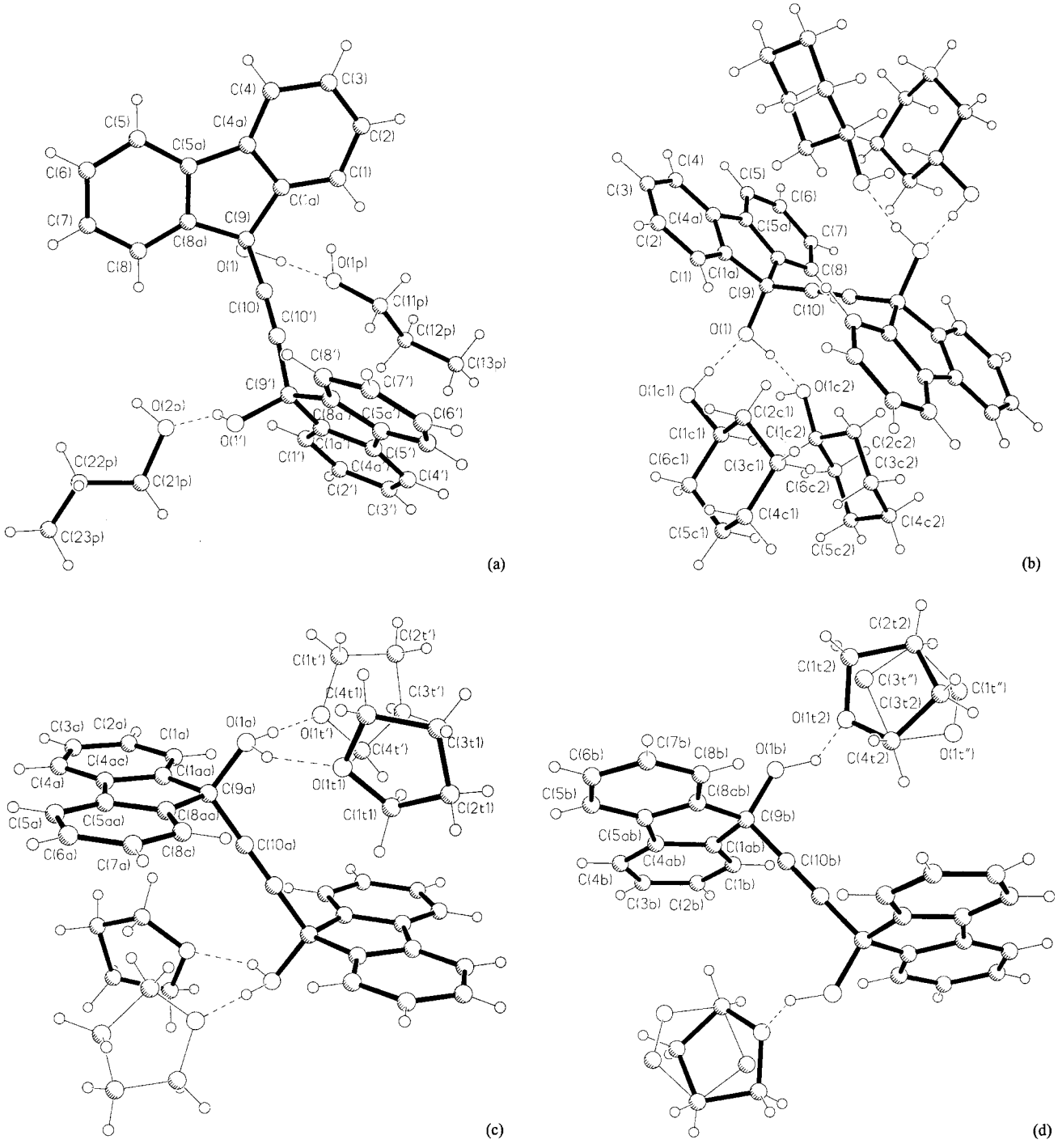


Figure 2. Perspective views of the stoichiometric host−guest units in compounds **2**·1-PrOH (1:2) (a), **2**·cyclohexylOH (1:4) (b), and **2**·THF (1:2) [molecule A (c) and molecule B (d)], including disorder sites of the guest molecules in (c) and (d); the THF rings of the minor disorder sites in (c) and (d) are drawn with thinner lines; the H disorder positions belonging to the minor guest disorder site T′′ in (d) are omitted for clarity; the unique non-hydrogen atoms are labeled as in the text; solid and dashed lines represent covalent and hydrogen bonds, respectively

H-bonded T1 and 11.4(6)° for the T2 guest. The packing of the 1:2 H-bonded host−guest units in the latter crystal gives rise to voids due to the elongated shape of molecule **10.** Consequently, additional guest molecules must be included in order to fill up the holes and stabilize the crystal structure. Accordingly, crystallization yields cocrystals of 1:4 host−guest stoichiometry [Figure 7 (b)] and with a space-filling coefficient[61] of 63.4% (calculated with the PLATON program).[62] This relatively low packing coefficient value is in accordance with our experience of the modest crystal quality and the limited tendency of the single crystals to grow to desirable size. Crystals of **2**·THF (1:2) [Figure 7 (a)], with a space-filling coefficient of 67.5%, have been grown to a more suitable size and are better looking

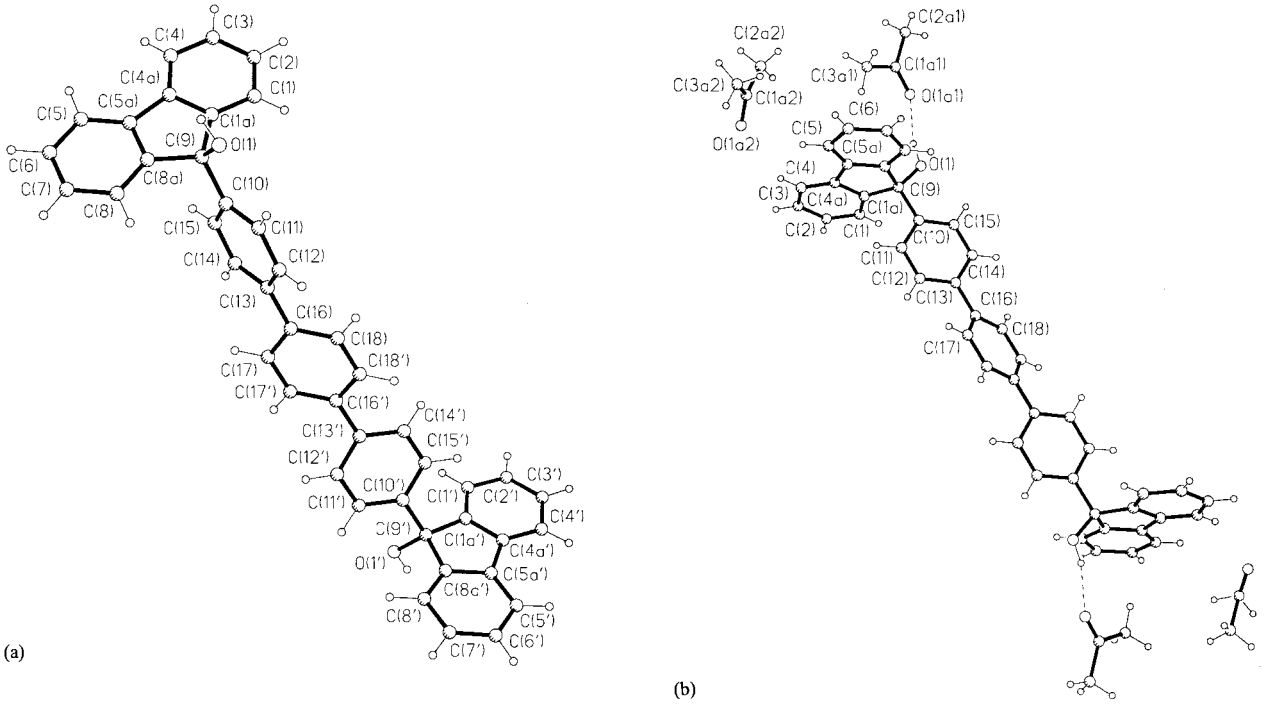


Figure 3. Perspective view of the guest-free compound **8** (a) and of the stoichiometric host−guest unit in **8**·acetone (1:4) (b); the unique non-hydrogen atoms are labeled as in the text; solid and dashed lines represent covalent and hydrogen bonds, respectively

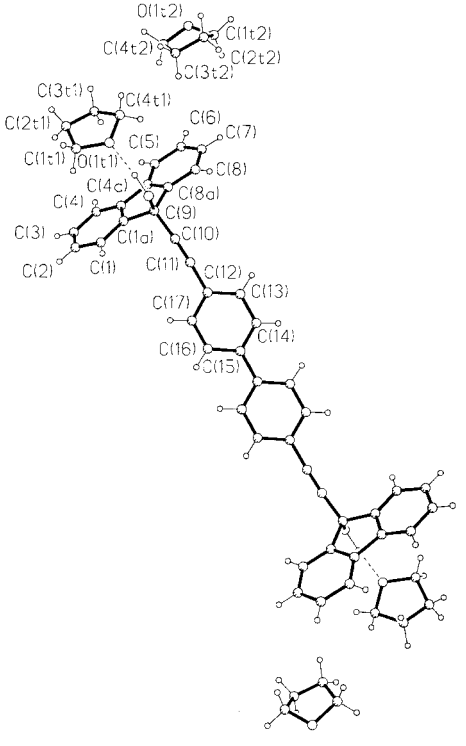


Figure 4. Perspective view of the stoichiometric host−guest unit in compound **10**·THF (1:4); the unique non-hydrogen atoms are labeled as in the text; solid and dashed lines represent covalent and hydrogen bonds, respectively

than the former ones. Nevertheless, refinement of the structural models was not straightforward with either of these two compounds, mostly depending on the dynamic or static disorder of the guest entities at room temperature. The atoms constituting the THF molecules in **10**·THF (1:4), particularly those of the space-filling guest, display lively vibrations. The average equivalent isotropic vibration amplitudes (U_{eq}) of the guest non-hydrogen atoms are 0.16[3] for the H-bonded T1 guest and 0.31[6] Å^2 for the space-filling T2 one, with the root mean square (rms) deviations around the arithmetic average values given in square brackets. The observed disorder in this compound could not be resolved to distinct disorder sites, however. On the contrary, two major disorder positions were revealed for each unique THF guest in **2**·THF (1:2) [Figure 2 (c), (d)], despite the fact that both guests (T1 and T2) are coordinated by either of hosts **2**A or **2**B through rather strong hydrogen bonds (Table 5). The mean values of U_{eq} of the partially occupied guest sites are 0.14[1] for T1, 0.15[2] for T′, 0.17[4] for T2, and 0.20[5] Å^2 for T′′. Interestingly enough, although the **2**·THF (1:2) crystals have denser packing, the average value of the calculated solvent-accessible volume for each guest molecule in the host framework of **2** is somewhat larger than in **10**·THF (1:4). Accordingly, there is 637.5 Å^3 free space for four THF guests (ca. 160 Å^3/molecule) between hosts **2** in **2**·THF (1:2), which proved to be enough to allow the guest molecules to take varying positions in different unit cells. On the other hand, the total solvent-accessible volume per unit cell in the host framework of **10**·THF (1:4), in which eight THF molecules reside, is 1165.5 Å^3 (ca. 146 Å^3/guest). It is worth mentioning that, in the latter case, the four H-bonded guests occupy only less

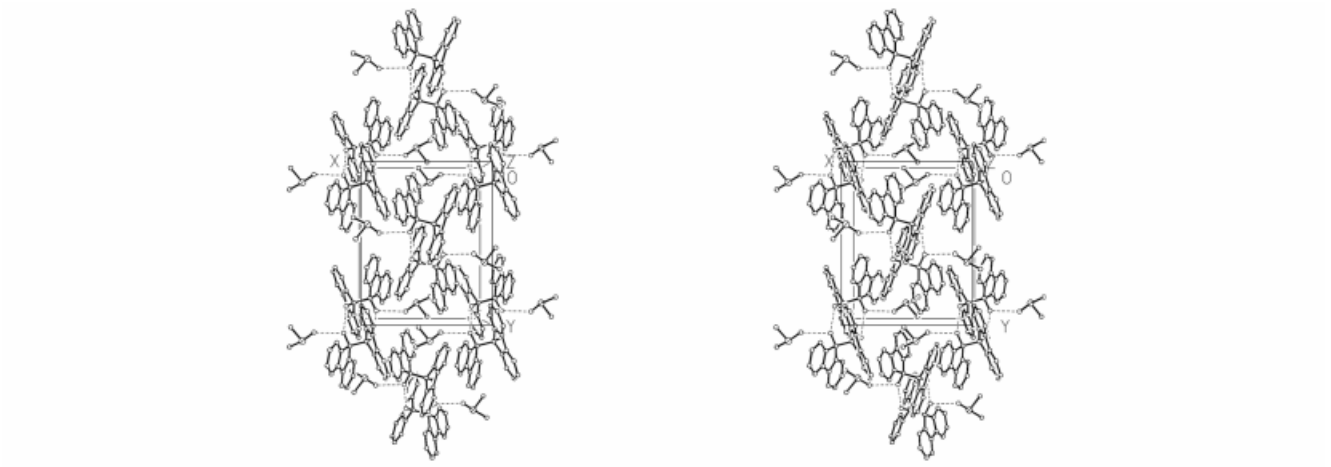


Figure 5. Stereopacking illustration of **1**·DMSO (1:1); solid and dashed lines represent covalent and hydrogen bonds, respectively; the H atoms are omitted for clarity

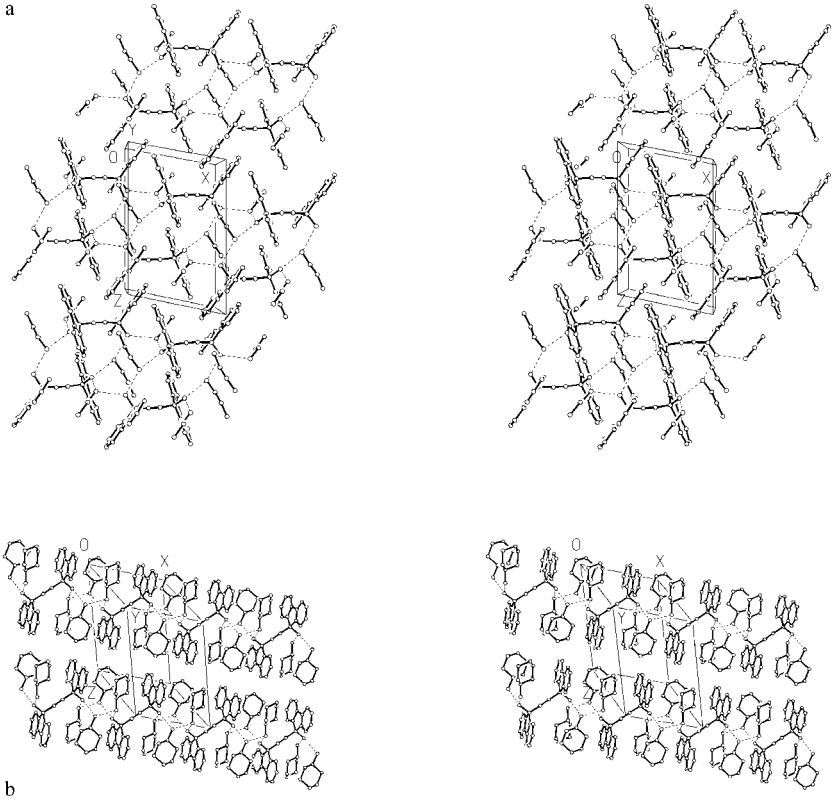


Figure 6. Stereopacking illustrations of **2**·1-PrOH (1:2) (a) and **2**·cyclohexylOH (1:4) (b); solid and dashed lines represent covalent and hydrogen bonds, respectively; the H atoms are omitted for clarity

than ca. 500 Å^3, while the remaining space of 667 Å^3 (ca. 167 Å^3/molecule) is large enough to allow high mobility for the weakly bound space-filling guests.

Molecule **8,** comprising a linear triphenylene group as spacer between the fluorenol moieties, is slightly shorter than host **10** (Table 4). Two crystal structures of **8**, one with acetone as guest (Figure 8) and one without a guest (Figure 9), were studied by X-ray diffraction. Although the solvent-free crystal has a higher space-group symmetry than the acetone inclusion compound (orthorhombic *Pbca* vs. monoclinic $P2_1/n$; Table 3), molecule **8** exhibits crystallographic inversion symmetry in **8**·acetone (1:4) but not in its solvent-free crystal (Table 4). The acetone inclusion compound (Figure 8) contains 1:2 H-bonded host−guest associates. The C(10)−C(9)−O(1)···O(1A1) torsion angle to the host-bonded A1 molecule is −159.4(1)°, indicating an approximate *trans* attachment for A1 to the linear triphenylene spacer unit. Packing of the inconveniently shaped 1:2

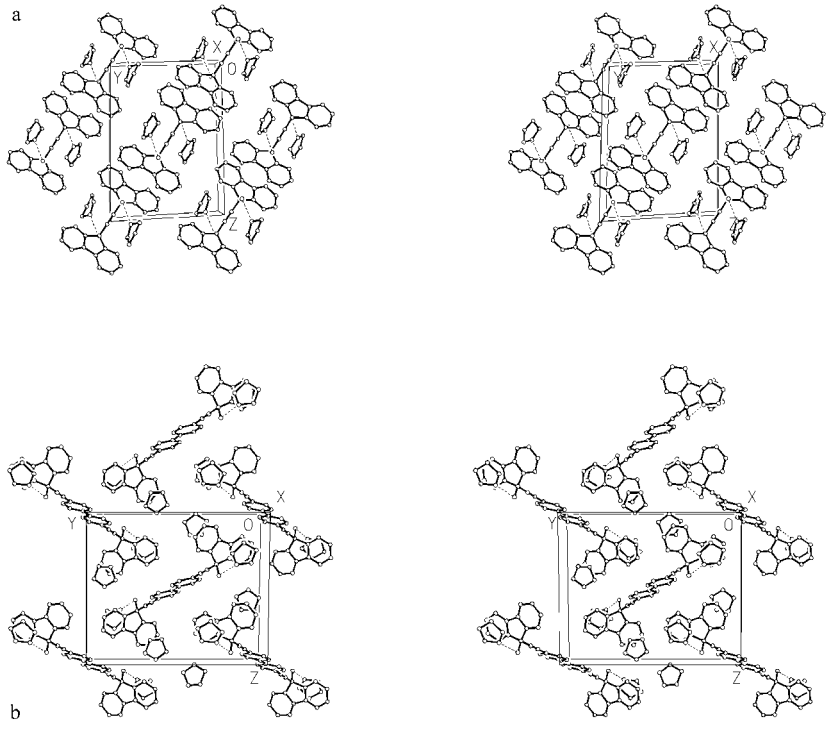


Figure 7. Stereopacking illustrations of compounds **2**·THF (1:2) (a) and **10**·THF (1:4) (b); solid and dashed lines represent covalent and hydrogen bonds, respectively; the minor guest disorder sites in (a) as well as the H-atom positions in both drawings are omitted for clarity

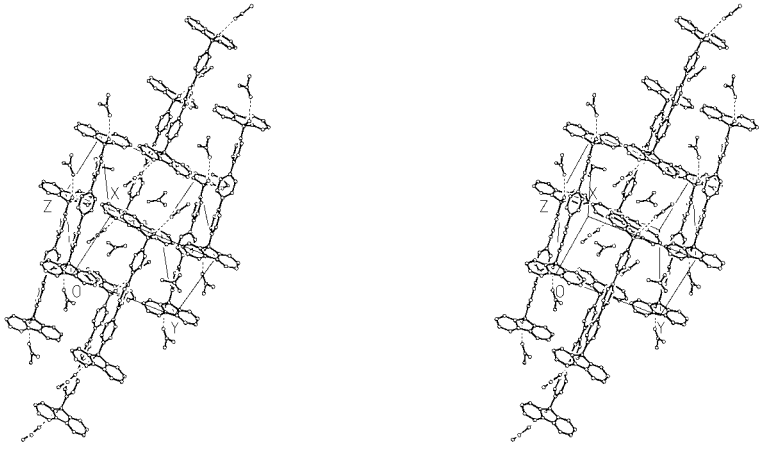


Figure 8. Stereopacking illustration of **8**·acetone (1:4); solid and dashed lines represent covalent and hydrogen bonds, respectively; the H atoms are omitted for clarity

supramolecular entities gives rise to holes of a total volume of 507 Å^3 in each unit cell, which are filled by eight guests [A2 molecules, cf. Figure 3 (b)], thus increasing the packing coefficient[61,62] to the acceptable value of 66.3%. Although the A1 molecules are coordinated to the host by ordinary O−H···O hydrogen bonds, whereas the A2 guests are trapped by lattice forces only, the atomic displacement parameters indicate comparable, rather modest mobility values for both acetone molecules at 170 K. The mean U_{eq} values of the guest non-hydrogen atoms are 0.06[2] for the H-bonded A1 and 0.07[2] Å^2 for the space-filling A2 molecule.

As can be seen, molecule **8** is also capable of forming stable crystals on its own (Figure 9). The remarkable feature of the crystal structure of compound **8** is the absence of O(H)···O hydrogen bonds between the molecules. This observation is similar to those made earlier in the solvent-free crystals of four 9-substituted 9-fluorenol host molecules.[58] These four crystal structures have demonstrated well that the presence of OH groups does not guarantee that

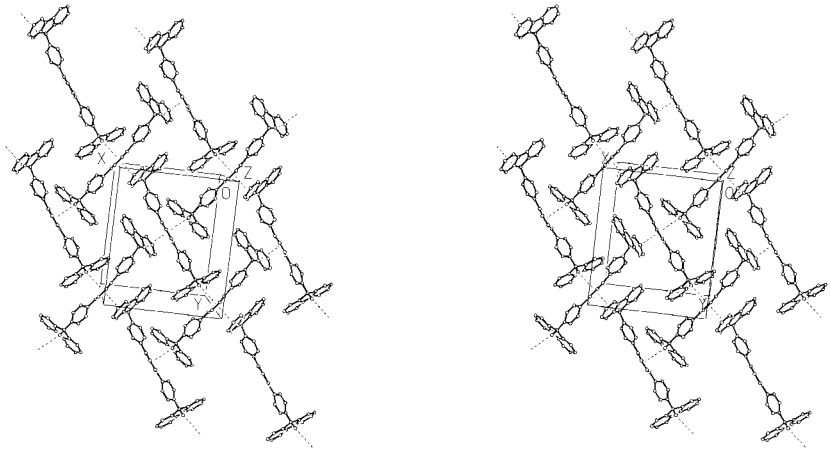


Figure 9. Stereopacking diagram of the solvent-free compound **8**; the H atoms are omitted for clarity; the shorter intermolecular O(−H)···π(aryl) connections (Table 5) are indicated by dotted lines

O−H···O bonding will occur. Hydrogen bonding will arise only if the H-bonded aggregates can achieve a packing of acceptable density. Accordingly, the 9-methylfluoren-9-ol molecules produce H-bonded tetramers linked through closed loops with full H-bond saturation, the 9-phenyl derivative forms H-bonded dimers without full H-bond saturation, whereas in the crystals of the 9-biphenyl and 9-naphthyl derivatives, weaker interactions of O−H···π(aryl) or van-der-Waals-type, respectively, connect the molecules to each other. Similarly to those in the 9-biphenylfluoren-9-ol compound, the OH groups in the solvent-free crystals of molecule **8** establish connections to the aryl π-electron clouds rather than the OH functions, and through these weaker but more flexible O−H···π(aryl) bonds (Table 5), two-dimensional endless supramolecular layers are created (Figure 9). Each molecule is involved in four such interactions with four other molecules, in two connections as proton donor, and in two others as proton acceptor. The two donor oxygen atoms are located on either side of the same phenyl ring, with shortest distances of 3.095(2) and 3.225(2) Å from O(1) and O(1′), respectively, to the attached ring plane. These distances are almost the same as the lengths of the corresponding O···π connections (Table 5) (π refers to the center of the phenyl ring), thus indicating that both donor oxygen atoms are directed towards the center of the acceptor aryl π-electron system.

Conclusions

A family of potential clathrate host molecules, containing two 9-hydroxy-9-fluorenyl or analogous terminal groups attached to linear oligoethynylene/phenylene spacer units of different lengths (**1**−**15**), has been designed and synthesized. Their abilities to form solid inclusion complexes were tested with a broad variety of solvents (25−28 different species), to yield 229 examples of solid inclusion compounds. X-ray diffraction analysis of six selected cocrystals indicated extensive involvement of the host alcoholic functions in the enclathration of smaller guest molecules with H-bond capability, in agreement with previous studies of some crystalline inclusion compounds of hosts **1**[40] and **3**.[51,52] Accordingly, recognition of guests with OH groups, such as propanols or cyclohexanol, by these diol hosts is characterized by closed H-bonded loops with full H-bond saturation. This interaction pattern is a consequence of the cooperativity of the alcoholic OH groups of both host and guest, simultaneously exhibiting good proton donor and acceptor capacity. As each host molecule is involved in at least two such loops, due to their bifunctionality, infinite H-bonded supramolecular ribbons are created in these alcoholic inclusion compounds. Nevertheless, as the size and shape of the guest alcohols and/or the host molecules varies, the host−guest stoichiometries may vary as well [cf. **2**·1-PrOH (1:2), **2**·cyclohexylOH (1:4), and **3**·2-PrOH (1:1)],[52] which may in turn affect the size of the H-bonded loops and/or the organization of the ribbons. Guests with dominating proton acceptor character, such as DMSO, THF, acetone, or lutidines,[51] are usually coordinated by these diol host molecules through single hydrogen bonds. However, DMSO and acetone have also been observed to function as double-acceptor guest molecules, when enclathrated by host **3**, for example,[52] thus giving rise to endless chains of alternating H-bonded host and guest molecules. Inclusion of single-acceptor guests, on the other hand, results in distinct supramolecular host−guest entities with 1:2 or sometimes with 2:2 stoichiometry, in the latter case through inter-host H bonds between the 1:1 host−guest units. These building blocks can either produce a packing of acceptable density on their own [**1**·DMSO (1:1) and **2**·THF (1:2)], or form crystals by including additional guests to fill the voids between the hydrogen-bonded entities [**8**·acetone (1:4) and **10**·THF (1:4)]. Increasing length of the spacer unit between the fluorenol moieties seems to favor inclusion of space-filling guests in the crystal, thus often resulting in a relatively high guest content, with a 1:4 host−guest ratio. Compound **8**, on the other hand, also proved to be able to form stable crystals without inclusion of a guest and without in-

termolecular O−H···O bonds. Instead, a network of O−H···π(aryl) bonds links the diol molecules into endless supramolecular layers.

Experimental Section

General: Melting points (uncorrected): Kofler melting point microscope. IR: Perkin−Elmer FT-IR 1600. ^{1}H NMR (internal standard TMS): Bruker WH 90 and MSL 300. ^{13}C NMR (internal standard TMS): Bruker WM 250 and MSL 300. MS: A.E.I. MS 50, Kratos FAB-MS Concept 1H and Hewlett−Packard GC-MS 5890. Elemental analyses: Heraeus CHN rapid analyzer. Column chromatography: Silica gel (63−100 μm), Woelm. Organic solvents were purified by standard procedures. Inclusion compounds (solvates; for composition see Tables 1 and 2), where obtained, were desolvated by heating the recrystallized material (clathrate) in vacuo (0.1 Torr) for 12 h at 120 °C. Starting compounds fluorenone (**16a**), xanthone (**18a**) thioxanthone (**18b**), dibenzosuberone (**18c**), dibenzosuberenone (**18d**), *p*-dibromobenzene, and 4,4′-dibromobiphenyl were purchased from Janssen. 2,7-Di-*tert*-butylfluorenone (**16b**),[36,63] 2,7-dichlorofluorenone (**16c**),[46] 2,7-dibromo-fluorenone (**16d**),[36,64] and 4,4′′-dibromo-1,1′:4′,1′′-terphenyl[65] were prepared according to literature procedures.

General Procedure. − Synthesis of 9-Ethynylfluoren-9-ols 17a and 17b:[47,48] A solution of ethylmagnesium bromide, prepared from magnesium (12.0 g, 0.50 mol) and bromoethane (41.9 mL, 0.55 mol) in dry THF (150 mL), was added to dry THF (200 mL) saturated with dried (H_2SO_4) gaseous ethyne below 40 °C, while additional ethyne gas was passed into the reaction mixture. After this had been stirred for 0.5 h, a solution of the appropriate fluorenone **16** (0.36 mol) in dry THF (300 mL) was added. The mixture was heated to reflux for 2 h, then cooled and quenched with saturated aqueous NH_4Cl solution. The ethereal phase was separated and the aqueous phase was extracted with diethyl ether. The combined organic phases were dried (Na_2SO_4) and the solvents were evaporated. Details for purification and data of the individual compounds are given below.

9-Ethynylfluoren-9-ol (17a): Fluorenone **16a** was used. The oily residue was extracted with refluxing *n*-hexane. The product precipitated on cooling to yield 45.3 g (61%) of a colorless powder. M.p. 108−109 °C (ref.[66] 107−108 °C).

2,7-*tert*-Butyl-9-ethynylfluoren-9-ol (17b): Fluorenone **16b** was used. The oily residue was extracted with toluene. The product precipitated on cooling to yield 61.9 g (54%) of a pale yellow powder. M.p. 158−159 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.33 (s, 18 H, *t*Bu), 2.47 (s, 1 H, C≡CH), 2.55 (s, 1 H, OH), 7.27−7.69 (m, 6 H, Ar-H. $C_{23}H_{26}O$ (GC MS): calcd. 318.46; found 318 [M^+].

9,9′-Bifluorenyl-9,9′-diol (1): This compound was produced from **16a**, iodine, and magnesium in benzene/diethyl ether (3:1) according to ref.[41] Recrystallization from MeOH and decomposition of the clathrate yielded 85% of a colorless powder. M.p. 190−192 °C (ref.[40] 190−192 °C).

9,9′-(Ethyne-1,2-diyl)bis(fluoren-9-ol) (2): In the procedure for preparation of **17a**, the residue that did not dissolve in *n*-hexane was extracted with refluxing THF and cooled to give colorless crystals of the clathrate. Recrystallization from toluene yielded 6.6 g (9.5%) of a colorless powder. M.p. 244−245 °C (ref.[67] 238 °C).

9,9′-(1,4-Phenylene)bis(fluoren-9-ol) (3): This compound was produced from *p*-dibromobenzene and fluorenone (**16a**) by a Grignard reaction and the usual workup.[42] Recrystallization from EtOH and decomposition of the clathrate yielded 38% of a colorless powder. M.p. 262−263 °C (ref.[68] 263−265 °C).

General Procedure. − Synthesis of Host Compounds 4−8 and 12−15:[43] The appropriate ketone (**16a−d** or **18a−d**) (100 mmol) was added in portions as a solid to a stirred solution of the corresponding aryllithium compound (50 mmol), prepared from the respective aryl dibromide (4,4′-dibromobiphenyl or 4,4′′-dibromo-1,1′:4′,1′′-terphenyl) (50 mmol) and *n*BuLi (1.6 M in hexane, 62.7 mL, 100 mmol) in diethyl ether (125 mL), at 0 °C and under argon. The mixture was heated to reflux for 15 h, then cooled and quenched with saturated aqueous NH_4Cl solution. Details for workup and purification, together with the data for the individual compounds, are given below.

9,9′-(Biphenyl-4,4′-diyl)bis(fluoren-9-ol) (4): Biphenyl-4,4′-diyldilithium (from 4,4′-dibromobiphenyl and *n*BuLi) and **16a** were used. The solid precipitate was collected, treated with refluxing diethyl ether, cooled to room temp., and filtered. Recrystallization from toluene yielded 17.7 g (69%) of a colorless powder. M.p. > 300 °C. IR (KBr): $\tilde{\nu}$ = 3630 (OH), 3100 (Ar−H), 3000−2900 (C−H), 1500 (Ar), 1460, 1410, 1340, 1325, 1215, 1190, 1120, 1050, 1020, 970, 925, 880, 830, 780, 770, 750, 690, 650, 620, 600, 520, 475 cm^{-1}. ^{1}H NMR (90 MHz, $CDCl_3$): δ = 7.15−7.76 (m, 20 H, Ar-H). ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 82.5, 120.2, 125.7, 126.3, 128.1, 128.6, 138.5, 139.2, 144.2, 151.3 (11 C). $C_{38}H_{26}O_2$ (HR-MS): calcd. 514.1926; found 514.1924.

2,2′,7,7′-Tetra-*tert*-butyl-9,9′-(biphenyl-4,4′-diyl)bis(fluoren-9-ol) (5): Biphenyl-4,4′-diyldilithium (from 4,4′-dibromobiphenyl and *n*BuLi) and **16b** were used. The solid precipitate was collected. The ethereal phase was separated. The water phase was extracted with diethyl ether and the combined ethereal phases were dried ($MgSO_4$). Evaporation of the solvent and recrystallization of the solid products from toluene yielded 10.9 g (29.5%) of a colorless powder. M.p. > 300 °C. IR (KBr): $\tilde{\nu}$ = 3550 , 3435 (OH), 3030 (Ar−H), 2960, 2900, 2860 (C−H), 1610, 1555 (Ar), 1475, 1390, 1365 (*t*Bu), 1260 (OH), 1200, 1170, 1130 (C−O), 1025, 890, 785, 743, 643, 520 cm^{-1}. ^{1}H NMR (90 MHz, [D$_6$]DMSO): δ = 1.17 (s, 36 H, *t*Bu), 6.26 (s, 2 H, OH), 6.95−7.79 (m, 20 H, Ar-H). ^{13}C NMR (62.89 MHz, [D$_6$]DMSO): δ = 31.2, 34.6, 81.0, 119.4, 121.0, 125.8, 126.0, 136.6, 137.9, 144.8, 150.3, 151.3 (12 C). $C_{54}H_{58}O_2$ (HR-MS): calcd. 738.4422; found 738.4456.

2,2′,7,7′-Tetrachloro-9,9′-(biphenyl-4,4′-diyl)bis(fluoren-9-ol) (6): Biphenyl-4,4′-diyldilithium (from 4,4′-dibromobiphenyl and *n*BuLi) and **16c** were used. The reaction solvents were evaporated to dryness and the remaining solid was treated with refluxing toluene and then with water. Extraction with refluxing chloroform and column chromatography of the concentrate (SiO_2; eluent: chloroform; R_f = 0.2) yielded 4.4 g (13.5%) of a colorless powder. M.p. > 300 °C. IR (KB_r): $\tilde{\nu}$ = 3551 (OH), 3100−3000 (Ar−H), 1632 (Ar), 1492, 1450, 1411, 1344, 1247 (OH), 1169, 1072 (C−O), 1036 cm^{-1}. ^{1}H NMR (90 MHz, [D$_6$]DMSO): δ = 7.19−7.32 (m, 10 H, Ar-H), 7.41−7.55 (m, 7 H, Ar-H), 7.85−7.92 (d, 3 H, Ar-H). ^{13}C NMR (62.89 MHz, [D$_6$]DMSO): δ = 82.3, 122.4, 124.8, 125.6, 126.7, 128.9, 132.9, 137.0, 138.8, 142.8, 153.1 (11 C). $C_{38}H_{22}Cl_4O_2$ (HR-MS): calcd. 650.0366; found 650.0367.

2,2′,7,7′-Tetrabromo-9,9′-(biphenyl-4,4′-diyl)bis(fluoren-9-ol) (7): Biphenyl-4,4′-diyldilithium (from 4,4′-dibromobiphenyl and *n*BuLi) and **16d** were used. Workup and purification were carried out as given for **6** (R_f = 0.32) to yield 4.9 g (12%) of a colorless powder. M.p. > 300 °C. IR (KBr): $\tilde{\nu}$ = 3540 (OH), 3025−300 (C−H), 1580, 1500 (Ar), 1450, 1402, 1350 (OH), 1250, 1206, 1165

(C−O), 1035, 928, 876, 814, 751 cm^{-1}. ^1H NMR (90 MHz, [D_6]DMSO): δ = 6.62−6.79 (d, 2 H, Ar-H), 7.12−8.06 (m, 17 H, Ar-H), 8.27−8.42 (t, 1 H, Ar-H). ^{13}C MNR (62.89 MHz, [D_6]DMSO): δ = 82.3, 121.4, 122.7, 125.6, 126.7, 127.6, 131.8, 137.4, 138.8, 142.7, 153.2 (11 C). $C_{38}H_{22}Br_4O_2$ (FAB-MS, *m*NBA + NaOAc): calcd. 830.1720; found 830.

9,9′-(1,1′:4,1′′-Terphenyl-4,4′′-diyl)bis(fluoren-9-ol) (8): 1,1′:4′,1′′-Terphenyl-4,4′′-diyldilithium (from 4,4′′-dibromo-1,1′:4′,1′′-terphenyl and *n*BuLi) and **16a** were used. The solid precipitate was collected and washed with diethyl ether. Recrystallization from toluene yielded 5.4 g (18.5%) of a colorless powder. M.p. 260−262 °C. IR (KBr): ṽ = 3544, 3348 (OH), 3030. 2974, 2887 (C−H), 1600 (Ar), 1480, 1445, 1384, 1289 (OH), 1168 (C−O), 1036, 918, 812, 735, 644, 513 cm^{-1}. ^1H NMR (90 MHz, $CDCl_3$): δ = 6.35 (s, 2 H, OH), 6.89−7.91 (m, 28 H, Ar-H). ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 76.4, 120.2, 124.7, 125.8, 126.3, 127.0, 127.2, 128.1, 128.6, 129.0, 131.9, 138.8, 139.3, 144.4, 151.3 (15 C). $C_{44}H_{30}O_2$ (HR-MS): calcd. 590.2238; found 590.2249.

9,9′-(Biphenyl-4,4′-diyl)bis(xanthen-9-ol) (12): Biphenyl-4,4′-diyldilithium (from 4,4′-dibromobiphenyl and *n*BuLi) and **18a** were used. The solid precipitate was collected, treated with methanol, and filtered. Recrystallization from DMF yielded 19.11 g (70%) of a colorless powder. M.p. > 300 °C. IR (KBr): ṽ = 3505 (OH), 3035 (C−H), 1603 (Ar), 1450, 1375 (OH), 1305, 1237, 1170 (C−O), 1100, 1001, 912, 875, 814, 748, 628, 589, 512 cm^{-1}. ^1H NMR (90 MHz, [D_6]DMSO): δ = 6.60 (s, 2 H, OH), 7.00−7.15 (m, 4 H, Ar-H), 7.15−7.50 (m, 20 H, Ar-H). ^{13}C NMR (62.89 MHz, [D_6]DMSO): δ = 74.6, 131.0, 138.4, 139.5, 140.0, 142.5, 142.8, 145.25, 145.47, 145.54, 153.0, 155.9 (12 C). $C_{38}H_{26}O_2$ (HR-MS): calcd. 546.1824; found 546.1828.

9,9′-(Biphenyl-4,4′-diyl)bis(thioxanthen-9-ol) (13): Biphenyl-4,4′-diyldilithium (from 4,4′-dibromobiphenyl and *n*BuLi) and **18b** were used. Workup and purification were carried out as given for **12** to yield 22.8 g (79%) of a colorless powder. M.p. > 290 °C (dec.). IR (KBr): ṽ = 3514 (OH), 3051 (C−H), 1632 (Ar), 1492, 1456, 1263 (OH), 1153 (C−O), 1062, 899, 863, 815, 758, 738, 631 cm^{-1}. ^1H NMR (90 MHz, [D_6]DMSO): δ = 6.75−6.93 (t, 5 H, Ar-H), 7.22−7.48 (m, 15 H. Ar-H), 7.97−8.07 (m, 4 H, Ar-H). ^{13}C NMR (62.89 MHz, [D_6]DMSO): δ = 75.1, 125.9, 126.1, 126.47, 126.63, 127.2, 130.3, 138.5, 140.6, 143.4 (10 C). $C_{38}H_{26}O_2S_2$ (HR-MS): calcd. 578.1366; found 578.1362.

5,5′-(Biphenyl-4,4′-diyl)bis(10,11-dihydro-5*H*-dibenzo[*a*,*d*]cyclohepten-5-ol) (14): Biphenyl-4,4′-diyldilithium (from 4,4′-dibromobiphenyl and *n*BuLi) and **18c** were used. The solid precipitate was collected and treated with refluxing diethyl ether. Recrystallization from toluene and decomposition of the clathrate yielded 11.1 g (39%) of a colorless powder. M.p. 237−240 °C. IR (KBr): ṽ = 3450 (OH), 3100 (C−H), 3000−2900 (C−H), 1620 (Ar), 1500, 1370 (OH), 1130 (C−O), 835, 760 cm^{-1}. ^1H NMR (90 MHz, $CDCl_3$): δ = 2.20−2.36 (s, 2 H, OH), 2.52−3.18 (m, 8 H, CH_2), 6.86−7.46 (m, 21 H, Ar-H), 7.90−8.15 (m, 3 H, Ar-H). ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 31.8, 77.7, 125.4, 125.9, 126.2, 127.2, 130.2, 137.4, 138.3, 144.5, 147.5 (11 C). $C_{42}H_{34}O_2$ (HR-MS): calcd. 570.2550; found 570.2550.

5,5′-(Biphenyl-4,4′-diyl)bis(5*H*-dibenzo[*a*,*d*]cyclohepten-5-ol) (15): Biphenyl-4,4′-diyldilithium (from 4,4′-dibromobiphenyl and *n*BuLi) and **18d** were used. Workup and purification was carried out as given for **14** to yield 10.2 g (36%) of a colorless powder. M.p. 279−282 °C. IR (KBr): ṽ = 3620 (OH), 3100−3090 (C−H), 1650 (Ar), 1500, 1350 (OH), 1130 (C−O), 840, 765, 700 cm^{-1}. ^1H NMR (90 MHz, [D_6]DMSO): δ = 6.32 (s, 2 H, OH), 6.41−6.55 (d, 4 H, CH=CH), 6.67 (s, 4 H, Ar-H), 7.07−7.40 (m, 12 H, Ar-H), 7.40−7.55 (m, 4 H, Ar-H), 8.01−8.15 (d, 4 H, Ar-H). ^{13}C NMR (62.89 MHz, [D_6]DMSO): δ = 77.2, 124.9, 125.1, 126.4, 127.3, 127.8, 128.3, 131.2, 133.0, 138.2, 143.0, 144.6 (12 C). $C_{42}H_{30}O_2$ (HR-MS): calcd. 566.2238; found 566.2245.

General Procedure. − Synthesis of Host Compounds 9−11:[69,70] A solution of the appropriate aryl dibromide (10 mmol) and of the corresponding ethynyl compound (**17a, 17b**) (22 mmol) in triethylamine/toluene (2:1) was degassed with argon. The catalyst, comprising palladium(II) acetate (25 mg), triphenylphosphane (75 mg), and copper(I) iodide (25 mg), was added and the mixture was refluxed for 5 h. After cooling down to room temperature, the solid (catalyst and triethylamine hydrobromide) was filtered off and washed with diethyl ether (100 mL). The solvent was removed and the residue was taken up in diethyl ether or chloroform (200 mL). The extract was washed with 10 % aqueous hydrochloric acid, water, saturated aqueous sodium bicarbonate, and water, in that sequence, and dried (Na_2SO_4), and the solvents were evaporated. Details for workup and purification, together with the data for the individual compounds, are given below.

9,9′-[1,4-Phenylenebis(ethyne-2,1-diyl)]bis(fluoren-9-ol) (9): 1,4-Dibromobenzene and **17a** were used. Recrystallization from ethanol and decomposition of the clathrate yielded 4.2 g (87%) of an off-white powder. M.p. 269−271 °C. IR (KBr): ṽ = 3472 (OH), 3065, 3044 (C−H), 2228 (C≡C), 1616, 1511 (Ar), 1448 (OH), 1060 (C−O), 836 cm^{-1} (1,4-disubst. Ar). ^1H NMR (300 MHz, $CDCl_3$): δ = 2.56 (s, 2 H, OH), 7.26−7.74 (m, 20 H, Ar-H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 75.2 (C−OH), 82.6 (C≡C), 90.9 (C≡C), 120.3, 122.6, 124.4, 128.6, 129.8, 131.7, 139.1, 147.1 (8 C, CH resp. Cq). $C_{36}H_{22}O_2$ (486.57): calcd. C 89.61, H 4.60; found C 89.84, H 4.49.

9,9′-[Biphenyl-4,4′-diylbis(ethyne-2,1-diyl)]bis(fluoren-9-ol) (10): 4,4′-Dibromobiphenyl and **17a** were used. Recrystallization from acetone/toluene (1:1) yielded 4.7 g (80%) of a pale brownish powder. M.p. 215−216 °C. IR (KBr): ṽ = 3437 (OH), 3072, 3044 (C−H), 2221 (C≡C), 1609, 1497 (Ar), 1448 (OH), 1047 (C−O), 829 cm^{-1} (1,4-disubst. Ar). ^1H NMR (300 MHz, $CDCl_3$): δ = 2.59 (s, 2 H, OH), 7.25−7.79 (m, 24 H, Ar-H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 75.3 (C-OH), 82.9 (C≡C), 89.9 (C≡C), 120.2, 121.7, 124.4, 126.7, 128.6, 129.7, 132.4, 139.2, 140.2, 147.2 (10 C, CH and C_q). $C_{42}H_{26}O_2$ (562.67): calcd. C 89.66, H 4.66; found C 89.34, H 4.45.

2,2′,7,7′-Tetra-*tert*-butyl-9,9′-[biphenyl-4,4′-diylbis(ethyne-2,1-diyl)]bis(fluoren-9-ol) (11): 4,4′-Dibromobiphenyl and **17b** were used. Recrystallization from chloroform yielded 4.7 g (60%) of a pale yellowish powder. M.p. 185−186 °C. IR (KBr): ṽ = 3452 (OH), 3079, 3058 (C−H), 2959 (*t*Bu), 2221 (C≡C), 1630 (Ar), 1443 (OH), 1391, 1363 (*t*Bu), 1058 (C−O), 822 cm^{-1} (1,4-disubst. Ar). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.35 (s, 36 H, *t*Bu), 2.55 (s, 2 H, OH), 7.25−7.80 (m, 20 H, Ar-H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 31.5 (CH_3), 35.1 [C-(CH_3)$_3$], 75.9 (C-OH), 82.8 (C≡C), 90.5 (C≡C), 119.5, 121.3, 122.0, 126.7, 127.8, 132.4, 136.5, 140.2, 147.4, 151.8 (10 C, CH and C_q). $C_{58}H_{58}O_2$ (787.09): calcd. C 88.50, H 7.43; found C 87.96, H 7.29.

Crystalline Inclusion Compounds: The appropriate host compound was dissolved with heating in a minimum amount of the respective guest solvent. After this had stood for 12 h at room temperature, the crystals that had formed were collected, washed with diethyl ether, and dried (1 h, 15 Torr, room temp.). Host−guest stoichiometric ratios were determined by ^1H NMR integration. Data for each compound are given in Tables 1 and 2.

Crystallography: The single crystals taken out of the mother liquors for X-ray diffraction analysis were immediately coated with epoxy glue in order to prevent possible solvent evaporation. Intensity data were collected with an STOE Imaging Plate Detection System,[71] in most cases at low temperature (193 ± 2 K). Nevertheless, a Siemens P4/RA diffractometer equipped with a high-intensity rotating anode, operating at room temperature, had to be used for compound **10**·THF (1:4) because of the rather small crystal size (Table 3). Moreover, although three low-temperature data sets were collected from three different crystals of **2**·THF (1:2), and the structure could be solved by using these data (193 ± 2 K), the refinement calculations in all three cases yielded unusually high crystallographic R values [$wR(F^2) > 30\%$; $R(F) > 15\%$], due to relatively high mosaicity and hence modest data quality. A fourth set of data collection at room temperature yielded data with considerably lower R_{int} and much better wR/R values for the refined structure model. Hence, the results presented here for this compound (Table 3) are based on the room-temperature data. The net intensities were corrected for Lorentz and polarization effects. Further information concerning crystal data and data collection is summarized in Table 3.[72] Application of direct methods[73] yielded preliminary structure models, which were then completed and refined, using the F^2 values of all independent reflections.[74] The non-hydrogen atoms and disorder sites were refined together with their anisotropic atomic displacement parameters in all compounds, whereas the treatment of the hydrogen atoms varied somewhat between the different structures. The hydroxy H atoms were located from difference electron density (Δρ) maps in all cases, whereas the positions of carbon-bonded H atoms were either deduced from Δρ maps [**1**·DMSO (1:1), **2**·cyclohexylOH (1:4), **8** (guest free)] or calculated [**2**·1-PrOH (1:2), **2**·THF (1:2), **8**·acetone (1:4), **10**·THF (1:4)] by using geometric evidence.[74] The hydrogen positions were refined together with their isotropic displacement parameters (U_{iso}) in **1**·DMSO (1:1) and **2**·cyclohexylOH (1:4), whereas only the U_{iso} parameters were refined for the H atoms in compounds **8**·acetone (1:4), **8** (guest-free), and **10**·THF (1:4). In the remaining two compounds, **2**·THF (1:2) and **2**·1-PrOH (1:2), the H atoms/disorder sites were given 1.2 or 1.5 times the U_{iso} value of their parent non-hydrogen atoms. The space-filling THF guest in **10**·THF (1:4) [i.e., the T2 guest without H-bond connection to the host], and both disordered guests in **2**·THF (1:2), had to be refined with a few distance constraints in order to obtain acceptable geometries for them. Moreover, the acetone methyl groups in **8**·acetone (1:4) were treated as rigid groups with free rotation around the $C-C_{methyl}$ bond.[74] Final crystallographic R values and details of the refinement calculations are shown in Table 3.

Acknowledgments

Financial support by the Deutsche Forschungsgemeinschaft (DFG), the Fonds der Chemischen Industrie, the Swedish National Science Research Council (NFR), and the Faculty of Mathematics and Natural Sciences of Stockholm University is gratefully acknowledged. This work is part of the Graduate School Program (GRK 208) of the TU Bergakademie Freiberg, supported by the DFG.

[1] J. W. Steed, J. L. Atwood, *Supramolecular Chemistry*, Wiley, Chichester, **2000**.
[2] Eds.: R. Bishop, D. D. MacNicol, F. Toda, *Comprehensive Supramolecular Chemistry*, vol. 6 ("Solid-state Supramolecular Chemistry − Crystal Engineering"), Elsevier, Oxford, **1996**.
[3] Ed.: G. R. Desiraju, *The Crystal as a Supramolecular Entity*, vol. 2 ("Perspectives in Supramolecular Chemistry"), Wiley, Chichester, **1996**.
[4] E. Weber, in *Kirk-Othmer Encyclopedia of Chemical Technology* (Ed.: J. I. Kroschwitz), 4th ed., Wiley, New York, **1995**, vol. 14, p. 122.
[5] H.-B. Bürgi, J. Hulliger, P. J. Langley, *Curr. Opin. Solid State Mater. Sci.* **1998**, *3*, 425.
[6] P. J. Langley, J. Hulliger, *Chem. Soc. Rev.* **1999**, *28*, 279.
[7] T. Müller, J. Hulliger, W. Seichter, E. Weber, T. Weber, M. Wübbenhorst, *Chem. Eur. J.* **2000**, *6*, 54.
[8] Eds.: J. L. Atwood, J. E. D. Davies, D. D. MacNicol, *Inclusion Compounds*, vol. 1−3, Academic Press, London, **1994**; vol. 4−5, Oxford University Press, Oxford, **1991**.
[9] Ed.: E. Weber, *Molecular Inclusion and Molecular Recognition − Clathrates I and II* (Top. Curr. Chem., vol. 140 and 149), Springer-Verlag, Berlin, Heidelberg, **1987** and **1988**.
[10] Ed.: Y. Ohashi, *Reactivity in Molecular Crystals*, VCH-Verlagsgesellschaft, Weinheim, **1993**.
[11] F. Toda, *Acc. Chem. Res.* **1995**, *28*, 480.
[12] F. Dickert, A. Haunschild, *Adv. Mater.* **1993**, *5*, 887.
[13] D. Meinhold, W. Seichter, K. Köhnke, J. Seidel, E. Weber, *Adv. Mater.* **1997**, *9*, 958.
[14] J. Reinbold, K. Cammann, E. Weber, T. Hens, C. Reutel, *J. Prakt. Chem.* **1999**, *341*, 252.
[15] F. Toda, *Supramol. Chem.* **1995**, *6*, 159.
[16] P. P. Korkas, E. Weber, M. Czugler, G. Náray-Szabó, *J. Chem. Soc., Chem. Commun.* **1995**, 2229.
[17] E. Weber, O. Hager, C. Foces-Foces, A. L. Llamas-Saiz, *J. Incl. Phenom.* **1999**, *34*, 197.
[18] G. R. Desiraju, *Crystal Engineering* (Mat. Sci. Monogr., vol. 54), Elsevier, Amsterdam, **1989**.
[19] Ed.: E. Weber, *Design of Organic Solids* (Top. Curr. Chem., vol. 198), Springer-Verlag, Berlin, Heidelberg, **1998**.
[20] A. Anthony, G. R. Desiraju, R. K. R. Jetti, S. S. Kudura, N. N. L. Madhavi, A. Nangia, R. Thaimattam, V. R. Thalladi, *Cryst. Eng.* **1998**, *1*, 1.
[21] E. Weber, *J. Mol. Graphics* **1989**, *7*, 12.
[22] R. Bishop, *Chem. Soc. Rev.* **1996**, *25*, 311.
[23] F. Toda, see ref.[2] vol. 6, p. 465.
[24] E. Weber, see ref.[2] vol. 6, p. 535.
[25] F. Toda, D. L. Ward, H. Hart, *Tetrahedron Lett.* **1981**, *22*, 3865.
[26] H. Hart, L. T. W. Lin, D. L. Ward, *J. Am. Chem. Soc.* **1984**, *106*, 4043.
[27] E. Weber, K. Skobridis, A. Wierig, L. R. Nassimbeni, L. Johnson, *J. Chem. Soc., Perkin Trans. 2* **1992**, 2123.
[28] E. Weber, K. S. Skobridis, A. Wierig, S. Stathi, L. R. Nassimbeni, M. L. Niven, *Angew. Chem.* **1993**, *105*, 616; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 606.
[29] L. J. Barbour, S. A. Bourne, M. R. Caira, L. R. Nassimbeni, E. Weber, K. Skobridis, A. Wierig, *Supramol. Chem.* **1993**, *1*, 331.
[30] S. A. Bourne, L. R. Nassimbeni, M. L. Niven, E. Weber, A. Wierig, *J. Chem. Soc., Perkin Trans. 2* **1994**, 1215.
[31] M. R. Caira, L. R. Nassimbeni, N. Winder, E. Weber, A. Wierig, *Supramol. Chem.* **1994**, *4*, 135.
[32] E. Weber, T. Hens, T. H. Brehmer, I. Csöregh, *J. Chem. Soc., Perkin Trans. 2* **2000**, 235.
[33] M. R. Caira, A. Coetzee, L. R. Nassimbeni, E. Weber, A. Wierig, *J. Chem. Soc., Perkin Trans. 2* **1995**, 281.
[34] M. R. Caira, A. Coetzee, L. R. Nassimbeni, E. Weber, A. Wierig, *J. Chem. Soc., Perkin Trans. 2* **1997**, 237.
[35] E. Weber, A. Wierig, K. Skobridis, *J. Prakt. Chem.* **1996**, *338*, 553.
[36] E. Weber, N. Dörpinhaus, I. Csöregh, *J. Chem. Soc., Perkin Trans. 2* **1990**, 2167.
[37] I. Csöregh, E. Weber, L. R. Nassimbeni, O. Gallardo, N. Dörpinhaus, A. Ertan, S. A. Bourne, *J. Chem. Soc., Perkin Trans. 2* **1993**, 1775.
[38] I. Csöregh, O. Gallardo, E. Weber, N. Dörpinghaus, *J. Chem. Soc., Perkin Trans. 2* **1994**, 303.

[39] I. Csöregh, O. Gallardo, E. Weber, S. A. Bourne, N. Dörpinghaus, *Bull. Chem. Soc. Jpn.* **1995**, *68*, 3111.
[40] L. J. Barbour, M. R. Caira, L. R. Nassimbeni, A. Wierig, E. Weber, *Supramol. Chem.* **1995**, *5*, 153.
[41] M. Gomberg, W. E. Bachmann, *J. Am. Chem. Soc.* **1927**, *49*, 236.
[42] K. Nützel, *Methoden Org. Chem. (Houben-Weyl)*, **1973**, vol. XIII/2a, p. 47.
[43] U. Schöllkopf, *Methoden Org. Chem. (Houben-Weyl)*, **1970**, vol. XIII/1, p. 87.
[44] K. Sonogashira, Y. Tohda, N. Hagihara, *Tetrahedron Lett.* **1975**, 4467.
[45] Y. Sprinzak, *J. Am. Chem. Soc.* **1958**, *80*, 5449.
[46] F. Dewhurst, P. K. J. Shah, *J. Chem. Soc., Sect. C* **1970**, 1737.
[47] L. Skatebol, E. R. H. Jones, M. C. Whiting, *Org. Synth. Coll. Vol.* **1963**, 4, 792.
[48] L. Brandsma, H. D. Verkruijsse, *Synthesis of Acetylenes, Allenes and Cumulenes*, Elsevier, Amsterdam, **1981**.
[49] E. Weber, T. Hens, Q. Li, T. C. W. Mak, *Eur. J. Org. Chem.* **1999**, 1115.
[50] E. Weber, see ref.[9], vol. 140, p. 1.
[51] M. R. Caira, L. R. Nassimbeni, D. Vujovic, E. Weber, A. Wierig, *Struct. Chem.* **1999**, *10*, 205.
[52] M. R. Caira, L. R. Nassimbeni, D. Vujovic, E. Weber, *J. Chem. Soc., Perkin Trans. 2* **2001**, 861.
[53] G. M. Sheldrick, *XP Molecular Graphics* in the *SHELXTL/PC program package* (version 4.3), Siemens Analytical X-ray Instruments, Madison, WI, **1992**.
[54] M. Nardelli, *Comput. Chem.* **1983**, *7*, 95 (updated 1995); and references therein.
[55] D. Cremer, J. A. Pople, *J. Am. Chem. Soc.* **1975**, *97*, 1354.
[56] M. C. Etter, *Acc. Chem. Res.* **1990**, *23*, 120.
[57] J. Bernstein, R. E. Davis, L. Shimoni, N.-L. Chang, *Angew. Chem.* **1995**, *107*, 1689; *Angew. Chem. Int. Ed. Eng.* **1995**, *34*, 1555; and references therein.
[58] I. Csöregh, M. Czugler, E. Weber, *J. Phys. Org. Chem.* **1993**, *6*, 171.
[59] E. Weber, T. Hens, O. Gallardo, I. Csöregh, *J. Chem. Soc., Perkin Trans. 2* **1996**, 737.
[60] I. Csöregh, E. Weber, in *Molecular Recognition and Inclusion* (Ed.: A. W. Coleman), Kluwer Academic Publishers, The Netherlands, **1998**, pp. 301−304.
[61] A. I. Kitaigorodsky, in *Molecular Crystals and Molecules*, vol. 29 ("Physical Chemistry") (Ed.: E. M. Loebl), Academic Press, New York, London, **1973**.
[62] A. L. Spek, *PLATON-92*, *Program for the Analysis of Molecular Geometry*, University of Utrecht, The Netherlands, **1992**.
[63] M. Bruch, M. Große, D. Rewicki, *Justus Liebigs Ann. Chem.* **1976**, 76.
[64] E. Bergmann, J. Hernay, *Ber. Dtsch. Chem. Ges.* **1929**, *62*, 893.
[65] J. v. Braun, G. Irmisch, J. Nelles, *Ber. Dtsch. Chem. Ges.* **1933**, *66*, 1471.
[66] O. F. Beumel, Jr., R. F. Harris, *J. Org. Chem.* **1964**, *29*, 1872.
[67] E. Bergmannm, H. Hoffmann, D. Winter, *Ber. Dtsch. Chem. Ges.* **1933**, *66*, 46.
[68] G. Wittig, E. Dreher, W. Reuther, H. Weidinger, R. Steinmetz, *Justus Liebigs Ann. Chem.* **1969**, *762*, 188.
[69] S. Takahashi, Y. Kuroyama, K. Sonogashira, N. Hagihara, *Synthesis* **1980**, 627.
[70] W. B. Austin, N. Bilow, W. J. Kelleghan, K. S. Y. Lan, *J. Org. Chem.* **1981**, *46*, 2280.
[71] STOE & CIE GmbH, Publications 4802−003, **1996**.
[72] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no. CCDC-161455 to -161461. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033, E-mail: deposit@ccdc.cam.ac.uk].
[73] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, *46*, 467.
[74] G. M. Sheldrick, *SHELXL-93: Program for the refinement of crystal structures*, University of Göttingen, Germany, **1993**.

Received July 10, 2001
[O01342]