Versatile and Convenient Lattice Hosts derived from Singly Bridged Triarylmethane Frameworks, X-Ray Crystal Structures of Three Inclusion Compounds

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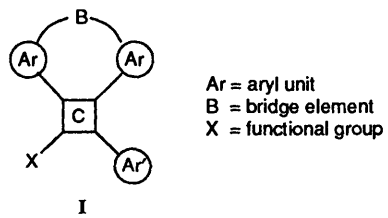
A new family of host molecules, based on the singly bridged triarylmethanol and triarylacetic acid frameworks, is described. These hosts form crystalline inclusions with a variety of uncharged organic molecules ranging from protic dipolar to apolar compounds (130 different species). The formation and stoicheiometry depend in a systematic manner on structural parameters of the host, such as the nature of the functional group and the substituents, and on the substituent positions. The crystal structures of three inclusion compounds [**1a**·benzene (8:3), **1a**·dioxane (4:3) and **4c**·EtOH (1:1)] have been studied by X-ray diffraction. They reveal the building principles of the new inclusion family. In the crystals of **1a**·benzene (8:3), the benzene is interstitially entrapped by H-bonded tetramer clusters of **1a**. Crystals of **1a**·dioxane (4:3) are built of H-bonded 2:1 host–guest complexes including interstitial molecules of dioxane. In the case of **4c**·EtOH (1:1), the building principle is formation of 2:2 host–guest clusters *via* a twelve-membered H-bonded ring.

Considerable interest in crystalline inclusion compounds and similar systems has arisen in the past few years.[1] Scientifically, the molecular recognition properties of inclusion hosts are attractive,[2] because they can sense subtle differences in shape and electronic structure between guest molecules, which is reminiscent of the high selectivities observed in biological systems.[3] Crystalline inclusion formation is also useful for analytical purposes; especially interesting is the possibility of separating constitutional and configurational isomers otherwise difficult to manage.[4] There are further applications to topochemical problems[5] and materials science.[6] All this has stimulated development of new strategies in crystalline inclusion formation and motivated the design of novel host types.[1b] There are a few host molecules, however, that have a simple constitution and are easily available for large-scale applications.

Recently, our attention was directed to triphenylmethanol (Ph_3COH) as a host molecule with amazing inclusion selectivity.[7] We now report on an extensive family of new lattice hosts which are simple, easily accessible and highly variable in structure. They are represented by the general formula **I** and are thus related to Ph_3COH in the clustering of



I

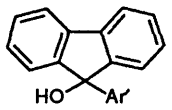
three aryl (or similar) units and one functional group around a carbon centre. Two of the aryl residues are bridged, however, and this gives rise to a distinct family of hosts with a new molecular shape. The parent compound of **I** is 9-phenylfluoren-9-ol (**1a**).[8] The possible structural modifications broadly include variation of the unbridged aryl group (Ar'), substitution at the bridged aryls (Ar), modification of the bridging unit (B), and variation of X. Compounds with different sites of modification (Ar', Y, B and X in formulae **1**–**4**) are **1a–i**, **2a–c**, **3a–d** and **4a–d**, respectively. Compound **5** is an analogue of **1a** with Ar' spaced by ethynylene, and **6** is a derivative of **5** having a modified bridge (B). Thus a vast number of variations are possible, where each individual among **1**–**4** may serve as a parent for new structural modifications.

We describe the preparation of the specified compounds, report in detail on their crystal inclusion properties, and give the X-ray crystal structure of three of the isolated host–guest species, *i.e.* **7** [**1a**·benzene (8:3)], **8** [**1a**·dioxane (4:3)] and **9** [**4c**·EtOH (1:1)].

Results and Discussion

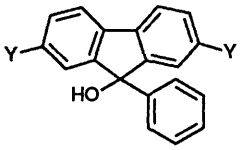
Synthesis.—Compounds **1**–**6** can be made as required from simple starting materials using common synthetic procedures.[9,10] Compounds **1a–i**, **2a–c**, **3a–d**, **5** and **6** were obtained by reaction of the corresponding fluorenones **11a–d** or ketones **12a–d** with Grignard or lithium reagents, prepared from corresponding aryl bromides or phenylethyne in 50–80% yield (see Experimental). For **4a** and **4d**, 9-phenylfluoren-9-ol **1a** was reduced with HI in HOAc[8a] or reacted with acetyl chloride,[8b] respectively. The methoxy compound **4b** was prepared from **4a** with MeOH;[11] the carboxylic acid **4c** was synthesized by lithiation of **4a** and quenching with CO_2.[12] The starting fluorenones **11b–d** were obtained by O_2 oxidation of the corresponding fluorenes **10b–d** under basic conditions.[13] Ketone **12d** was synthesized *via* a known Diels–Alder route from **12c**.[14]

Inclusion Properties.—In order to show the inclusion properties clearly, all potential host compounds **1**–**6** were tested with the same variety of solvents (17 examples, see Table 1). These include alcohols of different molecular sizes and degrees of ramification, dipolar aprotic compounds of different polarities, heterocycles of different ring sizes and with different numbers and types of heteroatoms, as well as aromatic and



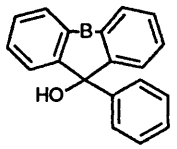
a; Ar′ = Ph
b; Ar′ = 4—MeC_6H_4
c; Ar′ = 4—$Bu^tC_6H_4$
d; Ar′ = 4—ClC_6H_4
e; Ar′ = mesityl
f; Ar′ = 2—biphenylyl
g; Ar′ = 4—biphenylyl
h; Ar′ = 1—naphthyl
i; Ar′ = 9—anthryl

1



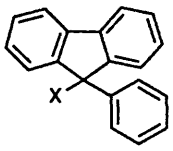
a; Y = Me
b; Y = Bu^t
c; Y = Br

2



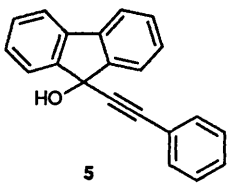
a; B = O
b; B = ethylene
c; B = vinylene
d; B = 1,2—phenylene

3



a; X = H
b; X = OMe
c; X = CO_2H
d; X = Cl

4



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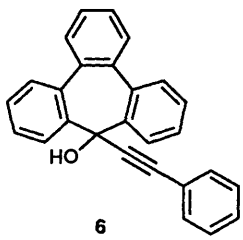

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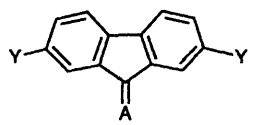
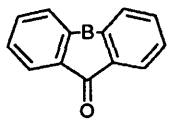
7 = **1a** • benzene (8:3)
8 = **1a** • dioxane (4:3)
9 = **4c** • EtOH (1:1)



a; Y = H
b; Y = Me
c; Y = Bu^t
d; Y = Br

10 A = H_2
11 A = O



a; B = O
b; B = ethylene
c; B = vinylene
d; B = 1,2—phenylene

12

alicyclic hydrocarbons. The ability of the new host type to form inclusion compounds is evident from Table 1, which specifies 130 different lattice inclusions. However, these are not uniformly distributed among the individual host molecules **1**–**6**. Compounds **2a**–**c**, **3b**–**d** and **6** are very efficient inclusion hosts (Table 1). Others (**1f**, **1g** and **1i**) allow only a few inclusions, while compounds **4a**, **4b** and **4d** have no host properties at all; compounds **1b** and **1e** do not crystallize from the solvents given in Table 1. These general findings show that H-donating groups are an essential structural feature of the present host design and that substituents are important. The following discussion of individual results will examine different structural criteria in more detail.

Nature of the included solvents. The presence of hydroxy or carboxy groups in the present host compounds makes inclusion of strong H bond acceptor and donor solvents very likely.[2a,15] In practice, however, all hosts form inclusion complexes with different proton acceptor solvents (dipolar aprotic compounds and heterocycles); however, inclusion formation with typical proton donor solvents, represented by the alcohols, is limited (Table 1). Only morpholine and piperidine, which may also be conceived of as H donor solvents, form crystal inclusions with virtually all of the hosts (an exception is **1g**). As expected, apolar hydrocarbons are rarely enclathrated by the present hosts; only benzene which yields a certain number of inclusions (seven examples, Table 1) is an exception, contrasting with cyclohexane that gives only one inclusion and toluene which gives none. Among the dipolar aprotic compounds, *N*,*N*-dimethylformamide (DMF) and dimethyl sulphoxide (DMSO) are special cases with respect to their high number of inclusions. Another remarkable point related to this solvent class is the large difference in guest behaviour between MeCN and $MeNO_2$, since $MeNO_2$ allows one single inclusion with **3d** while MeCN is much less selective. The heterocycles are thus the favoured guest molecules, followed by DMF and DMSO, and the hydrocarbons are not favoured (except benzene).

The polarities of the solvent molecules[16] that are accepted as guests range between 0 and 3.9 Debye, indicating no clear correlation between solvent polarity and inclusion formation. However, strict discrimination effects of the size and shape of potential and actual guest molecules are obvious from Table 1. For example, all of the efficient guest molecules of medium and low polarity are five- to six-membered rings with a maximum size of 6–7 Å,[17] while toluene with a maximum diameter of 7.8 Å[17] is inefficient.

Host constitution. The majority of compounds constitutionally modified according to the general formula **I** are potential host molecules (see above), but they exhibit different inclusion properties. There seems to be only one mandatory structural feature, namely that X must be a proton donor such as a hydroxy or carboxy group. Modifications, as in **I**, of the unsubstituted parent compound **1a** give rise to the following changes of inclusion properties.

The parent molecule **1a** yields inclusion compounds with DMF, DMSO and all heterocycles tested, as well as with benzene and cyclohexane (Table 1). Modification of the unbridged phenyl ring (Ar′ in formula **I**) as in **1c**–**d** and **1f**–**i** in general includes only gradual changes in the host properties, with one exception, namely the 2-biphenyl-substituted derivative **1f** which is completely unable to host dipolar aprotic compounds or tetrahydrofuran (THF), pyridine and benzene. The gradual change in the ability of the other **1**-type compounds (Table 1) to form inclusion compounds is shown with alcohols and benzene. Also, one may infer from the observed inclusion properties that the bulk of Ar is an important structural factor controlling the host behaviour, possibly by shielding the hydroxy group (*cf* **1f** and **1i**).

Most distinctly, host properties of the singly bridged triaryl-

Table 1. Crystalline inclusion compounds (host:guest stoicheoimetric ratios).[a]

Guest solvent[b]	Host compound																
	1a	**1c**	**1d**	**1f**	**1g**	**1h**	**1i**	**2a**	**2b**	**2c**	**3a**	**3b**	**3c**	**3d**	**4c**	**5**	**6**
MeOH	—	1:2	—	—	—	—	—	—	3:1	1:1	—	—	—	—	1:1	1:1	—
EtOH	—	—	—	—	—	1:1	1:1	—	—	1:1	—	—	—	—	1:1	1:1	—
Pr^{i}OH	—	—	—	—	—	—	—	1:1	—	2:1	—	—	—	—	1:1	1:1	—
Bu^{t}OH	—	—	—	—	—	—	—	1:1	—	—	3:2	—	2:1	—	1:1	2:3	—
Me_2CO	—	—	—	—	—	2:1	—	—	—	1:1	—	1:1	1:1	2:1	—	—	1:1
MeCN	—	—	—	—	—	—	—	—	3:1	1:1	—	2:1	—	1:1[d] 2:1	—	—	—
$MeNO_2$	—	—	—	—	—	—	—	—	—	—	—	—	—	3:1	—	—	—
DMF	1:1	—	4:3	—	2:1	1:1	—	1:1	2:1	1:1	1:1	1:1	1:1	1:1	—	—	1:1
DMSO	1:1	—	1:1	—	2:1	1:1	1:1	1:1	2:3[d] 1:1	1:1	1:1	1:1	2:3[d] 1:1	1:1	—	—	1:1
THF	*c*	1:1	8:1	—	2:1	1:1	—	1:1	4:1	1:1[d] 2:1	—	3:1	4:3	1:1	1:1	—	1:1
Dioxane	4:3	1:1	2:1	2:1	2:1	1:1	—	1:3	4:1	2:1	1:2	2:1	2:1	1:1	2:1	—	1:1
Morpholine	1:1	1:1	1:1	4:3	—	2:1	1:2	1:2	2:3	1:2	2:3[d] 1:1	1:1	1:1	2:1	—	1:1	1:1
Piperidine	1:1	1:1	1:1	1:1	—	—	1:1	1:1	2:3	1:1	1:1	1:1	1:1	1:2	—	1:1	1:1
Pyridine	*c*	1:1	2:1	—	—	2:3	—	1:1	1:1	2:1	1:1[d] 2:1	1:1	1:1	1:1	—	—	1:1
Cyclohexane	3:1	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Benzene	8:3	—	2:1	—	—	—	—	2:1	—	—	—	—	2:1	2:1	1:1	—	2:1

[a] See Experimental for methods of preparation, drying standard and characterization. [b] Toluene, which was also tested as guest solvent, yielded no inclusion compound. [c] Unstoicheiometric. [d] Ratio dependent on recrystallization conditions (concentration of components, rate of cooling).

type molecules are changed by modification of Y (*cf.* **2a–c**). This is demonstrated in the large number of inclusions with alcohols besides dipolar aprotic compounds and heterocycles (Table 1). Naturally, the individual inclusion behaviour of **2a–c** depends on the size and polarity of the Y-substituent (compare **2a** with **2b** or **2c**). In general, improvement of inclusion properties when bulky Y-substituents are introduced into **1a** may be interpreted as a steric effect resulting from more free space in the crystal lattice near the hydroxy groups (Y-substituents may act as lattice spacers).

Modification of the bridging element (B in **I**) as in **3a–d** also results in a general improvement of the inclusion properties compared to **1a**. This is mainly reflected in the dipolar aprotic type of inclusion compounds (Table 1). Generally, for the host series **3a–d**, the more rigid the bridging element (B), the more inclusion compounds are possible (**3a** and **3b** *vs.* **3c** and **3d**).

The change in X from hydroxy in **1a** to carboxy in **4c** amounts to replacement of a weak by a strong proton donor (and acceptor) site. Consequently, the inclusion of alcohols is much more pronounced in **4c** (Table 1). Unfortunately, this host molecule decomposes *via* decarboxylation when heated in high-boiling (DMF, DMSO) or basic solvents (the N-containing heterocycles). Thus, inclusion studies of **4c** are limited by experimental difficulties.

Apart from the change from hydroxy in **1a** to carboxy in **4c**, the introduction of an ethynylene spacer group in **1a** to give **5** has the most distinct influence on the inclusion of alcohols. Like **4c**, host **5** yields inclusion compounds with all tested alcohols (Table 1). Since neither aprotic dipolar solvents nor hydrocarbons, nor heterocycles such as THF, dioxane and pyridine, but only morpholine and piperidine form inclusion compounds with **5**, this host shows exclusive preference for proton-donating guests (alcohols and the mentioned secondary amines).

On the contrary, compound **6**, which is a spacered version of **3d**, gives no alcohol inclusion at all, rather its inclusion properties are close to those of the non-spacered parent molecule **3d**. The reason for the remarkable difference in inclusion behaviour between **5** and **6** is not yet obvious. However, for **5**, the presence of an ethynylene spacer may result in a favourable steric situation for H donor guests to interact with the host hydroxy group. In **6**, lattice factors may be against this interaction.

Host–Guest Stoicheiometry. A wide range of stoicheiometric host:guest ratios was found for the different inclusion compounds, *e.g.* 1:3, 1:2, 2:3, 1:1, 4:3, 2:1, 8:3, 4:1 and 8:1 (Table 1). None of the hosts, except **1g**, exhibit one single stoicheiometric ratio regardless of the guest, but some behave rather uniformly and have simple ratios (*e.g.* **1c**, **1i**, **4c**, **5** and **6**); others do not and show more complex ratios (*e.g.* **1a**, **1d**, **1f**, **2b** and **3c**). In a few cases (*cf.* **2b**, **3a**, **3c** and **3d**), depending on the recrystallization conditions, more than one single stoicheiometric ratio is found for the same host–guest combination, which indicates that different host–guest crystals (phases) are possible and suggests complex lattice energetics.[18]

Irrespective of this, the most frequently observed stoicheiometric ratio is 1:1—prevalent for the alcohol inclusions—followed by 2:1, while the higher ratios are rather rare. This suggests that H-bonded 1:1 complexes between host and guest or similar structures (*e.g.* 2:2 complexes, see refs. 2*a*, 7 and 15) are predominant for the alcohol inclusions (*cf.* **4c** and **5**) and should also exist in some of the 1:1 inclusions with other polar solvents (Table 1). However, clusters of H-bonded host–host aggregates are likely to occur in the inclusion compounds of apolar guests, as indicated by high stoicheiometric host:guest ratios for the dioxane, benzene and cyclohexane inclusions of **1a**. Such clusters suggest the recently reported inclusion structures of triphenylmethanol and of unsolvated triphenylmethanol.[7] More profound relationships between host and guest based on inclusion stoicheiometries are not evident from Table 1.

In view of these problems and in order to investigate the building principles of the new inclusion family, we studied the crystal structures of three inclusion species: **7** [**1a**·benzene (8:3)], **8** [**1a**·dioxane (4:3)] and **9** [**4c**·EtOH (1:1)] which are protic host/apolar guest, protic host/H acceptor guest, and protic host/protic guest inclusion compounds, respectively.

X-Ray Analysis. Structure Description of **7** [**1a**·*benzene* (8:3)],

Table 2. Crystal data and selected details of the refinement calculations for the three inclusion compounds.[a]

Compound	**7** **1a**·benzene (8:3)	**8** **1a**·dioxane (4:3)	**9** **4c**·EtOH (1:1)
Formula unit	$C_{85}H_{65}O_4$	$C_{44}H_{40}O_5$	$C_{44}H_{20}O_6$
Formula weight	1 150.45	648.80	664.80
Crystal	monoclinic	triclinic	triclinic
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
a/Å	18.520(1)	9.131(1)	8.935 5(4)
b/Å	16.810(1)	12.742(1)	13.475 0(7)
c/Å	21.109(1)	17.030(2)	15.584 4(7)
α/°	90.0	100.467(5)	91.485(8)
β/°	95.47(1)	100.197(7)	104.818(4)
γ/°	90.0	108.424(5)	94.418(5)
V_c/Å^3	6541.7(6)	1789.2(4)	1806.6(2)
Z	4	2	2
D_c/g cm^{-3}	1.17	1.20	1.22
$F(000)$	2428	688	704
μ/cm^{-1}	0.65	5.80	6.07
Radiation (λ/Å)	Mo-Kα(0.7107)	Cu-Kα(1.5418)	Cu-Kα(1.5418)
N_o(unique, non-zero)	14 127	4 474	6 471
θ_{max}/°	30	55	70
N_{ref}	5165	3038	4438
Limit	$F > 4\sigma(F)$	$F > 6\sigma(F)$	$F > 6\sigma(F)$
No. of variables	799	446	470
Final agreement factors			
$R = \Sigma\|\Delta F\|/\Sigma\|F_o\|$	0.063	0.060	0.085
$R_w = (\Sigma w\|\Delta F\|^2/\Sigma w\|F_o\|^2)^{\frac{1}{2}}$	0.105	0.097	0.116
Weighting: g in SHELX[b]	0.019	0.015	0.0001

[a] Esds are given in parentheses. [b] Weights of the structure factors in SHELX are estimated as $w = \text{const.}/[\sigma^2(F) + (gF^2)]$.

8 [**1a**·*dioxane* (4:3)] *and* **9** [**4c**·*EtOH* (1:1)].—Crystal data are given in Table 2. Perspective views of the stoicheiometric units of the inclusion compounds **7**, **8** and **9**, including atom labelling, are shown in Figs. 1(*a*)–(*c*), respectively and packing diagrams are shown in Figs. 2(*a*)–(*c*) respectively. Due to the space group symmetries each of the crystallographic asymmetric units in the crystal structures of **7** and **8** contains only one half of the respective stoicheiometric formula unit, *i.e.* four host and one and a half guest molecules for **7**, and two host and one and a half guest molecules for **8**. The geometries of the six crystallographically independent 9-phenylfluoren-9-ol **1a** host molecules in **7** and **8** are very similar and comparable with those reported earlier for related molecules.[19,20] The tricyclic fluorene moieties have a nearly, but not strictly planar conformation. The dihedral angles between the two benzene ring planes of each fluorene group (calculated according to Nardelli *et al.*[21]) vary between 1.8 and 5.1°. The mean value of 3.6[12]° (with the rms deviation in angular parentheses) for the present six molecules is in accordance with the values of 3.35 and 3.47 Å reported for the same dihedral angle.[20b] Nevertheless the thirteen carbon atoms of each fluorene group are located approximately in the same plane (within 0.135 Å), and the maximum deviation of the C atoms for their respective planes is less than 0.10 Å in the present structures (*cf.* ref. 19*a*). The phenyl substituent is approximately perpendicular to the fluorene plane in all cases, in agreement with, for example, the conformation of the related bis[9-(9-phenylfluorenyl)]peroxide molecule.[20a] The calculated dihedral angles between the least-squares planes through the fluorene and the phenyl moieties range from 84.3 to 95.8°, with an average value of 90.2[47]° for the present six 9-phenylfluoren-9-ol molecules. The C atoms of each phenyl substituent are coplanar within 0.008–0.026 Å in these structures.

The asymmetric unit in the structure of **9** [Fig. 1(*c*)] contains two host and two guest molecules, which is twice the stoicheiometric unit of **4c**·EtOH (1:1). The geometry of the 9-phenylfluorene-9-carboxylic acid host **4c** is similar to that of **1a**, but the conformations of the two host molecules in **9** are slightly different. The dihedral angles between the two benzene rings of each fluorene moiety are 4.3(2) and 1.0(2)°, the non-hydrogen atoms of these tricyclic groups are co-planar within 0.106 and 0.030 Å, and the phenyl substituents are planar within 0.009 and 0.016 Å in the unprimed and in the primed molecules, respectively. However, while the phenyl substituent is nearly perpendicular to the fluorene plane in the unprimed molecule, with a dihedral angle of 94.6(2)°, the same angle in the primed host is only 70.5(2)°. Moreover, the calculated dihedral angle between the planes of the fluorene moiety and of the carboxy group is 124.3(4)° in the unprimed host, but only 64.5(4)° in the primed host.

The bond lengths and angles in the host molecules of **7**, **8** and **9** generally conform to the expected values.[22] The guest molecules also have the assumed conformations, but the bond distances and angles within these molecules show significant deviations from the expected values, due to the high thermal mobility of the atoms involved (see below and Experimental).

In the inclusion compound of the aprotic, apolar benzene guest there is no possibility for H bonds between host and guest. However, because the alcoholic hydroxy group can function both as proton donor and acceptor in H bonds, the fluorenol hosts in this structure can form tetramer complexes. Fig. 3(*a*) illustrates the closed loop of H bonds (Table 3) formed by four **1a** host molecules in **7**. The benzene guests are trapped in the voids between the large host tetramers by steric forces only [*cf.* Fig. 2(*a*)], in the same manner as, for example, in the benzene inclusion compound of the 9,9′-bianthryl host.[17] Nevertheless, in the latter clathrate the benzene molecules are enclosed pairwise with nearly perfect fit in almost completely closed cages formed by the bianthryl hosts. In the present structure, however, the shape and the large size of the crystal cavities, depending on the huge size of the host tetramers, makes it possible for the benzene guests to have a relatively high thermal mobility, especially those located around the centre of symmetry.

The dioxane oxygen atoms can function as proton acceptors

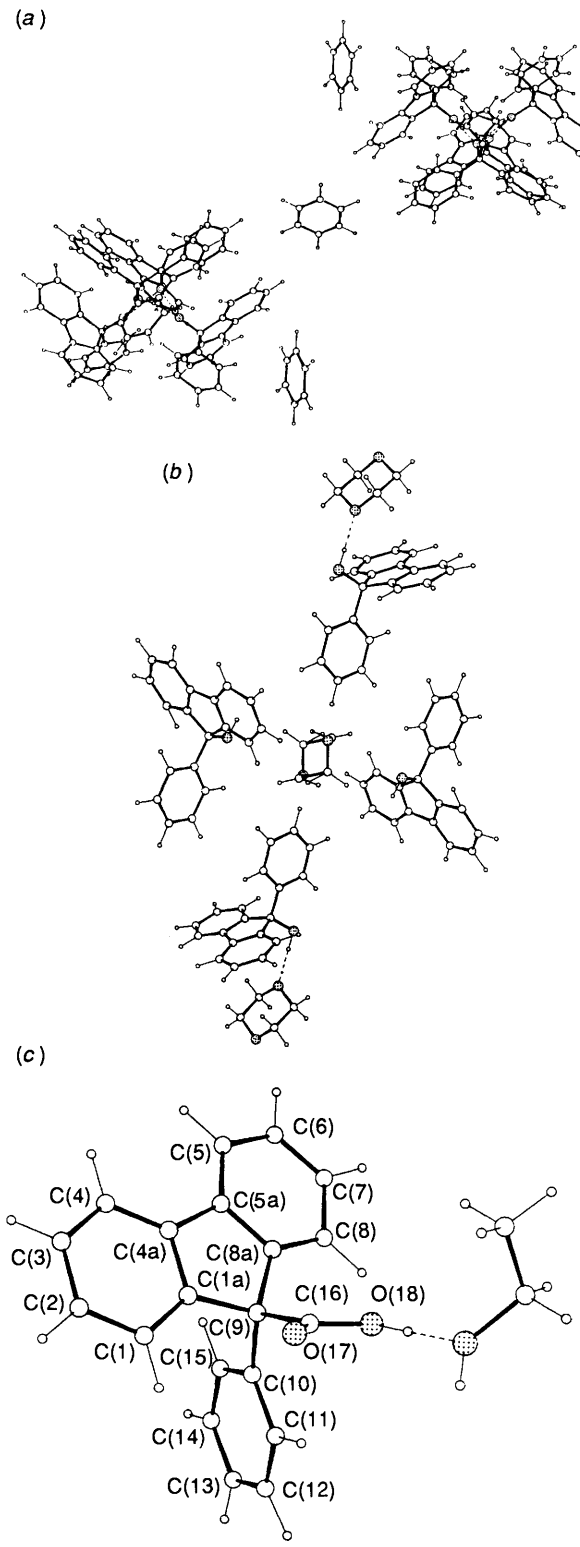


Fig. 1. Perspective views of the stoicheiometric units showing the conformation and the relative positioning of the host and the guest molecules: (*a*) **7** [**1a**·benzene (8:3)]; (*b*) **8** [**1a**·dioxane (4:3)]; (*c*) **9** [**4c**·EtOH (1:1)]. Solid and dashed lines represent covalent and hydrogen bonds, respectively; O atoms are shaded. The atom numbering of the skeletal atoms of **4c** in (*c*) applies also to **1a** in (*a*) and (*b*); the O atom of **1a** is numbered as O(9).

in H bonds.[23] This is also demonstrated by the structure of **8**, which consists of H-bonded (2:1) host–guest aggregates (see Table 3), held together by van der Waals' forces [*cf.* Fig. 2(*b*)]. Nevertheless, the crystal structure includes additional dioxane molecules which are located around the symmetry centres. These latter guests interact rather weakly with the H-bonded host–guest associates, and the voids around the symmetry centres are large enough to allow lively thermal motion for these loosely bonded guest entities.

Structure **9** is a new example of alcohol inclusion by a carboxylic host. Like the hosts 1,1′-binaphthyl-2,2′-dicarboxylic acid (2,2′-BNDA)[2a,15,24] and *trans*-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxylic acid (DEADA),[2a,15,25] 9-phenylfluorene-9-carboxylic acid **4c** also forms H-bonded loops with the guest alcohol (Table 3). A twelve-membered ring (including the H atoms) is closed *via* two $-CO_2H$ and two alcoholic –OH groups [*cf.* Fig. 3(*b*)]. In contrast to the structures of the alcoholic inclusions of 2,2′-BNDA with MeOH, EtOH, Pr^nOH and Pr^iOH, and that of DEADA with Bu^nOH, the twelve-membered H-bonded ring in the present structure has no crystallographic symmetry. In the crystals of **9**, the host–guest aggregates with 2:2 stoicheiometry that form the H-bonded closed loops are linked together by van der Waals' forces. The packing [*cf.* Fig. 2(*c*)] allows the loosely fixed ethyl moieties of the guests a high thermal mobility in the crystal.

Conclusions

Singly bridged triaryl methanols and analogues have proved to be a rewarding source of inclusion hosts. They form crystalline inclusions with a variety of uncharged organic molecules ranging from protic dipolar to apolar compounds (130 different species, Table 1). Inclusion formation depends on structural parameters of the hosts, such as the size and shape of the substituent, the bridging group, the spacer and the functional group.

The crystal structures illustrate the fact that inclusions of very different character (H-bonded complexes and true lattice-type clathrates)[15] are possible within this new host family, and even with the same host molecule. Host **1a** is capable of forming H-bonded aggregates with itself (as in **7**) or with a suitable guest (as in **8**). Then, these host–host or host–guest associates are able to act as the real host species for interstitial benzene or dioxane guests in van der Waals'-type inclusions. By this mode of action, a high adaptability to guests of different polarities is achieved by **1a** and by the other hosts of this type (*cf.* Table 1). Change of the –OH functional group of **1a** to $-CO_2H$ gives the host **4c**. Its inclusion of the protic EtOH guest follows the expected mode of binding between an efficient carboxylic host and an alcohol.[2a,15,24,25]

The triaryl methanols and analogues described here possess several properties which make their use as lattice hosts very favourable. They are simple in constitution, can easily be synthesized by common methods, allow structural modifications in many ways, and mostly yield inclusion compounds of good crystal quality. In the future, analogous hosts monosubstituted at the fluorene moiety may be prepared in optically active form. These are desirable features for practical applications.[1,2,6]

Experimental

General Methods and Materials.—All temperatures are uncorrected. M.p.s were determined with a Reichert hot-stage apparatus. High-resolution mass spectra were obtained using an A.E.I. MS 50 instrument. Proton and ^{13}C NMR spectra were measured for $CDCl_3$, solutions (Me_4Si as internal standard) with Varian EM-360 (60 MHz) and Bruker WH-90 (90 MHz) spectrometers, respectively. Microanalyses were carried out by the Microanalytical Laboratory of the Institut für Organische Chemie und Biochemie, Universität Bonn. For column

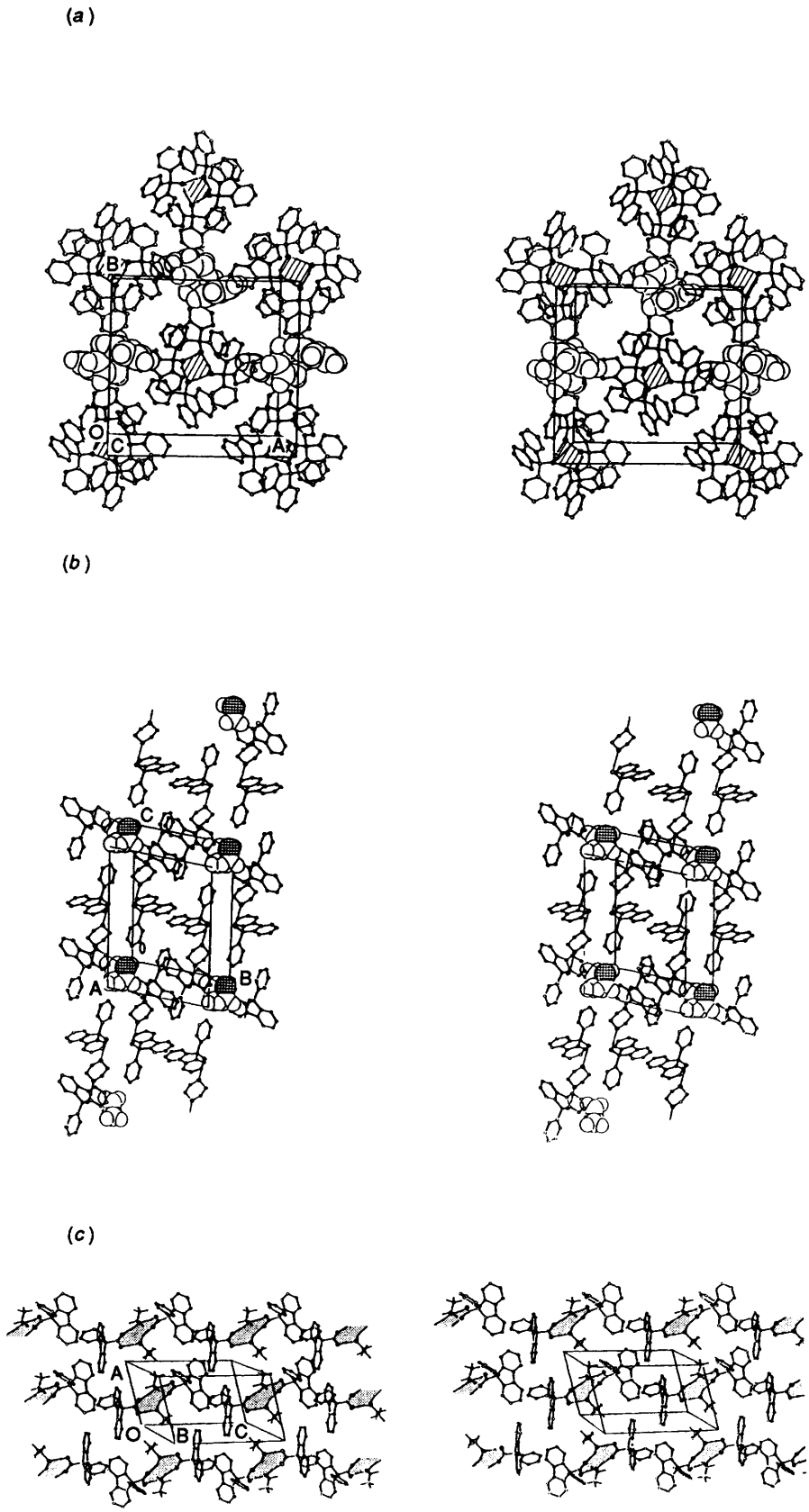


Fig. 2. Stereoscopic packing illustrations of inclusion compounds: (*a*) **7** [**1a**·benzene (8:3)]; (*b*) **8** [**1a**·dioxane (4:3)]; (*c*) **9** [**4c**·EtOH (1:1)]. The host molecules in (*a*)–(*c*) as well as the H-bonded dioxane species in (*b*), and the EtOH guests in (*c*) are represented in ball-and-stick fashion. The benzene guests in (*a*) and the uncoordinated dioxane species in (*b*) are given in van der Waals' representation. O atoms are shaded; H atoms of the host in (*a*)–(*c*), except those involved in H bonds, and in (*b*) also the hydrogens of the H-bonded guest, are omitted for clarity. H bonds are indicated as thin lines. The inter-host H-bonded ring systems in (*a*) are hatched; H-bonded ring systems in (*c*), involving host and guest, are dotted (*cf.* Fig. 3).

Table 3. Bond distances and angles in possible hydrogen bonds in the three inclusion compounds studied by X-ray diffraction.[a]

Atoms involved	Symmetry	Distances/Å			Angle/°
		$O_D \cdots O_A$	O_D–H	H $\cdots$ O_A	O_D–H $\cdots$ O_A
7 [**1a**·benzene (8:3)]					
O(9A)–H(9A) $\cdots$ O(9B)	x, y, z	2.734(4)	0.88	1.91	154
O(9B)–H(9B) $\cdots$ O(9D)	x, y, z	2.688(4)	0.87	1.84	163
O(9C)–H(9C) $\cdots$ O(9A)	x, y, z	2.750(3)	0.96	1.79	176
O(9D)–H(9D) $\cdots$ O(9C)	x, y, z	2.685(4)	0.90	1.80	164
8 [**1a**·dioxane (4:3)]					
O(9)–H(9) $\cdots$ O(D1)	x, y, z	2.724(4)	0.91	1.82	180
O(9′)–H(9′) $\cdots$ O(D4)	$1-x, 2-y, 1-z$	2.722(5)	0.94	1.80	165
9 [**4c**·EtOH (1:1)]					
O(18)–H(18) $\cdots$ O(E)	x, y, z	2.607(5)	1.04	1.56	179
O(18′)–H(18′) $\cdots$ O(E′)	x, y, z	2.585(5)	0.88	1.72	170
O(E)–H(OE) $\cdots$ O(17′)	$x, y, 1+z$	2.722(4)	1.08	1.72	152
O(E′)–H(OE′) $\cdots$ O(17)	$x, y, 1-z$	2.719(5)	1.12	1.69	150

[a] Esds are given in parentheses.

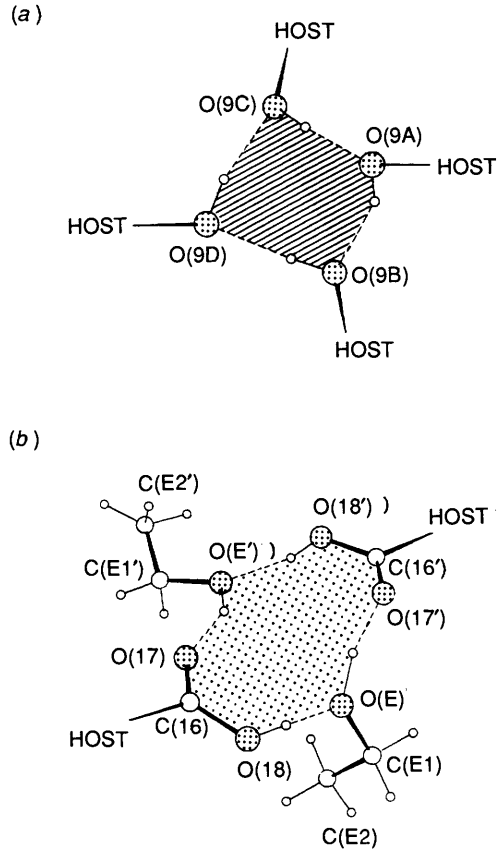


Fig. 3. Individual units of the H-bonded ring constitutions of inclusion compounds: (*a*) **7** [**1a**·benzene (8:3)]; (*b*) **9** [**4c**·EtOH (1:1)] [*cf.* Figs. 2(*a*) and 2(*c*), respectively]. (– – –) H bond interactions.

chromatography Al_2O_3 (grade II-III, Merck) and silica gel (0.063–0.1 mm, Merck) were used. All solvents were of reagent quality or purified by distillation before use. Starting compounds and all other reagents were purchased from Janssen unless otherwise stated.

2,7-Disubstituted Fluorenones **11b–d** *(General Procedure).*— To a solution of the respective fluorene compound **10b–d** (10 mmol) in pyridine (10 cm^3; freshly distilled over KOH) is added Triton B (40% in pyridine, 0.5 cm^3; obtained by the method given in ref. 13). Oxygen (dried over $CaCl_2$) is bubbled through the solution until the reaction is complete (DC-control). The reaction mixture is hydrolysed with water (seven fold volume) and neutralized (acetic acid). The precipitate is washed free of pyridine (H_2O) and dried. The crude material is dissolved in toluene and filtered through Al_2O_3. Evaporation yielded the pure compound. Specific details for each compound are given below.

2,7-*Dimethylfluorenone* **11b**. From 2,7-dimethylfluorene **10b**;[26] chromatography (Al_2O_3, toluene) and recrystallization from petroleum ether (b.p. 60–90 °C) yielded yellow crystals (68%), m.p. 156 °C (lit.,[26] 156 °C).

2,7-*Di-t-butylfluorenone* **11c**. From 2,7-di-t-butylfluorene **10c**;[27] chromatography (Al_2O_3, toluene) and recrystallization from isoamyl alcohol yielded a yellow powder (75%), m.p. 105–107 °C (lit.,[28] 107 °C).

2,7-*Dibromofluorenone* **11d**. From 2,7-dibromofluorene **10d**;[29] chromatography (Al_2O_3, toluene) yielded a yellow powder (81%), m.p. 200 °C (lit.,[13,30] 202 °C).

Bridged Triaryl Compounds and Analogues **1–6**. (i) Via *Grignard Reaction* (**1a–b, 1f–h, 2a–c, 3a–c**). *General Procedure.*— The Grignard reagents were prepared[9] from magnesium turnings (2.40 g, 100 mmol) in Et_2O (10 cm^3) and the respective aryl compound (100 mmol) in Et_2O (20 cm^3). The cooled Grignard solution was diluted with dry Et_2O (80 cm^3) and the respective ketone (50 mmol) added in ethereal solution (**11b–d, 12b–c, 11a** and **12a** were added as a solid). The mixture was refluxed for 2 h and then stirred for 2 h at room temperature. Work-up of the reaction mixture, including hydrolysis (saturated NH_4Cl solution), extraction with Et_2O, washing (brine), drying ($MgSO_4$) and evaporation of the solvent under reduced pressure, yielded the crude product as a viscous oil. Purification was effected by column chromatography (SiO_2) and recrystallization. Specific details for each compound are given below.

9-*Phenylfluoren*-9-*ol* (**1a**). From fluoren-9-one **11a** with bromobenzene; recrystallization from light petroleum (b.p. 60–90 °C), yielded colourless crystals (83%), m.p. 107–109 °C (lit.,[8] 107 °C).

9-(4-*Tolyl*)*fluoren*-9-*ol* **1b**. From fluoren-9-one **11a** and 4-bromotoluene; a colourless oil (83%). Unlike the literature

description (m.p. 85.5–86.5 °C[31]) the compound resisted crystallization from various solvents.

9-(2-*Biphenylyl*)*fluoren*-9-*ol* **1f**. From fluoren-9-one **11a** and 2-bromobiphenyl; recrystallization from toluene yielded a white powder (78%), m.p. 169–170 °C (lit.,[32] 169–170 °C).

9-(4-*Biphenylyl*)*fluoren*-9-*ol* **1g**. From fluoren-9-one **11a** and 4-bromobiphenyl; the crude product was chromatographed [SiO_2, elution with $CHCl_3$–toluene (5:1)]. Recrystallization from acetic acid yielded a white powder (68.5%), m.p. 149 °C (lit.,[33] 137–139 °C).

9-(1-*Naphthyl*)*fluoren*-9-*ol* **1h**. From fluoren-9-one **11a** with 1-bromonaphthalene; recrystallization from toluene yielded a white powder (55%), m.p. 156–157 °C (lit.,[34] 151.5 °C).

2,7-*Dimethyl*-9-*phenylfluoren*-9-*ol* **2a**. From 2,7-dimethylfluorenone **11b** and bromobenzene; recrystallization from petroleum ether (b.p. 60–90 °C) yielded a white powder (75%), m.p. 123–124 °C (Found: C, 88.00; H, 6.15. $C_{21}H_{18}O$ requires C, 88.08; H, 6.34%); δ_C(90 MHz; $CDCl_3$) 150.77, 143.65, 138.02, 137.14, 129.79, 128.24, 127.10, 125.52, 125.42, 119.60, 83.44 and 21.55; δ_H(60 MHz; $CDCl_3$) 2.30 (6 H, s, Me), 2.40 (1 H, s, OH) and 7.00–7.60 (11 H, m, Ar); *m/z* (Found: 286.1343; requires M^+, 286.1358).

2,7-*Di-t-butyl*-9-*phenylfluoren*-9-*ol* **2b**. From 2,7-di-t-butylfluorenone **11c** and bromobenzene; recrystallization from petroleum ether (b.p. 60–90 °C) and subsequently from $MeNO_2$ yielded colourless crystals (72%), m.p. 165 °C (Found: C, 86.71; H, 8.41. $C_{27}H_{30}O$ requires C, 87.52; H, 8.16%); δ_C(90 MHz; $CDCl_3$) 151.42, 150.83, 143.91, 137.04, 128.14, 126.98, 126.01, 125.55, 121.67, 119.31, 83.80, 34.99 and 31.49; δ_H(60 MHz; $CDCl_3$) 1.20 (18 H, s, Bu^t), 2.40 (1 H, s, OH) and 7.00–7.60 (11 H, m, Ar); *m/z* (Found: 370.2272; $C_{27}H_{30}O$ requires M^+, 370.2297).

2,7-*Dibromo*-9-*phenylfluoren*-9-*ol* **2c**. From 2,7-dibromofluorenone **11d** and bromobenzene in THF; successive recrystallizations from CCl_4 and MeCN yielded colourless crystals (73%), m.p. 163–164 °C (Found: C, 54.26; H, 2.90. $C_{19}H_{12}Br_2O$ requires C, 54.84; H, 2.91%); δ_C(90 MHz; $CDCl_3$) 152.35, 141.99, 137.56, 132.29, 128.47, 128.37, 127.66, 125.29, 122.45, 121.51 and 83.18; δ_H(60 MHz; $CDCl_3$) 2.50 (1 H, s, OH) and 7.20–7.60 (11 H, m, Ar); *m/z* (Found: 413.9282; requires M^+, 413.9255).

9-*Phenylxanthen*-9-*ol* **3a**. From xanthone **12a** and bromobenzene; recrystallization from toluene gave a white powder (80%), m.p. 159 °C (lit.,[35] 159 °C).

1-*Phenyl*-2:3,6:7-*dibenzosuber*-1-*ol* **3b**. From dibenzosuberone **12b** and bromobenzene; recrystallization from MeOH gave colourless crystals (69%), m.p. 153 °C (lit.,[36] 151 °C).

1-*Phenyl*-2:3,6:7-*dibenzosuber*-4-*en*-1-*ol* **3c**. From dibenzosuberenone **12c** and bromobenzene; recrystallization from MeOH gave colourless crystals (75%), m.p. 150–151 °C (lit.,[36] 150 °C).

(ii) via *Aryllithium Compounds* (**1c–e**, **1i**, **3d**, **5**, **6**). *General Procedure*.—Lithiation of aryl compounds[10] was carried out at 0 °C under an argon atmosphere; Bu^nLi in hexane (51.5 cm^3, 82.5 mmol; 1.6 mol dm^{-3}) was added dropwise (*ca.* 0.5 h) to a solution of the respective aryl compound (75 mmol) in dry Et_2O (100 cm^3). The mixture was stirred for 2 h at room temperature, then cooled to 0 °C and diluted with dry Et_2O (60 cm^3). Fluoren-9-one **11a** (9.00 g, 50 mmol) was added as a solid and the mixture stirred for 2 h at room temperature, then 2 h under reflux. Work-up was as described in (*i*) above. Specific details for each compound are given below.

9-(4-*t-Butylphenyl*)*fluoren*-9-*ol* **1c**. From fluoren-9-one **11a** and 4-bromo-t-butylbenzene; recrystallization from dioxane gave the clathrate (see Table 1). The solvent-free compound was obtained by repeated recrystallization from MeOH (73%), m.p. 118–120 °C (Found: C, 87.19; H, 7.32. $C_{23}H_{22}O$ requires C, 87.86; H, 7.05%); δ_C(90 MHz; $CDCl_3$) 150.41, 149.74, 140.15, 139.45, 128.83, 128.26, 125.06, 125.03, 124.85, 119.93, 83.43, 34.34 and 31.33; δ_H(60 MHz; $CDCl_3$) 1.30 (9 H, s, Bu^t), 2.40 (1 H, s, OH) and 7.10–7.80 (12 H, m, Ar); *m/z* (Found: 314.1687; requires M^+, 314.1671).

9-(4-*Chlorophenyl*)*fluoren*-9-*ol* **1d**. From fluoren-9-one **11a** and 4-bromochlorobenzene; recrystallization from morpholine gave the clathrate (see Table 1). The solvent-free compound was obtained by heating the clathrate to 110 °C at 15 Torr (1 Torr = 133.322 Pa) for 15 h. Recrystallization from $MeNO_2$ gave colourless crystals (63%), m.p. 98–99 °C (lit.,[31] 93–94 °C).

9-*Mesitylfluoren*-9-*ol* **1e**. From fluoren-9-one **11a** and bromomesitylene; lithiation and addition of **11a** was carried out at 0 °C. Chromatography (SiO_2, $CHCl_3$) gave a colourless oil (40%). Unlike the literature description (m.p. 115–115.5 °C)[37] the compound resisted crystallization from various solvents.

9-*Anthrylfluoren*-9-*ol* **1i**. From fluoren-9-one **11a** with 9-bromoanthracene (130 ml Et_2O); recrystallization from toluene–petroleum ether (b.p. 60–90 °C) (1:1) gave yellow needles (77%), m.p. 201–203 °C (lit.,[38] 205–206 °C).

1-*Phenyl*-2:3,4:5,6:7-*tribenzocycloheptatrien*-1-*ol* **3d**. From tribenzocycloheptatrienone **12d**[14] and PhLi (obtained by the method of Gilman[39]); recrystallization from cyclohexane gave a white powder (80%), m.p. 197–198 °C (lit.,[14b] 198–199 °C).

(iii) *Triaryl Compounds* **4a–d**.—9-*Phenylfluorene* **4a**. From 9-phenylfluoren-9-ol **1a** and hydroiodic acid in acetic acid; recrystallization from MeOH gave colourless needles (84%), m.p. 146–147 °C (lit.,[8a] 145 °C).

9-*Methoxy*-9-*phenylfluorene* **4b**. From 9-chloro-9-phenylfluorene **4d** and MeOH; recrystallization from MeOH gave colourless crystals (91%), m.p. 92–93 °C (lit.,[11] 92–93 °C).

9-*Carboxy*-9-*phenylfluorene* **4c**. Lithiation of 9-phenylfluorene **4a** with Bu^nLi and carboxylation with CO_2 gas followed the literature procedure.[39] Recrystallization from toluene light petroleum (b.p. 60–90 °C) (1:1) gave a white powder (70%), m.p. 189 °C (lit.,[39] 193.5–195 °C, lit.,[12] 189–190.5 °C).

9-*Chloro*-9-*phenylfluorene* **4d**. From 9-phenylfluoren-9-ol **1a** and thionyl chloride in benzene; recrystallization from light petroleum (b.p. 40–60 °C) gave colourless crystals (82%), m.p. 78–79 °C (lit.,[8b] 78–79 °C).

(iv) *Spacered Triaryl Compounds* **5** *and* **6**.—9-(*Phenylethynyl*)-*fluoren*-9-*ol* **5**. From fluoren-9-one **11a** and phenylethyne; lithiation and addition of **11a** was carried out in THF at −40 °C. Recrystallization from Pr^iOH gave the clathrate (see Table 1). The solvent-free compound was obtained by heating the clathrate to 60 °C at 15 Torr for 24 h; white powder (66%), m.p. 80–81 °C (lit.,[40] 82–83 °C).

1-(*Phenylethynyl*)-2:3,4:5,6:7-*tribenzocycloheptatrien*-1-*ol* **6**. From tribenzocycloheptatrienone **12d** and phenylethyne; lithiation and addition of **12d** was carried out in THF at −40 °C. Recrystallization from light petroleum (b.p. 40–60 °C) gave a white powder (34%), m.p. 169–171 °C (Found: C, 89.84; H, 5.14. $C_{27}H_{18}O$ requires C, 90.47; H, 5.06%); δ_C(90 MHz, $CDCl_3$) 144.97, 139.44, 135.78, 131.54, 130.15, 129.31, 128.11, 127.82, 127.75, 127.69, 127.59, 122.03, 120.93, 101.44, 90.08, 84.48 and 70.08; δ_H(60 MHz, $CDCl_3$) 3.00 (1 H, s, OH) and 6.60–8.10 (17 H, m, Ar); *m/z* (Found: 358.1358; requires M^+, 358.1358).

Crystalline Inclusion Compounds.—The corresponding host compound was dissolved under heating in a minimum amount of the respective guest solvent. The solution was placed into a hot oil bath to prevent it from rapid cooling and to ensure slow crystallization of the inclusion compound. After storage for 12 h at room temperature, the crystals which formed were collected

Table 4. Fractional atomic co-ordinates of the non-hydrogen atoms and of the alcoholic and carboxylic H atoms of the inclusion compounds 7–9.[a–c]

Atoms	x/a	y/b	z/c
7 [1a·benzene (8:3)]			
C(1aA)	1.129 4(2)	−0.095 2(2)	0.401 6(2)
C(1A)	1.072 5(3)	−0.131 7(3)	0.428 6(2)
C(2A)	1.086 3(4)	−0.202 4(3)	0.460 8(3)
C(3A)	1.154 5(4)	−0.235 4(3)	0.465 8(3)
C(4A)	1.211 6(3)	−0.199 9(3)	0.438 2(2)
C(4aA)	1.198 4(2)	−0.128 5(3)	0.406 1(2)
C(5aA)	1.245 2(2)	−0.078 3(3)	0.370 5(2)
C(5A)	1.318 7(3)	−0.085 5(3)	0.360 7(3)
C(6A)	1.348 6(3)	−0.028 6(4)	0.323 9(3)
C(7A)	1.307 7(3)	0.034 1(3)	0.296 8(3)
C(8A)	1.235 2(3)	0.041 2(3)	0.308 2(2)
C(8aA)	1.204 6(2)	−0.014 7(2)	0.344 9(2)
C(9A)	1.127 6(2)	−0.017 6(2)	0.364 1(2)
O(9A)	1.074 2(2)	−0.019 4(2)	0.309 9(2)
H(9A)	1.0799	−0.0588	0.2833
C(10A)	1.111 8(2)	0.055 1(2)	0.403 9(2)
C(11A)	1.063 5(3)	0.113 4(3)	0.381 5(2)
C(12A)	1.055 4(3)	0.181 1(3)	0.416 9(3)
C(13A)	1.092 8(3)	0.190 6(3)	0.475 9(3)
C(14A)	1.139 3(3)	0.132 4(3)	0.499 5(2)
C(15A)	1.148 7(3)	0.065 4(3)	0.464 0(2)
C(1aB)	1.005 4(3)	−0.227 0(3)	0.135 1(2)
C(1B)	0.986 1(3)	−0.178 7(5)	0.085 0(3)
C(2B)	0.928 4(4)	−0.210 4(7)	0.036 4(4)
C(3B)	0.902 2(4)	−0.282 5(7)	0.050 5(4)
C(4B)	0.920 7(3)	−0.333 6(5)	0.100 2(4)
C(4aB)	0.973 9(3)	−0.304 4(4)	0.145 2(3)
C(5aB)	1.005 1(3)	−0.336 7(4)	0.204 7(3)
C(5B)	0.989 5(3)	−0.412 8(4)	0.236 1(4)
C(6B)	1.027 6(4)	−0.421 4(4)	0.294 5(4)
C(7B)	1.076 3(3)	−0.368 2(4)	0.324 5(3)
C(8B)	1.088 8(3)	−0.299 8(3)	0.292 3(3)
C(8aB)	1.053 7(3)	−0.285 0(3)	0.232 2(3)
C(9B)	1.061 5(2)	−0.211 2(2)	0.191 2(2)
O(9B)	1.045 8(2)	−0.141 6(2)	0.225 8(2)
H(9B)	1.0005	−0.1280	0.2256
C(10B)	1.138 5(2)	−0.204 1(3)	0.171 9(2)
C(11B)	1.180 7(2)	−0.137 4(3)	0.187 1(2)
C(12B)	1.251 6(3)	−0.133 8(3)	0.169 1(3)
C(13B)	1.279 4(3)	−0.195 2(3)	0.136 0(2)
C(14B)	1.237 8(3)	−0.261 1(3)	0.120 6(2)
C(15B)	1.167 4(3)	−0.265 6(3)	0.138 5(2)
C(1aC)	0.976 6(2)	0.186 5(3)	0.218 6(2)
C(1C)	0.915 1(3)	0.210 8(3)	0.245 9(2)
C(2C)	0.918 6(4)	0.281 7(4)	0.280 4(3)
C(3C)	0.981 8(5)	0.326 3(4)	0.286 2(3)
C(4C)	1.043 1(4)	0.302 3(3)	0.259 6(3)
C(4aC)	1.040 4(3)	0.231 6(3)	0.225 5(2)
C(5aC)	1.095 7(3)	0.188 7(3)	0.192 9(2)
C(5C)	1.169 4(3)	0.206 5(4)	0.188 0(3)
C(6C)	1.209 2(3)	0.152 6(5)	0.155 0(4)
C(7C)	1.178 5(3)	0.084 8(5)	0.127 5(3)
C(8C)	1.105 2(3)	0.067 2(3)	0.131 8(3)
C(8aC)	1.065 4(2)	0.120 1(3)	0.165 8(2)
C(9C)	0.986 3(2)	0.112 3(3)	0.179 8(2)
O(9C)	0.976 3(2)	0.041 9(2)	0.216 4(2)
H(9C)	1.0087	0.0189	0.2500
C(10C)	0.934 2(2)	0.108 0(3)	0.119 6(2)
C(11C)	0.894 8(3)	0.041 4(4)	0.102 7(3)
C(12C)	0.847 7(4)	0.041 1(5)	0.046 8(4)
C(13C)	0.840 7(4)	0.105 9(5)	0.008 4(3)
C(14C)	0.879 7(4)	0.172 3(4)	0.025 0(3)
C(15C)	0.926 2(3)	0.173 4(3)	0.080 6(2)
C(1aD)	0.784 2(3)	−0.092 1(3)	0.213 6(2)
C(1D)	0.775 6(4)	−0.142 6(4)	0.162 0(3)
C(2D)	0.718 0(8)	−0.123 9(7)	0.116 1(4)
C(3D)	0.674 5(8)	−0.064 1(10)	0.119 4(7)
C(4D)	0.682 5(4)	−0.013 8(6)	0.172 5(5)
C(4aD)	0.738 6(3)	−0.027 3(3)	0.218 6(3)
C(5aD)	0.764 0(3)	0.016 2(3)	0.276 4(3)
C(5D)	0.740 5(4)	0.087 5(4)	0.301 6(5)
C(6D)	0.777 0(6)	0.116 4(5)	0.354 3(5)
C(7D)	0.835 2(6)	0.078 3(4)	0.385 5(4)
C(8D)	0.861 0(4)	0.007 0(3)	0.361 2(3)
C(8aD)	0.824 4(2)	−0.022 9(3)	0.306 5(2)
C(9D)	0.841 5(2)	−0.097 2(2)	0.269 8(2)
O(9D)	0.912 9(2)	−0.093 3(2)	0.250 1(2)
H(9D)	0.9286	−0.0434	0.2432
C(10D)	0.835 6(2)	−0.173 0(2)	0.308 5(2)
C(11D)	0.895 4(3)	−0.218 6(3)	0.328 8(2)
C(12D)	0.888 0(4)	−0.286 3(3)	0.365 3(3)
C(13D)	0.820 9(4)	−0.308 7(3)	0.381 7(3)
C(14D)	0.761 0(3)	−0.264 3(3)	0.361 8(3)
C(15D)	0.768 0(3)	−0.197 2(3)	0.325 2(2)
C(B1)	0.076 4(5)	0.578 9(6)	0.002 9(4)
C(B2)	0.143 2(5)	0.554 3(5)	−0.008 0(5)
C(B3)	0.162 3(4)	0.553 4(5)	−0.068 9(6)
C(B4)	0.114 5(6)	0.577 6(6)	−0.116 4(4)
C(B5)	0.048 5(6)	0.601 1(5)	−0.106 3(5)
C(B6)	0.030 5(5)	0.603 1(5)	−0.046 7(6)
C(B7)	0.0621	0.5035	0.4679
C(B8)	0.0368	0.4319	0.4861
C(B9)	−0.0255	0.4305	0.5163
8 [1a·dioxane (4:3)]			
C(1a)	0.518 0(4)	0.786 3(3)	0.482 4(2)
C(1)	0.637 1(4)	0.892 2(3)	0.504 9(3)
C(2)	0.785 8(5)	0.897 9(4)	0.492 8(3)
C(3)	0.814 1(5)	0.800 9(5)	0.460 1(3)
C(4)	0.694 0(5)	0.695 8(4)	0.437 7(3)
C(4a)	0.545 0(4)	0.688 1(3)	0.449 0(2)
C(5a)	0.394 6(4)	0.589 8(3)	0.429 2(2)
C(5)	0.358 9(6)	0.474 6(3)	0.394 2(3)
C(6)	0.202 1(6)	0.399 9(3)	0.379 1(3)
C(7)	0.083 6(5)	0.438 4(3)	0.399 0(2)
C(8)	0.121 1(5)	0.554 9(3)	0.434 7(2)
C(8a)	0.277 0(4)	0.628 9(3)	0.449 9(2)
C(9)	0.345 0(4)	0.757 5(3)	0.486 9(2)
O(9)	0.264 1(3)	0.814 1(2)	0.439 4(2)
H(9)	0.2901	0.8022	0.3904
C(10)	0.327 4(4)	0.787 2(3)	0.574 2(2)
C(11)	0.418 2(6)	0.763 0(4)	0.637 5(3)
C(12)	0.398 2(8)	0.786 0(5)	0.717 1(3)
C(13)	0.290 2(8)	0.834 4(4)	0.734 0(3)
C(14)	0.202 6(6)	0.860 1(4)	0.673 1(4)
C(15)	0.219 5(5)	0.837 9(3)	0.592 5(3)
C(1a′)	0.232 6(4)	1.367 5(3)	0.877 3(2)
C(1′)	0.323 7(5)	1.483 0(4)	0.896 4(3)
C(2′)	0.313 4(5)	1.538 7(4)	0.834 3(3)
C(3′)	0.216 2(6)	1.485 0(5)	0.757 9(3)
C(4′)	0.123 8(5)	1.370 7(4)	0.737 9(3)
C(4a′)	0.134 6(4)	1.311 7(3)	0.799 0(2)
C(5a′)	0.056 2(5)	1.190 3(3)	0.795 7(3)
C(5′)	−0.050 2(5)	1.098 9(4)	0.730 6(3)
C(6′)	−0.105 2(6)	0.993 6(4)	0.744 6(4)
C(7′)	−0.057 4(7)	0.977 4(4)	0.821 6(5)
C(8′)	0.051 3(6)	1.067 1(4)	0.888 2(3)
C(8a′)	0.107 8(5)	1.174 5(4)	0.873 8(3)
C(9′)	0.224 4(5)	1.285 8(3)	0.932 8(2)
O(9′)	0.376 1(3)	1.279 0(3)	0.963 0(2)
H(9′)	0.4192	1.2579	0.9187
C(10′)	0.163 0(5)	1.317 6(3)	1.008 0(3)
C(11′)	0.231 2(6)	1.308 4(4)	1.083 5(3)
C(12′)	0.170 7(7)	1.335 4(4)	1.151 2(3)
C(13′)	0.044 4(8)	1.367 8(4)	1.144 0(4)
C(14′)	−0.022 3(8)	1.379 0(6)	1.070 1(4)
C(15′)	0.036 6(7)	1.353 6(6)	1.001 1(4)

Table 4 (*continued*).

Atoms	*x/a*	*y/b*	*z/c*
8 [**1a**·dioxane (4:3)]			
O(D1)	0.340 4(4)	0.777 7(3)	0.291 8(2)
C(D2)	0.432 8(7)	0.872 1(4)	0.266 2(3)
C(D3)	0.561 7(6)	0.846 0(5)	0.234 6(4)
O(D4)	0.494 5(4)	0.745 9(3)	0.168 4(2)
C(D5)	0.405 7(7)	0.651 8(4)	0.194 9(4)
C(D6)	0.278 3(6)	0.676 2(4)	0.227 7(3)
O(D1′)	0.567 1(21)	0.073 2(11)	1.069 4(6)
C(D2′)	0.612 4(24)	0.087 2(13)	0.995 4(12)
C(D6′)	0.412 4(24)	0.029 5(21)	1.043 5(9)
9 [**4c**·EtOH (1:1)]			
C(1a)	0.493 5(5)	0.486 1(3)	0.731 3(3)
C(1)	0.644 5(6)	0.463 9(4)	0.757 1(3)
C(2)	0.676 1(7)	0.363 3(4)	0.764 4(4)
C(3)	0.557 4(8)	0.289 1(4)	0.745 7(4)
C(4)	0.405 2(7)	0.310 3(4)	0.719 5(3)
C(4a)	0.372 3(5)	0.409 1(3)	0.711 8(3)
C(5a)	0.224 4(5)	0.453 0(4)	0.681 9(3)
C(5)	0.074 2(6)	0.406 4(5)	0.652 3(3)
C(6)	−0.045 4(7)	0.464 4(5)	0.625 1(4)
C(7)	−0.021 9(6)	0.567 3(6)	0.625 4(4)
C(8)	0.132 3(6)	0.616 7(4)	0.655 6(3)
C(8a)	0.251 2(5)	0.556 9(4)	0.683 6(3)
C(9)	0.427 4(5)	0.587 2(3)	0.716 3(3)
C(10)	0.491 1(5)	0.641 6(3)	0.646 1(3)
C(11)	0.603 9(6)	0.721 1(4)	0.667 5(3)
C(12)	0.667 1(6)	0.763 5(4)	0.603 2(3)
C(13)	0.617 9(6)	0.727 5(4)	0.515 8(3)
C(14)	0.505 2(6)	0.647 9(4)	0.493 8(3)
C(15)	0.441 8(6)	0.606 0(4)	0.558 7(3)
C(16)	0.466 6(5)	0.649 7(3)	0.803 8(3)
O(17)	0.563 3(5)	0.630 7(3)	0.867 9(2)
O(18)	0.388 1(5)	0.727 7(3)	0.801 0(2)
H(18)	0.4166	0.7683	0.8619
O(E)	0.458 2(5)	0.829 8(3)	0.952 5(3)
H(OE)	0.5784	0.8479	0.9887
C(E1)	0.3410	0.8552	0.9967
C(E2)	0.2778	0.7701	1.0324
C(1a′)	0.988 4(5)	0.899 3(3)	0.309 2(3)
C(1′)	1.131 8(5)	0.864 7(4)	0.316 1(3)
C(2′)	1.212 8(6)	0.831 0(4)	0.397 6(4)
C(3′)	1.152 0(6)	0.831 4(4)	0.469 4(4)
C(4′)	1.006 5(6)	0.867 5(4)	0.463 6(3)
C(4a′)	0.925 8(5)	0.901 6(3)	0.383 2(3)
C(5a′)	0.775 6(5)	0.943 6(3)	0.357 3(3)
C(5′)	0.668 2(6)	0.961 5(4)	0.406 7(4)
C(6′)	0.533 2(6)	1.000 4(4)	0.364 6(4)
C(7′)	0.500 8(6)	1.022 9(4)	0.275 8(4)
C(8′)	0.606 5(5)	1.005 3(4)	0.226 3(4)
C(8a′)	0.742 9(5)	0.964 8(3)	0.267 8(3)
C(9′)	0.877 3(5)	0.940 7(3)	0.228 9(3)
C(10′)	0.955 1(5)	1.030 4(4)	0.193 6(3)
C(11′)	0.942 7(6)	1.125 7(4)	0.222 0(3)
C(12′)	1.015 2(7)	1.207 7(5)	0.190 3(4)
C(13′)	1.099 7(7)	1.193 1(5)	0.129 8(4)
C(14′)	1.115 0(6)	1.096 1(5)	0.101 8(4)
C(15′)	1.042 6(5)	1.015 2(4)	0.132 9(3)
C(16′)	0.811 0(5)	0.863 0(4)	0.151 7(3)
O(17′)	0.719 2(4)	0.882 7(3)	0.084 8(2)
O(18′)	0.860 5(5)	0.775 6(3)	0.164 8(3)
H(18′)	0.8063	0.7343	0.1209
O(E′)	0.740 5(6)	0.642 4(3)	0.038 6(3)
H(OE′)	0.6698	0.6632	−0.0276
C(E1′)	0.748 1(13)	0.539 3(7)	0.054 3(6)
C(E2′)	0.884 2(14)	0.508 6(10)	0.103 1(7)

[a] Esds are given in parentheses. [b] The half benzene molecule of the asymmetric unit in **7**, and the carbon atoms of one of the alcohol molecules in **9** showed extremely high thermal mobility and could not be refined in the usual way. The benzene C atoms were held fixed and the alcoholic carbons were held riding on their O(E) atom during the refinement calculations. [c] The positions of the alcoholic and the carboxylic H atoms were taken from difference Fourier calculations and were held riding on their 'mother' atoms during the subsequent calculations.

by suction filtration, washed with Et_2O or MeOH, and dried (2 h, 15 Torr, room temperature). Data for each compound are given in Table 1.

Crystal Structure Determination.—Sample preparation. Colourless, transparent crystals of the inclusion compounds **7**–**9**, suitable for X-ray diffraction, were grown from solutions of the host compounds **1a** and **4c** in the corresponding solvents (benzene, dioxane and EtOH). In order to prevent solvent evaporation during X-ray data collection, the selected single crystals of **7** and **8** were carefully sealed in epoxy glue, and the crystal of **9** was enclosed in a glass capillary.

Data collection and processing. The intensity data were obtained at room temperature on a Siemens STOE/AED2 diffractometer equipped with a graphite monochromator and using the ω–2θ scan technique. Data reduction included corrections for background, Lorentz, polarization and decay effects, but the relatively low absorption effects (*cf.* Table 2) were ignored. Reference reflections (five for **7**, five for **8** and four for **9**), measured at intervals of approximately 90 (**7** and **9**) or 60 min (**8**), showed a decrease in intensity of about 5% for **7** and **9**, and about 22% for **8** during the period of the data collection. The unit cell parameters were refined by the least squares method, using the angular settings (θ values) of strong, well-centred reflections ($54_{7.5<2\theta<30°}$ for **7**, $80_{40.5<2\theta<77.5°}$ for **8** and $45_{61<2\theta<81.5°}$ for **9**), accurately measured on the diffractometer. Crystal data and some experimental details are summarized in Table 2.

Structure analysis and refinement. The structures were solved by direct methods, using the program systems of SHELXS[41] for **7** and MULTAN[42] for **8** and **9**. Difference electron density and full-matrix least-squares calculations by means of different versions of the SHELX program system[43,44] were then used for completion and refinement of the initial structural models. The oxygen-bonded hydrogens were in all cases located from difference electron density maps and were held riding on their 'mother' atoms during the subsequent calculations. The carbon-bonded H atom sites were generated in geometrically assumed positions (C–H = 1.08 Å) after each cycle of the refinement calculations.

In the last stage of the refinements, the C and O atomic positions, except C(B7), C(B8) and C(B9) benzene atoms in **7**, and C(E1) and C(E2) ethanol atoms in **9**, which could not be treated in the usual way (see below), were refined together with their anisotropic thermal parameters in all three structures. Isotropic temperature factors (six in **7** and four in **8**) were refined for the H atoms in the two inclusion compounds of the **1a** host. In the structure of **9**, however, each hydrogen of the two host molecules and the two hydroxy groups of the guests had its own isotropic temperature parameter refined, and one temperature factor was refined for the methylene and one for the methyl H atoms of the primed guest alcohol. The methyl group of this guest was treated as a rigid group with free rotation around the C(E1′)–C(E2′) bond. The (C)–H atoms of the other guest were given fixed temperature parameters (see below).

The atoms of the guest molecules in these structures have considerably higher temperature factors than those of the host molecules (*cf.* Table 4). Due to the very high thermal mobility of some of the guest atoms, the solution of the present structures was not straightforward. Although the guest atomic positions could be located from maps with some trouble, it was

impossible, in some cases, to refine them in the usual way by least-squares techniques. In the case of **7**, for example, the refinement of the structural model converged satisfactorily only when the three independent benzene carbon positions [C(B7), C(B8) and C(B9)] were held fixed. Similarly, in the refinement of the ethanol inclusion compound of the **4c** host, it was necessary to keep the positions of C(E1) and C(E2) atoms riding on their ethanolic oxygens, O(E), and to fix the temperature factors of the H atoms bonded to these two guest carbon atoms.

Some of the stronger low-θ reflections (four for **7**, two for **8** and 24 for **9**) with F_o considerably less than F_c, probably due to extinction, were excluded from the last refinements, which resulted in the final reliability indices listed in Table 2. Final atomic co-ordinates for compounds **7**–**9** are given in Table 4.

Supplementary Data. Lists of bond lengths and bond angles involving the non-H atoms, fractional atomic co-ordinates of the calculated H positions, and details of least-squares planes have been deposited as supplementary data at the Cambridge Crystallographic Data Centre.* Lists of the anisotropic thermal parameters of the non-hydrogen atoms and the observed and calculated structure factors may be obtained from the authors (I. C.).

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* For details of the CCDC deposition scheme see 'Instructions for Authors, (1990),' *J. Chem. Soc., Perkin Trans. 2*, issue 1.

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