New Trigonal Lattice Hosts: Stoicheiometric Crystal Inclusions of Laterally Trisubstituted Benzenes—*X*-Ray Crystal Structure of 1,3,5-Tris-(4-carboxyphenyl)benzene·Dimethylformamide

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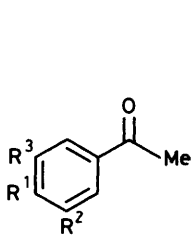
New host molecules with a central 1,3,5-trisubstituted benzene ring and rigidly attached lateral arms composed of aryl or arylethynyl and extra functional groups are reported. They are shown to give more than thirty clathrates with a wide variety of organic solvents comprising alicyclic, aromatic, heterocyclic, dipolar aprotic, and protic molecules. Inclusion selectivities and stoicheiometries of the different clathrates are discussed. The crystal structure of (**2a**)·dimethylformamide (DMF) (1:3) inclusion compound has been determined from single-crystal *X*-ray diffraction. The crystals show $R\bar{3}$ symmetry. There are six host and eighteen guest molecules in the hexagonal unit cell with $a = b = 23.160(9)$ and $c = 11.812(3)$ Å. The final linear R is 0.082 for 1 518 unique reflections. The host molecule adopts a propeller conformation with perfect three-fold symmetry and acts as a donor in hydrogen bonds to three DMF molecules. In the crystal structure the host–guest units are arranged stack-wise.

Organic molecules are predestinated to form crystalline interspace inclusions (clathrates†) when having a bulky and spatially unbalanced molecular constitution.[1] It is also established that molecules of a certain symmetry tend to exhibit clathrate behaviour,[2] *e.g.*, trigonal symmetry being very effective.[3] Unfortunately, existing host compounds which have this merit are rather complex in structure or are individual units not allowing extensive modifications.[1] The recent interest in the practical applications of crystal inclusions[4] stimulated us to seek for alternative clathrate hosts characterized as simple, easily accessible, and highly variable in structure. Compounds based on a trifunctional aromatic core and—unlike a former report[5]—rigidly attached non-flexible but bulky side arms (if possible with functional groups on them)[2c] are promising candidate molecules in this respect. We now describe the preparation of several new compounds of this type, (**1**)—(**5**), report on their crystal inclusion properties, and give an *X*-ray crystal structure demonstration of one of the isolated host–guest species [(**2a**)·DMF].

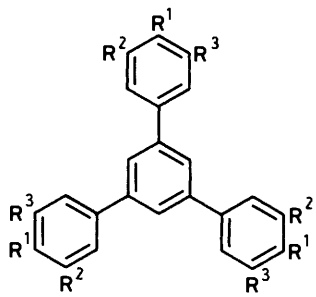
Results and Discussion

Synthesis.—The 1,3,5-triaryl substituted benzenes (**1**) were obtained by cyclization reaction of the corresponding acetophenones (**6**) (Scheme 1).[6] Different condensation reagents were used in individual cases (see the Experimental section). The triacids (**2a**)[7] and (**3**) were synthesized from the tribromo derivatives (**1g**)[6,8] and (**1h**),[9] respectively, by reaction with n-BuLi–CO_2. Tris-aldehyde (**2b**) was prepared from tribromide (**1g**) with Bu^{n}Li and *N*-formylpiperidine (*cf.* ref. 10).

In contrast to the triaryl-substituted benzenes (**1**), the analogous tris(arylethynyl)-substituted arenes (**4**) and (**5**) are not documented in the literature. Known methods which may lead to compounds of this class [*cf.* (**8**)][11] are unfavourable owing to multi-step reactions and low yields. Recently, Hagihara[12] has demonstrated an elegant synthetic approach to mono- and di-ethynylarenes in which aryl halides and



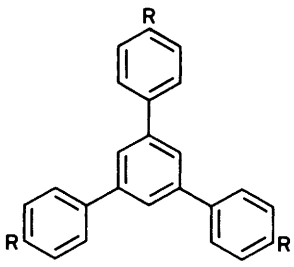
(**6**)



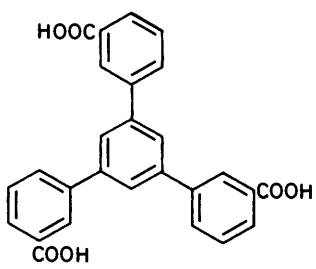
(**1**)

a; $R^1 = R^2 = R^3 = H$
b; $R^1 = Me$, $R^2 = R^3 = H$
c; $R^1 = H$, $R^2 = R^3 = Me$
d; $R^1 = Bu^t$, $R^2 = R^3 = H$
e; $R^1 = OMe$, $R^2 = R^3 = H$
f; $R^1 = Ph$, $R^2 = R^3 = H$
g; $R^1 = Br$, $R^2 = R^3 = H$
h; $R^1 = R^2 = H$, $R^3 = Br$

Scheme 1.

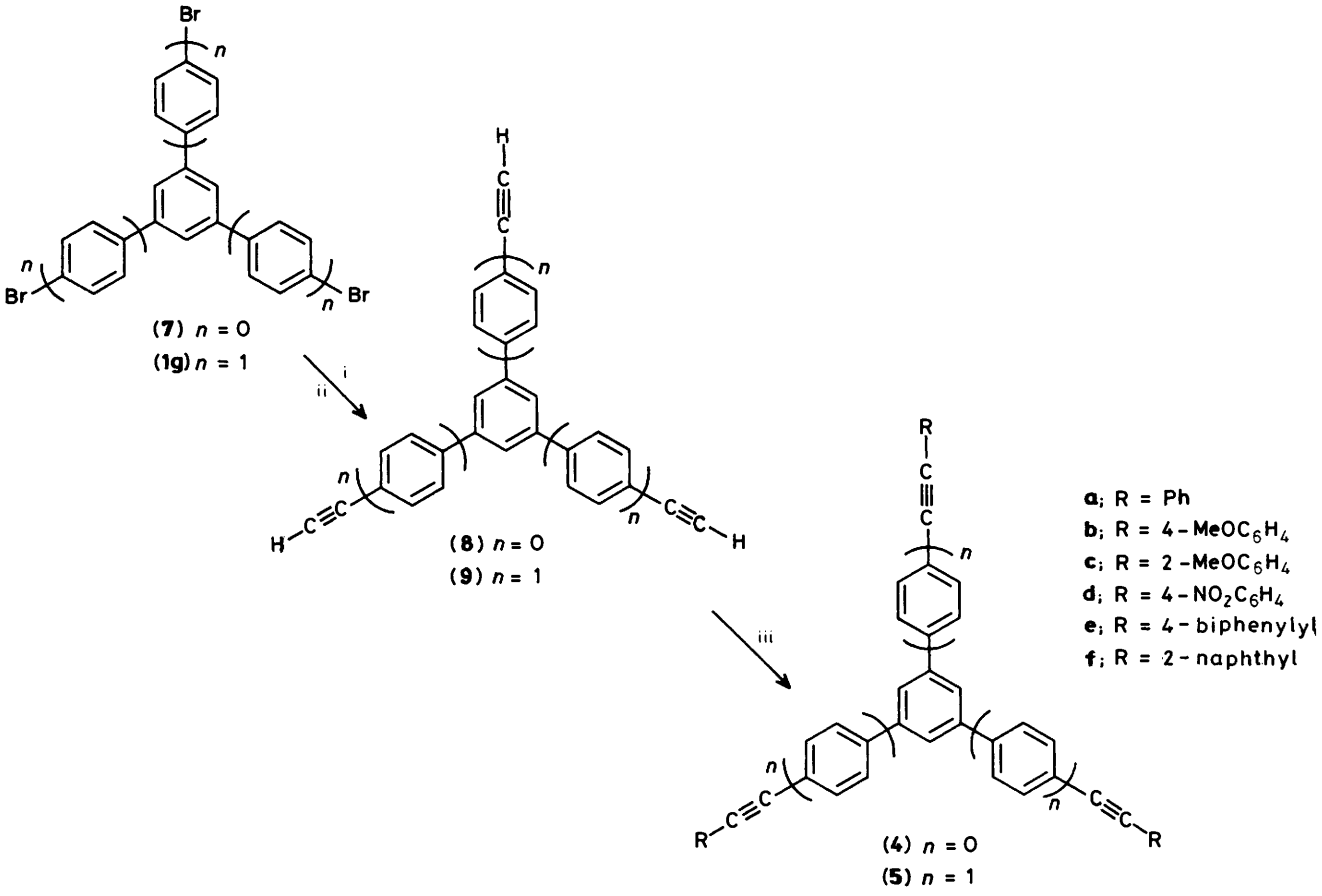


(**2**)**a**; R = COOH
b; R = CHO



(**3**)

† Classification and nomenclature of inclusion-type compounds, see E. Weber and H.-P. Josel, *J. Incl. Phenom.*, 1983, **1**, 79.



Scheme 2. *Reagents and conditions:* (i) 3 $HC{\equiv}CSiMe_3$, $Pd(PPh_3)_2Cl_2$–CuI, Et_2NH; (ii) NaOH; (iii) 3 RI (**10**), $Pd(PPh_3)Cl_2$–CuI

trimethylsilylacetylene are coupled in the presence of the catalytic system copper(I) iodide–dichlorobis(triphenylphosphine)palladium(II) and secondary or tertiary amines as solvent and base. We were successful in developing efficient synthetic procedures to triethynyl arenes using this reaction (Scheme 2).* For the synthesis of 1,3,5-triethynylbenzene (**8**),[11c] 1,3,5-tribromobenzene (**7**) in diethylamine was treated under mild conditions with trimethylsilylacetylene in the presence of the Pd–Cu catalytic system. The resulting silyl intermediate was hydrolysed without prior isolation to yield 86% of (**8**). Analogously 1,3,5-tris-(4-ethynylphenyl)benzene (**9**) was obtained from 1,3,5-tris-(4-bromophenyl)benzene (**1g**) in 80% yield.

Conversion of (**8**) and (**9**) into the corresponding aryl-substituted triethynyl compounds (**4b**—**f**) and (**5b**) was also accomplished by the Pd–Cu catalytic system[13] (Scheme 2). Yields ranging between 40—80% were obtained by using aryl iodides (**10**) as the second component. Replacement by aryl bromides (*e.g.* bromobenzene or 4-bromotoluene) failed. Likewise the reaction of (**8**) with non-aromatic iodides, *e.g.* t-butyl iodide or iodocyclohexane, did not proceed under the catalytic conditions. In a different procedure, 1,3,5-tris(phenylethynyl)benzene (**4a**) was synthesized in 42% yield from tribromobenzene (**7**) and phenylacetylene in the presence of copper bronze and potassium carbonate in dimethylformamide (*cf.* ref. 14).

* Very recently hexaethynylbenzene was also obtained by this method, K. P. C. Vollhardt and R. Diercks, *J. Am. Chem. Soc.*, 1986, **108**, 3150.

Inclusion Properties.—A variety of solvents, including aliphatic and alicyclic compounds, unsaturated hydrocarbons, aromatic compounds, heterocycles, dipolar aprotic compounds, amines, alcohols, and an acid (see Table 1), were used to investigate the inclusion capabilities of potential host compounds (**1**)—(**5**) (see Table 2). By far the most efficient host is (**1e**) followed by (**2a**) and (**2b**), while (**1a**), (**1d**), (**1f**), (**3**), and (**4e**) are less effective at inclusion formation; none of the other compounds [(**1b**), (**1c**), (**1g**), (**1h**), (**4a**—**d**), (**4f**), and (**5b**)] have inclusion properties.

For the hosts of types (**1**) and (**4**), the guest molecules included exclusively range between alicyclic, aromatic, and heterocyclic solvents (Table 2). In contrast, the polar group containing hosts (**2**) and (**3**) mostly form inclusion compounds with dipolar aprotic solvents such as acetonitrile, DMF, and DMSO. The only examples of protic solvent inclusions are that of (**2a**) with ethanol and acetic acid. Guest preferences, as observed, are in accordance with expectations of former findings.[1,2] The relation is: non-polar hosts favour non-polar guests in the formation of inclusion crystals and polar hosts favour polar guests [*cf.* (**1a**) with (**2a**)]. Stoicheiometries of the different inclusions are between 4:1 and 1:3 (host:guest, see Table 2).

It is generally noticed that (**1a**) and (**1f**), which are composed of benzene nuclei only, but with a different number, tend to form 3:1 (host:guest) stoicheiometry, and the guest over-all size and shape (unsubstituted and substituted six-membered rings, respectively) are rather constant. On the other hand (**1e**) is typical of the 2:1 ratio largely irrespective of the nature (*cf.* benzene and pyridine) and over-all size of the guest (*cf.* benzene

Table 1. Solvent compounds tested for inclusion formation

n-Hexane, n-heptane, cyclopentane, cyclohexane, cycloheptane, methylcyclohexane, cyclopentene, cyclohexene, cycloheptene, cycloheptatriene;

benzene, toluene, *o*-xylene, *m*-xylene, *p*-xylene, mesitylene, 1,2,3,5-tetramethylbenzene, 1-bromo-2,3-dimethylbenzene;

tetrahydrofuran (THF), dioxolane, dioxane, morpholine, pyridine, 2-methylpyridine, 4-methylpyridine, 2-ethylpyridine;

dichloromethane, acetone, cyclopentanone, cyclohexanone, acetonitrile, nitromethane, nitroethane, dimethyl sulphoxide (DMSO), DMF;

diethylamine, triethylamine, methanol, ethanol, propan-1-ol, propan-2-ol, butan-1-ol, butan-2-ol, 2-methylpropan-2-ol, cyclopentanol, cyclohexanol, acetic acid.

Table 2. Crystalline inclusion compounds[a]

(**1a**): Benzene (3:1),[b] cyclohexane (3:1), cyclohexene (3:1)

(**1d**): Morpholine (4:1)

(**1e**): Benzene (2:1), toluene (2:1), *o*-xylene (2:1), *m*-xylene (2:1), *p*-xylene (2:1), mesitylene (2:1), 1,2,3,5-tetramethylbenzene (2:1), 1-bromo-2,3-dimethylbenzene (2:1), pyridine (≈2:1), 2-methylpyridine (≈2:1), 4-methylpyridine (≈2:1), 2-ethylpyridine (≈2:1), dioxane (≈2:1)

(**1f**): Toluene (3:1), xylene (3:1)[c]

(**2a**): Dioxane (2:3), DMSO (1:2), DMF (1:3), ethanol (1:1), acetic acid (3:1, 1:1)[d]

(**2b**): Toluene (2:1), acetonitrile (1:1), DMSO (1:1), DMF (2:1)

(**3**): DMSO (1:1), DMF (2:3)

(**4e**): Dioxane (≈2:1)

[a] See Experimental section for method of preparation, drying standard and characterization; stoicheiometric ratios (host:guest) are given in parentheses. [b] Ratio difficult to observe by n.m.r. integration. [c] *Cf.* ref. 15. [d] Ratio dependent on recrystallization conditions (concentration of components, rate of cooling).

and 1,2,3,5-tetramethylbenzene). This suggests the existence of relatively invariant host lattices[1] for (**1a**) and (**1f**), possibly with a channel structure (*cf.* ref. 16), whereas (**1e**) is indicative of a more deformable host matrix. Indeed, among the three hosts, only (**1e**) has a flexible group (OMe) which may be responsible for the more deformable lattice structure in the case of (**1e**). A further conclusion from Table 2 is that (**1a**) not only involves the least deformable crystal voids of all three hosts, but also the most narrow. Compound (**1e**) is unique in forming clathrates both with non-polar and polar guests (aromatic hydrocarbons and pyridines, respectively); alicyclic molecules, however, are not included.

While the clathrates of (**1a**), and (**1d**—**f**), naturally, are not concerned with co-ordinative host–guest interaction,[2d] that of the more polar hosts (**2a**), (**2b**), and (**3**) certainly are. Most evidently this behaviour (co-ordinatoclathrate formation[2c]) appears from the 1:3 stoicheiometry of (**2a**)·DMF. It suggests involvement of the complete carboxylic group capacity in host–guest binding, *e.g. via* hydrogen bonds. Former findings are corroborative with this assumption.[17,18] Binding of (**2a**) to DMSO which demonstrates a restricted carboxylic group involvement on host–guest interaction (1:2 stoicheiometry) is also in line with previous facts.[19,20] As formerly shown and suggested here, DMSO tends to bind in an intercalate fashion

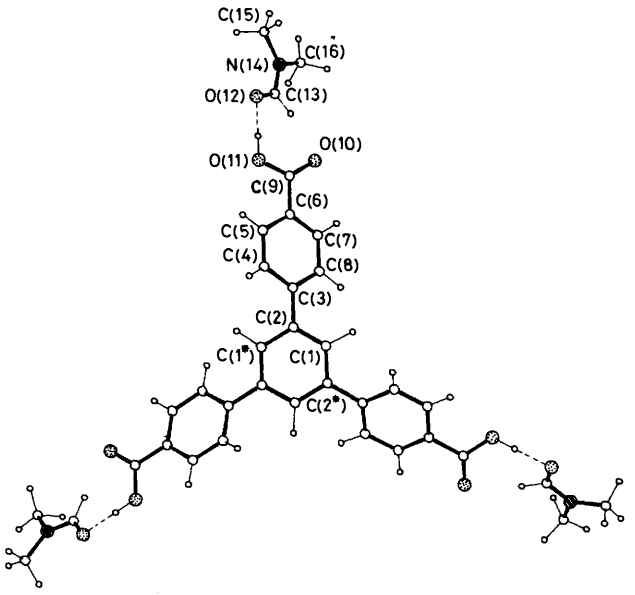


Figure 1. Molecular structure of (**2a**)·DMF (1:3): top view giving indication of the numbering scheme for the atoms (O atoms dotted, N atoms hatched; solid and dashed lines represent covalent and hydrogen bonds, respectively)

with carboxylic-group-containing hosts, while DMF is characteristic of displaying a concrete one-to-one co-ordination to each COOH group appended to the host. Since acetic acid is known to behave as a self-clustering species in host crystals,[21] 3:1 or 1:1 stoicheiometry with (**2a**) (contingent on the conditions, see Table 2) may not be interpreted as a surprising result. However, the 1:1 stoicheiometry of (**2a**) with ethanol is difficult to explain in the light of former data.[2c] But other authors have shown that benzene-1,3,5-tricarboxylic acid, in a way related to (**2a**), also resulted in unpredictable inclusion stoicheiometries.[19]

Host (**2b**) with less hydrogen bond potential gave inclusion stoicheiometries (*cf.* toluene, DMF) closely connected with (**1e**) rather than with (**2a**). The positional isomer (**3**) [*cf.* (**2a**)] is far less prone to form inclusion compounds (only with DMSO and DMF) showing that placement of the functional groups is an essential parameter in host capacity. The ethynylene-modified analogues (**4a**—**f**), and (**5b**) are inefficient in inclusion formation, except for (**4e**) which yields a 2:1 clathrate with dioxane, but this inclusion compound is rather weak (see below).

Inclusion selectivities of (**1a**) and (**2a**) have been determined for several solvent mixtures (equimolar ratio). It is shown for (**1a**) that both from mixtures of cyclohexane with cyclohexene or with benzene, the cyclohexane inclusion compound (3:1) is formed, exclusively. Host (**2a**) has a high affinity to co-crystallize with DMF. Hence, the respective inclusion compound, (**2a**)·DMF (1:3), is formed from all solvent mixtures involving DMF and other potential guests of Table 2. It is also noted that (**2a**)·DMF shows the highest stability under vacuum drying conditions, and on storage of all isolated inclusion compounds. The cathrates composed of only hydrocarbons (see Table 2) are unstable on storage.

The particular solvent inclusion and binding behaviour of several hosts, *e.g.* of (**2a**), made the *X*-ray structure of a respective inclusion compound desirable. Fortunately crystals of (**2a**)·DMF (1:3) were found to be suitable for an *X*-ray study.

X-Ray Analysis: Structure Description of (**2a**)·*DMF* (1:3).—A perspective view of the structure including atom numbering is presented in Figure 1, atomic co-ordinates are listed in Table

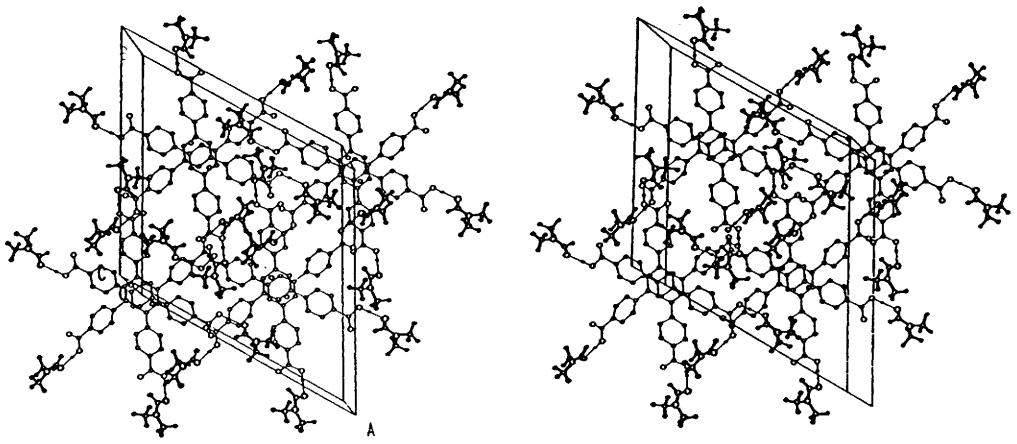


Figure 2. Stereoscopic packing illustration of the (**2a**)·DMF (1:3) co-ordinatoclathrate (for clearness, hydrogen atoms of the aromatic rings are omitted)

Table 3. Fractional atomic co-ordinates (the e.s.d.s, where given, are in parentheses; the atoms are numbered according to Figure 1)

Atom	*x*	*y*	*z*
C(1)	0.006 2(2)	−0.056 5(2)	0.156 2(3)
C(2)	0.063 8(2)	0.006 7(2)	0.155 1(3)
C(3)	0.135 5(2)	0.013 3(2)	p.143 2(3)
C(4)	0.187 2(2)	0.066 8(2)	0.190 4(4)
C(5)	0.249 7(2)	0.074 7(2)	0.172 8(4)
C(6)	0.256 5(2)	0.028 6(2)	0.107 1(3)
C(7)	0.201 0(2)	−0.024 2(2)	0.059 0(4)
C(8)	0.137 8(2)	−0.032 6(2)	0.078 4(4)
C(9)	0.322 7(2)	0.035 6(2)	0.083 1(4)
O(10)	0.329 0(2)	−0.008 6(2)	0.041 2(4)
O(11)	0.373 5(2)	0.094 3(2)	0.109 9(3)
O(12)	0.487 6(2)	0.109 7(2)	0.041 6(4)
C(13)	0.483 2(3)	0.078 8(3)	−0.045 8(5)
N(14)	0.532 5(2)	0.075 2(2)	−0.093 7(3)
C(15)	0.597 5(3)	0.106 6(6)	−0.042 6(7)
C(16)	0.525 6(4)	0.038 7(5)	−0.196 9(6)
O(W)	0.0000	0.0000	0.5000
H(1)	0.008	−0.104	0.166
H(4)	0.182	0.091	0.244
H(5)	0.290	0.112	0.212
H(7)	0.207	−0.057	0.004
H(8)	0.094	−0.073	0.039
H(11)	0.416	0.100	0.082
H(13)	0.438	0.047	0.095
H(151)	0.630	0.102	0.104
H(152)	0.594	0.078	0.032
H(153)	0.618	0.158	0.020
H(161)	0.572	0.047	0.234
H(162)	0.505	0.062	0.249
H(163)	0.491	−0.014	0.192

3. Since the three-fold molecular symmetry perfectly coincides with a crystallographic three-fold rotor, the asymmetric unit consists of only 1/3 of the depicted host–guest aggregate.

Bond lengths and bond angles generally conform to the expected values. The five non-hydrogen atoms of the DMF guest are co-planar within 0.017 Å, but the host molecule deviates considerably from planarity, as expected. The pair of planar phenyl rings is twisted around the C(2)–C(3) bond. The dihedral angle between the LS plane of the rings is 31.8(3)°. This is comparable with the phenyl twist angles (+34, −27, and +24°) reported in the first study of the parent compound 1,3,5-triphenylbenzene,[20a] but slightly less than the refined values (+40.7, −37.2, and 36.1°) later published for these angles.[20b] The carboxy groups are inclined by 13.1(2)° with reference to the plane of the attached phenyl substituent. Consequently the host molecule has the shape of a propeller.

The bonding of the DMF guest in the present structure (Figure 1) is somewhat different from that expected.[17] The DMF molecule may be engaged in hydrogen bonding primarily as proton acceptor, but also as donor making a C–H···O type of interaction possible. In one way, this mode of interaction is usual and has previously been demonstrated by the crystal structures of DMF inclusions with hosts such as 9,9′-spirobifluorene-2,2′-dicarboxylic acid,[17] 1,1′-binaphthene-2,2′-dicarboxylic acid,[18] and *trans*-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxylic acid.[22] In the present structure, however, the DMF guest is the acceptor in an O–H···O bond from the host [O···O = 2.611(5), O–H = 0.99, H···O = 1.62 Å, O–H···O = 178°] but makes no advantage of a C–H···O-type interaction. On the contrary, probably due to crystal forces, the DMF molecule is turned around the O–H···O bond so as to incline its molecular plane though 36.2(2)° to the plane of the carboxyl group it co-ordinates.

Packing in the crystal (Figure 2) is such that the (**2a**)·DMF (1:3) aggregates are stacked along the short *c* axis. The interplanar spacing between the central benzene rings of succeeding aggregates is either *ca.* 3.66 Å, a common van der Waals' contact distance, or as long as *ca.* 8.15 Å. In the latter case there are voids formed between succeeding pairs of host–guest units, in which small molecules, *e.g.* disordered water molecules, can be located. Thus, it seems, the hydrogen bonded host–guest (1:3) aggregates are held together by side-arm interlocking and weak van der Waals' interactions.

Conclusions

The present results show that 1,3,5-triaryl-substituted benzenes are a rich source of crystalline inclusion hosts. Whether inclusion compounds are formed with these molecules, and if so, what type, depends on the nature and the position of substituents appended to the peripheral nuclei. The data in Table 2 indicate that similarity in polarities of host and guest is a decisive factor to predict inclusion properties. This relation may also be useful in the development of new selective host molecules in the future. However, the apparent lack of inclusion ability, *e.g.* of (**1b**) and (**1c**) [compared with (**1a**), and (**1d**—**f**)], highlights the care required in the design of new trigonal hosts based on

Table 4. Analytical data for the new compounds

Compd.	Yield (%)	M.p. (°C)	Found (%) C	Found (%) H	Mol formula	Required (%) C	Required (%) H	*m/z*, M^+ (required)
(2b)	51	231—232	83.1	4.8	$C_{27}H_{18}O_3$	83.1	4.65	390.1269 (390.1256)
(3)	66	>320	74.2	4.0	$C_{27}H_{18}O_6$	74.0	4.1	438.1104 (438.1103)
(4a)	42	145—147	95.5	5.0	$C_{30}H_{18}$	95.2	4.8	378.1426 (378.1404)
(4b)	82	130—131	84.5	5.3	$C_{33}H_{24}O_3$	84.6	5.2	468.1722 (468.1723)
(4c)	51	132—133	85.1	5.3	$C_{33}H_{24}O_3$	84.6	5.2	468.1711 (468.1723)
(4d)	44	>300	70.2	3.1[c]	$C_{30}H_{15}N_3O_6$	70.2	2.9[c]	513.0966 (513.0957)
(4e)	40	222	95.0	5.1	$C_{48}H_{30}$	95.0	5.0	606.2335 (606.2340)
(4f)	76	206	95.1	5.0	$C_{42}H_{24}$	95.4	4.6	528.1836 (528.1872)
(5b)	54	227—229[a]	87.7	5.3	$C_{51}H_{36}O_3$	87.9	5.2	696.2685 (696.2655)
(9)	80	>200[b]	94.95	4.9	$C_{30}H_{18}$	95.2	4.8	378.1408 (378.1404)

[a] Phase transformation at 150 °C. [b] Decomposition. [c] Found: N, 8.0; required: N, 8.2%.

Table 5. Spectroscopic data for the new compounds

Compd.	I.r. $\nu_{max.}$ (KBr)	^{1}H N.m.r. (δ, p.p.m.; *J*, Hz; $CDCl_3$)
(2b)	2 870, 2 780 (CHO); 1 700 (C=O); 1 615, 1 580 (Ar)	7.89 and 8.01 (12 H, AA'BB', J_{AB} 8, disubst. Ar), 7.95 (3 H, s, trisubst. Ar), and 10.07 (3 H, s, CHO)[a]
(3)	1 715 (C=O); 1 620, 1 590 (Ar)	7.40—8.50 (m, Ar)[b]
(4a)	2 200 (C≡C); 1 590, 1 500 (Ar)	7.29—7.64 (m, Ar)
(4b)	2 220 (C≡C); 1 580, 1 510 (Ar)	3.81 (9 H, s, OMe), 6.82 and 7.41 (12 H, AA'BB', J_{AB} 8, disubst. Ar), and 7.57 (3 H, s, trisubst. Ar)[c]
(4c)	2 200 (C≡C); 1 585, 1 500 (Ar)	4.00 (9 H, s, OMe) and 6.93—7.21 (15 H, m, Ar)
(4d)	2 210 (C≡C); 1 600, 1 510 (Ar); 1 530, 1 340 (NO_2)	*d*
(4e)	2 220 (C≡C); 1 585, 1 490 (Ar)	7.30—7.70 (m, Ar)[c]
(4f)	2 220 (C≡C); 1 590, 1 510 (Ar)	7.39—8.57 (m, Ar)
(5b)	2 220 (C≡C); 1 610, 1 540 (Ar)	3.93 (9 H, s, OMe) and 6.98—8.13 (27 H, m, Ar)
(9)	3 310 (≡C–H); 2 110 (C≡C); 1 605, 1 510 (Ar)	3.08 (3 H, s, ≡CH) and 7.53—7.78 (15 H, m, Ar)

[a] In CD_2Cl_2. [b] In [$^2H_6$]DMSO. [c] In CCl_4. [d] Sparingly soluble.

these simple considerations only. Specific packing effects, which are difficult to assess, may play a primary role and make a prediction problematic. Nevertheless, the crystal structure of (**2a**)·DMF (1:3) meets our expection with regard to the general construction. It has already been shown that hydrogen-bonded rings composed of one COOH and one CHO group are not the one and only mode of interaction between carboxylic acid hosts and DMF.[17,18,22] As in the present case, carboxylic acid hosts and DMF may also form a single hydrogen bond, if crystal packing requires.

It is now established that part of the host properties which were originally ascribed to a six-fold substituted benzene nucleus in the so-called 'hexa-hosts',[3,5] are also made with only three side-arms at the central ring, provided they are rigidly attached, non-flexible, and bulky.

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 from a A.E.I. MS 50 instrument. I.r. spectra were recorded as KBr pills on a Unicam SP-1100 infrared spectrophotometer. ^{1}H N.m.r. spectra were measured, unless otherwise stated, for $CDCl_3$ solutions (Me_4Si as internal standard) with Varian EM-360 (60 MHz) and Bruker WH-90 (90 MHz) spectrometers. Microanalyses were carried out by the Microanalytical Laboratory of the Institute für Organische Chemie und Biochemie, Bonn. For column chromatography Al_2O_3 (Brockmann, grade II—III, Woelm) 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 [acetophenones (**6a—h**), 1,3,5-tribromobenzene (**7**), phenylacetylene] and all other reagents were purchased from Janssen. Analysis figures, yields, and other relevant data of the new compounds are given in Table 4. Spectroscopic data of the new compounds are listed in Table 5.

1,3,5-*Trisubstituted benzenes* (**1a—h**). These compounds were prepared from the corresponding acetophenones (**6a—h**) (*cf.* Scheme 1) using the literature procedures.[6,8b,9,23—25] Methods of condensing involved triethyl orthoformate for compounds (**1a—c**), and for (**1g**), (**1h**), HCl for (**1d**), 'sulfoacetic acid' for (**1e**) and anilinium chloride for (**1f**). (**1a**),[6] 60%, m.p. 175—176 °C; (**1b**),[23] 45%, m.p. 172—174 °C; (**1c**),[23] 21%, m.p. 286—287 °C; (**1d**),[8b] 40%, m.p. 294 °C; (**1e**),[24] 15%, m.p. 145 °C; (**1f**),[25] 18%, m.p. 234—236 °C; (**1g**),[6,8b] 41%, m.p. 259—262 °C; (**1h**),[9] 44%, m.p. 163—165 °C.

1,3,5-*Tris*-(4-*carboxyphenyl*)*benzene* (**2a**). 1,3,5-Tris-(4-bromophenyl)benzene (**1g**) (5.00 g, 9.20 mmol) was dissolved in dry THF (70 ml) under an atmosphere of argon. The stirred solution was cooled to −60 °C and Bu^{n}Li in n-hexane (19.1 ml, 27.6 mmol; 1.6M) was added dropwise. A light-green precipitate of the organyl lithium compound was formed. Then, gaseous CO_2 was passed into the mixture at −60 °C to give a colourless precipitate of the lithium salt of (**2a**). The mixture was acidified with glacial acetic acid, and water was added to cause quantitative deposit of the salt. The precipitate was collected and recrystallized from glacial acetic acid to yield (**2a**) (2.40 g, 60%) as a colourless microcrystalline solid, m.p. 315—318 °C (lit.,[7b] 325 °C).

1,3,5-*Tris*-(4-*formylphenyl*)*benzene* (**2b**). 1,3,5-Tris-(4-bromophenyl)benzene (**1g**) (4.50 g, 8.29 mmol) was dissolved in dry benzene (350 ml) under an atmosphere of argon. To the stirred

solution over a period of 3 h at room temperature was added dropwise n-BuLi in n-hexane (50 ml, 80 mmol; 1.6M). The mixture was stirred for 6—7 h at 55—60 °C to afford the organyl lithium compound of (**1g**) as a brownish-violet precipitate. After cooling the mixture to 0 °C, *N*-formylpiperidine (15 ml, 135 mmol) was added in portions, and slowly warming up the mixture to room temperature led to the formation of a yellow precipitate. The mixture was acidified with HCl (100 ml; 3M), and stirring was continued for 5 h. The formed colourless precipitate was collected by suction filtration. The organic phase of the filtrate was separated and freed from solvent. The residue and the previously collected precipitate were combined and dissolved in $CHCl_3$. The solution was washed (water), dried ($MgSO_4$), and evaporated. Digestion of the crude material with Et_2O and purification by column chromatography (SiO_2, CH_2Cl_2) yielded (**2b**) as colourless crystals.

1,3,5-*Tris*-(3-*carboxyphenyl*)*benzene* (**3**). The same procedure as for (**2a**) applies; (**1h**) was used instead of (**1g**) to yield (**3**) as a colourless powder.

1,3,5-*Triethynylbenzene* (**8**). 1,3,5-Tribromobenzene (**7**) (9.45 g, 30.0 mmol) was dissolved in diethylamine (250 ml) under an atmosphere of argon. Copper(I) iodide (50 mg) and dichlorobis-(triphenylphosphine)palladium(II) (400 mg) were added to the stirred solution. Trimethylsilylacetylene (10.6 g, 108 mmol) was dropped in and the mixture was heated to 50 °C for 7 h. After cooling, the formed precipitate of diethylamine hydrobromide was filtered off and washed (ether). The combined filtrates were evaporated under reduced pressure, and the residue was chromatographed on a column [Al_2O_3, light petroleum (b.p. 40—60 °C)] to yield 1,3,5-tris(trimethylsilylethynyl)benzene as an intermediate. Hydrolysis of this compound was carried out by treatment with a mixture of MeOH–NaOH (50 ml; 30 ml, 1M) under stirring at room temperature for 1 h. A standard work-up procedure involving evaporation of the organic solvent, extraction of the residue with ether, drying (Na_2SO_4), and removal of the solvent under reduced pressure yielded almost pure (**8**) (3.90 g, 85%) as a nearly colourless powder. Sublimation at 0.5 Torr gave colourless needles, m.p. 102—103 °C (lit.,[11c] 104—105 °C).

1,3,5-*Tris*-(4-*ethynylphenyl*)*benzene* (**9**). The same procedure as for (**8**) applies; (**1g**) [5.43 g, 10 mmol, in diethylamine (400 ml)] was used instead of (**7**). The intermediate 1,3,5-tris-[(4-trimethylsilylethynyl)phenyl]benzene was chromatographed on Al_2O_3 using $CHCl_3$–light petroleum (b.p. 40—60 °C) (1:1) as eluant. Hydrolysis and standard work-up as before afforded the crude (**9**) which was chromatographed [Al_2O_3, elution with a mixture of $CHCl_3$–light petroleum (b.p. 40—60 °C) (1:20)] to yield pure (**9**) as colourless crystals.

1,3,5-*Tris*(*phenylethynyl*)*benzene* (**4a**). A stirred mixture of 1,3,5-tribromobenzene (**7**) (3.15 g, 10.0 mmol), phenylacetylene (4.60 g, 45.0 mmol), copper bronze (2.85 g, 45.0 mmol), and potassium carbonate (15.5 g, 112 mmol) in dry DMF (50 ml) was heated to 140 °C for 10 h under an atmosphere of argon. The reaction mixture was filtered, the residue washed ($CHCl_3$), and the collected filtrate and washings were evaporated under reduced pressure. Purification by column chromatography [Al_2O_3, elution with a mixture of $CHCl_3$–light petroleum (b.p. 40—60 °C) (1:20)] gave compound (**4a**) (42%) as colourless crystals.

Triaryl-substituted triethynylbenzenes (**4b**—**f**) *and* 1,3,5-*tris*-[2-(4-*methoxyphenyl*)*ethynylphenyl*]*benzene* (**5b**). Triethynyl compounds (**8**) and (**9**) were treated with the corresponding aryl iodides (**10b**—**f**) using the copper(I) iodide–dichlorobis-(triphenylphosphine)palladium(II) catalytic system as described for (**8**). The reaction mixture was evaporated under reduced pressure and extracted with toluene–H_2O [(**4b**), (**4c**), and (**4e**)] or $CHCl_3$–H_2O [(**4d**), (**4f**), and (**5b**)]. Purification of the crude products was accomplished by column chromatography [Al_2O_3, elution with a mixture of $CHCl_3$–light petroleum (b.p. 40—60 °C (1:20)], in the case of (**4d**) and (**4e**) by additional recrystallization from DMF. Compounds (**4b**), (**4c**), (**4e**), and (**4f**) were isolated as colourless crystals, (**4d**) and (**5b**) as light green and colourless powders, respectively.

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

Crystal Structure Determination.—*X*-Ray intensity data were collected from a single crystal of (**2a**)·DMF (1:3) with approximate dimensions 0.72 × 0.47 × 0.55 mm at room temperature on a computer-controlled Siemens/STOE AED 2 diffractometer. The net intensities of 1 884 reflections ($\lambda_{Cu\text{-}K_\alpha}$ = 1.5418 Å, $\theta_{max.}$ = 70°) were corrected for Lorentz and polarization effects, but the rather low absorption effect (μ = 0.67 mm^{-1}) was neglected.

The crystal shows rhombohedral ($R\bar{3}$) symmetry. The dimensions of the hexagonal unit cell, $a = b$ = 23.160(9) and c = 11.812(3) Å (Z = 6), have been refined using the angular settings of 29 well-centred reflections (19° < 2θ < 41°) accurately measured by the diffractometer. The initial structural model, consisting of all the crystallographically independent non-hydrogen atoms but one, O(W), was achieved by application of the direct method (SHELXS 84[26]). The full-matrix least-squares procedure of the SHELX 76 program system[27] was used for the refinement. The hydrogen atoms were located from difference Fourier calculations and were refined as 'riding' on their bonds to the respective 'mother' atom. The methyl hydrogen positions, however, were calculated geometrically. The non-hydrogens were allowed to vibrate anisotropically whereas only one isotropic group temperature factor was refined for the hydrogen atoms. The methyls were treated as rigid groups. The last refinement included also a fixed site of a possible disordered water oxygen with a site occupancy as a half and with an isotropic temperature factor. It coverged to the final linear R value of 0.082 for 1 518 reflections, all with $F > 6\sigma(F)$; 11 reflections with $\Delta F/\sigma(F) > 4.5$, probably affected by extinction, were omitted from this calculation. The final R_w index[27] became 0.092. The weights of the structure factors were calculated as $w = 30.22/[\sigma^2(F) + 0.000\,15\ F^2]$ with $\sigma(F)$ derived from counter statistics.*

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* *Supplementary data* (see section 5.6.3 of Instructions for Authors, in the January issue). Lists of bond lengths and bond angles and of thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

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