A New Approach for the Design of Inclusion Compounds

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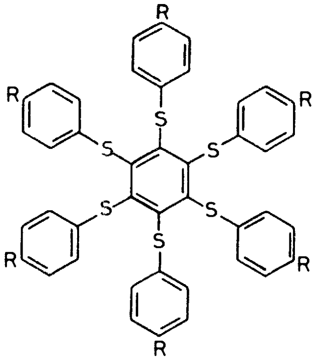
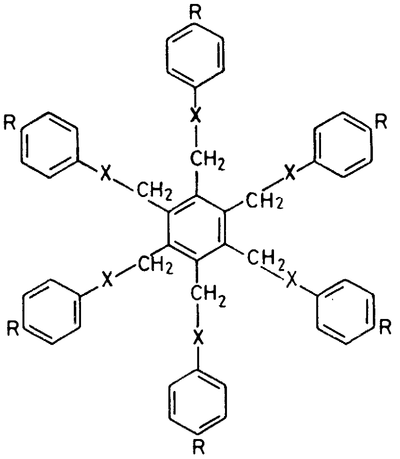
A new strategy for the design of inclusion compounds is described. The approach is based on the analogy between the hydrogen-bonded hexamer unit present in the clathrates of phenol, quinol, Dianin's compound, and other hydroxyaromatic hosts, and a hexasubstituted benzene. Suitable hexasubstituted benzenes have been prepared, and on recrystallisation from various solvents, a wide range of inclusion behaviour has been found for compounds (I), (III), (VIII)—(XIII), (XV), and (XVIII)—(XX). In addition, several of these hosts, for example, (III), (VIII), (IX), and (XIII), exhibit remarkable guest selectivity properties when recrystallised from solvent mixtures. A detailed *X*-ray study of the carbon tetrachloride adduct of hexakisphenylthiobenzene (I) has been carried out. The crystals are trigonal, space group $R\bar{3}$, with a = 14.263; c = 20.717 Å, and three host and six guest molecules in the hexagonal unit cell. A true clathrate structure is found and two CCl_4 guest molecules fit snugly into a cavity of effective length *ca.* 17 Å, a C–Cl bond of each guest being collinear with the *c* axis of the crystal.

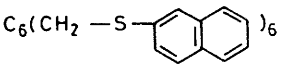
A MAJOR stumbling block in the study of clathrates[1] and other multimolecular inclusion compounds has been the lack of ability to design and synthesise new host materials.



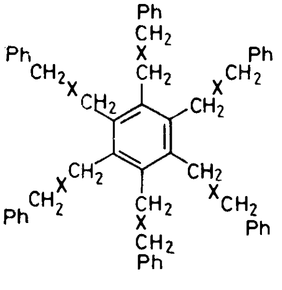
(I) R = H
(II) R = Me



(III) X = O, R = H
(IV) X = O, R = Pr^i
(V) X = O, R = Bu^t
(VI) X = O, R = 1-adamantyl
(VII) X = O, R = OMe
(VIII) X = S, R = H
(IX) X = S, R = Bu^t
(X) X = S, R = 1-adamantyl
(XI) X = S, R = OH
(XII) X = S, R = NH_2
(XIV) X = Se, R = H
(XV) X = Se, R = Bu^t
(XVI) X = NH, R = H



(XIII)



(XVII) X = O
(XVIII) X = S

$C_6(CH_2XR)_6$

(XIX) X = O, R = cyclopentyl
(XX) X = S, R = cyclohexyl

In recent studies[2] we have successfully employed the idea that judicious modification of a known host might lead to new hosts with properties significantly different from those of the parent. Both cavity shape[3] and selective inclusion behaviour[4] have been fundamentally altered.

In the present work a new and different strategy (*vide infra*) is employed,[5] the main objective being the design and synthesis of new hosts with no *direct* structural relationship to any known host.

An intrinsic factor involved in the molecular packing of the clathrates formed by Dianin's compound[6] and related systems[7-10] and also those formed by hydroquinone[11] and phenol[12] is the linking of the OH groups of six host molecules by a network of hydrogen bonds such that the oxygen atoms form a hexagonal arrangement (A), shown in Figure 1. Struck by the parallel between this temporary unit, which is subject to collapse as the groups R are varied and the permanent consolidated structure of a benzene (B), we have prepared a number of hexasubstituted benzenes (I)—(XX) in order to ascertain if these latter compounds might possess an increased tendency to crystallise forming non-close-packed structures with possible inclusion properties. It may be noted that unit (A) corresponds to (B) both in terms of overall geometric aspects and ' hexamer ' dimensions (*cf.* distances *d* and *d'* in Figure 1, where Z denotes a general atom or group attached directly to the central benzene ring). A literature search revealed that a few of these compounds had been prepared previously and encouragingly a number of these materials had been found to retain certain solvents, though at the time of publication the nature of inclusion compounds was less well understood. While the present work was in progress, a number of ' octopus ' molecules based on a hexasubstituted benzene nucleus, have been shown to be capable of binding metal cations in solution.[13]

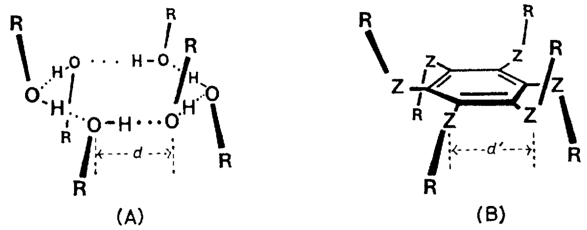


FIGURE 1 Comparison of (A) hydrogen-bonded hexamer unit with (B) hexasubstituted benzene analogue

Compound (I) was prepared[14] by reaction of hexachlorobenzene with phenylthiocuprate, and (II) was synthesised analogously employing *p*-tolylthiocuprate. All the other hexasubstituted benzenes were prepared by the action of the appropriate phenol, thiol, selenol, amine, or alcohol on hexakisbromomethylbenzene, $C_6(CH_2Br)_6$ in the presence of base. *p*-(1-Adamantyl)-thiophenol, required for the preparation of compound (X), was prepared from the corresponding phenol[15] by the method of Newman and Karnes.[16] On recrystallisation from suitable solvents, a wide range of inclusion behaviour was found for compounds (I), (III), (VIII)—(XIII), (XV), and (XVIII)—(XX) (Table 1). Certain of these hosts, for example (III), (VIII), (IX), and (XIII), also show remarkable selective inclusion behaviour (Table 2). In addition, we report the results of a detailed single crystal *X*-ray study of the carbon tetrachloride clathrate of hexakisphenylthiobenzene (I).

EXPERIMENTAL

^1H N.m.r. spectra were recorded on Varian T-60, HA 100, XL-100, and HR 220 instruments with $CDCl_3$ as solvent and tetramethylsilane as internal standard. ^{13}C N.m.r. spectra were recorded on the Varian XL-100 machine. U.v. spectra were recorded on a Unicam SP 8000 spectrometer, and mass spectra were measured on A.E.I.–G.E.C. MS 12 and MS 902 instruments. I.r. spectra were recorded on Perkin-Elmer 225 and Unicam SP 1000 instruments. M.p.s were determined on a Kofler hot-stage apparatus and are uncorrected.

TABLE 1

Representative inclusion compounds formed by hosts (I), (III), (VIII)—(XIII), (XV), and (XVIII)—(XX)

Host	Guest	Mole ratio of host : guest[a]	Method of analysis
(1)	CCl_4	1 : 2	*b*
	CCl_3CH_3	1 : 2	*c*
	CCl_3Br	1 : 1	*b*
	CCl_3SCl	1 : 2	*b*
	CCl_3NO_2	1 : 1	*b*
(III)	Toluene	1 : 2	*c*
	1,4-Dioxan	1 : 3	*c*
	Tetrahydrothiophen	1 : 1	*c*
(VIII)	Toluene	1 : 1	*c*
	1,4-Dioxan	1 : 2	*c*
(IX)	Cyclohexane	1 : 2	*c*
	Cycloheptane	1 : 2	*c*
	Cyclo-octane	1 : 2	*c*
	Toluene	1 : 2	*c*
	Iodobenzene	1 : 2	*b*
	Phenylacetylene	1 : 2	*c*
	1-Methylnaphthalene	1 : 2	*c*
	2-Methylnaphthalene	1 : 2	*c*
	Bromoform	1 : 2	*b*
	Squalene	2 : 1	*c*
	Hexamethyldisilane	2 : 1	*c*
(X)	Toluene[e]	1 : 1	*c*
	1,4-Dioxan	1 : 1	*c*
	o-Xylene	1 : 2	*c*
(XI)	Acetone	1 : 3	*c*
	Methanol	1 : 4	*c*
(XII)	1,4-Dioxan	1 : 3	*c*
(XIII)	Toluene[e]	1 : 1	*c*
	o-Xylene	2 : 1	*c*
(XV)	Cyclo-octane	2 : 3	*c*
	Toluene	2 : 3	*c*
	1,4-Dioxan	2 : 3	*c*
(XVIII)	Cyclohexane	1 : 1	*c*
	Toluene	1 : 1	*c*
	1,4-Dioxan	1 : 1	*c*
	Acetone	1 : 2	*c*
(XIX)	Chloroform	1 : 1	*d*
	1,1,1-Trichloroethane	1 : 1	*d*
(XX)	Benzene	2 : 3	*c*
	Toluene	2 : 3	*c*
	Methyl acetate	2 : 3	*c*
	o-Xylene	2 : 3	*c*
	1,4-Dioxan	2 : 3	*c*

[a] Given to nearest integral ratio. [b] Mole ratio of host : guest determined by microanalysis for halogen. [c] Mole ratio of host : guest determined by multiple integration of the ^1H n.m.r. spectrum employing $CDCl_3$ or [$^2H_6$]acetone as solvent. [d] Mole ratio of host : guest determined by weight loss. [e] Unsolvated material has also been obtained from this solvent.

Hexakisphenylthiobenzene (I). PhSCu was prepared by the reaction of freshly prepared Cu_2O and thiophenol in refluxing ethanol for 24 h with efficient mechanical stirring. The yield of pink-yellow material was 90%, m.p. 285° (decomp.). Compound (I) was synthesised by a literature route[14] by reaction of PhSCu and hexachlorobenzene in quinoline–pyridine at 210° in a Wood's metal-bath for 24 h. The crude mixture was poured on to concentrated HCl in ice and the black rubbery solid thus isolated extracted with

TABLE 2

Guest selectivity properties of hosts (III), (VIII)—(X), (XIII), (XV), (XVIII), and (XX)

Host	Recrystallisation solvent mixture (mol %)	Respective mole percentage of guest included [a]			Overall host : guest ratio [b]
(III)	50 : 50; *o*-Xylene–*p*-xylene	85		15 [c]	1 : 2
	50 : 50; *o*-Xylene–*p*-xylene	90		10 [d]	2 : 1
	50 : 50; Mesitylene–pseudocumene	65		35	1 : 2
(VIII)	50 : 50; *o*-Xylene–*p*-xylene	90		10	1 : 2
	50 : 50; *o*-Xylene–*m*-xylene	45		55	1 : 1
(IX)	50 : 50; *o*-Xylene–*p*-xylene	95		5 [c,e]	1 : 2
	50 : 50; *o*-Xylene–*m*-xylene	85		15	2 : 3
	50 : 50; Mesitylene–pseudocumene	10		90	1 : 2
	33 : 33 : 33; Cyclopentane–cyclohexane–cycloheptane	20	45	35	1 : 2
(X)	50 : 50; *o*-Xylene–*m*-xylene	70		30 [c]	1 : 2
(XIII)	50 : 50; *o*-Xylene–*p*-xylene	20		80 [e]	1 : 1
(XV)	50 : 50; *o*-Xylene–*p*-xylene	90		10 [e]	1 : 1
	50 : 50; *o*-Xylene–*m*-xylene	80		20 [e]	1 : 2
	33 : 33 : 33; Cyclopentane–cyclohexane–cycloheptane	20	45	35	1 : 2
(XVIII)	50 : 50; *o*-Xylene–*p*-xylene	25		75	1 : 1
(XX)	50 : 50; *o*-Xylene–*p*-xylene	80		20	2 : 3
	50 : 50; *o*-Xylene–*m*-xylene	80		20	2 : 3

[a] Measured by multiple ^{1}H n.m.r. integration and given to nearest 5%. [b] Given to nearest integral ratio. [c] Average for solvated material formed in two experiments. [d] For sorption experiment in which 200 mg of host (III) was stirred at room temperature for 24 h in 8 ml solvent mixture. [e] Shows duality of crystallisation behaviour: on one occasion, unsolvated material was deposited.

$CHCl_3$ (Soxhlet) for 48 h. After removing the solvent, a brown oil remained which crystallised well from carbon tetrachloride.

Further recrystallisation from CCl_4 resulted in the formation of magnificent, trigonal, yellow crystals (30%) of the CCl_4 inclusion compound, m.p. 186—186.5°, after apparent loss of guest at *ca.* 90° (Found: C, 51.75; H, 3.25; S, 18.0; Cl, 25.1. $C_{42}H_{30}S_6,2CCl_4$ requires C, 51.05; H, 2.9; S, 18.6; Cl, 27.4%); *m/e* 726; $\nu_{max.}$(KBr) 1 577, 1 476, 1 438, 1 024, 744, 738, 704, and 689 cm^{-1}; τ($CDCl_3$) *ca.* 2.7—3.2; δ_C($CDCl_3$) 148.1 (s), 137.7 (s), 128.9 (d), 128.2 (d), and 126.1 (d) p.p.m.; $\lambda_{max.}$(CCl_4) 323 nm (ε 108). Inclusion compounds are also formed with CCl_3CH_3, host : guest ratio 1 : 2 determined by ^{1}H n.m.r.; CCl_3Br (Found: halogen, 22.4. $C_{42}H_{30}S_6,CCl_3Br$ requires halogen, 20.15%); CCl_3SCl (Found: Cl, 24.8. $C_{42}H_{30}S_6,2CCl_3SCl$ requires Cl, 25.8%); CCl_3NO_2 (Found: Cl, 13.8. $C_{42}H_{30}S_6,CCl_3NO_2$ requires Cl, 11.95%). These four adducts all show apparent guest escape below 100°, on a Kofler hot-stage apparatus.

p-*Tolylthiocuprate.*—Redistilled *p*-thiocresol (41.3 g, 0.33 mol), b.p. 74° at 10 mmHg, freshly prepared Cu_2O (18.6 g, 0.13 mol), and 95% ethanol (400 ml) were stirred under reflux in pure nitrogen for 40 h. The filtered product was washed with ethanol to give a grey-pink powder (44 g, 93%), m.p. 260° (decomp.) (Found: C, 44.8; H, 3.75; S, 17.3. C_7H_7SCu requires C, 45.05; H, 3.8; S, 17.15%); $\nu_{max.}$(KBr) 1 488, 1 185, 1 087, 804, 799, and 493 cm^{-1}.

Hexakis-p-tolylthiobenzene (II).—*p*-Tolylthiocuprate (42 g, 0.225 mol), hexachlorobenzene (9.5 g, 0.033 mol), redistilled quinoline (150 ml), b.p. 100° at 10 mmHg, and pyridine (15 ml) were heated in a 500 ml flask under pure nitrogen in a Wood's metal-bath for 25.5 h, at 210°. After cooling, the mixture was poured into concentrated HCl (140 ml) in crushed ice with stirring. The black rubbery solid was collected next day and Soxhlet-extracted with chloroform (350 ml) for two days. T.l.c. indicated the presence of four compounds so the entire extracted material was purified by silica column chromatography, with $CHCl_3$ as eluant. The first yellow band contained the desired material, but large amounts of polymeric material were strongly absorbed onto the silica. Recrystallisation of the first yellow material from ethanol–benzene gave the product as fine yellow needles, m.p. 197—200°, in very modest yield (Found: C, 70.8; H, 5.35; S, 23.65. $C_{48}H_{42}S_6$ requires C, 71.1; H, 5.2; S, 23.7%); *m/e* 810; $\nu_{max.}$(KBr) 1 487, 1 177, 1 016, 810, and 492 cm^{-1}; τ($CDCl_3$) 7.76 (18 H, s, Me) and *ca.* 2.9—3.4 (24 H, m, aromatic H); $\lambda_{max.}$(CCl_4) 325 nm (ε 143). No inclusion compounds were formed with CCl_4 or CCl_3CH_3.

Hexakisbromomethylbenzene.—To a boiling solution of hexamethylbenzene (65 g, 0.4 mol) in 1,2-dibromoethane (1.5 l) was added [17] slowly over 2 h AnalaR bromine (175 ml; 40% excess) and refluxing continued for 30 h. On cooling the product (250 g, 98%) was collected by filtration and recrystallised from 1,2-dibromoethane, m.p. 309—310° (301° with decomposition in sealed tube) (Found: C, 22.8; H, 2.0; Br, 75.0. $C_{12}H_{12}Br_6$ requires C, 22.65; H, 1.9; Br, 75.35%); *m/e* centred on 635, with 1 : 6 : 15 : 20 : 15 : 6 : 1 isotope pattern; $\nu_{max.}$(KBr) 3 037, 1 489, 1 447, 1 221, 1 194, 800, 725, 654, 603, and 524 cm^{-1}.

Hexakisphenoxymethylbenzene (III).—Sodium phenoxide in phenol was reacted with hexakisbromomethylbenzene (6.36 g, 0.01 mol) as described in the literature,[18] but under nitrogen and heating at 110° for 24 h, and after suitable work-up, the yield of (III) was 70%. Purification was readily achieved by recrystallisation from toluene giving the di-toluene adduct, m.p. 227—228° (guest escape, 90°) (Found: C, 80.8; H, 6.05. $C_{48}H_{42}O_6$ requires C, 80.65; H, 5.9%); *m/e* 714; $\nu_{max.}$ 1 597, 1 496, 1 223, 1 168, and 752 cm^{-1}; τ($CDCl_3$) 4.80br (12 H, CH_2) and *ca.* 2.6—3.3 (3 H, m, aromatic H). Compound (III) forms adducts with toluene, 1,4-dioxan, and tetrahydrothiophen (Table 1), there being apparent release of guest below 100° in each case (Kofler apparatus). Solvents which were not included are cyclohexane, tetrahydrofuran, tetrahydropyran, 1,1,1-trichloroethane, and acetone. Host (III) exhibits significant selective inclusion behaviour (Table 2).

Hexakis-(p-*isopropylphenoxymethyl*)*benzene* (IV).—Sodium (2.3 g, 0.10 mol), redistilled *p*-isopropylphenol (13.62 g, 0.10 mol), b.p. 104—106° at 10 mmHg, and dry redistilled diglyme (110 ml), b.p. 53° at 8 mmHg, were heated under nitrogen and, when all dissolved, $C_6(CH_2Br)_6$ (6.36 g, 0.01 mol) was added and the mixture stirred under reflux for 22 h. When cool, water was added, the crude product collected by filtration and washed with base yielding product (8.9 g, 90%). This was recrystallised from toluene giving the product as fine needles, m.p. 212.5—214° (Found: C, 82.05; H, 8.3. $C_{66}H_{78}O_6$ requires C, 81.95; H, 8.15%); *m/e* 966; $\nu_{max.}$(KBr) 2 956, 1 610, 1 511, 1 232, 1 178, 1 012, and 826 cm^{-1}; τ($CDCl_3$) 8.81 (36 H, d, *J* 6.5 Hz, CH_3), 7.17 [6 H, heptet, *J* 6.5 Hz, $C(CH_3)_2H$], 4.84br (12 H, CH_2), and *ca.* 2.8—3.3 (24 H, AA′BB′, aromatic H).

Dioxan, tetrahydrofuran, and tetrahydrothiophen did not form inclusion compounds.

Hexakis-(p-*t-butylphenoxymethyl*)*benzene* (V).—The procedure described for (IV) was followed but using *p*-t-butylphenol (15 g, 0.1 mol) and $C_6(CH_2Br)_6$ (6.36 g, 0.01 mol) to yield crude (V) (8.31 g, 80%). Fine needles were obtained from toluene, m.p. 253—257° (Found: C, 82.25; H, 8.65. $C_{72}H_{90}O_6$ requires C, 82.35; H, 8.65%); *m/e* 1 050; $\nu_{max.}$ (KBr) 2 960, 1 512, 1 233, 1 182, 1 011, and 829 cm^{-1}; τ($CDCl_3$) 8.72 (54 H, s, t-butyl), 4.87br (12 H, CH_2), and *ca.* 2.7—3.3 (24 H, AA′BB′ aromatic H); δ_C($CDCl_3$) 156.4 (s), 143.9 (s), 138.0 (s), 126.2 (d), 114.3 (d), 63.6 (t), 34.0 (s), and 31.5 (q) p.p.m.

Inclusion compounds were not formed with cyclohexane, cyclo-octane, squalene, *p*-xylene, or dioxan.

1-*Adamantyl Bromide.*—This was prepared by a simplified modification of the literature method.[19] Adamantane (100 g, 0.735 mol) was refluxed with Br_2 (150 ml, 2.925 mol) for 5.5 h. On cooling, aqueous $Na_2S_2O_5$ was added and when colourless, aqueous Na_2CO_3 was added. After stirring overnight, the slurry was filtered in a large sintered glass funnel and washed with carbonate till slightly basic and then brine till neutral. The crude material (80%) was recrystallised twice from methanol, giving a 71% yield of pure material, m.p. 118—119° (Found: C, 55.9; H, 7.1; Br, 36.95. $C_{10}H_{15}Br$ requires C, 55.85; H, 7.05; Br, 37.15%); *m/e* 215; $\nu_{max.}$(KBr) 2 905, 2 852, 1 455, 1 342, 1 276, 1 025, 805, 765, and 674 cm^{-1}; τ($CDCl_3$) 8.24 (6 H), 7.88 (3 H), and 7.62 (6 H).

p-1-*Adamantylphenol.*—Adamantyl bromide (69 g, 0.321 mol) and phenol (345 g, 10-fold excess) were heated with stirring at 100—110° for 30 h.[15] On cooling, water was added with vigorous stirring to form a slurry. This slurry in a large sinter, was washed with boiling water (8 × 1 l) to remove the phenol leaving the product (64 g, 87.5%) which was recrystallised from methanol giving very fine needles, m.p. 181.5—182.5° (Found: C, 83.95; H, 9.0. $C_{16}H_{20}O$ requires C, 84.15; H, 8.85%); *m/e* 288; $\nu_{max.}$(KBr) 3 240, 2 904, 2 823, 1 513, 1 446, 1 246, 833, 806, and 538 cm^{-1}; τ($CDCl_3$) *ca.* 7.8—8.5 (15 H, adamantyl H), 5.32 (1 H, s, OH), and *ca.* 2.7—3.4 (4 H, aromatic H).

Hexakis-(p-1-*adamantylphenoxymethyl*)*benzene* (VI).—To adamantylphenol (1.35 g, 0.0047 mol) in dry diglyme (12 ml) was added sodium (0.14 g, 0.006 09 mol) and the mixture heated till dissolved. $C_6(CH_2Br)_6$ (0.419 g, 0.000 66 mol) was then added and the mixture refluxed for 21 h under dry nitrogen. When cool, water was added giving a milky nonfilterable solution. This was transferred to a separating funnel with ether and washed with water to remove the diglyme. Some organic material floated on top of the water layer. The solid and dried ether extracts were combined and digested with $CHCl_3$ and transferred to another flask. There remained a residue which was unchanged hexabromide. The chloroform was removed, the residue washed with ether, and recrystallised from toluene to give the product in *ca.* 60% yield, m.p. >350°. It is very insoluble and tends to creep up the sides of vessels. A satisfactory microanalysis was not obtained; $\nu_{max.}$(KBr) 2 894, 2 840, 1 510, 1 234, 1 008, 832, 807, and 544 cm^{-1}; τ($CDCl_3$) *ca.* 7.7—8.6 (90 H, adamantyl H), 4.88br (12 H, s, CH_2), and *ca.* 2.7—3.4 (24 H, AA′BB′, aromatic H).

Toluene and dioxan did not form inclusion compounds with (VI).

Hexakis-(p-*methoxyphenoxymethyl*)*benzene* (VII).—*p*-Methoxyphenol was redistilled under reduced pressure giving material, b.p. 152—154° at 10 mmHg, m.p. 53°. The procedure was the same as that described for (IV), being carried out on a 0.01 molar scale but using *p*-methoxyphenol (11.16 g, 0.09 mol) and refluxing was continued for 27 h. The usual work-up afforded brown-white material (7.74 g, 87%) which was recrystallised from toluene to give very fine needles, m.p. 225—227° (Found: C, 72.55; H, 6.1. $C_{54}H_{54}O_6$ requires C, 72.5; H, 6.05%); *m/e* 894; $\nu_{max.}$(KBr) 1 506, 1 220, 1 038, and 822 cm^{-1}; τ($CDCl_3$) 6.26 (18 H, s, OCH_3), 4.87br (12 H, CH_2), and *ca.* 3.0—3.4 (24 H, aromatic H). No inclusion compounds were formed with toluene, cyclohexane, or xylene mixtures.

Hexakis(*phenylthiomethyl*)*benzene* (VIII).—Sodium (2.3 g, 0.1 mol) was dissolved in pentyl alcohol (100 ml), then thiophenol (9 g, 0.09 mol) and $C_6(CH_2Br)_6$ (6.36 g, 0.01 mol) added and stirred under reflux for 9 h, under nitrogen.[20] When cold, the mixture was added to iced water (400 ml) and the solid collected by filtration and dried yielding (VIII) (7.55 g, 92%). This was recrystallised from toluene giving a 1 : 1 adduct. Solvent free material was obtained by crystallising from cyclohexane, m.p. 192—193° (Found: C, 71.15; H, 5.4; S, 23.5. $C_{48}H_{42}S_6$ requires C, 70.8; H, 5.2; S, 23.65%); *m/e* 810; $\nu_{max.}$(KBr) 1 581, 1 479, 1 437, 1 025, 752, 732, and 689 cm^{-1}; τ($CDCl_3$) 5.71br (12 H, CH_2) and *ca.* 2.6—2.9 (30 H, aromatic H). An inclusion compound is also formed with dioxan (host : guest = 1 : 2); see Table 1. The toluene and dioxan adducts undergo apparent solvent loss below 100° (Kofler). The following solvents were not included: cyclohexane, cyclopentane, tetrahydrofuran, tetrahydropyran, and tetrahydrothiophen. Compound (VIII) shows selective inclusion behaviour (Table 2).

Hexakis(p-*t-butylphenylthiomethyl*)*benzene* (IX).—The procedure described for (VIII) was adopted [20] but using *p*-t-butylthiophenol (13 g, 0.08 mol) and $C_6(CH_2Br)_6$ (6.36 g, 0.01 mol). The crude product amounted to 10.5 g (91.5%). Glassy needles were obtained on recrystallisation from toluene, which were desolvated for analysis, m.p. 182—183° (Found: C, 75.3; H, 7.85; S, 16.8. $C_{72}H_{90}S_6$ requires C, 75.35; H, 7.9; S, 16.75%); $\nu_{max.}$(KBr) 2 954, 1 496, 1 119, 1 012, 814, and 543 cm^{-1}; τ($CDCl_3$) 8.70 (54 H, s, t-butyl H), 5.87br (12 H, s, CH_2), and *ca.* 2.6—2.9 (24 H, AA′BB′, aromatic H); δ_C($CDCl_3$) 150.1 (s), 135.9 (s), 132.2 (s), 130.6 (d), 126.0 (d), 34.5 (s), 33.4 (t), and 31.3 (q) p.p.m.

Results of single solvent and selective inclusion experiments are given in Tables 1 and 2, respectively.

Mesitylene, hexamethyldistannane, bistrimethylsilylacetylene, and ethanol were not included.

O-[*p*-(1-*Adamantyl*)*phenyl*] *Dimethylthiocarbamate.*—This compound was prepared [16] on a 0.05 molar scale under pure nitrogen. To sodium (1.15 g) in dry ethanol (60 ml) was added *p*-1-adamantylphenol (11.42 g), then the ethanol removed under vacuum (0.005 mmHg for 2 h) and dimethylthiocarbamoyl chloride (10.5 g, 0.085 mol) in dry redistilled dimethylformamide (60 ml) added and the mixture stirred for 2 h at 60°. After extraction with benzene–hexane (4 : 1, 4 × 200 ml) and washing with KOH (5%) then brine, product (14.2 g, 88%) was obtained. This was recrystallised from methanol (2 l) giving fine needles, m.p. 201.5—203° (Found: C, 72.3; H, 7.9; N, 4.6; S, 10.35. $C_{19}H_{25}NOS$ requires C, 72.35; H, 8.0; N, 4.45; S, 10.15%); *m/e* 315; $\nu_{max.}$(KBr) 2 900, 2 843, 1 503, 1 392, 1 287, 1 207, 1 171, and 1 135 cm^{-1}; τ($CDCl_3$) *ca.* 7.8—8.5 (15 H, adamantyl H), 6.58, 6.71 (each 3 H, s, NCH_3), and 2.6—3.2 (4 H, AA′BB′, aromatic H).

S-[p-(1-*Adamantyl*)*phenyl*] *Dimethylthiocarbamate*.—The corresponding *O*-carbamate (5.1 g, 0.0162 mol) was heated [16] in an evacuated sealed tube at 270° for 70 min. The yield of product was quantitative, being pure enough for direct hydrolysis. A little was recrystallised from benzene to give large glassy needles, m.p. 137—138° (Found: C, 72.35; H, 8.0; N, 4.7; S, 10.25. $C_{19}H_{25}NOS$ requires C, 72.35; H, 8.0; N, 4.45; S, 10.15%); *m/e* 315; $\nu_{max.}$(KBr) 2 890, 1 656, 1 353, 1 086, 1 009, 803, 686, and 554 cm^{-1}; τ($CDCl_3$) *ca.* 7.8—8.4 (15 H, adamantyl H), 6.97 (6 H, s, NCH_3), and *ca.* 2.5—2.8 (4 H, aromatic H).

p-(1-*Adamantyl*)*thiophenol*.—The crude *S*-carbamate (5 g, 0.0159 mol) in methanol (100 ml) and NaOH pellets (3.18 g, 0.079 mol) in water (30 ml) were heated under reflux in pure nitrogen for 22 h. On cooling, dilute HCl was added with stirring to pH 5 and the mixture extracted with benzene (4 × 200 ml) and washed with brine. The solvent was evaporated to give the crude thiol (4 g, 100%) which was pure enough for further reaction. The thiol was recrystallised from cyclohexane, m.p. 106—106.5° (Found: C, 78.85; H, 8.45; S, 11.9. $C_{16}H_{20}S$ requires C, 78.6; H, 8.0; S, 13.1%); *m/e* 244.128 38; $\nu_{max.}$(KBr) 2 890, 2 840, 2 546 (S–H), 1 493, 799, and 531 cm^{-1}; τ($CDCl_3$) *ca.* 7.8—8.4 (15 H, adamantyl H), 6.66 (1 H, s, SH), and *ca.* 2.6—2.9 (4 H, aromatic H). This thiol is unstable in solution with respect to oxidation to the corresponding disulphide but appears to be perfectly stable in the solid state.

Hexakis-[p-(1-*adamantyl*)*phenylthiomethyl*]*benzene* (X).—*p*-(1-Adamantyl)thiophenol (3.7 g, 0.0152 mol) was added to a solution of sodium (0.35 g, 0.0152 mol) in pentyl alcohol (25 ml) in pure nitrogen with stirring and then $C_6(CH_2Br)_6$ (1.07 g, 0.001 68 mol) added and the mixture heated under reflux for 15 h, with 25 ml further degassed pentyl alcohol being added half-way through to wash sublimed thiol back into the reaction flask. On cooling, iced water was added, the solid filtered, washed with base and then brine to give the product (2.51 g, 92%). This was recrystallised from toluene to give very fine needles, m.p. 308—308.5° (slight decomp.) (Found: C, 80.0; H, 7.9; S, 12.25. $C_{108}H_{126}S_6$ requires C, 80.25; H, 7.85; S, 11.9%); $\nu_{max.}$(KBr) 2 894, 2 840, 1 492, 1 445, 1 010, and 802 cm^{-1}; τ($CDCl_3$) *ca.* 7.8—8.4 (90 H, adamantyl H), 5.88br (12 H, CH_2S), and 2.6—2.9 (24 H, aromatic H). The results of inclusion experiments are shown in Tables 1 and 2. Cyclo-octane was not included in (X).

Hexakis-(p-*hydroxyphenylthiomethyl*)*benzene* (XI).—Under pure nitrogen, to a solution of sodium (1.53 g, 0.066 mol) in absolute alcohol (75 ml) was added *p*-mercaptophenol (8.42 g, 0.0667 mol) and then $C_6(CH_2Br)_6$ (4.24 g, 0.006 66 mol) and the mixture stirred for 20 h under reflux. Appropriate acid work-up gave a solid (4.35 g, 72%) which was recrystallised from anisole, m.p. 228—230° (Found: C, 63.35; H, 4.9; S, 20.9. $C_{48}H_{42}O_6S_6$ requires C, 63.55; H, 6.45; S, 21.2%); $\nu_{max.}$ (KBr) 3 365, 1 602, 1 583, 1 496, 1 236, and 831 cm^{-1}; τ([$^2H_6$]acetone) 5.81br (12 H, s, CH_2), *ca.* 2.6—3.3 (24 H, AA′BB′, aromatic H), and 1.38 (6 H, s, OH). For adducts formed by (XI), see Table 1 (on the Kofler apparatus, each adduct shows apparent solvent loss below 100°). No evidence for adduct formation was found for ethanol, t-butyl alcohol, or methyl acetate.

Hexakis-(p-*aminophenylthiomethyl*)*benzene* (XII).—To a solution of sodium (2.3 g, 0.1 mol) in absolute alcohol (90 ml) under pure nitrogen was added 4-aminothiophenol (11.27 g, 0.09 mol) and then $C_6(CH_2Br)_6$ (6.36 g, 0.01 mol) and the mixture stirred under reflux for 17 h. When cool, ice was added, the solid filtered, washed with base, brine, and then water yielding a powder (8.69 g, 97%). This was recrystallised from anisole to give fine needles, m.p. 210—212° (Found: C, 64.1; H, 5.45; N, 9.5; S, 21.8. $C_{48}H_{48}N_6S_6$ requires C, 63.9; H, 5.35; N, 9.3; S, 21.35%); $\nu_{max.}$(KBr) 3 410, 3 327 (N–H), 1 623, 1 600, 1 497, 1 286, 1 177, 826, and 511 cm^{-1}; τ([$^2H_6$]acetone) 5.76br (12 H, CH_2), 5.14br (12 H, NH_2), and *ca.* 2.7—3.5 (24 H, AA′BB′, aromatic H). 1,4-Dioxan forms an inclusion compound with a host : guest ratio of 1 : 3, from which guest escapes over the range 25—70° (Kofler). However, it requires 16 h at 0.5 mmHg and room temperature to remove half the guest component. Acetone, tetrahydrofuran, and tetrahydropyran did not form inclusion compounds.

Hexakis-(2-*naphthylthiomethyl*)*benzene* (XIII).—This was prepared similarly to (VIII) on a 0.01 molar scale but using naphthalene-2-thiol (14.4 g, 0.09 mol) in pure nitrogen. The yield of crude yellowish material was 8.6 g (77.5%), m.p. 209—211° (from CCl_4–$CHCl_3$) (Found: C, 77.65; H, 4.8; S, 17.3. $C_{72}H_{54}S_6$ requires C, 77.85; H, 4.85; S, 17.35%); $\nu_{max.}$(KBr) 3 047, 1 627, 1 586, 1 501, 1 132, 944, 857, 812, 743, and 473 cm^{-1}; τ($CDCl_3$) 5.54br (12 H, CH_2), and *ca.* 2.2—2.9 (42 H, aromatic H). Results of inclusion experiments are shown in Tables 1 and 2. Attempts to prepare adducts of cyclohexane, cyclo-octane and 1,4-dioxan were unsuccessful.

Hexakis(*phenylselenomethyl*)*benzene* (XIV).—The procedure adopted is analogous to the preparation of (VIII) but using PhSeH and pure nitrogen. The yield was 86% for a 0.01 molar preparation. Glassy needles were obtained when recrystallised from toluene, m.p. 161—162° (Found: C, 52.9; H, 4.15. $C_{48}H_{42}Se_6$ requires C, 52.8; H, 3.9%); $\nu_{max.}$(KBr) 1 572, 1 475, 1 434, 1 069, 1 019, 1 000, 736, 725, and 686 cm^{-1}; τ($CDCl_3$) 5.74br (12 H, CH_2) and *ca.* 2.4—2.9 (30 H, aromatic H). Dioxan and toluene did not form inclusion compounds.

p-*Bromo-t-butylbenzene*.—t-Butylbenzene (67 g, 0.5 mol) [21] and bromine (80 g, 0.5 mol) were stirred [22] in a 500 ml round-bottomed flask with a reflux condenser and a drying tube at 0° and the flask illuminated with a 150-W tungsten bulb. The reaction started after 15 min and illumination at ambient temperature was continued for 5 d. $Na_2S_2O_5$ solution was added, the solution made slightly basic and then extracted with n-pentane (3 × 150 ml) and the extracts washed with brine and water and then the solvent removed. Distillation at atmospheric pressure gave product (90 g, 84%) (lit.,[22] 60%) (Found: C, 56.1; H, 5.9; Br, 37.9. $C_{10}H_{13}Br$ requires C, 56.35; H, 6.15; Br, 37.5%); *m/e* 213; $\nu_{max.}$ (neat liquid) 2 948, 1 490, 1 107, 1 006, 820, 726, and 540 cm^{-1}; τ($CDCl_3$) 8.74 (9 H, s, t-butyl H) and *ca.* 2.5—2.9 (4 H, AA′BB′, aromatic H).

p-*t-Butylbenzeneselenol*.—This selenol, obtained as an almost colourless liquid, b.p. 112—114° at 8 mmHg, was prepared [23] from *p*-bromo-t-butylbenzene employing essentially a literature route.[24] This material was used at once in the next synthesis (Found: *m/e* 212.026 67, 214.025 88. $C_{10}H_{14}{}^{78}Se$ and $C_{10}H_{14}{}^{80}Se$ require *M*, 212.026 85 and

214.026 05, respectively); $\tau(CDCl_3)$ 8.73 (9 H, s, t-butyl H), 8.59 (1 H, SeH), and *ca.* 2.6—2.9 (4 H, AA′BB′, aromatic H).

Hexakis(p-t-butylphenylselenomethyl)benzene (XV).—The above selenol (4 g) was added to a solution of sodium (1 g) in n-pentanol (50 ml) and then $C_6(CH_2Br)_6$ (1 g) added and the mixture stirred for 3.5 h at 140° under pure nitrogen. NaBr precipitated the instant the hexabromide was added. When cool, ice was added, the mixture filtered, and the solid washed with NaOH, brine, and water giving fairly pure (XV) (2.04 g, 91%). This material was recrystallised from toluene giving needles of the adduct which was desolvated for analysis, m.p. 179.5—181.5° (Found: C, 60.65; H, 6.4. $C_{72}H_{90}Se_6$ requires C, 60.5; H, 6.35%); $\nu_{max.}$(KBr) 2 964, 1 396, 1 116, 1 013, 824, and 551 cm^{-1}; $\tau(CDCl_3)$ 8.69 (54 H, s, t-butyl H), 5.82br (12 H, CH_2), and *ca.* 2.6—2.9 (24 H, aromatic H); $\delta_C(CDCl_3)$ 150.7 (s), 135.7 (s), 133.7 (d), 126.4 (s), 126.3 (d), 34.5 (s), 31.3 (q), and 26.6 (t) p.p.m.

Hexakis(phenylaminomethyl)benzene (XVI).—In pure nitrogen, $C_6(CH_2Br)_6$ (6.36 g, 0.01 mol) and redistilled aniline (100 ml), b.p. 93—94° at 10 mmHg, were stirred for 27 h at 150°, then the aniline was removed at the water pump to leave a crude red solid which was digested with toluene and decolourised with animal charcoal. Needles (3.4 g, 47%) crystallised, m.p. 214.5—215.5° (Found: C, 81.45; H, 7.0; N, 11.65. $C_{48}H_{48}N_6$ requires C, 81.3; H, 6.8; N, 11.85%); *m/e* 696; $\nu_{max.}$(KBr) 3 392 and 3 293 cm^{-1} (N–H); $\tau(CDCl_3$; 220 MHz) *ca.* 6.0br (6 H, s, NH), 5.55br (12 H, CH_2), 3.40 (12 H, m, *o*-aromatic H), 3.25 (6 H, m, *p*-aromatic H), and 2.87 (12 H, m, *m*-aromatic H); $\delta_C(CDCl_3)$ 147.6 (s), 138.6 (s), 129.3 (d), 118.8 (d), 113.8 (d), and 43.3 (t). Toluene, 1,4-dioxan, CCl_4, and $CHCl_3$ did not form inclusion compounds.

Hexakis(benzyloxymethyl)benzene (XVII).—The procedure and scale (0.01 molar) were similar to those used for (III). Heating at 165° was maintained for 30 h as the sodium salt of benzyl alcohol precipitated out. Excess of benzyl alcohol was removed by distillation, b.p. 102—104° at 10 mmHg, and and the residual oil recrystallised from toluene, giving needles (37.5%), m.p. 121.5—123.5° (Found: C, 81.15; H, 6.8. $C_{54}H_{54}O_6$ requires C, 80.9; H, 6.9%); *m/e* 798; $\nu_{max.}$(KBr) 1 512, 1 451, 1 354, 1 347, 1 057, and 702 cm^{-1}; $\tau(CDCl_3)$ 5.69 (12 H, s, CH_2), 5.50 (12 H, s, CH_2), and *ca.* 2.5—2.9 (30 H, aromatic H). Toluene, cyclohexane, t-butyl alcohol, nitromethane, tetrahydrofuran, and tetrahydropyran were not included.

Hexakis(benzylthiomethyl)benzene (XVIII).—This was prepared [20] similarly to (VIII) on a 0.01 molar scale but using phenylmethanethiol. The yield of (XVIII) was quantitative. Purification was readily achieved by recrystallisation from toluene giving a 1 : 1 adduct, which was desolvated by heating overnight at 60° and 0.5 mmHg, m.p. 150—152° (Found: C, 72.45; H, 6.2; S, 21.55. $C_{54}H_{54}S_6$ requires C, 72.45; H, 6.1; S, 21.5%); *m/e* 894; $\nu_{max.}$(KBr) 1 599, 1 492, 1 448, 1 229, 726, 706, and 696 cm^{-1}; $\tau(CDCl_3)$ 6.48 (12 H, s, CH_2), 6.64 (12 H, s, CH_2), and *ca.* 2.4—2.9 (30 H, aromatic H). Details of the inclusion compounds are given in Tables 1 and 2.

Hexakis(cyclopentyloxymethyl)benzene (XIX).—To a solution of sodium (2.3 g, 0.1 mol) in cyclopentanol (100 ml), magnetically stirred under nitrogen, was added $C_6(CH_2Br)_6$ (6.36 g, 0.01 mol) and the mixture maintained at 140° for 22 h. When cool, the solvent was removed, then water and ethanol added, giving a yellow solid (2.4 g, 36%). Silica column chromatography (eluant $CHCl_3$) and recrystallisation from benzene gave m.p. 167—169° (Found: C, 75.45; H, 9.95. $C_{42}H_{60}O_6$ requires C, 75.65; H, 9.95%); $\nu_{max.}$(KBr) 2 943, 2 862, 1 338, 1 176, 1 076, and 1 046 cm^{-1}; $\tau(CDCl_3)$ *ca.* 7.9—8.7 (48 H, ring CH_2), 6.02 (6 H, m, methine H), and 5.54br (12 H, s, CH_2O). Results of inclusion experiments are given in Table 1.

Hexakis(cyclohexylthiomethyl)benzene (XX).—This was prepared similarly to (VIII) on a 0.01 molar scale but using cyclohexanethiol (10.44 g, 0.09 mol). The crude solid (7.38 g, 86%) was recrystallised from toluene and desolvated for analysis, m.p. 248—250.5° (Found: C, 68.1; H, 9.4; S, 22.5. $C_{48}H_{78}S_6$ requires C, 68.05; H, 9.3; S, 22.7%); *m/e* 846; $\nu_{max.}$(KBr) 2 922, 2 844, 1 447, 1 197, and 999 cm^{-1}; $\tau(CDCl_3)$ *ca.* 7—9 (66 H, cyclohexyl H) and 5.92br (12 H, CH_2S). Results of inclusion experiments are given in Tables 1 and 2.

Procedure for Inclusion Experiments.—Single-solvent inclusion experiments were routinely carried out by recrystallisation of the unsolvated prospective host from the appropriate pure solvent, sealed tubes being employed for the less soluble materials. Where necessary, crystals were washed with cold or room temperature n-pentane to remove surface liquid. Typical selectivity experiments involved recrystallisation of *ca.* 100 mg of unsolvated host from *ca.* 2 ml of solvent mixture in a sealed tube. Following collection on a small sinter, the crystals of the adduct were washed with 10 ml of cold or room temperature n-pentane to remove surface liquid, and then analysed by ^1H n.m.r. spectroscopy.

X-*Ray Crystal Structure Analysis of the Carbon Tetrachloride Adduct of Compound* (I).—*Crystal data.* $C_{42}S_6H_{30}$,$2CCl_4$; $M = 1\,034.7$; a host : guest ratio of 1 : 2 was found by microanalysis for chlorine; trigonal space group $R\bar{3}$ (or $R3$), referred to a rhombohedral unit cell with $a = 10.747$ Å, $\alpha = 83.15°$, $Z = 1$ (*i.e.* 1 host and 2 guest molecules), $U = 1\,216.6$ Å^3, $D_c = 1.41$ g cm^{-3}, $F(000) = 526$; Mo-K_α radiation, $\lambda = 0.7107$ Å, μ(Mo-K_α) = 7.38 cm^{-1}. The crystal used was a light yellow rectangular slab of approximate dimensions 0.85 × 0.70 × 0.55 mm; the crystal being sealed in a thin-walled glass capillary (with a small amount of solvent) to prevent crystal decomposition during data collection.

Crystallographic measurements. Least-squares best cell dimensions were obtained by a treatment of the θ, χ, ϕ setting angles of 22 reflections measured on a Hilger and Watts automatic diffractometer. The intensities were measured by the θ—2θ step scan procedure with Zr-filtered Mo-K_α radiation. Background counts were taken at each end of the scan range. The intensities of three standard reflections were monitored after every 60 intensity measurements, and the results used to place the reflections on a common scale; the changes in the standard intensities during data collection were small (<10%). Reflections were surveyed out to $\theta \leqslant 30°$, with an option whereby those intensities with $I < 2\sigma(I)$ were not measured when $25° < \theta \leqslant 30°$. The intensity values were corrected for Lorentz-polarisation effects, but not for absorption, and from the 6 232 reflections originally scanned 2 071 independent reflections were obtained [where 1 859 reflections had $I/\sigma(I) > 2.0$].

Structure analysis. The structure was initially solved in the space group $P\bar{1}$ (a centrosymmetric space group was strongly indicated from the distribution of the $|E|$ magnitudes, and the choice was justified by successful analysis), by direct phase-determining methods using MULTAN [25] and the 250 reflections having the largest $|E|$ magnitudes. An E-map computed with that set of phases which gave the

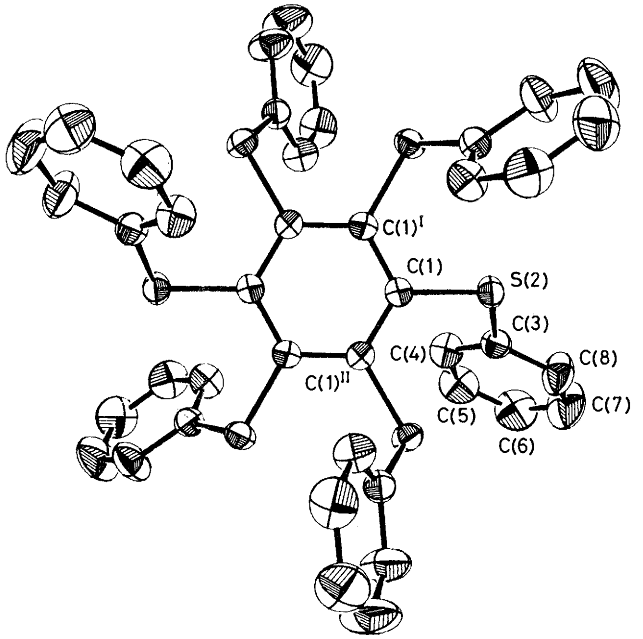


FIGURE 2 An ORTEP drawing showing the molecular structure of the host hexakisphenylthiobenzene (I) in the crystal of its CCl_4 clathrate, as viewed along the *c* axis of the hexagonal unit cell (see Experimental section)

highest figure of merit and the lowest residual revealed 21 of the 24 (host) non-hydrogen atom positions in the asymmetric unit (a half molecule). A subsequent difference electron-density distribution revealed the remaining three carbon atom positions of the host molecule as well as the positions of the CCl_4 guest molecule. Minor peaks on a final difference map may indicate a very low occupancy secondary guest orientation. These approximate atomic parameters were adjusted by several cycles of full-matrix least-squares calculations employing the program CRYLSQ from the *X*-RAY '72 system,[26] and for anisotropic temperature factors for all the atoms *R* was reduced to 9.3%.

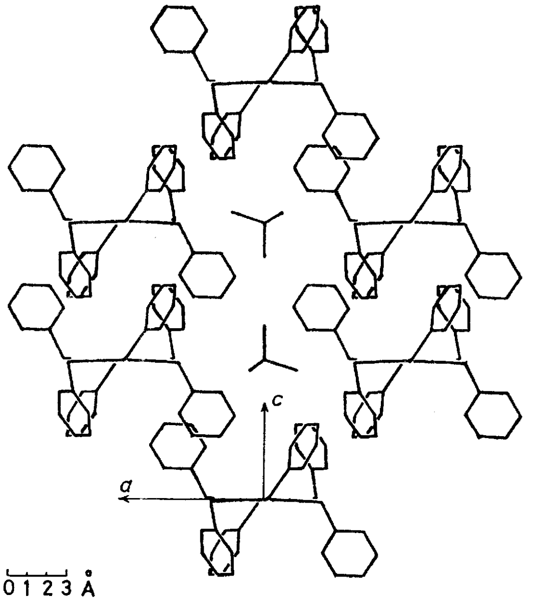


FIGURE 3 An illustration of the host–guest packing in the crystal of the CCl_4 clathrate of (I) as viewed onto the *ac* plane. Two host molecules which lie above and below the cavity as viewed in this direction have been excluded to show the guest molecules more clearly

The 15 hydrogen atoms in the asymmetric unit were located in a difference electron-density distribution, and when included in a subsequent cycle of least-squares calculations (with isotropic temperature factors, their positional and thermal parameters being fixed) the *R* value was lowered to 7.1%.

At this stage trigonal symmetry was introduced, the space group changed from $P\bar{1}$ to $R\bar{3}$, and using the averaged data and the entire contents of the reduced asymmetric unit further cycles of least-squares calculations were performed with all positional and thermal parameters being refined. The final *R* value was 5.5% (R_w 8.9%). The weighting scheme employed in the last cycles of the least-squares calculations was $w = (0.802 - 0.061\ |F| - 0.017\ |F|^2)^{-1}$.

Calculations were carried out on an IBM 370/168 computer at Newcastle. Observed and calculated structure factors and anisotropic thermal parameters are listed in Supplementary Publication No. 22502 (11 pp.).* The scattering factors employed for S, Cl, and C atoms were those listed in ref. 27, those for H in ref. 28. The anomalous dispersion was allowed for in the least-squares calculations, with values of $\Delta f'$ and $\Delta f''$ for sulphur and chlorine taken from ref. 29. Atomic fractional co-ordinates and isotropic temperature factors are listed in Table 3, and various parameters connected with the clathrate's molecular geometry are listed in Tables 4—7. In Figure 4 the hydrogen atom positions used were those generated by the program BONDAT in the *X*-RAY '72 suite of programs[26] (with C–H, 1.00 Å and $H-\hat{C}-C$, 120°). In Figures 2—4 the axes employed are referred to a hexagonal unit cell with $a = b = 14.263$, $c = 20.717$ Å, $\alpha = \beta = 90°$, $\gamma = 120°$, and $Z = 3$ (host).

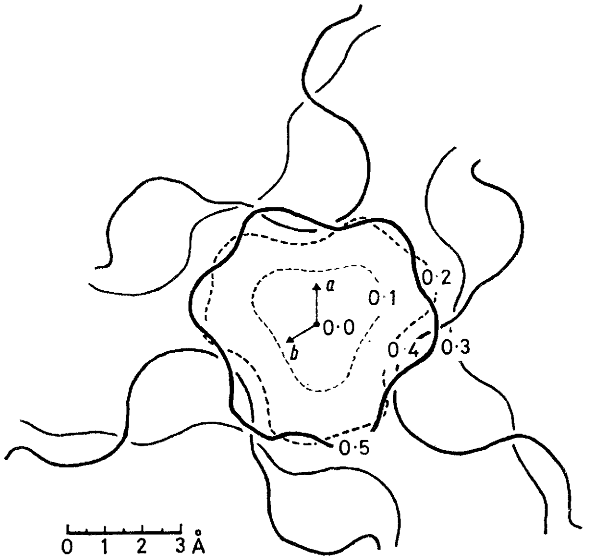


FIGURE 4 The space available in the cage of (I) in cross section at various fractional levels parallel to the *ab* plane. The contours shown represent only half the centrosymmetric cage

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* For details of supplementary publications see Notice to Authors No. 7 in *J.C.S. Perkin II*, 1978, Index issue.

DISCUSSION

Inclusion Properties of Compounds (I), (III), (VIII)—(XIII), (XV), *and* (XVIII)—(XX).—The host : guest ratios of representative adducts formed by the above compounds are given in Table 1. Compound (I), hexakisphenylthiobenzene, forms inclusion compounds with several guests possessing a CCl_3 group, a property not shared by its close analogue, hexakis-*p*-tolylthiobenzene (II). The structure of the CCl_4 adduct of (I) is discussed in detail below. Interesting differences in inclusion ability are found among compounds (III), (VIII), (XIV), and (XVI) which have a two atom CH_2X chain linking each phenyl group to the central aromatic core of the molecule. Whereas hexakis(phenoxymethyl)benzene (III) and its sulphur analogue (VIII) retain toluene and other guests, no parallel behaviour has yet been found for the related selenium compound (XIV) or the hexamine (XVI). Introduction of isopropyl, t-butyl, 1-adamantyl, or methoxy *para*-substituents into each of the phenyl groups of hexakis(phenoxymethyl)benzene (III), to give compounds (IV)—(VII) respectively, yielded no further evidence of inclusion behaviour. In marked contrast, four new hosts (IX)—(XII) are produced by substitution of the phenyl groups of hexakis(phenylthiomethyl)benzene (VIII). Of these derived hosts, hexakis(*p*-t-butylphenylthiomethyl)benzene (IX) is particularly versatile forming a beautifully crystalline inclusion compound with the large guest molecule squalene, $C_{30}H_{50}$ (host : guest ratio 2 : 1), and many 1 : 2 adducts with medium sized guest species. Notably, compounds (XIX) and (XX) which have saturated rather than aromatic 'side-chain' rings retain the ability to form inclusion compounds. Hexakis(benzylthiomethyl)benzene (XVIII) which has a three atom chain linking each side chain phenyl to the central molecular core also has inclusion ability, though this property is not shared by its oxygen counterpart (XVII).

TABLE 3

Fractional atomic co-ordinates, with standard deviations in parentheses, and isotropic thermal parameters; hydrogen atoms are numbered according to the atoms to which they are attached

	X	*Y*	*Z*	$U \times 10^2$
C(1)	0.066 0(2)	−0.112 7(2)	0.049 5(2)	
S(2)	0.148 6(1)	−0.252 1(1)	0.116 6(1)	
C(3)	0.299 4(2)	−0.205 9(2)	0.127 7(2)	
C(4)	0.322 7(3)	−0.084 5(3)	0.140 7(3)	
C(5)	0.444 4(3)	−0.061 0(4)	0.156 1(4)	
C(6)	0.540 0(3)	−0.156 4(4)	0.162 7(5)	
C(7)	0.516 9(3)	−0.276 7(4)	0.152 6(5)	
C(8)	0.396 9(3)	−0.302 5(3)	0.130 5(4)	
C(111)	0.335 5(8)	0.335 5(8)	0.335 5(8)	
Cl(1)	0.192 4(2)	0.421 8(3)	0.316 9(2)	
Cl(4)	0.417 7(5)	0.417 7(5)	0.417 7(5)	
H(4)	0.255 3(82)	−0.021 5(82)	0.146 8(80)	5.5(0.7)
H(5)	0.479 5(100)	0.018 8(101)	0.191 9(100)	8.8(1.0)
H(6)	0.624 3(90)	−0.130 1(88)	0.162 4(87)	9.2(1.1)
H(7)	0.580 2(117)	−0.356 2(115)	0.146 3(114)	11.7(1.4)
H(8)	0.375 0(90)	−0.381 3(82)	0.129 7(95)	5.8(0.8)

TABLE 4

Interatomic distances (Å) and valency angles (°), with standard deviations in parentheses

(*a*) Bond lengths

C(1)–C(1$^{\mathrm{I}}$)	1.409(3)	C(5)–C(6)	1.364(5)
C(1)–S(2)	1.769(2)	C(6)–C(7)	1.364(7)
S(2)–C(3)	1.772(2)	C(7)–C(8)	1.403(5)
C(3)–C(4)	1.384(4)	C(111)–Cl(1)	1.719(8)
C(3)–C(8)	1.385(4)	C(111)–Cl(4)	1.702(11)
C(4)–C(5)	1.393(5)		

Average C(*sp*^{2})–H is 0.99 Å

(*b*) Valency angles

C(1$^{\mathrm{I}}$)–C(1)–C(1$^{\mathrm{II}}$)	119.9(2)	C(3)–C(4)–C(5)	119.5(3)
C(1$^{\mathrm{I}}$)–C(1)–S(2)	118.8(1)	C(4)–C(5)–C(6)	121.1(3)
C(1$^{\mathrm{II}}$)–C(1)–S(2)	121.2(1)	C(5)–C(6)–C(7)	119.7(3)
C(1)–S(2)–C(3)	103.2(1)	C(6)–C(7)–C(8)	120.6(3)
S(2)–C(3)–C(4)	124.7(2)	C(7)–C(8)–C(3)	119.3(3)
S(2)–C(3)–C(8)	115.5(2)	Cl(1)–C(111)–Cl(1$^{\mathrm{III}}$)	111.3(4)
C(4)–C(3)–C(8)	119.7(2)	Cl(1)–C(111)–Cl(4)	107.6(5)

Average C(*sp*^{2})–C(*sp*^{2})–H is 119.5°

TABLE 5

Torsion angles (°)

C(1$^{\mathrm{I}}$)–C(1)–S(2)–C(3)	−125	C(3)–C(4)–C(5)–C(6)	−2
C(1$^{\mathrm{II}}$)–C(1)–S(2)–C(3)	56	C(4)–C(5)–C(6)–C(7)	1
C(1)–S(2)–C(3)–C(4)	28	C(5)–C(6)–C(7)–C(8)	2
C(1)–S(2)–C(3)–C(8)	−156	C(6)–C(7)–C(8)–C(3)	−4
S(2)–C(3)–C(4)–C(5)	176	C(4)–C(3)–C(8)–C(7)	3
S(2)–C(3)–C(8)–C(7)	−173	C(8)–C(3)–C(4)–C(5)	0

TABLE 6

Some short intramolecular separations (<3.5 Å)

C(4) ··· C(1)	3.09	S(2) ··· S(2$^{\mathrm{II}}$)	3.18
C(4) ··· C(1$^{\mathrm{II}}$)	3.31	C(3) ··· C(1$^{\mathrm{II}}$)	3.25
C(4) ··· S(2$^{\mathrm{II}}$)	3.35	C(3) ··· S(2$^{\mathrm{II}}$)	3.09

TABLE 7

Displacements (Å) of atoms from planes through various sets of atoms

Plane A: C(1), C(1$^{\mathrm{I}}$), C(1$^{\mathrm{II}}$), C(1$^{\mathrm{III}}$), C(1$^{\mathrm{IV}}$), C(1$^{\mathrm{V}}$)

C(1) 0.019, C(1$^{\mathrm{I}}$) −0.019, C(1$^{\mathrm{IV}}$) 0.019, C(1$^{\mathrm{V}}$) −0.019, C(1$^{\mathrm{III}}$) 0.019, C(1$^{\mathrm{II}}$) −0.019, *S*(*2*) *0.090*

Plane B: C(3)—(8)

C(3) 0.006, C(4) 0.012, C(5) −0.014, C(6) −0.002, C(7) 0.020, C(8) −0.022, *S*(*2*) *0.135*

Angle between plane normals A–B is 66.8°.

The superscripts refer to the following transformations of the atomic co-ordinates (used in Tables 4—7):

I, $-z, -x, -y$
II, $-y, -z, -x$
III, z, x, y
IV, y, z, x
V, $-x, -y, -z$

As can be seen from Table 2 many of these new hosts exhibit remarkable selective inclusion behaviour. On recrystallisation from an equimolar mixture of *o*- and *p*-xylene, for example, hosts (III), (VIII), (IX), (XV), and (XX) favour inclusion of the *ortho*-isomer. On the other hand, a preference for the *para*-isomer is found for hexakis-(2-naphthylthiomethyl)benzene (XIII) and hexakis(benzylthiomethyl)benzene (XVIII).

Structural Properties of the Carbon Tetrachloride Adduct of (I).—A view looking directly onto the plane of the central benzene ring of the host molecule (I) is shown in Figure 2. It is located on a point of $\bar{3}$ symmetry so that the crystallographically equivalent 'legs' of the molecule point alternately above and below the plane of the central benzene ring. The relative orientation of the central and side-chain aromatic rings may be appreciated by a consideration of the torsion angles C(1^{II})–C(1)–S(2)–C(3) and C(1)–S(2)–C(3)–C(4), which are 56 and 28°, respectively. All bond lengths and angles in (I) are normal, with the exception of lengths C(5)–C(6) and C(6)–C(7), which are artificially shortened by thermal motion effects [30] (see Table 4). In this hexa-substituted molecule the central and side-chain benzene rings are near planar, with the sulphur atom displaced from these planes by 0.09 and 0.13 Å respectively.

The host–guest packing arrangement in the crystal is illustrated in Figure 3; the host molecules which complete the cage (which lie above and below the cavity in the view shown) have been omitted for clarity. The two CCl_4 guest molecules in the clathrate cage are orientated such that a C–Cl bond of each is collinear with the *c* axis. No evidence has been found to suggest distortion from tetrahedral geometry for the CCl_4 guest molecule (see Table 4); however, there is considerable thermal motion of the guest species in the cavity and this causes artificial shortening of the C–Cl bonds. The space available for guest accommodation may be appreciated from the contours shown in Figure 4, which are at various fractional levels parallel to the *ab* plane and represent only half the centrosymmetric cage. These contours were obtained after allowing for the van der Waals volumes of the cage wall atoms, and represent the greatest degree of freedom for a hydrogen atom at each fractional level. The effective cavity length is *ca.* 17 Å and although gaps have been detected in the cage wall, these are small compared with the size of the CCl_4 guest species. The cavity may therefore be considered to be of the closed cage type. Nevertheless, solvent loss does in fact occur slowly when the crystals are left in air, with apparent complete disruption of the crystal lattice. Although the guest molecules for (I), in Table 1, all possess a CCl_3 group, the presence of this group is not a sufficient condition for inclusion. For example, no inclusion behaviour is found on recrystallisation from CCl_3H, CCl_3F, or CCl_3CN; also recrystallisation from CCl_3CCl_2H gives unsolvated crystals of (I) which have been found to be triclinic with one molecule in the unit cell.

In summary, the analogy presented earlier has led to the discovery of a wide range of inclusion behaviour for compounds with a one, two, or three atom chain linking each side-chain ring to the central hexasubstituted benzene core of the molecule. The name 'hexa-host' seems particularly appropriate for this type of host molecule since it not only suggests the substitution pattern of the central ring, but also reflects the key relationship to the pre-existing hydrogen-bonded hexamer unit commonly encountered in hydroxyaromatic clathrate systems.

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