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Decakis(phenylthio)benzophenone: A Representative of a Novel Class of Host Molecule Comprised of Two Linked Persubstituted Aromatic Cores

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The title compound 1, prepared by reaction of decafluorobenzophenone 5 with PhSNa in DMEU, forms a 1:1 adduct with DMF; in this adduct the molecule's central V-shaped twin core possesses approximate C_2 symmetry, though this does not extend to the molecular periphery owing to the ababababab side-chain orientational distribution [a, above core benzene plane; b, below]. The adduct crystallizes in the monoclinic space group $P2_1/c$ with $a = 16.559(3)$, $b = 23.233(5)$, $c = 18.640(4)$, Å, $\beta = 114.49(3)°$ and $D_c = 1.363\,\mathrm{gcm}^{-3}$ for $Z = 4$. The refinement is based on 4621 observed reflections and gives a final R value of 0.069.

Keywords: Clathrate, linked hexa-host, host design, X-ray

INTRODUCTION

Several strategies have proved effective in producing new series of host molecules capable of forming crystalline inclusion compounds [1], with already realised or potential applications [2]. We now report a new approach, concerned with the design of hosts which have a central skeleton comprised of more than one (persubstituted) aromatic unit. In the present work we describe the successful construction of novel hosts by linking two hexa-hosts [3] together. Figure 1 shows a schematic representation of a linked hexa-host system, in which the linking unit *L* joining the two pentasubstituted phenyl units may correspond to a single atom, a chain of atoms or even a single covalent bond; the outer groups, *R*, are connected to a benzene nucleus by link Z which is comprised of one or more atoms.

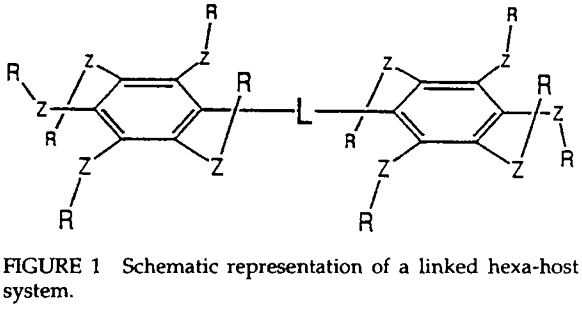

FIGURE 1 Schematic representation of a linked hexa-host system.

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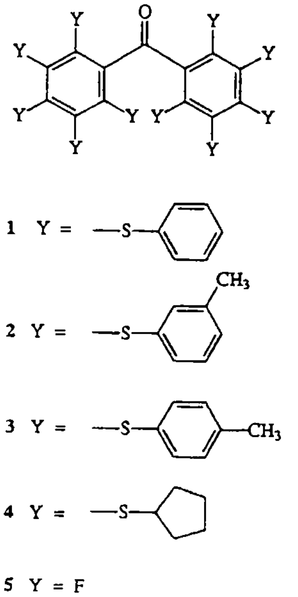
In initial studies it rapidly became apparent that the length of the link L was of critical importance. For example, when a two-atom link, $—CH_2—CH_2—$, was introduced as in 1,2-bis[2,3,4,5,6-pentakis(phenylthio)phenyl]-ethane [4] the centrosymmetric molecules were found to pack together efficiently leaving no voids for guest incorporation. Also, where the link is a direct covalent bond, as in decakis-(phenylthio)biphenyl [5], no host properties were found. However, the above cases contrast with the significant host properties described here for the one-atom link molecule decakis-(phenylthio)benzophenone **1** and related molecules **2**–**4**.

EXPERIMENTAL

Synthesis

Compounds **1**–**4** were prepared from decafluorobenzophenone **5** and had spectroscopic (^{1}H NMR, ^{13}C NMR) and microanalytical data in keeping with their formulated structures. Preparation of decakis(phenylthio)benzophenone **1**. PhSNa, 2.0 g (15.1 mmols), prepared from sodium in dry EtOH, was dissolved in DMEU and the solution degassed. Perfluorobenzophenone **5** (0.274 g, 0.78 mmols) was then added and the mixture degassed again and stirred at ambient temperature for two hours. Toluene (200 mL) was then added and the organic layer washed with water (10 × 100 mL). After removal of solvent, the yellow oil was purified by column chromatography (silica, toluene elution) to yield a yellow powder which was recrystallised from $CHCl_3/MeOH$ to yield yellow crystals 0.903 g (95%), m.p. 238–240°C; TLC $R_f = 0.58$ toluene. Found (recrystallised from $CHCl_3/CH_3COOH$ and dried) C, 64.16; H, 3.56; S, 23.61%. $C_{73}H_{50}S_{10}O \cdot CHCl_3$ requires C, 64.28; H, 3.69; S, 23.16%; δ_H(200 MHz, CD_2Cl_2) *ca.* 7.2–6.9 (*m*, 38H, ArH), *ca.* 6.57–6.6 (*m*, 12H, ArH); δ_c(50 MHz, CD_2Cl_2) 191.9, 152.0, 151.1, 150.0, 139.9, 138.1, 137.7, 137.6, 129.4, 129.3 (overlapping resonances), 128.7, 128.2, 127.6, 126.7, 126.4 (overlapping resonances). Compounds **2**, **3** and **4** were prepared analogously in respective unoptimised yields of 40%, 36% and 39% and had m.p.s 121–122, 126–127 and 193–194°C (1,4-dioxane clathrate), respectively. The parent decakis(phenylthio)benzophenone **1**, the first of the series prepared, proved to be a novel host forming adducts from a range of solvent mixtures. For example, a ternary monoclinic 1 : 1 : 1 adduct was produced on recrystallisation of **1** from a mixture of chloroform and acetic acid (see below).



SCHEME 1

X-ray Data Collection, Structure Determination and Refinement

Crystal data for **1**. $C_{76}H_{57}NO_2S_{10}$, $Mr = 1336.84$ yellow cuboidal crystal with dimensions 0.2 × 0.2 × 0.3 mm, space group $P2_1/c$ (No. 14), monoclinic, $a = 16.559(3)$, $b = 23.223(5)$, $c = 18.640(4)$ Å, $\beta = 114.49(3)°$, $V = 6523(2)$ Å^3 [3], $Z = 4$, $D_c = 1.363$ gcm^{-3}, μ(Mo-K$_\alpha$) = 0.39 mm^{-1}, $F(000) = 2792$. Data were obtained at 120 ± 1 K on a

CAD-4 diffractometer using graphite monochromated Mo-K_α radiation. A total of 15950 reflections (11371 unique) were collected using the $\omega-2\theta$ technique with $\theta_{max} = 24.91°$. The structure was solved by direct methods and refined by full matrix least squares method on F^2. For the 4621 reflections with $[I > 2\sigma(I)]$, $R = 0.0688$, $R_w = 0.1290$. The hydrogen atom coordinates are constrained to ride on those of the atom to which they are bonded. One of the phenyl groups of the host, and the carbonyl group of the solvent molecule are disordered. In both groups two positions can be located for each atom. The site occupancies refine to around 0.5 in all cases.

A preliminary study of the 1 : 1 : 1 adduct of **1** with joint guests $CHCl_3$ and CH_3COOH showed that it crystallises in space group $P2_1/c$, with $a = 17.785(3)$, $b = 23.081(4)$, $c = 19.310(2)$ Å, $\beta = 116.75(1)°$, $Z = 4$. The X-ray study of this adduct at 293 K revealed high thermal motion of host atoms and disorder of both guest components. Interestingly, when this adduct is heated at 80°C, under vacuum for 4 hours, the acetic acid is removed but the chloroform remains in the host lattice.

RESULTS AND DISCUSSION

The low-temperature (120 K) X-ray crystallographic structure analysis of the 1 : 1 crystalline inclusion compound of **1** with DMF (obtained using a DMF/$CHCl_3$/MeOH solvent mixture; ^{1}H NMR analysis) was undertaken to elucidate precisely the conformation of **1** and the nature of the host-guest packing in this adduct. The crystals are monoclinic space group $P2_1/c$ and both the host and the DMF molecules occupy general positions in the unit cell; the contents of the asymmetric unit are shown in Figure 2. The host molecule's V-shaped twin core possesses approximate C_2 symmetry; however, this does C_2 symmetry does not extend to the side-chain distribution. The molecule of **1** has an **abababab** conformation, where **a** represents a side-chain oriented above the plane of its core benzene (on same side as carbonyl O), and **b** the opposite orientation.

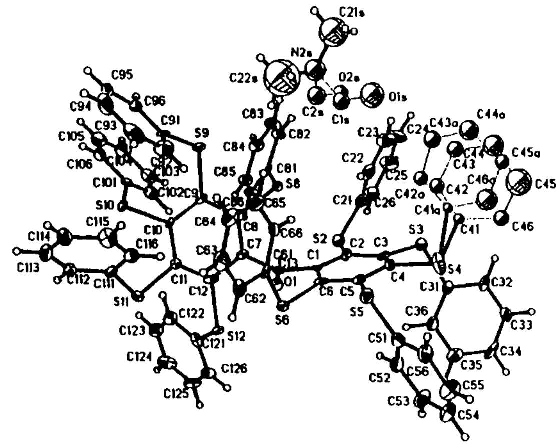


FIGURE 2 The contents of the asymmetric unit in the 1 : 1 inclusion compound of decakis(phenylthio)benzophenone **1** with DMF. Selected host bond lengths, angles and torsion angles are: O1—C13, 1.211(9); C13—C1, 1.508(2); C13—C7, 1.493(12) Å C1—C13—C7, 122.8(7); O1—C13—C1, 118.6(7); O1—C13—C7, 118.6(7)° O1—C13—C1—C2, 44.7(10); O1—C13—C7—C12, 61.1(10)°.

As can be seen from Figure 2, one side-chain exhibits disorder over two positions; whilst the DMF guest possesses two orientations in the host void. The host-guest packing is illustrated in Figure 3, in which the main orientation of four DMF molecules, roughly half-way along the a axis, may be seen; also, for clarity, only the principal position of the disordered side chain of **1** is represented.

To examine the effect of substitution on the aryl side-chains, the *m*-tolyl and *p*-tolyl analogues **2** and **3** were prepared. Both molecules possess the ability to from clathrates, including 1,4-dioxane on recrystallisation from this solvent, the respective host-guest ratios being 1 : 1 and *ca.* 1 : 2. Encouragingly, decakis(cyclopentylthio)benzophenone **4**, featuring a non-aromatic side-chain, was also found to form (*ca.* 1 : 1) crystalline 1,4-dioxane adduct, from which thermogravimetric analysis (TGA) revealed guest loss only between 125–145°C.

Finally, recrystallisation of the aromatic parent **1** from an ethane-1,2-dithiol/$CHCl_3$/MeOH

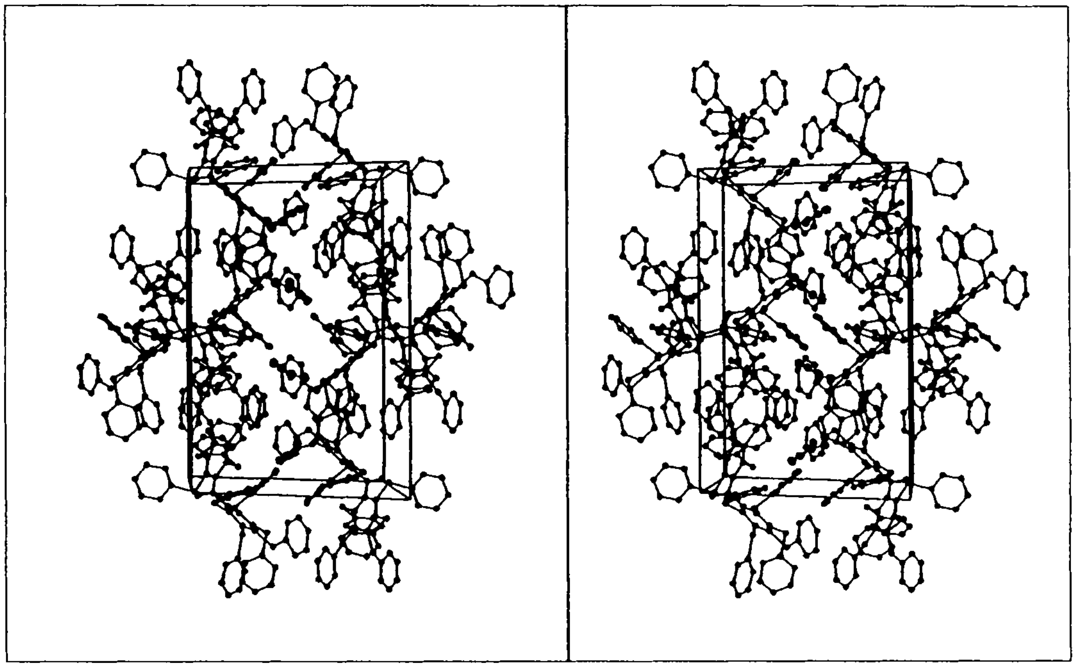


FIGURE 3 A stereoview looking onto the *ab* plane (*a* horizontal, *b* vertical) illustrating the host–guest packing in the 1 : 1 adduct of **1** with DMF. The DMF molecules are indicated by larger spheres.

TABLE I Positional and thermal parameters

Atom	x	y	z	U_{equiv} Å^2
O1	0.9671(4)	−0.5123(3)	0.2957(3)	0.0219(14)
S2	0.8897(2)	−0.53690(10)	0.40363(14)	0.0257(6)
S3	0.7552(2)	−0.63514(10)	0.40591(13)	0.0242(6)
S4	0.6050(2)	−0.68142(13)	0.2357(2)	0.0382(7)
S5	0.62258(15)	−0.64762(10)	0.07983(14)	0.0246(6)
S6	0.78320(14)	−0.56952(10)	0.08779(12)	0.0188(5)
S8	0.76879(14)	−0.42576(10)	0.26087(12)	0.0181(5)
S9	0.76249(15)	−0.30786(9)	0.17945(13)	0.0202(5)
S10	0.89900(14)	−0.28975(9)	0.08947(12)	0.0176(5)
S11	0.95782(14)	−0.40567(10)	0.02915(13)	0.0206(5)
S12	0.97988(14)	−0.51833(9)	0.13045(13)	0.0179(5)
C1	0.8203(5)	−0.5543(4)	0.2437(5)	0.015(2)
C2	0.8158(5)	−0.5684(4)	0.3158(5)	0.020(2)
C21	0.8252(6)	−0.5160(4)	0.4549(5)	0.028(2)
C22	0.7346(7)	−0.4984(4)	0.4170(5)	0.031(2)
C23	0.6906(7)	−0.4811(5)	0.4621(6)	0.041(3)
C24	0.7336(7)	−0.4814(5)	0.5428(6)	0.046(3)
C25	0.8232(7)	−0.4971(5)	0.5804(6)	0.042(3)
C26	0.8673(7)	−0.5137(4)	0.5353(6)	0.035(3)
C3	0.7527(6)	−0.6114(4)	0.3150(5)	0.020(2)
C31	0.7797(5)	−0.7097(4)	0.4059(5)	0.020(2)
C32	0.7497(6)	−0.7442(4)	0.4494(5)	0.025(2)
C33	0.7738(7)	−0.8016(4)	0.4607(6)	0.032(2)
C34	0.8270(6)	−0.8242(4)	0.4279(6)	0.034(3)
C35	0.8563(6)	−0.7903(4)	0.3828(6)	0.031(2)
C36	0.8330(6)	−0.7326(4)	0.3709(6)	0.026(2)
C4	0.6907(6)	−0.6317(4)	0.2431(5)	0.021(2)
C41	0.5520(17)	−0.6325(30)	0.2895(15)	0.010(12)
C42	0.5479(18)	−0.5749(22)	0.2883(14)	0.024(11)
C43	0.5032(15)	−0.5452(14)	0.3254(13)	0.036(11)
C44	0.4586(19)	−0.5734(15)	0.3574(18)	0.052(13)
C45	0.4551(19)	−0.6414(26)	0.3569(15)	0.023(14)

TABLE I (Continued)

Atom	x	y	z	U_{equiv} Å^2
C46	0.5087(15)	−0.6639(15)	0.3238(13)	0.040(11)
C41A	0.5457(13)	−0.6557(18)	0.2828(12)	0.008(9)
C42A	0.5372(15)	−0.5992(21)	0.2971(11)	0.021(10)
C43A	0.4877(14)	−0.5793(11)	0.3317(12)	0.028(10)
C44A	0.4465(12)	−0.6154(20)	0.3603(11)	0.048(9)
C45A	0.4531(12)	−0.6785(13)	0.3485(11)	0.072(10)
C46A	0.5040(11)	−0.6982(10)	0.3124(10)	0.025(8)
C5	0.6965(6)	−0.6183(4)	0.1709(5)	0.022(2)
C51	0.6490(6)	−0.7214(4)	0.0911(5)	0.024(2)
C52	0.7332(6)	−0.7420(4)	0.1396(6)	0.028(2)
C53	0.7483(7)	−0.8015(4)	0.1411(6)	0.034(3)
C54	0.6834(6)	−0.8390(4)	0.0953(6)	0.033(2)
C55	0.6021(7)	−0.8183(5)	0.0486(6)	0.037(3)
C56	0.5827(6)	−0.7606(4)	0.0451(5)	0.027(2)
C6	0.7633(5)	−0.5797(4)	0.1724(5)	0.020(2)
C61	0.6959(5)	−0.5247(4)	0.0260(5)	0.018(2)
C62	0.6835(6)	−0.5215(4)	−0.0521(5)	0.028(2)
C63	0.6186(6)	−0.4851(4)	−0.1037(6)	0.033(2)
C64	0.5682(6)	−0.4516(4)	−0.0762(6)	0.029(2)
C65	0.5804(6)	−0.4556(4)	0.0008(6)	0.028(2)
C66	0.6450(5)	−0.4915(4)	0.0532(5)	0.021(2)
C7	0.8751(5)	−0.4632(4)	0.1922(5)	0.015(2)
C8	0.8237(5)	−0.4166(4)	0.1973(4)	0.017(2)
C81	0.8388(6)	−0.3848(4)	0.3441(5)	0.017(2)
C82	0.7990(6)	−0.3556(4)	0.3866(6)	0.028(2)
C83	0.8516(6)	−0.3267(4)	0.4526(6)	0.033(2)
C84	0.9428(6)	−0.3244(4)	0.4788(6)	0.029(2)
C85	0.9814(6)	−0.3543(4)	0.4365(5)	0.024(2)
C86	0.9310(6)	−0.3843(4)	0.3704(5)	0.022(2)
C9	0.8228(5)	−0.3643(3)	0.1613(5)	0.014(2)
C91	0.7123(5)	−0.2704(4)	0.0884(5)	0.018(2)
C92	0.6643(6)	−0.2998(5)	0.0185(6)	0.033(3)
C93	0.6223(6)	−0.2666(6)	−0.0497(6)	0.045(3)
C94	0.6260(7)	−0.2076(7)	−0.0483(8)	0.052(4)
C95	0.6725(7)	−0.1796(5)	0.0220(8)	0.043(3)
C96	0.7176(6)	−0.2109(4)	0.0911(7)	0.033(3)
C10	0.8748(5)	−0.3580(3)	0.1177(5)	0.012(2)
C101	0.9494(5)	−0.2531(4)	0.1815(5)	0.017(2)
C102	0.9974(5)	−0.2789(4)	0.2533(5)	0.025(2)
C103	1.0418(6)	−0.2455(4)	0.3201(5)	0.026(2)
C104	1.0399(6)	−0.1861(5)	0.3155(6)	0.034(3)
C105	0.9926(6)	−0.1601(4)	0.2432(6)	0.032(2)
C106	0.9473(6)	−0.1928(4)	0.1770(5)	0.023(2)
C11	0.9126(5)	−0.4076(4)	0.1000(4)	0.013(2)
C111	0.8772(6)	−0.3656(4)	−0.0491(5)	0.019(2)
C112	0.9064(6)	−0.3233(4)	−0.0850(5)	0.023(2)
C113	0.8458(7)	−0.2947(4)	−0.1508(6)	0.032(2)
C114	0.7559(6)	−0.3084(4)	−0.1795(5)	0.029(2)
C115	0.7278(6)	−0.3492(5)	−0.1417(5)	0.029(2)
C116	0.7865(6)	−0.3787(4)	−0.0768(5)	0.025(2)
C12	0.9191(5)	−0.4581(4)	0.1413(5)	0.017(2)
C121	1.0931(5)	−0.4972(4)	0.1836(5)	0.018(2)
C122	1.1234(6)	−0.4415(4)	0.1998(5)	0.024(2)
C123	1.2138(6)	−0.4310(4)	0.2374(5)	0.028(2)
C124	1.2743(6)	−0.4763(5)	0.2582(6)	0.033(3)
C125	1.2426(6)	−0.5316(4)	0.2423(6)	0.031(2)
C126	1.1521(5)	−0.5430(4)	0.2055(5)	0.022(2)
C13	0.8925(6)	−0.5138(4)	0.2460(5)	0.016(2)
N2S	0.4820(7)	−0.3643(4)	0.2087(6)	0.051(3)
O1S	0.5081(12)	−0.4391(9)	0.3018(11)	0.082(10)
C1S	0.5236(18)	−0.4164(15)	0.2510(16)	0.045(13)
C2S	0.5486(20)	−0.3842(16)	0.2439(16)	0.050(13)
O2S	0.5665(14)	−0.3999(10)	0.3128(13)	0.036(10)
C21S	0.4107(10)	−0.3474(8)	0.2255(10)	0.095(5)
C22S	0.4810(14)	−0.3477(11)	0.1346(13)	0.144(8)

mixture leads to formation of odourless yellow crystals of the dithiol adduct, host–guest ratio *ca.* 4:3 [^{1}H NMR analysis], which are stable [6] (by TGA) up to 170°C.

Acknowledgments

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