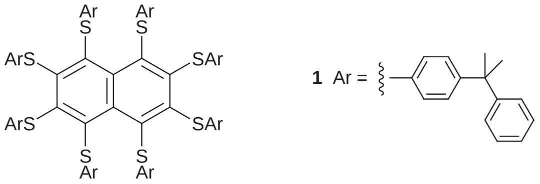
Octakis[4-(2-phenylpropan-2-yl)phenylthio]naphthalene: a conformationally unique host allowing direct observation of a well-defined solid-state acetone conformation

Gary A. Downing,[a] **Christopher S. Frampton**[b] **and David D. MacNicol***[a]†

[a] *Department of Chemistry, University of Glasgow, Glasgow, UK G12 8QQ*
[b] *Roche Discovery Welwyn, Broadwater Road, Welwyn Garden City, Herefordshire, UK AL7 3AY*

In its stoichiometric 1:1 clathrate with acetone, studied by X-ray diffraction at 123 K, the title host molecule possesses a unique abbbabbb conformation with six side-chain units anti-parallel to the other two; the guest acetone's conformation exhibits non-crystallographic C_2 symmetry, and the observed lowering in symmetry from C_{2v} in the vapour is accompanied by a significant opening of the guest's C–C–C angle, in accord with a key theoretical prediction in the literature (*J. Chem. Phys.*, 1993, 98, 2754).

In the design of new spider host molecules, suitably persubstituted naphthalenes, a challenging goal is to establish the precise way in which the structure of the side-chain unit of a given host controls its ability to form crystalline inclusion compounds.[1] For this host series we have stressed the critical role of the host's molecule conformation; this is well illustrated in the case of octakis(3,4-dimethylphenylthio)naphthalene which, in the course of its self-assembly to form nano-scale cavities capable of trapping diverse guest species,[2] adopts an exactly D_2-symmetric **aabbaabb** conformation, (**a** and **b** denoting side-chain units projecting, respectively, above and below the aromatic core). We now report the synthesis of the new spider host octakis[4-(2-phenylpropan-2-yl)phenylthio]-napthalene **1**, possessing a more extended side-chain unit,



which was initially characterised by ^{1}H NMR, ^{13}C NMR and microanalytical data.‡ The new host **1**, contrasting with the broad inclusion spectrum found for its above-mentioned counterpart, appears to be specific[3] to acetone alone, suggesting the efficiency with which this guest is embedded in the host lattice of **1**. A strictly 1:1 crystalline inclusion compound was formed on recrystallisation of unsolvated **1** from neat acetone.

A low-temperature (123 K) X-ray diffraction analysis was undertaken to determine the host conformation, the conformation of the acetone guest, and the nature of host–guest interactions in this unique adduct of **1**. The 1:1 acetone adduct of **1** is triclinic, space group $P\bar{1}$, with two host and two acetone guest molecules per unit cell.§ The striking host conformation of **1**, illustrated in Fig. 1(*b*) (the enantiomeric form is also present in the centrosymmetric crystal), is of the previously unknown **abbbabbb** type, with six of the eight side chain units projecting in the opposite direction to the other two. The conformation is close to C_2-symmetric, with the non-crystallographic two-fold axis running normal to the mean plane of the naphthalene core, and bisecting its central carbon–carbon bond. The naphthalene core is markedly non-planar, but almost exactly C_2 in character; corresponding displacements form the ten-carbon mean plane are C(1), C(5), −0.22, −0.23; C(2), C(6), −0.25, −0.25; C(3), C(7), 0.07, 0.08; C(4), C(8), 0.31,

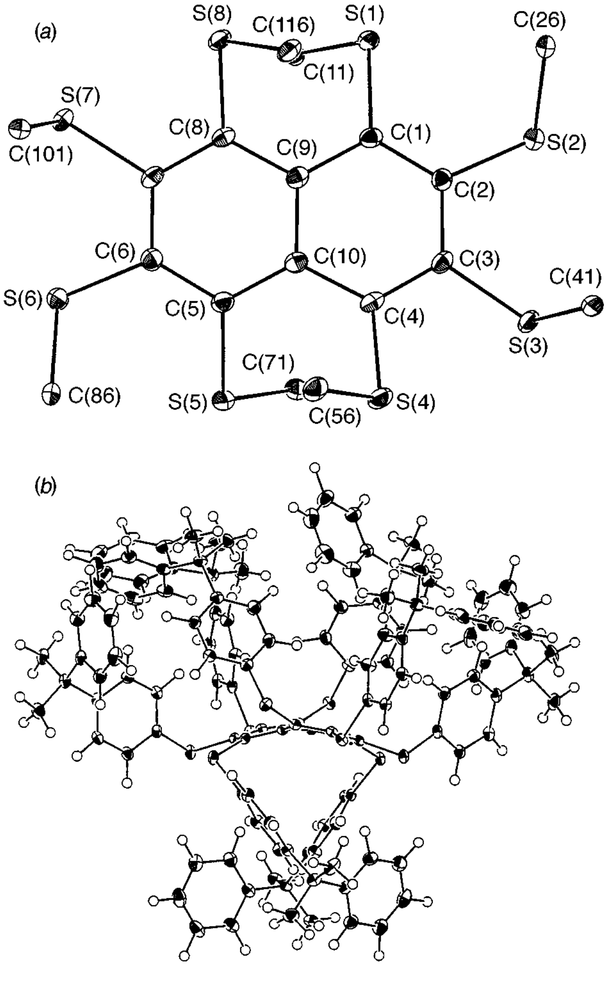


Fig. 1 (*a*) Atomic numbering scheme for the central region of **1** in its acetone clathrate; (*b*) a view illustrating the structure and conformation of the host molecule **1** in its 1 : 1 triclinic adduct with acetone. The host molecule's non-crystallographic C_2 axis is vertical in this view. The distribution of bond lengths (Å) about the naphthalene core is: C(1)–C(2), 1.386(3); C(3)–C(4), 1.386(3); C(5)–C(6), 1.393(3); C(7)–C(8), 1.388(3); C(2)–C(3), 1.424(3); C(6)–C(7), 1.424(3); C(1)–C(9), 1.442(3); C(4)–C(10), 1.439(3); C(5)–C(10), 1.444(3); C(8)–C(9), 1.439(3); C(9)–C(10), 1.427(3). The core bond angles (°) are C(9)–C(1)–C(2), 120.4(2); C(1)–C(2)–C(3), 119.3(2); C(2)–C(3)–C(4), 120.9(2); C(3)–C(4)–C(10), 119.8(2), C(10)–C(5)–C(6), 120.0(2); C(5)–C(6)–C(7), 119.5(2); C(6)–C(7)–C(8), 120.7(2); C(7)–C(8)–C(9), 120.0(2); C(10)–C(9)–C(1), 118.7(2); C(8)–C(9)–C(10), 117.0(2); C(8)–C(9)–C(1), 124.2(2); C(9)–C(10)–C(5), 118.4(2); C(4)–C(10)–C(9), 116.8(2); C(4)–C(10)–C(5), 124.5(2).

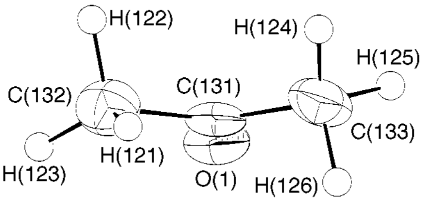


Fig. 2 The near C_2-symmetric conformation of acetone in its 1:1 adduct with host **1** as viewed at a narrow angle to the C=O bond direction

0.30 Å. The average esd for the carbon displacements is 0.002 Å. The corresponding displacements for S(1), S(5); S(2), S(6); S(3), S(7); S(4), S(8): −0.92, −0.89; −0.78, −0.76; 0.18, −0.05; 1.03, 1.00 Å [for other structural data, see caption to Fig. 1(*b*)].

The acetone guest molecule, which also occupies a general position in the unit cell, is shown in Fig. 2. As for the host molecule **1**, all hydrogen atoms were located and, again, the molecule possesses non-crystallographic C_2 symmetry. The non-hydrogen atoms of the guest are exactly coplanar, the angles being C(132)–C(131)–C(133) = 118.3(3), O(1)–C(131)–C(132) = 120.7(3) and O(1)–C(131)–C(133) = 121.0(3)°. The bond lengths are similar to those found for acetone in the vapour phase from a combined analysis of microwave and electron diffraction data[4] [given in parenthesis, for comparison]: O(1)–C(131) = 1.211(3) [1.210(4)], C(131)–C(132) = 1.499(4) [1.517(3)] and C(131)–C(133) = 1.498(4) [1.517(3) Å].

The acetone *conformation* in host **1**, subject to a number of weak host–guest hydrogen–hydrogen interactions (*vide infra)*, is distinct from the C_{2v} equilibrium symmetry situation in the vapour phase, where the in-plane methyl hydrogens eclipse the oxygen atom. It is interesting to note that Smeyers and coworkers[5] have predicted that methyl group rotation, away from the above C_{2v} conformation, will lead to an increase in the C–C–C bond angle. This is in keeping with observation; the C–C–C bond angle for the C_2 guest conformation, 118.2(3)°, is indeed significantly opened compared to the value, 116.0(3)°, for this angle in the C_{2v} vapour phase conformation of acetone. It must be said, of course, that the guest acetone's skeletal geometry may be subject to other host–guest influences, in addition to conformational control by the host lattice.[6] The acetone guest molecule experiences no strong host–guest interactions, and is present in an environment of low polarity. There are no fewer than 17 hydrogen–hydrogen host–guest contacts in the range 2.340–2.959 Å. The closest contact between the host molecule **1** and acetone is of the C–H···O type[7] and has length 2.320 Å. In all, there are five intermolecular contacts between O(1) and hydrogen atoms of **1** and these span the distance range 2.320–2.912 Å.

We thank the EPSRC (UK) for support (to G. A. D.).

Notes and References

† E-mail: D.MacNicol@chem.gla.ac.uk

‡ Compound **1** was prepared by persubstitution of perfluoronaphthalene with an excess of the appropriate thiolate nucleophile in dipolar aprotic solvent, the required thiol, 4-(2-phenylpropan-2-yl)benzenethiol, being prepared from the corresponding phenol by a general literature method (M.S. Newman and H.A. Karnes, *J. Org. Chem.*, 1966, **31**, 3980), and having mp 43–44 °C (Calc. for $C_{15}H_{16}S$: C, 78.90; H, 7.02. Found: C, 78.78; H, 7.15%). Perfluoronaphthalene (0.26g, 0.96 mmol) and sodium 4-(2-phenylpropan-2-yl)benzenethiolate (3.74g, 15.3 mmol), prepared from the above thiol and sodium in absolute ethanol, were stirred in dry, degassed 1,3-dimethylimidazolidin-2-one (DMEU) (40 ml) for 3 h at ambient temperature, under N_2. The red–orange reaction mixture was then added to toluene (200 ml), washed with water (10 × 250 ml), and evaporation of the solvent gave a red oil, from which compound **1** was obtained by column chromatography (silica, hexane–EtOAc) as a orange–red microcrystalline material, 1.51g (81%), mp 161–162 °C. *Selected data* for **1**: δ_H(200 MHz, $CDCl_3$) 1.51 (s, 24H), 1.54 (s, 24H), *ca.* 6.6–6.9 (two AA′BB′ spectra, 32H), *ca.* 7.0–7.3 (m, 40H); δ_C(50 MHz, $CDCl_3$) 30.6, 30.7, 42.6, 42.7, 125.6, 125.7, 126.6, 126.7, 126.9, 127.4, 127.5, 128.0, 128.1, 128.9, 134.8, 135.7, 139.6 (overlapping resonances), 143.7, 148.4, 148.9, 150.1, 150.5 (Calc. for $C_{130}H_{120}S_8$: C, 80.57; H, 6.20. Found: C, 80.52; H, 6.29%).

§ *Crystal data* for **1**·$(CH_3)_2CO$: $C_{133}H_{126}O_1S_8$, M_r = 1996.82, triclinic, space group $P1$, a = 19.299(9), b = 20.235(11), c = 16.338(5) Å, α = 92.15(4), β = 104.71(3), γ = 118.47(4)°, U = 5330(4) Å^3, Z = 2, ρ_{calc} = 1.244 Mg m^{-3}, $F(000)$ = 2120, μ = 0.221 mm^{-1}, T = 123(1) K. Crystal dimensions, orange prism, 0.80 × 0.38 × 0.22 mm. Mo-Kα radiation (0.71069 Å), θ_{max} = 25.02°, 19 349 reflections collected, 18 743 unique reflections R_{int} = 0.0216, 15 294 reflections observed [$> 2\sigma(I)$]. Final R (on F using observed data) a $wR2$ (on F^2 using all data) were 0.0372 and 0.1044 respectively for 1279 parameters. Final GOF = 1.002. Maximum and minimum residual density 0.416 and −0.415 e Å^{-3} respectively. Data were collected on a Rigaku AFC7R diffractometer equipped with an Oxford Cryosystems cryostream cooler (ref. 8). The structure was solved using direct methods (SHELXS-86) (ref. 9) and refined on F^2 using all unique data by full-matrix least-squares (SHELXL-93) (ref. 10). All non-hydrogen atoms have anisotropic displacement parameters. All hydrogen atoms were located in difference syntheses, these were assigned a common temperature factor and included in the model but not refined. CCDC 182/983.

1 For a review see, D. D. MacNicol and G. A. Downing, in *Comprehensive Supramolecular Chemistry*, ed. D. D. MacNicol, F. Toda and R. Bishop, Pergamon, Oxford, 1996, vol. 6, ch. 14, pp. 434–444.
2 G. A. Downing, C. S. Frampton, J. H. Gall and D. D. MacNicol, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1547.
3 Unsolvated crystals of **1** were obtained on recrystallisation of **1** from neat DMF, DMSO, CH_2Cl_2, 1,4-dioxane, and other solvents.
4 T. Iijima, *Bull. Chem. Soc. Jpn.*, 1972, **45**, 3526; see also J. M. Vacherand, B. P. Van Eijck, J. Burie and J. Demaison, *J. Mol. Spectosc.*, 1986, **118**, 355.
5 Y. G. Smeyers, M. L. Senent, V. Botella and D. C. Moule, *J. Chem. Phys.*, 1993, **98**, 2754 and references cited therein.
6 With regard to the crystalline state, 1109 X-ray crystal structure analyses have been reported for systems in which acetone is present as a ligand component coordinated to a metal (*e.g.* R. Amstutz, J. D. Dunitz, T. Laube, W. B. Schweizer and D. Seebach, *Chem. Ber.*, 1986, **119**, 434; M. Hoyer and H. Hartl, *Z. Anorg. Allg. Chem.*, 1992, 612) or is 'anchored' in the lattice by one or more hydrogen bonds (*e.g.* C. P. Brock and G. L. Morelan, *J. Phys. Chem.*, 1986, **90**, 5631). Both these situations tend to attenuate thermal motion, favouring direct observation of the acetone's hydrogen atoms, but represent relatively strong host–guest interactions. When such motion-reducing interactions are absent, the acetone molecule normally exhibits high thermal motion and/or disorder, however, see for example, A. Dietrich, K. A. Fidelis, D. R. Powell, D. van der Helm and D. L. Eng-Wilmot, *J. Chem. Soc., Dalton Trans.*, 1991, 231; A. Avdeef and W. P. Scheafer, *J. Am. Chem. Soc.*, 1976, **98**, 5153. Interestingly, no X-ray results from the molecular crystal of acetone itself have yet appeared in the literature.
7 For a recent review of C–H···O interactions see, T. Steiner, *Chem. Commun.*, 1997, 727.
8 J. Cosier and A. M. Glazer, *J. Appl. Crystallogr.*, 1986, **19**, 105.
9 G. M. Sheldrick, *Acta Crystallogr., Sect. A.*, 1990, **46**, 467.
10 G. M. Sheldrick, SHELXL-93, program for the refinement of crystal structures, University of Göttingen, Germany, 1993.

Received in Liverpool, UK, 29th July 1998; 8/05967E