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Structurally Dissimilar Clathrates from Isomeric Spider Hosts: Octakis(*m*-tolylthio)naphthalene and its *p*-Tolylthio Analogue

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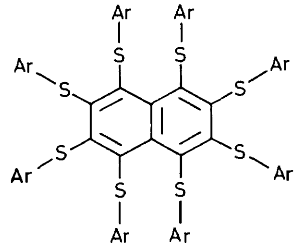
The title isomeric hosts (**1**) and (**2**), adopting different molecular conformations, form distinct types of closed cage accommodating the common guest 1,4-dioxane; it is remarkable that the symmetrical multimolecular cage structure of (**1**), not consolidated by hydrogen bonding, can exist even in the absence of guest.

As part of our work[1] directed towards the discovery of new classes of host molecule we have recently described[2] the first synthesis of octakis(arylthio)naphthalenes; also, preliminary information on guest inclusion was briefly reported. We now present the first detailed structural information on crystalline inclusion compounds formed by members of this novel, eight-legged or 'spider' host series. In addition, an unusual isostructural empty-cage form, lacking stabilisation by hydrogen bonding, has been defined by X-ray methods. The hosts initially selected for structural study were octakis(*m*-tolylthio)naphthalene (**1**) and octakis(*p*-tolylthio)naphthalene (**2**). The isomeric octa-substituted naphthalenes (**1**) and (**2**) were readily obtained in excellent yields by reaction of octafluoronaphthalene with the appropriate sodium arenethiolate employing the solvent 1,3-dimethylimidazolidin-2-one (DMEU) to promote complete displacement of the fluorine atoms, the method being directly analogous to that previously employed for the synthesis[2] of the parent molecule, octakis(phenylthio)naphthalene (**4**) itself. Compounds (**1**) and (**2**), m.p. 157—158 °C and 195—196 °C (unsolvated forms) respectively, gave satisfactory microanalytical data and had spectroscopic properties (^{1}H and ^{13}C n.m.r., i.r., and mass) fully in accord with their formulated structures.



(**1**) Ar = *m*-MeC_6H_4

(**2**) Ar = *p*-MeC_6H_4

(**3**) Ar = *o*-MeC_6H_4

(**4**) Ar = Ph

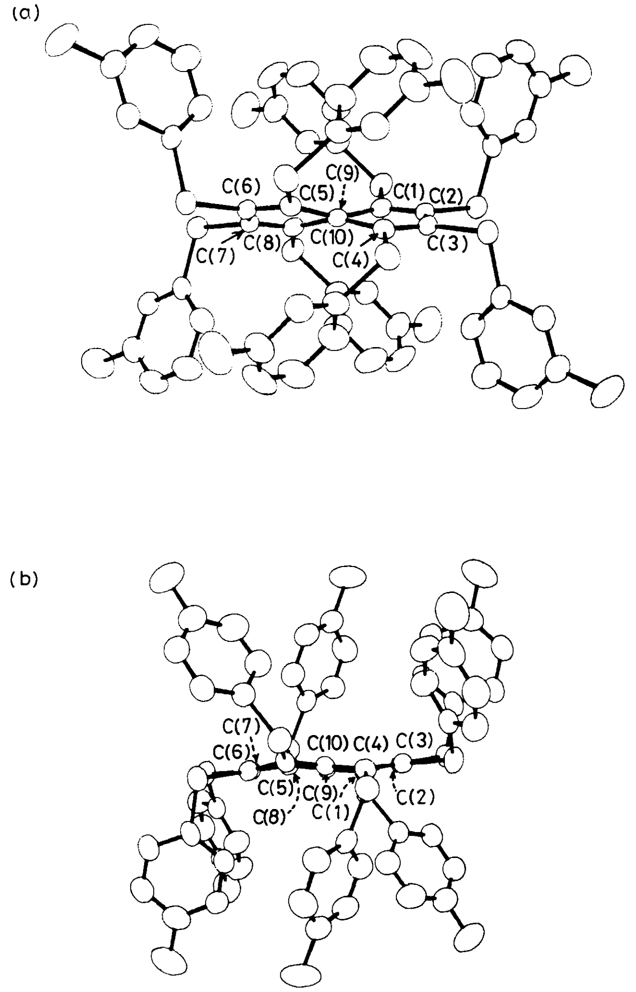


Figure 1. Views illustrating the molecular structures of (a) octakis(*m*-tolylthio)naphthalene (**1**), in the unsolvated tetragonal crystal and (b) octakis(*p*-tolylthio)naphthalene (**2**) in its 1,4-dioxane adduct.

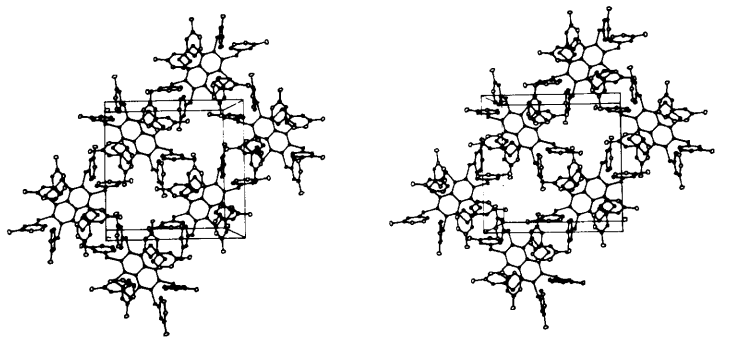


Figure 2. A stereoview, looking down *c*, showing the molecular packing of octakis(*m*-tolylthio)naphthalene (**1**) in its empty-cage form.

Recrystallisation of unsolvated (**1**) and (**2**) from the common solvent 1,4-dioxane yields red, highly crystalline adducts with respective host–guest ratios of 1:*ca.* 1 and 1:2, as determined by ^{1}H n.m.r. spectroscopy. Prepared analogously, the third isomer, octakis(*o*-tolylthio)naphthalene (**3**), also forms an inclusion compound with the same guest, though the structure of this 1,4-dioxane adduct [host–guest ratio 1:2] has not yet been determined.

Crystal data: $C_{66}H_{56}S_8$, (**1**), unsolvated form: $M = 1\,105.68$, tetragonal, space group $P4/ncc$, $a = 15.875(2)$, $c = 23.654(3)$ Å, $U = 5\,961.2$ Å^3, $Z = 4$, $D_c = 1.23$ g cm^{-3}, μ(Mo-K_α) = 3.25 cm^{-1}. Number of independent intensities:† 3 256 from red prism, 0.3 × 0.2 × 0.2 mm, mounted on fibre. Final R for 1 492 reflections considered observed: 0.042; R' 0.034. $C_{66}H_{56}S_8$, (**1**)·$C_4H_8O_2$: $M = 1\,193.79$, tetragonal, space group $P4/ncc$, $a = 16.040(2)$, $c = 23.793(2)$ Å, $U = 6\,121.4$ Å^3, $Z = 4$, $D_c = 1.29$ g cm^{-3}, μ(Mo-K_α) = 3.23 cm^{-1}. Number of independent intensities: 3 512 from red prism, 0.3 × 0.3 × 0.2 mm, mounted in capillary. Final R for 1 369 reflections considered observed: 0.045; R' 0.038. $C_{66}H_{56}S_8$, (**2**)·2[$C_4H_8O_2$]: $M = 1\,281.90$, monoclinic, space group $P2_1/n$, $a = 11.225(4)$, $b = 14.602(2)$, $c = 21.083(2)$ Å, $\beta = 101.30(3)°$, $U = 3\,388.6$ Å^3, $Z = 2$, $D_c = 1.26$ g cm^{-3}, μ(Mo-K_α) = 2.98 cm^{-1}. Number of independent intensities: 7 363 from red prism, 0.7 × 0.2 × 0.2 mm, mounted in capillary. Final R for 3 836 reflections considered observed: 0.066; R' 0.095.

Figure 1(a) shows an edge-on view of octakis(*m*-tolylthio)naphthalene (**1**) in the unsolvated crystal,‡ the molecular conformation being almost identical to that found for (**1**) in its 1,4-dioxane adduct. The molecule, located on a point of 222 symmetry, is constrained to have exact D_2 symmetry, and both enantiomeric conformations are present in the crystal. The significant non-planarity of the naphthalene core is characterised by the torsion angle C(1)–C(9)–C(10)–C(4), −26(1)°, with a corresponding value of −27(1)° for the dioxane adduct; the atoms C(1) to C(4) are close to coplanar in each case. It is convenient to introduce a new classification, given below,§ for the economical description of 'leg' distributions in spider host molecules: whereby the conformation of (**1**), with its regular alternation of *pairs* of legs, **aabbaabb**, is called type II; this type, corresponding to lower (C_2) *exact* symmetry, was previously encountered[2] in the unsolvated yellow monoclinic crystal of the parent (**4**) itself. By contrast, the octakis(*p*-tolylthio)naphthalene (**2**) host molecule, shown in Figure 1(b), is centrosymmetric and exhibits the previously unknown type III (**abbabaab**) conformation. The central six carbon atoms of the molecule are now essentially coplanar, the torsion angle C(1)–C(9)–C(10)–C(4) being −3(1)°; the naphthalene's six-membered rings are shallow boats and C(1) and C(4) are both displaced by 0.17(1) Å below the plane defined by the essentially coplanar directly attached atoms C(2), C(3), C(10), and C(9).

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† *X*-Ray intensity measurements for all possible reflections with sin $\theta/\lambda < 0.64$ Å^{-1} were made at room temperature (20 °C) by θ—ω scan on a Nonius CAD4 diffractometer, using graphite-monochromated Mo-K_α radiation ($\lambda = 0.7107$ Å). Reflections having $F^2 > 2\sigma(F^2)$ were considered observed. The principal computer programs used in structure solution and refinement are listed in ref. 3. Hydrogen atoms were located in difference-Fourier maps calculated during the anisotropic least-squares refinement, isotropic hydrogen parameters being included in subsequent refinement. For the adduct of (**2**), however, some of the methyl hydrogens were placed in theoretical positions and allowed to ride on their attached carbon atoms. No dioxane guest hydrogens could be located, and the oxygen atoms could not be distinguished from the carbon atoms. All the guest's ring atoms were therefore treated as isotropic carbon atoms. In the 1,4-dioxane adduct of (**1**), peaks associated with the guest were observed on or near the four-fold symmetry axis and included in the calculations, although it was not possible to model the disordered guest molecule using these peaks.

The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

‡ This material was obtained by recrystallisation of unsolvated (**1**) from dry toluene and gave no evidence (^{1}H n.m.r. or *X*-ray) for inclusion of significant amounts of guest (toluene or air) consolidating the structure.

§ The suggested classification for the description of possible 'leg' orientations in spider host molecules comprises fourteen types; the descriptors **a** and **b** denoting a side-chain hydrocarbon (or other) moiety projecting above or below, respectively, the mean plane of the naphthalene core. These types, specified below, correspond to *trans* arrangements for *peri*-related groups and are ordered on the basis of the *maximum possible* symmetry for a uniform array of achiral 'legs' (shown in parenthesis), with most weight placed on *proper rotation axes*; primary ranking is in the order D_2, C_{2h}, C_2, C_s, C_i, and C_1; secondary ranking reflecting a higher degree of alternation of 'legs'; lower ranking criteria being maximum (non-exact) symmetry of the central six carbon atoms and four attached groups; with, if required, an exact C_2 axis along the C(9)–C(10) bond outweighing other C_2 orientations. Type I, **abababab** (D_2); type II, **aabbaabb** (D_2); type III, **abbabaab** (C_{2h}); type IV, **aaaabbbb** (C_{2h}); type V, **ababaabb** (C_2); type VI, **aabababb** (C_2); type VII, **aaababbb** (C_2); type VIII, **abbbabbb** (C_2); type IX, **abbabbbb** (C_s); type X, **abaababb** (C_i); type XI, **abababbb** (C_1); type XII, **abbabbab** (C_1); type XIII, **aabbabbb** (C_1); type XIV, **aababbbb** (C_1).

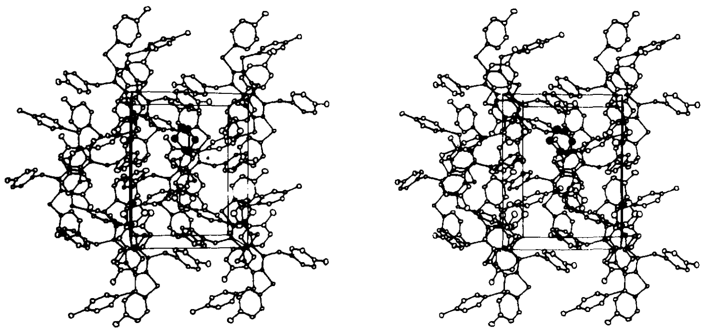

Figure 3. A stereoview, looking down the *c*-axis, of the host-guest packing in the 1,4-dioxane clathrate of octakis(*p*-tolylthio)naphthalene (**2**). The atoms of the chair-shaped guest molecule closest to the viewer have been represented by filled circles for clarity.

The packing of the octakis(*m*-tolylthio)naphthalene (**1**) molecules in the unsolvated tetragonal crystal is illustrated in the stereoview shown in Figure 2; and this corresponds directly to the host packing in the 1,4-dioxane adduct of (**1**). The cages, unoccupied in Figure 2, possess exact four-fold symmetry, and of the four host molecules present in the centrosymmetric unit cell only those located at ($\frac{1}{4}$,$\frac{3}{4}$,$\frac{3}{4}$) and ($\frac{3}{4}$,$\frac{1}{4}$,$\frac{3}{4}$) are shown for clarity. The remarkable stability of the empty cage form may reflect efficient edge-on packing of the molecules of (**1**) which all have the same conformational chirality within a given layer, parallel to the *ab* plane. By means of van der Waals sections[4] it has been established that closed cages, four per cell, exist; and in the 1,4-dioxane adduct the four (necessarily disordered) guest molecules are located at heights approximately 1/4 and 3/4 along *c*. The host–guest packing in the 1,4-dioxane clathrate of octakis(*p*-tolylthio)-naphthalene (**2**), shown in the stereoview in Figure 3, corresponds to complete loss of cavity symmetry, and the chair-shaped dioxane guest molecule now occupies a general position in the unit cell. The closed nature of the cage was again established by van der Waals section analysis.[4] It is fascinating that despite the contrasting type II and type III host conformations of (**1**) and (**2**) respectively the ability to form clathrates is retained.

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1 See, for example, D. D. MacNicol in 'Inclusion Compounds,' ed. J. L. Atwood, J. E. D. Davies, and D. D. MacNicol, Academic Press, London, 1984, vol. 2, chap. 5.

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