The First Synthesis of Octakis(arylthio)naphthalenes: an *X*-Ray Study of a Novel Pressure-induced Colour and Conformational Change in Crystalline Octakis(phenylthio)naphthalene

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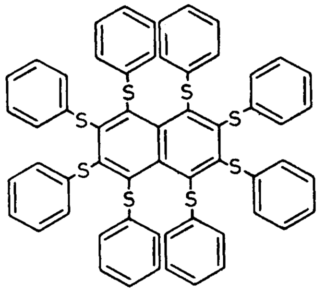
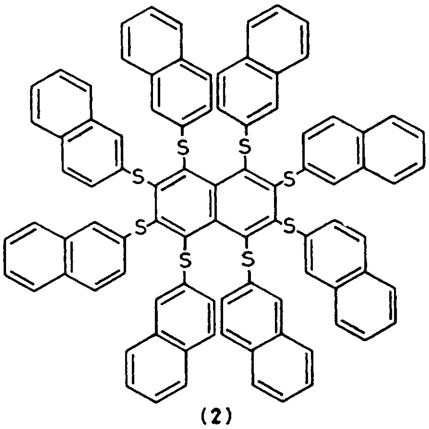
The title compound (**1**) and its octakis(β-naphthylthio) analogue (**2**), the first examples of per(arylthio)naphthalenes, have been synthesised in essentially quantitative yield by the reaction of octafluoronaphthalene with the sodium salt of the appropriate arenethiol in 1,3-dimethylimidazolidin-2-one as solvent; a remarkable pressure-induced crystal transformation of *unsolvated* (**1**), studied by *X*-ray methods, has been discovered.

It is now well known[1] that many suitably hexasubstituted benzenes exhibit the property of forming crystalline inclusion compounds, a possibility originally suggested by the hexa-host analogy;[2] and, subsequently, the role of three-fold[3] and two-fold[4] molecular symmetry in host design has also been considered. With new potential aromatic-based hosts in mind, we were attracted to the synthesis of candidate molecules (**1**) and (**2**) based on a naphthalene core, which possesses two-fold molecular symmetry. Our recently reported discovery[5] of an efficient synthesis of hexasubstituted benzenes, such as hexakis(phenylthio)benzene and hexakis(β-naphthylthio) benzene, suggested extension of the method to naphthalene synthesis. We now report that the reaction of octafluoronaphthalene with 16 mol. equiv. of PhSNa in 1,3-dimethylimidazolidin-2-one, for 2 days† at ambient temperature, leads to the ready complete displacement of all the fluorine atoms, giving, after appropriate work-up, a near quantitative yield of (**1**), m.p. 207—208 °C (unsolvated). Compound (**1**) gave a satisfactory microanalysis and had spectroscopic properties (^1H and ^{13}C n.m.r., i.r., and m.s.) compatible with its formulated structure (**1**). The larger molecule (**2**) was prepared, also in near quantitative yield, in an analogous process using 16 mol. equiv. of the sodium salt of naphthalene-β-thiol; (**2**) showed the expected spectroscopic properties and microanalysis. Both (**1**) and (**2**) form crystalline inclusion compounds; *e.g.*, when crystallised from 1,4-dioxan at ambient temperature. A detailed description of the inclusion properties of (**1**) and (**2**), the first representatives of the new class of eight-legged, or 'spider', hosts, will be given elsewhere. Of particular immediate relevance however, is that two distinct *unsolvated* forms of (**1**) have been obtained; a yellow form (from dimethylformamide at ambient temperature) and a red form (from anisole at *ca.* 50 °C). When pressure is applied to crystals of the yellow form on a glass slide for example, a striking colour change to red is observed at the point of pressure application. Intrigued as to the origin of the different colours of these unsolvated forms, and indeed how the chromophoric region of (**1**) could differ significantly in the two forms, an *X*-ray study was undertaken.

Crystal data: (**1**), yellow form, $C_{58}H_{40}S_8$, $M = 993.47$, monoclinic, space group $I2/c$, $a = 20.469(3)$, $b = 10.567(2)$, $c = 25.415(3)$ Å, $\beta = 118.13(2)°$, $U = 4848.1$ Å^3, $F(000) = 2064$, $Z = 4$, $D_c = 1.36$ g cm^{-3}, $\mu(\text{Mo-}K_\alpha) = 4.0$ cm^{-1}. Red form, $C_{58}H_{40}S_8$, $M = 993.47$, triclinic, space group $P\bar{1}$, $a = 9.149(2)$, $b = 11.473(3)$, $c = 12.466(2)$ Å, $\alpha = 101.42(2)$, $\beta = 96.37(1)$, $\gamma = 109.67(2)°$, $U = 1185.4$ Å^3, $F(000) = 516$, $Z = 1$, $D_c = 1.39$ g cm^{-3}, $\mu(\text{Mo-}K_\alpha) = 4.0$ cm^{-1}.



(**1**)



(**2**)

Diffraction intensities for both crystals were measured on an Enraf–Nonius CAD-4 diffractometer with graphite monochromatized Mo-K_α radiation. 2771 and 3937 Independent reflections [$I \geqslant 2.5\sigma(I)$] were recorded for the yellow and red forms, respectively.‡ The structures were solved by the direct methods package MITHRIL.[6] Block-diagonal least-squares with unit weights converged at *R* factors of 0.052 and 0.058 for the yellow and red unsolvated forms, respectively; whereupon a final difference electron-density calculation revealed, in each case, the positions of all the hydrogen atoms. Final, full-matrix, refinement (with isotropic thermal parameters for hydrogens) gave final *R* factors of 0.028 ($R_w = 0.034$) and

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† The minimum time required for this complete substitution has not yet been established.

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

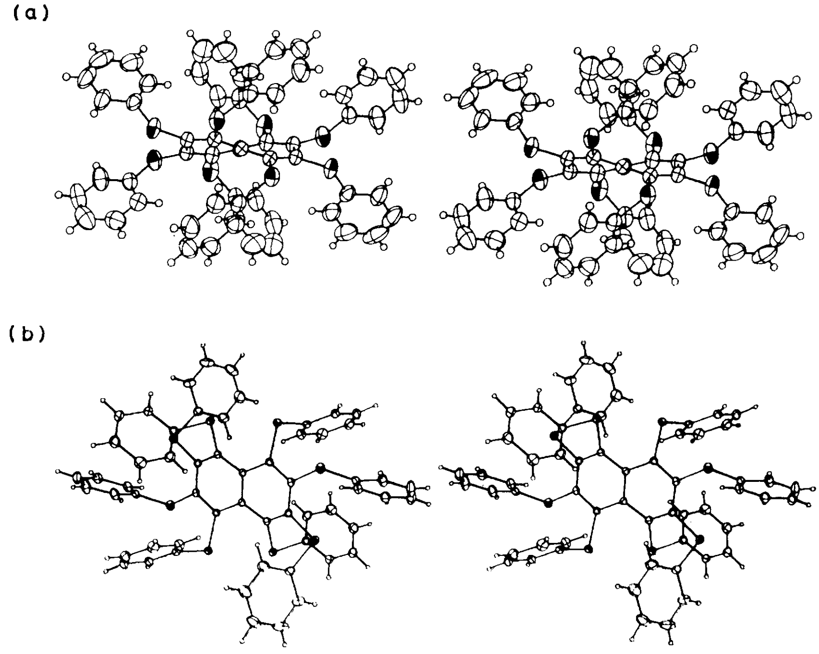

Figure 1. Stereoviews illustrating the molecular structure of octakis(phenylthio)naphthalene in unsolvated (**1**), for (a) the yellow monoclinic crystal and (b) the red triclinic crystal.

0.032 ($R_w = 0.045$) for the yellow and red unsolvated forms, respectively.

Just how fundamentally the structures differ may be appreciated from Figure 1. The molecule of (**1**) in the yellow form is chiral and has exact C_2 symmetry, and approximate D_2 symmetry; both enantiomers are present in the crystal. A very pronounced twist around the bond at the ring fusion for the yellow form can be seen in Figure 1(a), the intra-ring torsion angle corresponding to this bond being −31°. The structure of (**1**) in the red form, Figure 1(b), is quite different: the molecule is now achiral, with the central region not far from planar; the two six-membered rings comprising the centrosymmetric naphthalene unit, may now be described as enantiomerically related (distorted) boat conformations. In the yellow form pairs of adjacent 'legs' alternate above and below the mean plane of the naphthalene ring; in the red form, however, there are only two such pairs, centrosymmetrically related, and interconversion between the two forms corresponds to relocation of any one pair of 'legs' of the yellow form on the opposite face of the molecule with the two neighbouring groups moving in the opposite sense, thereby giving the achiral leg distribution of the red form. Interestingly, the molecule of (**1**) in the red, triclinic, crystal occupies 2% less volume than in the yellow form; and, if one assumes[§] that there is only one red, unsolvated, form, it follows that the above apparently formal transformation may actually occur, in one or more steps, within the crystal lattice of (**1**).

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References

1 See, for example, A. A. Freer, J. H. Gall, and D. D. MacNicol, *J. Chem. Soc., Chem. Commun.*, 1982, 674, and references therein.

2 D. D. MacNicol and D. R. Wilson, *J. Chem. Soc., Chem. Commun.*, 1976, 494.

3 D. D. MacNicol and S. Swanson, *Tetrahedron Lett.*, 1977, 2969; see also, D. D. MacNicol, J. J. McKendrick, and D. R. Wilson, *Chem. Soc. Rev.*, 1978, 7, 65.

4 N. Z. Huang and T. C. W. Mak, *J. Chem. Soc., Chem. Commun.*, 1982, 543, and references therein.

5 D. D. MacNicol, P. R. Mallinson, A. Murphy, and G. J. Sym, *Tetrahedron Lett.*, 1982, 4131.

6 C. J. Gilmore, personal communication.

[§] At present, evidence is being sought (by spectroscopic and *X*-ray methods) to establish rigorously whether or not the red form, produced by pressure, is the same as that produced by crystallisation under suitable conditions (see text).