

Novel Conformation and Synthesis of Octakis(cyclohexylthio)naphthalene

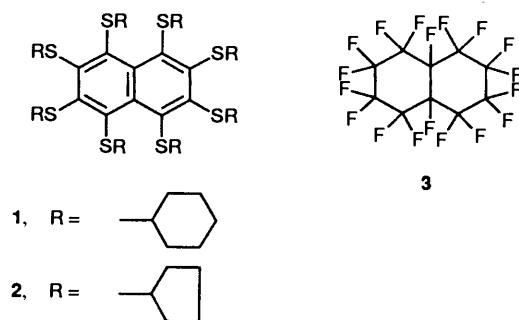
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The crystalline title compound **1**, prepared from both perfluoronaphthalene and, in a remarkable new reaction, perfluorodecalin **3** has been shown by X-ray and solid-state NMR spectroscopic methods to have an axial C–S bond in one of the four crystallographically independent cyclohexane rings.

We have recently reported¹ an unprecedented reaction of arenethiolate nucleophiles with perfluorodecalin **3**, a saturated fluorocarbon of the type generally considered totally inert under all but extreme conditions.² While investigating the scope of this aprotic solvent-promoted reaction, an aim being to synthesise octa-hosts belonging to new classes of compound,⁴ octakis-(cyclohexylthio)naphthalene **1**, as well as its cyclopentyl analogue **2**, was prepared. A favoured mechanism for this reaction involves single electron transfer (SET). Experimental evidence for this includes significantly enhanced yields in the presence of metallic sodium, observed for arenethiolate nucleophiles.⁵

Compound **1** was prepared from the reaction of perfluorodecalin **3** (mixture of *cis* and *trans* isomers) with sodium cyclohexanethiolate (36 mol equiv.) in DMEU (1,3-dimethylimidazolidin-2-one) at 60 °C over 14 d in 34% yield, after chromatographic purification of silica with cyclohexane–ether eluent. The identity of this compound was established by comparison with a sample of **1** made from perfluoronaphthalene in 87% yield by more conventional nucleophilic aromatic substitution.³ This material had spectroscopic properties (¹H, ¹³C NMR, IR and mass) in agreement with the formulated structure (Found: C, 66.8; H, 8.6; S, 24.4. C₅₈H₈₈S₈ requires C, 66.9; H, 8.5; S, 24.6%).



During the attempted preparation of adducts of **1** with various solvents, stable, yellow, unsolvated prisms, m.p. 250–252 °C, were grown from hexane–toluene solution. Octakis-(cyclopentylthio)naphthalene **2**, m.p. 255–257 °C, was prepared similarly from perfluorodecalin **3** in 23% yield, unoptimised (Found: C, 64.5; H, 8.0; S, 27.7. C₅₀H₇₂S₈ requires C, 64.4; H, 7.8; S, 27.6%). To completely characterise **1** and **2** we have carried out crystal structure analyses.† The structure and conformation are discussed in detail below for **1**, whereas the refinement of **2** (space group *P2₁/c*, *a* = 11.860(1), *b* = 18.768(4), *c* = 22.762(3) Å, β = 102.24(1)°, current *R* factor 7.7%) is in progress.

Fig. 1 gives a view approximately edge-on to the central naphthalene core of **1**, illustrating the molecular conformation in the unsolvated crystal. A salient feature is that three of the cyclohexane rings have an equatorially oriented C–S bond, whilst the fourth crystallographically independent ring exhibits an extremely rare‡ feature for an X-ray analysis of a mono-

substituted cyclohexane, namely an axially oriented C-substituent bond, here to sulfur. This may be more readily appreciated from the stereoview shown in Fig. 2, which also illustrates the molecular packing viewed along the *a*-axis. Using our earlier nomenclature,⁸ the centrosymmetric conformation is of the *abbabaab* type. Although the central six naphthalene carbon atoms are accurately coplanar, with torsion angle C(1)–C(9)–C(10)–C(4) 0.0(2)°, the entire naphthalene core comprises two fused, centrosymmetrically related, shallow boats with C(1) and C(4) displaced from the mean plane of C(2), C(3), C(9) and C(10) by –0.204(2) and –0.159(2) Å respectively. The sulfur atoms S(1) to S(4) are displaced from the mean plane of the naphthalene ring by respective distances of –0.826(1), 0.330(1), 0.037(1) and –0.696(1) Å, and the mean C(sp²)–S and C(sp³)–S distances are 1.775(1) and 1.819(2) Å, respectively. The mean of the angles C(11)–C(12)–C(13) and C(11)–C(16)–C(15), β to sulfur in the axially substituted cyclohexane ring, 113.3(2)° is significantly greater than the corresponding average β ring angle of 110.5(1)° for the other three, equatorial, rings. The equatorially substituted rings have a mean intraannular torsion angle of 56°, close to experimental and calculated values for cyclohexane itself;⁹ the cyclohexane ring bearing an axial sulfur is, however, significantly distorted, the mean (magnitude) of torsion angles C(16)–C(11)–C(12)–C(13) and C(15)–C(16)–C(11)–C(12) being 52°. To facilitate discussion of the solid state NMR results discussed below, it is useful to note that the conformation around the C(sp³)–S bond is similar for all three equatorial side chains; this is shown by torsion angles give in pairs with *gauche* and *anti* sense respectively: C(2)–S(2)–C(21)–C(26), C(2)–S(2)–C(21)–C(22), 48°, 171°; C(3)–S(3)–C(31)–C(36), C(3)–S(3)–C(31)–C(32), 51°, 175°; C(4)–S(4)–C(41)–C(42), C(4)–S(4)–C(41)–C(46), –62°, 177°. The corresponding torsion angles for the axially substituted ring, C(1)–S(1)–C(11)–C(12) and C(1)–S(1)–C(11)–C(16), are 46° and 168°, respectively.

Fig. 3 shows the ¹³C solid state NMR spectrum of crystalline unsolvated octakis(cyclohexylthio)naphthalene **1** recorded with cross-polarisation and magic angle spinning (CPMAS). This

† Crystal data for C₅₈H₈₈S₈ **1**. *M* = 1041.9, triclinic, space group *P* $\bar{1}$, *a* = 10.630(1), *b* = 11.011(4), *c* = 12.304(2) Å, α = 86.82(2), β = 87.31(2), γ = 86.93(2)°, *U* = 1434(1) Å³, *Z* = 1, *D_c* = 1.21 g cm⁻³, λ(Mo-Kα) = 0.7107 Å, μ = 3.33 cm⁻¹, *T* = 293 K. Number of independent intensities = 6244 from orange prism, 0.5 × 0.5 × 0.4 mm. *R* = 0.045, *R_w* = 0.064 for 5092 observed [*I*/σ(*I*) > 2.0] reflections.

X-ray intensity measurements for all possible reflections with sin θ/λ < 0.64 Å⁻¹ were made by 2θ – ω scans on a Nonius CAD4 diffractometer. The principal computer programs used in structure solution and refinement are listed in ref. 6. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See 'Instructions to Authors,' *J. Chem. Soc., Perkin Trans. 1*, 1991, Issue 1.

‡ An axial-Cl chair has been assigned for the predominant conformation of chlorocyclohexane, present as guest in the tri-*o*-thymotide clathrate.⁷ However, extensive guest disorder severely limited the precision of the X-ray structure analysis of the guest species.

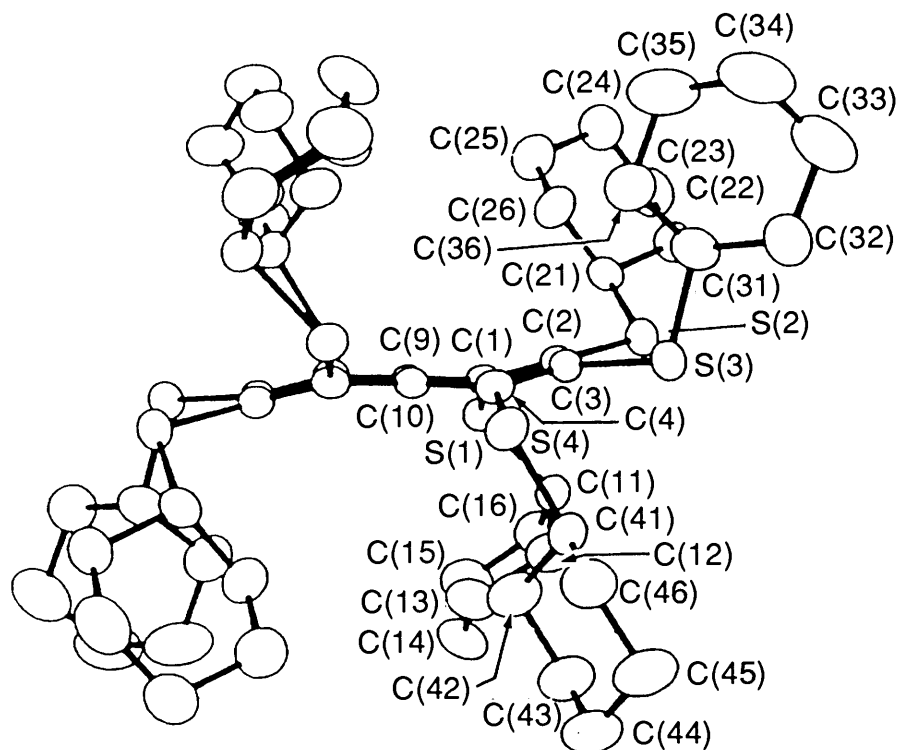


Fig. 1 A view of the molecular structure of octakis(cyclohexylthio)naphthalene **1** in its unsolvated molecular crystal, showing the atomic numbering scheme

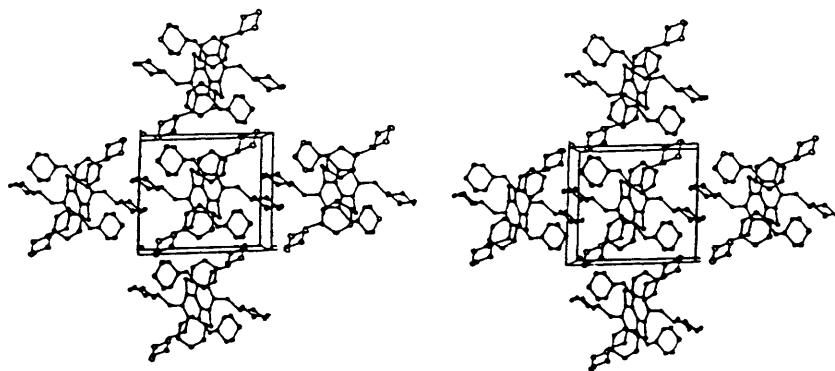


Fig. 2 A stereoview illustrating the molecular packing in the unsolvated molecular crystal of **1**, triclinic, space group $P\bar{1}$

CPMAS spectrum gives very distinct and clear evidence of the special conformation of the axially oriented C–S bond in the side chain moiety attached to C(1), and of the whole molecule in general. Immediately apparent in Fig. 3 is the well-resolved group of lines arising from the centrosymmetric naphthalene core, five independent carbons in total. This neatly corresponds to the type III, *abbabaab*,⁷ conformation observed independently in the single-crystal X-ray diffraction analysis. At least as interesting are the high-field signals, which also show remarkable resolution. These are provisionally assigned (subject to possible labelling experiments) in the following way: the methine carbons C(21), C(31) and C(41) of the three independent equatorial rings occur at δ_c 52.8, and the methine carbon in the axial ring, C(11), at δ_c 49.4. The peaks at δ_c 43.3 and δ_c 32.7 are carbon atoms β to sulfur and are assigned to the six carbon atoms of the equatorial rings C(22), C(32), C(46); and C(26), C(36), C(42) respectively. The presence of only two signals at mean shift δ_c 38.0, from the above six carbon atoms is compatible with the approximately equal torsion angles around the C(sp³)–S bonds described above; that is, similar γ -*gauche* and γ -*anti* effects¹⁰ involving

an aromatic ring carbon may be expected in each case. Waugh–Fessenden–Johnson–Bovey ring current calculations¹¹ employing X-ray coordinates indicate that the diamagnetic anisotropy of the naphthalene core affects only marginally the chemical shifts of all saturated β carbons and contributes ≤ 1 ppm to the splitting of 10.6 ppm of the β carbons of the equatorial rings; a similar estimated maximum contribution from ring current effects also applies to the 4.7 ppm splitting of the β carbons C(16) and C(12) of the axial ring. The signals at δ_c 35.2 and 30.5, at higher field,^{10,12} mean position δ_c 32.9, are assigned, respectively, to the β carbon atoms C(16) and C(12) of the axial ring. In keeping with above-quoted torsion angles, significant γ -effects are again expected for these β carbon atoms. The above splittings reflect conformational ‘locking’ in the crystal, this situation contrasting with the conformational mobility of **1** in CDCl₃ solution where all carbon atoms β to sulfur in the cyclohexane rings resonate at δ_c 33.0. In good agreement with literature studies on cyclohexane derivatives, the γ -carbons of the equatorial rings and the δ -carbons of all the rings are fairly closely grouped around δ_c 27.⁹ Finally, the two crystallographically non-equivalent carbon atoms C(13) and C(15), γ to

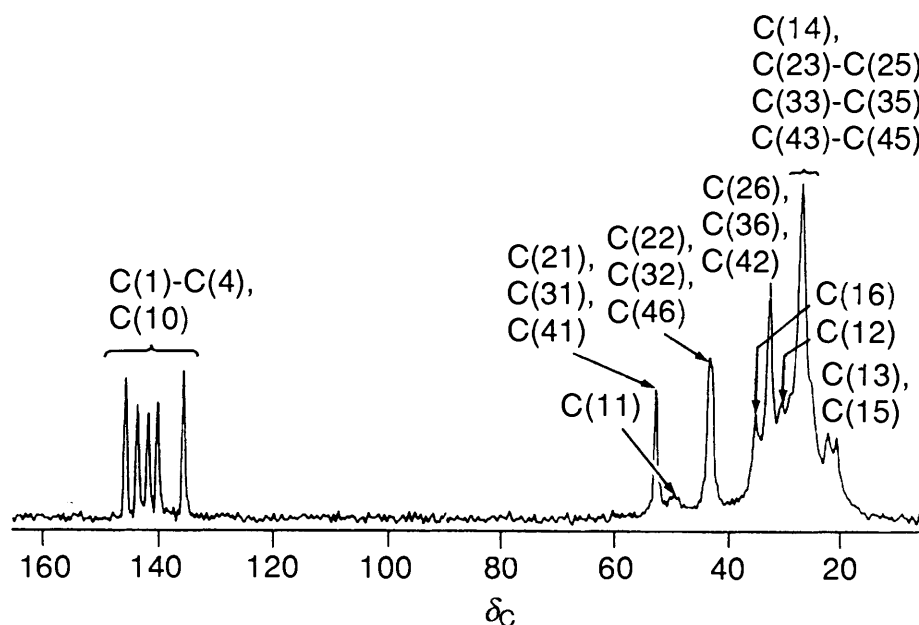


Fig. 3 A ^{13}C solid-state NMR spectrum of unsolvated crystalline octakis(cyclohexylthio)naphthalene **1** measured under CPMAS conditions on a Varian VXR 300 spectrometer, at carbon frequency 75.4 MHz; a 30 s relaxation delay, 2.5 ms contact time and spin-rate of 8.8 kHz were used, 616 transients being accumulated. The chemical shift scale is relative to an external sample of tetramethylsilane.

sulphur in the axial ring, resonate at δ_{C} 22.1 and 20.5, these being in keeping with low-temperature solution measurements on monosubstituted cyclohexanes.¹²

The fact that two centrosymmetrically related rings of **1** adopt axial conformations may reflect Kitaigorodsky's close-packing principle;¹³ that is, although the energy of the individual molecule of **1** is almost certainly raised in such a conformational situation, this is more than off-set by increased efficiency in intermolecular packing, leading to an overall lowering of the potential energy of the molecular crystal of **1**.

Preliminary observations have indicated host properties for **1** and **2**. In particular, unstable adducts of **1** with chlorinated solvents have been found. It remains of interest to establish whether **1** undergoes conformational relaxation on adduct formation.

Acknowledgements

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