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Synthesis and structure of the first per-substituted anthracene host: decakis(cyclopentylthio)anthracene

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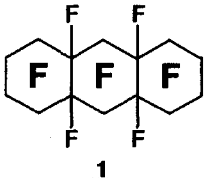
The title compound, a novel host molecule, has been prepared both from mixtures of unsaturated fluorocarbons related to perfluoroperhydroanthracene and, in an extension of a remarkable new reaction, perfluoroperhydroanthracene itself. The 1,4-dioxane inclusion compound of this anthracene-based host is triclinic, space group $P\bar{1}$, with $a = 11.826(1)$, $b = 15.297(1)$, $c = 20.280(1)$ Å, $\alpha = 98.77(1)$, $\beta = 99.85(1)$, and $\gamma = 95.83(1)°$, with two host, and *ca.* three 1,4-dioxane guest molecules per unit cell. The host molecule occupies a general position in the unit cell and its anthracene core is markedly non-planar; each of the three crystallographically independent six-membered rings possesses a shallow twist-boat conformation. The host's side-chain moieties display an asymmetrical conformational distribution of the abbabaabab **type (a = above, b = below, mean core plane).**



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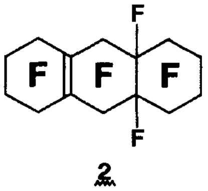

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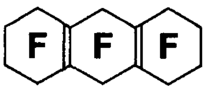

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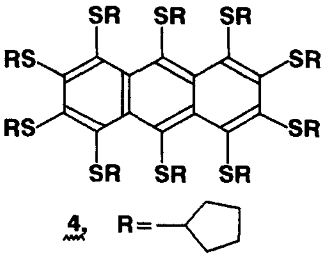

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INTRODUCTION

For many years saturated fluorocarbons were regarded as totally inert except under extreme conditions.[1] Recently, however, we have reported that perfluorodecalin undergoes complete aromatisation and persubstitution promoted by arenethiolate nucleophiles in DMEU;[2,3] whilst others have shown that the same tertiary carbon-containing substrate is converted to perfluoronaphthalene by sodium benzophenone ketyl in THF.[4] Also, a very recent paper[5] describes reductive defluorination of perfluorodecalin using organometallic nucleophiles.

Our initial report,[2] in addition to mechanistic interest, also provides direct synthetic entry to molecules of the naphthalene-based spider host type.[6] We now describe successful extension of this reaction to the substrate perfluoroperhydroanthracene, 1, yielding the persubstituted anthracene host decakis(cyclopentylthio)anthracene, 4. Also, we describe a detailed single-crystal X-ray study of this ten-armed host as its 1,4-dioxane adduct, undertaken with a view to elucidation of the host-guest packing, and the conformational arrangement adopted by the host molecule. A higher-yield preparation of host 4 employing mixtures of the unsaturated fluorocarbons 2 and 3, structurally related to perfluoroperhydroanthracene, is also described.

EXPERIMENTAL

Preparation of decakis(cyclopentylthio)anthracene 4

Method A, from perfluoroperhydroanthracene 1. Perfluoroperhydroanthracene[7] (0.312 g, 0.5 mmol)

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and sodium cyclopentanethiolate (3.10 g, 25 mmol), prepared from cyclopentanethiol and sodium in absolute ethanol, were stirred in 30 mL of degassed 1,3-dimethylimidazolidin-2-one (DMEU), under vacuum at 60°C for 7 days in absence of light. The mixture was added to toluene (200 mL), washed with water (10 x 100 mL), and evaporation of the solvent gave a dark red oil, from which compound **4** was obtained (as its 1,4-dioxane adduct) on recrystallisation from 1,4-dioxane/methanol; yield 0.057 g (9.7%); m.p. 243–244 °C. TLC, Rf = 0.31, diethyl ether/pet. ether (40–60 °C) [1:30]. ^{1}H NMR, δ_H (200 M Hz, $CDCl_3$), *ca.* 0.7–2.2 (80H), 3.09 (m, 2H), 4.05 (m, 4H), 4.32 (m, 4H). FAB MS *m/e* ($M^+ + H$) 1179. Microanalysis and high resolution MS given in Method B.

Method B, from fluorocarbon mixture 2/3. Cyclopentanethiol (3.50 g, 34 mmol) and (95%) NaH (0.85 g, 34 mmol) were added to 30 mL degassed DMEU under N_2. Once reaction was complete, the mixture was again degassed and the fluorocarbon mixture **2**/**3**[8] (0.415 g, *ca.* 0.71 mmol) added. The reaction was stirred in the absence of light for 20 hours, and worked up as in Method A, giving purple crystals of the 1,4-dioxane adduct, yield 0.34 g (*ca.* 37%), m.p. 243–244 °C. TLC and ^{1}H NMR as Method A. Microanalysis, Found: C, 63.7; H, 7.8; S, 24.0. $2C_{64}H_{90}S_{10}\cdot 3C_4H_8O_2$ requires C, 64.1; H, 7.8; S, 24.4%. FAB MS *m/e* ($M^+ + H$) 1179.4330, $C_{64}H_{90}S_{10}$ requires 1179.4328. TGA, heating rate 10 °C/min, indicates loss of 1,4-dioxane guest between 90 and 140°C and confirms host/guest ratio of *ca.* 2:3.

Crystal data

$C_{64}H_{90}S_{10}\cdot 1.5C_4H_8O_2$, $M = 1312.2$, Triclinic, space group $P\bar{1}$, $a = 11.826(1)$, $b = 15.297(1)$, $c = 20.280(1)$ Å, $\alpha = 98.77(1)$, $\beta = 99.85(1)$, $\gamma = 95.83(1)$°, $V = 3542(1)$ Å^3, $Z = 2$, $D_c = 1.230$ g cm^{-3}, Mo K_α radiation, $\lambda = 0.71069$ Å, cell parameters from 25 reflections, $\theta = 12$–14°, $\mu = 3.40$ cm^{-1}, $T = 295$K, prism $0.2 \times 0.2 \times 0.2$ mm.

Data collection

Enraf-Nonius CAD-4 diffractometer, $R_{int} = 0.023$, $\theta_{max} = 23$°, $\omega - 2\theta$ scans, absorption correction: none, 8890 independent reflections, 4851 observed reflections $[I > 3\sigma(I)]$.

Structure determination

The structure was solved by direct methods[9] using SHELXS86 and refined on F to $R = 0.077$, $R_w = 0.110$ for the 4851 observed reflections. $w = 1/\sigma^2(F)$. Hydrogen atoms were placed in calculated positions and not refined. Oxygen atoms of the dioxan guest molecules were treated as carbon, and hydrogen atoms of the dioxan were not included in the calculations. Least squares refinement was carried out using the NRC package.[10] Other calculations used GX,[11] which incorporates a locally-modified version of ORTEP.[12]

RESULTS AND DISCUSSION

Decakis(cyclopentylthio)anthracene **4** was prepared from perfluoroperhydroanthracene **1**, and a mixture of fluorocarbons **2** and **3**, Methods A and B respectively, as described in the Experimental section. The structure of **4** was initially established spectroscopically and by microanalysis, as its 1,4-dioxane adduct; and mass spectrometry, as described above. Results of a single-crystal X-ray analysis of the 1,4-dioxane inclusion compound of **4** are now discussed. The adduct is triclinic, space group $P\bar{1}$, and the unit cell contains two centrosymmetrically related host molecules and close to three 1,4-dioxane guest molecules. A view illustrating the structure and conformation of molecule **4**, which occupies a general position is shown in Fig 1. Using an extension of our earlier nomenclature[6] the molecule can be seen to possess an asymmetric **abbabaabab** conformation, where **a** and **b** denote side-chain moieties projecting above and below, respectively, the mean plane of the central aromatic core. (Sequences are given with leading **a**.) In marked contrast to anthracene itself,[13] which is coplanar to within 0.01 Å, the central aromatic core of **4** is markedly non-planar, reflecting pronounced *peri* interactions. Interestingly, each of the three crystallographically independent six membered rings approximates quite well to a shallow twist boat conformation, as may be appreciated from the torsion angles in Fig 2, which also gives displacements of the sulphur atoms from the mean plane of the aromatic core. For mean planes of the *individual* six-membered rings, the respective atom displacements are: C(2), C(3), C(4), C(12), C(11), C(1), 0.01, −0.14, 0.13, 0.00, −0.12, 0.12; C(12), C(10), C(13), C(14), C(9), C(11), 0.02, 0.12, −0.13, −0.01, 0.15, −0.15; C(6), C(7), C(8), C(14), C(13), C(5), 0.02, −0.13, 0.10, 0.03, −0.14, 0.12. Within a given molecule, all twist boats have similar conformations and the same chiral sense; this imparts approximate C_2 symmetry to the entire anthracene core, the non-crystallographic two-fold rotation axis running through its centre, and roughly normal to its mean plane. This approximate C_2 symmetry, which encompasses to some extent the location of the sulphur atoms (Fig 2), does not, however, extend to the molecular periphery, owing to the asymmetric side-chain distribution. Figure 3 shows a stereoview

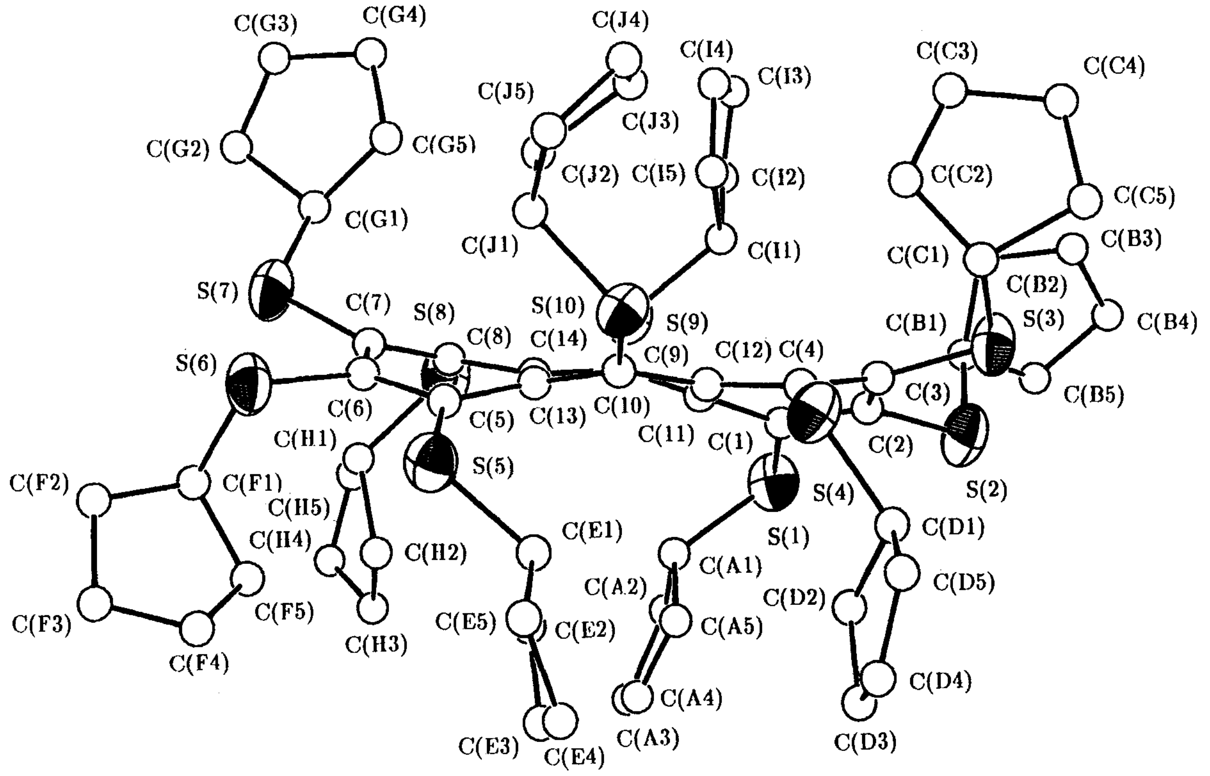

Figure 1 A view of the molecular structure of decakis(cyclopentylthio)anthracene 4 in its 1,4-dioxane inclusion compound, showing the host's atomic numbering scheme.

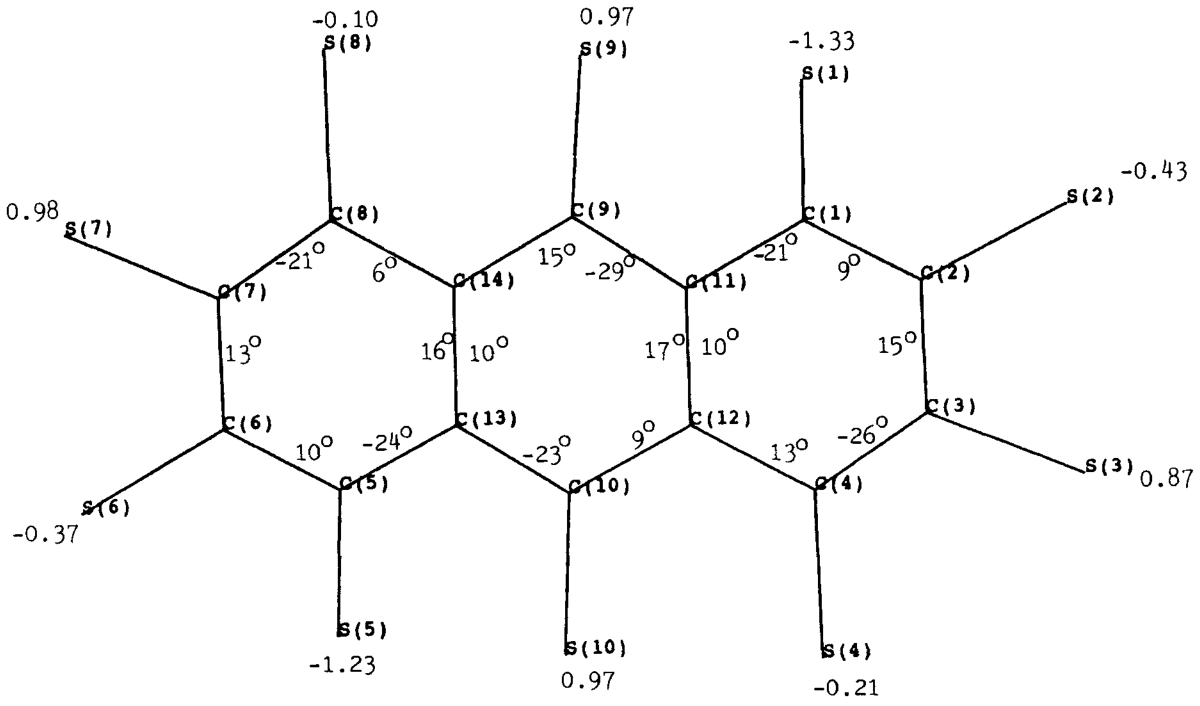

Figure 2 Torsion angles, and displacements (Å) of the sulphur atoms from the mean plane defined by atoms C(1) to C(14) inclusive, for decakis(cyclopentylthio)anthracene 4 [1,4-dioxane adduct], indicating approximate C_2 core symmetry. This local non-crystallographic two-fold symmetry is also apparent from displacements of related pairs of atoms from the same mean anthracene plane: C(1), C(5), −0.43, −0.42; C(2), C(6), −0.12, −0.13; C(3), C(7), 0.32, 0.30; C(4), C(8), 0.13, 0.16; C(12), C(14), 0.05, 0.02; C(10), C(9), 0.16, 0.18; C(13), C(11), −0.09, −0.12 Å. (E.s.d.'s on torsion angles and C displacements, *ca.* 1°, and 0.01 Å.)

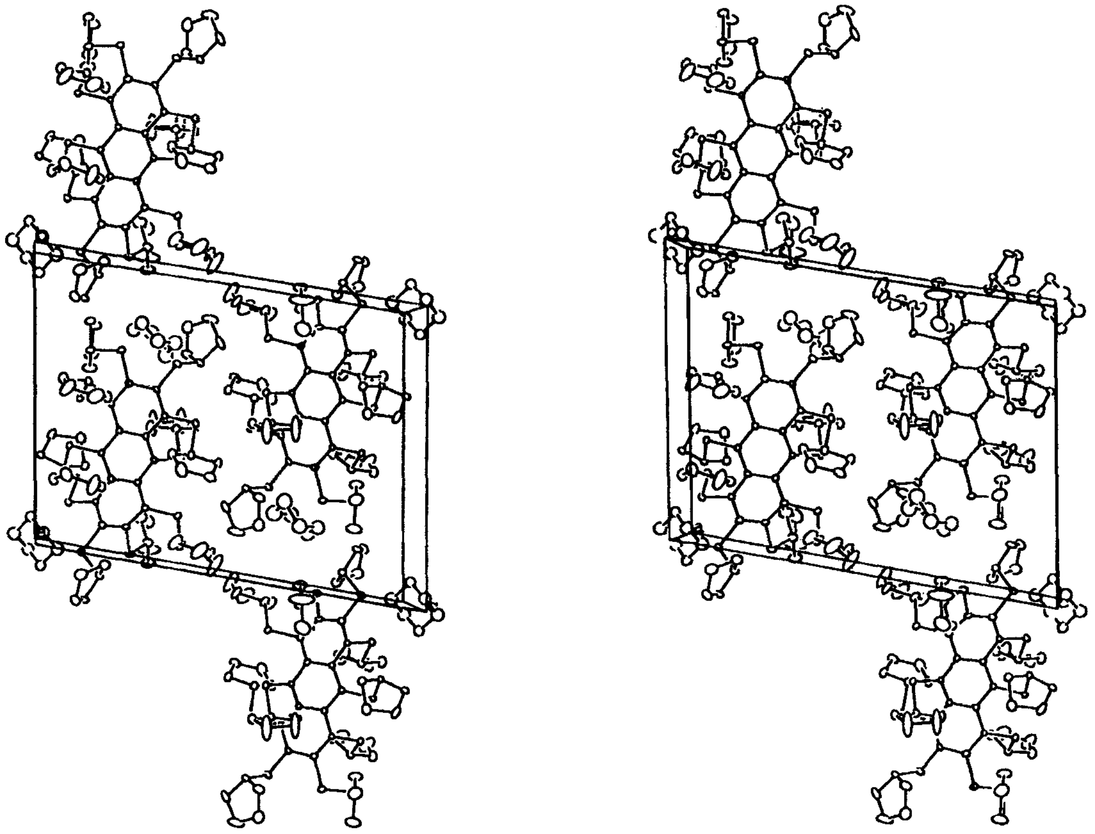

Figure 3 A stereoview looking along the *a* axis illustrating the host-guest packing in 1,4-dioxane inclusion compound of host **4**.

illustrating the host-guest packing in the 1,4-dioxane adduct of **4**. There are two distinct locations for the 1,4-dioxane guest molecules; one corresponds to a general position in the unit cell, the other a centre of inversion $\bar{1}$, half way along the *a* axis. Both 1,4-dioxane guest types have a chair conformation.

A crystalline inclusion compound of host **4**, with a host-guest ratio of 2:3, has also been found for guest 1,4-thioxane; whilst adducts, analysed by ^{1}H NMR, with host-guest ratios closer to 1:1 are formed with guest species pyridine, toluene, *N*-methylmorpholine, or cyclohexanone.

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