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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HA1166). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Octakis(3,5-dimethylphenylthio)-naphthalene

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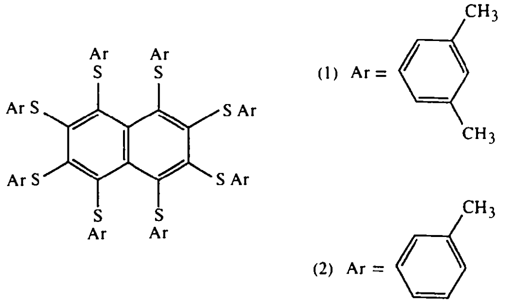
Abstract

The title compound, $C_{74}H_{72}S_8$, possesses a conformation which is unique for a per(arylthio)naphthalene in that the side chains at one of the *peri* positions adopt a *syn* arrangement, whereas all molecules of this class studied previously uniformly exhibit *anti* arrangements at the *peri* positions. This asymmetric conformation is of the previously uncategorized *abbaabab* type, where *a* and *b* denote side chains projecting, respectively, above and below the mean plane of the naphthalene core. A significant non-planarity of the naphthalene core is imparted by a substantial twist around its central carbon–carbon bond characterized by the symmetry-independent intra-ring torsion angles.

Comment

In the course of a study of spider hosts (Downing & MacNicol, 1996), a conformationally mobile class of molecule (Barbour, Freer & MacNicol, 1983; MacNicol, 1984; MacNicol, Mallinson & Robertson, 1985; Freer, MacNicol, Mallinson & Robertson, 1989), we prepared octakis(3,5-dimethylphenylthio)naphthalene, (1), which corresponds to the formal introduction of a second *meta*-methyl substituent to the side chain of octakis(*m*-tolylthio)naphthalene, (2). The introduction of this second methyl group precludes adoption of a conformation directly analogous to that of (2), owing to prohibitive transannular interactions.



In contrast to the exactly D_2-symmetric conformation of compound (2) (MacNicol, Mallinson & Robertson, 1985), the molecule of (1), which occupies a general position in the unsolvated triclinic crystal, possesses a highly asymmetric conformation (Fig. 1). A conformational feature of compound (1), unique for a per(arylthio)-substituted naphthalene, is that two per related side chains, linked to the naphthalene core by S4 and S5, possess a *syn* relationship. As a consequence, the *abbaabab* conformation observed, where *a* and *b* denote side chains projecting, respectively, above and below the mean plane of the naphthalene core, corresponds to none of the 14 previously identified side-chain orientational distributions for spider host molecules (MacNicol, Mallinson & Robertson, 1985). The naphthalene core of compound (1) is markedly non-planar, the largest displacements from its mean plane being −0.29 (1), 0.25 (1), −0.30 (1) and 0.23 (1) Å for atoms C1, C3, C5 and C8, respectively. Although the naphthalene core lacks symmetry, one of the six-membered rings (but not the substituent arrangement) is approximately C_s symmetric, with the approximate mirror plane passing

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through the C7 and C10 atoms, which are displaced by −0.01 (1) and 0.23 (1) Å, respectively, from the plane defined by the accurately coplanar atoms C5, C6, C8 and C9. A marked twist around the central C9—C10 bond is characterized by the torsion angles C1—C9—C10—C4 of 25° and C5—C10—C9—C8 of 21°, and these may be compared with the value of 26 (1)° found for the exactly D_2-symmetric conformation of compound (2) in its unsolvated crystal; other intra-ring torsion angles for compound (1) are given in Table 2.

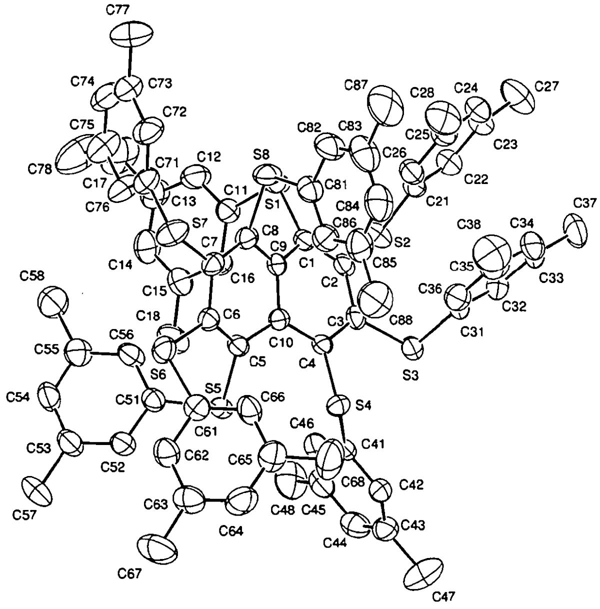

Fig. 1. The structure and conformation of octakis(3,5-dimethylphenylthio)naphthalene in its unsolvated crystal, showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

The S atoms are all markedly displaced from the mean plane of the naphthalene ring; the respective values for atoms S1–S8 are −1.17 (1), −0.46 (1), 0.72 (1), 0.88 (1), −1.14 (1), −0.09 (1), 0.44 (1) and 1.00 (1) Å. The geometries of the 3,5-dimethylphenyl moieties show no unusual features. The conformations of the *syn*-related substituents at S4 and S5 bear no relation to those of the corresponding *cis*-related substituents in aryloxynaphthalene compounds (Freer *et al.*, 1989). There are some short intermolecular contacts, however, involving C atoms of the *peri*-substituted phenyl rings, *viz.* C41···C57(1 − *x*, −*y*, 2 − *z*) 3.56 (1), C42···C57(1 − *x*, −*y*, 2 − *z*) 3.50 (1), C44···C15(−*x*, −*y*, 2 − *z*) 3.44 (1), C44···C18(−*x*, −*y*, 2 − *z*) 3.59 (1) and C54···C38(*x*, 1 + *y*, *z*) 3.55 (1) Å. This suggests that the rotational orientations of these rings are at least partly determined by crystal-packing effects.

Experimental

Perfluoronaphthalene (0.25 g, 0.92 mmol) and sodium 3,5-dimethylbenzene thiolate (2.16 g, 13.5 mmol), prepared from 3,5-dimethylbenzenethiol and sodium hydride in tetrahydrofuran, were stirred in 20 ml of dry degassed DMEU for 3 h at ambient temperature under an N_2 atmosphere. The red 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 as red crystals. Recrystallization from 1,4-dioxane/methanol gave a yield of 0.98 g (87.6%). M.p. 453–454 K; analysis found: C 72.93, H 5.87, S 21.24%; $C_{74}H_{72}S_8$ requires: C 73.02, H 5.92, S 21.06%. The absence of 1,4-dioxane in the crystals was confirmed by ^{1}H NMR spectroscopy.

Crystal data

$C_{74}H_{72}S_8$
$M_r = 1217.87$
Triclinic
$P\bar{1}$
$a = 13.907\ (1)$ Å
$b = 14.476\ (1)$ Å
$c = 17.174\ (1)$ Å
$\alpha = 80.993\ (5)°$
$\beta = 87.729\ (4)°$
$\gamma = 74.382\ (5)°$
$V = 3288.7\ (3)$ Å^3
$Z = 2$
$D_x = 1.23$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 13$–$15°$
$\mu = 0.300$ mm^{-1}
$T = 298$ K
Plate
0.5 × 0.3 × 0.1 mm
Red

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: none
16 150 measured reflections
10 223 independent reflections
6507 observed reflections [$I > 3\sigma(I)$]

$R_{\rm int} = 0.048$
$\theta_{\rm max} = 25.4°$
$h = -17 \rightarrow 2$
$k = -18 \rightarrow 17$
$l = -21 \rightarrow 21$
3 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F
$R = 0.042$
$wR = 0.063$
$S = 0.67$
6507 reflections
808 parameters
H-atom parameters not refined
$w = 4F^2/[\sigma^2(F^2) + 0.001F^4]$

$(\Delta/\sigma)_{\rm max} = 0.47$
$\Delta\rho_{\rm max} = 0.33$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.23$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Tables 2.2B and 2.3.1)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	$U_{\rm eq}$
C1	0.1313 (3)	−0.1751 (2)	0.7212 (2)	0.036 (2)
C2	0.0804 (3)	−0.2044 (2)	0.7869 (2)	0.038 (2)
C3	0.1325 (3)	−0.2365 (2)	0.8604 (2)	0.036 (2)
C4	0.2253 (3)	−0.2213 (2)	0.8678 (2)	0.033 (2)

C5	0.3658 (3)	−0.1547 (2)	0.8037 (2)	0.035 (2)
C6	0.4269 (3)	−0.1538 (2)	0.7385 (2)	0.037 (2)
C7	0.3935 (3)	−0.1667 (2)	0.6643 (2)	0.040 (2)
C8	0.3007 (3)	−0.1815 (2)	0.6583 (2)	0.040 (2)
C9	0.2361 (3)	−0.1811 (2)	0.7249 (2)	0.035 (2)
C10	0.2753 (3)	−0.1848 (2)	0.8001 (2)	0.032 (2)
C11	0.0493 (3)	0.0137 (3)	0.6593 (2)	0.040 (2)
C12	0.0030 (3)	0.0900 (3)	0.6027 (2)	0.058 (2)
C13	−0.0100 (4)	0.1852 (3)	0.6136 (3)	0.062 (2)
C14	0.0249 (3)	0.2031 (3)	0.6829 (3)	0.061 (2)
C15	0.0677 (3)	0.1286 (3)	0.7415 (2)	0.048 (2)
C16	0.0812 (3)	0.0334 (3)	0.7292 (2)	0.044 (2)
C17	−0.0582 (5)	0.2672 (4)	0.5503 (3)	0.101 (4)
C18	0.0996 (4)	0.1494 (3)	0.8184 (3)	0.067 (3)
C21	−0.0569 (3)	−0.2869 (2)	0.7267 (2)	0.039 (2)
C26	0.0208 (3)	−0.3425 (3)	0.6874 (2)	0.047 (2)
C25	0.0045 (3)	−0.4137 (3)	0.6476 (2)	0.054 (2)
C24	−0.0909 (3)	−0.4257 (3)	0.6470 (2)	0.058 (2)
C23	−0.1696 (3)	−0.3708 (3)	0.6846 (2)	0.055 (2)
C22	−0.1524 (3)	−0.3006 (3)	0.7250 (2)	0.051 (2)
C28	0.0893 (4)	−0.4774 (4)	0.6080 (3)	0.079 (3)
C27	−0.2741 (4)	−0.3826 (4)	0.6827 (3)	0.089 (4)
C31	0.0642 (3)	−0.3951 (2)	0.9047 (2)	0.043 (2)
C36	0.1472 (3)	−0.4544 (3)	0.8721 (2)	0.050 (2)
C35	0.1377 (4)	−0.5351 (3)	0.8427 (3)	0.062 (2)
C34	0.0458 (4)	−0.5559 (3)	0.8485 (3)	0.071 (3)
C33	−0.0365 (3)	−0.4983 (3)	0.8798 (2)	0.059 (2)
C32	−0.0265 (3)	−0.4172 (3)	0.9089 (2)	0.049 (2)
C37	−0.1366 (5)	−0.5203 (4)	0.8812 (3)	0.096 (4)
C38	0.2269 (5)	−0.5975 (4)	0.8053 (3)	0.092 (4)
C41	0.2396 (3)	−0.2230 (3)	1.0328 (2)	0.040 (2)
C46	0.1811 (3)	−0.1274 (3)	1.0261 (2)	0.045 (2)
C45	0.1390 (3)	−0.0909 (3)	1.0932 (2)	0.053 (2)
C44	0.1586 (3)	−0.1490 (3)	1.1653 (2)	0.056 (2)
C43	0.2159 (3)	−0.2444 (3)	1.1731 (2)	0.053 (2)
C42	0.2562 (3)	−0.2813 (3)	1.1057 (2)	0.043 (2)
C48	0.0735 (4)	0.0115 (3)	1.0878 (3)	0.079 (3)
C47	0.2322 (4)	−0.3068 (4)	1.2531 (3)	0.087 (3)
C51	0.3994 (3)	0.0116 (3)	0.8412 (2)	0.041 (2)
C52	0.4596 (3)	0.0503 (3)	0.8816 (2)	0.048 (2)
C53	0.4717 (3)	0.1419 (3)	0.8546 (2)	0.056 (2)
C54	0.4230 (3)	0.1926 (3)	0.7859 (3)	0.056 (2)
C55	0.3643 (3)	0.1549 (3)	0.7439 (2)	0.052 (2)
C56	0.3511 (3)	0.0645 (3)	0.7735 (2)	0.047 (2)
C57	0.5385 (4)	0.1839 (4)	0.8982 (3)	0.086 (3)
C58	0.3158 (4)	0.2105 (3)	0.6669 (3)	0.078 (3)
C61	0.5954 (3)	−0.2023 (3)	0.8328 (2)	0.045 (2)
C62	0.6552 (3)	−0.1630 (3)	0.8745 (3)	0.054 (2)
C63	0.6995 (3)	−0.2134 (3)	0.9451 (3)	0.063 (3)
C64	0.6829 (4)	−0.3016 (4)	0.9736 (3)	0.071 (3)
C65	0.6227 (3)	−0.3415 (3)	0.9334 (3)	0.060 (2)
C66	0.5818 (3)	−0.2922 (3)	0.8624 (3)	0.054 (2)
C67	0.7638 (4)	−0.1716 (5)	0.9913 (3)	0.097 (4)
C68	0.6011 (5)	−0.4367 (4)	0.9678 (4)	0.094 (4)
C71	0.3948 (3)	−0.0834 (3)	0.5084 (2)	0.051 (2)
C72	0.3936 (4)	−0.1113 (3)	0.4351 (2)	0.063 (3)
C73	0.3323 (4)	−0.0523 (3)	0.3758 (2)	0.067 (3)
C74	0.2718 (4)	0.0345 (4)	0.3914 (3)	0.073 (3)
C75	0.2724 (4)	0.0655 (3)	0.4633 (3)	0.071 (3)
C76	0.3357 (4)	0.0049 (3)	0.5222 (2)	0.064 (3)
C77	0.3284 (6)	−0.0824 (5)	0.2963 (3)	0.115 (5)
C78	0.2054 (6)	0.1621 (4)	0.4775 (3)	0.115 (4)
C81	0.3391 (3)	−0.3550 (3)	0.6046 (2)	0.049 (2)
C82	0.3412 (4)	−0.4162 (3)	0.5490 (3)	0.064 (3)
C83	0.3907 (4)	−0.5143 (3)	0.5651 (3)	0.074 (3)
C84	0.4381 (4)	−0.5493 (3)	0.6358 (3)	0.075 (3)
C85	0.4384 (4)	−0.4908 (3)	0.6917 (3)	0.064 (3)
C86	0.3875 (3)	−0.3938 (3)	0.6760 (2)	0.053 (2)
C87	0.3913 (6)	−0.5792 (4)	0.5041 (4)	0.111 (4)
C88	0.4916 (5)	−0.5300 (3)	0.7696 (4)	0.091 (3)
S5	0.38222 (9)	−0.10203 (8)	0.88725 (6)	0.0426 (5
S2	−0.04873 (7)	−0.19651 (7)	0.78285 (6)	0.0462 (5
S3	0.07705 (8)	−0.29190 (7)	0.94327 (5)	0.0455 (5
S4	0.30245 (7)	−0.27436 (6)	0.95162 (5)	0.0372 (4
S1	0.06528 (8)	−0.10493 (7)	0.63543 (5)	0.0458 (5
S6	0.54801 (8)	−0.13616 (7)	0.74032 (6)	0.0486 (5
S8	0.26950 (8)	−0.23192 (7)	0.57747 (5)	0.0499 (5
S7	0.47566 (8)	−0.16222 (8)	0.58292 (6)	0.0550 (6

Table 2. *Selected geometric parameters (Å, °)*

C1—C2	1.380 (5)	C7—C8	1.375 (6)
C1—C9	1.439 (5)	C7—S7	1.774 (4)
C1—S1	1.783 (4)	C8—C9	1.426 (5)
C2—C3	1.429 (5)	C8—S8	1.783 (4)
C2—S2	1.772 (4)	C9—C10	1.411 (5)
C3—C4	1.380 (5)	C11—S1	1.781 (4)
C3—S3	1.776 (4)	C21—S2	1.773 (4)
C4—C10	1.433 (5)	C31—S3	1.780 (4)
C4—S4	1.774 (4)	C41—S4	1.771 (4)
C5—C6	1.378 (5)	C51—S5	1.782 (4)
C5—C10	1.445 (5)	C61—S6	1.773 (4)
C5—S5	1.777 (4)	C71—S7	1.781 (5)
C6—C7	1.431 (5)	C81—S8	1.782 (5)
C6—S6	1.772 (4)		
C9—C1—C2—C3	3.3 (4)	C6—C5—C10—C9	−20.5 (4)
C2—C1—C9—C8	159.8 (6)	C5—C6—C7—C8	−1.0 (4)
C2—C1—C9—C10	−21.6 (4)	C6—C7—C8—C9	2.0 (4)
C1—C2—C3—C4	11.7 (4)	C7—C8—C9—C1	166.0 (6)
C2—C3—C4—C10	−7.9 (4)	C7—C8—C9—C10	−12.5 (4)
C3—C4—C10—C5	171.5 (5)	C1—C9—C10—C4	25.0 (3)
C3—C4—C10—C9	−10.9 (4)	C1—C9—C10—C5	−157.3 (5)
C6—C5—C10—C4	157.1 (5)	C8—C9—C10—C4	−156.3 (5)
C10—C5—C6—C7	10.3 (4)	C8—C9—C10—C5	21.4 (4)

The structure was solved using the *SIR* program (Altomare *et al.*, 1992) of the *CRYSTAN* package (MacScience, 1995). H atoms were placed in calculated fixed positions and only their isotropic displacement parameters were varied. The structure was refined using *CRYSTAN*'s block-diagonal least-squares program, in which each normal matrix block is composed of the coordinates and the isotropic or anisotropic displacement parameters of one atom. Appreciable thermal motion of some of the methyl C atoms of the 3,5-dimethylphenyl moieties is indicated by their displacement parameters.

Data collection: *CAD*-4 *Express* (Enraf–Nonius, 1995). Cell refinement: *CAD*-4 *Express*. Data reduction: *GX* (Mallinson & Muir, 1985) in *CRYSTAN*. Molecular graphics: *CRYSTAN*. Software used to prepare material for publication: *CRYSTAN*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1379). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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