sites for the water H atoms. The water H atoms were placed along the Br(2)—O(1) vector and the O(1)—H(1) length fixed at 0.86 Å. The twofold axis generates the other water H atom such that the H—O—H angle is 102.7°.

Data collection: Siemens *R3m/V* software. Data reduction: *SHELXTL-Plus* (VMS) (Sheldrick, 1991). Program(s) used to solve structure: *SHELXTL-Plus* (VMS). Program(s) used to refine structure: *SHELXTL-Plus* (VMS).

RTP recognizes financial support for this study from US Department of Energy, Office of Basic Energy Sciences Grant No. DE-FG03-94ER14446 and Los Alamos National Laboratory.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: PT1017). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Bryant, L. H. Jr, Lachgar, A., Coates, K. S. & Jackels, S. C. (1994). *Inorg. Chem.* **33**, 2219–2226.

Rothermel, G. L., Miao, L., Hill, A. L. & Jackels, S. C. (1992). *Inorg. Chem.* **31**, 4854–4859.

Sheldrick, G. M. (1991). *SHELXTL-Plus*. Release 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Acta Cryst. (1996). C**52**, 207–210

Two *cis* Ring-Fused *exo* *N*-Aryl Heterocycles: 1-Phenyl-2-(2,4,6-trimethylphenyl)-decahydroquinolin-4-one and 1-(4-Trifluoromethylphenyl)-2-phenyldecahydroquinolin-4-one

Denise Nogue,[a] Renée Paugam,[a] Lya Wartski,[a] Martine Nierlich,[b] Daniel Vigner[b] and Monique Lance[b]

[a]*ICMO Laboratoire des Carbocycles, CNRS-URA 478, Bâtiment 420, 91405 Orsay CEDEX, France, and* [b]*CEA, DRECAM, SCM, Saclay, Bâtiment 125, 91191 Gif sur Yvette CEDEX, France*

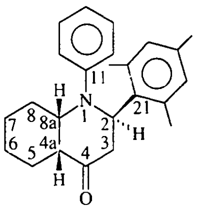
(*Received 12 April 1995; accepted 3 July 1995*)

Abstract

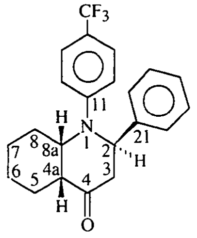
For the title compounds, $C_{24}H_{29}NO$ (I) and $C_{22}H_{22}F_3NO$ (II), the cyclohexane ring adopts a chair conformation. Both compounds exhibit a *cis* ring-fused *exo* configuration. When the N atom bears a phenyl ring and the C(2) atom is substituted by a 2,4,6-trimethylphenyl group (I) ring *B* lies in a chair conformation, the N atom being tetrahedral. When the N atom is substituted by a 4-trifluoromethyl group and the C(2) atom by a phenyl moiety as in (II), however, the *B* ring adopts a quasi-boat conformation, the N atom being planar.

Comment

1-Phenyl-2-(2,4,6-trimethylphenyl)decahydroquinolin-4-one (I) and 1-(4-trifluoromethylphenyl)-2-phenyldecahydroquinolin-4-one (II), are obtained by stereospecific hydrolysis of the cycloadducts formed by imino Diels–Alder reaction between substituted imines and the trimethylsilylenol ether of 1-acetylcyclohexene (Nogue, Paugam & Wartski, 1992). The determination of the structure of these heterocycles is necessary to understand their reactivity and to assign the configuration of the starting cycloadducts.



(I)



(II)

For both compounds, the ^1H-NMR data allow the determination of the *cis* relationship between C(4a)—H(4a) and C(8a)—H(8a) bonds and the axial and equatorial position of the H(8a) and H(4a) atoms in the cyclohexane ring. However, no information is given about the relationship between C(2)—H(2) and C(8a)—H(8a) bonds. Moreover, the N-atom geometry as well as the conformation of the *A* and *B* rings is unknown. Unambiguous assignment of these structures has to be obtained by single-crystal X-ray structure analysis.

In both compounds, the value of the torsion angle H(8a)—C(8a)—C(4a)—H(4a) of 57.8 (6) (I) and 56.4 (8)° (II) confirms the *cis* relationship between the

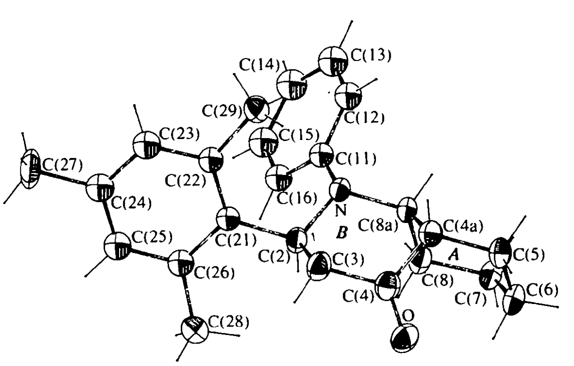


Fig. 1. Drawing of the molecule of (I) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 40% probability level.

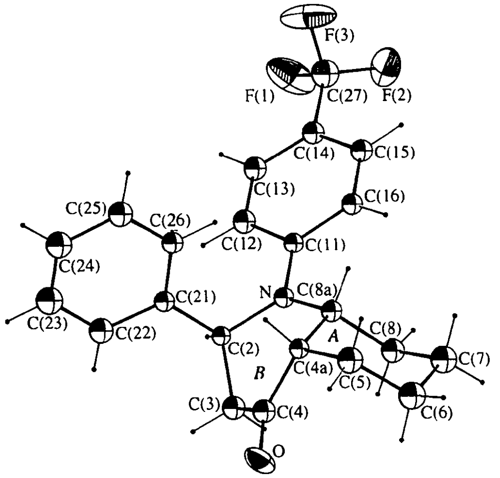


Fig. 2. Drawing of the molecule of (II) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 40% probability level.

C(8a)—H(8a) and C(4a)—H(4a) bonds. The *A* ring lies in a chair conformation for both compounds: the C(6) and C(8a) atoms are located at 0.65 and −0.68 Å, respectively, from the C(5),C(7),C(8),C(4a) (±0.02 Å) plane for (I) and at 0.64 Å and −0.70 Å, respectively, from the same plane (±0.01 Å) for (II). On the other hand, the conformation of the *B* ring is different in the two compounds. For (I), the *B* ring adopts a chair conformation, the C(2) and C(4a) atoms being located at 0.64 and −0.66 Å from the N,C(3),C(4),C(8a) (±0.014 Å) plane; moreover, a *trans* (*exo*) relationship between the C(2)—C(21) and C(8a)—C(8) bonds is assigned, C(21) and C(8) being located at 0.54 and 1.41 Å, respectively, from the previously defined plane of the *B* ring. For (II), the *B* ring adopts a quasi-boat conformation, C(2) and C(4a) located at 0.56 and 0.53 Å, respectively, from the least-squares plane of N,C(3),C(4),C(8a) (±0.13 Å). As in (I), the C(2)—C(21) and C(8a)—C(8) bonds of (II) are in a *trans* (*exo*) relationship, the distances of C(21) and C(8) to the previously defined least-squares plane being 2.08 and −1.62 Å, respectively. The aryl substituent of the C(2) atom occupies an equatorial position in (I) as shown by the C(21)—C(2)—C(3)—H(31) and C(21)—C(2)—C(3)—H(32) torsion angles of 63.1 (5) and −55.9 (5)°, respectively. On the other hand, an axial position of the C(2) aryl group in (II) is indicated by the values of 170.6 (6) and 51.6 (8)°, respectively, for the same torsion angle. Finally, the bond angles around the N atom are close to tetrahedral values for (I) [116.5 (4), 113.6 (4) and 111.5 (4)°] whereas for (II) these values are in agreement with a planar geometry [120.8 (6), 119.3 (7) and 119.2 (7)°].

Experimental

Crystals suitable for X-ray analysis were obtained by slow evaporation of a methanol solution [for (I)] and a cyclohexane–methanol (1/1) solution [for (II)].

Compound (I)

Crystal data

$C_{24}H_{29}NO$
$M_r = 347.5$
Monoclinic
$P2_1/c$
$a = 12.661\ (3)$ Å
$b = 16.540\ (5)$ Å
$c = 9.677\ (2)$ Å
$\beta = 101.57\ (2)°$
$V = 1985\ (1)$ Å^3
$Z = 4$
$D_x = 1.163$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 8–12°$
$\mu = 0.065$ mm^{-1}
$T = 294$ K
Needle
$0.90 \times 0.65 \times 0.40$ mm
Colourless

Data collection

CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
3082 measured reflections
2751 independent reflections
1327 observed reflections [$I > 3\sigma(I)$]

$R_{\rm int} = 0.015$
$\theta_{\rm max} = 23°$
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 18$
$l = -10 \rightarrow 10$
2 standard reflections
frequency: 60 min
intensity decay: 0.12%

Refinement

Refinement on F
$R = 0.057$
$wR = 0.056$
$S = 1.34$
1327 reflections
176 parameters
H atoms: see text
Unit weights applied

$(\Delta/\sigma)_{\rm max} = 0.03$
$\Delta\rho_{\rm max} = 0.341$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.258$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Compound (II)

Crystal data

$C_{22}H_{22}F_3NO$
$M_r = 373.42$
Monoclinic
$P2_1$
$a = 7.150\ (1)$ Å
$b = 12.214\ (2)$ Å
$c = 10.944\ (1)$ Å
$\beta = 101.20\ (1)°$
$V = 937.6\ (3)$ Å^3
$Z = 2$
$D_x = 1.323$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 8–12°$
$\mu = 0.095$ mm^{-1}
$T = 294$ K
Irregular
$0.40 \times 0.40 \times 0.30$ mm
Colourless

Data collection

CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
1397 measured reflections
1331 independent reflections
1043 observed reflections [$I > 3\sigma(I)$]

$R_{\rm int} = 0.02$
$\theta_{\rm max} = 22°$
$h = 0 \rightarrow 7$
$k = 0 \rightarrow 12$
$l = -11 \rightarrow 11$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F
$R = 0.059$
$wR = 0.061$
$S = 0.87$
1043 reflections
130 parameters
H atoms: see text
Unit weights applied
$(\Delta/\sigma)_{\max} = 0.04$
$\Delta\rho_{\max} = 0.382$ e Å^{-3}
$\Delta\rho_{\min} = -0.320$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for* (I)

$^*B_{eq} = (4/3)\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	B_{iso}/B_{eq}*
O	0.7851 (3)	0.1316 (2)	0.2797 (4)	5.8 (1)*
N	0.7617 (3)	0.0312 (2)	0.6505 (4)	3.43 (9)*
C(2)	0.7684 (4)	−0.0198 (3)	0.5278 (5)	3.4 (1)*
C(3)	0.8401 (4)	0.0219 (3)	0.4376 (5)	4.4 (1)*
C(4)	0.8052 (4)	0.1079 (3)	0.3998 (5)	4.1 (1)*
C(4a)	0.7961 (4)	0.1584 (3)	0.5265 (5)	4.1 (1)*
C(5)	0.7585 (5)	0.2456 (3)	0.4898 (6)	5.0 (1)*
C(6)	0.6397 (5)	0.2498 (3)	0.4192 (6)	5.1 (1)*
C(7)	0.5684 (5)	0.2070 (3)	0.5057 (6)	5.0 (1)*
C(8)	0.6051 (4)	0.1190 (3)	0.5341 (6)	4.2 (1)*
C(8a)	0.7227 (4)	0.1150 (3)	0.6122 (5)	3.6 (1)*
C(11)	0.7088 (4)	−0.0032 (3)	0.7538 (5)	3.3 (1)
C(12)	0.7304 (4)	0.0301 (3)	0.8891 (5)	4.3 (1)
C(13)	0.6791 (4)	−0.0002 (4)	0.9925 (6)	5.0 (1)
C(14)	0.6080 (5)	−0.0627 (4)	0.9637 (6)	5.4 (1)
C(15)	0.5877 (5)	−0.0981 (4)	0.8318 (6)	5.0 (1)
C(16)	0.6378 (4)	−0.0678 (3)	0.7261 (5)	4.0 (1)
C(21)	0.8158 (4)	−0.1041 (3)	0.5658 (5)	3.2 (1)
C(22)	0.9018 (4)	−0.1187 (3)	0.6776 (5)	3.6 (1)
C(23)	0.9402 (4)	−0.1983 (3)	0.7032 (6)	4.4 (1)
C(24)	0.8956 (4)	−0.2622 (3)	0.6185 (6)	4.5 (1)
C(25)	0.8138 (4)	−0.2465 (3)	0.5058 (5)	4.3 (1)
C(26)	0.7730 (4)	−0.1684 (3)	0.4764 (5)	3.9 (1)
C(27)	0.9380 (5)	−0.3480 (3)	0.6519 (8)	7.1 (2)*
C(28)	0.6855 (5)	−0.1578 (4)	0.3457 (5)	5.1 (2)*
C(29)	0.9595 (4)	−0.0551 (3)	0.7775 (6)	4.6 (1)*

Table 2. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for* (II)

$^*B_{eq} = (4/3)\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	B_{iso}/B_{eq}*
F(1)	0.093 (1)	0.6709 (6)	0.3537 (8)	11.7 (2)*
F(2)	0.1554 (9)	0.7779 (7)	0.4981 (5)	11.9 (2)*
F(3)	0.2528 (8)	0.8044 (7)	0.3357 (7)	12.5 (2)*
O	−1.0541 (8)	1.1978 (6)	0.0536 (6)	6.4 (2)*
N	−0.5663 (8)	1.017	0.1854 (5)	3.0 (1)
C(2)	−0.702 (1)	0.9782 (7)	0.0745 (6)	3.3 (2)
C(3)	−0.902 (1)	1.0214 (6)	0.0774 (7)	3.7 (2)
C(4)	−0.909 (1)	1.1456 (6)	0.0865 (7)	3.7 (2)
C(4a)	−0.722 (1)	1.2002 (6)	0.1373 (6)	3.0 (1)
C(5)	−0.740 (1)	1.3145 (7)	0.1905 (7)	4.8 (2)
C(6)	−0.806 (1)	1.3114 (8)	0.3132 (7)	5.3 (2)
C(7)	−0.681 (1)	1.2378 (7)	0.4086 (8)	5.2 (2)
C(8)	−0.670 (1)	1.1231 (7)	0.3555 (7)	4.1 (2)
C(8a)	−0.592 (1)	1.1264 (6)	0.2346 (6)	3.2 (1)
C(11)	−0.402 (1)	0.9595 (6)	0.2317 (6)	2.9 (1)
C(12)	−0.358 (1)	0.8602 (7)	0.1754 (7)	3.8 (2)
C(13)	−0.199 (1)	0.8029 (7)	0.2231 (7)	3.8 (2)
C(14)	−0.072 (1)	0.8364 (7)	0.3272 (7)	3.5 (2)
C(15)	−0.108 (1)	0.9357 (6)	0.3810 (7)	3.5 (2)
C(16)	−0.268 (1)	0.9956 (7)	0.3350 (6)	3.2 (1)
C(21)	−0.639 (1)	1.0048 (6)	−0.0473 (6)	3.0 (1)
C(22)	−0.749 (1)	0.9666 (7)	−0.1589 (7)	4.3 (2)
C(23)	−0.695 (1)	0.9949 (8)	−0.2716 (8)	5.4 (2)
C(24)	−0.541 (1)	1.0548 (8)	−0.2747 (8)	5.0 (2)
C(25)	−0.427 (1)	1.0904 (7)	−0.1654 (7)	4.3 (2)
C(26)	−0.476 (1)	1.0633 (6)	−0.0525 (6)	3.3 (1)
C(27)	0.106 (1)	0.7757 (8)	0.3783 (8)	5.4 (2)

Table 3. *Selected geometric parameters (Å, °)*

	(I)	(II)
N—C(2)	1.474 (6)	1.477 (9)
N—C(11)	1.429 (6)	1.38 (1)
C(2)—C(3)	1.543 (7)	1.53 (1)
C(3)—C(4)	1.511 (8)	1.52 (1)
C(4a)—C(5)	1.538 (8)	1.53 (1)
C(6)—C(7)	1.523 (8)	1.53 (1)
C(8)—C(8a)	1.530 (7)	1.53 (1)
C(11)—C(12)	1.397 (7)	1.42 (1)
C(13)—C(14)	1.363 (8)	1.37 (1)
C(15)—C(16)	1.400 (8)	1.37 (1)
C(2)—C(21)	1.535 (7)	1.52 (1)
C(22)—C(23)	1.406 (8)	1.40 (1)
C(23)—C(24)	1.386 (8)	1.33 (1)
C(24)—C(25)	1.370 (7)	1.38 (1)
C(26)—C(28)	1.516 (7)	–
C(27)—F(1)	–	1.31 (1)
C(27)—F(3)	–	1.28 (1)
N—C(8a)	1.491 (6)	1.46 (1)
O—C(4)	1.203 (7)	1.21 (1)
C(4)—C(4a)	1.507 (8)	1.50 (1)
C(5)—C(6)	1.525 (8)	1.51 (1)
C(7)—C(8)	1.538 (7)	1.52 (1)
C(8a)—C(4a)	1.541 (7)	1.56 (1)
C(12)—C(13)	1.392 (8)	1.35 (1)
C(14)—C(15)	1.381 (8)	1.39 (1)
C(16)—C(11)	1.386 (7)	1.40 (1)
C(21)—C(22)	1.393 (7)	1.40 (1)
C(22)—C(29)	1.516 (7)	–
C(24)—C(27)	1.528 (8)	–
C(25)—C(26)	1.398 (8)	1.39 (1)
C(26)—C(21)	1.409 (7)	1.37 (1)
C(27)—F(2)	–	1.29 (1)
C(2)—N—C(11)	116.5 (4)	120.8 (6)
C(11)—N—C(8a)	111.5 (4)	119.3 (7)
N—C(8a)—C(4a)	111.2 (4)	112.1 (6)
C(4)—C(3)—C(2)	112.4 (5)	112.8 (8)
C(8a)—C(8)—C(7)	111.0 (5)	111.1 (7)
C(7)—C(6)—C(5)	111.8 (5)	112.3 (9)
C(2)—N—C(8a)	113.6 (4)	119.2 (7)
N—C(8a)—C(8)	113.8 (4)	112.8 (7)
C(4a)—C(4)—C(3)	112.9 (5)	115.4 (8)
C(3)—C(2)—N	109.5 (4)	109.7 (6)
C(8)—C(7)—C(6)	110.3 (5)	110.3 (8)
C(6)—C(5)—C(4a)	112.2 (5)	112.5 (8)

The structure was solved by direct methods and using full-matrix least-squares techniques, with all non-benzene C atoms for (I) and F and O atoms for (II) refined anisotropically. H atoms were included at calculated positions and constrained to ride on their parent C atoms. All calculations were performed on a VAX 4200 computer.

For both compounds, data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *MolEN* (Fair, 1990); program(s) used to solve structures: *SIR*88 (Burla *et al.*, 1989); program(s) used to refine structures: *MolEN*; molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *MolEN*.

Lists of structure factors, torsion angles, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: PA1188). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Burla, M. C., Camalli, M., Cascarano, G., Giacovazzo, C., Polidori, G., Spagna, R. & Viterbo, D. (1989). *J. Appl. Cryst.* **22**, 389–393.
Enraf–Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf–Nonius, Delft, The Netherlands.
Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Nogue, D., Paugam, R. & Wartski, L. (1992). *Tetrahedron Lett.* **33**, 1265–1268.

Acta Cryst. (1996). C**52**, 210–212

1,2-Bis[2,3,4,5,6-pentakis(phenylthio)-phenyl]ethane

Robert K. Henderson, David D. MacNicol and Stuart J. Rowan

Department of Chemistry, University of Glasgow, Glasgow G12 8QQ, Scotland

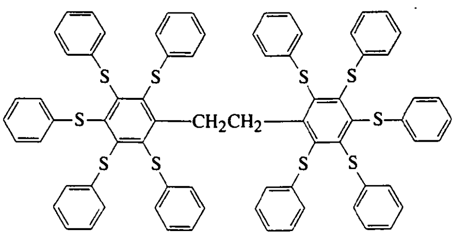
(*Received 15 February 1995; accepted 12 September 1995*)

Abstract

In its molecular crystal the title compound, $C_{74}H_{54}S_{10}$, has an *anti* conformation about the central C—C bond. The molecule is centrosymmetric and exhibits regular alternation of the phenylthio side-chain units above and below the mean plane of the 14 C atoms of the diphenylethane skeleton. In contrast, the ethylene link unit has a *syn* relationship with respect to the phenyl groups of the phenylthio substituents in the *ortho* positions.

Comment

Previous studies on the design of host molecules capable of forming crystalline inclusion compounds have been concerned with the per-substitution of single or fused aromatic cores (MacNicol, 1984; Downing, Frampton, MacNicol & Mallinson, 1994). In order to investigate the attractive possibility of linking aromatic cores, we have prepared 1,2-bis[pentakis(phenylthio)phenyl]-ethane, (I). Unlike the inclusion behaviour found for molecules incorporating a one-atom link, such as carbonyl or methylene (to be reported elsewhere), the two-atom link molecule, (I), crystallizes unsolvated from a range of solvents such as EtOEt/petroleum ether (313–333 K), $CHCl_3$/MeOH and 1,4-dioxane/MeOH. The present work was undertaken in order to elucidate the structure and conformation of (I) in its molecular crystal.



(I)

The molecule of (I), illustrated in Fig. 1, occupies a crystallographic inversion centre. In an extension of our earlier nomenclature (MacNicol, Mallinson & Robertson, 1985), the conformation is notated as *ababa*(*a,l*)(*b,l*)*babab*, the new symbols *a,l* and *b,l* referring to the orientation of the first non-directly attached link atom or group, here CH_2, above or below the mean plane of the molecule.

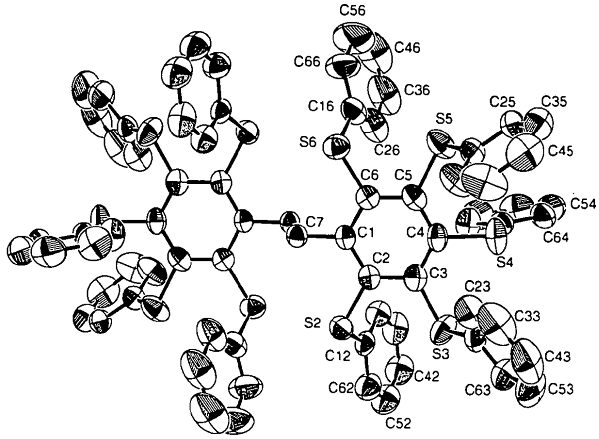


Fig. 1. The molecular structure of (1), with selected atoms indicating the numbering scheme, which is consistent for all rings. Displacement ellipsoids are at the 50% probability level.

The SPh units exhibit the maximum possible degree of alternation above and below the mean plane of the 14 central C atoms. The disposition of the five independent SPh units is described by the representative torsion angles given in Table 2. These may be compared with the corresponding values of 56 and 28° found for the unique SPh side chain of hexakis(phenylthio)benzene in its trigonal CCl_4 clathrate (Hardy, MacNicol & Wilson, 1979). Bond lengths and angles are in keeping with expected values (Table 2).

The C1–C6 atoms of the benzene core unit deviate significantly from planarity, the respective displacements from the mean plane of the ring being 0.043 (3), −0.012 (4), −0.035 (4), 0.052 (4), −0.021 (4) and −0.027 (4) Å. With the exception of atom S5, which lies close to the mean benzene plane [0.006 (7) Å], the S atoms also show significant departures from the mean benzene plane, the respective values for atoms S2, S3,

Acta Crystallographica Section C
ISSN 0108-2701 ©1996