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

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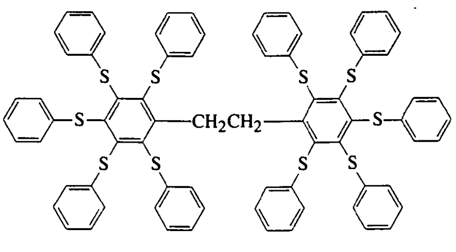
## Abstract

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.

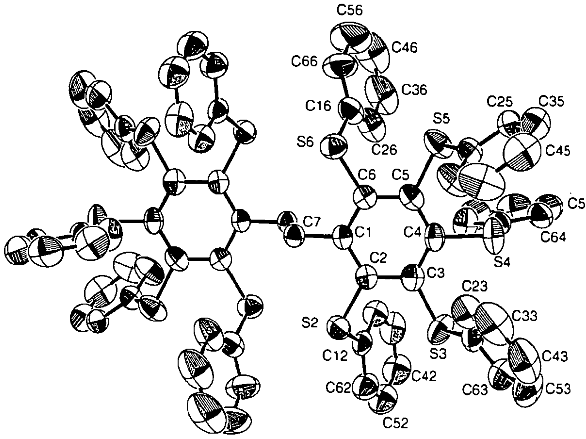


Fig. 1. The molecular structure of (I), with selected atoms indicating the numbering scheme, which is consistent for all rings. Displacement ellipsoids are at the 50% probability level.

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,

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S4 and S6 being −0.051 (7), −0.044 (7), 0.324 (7) and −0.181 (7) Å.

Although the outer phenyl groups are close to planarity all the S atoms are significantly displaced from their respective mean planes, the displacements for atoms S2–S6 being −0.028 (8), −0.110 (10), −0.072 (9), 0.149 (9) and 0.036 (10) Å, respectively.

A number of similar compounds have been prepared, for example, 1,2-bis[pentakis(*p*-tolylthio)phenyl]ethane, 1,2-bis[pentakis(*p*-tertbutylthio)phenyl]ethane, 1,2-bis[pentakis(3,5-dimethylphenylthio)phenyl]ethane and 1,2-bis[pentakis(cyclohexylthio)phenyl]ethane. None of these compounds has shown any indication of inclusion behaviour as evidenced by both microanalysis and $^1$H-NMR analysis (unpublished work). Sections of the crystal structure of the title compound show no voids of sufficient size to hold a solvent molecule.

## Experimental

For the preparation of 1,2-bis[pentakis(phenylthio)phenyl]ethane, 1,2-bis(pentabromophenyl)ethane from Ethyl S. A. (0.200 g, 0.21 mmol) and sodium thiophenolate (0.545 g, 4.13 mmol), prepared from thiophenol and sodium in absolute ethanol, were stirred in 30 ml of degassed 1,3-dimethylimidazolidin-2-one (DMEU) under vacuum at 333 K for 3 d. The mixture was added to toluene (200 ml), washed with water (10 × 100 ml) and the solvent evaporated to give a yellow oil. This was purified by gravity column chromatography [petroleum ether (313–333 K)/diethyl ether (1:1)] and recrystallized from 1,4-dioxane/methanol to yield yellow crystals (0.210 g, 80.9% yield, m.p. 491–493 K). TLC: $R_F$ = 0.41 [petroleum ether (313–333 K)/diethyl ether (1:1)]. The compound was initially characterized by $^1$H- and $^{13}$C-NMR spectral analysis.

### *Crystal data*

$C_{74}H_{54}S_{10}$
$M_r$ = 1263.77
Monoclinic
$P2_1/n$
$a$ = 12.0031 (10) Å
$b$ = 19.527 (3) Å
$c$ = 13.953 (2) Å
$\beta$ = 102.300 (9)°
$V$ = 3195.3 (7) Å$^3$
$Z$ = 2
$D_x$ = 1.313 Mg m$^{-3}$
$D_m$ not measured

Mo $K\alpha$ radiation
$\lambda$ = 0.71073 Å
Cell parameters from 25 reflections
$\theta$ = 16.27–21.06°
$\mu$ = 0.388 mm$^{-1}$
$T$ = 293 (2) K
Needle
0.4 × 0.2 × 0.2 mm
Yellow

### *Data collection*

Enraf–Nonius CAD-4 diffractometer
$\omega$–2$\theta$ scans
Absorption correction: none
6207 measured reflections
5955 independent reflections
2408 observed reflections [$I > 2\sigma(I)$]

$R_{\rm int}$ = 0.0355
$\theta_{\rm max}$ = 25.52°
$h = -14 \rightarrow 14$
$k = 0 \rightarrow 23$
$l = -16 \rightarrow 0$
3 standard reflections
frequency: 120 min
intensity decay: 15.4%

### *Refinement*

Refinement on $F^2$
$R(F)$ = 0.0609
$wR(F^2)$ = 0.1877
$S$ = 0.998
5953 reflections
379 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0631P)^2 + 2.1159P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max}$ = −0.041
$\Delta\rho_{\rm max}$ = 0.388 e Å$^{-3}$
$\Delta\rho_{\rm min}$ = −0.267 e Å$^{-3}$
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

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

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

| | $x$ | $y$ | $z$ | $U_{\rm eq}$ |
|---|---|---|---|---|
| C7 | 0.0544 (4) | 0.0179 (3) | 0.9928 (4) | 0.0464 (13) |
| C1 | 0.1326 (4) | −0.0313 (2) | 0.9544 (4) | 0.0423 (13) |
| C2 | 0.1333 (4) | −0.0353 (3) | 0.8553 (4) | 0.0458 (14) |
| C3 | 0.2016 (4) | −0.0850 (3) | 0.8202 (4) | 0.054 (2) |
| C4 | 0.2645 (4) | −0.1315 (3) | 0.8850 (5) | 0.0514 (15) |
| C5 | 0.2732 (4) | −0.1240 (3) | 0.9851 (5) | 0.054 (2) |
| C6 | 0.2068 (4) | −0.0734 (3) | 1.0208 (4) | 0.0458 (14) |
| S2 | 0.04782 (13) | 0.02197 (8) | 0.77202 (11) | 0.0577 (4) |
| C12 | −0.0470 (5) | −0.0346 (3) | 0.6947 (4) | 0.054 (2) |
| C22 | −0.0852 (5) | −0.0952 (4) | 0.7281 (5) | 0.067 (2) |
| C32 | −0.1573 (6) | −0.1366 (4) | 0.6634 (6) | 0.081 (2) |
| C42 | −0.1926 (6) | −0.1188 (5) | 0.5676 (6) | 0.089 (2) |
| C52 | −0.1582 (6) | −0.0579 (5) | 0.5350 (6) | 0.089 (2) |
| C62 | −0.0849 (6) | −0.0157 (4) | 0.5983 (5) | 0.074 (2) |
| S3 | 0.19438 (13) | −0.08933 (10) | 0.69216 (12) | 0.0738 (6) |
| C13 | 0.3369 (5) | −0.0800 (3) | 0.6791 (5) | 0.062 (2) |
| C23 | 0.4263 (6) | −0.0598 (4) | 0.7534 (6) | 0.085 (2) |
| C33 | 0.5323 (7) | −0.0507 (4) | 0.7319 (9) | 0.116 (3) |
| C43 | 0.5499 (10) | −0.0595 (5) | 0.6411 (11) | 0.137 (5) |
| C53 | 0.4603 (11) | −0.0788 (5) | 0.5672 (9) | 0.136 (4) |
| C63 | 0.3538 (7) | −0.0898 (4) | 0.5861 (6) | 0.093 (2) |
| S4 | 0.32938 (14) | −0.20278 (9) | 0.83924 (15) | 0.0754 (6) |
| C14 | 0.2228 (5) | −0.2661 (3) | 0.8335 (4) | 0.057 (2) |
| C24 | 0.1136 (6) | −0.2535 (4) | 0.8462 (5) | 0.078 (2) |
| C34 | 0.0365 (7) | −0.3064 (4) | 0.8363 (5) | 0.093 (2) |
| C44 | 0.0675 (9) | −0.3716 (4) | 0.8125 (6) | 0.097 (3) |
| C54 | 0.1767 (9) | −0.3836 (4) | 0.7989 (5) | 0.092 (2) |
| C64 | 0.2532 (6) | −0.3308 (3) | 0.8101 (5) | 0.072 (2) |
| S5 | 0.35817 (14) | −0.17971 (9) | 1.07201 (14) | 0.0776 (6) |
| C15 | 0.4984 (5) | −0.1671 (3) | 1.0518 (4) | 0.056 (2) |
| C25 | 0.5729 (5) | −0.2220 (3) | 1.0753 (4) | 0.061 (2) |
| C35 | 0.6848 (5) | −0.2142 (4) | 1.0712 (5) | 0.077 (2) |
| C45 | 0.7221 (6) | −0.1538 (5) | 1.0415 (6) | 0.096 (3) |
| C55 | 0.6476 (7) | −0.0992 (5) | 1.0146 (6) | 0.112 (3) |
| C65 | 0.5345 (6) | −0.1053 (4) | 1.0224 (5) | 0.084 (2) |
| S6 | 0.22035 (14) | −0.06069 (8) | 1.14825 (12) | 0.0636 (5) |
| C16 | 0.1709 (5) | −0.1367 (4) | 1.1922 (5) | 0.067 (2) |
| C26 | 0.1036 (6) | −0.1836 (4) | 1.1351 (7) | 0.091 (2) |
| C36 | 0.0683 (8) | −0.2414 (5) | 1.1798 (9) | 0.128 (4) |
| C46 | 0.0987 (11) | −0.2505 (6) | 1.2792 (13) | 0.148 (6) |
| C56 | 0.1651 (11) | −0.2021 (7) | 1.3342 (9) | 0.157 (5) |
| C66 | 0.2021 (7) | −0.1453 (5) | 1.2937 (6) | 0.107 (3) |

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

| | | | |
|---|---|---|---|
| C7—C1 | 1.519 (7) | C4—S4 | 1.779 (6) |
| C7—C7$^{\rm i}$ | 1.532 (9) | C5—C6 | 1.425 (8) |
| C1—C2 | 1.387 (7) | C5—S5 | 1.780 (6) |
| C1—C6 | 1.405 (7) | C6—S6 | 1.768 (6) |
| C2—C3 | 1.423 (7) | S2—C12 | 1.777 (6) |
| C2—S2 | 1.773 (6) | S3—C13 | 1.768 (6) |
| C3—C4 | 1.386 (8) | S4—C14 | 1.769 (6) |
| C3—S3 | 1.772 (6) | S5—C15 | 1.782 (6) |
| C4—C5 | 1.386 (7) | S6—C16 | 1.757 (7) |

| | | | |
|---|---|---|---|
| C1—C7—C7$^{i}$ | 111.5 (5) | C1—C6—S6 | 119.4 (4) |
| C2—C1—C6 | 119.1 (5) | C5—C6—S6 | 120.7 (4) |
| C2—C1—C7 | 121.5 (5) | C2—S2—C12 | 102.2 (3) |
| C6—C1—C7 | 119.3 (5) | C62—C12—S2 | 117.5 (5) |
| C1—C2—C3 | 120.5 (5) | C22—C12—S2 | 122.8 (5) |
| C1—C2—S2 | 119.5 (4) | C13—S3—C3 | 105.0 (3) |
| C3—C2—S2 | 119.9 (4) | C63—C13—S3 | 115.2 (6) |
| C4—C3—C2 | 119.7 (5) | C23—C13—S3 | 124.5 (5) |
| C4—C3—S3 | 122.0 (5) | C14—S4—C4 | 101.3 (3) |
| C2—C3—S3 | 118.2 (4) | C64—C14—S4 | 115.3 (5) |
| C3—C4—C5 | 120.2 (5) | C24—C14—S4 | 124.5 (5) |
| C3—C4—S4 | 119.9 (5) | C5—S5—C15 | 103.4 (3) |
| C5—C4—S4 | 119.9 (5) | C65—C15—S5 | 122.5 (5) |
| C4—C5—C6 | 119.8 (5) | C25—C15—S5 | 116.0 (5) |
| C4—C5—S5 | 122.1 (5) | C16—S6—C6 | 105.5 (3) |
| C6—C5—S5 | 117.9 (5) | C26—C16—S6 | 124.5 (6) |
| C1—C6—C5 | 119.9 (5) | C66—C16—S6 | 114.8 (7) |
| | | | |
| C7$^{i}$—C7—C1—C6 | −83.3 (7) | C5—C4—S4—C14 | 84.6 (5) |
| C7—C1—C2—S2 | 4.1 (7) | C4—S4—C14—C24 | 9.8 (6) |
| C7—C1—C6—S6 | −7.9 (6) | C4—C5—S5—C15 | 61.2 (5) |
| C3—C2—S2—C12 | 62.0 (5) | C5—S5—C15—C65 | 32.4 (7) |
| C2—S2—C12—C22 | 33.2 (5) | C5—C6—S6—C16 | −65.4 (5) |
| C4—C3—S3—C13 | −60.2 (5) | C6—S6—C16—C26 | −19.0 (6) |
| C3—S3—C13—C23 | −11.7 (6) | | |

Symmetry codes: (i) $-x, -y, 2-z$.

H atoms were placed geometrically and refined with riding model constraints and $U(\mathrm{H}) = 1.5U_{\mathrm{eq}}(\mathrm{C})$.

Data collection: *CAD*-4 *EXPRESS Software* (Enraf–Nonius, 1992). Cell refinement: Enraf–Nonius *SET*4 (de Boer & Duisenberg, 1984). Data reduction: *GX* (Mallinson & Muir, 1985). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1971).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: CF1010). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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# (22*S*)-21-Acetoxy-11$\beta$-hydroxy-16$\alpha$,17$\alpha$-methylorthoacetoxypregna-1,4-diene-3,20-dione

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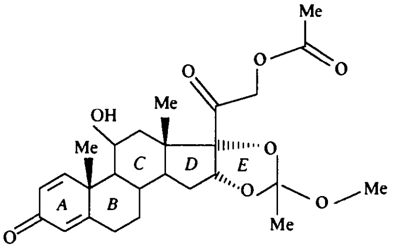
## Abstract

In the title compound, methyl (22*S*)-11$\beta$-hydroxy-16$\alpha$,17$\alpha$-[(methoxy)(methyl)methylenedioxy]pregna-1,4-diene-3,20-dione-21-acetate, $C_{26}H_{34}O_8$, part of the orthoacetate group forms the dioxolane ring (*E*) fused with the steroid skeleton at the C16 and C17 atoms. Ring *A* is planar, rings *B* and *C* adopt chair conformations, while rings *D* and *E* have conformations midway between half-chair and envelope. Intermolecular O11—H···O3 hydrogen bonds are formed. The new chiral center at atom C22 of the dioxolane ring has an *S* configuration and the conformation of the ring, closed at C22, is comparable with the conformations found for the (22*R*) diastereoisomers of similar compounds.

## Comment

This investigation is the fourth in a series of structure determinations of pregnadiene derivatives having a dioxolane ring attached to the C16 and C17 atoms. The compound was prepared by Infarm Co. Ltd as part of a study of new glucocorticosteroid drugs. The crystal structure analysis of (22*S*)-21-acetoxy-11$\beta$-hydroxy-16$\alpha$,17$\alpha$-methylorthoacetoxypregna-1,4-diene-3,20-dione, (I), was undertaken in order to confirm the structural formula and to establish the configuration at the C22 atom, *i.e.* the new chiral center of the molecule. Compounds having a (22*S*) configuration are either biologically less active than their (22*R*) diastereoisomers or inactive.

A view of the molecule is shown in Fig. 1. The bond lengths and valency angles (Table 2) are within the range



(I)

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