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Chiral and *meso*-bis([2.2]paracyclophan-4-yl)methane and *meso*-bis([2.2]paracyclophan-4-yl) sulfide

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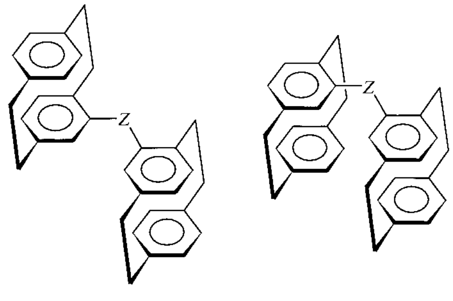
The [2.2]paracyclophane groups of the title compounds, chiral and *meso*-bis(tricyclo[8.2.2.2^{4,7}]hexadeca-4,6,10,12,13,15-hexaen-5-yl)methane (the former as a racemate), $C_{33}H_{32}$, and *meso*-bis(tricyclo[8.2.2.2^{4,7}]hexadeca-4,6,10,12,13,15-hexaen-5-yl) sulfide, $C_{32}H_{30}S$, show the characteristic structural features of the parent compound [2.2]paracyclophane and the related compound dimethylbis([2.2]paracyclophan-4-yl)silane, $C_{34}H_{36}Si$: the aromatic rings are puckered, resulting in a boat conformation. The planes of the four coplanar C atoms are slightly twisted with respect to each other. The Csp^3-Csp^3 bond lengths of the ethylene bridges are elongated by the electronic and steric effects of the skeleton.

Comment

Because of the (planar) chirality of monosubstituted [2.2]paracyclophanes (Q), compounds ZQ_2 composed of a central atom or group (Z) carrying two Q ligands can occur as *meso* and chiral diastereomers. Some time ago we reported the X-ray structures of the first pair of such diastereomers, in which Z was $Si(CH_3)_2$ (Jones *et al.*, 1997), and recently the structure of *meso*-bis[2.2]paracyclophan-4-yl (Z = nil) has been determined (Jones & Kuś, 1998). The configurations of the title compounds, (1*c*) and (1*m*), as determined by NMR data, where the chemical equivalence or non-equivalence of the H atoms of the central methylene group indicate the chiral or *meso*-configuration, respectively, were confirmed by the X-ray structures; (1*c*) crystallizes as a racemate with imposed twofold symmetry. The X-ray diffraction study of the sulfide, (2*m*), was necessary because NMR data gave no indication of its configuration.

The paracyclophanyl groups in the title compounds show the characteristic structural features of substituted [2.2]paracyclophanes, similar to the diastereomeric pair of dimethylbis[2.2]paracyclophan-4-yl)silanes, $C_{34}H_{36}Si$, (3) (Jones *et al.*, 1997) (Figs. 1–3). The aromatic rings are distorted into boat shapes and the C atoms bearing the ethylene bridges are displaced out of the plane of the four other atoms. The mean aromatic planes are slightly inclined with respect to one another; the angles within paracyclophanyl groups vary from 0.3 (2) in (2*m*) to 1.7 (1)° in (1*m*), *cf.* 1.6 (4) to 4.5 (4)° in (3).



(1*c*) $Z = CH_2$

(1*m*) $Z = CH_2$
(2*m*) $Z = S$

The *para*-C atoms are displaced out of the planes by amounts similar to those in the parent compound (4), [2.2]paracyclophane (0.156 and 0.157 Å; Stalke, 1996). The values vary from 0.153 (2) to 0.172 (2) in (1*c*), 0.146 (2) to 0.160 (2) in (1*m*) and 0.140 (3) to 0.167 (3) Å in (2*m*). In contrast to the diastereomeric pair (3), no differences in the displacements between the substituted and non-substituted rings can be recognized.

The non-bonded distances of the corresponding bridgehead C atoms, which eclipse one another transannularly, are less than 2.8 Å [2.780 (2) and 2.792 (2) in (1*c*), 2.767 (2) to 2.774 (2) in (1*m*) and 2.763 (3) to 2.777 (3) Å in (2*m*)]. The intramolecular separation of the planes results in values of 3.084 (2) to 3.135 (2) in (1*c*), 3.041 (2) to 3.128 (2) in (1*m*) and 3.052 (3) to 3.098 (3) Å in (2*m*). The deviations from the geometry of the parent compound (4) (2.779 and 3.093 Å;

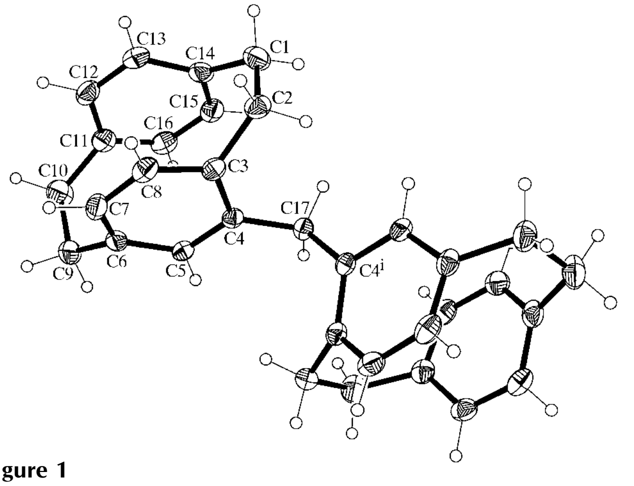


Figure 1
The molecule of compound (1*c*) in the crystal. Ellipsoids correspond to 50% probability levels. H atom radii are arbitrary. [Symmetry code: (i) $1-x, y, \frac{3}{2}-z$].

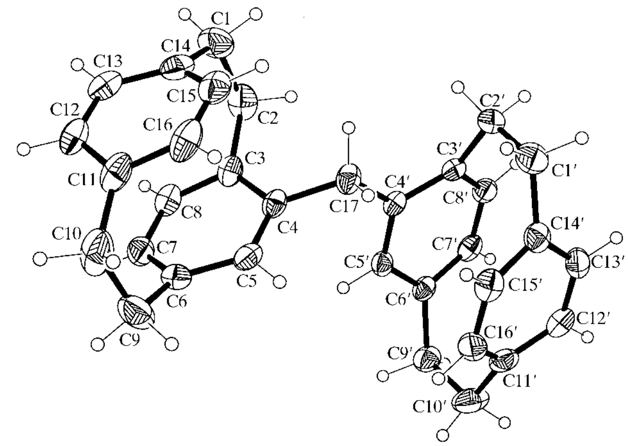


Figure 2
The molecule of compound (1*m*) in the crystal. Ellipsoids correspond to 50% probability levels. H atom radii are arbitrary.

Stalke, 1996) are less pronounced than in the diastereomeric pair of (3) with their bulkier central $Si(CH_3)_2$ moieties.

The torsion angle C9···C2—C1···C10 indicates a mutual twist of the aromatic rings. Individual values are 4.61 (3) (C9···C2—C1···C10) in (1*c*), −1.26 (4) (C9···C2—C1···C10) and 2.00 (4)° (C9′···C2′—C1′···C10′) in (1*m*). The sulfur-bridged compound, (2*m*), displays values of 4.64 (5) (C9···C2—C1···C10) and −0.90 (5)° (C9′···C2′—C1′···C10′).

As usual, the Csp^3—Csp^3 bonds of the ethylene bridges are characteristically elongated to values of 1.581 (2) and 1.585 (2) in (1*c*), 1.577 (2) to 1.582 (3) in (1*m*) and 1.572 (3) to 1.580 (3) Å in (2*m*), similar to the parent compound (4) (1.571 Å; Stalke, 1996).

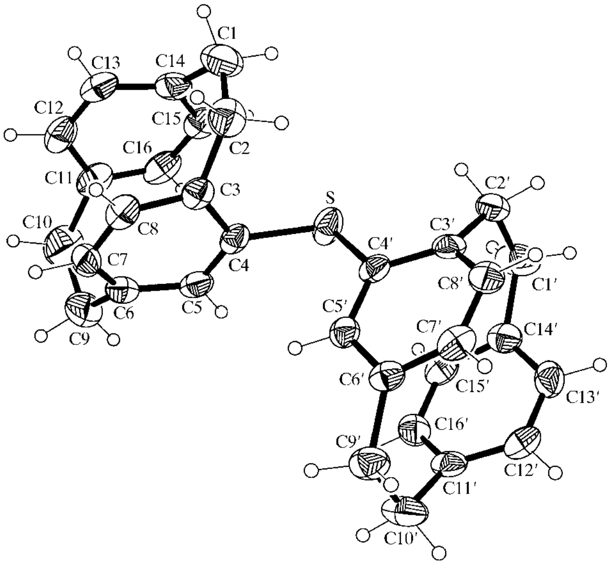


Figure 3
The molecule of compound (2*m*) in the crystal. Ellipsoids correspond to 50% probability levels. H atom radii are arbitrary.

The carbon–carbon bonds in (1*c*) and (1*m*) and the sulfur–carbon bonds in (2*m*) between the two halves of the molecules lie in the range of the mean standard bond length of 1.513 Å for a Csp^3—C_{ar} (Allen *et al.*, 1987) and 1.768 Å for a C_{ar}—S bond length (Allen *et al.*, 1987): 1.518 (2) in (1*c*), 1.513 (2) and 1.521 (2) in (1*m*), and 1.778 (2) and 1.780 (2) Å in (2*m*).

The torsion angles C5—C4—*Z*—C4′ and C4—*Z*—C4′—C5′ indicate the orientation of the paracyclophane groups with respect to each other. The central bond C4—*Z* in all cases shows torsion angles close to 120° and thus an *ac* conformation: −113.80 (12) [C5—C4—C17—C4^{i}; symmetry code: (i) $1 - x, y, \frac{3}{2} - z$] in (1*c*), 106.24 (15) (C5—C4—C17—C4′) in (1*m*) and −111.86 (16)° (C5—C4—S—C4′) in (2*m*). In contrast, the bond *Z*—C4′ has a flattened *sc* conformation: −30.64 (19) (C4—C17—C4′—C5′) in (1*m*) and 33.75 (18)° (C4—S—C4′—C5′) in (2*m*).

Experimental

The title compounds were prepared according to the method of Ernst & Wittkowski (1999).

Compound (1c)

Crystal data

$C_{33}H_{32}$
$M_r = 428.59$
Monoclinic, $C2/c$
$a = 24.928$ (3) Å
$b = 7.8409$ (6) Å
$c = 11.5716$ (12) Å
$\beta = 92.256$ (8)°
$V = 2260.0$ (4) Å^3
$Z = 4$
$D_x = 1.260$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 64 reflections
$\theta = 4.8$–12.5°
$\mu = 0.071$ mm^{-1}
$T = 173$ (2) K
Hexagonal tablet, colourless
0.76 × 0.46 × 0.22 mm
Crystal source: Ernst & Wittkowski (1999)

Data collection

Siemens *P*4 diffractometer
ω scans
3066 measured reflections
2589 independent reflections
1912 reflections with $I > 2\sigma(I)$
$R_{int} = 0.025$
$\theta_{max} = 27.49°$

$h = 0 \rightarrow 32$
$k = -10 \rightarrow 2$
$l = -15 \rightarrow 15$
3 standard reflections
every 247 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.131$
$S = 1.024$
2587 reflections
151 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0763P)^2 + 0.4887P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.27$ e Å^{-3}
$\Delta\rho_{min} = -0.21$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0080 (12)

Table 1
Selected geometric parameters (Å, °) for (1*c*).

C4—C17	1.518 (2)	C17—C4^{i}	1.518 (2)
C5—C4—C17—C4^{i}	−113.80 (12)		

Symmetry code: (i) $1 - x, y, \frac{3}{2} - z$.

Compound (1*m*)

Crystal data

$C_{33}H_{32}$
$M_r = 428.59$
Monoclinic, $C2/c$
$a = 25.969$ (3) Å
$b = 7.7200$ (10) Å
$c = 23.329$ (3) Å
$\beta = 94.044$ (6)°
$V = 4665.3$ (10) Å^3
$Z = 8$
$D_x = 1.220$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 64 reflections
$\theta = 5.3$–12.5°
$\mu = 0.069$ mm^{-1}
$T = 173$ (2) K
Tablet, colourless
1.20 × 0.64 × 0.34 mm
Crystal source: Ernst & Wittkowski (1999)

Data collection

Siemens $P4$ diffractometer
ω scans
4268 measured reflections
4095 independent reflections
3240 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.011$
$\theta_{\rm max} = 25°$

$h = -30 \rightarrow 30$
$k = -9 \rightarrow 1$
$l = -27 \rightarrow 0$
3 standard reflections
every 247 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.116$
$S = 1.037$
4094 reflections
298 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0671P)^2 + 1.7940P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{\rm max} = 0.18$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.23$ e Å^{-3}

Table 2
Selected geometric parameters (Å, °) for (1*m*).

C4—C17	1.513 (2)	C17—C4′	1.521 (2)
C5—C4—C17—C4′	106.2 (2)	C4—C17—C4′—C5′	−30.6 (2)

Compound (2*m*)

Crystal data

$C_{32}H_{30}S$
$M_r = 446.62$
Triclinic, $P\overline{1}$
$a = 8.1084$ (12) Å
$b = 12.334$ (2) Å
$c = 12.826$ (2) Å
$\alpha = 94.525$ (12)°
$\beta = 105.516$ (12)°
$\gamma = 105.779$ (8)°
$V = 1173.3$ (3) Å^3
$Z = 2$

$D_x = 1.264$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 55 reflections
$\theta = 5.5$–12.5°
$\mu = 0.157$ mm^{-1}
$T = 173$ (2) K
Tablet, colourless
0.60 × 0.30 × 0.08 mm
Crystal source: Ernst & Wittkowski (1999)

Data collection

Siemens $P4$ diffractometer
ω scans
5091 measured reflections
4117 independent reflections
2443 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.019$
$\theta_{\rm max} = 25°$

$h = -9 \rightarrow 5$
$k = -14 \rightarrow 14$
$l = -14 \rightarrow 15$
3 standard reflections
every 247 reflections
intensity decay: 3%

Table 3
Selected geometric parameters (Å, °) for (2*m*).

S—C4	1.778 (2)	S—C4′	1.780 (2)
C4′—S—C4—C5	−111.9 (2)	C4—S—C4′—C5′	33.8 (2)

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.090$
$S = 0.817$
4115 reflections
298 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0439P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{\rm max} = 0.27$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.18$ e Å^{-3}

For compound (1*m*) very few single crystals were available, and these could not be cut because they deformed: the crystal size is therefore greater than would normally be acceptable. For (2*m*), which diffracted more weakly, 307 similarity restraints were applied to the U^{ij} components of C atoms.

For all compounds, data collection: *XSCANS* (Fait, 1991); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *XP*5 (Siemens, 1994); software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1382). Services for accessing these data are described at the back of the journal.

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. S1–S19.
Ernst, L. & Wittkowski, L. (1999). *Eur. J. Org. Chem.* pp. 1653–1663.
Fait, J. (1991). *XSCANS User's Manual.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Jones, P. G., Ernst, L., Dix, I. & Wittkowski, L. (1997). *Acta Cryst.* C**53**, 612–615.
Jones, P. G. & Kuś, P. (1998). *Pol. J. Chem.* **72**, 1106–1111.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1993). *SHELXL*93. University of Göttingen, Germany.
Siemens (1994). *XP*. Version 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Stalke, D. (1996). Private communication.