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A Diastereomeric Pair of Cyclophane Derivatives: Planar–Chiral and *meso*-Dimethylbis([2.2]paracyclophan-4-yl)silane

Peter G. Jones,[a] Ludger Ernst,[a] Ina Dix[a] and Lars Wittkowski[b]

[a]*Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Postfach 3329, 38023 Braunschweig, Germany, and* [b]*Institut für Organische Chemie, Technische Universität Braunschweig, Hagenring 30, 38106 Braunschweig, Germany. E-mail: jones@xray36.anchem.nat.tu-bs.de*

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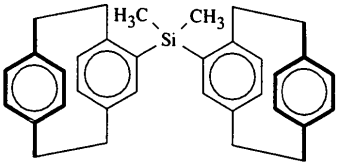
Abstract

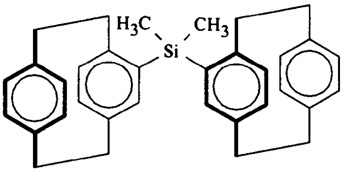
The cyclophane groups of the two title compounds, planar–chiral dimethylbis(tricyclo[8.2.2.2^{4,7}]tetradeca-4,6,10,12,13,15-hexaen-5-yl)silane, $C_{34}H_{36}Si$, and its *meso* analogue, display similar geometric features to the parent compound [2.2]paracyclophane and also to [2.2]paracyclophane units in other structures; the aromatic rings are distorted in the typical way. The *para*-C atoms are bent out of the plane of the other four approximately coplanar atoms into a boat conformation. The aromatic rings are twisted with respect to one another. The C_{sp^3}—C_{sp^3} bond lengths of the methylene bridges are slightly longer than standard values in unstrained systems.

Comment

As far as we are aware, the two title compounds are the first examples of bis([2.2]paracyclophan-4-yl) compounds of which the chiral and *meso* diastereomers have been isolated and this is the first structural characterization of a diastereomeric pair of such compounds. Both crystallize in centrosymmetric space groups and compound (1) crystallizes with two independent molecules in the asymmetric unit; each molecule displays a *meso* configuration, with one paracyclophanyl group *R* and the other *S*. In contrast, the chiral compound (2) crystallizes with only one independent molecule and the paracyclophanyl groups are either both *R* or both *S*.



(1)



(2)

The paracyclophanyl groups are similar to each other and also to the parent hydrocarbon [2.2]paracyclophane, (3) (Keehn & Rosenfeld, 1983; Stalke, 1996). The aromatic rings are puckered into a boat form whereby the C atoms bearing the methylene bridges are displaced out of the plane of the other four atoms. These planes are not exactly parallel to one another; the interplanar angles within the paracyclophanyl groups range from 1.6 (4) to 4.5 (4)°.

The displacement of the *para*-C atoms from the planes varies from 0.174 (4) to 0.190 (5) Å in the substituted rings and from 0.143 (6) to 0.161 (5) Å in the non-substituted rings of (1). The *para*-C atoms of compound (2) are displaced out of the planes by 0.161 (3)–0.180 (3) Å in the substituted rings and by 0.154 (3)–0.161 (4) Å in the non-substituted rings. The displacement is thus slightly more pronounced in the substituted rings. The rings of the parent non-substituted compound (3) show similar values (0.156 and 0.157 Å; Stalke, 1996).

The displacements are also significantly greater for the C atoms (C3, *etc.*) nearest to the silicon bridges, with values of 0.174 (5)–0.190 (5) Å in (1) and 0.175 (3)–0.180 (3) Å in (2); the Si atoms are displaced by 0.225 (4)–0.473 (6) Å in the opposite direction from the substituted planes.

The planes described by the two sets of four coplanar C atoms are separated by 3.011 (5)–3.222 (5) Å in (1) and 3.036 (3)–3.183 (3) Å in (2). The bridgehead distances C3···C14 and C6···C11 range from 2.766–2.792 Å in (1) and (2) [e.s.d.'s: 0.005 in (1) and 0.003 Å in (2)]. In the parent compound (3), the planes are exactly parallel to one another (crystallographic inversion symmetry), with a bridgehead distance of

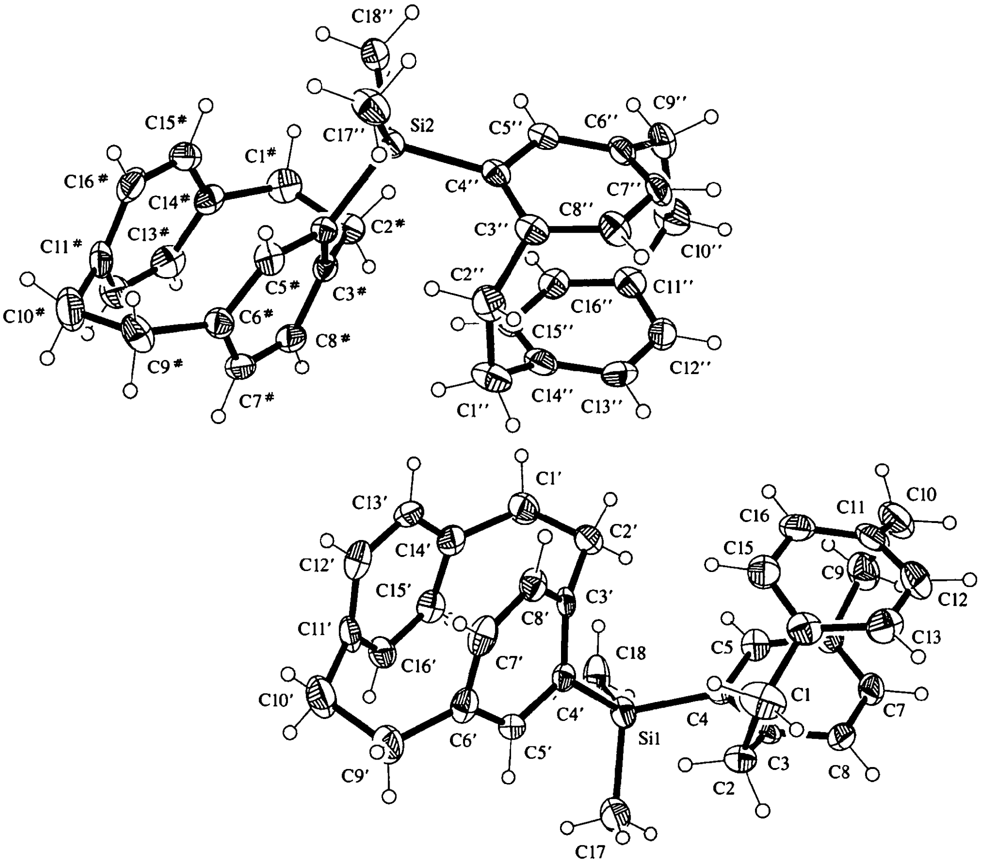


Fig. 1. View of both the independent molecules of compound (1) in the crystal. Ellipsoids correspond to 50% probability levels and H-atom radii are arbitrary.

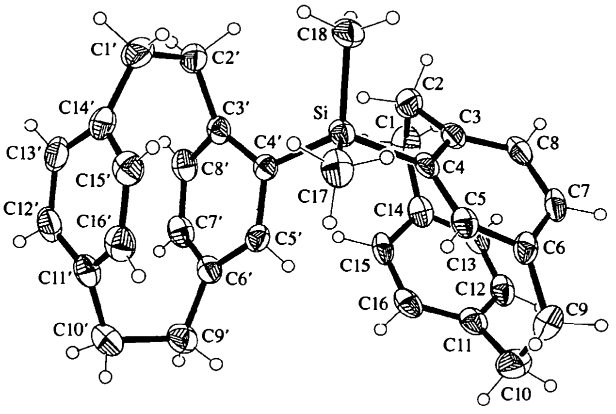


Fig. 2. The molecule of compound (2) in the crystal. Ellipsoids correspond to 50% probability levels and H-atom radii are arbitrary.

2.779 Å and an inter-ring contact of 3.093 Å (Stalke, 1996).

The aromatic rings are slightly twisted with respect to each other, as shown by the torsion angles C9···C2—C1···C10, which amount to −2.18 (9) at C9 and 3.13 (8)° at C9′ in the first independent molecule of (1), and 2.45 (8) at C9″ and −4.54 (8)° at C9# in the second molecule. Compound (2) shows values of 5.79 (5) at C9 and −6.23 (5)° at C9′.

The C_{sp^3}—C_{sp^3} bond lengths of the methylene bridges range from 1.574 (5) to 1.595 (5) Å in (1) and from 1.580 (4) to 1.586 (4) Å in (2), showing a significant extension from standard values that is characteristic of paracyclophanes (Keehn & Rosenfeld, 1983; Allen *et al.*, 1987). The value in the parent compound (3) is 1.571 Å (Stalke, 1996).

The silicon–carbon bonds (Si—C4, *etc.*) to the paracyclophane groups are marginally lengthened [distances of 1.882 (3)–1.888 (3) Å in (1), and 1.885 (2) and 1.889 (2) Å in (2)] from the mean standard value of 1.868 Å (Allen *et al.*, 1987).

The mutual orientation of both paracyclophane groups is described by the torsion angles C5—C4—Si—C4′ and C4—Si—C4′—C5′. In the *meso* diastereomer (1), these torsion angles are close to 120°, *viz.* an *ac* conformation [C5—C4—Si1—C4′ 113.8 (3), C4—Si1—C4′—C5′ −128.6 (3), C5″—C4″—Si2—C4# −119.0 (3) and C4″—Si2—C4#—C5# 118.0 (3)°]. In contrast, the chiral diastereomer (2) displays different torsion angles; *ac* about C4—Si [C5—C4—Si—C4′ 100.58 (18)°], but *sc* about Si—C4′ [C4—Si—C4′—C5′ 65.06 (18)°].

Experimental

Compounds (1) and (2) were prepared by lithiation of 4-bromo[2.2]paracyclophane with ^{t}BuLi in tetrahydrofuran at 195 K, followed by addition of dichlorodimethylsilane. The diastereomeric products were separated by crystallization from dichloromethane/2-propanol solution. The less soluble *meso* isomer has a melting point of 527 K, while the chiral diastereomer has a melting point of 453 K. Crystals were obtained at room temperature from dichloromethane/2-propanol for (1) and from *n*-hexane for (2).

Compound (1) (*meso*)

Crystal data

$C_{34}H_{36}Si$
$M_r = 472.72$
Triclinic
$P\overline{1}$
$a = 11.115\,(2)$ Å
$b = 15.077\,(3)$ Å
$c = 17.182\,(3)$ Å
$\alpha = 65.191\,(12)°$
$\beta = 87.299\,(10)°$
$\gamma = 79.709\,(12)°$
$V = 2570.5\,(8)$ Å^3
$Z = 4$
$D_x = 1.222$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 64 reflections
$\theta = 3.1–11.5°$
$\mu = 0.113$ mm^{-1}
$T = 173\,(2)$ K
Tablet
0.76 × 0.18 × 0.06 mm
Colourless

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction: none
9147 measured reflections
8779 independent reflections
3765 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.0272$

$\theta_{\rm max} = 25°$
$h = -13 \rightarrow 13$
$k = 0 \rightarrow 16$
$l = -18 \rightarrow 20$
3 standard reflections every 247 reflections intensity decay: 2%

Refinement

Refinement on F^2
$R(F) = 0.0531$
$wR(F^2) = 0.1106$
$S = 0.788$
8777 reflections
635 parameters
H atoms: methyl H atoms rigid, others riding

$w = 1/[\sigma^2(F_o^2) + (0.0323P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.651$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.224$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Compound (2) (planar-chiral)

Crystal data

$C_{34}H_{36}Si$
$M_r = 472.72$
Monoclinic
$P2_1/c$
$a = 13.941\,(2)$ Å
$b = 17.694\,(2)$ Å
$c = 10.4379\,(14)$ Å
$\beta = 93.089\,(10)°$
$V = 2571.0\,(6)$ Å^3
$Z = 4$
$D_x = 1.221$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 63 reflections
$\theta = 4.7–12.5°$
$\mu = 0.113$ mm^{-1}
$T = 173\,(2)$ K
Prism
0.56 × 0.48 × 0.26 mm
Colourless

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction: none
4837 measured reflections
4530 independent reflections
2972 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.0286$

$\theta_{\rm max} = 25°$
$h = -16 \rightarrow 16$
$k = -1 \rightarrow 21$
$l = 0 \rightarrow 12$
3 standard reflections every 247 reflections intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.0457$
$wR(F^2) = 0.1144$
$S = 0.920$
4527 reflections
318 parameters
H atoms: methyl H atoms rigid, others riding

$w = 1/[\sigma^2(F_o^2) + (0.0599P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = -0.001$
$\Delta\rho_{\rm max} = 0.676$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.206$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

All H atoms were refined using a riding model. For (1), which diffracted more weakly, 628 similarity restraints were applied to the *U* components of the C atoms.

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

The authors thank the Fonds der Chemischen Industrie for financial support, Mr A. Weinkauf for technical assistance and Professor D. Stalke for making available his new data on [2.2]paracyclophane.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: FG1229). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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trans-3,5-Diphenyl-1,4,2,6-oxathiadiphosphorinane-3,5-dione

Peter G. Jones and Andreas Weinkauf

Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Postfach 3329, 38023 Braunschweig, Germany. E-mail: jones@xray36.anchem.nat.tu-bs.de

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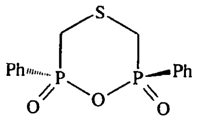
Abstract

The title compound, $C_{14}H_{14}O_3P_2S$, exhibits a flattened chair conformation of the heterocycle. The ring bond angle at oxygen is extremely wide at 137.12 (9)°, whereas that at sulfur is narrow at 98.78 (9)°.

Comment

The title compound, (I), was synthesized as part of a study of the oxidations of various diphosphanes and diphospholanes (Sebastian, 1992). As far as we are aware, no structures of the ring system 1,4,2,6-oxathiadiphosphorinane have been published [Cambridge Structural Database (version of April 1996); Allen & Kennard, 1993]. The X-ray structure determination revealed the *trans* disposition of the phenyl substituents [torsion angles O2—P3···P5—O3 −140.0 (1) and C7—P3···P5—C13 129.9 (1)°].



(I)

The heterocycle adopts a distorted chair conformation; the absolute torsion angles in the flatter region C2—P3—O4—P5 lie in the range 28–40°, while the others are in the range 58–74° (Table 1). If the atoms C2, P3, P5 and C6 are regarded as defining a ring plane (mean deviation 0.08 Å), then the S1 and O4 atoms lie 1.017 (2) and 0.301 (1) Å, respectively, on opposite sides of this plane.

The ring angle P3—O4—P5 is extremely wide at 137.12 (9)° [P3···P5 3.001 (2) Å], whereas C2—S1—C6 is narrow at 98.78 (9)°. A similarly wide P—O—P angle of 135.2 (1)° was observed in the P—O—P—C—O—C ring of *cis*-2,4-dimethyl-1,5-diphenyl-3,9-dioxa-2,4-diphosphabicyclo[3.3.1]nonane-2,4-dione, whereas the corresponding angle in the *trans* isomer was narrower [128.4 (1)°; Rudi, Reichman, Goldberg & Kashman, 1983]. C—S—C angles of 100.47, 101.01 (14) and 102.2, 101.6 (2)° were observed in the P—C—P—C—S—C rings of two independent molecules of *trans*- and *cis*-3,5-diisopropoxy-3,5-dioxo-1,3,5-thiadiphosphorinane (Jones & Weinkauf, 1994).

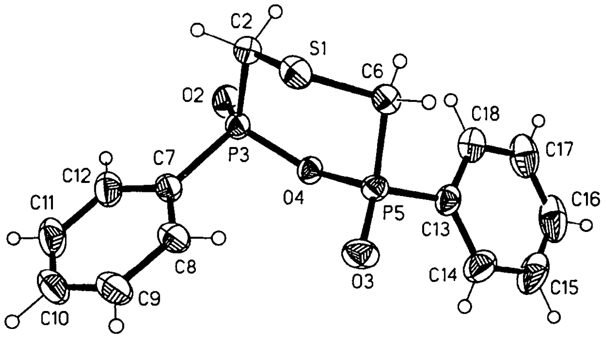


Fig. 1. The molecule of the title compound in the crystal. Ellipsoids represent 50% probability levels and H-atom radii are arbitrary.

Experimental

The title compound was obtained by air oxidation of 3,4-diphenyl-1,3,4-thiadiphospholane and recrystallized from dichloromethane–petroleum ether (30/40) solution (Sebastian, 1992).

Crystal data

$C_{14}H_{14}O_3P_2S$
$M_r = 324.25$
Triclinic
$P\overline{1}$
$a = 9.142\,(4)$ Å
$b = 9.687\,(4)$ Å
$c = 10.449\,(5)$ Å
$\alpha = 113.07\,(3)°$
$\beta = 94.14\,(3)°$
$\gamma = 115.15\,(3)°$
$V = 738.3\,(6)$ Å^3
$Z = 2$
$D_x = 1.459$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 50 reflections
$\theta = 10–12°$
$\mu = 0.439$ mm^{-1}
$T = 178\,(2)$ K
Block
0.65 × 0.60 × 0.40 mm
Colourless

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