

$S = 1.070$   
 1709 reflections  
 94 parameters  
 H-atom parameters  
 constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0303P)^2 + 0.3539P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

Extinction correction:  
*SHELXL93* (Sheldrick, 1993)  
 Extinction coefficient:  
 0.033 (2)  
 Scattering factors from  
*International Tables for Crystallography* (Vol. C)

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Table 1. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

S1—O2	1.4249 (11)	S2—O4	1.4272 (10)
S1—O1	1.4272 (11)	S2—N	1.6992 (12)
S1—N	1.7260 (11)	S2—C2	1.7505 (15)
S1—C1	1.7531 (15)	Cl—N	1.7138 (11)
S2—O3	1.4251 (11)		
O2—S1—O1	119.52 (7)	O4—S2—N	103.43 (6)
O2—S1—N	105.16 (6)	O3—S2—C2	110.27 (7)
O1—S1—N	108.61 (6)	O4—S2—C2	110.42 (7)
O2—S1—C1	110.71 (7)	N—S2—C2	106.04 (7)
O1—S1—C1	109.76 (7)	S2—N—Cl	114.34 (6)
N—S1—C1	101.40 (7)	S2—N—S1	120.24 (6)
O3—S2—O4	119.72 (7)	Cl—N—S1	115.71 (7)
O3—S2—N	105.77 (6)		
O3—S2—N—Cl	−45.65 (9)	O2—S1—N—S2	157.69 (8)
O4—S2—N—Cl	−172.30 (7)	O1—S1—N—S2	28.64 (10)
C2—S2—N—Cl	71.47 (9)	Cl—S1—N—S2	−86.94 (9)
O3—S2—N—S1	169.79 (8)	O2—S1—N—Cl	13.59 (9)
O4—S2—N—S1	43.14 (9)	O1—S1—N—Cl	−115.46 (8)
C2—S2—N—S1	−73.09 (9)	Cl—S1—N—Cl	128.96 (8)

Table 2. Hydrogen-bonding geometry ( $\text{\AA}$ ,  $^\circ$ )

D—H...A	D—H	H...A	D...A	D—H...A
Cl—H1A...O4 <sup>i</sup>	0.98	2.45	3.208 (2)	134
Cl—H1B...O2 <sup>ii</sup>	0.98	2.69	3.628 (2)	161
Cl—H1C...O3 <sup>iii</sup>	0.98	2.39	3.316 (2)	157
C2—H2A...O2 <sup>iv</sup>	0.98	2.69	3.374 (2)	127
C2—H2B...O4 <sup>v</sup>	0.98	2.58	3.417 (2)	144

Symmetry codes: (i)  $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$ ; (ii)  $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$ ; (iii)  $1 - x, 1 - y, -z$ ; (iv)  $\frac{3}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$ ; (v)  $1 - x, 1 - y, 1 - z$ .

Data collection: *XSCANS* (Fait, 1991). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93*. Molecular graphics: *XP* (Siemens, 1994b). Software used to prepare material for publication: *SHELXL93*.

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*Acta Cryst.* (1997). **C53**, 1307–1310

## 2,13-Dithia[3]metacyclo[3](2,3)naphthalenophane and 2,13-Dithia[3]metacyclo[3](1,7)-naphthalenophane †

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## Abstract

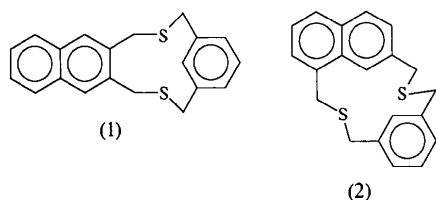
The title compounds are isomeric,  $C_{20}H_{18}S_2$ . The (2,3) isomer has an *anti* conformation, parallel ring systems and approximate mirror symmetry. The (1,7) isomer has

† Alternative names: 3,16-dithiatetracyclo[16.3.1.0<sup>5,14</sup>.0<sup>7,12</sup>]docosane-1(22),5,7(12),8,10,13,18,20-octaene and 3,11-dithiatetracyclo[11-6.2.1<sup>5,9</sup>.0<sup>17,21</sup>]docosane-1(20),5(22),6,8,13,15,17(21),18-octaene.

perpendicular ring systems and the bridge conformations reflect the inherent asymmetry of the substitution pattern.

### Comment

We are interested in the structures of dithianaphthalenophanes and have most recently reported the structure of 2,13-dithia[3]orthocyclo[3](2,3)-naphthalenophane (Jones & Kuš, 1997; further related references are presented therein). In the *meta* series, we have reported the structure of 17-methyl-2,13-dithia[3]metacyclo[3](2,3)-naphthalenophane (Jones, Hopf & Kuš, 1996a). We publish here the structures of the isomeric compounds 2,13-dithia[3]metacyclo[3](2,3)naphthalenophane, (1), and 2,13-dithia[3]metacyclo[3](1,7)naphthalenophane, (2).



In the (2,3) isomer, (1) (Fig. 1), the ring systems are approximately parallel [interplanar angle 12.59 (7)°] and adopt the *anti* conformation, as observed in the 17-methyl derivative (Jones *et al.*, 1996a). The perpendicular distance between the ring planes (as given by the distances of atoms C15–C20 from the naphthalene best plane) varies from 2.8 to 3.4 Å. Surprisingly, the corresponding benzene plane, 2,11-dithia[3.3]orthometacyclophane, adopts a *syn* conformation in the crystal (Bodwell *et al.*, 1990). Dimensions of the central ten-membered ring of (1) are presented in Table 1; starting with C1–S2–C3–C4 and moving to increasing atom number, the torsion angle sequence is  $-ac$ ,  $+ac$ ,  $sp$ ,  $-sc$ ,  $+sc$ ,  $+sc$ ,  $-sc$ ,  $+ap$ ,  $-ap$ ,  $-ac$ . The molecule, and in particular the bridge geometry, displays mirror symmetry to a good approximation.

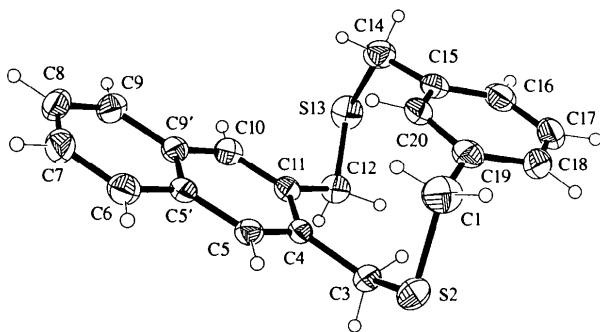


Fig. 1. The molecule of the (2,3) isomer, (1), in the crystal. Ellipsoids represent 50% probability levels. H-atom radii are arbitrary.

In the (1,7) isomer, (2) (Fig. 2), the ring systems are approximately orthogonal [interplanar angle 72.36 (8)°]. Dimensions of the central 13-membered ring of (1) are presented in Table 2; starting with C1–S2–C3–C4 and moving anticlockwise in the figure, the torsion-angle sequence is  $+ac$ ,  $-ac$ ,  $ap$ ,  $ap$ ,  $sp$ ,  $+sc$ ,  $-ap$ ,  $+sc$ ,  $+sc$ ,  $ap$ ,  $ap$ ,  $-ac$ ,  $-ac$ . The bridges, in which the corresponding torsion angles necessarily have opposite signs, display similar conformations; the most significant difference of *ca* 33° is observed for C14–S13–C12–C10  $-157.0$  (2) and C1–S2–C3–C4 124.1 (3)°, and compensates for the inherent asymmetry of the (1,7) substitution pattern. As far as we are aware, there are no other reported structures of [3.3]naphthalenophanes with (1,7) substitution; we have determined the (disordered) structure of the corresponding *para*-(1,6) isomer (Jones, Hopf & Kuš, 1996b).

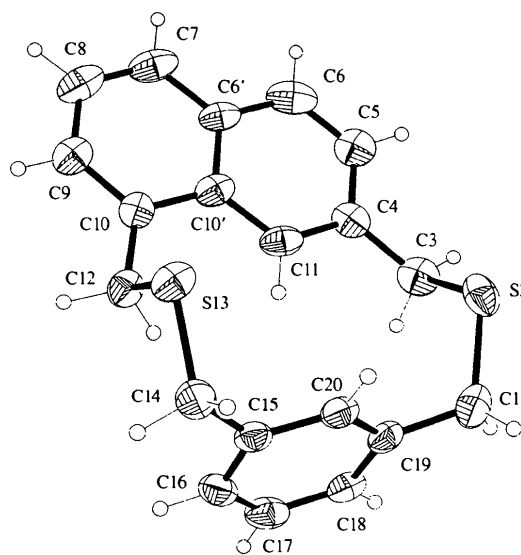


Fig. 2. The molecule of the (1,7) isomer, (2), in the crystal. Ellipsoids represent 50% probability levels. H-atom radii are arbitrary.

The shortest intramolecular contacts (excluding H atoms) are, for (1), S2···S2( $\frac{3}{2}-x, \frac{3}{2}-y, 1-z$ ) 3.936 (1) and C7···C8( $1-x, -y, 1-z$ ) 3.462 (2) Å, and for (2), C6···C18( $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$ ) 3.461 (5) Å (no S···S contacts).

### Experimental

The title compounds were prepared by cyclization of 1,3-di-(mercaptomethyl)benzene and 2,3- or 1,7-di(bromomethyl)-naphthalene by the well known high-dilution method (Kuš, 1987, 1991) and recrystallized from carbon tetrachloride for (1) or ethanol for (2) by slow evaporation.

**Compound (1)***Crystal data*

$C_{20}H_{18}S_2$   
 $M_r = 322.46$   
 Monoclinic  
 $C2/c$   
 $a = 19.604 (2) \text{ \AA}$   
 $b = 9.7659 (12) \text{ \AA}$   
 $c = 17.8787 (18) \text{ \AA}$   
 $\beta = 105.524 (8)^\circ$   
 $V = 3298.1 (6) \text{ \AA}^3$   
 $Z = 8$   
 $D_x = 1.299 \text{ Mg m}^{-3}$   
 $D_m$  not measured

*Data collection*

Siemens *P4* diffractometer  
 $\omega$  scans  
 Absorption correction: none  
 4740 measured reflections  
 3775 independent reflections  
 2942 reflections with  
 $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.020$

*Refinement*

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.035$   
 $wR(F^2) = 0.098$   
 $S = 1.025$   
 3775 reflections  
 199 parameters  
 H atoms riding: see below  
 $w = 1/[\sigma^2(F_o^2) + (0.0594P)^2 + 0.4203P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

Mo  $K\alpha$  radiation  
 $\lambda = 0.71073 \text{ \AA}$   
 Cell parameters from 62 reflections  
 $\theta = 3.5\text{--}12.5^\circ$   
 $\mu = 0.317 \text{ mm}^{-1}$   
 $T = 173 (2) \text{ K}$   
 Tablet  
 $0.80 \times 0.60 \times 0.20 \text{ mm}$   
 Colourless

$\theta_{\text{max}} = 27.5^\circ$   
 $h = -25 \rightarrow 4$   
 $k = -12 \rightarrow 0$   
 $l = -22 \rightarrow 22$   
 3 standard reflections  
 every 247 reflections  
 intensity decay: none

$(\Delta/\sigma)_{\text{max}} = -0.001$   
 $\Delta\rho_{\text{max}} = 0.297 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.277 \text{ e \AA}^{-3}$   
 Extinction correction: none  
 Scattering factors from  
*International Tables for Crystallography* (Vol. C)

Table 1. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ) for (1)

C1—C19	1.501 (2)	C12—S13	1.8152 (15)
C1—S2	1.8310 (18)	S13—C14	1.8292 (17)
S2—C3	1.8093 (15)	C14—C15	1.500 (2)
C3—C4	1.5204 (19)	C15—C20	1.394 (2)
C4—C11	1.4347 (19)	C19—C20	1.393 (2)
C11—C12	1.518 (2)		
C19—C1—S2	112.37 (12)	C12—S13—C14	102.75 (7)
C3—S2—C1	102.68 (7)	C15—C14—S13	112.62 (11)
C4—C3—S2	117.53 (10)	C20—C15—C14	118.84 (14)
C11—C4—C3	121.24 (12)	C20—C19—C1	118.70 (15)
C4—C11—C12	121.37 (13)	C19—C20—C15	121.96 (14)
C11—C12—S13	116.86 (11)		
C19—C1—S2—C3	-40.99 (14)	C11—C12—S13—C14	58.54 (13)
C1—S2—C3—C4	-61.88 (12)	C12—S13—C14—C15	43.56 (13)
S2—C3—C4—C11	145.89 (11)	S13—C14—C15—C20	-99.20 (14)
C3—C4—C11—C12	0.1 (2)	C1—C19—C20—C15	-169.65 (14)
C4—C11—C12—S13	-141.70 (12)	C14—C15—C20—C19	170.85 (14)

**Compound (2)***Crystal data*

$C_{20}H_{18}S_2$   
 $M_r = 322.46$

Mo  $K\alpha$  radiation  
 $\lambda = 0.71073 \text{ \AA}$

## Monoclinic

$P2_1/n$   
 $a = 8.846 (2) \text{ \AA}$   
 $b = 13.178 (3) \text{ \AA}$   
 $c = 13.876 (3) \text{ \AA}$   
 $\beta = 101.28 (2)^\circ$   
 $V = 1586.3 (6) \text{ \AA}^3$   
 $Z = 4$   
 $D_x = 1.350 \text{ Mg m}^{-3}$   
 $D_m$  not measured

*Data collection*

Siemens *P4* diffractometer  
 $\omega$  scans  
 Absorption correction: none  
 3132 measured reflections  
 2792 independent reflections  
 1766 reflections with  
 $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.026$

*Refinement*

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.051$   
 $wR(F^2) = 0.127$   
 $S = 0.921$   
 2792 reflections  
 199 parameters  
 H atoms riding: see below  
 $w = 1/[\sigma^2(F_o^2) + (0.0671P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

## Cell parameters from 59 reflections

$\theta = 4.5\text{--}11.5^\circ$   
 $\mu = 0.329 \text{ mm}^{-1}$   
 $T = 173 (2) \text{ K}$   
 Plate  
 $0.80 \times 0.25 \times 0.08 \text{ mm}$   
 Colourless

$\theta_{\text{max}} = 25.0^\circ$   
 $h = 0 \rightarrow 10$   
 $k = -15 \rightarrow 1$   
 $l = -16 \rightarrow 16$   
 3 standard reflections  
 every 247 reflections  
 intensity decay: none

$(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.671 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.379 \text{ e \AA}^{-3}$   
 Extinction correction: none  
 Scattering factors from  
*International Tables for Crystallography* (Vol. C)

Table 2. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ) for (2)

C1—C19	1.509 (5)	C10'—C11	1.395 (5)
C1—S2	1.809 (4)	C12—S13	1.828 (3)
S2—C3	1.832 (4)	S13—C14	1.830 (4)
C3—C4	1.493 (5)	C14—C15	1.511 (5)
C4—C11	1.390 (5)	C15—C20	1.391 (5)
C10—C10'	1.452 (5)	C19—C20	1.384 (5)
C10—C12	1.487 (5)		
C19—C1—S2	113.9 (2)	C10—C12—S13	109.9 (2)
C1—S2—C3	101.15 (17)	C12—S13—C14	102.02 (16)
C4—C3—S2	114.2 (2)	C15—C14—S13	111.5 (2)
C11—C4—C3	119.9 (3)	C20—C15—C14	120.3 (3)
C10'—C10—C12	121.4 (3)	C20—C19—C1	120.4 (3)
C11—C10'—C10	122.6 (3)	C19—C20—C15	121.9 (3)
C19—C1—S2—C3	-66.4 (3)	C10—C12—S13—C14	-157.0 (2)
C1—S2—C3—C4	124.1 (3)	C12—S13—C14—C15	57.7 (3)
S2—C3—C4—C11	-72.3 (4)	S13—C14—C15—C20	69.0 (4)
C12—C10—C10'—C11	4.1 (5)	S2—C1—C19—C20	-55.8 (4)
C3—C4—C11—C10'	-177.2 (3)	C1—C19—C20—C15	176.3 (3)
C10—C10'—C11—C4	-179.9 (3)	C14—C15—C20—C19	-173.4 (3)
C10'—C10—C12—S13	77.7 (3)		

In both (1) and (2), H atoms were treated as riding atoms with C—H 0.99  $\text{\AA}$  for  $\text{CH}_2$  groups and 0.95  $\text{\AA}$  for aromatic CH groups.

For both compounds, data collection: XSCANS (Fait, 1991); cell refinement: XSCANS; data reduction: XSCANS; program(s) used to solve structures: SHELXS86 (Sheldrick, 1990); program(s) used to refine structures: SHELXL93 (Sheldrick, 1993); molecular graphics: XP (Siemens, 1994); software used to prepare material for publication: SHELXL93.

We thank the Fonds der Chemischen Industrie for financial support and Mr A. Weinkauff for technical assistance.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1295). Services for accessing these data are described at the back of the journal.

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*Acta Cryst.* (1997). **C53**, 1310–1312

## An Unusual Calix[4]arene Derivative Containing Phosphorus with Coordination Numbers 4, 5 and 6

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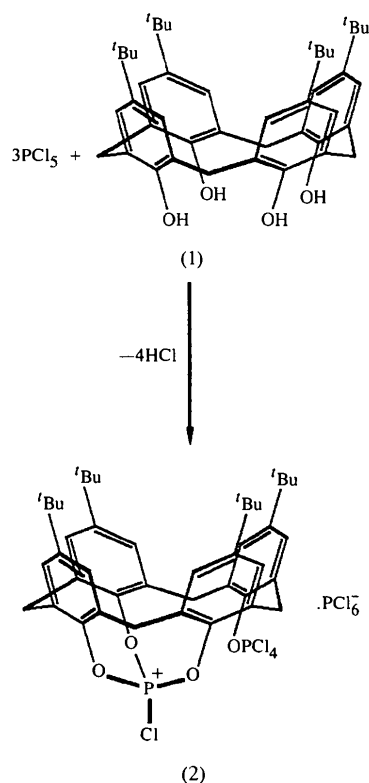
(Received 11 March 1997; accepted 25 March 1997)

### Abstract

The title compound, chloro[5,11,17,23-tetra-*tert*-butyl]-28-(tetrachlorophosphoranyloxy)calix[4]arene-25,26,27-trioxy]phosphonium hexachlorophosphate dichloromethane solvate, C<sub>44</sub>H<sub>52</sub>Cl<sub>5</sub>O<sub>4</sub>P<sub>2</sub><sup>+</sup>.PCl<sub>6</sub><sup>-</sup>.CH<sub>2</sub>Cl<sub>2</sub>, contains pentavalent phosphorus with three different coordination numbers, 4, 5 and 6. The calixarene adopts a non-standard conformation between the partial cone and 1,2-alternate conformations.

### Comment

The introduction of phosphorus-containing substituents into calix[4]arene systems *via* oxygen linkages has been achieved during the past few years in a number of ways, some of which we have described (Neda *et al.*, 1995; Gloede, Keitel, Costisella, Kunath & Schneider, 1996, and references therein). The reaction of *p-tert*-butylcalix[4]arene, (1), with phosphorus pentachloride was reported (Gloede, Costisella, Ramm & Bienert, 1993; Gloede & Keitel, 1995) to proceed as shown in the scheme, forming an unusual phosphorus-containing derivative, (2), that involves P atoms with coordination numbers 4, 5 and 6; the conformation of the calix[4]arene was, however, not established. (In the scheme the common cone conformation is presented for clarity.)



The proposed structure of (2) was originally based on the <sup>31</sup>P NMR spectrum in solution, with three  $\delta$  values of equal intensity at 8.1, -66.0 and -296 p.p.m. These values agree well with the presence of P with coordination numbers 4, 5 and 6 (Gloede *et al.*, 1993; Mark, Dungan, Crutchfield & van Wazer, 1967; Brazier, Lamandé & Wolf, 1991).

Compound (2) was originally reported as being highly deliquescent. This was not confirmed during the studies reported here. After crystallization from CH<sub>2</sub>Cl<sub>2</sub>/hexane under absolutely anaerobic conditions, (2) proved to be remarkably stable towards atmospheric moisture. We report here the crystal structure of its dichloro-