Structures of 2,11-Dithia[3.3]parabenzenophane (V) and 2,3,12,13-Tetrathia[4.4]parabenzenophane (VI)*

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Abstract. $C_{16}H_{16}S_2$ (V): $M_r = 272.43$, monoclinic, $P2_1/c$, $a = 6.182$ (1), $b = 13.079$ (3), $c = 8.689$ (2) Å, $\beta = 107.41$ (2)°, $V = 670.4$ (2) Å^3, $Z = 2$, $D_x = 1.350$, $D_m = 1.352$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 3.60$ cm^{-1}, $F(000) = 287.97$, $T = 295$ K, $R = 0.033$ for 1305 observed reflections. $C_{16}H_{16}S_4$ (VI): $M_r = 336.56$, monoclinic, $P2_1/c$, $a = 6.333$ (1), $b = 13.974$ (3), $c = 8.779$ (2) Å, $\beta = 92.58$ (1)°, $V = 776.1$ (2) Å^3, $Z = 2$, $D_x = 1.440$, $D_m = 1.437$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 5.75$ cm^{-1}, $F(000) = 351.97$, $T = 295$ K, $R = 0.034$ for 1485 observed data. Both molecules are centrosymmetric, with boat-shaped deformation of the benzenoid rings and measured dimensions which reflect the presence of intramolecular strain. The aromatic rings are virtually eclipsed in (V) but displaced laterally relative to each other in (VI).

Introduction. Dithia-bridged and tetrathia-bridged cyclophanes of types (I) and (II), in which two aryl rings are joined in various ways, are useful intermediates in cyclophane synthesis (Boekelheide & Mondt, 1970; Boekelheide, 1980).
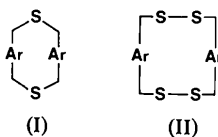
The static and dynamic stereochemistry of these sulfur-containing cyclophanes in relation to the carbon analogs has been a subject of interest for more than a decade (Lai, 1981; Keehn, 1983; Mitchell, 1983). Indeed, the variable-temperature NMR spectra and/or the X-ray crystal structures of a number of systems related to 2,11-dithia[3.3]metabenzenophane (III) and 2,3,12,13-tetrathia[4.4]metabenzenophane (IV) have been studied extensively (Davis & Bernal, 1971; Mitchell & Boekelheide, 1974; Anker, Bushnell & Mitchell, 1979; Kamp & Boekelheide, 1978; Newkome,

Pappalardo & Fronczek, 1983; Dixon & Mitchell, 1983; Beveridge, Bushnell & Mitchell, 1983).
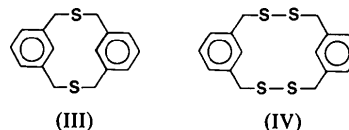
However, surprisingly little is known about the stereochemistry of the corresponding *para* series where transannular π–π interaction is expected to have a profound effect on molecular geometry. The possible existence of such interaction in 2,11-dithia[3.3]parabenzenophane (V) and the anticipated absence of it in 2,3,12,13-tetrathia[4.4]parabenzenophane (VI) prompted us to conduct a comparative study on these two compounds by X-ray diffraction. The present work constitutes a sequel to our previous report on the crystal and molecular structure of 2,11,20,29-tetrathia[3.3.3.3]parabenzenophane (XI) (Chan & Mak, 1984).
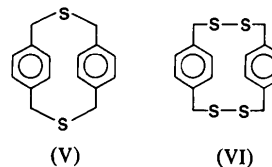
Experimental. 2,11-Dithia[3.3]parabenzenophane (V) was prepared from 1,4-bis(bromomethyl)benzene and *p*-xylene-α,α′-dithiol as previously described (Chan & Mak, 1984). Recrystallization of the crude product first from benzene and then from acetone gave pure (V) as colorless prisms, m.p. 499–501 K, lit. 497 K (Brink, 1975).

2,3,12,13-Tetrathia[4.4]parabenzenophane (VI) was prepared from *p*-xylene-α,α′-dithiol by an oxidative coupling procedure developed earlier by us (Tam, Wong, Siu & Chan, 1975). Product isolation by column chromatography over silica gel using petroleum ether (b.p. 323–348 K)–benzene (4:1) as eluent followed by recrystallization from acetone gave pure (VI) as colorless thick prisms, m.p. 523–525 K.

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* These compounds are known as thia-bridged paracyclophanes in common usage.

Unit-cell and intensity measurements were conducted according to established procedures (Sparks, 1976). Experimental parameters are listed in Table 1. Intensities processed with learnt-profile fitting (Diamond, 1969); empirical absorption based on ψ-scan data (Kopfmann & Huber, 1968; North, Phillips & Mathews, 1968). Both structures solved by direct phasing guided by negative quartets (DeTitta, Edmonds, Langs & Hauptman, 1975); S and C atoms anisotropic; H atoms generated geometrically (C—H fixed at 0·96 Å), assigned isotropic thermal parameters, and allowed to ride on their respective parent C atoms; refinement by blocked-cascade least squares (Schilling, 1970) using *SHELXTL* program system (Sheldrick, 1982) on Data General Nova 3/12 minicomputer, Nicolet Zeta 1553 digital plotter; analytic expressions of neutral-atom scattering factors with incorporation of anomalous-dispersion corrections (*International Tables for X-ray Crystallography*, 1974); refinement parameters are in Table 1.

Discussion. Atomic coordinates are listed in Table 2.* Perspective views of molecules (V) and (VI) with atom labeling are shown in Figs. 1 and 2, respectively. Bond distances, bond angles and selected torsion angles are displayed in Table 3.

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* Lists of structure factors, anisotopic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42810 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
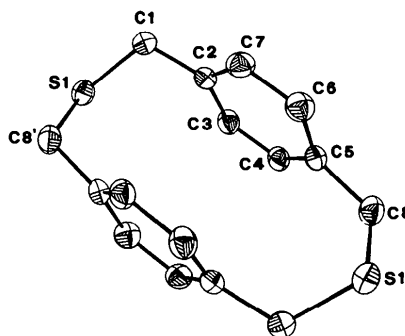

Fig. 1. Perspective view of molecule (V) with atom labeling. Primed atoms are related to the corresponding unprimed ones by inversion through the molecular center at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$. Thermal ellipsoids are drawn at the 40% probability level.
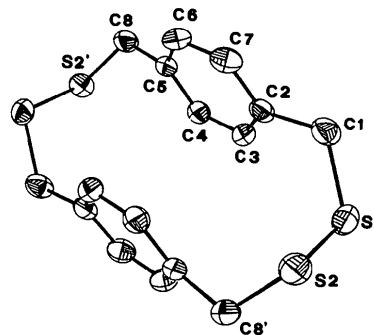

Fig. 2. Perspective view of molecule (VI) with atom labeling. Primed atoms are related to the corresponding unprimed ones by inversion through the molecular center at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$. Thermal ellipsoids are drawn at the 40% probability level.

Table 1. *Data collection and processing parameters*

	(V)	(VI)
Habit	Prisms elongated along **a**	
Crystal size	0·32 × 0·28 × 0·20 mm	0·26 × 0·24 × 0·12 mm
No. of reflections for lattice parameters	21	21
Diffractometer	Nicolet $R3m$	Nicolet $R3m$
Standard reflections	142, 22$\bar{2}$	11$\bar{1}$, 122
Intensity variation	±1%	±1%
R_{int} (from merging equivalent reflections)	0·007	0·006
Absorption coefficient	3·60 cm^{-1}	5·75 cm^{-1}
Mean μr	0·058	0·069
Transmission factors	0·876 to 0·906	0·794 to 0·863
Scan mode and rate	ω–2θ; 2·02–8·37° min^{-1}	
Scan range	1° below $K\alpha_1$ to 1° above $K\alpha_2$	
Background counting	Stationary counts for one-half of scan time at each end of scan	
$2\theta_{max}$	54°	54°
hkl ranges	0 to 7; 0 to 16; 10 to −10	0 to 8; 0 to 17; 11 to −11
Unique data measured	1436	1699
Observed data with $|F_o| > 3\sigma(|F_o|)$, n	1305	1485
Number of variables, p	82	91
R	0·033	0·034
g in $w = [\sigma^2(F_o) + g|F_o|^2]^{-1}$	0·005	0·008
wR	0·049	0·049
S	1·648	1·279
$(\Delta/\sigma)_{max}$	0·007	0·010
Residual extrema in final difference map	+0·23 to −0·27 e Å^{-3}	+0·22 to −0·23 e Å^{-3}

Table 2. *Fractional atomic coordinates* ($\times 10^5$ *for* S; $\times 10^4$ *for* C) *and equivalent isotropic thermal parameters* (Å$^2 \times 10^4$)

U_{eq} is defined as one third of the trace of the orthogonalized U matrix.

	Compound (V)				Compound (VI)			
	x	y	z	U_{eq}	x	y	z	U_{eq}
S(1)	11258 (7)	36112 (3)	16852 (5)	383 (2)	25684 (9)	57020 (4)	9253 (6)	504 (2)
S(2)					4403 (8)	63116 (3)	22810 (6)	493 (2)
C(1)	2859 (4)	2876 (1)	3390 (2)	424 (6)	2598 (4)	4448 (1)	1478 (3)	506 (7)
C(2)	3852 (3)	3465 (1)	4931 (2)	325 (5)	3950 (3)	4154 (1)	2860 (2)	376 (5)
C(3)	2509 (3)	4102 (1)	5543 (2)	366 (5)	5983 (3)	4501 (1)	3128 (2)	385 (5)
C(4)	3475 (3)	4737 (1)	6849 (2)	346 (5)	7271 (3)	4137 (1)	4299 (2)	395 (5)
C(5)	5797 (3)	4746 (1)	7584 (2)	319 (5)	6559 (3)	3413 (1)	5239 (2)	397 (5)
C(6)	7114 (3)	4042 (1)	7064 (2)	383 (5)	4500 (3)	3100 (1)	5006 (2)	480 (6)
C(7)	6149 (3)	3414 (1)	5749 (2)	375 (6)	3213 (3)	3460 (1)	3827 (3)	475 (6)
C(8)	6853 (3)	5548 (1)	8833 (2)	408 (6)	7999 (4)	2932 (1)	6416 (2)	537 (7)

Table 3. *Bond lengths* (Å), *bond angles* (°) *and selected torsion angles* (°)

	(V)	(VI)
S(1)—S(2)	—	2·206 (1)
S(1)—C(1)	1·821 (2)	1·818 (2)
S(1)—C(8')	1·820 (2)	—
S(2)—C(8')	—	1·817 (2)
C(1)—C(2)	1·508 (2)	1·510 (3)
C(5)—C(8)	1·510 (2)	1·506 (3)
C(2)—C(3)	1·389 (3)	1·386 (3)
C(2)—C(7)	1·386 (2)	1·384 (3)
C(4)—C(5)	1·386 (2)	1·393 (3)
C(5)—C(6)	1·391 (3)	1·382 (3)
C(3)—C(4)	1·389 (2)	1·380 (3)
C(6)—C(7)	1·389 (2)	1·383 (3)
C(1)—S(1)—S(2)	—	104·3 (1)
S(1)—S(2)—C(8')	—	104·9 (1)
C(1)—S(1)—C(8')	103·9 (1)	—
S(1)—C(1)—C(2)	115·9 (1)	118·4 (1)
S(1')—C(8)—C(5)	115·0 (1)	—
S(2')—C(8)—C(5)	—	117·9 (1)
C(1)—C(2)—C(3)	121·0 (1)	122·1 (2)
C(1)—C(2)—C(7)	120·9 (2)	119·2 (2)
C(4)—C(5)—C(8)	120·2 (2)	121·9 (2)
C(6)—C(5)—C(8)	121·6 (1)	119·9 (2)
C(2)—C(3)—C(4)	120·7 (1)	120·7 (2)
C(3)—C(4)—C(5)	121·0 (2)	120·9 (2)
C(5)—C(6)—C(7)	120·6 (1)	121·1 (2)
C(6)—C(7)—C(2)	121·0 (2)	120·7 (2)
C(7)—C(2)—C(3)	118·1 (1)	118·5 (2)
C(4)—C(5)—C(6)	118·1 (1)	118·1 (2)
C(8')—S(2)—S(1)—C(1)	—	110·7 (1)
S(2)—S(1)—C(1)—C(2)	—	−82·8 (2)
C(8')—S(1)—C(1)—C(2)	68·4 (2)	—
S(1)—C(1)—C(2)—C(3)	49·2 (2)	−43·0 (3)

Primed atoms are generated by the symmetry transformation (1−x, 1−y, 1−z).

Both 2,11-dithia[3.3]parabenzenophane (V) and 2,3,12,13-tetrathia[4.4]parabenzenophane (VI) have crystallographically imposed 1̄ molecular symmetry, so that the two bridging chains are oriented *anti* to each other, and the mean planes of each pair of benzenoid rings are necessarily parallel. The set of atoms C(3), C(4), C(6) and C(7) conforms to planarity, the maximum deviations from the corresponding best planes being 0·0028 and 0·0023 Å for (V) and (VI), respectively. The presence of intramolecular steric strain in (V) is reflected by the fact that each benzenoid ring is boat-shaped, with its bow and stern [C(2) and C(5)] displaced inward towards the other ring by $\delta = 0·06$ Å, which is consistent with the corresponding values of 0·8, 0·7 and 0·13 Å found for [3·3]-paracyclophane (VII) (Gantzel & Trueblood, 1965), 2,11-dithia[3.3](13,16)-*cis*-1,4-cyclohexanoparacyclophane (VIII) (Swepston, Lin, Hawkins, Humphrey, Siegel & Cordes, 1981) and 2,6-dithia[7]paracyclophane (IX) (Pfisterer & Ziegler, 1983), respectively. On the other hand, the boat-like contortion of the benzenoid ring in (VI) is barely detectable, with an average inward displacement of $\delta = 0·03$ Å for C(2) and C(5).

Interestingly, atoms C(1) and C(8) ($\delta = -0·19$ and $-0·18$ Å, respectively) in (VI) lie on one side of the mean plane defined by C(3,4,6,7) and the S ($\delta = 0·74$ and 2·76 Å) atoms lie on the other, whereas the corresponding C ($\delta = 0·23$ and 0·27 Å) and S ($\delta = 1·57$ and 1·79 Å) atoms lie on the same side in (V). Alternatively, the 'out-of-plane' deformation associated with the aromatic ring may be gauged by the angles of type α [e.g. between the C(3,4,6,7) plane and the C(2,3,7) plane] and type β [e.g. between the C(2,3,7) plane and the C(2)–C(1) bond vector] (see p. 76 in Keehn, 1983). This set of mean (α, β) angles is (4·7, 2·7°) for (V) and (1·9, −3·9°) for (IV), as compared to the values (6·4, 3·6°), (6·0, 4·4°) and (11·3, 10·9°) for paracyclophanes (VII), (VIII) and (IX), respectively.

(VII)   (VIII)   (IX)

(X)   (XI)
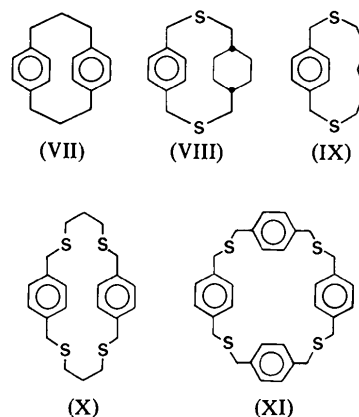
The molecular conformations of (V) and (VI) are specified by the torsion angles given in Table 3. Compound (V) nearly attains idealized $2/m$ molecular symmetry with its two *para*-connected aromatic rings virtually eclipsing each other, as the vector joining their centroids makes an inclination angle (φ) of only 4·3° with the plane normal. In contrast to this, the two parallel benzenoid rings in (VI) are laterally displaced relative to each other, the relevant inclination angle φ being 21·1°.

There is generally good agreement between matching bond distances and angles in the two thia-bridged paracyclophanes, the largest deviation being the bond angle at the methylene C atom (Table 3). As compared to the strain-free and centrosymmetric molecules 2,6,15,19-tetrathia[7.7]paracyclophane (X) [av. S—C = 1·812 (4) Å, C—S—C = 101·2 (2)°, S—C—C(Ar) = 115·2 (2)°] (Pfisterer & Ziegler, 1983) and 2,11,20,29-tetrathia[3.3.3.3]parabenzenophane (XI) [av. S—C = 1·800 (3) Å, C—S—C = 102·2 (1)°, S—C—C = 116·6 (2)°] (Chan & Mak, 1984), the observed S—C and C—S—C values for (V) and S—C values for (VI) are significantly larger, attesting to the presence of intramolecular strain in the latter two cyclic systems.
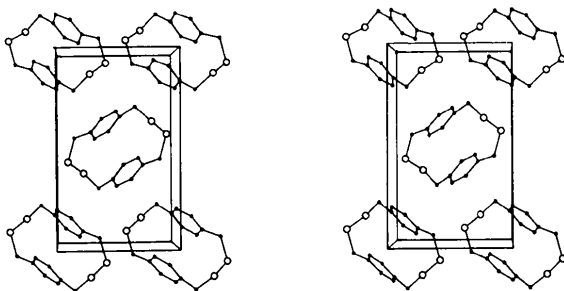
Fig. 3. Stereoview of the molecular packing in compound (VI). The origin of the unit cell lies at the upper left corner, with a pointing towards the reader, b downwards, and c from left to right. Hydrogen atoms have been omitted for clarity. Compound (V) has a similar mode of molecular packing.

A stereoview of the molecular packing in (VI) is illustrated in Fig. 3; compound (V) has a similar mode of herringbone arrangement of structural units in the unit cell with no unusual van der Waals interactions. Finally, we conclude with the observation that para-cyclophanes of inherent $\bar{1}$ molecular symmetry generally occupy an inversion center in the crystalline state. Besides compounds (V), (VI), (VII), (X) and (XI), many more examples are found in the literature (Keehn, 1983).

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Structure of an Eight-Membered CN₄S₃ Ring with a Ph₃P=N Substituent

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Abstract. 7-Phenyl-3-(triphenylphosphinimino)-1,3,5,-2,4,6,8-trithiatetrazocine, $C_{25}H_{20}N_5PS_3$, $M_r = 517.64$, monoclinic, $P2_1/c$, $a = 13.957$ (3), $b = 9.242$ (3), $c = 19.473$ (4) Å, $\beta = 102.80$ (2)°, $V = 2449.4$ Å³, $Z = 4$, $D_x = 1.40$ g cm⁻³, $\lambda(\text{Mo}K\alpha) = 0.71069$ Å, $\mu = 3.8$ cm⁻¹, $F(000) = 1072$, $T = 293$ (1) K, final $R = 0.038$ for 2430 observed reflections. The molecule has a phenyl ring substituted at a planar carbon, and a Ph₃P=N group substituted at S in the 3-position. The CN₄S₃ ring is folded by 114.5°, with an almost planar SNCNS fragment, and an endo-S-envelope SNSNS fragment (dihedral 145.0°). The Ph₃P=N substituent at S is endo and the transannular S···S contact is 2.415 (1) Å.