Table 4. *Hydrogen-bond distances* (Å) *and angles* (°) *in the structure of jacobine methanol solvate*

The e.s.d.'s are given in parentheses.

D—H···A	D—H	H···A	D···A	∠ D—H···A
O(M)—H···O(22) [x,y,z]	0·89 (7)	2·04 (8)	2·767 (4)	139 (5)
O(22)—H···N(4) [$\frac{1}{2}+x,\frac{3}{2}-y,-z$]	0·87 (3)	1·99 (3)	2·819 (2)	159 (2)

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Structure of 2,11,20,29-Tetrathia[3.3.3.3]parabenzenophane, $C_{32}H_{32}S_4$

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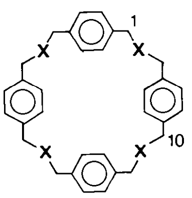
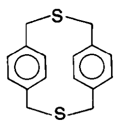
Abstract. $M_r = 544{\cdot}86$, orthorhombic, $Pccn$, $a = 20{\cdot}607\,(3)$, $b = 20{\cdot}121\,(3)$, $c = 6{\cdot}622\,(1)$ Å, $V = 2745{\cdot}7\,(7)$ Å^3, $Z = 4$, $D_m = 1{\cdot}316$ (flotation in KI/H_2O), $D_x = 1{\cdot}318$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 3{\cdot}51$ cm^{-1}, $F(000) = 1152$, $T = 295$ K, final $R_F = 0{\cdot}045$ for 2151 observed reflections. An improved synthesis of the title compound yielded a product whose m.p. of 527–529 K is 55 K higher than the literature value. The four S atoms are coplanar as are each benzene ring and its two methylene carbons. The conformation reduces the size of the central cavity. There are no unusual close contacts.

Introduction. Macrocyclic heterocyclophanes 2,11,20,29-tetrathia[3.3.3.3]parabenzenophane (I) (Tabushi, Sasaki & Kuroda, 1976) and *N,N′,N″,N‴*-tetramethyl-2,11,20,29-tetraaza[3.3.3.3]parabenzenophane (II) (Tabushi, Kimura & Kuroda, 1976; Tabushi, Kimura & Yamamura, 1978, 1981) have recently emerged as a novel class of compounds in the area of inclusion chemistry. The alkylatable exterior heteroatoms together with the hydrophobic cavity in these cyclic systems endow them with the unique ability to form water-soluble host molecules which exhibit marked binding capacity and catalytic specificity toward certain organic substrates. By analogy to the [2^n]paracyclophanes whose conformations in solution (Tabushi, Yamada & Kuroda, 1975) were well analyzed by variable-temperature NMR, the shapes of the cavities in both (I) and (II) were assumed to be approximately square with the benzene rings lying perpendicular to the mean plane of the four heteroatoms (Tabushi, Sasaki & Kuroda, 1976; Tabushi, Kimura & Kuroda, 1976). However, direct structural determination of these compounds has not



(I) X = S

(II) X = NCH_3



(III)

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appeared in the literature. We report here the crystal and molecular structure of (I) as established by X-ray diffraction.

Experimental. A solution of 5·28 g (0·02 mol) of 1,4-bis(bromomethyl)benzene and 3·40 g (0·02 mol) of 1,4-bis(mercaptomethyl)benzene* in 200 ml of ethanol was added dropwise over 10 h to a vigorously stirred solution of 1 liter of ethanol containing 4·0 g of potassium hydroxide. On further stirring for 12 h, the solvent was evaporated *in vacuo* and to the residue was added 300 ml of water. The resulting aqueous suspension was extracted with 4 × 200 ml of chloroform and the combined extracts were washed with water. Evaporation of the dried ($MgSO_4$) chloroform solution left an off-white powder from which the major product 2,11-dithia[3.3]parabenzenophane (III) was separated by extraction with 70 ml of boiling benzene. The benzene-insoluble substance was retained by filtration. The filtrate, on concentration to *ca* 50 ml and on standing at room temperature overnight, gave a white solid. Recrystallization of this substance from benzene yielded 3·3 g (61%) of (III) as white prisms, m.p. 499–501 K, lit. 497 K (Brink, 1975). The benzene-insoluble fraction above was extracted with 3 × 100 ml of boiling carbon tetrachloride. Evaporation of the combined extracts gave an off-white solid. Recrystallization of this material from chloroform yielded 0·34 g (3%) of 2,11,20,29-tetrathia[3.3.3.3]parabenzenophane (I) as colorless prisms, m.p. 527–529 K, lit. 472–473 K (Tabushi, Sasaki & Kuroda, 1976); mass spectrum *m*/*e* (rel. intensity), 544 (M^+, 8·8), 272 (8·5), 271 (16·8), 240 (16·1), 137 (19·2), 136 (45·3), 135 (33·1), 123 (13·8), 105 (79·9), 104 (100); NMR ($CDCl_3$), δ 3·55 (*s*, 1H), 7·05 (*s*, 1H). Analysis: found: C 70·65, H 5·78, S 23·3; calc. for $C_{32}H_{32}S_4$: C 70·54, H 5·92, S, 23·53.

Prisms elongated along **c**, well developed on (100), crystal block 0·3 × 0·2 × 0·4 mm, Nicolet *R*3*m* diffractometer (Sparks, 1976), graphite-monochromated Mo $K\alpha$ radiation, ω–2θ variable scan (2·02 to 8·37° $\min^{-1}$), range 1° below $K\alpha_1$ to 1° above $K\alpha_2$, background counting for one-half of scan time on each side of peak, $2\theta_{\max} = 54°$, collection range $0 \leq h \leq 27$, $0 \leq k \leq 26$, $0 \leq l \leq 9$, three standard reflections monitored every 100 measurements, intensity variation ±2%, 3024 unique data measured, 2151 observed with $I > 1{\cdot}5\sigma(I)$, Lorentz and polarization factors applied, no absorption correction. Structure solution by direct phasing based on negative quartets (De Titta, 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) with $\sum w(|F_o| - |F_c|)^2$ minimized, $w = [\sigma^2(|F_o|) + 0{\cdot}0005|F_o|^2]^{-1}$; empirical isotropic extinction correction applied by multiplying $|F_c|$ by $(1{\cdot}0 + 0{\cdot}002\ g|F_c|^2/\sin 2\theta)^{-1/4}$, where *g* refined to 0·0002 (Larson, 1970); final $R_F = 0{\cdot}045$, $R_{wF} = 0{\cdot}052$, $S = 1{\cdot}42$, max. Δ/σ 0·04; residual extrema in final difference map +0·21 and $-0{\cdot}20$ e Å^{-3}. *SHELXTL* program system (Sheldrick, 1982) on Data General Corporation Nova 3/12 minicomputer, Nicolet Zeta 1553 digital plotter; analytic expressions of neutral-atom scattering factors, anomalous-dispersion corrections incorporated (*International Tables for X-ray Crystallography*, 1974).

Table 1. *Fractional atomic coordinates* ($\times 10^5$ *for* S; $\times 10^4$ *for* C) *and equivalent isotropic thermal parameters* (Å^2 × 10^4 *for* S; × 10^3 *for* C)

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

	x	y	z	U_{eq}
S(1)	−18040 (3)	−18257 (3)	−11209 (11)	568 (2)
S(2)	−18138 (3)	18741 (3)	32499 (13)	643 (3)
C(1)	−1337 (1)	−1402 (1)	800 (4)	57 (1)
C(2)	−1412 (1)	−657 (1)	834 (3)	46 (1)
C(3)	−1952 (1)	−356 (1)	1673 (4)	53 (1)
C(4)	−2012 (1)	327 (1)	1726 (4)	53 (1)
C(5)	−1523 (1)	731 (1)	959 (3)	44 (1)
C(6)	−984 (1)	431 (1)	165 (4)	54 (1)
C(7)	−929 (1)	−255 (1)	97 (4)	57 (1)
C(8)	−1572 (1)	1478 (1)	930 (4)	54 (1)
C(9)	−1279 (1)	1501 (1)	5069 (4)	62 (1)
C(10)	−559 (1)	1511 (1)	4584 (3)	47 (1)
C(11)	−258 (1)	2040 (1)	3629 (4)	50 (1)
C(12)	402 (1)	2028 (1)	3222 (4)	49 (1)
C(13)	781 (1)	1488 (1)	3762 (3)	45 (1)
C(14)	478 (1)	962 (1)	4717 (4)	56 (1)
C(15)	−181 (1)	973 (1)	5115 (4)	58 (1)
C(16)	1499 (1)	1453 (1)	3391 (4)	56 (1)

Discussion. Atomic coordinates are listed in Table 1.* A perspective view of the molecule and atom-labeling scheme is shown in Fig. 1. Bond distances, bond angles and selected torsion angles are given in Table 2.

Tetrathiaparabenzenophane (I) has crystallographically imposed $\bar{1}$ molecular symmetry. The four S atoms are necessarily coplanar, and the aromatic moieties constitute two independent pairs of parallel rings (Fig. 1). The pair comprising benzene ring C(2)–C(7) and centrosymmetrically-related atoms has an interplanar spacing of 1·58 (1) Å and makes a dihedral angle of 26·4 (4)° with the planar S_4 system; the corresponding parameters for the C(10)–C(15) ring are 7·54 (1) Å and 45·9 (4)°, respectively. The conformation adopted by molecule (I) thus effectively

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* IUPAC name: *p*-xylene-α,α′-dithiol.

* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39405 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond lengths* (Å), *bond angles* (°) *and selected torsion angles* (°)

S(1)—C(1)	1·809 (3)	S(2)—C(8)	1·801 (3)
S(1)—C(16^{i})	1·794 (3)	S(2)—C(9)	1·797 (3)
C(1)—C(2)	1·506 (3)	C(9)—C(10)	1·519 (3)
C(5)—C(8)	1·505 (3)	C(13)—C(16)	1·502 (3)
C(2)—C(3)	1·385 (3)	C(10)—C(11)	1·383 (3)
C(2)—C(7)	1·373 (3)	C(10)—C(15)	1·379 (3)
C(4)—C(5)	1·391 (3)	C(12)—C(13)	1·385 (3)
C(5)—C(6)	1·369 (3)	C(13)—C(14)	1·382 (3)
C(3)—C(4)	1·381 (3)	C(11)—C(12)	1·388 (3)
C(6)—C(7)	1·386 (4)	C(14)—C(15)	1·383 (4)
C(1)—S(1)—C(16^{i})	101·9 (1)	C(8)—S(2)—C(9)	102·5 (1)
S(1)—C(1)—C(2)	115·2 (2)	S(2)—C(8)—C(5)	116·7 (2)
S(1)—C(16^{i})—C(13^{i})	117·6 (2)	S(2)—C(9)—C(10)	116·9 (2)
C(1)—C(2)—C(3)	121·6 (2)	C(9)—C(10)—C(11)	123·0 (2)
C(1)—C(2)—C(7)	120·4 (2)	C(9)—C(10)—C(15)	119·2 (2)
C(4)—C(5)—C(8)	122·6 (2)	C(12)—C(13)—C(16)	123·3 (2)
C(6)—C(5)—C(8)	119·3 (2)	C(14)—C(13)—C(16)	119·0 (2)
C(2)—C(3)—C(4)	121·2 (2)	C(10)—C(11)—C(12)	121·0 (2)
C(3)—C(4)—C(5)	120·5 (2)	C(11)—C(12)—C(13)	121·1 (2)
C(5)—C(6)—C(7)	121·3 (2)	C(13)—C(14)—C(15)	121·2 (2)
C(6)—C(7)—C(2)	121·1 (2)	C(14)—C(15)—C(10)	121·1 (2)
C(3)—C(2)—C(7)	117·9 (2)	C(11)—C(10)—C(15)	117·9 (2)
C(4)—C(5)—C(6)	118·0 (2)	C(12)—C(13)—C(14)	117·7 (2)
C(3)—C(2)—C(1)—S(1)	77·8 (3)	C(4)—C(5)—C(8)—S(2)	48·8 (3)
C(2)—C(1)—S(1)—C(16^{i})	59·1 (2)	C(5)—C(8)—S(2)—C(9)	49·7 (2)
C(1)—S(1)—C(16^{i})—C(13^{i})	56·2 (2)	C(8)—S(2)—C(9)—C(10)	51·4 (2)
S(1)—C(16^{i})—C(13^{i})—C(12^{i})	35·7 (3)	S(2)—C(9)—C(10)—C(11)	36·9 (3)

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

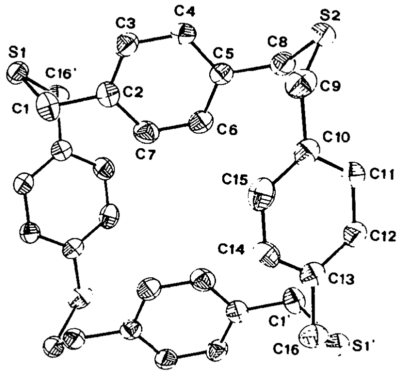

Fig. 1. Perspective view of molecule (I) with atom labeling. Primed atoms are related to the corresponding unprimed ones by inversion through the molecular center at (0,0,0). Thermal ellipsoids are drawn at the 40% probability level.

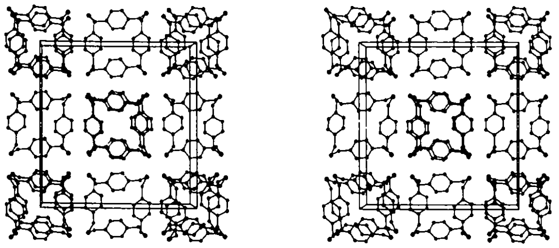

Fig. 2. Stereoview of the molecular packing in compound (I). The origin of the unit cell lies at the upper left corner, with **a** pointing downwards, **b** from left to right, and **c** towards the reader. Hydrogen atoms have been omitted for clarity.

closes up the central cavity, and it will be of interest to determine whether a more favorable conformation for accommodating hydrophobic guest species exists in the peralkylated tetrasulfonium salt.

Each benzene ring and its two attached methylene carbon atoms are coplanar within the limits of experimental error, indicating that the cyclic system is virtually free from intermolecular steric strain. This conclusion is supported by the observed S—C bond distances and C—S—C angles (Table 2), which agree well with those observed in the strain-free molecule 2,6,15,19-tetrathia[7.7]parabenzenophane [C—S 1·819 (3), 1·818 (3), 1·809 (3), 1·802 (4) Å; C—S—C 101·4 (2), 102·9 (2)°] (Pfisterer & Ziegler, 1983). These values are significantly smaller than those in strained systems such as 2,11,20-trithia[3.3.3](1,2,4)-benzeno(1,3,5)benzenophane [C—S from 1·817 (8) to 1·840 (8), av. 1·827 Å; C—S—C 103·9 (3), 103·5 (3), 103·1 (3)°] (Kai, Mizuma, Yasuoka & Kasai, 1983) and 2,11,20-trithia[3.3.3](1,3,5)benzenophane [for the ordered sulfide bridge, S—C 1·821 (7), 1·823 (6) Å; C—S—C 104·7 (3)°] (Hanson & Macaulay, 1972).

A stereoview of the molecular packing in (I) is shown in Fig. 2. The molecular centers constitute a pseudo *F* lattice, and there are no unusual van der Waals contacts.

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