

6,22-Dioxaparazylenyl 2,10,18,26-tetrathia-33,35 diazapentacyclo[27.3.1.1^{4,8}.1^{12,16}.1^{20,24}]-hexatriaconta-4,6,8(36),12,14,16(35),20,22,-24(34),28,30,32-dodecaene

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Key indicators

Single-crystal X-ray study

$T = 293\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.004\text{ \AA}$

R factor = 0.044

wR factor = 0.126

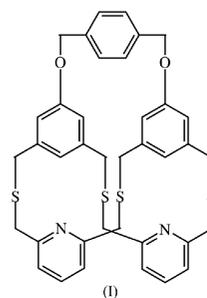
Data-to-parameter ratio = 14.3

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The structure of the title molecule, $\text{C}_{38}\text{H}_{36}\text{N}_2\text{O}_2\text{S}_4$, is stabilized by intramolecular $\text{C}-\text{H}\cdots\text{N}$ hydrogen bond and $\pi-\pi$ interactions. The molecular packing in the crystal is stabilized by $\text{C}-\text{H}\cdots\text{O}$, $\text{C}-\text{H}\cdots\text{S}$, and $\text{C}-\text{H}\cdots\pi$ interactions.

Comment

Cyclophanes are cyclic systems, consisting of at least one aromatic moiety bridged by one or more aliphatic chains (De Ridder *et al.*, 2001). Paracyclophane and other π -electron-rich hydrocarbons possessing a cavity-forming topology are known to form endohedral π -complexes with silver and other soft metal atoms (Addad *et al.*, 1983; Heirtzler *et al.*, 1995; Faust, 1995). Cyclophane derivatives constitute a novel building block for the potent human immunodeficiency virus (HIV) protease inhibitor (Ettmayer *et al.*, 1996). Cyclophane derivatives act catalytically as cholesterol shuttles to accelerate the exchange of free cholesterol between cells and serum lipoproteins (Christian *et al.*, 1999), and also act as potential reversal agents of muscle relaxants by chemical chelation (Cameron *et al.*, 2002). The importance of cyclophane derivatives prompted us to undertake the structure analysis of the title compound, (I).



The structure of (I), with the atom-numbering scheme, is shown in Fig. 1. The $\text{C}-\text{C}$ bond lengths in the benzene and pyridine rings are comparable to the reported mean values of 1.384 (13) and 1.379 (12) \AA , respectively (Allen *et al.*, 1987). The $\text{C}-\text{N}$ bond lengths in the pyridine rings also agree with the reported mean value of 1.337 (12) \AA . The $\text{S}-\text{C}$ and $\text{C}-\text{O}$ distances are comparable to those reported for related structures (Itoh *et al.*, 1999; Weber & Jones, 1983). The exocyclic angles around atoms C13 and C27 show considerable asymmetry, with the angle $\text{O}33-\text{C}13-\text{C}12$ [125.3 (3) $^\circ$] wider than $\text{O}33-\text{C}13-\text{C}14$ [114.5 (3)], and the angle $\text{O}42-\text{C}27-\text{C}28$ [124.1 (3) $^\circ$] wider than $\text{O}42-\text{C}27-\text{C}26$ [115.6 (3) $^\circ$]. This asymmetry may be due to the short contacts $\text{H}12\cdots\text{H}34\text{B}$ (2.14 \AA) and $\text{H}28\cdots\text{H}41\text{B}$ (2.19 \AA). Similar effects have been

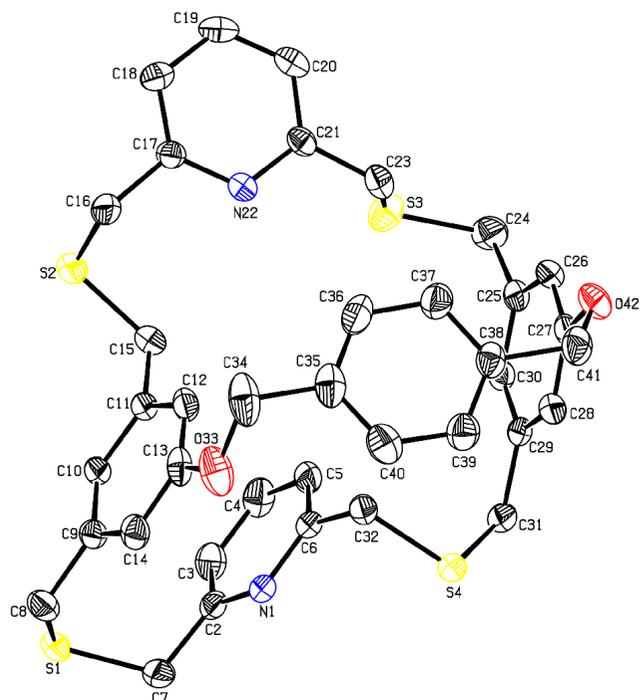


Figure 1
The molecular structure of (I), showing 30% probability displacement ellipsoids. For clarity, H atoms are omitted.

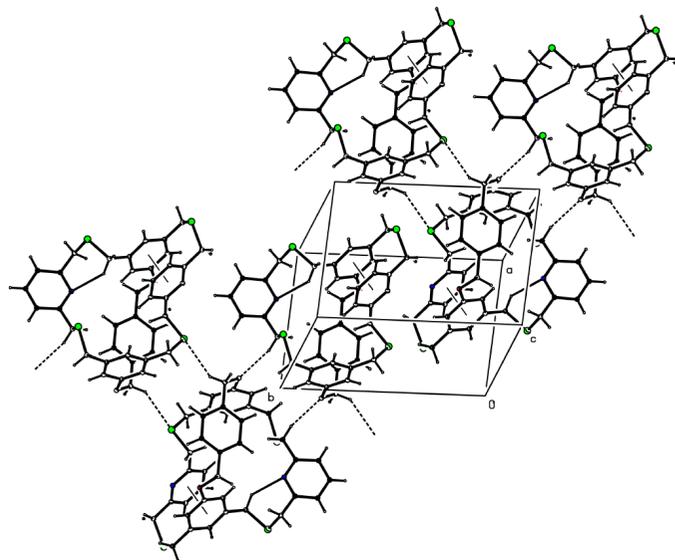


Figure 2
A view of the molecular packing of (I), showing π - π , C-H...O and C-H...S interactions.

observed in a related structure (Bhaskaran *et al.*, 2003). The dihedral angles between the -C-S-C- linkage and the bridged benzene and pyridine rings lie in the ranges 66.3 (1)–87.5 (1)° and 67.9 (1)–89.7 (1)°, respectively.

The molecular structure is influenced by C15–H15B...N22 and π - π interactions between the pyridine ring (N1/C2–C6) and the benzene ring (C9–C14), with a centroid separation of 3.546 (2) Å (Fig. 2). In the crystal structure, C23–H23B...O42ⁱ and C41–H41B...S4ⁱⁱ hydrogen bonds link inversion-related molecules, forming chains along the *b* axis (Fig. 2 and

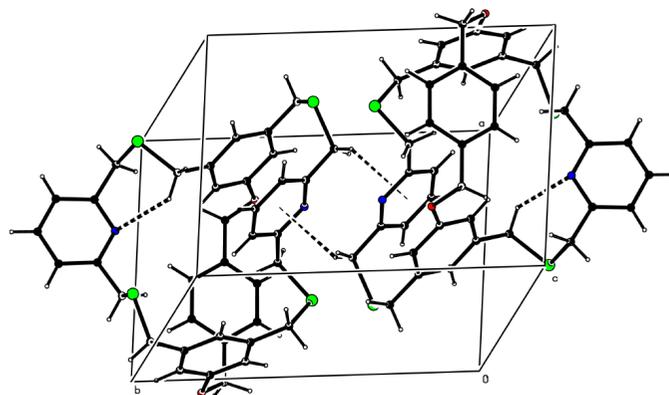


Figure 3
A view of the molecular packing, showing C-H... π interactions.

Table 2). In addition, inversion-related molecules are also linked by weak C-H... π interactions, such that atom H7B is 2.80 Å from the centroid of the pyridine ring (N1/C2–C6) at (1 - *x*, 1 - *y*, 1 - *z*), with a C7–H7B...centroid angle of 136° and a C7...centroid distance of 3.553 (3) Å.

Experimental

A solution containing α,α' -bis[3,5-bis(mercaptomethyl)phenoxy]-*p*-xylene (0.5 mmol) and 2,6-bis(bromomethyl)pyridine (1 mmol) in nitrogen-degassed benzene (100 ml) was added dropwise, over 10–12 h, to a well stirred solution of KOH in EtOH (95%, 850 ml). After the addition was complete, the mixture was stirred for an additional 8 h and then evaporated to dryness. The crude product was purified by column chromatography, using ethyl acetate and hexane (2:8) as eluants, to afford (I). Single crystals of (I) were obtained by recrystallization from ethyl acetate, by slow evaporation.

Crystal data

$C_{38}H_{36}N_2O_2S_4$	$Z = 2$
$M_r = 680.93$	$D_x = 1.340 \text{ Mg m}^{-3}$
Triclinic, <i>P1</i>	Mo $K\alpha$ radiation
$a = 10.2571 (10) \text{ \AA}$	Cell parameters from 25 reflections
$b = 12.3622 (7) \text{ \AA}$	$\theta = 19.7\text{--}28.2^\circ$
$c = 14.2374 (10) \text{ \AA}$	$\mu = 0.32 \text{ mm}^{-1}$
$\alpha = 94.326 (5)^\circ$	$T = 293 (2) \text{ K}$
$\beta = 108.527 (6)^\circ$	Block, colourless
$\gamma = 96.725 (6)^\circ$	$0.30 \times 0.25 \times 0.20 \text{ mm}$
$V = 1687.8 (2) \text{ \AA}^3$	

Data collection

Enraf-Nonius CAD-4 diffractometer	$\theta_{\text{max}} = 25.0^\circ$
ω -2 θ scans	$h = 0 \rightarrow 12$
6283 measured reflections	$k = -14 \rightarrow 14$
5919 independent reflections	$l = -16 \rightarrow 16$
3917 reflections with $I > 2\sigma(I)$	3 standard reflections
$R_{\text{int}} = 0.023$	every 100 reflections
	intensity decay: none

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0668P)^2 + 0.2974P]$
$R[F^2 > 2\sigma(F^2)] = 0.044$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.126$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 0.99$	$\Delta\rho_{\text{max}} = 0.67 \text{ e \AA}^{-3}$
5919 reflections	$\Delta\rho_{\text{min}} = -0.29 \text{ e \AA}^{-3}$
415 parameters	
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

S1—C8	1.797 (3)	N1—C2	1.332 (3)
S1—C7	1.810 (3)	N1—C6	1.349 (3)
S2—C16	1.806 (3)	C13—O33	1.373 (4)
S2—C15	1.811 (3)	C17—N22	1.340 (3)
S3—C23	1.801 (3)	C21—N22	1.337 (3)
S3—C24	1.811 (3)	C27—O42	1.376 (3)
S4—C31	1.798 (3)	O33—C34	1.430 (4)
S4—C32	1.810 (3)	C41—O42	1.423 (4)
O33—C13—C12	125.3 (3)	O42—C27—C26	115.6 (3)
O33—C13—C14	114.5 (3)	O42—C27—C28	124.1 (3)

Table 2
Hydrogen-bonding geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C15—H15 <i>B</i> ...N22	0.97	2.46	3.220 (4)	135
C23—H23 <i>B</i> ...O42 ⁱ	0.97	2.48	3.399 (3)	158
C41—H41 <i>B</i> ...S4 ⁱⁱ	0.97	2.77	3.604 (3)	145

Symmetry codes: (i) $-x, 2 - y, -z$; (ii) $-x, 1 - y, -z$.

H atoms were positioned geometrically and were treated as riding on their parent C atoms, with C—H distances of 0.93 (aromatic) and 0.97 Å (methylene), and a $U_{\text{iso}}(\text{H})$ value of $1.2U_{\text{eq}}(\text{C})$.

Data collection: *CAD-4 EXPRESS* (Enraf-Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PARST* (Nardelli, 1995).

SSN and DV thank the University Grants Commission (UGC), New Delhi, for financial support under the University With Potential For Excellence Programme. VRK thanks the Council of Scientific and Industrial Research (CSIR) for providing a Senior Research Fellowship.

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