Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.125$
$S = 1.222$
5754 reflections
502 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0799P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.650$ e Å^{-3}
$\Delta\rho_{\min} = -0.478$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.113 (5)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected torsion angles (°)*

C11—N1—C2—C3	39.2 (3)
N1—C2—C3—C4	50.4 (3)
C2—C3—C4—N5	−69.9 (2)
C3—C4—N5—C10	−5.7 (3)
C4—N5—C10—C11	53.7 (3)
N5—C10—C11—N1	−2.2 (3)
C2—N1—C11—C10	−69.4 (3)
C11*A*—N1*A*—C2*A*—C3*A*	−41.9 (3)
N1*A*—C2*A*—C3*A*—C4*A*	−49.3 (2)
C2*A*—C3*A*—C4*A*—N5*A*	68.9 (2)
C3*A*—C4*A*—N5*A*—C10*A*	8.7 (3)
C4*A*—N5*A*—C10*A*—C11*A*	−54.1 (3)
N5*A*—C10*A*—C11*A*—N1*A*	−1.5 (3)
C2*A*—N1*A*—C11*A*—C10*A*	75.8 (3)

The H atoms attached to N5 and N5*A* were located from the difference map and were refined with isotropic displacement parameters in the subsequent cycles of refinement. All the other H atoms were fixed using geometrical considerations.

Data collection: R-AXIS image plate software. Cell refinement: R-AXIS image plate software. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1997). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *ZORTEP* (Zsolnai, 1997). Software used to prepare material for publication: *SHELXL*97. Geometrical calculations: *PARST*96 (Nardelli, 1983).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: VJ1098). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1999). C**55**, 1357–1360

2,11-Dithia[3.3.1]paracyclophane, (I), and 2,11-dithia[3.3.2]paracyclophane, (II)†

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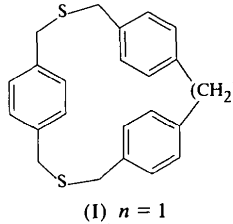
Abstract

In the title compounds [$C_{23}H_{22}S_2$, (I), and $C_{24}H_{24}S_2$, (II)], the thio-bridging chains on either side of the benzene ring (*A*) are oriented *anti* to each other. Ring *A* is located nearly perpendicular to the other benzene rings (*B* and *B*′) to give a short contact between an H atom of ring *A* and the center of ring *B* (*B*′). The thio-bridging moieties in (I) and (II) seem to be almost strain-free.

Comment

In relation to the cyclophanes, thio analogs are interesting substances and the stereochemistry of a few thiocyclophanes has been studied by means of X-ray crystallography (Lai, 1981; Keehn, 1983; Mitchell, 1983; Chan *et al.*, 1986). The title compounds, (I) and (II), are expected to show ring flexibility similar to that



(I) $n = 1$
(II) $n = 2$

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† Alternative names: (I) is 8,15-dithiatetracyclo[15.2.2.$2^{3,6}$.$2^{10,13}$]pentacosa-3,5,10,12,17,19(1),20,22,24-nonaene and (II) is 9,16-dithiatetracyclo[16.2.2.$2^{4,7}$.$2^{11,14}$]hexacosa-4,6,11,13,18,20(1),21,23,25-nonaene.

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of the previously studied [14]paracyclophane. One of the authors (HY) has studied the kinetics of the thermal motion in the benzene rings of (I) and (II) under high pressure using ^1H NMR (Imashiro *et al.*, 1976, 1981). The ^1H NMR spectra showed unusual high-field shifts (6.30 p.p.m.) for the H atoms [H3 and H4 of (I) and H5 and H6 of (II)] in benzene ring *A* (see Figs. 1 and 2). In order to investigate the origin of these shifts in the ^1H NMR spectra, we have determined the crystal structures of (I) and (II).

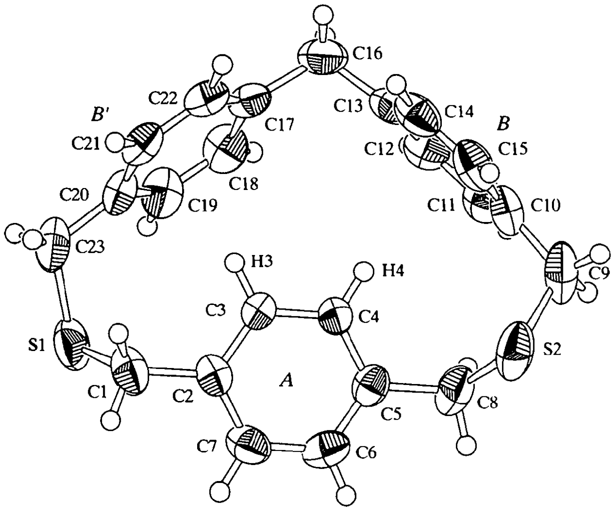

Fig. 1. Molecular structure of (I) showing 50% probability displacement ellipsoids.

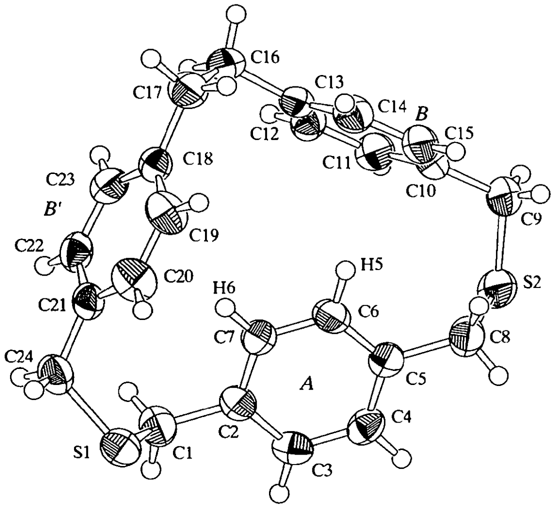

Fig. 2. Molecular structure of (II) showing 50% probability displacement ellipsoids.

In both compounds, the thio-bridging chains $-CH_2S-$ are oriented *anti* to each other across the plane of the benzene ring *A*. The angle between the *B*/*B'* pair of benzene rings is 78.7 (2) in (I) and 92.5 (3)° in (II). In (I), the C3—H3 bond axis of the benzene ring *A* is directed to the center of the benzene ring *B'* with an H3···*B'* distance of 2.63 (2) Å and an approach angle of 85.5 (3)°. In (II), the C6—H5 bond axis of the benzene ring *A* is directed to the center of benzene ring *B* with an H5···*B* distance of 2.72 (2) Å and an approach angle of 79.3 (3)°. The H3···C21 distance of 2.75 (1) Å in (I), and the H5···C15 distance of 2.69 (1) Å in (II) are nearly equal to the sum of van der Waals radii of aromatic H and C atoms (2.77 Å; Bondi, 1964). Molecules (I) and (II) have a chemical twofold axis which exchanges the positions of *B* and *B'* rings. It is evident that the diamagnetic effect of the ring current in *B* and *B'* contributes to the unusual chemical shifts of H3 and H4 in (I) [H5 and H6 in (II)] in solution.

Observed S—C bond lengths [1.806 (3)–1.826 (3) Å] and S—C—C bond angles [112.7 (2)–115.8 (2)°] for (I) and (II) are closer to the values reported for strain-free 2,11,20,29-tetrathia[3.3.3.3]parabenzophenone [S—C 1.812 (4) Å and S—C—C 115.2 (2)° (Pfisterer & Ziegler, 1983)] than for those for the strained 1,9-dithia[2.2]paracyclophane [S—C 1.774 (4) and 1.860 (8) Å, S—C—C 120.0 (3) and 120.8 (3)° (Itoh *et al.*, 1996)]. This observation indicates that the thio-bridging moieties in (I) and (II) are almost strain-free.

Experimental

Compound (I) was prepared from 4,4'-bis(chloromethyl)diphenylmethane and *p*-xylene-α,α'-dithiol in benzene by a previously described method (Imashiro *et al.*, 1976). Recrystallization of (I) from dimethyl ether/*n*-hexane gave colorless prisms (m.p. 492.3–493.2 K). Compound (II) was prepared from 4,4'-bis(chloroethyl)diphenylmethane and *p*-xylene-α,α'-dithiol in benzene. The product was isolated by column chromatography over silica gel using *n*-hexane/ethyl acetate (5:1) as eluate. Recrystallization of (II) from dimethylether/*n*-hexane gave pure compound (II) as colorless prisms (m.p. 435.7–436.2 K). The crystals of (I) and (II) used in the study were obtained by slow diffusion of hexane into dichloromethane solutions.

Compound (I)

Crystal data

$C_{23}H_{22}S_2$
$M_r = 362.55$
Monoclinic
$P2_1/n$
$a = 12.565 (2)$ Å
$b = 10.784 (1)$ Å
$c = 14.512 (1)$ Å
$\beta = 105.716 (8)°$
$V = 1892.8 (3)$ Å^3
$Z = 4$
$D_x = 1.272$ Mg m^{-3}
$D_m = 1.23$ Mg m^{-3}
D_m measured by flotation in aqueous NaI solution

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 13.9$–$15.0°$
$\mu = 0.284$ mm^{-1}
$T = 296.2$ K
Prismatic
0.55 × 0.50 × 0.35 mm
Colorless

Data collection

Rigaku AFC-5*R* diffractometer
ω–2θ scans
Absorption correction:
 ψ scan (North *et al.*, 1968)
 $T_{\min} = 0.873$, $T_{\max} = 0.905$
4772 measured reflections
4574 independent reflections
2880 reflections with $I > \sigma(I)$
$R_{\rm int} = 0.017$
$\theta_{\max} = 27.49°$
$h = 0 \rightarrow 16$
$k = 0 \rightarrow 14$
$l = -18 \rightarrow 18$
3 standard reflections
 every 150 reflections
 intensity decay: none

Refinement

Refinement on F
$R = 0.061$
$wR = 0.054$
$S = 1.341$
2880 reflections
227 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o) + 0.00042|F_o|^2]$
$(\Delta/\sigma)_{\max} = 0.0038$
$\Delta\rho_{\max} = 0.26$ e Å^{-3}
$\Delta\rho_{\min} = -0.30$ e Å^{-3}
Extinction correction: Zachariasen (1967)
Extinction coefficient: 0.055 (3)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °) for (I)*

S1—C1	1.806 (3)	C5—C8	1.511 (3)
S1—C23	1.826 (3)	C9—C10	1.505 (4)
S2—C8	1.825 (3)	C13—C16	1.509 (4)
S2—C9	1.812 (3)	C16—C17	1.511 (4)
C1—C2	1.504 (3)	C20—C23	1.502 (4)
C1—S1—C23	102.8 (2)	C9—C10—C15	121.3 (3)
C8—S2—C9	102.9 (2)	C12—C13—C16	120.0 (2)
S1—C1—C2	115.8 (2)	C14—C13—C16	122.9 (3)
C1—C2—C3	121.2 (2)	C13—C16—C17	111.7 (2)
C1—C2—C7	121.2 (2)	C16—C17—C18	121.7 (3)
C4—C5—C8	121.5 (2)	C16—C17—C22	121.1 (2)
C6—C5—C8	120.6 (2)	C19—C20—C23	121.7 (3)
S2—C8—C5	115.6 (2)	C21—C20—C23	119.9 (3)
S2—C9—C10	115.7 (2)	S1—C23—C20	112.7 (2)
C9—C10—C11	121.1 (3)		

Compound (II)

Crystal data

$C_{24}H_{24}S_2$
$M_r = 376.57$
Monoclinic
$P2_1/n$
$a = 14.345$ (3) Å
$b = 7.585$ (3) Å
$c = 19.248$ (2) Å
$\beta = 105.57$ (1)°
$V = 2017.4$ (9) Å^3
$Z = 4$
$D_x = 1.240$ Mg m^{-3}
$D_m = 1.20$ Mg m^{-3}
D_m measured by flotation in aqueous NaI solution
Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 23 reflections
$\theta = 13.3$–$14.8°$
$\mu = 2.401$ mm^{-1}
$T = 298.2$ K
Prismatic
0.40 × 0.30 × 0.15 mm
Colorless

Data collection

Rigaku AFC-5*R* diffractometer
ω–2θ scans
Absorption correction:
 ψ scan (North *et al.*, 1968)
 $T_{\min} = 0.478$, $T_{\max} = 0.698$
2966 measured reflections
2863 independent reflections
2182 reflections with $I > \sigma(I)$
$R_{\rm int} = 0.015$
$\theta_{\max} = 60.08°$
$h = 0 \rightarrow 16$
$k = 0 \rightarrow 7$
$l = -21 \rightarrow 20$
3 standard reflections
 every 150 reflections
 intensity decay: 4.1%

Refinement

Refinement on F
$R = 0.042$
$wR = 0.044$
$S = 1.484$
2182 reflections
236 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o) + 0.00029|F_o|^2]$
$(\Delta/\sigma)_{\max} = 0.0005$
$\Delta\rho_{\max} = 0.19$ e Å^{-3}
$\Delta\rho_{\min} = -0.21$ e Å^{-3}
Extinction correction: Zachariasen (1967)
Extinction coefficient: 0.059 (4)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 2. *Selected geometric parameters (Å, °) for (II)*

S1—C1	1.819 (3)	C9—C10	1.506 (4)
S1—C24	1.822 (3)	C13—C16	1.510 (4)
S2—C8	1.821 (3)	C14—C15	1.389 (4)
S2—C9	1.816 (3)	C16—C17	1.520 (4)
C1—C2	1.505 (3)	C21—C24	1.497 (4)
C5—C8	1.509 (3)	C22—C23	1.387 (4)
C6—C7	1.382 (4)		
C1—S1—C24	103.7 (1)	C9—C10—C15	121.0 (3)
C8—S2—C9	102.3 (1)	C12—C13—C16	119.2 (3)
S1—C1—C2	114.2 (2)	C14—C13—C16	122.7 (2)
C1—C2—C3	121.4 (3)	C13—C16—C17	116.3 (3)
C1—C2—C7	120.7 (2)	C16—C17—C18	116.2 (2)
C4—C5—C6	118.4 (2)	C17—C18—C19	120.9 (3)
C4—C5—C8	121.3 (2)	C17—C18—C23	121.9 (3)
C6—C5—C8	120.3 (2)	C20—C21—C24	121.2 (3)
S2—C8—C5	114.2 (2)	C22—C21—C24	121.1 (3)
S2—C9—C10	115.3 (2)	S1—C24—C21	114.7 (2)
C9—C10—C11	121.1 (3)		

Table 3. *Comparison of S—C bond lengths (Å), and C—S—C and S—C—C bond angles (°) observed for (I), (II), (III) and (IV)*

	S—C	C—S—C	S—C—C
(I)	1.826 (3), 1.825 (3)	102.9 (2), 102.8 (2)	115.8 (2), 115.7 (2)
	1.812 (3), 1.806 (3)		115.6 (2), 112.7 (2)
(II)	1.822 (3), 1.821 (3)	103.7 (1), 102.3 (1)	115.3 (2), 114.7 (2)
	1.819 (3), 1.816 (3)		114.2 (2), 114.2 (2)
(III)	1.812 (4)	101.2 (2)	115.2 (2)
(IV)	1.860 (8), 1.774 (4)	103.4 (3)	120.8 (3), 120.0 (3)

H atoms were included in the cycles of least-squares calculations, where the coordinates of the H atoms were fixed to those obtained in the penultimate calculation.

For both compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1992). Program(s) used to solve structures: *SIR*88 (Burla *et al.*, 1989) for (I); *DIRDIF*92 (*PATTY*; Beurskens *et al.*, 1992) for (II). For both compounds, program(s) used to refine structures: *TEXSAN*; software used to prepare material for publication: *TEXSAN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1006). Services for accessing these data are described at the back of the journal.

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trans-(6-Bromo-2-cyclohexen-1-yl)-pyridinium bromide

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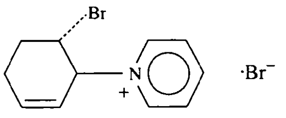
(*Received 6 January 1999; accepted 30 March 1999*)

Abstract

The title compound, $C_{11}H_{13}BrN^+\cdot Br^-$, was prepared by bromination of 1,3-cyclohexadiene in the presence of stoichiometric amounts of bromine and pyridine. Bromine and pyridine are found to add by *anti* 1,2-addition, with pyridine occupying the allylic position. The bromide resides relatively close [3.490 (1) Å] to the covalent bromine, whereas it is 4.232 (5) Å from the nearest nitrogen cation.

Comment

Several reports concerning the structure of the products of bromination of 1,3-cyclohexadiene are in disagreement (Hassel & Lunde, 1950; Heasley *et al.*, 1973; Khedekar, 1997; McMillen & Grutzner, 1994; Lund, 1950). The first-formed dibromocyclohexenes are unstable liquids which undergo rearrangements at room temperature. Therefore, the bromination was conducted in the presence of pyridine at low temperature, and afforded the title compound, (I). Its structure was determined in order to establish the stereochemistry of addition of nucleophiles during the initial steps of bromination of 1,3-dienes. Because the nucleophile (pyridine) differs from the electrophile (bromine), the structure establishes the regiochemistry of the addition as well.



(I)

The structure shown in Fig. 1 demonstrates that the product is formed by *anti* 1,2-addition of the elements of bromine and pyridine across one of the double bonds of the diene. The pyridine attaches to the allylic-C atom. The pyridinium moiety is essentially planar and resembles that found in other *N*-alkylpyridinium derivatives (van Havere *et al.*, 1982), with relatively short (about 1.36 Å) carbon–carbon bonds and bond angles all near 120°. Bond distances and angles in the cyclohexene moiety are close to those in cyclohexene (Chiang & Bauer, 1969). For example, C1, C2, C3 and C4 are coplanar. Interior bond angles about the C=C double bond average 123.1° (123.5° in cyclohexene),

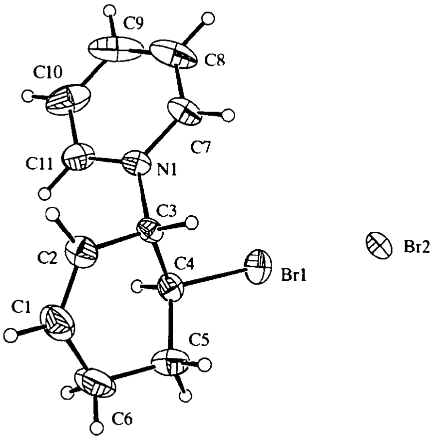


Fig. 1. *ORTEP*II (Johnson, 1976) representation showing the atom-numbering scheme with displacement ellipsoids at the 30% probability level.