For data collection, a scan width of $(1.00 + 0.30\tan\theta)^\circ$ (in ω) and a scan speed of 16.0° min^{-1} were used. A colorless prism crystal was mounted on a glass fiber. Cell constants and an orientation matrix for data collection were obtained from a least-squares refinement. The structure was solved by direct methods (*SHELXS*86; Sheldrick, 1985) and expanded using Fourier techniques (*DIRDIF*; Beurskens *et al.*, 1992). The non-H atoms were refined anisotropically by full-matrix least squares. H atoms were placed in calculated positions (C—H 0.96 Å), assigned fixed isotropic displacement parameters and allowed to ride on their respective parent atoms. The contributions of these H atoms were included in the structure-factor calculations. The C(29) H atoms [s.o.f.'s for H(29*B*) and H(29*C*) were fixed at 0.6 and 0.4, respectively], and the C(30) and C(30′) H atoms [s.o.f.'s for atoms H(30*A*)–H(30*C*) and H(30*D*)–H(30*F*) were fixed at 0.6 and 0.4, respectively] were found to be highly disordered. Neutral atom scattering factors were taken from Cromer & Waber (1974). Anomalous dispersion effects were included in F_{calc} (Ibers & Hamilton, 1964). The values for the mass attenuation coefficients are those of Creagh & Hubbel (1992). All calculations were performed on a PC586 using the *SHELXTL-Plus* (Sheldrick, 1991) program package.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1985, 1992). Program(s) used to refine structure: *SHELXTL-Plus*. Software used to prepare material for publication: *SHELXL*93 (Sheldrick, 1993).

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: NA1249). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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4,6,10,12-Tetraphenyl-7,9-dioxa-1,3-dithiacyclododecane

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Abstract

The title compound, $C_{32}H_{32}O_2S_2$, is a mixed oxa–thia crown macrocycle. The molecule has all heteroatoms at side positions of a quadrangular skeleton. Both sulfur and oxygen conformational arrangements are virtually the same.

Comment

Sulfur coronands possess solid-state conformations that differ significantly from those of their oxygen counterparts and yield metal complexes with unexpected reactivity and redox properties (Cooper, 1988). In this context, we have isolated the title compound, (I), which, in addition to its potential as a transition metal complexing agent, is an interesting candidate for conformational studies since it contains both S and O heteroatoms in a novel arrangement.

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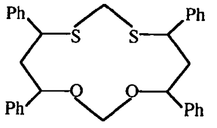

(I)

The ring skeleton has an approximate twofold axis through atoms C2 and C8, and can be denoted as quadrangular with sides composed of *anti* segments and each of the four corners formed by two *gauche* torsion angles of the same sign. The same conformation was found for cyclododecane (Dunitz & Shearer, 1960). Both S and O atoms are located at side positions of the quadrilateral, as has been reported for the solution structure of the oxygen analogue 1,3,7,9-tetraoxacyclododecane (Borgen & Dale, 1974) determined by NMR spectroscopy. In contrast, the selenium analogue 1,3,7,9-tetraselenacyclododecane contains Se atoms at both side and corner positions (Batchelor *et al.*, 1989). Since the ring skeleton has only four C—C bonds (all in *gauche* arrangements) and the cyclic structure requires at least eight *gauche* bonds, four of the C—*X* bonds (*X* = O, S) are forced to adopt *gauche* arrangements. All four *X*—C—*X*—C sequences display *gauche* torsion angles, but none of the four C—*X*—C—C sequences display this arrangement. The preference for *gauche* arrangements in the *X*—C—*X*—C units is interpreted as a manifestation of heteroatom anomeric effects, as has been noted in oxygen (Dale, 1974) and selenium (Batchelor *et al.*, 1989) coronands containing 1,3-dioxa groupings.

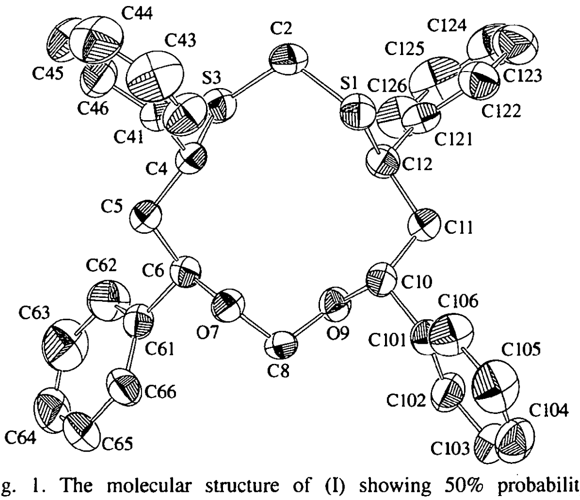

Fig. 1. The molecular structure of (I) showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

Experimental

Stereoisomeric 1,3-diphenyl-3-mercapto-1-propanol (0.5 g, 2.05 mmol; Flores-Vela, 1996), paraformaldehyde (0.27 g, 9 mmol), a few crystals of *p*-toluenesulfonic acid and 10 ml of water were mixed in a 25 ml round-bottomed flask. The mixture was heated so that the water distilled slowly. When about half of the water had distilled, 10 ml of water was added and the distillation was continued. This procedure was repeated twice. The residue was extracted twice with 20 ml portions of ether. The combined ether layers were washed once with dilute aqueous potassium carbonate, dried over anhydrous potassium carbonate, filtered and concentrated to give 4.9 g of the crude product which consisted mainly of a mixture of *cis*- and *trans*-4,6-diphenyl-1,3-oxathiane. Fractional crystallization from ethyl acetate afforded 0.84 g (19.5% yield) of the title heterocycle (m.p. 546.5–547.0 K).

Crystal data

$C_{32}H_{32}O_2S_2$
$M_r = 512.70$
Monoclinic
$P2_1/a$
$a = 16.179\,(2)$ Å
$b = 10.992\,(2)$ Å
$c = 16.695\,(2)$ Å
$\beta = 106.42\,(1)^\circ$
$V = 2847.9\,(7)$ Å^3
$Z = 4$
$D_x = 1.196$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 13$–18°
$\mu = 0.213$ mm^{-1}
$T = 293\,(2)$ K
Plate
0.45 × 0.40 × 0.12 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
8214 measured reflections
7180 independent reflections
3030 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.132$
$\theta_{\rm max} = 28.46^\circ$
$h = -21 \rightarrow 0$
$k = -14 \rightarrow 0$
$l = -21 \rightarrow 22$
3 standard reflections frequency: 60 min intensity decay: 0.7%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0457$
$wR(F^2) = 0.1828$
$S = 0.684$
7180 reflections
327 parameters
H atoms riding with a group $U_{\rm iso}$

$w = 1/[\sigma^2(F_o^2) + (0.1438P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.052$
$\Delta\rho_{\rm max} = 0.256$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.251$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

S1—C2	1.804 (3)	O9—C8	1.404 (3)
S1—C12	1.822 (3)	O9—C10	1.434 (3)
S3—C2	1.796 (3)	C4—C5	1.527 (4)
S3—C4	1.823 (3)	C5—C6	1.524 (4)
O7—C8	1.403 (3)	C10—C11	1.523 (4)
O7—C6	1.430 (3)	C11—C12	1.530 (4)
C2—S1—C12	101.19 (13)	C6—C5—C4	113.4 (2)
C2—S3—C4	101.02 (14)	O7—C6—C5	105.7 (2)
C8—O7—C6	114.0 (2)	O7—C8—O9	113.1 (2)
C8—O9—C10	114.6 (2)	O9—C10—C11	105.5 (2)
S3—C2—S1	116.2 (2)	C10—C11—C12	113.8 (2)
C5—C4—S3	107.8 (2)	C11—C12—S1	108.0 (2)
C4—S3—C2—S1	58.2 (2)	C6—O7—C8—O9	74.9 (3)
C12—S1—C2—S3	58.5 (2)	C10—O9—C8—O7	79.4 (3)

C2—S3—C4—C5	−162.9 (2)	C8—O9—C10—C11	−167.0 (2)
S3—C4—C5—C6	71.8 (3)	O9—C10—C11—C12	64.0 (3)
C8—O7—C6—C5	−163.7 (2)	C10—C11—C12—S1	71.8 (2)
C4—C5—C6—O7	67.3 (3)	C2—S1—C12—C11	−161.9 (2)

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1992). Cell refinement: *CAD-4 EXPRESS*. Data reduction: local program. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *PC-ORTEP* (Schmid & Brueggemann, 1990). Software used to prepare material for publication: *SHELXL93*.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: CF1105). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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N-Methylmorpholinium Chloride

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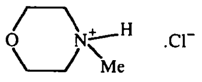
Abstract

The hydrochloride salt of *N*-methylmorpholine, $C_5H_{12}NO^+.Cl^-$, was isolated from water as deliquescent crystals. There are hydrogen bonds between the halide ions and the morpholinium protons. Differences in the lattice dimensions of the hydrochloride and the hydrobromide are commensurate with the radii of the halide ions.

Comment

As a result of our interest in low-dimensional magnetic lattices, we have been studying complexes of the family $(LH)_2MX_4$, where M is a 2+ first-row transition metal ion, X = Cl, Br and L is an organic base. These compounds are known to pack in the crystal lattice such that low-dimensional magnetic lattices, arising from van der Waals interactions between the MX_4 ions, are frequently obtained (for example, Place & Willett, 1987*a*,*b*). The nature of these contacts is determined by *L*. To determine whether *N*-methylmorpholine might be suitable for the preparation of these types of complexes, we determined the structure of its hydrochloride salt, (I).



(I)

N-Methylmorpholinium chloride crystallized from water as large blocks in space group $P2_1/m$, the same as the related compounds *N*-methylmorpholine *N*-oxide (Maia, Peguy & Perez, 1981) and *N*,*N*-dimethylmorpholinium iodide (Sishen & Geller, 1987). The molecular structure is shown in Fig. 1.

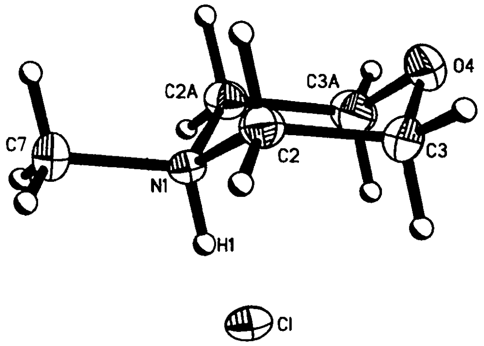


Fig. 1. The molecular structure of *N*-methylmorpholinium chloride showing 50% probability ellipsoids.

The position of the N—H proton was allowed to refine with fixed displacement parameters. The structure shows moderately strong hydrogen bonding between the halide ion and the morpholinium N—H proton. The associated distances and angles are: Cl···H—N 3.04 (1) Å and 178.4 (2)°. The packing diagram (Fig. 2) shows that the N—H···Cl hydrogen bonds are aligned roughly parallel to the *c* axis.

Unit-cell parameters and a partial data set were also collected for the corresponding bromide salt which were

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