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4,4'-Dimethoxy-2,2'-[dithiobis(o-phenylene-nitrilomethylidyne)]diphenol

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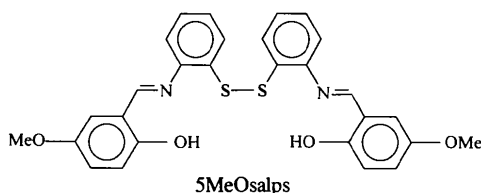
Abstract

The molecule of the title compound, $C_{28}H_{24}N_2O_4S_2$, sits on a crystallographic twofold axis that bisects the S—S bond. The S—S distance is 2.021 (1) Å and the C—S—S—C torsion angle is −83.1 (1)°.

Comment

In recent years, the synthesis and study of new organic ligands containing the R—S—S—R group and their complexes with metals containing the metal–sulfur bond has progressed considerably (West & Pannell, 1989; Manzur *et al.*, 1989; Gon, You, Xu, Yu & Ju, 1991). This interest is probably based on the relevancy of the research to certain redox processes in metalloenzymes and metalloproteins. The disulfide bond in chemical systems has been studied widely, both experimentaly and theoretically. Apart from the intrinsic chemical value of these studies, they also help to shed light on the behaviour of many biologically important molecules that contain disulfide links. The chemical, physical and other properties of disulfides are intimately linked to the torsion angle R—S—S—R' (φ).

There have been a number of in-depth theoretical studies on prototype molecules, *e.g.* H_2S_2 (Marsden & Smith, 1988; Rauk, 1984), Me—S—S—Me (Rauk, 1984) and Et—S—S—Et (Ohsaku & Allinger, 1988). The 'natural' S—S dihedral angle for strain-free disulfides is well established as 80–85°. In this paper we describe the synthesis and molecular structure of a new ligand containing an R—S—S—R group: 4,4'-dimethoxy-1,1'-[dithiobis(o-phenylenenitrilomethylidyne)]diphenol [designated 5MeOsalps, after a 'common' type of name of this compound: *N,N'*-dithiobis(o-phenylene)bis(5-methoxysalicylideneamine)]. Metal complexes of this ligand are described elsewhere.

5MeOsalps

The S—S distance is 2.021 (1) Å. The intermediate value for the same group in Fe(salps)Cl is 2.046 (5) Å (Bertrand & Eller, 1974) and that in [Ni(salps)MeOH]MeOH is 2.006 (1) Å (Manzur *et al.*, 1989). The C—S distance is 1.778 (2) Å and the S—S—C angle is 104.4 (1)°. The torsion angle C—S—S—C is −83.1 (1)°. The N1—C7 bond length [1.274 (2) Å] is of the same order as those found for imino groups of the compounds salTPA {salTPA = 2-[2-(1*H*-indol-3-yl)ethyl]iminomethylphenol (Rodríguez *et al.*, 1987)} and 3'-MeOsalTPA (Martín-Zarza *et al.*, 1988). The C—N=C—C torsion angle is 176.2 (1)° and the dihedral angle between the planes of the aromatic rings is 28.7 (1)°.

An intramolecular hydrogen bond is observed between the O atom of the hydroxy group and the iminic N atom. The N—O distance is 2.647 (2) Å. The packing of the molecules in the crystal involves van der Waals forces.
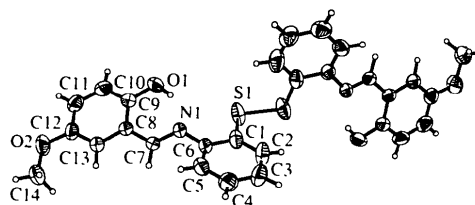

Fig. 1. A view of the molecule showing the atomic numbering scheme. Displacement ellipsoids are plotted at the 50% probability level.

Experimental

for 2 h. On cooling, the resulting yellow solid was filtered, washed with cold ethanol and dried. Crystals suitable for X-ray crystallography were grown by liquid–vapour diffusion, using chloroform as a solvent and *n*-hexane as a precipitant.

Crystal data

$C_{28}H_{24}N_2O_4S_2$	Mo $K\alpha$ radiation
$M_r = 516.61$	$\lambda = 0.71073$ Å
Monoclinic	Cell parameters from 25
$C2/c$	reflections
$a = 24.166\,(3)$ Å	$\theta = 6–18°$
$b = 8.903\,(3)$ Å	$\mu = 0.248$ mm^{-1}
$c = 11.840\,(3)$ Å	$T = 293\,(2)$ K
$\beta = 95.074\,(3)°$	Prism
$V = 2537.4\,(2)$ Å^3	$0.4 \times 0.2 \times 0.1$ mm
$Z = 4$	Colourless
$D_x = 1.352$ Mg m^{-3}	

Data collection

Enraf–Nonius CAD-4	$R_{int} = 0.032$
diffractometer	$\theta_{max} = 25.25°$
$\omega–2\theta$ scans	$h = -9 \rightarrow 28$
Absorption correction:	$k = -10 \rightarrow 9$
none	$l = -14 \rightarrow 14$
4576 measured reflections	1 standard reflection
2266 independent reflections	frequency: 60 min
1970 observed reflections	intensity decay: none
$[I > 2\sigma(I)]$	

Refinement

Refinement on F	$(\Delta/\sigma)_{max} = -0.368$
$R = 0.039$	$\Delta\rho_{max} = 0.131$ e Å^{-3}
$wR = 0.065$	$\Delta\rho_{min} = -0.265$ e Å^{-3}
$S = 0.879$	Extinction correction: none
1913 reflections	Atomic scattering factors
211 parameters	from *International Tables*
All H-atom parameters	*for X-ray Crystallography*
refined	(1974, Vol. IV, Table
$w = 1/[\sigma^2(F) + 0.004623F^2]$	2.3.1)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
S1	0.45929 (2)	0.04313 (5)	0.72175 (5)	0.0704 (2)
O1	0.30660 (6)	0.10293 (17)	0.76474 (9)	0.0616 (4)
O2	0.12317 (5)	0.16347 (17)	0.46009 (12)	0.0704 (4)
N1	0.35518 (5)	−0.04952 (14)	0.60894 (10)	0.0433 (4)
C1	0.45311 (7)	−0.1016 (2)	0.61794 (15)	0.0538 (5)
C2	0.49739 (9)	−0.1833 (3)	0.5821 (2)	0.0727 (7)
C3	0.48888 (9)	−0.2943 (2)	0.50218 (19)	0.0733 (8)
C4	0.43610 (9)	−0.3274 (2)	0.45575 (16)	0.0657 (7)
C5	0.39166 (8)	−0.2459 (2)	0.48992 (13)	0.0551 (5)
C6	0.39946 (6)	−0.13247 (16)	0.56950 (12)	0.0443 (5)
C7	0.31176 (6)	−0.02478 (17)	0.54247 (11)	0.0422 (5)
C8	0.26354 (6)	0.05113 (15)	0.57821 (12)	0.0421 (4)
C9	0.26244 (7)	0.11268 (19)	0.68706 (12)	0.0477 (5)
C10	0.21540 (8)	0.1892 (2)	0.71500 (14)	0.0588 (6)
C11	0.17011 (7)	0.2025 (2)	0.63819 (15)	0.0589 (6)
C12	0.17052 (7)	0.14122 (19)	0.53056 (14)	0.0518 (5)
C13	0.21694 (7)	0.06702 (18)	0.50053 (13)	0.0466 (5)
C14	0.12104 (9)	0.0993 (3)	0.35086 (17)	0.0688 (7)

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

S1—S1^i	2.021 (1)	C3—C4	1.375 (3)
S1—C1	1.778 (2)	C4—C5	1.386 (3)
O1—C9	1.349 (2)	C5—C6	1.383 (2)
O2—C12	1.370 (2)	C7—C8	1.442 (2)
O2—C14	1.411 (3)	C8—C9	1.403 (2)
N1—C6	1.413 (2)	C8—C13	1.397 (2)
N1—C7	1.274 (2)	C9—C10	1.390 (3)
C1—C2	1.391 (3)	C10—C11	1.365 (2)
C1—C6	1.398 (2)	C11—C12	1.387 (2)
C2—C3	1.372 (3)	C12—C13	1.375 (2)
S1—S1^i—C1^i	104.40 (7)	N1—C7—C8	122.8 (1)
C12—O2—C14	117.4 (2)	C7—C8—C13	118.6 (1)
C6—N1—C7	119.5 (1)	C7—C8—C9	122.3 (1)
S1—C1—C6	116.4 (1)	C9—C8—C13	119.1 (1)
S1—C1—C2	124.7 (1)	O1—C9—C8	121.5 (2)
C2—C1—C6	118.8 (2)	C8—C9—C10	119.5 (1)
C1—C2—C3	121.0 (2)	O1—C9—C10	118.9 (1)
C2—C3—C4	120.5 (2)	C9—C10—C11	120.6 (2)
C3—C4—C5	119.1 (2)	C10—C11—C12	120.5 (2)
C4—C5—C6	121.3 (2)	O2—C12—C11	115.4 (2)
C1—C6—C5	119.3 (2)	C11—C12—C13	119.9 (2)
N1—C6—C5	123.0 (1)	O2—C12—C13	124.6 (2)
N1—C6—C1	117.6 (1)	C8—C13—C12	120.5 (1)
S1^i—S1—C1—C2	−4.5 (2)	C1—S1—S1^i—C1^i	−83.1 (1)
S1^i—S1—C1—C6	176.0 (1)	C6—N1—C7—C8	176.2 (1)

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1—H10$\cdots$N1	0.89 (3)	1.87 (2)	2.647 (2)	144 (2)
C2—H2$\cdots$S1^i	0.88 (3)	2.72 (3)	3.181 (2)	114 (2)
C3—H3$\cdots$O2^{ii}	0.96 (3)	2.54 (3)	3.348 (3)	142 (2)
C7—H7$\cdots$O1^{iii}	0.97 (3)	2.39 (3)	3.353 (2)	172 (1)

Symmetry codes: (i) $1 - x, y, \frac{3}{2} - z$; (ii) $\frac{1}{2} + x, y - \frac{1}{2}, z$; (iii) $x, -y, z - \frac{1}{2}$.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1995). Program(s) used to refine structure: *SHELX76* (Sheldrick, 1976). Molecular graphics: *PLUTO* (Motherwell & Clegg, 1978). Molecular geometry calculations: *PARST* (Nardelli, 1983).

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Fig. 1. Displacement ellipsoid plot (50% probability) of benzyl 2-acetamido-4-azido-3-O-benzoyl-6-O-(tert-butyldiphenylsilyl)-2,4-dideoxy-β-D-glucopyranoside perpendicular to the glucose ring.

Benzyl 2-Acetamido-4-azido-3-O-benzoyl-6-O-(tert-butyldiphenylsilyl)-2,4-dideoxy-β-D-glucopyranoside

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Abstract

The title compound, $C_{38}H_{42}N_4O_6Si$, is a key intermediate in the preparation of inhibitors for bovine β-1,4-galactosyl transferase. The configuration of the sugar was as expected. Libration of the *tert*-butyldiphenylsilyl group about an axis normal to the glucose ring is not coupled to the glucose. Intermolecular hydrogen bonding at the acetamido group leads to a sixfold screw axis.

Comment

During a recent study of inhibitors of bovine β-1,4-galactosyl transferase, acceptor analogues were prepared by a sequence of reactions starting from benzyl *N*-acetyl-β-D-galactosaminide. The title compound, (I), is a key intermediate in this sequence, representing the stage at which the configuration is reversed to give the required glucosaminide products (Field, Neville, Smith & Ferguson, 1994). The stereochemistry was found to be as expected, confirming the validity of the reaction sequence.
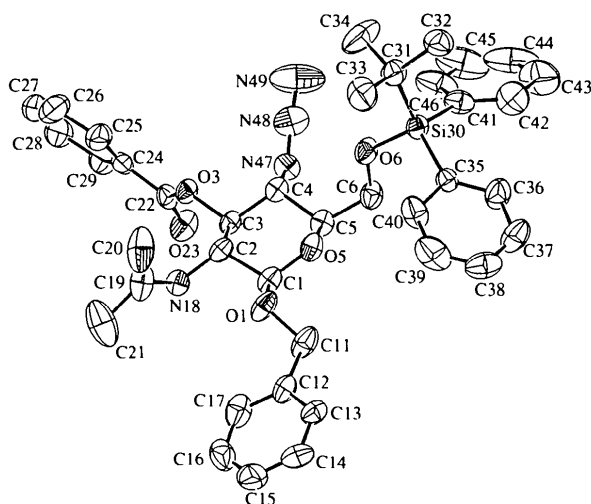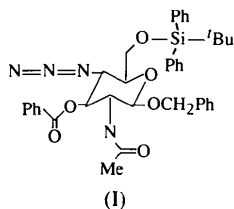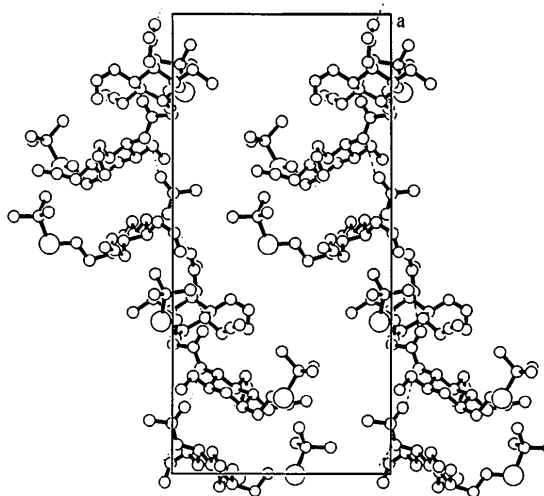

Fig. 2. Packing diagram showing the hydrogen bonds (O20···N18′) forming the sixfold screw axis parallel to *c*. Phenyl groups have been omitted for clarity.
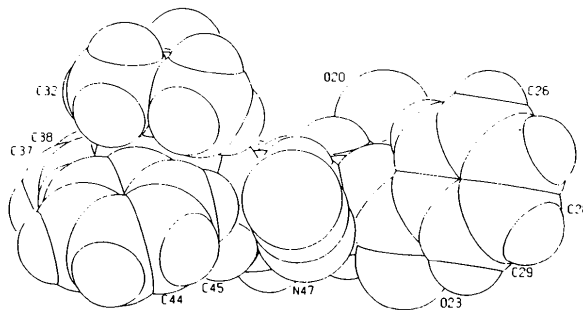
(I)

Fig. 3. Space-filling diagram looking from N49 towards C15, showing the cleft in the molecule.