

O(12)···O(13)	2.828 (2)	O(32)···O(33)	2.856 (2)	2.711
O(13)···O(14)	2.686 (2)	O(33)···O(34)	2.737 (2)	2.838
O(15)···O(16)	2.852 (2)	O(35)···O(36)	2.847 (2)	2.868

* Ollis, James, Angyal & Pojer (1978).

Table 5. Puckering parameters (Cremer & Pople, 1975) for the pyranose rings of the two symmetry-independent molecules of (I)

	Molecule A		Molecule B	
	Ring containing:		Ring containing:	
	O(5)	O(15)	O(25)	O(35)
Q (Å)	0.538	0.531	0.556	0.539
q ₂ (Å)	0.080	0.074	0.106	0.085
q ₃ (Å)	0.532	0.526	0.546	0.532
φ ₂ (°)	314	309	289	306
θ (°)	8.53	8.04	11.0	9.10

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1991). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1989). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *TEXSAN LS*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *TEXSAN FINISH*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: SH1108). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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α,α-galacto-Trehalose†

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Abstract

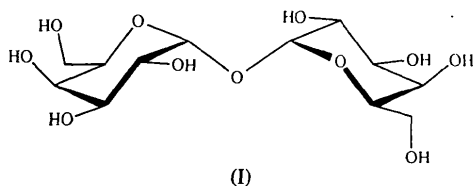
The low-temperature X-ray structure of α,α-galacto-trehalose (α-D-galactopyranosyl α-D-galactopyranoside, C₁₂H₂₂O₁₁) is reported. Each galactopyranosyl residue in the molecule has the ⁴C₁ conformation. The molecule does not possess any internal crystallographic symmetry, although the conformational differences between the two halves of the molecule are almost negligible. The molecules are linked by a large number of hydrogen bonds to form a complex three-dimensional network.

Comment

Shallenberger (1963) attributed the low intensity of the sweetness of 'crystal' D-galactose, which is only approximately half as sweet as D-glucose, to an intramolecular hydrogen bond between its axial C(4) hydroxy group and its ring O atom. IR studies (Shallenberger, 1963) suggested this and it was also observed that as the temperature is raised, D-galactose increases in sweet-

† Crystal Structures of Trehalose Derivatives, Part 11. For Part 10, see Linden & Lee (1995).

ness twice as fast as D-glucose, so that the two sugars eventually approach the same sweetness value. This observation is consistent with the expectation that raising the temperature would sever the intramolecular hydrogen bond, thus allowing C(4)—OH to function as AH of the Shallenberger AH,B glucophore (Shallenberger & Acree, 1967). We are interested, therefore, in the crystal structures of D-galactopyranosyl compounds, and in particular that of α,α -galacto-trehalose, (I).



A view of (I), showing the displacement ellipsoids and the atomic numbering, is given in Fig. 1. The figure depicts the correct absolute configuration of the molecule which was assigned to agree with that of its known precursor (Birch & Richardson, 1970). All bond lengths and angles (Table 2) are within expected ranges and generally agree with the corresponding values in other α,α -trehalose analogues and other sugars. The C—O bond lengths associated with the anomeric C atoms and the ring O atoms show systematic trends similar to those observed in other α -pyranose sugars (Berman, Chu & Jeffrey, 1967).

The two D-galactopyranosyl residues of (I) each have approximate C_2 symmetry. The conformational differences between the two halves are very slight. The torsion angles about the glycosidic linkage differ

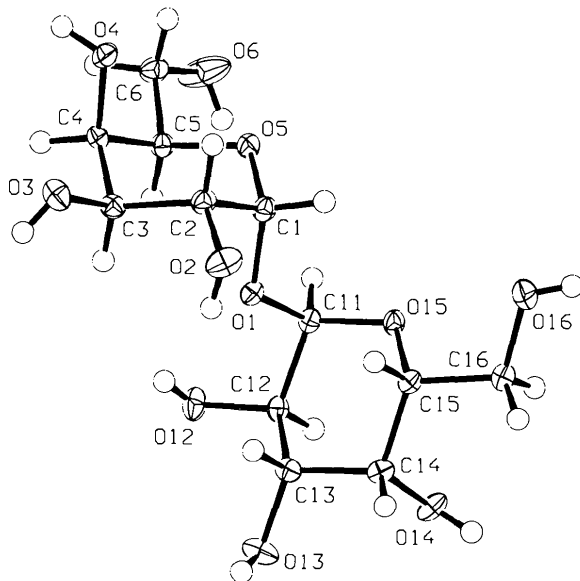


Fig. 1. View of the molecule of (I) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by spheres of arbitrary size.

by only 4° [$O(5)—C(1)—O(1)—C(11) = 66.2(2)$ and $O(15)—C(11)—O(1)—C(1) = 62.4(2)^\circ$]. Similar small differences ($<2^\circ$) in the glycosidic torsion angles are observed in α,α -allo-trehalose (Linden & Lee, 1995) and anhydrous α,α -trehalose (Jeffrey & Nanni, 1985). In α,α -trehalose dihydrate (Brown *et al.*, 1972), where these angles are 74.8 and 61.7° , respectively, the pyranosyl residues are less symmetrically oriented about the glycosidic O atom. These variations suggest that the glycosidic torsion angles are readily influenced by the crystal-packing environment.

The conformations of the hydroxymethyl substituents at C(5) and C(15) are both *gauche-trans*. In all other α,α -trehalose derivatives which do not possess internal crystallographic symmetry, these substituents adopt completely different conformations, very often with one substituent having the *gauche-trans* conformation and the other the *gauche-gauche* conformation (Brown *et al.*, 1972; Taga, Senma & Osaki, 1972; Jeffrey & Nanni, 1985; Lee & Koh, 1994; Lee, Koh, Xu & Linden, 1994; Lee & Linden, 1994a; Linden & Lee, 1995).

Both D-galactopyranosyl rings have the 4C_1 conformation, with the torsion angles showing the normal variations commonly observed in pyranose systems. The puckering parameters (Cremer & Pople, 1975) describe slightly distorted chair conformations. For the ring containing O(5), $Q = 0.557(2)$ Å, $q_2 = 0.042(2)$ Å, $q_3 = 0.555(2)$ Å, $\varphi_2 = 168(3)^\circ$ and $\theta = 4.3(2)^\circ$, and for that containing O(15), $Q = 0.561(2)$ Å, $q_2 = 0.051(2)$ Å, $q_3 = 0.559(2)$ Å, $\varphi_2 = 173(2)^\circ$ and $\theta = 5.2(2)^\circ$. The φ_2 values are close to 180° , which indicates that the pyranoid rings are being distorted towards the E_3 conformation. The flattening of the oxygen apex allows the two ring C—O—C angles to increase to $114.2(1)$ and $115.4(1)^\circ$, which is also observed in many pyranose structures (Berman, 1970; Brown *et al.*, 1972; Cremer & Pople, 1975; Jeffrey & Nanni, 1985; Kanters, Scherrenberg, Leeflang, Kroon & Mathlouthi, 1988; Lee & Linden, 1994a,b,c).

The molecules of (I) interact *via* a complex system of intermolecular hydrogen bonds (Table 3) to form a three-dimensional network (Fig. 2). With the exception of O(2)—H and O(12)—H, each hydroxy group acts as both a donor and an acceptor for intermolecular hydrogen bonds. O(12)—H acts as a donor only and O(2)—H is not involved in any intermolecular interactions. The O atom of one ring, O(15), is also an intermolecular hydrogen-bond acceptor. In addition, there may be two very weak intramolecular hydrogen bonds from O(2)—H and O(12)—H to the bridging O atom, O(1); in which case, O(12)—H is involved in bifurcated hydrogen bonding. However, the acute O—H \cdots O angles suggest that the relatively short H \cdots O distances may only be the consequence of the geometry of the molecule, rather than being true hydrogen bonds.

IR studies (Barker, Brimacombe, Foster, Whiffen & Zweifel, 1959; Foster, 1961) indicated that, in solution,

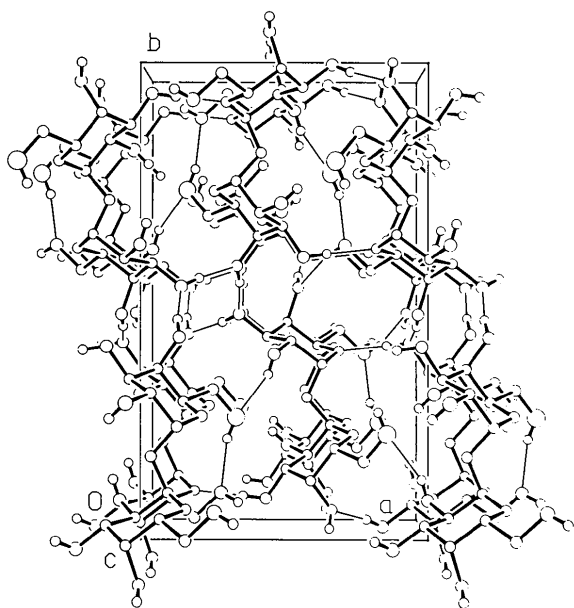


Fig. 2. The packing of (I) viewed down *c*. Thin lines indicate the hydrogen-bonding interactions.

the axial C(4)—OH in D-galactose may form an intramolecular hydrogen bond with the ring atom O(5). However, the solid-state structures of (I) and D-galactose (Sheldrick, 1976) show no such intramolecular hydrogen bond; the O(4)···O(5) and O(14)···O(15) distances in (I) are 2.959 (2) and 2.977 (2) Å, respectively. In solution, with the absence of the more attractive closer intermolecular contacts that are present in the solid state, intramolecular hydrogen bonding could occur. Even so, with an O···O distance of about 2.96 Å, the hydrogen bond would be rather weak and so is unlikely to significantly hinder the formation of any hydrogen-bonding interactions with another substrate, such as a taste receptor. Yet the intensity of the sweetness of D-galactose and α,α -galacto-trehalose is only half that of D-glucose (Shallenberger & Acree, 1971; Lee, 1994). Since the O(3)···O(4) and O(13)···O(14) distances [2.765 (2) and 2.808 (2) Å, respectively] are within the limits which permit these groups to function as the Shallenberger AH,B glucophore (Shallenberger & Acree, 1967), it is possible that the low intensity of the sweetness of D-galactose and α,α -galacto-trehalose is due to the axial disposition of the C(4)—OH group. Methyl α -D-allopyranoside and α,α -allo-trehalose, where the C(3)—OH group is axial, are also only about half as sweet as methyl α -D-glucopyranoside (Linden & Lee, 1995), in which the C(3) and C(4) hydroxy groups occupy equatorial positions. We are presently studying the taste properties of methyl α -D-allopyranoside and α,α -alatro-trehalose to determine the importance of the stereo arrangement of the C(3) and C(4) hydroxy groups upon their role as the sweet glucophore.

Experimental

Synthesis was performed according to the procedure of Birch & Richardson (1970). Suitable crystals were obtained from an aqueous acetone solution.

Crystal data

C₁₂H₂₂O₁₁
M_r = 342.30
 Orthorhombic
*P*2₁2₁2₁
a = 11.071 (3) Å
b = 18.283 (3) Å
c = 6.865 (4) Å
V = 1389.5 (8) Å³
Z = 4
D_x = 1.636 Mg m⁻³

Mo *K*α radiation
 λ = 0.71069 Å
 Cell parameters from 25 reflections
 θ = 19.0–20.0°
 μ = 0.137 mm⁻¹
T = 173 (1) K
 Prism
 0.45 × 0.32 × 0.30 mm
 Colourless

Data collection

Rigaku AFC-5R diffractometer
 $\omega/2\theta$ scans
 Absorption correction: none
 2824 measured reflections
 2706 independent reflections
 2514 observed reflections
 [*I* > 2σ(*I*)]
R_{int} = 0.009 for 118 Friedel pairs

θ_{\max} = 30°
h = 0 → 15
k = -1 → 25
l = -1 → 9
 3 standard reflections monitored every 150 reflections
 intensity decay: insignificant

Refinement

Refinement on *F*
R = 0.0315
wR = 0.0306
S = 1.949
 2514 reflections
 296 parameters
 All H-atom parameters refined
 $w = 1/[\sigma^2(F_o) + (0.005F_o)^2]$
 $(\Delta/\sigma)_{\max} = 0.0003$
 $\Delta\rho_{\max} = 0.30 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.21 \text{ e } \text{Å}^{-3}$

Extinction correction: none
 Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
 Absolute configuration: assigned to agree with the known chirality at C(5), as established by the synthesis of the compound

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{\text{eq}} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
O(1)	0.5781 (1)	0.29801 (6)	0.0338 (2)	0.0160 (3)
O(2)	0.5106 (1)	0.19168 (7)	-0.2329 (2)	0.0259 (4)
O(3)	0.4364 (1)	0.08810 (7)	0.0559 (2)	0.0208 (4)
O(4)	0.6605 (1)	0.07087 (7)	0.2280 (2)	0.0200 (4)
O(5)	0.7355 (1)	0.22375 (7)	0.1544 (2)	0.0169 (3)
O(6)	0.8392 (1)	0.23420 (8)	0.5470 (3)	0.0454 (6)
O(12)	0.4655 (1)	0.39090 (7)	0.2897 (2)	0.0217 (4)
O(13)	0.3425 (1)	0.47203 (7)	-0.0048 (2)	0.0227 (4)
O(14)	0.5494 (1)	0.52806 (6)	-0.1881 (2)	0.0200 (4)
O(15)	0.6920 (1)	0.39398 (6)	-0.1005 (2)	0.0155 (3)
O(16)	0.7896 (1)	0.38359 (7)	-0.4797 (2)	0.0242 (4)

C(1)	0.6604 (2)	0.24002 (9)	-0.0073 (3)	0.0163 (4)
C(2)	0.5806 (2)	0.17532 (9)	-0.0645 (3)	0.0164 (4)
C(3)	0.5058 (2)	0.15112 (9)	0.1097 (3)	0.0154 (4)
C(4)	0.5895 (1)	0.13338 (9)	0.2795 (3)	0.0149 (4)
C(5)	0.6707 (2)	0.19900 (9)	0.3257 (3)	0.0153 (4)
C(6)	0.7639 (2)	0.1777 (1)	0.4766 (3)	0.0189 (5)
C(11)	0.6300 (2)	0.36795 (9)	0.0656 (3)	0.0146 (4)
C(12)	0.5238 (2)	0.41746 (9)	0.1204 (3)	0.0145 (4)
C(13)	0.4402 (1)	0.42504 (9)	-0.0549 (3)	0.0151 (4)
C(14)	0.5109 (2)	0.45467 (9)	-0.2295 (3)	0.0147 (4)
C(15)	0.6180 (2)	0.40455 (9)	-0.2730 (3)	0.0141 (4)
C(16)	0.7006 (2)	0.43650 (9)	-0.4251 (3)	0.0173 (5)

Table 2. Selected geometric parameters (Å, °)

O(1)—C(1)	1.426 (2)	O(1)—C(11)	1.419 (2)
O(2)—C(2)	1.424 (2)	O(12)—C(12)	1.416 (2)
O(3)—C(3)	1.433 (2)	O(13)—C(13)	1.423 (2)
O(4)—C(4)	1.431 (2)	O(14)—C(14)	1.436 (2)
O(5)—C(1)	1.419 (2)	O(15)—C(11)	1.414 (2)
O(5)—C(5)	1.450 (2)	O(15)—C(15)	1.453 (2)
O(6)—C(6)	1.413 (2)	O(16)—C(16)	1.431 (2)
C(1)—C(2)	1.527 (2)	C(11)—C(12)	1.531 (2)
C(2)—C(3)	1.521 (2)	C(12)—C(13)	1.524 (2)
C(3)—C(4)	1.524 (2)	C(13)—C(14)	1.531 (3)
C(4)—C(5)	1.532 (2)	C(14)—C(15)	1.528 (2)
C(5)—C(6)	1.513 (2)	C(15)—C(16)	1.505 (2)
C(1)—O(5)—C(5)	114.2 (1)	C(11)—O(15)—C(15)	115.4 (1)
O(1)—C(1)—O(5)	112.1 (1)	O(1)—C(11)—O(15)	112.1 (1)
O(1)—C(1)—C(2)	104.9 (1)	O(1)—C(11)—C(12)	105.0 (1)
O(5)—C(1)—C(2)	112.2 (1)	O(15)—C(11)—C(12)	111.8 (1)
O(2)—C(2)—C(1)	111.1 (1)	O(12)—C(12)—C(11)	110.4 (1)
O(2)—C(2)—C(3)	113.8 (1)	O(12)—C(12)—C(13)	113.7 (1)
C(1)—C(2)—C(3)	109.8 (1)	C(11)—C(12)—C(13)	109.0 (1)
O(3)—C(3)—C(2)	108.9 (1)	O(13)—C(13)—C(12)	109.0 (1)
O(3)—C(3)—C(4)	110.6 (1)	O(13)—C(13)—C(14)	111.4 (1)
C(2)—C(3)—C(4)	109.4 (1)	C(12)—C(13)—C(14)	109.9 (1)
O(4)—C(4)—C(3)	108.4 (1)	O(14)—C(14)—C(13)	109.1 (1)
O(4)—C(4)—C(5)	110.8 (1)	O(14)—C(14)—C(15)	111.6 (1)
C(3)—C(4)—C(5)	110.4 (1)	C(13)—C(14)—C(15)	109.7 (1)
O(5)—C(5)—C(4)	111.5 (1)	O(15)—C(15)—C(14)	111.0 (1)
O(5)—C(5)—C(6)	107.3 (1)	O(15)—C(15)—C(16)	105.9 (1)
C(4)—C(5)—C(6)	109.9 (1)	C(14)—C(15)—C(16)	112.0 (1)
O(6)—C(6)—C(5)	116.6 (2)	O(16)—C(16)—C(15)	109.7 (1)
C(1)—O(1)—C(11)	116.2 (1)		
O(1)—C(1)—O(5)—C(5)	61.9 (2)		
O(1)—C(1)—C(2)—O(2)	61.1 (2)		
O(1)—C(1)—C(2)—C(3)	-65.7 (2)		
O(2)—C(2)—C(3)—O(3)	57.7 (2)		
O(3)—C(3)—C(4)—O(4)	54.0 (2)		
O(4)—C(4)—C(5)—C(6)	-52.8 (2)		
O(5)—C(1)—O(1)—C(11)	66.2 (2)		
O(5)—C(1)—C(2)—C(3)	56.2 (2)		
O(5)—C(5)—C(4)—C(3)	-53.9 (2)		
O(5)—C(5)—C(6)—O(6)	63.8 (2)		
O(6)—C(6)—C(5)—C(4)	-174.7 (2)		
C(1)—O(1)—C(11)—C(12)	-176.0 (1)		
C(1)—O(5)—C(5)—C(4)	54.6 (2)		
C(1)—C(2)—C(3)—C(4)	-56.1 (2)		
C(2)—C(1)—O(5)—C(5)	-55.9 (2)		
C(2)—C(3)—C(4)—C(5)	55.5 (2)		
O(1)—C(11)—O(15)—C(15)	61.8 (2)		
O(1)—C(11)—C(12)—O(12)	59.6 (2)		
O(1)—C(11)—C(12)—C(13)	-66.1 (2)		
O(12)—C(12)—C(13)—O(13)	57.2 (2)		
O(13)—C(13)—C(14)—O(14)	55.0 (2)		
O(14)—C(14)—C(15)—C(16)	-50.9 (2)		
O(15)—C(15)—O(1)—C(1)	62.4 (2)		
O(15)—C(15)—C(12)—C(13)	55.7 (2)		
O(15)—C(15)—C(14)—C(13)	-53.9 (2)		
O(15)—C(15)—C(16)—O(16)	66.7 (2)		
O(16)—C(16)—C(15)—C(14)	-172.1 (1)		
C(11)—O(1)—C(1)—C(2)	-171.8 (1)		
C(11)—O(15)—C(15)—C(14)	54.8 (2)		
C(11)—C(12)—C(13)—C(14)	-56.8 (2)		
C(12)—C(13)—O(15)—C(15)	-55.8 (2)		
C(12)—C(13)—C(14)—C(15)	56.7 (2)		

Table 3. Hydrogen-bonding geometry (Å, °)

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O(3)—H(3)···O(15 ⁱ)	0.79 (2)	1.97 (2)	2.743 (2)	167 (3)
O(4)—H(4)···O(13 ⁱⁱ)	0.82 (3)	1.82 (3)	2.623 (2)	170 (3)
O(6)—H(6)···O(16 ⁱⁱⁱ)	0.81 (2)	2.00 (2)	2.792 (2)	165 (2)
O(12)—H(12)···O(6 ^{iv})	0.78 (2)	2.28 (2)	2.905 (2)	137 (2)
O(13)—H(13)···O(4 ^v)	0.78 (2)	1.87 (2)	2.650 (2)	174 (2)
O(14)—H(14)···O(3 ^v)	0.80 (2)	1.97 (2)	2.758 (2)	166 (2)
O(16)—H(16)···O(14 ^{vi})	0.76 (2)	2.06 (2)	2.799 (2)	164 (2)
O(2)—H(2)···O(1)	0.80 (2)	2.48 (2)	2.773 (2)	103 (2)
O(12)—H(12)···O(1)	0.78 (2)	2.41 (2)	2.743 (2)	107 (2)

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

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1991). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1989). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *TEXSAN LS*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *TEXSAN FINISH*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1050). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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

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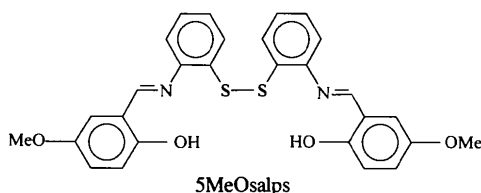
Abstract

The molecule of the title compound, C₂₈H₂₄N₂O₄S₂, 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 experimentally 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.* H₂S₂ (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*-phenylenitrilomethylidyne)]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.



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.

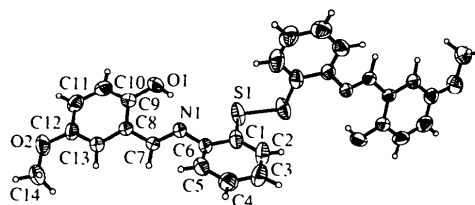


Fig. 1. A view of the molecule showing the atomic numbering scheme. Displacement ellipsoids are plotted at the 50% probability level.

Experimental

5'-Methoxysalicylaldehyde (20 mmol) was dissolved in 50 cm³ of ethanol and then added to bis(2-aminophenyl)disulfide (10 mmol) in ethanol, and the reaction mixture was refluxed