Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2939 measured reflections
2771 independent reflections
1676 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.0372$
$\theta_{\text{max}} = 25°$
$h = -13 \rightarrow 0$
$k = -23 \rightarrow 0$
$l = -9 \rightarrow 9$
3 standard reflections
every 100 reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0678$
$wR(F^2) = 0.2370$
$S = 1.017$
2726 reflections
229 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.1112P)^2 + 2.3877P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\text{max}} = -0.008$
$\Delta\rho_{\text{max}} = 0.552$ e Å^{-3}
$\Delta\rho_{\text{min}} = -0.600$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Cl1—C19	1.688 (5)	O4—C6	1.425 (5)
O1—C1	1.352 (5)	C3—C15	1.395 (7)
O2—C13	1.225 (5)	C15—C16	1.333 (7)
O3—C16	1.355 (6)	C18—C19	1.477 (6)
O3—C4	1.363 (5)	C19—C20	1.416 (7)
C18—C19—Cl1	115.2 (4)	C5—C6—O4	110.6 (3)
C20—C19—Cl1	118.2 (4)	C7—C6—O4	108.0 (3)
C14—C13—O2	120.3 (4)	C4—O3—C16	104.1 (4)
C12—C13—O2	121.1 (4)	C2—C1—O1	116.8 (4)
C14—C1—O1	121.8 (4)		
C5—C6—C18—C19	68.0 (5)	C6—C18—C19—Cl1	106.8 (4)

The diffraction pattern was rather weak, falling off rapidly with θ. The low intensity of the data, particularly for high θ reflections, contributes to the rather high residual. H atoms were placed geometrically and refined with a riding model (including free rotation about C—C bonds for the methyl group), and with U_{iso} constrained to be $1.2U_{\text{eq}}$ of the carrier atom.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: local programs. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL* (Siemens, 1994). Software used to prepare material for publication: *SHELXL*93.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1287). Services for accessing these data are described at the back of the journal.

References

Enraf–Nonius (1989). *CAD*-4 *Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
Harrington-Frost, N. M., Milbank, J. M. J. & Rutledge, P. S. (1997). *Aust. J. Chem.* In the press.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.
Siemens (1994). *SHELXTL*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Acta Cryst. (1997). C**53**, 1103–1105

2,2′-Diaminodiphenyl Disulfide Hemihydrate

Branko Kaitner and Gordana Pavlović

Chemistry Department, Laboratory of General and Inorganic Chemistry, Faculty of Science, University of Zagreb, Ul. kralja Zvonimira 8, 10000 Zagreb, Croatia. E-mail: kaitner@olimp.irb.hr

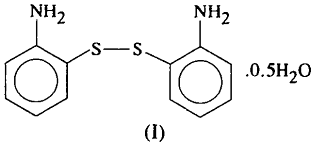
(*Received 1 February 1996; accepted 20 March 1997*)

Abstract

The stereochemistry of 2,2′-diaminodiphenyl disulfide hemihydrate, $C_{12}H_{12}N_2S_2.0.5H_2O$, differs significantly from that of the corresponding anhydrous compound. The conformational difference is a consequence of the O—H···N and N—H···O intermolecular hydrogen bonding between the $C_{12}H_{12}N_2S_2$ and water molecules. The molecule is characterized by a skewed central moiety with a C—S—S—C torsion angle of 75.2 (1)°.

Comment

Two products were obtained in an attempt to prepare the tridentate Schiff base *N*-(2-mercaptophenyl)-2-hydroxy-1-naphthaldimine from 2-hydroxy-1-naphthaldehyde and 2-aminothiophenol in a template condensation reaction, namely, *N*,*N*′-[dithiobis(*o*-phenylene)]bis(2-hydroxy-1-naphthaldimine), as a yellow precipitate in lower yield, and 2,2′-diaminodiphenyl disulfide in higher yield. The latter crystallized as a hemihydrate, (I), in the form of regular transparent ochre prisms from a red–brown solution in methanol at low temperature.



(I)

The stereochemistry of diphenyl disulfide is known (Lee & Bryant, 1969; Sacerdoti, Gilli & Domiano, 1975), together with many substituted diaryl disulfides (Lee & Bryant, 1970; Spirlet, Van den Bossche, Dideberg & Dupont, 1979; Ricci & Bernal, 1969, 1970; Mak, Yip, Chan, Smith & Kennard, 1989). The results of our investigation revealed that the presence of a water molecule significantly changes the molecular conformation. The structure (Fig. 1) exhibits essentially the same bond-length pattern as the anhydrous form (Lee & Bryant, 1970). The main feature of the central part of both the hemihydrate and anhydrous 2,2′-diaminodiphenyl disulfide (Lee & Bryant, 1970) is a skewed conformation with very different C—S—S—C torsion angles [75.2 (1) and 90.5 (3)°]. The S—S bond length in disulfide compounds is correlated with the C—S—S—C torsion angles, being around 2.031 (τ = 75–105°) or 2.070 Å (τ = 0–20°) (Allen *et al.*, 1987). The anomalous S1—S2 bond distance of 2.073 (1) Å, with a C11—S1—S2—C21 torsion angle of 75.2 (1)°, could be explained only by the presence of the phenyl-ring amino substituents. The C—N bond distances of 1.382 (4) and 1.384 (4) Å imply that the NH_2 groups are pyramidal, containing an sp^3-hybridized N atom (Allen *et al.*, 1987). The existence of O—H···N-type hydrogen bonds also depends on the presence of nitrogen lone-pair electron density. All other bond distances are normal. The dihedral angle between the phenyl rings is 35.9 (1)°. The water molecule is disordered over two sites, each 0.37 Å from the twofold axis. The 2,2′-diaminodiphenyl disulfide and water molecules are linked through three moderately strong and a relatively weak hydrogen bond (Table 2). Through these, the disulfide molecules are connected by the water molecules into infinite puckered ribbons along the *a* axis.

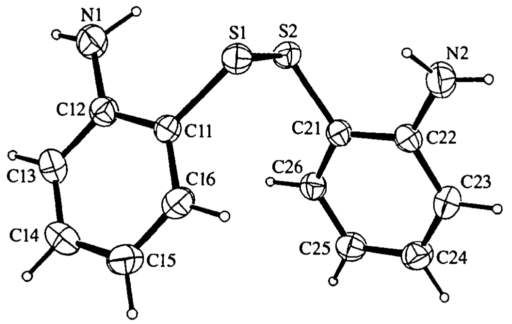


Fig. 1. The molecular structure of (I) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

Experimental

The title compound crystallized as a hemihydrate in the form of regular transparent ochre prisms from a methanol solution at low temperature.

Crystal data

$C_{12}H_{12}N_2S_2.0.5H_2O$
M_r = 257.37
Monoclinic
$I2/a$
a = 18.781 (5) Å
b = 5.292 (1) Å
c = 24.948 (7) Å
β = 90.47 (2)°
V = 2479 (1) $Å^3$
Z = 8
D_x = 1.38 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 24 reflections
θ = 9.0–14.5°
μ = 0.41 mm^{-1}
T = 295 K
Prism
0.60 × 0.43 × 0.30 mm
Ochre

Data collection

Phillips PW1100 diffractometer
ω scans
Absorption correction: semi-empirical ψ scan (Stoe & Cie, 1992*c*)
T_{min} = 0.781, T_{max} = 0.858
3086 measured reflections
2784 independent reflections

1343 reflections with $I > 2\sigma(I)$
R_{int} = 0.015
θ_{max} = 27°
$h = -24 \rightarrow 24$
$k = 0 \rightarrow 6$
$l = 0 \rightarrow 31$
3 standard reflections frequency: 90 min intensity decay: 2.3%

Refinement

Refinement on F
R = 0.031
wR = 0.051
S = 1.12
1343 reflections
154 parameters
H atoms riding (C—H 0.95 Å), others from ΔF map

$w = 1/[\sigma^2(F_o) + 0.0015F_o^2]$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.19 e $Å^{-3}$
$\Delta\rho_{min}$ = −0.19 e $Å^{-3}$
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

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

S1—S2	2.073 (1)	N1—C12	1.382 (4)
S1—C11	1.769 (3)	N2—C22	1.384 (4)
S2—C21	1.769 (3)		
S2—S1—C11	101.9 (1)	S1—S2—C21	103.1 (1)

Table 2. *Contact distances (Å)*

$N1\cdots OW^{i}$	3.076 (8)	$OW\cdots N1^{iii}$	3.330 (7)
$N1\cdots OW^{ii}$	3.001 (7)	$OW\cdots N2^{iv}$	3.038 (9)

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

H atoms attached to C atoms were calculated as riding atoms, with C—H = 0.95 Å. The amino and disordered water H atoms were revealed from a ΔF map with one of the two water H atoms placed on the twofold axis. All H atoms were included in the structure-factor calculations with isotropic displacement parameters set at $1.2U_{eq}$ of the atom to which they were attached. The water molecule occupancy factor of 0.5 was unambiguously proved by the refinement procedure.

Data collection: *DIF*4 (Stoe & Cie, 1992*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1992*b*). Program(s) used to solve structure: *NRCVAX SOLVER* (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to refine structure: *NRCVAX LSTSQ*. Molecular graphics: *NRCVAX ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *NRCVAX TABLES* (version of January 1994).

BK thanks the Ministry of Science and Technology, Republic of Croatia, for a research grant.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1091). Services for accessing these data are described at the back of the journal.

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L. & Orpen, A. G. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. S1–S19.
Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Lee, J. D. & Bryant, M. W. R. (1969). *Acta Cryst.* B**25**, 2094–2101.
Lee, J. D. & Bryant, M. W. R. (1970). *Acta Cryst.* B**26**, 1729–1735.
Mak, T. C. W., Yip, W.-H., Chan, W.-H., Smith, G. & Kennard, C. H. L. (1989). *Aust. J. Chem.* **42**, 1403–1406.
Ricci, J. S. & Bernal, I. (1969). *J. Am. Chem. Soc.* **91**, 4078–4082.
Ricci, J. S. & Bernal, I. (1970). *J. Chem. Soc. B*, pp. 806–811.
Sacerdoti, M., Gilli, G. & Domiano, P. (1975). *Acta Cryst.* B**31**, 327–329.
Spirlet, M. R., Van den Bossche, G., Dideberg, O. & Dupont, L. (1979). *Acta Cryst.* B**35**, 203–205.
Stoe & Cie (1992*a*). *DIF4. Diffractometer Control Program.* Version 7.0. Stoe & Cie, Darmstadt, Germany.
Stoe & Cie (1992*b*). *REDU4. Data Reduction Program.* Version 7.0. Stoe & Cie, Darmstadt, Germany.
Stoe & Cie (1992*c*). *EMPIR. Program for Empirical Absorption Correction.* Version 7.0. Stoe & Cie, Darmstadt, Germany.

Acta Cryst. (1997). C**53**, 1105–1107

Methyl 2-*O*-α-D-Mannopyranosyl-β-D-glucopyranoside

Lars Eriksson,[a] Roland Stenutz[b] and Gőran Widmalm[b]

[a]*Department of Structural Chemistry, Arrhenius Laboratory, Stockholm University, S-106 91 Stockholm, Sweden, and* [b]*Department of Organic Chemistry, Arrhenius Laboratory, Stockholm University, S-106 91 Stockholm, Sweden. E-mail: lerik@struc.su.se*

(*Received 2 May 1996; accepted 26 March 1997*)

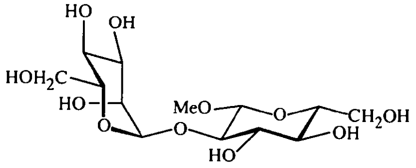
Abstract

The structure of the title compound, $C_{13}H_{24}O_{11}$, has been determined. The torsion angles of the glycosidic linkage connecting the two sugar residues, φ_H (H1′—C1′—O2—C2) and ψ_H (C1′—O2—C2—H2), have values of −62.7 (2)° and −28.6 (2)°, respectively. The conformation in the crystal is similar to that obtained by energy minimization *in vacuo* using the HSEA (hard-sphere *exo*-anomeric) force field. A chain of seven inter-residue hydrogen bonds, involving all possible H-atom donors in the molecule is observed. The chain is terminated by a ring O atom as an acceptor.

Comment

The three-dimensional structure of an oligosaccharide is governed by the glycosidic torsion angles φ_H and ψ_H. Their values determine the overall shape of an oligosaccharide and it is important to have an accurate measurement of these for an understanding of conformational aspects of the glycosidic linkage and for recognition processes between proteins and carbohydrates.

We have determined the crystal structure of methyl 2-*O*-α-D-mannopyranosyl-β-D-glucopyranoside, (I) (Fig. 1). The major degrees of freedom, the glycosidic torsion angles φ_H and ψ_H, and the exocyclic torsion angles for hydroxymethyl groups, ω, show values in the expected regions of conformational space. Thus, for the glycosidic linkage between the two sugar residues, the torsion angles φ_H and ψ_H are −62.7 (2) and −28.6 (2)°, respectively. The φ_H (H1—C1—O1—C7) torsion angle for the glucose residue is 49.7 (2)°. For both φ_H torsion angles, the values are in the conformational region where the *exo*-anomeric effect (Thøgersen, Lemieux, Bock & Meyer, 1982) contributes to energy stabilization.



(I)

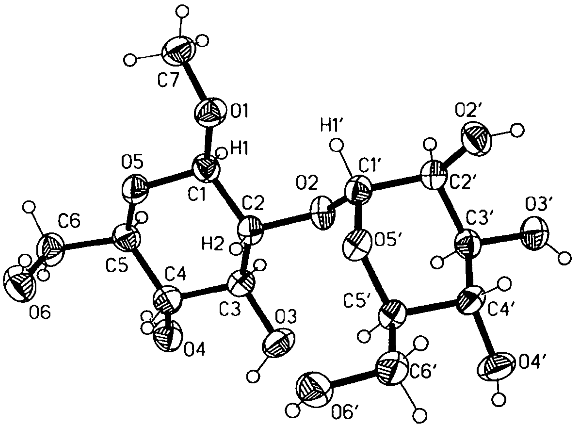


Fig. 1. The molecular structure of (I) showing 50% probability displacement ellipsoids. H atoms are drawn as small circles of arbitrary radii.

The exocyclic torsion angles for the constituent monosaccharides have ω′ (O5′—C5′—C6′—O6′) = 63.5 (2)° (*gauche–trans*) for the mannose residue and ω (O5—C5—C6—O6) = −65.2 (2)° (*gauche–gauche*)