## References

Buemi, G. (1990). *J. Chem. Soc. Faraday Trans.* **86**, 2813–2818.
Burla, M. C., Camalli, M., Cascarano, G., Giacovazzo, C., Polidori, G., Spagna, R. & Viterbo, D. (1989). *J. Appl. Cryst.* **22**, 389–393.
Cambridge Structural Database Centre (1996). Cambridge Structural Database System. Version 5.1.1. Cambridge Structural Data Centre, 12 Union Road, Cambridge CB2 1EW, England.
Dolling, W., Kischkies, K., Heinemann, F. & Hartung, H. (1993). *Monatsh. Chem.* **124**, 707–719.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Karcher, B., Helland, B., Dudis, D., Miller, L., Hendrixson, T. & Jacobson, R. A. (1989). *Theta-Dependent Psi-scan Correction.* Ames Laboratory, Iowa State University, USA.
Molecular Structure Corporation (1988). *MSC/AFC Diffractometer Control Software.* MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Molecular Structure Corporation. (1994). *TEXSAN. Single Crystal Structure Analysis Software.* MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Norskov-Lauritsen, L., Carlsen, L. & Duus, F. (1983). *J. Chem. Soc. Chem. Commun.* pp. 496–498.
Richter, R., Sieler, J., Kaiser, J. & Uhlemann, E. (1976). *Acta Cryst.* **B32**, 3290–3294.
Richter, R., Sieler, J., Mootz, D., Hocken, J., Ludwig, E. & Uhlemann, E. (1989). *Acta Cryst.* **C45**, 1606–1609.
Tsuchiya, T., Oishi, A., Shibuya, I., Taguchi, Y. & Honda, K. (1996). *Chem. Commun.* pp. 1621–1622.
Tsuchiya, T., Shibuya, I., Taguchi, Y., Oishi, A. & Honda, K. (1996). *Jpn Kokai*, pp. 1996–2203.

---

*Acta Cryst.* (1997). **C53**, 376–378

# *N*,*N*′-Bis(4-chlorobenzylidene)-2,2′-diaminodiphenyl Disulfide

SEMRA İDE,[a] GÜL ÖZTAŞ,[b] NİLGÜN ANCIN[b] AND MÜRŞİDE TÜZÜN[b]

[a]*Hacettepe University, Department of Engineering Physics, Beytepe 06532, Ankara, Turkey, and* [b]*Ankara University, Faculty of Science, Department of Chemistry, Ankara, Turkey. E-mail: side@eti.cc.hun.edu.tr*

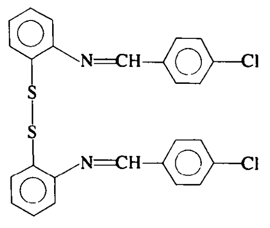
(*Received 14 June 1996; accepted 6 November 1996*)

## Abstract

In the title compound, *N*,*N*′-bis(4-chlorobenzylidene)-disulfanediylbis(2-aniline), $C_{26}H_{18}Cl_2N_2S_2$, two 2-(4-chlorobenzylideneamino)phenyl sulfide moieties, which can act as tridentate ligands, are joined through their S atoms. The molecule has a *trans* configuration about the S—S bond. The bond lengths and angles are nearly identical between the two halves of the molecule.

## Comment

Schiff's bases bearing imine N and anionic S atoms constitute an important class of polydentate ligands and their metal complexes have previously been used as models for biological systems (Sugiura & Hirayama, 1976; Casella, 1984). The direct approach in synthesizing a free Schiff's base from the condensation of 2-mercaptoaniline with a carbonyl compound often results in an undesirable side reaction involving ring closure with the formation of a heterocyclic compound (Jadamus, Fernando & Freiser, 1964; Charles & Freiser, 1953; Sugiura, Hirayama, Tanaka & Ishizu, 1975; İde, Öztaş, Ancın & Tüzun, 1996). The title compound, (I), was obtained by the condensation of 4-chlorobenzaldehyde with 2,2′-diaminodiphenyl disulfide. This preformed Schiff's base can then be used to obtain $Ni^{II}$, $Zn^{II}$, $Cu^{II}$ and $Cd^{II}$ complexes by an electrochemical reductive cleavage of the disulfide bond (Castro *et al.*, 1990). Disulfides including a C—S—S—C chain have been used also as antiwear and extreme-pressure additives in lubricating oils.



(I)

The present investigation is part of a research program involving the structural studies of disulfides. Structural properties of such compounds have been discussed previously by Hordvik (1966), Lee (1972), Meyer (1976), Muller & Diemann (1987), Marsden & Smith (1988) and Krasinski & Fackler (1994). The observed S—S and S—C bond lengths (Table 1) are in agreement with the values reported in the literature (Allen *et al.*, 1987; Orpen *et al.*, 1989). The torsion angles C7—C1—S1—S1′ of 19.8 (4) and C7′—C1′—S1′—S1 of 0.4 (4)° are similar to the corresponding angles in diphenyl disulfide (17.7 and 0.2°), but different from the values in 2,2′-diaminodiphenyl disulfide (83.6 and 83.4°; Lee & Bryant, 1970), which indicates a $p\pi$–$d\pi$ interaction between the fully occupied $p_z$ orbital on the C atom with an empty $d$ orbital on the S atom in the latter compound. Such a $\pi$ overlap does not seem as favourable in the title compound. In a disulfide group, the regular dihedral angle of about 90° corresponds to S—S bond lengths of about 2.03 Å (Hordvik, 1966). In the title compound, the C1—S1—S1′—C1′ torsion angle of −89.8 (2)° and the S—S bond length of 2.032 (2) Å agree with this observation.

Mean plane *A* (formed by atoms C1–C3 and C5–C7) makes an angle of 86.3 (1)° with mean plane *A*′ (formed by atoms C1′–C7′). The S1 atom deviates by 0.081 (1) Å from plane *A*, while there is no deviation of the S1′ atom from plane *A*′. The N atoms

*Acta Crystallographica Section C*
ISSN 0108-2701 © 1997

are coplanar with their respective rings. The torsion angles C2—N1—C8—C9 and C2′—N1′—C8′—C9′ are 178.3 (4) and −178.3 (4)°, respectively. The other bond distances and angles are close to those reported for *N*,*N*′-bis(*p*-chlorobenzylidene)-1,3-propanediamine (Tinant & Declercq, 1986) and *N*-(4-chlorobenzylidene)-2-(4-imidazolyl)ethylamine (Bocelli & Cantoni, 1992). There are weak intermolecular contacts. In the crystal structure, the molecules thus appear to be held together by van der Waals forces.

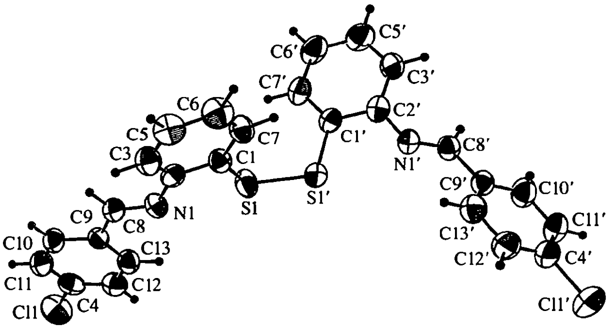


Fig. 1. The molecular structure of the title compound with the atomic labelling. The displacement ellipsoids are drawn at the 50% probability level. Unlabelled H atoms possess the same numerical label as their parent C atoms.

## Experimental

To obtain the title compound, 4-chlorobenzaldehyde (0.283 g, 2 mmol) in alcohol (10 ml) was added to a solution of 2,2′-diaminodiphenyl disulfide (0.248 g, 1 mmol) in alcohol (20 ml). The solution was heated to 323 K for 5–6 h. During this time, a yellow crystalline product was deposited. It was recrystallized from chloroform (m.p. 411 K). IR (KBr) $\nu_{max}$: 1574 (*s*), 1500 (*s*, C=N), 680 (*m*, C—S), 476 (*m*, S—S), 1290 (*m*, C—N). $^1$H NMR ($\delta_H$, 400 MHz, $CDCl_2$): 8.46 (2H, *s*, 2CH=N), 7.91 (4H, *d*, Ar-12,12′,11,11-H), 7.70 (2H, *d*, Ar-7,7′-H), 7.48 (4H, *d*, Ar-13,13′-10,10′-H), 7.19 (4H, *m*, Ar-3,3′,6,6′-H), 7.06 (2H, *dd*, Ar-5,5′-H). UV (acetone) $\lambda_{max}$: 327.7 nm ($\varepsilon$ = 25240 dm$^3$ mol$^{-1}$cm$^{-1}$).

### *Crystal data*

$C_{26}H_{18}Cl_2N_2S_2$
$M_r$ = 493.48
Monoclinic
$P2_1/c$
$a$ = 11.7998 (12) Å
$b$ = 10.1564 (11) Å
$c$ = 19.5352 (18) Å
$\beta$ = 93.410 (9)°
$V$ = 2337 (5) Å$^3$
$Z$ = 4
$D_x$ = 2.805 Mg m$^{-3}$
$D_m$ not measured

Mo $K\alpha$ radiation
$\lambda$ = 0.71073 Å
Cell parameters from 25 reflections
$\theta$ = 10.31–18.01°
$\mu$ = 0.948 mm$^{-1}$
$T$ = 293 (1) K
Prismatic
0.56 × 0.32 × 0.10 mm
Yellow

### *Data collection*

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical *via* $\psi$ scan (*MolEN*; Fair, 1990)
$T_{min}$ = 0.876, $T_{max}$ = 0.910
4755 measured reflections
4477 independent reflections

2418 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.037
$\theta_{max}$ = 26.32°
$h = -14 \rightarrow 14$
$k = 0 \rightarrow 12$
$l = -23 \rightarrow 0$
3 standard reflections
frequency: 120 min
intensity decay: 5.17%

### *Refinement*

Refinement on $F$
$R$ = 0.046
$wR$ = 0.045
$S$ = 0.71
2418 reflections
289 parameters
H atoms: see below
Weighting scheme: see below

$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.285 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.114 e Å$^{-3}$
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

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

| | | | |
|---|---|---|---|
| N1—C2 | 1.406 (5) | N1′—C2′ | 1.415 (5) |
| N1—C8 | 1.258 (5) | N1′—C8′ | 1.259 (5) |
| C6—C7 | 1.364 (7) | C6′—C7′ | 1.375 (7) |
| C8—C9 | 1.457 (6) | C8′—C9′ | 1.472 (6) |
| Cl1—C4 | 1.735 (5) | Cl1′—C4′ | 1.740 (5) |
| S1—C1 | 1.770 (4) | S1′—C1′ | 1.781 (4) |
| S1—S1′ | 2.032 (2) | | |
| S1—C1—C7 | 125.4 (3) | S1′—C1′—C7′ | 125.1 (3) |
| S1—C1—C2 | 115.1 (3) | S1′—C1′—C2′ | 114.5 (3) |
| S1′—S1—C1 | 104.6 (1) | S1—S1′—C1′ | 106.4 (1) |
| N1—C2—C1 | 114.9 (3) | N1′—C2′—C1′ | 116.3 (4) |
| N1—C2—C3 | 126.6 (4) | N1′—C2′—C3′ | 125.0 (4) |
| C2—N1—C8 | 122.0 (4) | C2′—N1′—C8′ | 120.2 (3) |
| N1—C8—C9 | 121.8 (4) | N1′—C8′—C9′ | 121.9 (4) |
| C8—C9—C10 | 120.2 (4) | C8′—C9′—C10′ | 120.3 (4) |
| C8—C9—C13 | 121.1 (4) | C8′—C9′—C13′ | 120.4 (4) |
| Cl1—C4—C11 | 120.1 (4) | Cl1′—C4′—C11′ | 119.7 (4) |
| Cl1—C4—C12 | 119.0 (3) | Cl1′—C4′—C12′ | 118.2 (4) |

The weighting scheme applied was $w = (197.30/F)^2$ if $F \geq 197.30$ and $w$ = 1.0 if $197.3 > F$ and $F^2 < 2\sigma F^2$, otherwise $w$ = 0. H atoms were placed geometrically at a distance of 0.95 Å from their corresponding C atoms, while the H atoms of the C8 and C8′ atoms were taken from a difference map. For all H atoms, a riding model was used with $U_{iso}(H) = 1.3U_{eq}(C)$.

Data collection: *CAD-4 Express* (Enraf–Nonius, 1993). Cell refinement: *CAD-4 VAX/PC Fortran System* (Enraf–Nonius, 1988). Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SIR* (Burla *et al.*, 1989) in *MolEN*. Program(s) used to refine structure: *LSFM* in *MolEN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *MolEN*.

The authors wish to acknowledge the purchase of the CAD-4 diffractometer under Grant DPT/TBAG1 of the Scientific and Technical Research Council of Turkey.

---

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: AB1401). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

## References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. S1–S19.

Bocelli, G. & Cantoni, A. (1992). *Acta Cryst.* **C48**, 961–963.

Burla, M. C., Camalli, M., Cascarano, G., Giacovazzo, C., Polidori, G., Spagna, R. & Viterbo, D. (1989). *J. Appl. Cryst.* **22**, 389.

Casella, L. (1984). *Inorg. Chem.* **23**, 2781–2787.

Castro, J., Romero, J., Vázquez, J. A. G., Durán, M. L., Castineiras, A. & Sousa, A. (1990). *J. Chem. Soc. Dalton Trans.* pp. 3255–3258.

Charles, R. G. & Freiser, H. (1953). *J. Org. Chem.* **18**, 422–425.

Enraf–Nonius (1988). *CAD-4 VAX/PC Fortran System. Operator's Guide to the Enraf–Nonius CAD-4 Diffractometer Hardware, its Software and the Operating System.* Enraf–Nonius, Delft, The Netherlands.

Enraf–Nonius (1993). *CAD-4 Express Software.* Version 1.1. Enraf–Nonius, Delft, The Netherlands.

Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis.* Enraf–Nonius, Delft, The Netherlands.

Hordvik, A. (1966). *Acta Chem. Scand.* **20**, 1885–1891.

İde, S., Öztaş, S. G., Ancın, N. & Tüzün, M. (1996). *Cryst. Res. Technol.* **31**, 427–431.

Jadamus, H., Fernando, Q. & Freiser, H. (1964). *J. Am. Chem. Soc.* **86**, 3056–3059.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Krasinski, R. A. & Fackler, J. P. Jr (1994). *Acta Cryst.* **C50**, 2039–2041.

Lee, J. D. (1972). *Naturwissenchaften*, **15**, 36.

Lee, J. D. & Bryant, M. W. R. (1970). *Acta Cryst.* **B26**, 1729–1735.

Marsden, C. J. & Smith, B. J. (1988). *J. Phys. Chem.* **92**, 347–353.

Meyer, B. (1976). *Adv. Inorg. Chem. Radiochem.* **18**, 287–317.

Muller, A. & Diemann, E. (1987). *Adv. Inorg. Chem.* **31**, 89–122.

Orpen, A. G., Brammer, L., Allen, F. H., Kennard, O., Watson, D. G. & Taylor, R. (1989). *J. Chem. Soc. Dalton Trans.* pp. S1–S83.

Sugiura, Y. & Hirayama, Y. (1976). *Inorg. Chem.* **15**, 679–681.

Sugiura, Y., Hirayama, Y., Tanaka, H. & Ishizu, K. (1975). *J. Am. Chem. Soc.* **97**, 5577–5581.

Tinant, B. & Declercq, J.-P. (1986). *Acta Cryst.* **C42**, 383–384.

---

*Acta Cryst.* (1997). **C53**, 378–379

# *N*-Acetyl-2,3,4,6-tetra-*O*-acetyl-*N*-benzyl-*β*-D-glucopyranosylamine

MARÍA JESÚS DIÁNEZ, MARÍA DOLORES ESTRADA, AMPARO LÓPEZ-CASTRO AND SIMEÓN PÉREZ-GARRIDO

*Instituto de Ciencias de Materiales de Sevilla, and*
*Departamento de Física de la Materia Condensada,*
*CSIC-Universidad de Sevilla, Apartado 1065, 41080*
*Sevilla, Spain. E-mail: amparo@cica.es*

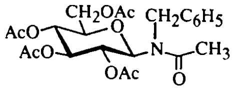
(*Received 16 May 1996; accepted 21 October 1996*)

## Abstract

The solid-state conformation of the title compound, $C_{23}H_{29}NO_{10}$, has been unequivocally established. The configuration at C1 is *β*-D-glucopyranose and the pyranose ring is essentially a perfect chair. Only the *E* rotamer along the N—C bond is observed.

## Comment

Many natural products and their derivatives have an *N*-acyl group joined to a sugar moiety and as the chemical and biological properties of these compounds depend on their structure and conformation, the correct determination is important. In some *N*-alkyl-*N*-glycosylamides, the presence of two conformational isomers is observed in solution due to hindered rotation about the amide C—N bond. In the present case, (I), no preferred conformation was established in solution so we undertook a crystal structure determination.



(I)

Crystals of (I) were obtained (Avalos, Babiano, Durán, Jiménez & Palacios, 1992) from the reaction of acetic anhydride with *N*-benzylglucopyranosylamine in pyridine. The same authors studied several sugar amides and thioamides, including the title compound, by NMR spectroscopy. Our structural analysis shows that only one anomer, *i.e.* *β*-D-glucopyranose, and one rotamer along the N—C bond (*E*) are present in the crystal.

A *PLATON* view (Spek, 1994) of the title molecule viewed along the *z* axis, together with the atomic numbering, is shown in Fig. 1. Bond lengths and angles agree with those of analogous compounds (Banic, Kojic-Prodic, Kroon-Beterburg & Keglevic, 1994; Vega, López-Castro & Márquez, 1986), although the pyranose endocyclic bond lengths [O1—C2 1.435 (3) and O—C5 1.427 (3) Å] do not show the anomeric effect characteristic of this ring. The phenyl, acetoxy and acetamide groups are essentially planar.

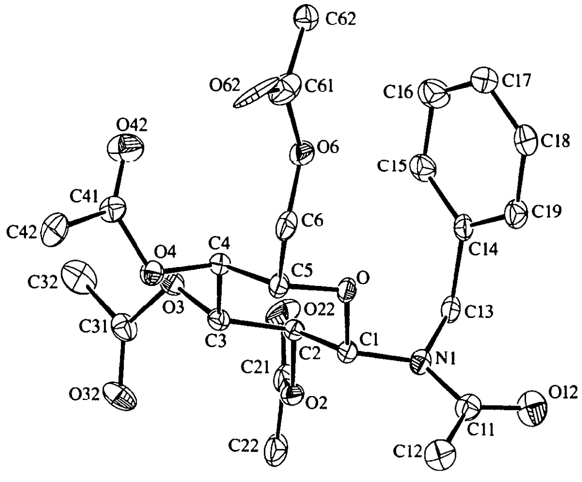


Fig. 1. A *PLATON* (Spek, 1994) plot of the title compound showing 30% probability displacement ellipsoids and the atom-numbering scheme. H atoms have been omitted for clarity.

*Acta Crystallographica Section C*
ISSN 0108-2701 © 1997