

most stable and that the enethiol S—H···O form was more stable than the corresponding enol O—H···S form (Buemi, 1990). In the present crystal structure, however, the molecule adopts the enol form. A Cambridge Structural Database search (Cambridge Structural Database Centre, 1996) for the 3-oxothioketone structures revealed that there had been four O—H···S forms (Richter, Sieler, Kaiser & Uhlemann, 1976; Norskov-Lauritsen, Carlsen & Duus, 1983; Richter *et al.*, 1989; Dolling, Kischkies, Heinemann & Hartung, 1993), but no S—H···O forms. The hydrogen-bonding geometry in the molecule [O(1)—H(8) 0.94 (7), H(8)···S(1) 2.01 (7), O(1)···S(1) 2.895 (4) Å, C(3)—O(1)—H(18) 106 (4) and O(1)—H(8)···S(1) 156 (6)°] shows typical values for chelated enol structures.

All the atoms of the molecule, except for the H(2), H(4) and H(7) atoms of the terminal methyl groups, lie on the crystallographic mirror plane.

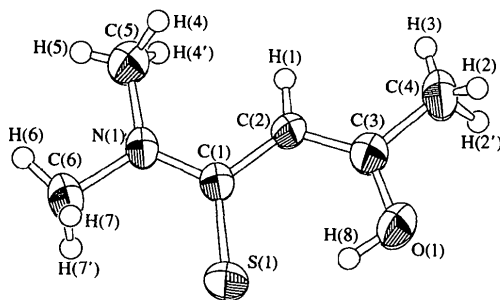


Fig. 1. View of the title compound with the atomic numbering system. Displacement ellipsoids are drawn at the 50% probability level.

Experimental

The title compound was obtained from the reaction of bis(tri-methylsilyl)thioketene and *N,N*-dimethylacetamide (Tsuchiya, Shibuya, Taguchi, Oishi & Honda, 1996). The single crystal was prepared by evaporation of a diethyl ether solution.

Crystal data

C₆H₁₁NOS
M_r = 145.22
 Monoclinic
*P*2₁/*m*
a = 8.472 (2) Å
b = 7.107 (2) Å
c = 6.533 (2) Å
 β = 99.84 (2)°
V = 387.6 (2) Å³
Z = 2
D_x = 1.244 Mg m⁻³
D_m not measured

Data collection

Rigaku AFC-5S diffractometer

Mo *K*α radiation
 λ = 0.7107 Å
 Cell parameters from 25 reflections
 θ = 12.5–14.8°
 μ = 0.341 mm⁻¹
T = 299 K
 Block
 0.2 × 0.2 × 0.1 mm
 Yellow transparent

541 reflections with *I* > $\sigma(I)$

ω scans

Absorption correction:
 empirical via ψ scan
 (Karcher *et al.*, 1989)
T_{min} = 0.858, *T_{max}* = 0.995
 1193 measured reflections
 1057 independent reflections

R_{int} = 0.0116

θ_{\max} = 27.5°

h = 0 → 10

k = 0 → 10

l = -9 → 9

3 standard reflections

every 100 reflections

intensity decay: 10.06%

Refinement

Refinement on *F*

R = 0.053

wR = 0.058

S = 1.29

541 reflections

82 parameters

All H atoms refined

w = 1/[$\sigma^2(F_o) + 0.0009|F_o|^2$]

(Δ/σ)_{max} = 0.092

$\Delta\rho_{\max}$ = 0.27 e Å⁻³

$\Delta\rho_{\min}$ = -0.30 e Å⁻³

Extinction correction: none

Scattering factors from

International Tables for Crystallography (Vol. C)

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

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

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
S(1)†	0.1853 (2)	1/4	0.1400 (2)	0.0598 (4)
O(1)†	0.4845 (4)	1/4	0.4305 (6)	0.073 (1)
N(1)†	-0.0287 (4)	1/4	0.3911 (5)	0.044 (1)
C(1)†	0.1273 (5)	1/4	0.3761 (6)	0.038 (1)
C(2)†	0.2432 (5)	1/4	0.5674 (7)	0.043 (1)
C(3)†	0.4038 (5)	1/4	0.5839 (7)	0.052 (1)
C(4)†	0.5120 (7)	1/4	0.7908 (10)	0.076 (2)
C(5)†	-0.0883 (7)	1/4	0.5868 (9)	0.056 (2)
C(6)†	-0.1522 (7)	1/4	0.2007 (9)	0.064 (2)
H(8)†	0.408 (9)	1/4	0.31 (1)	0.12 (2)

† Site occupancy = 0.5.

Table 2. Selected geometric parameters (Å, °)

S(1)—C(1)	1.697 (4)	N(1)—C(6)	1.482 (6)
O(1)—C(3)	1.306 (6)	C(1)—C(2)	1.451 (6)
N(1)—C(1)	1.342 (5)	C(2)—C(3)	1.346 (6)
N(1)—C(5)	1.453 (6)	C(3)—C(4)	1.497 (7)
C(1)—N(1)—C(5)	124.0 (4)	N(1)—C(1)—C(2)	117.8 (4)
C(1)—N(1)—C(6)	120.1 (4)	C(1)—C(2)—C(3)	126.5 (4)
C(5)—N(1)—C(6)	115.9 (4)	O(1)—C(3)—C(2)	126.3 (4)
S(1)—C(1)—N(1)	120.5 (3)	O(1)—C(3)—C(4)	111.9 (4)
S(1)—C(1)—C(2)	121.6 (3)	C(2)—C(3)—C(4)	121.8 (5)

The crystal density could not be measured due to high solubility in organic solvents and decomposition in aqueous solutions. The compound is air sensitive. The standard reflections indicated an intensity decay of 10.06% even though the crystal was sealed in a glass capillary. A polynomial correction was applied. All H atoms were located in difference Fourier maps.

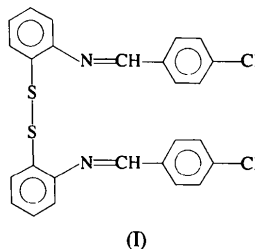
Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1994). Program(s) used to solve structure: *SIR88* (Burla *et al.*, 1989). Program(s) used to refine structure: *TEXSAN LS*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *TEXSAN FINISH*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FR1014). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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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 & Tüzün, 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.



Acta Cryst. (1997). **C53**, 376–378

N,N'-Bis(4-chlorobenzylidene)-2,2'-diaminodiphenyl Disulfide

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(Received 14 June 1996; accepted 6 November 1996)

Abstract

In the title compound, *N,N'*-bis(4-chlorobenzylidene)-disulfanediybis(2-aniline), C₂₆H₁₈Cl₂N₂S₂, 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

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 *pπ*–*dπ* 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 *π* 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