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N,*N*′-Dibenzyldithiooxamide

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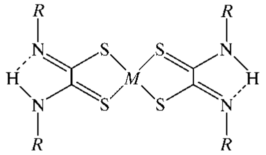
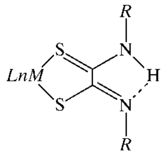
The title compound, alternatively known as *N*,*N*′-dibenzylethanedithioamide, $C_{16}H_{16}N_2S_2$, lies about an inversion centre and contains a planar *trans*-dithiooxamide fragment characterized by a strong intramolecular hydrogen bond between the S atom and the adjacent amide H atom in the solid state, with an S···N distance of 2.926 (1) Å. The aryl substituent is oriented orthogonal to the mean plane of the *trans*-dithiooxamide fragment due to steric hindrance and this effect is discussed.

Comment

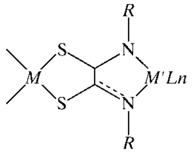
We are interested in building polymetallic complexes through the combined use of both bi- and monofunctionalized metal complexes of types (I) and (II). In both classes of compound, the ═N—H···N═ moiety splits the Cl-bridged $[L'_nM'\mathrm{Cl}]_2$ dimers and gives rise to the heterobimetallic fragment (III).



(I)

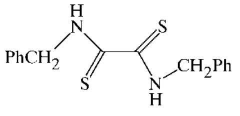


(II)



(III)

To date, we have prepared and fully characterized a number of heterobimetallic complexes (Lanza *et al.*, 1996, 2000; Bruno *et al.*, 2002). The synthesis of tri- and tetrametallic species is at an advanced stage. In this context, we have found that steric hindrance on nitrogen and nitrogen basicity are important factors in determining the reactivity of secondary dithiooxamides in the stepwise construction of our polymetallic systems (Lanza *et al.*, 2002). For this reason, it is useful to collect structural information on the *R* substituents of secondary dithiooxamides, both free and coordinated, with regard to both their steric congestion and their electronic influence on the N—C—S fragment. Hence, the title compound, (IV), has been crystallized and its structure is presented here.



(IV)

The molecule of (IV) lies on a crystallographic centre and consists of a central N—CS—CS—N moiety and two benzyl substituents attached to the N atoms. A detailed analysis of the bond distances reveals a strong double-bond character for both C1—S and C1—N [1.660 (1) and 1.316 (2) Å, respectively], confirming that the important electronic π-delocalization of the N—C—S system does not affect the central C—C single bond [1.533 (2) Å].

The central dithiooxamide (DTO) fragment is perfectly planar, with a maximum deviation of −0.003 (1) Å for atom C1. The bond parameters for C1—N show the typical slightly distorted trigonal geometry, the sums of the valence bond angles both being 360 (1)°. The planarity of the *trans*-thiooxamide fragment, as required by the intermediate inversion centre, allows the formation of a significant intramolecular interaction between the H atom on the N atom and the S($-x$, $-y$, $-z$) atom. The intramolecular hydrogen bond detected in the solid state has also been observed in solution; the ^{1}H NMR spectrum of (IV) in $CDCl_3$ shows an N—H resonance at 10.55 p.p.m. Chemical-shift (Emsley, 1980), line-broadening and dilution experiments also indicate that the N—H group is involved in a strong intramolecular -*R*N—H···S═ interaction in solution.

The tetrahedral atom C2 of the *N*-benzyl substituent is almost in the same plane as the DTO fragment [deviation 0.020 (1) Å]; the phenyl ring forms a dihedral angle of 82.91 (6)° with this plane. This orthogonal arrangement, and the enlargement of the C1—N—C2 and N—C2—C3 *endo* angles with respect to the idealized values [126.1 (1) and 113.4 (1)°, respectively], might be related to steric hindrance between the H atoms linked to atoms N and C8. This is confirmed by the complete planarity observed for the molecule of *N*,*N*′-bis(2-pyridylmethyl)dithiooxamide (Bermejo *et al.*, 1998), where atom C8 is formally replaced by an N atom carrying no H atom. In such a case, the amide H atom interacts either with the S atom or with the pyridine N atom on the same plane, in a three-atom/four-electron bond, which further stabilizes of the coplanar arrangement.

The same situation is observed in the analogous *N*,*N*′-bis(pyridylmethyl)diooxamides reported in the literature. The two 4-pyridyl structures reported by Nguyen *et al.* (1998) have the *ortho* position occupied by the hindering CH group, which causes the same orthogonal disposition; the OC—NH—CH_2—C_{py} torsion angles are 97.4 (2) and 100.9 (2)°, comparable with

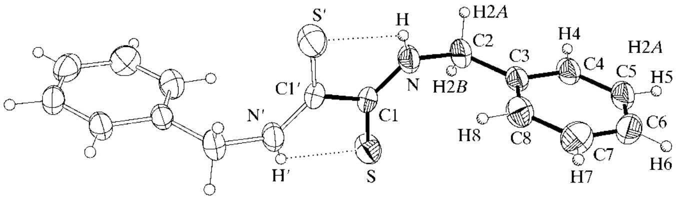


Figure 1
A perspective molecular view of (IV), showing the atomic numbering scheme for the asymmetric unit. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Open atoms and bonds represent the equivalent part of the molecule obtained by the symmetry operation ($-x$, $-y$, $-z$). Dotted lines represent intramolecular hydrogen-bond interactions.

the corresponding value of 99.6 (1)° in (IV). On the other hand, the 4-pyridyl isomer reported by Liu *et al.* (1999) shows the planar conformation, with the amide H atom interacting with both the adjacent O and pyridine N atoms.

Experimental

Dibenzyldithiooxamide was synthesized by a slight modification of the method of Hurd *et al.* (1961). Benzylamine (two equivalents, 2.14 g) was mixed with dithiooxamide (0.002 mol). The mixture was homogenized in a mortar and, after a few minutes, the crude dibenzyldithiooxamidate solidified. The pure compound was crystallized from ethanol. For the diffraction study, suitable crystals of (IV) were grown by slow evaporation of an ethanol solution at room temperature. The compound was initially identified from the NMR spectra. Spectroscopic analysis, ^{1}H NMR (300.13 MHz, $CDCl_3$, δ, p.p.m): 10.55 (*bs*, 1H, NH), 7.2–7.4 (*mm*, 5H, phenyl H), 4.93 (*d*, $^3J_{HH}$ = 6.10 Hz, 2H, $N-CH_2$); $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$, δ, p.p.m.): C_S 184.5, C_1 131.01, C_2–C_6 129.00, C_3–C_5 128.09, C_4 128.20 (four aromatic C), 51.5 ($N-CH_2$).

Crystal data

$C_{16}H_{16}N_2S_2$
$M_r = 300.43$
Monoclinic, $P2_1/c$
$a = 7.665$ (2) Å
$b = 10.533$ (2) Å
$c = 9.263$ (2) Å
$\beta = 98.57$ (2)°
$V = 739.5$ (3) Å^3
$Z = 2$

$D_x = 1.349$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 34 reflections
$\theta = 6.8$–12.9°
$\mu = 0.35$ mm^{-1}
$T = 293$ (2) K
Irregular, orange
0.68 × 0.40 × 0.12 mm

Data collection

Siemens *P*4 diffractometer
$\omega/2\theta$ scans
2167 measured reflections
1986 independent reflections
1568 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.014$
$\theta_{\rm max} = 29.1°$

$h = 0 \rightarrow 10$
$k = 0 \rightarrow 14$
$l = -12 \rightarrow 12$
3 standard reflections
every 197 reflections
intensity decay: 2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.096$
$S = 1.03$
1986 reflections
124 parameters

All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0642P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.29$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.27$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S—C1	1.660 (1)	C1—C1^i	1.533 (2)
N—C1	1.316 (2)	C2—C3	1.513 (2)
N—C2	1.455 (2)	C3—C8	1.379 (2)
C1—N—C2	126.1 (1)	C1^i—C1—S	121.3 (1)
N—C1—C1^i	113.4 (1)	N—C2—C3	113.4 (1)
N—C1—S	125.3 (1)		
C2—N—C1—C1^i	179.2 (1)	C1—N—C2—C3	−99.6 (1)

Symmetry code: (i) $-x$, $-y$, $-z$.

Table 2
Intramolecular contact geometry (Å, °).

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N—H⋯S^i	0.80 (2)	2.42 (2)	2.926 (1)	122 (1)
C8—H8⋯N	0.96 (2)	2.51 (2)	2.855 (2)	101 (1)

Symmetry code: (i) $-x$, $-y$, $-z$.

All H atoms were located in difference Fourier syntheses and were included in the refinement as free isotropic atoms.

Data collection: *P*3/*V* (Siemens, 1989); cell refinement: *P*3/*V*; data reduction: *SHELXTL-Plus* (Siemens, 1990); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XPW* (Siemens, 1996); software used to prepare material for publication: *PARST*97 (Nardelli, 1995) and *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1132). Services for accessing these data are described at the back of the journal.

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