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N,N'-Bis(2-pyridylmethyl)dithiooxamide

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Abstract

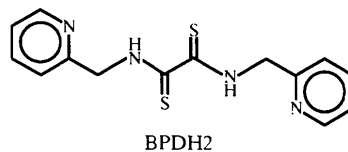
Molecules of the title compound (BPDH2, C₁₄H₁₄N₄S₂) belong to the C_i point group, with only half of the molecule in an asymmetric unit. The molecule is planar to within 0.006 Å, with intramolecular N—H···S and N—H···N hydrogen bonds [H···N 2.10 (4) and H···S 2.48 (4) Å].

Comment

In the last twenty years, the study of the magnetic properties of polynuclear complexes has attracted considerable interest, due to the occurrence in many such compounds of interactions between the metal centres which considerably alter their magnetic behaviour (Ginsberg, 1971; Daudey *et al.*, 1985). Specifically, many studies have been carried out on dinuclear species, with copper(II) or nickel(II) as metal centres, and with bichelating dianions such as oxalate

(Alvarez *et al.*, 1985) or oxamide (Sigel & Martin, 1982) as ligands. However, few compounds in which the ligands are dithiooxamide or its *N,N'*-disubstituted derivatives have been studied. Recently, a number of compounds have been designed, synthesized and characterized, which consist of dithiooxamides *N,N'*-disubstituted with coordinating groups (Ali Deveci & Irez, 1994; Castiñeiras *et al.*, 1995). In many cases, these compounds, in the presence of copper(II) or nickel(II), yield dinuclear complexes with antiferromagnetic properties (Vidal, 1994).

The title molecule, BPDH2, adopts a *trans* conformation (Fig. 1), which is crystallographically imposed by the inversion centre. This conformation is also found in dithiooxamide (DTO; Wheatley, 1965)



and in some *N,N'*-disubstituted dithiooxamides, such as *N,N'*-bis(trimethylsilyl)dithiooxamide (BTMDTO; Rinne & Thewalt, 1978), *N,N'*-diisopropylidithiooxamide (DIPDTO; Klaska *et al.*, 1980; Drew *et al.*, 1984), *N,N'*-diethyldithiooxamide (DEDTO; Drew *et al.*, 1982) and *N,N'*-bis(2-hydroxypropyl)dithiooxamide (BHPDTO; Drew *et al.*, 1984).

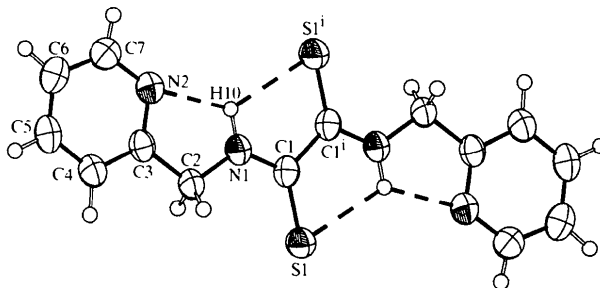


Fig. 1. Plot of BPDH2, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level, and H atoms are shown as spheres with small arbitrary radii. [Symmetry code: (i) 1 - x, 1 - y, 1 - z.]

The structural parameters found for BPDH2 (Table 1) are comparable to those reported for other *N,N'*-disubstituted dithiooxamides (Rinne & Thewalt, 1978; Klaska *et al.*, 1980; Drew *et al.*, 1982, 1984; Jean, 1994), with typical bond distances which do not deviate significantly from those reported for compounds containing the thioamide group (Orpen *et al.*, 1994).

The overall molecule is planar to within 0.006 Å; not only is the dithiooxamide unit planar, as expected for a dithiooxamide function lying across a crystallographic inversion centre, but the pyridine ring also occupies the same plane. This conformation is favoured by the presence of intramolecular hydrogen bonds (Jeffrey &

Saenger, 1991), involving the N—H units participating in bifurcated interactions with the thiocarbonyl S and the heterocyclic N atoms (Table 2).

Experimental

The synthesis of the title compound was carried out according to the method described in the literature (Ali Deveci & Irez, 1994). To a suspension of dithiooxamide (4.66 g, 39.8 mmol) in ethanol (80 ml), 2-(aminomethyl)pyridine (8 ml, 77.6 mmol) was added dropwise over a period of 30 min. The mixture was then heated under reflux for 2 h. The resulting yellow-brown solid was filtered, washed with cold ethanol, vacuum dried and finally recrystallized from ethanol/methyl cyanide (1:1) (yield: 72%).

Crystal data

C₁₄H₁₄N₄S₂
M_r = 302.41
 Monoclinic
*P*2₁/*c*
a = 8.108 (5) Å
b = 5.345 (1) Å
c = 16.680 (11) Å
 β = 94.16 (3)°
V = 720.9 (7) Å³
Z = 2
D_x = 1.393 Mg m⁻³
D_m not measured

Data collection

Enraf-Nonius CAD-4
 diffractometer
 ω scans
 Absorption correction:
 empirical (North *et al.*,
 1968; Nonius BV, 1997)
T_{min} = 0.577, *T_{max}* = 0.848
 1504 measured reflections
 1242 independent reflections

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.052
wR (*F*²) = 0.146
S = 1.027
 1242 reflections
 119 parameters
 H atoms: see below
w = 1/[σ²(*F_o*²) + (0.0681*P*)²
 + 0.2519*P*]
 where *P* = (*F_o*² + 2*F_c*²)/3

Cu *K*α radiation
 λ = 1.54184 Å
 Cell parameters from 25
 reflections
 θ = 11.47–28.24°
 μ = 3.301 mm⁻¹
T = 291 (2) K
 Needle
 0.35 × 0.05 × 0.05 mm
 Yellow-brown

826 reflections with
I > 2σ(*I*)
R_{int} = 0.073
 θ_{\max} = 67.13°
h = -1 → 9
k = 0 → 5
l = -19 → 19
 3 standard reflections
 frequency: 60 min
 intensity decay: none

(Δ/σ)_{max} < 0.001
 $\Delta\rho_{\max}$ = 0.23 e Å⁻³
 $\Delta\rho_{\min}$ = -0.21 e Å⁻³
 Extinction correction: none
 Scattering factors from
*International Tables for
 Crystallography* (Vol. C)

Table 1. Selected geometric parameters (Å, °)

S1—C1	1.657 (4)	N1—C2	1.438 (5)
N1—C1	1.311 (5)	C1—C1'	1.524 (7)
C1—N1—C2	124.6 (3)	N1—C1—S1	124.3 (3)
N1—C1—C1'	113.3 (4)	C1'—C1—S1	122.4 (4)

Symmetry code: (i) 1 - x, 1 - y, 1 - z.

Table 2. Hydrogen-bonding geometry (Å, °)

D—H...A	D—H	H...A	D...A	D—H...A
N1—H10...N2	0.94 (4)	2.10 (4)	2.626 (5)	114 (3)
N1—H10...S1'	0.94 (4)	2.48 (4)	2.935 (4)	110 (3)

Symmetry code: (i) 1 - x, 1 - y, 1 - z.

The structure was solved by direct methods and refined by full-matrix least-squares techniques. All H atoms were located from difference maps and refined isotropically.

Data collection: *CAD-4 Software* (Enraf-Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *OpenMolEN* (Nonius BV, 1997). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *PLATON* (Spek, 1997). Software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1197). Services for accessing these data are described at the back of the journal.

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