

Table 2. Selected geometric parameters (Å, °)

N1—C2	1.460 (5)	C11—N12	1.451 (4)
N1—C9a	1.373 (4)	N12—C13	1.350 (4)
N1—C10	1.472 (7)	C13—O14	1.226 (5)
C2—C3	1.516 (5)	C13—C15	1.475 (5)
C2—C11	1.514 (5)	C15—C16	1.352 (5)
C3—N4	1.447 (5)	C15—C19	1.419 (5)
N4—C5	1.306 (4)	C16—O17	1.362 (5)
C5—C5a	1.447 (5)	O17—C18	1.350 (6)
C5—C1'	1.479 (5)	C18—C19	1.350 (5)
C5a—C6	1.422 (4)	C1'—C2'	1.391 (5)
C5a—C9a	1.428 (5)	C1'—C6'	1.397 (5)
C6—C7	1.356 (5)	C2'—C3'	1.373 (6)
C7—C8	1.395 (5)	C3'—C4'	1.392 (6)
C8—C8M	1.506 (6)	C4'—C5'	1.380 (6)
C8—C9	1.370 (5)	C5'—C6'	1.385 (6)
C9—C9a	1.421 (5)		
C9a—N1—C10	118.6 (4)	N1—C9a—C5a	126.2 (3)
C2—N1—C10	113.4 (3)	C2—C11—N12	113.1 (3)
C2—N1—C9a	126.7 (3)	C11—N12—C13	121.8 (3)
N1—C2—C11	110.5 (3)	N12—C13—C15	115.2 (3)
N1—C2—C3	112.2 (3)	N12—C13—O14	122.6 (3)
C3—C2—C11	113.8 (3)	O14—C13—C15	122.2 (3)
C2—C3—N4	111.4 (3)	C13—C15—C19	130.2 (3)
C3—N4—C5	124.1 (3)	C13—C15—C16	123.6 (3)
N4—C5—C1'	114.8 (3)	C16—C15—C19	106.2 (3)
N4—C5—C5a	122.3 (3)	C15—C16—O17	110.4 (3)
C5a—C5—C1'	122.9 (3)	C16—O17—C18	106.3 (3)
C5—C5a—C9a	127.5 (3)	O17—C18—C19	110.9 (4)
C5—C5a—C6	115.0 (3)	C15—C19—C18	106.2 (4)
C6—C5a—C9a	117.5 (3)	C5—C1'—C6'	121.8 (3)
C5a—C6—C7	123.4 (3)	C5—C1'—C2'	119.3 (3)
C6—C7—C8	119.6 (3)	C2'—C1'—C6'	118.8 (3)
C7—C8—C9	119.0 (3)	C1'—C2'—C3'	120.8 (3)
C7—C8—C8M	120.8 (4)	C2'—C3'—C4'	120.2 (4)
C8M—C8—C9	120.2 (4)	C3'—C4'—C5'	119.5 (4)
C8—C9—C9a	123.5 (3)	C4'—C5'—C6'	120.6 (4)
C5a—C9a—C9	117.0 (3)	C1'—C6'—C5'	120.0 (3)
N1—C9a—C9	116.7 (3)		
C2—N1—C9a—C5a	24.4 (6)	N4—C5—C1'—C2'	-41.8 (5)
C9a—N1—C2—C11	-109.3 (4)	N4—C5—C5a—C9a	-28.8 (5)
C9a—N1—C2—C3	18.8 (5)	C5—C5a—C9a—N1	-3.8 (6)
N1—C2—C11—N12	-172.9 (3)	C2—C11—N12—C13	89.3 (4)
N1—C2—C3—N4	-75.7 (4)	C11—N12—C13—O14	-2.7 (6)
C2—C3—N4—C5	69.4 (4)	C11—N12—C13—C15	176.4 (3)
C3—N4—C5—C5a	-4.4 (5)	N12—C13—C15—C19	0.5 (6)

The data were collected with a scan width of 60 steps of 0.02° with extra steps for the  $\alpha_1$ - $\alpha_2$  dispersion. The variable scan speed ranged from 0.5 to 1.5 s per step. The ratio of total background to scan time was 0.5. The structure was solved by direct methods and refined anisotropically by full-matrix least squares on  $F^2$ . H atoms were positioned geometrically and allowed to ride on their parent atoms.

Data collection: *DIF4* (Stoe & Cie, 1988). Cell refinement: *DIF4*. Data reduction: *REDU4* (Stoe & Cie, 1992b). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEX2.1* (McArdle, 1994). Software used to prepare material for publication: *PARST* (Nardelli, 1983).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1182). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

## References

- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.  
 McArdle, P. (1994). *J. Appl. Cryst.* **27**, 438–439.  
 Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.  
 Peeters, O. M., Blaton, N. M., Meurisse, R. L. & De Ranter, C. J. (1994a) *Acta Cryst.* **C50**, 1350–1352.  
 Peeters, O. M., Blaton, N. M., Meurisse, R. L. & De Ranter, C. J. (1994b) *Acta Cryst.* **C50**, 1352–1354.  
 Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. Univ. of Göttingen, Germany.  
 Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. Univ. of Göttingen, Germany.  
 Stoe & Cie (1988). *DIF4. Diffractometer Control Program*. Version 6.2. Stoe & Cie, Darmstadt, Germany.  
 Stoe & Cie (1992a). *EMPIR. Empirical Absorption Correction Program*. Version 1.2. Stoe & Cie, Darmstadt, Germany.  
 Stoe & Cie (1992b). *REDU4. Data Reduction Program*. Version 7.08. Stoe & Cie, Darmstadt, Germany.

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## Pyridoxal Isonicotinoyl Hydrazone (PIH), a Synthetic Ion-Chelating Agent

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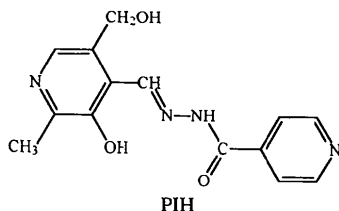
## Abstract

Pyridoxal isonicotinoyl hydrazone [3-hydroxy-5-(hydroxymethyl)-2-methyl-4-pyridinecarboxaldehyde 4-pyridinecarbonylhydrazone,  $C_{14}H_{14}N_4O_3$ ] exhibits a non-planar conformation. Non-H atoms lie almost in two planes, one of the isonicotinoyl ring, the other of the remainder of the molecule, with a dihedral angle of 17.41° between them. The central C=N—N'—C=O chain has an *E* configuration around the C=N double bond of the hydrazone bridge, a *trans* motif of the amide group along —N'—C= and an *S-trans* conformation along

the N—N' bond. This geometry allows intramolecular hydrogen bonding between the hydrazone N atom and the 3-hydroxy group.

### Comment

As part of our studies of synthetic chelating agents able to eliminate excess *p*<sup>6</sup> and 3*d* metal ions *in vivo*, we are currently investigating the capability of aroyl hydrazones, and in particular pyridoxal isonicotinoyl hydrazone (PIH), to monitor iron concentration in blood.



The biological properties of PIH are becoming fairly well documented (Ponka, Borova, Neuwirt, Fuchs & Necas, 1979; Ponka, Borova, Neuwirt & Fuchs, 1979; Huang & Ponka, 1983; Avramovici-Grisaru, Sarel, Link & Hershko, 1983; Ponka, Richardson, Baker, Schulman & Edwards, 1988). However, little is known about the structure of the title compound, although some spectroscopic and physico-chemical data are now available (Fakhrayan, Doucet & El-Hage Chahine, 1993; Dubois, Fakhrayan, Doucet & El-Hage Chahine, 1992; Richardson *et al.*, 1990; Wis Vitolo, Hefter, Clare & Webb, 1990; Avramovici-Grisaru, Sarel, Cohen & Bauminger, 1985; Aruffo, Murphy, Johnson, Rose & Schomaker, 1982; Murphy, Rose, Schomaker & Aruffo, 1985; Murphy, Johnson, Rose, Aruffo & Schomaker, 1982; Colonna, Cossé-Barbi, Massat & Doucet, 1993; Colonna, Cossé-Barbi, Massat, Ben Abdelmoumene & Doucet, 1993). For this compound, various conformers are possible *a priori*, but neither IR nor NMR results, nor semi-empirical quantum calculations can give definitive conclusions (Colonna, Cossé-Barbi, Massat, Ben Abdelmoumene & Doucet, 1993). Determination of the crystal structure of PIH is therefore required for a better understanding of its complexation ability and interpretation of its *in vitro* and *in vivo* behaviour.

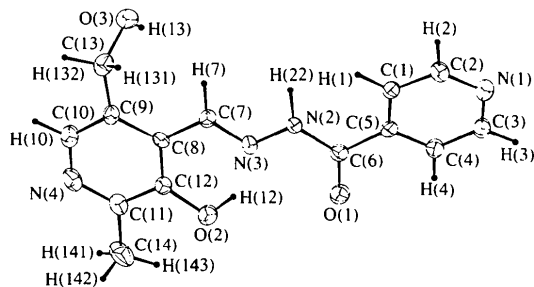


Fig. 1. ORTEP (Johnson, 1976) drawing of the PIH molecule showing 50% probability displacement ellipsoids for non-H atoms.

All non-H atoms in the molecule almost lie in two planes: one plane corresponds to the isonicotinoyl ring (maximum deviation 0.01 Å), the other to the remaining part of the molecule (maximum deviation 0.06 Å). These two planes make a dihedral angle along the C(5)—C(6) bond (Fig. 1) of 17.41°. The central chain is best described as C(7)=N(3)—N(2)—C(6)=O(1). As in the comparable molecules salicylaldehyde benzoyl hydrazone (SBH) and *N*-pyridoxylidene-*N'*-picolinoyl-hydrazine monohydrochloride monohydrate (Damiano, Musatti, Pelizzi & Predieri, 1978), this chain is of *E* configuration around the double bond of the hydrazone bridge, C(7)=N(3). An amide *trans* motif can be observed along C(6)—N(2) as can an *S-trans* conformation along the N(2)—N(3) bond. This geometry allows an intramolecular hydrogen bond between H(12) and N(3). As to the crystal structure, it is noteworthy that in contrast to SBH, the carbonyl O(1) atom is not involved in the hydrogen-bonding network. This shows the major importance of the pyridoxal CH<sub>2</sub>OH group in the lattice cohesion; only intermolecular H(13)⋯N(1) and H(22)⋯O(3) bonds take part in the crystal formation (Fig. 2).

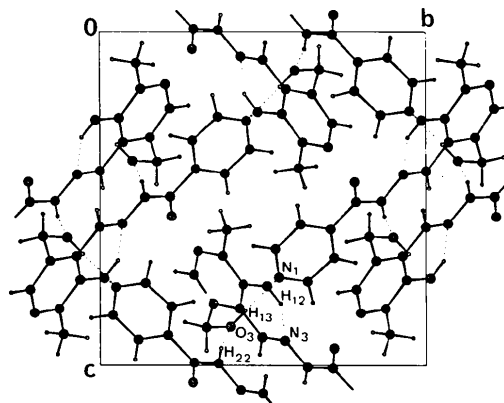


Fig. 2. Projection of the structure on (100) showing the repartition of hydrogen bonds.

### Experimental

Pyridoxal isonicotinoyl hydrazone was synthesized by condensing isonicotinoylhydrazide with pyridoxal hydrochloride in equimolar amounts, in the presence of sodium acetate, at pH 5. The precipitate was recrystallized from methanol. The picnometric density at 293 K was obtained by immersion of *ca* 1 g of powder in xylene (*D* = 0.861). Single crystals for X-ray analysis were obtained under isostatic conditions [298 (1) K]. Their morphology, elongated along [111], was established by means of a Nedinsco double-circle optic goniometer and X-ray precession method.

#### Crystal data

C<sub>14</sub>H<sub>14</sub>N<sub>4</sub>O<sub>3</sub>  
*M*<sub>r</sub> = 286.3

Mo Kα radiation  
 λ = 0.71069 Å

Monoclinic  
 $P2_1/n$   
 $a = 8.156(2) \text{ \AA}$   
 $b = 13.017(3) \text{ \AA}$   
 $c = 13.035(3) \text{ \AA}$   
 $\beta = 89.81(2)^\circ$   
 $V = 1383.9(5) \text{ \AA}^3$   
 $Z = 4$   
 $D_x = 1.374 \text{ Mg m}^{-3}$   
 $D_m = 1.37(2) \text{ Mg m}^{-3}$

Cell parameters from 24 reflections  
 $\theta = 10\text{--}16^\circ$   
 $\mu = 0.0934 \text{ mm}^{-1}$   
 $T = 293 \text{ K}$   
 Elongated along [111]  
 $0.250 \times 0.160 \times 0.100 \text{ mm}$   
 Colourless

C(1)—C(2)	1.393 (7)	C(1)—C(5)	1.375 (6)
C(3)—C(4)	1.388 (7)	C(4)—C(5)	1.371 (7)
C(5)—C(6)	1.499 (6)	C(7)—C(8)	1.464 (6)
C(8)—C(9)	1.407 (7)	C(8)—C(12)	1.385 (7)
C(9)—C(10)	1.383 (7)	C(9)—C(13)	1.495 (7)
C(11)—C(12)	1.398 (7)	C(11)—C(14)	1.502 (8)
C(3)—N(1)—C(2)	117.3 (5)	C(6)—N(2)—N(3)	116.1 (4)
C(7)—N(3)—N(2)	118.6 (4)	C(11)—N(4)—C(10)	118.0 (5)
C(5)—C(1)—C(2)	119.1 (5)	C(1)—C(2)—N(1)	123.0 (5)
C(4)—C(3)—N(1)	123.1 (5)	C(5)—C(4)—C(3)	119.3 (5)
C(4)—C(5)—C(1)	118.2 (5)	C(6)—C(5)—C(1)	125.5 (5)
C(6)—C(5)—C(4)	116.3 (4)	O(1)—C(6)—N(2)	122.4 (5)
C(5)—C(6)—N(2)	116.1 (4)	C(5)—C(6)—O(1)	121.5 (5)
C(8)—C(7)—N(3)	117.3 (4)	C(9)—C(8)—C(7)	120.9 (4)
C(12)—C(8)—C(7)	121.5 (5)	C(12)—C(8)—C(9)	117.6 (4)
C(10)—C(9)—C(8)	117.7 (5)	C(13)—C(9)—C(8)	122.8 (4)
C(13)—C(9)—C(10)	119.5 (5)	C(9)—C(10)—N(4)	124.4 (5)
C(12)—C(11)—N(4)	121.6 (5)	C(14)—C(11)—N(4)	118.1 (5)
C(14)—C(11)—C(12)	120.3 (5)	C(8)—C(12)—O(2)	123.7 (4)
C(11)—C(12)—O(2)	115.6 (5)	C(11)—C(12)—C(8)	120.6 (5)
C(9)—C(13)—O(3)	113.9 (4)		

#### Data collection

Enraf—Nonius CAD-4 diffractometer  
 $\omega$ - $2\theta$  scans  
 Absorption correction: none  
 2705 measured reflections  
 2409 independent reflections  
 882 observed reflections  
 $[I \geq 3\sigma(I)]$

$R_{\text{int}} = 0.042$   
 $\theta_{\text{max}} = 25^\circ$   
 $h = -9 \rightarrow 9$   
 $k = 0 \rightarrow 15$   
 $l = 0 \rightarrow 15$   
 3 standard reflections  
 frequency: 60 min  
 intensity decay: <1%

#### Refinement

Refinement on  $F$   
 $R = 0.0389$   
 $wR = 0.0383$   
 $S = 1.138$   
 882 reflections  
 191 parameters  
 H-atom parameters not refined  
 Unit weights applied

$(\Delta/\sigma)_{\text{max}} = 0.005$   
 $\Delta\rho_{\text{max}} = 0.16 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.06 \text{ e \AA}^{-3}$   
 Extinction correction: none  
 Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

The  $\omega$ -scan width was  $(0.8 + 0.345\tan\theta)^\circ$  with an  $\omega$ -scan rate of  $1^\circ \text{ min}^{-1}$  and background counts for 5 s on each side of every scan. The positions of the non-H atoms were obtained by direct methods with the *SHELXS86* program (Sheldrick, 1985) and H atoms were found in difference Fourier maps. Non-H atoms were refined with anisotropic displacement parameters; isotropic displacement parameters of H atoms were fixed at  $U = 0.069 \text{ \AA}^2$ , the mean value obtained during a precedent refinement cycle with the *CRYSTALS* program (Watkin, Carruthers & Betteridge, 1985). The highest peak on the final difference Fourier map ( $0.16 \text{ e \AA}^{-3}$ ) was situated near N(4).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: PA1163). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	$x$	$y$	$z$	$U_{\text{eq}}$
N(1)	0.0567 (5)	0.5501 (4)	0.7351 (3)	0.0439
N(2)	0.1252 (5)	0.8633 (3)	0.5056 (3)	0.0304
N(3)	0.1119 (5)	0.9316 (3)	0.4259 (3)	0.0325
N(4)	0.1827 (6)	1.1993 (4)	0.1568 (3)	0.0488
O(1)	-0.1019 (4)	0.7822 (3)	0.4483 (3)	0.0445
O(2)	-0.0351 (4)	0.9861 (3)	0.2623 (3)	0.0476
O(3)	0.5834 (4)	1.0994 (3)	0.3846 (3)	0.0449
C(1)	0.1296 (6)	0.7181 (4)	0.6764 (4)	0.0350
C(2)	0.1361 (6)	0.6383 (4)	0.7474 (4)	0.0407
C(3)	-0.0337 (6)	0.5396 (4)	0.6506 (4)	0.0427
C(4)	-0.0488 (6)	0.6164 (4)	0.5773 (4)	0.0388
C(5)	0.0336 (6)	0.7072 (4)	0.5906 (3)	0.0298
C(6)	0.0116 (6)	0.7864 (4)	0.5083 (4)	0.0322
C(7)	0.2215 (6)	1.0010 (4)	0.4159 (3)	0.0323
C(8)	0.2063 (6)	1.0710 (4)	0.3285 (3)	0.0283
C(9)	0.3183 (6)	1.1520 (4)	0.3142 (4)	0.0324
C(10)	0.3002 (7)	1.2126 (4)	0.2278 (4)	0.0451
C(11)	0.0763 (7)	1.1233 (4)	0.1705 (4)	0.0444
C(12)	0.0832 (6)	1.0593 (4)	0.2565 (4)	0.0352
C(13)	0.4549 (7)	1.1736 (4)	0.3873 (4)	0.0447
C(14)	-0.0583 (8)	1.1107 (5)	0.0932 (5)	0.0641

Table 2. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

N(1)—C(2)	1.329 (6)	N(1)—C(3)	1.335 (6)
N(2)—N(3)	1.372 (5)	N(2)—C(6)	1.365 (6)
N(3)—C(7)	1.277 (6)	N(4)—C(10)	1.346 (7)
N(4)—C(11)	1.327 (7)	O(1)—C(6)	1.215 (5)
O(2)—C(12)	1.358 (6)	O(3)—C(13)	1.425 (6)

#### References

- Aruffo, A., Murphy, T. B., Johnson, D. K., Rose, N. J. & Schomaker, V. (1982). *Inorg. Chim. Acta*, **67**, L25–27.
- Avramovici-Grisaru, S., Sarel, S., Cohen, S. & Bauminger, R. E. (1985). *Isr. J. Chem.* **25**, 288–292.
- Avramovici-Grisaru, S., Sarel, S., Link, G. & Hershko, C. (1983). *J. Med. Chem.* **26**, 298–302.
- Colonna, C., Cossé-Barbi, A., Massat, A., Ben Abdelmoumene, R. & Doucet, J. P. (1993). *Bull. Soc. Chim. Belg.* **102**, 411–430.
- Colonna, C., Cossé-Barbi, A., Massat, A. & Doucet, J. P. (1993). *Spectrosc. Lett.* **26**, 1065–1072.
- Damiano, P., Musatti, A., Pelizzi, C. & Predieri, G. (1978). *Cryst. Struct. Commun.* **7**, 751–755.
- Dubois, J. E., Fakhryan, H., Doucet, J. P. & El-Hage Chahine, J. M. (1992). *Inorg. Chim.* **31**, 853–859.
- Fakhryan, H., Doucet, J. P. & El-Hage Chahine, J. M. (1993). *Bull. Soc. Chim. Belg.* **102**, 377–389.
- Huang, A. R. & Ponka, P. (1983). *Biochim. Biophys. Acta*, **757**, 306–315.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Murphy, T. B., Johnson, D. K., Rose, N. J., Aruffo, A. & Schomaker, V. (1982). *Inorg. Chim. Acta*, **66**, L67–68.
- Murphy, T. B., Rose, N. J., Schomaker, V. & Aruffo, A. (1985). *Inorg. Chim. Acta*, **108**, 183–194.
- Ponka, P., Borova, J., Neuwirt, J. & Fuchs, O. (1979). *FEBS Lett.* **97**, 317–321.

- Ponka, P., Borova, J., Neuwirt, J., Fuchs, O. & Necas, E. (1979). *Biochim. Biophys. Acta*, **586**, 278–297.
- Ponka, P., Richardson, D., Baker, E., Schulman, H. M. & Edwards, J. T. (1988). *Biochim. Biophys. Acta*, **967**, 122–129.
- Richardson, R., Wis Vitolo, L. M., Hefter, G. T., May, P. M., Clare, B. W. & Webb, J. (1990). *Inorg. Chim. Acta*, **170**, 165–170.
- Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. Univ. of Göttingen, Germany.
- Watkin, D. G., Carruthers, J. R. & Betteridge, P. W. (1985). *CRYSTALS User Guide*. Chemical Crystallography Laboratory, Univ. of Oxford, England.
- Wis Vitolo, L. M., Hefter, G. T., Clare, B. W. & Webb, J. (1990). *Inorg. Chim. Acta*, **170**, 171–176.

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### *N,N'*-Dicyclohexyldithiooxamide

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#### Abstract

The crystal structure determination of *N,N'*-dicyclohexyldithiooxamide, C<sub>14</sub>H<sub>24</sub>N<sub>2</sub>S<sub>2</sub>, has confirmed the *trans* conformation for the molecule. The C—S and C—N bond lengths indicate that the molecule consists of two coupled thioamide functions (S—C—N), where net delocalization of  $\pi$  electrons occurs, bonded through a single C—C bond.

#### Comment

Dithiooxamide molecules are a versatile class of ligands built up of two thioamide (S—C—N) moieties (Green, Jubran, Buersten & Busch, 1987). The dihedral angle  $\theta$  between these groups can vary depending on the substituents *R* at the N atoms (Servaas, Stufkens, Oskam, Vernooijs, Baerends, De Ridder & Stam, 1989). Structure determinations of *N,N'*-R<sub>2</sub>dto (R = Et, <sup>i</sup>Pr, H; dto = dithiooxamide) have confirmed

a *trans* conformation in these molecules ( $\theta = 180^\circ$ ) (Drew, Kisenyi & Willey, 1982; Drew, Kisenyi, Willey & Wandiga, 1984; Weatley, 1965). The existence of the *cis* conformation is not expected because of steric interactions. However, upon complexation, *S,S*-chelate coordination has been found in most of the metal complexes of neutral *N,N'*-R<sub>2</sub>dto ligands. In these, the planarity imposed by the *cis* form is prohibited by the steric hindrance between the two thioamide protons; dihedral angles of around  $36^\circ$  have been reported in Zn(Me<sub>2</sub>dto)Cl<sub>2</sub> and [Cu(Bz<sub>2</sub>dto)<sub>2</sub>]ClO<sub>4</sub> (Bz = benzyl) (Antolini, Fabretti, Franchini, Menabue, Pellacani, Desseyn, Dommissie & Hofmans, 1987). *S,S*-Bidentate bridging coordination has been reported only in polymeric SbCl<sub>3</sub>L<sub>1.5</sub> (L = *N,N'*-diethyldithiooxamide), in which each bridging dithiooxamide molecule that separates the SbCl<sub>3</sub> moieties adopts a *trans* conformation as found for the uncomplexed ligand. We have recently determined the X-ray crystal structure of the dinuclear mixed ligand complex [Hg(H<sub>2</sub>dcdto)Cl<sub>2</sub>]<sub>2</sub>.EtOH (H<sub>2</sub>dcdto is *N,N'*-dicyclohexyldithiooxamide), in which one *S,S'*-chelating and one *S,S'*-bridging ligand coexist in a dinuclear unit (Baggio, Perek & Garland, 1995). The calculated dihedral angles are 52.6 and 66.4°, respectively. The latter value shows that the bridging ligand in which the S atoms are free from any constraint arising from *S,S*-chelation is also strongly distorted, contrasting with the near-planar *trans* conformation in polymeric SbCl<sub>3</sub>L<sub>1.5</sub>. Such a distorted conformation of the bridging ligand had not been reported previously and was attributed to Hg...S secondary interactions due to the high affinity of mercury for sulfur-donor ligands. In order to confirm this point an X-ray structure determination of the free H<sub>2</sub>dcdto ligand, (I), was undertaken.

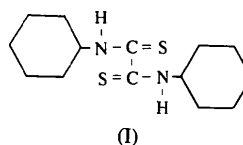


Fig. 1 shows a structural diagram and the atomic numbering scheme of the H<sub>2</sub>dcdto molecule. Note that just half of the molecule is crystallographically independent, as it lies on a center of symmetry, so only two complete molecules are found in the unit cell. They display a *trans* conformation as in the previously reported structures mentioned above. Also, the S1—C1—N1—C2 torsion angle is close to zero, having a value of  $-0.5(3)^\circ$ . The C—S and C—N bond lengths in the thioamide groups are 1.656(2) and 1.318(3) Å, respectively. These values, like those of the other known structures, confirm the importance of the resonance forms, *i.e.* S=C—NHR  $\leftrightarrow$  S<sup>-</sup>—C=N<sup>+</sup>HR. The central C—C distance between the two coupled thioamide groups of 1.534(4) Å is in accordance with the value of 1.53 Å for a normal C<sub>sp<sup>3</sup></sub>—C<sub>sp<sup>3</sup></sub> bond,