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N,N'-Dicyclohexyldithiooxamide

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Abstract

The crystal structure determination of *N,N'*-dicyclohexyldithiooxamide, C₁₄H₂₄N₂S₂, 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 π 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 θ 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*₂dto (*R* = Et, ^{*i*}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*₂dto 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° have been reported in Zn(Me₂dto)Cl₂ and [Cu(Bz₂dto)₂]ClO₄ (Bz = benzyl) (Antolini, Fabretti, Franchini, Menabue, Pellacani, Desseyn, Dommissie & Hofmans, 1987). *S,S*-Bidentate bridging coordination has been reported only in polymeric SbCl₃L_{1.5} (*L* = *N,N'*-diethyldithiooxamide), in which each bridging dithiooxamide molecule that separates the SbCl₃ 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(H₂dcdto)Cl₂]₂.EtOH (H₂dcdto 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 SbCl₃L_{1.5}. 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 H₂dcdto ligand, (I), was undertaken.

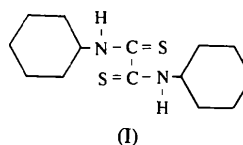


Fig. 1 shows a structural diagram and the atomic numbering scheme of the H₂dcdto molecule. Note that just half of the molecule is crystallographically independent, as it lies on a center of symmetry, so only two complete molecules are found in the unit cell. They display a *trans* conformation as in 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⁻—C=N⁺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_{sp³}—C_{sp³} bond,

suggesting that delocalization of π electrons is limited in the free molecule to the thioamide moieties only. The N1—C2 distance of 1.464 (3) Å is also in accordance with the normal value of about 1.47 Å for such bonds [e.g. 1.466 (7) (Antolini *et al.*, 1987) and 1.477 (9) Å (Baggio *et al.*, 1995)]. With regard to the geometry of the cyclohexyl groups (in chair conformations), angles and other metric parameters are unexceptional. There are no close contacts less than the sum of the van der Waals radii involving the ligand molecule (Fig. 2). This expected result confirms the high versatility of coordination of the dithioamide ligand in its metal complexes.

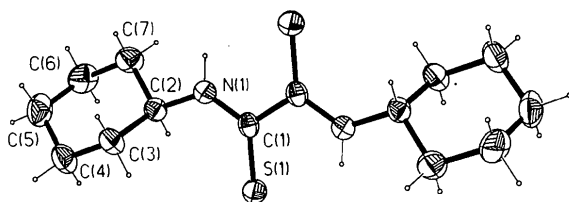


Fig. 1. Schematic view of the title molecule showing the numbering scheme used. Displacement ellipsoids are drawn at the 40% probability level.

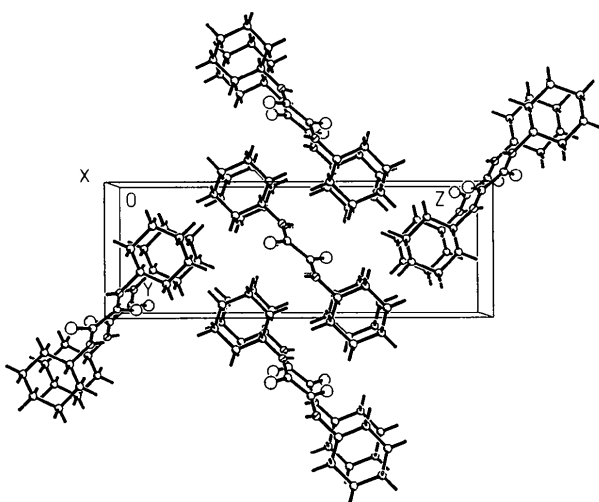


Fig. 2. Diagram showing the packing along the [100] direction.

Experimental

The title compound was commercially available (97%, Aldrich). Crystals were obtained by recrystallization from a toluene–tetramethoxysilane (1:1) solution.

Crystal data

$C_{14}H_{24}N_2S_2$
 $M_r = 284.47$
 Monoclinic
 $P2_1/c$
 $a = 5.923 (1) \text{ \AA}$
 $b = 6.803 (1) \text{ \AA}$
 $c = 19.554 (5) \text{ \AA}$
 $\beta = 90.00 (3)^\circ$

Mo $K\alpha$ radiation
 $\lambda = 0.71073 \text{ \AA}$
 Cell parameters from 25 reflections
 $\theta = 7.5\text{--}12.5^\circ$
 $\mu = 0.323 \text{ mm}^{-1}$
 $T = 293 (2) \text{ K}$
 Irregular block

$V = 787.9 (3) \text{ \AA}^3$
 $Z = 2$
 $D_x = 1.199 \text{ Mg m}^{-3}$

$0.48 \times 0.45 \times 0.38 \text{ mm}$
 Orange

Data collection

Siemens R3m diffractometer
 $\theta/2\theta$ scans (4.19–
 $29.3^\circ \text{ min}^{-1}$)
 Absorption correction:
 none
 1275 measured reflections
 1041 independent reflections
 1010 observed reflections
 $[I > 2\sigma(I)]$

$R_{int} = 0.0082$
 $\theta_{max} = 22.54^\circ$
 $h = 0 \rightarrow 6$
 $k = 0 \rightarrow 7$
 $l = -21 \rightarrow 21$
 2 standard reflections
 monitored every 98
 reflections
 intensity decay: <1%

Refinement

Refinement on F^2
 $R(F) = 0.0254$
 $wR(F^2) = 0.0747$
 $S = 0.267$
 1041 reflections
 84 parameters
 H atoms refined riding on
 their host atoms
 $w = 1/[\sigma^2(F_o^2) + (0.1755P)^2$
 $+ 4.0742P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = 0.298$

$\Delta\rho_{max} = 0.170 \text{ e \AA}^{-3}$
 $\Delta\rho_{min} = -0.120 \text{ e \AA}^{-3}$
 Extinction correction:
 $F_c^* = kF_c[1 + (0.000113$
 $\times F_c^2 \lambda^3 / \sin 2\theta)]^{-1/4}$
 (SHELXL93; Sheldrick,
 1993)
 Atomic scattering factors
 from *International Tables*
 for *Crystallography* (1992,
 Vol. C, Tables 4.2.6.8 and
 6.1.1.4)

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

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

	x	y	z	U_{eq}
S1	0.26896 (12)	0.05432 (9)	-0.07218 (3)	0.0544 (3)
N1	-0.1360 (3)	0.1949 (3)	-0.04336 (9)	0.0415 (5)
C1	0.0269 (4)	0.0685 (3)	-0.03008 (11)	0.0382 (6)
C2	-0.1295 (4)	0.3446 (3)	-0.09714 (10)	0.0407 (5)
C3	-0.1971 (4)	0.2587 (3)	-0.16621 (11)	0.0499 (6)
C4	-0.1842 (5)	0.4171 (4)	-0.22095 (13)	0.0614 (8)
C5	-0.3283 (5)	0.5907 (4)	-0.20349 (15)	0.0694 (9)
C6	-0.2679 (7)	0.6743 (4)	-0.13364 (14)	0.0682 (8)
C7	-0.2794 (5)	0.5161 (3)	-0.07819 (12)	0.0547 (7)

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

S1—C1	1.656 (2)	C2—C3	1.525 (3)
N1—C1	1.318 (3)	C3—C4	1.521 (3)
N1—C2	1.464 (3)	C4—C5	1.497 (4)
C1—C1 ¹	1.534 (4)	C5—C6	1.522 (4)
C2—C7	1.513 (3)	C6—C7	1.529 (3)
C1—N1—C2	125.2 (2)	C7—C2—C3	111.0 (2)
N1—C1—C1 ¹	113.3 (2)	C2—C3—C4	109.8 (2)
N1—C1—S1	125.0 (2)	C5—C4—C3	111.7 (2)
C1 ¹ —C1—S1	121.7 (2)	C4—C5—C6	111.4 (2)
N1—C2—C7	110.2 (2)	C5—C6—C7	111.3 (2)
N1—C2—C3	111.2 (2)	C2—C7—C6	110.1 (2)

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

The non-crystallographic β value of $90.00 (3)^\circ$ in the monoclinic title compound made it very difficult to obtain single crystals suitable for X-ray analysis, since attempts to recrystallize it from different protic solvents invariably afforded twinned ($\bar{1}00/010/001$) specimens displaying an almost perfect mmm Laue symmetry. Quite by chance, recrystallization of N,N' -dicyclohexyldithioamide (97%, Aldrich) from a

toluene–tetramethoxysilane (1:1) solution yielded large transparent orange crystals, which upon cleavage produced some specimens with an adequate bias (~ 30/70%) towards one of the two twinned components. The degree of their 'monoclinic' character (*2/m* Laue symmetry) was tested through the screening of their (*h0l*) diffraction pattern and a small crystal was chosen to attempt the structure solution. Direct methods processing of a preliminary data set resulted in a clear *E* map which distinctly suggested the whole non-H structure out of its ghost image. A second, complete data set was then gathered on a robust perfectly twinned (52/48% after refinement) specimen, for which the previous model was refined by full-matrix least squares making use of the *SHELXL93 TWIN* option (Sheldrick, 1993). Non-H atoms were refined anisotropically, while H atoms were added at their expected positions and allowed to ride on their host atoms with an overall isotropic displacement parameter of 0.08 Å². Almost no remaining electron density could be found in the unusually flat final difference Fourier map.

Data collection: *P3/P4-PC Diffractometer Program* (Siemens, 1991). Cell refinement: *P3/P4-PC Diffractometer Program*. Data reduction: *XDISK* in *SHELXTL/PC* (Sheldrick, 1991). Program(s) used to solve structure: *XS* in *SHELXTL/PC*. Program(s) used to refine structure: *SHELXL93*. Molecular graphics: *XP* in *SHELXTL/PC*. Software used to prepare material for publication: *CIFTAB* in *SHELXL93*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: SZ1025). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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2 α ,5 α ,9 α -Trihydroxy-10 β ,13 α -diacetoxy-4 β ,20-epoxy-taxa-11-en, ein neues Taxan aus *Taxus chinensis*

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Abstract

The title compound, 2,3,4a,5,6,7,8,11,12,12a-decahydro-3,5,12-trihydroxy-9,12a,13,13-tetramethyl-6,10-methano-[benzocyclodecene-4(1*H*)-spiro-2'-oxirane]-8,11-diyl diacetate, C₂₄H₃₆O₈, is a structurally new taxane from *Taxus chinensis*. This X-ray diffraction study reveals the configurations at positions 2, 5, 9, 10 and 13 (IUPAC numbering: 5, 3, 12, 11 and 8, respectively), thus establishing that the investigated compound is the 2,9-desacetyl derivative of the already known taxane Baccatin I. Notably, the positions of the methyl groups of the dimethylmethano bridge of the cyclodecene ring (C16 and C17), which have been the subject of conflicting discussions in some papers, are proven, as is the *trans* junction of the *B/C* rings. Furthermore, the *trans* positioning of the substituents at C atoms 9 and 10 is shown. The six-membered rings adopt chair conformations and the eight-membered *B* ring is severely puckered.

Kommentar

Taxane spielen in der Therapie der malignen Tumore eine wichtige Rolle. Seit den ersten Untersuchungen zur Wirksamkeit von Extrakten der Rinde von *Taxus brevifolia* und der Isolierung der aktiven Komponente Taxol und deren Röntgenstrukturanalyse (Wani, Taylor, Wall, Coggon & McPhail, 1971) sind eine Vielzahl von Untersuchungen zur Gewinnung und Darstellung von Taxanen publiziert worden. Hierbei zeigte es sich, daß lediglich Taxol und sein strukturell verwandtes Molekül Taxotere eine ausreichende Wirksamkeit aufweisen. Problematisch hierbei ist jedoch die Gewinnung aus der