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Structure of 2-Iminocyclopentanedithioic Acid

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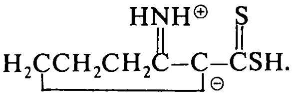
Abstract. $C_6H_9NS_2$, $M_r = 159{\cdot}3$, monoclinic, $A2/a$, $a = 13{\cdot}265\,(1)$, $b = 10{\cdot}310\,(1)$, $c = 12{\cdot}198\,(1)$ Å, $\beta = 114{\cdot}03\,(1)°$, $U = 1523{\cdot}8\,(2)$ Å^3, $Z = 8$, $D_x = 1{\cdot}388$, D_m(flotation in KI solution) = $1{\cdot}318$ Mg m^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}5418$ Å, $\mu = 5{\cdot}53$ mm^{-1}, $F(000) = 624$, room temperature, final $R = 0{\cdot}051$ for 1135 unique observed reflections. All the non-H atoms lie on a plane. The C—N bond distance of 1·305 (4) Å is consistent with a C=N double bond, whereas two H atoms are located around the N atom. Bond distances around the C atom at the α position of the dithiocarboxy group [C(2)] of 1·394 (4) [C(1)—C(2)], 1·400 (4) [C(2)—C(3)] and 1·500 (4) Å [C(2)—C(6)] indicate that the atom is sp^2 hybridized.

Introduction. Derivatives of β-iminodithioic acids have been used to study the coordination chemistry of transition metals as a model of metal–sulfur compounds in the body system (Nag & Joardar, 1976; Chaudhury, 1984). However, a few of the compounds have been studied by means of the X-ray diffraction method (Miyamae & Takato, 1982), and they are sometimes referred to as β-aminodithioic acids. To confirm the structure, the present crystal structure determination was carried out.

Experimental. Compound prepared according to the method reported by Takeshima, Fukuda, Miyauchi, Muraoka, Yamamoto & Hayashi (1974). Crystal dimensions *ca* 0·77 × 0·26 × 0·21 mm; Rigaku AFC-5 four-circle diffractometer, graphite monochromator; cell parameters refined by least-squares fit on the basis of 30 unique 2θ values ($24{\cdot}9 < 2\theta < 30{\cdot}0°$); $2\theta_{\max} = 130°$; h −15 to 13, k 0 to 12, l 0 to 14; θ–2θ scan mode, scan speed 8° min^{-1} (θ); 1464 reflections measured; 1135 intensities with $|F_o|/\sigma(|F_o|) \geq 3{\cdot}0$ considered as observed and used for structure determination; 2 standard reflections showed no significant change in $|F|$ (< 1%); corrections for Lorentz and polarization but not for absorption or extinction; all non-H atoms located by direct method using *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978); H atoms located on a difference electron density map; positional parameters for all atoms, anisotropic thermal parameters for non-H atoms and isotropic for H atoms refined by block-diagonal least squares; $R = 0{\cdot}051$, $wR = 0{\cdot}059$, $S = 4{\cdot}569$ with $w = 1/[\sigma^2 + (0{\cdot}02F_o)^2]$; $\sum(w|\Delta F|^2)$ minimized; final $\Delta/\sigma < 0{\cdot}1$ for non-H atoms; max. $\Delta\rho$ excursion in final difference map 0·5 e Å^{-3}; complex neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974); calculations carried out on a FACOM M-160F computer at the computer center of this university with *UNICS*III (Sakurai & Kobayashi, 1979).

Discussion. Final atomic coordinates are given in Table 1.† Fig. 1 shows the molecular structure with the atom numbering and deviation of each non-H atom from the molecular plane. Bond distances and angles within the molecule are listed in Table 2.

The short N(1)—C(3) distance certainly indicates double-bond character. However, two H atoms have been located around the N(1) atom. The H atoms are on the molecular plane.

C(2) is surrounded by two π-bond systems, —C=S and —C=N. The C(1)—C(2) and C(2)—C(3) bond distances are short enough to indicate that the C(2) atom is sp^2 hybridized. This is supported by the fact that all of the non-H atoms are almost on a plane as shown in Fig. 1. Thus it should be considered that an H atom has migrated to the N(1) atom, though a chemical formula suggests that it should be bonded to the C(2) atom. The molecule should be assigned as  $H_2CCH_2CH_2\overset{HNH^{\oplus}}{\overset{\|}{C}}-\underset{\ominus}{C}-\overset{S}{\overset{\|}{C}}SH$. This situation is similar to that previously observed (Miyamae & Takato, 1982), where the C atom at the α position of the dithiocarboxy group is also sp^2 hybridized.

Takeshima *et al.* (1974) reported that cyclohexane derivatives of this compound are unstable in ambient conditions and are easily converted into 2,4-dinitrophenyl esters. Generally, a cyclopentene ring is

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† Lists of anisotropic thermal parameters, structure factors and an equation of the least-squares plane of the molecule have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42312 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Positional parameters* ($\times 10^4$) *and equivalent isotropic thermal parameters*

$$B_{\rm eq} = \tfrac{8}{3}\pi^2 \textstyle\sum_i \sum_j U_{ij} a^*_i a^*_j \mathbf{a}_i . \mathbf{a}_j .$$

	x	y	z	$B_{\rm eq}$(Å^2)
S(1)	3689 (1)	530 (1)	2023 (1)	4·75 (0·04)
S(2)	6062 (1)	756 (1)	3672 (1)	5·51 (0·04)
N	3005 (2)	−2084 (3)	2648 (3)	4·33 (0·10)
C(1)	4809 (3)	−112 (3)	3141 (3)	3·25 (0·10)
C(2)	4879 (2)	−1311 (3)	3696 (3)	2·82 (0·09)
C(3)	4019 (2)	−2203 (3)	3444 (3)	3·03 (0·10)
C(4)	4397 (3)	−3390 (3)	4197 (3)	4·10 (0·12)
C(5)	5569 (3)	−3095 (3)	5074 (3)	4·93 (0·13)
C(6)	5913 (3)	−1844 (3)	4659 (3)	3·72 (0·11)

Table 2. *Bond distances* (Å) *and angles* (°) *within the molecule*

S(1)–C(1)	1·690 (3)	S(1)–C(1)–S(2)	119·0 (2)
S(2)–C(1)	1·762 (3)	S(1)–C(1)–C(2)	127·0 (2)
N–C(3)	1·305 (4)	S(2)–C(1)–C(2)	113·9 (2)
C(1)–C(2)	1·394 (4)	C(1)–C(2)–C(3)	126·1 (2)
C(2)–C(3)	1·400 (4)	C(1)–C(2)–C(6)	124·4 (3)
C(3)–C(4)	1·489 (4)	C(3)–C(2)–C(6)	109·5 (2)
C(4)–C(5)	1·517 (4)	N–C(3)–C(2)	127·0 (3)
C(5)–C(6)	1·522 (5)	N–C(3)–C(4)	121·5 (3)
C(6)–C(2)	1·500 (4)	C(2)–C(3)–C(4)	111·4 (2)
		C(3)–C(4)–C(5)	105·2 (3)
		C(4)–C(5)–C(6)	107·2 (3)
		C(5)–C(6)–C(2)	105·6 (3)

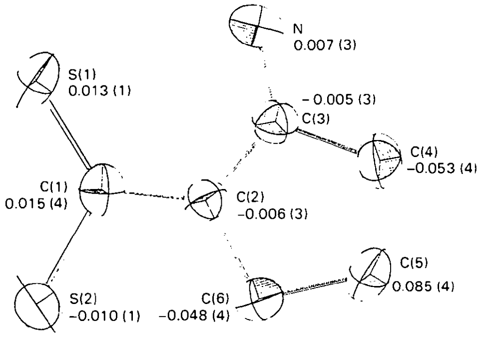

Fig. 1. Molecular structure with deviations (Å) of the atoms from the molecular plane.

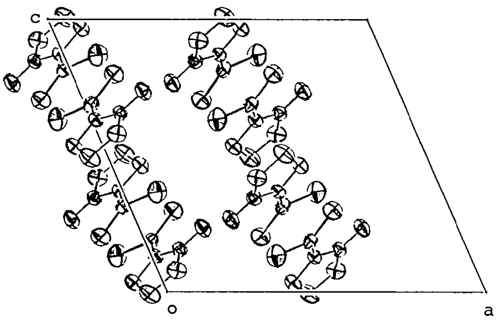

Fig. 2. An *ORTEP* (Johnson, 1971) projection of the crystal along −**b**.

much more stable than a cyclohexane ring. Thus the stability of these compounds should be related to the fact that the α carbon at the dithiocarboxy group takes part in π-electron delocalization of —C=S and —C=N double bonds.

Although all bonds within the five-membered ring except C(2)—C(3) are expected to be normal single bonds (1·54 Å), the C(3)—C(4) and C(2)—C(6) bonds are shorter than this. A similar shortening is also observed in the previous study. This should be a result of hyperconjugation of the C(3) and C(6) atoms with the π-bond system.

Bond angles S(1)—C(1)—C(2), C(1)—C(2)—C(3) and C(2)—C(3)—N are all greater than 120°, which is the expected value for simple sp^2 hybridization. These values probably result from the short S(1)···H—N hydrogen bond [S(1)···N 3·038 (4) Å]. The S(1)···N distance is much shorter than the sum of the van der Waals radii of these atoms (3·35 Å: calculated from the data of Huheey, 1978). On the other hand, the expansion of the three bond angles mentioned above brings S(2) close to C(6) at 2·977 (4) Å, which is *ca* 0·45 Å shorter than the sum of the van der Waals radii.

A packing diagram viewed along −**b** is depicted in Fig. 2. There are two intermolecular distances shorter than 3·5 Å: S(1)···N$^{\rm i}$ 3·463 (3) and N···C(5)$^{\rm ii}$ 3·474 (4) Å [symmetry operations (i) $\frac{1}{2}-x$, $\frac{1}{2}+y$, $\frac{1}{2}-z$; (ii) $-\frac{1}{2}+x$, $\frac{1}{2}-y$, $-\frac{1}{2}+z$]. The former can be regarded as the result of an intermolecular hydrogen bond between S(1) and N$^{\rm i}$ [S(1)···H(N2$^{\rm i}$) 2·58 (4) Å]. A couple of centrosymmetrically related molecules almost overlap each other.

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