Acta Cryst. (1982). B**38**, 3166–3168

Structure of Methyl 2-Cyano-3-iminodithiobutyrate

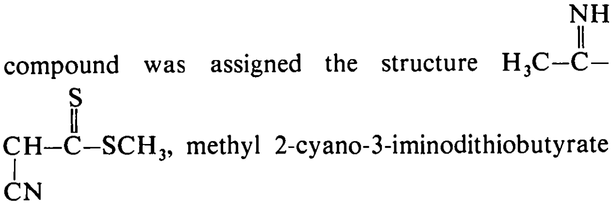
By Hiroshi Miyamae and Haruko Takato

Department of Chemistry, Faculty of Science, Josai University, Keyaki-dai, Sakado-shi, Saitama 350-02, *Japan*

(*Received* 31 *May* 1982; *accepted* 6 *July* 1982)

Abstract. $C_6H_8N_2S_2$, $M_r = 172{\cdot}1$, monoclinic, space group $P2_1/c$, $a = 8{\cdot}655\,(2)$, $b = 12{\cdot}556\,(2)$, $c = 8{\cdot}836\,(2)$ Å, $\beta = 119{\cdot}29\,(1)°$, $U = 837{\cdot}5\,(3)$ Å^3, $Z = 4$, $D_x = 1{\cdot}366$, D_m (flotation in KI solution) $= 1{\cdot}374$ Mg m^{-3}, μ(Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å) $= 0{\cdot}54$ mm^{-1}, $F(000) = 360$. The final R dropped to 0·039 for 802 independent observed reflections. All of the atoms except H are on a plane. The C—N(imino) bond length of 1·306 (5) Å is consistent with a C=N double bond. The C atom at the α position of the dithiocarboxyl group [C(2)] is surrounded by three π-bond systems of —C=S, —C=N and —C≡N, and the averaged C—C bond distance around the C(2) atom of 1·428 (6) Å indicates that the C(2) atom is sp^2 hybridized.

Introduction. The structure analysis of a derivative of an iminodithiocarboxylic acid was carried out. The compound was assigned the structure



$$H_3C{-}\overset{\overset{\displaystyle NH}{\|}}{C}{-}\underset{\underset{\displaystyle CN}{|}}{CH}{-}\overset{\overset{\displaystyle S}{\|}}{C}{-}SCH_3$$

, methyl 2-cyano-3-iminodithiobutyrate (CIDT-Me), from chemical analysis and on the basis of the IR spectra (Muraoka, Yamamoto, Yamaguchi, Tonosaki, Takeshima & Fukuda, 1977). However, a question remained unsolved: why is the imino group stabilized in this structure?

The compound was prepared according to the method reported by Muraoka *et al.* (1977). The crystals were grown from ethanol solution by evaporation at 278 K. The yellow-colored, transparent crystal specimen used for intensity measurements had dimensions 0·48 × 0·38 × 0·41 mm.

Lattice parameters were obtained by a least-squares refinement of 24 values of 2θ ($32 \le 2\theta \le 34°$) measured on a Rigaku AFC-5 automated four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0{\cdot}71069$ Å). Intensities of 2701 reflections were measured by the θ–2θ scan mode ($2\theta_{\rm max} = 65°$) at a speed of 3° min^{-1} in θ of which 802 independent intensities with $|F| \ge 3\sigma(|F|)$ were regarded as 'observed'. Corrections were applied for Lp effects but not for absorption [μ(Mo $K\alpha$) $= 0{\cdot}54$ mm^{-1}].

The structure was solved by the heavy-atom method. The coordinates of the two S atoms were obtained from a Patterson map and the following Fourier syntheses gave the positions of all the remaining non-H atoms. They were refined by block-diagonal least squares with anisotropic thermal parameters. The positions of all of the H atoms except that bonded to C(2) (see Fig. 1) were determined from difference Fourier maps. The remaining H atom was located later around the N(1) atom. They were refined isotropically. The final R and R_w were 0·039 and 0·041 for 802 unique reflections. Final atomic parameters are listed in Table 1.* The final shifts of all parameters were less than $\frac{1}{3}$ of the e.s.d. except for those of the H atoms. Atomic scattering factors including anomalous scattering were taken from *International Tables for X-ray Crystallography* (1974). The structure determination and refinement were carried out on the FACOM M-150F and FACOM M-160F computers of this University using the *Universal Crystallographic Computer Program System UNICS* III (Sakurai & Kobayashi, 1978).

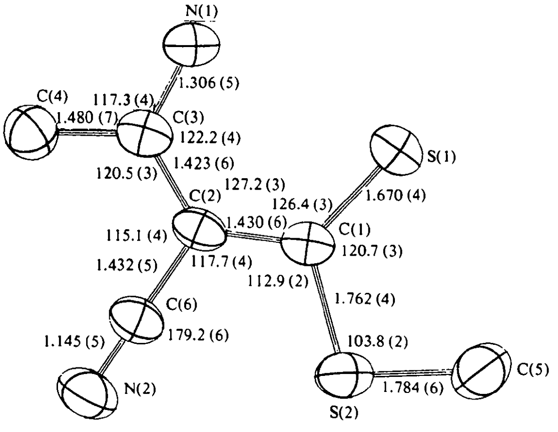


Fig. 1. Molecular structure with bond lengths (Å) and angles (°).

---

* Lists of anisotropic thermal parameters and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38052 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

0567-7408/82/123166-03$01.00

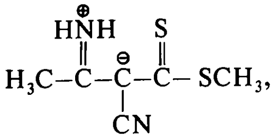
Table 1. *Atomic coordinates* ($\times 10^4$; $\times 10^3$ *for* H) *and isotropic thermal parameters* (Å^2)

	x	y	z	B_{eq}/B
S(1)	409 (1)	286 (1)	2648 (1)	4·11 (4)
S(2)	2018 (2)	2304 (1)	4550 (2)	4·48 (4)
N(1)	3113 (5)	−563 (3)	1770 (5)	4·26 (13)
N(2)	5984 (5)	2572 (3)	4746 (5)	4·80 (15)
C(1)	2093 (5)	1149 (3)	3455 (4)	3·05 (12)
C(2)	3689 (5)	1065 (3)	3358 (4)	3·04 (12)
C(3)	4148 (5)	249 (3)	2531 (4)	3·22 (12)
C(4)	5842 (5)	297 (3)	2502 (5)	4·18 (15)
C(5)	−76 (6)	2218 (4)	4473 (6)	5·16 (18)
C(6)	4968 (5)	1901 (3)	4122 (5)	3·46 (13)
H(1)	622 (6)	−25 (4)	205 (6)	7·9 (1·4)
H(2)	679 (6)	50 (4)	365 (6)	6·7 (1·2)
H(3)	589 (6)	95 (4)	194 (6)	6·8 (1·2)
H(4)	−23 (7)	144 (4)	504 (7)	9·7 (1·4)
H(5)	−110 (6)	224 (4)	326 (6)	5·8 (1·1)
H(6)	−25 (6)	262 (4)	516 (6)	6·5 (1·2)
H(7)	222 (6)	−65 (4)	178 (6)	6·5 (1·2)
H(8)	331 (6)	−107 (3)	112 (5)	5·4 (1·1)

Discussion. Fig. 1 shows the molecular structure with atomic numbering. The bond lengths and angles within the molecule are also given in Fig. 1. The N(1)—C(3) bond distance certainly indicates that this bond can be designated as a double bond, in agreement with the assignment from the IR spectra (Muraoka *et al.*, 1977). However, two H atoms have been located around the N(1) atom.

The C(2) atom is surrounded by three π-bond systems, —C=S, —C=N and —C≡N. Furthermore, the averaged C—C bond length around the C(2) atom of 1·428 (6) Å is comparable with that observed in graphite (1·42 Å; Wells, 1975), indicating that C(2) is sp^2 hybridized. This is also suggested from the bond angles around the C(2) atom. The least-squares plane of the molecule calculated from all of the non-H atoms is given in Table 2. The maximum deviation from the plane is only 0·029 (4) Å, for the C(4) atom. It should be noted here that the observed geometry of the present molecule suggests extensive delocalization of the π-electrons through the C(2) atom. This could be a reason why the N(1)—C(3) bond remains as a double bond.

This implies 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. Thus the molecule should be assigned the structure



$$H_3C-\overset{\overset{\oplus}{HNH}}{\overset{\|}{C}}-\underset{\underset{CN}{|}}{\overset{\ominus}{C}}-\overset{S}{\overset{\|}{C}}-SCH_3,$$

though the negative charge should be delocalized over the π-bond systems.†

Table 2. *Equation of the least-squares plane of CIDT-Me and deviations of atoms from that plane* (Å)

Equation: $0{\cdot}01393x - 0{\cdot}50599y + 0{\cdot}74536z = 1{\cdot}55901$, where x, y and z are coordinates referred to the crystallographic cell edges.

S(1)	0·008 (1)	C(2)	0·020 (3)
S(2)	−0·002 (1)	C(3)	−0·000 (3)
N(1)	0·002 (4)	C(4)	−0·029 (4)
N(2)	0·005 (4)	C(5)	−0·023 (5)
C(1)	0·012 (3)	C(6)	0·008 (4)

E.s.d.'s are estimated from those of the atomic coordinates only.

According to the NMR spectra measured in solution, unexplained broad peaks have appeared at δ = 12·12 and 9·97 p.p.m. in deuterated Me_2SO and at δ = 12·50 and 9·03 p.p.m. in hexadeuterioacetone (Muraoka & Takeshima, 1981). Although there exists some difference between solid and liquid states, the results of the NMR spectra could be connected with the 'migrating' H atom.

The bond angles S(1)—C(1)—C(2), C(1)—C(2)—C(3) and C(2)—C(3)—N(1) are all greater than 120° which is the value expected from the sp^2 hybridization. These might be a result of the short S(1)···N(1) distance [2·999 (5) Å]. The sum of the van der Waals radii of the N and S atoms is 3·35 Å (calculated from the data of Pauling, 1967). However, the S(1) atom forms an intramolecular hydrogen bond with the N(1) atom. The S(1)···H(7)—N(1) angle is 139 (4)°.

The C(3)—C(4) bond length is shorter than that expected for a normal single bond (1·54 Å). This shortening probably results from hyperconjugation of the C(4) methyl group with the π-electron system in the molecule.

A packing diagram of the crystal viewed along the c^* axis is depicted in Fig. 2. There is only one intermolecular distance shorter than 3·5 Å; the N(2^{i})···N(1^{ii})‡ distance of 2·987 (6) Å suggests an

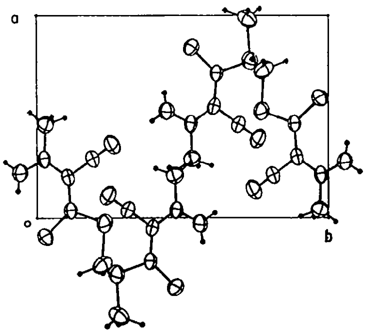


Fig. 2. *ORTEP* (Johnson, 1965) projection of the crystal structure on the *ab* plane.

---

† Otherwise the short C(2)—C(6) bond length could not be explained. This configuration is consistent with the N(1)—C(3) double bond and intra- and intermolecular hydrogen bonds mentioned below.

‡ Key to the symmetry operations: (i) x,y,z; (ii) $1+x, \frac{1}{2}-y, \frac{1}{2}+z$.

N—H···N hydrogen bond [the $N(2^{i})\cdots H(8^{ii})-N(1^{ii})$ angle is 165 (4)°].

The authors are grateful to Dr M. Muraoka of this University for helpful discussions. The authors also thank Professor M. Nagata for his continual interest throughout this investigation and the Ministry of Education for a grant towards the purchase of the diffractometer.

References

International Tables for X-ray Crystallography (1974). Vol. IV, pp. 72–102. Birmingham: Kynoch Press.

JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

MURAOKA, M. & TAKESHIMA, T. (1981). Private communication.

MURAOKA, M., YAMAMOTO, T., YAMAGUCHI, S., TONOSAKI, F., TAKESHIMA, T. & FUKUDA, N. (1977). *J. Chem. Soc. Perkin Trans.* 1, pp. 1273–1280.

PAULING, L. (1967). *The Chemical Bond*, p. 152. Ithaca Cornell Univ. Press.

SAKURAI, T. & KOBAYASHI, K. (1978). *Rikagaku Kenkyusho Hokoku* (*Rep. Inst. Phys. Chem. Res.*, in Japanese), **55**, 69–77.

WELLS, A. F. (1975). *Structural Inorganic Chemistry*, 4th ed., p. 734. Oxford: Clarendon Press.

Acta Cryst. (1982). B**38**, 3168–3171

(—)-2′-Hydroxy-2-(4-methoxybutyl)-5,9-dimethyl-6,7-benzomorphan Hydrobromide*†

BY O. M. PEETERS, C. J. DE RANTER‡ AND N. M. BLATON

Laboratorium voor Analytische Chemie en Medicinale Fysicochemie,
Instituut voor Farmaceutische Wetenschappen, KU Leuven, Van Evenstraat 4, *B*-3000 *Leuven, Belgium*

(*Received* 18 *January* 1982; *accepted* 8 *July* 1982)

Abstract. $C_{19}H_{29}NO_2.HBr$, $M_r = 384.36$, monoclinic, $P2_1$, $a = 12.2567$ (9), $b = 8.9898$ (9), $c = 17.5559$ (9) Å, $\beta = 92.63$ (1)°, $V = 1932$ Å^3, $D_m = 1.32$, $D_c = 1.32$ Mg m^{-3}, $Z = 4$, λ(Cu $K\alpha$) = 1.5418 Å, $\mu = 2.97$ mm^{-1}, $F(000) = 808$. The structure refined to an R of 0·041 for 3035 observed reflections. The two molecules in the asymmetric unit have different N side-chain conformations.

Introduction. As part of our study of structure–activity relationships in the 6,7-benzomorphan series (Gelders, De Ranter & Kokkes, 1980), the *N*-[(tetrahydrofuryl)alkyl] and the *N*-(alkoxyalkyl) derivatives of (—)-normetazocine [(—)-2′-hydroxy-5,9α-dimethyl-6,7-benzomorphan] are interesting since some compounds of this series possess action profiles distinctly different from those of morphine and other classical opiates (Merz & Stockhaus, 1979). Three groups may be distinguished: (*a*) morphine-like agonists, (*b*) non-morphine-like agonists and (*c*) nalorphine-like agonist–antagonists. The title compound is of the morphine-like agonist type and shows an analgesic activity twice that of morphine in the writhing test. Crystals were grown from an ethanol–diethyl ether solution. Intensities were measured on a Nonius CAD-4 computer-controlled diffractometer with graphite-monochromated Cu $K\alpha$ radiation using θ–2θ scans ($\theta_{max} = 65°$). Cell dimensions were obtained by least-squares refinement of the setting angles of 14 reflections with $37° < 2\theta < 44°$. A total of 3377 independent reflections were measured of which 3035 were considered as observed [$I > 3\sigma(I)$]. The intensities were corrected for Lorentz and polarization effects but not for absorption.

The positions of 38 of the 46 non-H atoms present in the asymmetric unit were obtained from a Patterson synthesis followed by a superposition map (minimum function). The missing ones were obtained from a Fourier synthesis. Subsequent isotropic and anisotropic refinements by block-diagonal least squares using XRAY (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) lowered the R value to 0·067. 48 H atoms were then located from a difference synthesis and were included as fixed-atom contributions with the isotropic temperature factor of their carrier atoms. Further refinement converged at $R = 0.041$. The weighting scheme employed was $w = (16.0 + |F_o| + 0.0125|F_o|^2)^{-1}$. The average and maximum parameter shifts during the final cycle were, respectively, 0·04 and 0·31 σ. The maximum electron density in a difference

---

* Structural Studies of Substituted 6,7-Benzomorphan Compounds. V. Part IV: Gelders, De Ranter & Kokkes (1980).

† *Chemical Abstracts* name: (—)-1,2,3,4,5,6-hexahydro-2,6-methano-3-(4-methoxybutyl)-6,11-dimethyl-3-benzazocin-8-ol hydrobromide.

‡ To whom correspondence should be addressed.

0567-7408/82/123168-04$01.00