MASAMBA, W. (1986). PhD Thesis, Univ. of Louvain, Belgium.
MOTHERWELL, W. D. S. & CLEGG, W. (1978). *PLUTO*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.
SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
SHELDRICK, G. M. (1985). *Crystallographic Computing* 3, edited by G. M. SHELDRICK, C. KRÜGER & R. GODDARD, pp. 175–189. Oxford Univ. Press.
TINANT, B., DE BLOCK, I., DECLERCQ, J.-P., GERMAIN, G., VAN MEERSSCHE, M., LEROY, G. & WEILER, J. (1982). *Bull. Soc. Chim. Belg.* **91**, 629–639.
TINANT, B., WU, S., DECLERCQ, J.-P., VAN MEERSSCHE, M., DE MESMAEKER, A., MASAMBA, S., MERENYI, R. & VIEHE, H. G. (1985). *J. Chem. Soc. Perkin Trans.* 2, pp. 535–540, 541–543.
TINANT, B., WU, S., DECLERCQ, J.-P., VAN MEERSSCHE, M., DE MESMAEKER, A., MASAMBA, S., MERENYI, R. & VIEHE, H. G. (1987). *J. Chem. Soc. Perkin Trans.* 2. Accepted.

Acta Cryst. (1987). C**43**, 2345–2347

Structure of Pyridoxal Homocysteine Thiolactone Enamine

BY KILMER S. MCCULLY

Veterans Administration Medical Center, Davis Park, Providence, Rhode Island 02908, *USA*

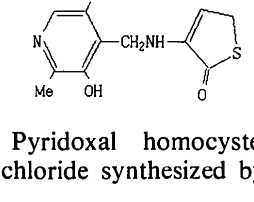
AND GENE B. CARPENTER

Department of Chemistry, Brown University, Providence, Rhode Island 02912, *USA*

(*Received* 9 *December* 1986; *accepted* 8 *July* 1987)

Abstract. 3-{[3-Hydroxy-5-(hydroxymethyl)-2-methyl-4-pyridyl]methylamino}-2(5*H*)-thiophenone, abbreviated name 2,5-dihydro-2-oxo-3-pyridoxaminothiophene, $C_{12}H_{14}N_2O_3S$, $M_r = 266{\cdot}3$, monoclinic, $P2_1/c$, $a = 10{\cdot}029$ (2), $b = 11{\cdot}472$ (4), $c = 11{\cdot}760$ (2) Å, $\beta = 112{\cdot}80$ (2)°, $V = 1247{\cdot}2$ Å^3, $Z = 4$, $D_x = 1{\cdot}42$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 2{\cdot}6$ cm^{-1}, $F(000) = 560$, $T = 298$ K, $R = 0{\cdot}044$ and $wR = 0{\cdot}054$ for 1537 unique observed reflections with $I > \sigma(I)$. The thiophene and pyridine rings are each planar with a dihedral angle of 95·0 (4)° between these planes. The C(O)—S and H_2C—S bonds are different [1·758 (3) and 1·784 (3) Å, respectively]. The CH_2OH group is disordered. The molecules are linked together by O—H···O and O—H···N hydrogen bonds.

Introduction. The title compound is one of a series prepared and investigated by McCully and co-workers for antineoplastic activity. Although high doses of the hydrochloride decreased growth of transplanted rhabdomyosarcoma in mice (McCully & Clopath, 1977), the free base was found to be inactive (McCully & Vezeridis, 1985). The structure of the free base was determined to verify the expected structure and to see the conformation of this rather crowded molecule.



Experimental. Pyridoxal homocysteine thiolactone enamine hydrochloride synthesized by the method of Okumura *et al.* (1971) from pyridoxal.HCl and homocysteine thiolactone (Sigma Chemical Co.). Free base crystallized from 0·07 *M* NaOH in methanol. Pale-yellow prismatic single crystal, 0·25 × 0·28 × 0·36 mm, mounted with epoxy cement. Nicolet *R*3*m* diffractometer, graphite monochromator; unit-cell parameters by least-squares refinement of 25 reflections ($26 \leq 2\theta \leq 28°$); θ–2θ scans at variable rates; $2\theta_{\max} = 45°$ for the range $0 \leq h \leq 10$, $0 \leq k \leq 12$, $-12 \leq l \leq 11$; three reflections monitored every 97 reflections with negligible change in intensity over the course of data collection; 1636 measured unique intensities, 1537 unique observed reflections (not including space-group absences) with $I > \sigma(I)$ used for refinement; absorption correction based on indexed and measured faces (max. and min. transmission factors 0·941, 0·925). Structure by direct methods; 10 of 14 H atoms found on difference map; for refinement, all C—H bond lengths fixed at 0·96 Å and refined with ideal geometry; anisotropic thermal parameters for all non-H atoms and fixed isotropic parameters for H atoms (20% greater than that of carrying atom). Refined by cascade block-diagonal least squares on *F* with max. $(\sin\theta)/\lambda = 0{\cdot}54$ Å^{-1}; refinement of 185 parameters converged to $R = 0{\cdot}044$, $wR = 0{\cdot}054$; $w = 1/[\sigma^2(F) + 0{\cdot}00040F^2]$ where $\sigma^2(F)$ is from counting statistics; goodness of fit = 1·791; $(\Delta/\sigma)_{\max} = -0{\cdot}05$ in final cycle; highest peak in final difference map 0·19, deepest hole, $-0{\cdot}23$ e Å^{-3}; atomic scattering factors from *International Tables for X-ray Crystallography* (1974); all calculations were performed on a Data General Eclipse S140 computer using the *SHELXTL* 4.1 program package (Sheldrick, 1984).

0108-2701/87/122345-03$01.50

Table 1. *Atom coordinates* (× 10^4) *and temperature factors* (Å^2 × 10^3)

	x	y	z	U_{eq}*
S	−24 (1)	1688 (1)	−1437 (1)	69 (1)
O(1)	5508 (2)	2704 (2)	4123 (1)	67 (1)
O(2)	1662 (4)	−485 (3)	5541 (3)	78 (2)
O(2*a*)	718 (5)	237 (4)	3784 (4)	69 (2)
O(3)	−258 (3)	2575 (2)	550 (2)	104 (1)
N(1)	4644 (2)	2028 (2)	6713 (2)	45 (1)
N(2)	2120 (2)	1406 (2)	2146 (2)	51 (1)
C(2)	5240 (2)	2496 (2)	5991 (2)	44 (1)
C(3)	4814 (2)	2147 (2)	4747 (2)	44 (1)
C(4)	3800 (2)	1262 (2)	4282 (2)	41 (1)
C(5)	3177 (2)	796 (2)	5062 (2)	44 (1)
C(6)	3627 (3)	1210 (2)	6250 (2)	47 (1)
C(7)	6382 (3)	3406 (3)	6515 (2)	63 (1)
C(8)	3382 (2)	808 (2)	2983 (2)	46 (1)
C(9)	2035 (3)	−143 (2)	4624 (2)	64 (1)
C(10)	398 (3)	1929 (2)	141 (2)	59 (1)
C(11)	1654 (2)	1245 (2)	899 (2)	44 (1)
C(12)	2172 (3)	577 (2)	249 (2)	57 (1)
C(13)	1416 (3)	668 (3)	−1128 (2)	65 (1)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 2. *Bond lengths* (Å) *and bond angles* (°)

S—C(10)	1·758 (3)	S—C(13)	1·784 (3)
O(1)—C(3)	1·352 (3)	O(2)—C(9)	1·330 (5)
O(2*a*)—C(9)	1·377 (5)	O(3)—C(10)	1·208 (4)
N(1)—C(2)	1·326 (3)	N(1)—C(6)	1·337 (3)
N(2)—C(8)	1·441 (3)	N(2)—C(11)	1·368 (3)
C(2)—C(3)	1·414 (3)	C(2)—C(7)	1·495 (3)
C(3)—C(4)	1·390 (3)	C(4)—C(5)	1·401 (4)
C(4)—C(8)	1·511 (3)	C(5)—C(6)	1·376 (3)
C(5)—C(9)	1·510 (3)	C(10)—C(11)	1·458 (3)
C(11)—C(12)	1·323 (4)	C(12)—C(13)	1·502 (3)

C(10)—S—C(13)	92·5 (1)	C(2)—N(1)—C(6)	119·1 (2)
C(8)—N(2)—C(11)	120·8 (2)	N(1)—C(2)—C(3)	121·1 (2)
N(1)—C(2)—C(7)	118·8 (2)	C(3)—C(2)—C(7)	120·0 (2)
O(1)—C(3)—C(2)	114·5 (2)	O(1)—C(3)—C(4)	125·7 (2)
C(2)—C(3)—C(4)	119·7 (2)	C(3)—C(4)—C(5)	117·7 (2)
C(3)—C(4)—C(8)	121·5 (2)	C(5)—C(4)—C(8)	120·7 (2)
C(4)—C(5)—C(6)	118·6 (2)	C(4)—C(5)—C(9)	121·4 (2)
C(6)—C(5)—C(9)	120·0 (2)	N(1)—C(6)—C(5)	123·6 (2)
N(2)—C(8)—C(4)	110·6 (2)	O(2)—C(9)—O(2*a*)	100·5 (3)
O(2)—C(9)—C(5)	110·3 (2)	O(2*a*)—C(9)—C(5)	114·1 (3)
S—C(10)—O(3)	124·8 (2)	S—C(10)—C(11)	111·0 (2)
O(3)—C(10)—C(11)	124·2 (2)	N(2)—C(11)—C(10)	115·9 (2)
N(2)—C(11)—C(12)	130·6 (2)	C(10)—C(11)—C(12)	113·5 (2)
C(11)—C(12)—C(13)	115·8 (2)	S—C(13)—C(12)	107·2 (2)

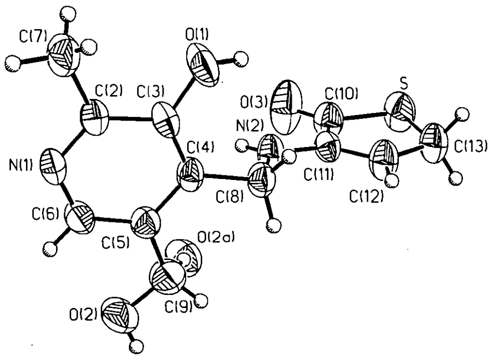


Fig. 1. Thermal-ellipsoid plot of 2,5-dihydro-2-oxo-3-pyridoxaminothiophene, showing the atom-numbering scheme. H atoms are drawn as small spheres with arbitrary radius.

Discussion. Atomic coordinates and equivalent isotropic thermal parameters are listed in Table 1, bond lengths and angles in Table 2.*

Fig. 1 is a thermal-ellipsoid plot of the molecule showing the atom-numbering scheme. The thiolactone enamine ring is nearly planar; the r.m.s. distance from the plane

$$6{\cdot}704\,(51)x + 8{\cdot}531\,(53)y - 3{\cdot}171\,(77)z = 1{\cdot}8760\,(70)$$

is only 0·0070 Å for atoms S and C(10) through C(13). Other distances from this plane are N(2), 0·0642, and C(8), 0·1350 Å. The pyridine ring is also planar; the r.m.s. distance from the plane

$$6{\cdot}541\,(18)x - 8{\cdot}012\,(45)y + 0{\cdot}224\,(14)z = 1{\cdot}5547\,(79)$$

is 0·0122 Å for atoms N(1) and C(2) through C(6). The angle between the planes of the two rings is 95·0 (4)°; most of the twist is about the C(4)—C(8) bond [torsion angle C(5)—C(4)—C(8)—N(2), 86·6 (3)°]. The S—C(10) bond is 1·758 (3) Å, somewhat shorter than S—C(13), 1·784 (3) Å, presumably because C(10) makes use of sp^2 hybridization. The —CH_2OH group on the pyridoxal portion exhibits some disorder, with two fractional O atoms near C(9). The fractional occupancies were taken as f and $1-f$, and f refined to the curiously round value 0·600 (3). The major portion [O(2)] was nearly coplanar with the pyridoxal ring [torsion angle C(6)—C(5)—C(9)—O(2), −3·1 (3)°], the minor portion [O(2*a*)] was twisted 109° away from that plane [torsion angle C(6)—C(5)—C(9)—O(2*a*), 109·2 (3)°]. Bond lengths and angles are all within normal ranges. The molecules are linked into a three-dimensional network by chains of hydrogen bonds along the **b** [O(2)···O(3) = 2·680 (4)] and **c** directions [O(1)···N(1) = 2·641 (2) Å]. Other intermolecular contacts are not remarkable.

The Nicolet *R*3*m*/*E* crystallographic system was purchased with an instrument grant to Brown University from the National Science Foundation (CHE-8206423).

---

* Tables of anisotropic thermal parameters, H-atom parameters and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44226 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
McCully, K. S. & Clopath, P. (1977). *Chemotherapy*, **23**, 44–49.
McCully, K. S. & Vezeridis, M. P. (1985). Unpublished observations.

Okumura, K., Oda, T., Kondo, K., Inoue, I., Danno, I., Yamaguchi, H. & Masukawa, K. (1971). *J. Med. Chem.* **14**, 226–229.

Sheldrick, G. M. (1984). *Nicolet SHELXTL Operations Manual*, version 4.1. Nicolet Instrument Company, Madison, Wisconsin, USA.

Acta Cryst. (1987). C**43**, 2347–2350

Structures of Isomeric *N*-(5-Methyl-2-aminobenzhydrylidene)amino-5-norbornene-2,3-*exo*-dicarboximide and *N*-(5-Methyl-2-aminobenzhydrylidene)amino-5-norbornene-2,3-*endo*-dicarboximide

By A. A. Dvorkin, T. Sh. Gifeysman, Yu. A. Simonov and T. I. Malinovsky

Institute of Applied Physics of Moldavian Academy of Sciences, Grosul Str. 5, Kishinev – 277028, USSR

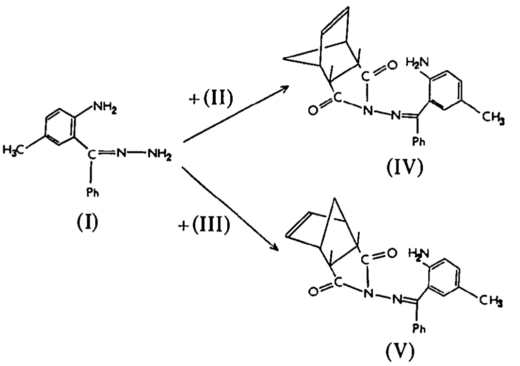
and S. A. Andronati, M. L. Bondarev and A. S. Yavorsky

A. V. Bogatsky Physico-Chemical Institute of the Ukrainian Academy of Sciences, Chernomorskaya doroga 86, Odessa – 277080, USSR

(*Received* 13 *June* 1986; *accepted* 8 *June* 1987)

Abstract. $C_{23}H_{21}N_3O_2$ (*exo* isomer), $M_r = 371{\cdot}44$, monoclinic, $P2_1/n$, $a = 15{\cdot}593$ (14), $b = 11{\cdot}206$ (7), $c = 10{\cdot}808$ (7) Å, $\gamma = 96{\cdot}72$ (2)°, $V = 1875{\cdot}6$ (2·4) Å^3, $Z = 4$, $D_x = 1{\cdot}315$ (4) Mg m^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 0{\cdot}551$ mm^{-1}, $F(000) = 784$, $T = 293$ K, $R = 0{\cdot}056$ for 2801 observed reflections. $C_{23}H_{21}N_3O_2$ (*endo* isomer), $M_r = 371{\cdot}44$, monoclinic, $P2_1/n$, $a = 15{\cdot}065$ (15), $b = 11{\cdot}560$ (12), $c = 10{\cdot}720$ (10) Å, $\gamma = 94{\cdot}53$ (2)°, $V = 1861{\cdot}1$ (3·2) Å^3, $Z = 4$, $D_x = 1{\cdot}325$ (4) Mg m^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 0{\cdot}551$ mm^{-1}, $F(000) = 784$, $T = 293$ K, $R = 0{\cdot}055$ for 2804 observed reflections. Both *exo* and *endo* isomers possess a *cis*-conformation for the *o*-aminophenyl ring, stabilized by strong intramolecular NH···N bonds. The crystal structures of the two isomers are similar. The molecules in the crystal are linked in spirals around the screw axes. The spirals are connected by van der Waals interactions.

Introduction. It is known that *o*-acylaniline and norbornene hydrazone derivatives, besides being biologically active by themselves, are used to obtain other compounds possessing psychotropic, anticonvulsant and antimicrobic activity (Minoru, Morio & Hiroyuki, 1974; Minoru, Morio, Hiroyuki & Yasuo, 1974; Tasihiko & Syundzi, 1971). Therefore, the combination of both *o*-aminophenyl and norbornene fragments in the same molecule is potentially interesting. At the same time, the opportunity arises of studying the influence of the conformational peculiarities of these compounds on their biological activity. Accordingly, by boiling equimolecular quantities of 5-methyl-2-aminobenzophenone hydrazone (I) with 5-norbornene-2,3-*exo*- (II) or 5-norbornene-2,3-*endo*-dicarboxylic anhydrides (III) in xylene we have prepared isomeric *N*-(5-methyl-2-aminobenzhydrylidene)amino-5-norbornene-2,3-*exo*- (IV) and *endo*-dicarboximide (V) (Andronati, Yavorsky, Bondarev, Salakov, Zakolodyajnaya & Terentev, 1985).



Experimental. Both compounds (IV) and (V) (melting points 526 and 516 K from toluene) gave satisfactory elemental analyses. Their X-ray structures are in full agreement with IR, PMR and mass spectra.

Pale yellow plate-like crystals 0·6 × 0·5 × 1·3 mm (IV) and 0·7 × 0·4 × 1·5 mm (V), three-circle single-crystal DAR-UMB diffractometer, graphite-monochromated Cu$K\alpha$ radiation, combined ω and $\theta/2\theta$ scan mode, scan speed 8° min^{-1}. Three reflections were used for the lattice-parameters determination; 3564 (IV) and 3634 (V) independent reflections were collected in the range $2 \leq \theta \leq 57°$ (h 0→13; k −13→13; l 0→15) for (IV), (h 0→13; k −14→14; l 0→16) for (V); 2801 (IV) and 2804 (V) reflections with $I \geq 3\sigma(I)$ were used for calculations. 16 standard reflections (one in each layer)

0108-2701/87/122347-04$01.50