0·0047 (17) Å respectively into the triple CN bond, when compared with the high-order refinement. This effect is generally observed in refinements of X-ray data (Coppens, 1974; Bats, 1976), and results from the aspherical distribution of the bonding electrons. As the structure is refined with a spherical atom model, the reported standard deviations in the atomic parameters do not contain these asphericity effects and are consequently underestimated.

Fig. 2 shows a difference Fourier synthesis in the plane containing the SSCN group, based on the low-order reflections and the high-order atomic parameters. The data cut-off in this difference Fourier synthesis has deliberately been taken low, in order to reduce the noise level. Although quantitative electron density studies require data of greater accuracy than in the present study, residuals due to the aspherical bonding density are apparent in Fig. 2.

Support of this work by the National Science Foundation is gratefully acknowledged.

References

Bats, J. W. (1976). *X-ray Diffraction and Chemical Bonding*. Thesis, Twente Univ. of Technology, The Netherlands.

Bats, J. W. & Coppens, P. (1977). *Acta Cryst.* B**33**, 1542–1548.

Bats, J. W., Coppens, P. & Kvick, Å. (1977). *Acta Cryst.* B**33**, 1534–1542.

Blessing, R. H., Coppens, P. & Becker, P. (1974). *J. Appl. Cryst.* **7**, 488–492.

Coppens, P. (1974). *Acta Cryst.* B**30**, 255–261.

Coppens, P., Yang, Y. W., Blessing, R. H., Cooper, W. F. & Larsen, F. K. (1977). *J. Amer. Chem. Soc.* **99**, 760–766.

Cromer, D. T. & Liberman, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.

Féher, F. & Linke, K. H. (1964). *Z. anorg. allgem. Chem.* **327**, 151–158.

Féher, F. & Weber, H. (1958). *Chem. Ber.* **91**, 642–650.

Hordvik, A. (1970). *Quart. Rep. Sulfur Chem.* **5**, 21–43.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

Schomaker, V. & Trueblood, K. N. (1968). *Acta Cryst.* B**24**, 63–76.

Acta Cryst. (1977). B**33**, 2266–2269

6-*endo*-Hydroxy-3-*endo*-aminomethylbicyclo[2.2.1]heptane-2-*endo*-carboxylic Acid Lactam*†

By Arthur J. Olson,‡ David H. Templeton and Lieselotte K. Templeton

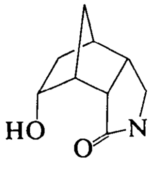
Materials and Molecular Research Division, Lawrence Berkeley Laboratory,
and Department of Chemistry, University of California, Berkeley, California 94720, *USA*

(*Received* 9 *December* 1976; *accepted* 31 *January* 1977)

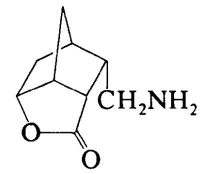
Abstract. $C_9H_{13}NO_2$, monoclinic, $P2_1/c$, 23°C, $a = 10{\cdot}870\,(3)$, $b = 7{\cdot}403\,(2)$, $c = 10{\cdot}721\,(4)$ Å, $\beta = 107{\cdot}46\,(2)°$, $Z = 4$, $D_x = 1{\cdot}350\,(2)$, $D_m = 1{\cdot}35\,(1)$ g cm^{-3}. For 1169 reflections with $I > \sigma$, $R = 0{\cdot}055$ and $R_w = 0{\cdot}051$. The O(hydroxyl)–C(carbonyl) distance is 2·832 Å, two H atoms are 2·00 Å from each other, and these distances would be even shorter except for distortion of some of the bond angles. Hydrogen bonds from the hydroxyl and amide groups to the carbonyl O atom link the molecules into chains.

Introduction. To explore effects of orientation on rates of chemical reactions analogous to those catalyzed by enzymes, Koshland and co-workers have measured intramolecular reaction rates for norbornane molecules substituted with a variety of functional groups (Storm & Koshland, 1972). The title compound, a hydroxylactam, was synthesized by Hackney (1975) to serve, in its base-catalyzed rearrangement to an aminolactone, as a model for the rate-determining step in the hydrolysis of amides by chymotrypsin.

We determined the crystal structure of this lactam as part of a program to establish the geometry of



hydroxylactam



aminolactone

---

[*] Structures of Bicyclo[2.2.1] Systems. IV.

[†] Work done in part with support from the US Energy Research and Development Administration.

[‡] Present address: Department of Chemistry, Harvard University, Cambridge, Mass., USA.

Table 1. *Positional parameters for the heavy atoms* ($\times 10^4$)

	x	y	z
C(1)	2119 (2)	5819 (3)	1390 (2)
C(2)	1548 (2)	3927 (3)	960 (2)
C(3)	2756 (2)	2730 (3)	1080 (3)
C(4)	3876 (2)	4061 (3)	1661 (3)
C(5)	3935 (2)	4582 (4)	3050 (3)
C(6)	2796 (2)	5904 (3)	2863 (3)
C(7)	3304 (3)	5780 (4)	893 (3)
C(8)	2605 (3)	1071 (4)	1879 (3)
C(9)	790 (2)	2932 (3)	1700 (2)
O(1)	−292 (1)	3361 (2)	1782 (2)
O(2)	2032 (2)	5427 (3)	3680 (2)
N(1)	1405 (2)	1408 (3)	2191 (2)

substituted norbornane molecules (Chapuis, Zalkin & Templeton, 1973, 1977*a*,*b*). A sample which had been recrystallized from ethyl acetate (m.p. 185°C) was kindly supplied to us by Professor D. E. Koshland and Dr D. D. Hackney.

A clear colorless crystal, 0·18 × 0·12 × 0·15 mm, was studied by photographic and diffractometric techniques. Laue symmetry $2/m$ and absent reflections $h0l$ ($l \neq 2n$) and $0k0$ ($k \neq 2n$) indicate space group $P2_1/c$. Setting angles for 12 reflections with $30° < 2\theta < 40°$ (Mo $K\alpha_1$, $\lambda = 0{\cdot}70926$ Å) were used for least-squares adjustment of the cell dimensions. The density was measured by flotation in solutions of CCl_4 and petroleum spirit. Intensities were measured with graphite-monochromatized Mo $K\alpha$ radiation and the θ–2θ scan technique for all the reflections in the half-sphere with l non-negative and $2\theta < 50°$, many of them twice (a total of 4685 measurements). The scan extended 2° in 2θ with a rate of 1° min^{-1}. Background was counted for 10 s near each end of the scan. After equivalent measurements were averaged there were 1467 unique reflections, of which 1169 had $I > \sigma$. Absorption was small ($\mu = 0{\cdot}89$ cm^{-1}) and no correction was made.

Table 2. *Parameters for the hydrogen atoms* ($\times 10^3$, *except B*)

The form of the temperature factor is exp $(-B\lambda^{-2}\sin^2\theta)$.

	x	y	z	B
H(1)	147 (2)	690 (3)	105 (2)	2·3 (5)
H(2)	98 (2)	396 (3)	−2 (2)	1·3 (4)
H(3)	278 (2)	232 (4)	13 (3)	3·2 (6)
H(4)	480 (2)	361 (3)	153 (2)	2·6 (5)
H(5)	377 (2)	344 (4)	360 (2)	3·0 (6)
H(6)	483 (3)	521 (4)	358 (3)	4·5 (7)
H(7)	316 (2)	728 (3)	309 (2)	2·4 (5)
H(8)	301 (2)	564 (3)	−20 (3)	2·5 (5)
H(9)	390 (2)	698 (3)	121 (2)	3·1 (5)
H(10)	343 (3)	93 (4)	290 (3)	3·7 (6)
H(11)	248 (2)	−10 (4)	130 (3)	3·6 (6)
H(12)	103 (3)	51 (4)	268 (3)	4·7 (7)
H(13)	139 (4)	635 (5)	361 (4)	6·7 (10)

The crystal structure was solved by direct methods with *MULTAN* (Germain, Main & Woolfson, 1971). All H atoms were found in a ΔF map. The structure was refined with Zalkin's full-matrix least-squares program, modified (Olson, 1975) to use polar scattering factors for H (Stewart, Davidson & Simpson, 1965), so that the H coordinates more nearly represent the positions of the protons. For other atoms we used the scattering factors of Doyle & Turner (1968) with dispersion corrections from Cromer & Liberman (1970). Zero weight was assigned to reflections with $I < \sigma$; otherwise, $w = [\sigma(F)]^{-2}$; $\sigma(F)$ was derived from $\sigma(I) = [s^2 + (0{\cdot}058I)^2]^{1/2}$, where s^2 is the variance due to counting statistics. In the last cycle no parameter shifted more than $0{\cdot}003\sigma$. The final residual $R = \Sigma\,|\Delta F|/\Sigma\,|F_o|$ was 0·055 for 1169 reflections and 0·078 for 1467 reflections including those of zero weight. The weighted residual minimized by the refinement was $R_w = [\Sigma\, w(\Delta F)^2/\Sigma\, wF_o^2]^{1/2} = 0{\cdot}051$. Final parameters are listed in Tables 1 and 2.*

Discussion. A view of the molecular structure (Fig. 1) shows the numbering of the atoms. The bond distances (Table 3) and most of the bond angles (Table 4) are normal. The angles C(2)–C(1)–C(6) (111·8°) and C(3)–C(4)–C(5) (110·7°) are larger than any of the experimental or theoretical values reported for norbornane (Altona & Sundaralingam, 1972); they indicate a distortion of the molecule in the direction which partially relieves the crowding of the substituent groups.

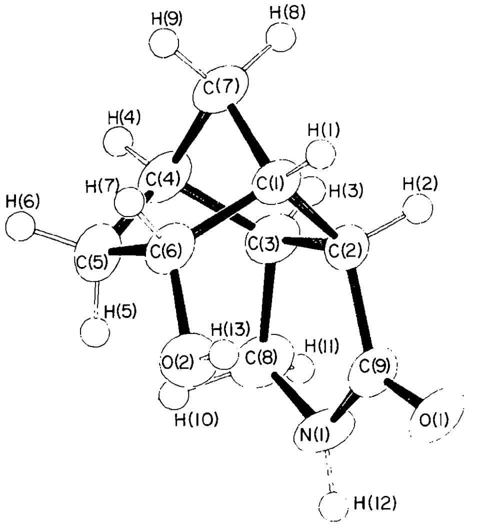


Fig. 1. Perspective view of a molecule with 50% probability thermal ellipsoids (*ORTEP*, Johnson, 1965). The size of the H atoms is arbitrary.

---

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32475 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. *Bond lengths* (Å)

C(1)–C(2)	1·545 (3)	C(1)–H(1)	1·06 (2)
C(1)–C(6)	1·530 (3)	C(2)–H(2)	1·05 (2)
C(1)–C(7)	1·533 (3)	C(3)–H(3)	1·08 (3)
C(2)–C(3)	1·557 (3)	C(4)–H(4)	1·11 (2)
C(2)–C(9)	1·499 (3)	C(5)–H(5)	1·08 (3)
C(3)–C(4)	1·545 (3)	C(5)–H(6)	1·07 (3)
C(3)–C(8)	1·534 (4)	C(6)–H(7)	1·09 (3)
C(4)–C(5)	1·521 (4)	C(7)–H(8)	1·13 (3)
C(4)–C(7)	1·539 (4)	C(7)–H(9)	1·09 (3)
C(5)–C(6)	1·544 (3)	C(8)–H(10)	1·19 (3)
O(1)–C(9)	1·246 (3)	C(8)–H(11)	1·05 (3)
O(2)–C(6)	1·420 (3)	N(1)–H(12)	1·00 (3)
N(1)–C(8)	1·462 (3)	O(2)–H(13)	0·97 (4)
N(1)–C(9)	1·336 (3)		

Table 4. *Bond angles* (°)

C(2)–C(1)–C(6)	111·8 (2)	C(1)–C(6)–C(5)	103·1 (2)
C(2)–C(1)–C(7)	100·6 (2)	C(1)–C(6)–O(2)	115·9 (2)
C(6)–C(1)–C(7)	99·4 (2)	C(5)–C(6)–O(2)	110·9 (2)
C(1)–C(2)–C(3)	103·8 (2)	C(1)–C(7)–C(4)	94·5 (2)
C(1)–C(2)–C(9)	121·5 (2)	C(3)–C(8)–N(1)	104·1 (2)
C(3)–C(2)–C(9)	105·1 (2)	C(2)–C(9)–N(1)	109·5 (2)
C(2)–C(3)–C(4)	102·3 (2)	C(2)–C(9)–O(1)	126·3 (2)
C(2)–C(3)–C(8)	105·9 (2)	O(1)–C(9)–N(1)	124·0 (2)
C(4)–C(3)–C(8)	119·3 (2)	C(8)–N(1)–C(9)	115·5 (2)
C(3)–C(4)–C(5)	110·7 (2)	C(6)–O(2)···C(9)	86·3 (1)
C(3)–C(4)–C(7)	99·8 (2)	C(2)–C(9)···O(2)	82·1 (1)
C(5)–C(4)–C(7)	101·7 (2)	O(1)–C(9)···O(2)	91·6 (2)
C(4)–C(5)–C(6)	103·7 (2)	N(1)–C(9)···O(2)	100·7 (2)

Table 5. *Hydrogen-bond distances* (Å) *and angles* (°)

X–H···Y	$d(X\cdots Y)$	$d(\mathrm{H}\cdots Y)$	X–H–Y
O(2)–H(13)···O(1^{i})	2·824 (2)	1·87 (4)	168 (3)
N(1)–H(12)···O(1^{ii})	2·926 (3)	1·95 (3)	164 (3)

Symmetry code
(i) $-x, \frac{1}{2}+y, \frac{1}{2}-z$ (ii) $-x, -\frac{1}{2}+y, \frac{1}{2}-z$

Angle C(1)–C(6)–O(2) (115·9°) is large for the same reason. The distance O(2)–C(9) [2·832 (3) Å] may be compared with 2·783 Å for an analogous distance in the Na salt of 2-*exo*-methyl-6-*endo*-hydroxybicyclo-[2.2.1]heptane-2-*endo*-carboxylic acid (Chapuis *et al.*, 1977*a*), where the C(2)–C(1)–C(6) angle is 112·2°. In the present case, the stress of the lactam ring results in a larger C(1)–C(2)–C(9) angle and thus a longer O(2)–C(9) distance with slightly less strain of the norbornane skeleton than in the salt of the 2,6,2-methylhydroxy acid. The enlargement of the C(3)–C(4)–C(5) angle probably results from the crowding of H(5) and H(10) which are at the abnormally short distance of 2·00 (4) Å. No other H atoms in the molecule are closer than 2·26 Å, except those which are attached to a common C atom. In the methylhydroxy acid salt mentioned above there was no corresponding crowding at the other end of the molecule, and the angle at C(4) was 107·6°.

For reference in discussion of the rates of conversion to the lactone (Hackney, 1975), in the context of the work reviewed by Bürgi (1975), we include in Table 4 some angles involving the O(2)–C(9) vector.

Fig. 2 shows the molecular packing. Hydrogen bonds from the amide and alcohol groups to the carbonyl O atom tie molecules together in strings along the screw axis. Table 5 gives distances and angles descriptive of these hydrogen bonds.

References

ALTONA, C. & SUNDARALINGAM, M. (1972). *Acta Cryst.* B**28**, 1806–1816.
BÜRGI, H. B. (1975). *Angew. Chem. Int. Ed.* **14**, 460–473.

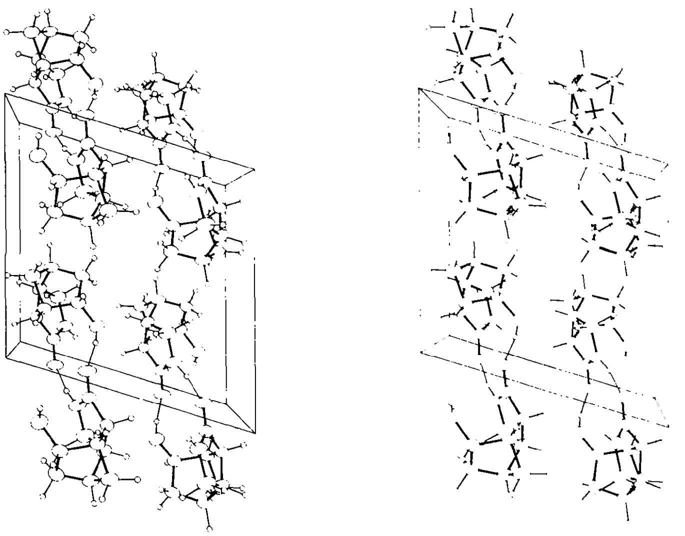


Fig. 2. Stereoscopic view of molecular packing, viewed along **b**.

Chapuis, G., Zalkin, A. & Templeton, D. H. (1973). *Acta Cryst.* **B29**, 2642–2644.

Chapuis, G., Zalkin, A. & Templeton, D. H. (1977*a*). *Acta Cryst.* **B33**, 560–563.

Chapuis, G., Zalkin, A. & Templeton, D. H. (1977*b*). *Acta Cryst.* **B33**, 1290–1293.

Cromer, D. T. & Liberman, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.

Doyle, P. A. & Turner, P. S. (1968). *Acta Cryst.* **A24**, 390–397.

Germain, G., Main, P. & Woolfson, M. M. (1971). *Acta Cryst.* **A27**, 368–376.

Hackney, D. D. (1975). *Models for Chymotrypsin and the Interaction of Lysozyme with Urea.* Thesis, Univ. of California, Berkeley.

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

Olson, A. J. (1975). *Polar Hydrogen Scattering Factors in X-ray Diffraction Analysis.* Thesis, Univ. of California, Berkeley.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Storm, D. R. & Koshland, D. E. (1972). *J. Amer. Chem. Soc.* **94**, 5815–5825.

Acta Cryst. (1977). B**33**, 2269–2270

O-Methyl[2-(2-Ethyl-5-nitroimidazol-1-yl)ethyl]thiocarbamate (sulnidazole)

By G. Germain, J. P. Declercq* and M. Van Meerssche

Laboratoire de Chimie Physique et de Cristallographie, Université de Louvain, 1 *place L. Pasteur,*
B-1348 *Louvain-la-Neuve, Belgium*

and M. H. J. Koch

Research Laboratories, Janssen Pharmaceutica, B-2340 *Beerse, Belgium*

(*Received* 2 *February* 1977; *accepted* 18 *February* 1977)

Abstract. $C_9H_{14}N_4O_3S$, $M_r = 258{\cdot}3$, monoclinic, $P2_1/c$, $a = 7{\cdot}313$ (2), $b = 15{\cdot}907$ (2), $c = 10{\cdot}868$ (2) Å, $\beta = 108{\cdot}02$ (3)°, 25 °C, $Z = 4$. The molecules are held together by packing forces only.

Introduction. Sulnidazole is an antiprotozoal drug. Transparent pale-green crystals were obtained by cooling a solution in ethanol. Cell dimensions and intensities were measured on a Picker four-circle diffractometer with the experimental conditions given in Table 1. The structure was solved with *MULTAN* (Germain, Main & Woolfson, 1971) and refined by block-diagonal anisotropic least squares (Ahmed, Hall, Pippy & Huber, 1966). The final $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ is 0·10 for all observed reflexions. The final coordinates are given in Table 2. The scattering factors were those given in *International Tables for X-ray Crystallography* (1962).†

Table 1. *Experimental conditions*

Source Cu $K\bar{\alpha}$; $\lambda = 1{\cdot}5418$ Å
ω–2θ scan; $\theta_{\max} = 50°$
Confidence level: 2·5
Total number of independent reflexions: 1230
Total observed: 1131

Table 2. *Final positional parameters* (×10⁴), *with standard deviations in parentheses*

	x	*y*	*z*
C(1)	7668 (6)	11781 (3)	2489 (5)
C(2)	8019 (6)	10868 (2)	2433 (4)
C(3)	9716 (5)	10669 (2)	2019 (3)
N(4)	10691 (4)	11208 (1)	1550 (2)
C(5)	12068 (4)	10753 (2)	1235 (3)
C(6)	11902 (4)	9937 (2)	1541 (3)
N(7)	10385 (4)	9880 (1)	2005 (3)
C(8)	9341 (6)	9129 (3)	2205 (4)
C(9)	10177 (6)	8799 (3)	3554 (4)
N(10)	8959 (4)	8132 (2)	3823 (3)
C(11)	7651 (5)	8328 (2)	4402 (3)
S(12)	6843 (2)	9262 (0)	4604 (1)
O(13)	7117 (3)	7614 (1)	4839 (2)
C(14)	5806 (5)	7677 (2)	5592 (4)
N(15)	13008 (4)	9255 (1)	1336 (3)
O(16)	14296 (3)	9421 (1)	845 (2)
O(17)	12704 (4)	8556 (1)	1637 (3)

---

* Chargé de Recherches du Fonds National de la Recherche Scientifique.

† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32506 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.