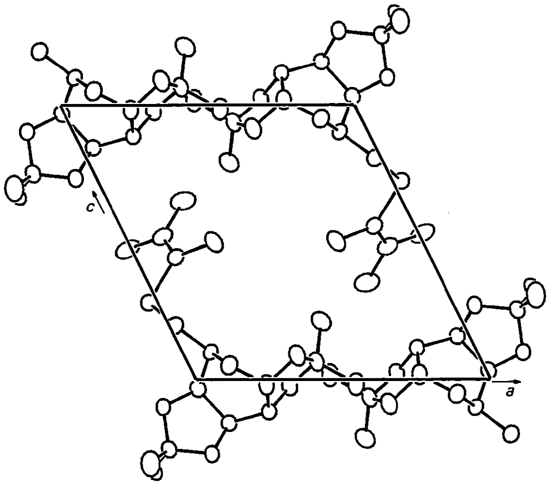


Fig. 2. Dessin de la structure vue selon [010].

Références

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans.* II, S1–S19.

Aubry, A., Protas, J., Duchaussoy, P., Di Cesaree, P. & Gross, B. (1981). *Acta Cryst.* B**37**, 1477–1480.

B. A. Frenz & Associates, Inc. (1982). *Structure Determination Package*. College Station, Texas, EU, et Enraf–Nonius, Delft, Pays-Bas.

Busing, W. R., Martin, K. O. & Levy, H. A. (1964). *ORFFE*. Rapport ORNL-TM-306. Oak Ridge National Laboratory, Tennessee, EU.

Johnson, C. K. (1976). *ORTEP*II. Rapport ORNL-5138. Oak Ridge National Laboratory, Tennessee, EU.

Julien, R., Ronco, G., Lemay, C., Khodadad, P. & Rodier, N. (1991). *Acta Cryst.* A paraître.

Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1982). *MULTAN*11/82. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univ. de York, Angleterre, et de Louvain, Belgique.

Acta Cryst. (1991). C**47**, 1338–1340

Structure of Benzyl 6-Methacryloylaminopenicillanate 1-Oxide

By Mitsuru Tashiro* and Yasushi Saotome†

Yokohama Laboratory, MD Research Co. Ltd, 760 *Morooka, Kohoku, Yokohama* 222, *Japan*

(*Received* 6 *September* 1990; *accepted* 14 *November* 1990)

Abstract. $C_{19}H_{22}N_2O_5S$, $M_r = 390·5$, monoclinic, $P2_1$, $a = 10·392\,(2)$, $b = 18·373\,(2)$, $c = 10·622\,(1)$ Å, $\beta = 103·73\,(1)°$, $V = 1970·2\,(5)$ Å^3, $Z = 4$, $D_x = 1·32$ Mg m^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1·54178$ Å, $\mu = 1·701$ mm^{-1}, $F(000) = 824$, $T = 296$ K, $R = 0·0411$ for 2254 observed reflections. The asymmetric unit contains two crystallographically independent molecules. The structure is stabilized by an intramolecular hydrogen bond between the amide N—H and the sulfoxide S—O [H(44*A*)···O(8*A*) = 2·14, H(44*B*)···O(8*B*) = 2·19 Å]. The geometry of the two independent molecules is identical except for small differences of bond lengths and angles. The distances and angles of the penicillin rings agree well with those observed in other penicillin sulfoxide molecules.

Experimental. Transparent needle from toluene/hexane, m.p. 409 K, dimensions 0·13 × 0·16 × 0·25 mm, Rigaku AFC5R diffractometer, lattice parameters determined from 25 reflections (53·31 <

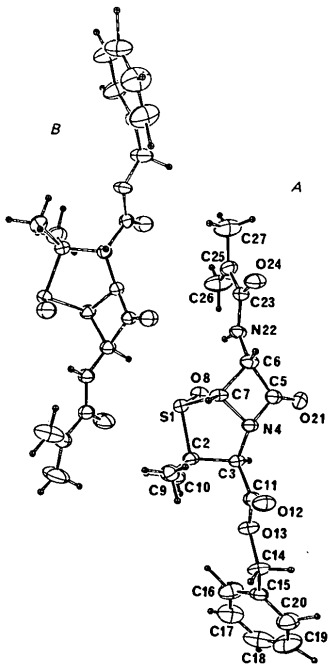


Fig. 1. A perspective view of the two molecules in the asymmetric unit.

---

* To whom correspondence should be addressed.

† Present address: Department of Biochemistry and Molecular Biophysics, Columbia University College of Physicians and Surgeons, New York, New York 10032, USA.

0108-2701/91/061338-03$03.00

Table 1. *Atomic parameters for molecules A and B with e.s.d.'s in parentheses*

$B_{\rm eq} = \frac{8}{3}\pi^2\sum_i\sum_j a_i a_j \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	$B_{\rm eq}$(Å^2)
S(1*A*)	0·1966 (2)	0·16240	0·9182 (1)	3·88 (6)
C(2*A*)	0·1475 (6)	0·0695 (3)	0·9531 (6)	3·8 (3)
C(3*A*)	0·1595 (6)	0·0703 (3)	1·1037 (6)	3·3 (2)
N(4*A*)	0·1264 (5)	0·1437 (2)	1·1352 (5)	3·5 (2)
C(5*A*)	0·2128 (7)	0·1902 (3)	1·2187 (7)	4·0 (3)
C(6*A*)	0·1700 (6)	0·2562 (3)	1·1291 (7)	4·1 (3)
C(7*A*)	0·1012 (6)	0·1978 (3)	1·0288 (6)	3·8 (2)
O(8*A*)	0·3387 (4)	0·1718 (2)	0·9912 (4)	4·3 (2)
C(9*A*)	0·0068 (7)	0·0590 (4)	0·8753 (7)	5·7 (3)
C(10*A*)	0·2404 (9)	0·0172 (4)	0·9140 (8)	6·2 (4)
C(11*A*)	0·0703 (7)	0·0139 (3)	1·1447 (6)	3·9 (3)
O(12*A*)	−0·0327 (5)	0·0240 (3)	1·1672 (5)	5·5 (2)
O(13*A*)	0·1304 (4)	−0·0514 (2)	1·1482 (4)	4·6 (2)
C(14*A*)	0·0529 (7)	−0·1128 (4)	1·1762 (8)	5·4 (3)
C(15*A*)	0·1435 (7)	−0·1789 (3)	1·1952 (7)	4·6 (3)
C(16*A*)	0·2195 (9)	−0·1939 (5)	1·112 (1)	7·2 (4)
C(17*A*)	0·298 (1)	−0·2577 (6)	1·125 (1)	8·7 (6)
C(18*A*)	0·297 (1)	−0·3033 (6)	1·228 (2)	9·5 (7)
C(19*A*)	0·221 (1)	−0·2876 (6)	1·310 (1)	9·5 (6)
C(20*A*)	0·143 (1)	−0·2260 (5)	1·2937 (9)	7·5 (4)
O(21*A*)	0·2934 (5)	0·1780 (3)	1·3182 (4)	4·9 (2)
N(22*A*)	0·2716 (5)	0·3009 (3)	1·1019 (5)	3·9 (2)
C(23*A*)	0·2635 (7)	0·3737 (3)	1·1042 (6)	3·9 (3)
O(24*A*)	0·1705 (5)	0·4046 (3)	1·1344 (5)	5·5 (2)
C(25*A*)	0·3767 (7)	0·4151 (4)	1·0743 (7)	4·9 (3)
C(26*A*)	0·4876 (9)	0·3799 (5)	1·055 (1)	8·4 (5)
C(27*A*)	0·358 (1)	0·4915 (5)	1·062 (1)	8·4 (5)
S(1*B*)	0·2924 (2)	0·3445 (1)	0·4453 (2)	4·56 (7)
C(2*B*)	0·3274 (6)	0·4390 (3)	0·5019 (6)	4·0 (3)
C(3*B*)	0·3266 (6)	0·4362 (3)	0·6480 (6)	3·4 (2)
N(4*B*)	0·3707 (5)	0·3638 (3)	0·6941 (4)	3·6 (2)
C(5*B*)	0·2911 (6)	0·3138 (3)	0·7378 (6)	3·7 (3)
C(6*B*)	0·3434 (7)	0·2497 (3)	0·6698 (6)	4·0 (3)
C(7*B*)	0·3998 (6)	0·3130 (3)	0·5975 (6)	3·9 (3)
O(8*B*)	0·1552 (4)	0·3285 (3)	0·4588 (5)	5·5 (2)
C(9*B*)	0·4590 (9)	0·4584 (5)	0·4776 (8)	6·7 (4)
C(10*B*)	0·2174 (8)	0·4868 (4)	0·4230 (7)	5·9 (3)
C(11*B*)	0·4140 (6)	0·4949 (4)	0·7229 (6)	4·0 (3)
O(12*B*)	0·5245 (5)	0·4874 (3)	0·7865 (5)	5·9 (2)
O(13*B*)	0·3486 (4)	0·5589 (2)	0·7048 (4)	4·7 (2)
C(14*B*)	0·4255 (7)	0·6216 (4)	0·7679 (8)	6·5 (4)
C(15*B*)	0·3380 (7)	0·6865 (4)	0·7351 (7)	4·7 (3)
C(16*B*)	0·3779 (8)	0·7427 (5)	0·671 (1)	7·6 (5)
C(17*B*)	0·297 (1)	0·8055 (6)	0·642 (1)	9·5 (6)
C(18*B*)	0·181 (1)	0·8094 (5)	0·672 (1)	7·7 (5)
C(19*B*)	0·141 (1)	0·7524 (7)	0·729 (1)	9·7 (7)
C(20*B*)	0·216 (1)	0·6909 (6)	0·764 (1)	9·4 (6)
O(21*B*)	0·2105 (5)	0·3212 (3)	0·8010 (4)	5·0 (2)
N(22*B*)	0·2489 (6)	0·2007 (3)	0·5976 (5)	4·5 (2)
C(23*B*)	0·2702 (9)	0·1275 (4)	0·6012 (7)	4·9 (3)
O(24*B*)	0·3704 (6)	0·1005 (3)	0·6649 (6)	7·2 (3)
C(25*B*)	0·1574 (9)	0·0834 (4)	0·5230 (7)	5·3 (4)
C(26*B*)	0·035 (1)	0·1105 (5)	0·480 (1)	8·7 (6)
C(27*B*)	0·189 (1)	0·0087 (5)	0·502 (1)	10·2 (6)

Table 2. *Selected geometrical parameters* (Å, °) *with e.s.d.'s in parentheses*

	Molecule *A*	Molecule *B*
S(1)—O(8)	1·506 (4)	1·495 (5)
S(1)—C(2)	1·845 (6)	1·847 (6)
S(1)—C(7)	1·828 (6)	1·827 (6)
O(12)—C(11)	1·166 (7)	1·194 (7)
O(13)—C(11)	1·349 (7)	1·348 (7)
O(13)—C(14)	1·458 (7)	1·471 (8)
O(21)—C(5)	1·204 (8)	1·200 (7)
O(24)—C(23)	1·227 (7)	1·206 (9)
N(4)—C(3)	1·450 (7)	1·453 (7)
N(4)—C(5)	1·396 (8)	1·388 (8)
N(4)—C(7)	1·481 (7)	1·471 (7)
N(22)—C(6)	1·421 (7)	1·416 (8)
N(22)—C(23)	1·341 (8)	1·363 (8)
C(2)—C(3)	1·575 (8)	1·555 (9)
C(2)—C(9)	1·512 (9)	1·49 (1)
C(2)—C(10)	1·49 (1)	1·52 (1)
C(3)—C(11)	1·521 (8)	1·510 (8)
C(5)—C(6)	1·541 (9)	1·547 (8)
C(6)—C(7)	1·562 (8)	1·581 (8)
C(14)—C(15)	1·52 (1)	1·49 (1)
C(23)—C(25)	1·498 (9)	1·50 (1)
C(25)—C(26)	1·38 (1)	1·34 (1)
C(25)—C(27)	1·42 (1)	1·44 (1)
O(8)—S(1)—C(2)	106·6 (3)	105·8 (3)
O(8)—S(1)—C(7)	104·1 (3)	104·4 (3)
C(2)—S(1)—C(7)	88·9 (3)	88·7 (3)
C(11)—O(13)—C(14)	114·8 (5)	114·6 (5)
C(3)—N(4)—C(5)	124·3 (5)	123·6 (5)
C(3)—N(4)—C(7)	117·2 (4)	116·5 (5)
C(5)—N(4)—C(7)	92·5 (4)	92·9 (4)
C(6)—N(22)—C(23)	121·3 (5)	121·6 (6)
S(1)—C(2)—C(3)	103·7 (4)	104·2 (4)
S(1)—C(2)—C(9)	106·6 (4)	106·6 (5)
S(1)—C(2)—C(10)	108·2 (5)	107·4 (5)
C(3)—C(2)—C(9)	112·9 (6)	113·7 (5)
C(3)—C(2)—C(10)	112·9 (5)	112·8 (6)
C(9)—C(2)—C(10)	111·9 (6)	111·5 (6)
N(4)—C(3)—C(11)	112·0 (5)	112·0 (5)
N(4)—C(3)—C(2)	106·1 (4)	107·0 (5)
C(11)—C(3)—C(2)	112·2 (5)	110·9 (5)
O(21)—C(5)—N(4)	130·8 (6)	131·5 (6)
O(21)—C(5)—C(6)	136·7 (6)	135·9 (6)
N(4)—C(5)—C(6)	92·4 (5)	92·6 (5)
N(22)—C(6)—C(5)	117·5 (5)	117·4 (5)
N(22)—C(6)—C(7)	120·1 (5)	119·6 (5)
C(5)—C(6)—C(7)	84·2 (4)	83·0 (4)
N(4)—C(7)—C(6)	88·4 (4)	88·1 (4)
S(1)—C(7)—N(4)	103·1 (4)	103·5 (4)
S(1)—C(7)—C(6)	116·9 (4)	116·3 (4)
O(12)—C(11)—O(13)	125·4 (6)	124·5 (6)
O(12)—C(11)—C(3)	126·9 (6)	126·3 (6)
O(13)—C(11)—C(3)	107·7 (5)	109·2 (5)
O(13)—C(14)—C(15)	106·9 (5)	106·6 (5)
O(24)—O(23)—N(22)	121·5 (6)	122·3 (7)
O(24)—C(23)—C(25)	121·9 (6)	123·0 (7)
N(22)—C(23)—C(25)	116·5 (6)	114·6 (7)
C(23)—C(25)—C(26)	121·4 (7)	122·8 (7)
C(23)—C(25)—C(27)	115·1 (7)	114·8 (8)
C(26)—C(25)—C(27)	123·4 (7)	122·4 (8)

$2\theta < 86{\cdot}80°$), $\omega/2\theta$ scan up to $2\theta = 120°$, index range $0 \leq h \leq 12$, $0 \leq k \leq 21$, $-12 \leq l \leq 12$; three standard reflections ($2\bar{2}0$, $\bar{2}\bar{2}0$, $\bar{1}0\bar{2}$) monitored every 150 measurements, no significant variation; 3229 reflections measured, 3046 unique, 2254 observed with $I \geq 3{\cdot}0\sigma(I)$. An empirical absorption correction, based on azimuthal scans of several reflections, was applied which resulted in transmission factors ranging from 0·91 to 1·00. Structure solved by direct methods (Gilmore, 1984) and refined by full-matrix least squares (Busing, Martin & Levy, 1962). All non-H atoms refined with anisotropic thermal parameters; H atoms included in the structure-factor calculation at difference map positions, and assigned isotropic thermal parameters which were 20% greater than the equivalent value of the atom to which they were bonded. $R = 0{\cdot}0411$, $wR = 0{\cdot}0495$, $w = 1/\sigma^2(F)$, $S = 1{\cdot}24$, maximum shift-to-e.s.d. ratio $(\Delta/\sigma)_{\rm max} = 0{\cdot}08$, $\Delta\rho_{\rm max} = 0{\cdot}18$ e Å^{-3}. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV). Figures were drawn with *PLUTO* (Motherwell & Clegg, 1978).

The refined atomic coordinates and equivalent isotropic temperature factors are given in Table 1;* selected bond distances and angles are presented in Table 2; the molecular structure and numbering of the atoms are shown in Fig. 1.

---

* Lists of structure factors, anisotropic thermal parameters, bond lengths and angles involving benzene ring C atoms and all H atoms, and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53759 (21 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Related literature. The title compound undergoes radical polymerization to yield a high molecular weight polymer (Saotome, Miyazawa & Endo, 1988), which serves as an efficient column packing for the chromatographic resolution of various aromatic racemates (Saotome, Miyazawa & Endo, 1989). The structures of other penicillin sulfoxides have been reported: phenoxymethylpenicillin sulfoxide (Cooper, DeMarco, Cheng & Jones, 1969), cloxacillin sulfoxide (Blanpain & Durant, 1976), and benzylpenicillin sulfoxide (Labischinski, Naumann, Barnickel, Dreissig, Gruszecki, Hofer & Bradaczek, 1987).

We thank Yoshio Kodama and Yasuo Takeuchi of Meiji Seika Kaisha for useful suggestions.

References

Blanpain, P. & Durant, F. (1976). *Cryst. Struct. Commun.* **5**, 89–94.

Busing, W. R., Martin, K. O. & Levy, H. A. (1962). *ORFLS*. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee, USA.

Cooper, R. D. G., DeMarco, P. V., Cheng, J. C. & Jones, N. D. (1969). *J. Am. Chem. Soc.* **91**, 1408–1415.

Gilmore, G. J. (1984). *J. Appl. Cryst.* **17**, 42–46.

Labischinski, H., Naumann, D., Barnickel, G., Dreissig, W., Gruszecki, W., Hofer, A. & Bradaczek, H. (1987). *Z. Naturforsch. Teil B*, **42**, 367–375.

Motherwell, S. & Clegg, W. (1978). *PLUTO*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.

Saotome, Y., Miyazawa, T. & Endo, T. (1988). *J. Polym. Sci. Polym. Lett. Ed.* **26**, 485–490.

Saotome, Y., Miyazawa, T. & Endo, T. (1989). *Chromatographia*, **28**, 505–508.

Acta Cryst. (1991). C**47**, 1340–1342

Structure of (±)-3-Benzyloxy-2,3,3a,7a-tetrahydrobenzo[*b*]thiophen-5(4*H*)-one 1,1-Dioxide

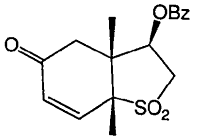
By V. M. Lynch, D. Daniel, S. F. Martin and B. E. Davis

Department of Chemistry and Biochemistry, University of Texas at Austin, Austin, Texas 78712, *USA*

(*Received* 27 *September* 1990; *accepted* 19 *November* 1990)

Abstracts. $C_{15}H_{16}O_4S$, (1), $M_r = 292\cdot35$, orthorhombic, $Pbca$, $a = 5\cdot9496\,(10)$, $b = 11\cdot483\,(3)$, $c = 40\cdot262\,(7)$ Å, $V = 2750\cdot7\,(10)$ Å^3, $Z = 8$, $D_x = 1\cdot41$ g cm^{-3}, $\mu = 2\cdot340$ cm^{-1}, Mo $K\alpha$ radiation, $\lambda = 0\cdot7107$ Å, $F(000) = 1232$, $T = 198$ K, $R = 0\cdot0451$ for 1703 reflections $[F_o \geq 4\sigma(F_o)]$. The two rings are *cis*-fused with the ring junction torsion angles being $-38\cdot2\,(3)°$ for C3—C3a—C7a—S1 and $-38\cdot4\,(4)°$ for C4—C3a—C7a—C7. The thiophene ring assumes the envelope conformation [C3a is 0·590 (3) Å from the plane through S1, C2, C3 and C7a] while the cyclohexanone moiety is in the sofa conformation [C3a is 0·530 (3) Å from the plane through C4, C5, C6, C7 and C7a].

Experimental. (1) was synthesized *via* an intermolecular Diels–Alder reaction of *trans*-1-methoxy-3-trimethylsiloxy-1,3-butadiene (Danishefski & Kitahara, 1974) and the benzyl protected allylic alcohol obtained from 2,5-dihydrothiophene 1,1-dioxide. Full synthetic details will be described elsewhere (Martin & Daniel, 1990). Crystals of (1) were obtained by slow evaporation from ethyl acetate. The data crystal was a colorless plate of approximate dimensions 0·09 × 0·49 × 0·51 mm. The data were collected on a Nicolet $R3$ diffractometer using a graphite monochromator and equipped with a Nicolet LT-2 low-temperature delivery system. Lattice parameters were obtained from the least-squares refinement of 40 reflections with $18\cdot2 < 2\theta < 24\cdot8°$. Data were collected using the ω-scan technique, with a 1·2° ω scan at 4–8° min^{-1} and 2θ range from 4·0–50·0° ($h = -7\rightarrow7$, $k = 0\rightarrow13$, $l = 0\rightarrow47$). 5196 reflections were collected, of which 2431 were unique, with an $R_{\rm int} = 0\cdot0185$. Three reflections $(\bar{1},\bar{2},\overline{17};\ \bar{1},3,\overline{15};\ 2,1,13)$ were remeasured every 97 reflections to monitor instrument and crystal stability. A smoothed curve of the intensities of these check reflections was used to scale the data. The scaling factor ranged from 0·996–1·05. The data were also corrected for Lp effects but not absorption. Reflections having $F_o < 4\sigma(F_o)$ were considered unobserved (728 reflections). Data reduction and decay correction were performed using the Nicolet XRD *SHELXTL-Plus* software package (Sheldrick,



(1)

0108-2701/91/061340-03$03.00