Acta Cryst. (1990). C46, 120–122

L-1-Benzyl-4-mesyloxymethyl-2-azetidinone

By Young Haeng Lee

Department of Chemistry, Wonkwang University, Iri, Chun Buck 510, *Korea*

Sung-il Cho*

Department of Chemical Engineering, Seoul City University, Seoul 131, *Korea*

Euisung Kim and Hyun-so Shin

Department of Chemical Engineering, Dongguk University, Seoul 100, *Korea*

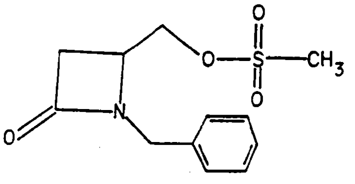
and J. R. Ruble and B. M. Craven

Department of Crystallography, University of Pittsburgh, Pittsburgh, PA 15260, *USA*

(*Received* 2 *December* 1988; *accepted* 3 *May* 1989)

Abstract. L-(1-Benzyl-2-oxo-4-azetidinyl)methyl methanesulfonate, $C_{12}H_{15}NO_4S$, $M_r = 269{\cdot}3$, orthorhombic, $P2_12_12_1$, $a = 5{\cdot}828\,(1)$, $b = 13{\cdot}263\,(1)$, $c = 17{\cdot}387\,(2)$ Å, $V = 1343{\cdot}8\,(1)$ Å^3, $Z = 4$, $D_x = 1{\cdot}33$, $D_m = 1{\cdot}32$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}7107$ Å, $\mu = 2{\cdot}68$ cm^{-1}, $F(000) = 568$, $T = 298$ K, final $R = 0{\cdot}046$ for 1356 observed reflections. In the β-lactam system, the four-membered ring is planar and the bond distances of the amide moiety are 1·342 (6) and 1·209 (5) Å for C—N and C═O, respectively.

Introduction. A new and versatile synthetic route to 4-substituted-2-azetidinones involving cyclization of α-substituted-*N*-benzyl-aspartate has recently been developed. The crystal structure determination of the title compound, (I), prepared in this way, confirms the synthesis and enables a comparison of the detailed stereochemistry of (I) with other β-lactams.



(I)

Experimental. Colorless needles of (I) were grown from chloroform solution. The crystal density was measured by flotation in benzene/CCl_4. Preliminary oscillation and Weissenberg X-ray photography showed the space group to be $P2_12_12_1$. A crystal 0·16 × 0·16 × 0·50 mm was then mounted with *b* close to the φ axis of an Enraf–Nonius CAD-4 diffractometer, and data were collected using Nb-filtered Mo $K\alpha$ radiation. Cell dimensions were derived from 25 reflections with $30 < 2\theta < 40°$. Integrated intensities were obtained from $\omega/2\theta$ scans for 2262 reflections with $\sin\theta/\lambda < 0{\cdot}70$ Å^{-1} in the octant $0 \le h \le 8$, $0 \le k \le 17$, $0 \le l \le 24$, with 1356 reflections having $I > 3\sigma$. Three monitor reflections ranged within $\pm 2\sigma$ from average intensity values. No corrections were made for X-ray absorption. *SHELX76* (Sheldrick, 1976) was used for the structure determination by direct methods and subsequent least-squares refinement to minimize the residual $\sum w\Delta^2$ with $\Delta = |F_o| - |F_c|$, $w = (\sigma^2 + 0{\cdot}02F_o^2)^{-1/2}$ and σ^2 the variance in $|F_o|$ owing to counting statistics. Variables included positional and isotropic thermal parameters for H atoms, which were all located in a difference Fourier map. Atomic scattering factors were those of Stewart, Davidson & Simpson (1965) for H and Cromer & Waber (1965) for other atoms, assuming $f' = 0{\cdot}110$ and $f'' = 0{\cdot}124$ for S. The refinement gave $R = 0{\cdot}046$, $wR = 0{\cdot}045$ and goodness of fit 0·83 for

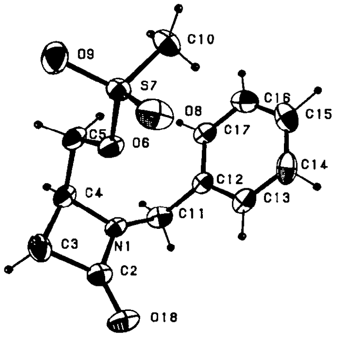


Fig. 1. Molecular structure and atom-numbering scheme. Atoms are shown as 20% probability thermal ellipsoids.

---

* To whom correspondence should be addressed.

Table 1. *Positional parameters* ($\times 10^4$) *and equivalent isotropic temperature factors* ($Å^2 \times 10^3$) *for non*-H *atoms*

$U_{eq} = (U_{11} + U_{22} + U_{33})/3.$

	x	y	z	U_{eq}
N1	5906 (6)	6051 (2)	7102 (3)	57 (2)
C2	7970 (8)	6430 (3)	7283 (2)	63 (3)
C3	7675 (12)	7299 (3)	6726 (3)	76 (3)
C4	5363 (9)	6832 (3)	6536 (2)	64 (2)
C5	4953 (10)	6461 (4)	5728 (3)	71 (3)
O6	6963 (5)	5846 (2)	5530 (1)	67 (2)
S7	7379 (2)	5562 (1)	4668 (1)	54 (1)
O8	9569 (6)	5098 (3)	4661 (2)	92 (2)
O9	6999 (7)	6410 (2)	4200 (2)	90 (2)
C10	5318 (11)	4662 (4)	4482 (3)	76 (3)
C11	4594 (10)	5231 (4)	7421 (3)	77 (3)
C12	4581 (7)	4299 (3)	6934 (2)	59 (2)
C13	6426 (9)	3649 (4)	6937 (3)	78 (4)
C14	6412 (14)	2787 (4)	6504 (4)	96 (4)
C15	4587 (16)	2559 (5)	6055 (4)	101 (5)
C16	2730 (14)	3197 (5)	6039 (3)	96 (4)
C17	2723 (9)	4061 (4)	6480 (3)	73 (3)
O18	9397 (6)	6147 (3)	7739 (2)	91 (2)

the structure with the absolute configuration shown in Fig. 1. The largest value for (shift/σ) = 0·06 and the maximum residual electron density was 0·67 e $Å^{-3}$. Final atom parameters are given in Table 1 and molecular parameters in Table 2.*

Discussion. The molecular conformation of (I) and the atom-numbering scheme are shown in Fig. 1. Bond lengths and angles in the central four-membered ring (Table 2) are similar to those in four other monocyclic β-lactams† except that the C3—C4 bond is shorter [1·519 (7) Å]. In (I), the atoms of the β-lactam ring, together with the amide O atoms, are coplanar within experimental error. The three bonds at the middle N atom form a flattened pyramid with N as apex. Possibly, this arises from intramolecular repulsions involving the benzyl and mesyloxymethyl groups. However, the pyramidal character of N in (I) is less than in certain other lactams. Thus, the displacement of the N atom from the plane through its bond atoms is 0·05 Å in (I), 0·13 Å in sulfazecin (Kamiya, Takamoto, Wada & Asai, 1981) and 0·37 Å in a carbapenam derivative (Désilets, Bélanger-Gariépy, Hanessian & Brisse, 1987).

Table 2. *Bond distances* (Å), *bond angles* (°) *and torsion angles* (°)

N1—C2	1·342 (6)	S7═O9	1·406 (3)
N1—C4	1·464 (5)	S7—C10	1·724 (6)
N1—C11	1·441 (6)	C11—C12	1·498 (7)
C2—C3	1·516 (6)	C12—C13	1·378 (7)
C2═O18	1·209 (5)	C12—C17	1·377 (7)
C3—C4	1·519 (7)	C13—C14	1·369 (8)
C4—C5	1·508 (6)	C14—C15	1·354 (11)
C5—O6	1·468 (6)	C15—C16	1·374 (11)
O6—S7	1·564 (2)	C16—C17	1·379 (8)
S7═O8	1·417 (4)		
C2—N1—C4	94·9 (4)	O6—S7—C10	103·8 (2)
C2—N1—C11	132·0 (4)	O8—S7—O9	119·0 (2)
C4—N1—C11	132·7 (4)	O8—S7—C10	109·0 (3)
N1—C2—C3	91·9 (4)	O9—S7—C10	109·6 (2)
N1—C2—O18	130·9 (4)	N1—C11—C12	114·1 (4)
C3—C2—O18	137·2 (5)	C11—C12—C13	120·7 (4)
C2—C3—C4	86·0 (4)	C11—C12—C17	121·1 (4)
N1—C4—C3	87·2 (3)	C13—C12—C17	118·2 (4)
N1—C4—C5	115·5 (4)	C12—C13—C14	121·0 (5)
C3—C4—C5	118·4 (4)	C13—C14—C15	120·5 (6)
C4—C5—O6	105·9 (4)	C14—C15—C16	119·5 (6)
C5—O6—S7	118·8 (3)	C15—C16—C17	120·2 (6)
O6—S7—O8	104·6 (2)	C12—C17—C16	120·5 (5)
O6—S7—O9	109·7 (2)		
C4—N1—C2—C3	0·6 (3)	C3—C4—C5—O6	48·5 (4)
C4—N1—C2═O18	179·2 (6)	C4—C5—O6—S7	−165·3 (5)
C11—N1—C2—C3	−173·2 (6)	C5—O6—S7═O8	172·3 (3)
C11—N1—C2═O18	5·5 (5)	C5—O6—S7═O9	43·6 (3)
C2—N1—C4—C3	−0·6 (4)	C5—O6—S7—C10	−73·5 (4)
C2—N1—C4—C5	119·7 (5)	N1—C11—C12—C13	79·1 (5)
C11—N1—C4—C3	173·1 (6)	N1—C11—C12—C17	−101·7 (6)
C11—N1—C4—C5	−66·6 (6)	C11—C12—C13—C14	178·9 (8)
C2—N1—C11—C12	−104·8 (6)	C17—C12—C13—C14	−0·3 (5)
C4—N1—C11—C12	83·7 (6)	C11—C12—C17—C16	−179·6 (8)
N1—C2—C3—C4	−0·6 (3)	C13—C12—C17—C16	−0·4 (5)
O18—C2—C3—C4	−179·0 (7)	C12—C13—C14—C15	0·7 (6)
C2—C3—C4—N1	0·5 (3)	C13—C14—C15—C16	−0·4 (6)
C2—C3—C4—C5	−117·1 (5)	C14—C15—C16—C17	−0·3 (7)
N1—C45—C5—O6	−52·8 (4)	C15—C16—C17—C12	0·7 (6)

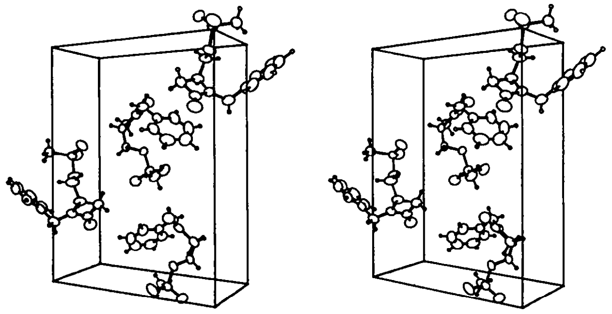


Fig. 2. Stereoscopic drawing of the crystal packing. The projection is down c and the b axis is horizontal.

Since the β-lactam ring is planar and the bonds at the amide N atom are nearly coplanar, the amide C—N bond is expected to be short owing to resonance effects. In (I) and in Δ^2-cephalosporin, which also has these stereochemical features (Sweet & Dahl, 1970), the amide C—N bond lengths are indeed short, 1·342 (6) and 1·339 (7) Å, respectively. In the carbapenam derivative noted above where the

---

* Lists of anisotropic thermal parameters, H-atom parameters, distances and angles involving H atoms, molecular least-squares planes, and the observed and calculated structure amplitudes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52186 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

† In these β-lactams (Parthasarathy, 1970; Kartha & Ambady, 1973; Colens, Declercq, Germain, Putzeys & Van Meerssche, 1974; Chambers & Doedens, 1980), the C3—C4 bond lengths range from 1·539 (7) to 1·602 (10) Å.

N-atom configuration is notably pyramidal (Désilets *et al.*, 1987), the amide C—N bond length is significantly longer, 1·381 (7) Å. The correlation between C—N bond length and pyramidal character of the amide N atom was first pointed out by Sweet & Dahl (1970) who went on to relate lengthening of the C—N bond to greater lability of the β-lactam ring system.

The molecular packing (Fig. 2) appears to be determined by van der Waals interaction. The shortest intermolecular approach [2·30 (5) Å] is between the amide O atom and an H atom from the C10 methyl group of the molecule at $(\frac{3}{2} - x, 1 - y, \frac{1}{2} + z)$.

This research is supported by BSRI administered by the Ministry of Education in Korea.

References

Chambers, R. & Doedens, R. J. (1980). *Acta Cryst.* **B36**, 1507–1510.

Colens, A., Declercq, J.-P., Germain, G., Putzeys, J. P. & Van Meerssche, M. (1974). *Cryst. Struct. Commun.* **3**, 119–122.

Cromer, D. T. & Waber, J. T. (1965). *Acta Cryst.* **18**, 104–109.

Désilets, D., Bélanger-Gariépy, F., Hanessian, S. & Brisse, F. (1987). *Acta Cryst.* **C43**, 919–922.

Kamiya, K., Takamoto, M., Wada, Y. & Asai, M. (1981). *Acta Cryst.* **B37**, 1626–1628.

Kartha, G. & Ambady, G. (1973). *J. Chem. Soc. Perkin Trans.* 2, pp. 2042–2044.

Parthasarathy, R. (1970). *Acta Cryst.* **B26**, 1282–1292.

Sheldrick, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

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

Sweet, R. M. & Dahl, L. F. (1970). *J. Am. Chem. Soc.* **92**, 5489–5507.

Acta Cryst. (1990). **C46**, 122–124

Structure of a Tetraphenyldiphosphine Monoxide Complex with Two Diphenylamine Molecules

By George Ferguson*

Chemistry Department, University of Guelph, Guelph, Ontario, Canada N1G 2W1

and Michael Myers and Trevor R. Spalding†

Chemistry Department, University College, Cork, Ireland

(*Received* 14 *March* 1989; *accepted* 3 *May* 1989)

Abstract. Tetraphenyldi-λ^3,λ^5-phosphane oxide–diphenylamine (1/2), $(C_6H_5)_2PP(O)(C_6H_5)_2.2(C_6H_5)_2NH$, $M_r = 724{\cdot}8$, monoclinic, $P2_1/n$, $a = 10{\cdot}587\ (2)$, $b = 18{\cdot}485\ (6)$, $c = 10{\cdot}026\ (2)$ Å, $\beta = 90{\cdot}59\ (3)°$, $V = 1962\ (2)$ Å^3, $Z = 2$, $D_x = 1{\cdot}23$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 1{\cdot}4$ cm^{-1}, $F(000) = 764$, 294 K. Final $R = 0{\cdot}042$ for 1466 observed reflections. The structure is disordered about an inversion centre (at the centre of the P—P bond); the O atom position is thus only 'half-occupied' and equally disordered in the sites adjacent to the P atoms. The unique diphenylamine molecule takes part in an N—H···O hydrogen-bond attachment to the O atom [N···O 2·690 (6) Å]. Whereas the P—P distance [2·228 (2) Å] is within the typical range of such bonds, the P═O distance [1·345 (6) Å] is remarkably short.

Introduction. As part of a study of the adducts of monoborane species BH_2X (X = H, CN) with aminophosphines, $R_2N—PR'_2$, we have serendipitously isolated a complex of $Ph_2PP(O)Ph_2$ with two molecules of Ph_2NH. Attempted recrystallization of diphenyl(diphenylamino)phosphineborane under aerobic conditions produced the title compound whose structure was elucidated by X-ray analysis. Confirmation of the presence of Ph_2NH came from the electron-impact mass spectrum of the complex which showed a parent ion at $m/z = 169$ ($^{12}C_{12}{}^1H_{11}N$; base peak) at highest mass. NMR spectroscopic studies also confirmed the presence of Ph_2NH (^1H, ^{13}C) and showed the presence of the $Ph_2P—P(O)Ph_2$ species (^1H, ^{13}C, ^{31}P) [δ ^{31}P at $-21{\cdot}6$ P^{III} and at 39·2 P^V; compare $-21{\cdot}6$ and 36·9 for $Ph_2P—P(O)Ph_2$ (Fluck & Binder, 1967)].

Experimental. Using a small colourless plate crystal, accurate cell dimensions and crystal orientation matrix were determined on a CAD-4 diffractometer by a least-squares treatment of the setting angles of 25 reflections in the range $10 < \theta < 14°$. Crystal dimensions 0·18 × 0·30 × 0·45 mm; intensities of

---

* E-mail address: CHFMFERG@UOGUELPH.

† E-mail address: STCH8006@IRUCCVAX.

0108-2701/90/010122-03$03.00