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Structure of Pivaloyloxymethyl (3*S*,5*R*,6*S*)-6-Bromopenicillanate

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Abstract. $C_{14}H_{20}BrNO_5S$, $M_r = 394{\cdot}3$, monoclinic, $P2_1$, $a = 5{\cdot}949$ (1), $b = 10{\cdot}470$ (1), $c = 14{\cdot}299$ (1) Å, $\beta = 94{\cdot}56$ (2)°, $V = 887{\cdot}8$ Å^3, $Z = 2$, $D_x = 1{\cdot}475$ g cm^{-3}, $\lambda(\text{Cu } K\alpha) = 1{\cdot}5418$ Å, $\mu = 42{\cdot}0$ cm^{-1}, $F(000) = 404$, room temperature, final $R = 0{\cdot}069$ for 1305 independent reflections. The thiazolidine ring is slightly puckered, with the C(3) atom, which is attached to the pivaloyl side chain, 0·47 (1) Å out of the plane formed by the remaining atoms. The nitrogen atom is 0·37 (1) Å above the plane defined by the three atoms to which it is bonded. Molecular packing results from normal van der Waals interactions.

Introduction. As pointed out in previous papers of this series, a crystal-structure determination of several penam derivatives was undertaken in our laboratory to establish the influence of 1,6-substituents on the conformation of the molecular nucleus. As part of these studies, the structure of the title compound was determined and is presented here.

Experimental. Crystallized by slow evaporation from methanol, colourless irregular-shaped crystal, approximate dimensions 0·25 × 0·22 × 0·07 mm; automatic four-circle Huber diffractometer; Ni-filtered Cu $K\alpha$ radiation; ω scans; integrated intensities as described by Lehmann & Larsen (1974); lattice parameters from setting angles of 20 reflections with 2θ values between 60 and 75°; space group $P2_1$ (No. 4); Lorentz–polarization and empirical absorption (see Alzari, Rivero, Punte & Ronco, 1986) corrections; min., max. transmission factors 1·00, 1·58; data collected to $2\theta_{\max} = 120°$; index range −6 to 6, 0 to 11, 0 to 16 for *h,k,l* respectively; 1362 unique reflections (not obscured by diffractometer geometry) measured, of which 1305 with $I > 2\sigma(I)$ considered observed; three standard reflections showed no significant fluctuations. Structure solved by Patterson and difference Fourier methods; refined by full-matrix least squares based on F's; weighting scheme: $w = 1/[\sigma^2(F) + 0{\cdot}0137F^2]$; H atoms stereochemically positioned with isotropic thermal parameters (not refined) equal to those of their bonded C atoms; all methyl groups refined as rigid bodies; remaining H atoms riding on corresponding heavy atoms. Isotropic extinction correction of form: $F' = F(1 - C\ F^2/\sin\theta)$ applied on F_{calc}, refined value of $C = 3{\cdot}0\ (4) \times 10^{-6}$. Agreement factors after last cycle $R = 0{\cdot}069$, $wR = 0{\cdot}067$ for 214 parameters refined; $(\Delta/\sigma)_{\max} = 0{\cdot}08$ for non-H parameters; max. and min. heights in difference map 1·2 e Å^{-3} (near Br atom) and −0·6 e Å^{-3}. An analytical absorption correction did not improve the quality of the final difference Fourier map, the two highest peaks ($\simeq$1 e Å^{-3}) reappeared in the same positions as before, close to the Br atom. Scattering factors from *International Tables for X-ray Crystallography* (1974); main computer programs those of *SHELX*76 (Sheldrick, 1976).

Discussion. Final atomic parameters are listed in Table 1,† bond lengths and angles in Table 2. Fig. 1 shows a general view of the molecule.

The compound presents a thiazolidine ring conformation with α-CH_3 equatorial, β-CH_3 axial and α-COO*R* equatorial, the C(3) atom being out of the plane formed by the other four atoms.

The nitrogen atom shows the characteristic pyramidal arrangement of penicillins, the sum of bond angles around N(4) being 339·5 (20)°.

The β-lactam ring is slightly puckered, as indicated by the distance from C(5) to the mean plane through N(4),C(6),C(7),O(8) [0·15 (1) Å] and by the dihedral angle between the planes defined by N(4)C(5)C(6) and N(4)C(7)C(6) [7·7 (8)°].

The dihedral angle between the mean planes through the β-lactam and thiazolidine rings is 62·5 (9)°, similar to those found in other penicillin derivatives having the same nuclear conformation (Belinzoni, Mascaretti, Alzari, Punte, Faerman & Podjarny, 1985; Domiano, Nardelli, Balsamo, Macchia & Macchia, 1979).

The orientation of the ester group is defined by the torsion angles C(2)—C(3)—C(11)—O(13) = 100·6 (8), C(3)—C(11)—O(13)—C(14) = −174·7 (7), C(11)—

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† Lists of structure factors, anisotropic temperature factors, H-atom positions and mean-plane calculations have been deposited with the British Library Lending Division, as Supplementary Publication No. SUP 42850 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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O(13)—C(14)—O(15) = 88·2 (9), O(13)—C(14)—O(15)—C(16) = 81·8 (8) and C(14)—O(15)—C(16)—C(18) = 178·1 (8)°. The dihedral angle between the carboxyl group and the C(2)C(3)N(4) plane is 78·9 (9)°; this torsion is caused by the intramolecular contact O(12)···N(4) [2·83 (1) Å].

Table 1. *Fractional coordinates and equivalent isotropic thermal parameters* (Å² × 10³), *with e.s.d.'s in parentheses*

$U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$.

	x	y	z	U_{eq}
S(1)	0·4934 (3)	0·3547 (3)	0·0720 (1)	57 (1)
C(2)	0·7677 (14)	0·3645 (9)	0·1439 (7)	51 (5)
C(3)	0·8842 (13)	0·4874 (9)	0·1064 (5)	46 (4)
N(4)	0·8070 (9)	0·4995 (8)	0·0087 (4)	42 (3)
C(5)	0·5724 (15)	0·4657 (8)	−0·0166 (6)	51 (5)
C(6)	0·6503 (15)	0·4097 (9)	−0·1081 (5)	52 (4)
C(7)	0·8874 (14)	0·4390 (8)	−0·0680 (6)	48 (4)
O(8)	1·0766 (11)	0·4210 (8)	−0·0881 (5)	64 (4)
C(9)	0·9153 (18)	0·2483 (10)	0·1251 (9)	69 (6)
C(10)	0·7202 (18)	0·3755 (11)	0·2459 (7)	69 (6)
C(11)	0·8246 (16)	0·6073 (9)	0·1591 (6)	50 (5)
O(12)	0·6459 (11)	0·6591 (8)	0·1481 (5)	67 (4)
O(13)	0·9922 (11)	0·6385 (7)	0·2228 (4)	58 (4)
C(14)	0·9510 (23)	0·7449 (10)	0·2846 (6)	70 (6)
O(15)	0·8506 (11)	0·7020 (7)	0·3640 (4)	60 (4)
C(16)	0·9907 (16)	0·6538 (11)	0·4329 (6)	61 (6)
O(17)	1·1872 (13)	0·6408 (16)	0·4257 (6)	119 (8)
C(18)	0·8713 (14)	0·6140 (10)	0·5169 (6)	57 (5)
C(19)	1·0504 (22)	0·5714 (15)	0·5950 (7)	82 (7)
C(20)	0·7152 (20)	0·5029 (15)	0·4923 (7)	78 (6)
C(21)	0·7374 (24)	0·7280 (15)	0·5512 (9)	88 (8)
Br(1)	0·5586 (2)	0·5000	−0·2233 (1)	71 (1)

Table 2. *Bond lengths* (Å) *and angles* (°), *with e.s.d.'s in parentheses*

C(2)—S(1)	1·861 (8)	C(5)—S(1)	1·809 (8)
C(3)—C(2)	1·575 (12)	C(9)—C(2)	1·537 (13)
C(10)—C(2)	1·512 (13)	N(4)—C(3)	1·441 (10)
C(11)—C(3)	1·520 (12)	C(5)—N(4)	1·457 (10)
C(7)—N(4)	1·385 (11)	C(6)—C(5)	1·539 (12)
C(7)—C(6)	1·511 (12)	Br(1)—C(6)	1·940 (8)
O(8)—C(7)	1·199 (11)	O(12)—C(11)	1·192 (11)
O(13)—C(11)	1·336 (11)	C(14)—O(13)	1·455 (12)
O(15)—C(14)	1·398 (12)	C(16)—O(15)	1·338 (11)
O(17)—C(16)	1·189 (12)	C(18)—C(16)	1·502 (13)
C(19)—C(18)	1·547 (12)	C(20)—C(18)	1·512 (15)
C(21)—C(18)	1·536 (15)		

C(5)—S(1)—C(2)	94·9 (4)	C(3)—C(2)—S(1)	104·3 (5)
C(9)—C(2)—S(1)	110·4 (7)	C(9)—C(2)—C(3)	108·4 (7)
C(10)—C(2)—S(1)	108·3 (6)	C(10)—C(2)—C(3)	112·8 (8)
C(10)—C(2)—C(9)	112·4 (8)	N(4)—C(3)—C(2)	106·7 (7)
C(11)—C(3)—C(2)	112·3 (7)	C(11)—C(3)—N(4)	109·8 (7)
C(5)—N(4)—C(3)	116·4 (6)	C(7)—N(4)—C(3)	128·7 (7)
C(7)—N(4)—C(5)	94·4 (6)	N(4)—C(5)—S(1)	106·2 (5)
C(6)—C(5)—S(1)	117·6 (6)	C(6)—C(5)—N(4)	87·5 (6)
C(7)—C(6)—C(5)	86·3 (6)	Br(1)—C(6)—C(5)	116·9 (6)
Br(1)—C(6)—C(7)	114·4 (6)	C(6)—C(7)—N(4)	91·3 (6)
O(8)—C(7)—N(4)	130·7 (8)	O(8)—C(7)—C(6)	138·0 (9)
O(12)—C(11)—C(3)	123·4 (8)	O(13)—C(11)—C(3)	110·4 (8)
O(13)—C(11)—O(12)	126·0 (9)	C(14)—O(13)—C(11)	116·6 (8)
O(15)—C(14)—O(13)	110·5 (8)	C(16)—O(15)—C(14)	116·0 (8)
O(17)—C(16)—O(15)	122·6 (10)	C(18)—C(16)—O(15)	112·8 (8)
C(18)—C(16)—O(17)	124·6 (9)	C(19)—C(18)—C(16)	108·3 (8)
C(20)—C(18)—C(16)	110·4 (8)	C(20)—C(18)—C(19)	108·7 (11)
C(21)—C(18)—C(16)	109·3 (9)	C(21)—C(18)—C(19)	109·8 (10)
C(21)—C(18)—C(20)	110·3 (9)		

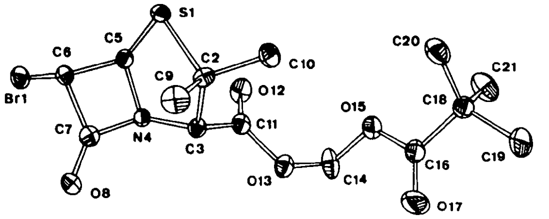

Fig. 1. *ORTEP* (Johnson, 1965) thermal ellipsoid (20%) plot, showing atomic numbering. Hydrogens omitted.

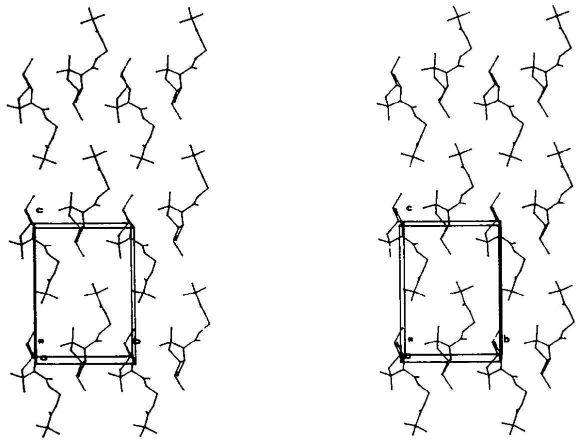

Fig. 2. Stereoview of the molecular packing.

No unusual values of bond lengths or angles have been found. The molecular packing may be described as layers of rigid penam nuclei (Fig. 2), with the pivaloyloxymethyl esters extended through the interlayer regions. The shortest intermolecular distances between non-H atoms are: C(5)···O(8) = 3·08 (1), C(6)···O(12) = 3·19 (1), S(1)···O(8) = 3·31 (1), O(8)···O(12) = 3·35 (2) and O(8)···C(14) = 3·35 (1) Å.

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