The authors thank Dr O. Mascaretti (IQUIOS, Universidad de Rosario, Argentina) for synthesizing the title compound, and CICPBA and CONICET (Argentina) for financial support.

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Structure of Pivaloyloxymethyl (3*S*,5*R*,6*S*)-6-Bromopenicillanate 1,1-Dioxide

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Abstract. $C_{14}H_{20}BrNO_7S$, $M_r = 426{\cdot}3$, orthorhombic, $P2_12_12_1$, $a = 6{\cdot}176\,(1)$, $b = 19{\cdot}965\,(5)$, $c = 17{\cdot}477\,(4)$ Å, $V = 1831{\cdot}2$ Å^3, $Z = 4$, $D_x = 1{\cdot}546$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}7107$ Å, $\mu = 23{\cdot}1$ cm^{-1}, $F(000) = 872$, room temperature, final $R = 0{\cdot}049$ for 1232 independent reflections. In the thiazolidine ring, the sulfur atom is 0·75 (1) Å out of the plane formed by the four other members of the ring. The distance from the N atom to the plane defined by its bonded atoms is 0·41 (1) Å. The ester group adopts an extended conformation, with thermal factors greater than those of the rigid molecular nucleus. Packing results from normal van der Waals contacts.

Introduction. This paper continues investigations on the influence of different 1,6-substituents on the penam nucleus of pivaloyloxymethyl penicillanates.

Experimental. Long needle-like transparent crystals by slow evaporation from mixture of petroleum ether/toluene/ethyl acetate at 291 K; automatic four-circle Huber diffractometer; graphite-monochromated Mo $K\alpha$ radiation; ω scans; integrated intensities as described by Lehmann & Larsen (1974); lattice parameters from setting angles of 16 reflections with 2θ values between 24 and 30°; space group $P2_12_12_1$ (No. 19). Lorentz and polarization corrections; no absorption corrections; data collected to $2\theta_{\max} = 45°$ in positive octant, index range 0 to 6, 0 to 18, 0 to 18 for h,k,l respectively; five standard reflections showed linear decay of intensities (corrected, limit values 1·0069 and 1·0687). 1271 unique reflections measured, of which 1232 with $I > 1{\cdot}5\sigma(I)$ considered observed. Structure solved by Patterson and Fourier methods; refined by full-matrix least squares based on F's; H atoms stereochemically positioned with isotropic thermal parameters (not refined) as those of bonded C atoms; all methyl groups refined as rigid bodies; remaining hydrogen positional parameters riding on corresponding C atoms. Secondary-extinction coefficient of form $F' = F(1 - CF^2/\sin\theta)$ applied on F_{calc}, refined value of $C = 1{\cdot}8\,(6) \times 10^{-7}$. Final agreement factors $R = 0{\cdot}0491$, $wR = 0{\cdot}0566$ for 233 parameters refined; weighting scheme $w = 1/[\sigma^2(F) + 0{\cdot}00244F^2]$; max. and min. heights in final difference Fourier synthesis 0·56 and $-0{\cdot}32$ e Å^{-3}; $(\Delta/\sigma)_{\max} = 0{\cdot}34$ for non-H atoms. Scattering factors from *International Tables for X-ray Crystallography* (1974); computer programs: *SHELX76* (Sheldrick, 1976).

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Table 1. *Fractional coordinates and equivalent isotropic thermal parameters* (Å^2 × 10^3), *with e.s.d.'s in parentheses*

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

	x	y	z	U_{eq}
S(1)	0·8627 (4)	0·7497 (1)	0·7639 (1)	65 (1)
C(2)	0·7370 (14)	0·6818 (5)	0·6960 (5)	55 (4)
C(3)	0·5675 (14)	0·7337 (5)	0·6550 (5)	50 (4)
N(4)	0·6470 (12)	0·8156 (4)	0·6584 (4)	48 (3)
C(5)	0·8461 (16)	0·8314 (5)	0·6997 (5)	59 (4)
C(6)	0·7397 (14)	0·9076 (6)	0·7317 (6)	63 (5)
C(7)	0·5330 (18)	0·8769 (5)	0·6937 (6)	63 (5)
O(8)	0·3476 (11)	0·8933 (4)	0·6920 (5)	83 (4)
C(9)	0·9138 (15)	0·6529 (6)	0·6417 (6)	64 (5)
C(10)	0·6258 (17)	0·6140 (5)	0·7416 (6)	68 (5)
C(11)	0·5313 (14)	0·7063 (5)	0·5739 (5)	54 (4)
O(12)	0·5979 (11)	0·7376 (4)	0·5171 (4)	70 (4)
O(13)	0·4127 (10)	0·6397 (3)	0·5778 (4)	62 (3)
C(14)	0·3776 (19)	0·5958 (6)	0·5090 (6)	72 (5)
C(15)	0·5317 (16)	0·5375 (4)	0·5003 (4)	81 (4)
C(16)	0·5176 (21)	0·4757 (7)	0·5433 (6)	84 (5)
O(17)	0·3784 (18)	0·4680 (6)	0·5901 (6)	118 (5)
C(18)	0·6913 (20)	0·4112 (6)	0·5254 (6)	74 (5)
C(19)	0·7912 (29)	0·3918 (12)	0·5995 (9)	155 (7)
C(20)	0·8441 (29)	0·4329 (12)	0·4674 (11)	156 (7)
C(21)	0·5579 (34)	0·3444 (8)	0·4928 (12)	164 (7)
Br(1)	0·8413 (2)	1·0050 (1)	0·6900 (1)	82 (1)
O(22)	1·0810 (13)	0·7274 (5)	0·7808 (5)	88 (4)
O(23)	0·7165 (15)	0·7643 (5)	0·8247 (4)	87 (4)

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

C(2)–S(1)	1·826 (9)	C(5)–S(1)	1·786 (10)
O(22)–S(1)	1·431 (8)	O(23)–S(1)	1·418 (8)
C(3)–C(2)	1·544 (12)	C(9)–C(2)	1·528 (13)
C(10)–C(2)	1·559 (12)	N(4)–C(3)	1·475 (10)
C(11)–C(3)	1·509 (13)	C(5)–N(4)	1·451 (12)
C(7)–N(4)	1·399 (12)	C(6)–C(5)	1·554 (13)
C(7)–C(6)	1·530 (14)	Br(1)–C(6)	1·912 (10)
O(8)–C(7)	1·179 (12)	O(12)–C(11)	1·198 (10)
O(13)–C(11)	1·347 (10)	C(14)–O(13)	1·431 (11)
O(15)–C(14)	1·382 (12)	C(16)–O(15)	1·294 (13)
O(17)–C(16)	1·193 (14)	C(18)–C(16)	1·563 (16)
C(19)–C(18)	1·472 (19)	C(20)–C(18)	1·432 (19)
C(21)–C(18)	1·513 (19)		

C(5)–S(1)–C(2)	93·3 (4)	O(22)–S(1)–C(2)	111·6 (5)
O(22)–S(1)–C(5)	112·9 (5)	O(23)–S(1)–C(2)	109·1 (5)
O(23)–S(1)–C(5)	107·4 (4)	O(23)–S(1)–O(22)	119·4 (5)
C(3)–C(2)–S(1)	103·3 (6)	C(9)–C(2)–S(1)	107·6 (6)
C(9)–C(2)–C(3)	112·3 (7)	C(10)–C(2)–S(1)	108·7 (6)
C(10)–C(2)–C(3)	111·1 (7)	C(10)–C(2)–C(9)	113·3 (8)
N(4)–C(3)–C(2)	107·0 (7)	C(11)–C(3)–C(2)	111·1 (7)
C(11)–C(3)–N(4)	112·2 (7)	C(5)–N(4)–C(3)	118·5 (7)
C(7)–N(4)–C(3)	123·4 (7)	C(7)–N(4)–C(5)	94·0 (7)
N(4)–C(5)–S(1)	102·6 (6)	C(6)–C(5)–S(1)	116·4 (7)
C(6)–C(5)–N(4)	88·5 (7)	C(7)–C(6)–C(5)	85·0 (7)
Br(1)–C(6)–C(5)	116·3 (6)	Br(1)–C(6)–C(7)	113·8 (7)
C(6)–C(7)–N(4)	91·4 (7)	O(8)–C(7)–N(4)	130·8 (9)
O(8)–C(7)–C(6)	137·7 (9)	O(12)–C(11)–C(3)	126·2 (8)
O(13)–C(11)–C(3)	106·9 (8)	O(13)–C(11)–O(12)	126·9 (9)
C(14)–O(13)–C(11)	118·4 (8)	O(15)–C(14)–O(13)	111·2 (8)
C(16)–O(15)–C(14)	118·0 (10)	O(17)–C(16)–O(15)	122·3 (13)
C(18)–C(16)–O(15)	113·8 (10)	C(18)–C(16)–O(17)	123·8 (11)
C(19)–C(18)–C(16)	105·5 (10)	C(20)–C(18)–C(16)	114·5 (9)
C(20)–C(18)–C(19)	113·8 (14)	C(21)–C(18)–C(16)	103·1 (11)
C(21)–C(18)–C(19)	113·1 (14)	C(21)–C(18)–C(20)	106·6 (13)

Discussion. Final atomic coordinates and equivalent isotropic thermal parameters for non-H atoms are listed in Table 1;* bond lengths and angles in Table 2. Fig. 1 is a view of the molecule, showing the atomic labelling.

The thiazolidine ring adopts the conformation with α-CH_3 axial, β-CH_3 equatorial and α-COO*R* axial, the S(1) atom being out of the plane formed by C(2)-C(3)N(4)C(5). The β-lactam ring is puckered, with C(5) 0·21 (1) Å out of the plane formed by N(4),-C(6),C(7),O(8). The dihedral angle between the planes defined by N(4)C(5)C(6) and N(4)C(7)C(6) is 10·8 (8)°.

The S(1)–C(2) [1·826 (9) Å] and S(1)–C(5) [1·786 (10) Å] bond lengths are appreciably shorter than the average values [1·842 (4) and 1·804 (5) Å, respectively] reported by Domiano, Nardelli, Balsamo, Macchia & Macchia (1979) for several compounds having the thiazolidine ring in the same conformation as that found here. The rest of the bond lengths and angles of the penam nucleus are in good agreement with the values found in similar compounds.

The molecule has three chiral centres, with configurations *S*[C(3), C(6)] and *R*[C(5)] (from starting material). The carboxyl group makes a dihedral angle of 64·4 (8)° with the plane defined by C(2)C(3)N(4), the reason for this torsion being the intramolecular contacts O(12)···N(4) [2·82 (1) Å] and O(13)···C(2) [2·96 (2) Å]. The orientation of the side chain is defined by the torsion angles: C(2)–C(3)–C(11)–O(13) = 74·5 (9), C(3)–C(11)–O(13)–C(14) = −172·4 (6), C(11)–O(13)–C(14)–O(15) = 93·4 (8), O(13)–C(14)–O(15)–C(16) = 74·1 (9), C(14)–O(15)–C(16)–C(18) = 176·5 (6)°.

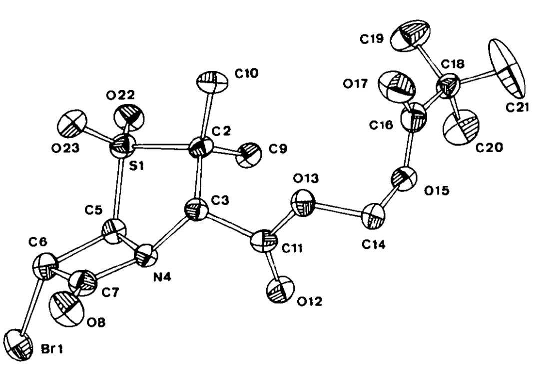

Fig. 1. *ORTEP* (Johnson, 1965) thermal ellipsoid (20%) plot, showing atomic numbering. Hydrogens omitted.

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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 42848 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

In view of the significantly short values of the C(14)—O(15) and O(15)—C(16) bond lengths (Table 2), site disorder was suspected, but a careful analysis with partial occupation factors and difference Fourier synthesis gave no definite results.

The atoms at the end of the ester group have large thermal factors; therefore the departure of bond lengths from their corresponding standard values cannot be considered statistically significant.

The rather large thermal factors associated with the ester group seem to be characteristic of the crystal packing of these compounds. Large temperature factors were found not only in compounds measured at room temperature (present work; Alzari, Rivero, Punte & Ronco, 1986; Alzari, Punte, Ronco & Rivero, 1986; Punte, Rivero & Alzari, 1986), but also in compounds measured at liquid-nitrogen temperature (Belinzoni, Mascaretti, Alzari, Punte, Faerman & Podjarny, 1985; Hope, 1985).

There are no unusually short intermolecular distances. The crystal packing (Fig. 2) is determined primarily by van der Waals contacts; however the distances C(6)—H(6)···O(17) [C(6)···O(17) = 3·36 (1), H(6)···O(17) = 2·34 (2) Å], C(9)—H2(C9)···O(12) [C(9)···O(12) = 3·53 (1), H2(C9)···O(12) = 2·62 (2) Å] and C(14)—H1(C14)···O(12) [C(14)···O(12) = 3·34 (2), H1(C14)···O(12) = 2·81 (3) Å] suggest a significant electrostatic contribution to the packing energy.

The authors are grateful to Dr O. Mascaretti (IQUIOS, Universidad de Rosario, Argentina) for the synthesis of the title compound, and to CICPBA and CONICET (Argentina) for financial support.

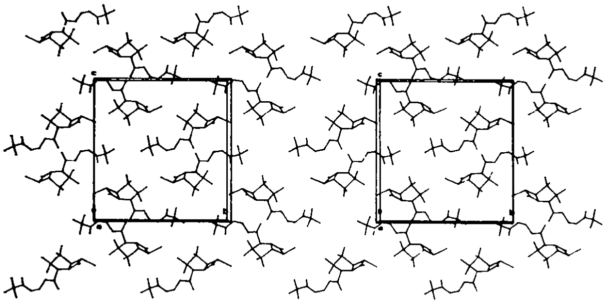

Fig. 2. Stereoview of the molecular packing.

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Structure of Pivaloyloxymethyl (1*S*,3*S*,5*R*)-6,6-Dibromopenicillanate 1-Oxide

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Abstract. $C_{14}H_{19}Br_2NO_6S$, $M_r = 489·2$, orthorhombic, $P2_12_12_1$, $a = 8·630$ (4), $b = 10·820$ (3), $c = 21·204$ (8) Å, $V = 1979·9$ Å^3, $Z = 4$, $D_x = 1·638$ g cm^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 41·2$ cm^{-1}, $F(000) = 976$, room temperature, final $R = 0·048$ for 1677 independent reflections. The thiazolidine ring is puckered; the S(1) atom is 0·945 (4) Å out of the plane formed by the other four atoms. The N atom of the β-lactam ring shows pyramidal geometry, the distance to the plane of its attached atoms being 0·37 (1) Å. No unusually short intermolecular distances were found.

Introduction. As part of a detailed study of 1,6-substituted penam derivatives, the crystal structure of the title compound is reported in the present paper.

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