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.

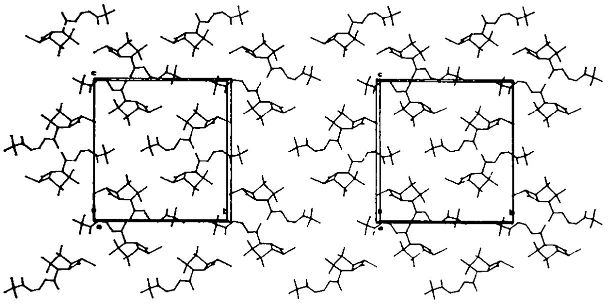

Fig. 2. Stereoview of the molecular packing.

References

Alzari, P. M., Punte, G., Ronco, A. E. & Rivero, B. E. (1986). *Acta Cryst.* C**42**, 1034–1036.

Alzari, P. M., Rivero, B. E., Punte, G. & Ronco, A. E. (1986). *Acta Cryst.* C**42**, 1032–1034.

Belinzoni, D. U., Mascaretti, O. A., Alzari, P. M., Punte, G., Faerman, C. H. & Podjarny, A. D. (1985). *Can. J. Chem.* **63**, 3177–3181.

Domiano, P., Nardelli, M., Balsamo, A., Macchia, B. & Macchia, F. (1979). *Acta Cryst.* B**35**, 1363–1372.

Hope, H. (1985). Private communication.

International Tables for X-ray Crystallography (1974). Vol. IV, pp. 99–149. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

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

Lehmann, M. S. & Larsen, F. K. (1974). *Acta Cryst.* A**30**, 580–584.

Punte, G., Rivero, B. E. & Alzari, P. M. (1986). *Acta Cryst.* C**42**, 1037–1038.

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

Acta Cryst. (1986). C**42**, 1034–1036

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

By Pedro M. Alzari,* Graciela Punte, Alicia E. Ronco and Blas E. Rivero

Laboratorio de Cristalografía, Departamento de Física, Universidad Nacional de La Plata, CC 67,
1900 *La Plata, Argentina*

(*Received* 6 *December* 1985; *accepted* 21 *February* 1986)

Abstract. $C_{14}H_{19}Br_2NO_6S$, $M_r = 489{\cdot}2$, orthorhombic, $P2_12_12_1$, $a = 8{\cdot}630\ (4)$, $b = 10{\cdot}820\ (3)$, $c = 21{\cdot}204\ (8)$ Å, $V = 1979{\cdot}9$ Å^3, $Z = 4$, $D_x = 1{\cdot}638$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}7107$ Å, $\mu = 41{\cdot}2$ cm^{-1}, $F(000) = 976$, room temperature, final $R = 0{\cdot}048$ 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.

---

* Present address: Immunologie Structurale, Institut Pasteur, 25 Rue du Dr Roux, 75724 Paris CEDEX 15, France.

0108-2701/86/081034-03$01.50

Experimental. Colourless irregular-shaped single crystal; grown by slow evaporation from petroleum ether/toluene/ethyl acetate; approximate dimensions 0·4 × 0·5 × 0·25 mm; automatic four-circle Huber diffractometer; graphite-monochromated Mo $K\alpha$ radiation; ω scans; integrated intensities as described by Lehmann & Larsen (1974); cell dimensions from setting angles of 18 reflections, 2θ values between 26 and 34°; space group $P2_12_12_1$ (No. 19). Lorentz, polarization and empirical absorption (see Alzari, Rivero, Punte & Ronco, 1986) corrections; min., max. transmission factors 1·00, 1·49; data collected to $2\theta_{\text{max}} = 60°$; index range 0 to 12, 0 to 15, 0 to 29 for h,k,l respectively; five standard reflections monitored every 90 min, gradual decrease in intensities (corrected, limit values 1·0 and 1·018); 2051 unique reflections measured, of which 1677 with $I > 1{\cdot}5\sigma(I)$ considered observed. Structure solved by Patterson and Fourier techniques; refined by full-matrix least squares based on F's; most H atoms located in difference map, all geometrically positioned with isotropic temperature factors (not refined) equal to those of corresponding heavy atoms; all methyl groups refined as rigid bodies; remaining H atoms riding on bonded C atoms. Isotropic extinction correction of form $F' = F(1 - CF^2/\sin\theta)$ applied on F_{calc}, refined $C = 1{\cdot}6\,(2) \times 10^{-7}$. Final agreement factors $R = 0{\cdot}0484$, $wR = 0{\cdot}0512$ for 233 refined parameters; $w = 1/[\sigma^2(F) + 0{\cdot}00068F^2]$; max. and min. heights in final difference Fourier synthêsis 0·45 and −0·56 e Å^{-3}; $(\Delta/\sigma)_{\text{max}} = 0{\cdot}20$ for non-H atoms. Scattering factors from *International Tables for X-ray Crystallography* (1974); main computer programs those of *SHELX*76 (Sheldrick, 1976).

Discussion. Final atomic coordinates and equivalent isotropic temperature factors for non-H atoms are listed in Table 1,* bond distances and angles in Table 2. Fig. 1 is a representation of the molecule showing the atom labelling.

As expected from steric restrictions (Alzari, Rivero, Punte & Ronco, 1986; Alzari, Ronco, Rivero & Punte, 1986), the thiazolidine ring adopts the conformation with the S atom out of the plane formed by the other four atoms. The same conformation was assigned, in solution, to the title compound and to its epimer, pivaloyloxymethyl (1*R*)-6,6-dibromopenicillanate 1-oxide, based on NMR–nuclear Overhauser effect spectroscopic evidence (Belinzoni, 1985). Although several attempts to crystallize the α-sulfoxide compound were unsuccessful, the structure of methyl

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

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

	x	y	z	U_{eq}
S(1)	−0·0238 (3)	0·3278 (2)	0·7671 (1)	54 (1)
C(2)	−0·0613 (11)	0·3572 (8)	0·8524 (4)	45 (5)
C(3)	0·1052 (10)	0·3474 (8)	0·8802 (4)	44 (5)
N(4)	0·2102 (8)	0·3981 (6)	0·8339 (3)	37 (4)
C(5)	0·1435 (10)	0·4315 (8)	0·7724 (4)	47 (5)
C(6)	0·3022 (11)	0·3992 (8)	0·7438 (4)	47 (5)
C(7)	0·3405 (11)	0·3442 (9)	0·8089 (4)	50 (5)
O(8)	0·4409 (8)	0·2807 (7)	0·8287 (3)	67 (4)
C(9)	−0·1282 (12)	0·4851 (9)	0·8582 (5)	66 (7)
C(10)	−0·1655 (12)	0·2583 (11)	0·8758 (5)	71 (7)
C(11)	0·1233 (12)	0·4188 (9)	0·9421 (4)	50 (6)
O(12)	0·2040 (12)	0·5057 (8)	0·9501 (3)	90 (6)
O(13)	0·0340 (8)	0·3669 (6)	0·9859 (3)	57 (4)
C(14)	0·0326 (13)	0·4234 (11)	1·0471 (4)	68 (7)
O(15)	−0·0673 (8)	0·5240 (6)	1·0466 (3)	56 (4)
C(16)	−0·2198 (15)	0·4970 (11)	1·0515 (5)	64 (7)
O(17)	−0·2667 (11)	0·3932 (8)	1·0517 (4)	98 (7)
C(18)	−0·3187 (15)	0·6080 (11)	1·0572 (5)	72 (7)
C(19)	−0·2550 (21)	0·6927 (14)	1·1089 (6)	126 (12)
C(20)	−0·3135 (18)	0·6797 (12)	0·9976 (5)	94 (9)
C(21)	−0·4813 (16)	0·5753 (18)	1·0756 (10)	151 (16)
Br(1)	0·4240 (1)	0·5431 (1)	0·7264 (1)	72 (1)
Br(2)	0·3124 (1)	0·2886 (1)	0·6732 (1)	72 (1)
O(23)	0·0366 (8)	0·1994 (6)	0·7645 (3)	68 (4)

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

C(2)–S(1)	1·865 (8)	C(5)–S(1)	1·832 (9)
O(23)–S(1)	1·485 (1)	C(3)–C(2)	1·556 (12)
C(9)–C(2)	1·504 (13)	C(10)–C(2)	1·484 (13)
N(4)–C(3)	1·445 (10)	C(11)–C(3)	1·531 (11)
C(5)–N(4)	1·470 (10)	C(7)–N(4)	1·373 (11)
C(6)–C(5)	1·538 (12)	C(7)–C(6)	1·540 (11)
Br(1)–C(6)	1·915 (9)	Br(2)–C(6)	1·918 (8)
O(8)–C(7)	1·183 (10)	O(12)–C(11)	1·182 (11)
O(13)–C(11)	1·331 (11)	C(14)–O(13)	1·436 (10)
O(15)–C(14)	1·389 (12)	C(16)–O(15)	1·353 (1-)
O(17)–C(16)	1·193 (13)	C(18)–C(16)	1·478 (15)
C(19)–C(18)	1·530 (18)	C(20)–C(18)	1·484 (14)
C(21)–C(18)	1·499 (18)		
C(5)–S(1)–C(2)	88·4 (4)	O(23)–S(1)–C(2)	104·9 (4)
O(23)–S(1)–C(5)	107·3 (4)	C(3)–C(2)–S(1)	101·3 (6)
C(9)–C(2)–S(1)	107·6 (7)	C(9)–C(2)–C(3)	112·8 (8)
C(10)–C(2)–S(1)	107·8 (7)	C(10)–C(2)–C(3)	112·6 (8)
C(10)–C(2)–C(9)	113·8 (8)	N(4)–C(3)–C(2)	107·2 (6)
C(11)–C(3)–C(2)	112·6 (7)	C(11)–C(3)–N(4)	109·1 (7)
C(5)–N(4)–C(3)	116·8 (7)	C(7)–N(4)–C(3)	127·9 (7)
C(7)–N(4)–C(5)	94·8 (6)	N(4)–C(5)–S(1)	102·3 (5)
C(6)–C(5)–S(1)	122·6 (6)	C(6)–C(5)–N(4)	86·9 (6)
C(7)–C(6)–C(5)	85·7 (6)	Br(1)–C(6)–C(5)	112·3 (6)
Br(1)–C(6)–C(7)	111·6 (6)	Br(2)–C(6)–C(5)	119·4 (6)
Br(2)–C(6)–C(7)	116·7 (6)	Br(2)–C(6)–Br(1)	109·4 (4)
C(6)–C(7)–N(4)	90·3 (4)	O(8)–C(7)–N(4)	135·2 (8)
O(8)–C(7)–C(6)	134·4 (9)	O(12)–C(11)–C(3)	125·7 (9)
O(13)–C(11)–C(3)	109·0 (8)	O(13)–C(11)–O(12)	125·3 (9)
C(14)–O(13)–C(11)	117·1 (8)	O(15)–C(14)–O(13)	109·4 (7)
C(16)–O(15)–C(14)	115·7 (9)	O(17)–C(16)–O(15)	122·3 (11)
C(18)–C(16)–O(15)	113·1 (9)	C(18)–C(16)–O(17)	124·7 (12)
C(19)–C(18)–C(16)	109·7 (11)	C(20)–C(18)–C(16)	109·8 (10)
C(20)–C(18)–C(19)	106·6 (11)	C(21)–C(18)–C(16)	111·7 (12)
C(21)–C(18)–C(19)	106·9 (13)	C(21)–C(18)–C(20)	111·9 (13)

---

* 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 42849 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

(1*R*)-6,6-dibromopenicillanate 1-oxide has been published (Peeters, Blaton & De Ranter, 1982). The thiazolidine ring in this molecule also has the conformation with α-CH_3 axial, *β*-CH_3 equatorial and α-COO*R* axial, the distance from S(1) to the mean plane through C(2)C(3)N(4)C(5) being the same as in the title compound, 0·945 (6) Å.

The puckering of the *β*-lactam ring is quite remarkable, as indicated by the distance from C(5) to the plane formed by N(4),C(6),C(7),O(8) [0·31 (1) Å] and by the dihedral angle between the N(4)C(5)C(6) and N(4)-C(7)C(6) planes [16·2 (5)°].

Bond lengths and angles of the penam nucleus (Table 2) are in good agreement with the values found by Peeters *et al.* (1982).

The dihedral angle between the mean planes of the thiazolidine and *β*-lactam rings [43·8 (4)°] is similar to that found in the sulfone (Alzari, Rivero, Punte & Ronco, 1986). In both cases, this angle is affected by the intramolecular contact O(23)···Br(2) [3·22 (1) Å for the sulfoxide, 3·17 (1) Å for the sulfone].

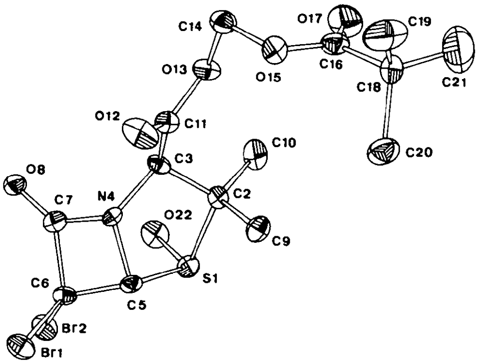

Fig. 1. *ORTEP* (Johnson, 1965) thermal ellipsoid (20%) plot, showing atomic numbering. Hydrogens omitted.

The configurations of the chiral centres in the molecule are *S* for S(1) and C(3), *R* for C(5) (from starting material).

The dihedral angle between the carboxyl group and the plane defined by C(2)C(3)N(4) is 59·1 (4)°; this torsion is determined by the intramolecular contacts O(12)···N(4) [2·73 (1) Å] and O(13)···C(2) [2·95 (1) Å]. The orientation of the ester group is defined by the torsion angles C(2)—C(3)—C(11)—O(13) = 65·1 (7), C(3)—C(11)—O(13)—C(14) = −178·5 (5), C(11)—O(13)—C(14)—O(15) = 81·2 (6), O(13)—C(14)—O(15)—C(16) = 79·2 (6) and C(14)—O(15)—C(16)—C(18) = 174·2 (5)°.

At the end of the pivaloyloxymethyl moiety, the atoms have large thermal factors (Table 1); therefore the differences between the observed (Table 2) and commonly accepted bond distances are probably not statistically significant.

Packing of molecules in the crystal (Fig. 2) is determined primarily by normal van der Waals contacts. The electrostatic contribution may also be significant, as suggested by the intermolecular contacts C(3)—H(3)···O(17) [C(3)···O(17) = 3·17 (1), H(3)···O(17) = 2·18 (1) Å], C(5)—H(5)···O(23) [C(5)···O(23) = 3·38 (1), H(5)···O(23) = 2·31 (2) Å], C(14)—H2(C14)···O(8) [C(14)···O(8) = 3·53 (1), H2(C14)···O(8) = 2·46 (2) Å] and C(10)—H2(C10)···O(8) [C(10)···O(8) = 3·55 (2), H2(C10)···O(8) = 2·48 (2) Å].

Apart from those cited above, the only intermolecular distances lower than 3·5 Å, involving non-H atoms, are Br(1)···O(8) = 3·06 (1) and O(13)···O(17) = 3·39 (1) Å.

The authors thank Dr O. Mascaretti (IQUIOS, University of Rosario, Argentina) for preparing the sample compound, and CICPBA and CONICET (Argentina) for financial support.

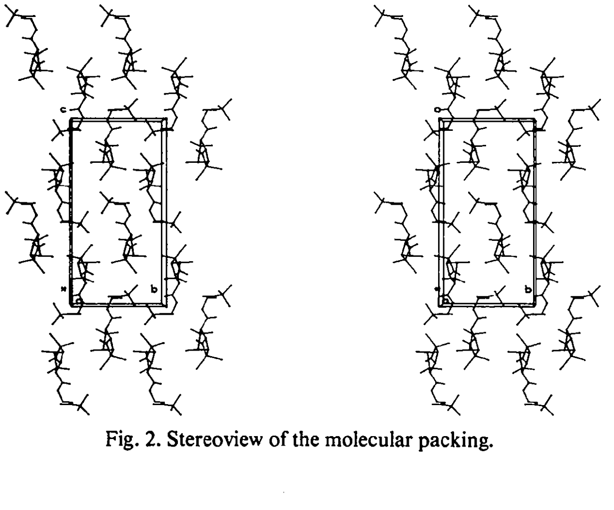

Fig. 2. Stereoview of the molecular packing.

References

Alzari, P. M., Rivero, B. E., Punte, G. & Ronco, A. E. (1986). *Acta Cryst.* C**42**, 1029–1032.

Alzari, P. M., Ronco, A. E., Rivero, B. E. & Punte, G. (1986). *Acta Cryst.* C**42**, 1032–1034.

Belinzoni, D. U. (1985). Doctoral thesis, Univ. de Buenos Aires, Argentina.

International Tables for X-ray Crystallography (1974). Vol. IV, pp. 99–149. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

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

Lehmann, M. S. & Larsen, F. K. (1974). *Acta Cryst.* A**30**, 580–584.

Peeters, O. M., Blaton, N. M. & De Ranter, C. J. (1982). *Cryst. Struct. Commun.* **11**, 787–791.

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