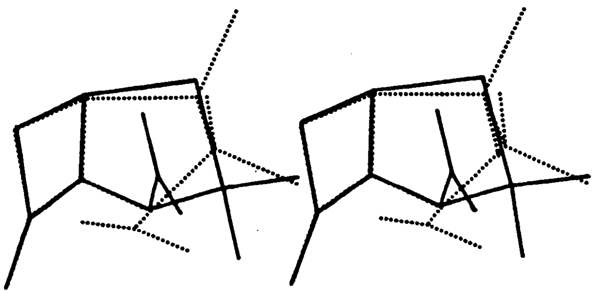

Fig. 3. Stereoscopic view of rigid fitting between penicillanic acid (full lines) and penicillanic acid 1,1-dioxide (dotted lines) by superposition of N(4), C(5), C(6), C(7) and O(8).

Table 2. *The* Na(14) *environment distances* (Å)

O(8)(*x,y,z*)···Na(14(*x,y,z*)	2·30 (1)
O(12)(*x,y,z*)···Na(14)(*x,y,z*−1)	2·29 (1)
O(13)(*x,y,z*)···Na(14)(−*x*+1,*y*−$\frac{1}{2}$,−*z*+$\frac{3}{2}$)	2·32 (1)

penicillin derivatives (Blanpain, Nagy, Laurent & Durant, 1980). The stereochemistry of the molecule can be seen from Fig. 2. The thiazolidine ring adopts a *C*3 conformation with α-CH_3 in pseudo-equatorial and *β*-CH_3 and the C(3) substituent in pseudo-axial positions. This geometry is opposite to that reported for the corresponding *S*-oxide compound, penicillanic acid 1,1-dioxide, which crystallizes in an *S*1 conformation (Brenner & Knowles, 1981) with α-CH_3 in pseudo-axial and *β*-CH_3 and the C(3) substituent in pseudo-equatorial positions.

A rigid fitting (Lejeune, Michel & Vercauteren, 1986) of both molecules, obtained by superposition of N(4), C(5), C(6), C(7) and O(8) atoms, is shown in Fig. 3. N(4) of the *β*-lactam ring lies 0·38 Å from the plane of C(3), C(5) and C(7) for both molecules. However, the dihedral angle between *β*-lactam and thiazolidine rings is 64° for the *S*-oxide, as for oxacillin (Blanpain & Durant, 1977) and penicillin G (Dexter & Van de Veen, 1978), and 49° for the title compound.

The crystal packing is shown in Fig. 2; the Na(14) environment is summarized in Table 2.

The authors are grateful to Dr D. A. Cox (Pfizer Central Research, Sandwich, Kent, England) for providing the title compound and to Dr R. Labia (Museum National d'Histoire Naturelle, Chimie Appliquée aux Corps Gras, Paris, France) for helpful discussions.

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Structure of 9-(2-Fluorobenzyl)-6-methylamino-9*H*-purine Hydrochloride, a Novel Anticonvulsant

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Abstract. $C_{13}H_{13}FN_5^+.Cl^-$, $M_r = 293·73$, monoclinic, $P2_1/n$, $a = 13·538$ (7), $b = 7·274$ (9), $c = 15·175$ (7) Å, $\beta = 116·06$ (3)°, $V = 1342·4$ (1) Å^3, $Z = 4$, $D_m = 1·45$ (2), $D_x = 1·45$ g cm^{-3}, $\mu = 24·89$ cm^{-1}, $F(000) = 608$, room temperature, $R = 0·065$ for 2217 observed reflections. Molecules are linked by Cl···N hydrogen bonds. The phenyl groups form spiraling stacks along **b**, perpendicular stacking separation $b/2 =$

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3·637 Å. The purine-ring planes are almost parallel to (001) and form offset stacks along [101]. The perpendicular inter-purine stacking distance is 3·408 Å.

Table 1. *Atom coordinates and equivalent isotropic thermal parameters for the non-hydrogen atoms with e.s.d.'s in parentheses*

$$U_{eq} = (U_{11}U_{22}U_{33})^{1/3}.$$

	x	y	z	U_{eq}(Å^2)
C(1*)	−0·1966 (2)	−0·1472 (4)	0·2033 (2)	0·0478 (13)
C(2*)	−0·2963 (2)	−0·1561 (4)	0·2074 (2)	0·0577 (15)
C(3*)	−0·3053 (3)	−0·1652 (6)	0·2934 (3)	0·0785 (22)
C(4*)	−0·2111 (4)	−0·1591 (5)	0·3805 (3)	0·0789 (27)
C(5*)	−0·1092 (3)	−0·1485 (6)	0·3794 (2)	0·0678 (20)
C(6*)	−0·1029 (3)	−0·1460 (5)	0·2911 (2)	0·0582 (16)
C(2)	0·0810 (2)	0·1951 (4)	0·1293 (2)	0·0477 (13)
C(4)	−0·0071 (2)	−0·0643 (4)	0·1175 (2)	0·0421 (12)
C(5)	0·0764 (2)	−0·1725 (3)	0·1188 (2)	0·0429 (12)
C(6)	0·1737 (2)	−0·0865 (3)	0·1284 (2)	0·0419 (13)
C(61)	0·3632 (3)	−0·0882 (4)	0·1437 (2)	0·0528 (17)
C(7)	−0·1968 (2)	−0·1377 (5)	0·1044 (2)	0·0517 (19)
C(8)	−0·0520 (3)	−0·3521 (4)	0·1020 (2)	0·0542 (16)
N(1)	0·1703 (2)	0·1001 (3)	0·1325 (2)	0·0469 (12)
N(3)	−0·0096 (2)	0·1221 (3)	0·1222 (2)	0·0496 (12)
N(6)	0·2610 (2)	−0·1736 (3)	0·1317 (2)	0·0488 (12)
N(7)	0·0493 (2)	−0·3565 (3)	0·1103 (2)	0·0512 (13)
N(9)	−0·0899 (2)	−0·1823 (3)	0·1071 (2)	0·0400 (11)
F(1)	−0·3894 (2)	−0·1585 (4)	0·1222 (2)	0·0751 (14)
Cl(1)	0·3108 (1)	0·4136 (1)	0·1216 (0)	0·0500 (4)

* Phenyl-ring atoms of fluorobenzyl group.

Table 2. *Bond lengths* (Å) *and angles* (°) *and hydrogen-bond data*

C(1*)–C(2*)	1·379 (4)	N(7)–C(5)	1·379 (3)
C(1*)–C(6*)	1·379 (4)	C(4)–C(5)	1·371 (4)
C(1*)–C(7)	1·503 (4)	C(4)–N(3)	1·359 (3)
C(2*)–C(3*)	1·366 (5)	N(3)–C(2)	1·297 (4)
C(3*)–C(4*)	1·376 (6)	N(1)–C(2)	1·375 (4)
C(4*)–C(5*)	1·389 (6)	N(1)–C(6)	1·361 (3)
C(5*)–C(6*)	1·380 (5)	C(6)–C(5)	1·407 (4)
C(7)–N(9)	1·466 (3)	N(6)–C(6)	1·322 (3)
N(9)–C(8)	1·353 (4)	N(6)–C(61)	1·454 (4)
N(9)–C(4)	1·364 (3)	F(2)–C(2*)	1·353 (4)
C(8)–N(7)	1·322 (4)		

C(2*)–C(1*)–C(6*)	117·4 (3)	N(7)–C(8)–N(9)	114·8 (2)
C(2*)–C(1*)–C(7)	118·4 (3)	N(9)–C(4)–N(3)	126·6 (3)
C(6*)–C(1*)–C(7)	124·2 (2)	N(9)–C(4)–C(5)	105·7 (2)
C(1*)–C(2*)–C(3*)	123·1 (3)	N(3)–C(4)–C(5)	127·7 (3)
C(1*)–C(2*)–F(2)	118·5 (3)	N(7)–C(5)–C(4)	111·9 (2)
C(3*)–C(2*)–F(2)	118·4 (3)	N(7)–C(5)–C(6)	129·8 (3)
C(2*)–C(3*)–C(4*)	118·8 (3)	C(4)–C(5)–C(6)	118·4 (2)
C(3*)–C(4*)–C(5*)	119·8 (3)	C(4)–N(3)–C(2)	111·6 (2)
C(4*)–C(5*)–C(6*)	119·9 (3)	N(3)–C(2)–N(1)	125·6 (3)
C(1*)–C(6*)–C(5*)	121·0 (3)	C(2)–N(1)–C(6)	123·2 (2)
C(1*)–C(7)–N(9)	113·2 (2)	N(6)–C(6)–N(1)	121·6 (2)
C(7)–N(9)–C(8)	126·5 (3)	N(6)–C(6)–C(5)	124·8 (2)
C(7)–N(9)–C(4)	127·3 (3)	N(1)–C(6)–C(5)	113·5 (2)
C(8)–N(9)–C(4)	105·6 (2)	C(61)–N(6)–C(6)	125·8 (2)
C(8)–N(7)–C(5)	102·0 (2)		

D–H···A	Symmetry code	D–H(Å)	$D\cdots A$(Å)	H···A(Å)	D–H···A(°)
N(6)–H(6)···Cl	(i)	1·134	3·03	2·071	174·8
N(1)–H(1)···Cl	(ii)	1·027	3·20	2·070	154·6

Symmetry code: (i) $x, -1+y, z$; (ii) x, y, z.

Introduction. The title compound is a novel orally active non-toxic anticonvulsant agent with potent activity against maximal electroshock-induced seizures (Kelly, McLean & Soroko, 1986). The structure analysis reported here was undertaken as part of a programme of study of convulsant and anticonvulsant compounds being carried out in this Department.

Experimental. Sample provided by Wellcome Research Laboratories. Colourless prisms by slow evaporation from ethanol/water. Crystal 0·12 × 0·18 × 0·60 mm used for data collection. Weissenberg photographs yielded approximate cell dimensions and showed monoclinic (2/m) Laue symmetry. Space group $P2_1/n$ from systematic absences ($h0l$, $h + l = 2n + 1$, $0k0$, $k = 2n + 1$); D_m by flotation (benzene/CCl_4); Enraf–Nonius CAD-4 automated diffractometer, graphite monochromator, Cu $K\alpha$ radiation, 25 high-angle reflections ($15 \le \theta \le 20°$) used to obtain accurate cell dimensions by least-squares fit; ω–2θ scan, scan width $(1·10 + 0·14\ \tan\theta)°$, vertical aperture = 4 mm; 2886 unique reflections measured ($0 \le h \le 16$, $0 \le k \le 8$, $-18 \le l \le 16$), 2217 with $I \ge 3\sigma(I)$, ($1 \le 2\theta \le 70°$); three intensity standards (114, 415 and 514) monitored at intervals of 50 measurements showed no significant variations during data collection; intensity data corrected for Lorentz–polarization factors; empirical absorption correction based on φ scan for each of two reflections (North, Phillips & Mathews, 1968) near $\varphi = 90°$ measured at 10° intervals from $\varphi = 0$ to $\varphi = 360°$, normalized transmission factors 0·99 to 0·92. Structure solution by direct methods with *SHELX76* (Sheldrick, 1976). Atomic scattering factors from *SHELX76*; E map gave positions of all non-hydrogen atoms. Refinement by full-matrix least squares with anisotropic thermal factors for all the non-hydrogen atoms, isotropic for H atoms located from difference synthesis. Function minimized was $\sum w(|F_o| - |F_c|)^2$, $w = [\sigma^2(|F|) + 0·0594|F_o|^2]^{-1}$, $R = 0·065$, $wR = 0·070$ for $I \ge 3\sigma(I)$, R (all data) = 0·076; max. $\Delta/\sigma = 0·76$. Final difference electron density ($\Delta\rho$) −0·58 to +0·55 e Å^{-3}. Calculations carried out on Amdahl 470/8 computer. Geometrical calculations were performed with *XANADU* (Roberts & Sheldrick, 1975) and molecular illustrations were drawn with *PLUTO* (Motherwell & Clegg, 1978).

Discussion. The refined atomic coordinates and equivalent isotropic thermal parameters for the non-H atoms are given in Table 1.* Bond distances and angles are listed in Table 2. The chemical formula with the

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44585 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

numbering scheme of the atoms is shown in Fig. 1. Fig. 2 shows the molecular conformation.

Rings *A* and *B*, constituting the purine moiety, are planar. The equation of the least-squares plane defined by atoms C(4), N(1), N(9), C(6), C(5), N(3), C(2), N(7), C(8) is $0{\cdot}375\,x' - 0{\cdot}063\,y' + 0{\cdot}0925\,z' - 1{\cdot}665 = 0$ where x', y', z' are coordinates in Å with respect to the orthogonal cell (Rollett, 1965). The root mean square displacement of the nine atoms from the plane is 0·013 Å. The adjacent carbon and nitrogen atoms, C(7) and N(6), are coplanar having deviations from the plane of 0·047 and 0·017 Å respectively. The methyl carbon on N(6) is also coplanar with a deviation of 0·046 Å. All nine C—N distances and the two C—C distances in the ring systems are intermediate between the expected single-bond lengths (1·47 and 1·54 Å respectively) and double-bond lengths (1·27 and 1·35 Å respectively). These data indicate electron delocalization within this group. N—C bond lengths were found to be *ca* 1·32 Å where the N was considered to have an unshared pair of electrons and *ca* 1·36 Å where the N formed a cyclic double bond. C—C bonds were uniformly of the order of 1·40 Å. These features are consistent with similar structures containing the purine group (Saenger, 1983).

The phenyl ring, *C*, comprising atoms C(1*) to C(6*) is planar. The equation of the least-squares plane through these six atoms and through the fluorine atom F(2) is $-0{\cdot}040x' + 0{\cdot}999y' + 0{\cdot}029z' + 0{\cdot}852 = 0$. The root mean square displacement of the atoms from the plane is 0·010 Å. No significant deviation from the average value of the bond lengths, 1·378 (5) Å, in the phenyl ring is observed. The average value for the bond angles in the phenyl ring is 120·0 (3)° – C(6*)—C(1*)—C(2*) = 117·4 (3), where C(1*) links to the purine, being significantly less and C(1*)—C(2*)—C(3*) = 123·1 (3)°, where C(2*) is attached to F(2), being significantly greater than this value. The dihedral angle between the phenyl plane and that defined for the purine group is 92·92°. The orientation of the phenyl ring with respect to the purine rings is governed by the torsion angles C(4)—N(9)—C(7)—C(1*) and N(9)—C(7)—C(1*)—C(6*) which have values of −93·03 and +18·13° respectively.

The molecules are linked by Cl···N hydrogen bonds of two types, through N(6) and N(1) respectively (see Table 2). Atom N(1) has become protonated in the solid state owing to this association. Two other interesting intermolecular associations occur, between the phenyl rings and between the purine rings respectively (see Fig. 3). The phenyl groups, which are almost exactly perpendicular to **b**, form spiraling stacks along **b** generated by the 2_1 axes. Overlap occurs such that C(2*) is almost exactly aligned with the centre of the adjacent layer on either side. The perpendicular stacking separation is $b/2 = 3{\cdot}637$ Å and the centre–centre separation = 3·878 Å. The purine ring planes are approximately parallel to (001) and form offset stacks along [101], molecules generated by centres of symmetry being sandwiched between molecules related by the *n*-glide operation. The perpendicular inter-purine stacking distance is thus $d(001)/4 = (c \sin \beta^*/4 = 3{\cdot}408$ Å, while the centre–centre purine distance is $d(101)/4 = 3{\cdot}817$ Å.

The interlocking π-bond systems and hydrogen-bond network thus form an extremely stable crystal structure.

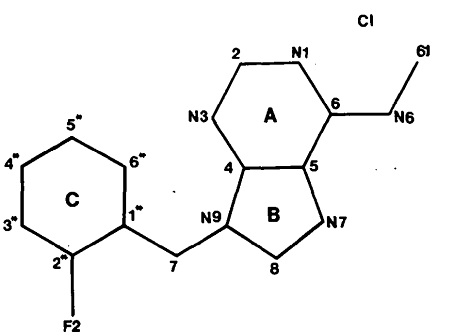

Fig. 1. Chemical formula and atom-numbering scheme.

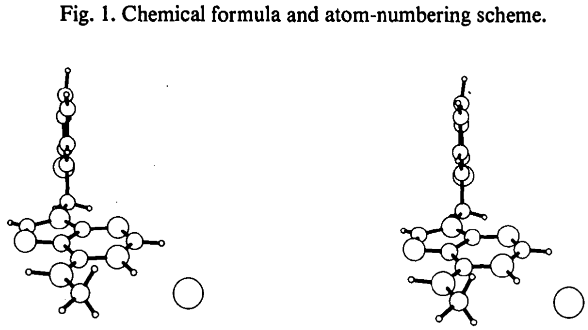
Fig. 2. Molecular conformation as seen edge-on to the phenyl group.

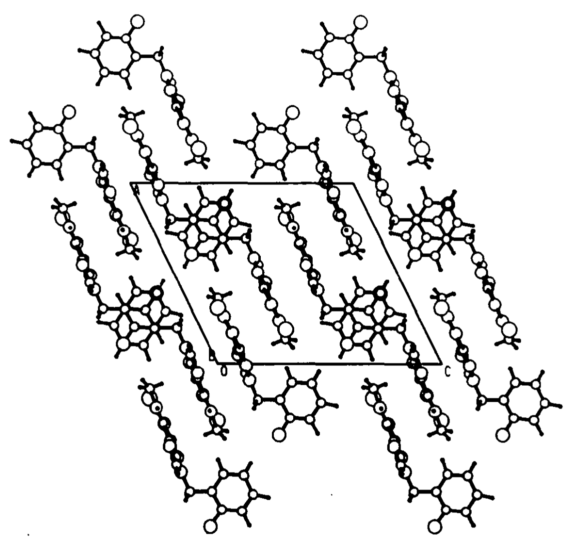

Fig. 3. View of the crystal structure along [010].

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Structure of Allyl 1-Deoxy-1-[(1-methyl-2-benzoylvinyl)amino]-α-D-fructofuranoside

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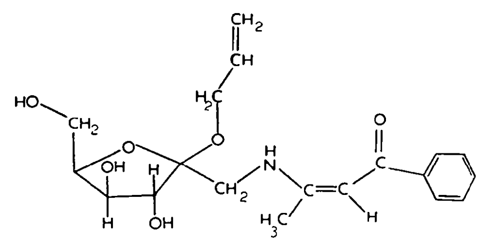
Abstract. $C_{19}H_{25}NO_6$, $M_r = 363{\cdot}4$, orthorhombic, $P2_12_12_1$, $a = 11{\cdot}946\,(2)$, $b = 18{\cdot}786\,(4)$, $c = 8{\cdot}366\,(2)$ Å, $V = 1877{\cdot}5\,(7)$ Å^3, $Z = 4$, $D_m = 1{\cdot}29$, $D_x = 1{\cdot}29$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 0{\cdot}089$ mm^{-1}, $F(000) = 776$, room temperature, final $R = 0{\cdot}09$, $wR = 0{\cdot}07$ for 1324 observed $[I > 2\sigma(I)]$ reflections. The C=C bond distance is as long as 1·398 (10) Å but the twist angle around this bond is 1·6 (10)°. The sugar has an α-D-configuration and bond lengths and angles of the furanose ring are normal. The two C—O glycosidic bond lengths, 1·464 (9) and 1·407 (8) Å, are not equal, owing to the anomeric effect. The furanose ring is in the twist ^2_1T conformation. The molecule has an intramolecular H bond between the NH and CO groups adopting the chelate form. The molecules are linked by van der Waals forces; additionally there is one intermolecular H bond between the furanose and carbonyl groups.

Introduction. A variety of substituted ethylenes have C=C bonds significantly longer than the bond in ethylene [1·336 (2) Å; Bartell, Roth, Hollowell, Kuchitsu & Young, 1965; Kuchitsu 1966], *e.g.* trivinylborane, 1·370 (6) Å (Foord, Beagley, Reade & Steer, 1975). In olefins substituted with electron-releasing and electron-withdrawing groups in the vicinal positions such lengthening of the C=C bond is more pronounced with low barriers to rotation, *e.g.* dimethyl (dimethylaminomethylene)malonate, 1·380 (5) Å (Shmueli, Shanan-Atidi, Horwitz & Shvo, 1973); α-(*p*-bromobenzoyl)-*β*,*β*′-bis(methylthio)acrylonitrile, 1·369 (7) Å, *p*-bromobenzoyl(1,3-dimethylimidazolidinylidene)acetonitrile, 1·448 (4) Å (Abrahamsson, Rehnberg, Liljefors & Sandstrom, 1974). X-ray crystallographic results on a few other polarized ethylenes and related compounds have been reported (Shimanouchi, Ashida, Sasada & Kakudo, 1967; Ammon & Plastas, 1971; Hazell & Mukhopadhyay, 1980; Adhikesavalu & Venkatesan, 1981; Diánez, López-Castro & Márquez, 1985*a*,*b*). In this paper we report X-ray results for allyl 1-deoxy-1-[(1-methyl-2-benzoylvinyl)amino]-α-D-fructofuranoside (1).



(1)

Samples kindly provided by Professor Gómez-Sánchez, University of Seville, Spain, were obtained by reaction with allylic alcohol in HCl of 1-deoxy-1-[(1-methyl-2-benzoylvinyl)amino]-α-D-fructofuranose (Gómez-Sánchez & Borrachero, 1984; Gómez-Sánchez, Garcia & Pascual, 1986; Diánez, López-Castro, Gómez-Sánchez, Garcia & Gasch, 1987). The structure determination was undertaken to confirm the identity of (1) and to determine its conformation, which has aroused interest as an 'enaminone', as well as for the bulky substituent (allyl deoxyfructofuranose group).

Experimental. D_m measured by flotation. Single crystal in form of colourless prism with approximate dimensions 0·30 × 0·31 × 0·43 mm used for intensity-data collection; preliminary Weissenberg photographs indicated crystals are orthorhombic with space group

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