used to solve structure: *SHELXTL* (Sheldrick, 1996). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL* and *PARST* (Nardelli, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1384). Services for accessing these data are described at the back of the journal.

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Pipemidic acid hydrochloride†

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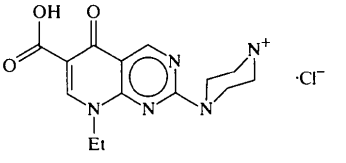
Abstract

The title compound exists as a $C_{14}H_{18}N_5O_3^+$ cation and a Cl^- anion. The apical N atom of the piperazine ring shows quaternary character due to proton transfer from HCl. The fused pyridine and pyrimidine rings are nearly coplanar and the piperazine ring adopts a chair conformation. The carboxyl and carbonyl O atoms are involved in an O—H···O intramolecular hydrogen bond and the Cl^- anion is involved in an N—H···Cl intermolecular hydrogen bond with the quaternary N atom.

Comment

Metal ions play a vital role in intricate biological processes. The interaction of these ions with drugs administered for therapeutic reasons is a subject of considerable interest. It is known that some drugs act *via* chelation (Albert, 1979) or by way of inhibiting the formation of metallo enzymes (Hughes, 1981). For most of the drugs that could act as potential ligands little is known about the metal-binding influences on their activities. In order to understand drug–metal ion interactions further, we have been studying pipemidic acid and its analogues. These antibiotics are used in the clinical treatment of urinary-tract infections caused by Gram-negative bacteria (Shen & Pernat, 1980). The X-ray structure determination of the title compound, (I), was carried out in order to elucidate the molecular conformation.



(I)

The asymmetric unit consists of a $C_{14}H_{18}N_5O_3^+$ cation and a Cl^- anion. The piperazine N atom, N17, shows quaternary character due to proton transfer from HCl. This is in contrast with the 'zwitterion' structure formed in pipemidic acid trihydrate (Fonseca *et al.*, 1986) where

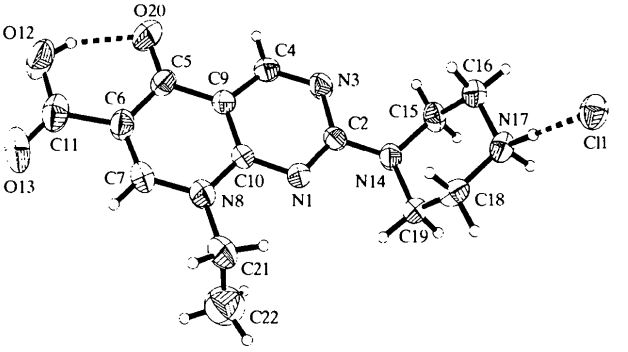


Fig. 1. The structure of the title compound showing 50% probability displacement ellipsoids and the atom-numbering scheme.

† Alternative name: 4-(6-carboxy-8-ethyl-5,8-dihydropyrido[2,3-*d*]-pyrimidin-2-yl)piperazin-1-ium chloride.
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the carboxyl group is deprotonated and the piperazine N atom is protonated. Bond lengths and angles in the fused ring and pyrimidine ring are comparable with those observed in the pipemidic acid trihydrate (Fonseca *et al.*, 1986) and the C—O distances in the carboxylic group agree with the reported mean values (Allen *et al.*, 1987). The C6—C11 distance [1.493 (4) Å] is slightly longer, which may be due to decreased resonance.

The pyridine ring is planar within ±0.030 (3) Å and it is nearly coplanar with the planar pyrimidine ring; the dihedral angle between these two rings is 1.3 (1)°. The carboxyl group is slightly twisted out of the pyridine ring with an average torsion angle of −7.2 (4)° around C6—C11. The piperazine ring adopts a chair conformation and the mean plane through that ring makes a dihedral angle of 52.8 (1)° with the pyrimidine ring.

In the cation, the carboxyl and carbonyl O atoms, O12 and O20, are involved in an O—H···O intramolecular hydrogen bond; in the asymmetric unit, the cation and anion are involved in an N17—H17*A*···Cl1 hydrogen bond (Table 2). Along the *b* axis, the screw-related molecules are linked by N17—H17*B*···Cl1^{i} hydrogen bonds to form a double-column structure (Fig. 2). Within each column, the molecules translated along the *b* axis are stacked stepwise without any π–π interactions and they are linked by weak C22—H22*B*···O13^{ii} hydrogen bonds. The adjacent columns are linked by weak C18—H18*B*···O20^{iii} hydrogen bonds.

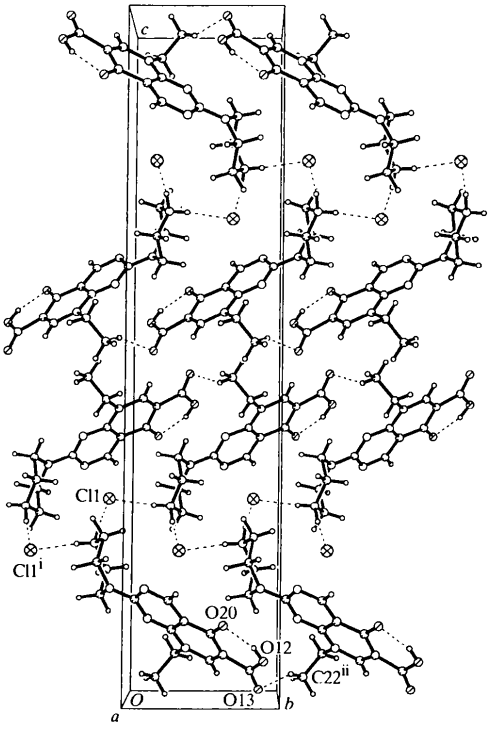

Fig. 2. Packing of the molecules viewed down the *a* axis.

Experimental

Single crystals of the title compound were obtained by slow evaporation of a solution of pipemidic acid in 10% HCl at room temperature.

Crystal data

$C_{14}H_{18}N_5O_3^+ \cdot Cl^-$
M_r = 339.78
Orthorhombic
$P2_12_12_1$
a = 6.8228 (1) Å
b = 7.1672 (2) Å
c = 31.9396 (6) Å
V = 1561.86 (6) Å^3
Z = 4
D_x = 1.445 Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 7398 reflections
θ = 2.91–33.22°
μ = 0.268 mm^{-1}
T = 293 (2) K
Plate
0.42 × 0.26 × 0.18 mm
Colourless

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
T_{min} = 0.896, T_{max} = 0.953
10 332 measured reflections
2102 independent reflections (plus 1478 Friedel-related reflections)
3219 reflections with $I > 2\sigma(I)$
R_{int} = 0.025
θ_{max} = 27.49°
h = −8 → 8
k = 0 → 9
l = 0 → 41

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.130
S = 1.118
3580 reflections
220 parameters
H atoms: see text
$w = 1/[\sigma^2(F_o^2) + (0.06P)^2 + 0.7411P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.66 e Å^{-3}
$\Delta\rho_{min}$ = −0.39 e Å^{-3}
Extinction correction: *SHELXTL* (Sheldrick, 1997)
Extinction coefficient: 0.004 (2)
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = −0.01 (9)

Table 1. *Selected geometric parameters (Å, °)*

N1—C10	1.334 (3)	N8—C21	1.478 (2)
N1—C2	1.338 (3)	C11—O13	1.194 (4)
C2—N14	1.355 (3)	C11—O12	1.324 (5)
C2—N3	1.365 (3)	N14—C15	1.459 (3)
N3—C4	1.317 (4)	N14—C19	1.466 (3)
C5—O20	1.252 (4)	C16—N17	1.494 (4)
C7—N8	1.365 (4)	N17—C18	1.499 (4)
N8—C10	1.388 (4)		
C7—C6—C11—O13	−7.9 (5)	C5—C6—C11—O12	−6.5 (4)

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O12—H12*A*···O20	0.82	1.79	2.551 (4)	155
N17—H17*A*···Cl1	1.02 (3)	2.09 (3)	3.104 (3)	172 (2)
N17—H17*B*···Cl1^{i}	1.02 (3)	2.07 (3)	3.083 (2)	170 (3)

C22—H22B···O13^{ii}	0.96	2.42	3.328 (6)	157
C18—H18B···O20^{iii}	0.96	2.41	3.168 (4)	135
C7—H7A···O13^{iv}	0.93	2.54	3.405 (4)	156

Symmetry codes: (i) $-x, y-\frac{1}{2}, \frac{1}{2}-z$; (ii) $x, y-1, z$; (iii) $x-1, y-1, z$; (iv) $x-\frac{1}{2}, \frac{3}{2}-y, -z$.

The data collection covered over a hemisphere of reciprocal space by a combination of three sets of exposures; each set had a different φ angle (0, 88 and 180°) for the crystal and each exposure of 30 s covered 0.3° in ω. The crystal-to-detector distance was 4 cm and the detector swing angle was −35°. Crystal decay was monitored by repeating 30 initial frames at the end of data collection and analysing the intensity of duplicate reflections, and was found to be negligible.

The structure was solved by direct methods and refined by full-matrix least-squares techniques. After checking the presence of all H atoms in the difference map, the H atoms belonging to the C and hydroxyl O atoms were geometrically fixed and allowed to ride on the parent atoms. Rotating group refinement was used for the methyl and OH groups. In order to allow slightly longer N—H distances upon protonation, the H atoms of N17 were initially isotropically refined, but the N17—H17*A* [1.08 (3) Å] distance was found to be longer than that of N17—H17*B* [0.88 (4) Å]. Hence the N—H distances were restrained by refining them as a free variable (using *DFIX*21 for N17, H17*A*, N17, H17*B*) and the final N—H distance was found to be 1.02 (3) Å. This value is in agreement with those observed (0.97 and 1.01 Å) in pipemidic acid trihydrate (Fonseca *et al.*, 1986).

Data collection: *SMART* (Siemens, 1996). Cell refinement: *SAINT* (Siemens, 1996). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1259). Services for accessing these data are described at the back of the journal.

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2,2-Bis(2-methoxyphenyl)-4-methyl-8,9-epoxy-7,8,9,10-tetrahydro-2*H*-benzo[*h*]-chromene

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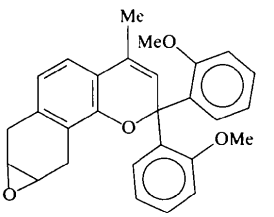
Abstract

In each independent molecule of the title compound, $C_{28}H_{26}O_4$, the pyran ring adopts a half-chair conformation and the tetrahydrobenzene ring is in a flattened-boat conformation. The phenyl rings are orthogonal to each other; in one of the enantiomers, they form dihedral angles of 74.66 (6) and 54.38 (6)° with the pyran ring, while in the other enantiomer, these angles are 76.42 (6) and 54.15 (5)°.

Comment

Epoxides are versatile reactive intermediates in organic synthesis because they are very susceptible to attack by several nucleophiles (Smith, 1984). Furthermore, the role of arene oxides in biological systems continues to attract attention due to their cytotoxicity, mutagenicity and carcinogenicity (Boyd & Sharma, 1986). The structure determination of the title compound, (I), was carried out in order to elucidate the molecular conformation.



(I)

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