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Narceine Hydrochloride Trihydrate

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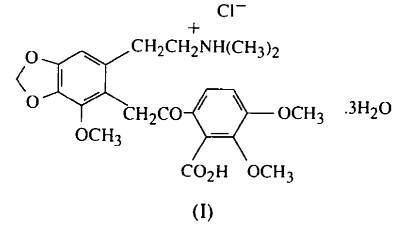
Abstract

The conformation of the title compound, {2-[5-(2-carboxy-3,4-dimethoxybenzoylmethyl)-4-methoxy-1,3-benzodioxol-6-yl]ethyl}dimethylammonium chloride trihydrate, $C_{23}H_{28}NO_8^+.Cl^-.3H_2O$, is presented. Bond lengths and angles are as expected. In the crystal, there are infinite chains comprising water molecules and Cl^- ions linked by hydrogen bonds; the alkaloid molecules are linked to these chains by strong hydrogen bonds.

Comment

Narceine was identified as a substituted phenyl benzyl ketone alkaloid by the work of Freund and co-workers, and the chemical structure confirmed by Addinall *et al.* (Addinall & Major, 1933, and references therein). The compound occurs in opium at 0.1–0.5% and can be extracted from the mother liquors in the preparation of morphine hydrochloride. The alkaloid can also be prepared from narcotine, by the methods of Roser & Hope and Hope & Robinson (Merck Index, 1983).

The crystal structure study of narceine was undertaken in order to determine its three-dimensional conformation. Different attempts to obtain crystals of the free base suitable for X-ray analysis proved unsuccessful. From the different derivatives tried, the chlorohydrate, (I), afforded the best specimens and was accordingly used for the crystal structure determination.



(I)

The bond lengths and angles do not deviate significantly from reported values. Both aromatic rings present in the structure are planar, within a 95% confidence level, and the angle between their normals is $\Phi = 74.3(1)°$. The puckering parameters for the five-membered ring of the benzodioxole group (Cremer & Pople, 1975; Nardelli, 1983), $q_2 = 0.197(3)$, $\varphi_2 = 284.5(8)°$, show that its conformation is near that of an envelope with a mirror plane through C15. The methoxy group on C5 forms a dihedral angle $\Phi = 42.2(1)°$ with the six-membered ring of benzodioxole, with a short intramolecular C20—H20C···O5 contact (H···O = 2.20 Å, C—H···O = 128.2°) that can be attributed to an attractive interaction (Taylor & Kennard, 1982). Atoms C1, C16, C17 and N in the fragment are almost coplanar (maximum deviation 0.05 Å), and this plane is almost perpendicular [$\Phi = 89.4(2)°$] to the six-membered ring. The N atom has sp^3 hybridization, as confirmed by the almost tetrahedral C—N—C angles.

Of the groups bonded to the phenyl ring (C9–C14), two are nearly perpendicular, namely the methoxy group at C11 [$\Phi = 89.2(1)°$] and the carboxy group at C10 [$\Phi = 89.5(1)°$], while the methoxy group at C12 is nearly coplanar [$\Phi = 8.9(1)°$] with it.

The structure is stabilized by a complex hydrogen-bonding scheme (see Fig. 1 and supplementary material). The water molecules and Cl^- ions are linked by hydrogen bonds in an 'anionic chain' parallel to *z*. Molecules of the alkaloid interact with one another through rather weak O8···C19 contacts and are also attached to the chain of anions through three very strong hydrogen bonds at O1, O3 and N, to form a double layer parallel to the crystallographic plane (010). The interaction between the double layers is of the van der Waals type.

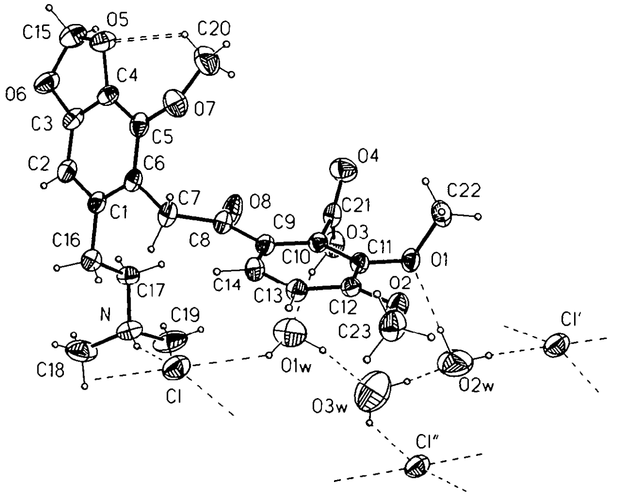


Fig. 1. View of the molecule showing the numbering scheme used, with non-H atom displacement ellipsoids drawn at the 30% probability level. Hydrogen-bonding interactions are shown by dashed lines, suggesting the formation of an anionic chain.

Experimental

Crystals were obtained by slow evaporation of a hydrochloric solution of narceine. (Free base from Merck.)

Crystal data

$C_{23}H_{28}NO_8^+.Cl^-.3H_2O$
$M_r = 535.96$
Triclinic
$P\bar{1}$
$a = 11.805\,(4)$ Å
$b = 12.428\,(3)$ Å
$c = 10.021\,(4)$ Å
$\alpha = 100.89\,(3)°$
$\beta = 114.89\,(3)°$
$\gamma = 77.51\,(3)°$
$V = 1294.0\,(7)$ Å^3
$Z = 2$
$D_x = 1.376$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 17.3$–$19.0°$
$\mu = 0.207$ mm^{-1}
$T = 293\,(2)$ K
Prism
0.40 × 0.32 × 0.30 mm
Colourless

Data collection

Rigaku AFC-7*S* diffractometer
ω–2θ scans
Absorption correction: none
4846 measured reflections
4572 independent reflections
2899 observed reflections $[I > 2\sigma(I)]$

$R_{\rm int} = 0.0449$
$\theta_{\rm max} = 25.28°$
$h = 0 \rightarrow 14$
$k = -14 \rightarrow 14$
$l = -11 \rightarrow 10$
3 standard reflections monitored every 150 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0485$
$wR(F^2) = 0.1627$
$S = 1.026$
4571 reflections
328 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0757P)^2 + 0.7150P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.022$
$\Delta\rho_{\rm max} = 0.369$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.420$ e Å^{-3}

Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0060 (23)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Cl	0.12247 (8)	0.33927 (8)	0.36092 (10)	0.0760 (3)
O1	0.3174 (2)	0.1498 (2)	−0.1724 (2)	0.0490 (5)
O2	0.1758 (2)	0.0031 (2)	−0.1886 (2)	0.0563 (5)
O3	0.4191 (2)	0.3614 (2)	0.0688 (2)	0.0625 (6)
O4	0.5718 (2)	0.2205 (2)	0.0967 (3)	0.0757 (7)
O5	0.9111 (2)	0.1658 (2)	0.8530 (3)	0.0662 (6)
O6	0.8645 (2)	0.3143 (2)	1.0087 (2)	0.0710 (7)
O7	0.7119 (2)	0.0813 (2)	0.5716 (3)	0.0688 (6)
O8	0.4999 (3)	0.2965 (2)	0.3667 (2)	0.0736 (7)
N	0.2580 (2)	0.5306 (2)	0.5703 (3)	0.0602 (7)
C1	0.5409 (3)	0.3118 (2)	0.7360 (3)	0.0468 (7)
C2	0.6379 (3)	0.3488 (2)	0.8631 (3)	0.0528 (7)
C3	0.7570 (3)	0.2960 (2)	0.8878 (3)	0.0522 (7)
C4	0.7845 (3)	0.2087 (2)	0.7937 (3)	0.0492 (7)
C5	0.6917 (3)	0.1706 (2)	0.6675 (3)	0.0490 (7)
C6	0.5672 (3)	0.2229 (2)	0.6388 (3)	0.0456 (7)
C7	0.4656 (3)	0.1786 (3)	0.5019 (3)	0.0517 (7)
C8	0.4504 (3)	0.2186 (2)	0.3614 (3)	0.0467 (7)
C9	0.3749 (3)	0.1622 (2)	0.2190 (3)	0.0423 (6)
C10	0.3802 (2)	0.1835 (2)	0.0886 (3)	0.0410 (6)
C11	0.3118 (3)	0.1289 (2)	−0.0444 (3)	0.0418 (6)
C12	0.2370 (3)	0.0523 (2)	−0.0526 (3)	0.0437 (6)
C13	0.2310 (3)	0.0325 (2)	0.0759 (3)	0.0483 (7)
C14	0.2992 (3)	0.0870 (2)	0.2084 (3)	0.0467 (7)
C15	0.9631 (3)	0.2493 (3)	0.9693 (4)	0.0735 (10)
C16	0.4111 (3)	0.3758 (3)	0.7072 (3)	0.0547 (7)
C17	0.3897 (3)	0.4702 (2)	0.6190 (3)	0.0531 (7)
C18	0.2224 (4)	0.5869 (4)	0.6939 (5)	0.0947 (14)
C19	0.2377 (4)	0.6086 (3)	0.4640 (5)	0.0951 (15)
C20	0.8158 (4)	0.0728 (4)	0.5343 (5)	0.0942 (13)
C21	0.4668 (3)	0.2569 (3)	0.0878 (3)	0.0500 (7)
C22	0.4071 (3)	0.0682 (3)	−0.2158 (4)	0.0629 (9)
C23	0.1136 (4)	−0.0868 (3)	−0.1989 (4)	0.0710 (10)
O1*w*	0.2084 (3)	0.4252 (3)	0.1085 (4)	0.1121 (11)
O2*w*	0.0808 (3)	0.2641 (3)	−0.3758 (4)	0.1364 (15)
O3*w*	0.0512 (5)	0.4476 (4)	−0.1732 (5)	0.166 (2)

Table 2. *Selected geometric parameters (Å)*

O1—C11	1.387 (3)	C1—C6	1.402 (4)
O1—C22	1.448 (4)	C1—C16	1.500 (4)
O2—C12	1.342 (3)	C2—C3	1.357 (4)
O2—C23	1.429 (4)	C3—C4	1.375 (4)
O3—C21	1.315 (4)	C4—C5	1.362 (4)
O4—C21	1.195 (4)	C5—C6	1.402 (4)
O5—C4	1.378 (4)	C6—C7	1.496 (4)
O5—C15	1.425 (4)	C7—C8	1.509 (4)
O6—C3	1.362 (3)	C8—C9	1.463 (4)
O6—C15	1.423 (4)	C9—C14	1.389 (4)
O7—C5	1.374 (4)	C9—C10	1.410 (4)
O7—C20	1.404 (5)	C10—C11	1.370 (4)
O8—C8	1.217 (3)	C10—C21	1.513 (4)
N—C18	1.478 (5)	C11—C12	1.402 (4)
N—C19	1.485 (5)	C12—C13	1.388 (4)
N—C17	1.488 (4)	C13—C14	1.366 (4)
C1—C2	1.387 (4)	C16—C17	1.516 (4)
O3···O1*w*	2.613 (5)	O3*w*···O2*w*	2.819 (7)
C20···O5	2.990 (5)	N···Cl	3.090 (3)
O1*w*···O3*w*	2.675 (6)	O1*w*···Cl	3.495 (5)
O2*w*···O1	2.925 (4)	C19···O8$^{\rm ii}$	3.204 (5)
O3*w*···Cl$^{\rm i}$	3.323 (5)	O2*w*···Cl$^{\rm iii}$	3.209 (5)

Symmetry codes: (i) $-x, 1-y, -z$; (ii) $1-x, 1-y, 1-z$; (iii) $x, y, z-1$.

The structure was solved through a combination of direct methods and difference Fourier synthesis. Refinement was performed on F^2 using the whole data set. H atoms from water molecules were detected in a difference Fourier synthesis and their positions refined with constrained distances (0.938 Å) to the corresponding water O atoms. Other H atoms, fixed by stereochemistry, were included at their expected positions and allowed to ride on their host atoms. In the case of terminal X—CH$_3$ groups (X = O, N), they were allowed to rotate as a rigid group around the X—C bond. In all cases fixed isotropic displacement parameters were used.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *MSC/AFC Diffractometer Control Software*. Program(s) used to solve structure: *XS* in *SHELXTL/PC* (Sheldrick, 1991). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *XP* in *SHELXTL/PC*. Software used to prepare material for publication: *CIFTAB* in *SHELXL*93, *PARST* (Nardelli, 1983).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HA1145). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Ethyl 2-[(*E*)-5-Chloro-2-hydroxy-4-nitrophenylazo]-3-(*E*)-amino-2-butenoate

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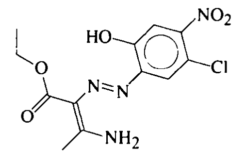
Abstract

The title molecule, $C_{12}H_{13}ClN_4O_5$, has two intramolecular hydrogen bonds (O1—H11···N3 and N4—H42···N2) and π-electron delocalization in the azoenamine group. Adjacent molecules in the crystal are linked through N—H···O hydrogen bonds and this results in an infinite chain structure.

Comment

Enaminones are compounds with interesting structural characteristics, such as distinct geometric forms (Eberlin, Takahata & Kascheres, 1990) and tautomerism between oxo, imino and enol forms (Naringrekar & Stella, 1990).

An *ORTEP* (Johnson, 1965) drawing of the title compound, (I), is presented in Fig. 1. The molecule has the oxo tautomeric form and the *E,s-Z* geometric form. The compound has two intramolecular hydrogen bonds, namely O1—H11···N3 [O1—H11 0.92 (6), O1···N3 2.568 (6) Å, O1—H11···N3 129 (5)°] and N4—H42···N2 [N4—H42 0.94 (6), N4···N2 2.584 (7) Å, N4—H42···N2 126 (5)°]. The hydrogen bond between atoms N4 and N2 may be responsible for the presence of the *E,s-Z* configuration in the compound.



(I)

The crystal packing involves N4—H41 ··O4$^{\rm i}$ intermolecular hydrogen bonds [N4—H41 0.92 (6), N4···O4$^{\rm i}$ 2.910 (7) Å, N4—H41···O4$^{\rm i}$ 169 (5)°; symmetry code: (i) x, $\frac{3}{2}-y$, $-\frac{1}{2}+z$], resulting in an infinite chain structure in the *c* direction. A stereoscopic view of the crystal packing is presented in Fig. 2.

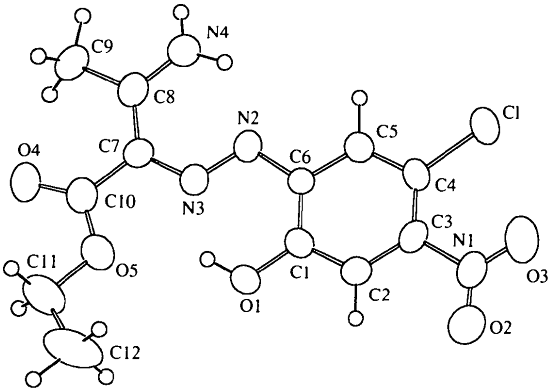


Fig. 1. View of the title compound (displacement ellipsoids are shown at 50% probability levels and H atoms as small circles of arbitrary radii) including the atom numbering.

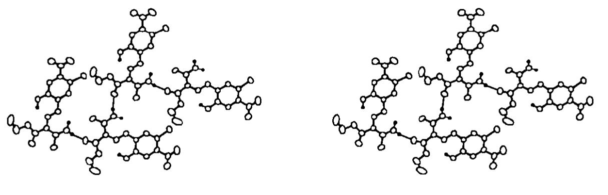


Fig. 2. Stereoscopic view of the crystal packing showing the intermolecular hydrogen bonding.