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Structure of Benzamidine Hydrochloride Monohydrate

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Abstract. $C_7H_9N_2^+.Cl^-.H_2O$, $M_r = 174{\cdot}5$, orthorhombic, $P2_12_12_1$, $a = 7{\cdot}328\,(2)$, $b = 8{\cdot}500\,(2)$, $c = 14{\cdot}573\,(3)$ Å, $V = 907{\cdot}7\,(4)$ Å^3, $Z = 4$, D_m(flotation) $= 1{\cdot}279$, $D_x = 1{\cdot}277$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}7107$ Å, $\mu = 3{\cdot}78$ cm^{-1}, $F(000) = 368$, $T = 293$ K, final $R = 0{\cdot}051$ for 707 observed reflections with $I > 2\sigma(I)$. The imine group is protonated. Chlorine is involved in five hydrogen bonds, three of N—H···Cl and two of O(W)—H···Cl type. The terminal C—C$\begin{smallmatrix}\diagup\mathrm{N}\\ \diagdown\mathrm{N}\end{smallmatrix}$ plane makes an angle of 36·6 (8)° with the benzene-ring plane, which prevents conjugation between the two unsaturated systems.

* Contribution No. 676.

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Introduction. Benzamidine hydrochloride, supplied by Sigma Chemicals, is reported to be of pharmaceutical importance. The activity of benzoyl-L-arginine ethyl ester esterase and the kinin-releasing activity of rat and horse kallikrein enzymes are inhibited by benzamidine hydrochloride (Diniz, Pereira, Barroso & Mares-Guia, 1965). Enzymes like trypsin, plasmin, thrombin and acrosin are inhibited by derivatives of benzamidine (Markwardt, Landmann & Walsmann, 1968; Beyler & Zaneveld, 1982). The study of the crystal structure was undertaken as part of a research project on drugs and related molecules.

Experimental. Colourless crystals (from water), 0·1 × 0·5 × 0·6 mm; Enraf–Nonius CAD-4F – 11M diffractometer, monochromatic Mo $K\alpha$ radiation; 911 reflections with $2\theta \leq 48°$, 707 with $I > 2\sigma(I)$; 202, 122, 006 as standard reflections, max. variation in intensity 6·2%; 25 reflections with $7 < \theta < 18°$ for lattice-parameter measurement and refinement; max. $h = 8$, max. $k = 9$, max. $l = 16$; Lp correction, no absorption correction. Chlorine from Patterson map; weighted Fourier synthesis with *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) revealed all non-hydrogen atoms; one water molecule located at $R = 0·31$; anisotropic full-matrix refinement with *LALS* (Gantzel, Sparks & Trueblood, 1961), using F_o; geometrically fixed hydrogen positions verified in ΔF synthesis, isotropic refinement, H(22) atom clamped during refinement as its temperature coefficient was increasing rapidly and no alternative position could be obtained from the ΔF map. Hydrogen atoms refined for a few cycles but not during last cycles of refinement to save computer time; Hughes's weighting scheme (Hughes, 1941) ($w = 1/\sigma^2$, $\sigma = F_o$ if $F_o > F_{omin}$ and $\sigma = F_{omin}$ if $F_o < F_{omin}$; $F_{omin} = 13·5$); final $R = 0·051$, $wR = 0·051$, for 100 parameters, goodness of fit $= 0·42$, $(\Delta/\sigma)_{max} = 0·17$, final ΔF had no peaks $>0·3$ e Å^{-3}; scattering factors from *International Tables for X-ray Crystallography* (1974).*

Discussion. Final atomic parameters and equivalent isotropic temperature coefficients are given in Table 1. Atom numbering, bond lengths and bond angles (with e.s.d.'s in parentheses) are given in Fig. 1. The average e.s.d. in bond lengths is 0·008 Å and in bond angles 0·5°. The average bond length and bond angle of the phenyl group are 1·385 (8) Å and 120·0 (5)° respectively.

The benzene-ring geometry is in agreement (within the 3σ level) with that of mono-substituted benzene rings (Domenicano, Vaciago & Coulson, 1975). The C–N bonds exhibit partial double-bond character and compare well with those in L-arginine L-aspartate (Salunke & Vijayan, 1982) and in guanidyl moieties (Chandrasekar, Pattabhi & Raghunathan, 1982; Thailambal, Pattabhi, Lee, Le Page & Gabe, 1985).

The benzene ring (A) and the terminal $C{-}C\begin{smallmatrix}N\\N\end{smallmatrix}$ group (B) are each planar. The planarity of the C–C(N)–N moiety is due to the protonation of the imine group and to π delocalization along the N–C–N system. The angle between the planes A and B is 36·6 (8)°. This is caused by the steric hindrance between the NH_2 groups and the benzene ring, as indicated by the N(2)···C(6) = 2·905 (8) and N(3)···C(10) = 2·900 (8) Å contacts. The resulting *gauche* conformation prevents conjugation between the N–C–N system and the benzene ring, in agreement with the value of the C(4)–C(5) = 1·471 (8) Å distance, which corresponds fairly well with a single C(sp^2)–C(sp^2) bond [1·482 (11) Å] (Dewar & Schmeising, 1960).

Table 1. *Fractional positional parameters* (×10⁴) *for non-hydrogen atoms with e.s.d.'s in parentheses and equivalent isotropic temperature factors*

$$B_{eq} = \tfrac{4}{3}(\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2).$$

	x	y	z	B_{eq}(Å²)
Cl	6269 (2)	349 (2)	6827 (1)	3·43 (4)
N(2)	6866 (7)	477 (6)	9866 (3)	3·5 (1)
N(3)	5945 (8)	2211 (6)	8758 (3)	3·5 (1)
C(4)	6427 (8)	1887 (7)	9616 (4)	2·7 (1)
C(5)	6448 (8)	3181 (7)	10286 (4)	2·8 (1)
C(6)	5901 (9)	2888 (8)	11193 (4)	3·5 (2)
C(7)	5956 (10)	4124 (8)	11822 (4)	4·3 (2)
C(8)	6535 (12)	5577 (8)	11549 (5)	5·0 (2)
C(9)	7082 (11)	5884 (8)	10662 (5)	4·6 (2)
C(10)	7010 (9)	4670 (8)	10029 (4)	3·5 (2)
O(W)	11774 (8)	6983 (5)	11451 (3)	4·7 (2)

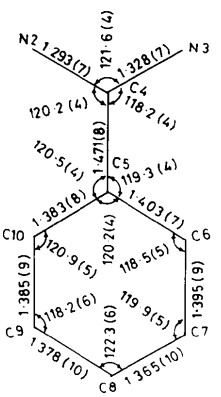

Fig. 1. Numbering of the atoms, bond lengths (Å) and bond angles (°) with e.s.d.'s in parentheses.

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and bond lengths and angles involving hydrogen have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42693 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Hydrogen-bond geometry (with e.s.d.'s in parentheses)*

	Symmetry code	$D\cdots A$ (Å)	D–H (Å)	H$\cdots A$ (Å)	D–H$\cdots A$ (°)	H–$D\cdots A$ (°)
N(3)–H(32)···Cl	(i)	3·237 (5)	1·19 (5)	2·16 (3)	148 (4)	21 (3)
N(2)–H(22)···Cl	(ii)	3·244 (5)	1·01 (5)	2·25 (5)	167 (4)	9 (2)
O(*W*)–H(*W*1)···Cl	(iii)	3·226 (5)	1·08 (8)	2·17 (10)	163 (6)	11 (5)
O(*W*)–H(*W*2)···Cl	(iv)	3·218 (5)	0·91 (10)	2·37 (9)	156 (7)	17 (6)
N(3)–H(31)···Cl	(v)	3·237 (6)	1·05 (5)	2·20 (5)	170 (4)	7 (3)
N(2)–H(21)···O(*W*)	(vi)	2·840 (6)	0·93 (6)	1·95 (6)	158 (4)	15 (4)

Symmetry code: (i) x, y, z; (ii) $\frac{3}{2}-x, \bar{y}, \frac{1}{2}+z$; (iii) $\frac{3}{2}-x, 1-y, \frac{1}{2}+z$; (iv) $\frac{1}{2}+x, \frac{1}{2}-y, 2-z$; (v) $1-x, \frac{1}{2}+y, \frac{3}{2}-z$; (vi) $x-\frac{1}{2}, \frac{1}{2}-y, 2-z$.

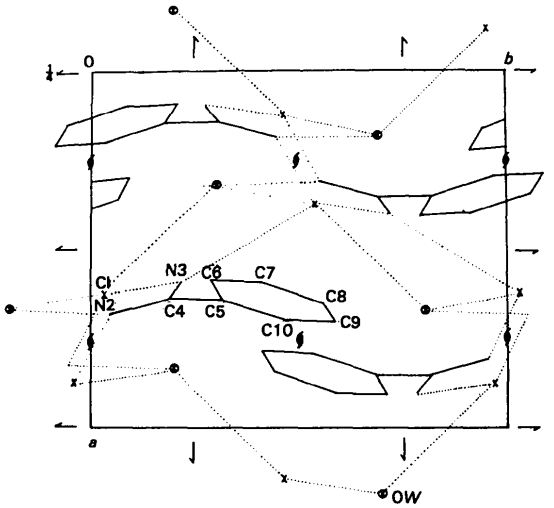

Fig. 2. Packing of the molecule viewed down the *c* axis.

Packing of the molecule viewed down the *c* axis is shown in Fig. 2. All the protons available from the amino groups and the water molecule take part in hydrogen bonding. Chlorine is involved in five hydrogen bonds, three N–H···Cl and two O(*W*)–H···Cl type. The sixth bond is between the water oxygen and N(2). The hydrogen-bond geometry is given in Table 2.

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(±)-*E*-6,6,6-Trichloro-3-methoxy-5-methyl-2-hexenoic Acid

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Abstract. $C_8H_{11}Cl_3O_3$, $M_r = 261{\cdot}52$, triclinic, $P\bar{1}$, $a = 5{\cdot}926$ (1), $b = 9{\cdot}641$ (2), $c = 11{\cdot}254$ (3) Å, $\alpha = 69{\cdot}57$ (2), $\beta = 80{\cdot}14$ (2), $\gamma = 75{\cdot}48$ (2)°, $V = 580{\cdot}8$ (6) Å^3, $Z = 2$, $D_x = 1{\cdot}50$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 7{\cdot}7$ cm^{-1}, $F(000) = 268$, $T = 295$ K. Final $R = 0{\cdot}0601$ for 1336 unique observed reflections.

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