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Stizolamine Chloride: A Novel Amine Isolated from *Stizolobium hassjoo*

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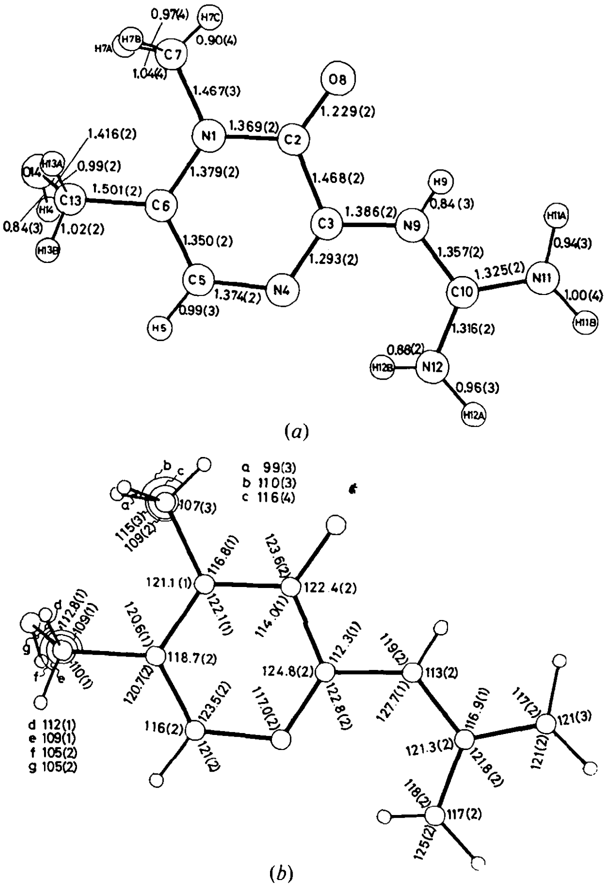
Abstract. $C_7H_{12}N_5O_2.Cl$, FW 233·6, monoclinic, $C2/c$, $a = 18{\cdot}441\ (2)$, $b = 7{\cdot}149\ (1)$, $c = 15{\cdot}138\ (2)$ Å, $\beta = 95{\cdot}30\ (1)°$, $Z = 8$, $D_x = 1{\cdot}56$, $D_m = 1{\cdot}55$ g cm^{-3}, $R = 0{\cdot}039$ for 1851 reflexions. X-ray analysis confirmed that stizolamine is 1-methyl-3-guanidino-6-hydroxymethylpyrazin-2-one. The pyrazine ring and guanidyl group are nearly coplanar (the dihedral angle between them being 2·9°). In the crystal, two-dimensional double-layered sheets are formed by one NH···O=C, one OH···Cl and four NH···Cl hydrogen bonds.

Introduction. Stizolamine was isolated as a novel amine from *Stizolobium hassjoo* and some other plants (Yoshida & Hasegawa 1977). From chemical studies the structure was supposed to be 1-methyl-3-guanidino-6-hydroxymethylpyrazin-2-one (Yoshida, 1977). In order to confirm this, the crystal structure analysis was undertaken as a part of the studies on the metabolites of stizolobium.

Crystals were prepared from aqueous solution as pale-yellow prisms. The space group was indicated from oscillation and Weissenberg photographs to be $C2/c$ or Cc (systematic absences: $h+k$ odd for hkl and l odd for $h0l$). The lattice constants and intensity data were obtained from measurements on a crystal, 0·2 × 0·3 × 0·15 mm, taken on a Rigaku four-circle diffractometer with graphite-monochromatized Cu $K\alpha$ radiation. The 2θ–ω scan mode was applied with a scan rate of 4° (2θ) min^{-1} and range (1·0 + 0·5 tan θ)°. Stationary background counts were accumulated for 10 s before and after each scan. Of 1925 independent reflexions measured within $2\theta < 150°$, 1851 had intensities greater than $3\sigma(|F_o|)$ and were used for structure determination. No correction was made for absorption ($\mu = 34{\cdot}17$ cm^{-1}).

The structure was solved by the symbolic addition procedure (Karle & Karle, 1966) on the basis of $C2/c$. Parameters were refined by the block-diagonal least-squares method. All the H atoms were located on a difference map at the stage $R = 0{\cdot}08$ and their positional and isotropic thermal parameters were included in refinement. The final R was 0·039. The weighting scheme was $w = 0{\cdot}3$ for $|F_o| < 3{\cdot}0$, $w = 1{\cdot}0$ for $3{\cdot}0 \le |F_o| < 20{\cdot}0$ and $w = 20{\cdot}0/|F_o|$ for $|F_o| \ge 20{\cdot}0$. Atomic scattering factors were taken from



(*a*)

(*b*)

Fig. 1. (*a*) Bond lengths (Å) and (*b*) angles (°). The estimated standard deviations are in parentheses.

Table 1. *Final fractional coordinates with estimated standard deviations in parentheses*

	x	*y*	*z*
Cl	0·68346 (2)	1·0569 (1)	0·03630 (3)
N(1)	0·40791 (7)	0·9318 (2)	0·17755 (9)
C(2)	0·47084 (8)	0·9227 (2)	0·13628 (11)
C(3)	0·49586 (8)	0·7313 (2)	0·12133 (10)
N(4)	0·46267 (7)	0·5812 (2)	0·14305 (10)
C(5)	0·39937 (8)	0·6045 (2)	0·18302 (12)
C(6)	0·37136 (8)	0·7734 (2)	0·20059 (10)
C(7)	0·37952 (10)	1·1191 (2)	0·19377 (15)
O(8)	0·50452 (7)	1·0610 (2)	0·11466 (10)
N(9)	0·56047 (7)	0·7278 (2)	0·08139 (9)
C(10)	0·60008 (8)	0·5757 (2)	0·06188 (10)
N(11)	0·66139 (9)	0·6074 (2)	0·02514 (11)
N(12)	0·57816 (7)	0·4052 (2)	0·07849 (10)
C(13)	0·30159 (8)	0·7889 (2)	0·24395 (11)
O(14)	0·24270 (6)	0·8536 (2)	0·18516 (9)
H(7*A*)	0·326 (2)	1·126 (5)	0·167 (2)
H(7*B*)	0·373 (2)	1·144 (6)	0·255 (3)
H(7*C*)	0·407 (2)	1·202 (6)	0·167 (2)
H(9)	0·579 (1)	0·830 (4)	0·068 (1)
H(11*A*)	0·675 (1)	0·731 (4)	0·019 (2)
H(11*B*)	0·694 (1)	0·502 (5)	0·013 (2)
H(12*A*)	0·608 (1)	0·305 (4)	0·062 (2)
H(12*B*)	0·537 (1)	0·392 (3)	0·102 (2)
H(5)	0·372 (1)	0·495 (4)	0·201 (2)
H(13*A*)	0·291 (1)	0·666 (3)	0·270 (1)
H(13*B*)	0·308 (1)	0·879 (3)	0·296 (1)
H(14)	0·235 (2)	0·768 (4)	0·147 (2)

International Tables for X-ray Crystallography (1962). The final atomic parameters are given in Table 1.*

Discussion. The molecular structure and numbering system used are shown in Fig. 1 which confirms the structure chemically proposed. The pyrazine ring is planar within a maximum deviation of 0·007 Å. The methyl C and carbonyl O are nearly in the plane, though the hydroxyl group is out of the plane as a result of rotation around C(6)–C(13) (109°). The guanidyl group is planar and makes a dihedral angle of 2·9° with the pyrazine ring.*

The pyrazine ring shows some localization of double bonds probably resulting from the C(2)=O(8) carbonyl group, although the C(3)=N(4) double bond corresponds to the largest value cited by Pendergrass, Paul & Curtin (1972) (1·27 to 1·29 Å) and the average of three N–C single-bond lengths (1·373 Å) is considerably shorter than the N–C(vinyl) length (1·40 Å) (Pendergrass *et al.*, 1972).

In the guanidyl group the averaged value of three C–N bond lengths (1·332 Å) is close to that of L-arginine dihydrate (1·332 Å) (Lehmann, Verbist, Hamilton & Koetzle, 1973) and biguanide chloride (1·335 Å) (Ernst, 1977), although C(10)–N(9) is somewhat longer than C(10)–N(11) and C(10)–N(12). The bond angle C(3)–N(9)–C(10) is large, probably because of the repulsion between N(4) and N(12) (2·73 Å).

The C(3)–N(9) distance is close to the bond lengths between trigonal N and ring C in 3-aminopyridine

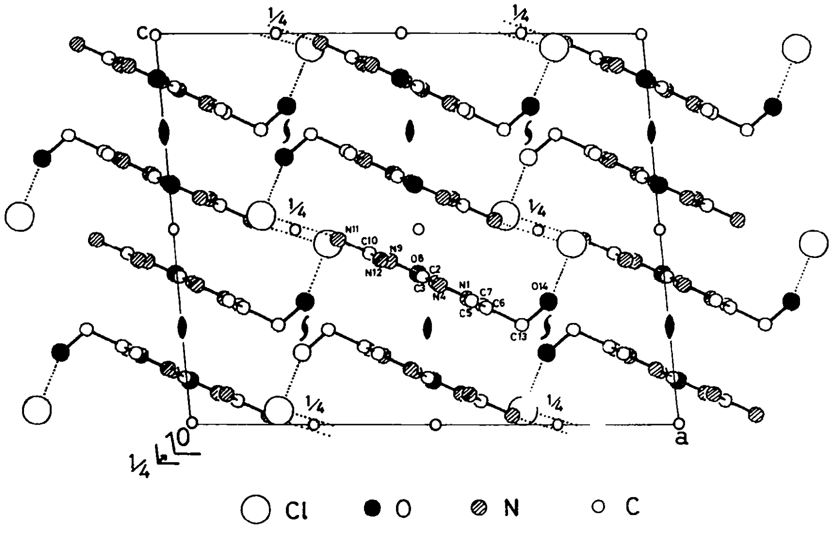


Fig. 2. The crystal structure viewed down **b**.

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* Lists of structure factors, thermal parameters and a table of deviations of atoms from some least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33176 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

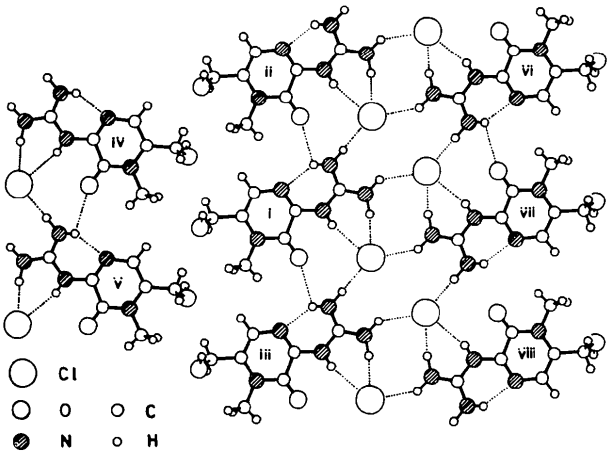

Fig. 3. The hydrogen-bond system within the (102) plane. Symmetry code: (i) x,y,z; (ii) $x,-1+y,z$; (iii) $x,1+y,z$; (iv) $\frac{1}{2}-x,\frac{1}{2}+y,-z$; (v) $\frac{1}{2}-x,\frac{3}{2}+y,\frac{1}{2}-z$; (vi) $\frac{1}{2}-x,-\frac{1}{2}-y,-z$; (vii) $\frac{1}{2}-x,\frac{1}{2}-y,-z$; (viii) $\frac{1}{2}-x,\frac{3}{2}-y,-z$.

Table 2. *Hydrogen-bond distances* (Å) *and angles* (°)

Donor atoms (D)	(H)	Acceptor atom (A)	Distances (Å) $D\cdots A$	$\mathrm{H}\cdots A$	Angle (°) $D-\mathrm{H}\cdots A$
N(9)	H(9)	Cl^{i}	3·381 (2)	2·59 (3)	156 (3)
N(11)	H(11*A*)	Cl^{i}	3·242 (2)	2·35 (4)	161 (4)
N(11)	H(11*B*)	$\mathrm{Cl}^{\mathrm{viii}}$	3·305 (2)	2·47 (5)	141 (4)
N(12)	H(12*A*)	$\mathrm{Cl}^{\mathrm{ii}}$	3·257 (2)	2·30 (4)	175 (4)
N(12)	H(12*B*)	$\mathrm{N}(4^{\mathrm{i}})$	2·731 (2)	2·06 (3)	133 (3)
N(12)	H(12*B*)	$\mathrm{O}(8^{\mathrm{ii}})$	2·877 (2)	2·45 (3)	111 (2)
O(14)	H(14)	$\mathrm{Cl}^{\mathrm{ix}}$	3·212 (2)	2·39 (4)	166 (3)

Symmetry code

(i) $x,\ y,\ z$
(ii) $x,\ -1+y,\ z$
(vii) $\frac{1}{2}-x,\ \frac{1}{2}-y,\ -z$
(ix) $-\frac{1}{2}+x,\ -\frac{1}{2}+y,\ z$

(1·338 Å) (Chao, Schempp & Rosenstein, 1975) and in 1,2-naphthoquinone 1-(2-nitro-4-chlorophenylhydrazone) (1·394 Å) (Guggenberger & Teufer, 1975), although somewhat longer than the values of N(amino)–C(ring) distances in aminopyrazine (1·341 Å) (Chao, Schempp & Rosenstein, 1976) and 2-amino-3-chloropyrazine (1·366 Å) (Morrow & Huddle, 1972). Hence, some double-bond character is expected in this bond.

The crystal structure viewed down **b** is shown in Fig. 2. All the molecules lie approximately on the (102) plane with an interplanar distance of 3·07 Å between those related by a centre of symmetry and 3·39 Å between those related by a twofold axis. The hydrogen-bond system within a plane is illustrated in Fig. 3, with distances and angles given in Table 2. The guanidyl groups and chloride ions are gathered around the centre of symmetry at $x=\frac{1}{4}, y=\frac{1}{4}, z=0$. The molecules form a two-stranded ribbon elongated along **b** with one NH···O and four NH···Cl hydrogen bonds. These ribbons are connected by the sixth intermolecular hydrogen bond, O(14)–H(14)···Cl, along **a** to form two-dimensional double-layered sheets which are stacked along [001].

H(12*B*) forms a bifurcated hydrogen bond, intramolecularly to N(4) and intermolecularly to O(8).

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