Fig. 2. Packing in the unit cell. Hydrogen bonds are indicated by broken lines.

observed (Alcock & Hough, 1972). The atoms forming ring A [C(1), C(2), C(3), C(4), C(5), C(10)] do not deviate significantly from the least-squares plane. Bond lengths and valence angles (Table 2) are comparable with the values found in similar molecules. The C—O bonds involved in the bridged O(20) are slightly elongated because of additional strain.

Puckering parameters (Cremer & Pople, 1975) are $Q = 0.538$ Å, $\theta = 128°$ and $\varphi = 262°$ for ring B [C(9), C(8), C(7), C(6), C(5), C(10)], and $Q = 0.558$ Å and $\theta = 179°$ for ring C [C(12), C(13), C(14), C(8), C(9), C(11)]. In the nomenclature of Boeyens (1978), the conformations of rings B and C are to be described as $^2H_3$ and $^4C_1$, respectively. The molecules are linked by

an O—H⋯O hydrogen bond (Fig. 2), with bond distances O(21)–H(21) = 0.87 (2) Å, O(21)⋯O(22) $(1 - x, \ y - x, \ \frac{5}{3} - z) = 2.77$ Å, and H(21)⋯O(22) $= 1.97$ Å.

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Structure of an Aminopyridazine Derivative

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Abstract. 2-(3-Carboxypropyl)-2,3-dihydro-6-phenyl-3-pyridaziniminium bromide, $C_{14}H_{16}N_3O_2^+.Br^-$, $M_r = 338.1$, triclinic, $P\bar{1}$, $a = 9.711$ (1), $b = 14.980$ (1), $c = 5.482$ (1) Å, $\alpha = 98.12$ (1), $\beta = 101.42$ (1), $\gamma = 98.84$ (1)°, $V = 760.1$ Å^3, $Z = 2$, $D_x = 1.48$ g cm^{-3}, Mo $K\bar{\alpha}$, $\lambda = 0.71069$ Å, $\mu = 26.29$ cm^{-1}, $F(000) = 344$, $T = 293$ K, final $wR = 0.040$ for 1610 observed reflections. For this molecule, which is a GABA A antagonist (GABA is γ-aminobutyric acid), the observed protonation site is the exocyclic N atom, giving rise to electronic delocalization in the aminopyridazine system. Crystal cohesion is assumed by a dense network of intermolecular H bonds involving the Br anion, the carboxylic function and the protonated N atom.

Introduction. The title compound is the demethylated analog of a new selective and competitive antagonist at the GABA A receptor site (Chambon, Feltz, Heaulme, Restlé, Schlichter, Bizière & Wermuth, 1985). Its crystal structure analysis has been undertaken in order to account for the structural and electronic features of

such 2,6-substituted 3-aminopyridazine derivatives. Our interest was increased by the possibility of comparing these results with those previously observed for several 4,6-substituted 3-aminopyridazines, analogs of minaprine (commercial name: Cantor, Clin-Midy, Montpellier), a potent antidepressant drug (Wermuth, 1985). As the major results reported for this family are similar (Van der Brempt, Evrard & Durant, 1985), these molecules and, for completeness, the dihydrochloride of the demethylated analog of minaprine (Michel, Gustin, Evrard & Durant, 1982), are used for comparative discussion.
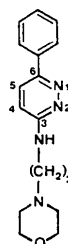
Demethylminaprine
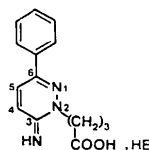
Title compound

Experimental. Crystal obtained by slow evaporation of chloroform/ethanol solution. Colourless prismatic crystal $0.35 \times 0.24 \times 0.17$ mm for all X-ray measurements, D_m not measured. Four-circle Enraf–Nonius diffractometer (CAD-4 system, graphite monochromator). Lattice parameters from least-squares refinement of 25 medium-angle reflections. $\omega-\theta$ scan, $4 \le 2\theta \le 52°$, $(\sin\theta/\lambda)_{max} = 0.62$ Å^{-1}; $-11 \le h \le 11$, $-17 \le k \le 17$, $0 \le l \le 6$. No absorption correction. 2976 reflections measured, 1610 observed $[I \ge 2.5\sigma(I)]$, no significant variation in intensity of 1 standard reflection. Bromide atom found with sharpened Patterson map, remaining 19 heavy atoms from weighted Fourier map. Full-matrix least-squares refinement on F. 8 of 16 H atoms located on difference Fourier map, others calculated [H(92), H(11), H(12), H(20), H(21), H(231), H(232) and H(26)]. Anisotropic temperature factors (U_{ij}) for C, N, O and Br atoms; isotropic for H atoms fixed at 0.05 Å^2. Final $R = 0.035$ and $wR = 0.040$; $w = 1/[\sigma^2(F) + 1.0F^2]$, $(\Delta/\sigma)_{max} = -0.540$ [parameter x of C(23) and y of N(9)]. $S = 0.38$; $-0.44 \le \Delta\rho \le 0.66$ e Å^{-3} in final difference map. Scattering factors from *SHELX* (Br factor used for bromide ion). All computational calculations with *SHELX*76 (Sheldrick, 1976). Structural analysis by *XRAY*76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976).*

Discussion. For an easier comparison, the same atomic numbering scheme as used previously for minaprine analogs has been retained. The atomic coordinates are given in Table 1. The bond lengths and angles are given in Fig. 1 with the atomic numbering.

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* Lists of structure factors, anisotropic thermal parameters, H-atom positions, H bonding, torsion angles and bonding around N(9) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42914 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
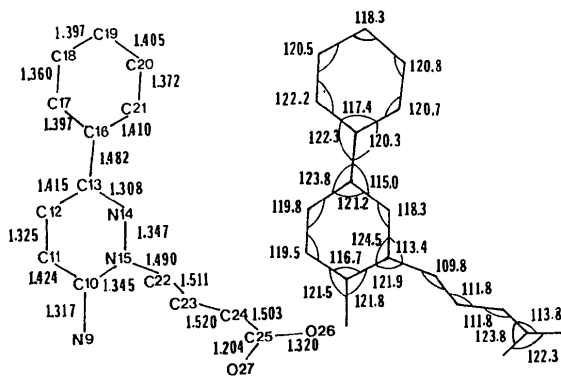
Table 1. *Final atomic coordinates* ($\times 10^4$) *and* B_{eq} *values with e.s.d.'s in parentheses*

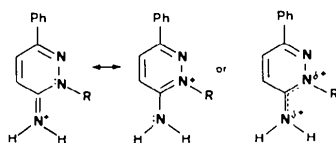$$B_{eq} = \tfrac{8}{3}\pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

	x	y	z	B_{eq}(Å^2)
Br(1)	2182 (1)	4036 (1)	240 (1)	7·25 (1)
N(9)	939 (4)	5715 (3)	3299 (8)	7·50 (1)
C(10)	1766 (4)	6117 (3)	5510 (8)	5·89 (1)
C(11)	3076 (5)	5840 (3)	6472 (11)	7·48 (2)
C(12)	3891 (5)	6278 (3)	8676 (11)	7·24 (1)
C(13)	3457 (4)	7018 (3)	10043 (8)	6·06 (1)
N(14)	2250 (4)	7273 (2)	9188 (6)	5·64 (1)
N(15)	1427 (3)	6817 (2)	6953 (6)	5·61 (1)
C(16)	4298 (4)	7552 (4)	12513 (9)	7·04 (1)
C(17)	5404 (5)	7238 (4)	13992 (12)	8·86 (2)
C(18)	6139 (6)	7712 (6)	16301 (13)	10·49 (3)
C(19)	5775 (6)	8528 (6)	17322 (12)	11·11 (3)
C(20)	4682 (6)	8866 (5)	15851 (12)	9·99 (2)
C(21)	3968 (5)	8395 (4)	13496 (10)	8·04 (2)
C(22)	142 (4)	7217 (3)	6075 (6)	5·43 (1)
C(23)	505 (4)	7942 (2)	4530 (6)	5·13 (1)
C(24)	−754 (4)	8405 (3)	3702 (8)	5·54 (1)
C(25)	−403 (4)	9113 (2)	2120 (6)	5·18 (1)
O(26)	−1265 (3)	9713 (2)	1988 (6)	6·73 (1)
O(27)	558 (4)	9131 (2)	1027 (6)	7·74 (1)
H(91)	−84	5934	2305	3·95
H(92)†	1208	5213	2357	3·95
H(26)†	−971	10189	747	3·95

† H positions calculated.

The exocyclic sp^2-hybridized atom N(9) is protonated by a hydrobromic acid molecule, giving rise to an electronic delocalization from N(15) to N(9) *via* C(10), which is confirmed by the bond lengths observed; N(9)—C(10) [1·317 (5) Å] is longer than a double C=N bond (1·27 Å), whereas N(15)—C(10) [1·345 (5) Å] is intermediate between a double C=N and a single C—N bond (1·47 Å) (Table 2). Consequently, the geometry of N(9) is quasi-trigonal as indicated by the sum of bond angles around N(9), 360·0°, and by the small deviation of N(9), H(91) and H(92) from the pyridazine mean plane (Table 2). It is interesting to note that similar bond-length modifications have been observed for the demethylminaprine analog (Michel *et al.*, 1982) (Table 2), although the electronic delocalization in the aminopyridazine moiety is inverted; indeed, in the case of demethylminaprine, the protonated heteroatom is N(15), and the N(9) atom stabilizes the positive charge through its mesomeric donor power. Consequently, this atom is sp^2 hybridized. The resonance scheme proposed by the authors accounts for these effects.
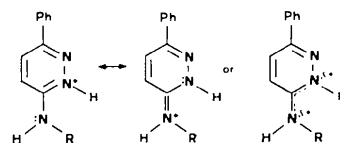
The following resonance forms could also explain the bond lengths observed in the title compound.

Fig. 1. Atom numbering, bond lengths (Å) and valence angles (°). Maximum e.s.d.'s are 0·007 Å and 0·5° (except for the phenyl ring for which e.s.d.'s vary between 0·007 and 0·012 Å and 0·5 and 0·6°).

$$C_{14}H_{16}N_3O_2^+.Br^-$$

Compared to unsubstituted pyridazine (Almenningen, Bjornsen, Ottersen, Seip & Strand, 1977), bond-length variations are observed in the title compound as well as in demethylminaprine (Table 2). The previously proposed scheme agrees with these modifications.

Crystal cohesion is assumed by a dense network of intermolecular H bonds involving, on the one hand, the bromide anion and the protonated N(9) atom and, on the other, the carboxylic function (Fig. 2). N(9) participates in two different H bonds, via H(91) and H(92); A: N(9)(x,y,z)–H(91)···Br(1)(–x,1–y,–z) = 3·364 (4) Å and B: N(9)(x,y,z)–H(92)···Br(1)(x,y,z) = 3·375 (5) Å. The O(26) atom of the carboxylic function is involved in a linear H bond with another –COOH function; C: O(26)(x,y,z)–H(26)···O(27)-(–x,2–y,–z) = 2·664 (5) Å with an angle of 179·7 (1)°. By symmetry, O(27)(x,y,z) participates in an H bond with O(26)(–x,2–y,–z).

As observed for the 3-amino-6-phenylpyridazine derivatives studied earlier, the valence angle N(14)–C(13)–C(16) [115·0 (4)°] is smaller than the opposite one C(12)–C(13)–C(16) [123·8 (4)°]. This effect, combined with the torsion between the phenyl and pyridazine rings [C(12)–C(13)–C(16)–C(17) = –16·0 (8)°], contributes to reduce van der Waals interactions between H(12) and H(17).

As for the demethylminaprine, the valence angle C(10)–N(15)–N(14) [124·5 (3)°] is greater than C(13)–N(14)–N(15) [118·4 (4)°]. The replacement of the lone pair on N(15) by an N–H⁺ bond or in this case by an alkyl group results in a diminution of repulsions

Table 2. *Comparison of the values of the main structural features in unsubstituted pyridazine (Almenningen et al., 1977), demethylminaprine (Michel et al., 1982) and the title compound*

	Pyridazine	4-Demethyl-minaprine	Title compound
Bond distances (Å)			
N(9)–C(10)	—	1·323 (10)	1·317 (5)
C(10)–C(11)	1·39	1·423 (9)	1·424 (6)
C(11)–C(12)	1·38	1·347 (11)	1·325 (7)
C(12)–C(13)	1·39	1·429 (14)	1·415 (7)
C(13)–N(14)	1·34	1·308 (8)	1·308 (6)
N(14)–N(15)	1·33	1·364 (9)	1·347 (4)
N(15)–C(10)	1·34	1·336 (13)	1·345 (5)
C(13)–C(16)	—	1·492 (9)	1·482 (6)
Sum of bond angles around N(9) (°)	—	359·7 (15)	360·0 (15)
Bond angles (°)			
C(12)–C(13)–C(16)	—	122·3 (5)	123·8 (4)
N(14)–C(13)–C(16)	—	116·0 (4)	115·0 (4)
C(13)–N(14)–N(15)	—	116·9 (4)	118·3 (4)
C(10)–N(15)–N(14)	—	126·0 (5)	124·5 (3)
Torsion angles (°)			
C(12)–C(13)–C(16)–C(17)	—	2·9 (8)	–16·0 (8)
Deviation (Å) from the mean plane of pyridazine of			
N(9)	—	0·251 (3)	0·042 (5)
H(91)	—	0·025 (3)	0·142 (5)

and an opening of the angle C(10)–N(15)–N(14), according to the Gillespie (1972) theory.

The alkyl lateral chain lies in an *anti* conformation, with torsion angles N(15)–C(22)–C(23)–C(24) –177·1 (3) and C(22)–C(23)–C(24)–C(25) –178·8 (3)°.

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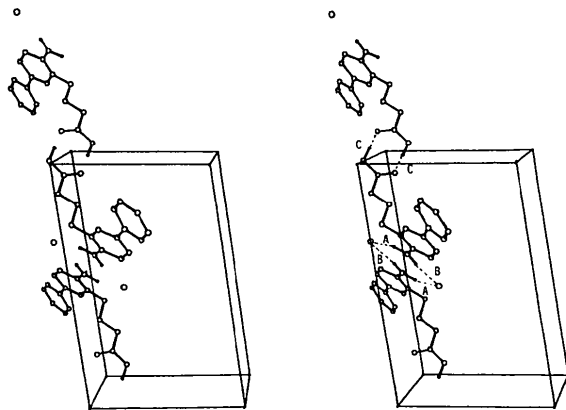

Fig. 2. Stereoview of the molecular conformation and crystal packing, with intermolecular H bonds indicated by dotted lines.