—NHCOOCH$_2$C$_6$H$_5$ moiety, the torsional barrier may well be low in solution.

Related molecules both with much greater and with no anti-5-HT activity are now under X-ray structural investigation.

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2-Amino-5-methylpyridine*

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Abstract. C$_6$H$_8$N$_2$, monoclinic, P2$_1$/c, a = 10·413 (5), b = 5·908 (3), c = 10·828 (5) Å, β = 116·69 (3)°, M$_r$ = 108·144, Z = 4, D$_x$ = 1·207 g cm^{-3}. The structure has been determined from four-circle X-ray diffractometer single-crystal data. The H atoms have been located and full-matrix least-squares refinement gave a final R(F) value of 0·048. The molecules are linked together by a very weak N—H···N bond (N···N, 3·113 Å) to produce cyclic dimers which, in turn, pack in a herringbone formation.

Introduction. Commercial 2-amino-5-methylpyridine was recrystallized several times from chloroform. A crystal with dimensions 0·18 × 0·18 × 0·23 mm was selected for data collection and was mounted in a glass capillary to prevent sublimation during the experiment. A preliminary film investigation indicated diffraction symmetry and systematic absences uniquely consistent with the monoclinic space group P2$_1$/c (No. 14, International Tables for X-ray Crystallography, 1952).

Cell parameters were refined from 18 θ values measured on a Guinier–Hägg powder camera at +24°C with monochromatized Cr Kα$_1$ radiation (λ = 2·28962 Å). CoP$_3$ (a = 7·7073 Å) was used as an internal standard. Intensity data were collected on a Stoe–Philips four-circle X-ray diffractometer with graphite-monochromatized Mo Kα radiation (λ = 0·7107 Å). An ω–2θ scan technique was used to obtain the intensities. Only small random fluctuations were observed in the intensities of the three standard reflexions measured every 50 reflexions. In all, 2708 reflexions were measured out to sin θ/λ = 0·703 Å^{-1}. An absorption correction (μ = 0·825 cm^{-1}) was made, with the Gaussian integration method with a grid of 216 points. After removal of systematic absences and averaging of hkl and h̄kl reflexions, 2118 reflexions remained of which 1112 were greater than 2σ(I) and were used in the refinement.

The structure was solved by direct methods following the iterative procedure programmed by Long (1965). The H atoms were located unambiguously in a difference Fourier synthesis, calculated after several cycles of full-matrix least-squares refinement of non-hydrogen atomic parameters with isotropic thermal

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Table 1. *Atomic coordinates* $(\times 10^4; for\ H \times 10^3)$

	x	y	z
C(2)	6236 (1)	−1529 (2)	3957 (1)
C(3)	6817 (1)	−2311 (2)	3094 (1)
C(4)	7801 (1)	−1002 (3)	2913 (2)
C(5)	8223 (1)	1083 (2)	3575 (1)
C(6)	7580 (1)	1717 (2)	4387 (2)
CM*	9301 (1)	2572 (3)	3396 (2)
N(1)	6605 (1)	481 (2)	4590 (1)
N(2)	5277 (2)	−2784 (3)	4205 (2)
H(1)	472 (2)	−211 (4)	457 (2)
H(2)	487 (2)	−393 (3)	367 (2)
H(3)	649 (1)	−378 (3)	265 (2)
H(4)	821 (2)	−154 (3)	231 (2)
H(6)	780 (1)	319 (3)	480 (2)
HMe(1)†	889 (3)	314 (7)	237 (3)
HMe(2)†	944 (4)	407 (7)	404 (5)
HMe(3)†	1032 (4)	174 (6)	374 (5)
HMe(4)†	900 (5)	399 (10)	308 (7)
HMe(5)†	963 (4)	190 (6)	276 (4)
HMe(6)†	1018 (5)	291 (11)	425 (5)

* The notation CM refers to the C atom in the methyl group.

† Two alternative positions for the methyl H atoms were refined with an occupation factor of 0·5.
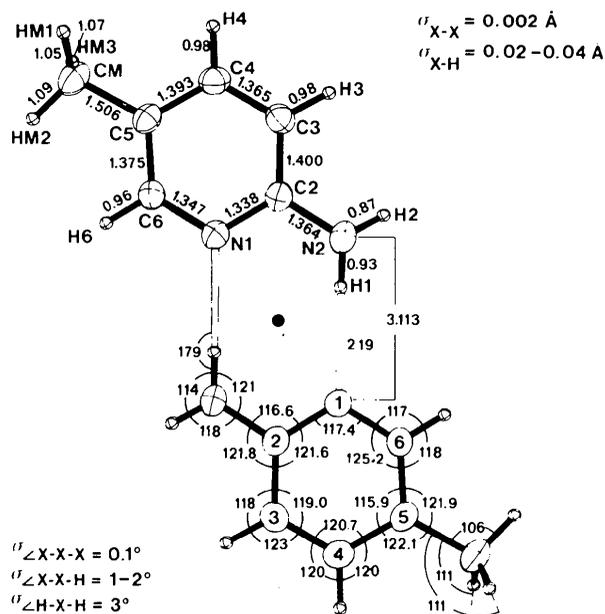

Fig. 1. Bond distances and angles with their estimated standard deviations. Covalent bonds are filled and hydrogen bonds are open. Only one of the two methyl-group orientations is shown; the other has a mean C—H distance of 0·96 Å and a mean C—C—H angle of 114°.

parameters. The subsequent refinement of the atomic parameters was carried out with anisotropic temperature factors for the heavy atoms (C and N) and isotropic ones for the H atoms. An isotropic extinction parameter, g, (Coppens & Hamilton, 1970) was also refined in the final cycles. Its final value was 126 (19).* The refinement was based on F^2 with reflexions weighted according to the expression: $w = 1/\sigma^2(F^2)$ where $\sigma^2(F^2) = \sigma^2_{count}(F^2) + (0·05F^2)^2$. Final $R(F^2)$ and $R_w(F^2)$ values were 0·075 and 0·119, equivalent to $R(F) = 0·048$. Final positional parameters are given in Table 1†.

Atomic scattering factors for C and N were those of Hanson, Herman, Lea & Skillman (1964), and for H those of Stewart, Davidson & Simpson (1965). All the calculations were performed on the IBM 370/155 computer in Uppsala with programs described by Lundgren (1975).

Discussion. This work is part of a systematic investigation of organic compounds which utilize hydrogen bonding to provide simple analogues to biologically interesting systems. Several substituted hydroxy- and aminopyridines have already been studied and are summarized by Kvick (1974).

The bond distances and angles are given in Fig. 1 together with the range of estimated standard deviations. The molecular bond distances are compared with those of other substituted aminopyridines in Table 2.

Two different sets of positions were found for the methyl H atoms indicating disorder of the methyl group. The coordinates for the methyl H atoms given in Table 1 were obtained by simultaneous refinement of six atom positions each with an occupancy factor of 0·5. Details of the best least-squares plane through the pyridine ring are given in Table 3. The pyridine ring itself deviates only slightly from planarity with the largest out-of-plane displacement for atom C(2) [0·007 (1) Å].

The largest deviations for exocyclic atoms occur for the amino H atoms H(1) [0·18 (2) Å] and H(2) [0·14 (2) Å]. The calculated dihedral angle between the plane of the amino group and the plane of the ring is 24°.

The aminopyridine molecules are linked *via* N—H···N hydrogen bonds to produce centrosymmetric dimers. The distance between the planes of the pyridine rings of the dimer is 0·74 Å. The dimers are packed in a herring-bone fashion with an angle of 52·5° between the planes of the two different sets of dimers (see Fig. 2). The structure is similar to the crystal structures of, for instance, 2-amino-5-chloropyridine (Kvick & Backéus, 1974) and 2-amino-4-methylpyridine (Kvick &

Table 2. *Comparison of covalent bond distances in substituted aminopyridines*

Bond (Å)

Compound	T(K)	C(2)—N(2)	C(3)—N(2)	N(1)—C(2)	N(1)—C(6)	C(2)—C(3)	C(3)—C(4)	C(4)—C(5)/C(5)—C(6)	C—CM
2-Aminopyridine[1]	302	1·351 (2)		1·345 (2)	1·340 (2)	1·405 (2)	1·364 (2)	1·380 (3) 1·367 (3)	–
2-Amino-3-nitropyridine[2]	302	1·336 (3)	–	1·364 (3)	1·326 (3)	1·412 (3)	1·389 (3)	1·367 (4) 1·379 (4)	–
2-Amino-4-methylpyridine[3]	100	1·363 (2)	–	1·347 (2)	1·348 (2)	1·410 (2)	1·383 (2)	1·397 (2) 1·383 (2)	1·507 (2)
2-Amino-5-methylpyridine[4]	302	1·364 (2)	–	1·338 (2)	1·347 (2)	1·400 (2)	1·365 (2)	1·393 (2) 1·375 (2)	1·506 (2)
2-Amino-5-methylpyridine[5] hydrochloride	302	1·338 (7)	–	1·333 (7)	1·356 (7)	1·405 (7)	1·357 (7)	1·397 (7) 1·353 (7)	1·494 (7)
2-Amino-5-chloropyridine[6]	302	1·355 (2)	–	1·342 (2)	1·341 (2)	1·408 (2)	1·368 (2)	1·389 (2) 1·377 (2)	–
3-Aminopyridine[1]	302	–	1·384 (4)	1·336 (4)	1·331 (5)	1·399 (4)	1·391 (4)	1·376 (4) 1·372 (4)	–

References: (1) Chao, Schempp & Rosenstein (1975, 1976). (2) Destro, Pilati & Simonetta (1975). (3) Kvick & Noordik (1977). (4) Present work. (5) Sherfinski & Marsh (1975). (6) Kvick & Backéus (1974).
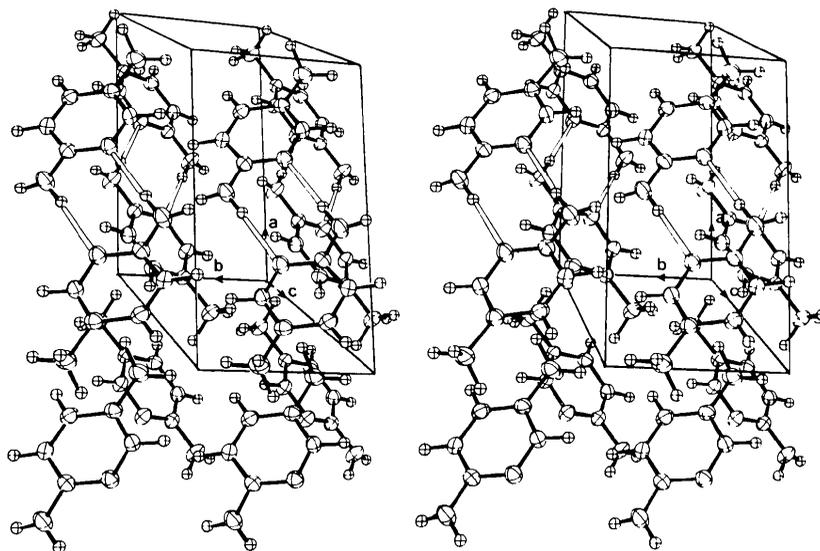

Fig. 2. Stereoscopic illustration of the crystal structure of 2-amino-5-methylpyridine. The thermal ellipsoids are scaled to 30% probability except for the H atoms, which are represented by spheres of radius 0·15 Å.

Table 3. *Deviations (Å) from the best least-squares plane through the pyridine ring*

The equation of the plane is $4·4887x - 2·6135y + 5·5117z = 5·3729$.

N(1)*	0·004 (1)	H(3)	0·01 (2)
C(2)*	−0·007 (1)	H(4)	0·01 (2)
C(3)*	0·004 (1)	H(6)	0·06 (2)
C(4)*	0·004 (2)	H(Me1)	0·89 (4)
C(5)*	−0·005 (1)	H(Me2)	−0·03 (5)
C(6)*	0·001 (1)	H(Me3)	−0·87 (5)
N(2)	−0·041 (2)	H(Me4)	0·68 (7)
CM	−0·002 (2)	H(Me5)	0·03 (4)
H(1)	0·18 (2)	H(Me6)	−0·78 (6)
H(2)	0·14 (2)		

* Atoms defining the plane.

Noordik, 1977), where alternating hydrogen-bonded and van der Waals bonded zones are also found.

The N—H···N hydrogen bond is linear [∠N(2)—H(1)···N(1) = 179(2)°]. The N(1)···H(1) distance is 2·19 (2) Å and the N(1)···N(2) distance 3·113 (2) Å. The hydrogen bond is slightly longer than the comparable bonds in 2-amino-5-chloropyridine [N···N = 3·058 (2) Å] and in 2-amino-4-methyl-pyridine [N···N = 2·996 (2) Å]. The unsubstituted 2-aminopyridine has an N···N distance of 3·071 (7) Å (Chao, Schempp & Rosenstein, 1975, 1976).

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Calcium Bromide Hexaurea

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Abstract. [Ca.6CO(NH$_2$)$_2$]Br$_2$ is monoclinic, space group $P2_1/c$, $a = 10\cdot203$ (1), $b = 7\cdot881$ (1), $c = 13\cdot336$ (2) Å, $\beta = 94\cdot07$ (2)°, $Z = 2$, $D_m = 1\cdot716$, $D_x = 1\cdot739$ g cm^{-3}. Six O atoms of the urea molecules form a nearly regular octahedron around the Ca ion. The Br ions are not included in the first coordination sphere of the cation.

Introduction. Crystals were obtained by slow evaporation of an aqueous solution of calcium bromide and urea with the molar ratio 1:6. A crystal, ground to a sphere of diameter 0·30 mm, was used to collect intensity data on an Enraf–Nonius CAD-4 diffractometer. The cell parameters were obtained from the least-squares fit of the φ, χ, ω, 2θ values for 15 reflexions. They agree with the values previously reported by Durski (1970). The intensities were measured out to $\theta = 27°$ with graphite-monochromated Mo $K\alpha$ radiation. A $\theta/2\theta$ scan was used, with scan width varying as $0\cdot80° + 0\cdot42°$ tan θ. The background was measured at both ends of the reflexions over one quarter of the scan range. Deviations in the intensity of a standard reflexion, monitored after each group of 23 measurements, were less than 2%. Lorentz, polarization and absorption corrections (*International Tables for X-ray Crystallography*, 1968) were applied to the intensity-data set. Of the 1913 measured independent reflexions, 1867 had positive net intensities and were used in further calculations.

The structure was determined by the heavy-atom method and refined by full-matrix least squares, minimizing $\Sigma w[F_o - (1/K)F_c]^2$. The weights used were the product of those resulting from counting statistics combined with the Cruickshank (1969) scheme. All H atoms were identified in difference Fourier maps but the refinement of their parameters resulted in unrealistic temperature factors. In the final least-squares cycles, the positions of the H atoms were therefore calculated from the geometry of the urea molecule and kept fixed. Neutral-atom scattering factors (Cromer & Waber,

Table 1. *Atomic positional parameters* ($\times 10^4$) *and their standard deviations for non-hydrogen atoms*

	x	y	z
Ca	0	5000	5000
Br	5102·7 (4)	6418·5 (5)	8558·3 (3)
O(1)	2120 (2)	4180 (4)	4710 (2)
N(1)	4041 (3)	3518 (5)	4083 (3)
N(2)	2389 (3)	4699 (5)	3071 (3)
C(1)	2821 (3)	4121 (5)	3973 (3)
O(2)	722 (2)	7784 (3)	5225 (2)
N(3)	2892 (3)	7914 (5)	5653 (3)
N(4)	1704 (3)	10332 (4)	5436 (3)
C(2)	1730 (4)	8643 (4)	5418 (3)
O(3)	480 (2)	4512 (3)	6711 (2)
N(5)	2647 (3)	4427 (5)	7127 (3)
N(6)	1372 (4)	6201 (6)	7948 (3)
C(3)	1462 (4)	5012 (5)	7250 (3)