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4-Dimethylaminopyridine Hydrochloride Dihydrate*

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$C_7H_{11}N_2^+ \cdot Cl^- \cdot 2H_2O$ is triclinic $P\bar{1}$ with $a = 16.162$ (4), $b = 7.066$ (4), $c = 9.584$ (4) Å, $\alpha = 104.51$ (9), $\beta = 90.01$ (8), $\gamma = 94.44$ (8)°, $M_r = 194.66$, $Z = 4$, $D_m = 1.218$ g cm⁻³, $D_x = 1.223$ g cm⁻³. The amino group is essentially planar with a N(7)–C(4) bond length of about 1.340 Å. Protonation takes place at the ring N. There are two independent molecules in the structure with significantly different geometries, apparently related to the formation of a very short N–H···Cl hydrogen bond (3.081 Å) in one case, and a N–H···O bond (2.675 Å) in the other.

Introduction

¹⁴N NQR studies of 2-aminopyridine (Marino, Guibé & Bray, 1968) and 2-aminopyrimidine (Schempp & Bray, 1971) have suggested that the two *ortho* ring N atoms in the pyrimidine are almost twice as effective as one ring N in withdrawing charge from the amino group. The C–NH₂ bond reflects this situation; the bond length is 0.009 Å longer in 2-aminopyridine than in 2-aminopyrimidine (Scheinbeim & Schempp, 1976). NQR study of 4-aminopyridine hydrochloride (Chao, 1975) shows that the quadrupole coupling constant (3315.6 kHz) and the asymmetry parameter (0.431) for the amino group change from their values in 4-aminopyridine (3506.3 kHz and 0.385) (Marino *et al.*, 1968) toward those in 2-aminopyrimidine (3270.3 kHz and 0.406); this seems to signal a limit to the amino group's electron-donating power. We then expect that the C–N(amino) bond length will reflect this (Chao & Schempp, 1977); unfortunately the structure of 4-aminopyridine hydrochloride has not been determined. The present structure determination was undertaken as part of planned NQR and X-ray studies of 4-dimethylaminopyridine and its hydrochloride.

A clear needle-shaped crystal of 4-dimethylaminopyridine.HCl dihydrate was obtained by adding dilute hydrochloric acid to an ethanol solution of the parent pyridine and letting this solution evaporate to dryness. The crystals lose water of hydration to form a white powder when they are exposed to the air for 1–2 days. A single crystal with approximate dimensions 0.2 × 0.3 × 0.3 mm was sealed in a Lindemann glass capillary. The unit-cell constants and the three-dimensional intensity data were measured by using a four-circle computer-controlled diffractometer (Nonius CAD-4) in the variable $\theta/2\theta$ scan mode. There were 4334 independent reflections measured with $\theta \leq 75^\circ$, of which 1227 had an integrated intensity less than $2\sigma(I)$. These were assigned an intensity $I = \sigma(I)/2$ and given zero weight during the least-squares refinement.

The structure was solved by the heavy-atom method and the atomic positional parameters were refined with a block-diagonal least-squares program (Shiono, 1971). H atoms were located in a difference electron density map, although the methyl H atoms turned out to have large temperature factors which did not converge during refinement. The ten strongest reflections gave large ratios of F_o/F_m and were given zero weight in the subsequent refinement. The reflections were weighted according to the Cruickshank (1965) scheme where $w = 0.9447 - 0.0073 |F_m| - 0.0008 |F_m|^2$ for the final refinement. The atomic scattering factors used were those of Cromer & Waber (1965) for Cl, O, N and C

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Table 1. Atomic parameters of 4-dimethylaminopyridine hydrochloride dihydrate

Positional parameters are given as fractions of the lattice translations. Thermal parameters are given according to the expression $T = \exp(-\sum_j \beta_{ij} h_i h_j)$, and isotropic temperature factors to the expression $T = \exp(-B \sin^2 \theta / \lambda^2)$. Estimated standard deviations given in parentheses refer to the least significant figure in parameter values. Positional and thermal parameters for atoms other than H are $\times 10^4$, for H positional parameters, $\times 10^3$. H thermal parameters are in \AA^2 .

	<i>x</i>	<i>y</i>	<i>z</i>	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cl(1)	8418 (1)	7672 (1)	8780 (1)	54 (1)	309 (2)	148 (1)	4 (1)	-0 (1)	51 (1)
Cl(2)	6410 (1)	3979 (1)	4628 (1)	57 (1)	335 (2)	137 (1)	18 (1)	-30 (1)	39 (1)
N(1A)	9002 (2)	2445 (3)	3421 (2)	57 (1)	229 (5)	139 (3)	8 (2)	-8 (2)	42 (3)
C(2A)	9841 (2)	2411 (3)	3446 (3)	58 (1)	203 (5)	146 (3)	15 (2)	16 (2)	48 (4)
C(3A)	10262 (2)	2507 (3)	4677 (3)	42 (1)	198 (5)	153 (3)	10 (2)	17 (2)	47 (3)
C(4A)	9842 (2)	2616 (3)	5981 (3)	38 (1)	157 (4)	137 (3)	6 (2)	2 (2)	22 (3)
C(5A)	8964 (2)	2626 (4)	5904 (3)	39 (1)	266 (6)	141 (3)	9 (2)	5 (2)	30 (4)
C(6A)	8577 (2)	2542 (4)	4641 (3)	42 (1)	252 (6)	165 (3)	5 (2)	-4 (2)	38 (4)
N(7A)	10238 (2)	2695 (3)	7225 (2)	45 (1)	247 (5)	147 (3)	8 (2)	-10 (2)	42 (3)
C(8A)	11145 (2)	2753 (4)	7320 (4)	44 (2)	306 (7)	227 (5)	10 (3)	-23 (2)	75 (5)
C(9A)	9770 (2)	2668 (5)	8526 (3)	70 (2)	378 (9)	131 (4)	18 (3)	4 (2)	42 (4)
N(1B)	5215 (2)	3066 (3)	1997 (2)	59 (1)	261 (5)	117 (3)	0 (2)	-18 (2)	47 (3)
C(2B)	5676 (2)	2766 (4)	809 (3)	41 (1)	248 (6)	141 (3)	2 (2)	-9 (2)	56 (4)
C(3B)	5324 (2)	2359 (3)	-526 (3)	38 (1)	210 (5)	127 (3)	7 (2)	-1 (1)	45 (3)
C(4B)	4455 (2)	2241 (3)	-703 (2)	37 (1)	169 (4)	104 (3)	7 (2)	0 (1)	32 (3)
C(5B)	3991 (2)	2537 (4)	582 (3)	41 (1)	268 (6)	115 (3)	21 (2)	9 (2)	41 (3)
C(6B)	4385 (2)	2945 (4)	1881 (3)	59 (2)	264 (6)	110 (3)	25 (3)	8 (2)	42 (4)
N(7B)	4086 (1)	1891 (3)	-2003 (2)	39 (1)	292 (5)	102 (3)	6 (2)	-3 (1)	39 (3)
C(8B)	4553 (2)	1541 (4)	-3336 (3)	57 (2)	367 (8)	104 (3)	14 (3)	7 (2)	40 (4)
C(9B)	3185 (2)	1790 (5)	-2189 (3)	40 (1)	542 (11)	167 (4)	6 (3)	-19 (2)	85 (5)
O(1)	7512 (2)	3875 (3)	9310 (2)	71 (1)	358 (6)	191 (3)	11 (2)	-14 (2)	83 (3)
O(2)	8204 (2)	1724 (3)	874 (2)	127 (2)	347 (6)	114 (3)	31 (3)	-24 (2)	44 (3)
O(3)	6766 (2)	1460 (3)	6819 (2)	70 (1)	426 (7)	152 (3)	33 (2)	8 (2)	83 (3)
O(4)	7534 (2)	7937 (3)	5879 (2)	70 (1)	375 (6)	180 (3)	0 (2)	-10 (2)	88 (3)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>		<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
H(1A)	868 (2)	225 (4)	248 (3)	7.5 (6)	H(6B)	408 (2)	324 (3)	283 (2)	5.1 (5)
H(2A)	1015 (2)	248 (4)	256 (3)	6.0 (7)	H(7B)	496 (3)	65 (6)	-348 (4)	11.1 (12)
H(3A)	1087 (2)	256 (4)	454 (3)	7.1 (7)	H(8B)	507 (2)	259 (4)	-318 (3)	9.4 (9)
H(5A)	867 (2)	270 (4)	675 (3)	7.2 (7)	H(9B)	422 (4)	170 (9)	-430 (6)	21.0 (24)
H(6A)	798 (2)	252 (4)	454 (3)	6.9 (7)	H(10B)	302 (4)	123 (8)	-326 (5)	15.3 (19)
H(7A)	1139 (3)	222 (7)	648 (5)	14.3 (19)	H(11B)	293 (2)	54 (5)	-202 (4)	8.8 (10)
H(8A)	1132 (3)	391 (7)	748 (5)	16.0 (18)	H(12B)	295 (2)	302 (4)	-134 (3)	9.1 (7)
H(9A)	1128 (3)	207 (5)	821 (4)	13.5 (10)	H(13)	733 (2)	332 (4)	849 (3)	5.6 (6)
H(10A)	1015 (2)	252 (5)	941 (4)	11.4 (10)	H(14)	783 (2)	501 (5)	898 (3)	8.9 (8)
H(11A)	946 (3)	166 (6)	829 (4)	14.1 (13)	H(15)	834 (2)	70 (4)	23 (3)	7.6 (6)
H(12A)	949 (2)	393 (5)	885 (3)	9.5 (8)	H(16)	813 (2)	259 (4)	45 (3)	11.3 (9)
H(1B)	557 (3)	349 (5)	300 (4)	7.9 (10)	H(17)	678 (2)	223 (4)	597 (3)	7.4 (8)
H(2B)	631 (2)	289 (4)	93 (3)	6.8 (7)	H(18)	701 (2)	33 (4)	638 (3)	8.2 (7)
H(3B)	569 (2)	204 (3)	-152 (3)	5.2 (6)	H(19)	768 (2)	775 (5)	682 (3)	9.3 (9)
H(5B)	344 (2)	245 (4)	55 (3)	6.8 (6)	H(20)	716 (3)	694 (6)	564 (4)	11.8 (12)

and those of Stewart, Davidson & Simpson (1965) for H. The final R ($= \sum |F_m| - |F_c| / \sum |F_m|$) was 0.069 for all reflections and 0.060 for those reflections with non-zero weight.* The final atomic parameters are listed in Table 1. Bond lengths and bond angles in the 4-dimethylaminopyridine cations are shown in Fig. 1(a) and (b). The bond angles of the water molecules are: H(13)—O(1)—H(14), 93(2); H(15)—O(2)—H(16),

107(3); H(17)—O(3)—H(18), 102(2); H(19)—O(4)—H(20), 96 (3)°.

Discussion

The difference electron density map clearly showed the acid hydrogens H(1A) and H(1B) at the ring N positions. The ring angles C(2A)—N(1A)—C(6A) and C(2B)—N(1B)—C(6B) are 119.7 (2) and 120.1 (2)°, respectively, which are 2.8 and 3.2° larger than the CNC angle in pyridine, 116.94° (Sørensen, Mahler & Rastrup-Andersen, 1974). This is another indication that protonation has taken place on the ring N (Singh,

* A list of measured and calculated structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32317 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

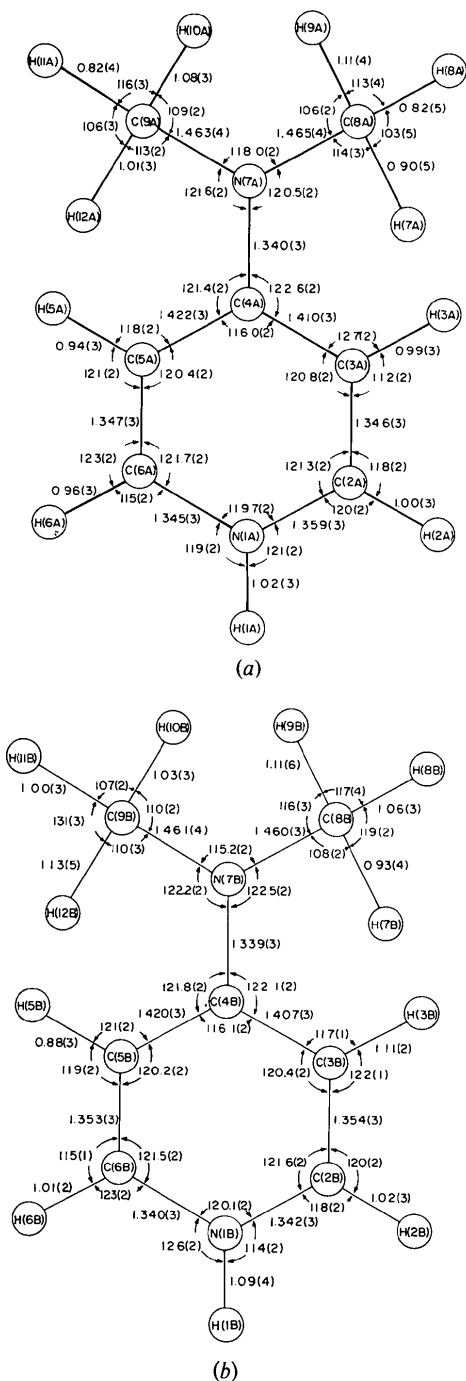


Fig. 1. (a) Bond lengths (Å) and angles (°) and atomic numbering in cation *A* of 4-dimethylaminopyridine hydrochloride dihydrate (e.s.d.'s given in parentheses refer to the last decimal position). (b) Cation *B* in 4-dimethylaminopyridine hydrochloride dihydrate; H(1*B*) is hydrogen-bonded to a Cl⁻ anion.

1965) and is consistent with the conclusion of a theoretical calculation by Konishi, Kato & Yonezawa (1970) which shows that protonation is easier at the ring N than at the amino N in aminopyridines.

The pyridine-ring atoms are coplanar in the 4-dimethylaminopyridine cation (Table 2). In molecule *A*, the amino N is essentially on the plane (-0.004 Å) but in *B*, it is not (0.042 Å). The fact that the sum of the bond angles at the amino N is 360° for both molecules indicates that the amino group is planar even though the individual CNC angles at each amino N depart from 120° . The angle between the ring plane and the plane determined by atoms N(7*A*), C(8*A*) and C(9*A*) in molecule *A* is 3.8° while the corresponding angle in molecule *B* is 1.1° . This geometric conformation favours conjugation between the lone pair of the amino N and the π system of the ring as indicated by the short amino-ring C(4)–N(7) bond lengths [$1.339(3)$ and $1.340(3)$ Å]. These bond lengths are nearly equal to the corresponding bond lengths in 2-amino-5-methylpyridine hydrochloride (Sherfinski & Marsh, 1975) and in aminopyrazine (see Chao & Schempp, 1977).

The hydrogen-bonding network appears to exert a marked influence on the packing and the molecular geometries. It is interesting that the ring N of molecule *A* is hydrogen-bonded to a water O atom, while in molecule *B* there is a hydrogen bond to a Cl⁻ anion (Fig. 2). Both cations depart noticeably from their nominal C_{2v} symmetry, but this is most pronounced in *A* where the N(1)–C(2) and N(1)–C(6) bond lengths [$1.345(3)$ and $1.359(3)$ Å] differ by $0.014(3)$ Å (Fig. 1*a*). The N–H...O distance here is $2.675(3)$ Å, which is unusually short (Pimentel & McClellan, 1960). In *B* the N(1)–C(2) and N(1)–C(6) bond lengths [$1.340(3)$ and $1.342(3)$ Å] are almost equal, but shorter than the mean length in *A* by about 0.01 Å. The N–H...Cl distance in this case is $3.081(2)$ Å (Table 3), which appears to be one of the shortest N...Cl distances observed. Hamilton & Ibers (1968) have dis-

Table 2. Least-squares planes and atom deviations of the 4-dimethylaminopyridine cations

The equations of the planes are relative to the crystal axes *a*, *b*, and *c*. Asterisks mark atoms not included in the calculation of the plane.

Molecule <i>A</i>		Molecule <i>B</i>	
$0.011x + 0.976y - 0.055z = 2.010$ Å		$-0.042x + 0.998y - 0.206z = 1.408$ Å	
N(1 <i>A</i>)	0.005 Å	N(1 <i>B</i>)	0.005 Å
C(2 <i>A</i>)	-0.006	C(2 <i>B</i>)	-0.003
C(3 <i>A</i>)	0.003	C(3 <i>B</i>)	-0.003
C(4 <i>A</i>)	0.002	C(4 <i>B</i>)	0.007
C(5 <i>A</i>)	-0.003	C(5 <i>B</i>)	-0.006
C(6 <i>A</i>)	-0.000	C(6 <i>B</i>)	-0.001
N(7 <i>A</i>)*	-0.004	N(7 <i>B</i>)*	0.042
C(8 <i>A</i>)*	0.047	C(8 <i>B</i>)*	0.026
C(9 <i>A</i>)*	-0.099	C(9 <i>B</i>)*	0.069
H(1 <i>A</i>)*	-0.089	H(1 <i>B</i>)*	0.080
O(2)*	-0.371	Cl(2)*	0.050

The angle between the plane of (*A*) and the plane of (*B*) is 9.2° .

cussed the N—H...Cl⁻ bonds in methyl glyoxal bis-guanylhydrazone.2HCl.H₂O which range in length from 3.15 to 3.51 Å with a mean N...Cl⁻ distance of 3.33 Å and a mean N—H...Cl⁻ angle of 149° (Gorter, van Ingen Schenau & Verschoor, 1974).

The water molecules and the N atoms of both rings serve as hydrogen donors (every water H is hydrogen-bonded) and the Cl anions and water O atoms are hydrogen-bond acceptors (Fig. 2 and Table 3). Cl(1) is involved in three O—H...Cl hydrogen bonds while Cl(2) has two O—H...Cl bonds in addition to the N(1B)—H...Cl hydrogen bond. The packing of the molecules and ions forms a three-dimensional net through the hydrogen bonds, as shown in Fig. 2.

Table 3. *Hydrogen-bonding distances and angles in 4-dimethylaminopyridine hydrochloride dihydrate*

Symmetry code: None *x, y, z*; (i) *x, 1 - y, z*.

<i>i</i>	<i>j</i>	<i>k</i>	<i>D_{ij}</i> (Å)	<i>D_{ik}</i> (Å)	<i>D_{jk}</i> (Å)	∠ <i>ijk</i> (°)
N(1A)—H(1A)...	O(2)		1.02 (2)	2.675 (3)	1.66 (3)	174 (2)
N(1B)—H(1B)...	Cl(2)		1.09 (4)	3.081 (2)	2.01 (3)	169 (3)
O(1)—H(13)...	O(3)		0.83 (2)	2.775 (3)	1.97 (2)	164 (2)
O(1)—H(14)...	Cl(1)		1.03 (3)	3.111 (2)	2.10 (3)	167 (2)
O(2)—H(15)...	Cl(1)		0.87 (2)	3.101 (2)	2.25 (2)	166 (2)
O(2)—H(16)...	O(1)		0.83 (3)	2.686 (3)	1.92 (3)	154 (3)
O(3)—H(17)...	Cl(2)		1.09 (3)	3.153 (2)	2.11 (3)	160 (2)
O(3)—H(18)...	O(4)		0.92 (3)	2.811 (3)	1.90 (3)	168 (3)
O(4)—H(19)...	Cl(1)		0.97 (3)	3.180 (2)	2.24 (3)	161 (3)
O(4)—H(20)...	Cl(2)		0.87 (4)	3.177 (2)	2.33 (4)	167 (4)

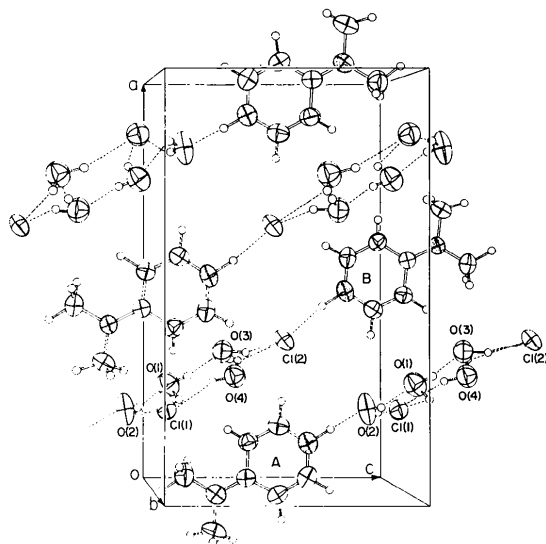


Fig. 2. Packing diagram of 4-dimethylaminopyridine.HCl.2H₂O. In addition to the hydrogen bonds shown, H(18) at O(3) is hydrogen-bonded to O(4) at (*x, 1 - y, z*); see Table 3. N atoms are stippled.

Because the crystal structure of 4-dimethylaminopyridine remains unknown, the most closely related molecule for comparison is 4-aminopyridine (Chao & Schempp, 1977). In this case the amino N(7)-to-ring C(4) distance is 1.363 (3) Å, fully 0.02 Å longer than in the hydrochloride, and the angle between the amino and ring planes is 22 (4)° in contrast to the practically coplanar structures found here. It is interesting that the ring C(2)—C(3) and C(5)—C(6) bond lengths in 4-aminopyridine [1.372 (3) Å] are about 0.02 Å longer than the corresponding bonds in 4-dimethylaminopyridine.HCl [1.347 (3) and 1.354 (3) Å in molecules *A* and *B* respectively]. On the other hand, the ring C—C bonds adjacent to the amino substituent appear longer in the hydrochloride [1.415 (8) Å average] than in 4-aminopyridine [1.404 (3) Å].

Both the configurations of the amino groups and the changes in bond lengths are consistent with a higher degree of conjugation in 4-dimethylaminopyridine.HCl and more double-bond character in the ring C(2)—C(3) and C(5)—C(6) bonds, suggestive of a trend toward a quinoidal structure.

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