Crystal structure of 2,6-dimethylpyridinium hydrochloride, $(C_7H_{10}N)Cl$

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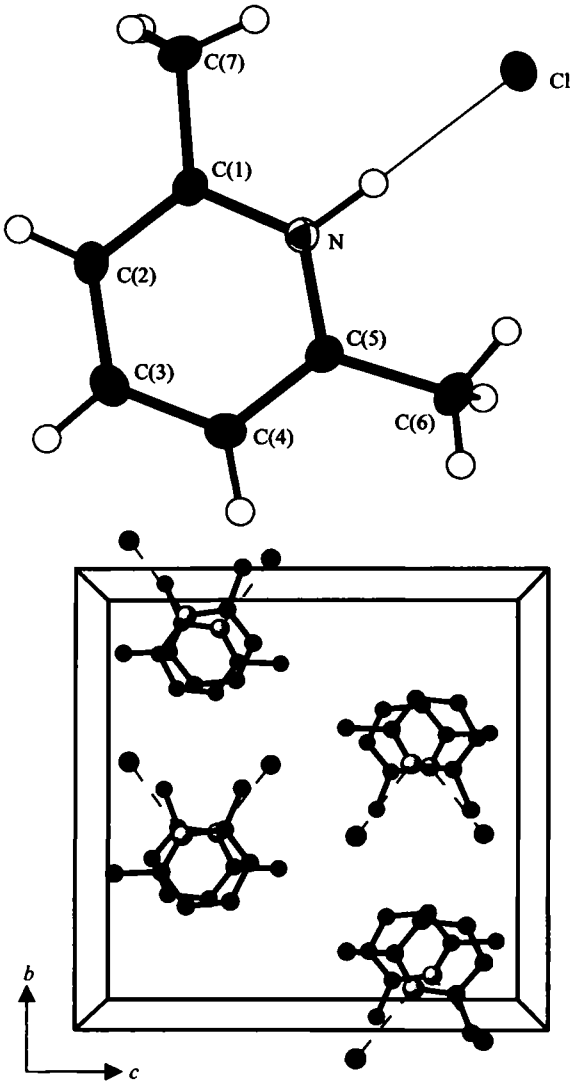

Abstract

$C_7H_{10}ClN$, orthorhombic, *Pbca* (no. 61), $a = 7.2466(6)$ Å, $b = 14.242(1)$ Å, $c = 14.506(1)$ Å, $V = 1497.1$ Å^3, $Z = 8$, $R_{gt(F)} = 0.049$, $wR_{ref(F^2)} = 0.137$, $T = 100$ K.

Source of material

2,6-dimethylpyridinium hydrochloride was obtained, according to a literature procedure [1], by adding an excess of 35 % aqueous HCl to 2,6-lutidine. After drying at the rotavapor the colorless residue was recrystallized from CH_2Cl_2 at –4 °C to give colorless needles.

Discussion

The weak acid ($pK_a = 14.1$) 2,6-dimethylpyridinium hydrochloride, or 2,6-lutidine hydrochloride, is known as a useful reagent for the investigation of reduction mechanisms in biochemistry [2], as well as for chlorination processes to produce for example several agrochemically important 2,2-dichloroaldehydes in the laboratory [1] and in industrial scale [3].

The bond lengths between the carbon atoms and carbon and nitrogen atoms, respectively, are all in the range of usual aromatic bonding. Compared to pyridine, the C–N–C angle (124.1(1)°) is widened so that this compound forms a queue with other known salts of the 2,6-dimethylpyridinium cation like its hydrogen phthalate (123.83(2)°) [4], hydrogen fumarate (123.9(2)°) [5] and nitrate (124.9(1)°) [6].

The Cl^- anion is connected via an hydrogen bond, d(N–H···Cl) = 3.014(1) Å, to the nitrogen at an angle N–H···Cl of 174(2)°. The deviation from linearity is apparently due to the sterical influence of the methyl substituents at the ortho positions of the aromatic ring.

Table 1. Data collection and handling.

Crystal:	colorless needle, size 0.15 × 0.20 × 0.80 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	4.19 cm^{-1}
Diffractometer, scan mode:	Bruker AXS SMART APEX, ω
$2\theta_{max}$:	69.72°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	21669, 3136
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2398
$N(param)_{refined}$:	122
Programs:	SHELXTL [7], ATOMS [8]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(1)	8c	0.695(3)	0.471(2)	0.680(2)	0.035(5)
H(2)	8c	0.606(3)	0.369(1)	0.930(1)	0.026(5)
H(3)	8c	0.503(3)	0.226(1)	0.864(1)	0.027(5)
H(4)	8c	0.511(3)	0.210(1)	0.706(1)	0.026(5)
H(6A)	8c	0.709(3)	0.379(2)	0.552(2)	0.039(6)
H(6B)	8c	0.497(4)	0.360(2)	0.553(2)	0.049(6)
H(6C)	8c	0.629(3)	0.276(2)	0.556(2)	0.046(6)
H(7A)	8c	0.635(3)	0.554(2)	0.882(2)	0.044(6)
H(7B)	8c	0.768(4)	0.562(2)	0.802(2)	0.053(8)
H(7C)	8c	0.828(4)	0.515(2)	0.891(2)	0.043(6)

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Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cl	8*c*	0.74970(4)	0.08380(2)	0.59740(2)	0.0226(2)	0.0174(2)	0.0169(2)	0.00014(9)	–0.0005(1)	0.00284(9)
N	8*c*	0.6572(2)	0.41994(7)	0.72041(7)	0.0164(4)	0.0144(4)	0.0134(4)	0.0009(3)	–0.0005(3)	0.0006(3)
C(1)	8*c*	0.6625(2)	0.43244(8)	0.81267(8)	0.0142(5)	0.0178(5)	0.0135(5)	0.0011(4)	–0.0008(4)	–0.0009(4)
C(2)	8*c*	0.6045(2)	0.35946(9)	0.86908(9)	0.0189(5)	0.0226(6)	0.0140(5)	–0.0008(4)	0.0008(4)	0.0014(4)
C(3)	8*c*	0.5446(2)	0.27613(9)	0.82922(9)	0.0181(5)	0.0199(5)	0.0205(5)	–0.0012(4)	0.0015(4)	0.0041(4)
C(4)	8*c*	0.5441(2)	0.26581(9)	0.73416(9)	0.0187(5)	0.0156(5)	0.0202(5)	–0.0009(4)	–0.0015(4)	–0.0008(4)
C(5)	8*c*	0.6014(2)	0.33965(8)	0.67891(8)	0.0160(5)	0.0162(5)	0.0150(5)	0.0022(4)	–0.0024(4)	–0.0010(4)
C(6)	8*c*	0.6066(2)	0.3360(1)	0.57613(9)	0.0297(7)	0.0223(6)	0.0142(5)	0.0035(5)	–0.0033(5)	–0.0025(4)
C(7)	8*c*	0.7297(2)	0.5244(1)	0.8485(1)	0.0217(6)	0.0192(5)	0.0198(6)	–0.0015(4)	–0.0016(4)	–0.0043(4)

References

1. Bellesia, F.; De Buyck, L.; Ghelfi, F.; Libertini, E.; Pagnoni, U. M.; Roncaglia, F.: 2,2-Dichlorination of Aldehydes with the 2,6-Lutidine · $HCl/Cl_2/CH_2Cl_2$ System: an Environmentally Benign Process Suitable for Scale Up. Tetrahedron **56** (2000) 7507-7511.
2. Grönberg, K. L. C.; Henderson, R. A.; Oglieve, K. E.: A unified mechanism for stoichiometric reduction of H^+ and C_2H_2 by $[Fe_4S_4(SPh)_4]^{3+}$ in MeCN. J. Chem. Soc., Dalton Trans. (1998) 3093-3104.
3. Brooks, G. T.: Chlorinated Insecticides: Technology and Application. CRC Press, Cleveland 1976.
4. Jin, Z. M.; Pan, Y. L.; Xu, D. J.; Xu, Y. Z.: Crystal structure of 2,6-dimethylpyridinium hydrogen phthalate. J. Chem. Crystallogr. **30** (2000) 119-122.
5. Pan, Y. J.; Jin, Z. M.; Sun, C. R.; Jiang, C. W.: Crystal Structure of 2,6-Dimethylpyridinium Hydrogen Fumarate: Hydrogen Bonds of $C(sp^3)$–H···O, $C(sp^2)$–H···O and N^+–H···$O^-(sp^3)$. Chem. Lett. **10** (2001) 1008-1009.
6. Jin, Z. M.; Li, Z. G.; Li, M. C.; Hu, M. L.; Shen, L.: 2,6-Dimethylpyridinium nitrate. Acta Crystallogr. E**59** (2003) o903-o904.
7. Sheldrick, G. M.: SHELXTL. Structure Determination Software Suite. V. 6.14. Bruker AXS, Madison, USA 2000.
8. Dowty, E.: ATOMS for Windows and Macintosh. V 6.1. Shape Software, Kingsport, Tennessee, USA 2002.