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Structure of 2-(2-Hydroxyethyl)-1-(2-pyridyl)imidazo[1,5-*a*]pyridinium Perchlorate

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Abstract. $C_{14}H_{14}N_3O^+.ClO_4^-$, $M_r = 339\cdot7$, monoclinic, $P2_1/n$, $a = 10\cdot781\ (3)$, $b = 17\cdot519\ (6)$, $c = 8\cdot155\ (3)$ Å, $\beta = 105\cdot08\ (3)°$, $V = 1487\cdot1\ (9)$ Å^3, $Z = 4$, $D_m = 1\cdot52$, $D_x = 1\cdot52$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0\cdot71069$ Å, $\mu = 2\cdot83$ cm^{-1}, $F(000) = 704$, room temperature, $R = 0\cdot053$ for 1804 observed reflections. X-ray and NMR data indicate bond localization in the imidazo[1,5-*a*]pyridinium ring system. The angle between the mean planes of the fused ring system and the pyridine ring is 43·2°. There is no indication of hydrogen bonding involving either the hydroxyl group or the perchlorate anion.

Introduction. Crystals of the title compound (1) were isolated from an attempt to prepare the Schiff-base *N*-(2-hydroxyethyl)-2-pyridinemethanimine by condensation of 2-pyridinecarbaldehyde and ethanolamine in the presence of manganese(II) perchlorate. Although the imidazo[1,5-*a*]pyridine ring system is known (Montgomery & Secrist, 1984), a 1,2-disubstituted quaternary salt has not been characterized previously. The ^{1}H NMR spectrum of the compound shows some unusual features which can be related to the structure of the salt.

Experimental. 2-Pyridinecarbaldehyde (9·3 mmol) dissolved in ethanol (20 ml) was slowly added to a refluxing ethanolic solution of ethanolamine (9·5 mmol in 30 ml), $Mn(ClO_4)_2.6H_2O$ (9·4 mmol) in ethanol (20 ml) was added and refluxing continued for 2·5 h. On cooling and evaporation of solvent a crystalline product was obtained. Recrystallization from methanol by ether diffusion yielded colourless crystals.

Crystal density was measured by flotation in $CHCl_3/CCl_4$. A triangular prism approximately 0·45 × 0·45 × 0·60 × 0·20 mm was used for data collection on a Nicolet *R*3*m* four-circle diffractometer. Lattice parameters determined from 18 reflections with $24 < 2\theta < 36°$, ω-scan data collection with $4 < 2\theta < 50°$, index ranges h 0/13, k 0/21, $l \pm 10$. Standard reflections (and intensity variations) 004, 080, 600 (0·3%) monitored every 100 measurements; 2859 reflections measured, 2611 unique reflections, R_{int} 0·019, 1804 observed reflections $[I > 3\sigma(I)]$. Corrections were applied for Lorentz and polarization effects but not for absorption.

The structure was solved from a Patterson calculation and refined on $|F|$ by blocked-cascade least-squares methods. All non-H atoms were refined anisotropically, H atoms were inserted at calculated positions with isotropic thermal parameters equal to 1·2 times the isotropic equivalent of their carrier atoms. $R = 0\cdot053$, $wR = 0\cdot067$, $g = 0\cdot0004$, $S = 2\cdot33$, 208 parameters. $(\Delta/\sigma)_{\max} = 0\cdot012$. $\Delta\rho_{\min} = 0\cdot38$ e Å^{-3}. Scattering factors from *International Tables for X-ray Crystallography* (1974). All calculations on a Nova 4x computer using *SHELXTL* (Sheldrick, 1984).

^{1}H NMR, d_4-methanol, δ 3·97 [H(1*A*), H(1*B*)]; 4·68 [H(2*A*), H(2*B*)]; 8·53 [H(11)]; 7·20 [H(12)]; 7·38 [H(13)]; 7·91 [H(14)]; 8·35 [H(16)]; 8·95 [H(21)]; 7·75 [H(22)]; 8·20 [H(23)]; 8·12 [H(24)]; ^{13}C NMR, d_4-methanol, δ 53·93 [C(1)]; 61·79 [C(2)]; 124·14 [C(11)]; 119·97 [C(12)]; 126·88 [C(13)]; 119·84 [C(14)]; 116·46 [C(16)]; 152·70 [C(21)]; 128·04 [C(22)]; 139·87 [C(23)]; 128·68 [C(24)].

Discussion. Final atom coordinates are listed in Table 1, bond distances and angles are given in Table 2.* Fig. 1 shows a perspective view of the cation and includes the atom labelling. Fig. 2 shows the packing of the unit cell. Assignments for the ^{1}H and ^{13}C NMR spectra are given in *Experimental* with the atom numbering as in Fig. 1. The ^{1}H NMR spectrum was assigned using homonuclear decoupling experiments and the ^{13}C NMR spectrum was unambiguously assigned by ^{1}H–^{13}C heteronuclear two-dimensional correlation spectroscopy.

A possible route for the cyclization, based on those observed for similar compounds (Montgomery & Secrist, 1984), is shown in the Scheme. The bond lengths show that the imidazo[1,5-*a*]pyridinium ring is not aromatic; double bonds are localized at C(11)—C(12) and C(13)—C(14) [1·326 (6) and 1·330 (6) Å respectively]. This is also evident from the ^3J coupling constants shown (in Hz) in the Scheme. The double-bond localization indicates that the positive charge

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44449 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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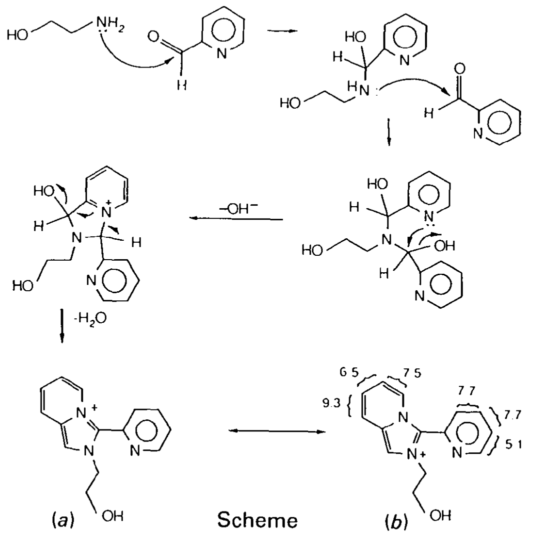
Table 1. *Atom coordinates* (× 10^4) *and equivalent isotropic temperature factors* (Å^2 × 10^3)

	x	y	z	U_{eq}*
N(11)	2689 (2)	4165 (2)	457 (4)	38 (1)
C(11)	3039 (3)	3466 (2)	1265 (4)	44 (1)
C(12)	2606 (4)	3285 (2)	2595 (5)	51 (1)
C(13)	1817 (4)	3795 (2)	3236 (5)	54 (1)
C(14)	1478 (3)	4469 (2)	2507 (5)	50 (1)
C(15)	1911 (3)	4683 (2)	1059 (4)	42 (1)
C(16)	1771 (3)	5302 (2)	4 (5)	45 (1)
N(21)	4655 (3)	4560 (2)	−2341 (4)	55 (1)
C(21)	5392 (4)	4225 (3)	−3213 (5)	66 (2)
C(22)	5332 (4)	3465 (3)	−3660 (5)	65 (2)
C(23)	4429 (4)	3022 (3)	−3227 (5)	57 (2)
C(24)	3630 (3)	3343 (2)	−2358 (4)	47 (1)
C(25)	3790 (3)	4106 (2)	−1912 (4)	42 (1)
C(26)	3000 (3)	4470 (2)	−907 (4)	39 (1)
N(1)	2427 (3)	5155 (2)	−1162 (4)	42 (1)
C(1)	2394 (4)	5676 (2)	−2610 (5)	54 (1)
C(2)	3363 (4)	6303 (2)	−2141 (6)	63 (2)
O(1)	3070 (3)	6760 (2)	−884 (4)	75 (1)
Cl	213 (1)	6557 (1)	3198 (1)	45 (1)
O(11)	1525 (3)	6419 (2)	3395 (4)	83 (1)
O(12)	89 (3)	7087 (2)	4487 (4)	77 (1)
O(13)	−429 (3)	5870 (2)	3415 (4)	71 (1)
O(14)	−339 (4)	6877 (3)	1599 (4)	120 (2)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

resides in the imidazo[1,5-*a*]pyridinium ring which can exist in the two resonance forms (*a*) and (*b*) (Scheme). Similar ring-closure products have been reported for other 2-substituted pyridines with α-amino substituents but these were not isolated as salts. Formation of an ionic compound in this case is likely to be due to the poor leaving ability of the hydroxyethyl substituent.



Scheme

The angle between the mean planes of the imidazo[1,5-*a*]pyridinium ring and the pyridine ring is 43·2°. There is no indication of hydrogen bonding involving either the hydroxyl group or the perchlorate anion.

We are grateful to Dr Peter J. Steel for his assistance with NMR spectroscopy.

Table 2. *Bond lengths* (Å) *and angles* (°)

N(11)–C(11)	1·396 (4)	N(11)–C(15)	1·407 (5)
N(11)–C(26)	1·352 (5)	C(11)–C(12)	1·326 (6)
C(12)–C(13)	1·424 (6)	C(13)–C(14)	1·330 (6)
C(14)–C(15)	1·428 (6)	C(15)–C(16)	1·368 (5)
C(16)–N(1)	1·349 (5)	N(21)–C(21)	1·332 (6)
N(21)–C(25)	1·339 (5)	C(21)–C(22)	1·379 (7)
C(22)–C(23)	1·361 (6)	C(23)–C(24)	1·370 (6)
C(24)–C(25)	1·385 (5)	C(25)–C(26)	1·473 (5)
C(26)–N(1)	1·342 (4)	N(1)–C(1)	1·484 (5)
C(1)–C(2)	1·496 (6)	C(2)–O(1)	1·399 (6)
Cl–O(11)	1·402 (3)	Cl–O(12)	1·435 (3)
Cl–O(13)	1·422 (3)	Cl–O(14)	1·402 (4)
C(11)–N(11)–C(15)	120·9 (3)	C(1)–N(11)–C(26)	129·8 (3)
C(15)–N(11)–C(26)	109·3 (3)	N(11)–C(11)–C(12)	119·1 (3)
C(11)–C(12)–C(13)	121·4 (4)	C(12)–C(13)–C(14)	121·0 (4)
C(13)–C(14)–C(15)	119·4 (4)	N(11)–C(15)–C(14)	118·2 (3)
N(11)–C(15)–C(16)	105·6 (3)	C(14)–C(15)–C(16)	136·1 (4)
C(15)–C(16)–N(1)	107·5 (3)	C(21)–N(21)–C(25)	115·5 (4)
N(21)–C(21)–C(22)	124·9 (4)	C(21)–C(22)–C(23)	118·1 (4)
C(22)–C(23)–C(24)	119·2 (4)	C(23)–C(24)–C(25)	118·7 (4)
N(21)–C(25)–C(24)	123·6 (4)	N(21)–C(25)–C(26)	115·5 (3)
C(24)–C(25)–C(26)	120·9 (3)	N(11)–C(26)–C(25)	126·1 (3)
N(11)–C(26)–N(1)	106·2 (3)	C(25)–C(26)–N(1)	127·6 (3)
C(16)–N(1)–C(26)	111·4 (3)	C(16)–N(1)–C(1)	122·4 (3)
C(26)–N(1)–C(1)	126·0 (3)	N(1)–C(1)–C(2)	112·2 (3)
C(1)–C(2)–O(1)	109·4 (4)	O(11)–Cl–O(12)	108·2 (2)
O(11)–Cl–O(13)	110·4 (2)	O(12)–Cl–O(13)	108·3 (2)
O(11)–Cl–O(14)	110·3 (2)	O(12)–Cl–O(14)	109·0 (2)
O(13)–Cl–O(14)	110·6 (2)		

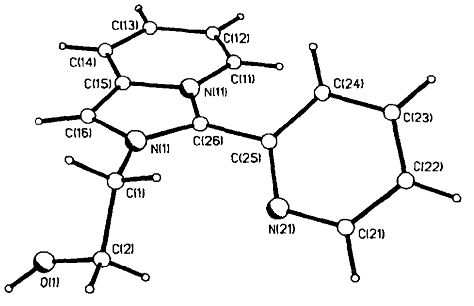


Fig. 1. Perspective view of the cation.

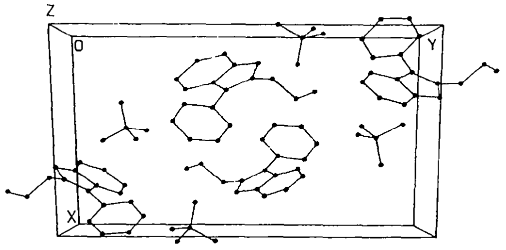


Fig. 2. Unit-cell packing diagram.

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