

Victor B. Rybakov,<sup>a\*</sup> Eugene V. Babaev,<sup>a</sup> Eduard J. Sonneveld,<sup>b</sup> Sergei G. Zhukov<sup>a</sup> and Vladimir V. Chernyshev<sup>a</sup>

<sup>a</sup>Department of Chemistry, Moscow State University, 119992 Moscow, Russian Federation, and <sup>b</sup>Laboratory of Crystallography, University of Amsterdam, Nieuwe Achtergracht, 166 Amsterdam, 1018 WV, The Netherlands

Correspondence e-mail: rybakov20021@yandex.ru

#### Key indicators

Powder X-ray study  
 T = 295 K  
 Mean  $\sigma(\text{C}-\text{C}) = 0.043 \text{ \AA}$   
 R factor = 0.000  
 wR factor = 0.000  
 Data-to-parameter ratio = 0.0

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

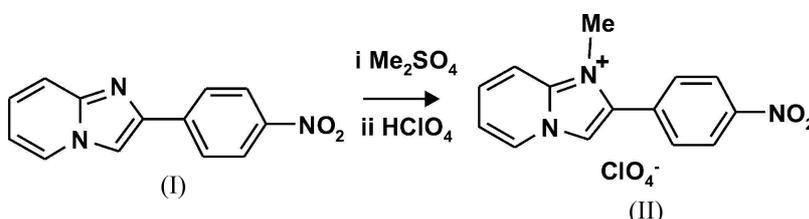
## 1-Methyl-2-(4-nitrophenyl)imidazo[1,2-a]pyridinium perchlorate: a powder study

The title compound,  $\text{C}_{14}\text{H}_{12}\text{N}_3\text{O}_2^+ \cdot \text{ClO}_4^-$ , crystallizes with two cations and two anions in the asymmetric unit,  $Z' = 2$ . All bond lengths and angles show normal values. Short intermolecular O(perchlorate)  $\cdots$  N(imidazole) contacts of 2.94 (3) and 2.95 (3)  $\text{Å}$ , respectively, indicate the principal location of positive charge near the imidazole N atom in both independent cations. The crystal packing is stabilized by weak intermolecular C—H  $\cdots$  O hydrogen bonds.

Received 9 March 2007  
 Accepted 15 March 2007

#### Comment

In continuation of a structural study of imidazo[1,2-a]pyridinium salts (Pointer *et al.*, 1986; Tafeenko *et al.*, 1996), we present here the crystal structure of the title compound, (II), determined from powder diffraction data.



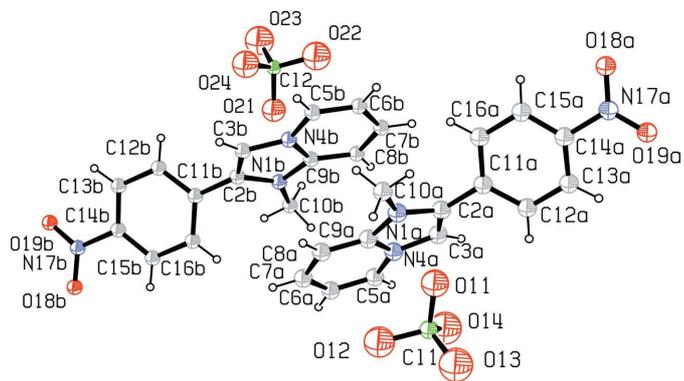
In compound (II) (Fig. 1), all bond lengths and angles show normal values (Allen *et al.*, 1987). The asymmetric unit consists of two cations and two anions. The mean planes of the bicyclic fragment and the benzene ring in the two independent cations make dihedral angles of 50.7 (9) and 53.2 (9)°, which are in agreement with those observed in 1-methyl-2-phenyl-3-hydroxymethyl-imidazo[1,2-a]pyridinium chloride (51.4°; Pointer *et al.*, 1986), 1-methyl-2-phenyl-imidazo[1,2-a]pyridinium iodide (59.4°; Tafeenko *et al.*, 1996) and 1-methyl-2-phenyl-6-nitroimidazo[1,2-a]pyridinium iodide (39.8°; Tafeenko *et al.*, 1996).

Short intermolecular anion–cation contacts  $\text{O11} \cdots \text{N1A} = 2.94 (3) \text{ \AA}$  and  $\text{O21} \cdots \text{N1B} = 2.95 (3) \text{ \AA}$ , indicate that the principal location of positive charge is near the imidazole N atom in both independent cations.

The crystal packing is stabilized by weak intermolecular C—H  $\cdots$  O hydrogen bonds (Table 1).

#### Experimental

The title compound was synthesized as described by Babaev & Goncharenko (1998*a,b*) (see scheme) and recrystallized from a solution in a  $\text{C}_2\text{H}_5\text{OH}-\text{H}_2\text{O}$  mixture (1:1 *v/v*).



**Figure 1**  
The asymmetric unit of (II), showing the atom-labelling scheme. Displacement spheres are drawn at the 50% probability level.

#### Crystal data

$C_{14}H_{12}N_3O_2^+ \cdot ClO_4^-$   
 $M_r = 353.72$   
 Orthorhombic,  $Pbca$   
 $a = 31.393$  (18) Å  
 $b = 25.527$  (17) Å  
 $c = 7.800$  (5) Å  
 $V = 6251$  (7) Å<sup>3</sup>  
 $Z = 16$   
 Cu  $K\alpha_1$  radiation

$\lambda = 1.54059$  Å  
 $\mu = 2.52$  mm<sup>-1</sup>  
 $T = 295$  (2) K  
 Specimen shape: flat sheet  
 $7 \times 7 \times 1.5$  mm  
 Specimen prepared at 293 K  
 Particle morphology: plate,  
 yellowish-brown

#### Data collection

Enraf-Nonius Guinier Johansson camera FR 552 diffractometer  
 Specimen mounting: pressed as a thin layer in the specimen holder of the camera

Specimen mounted in transmission mode  
 Scan method: fixed  
 Absorption correction: none  
 $2\theta_{\min} = 4.0$ ,  $2\theta_{\max} = 82.8^\circ$   
 Increment in  $2\theta = 0.01^\circ$

#### Refinement

$R_p = 0.049$   
 $R_{wp} = 0.063$   
 $R_{exp} = 0.030$   
 $R_B = 0.043$   
 $S = 2.11$   
 Excluded region(s): 4.04–4.99°  
 Profile function: split-type pseudo-Voigt (Toraya, 1986)  
 2079 reflections

156 parameters  
 220 restraints  
 H-atom parameters constrained  
 Preferred orientation correction: March–Dollase (Dollase, 1986); direction of preferred orientation (001), texture parameter  $r = 0.93$ (2)

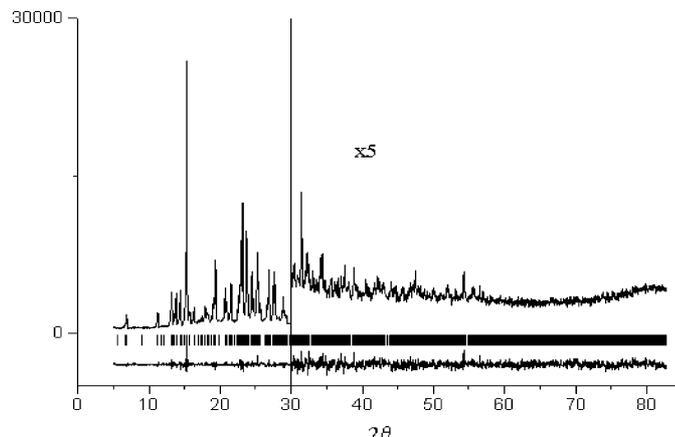
**Table 1**

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$C3A-H3A \cdots O13^i$	0.93	2.37	3.18 (3)	145
$C3B-H3B \cdots O23^{ii}$	0.93	2.26	2.99 (3)	135
$C3B-H3B \cdots O18A^{iii}$	0.93	2.48	3.29 (4)	145
$C6A-H6A \cdots O12^{iv}$	0.93	2.17	2.99 (4)	146
$C7A-H7A \cdots O19B^v$	0.93	2.29	3.17 (3)	157
$C15A-H15A \cdots O24^{vi}$	0.93	2.46	3.08 (4)	124

Symmetry codes: (i)  $x, y, z - 1$ ; (ii)  $x, y, z + 1$ ; (iii)  $-x + 1, y - \frac{1}{2}, -z + \frac{3}{2}$ ; (iv)  $-x + \frac{3}{2}, -y + 1, z - \frac{1}{2}$ ; (v)  $x, -y + \frac{1}{2}, z + \frac{1}{2}$ ; (vi)  $-x + 1, -y + 1, -z + 1$ .

During the exposure, the specimen was spun in its plane to improve particle statistics. The orthorhombic unit-cell dimensions were determined from a Guinier photograph using the indexing



**Figure 2**  
The Rietveld plot, showing the observed and difference profiles for (II). The reflection positions are shown above the difference profile.

program *ITO* (Visser, 1969) and refined using the program *LSPAID* (Visser, 1986) to  $M_{20} = 39$  and  $F_{30} = 75$  (0.009, 53) using the first 50 peak positions. The space group  $Pbca$  was chosen on the basis of systematic extinction rules and confirmed later by the crystal structure solution. Intensities for the structure determination and refinement were measured from the Guinier photographs in  $0.01^\circ$  steps using a Johansson LS18 line scanner. The structure of (II) was solved by the simulated annealing procedure (Zhukov *et al.*, 2001) following the methodology described in detail elsewhere (Chernyshev, 2004). The initial geometry of the cation was optimized by density functional theory calculations performed with the *PRIRODA* program (Laikov, 1997) employing the B3LYP exchange-correlation function (Becke, 1998; Lee *et al.*, 1988). For the representation of the Kohn–Sham one-electron wave functions, the sets of contracted Gaussian-type functions were used. The contracted patterns were (311/1) for H and (611111/411/11) for C, N and O. Geometry optimization was performed using the quasi-Newton method to a final gradient of  $3 \times 10^{-5}$  Hartree Å<sup>-1</sup>. Simulated annealing was used in a search of possible solutions, varying 24 degrees of freedom for the four rigid units, namely two cations and two perchlorate anions. A unique solution was found and subjected to subsequent bond-restrained Rietveld refinement using the program *MRIA* (Zlokazov & Chernyshev, 1992) using a split-type pseudo-Voigt peak profile function (Toraya, 1986) and taking into account anisotropic line-broadening (Popa, 1998). The strength of the restraints was a function of interatomic separation and, for intramolecular bond lengths, corresponds to an r.m.s. deviation of 0.03 Å. Additional restraints were applied to the planarity of three fragments in cations *A* and *B*, namely the bicyclic system, the benzene ring and C14/N17/O18/O19. All atoms in the perchlorate anions were refined isotropically, and two overall  $U_{iso}$  parameters were refined for cations *A* and *B*, respectively. All H atoms were placed in geometrically calculated positions ( $C-H = 0.93-0.96$  Å) and allowed to ride on their parent atoms with  $U_{iso}(H)$  fixed to  $0.05$  Å<sup>2</sup>. The March–Dollase texture formalism (Dollase, 1986), with (001) as the direction of preferred orientation and texture parameter  $r$  refined to 0.93 (2), was applied for (II). The diffraction profiles and the differences between the measured and calculated profiles are shown in Fig. 2.

Data collection: local program; cell refinement: local program; data reduction: local program; program(s) used to solve structure: *MRIA* (Zlokazov & Chernyshev, 1992); program(s) used to refine structure: *MRIA*; molecular graphics: *ORTEP-3* (Farrugia, 1997);

software used to prepare material for publication: *MRIA* and *SHELXL97* (Sheldrick, 1997).

This work was supported by ICDD Grant-in-Aid No. 00–16.

## References

- Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
- Babaev, E. V. & Goncharenko, L. V. (1998a). *Pharm. Chem. J.* **32**, 310–314.
- Babaev, E. V. & Goncharenko, L. V. (1998b). *Khim. Farm. Zh.* **6**, 24–28. (In Russian).
- Becke, A. D. (1988). *Phys. Rev. A*, **38**, 3098–3100.
- Chernyshev, V. V. (2004). *IUCr Commission on Powder Diffraction Newsletter*, **31**, 5–15.
- Dollase, W. A. (1986). *J. Appl. Cryst.* **19**, 267–272.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Laikov, D. N. (1997). *Chem. Phys. Lett.* **281**, 151–156.
- Lee, C. T., Yang, W. T. & Parr, R. G. (1988). *Phys. Rev. B*, **37**, 785–789.
- Pointer, D. J., Wilford, J. B., Hursthouse, M. B. & Walker, N. P. C. (1986). *J. Chem. Soc. Perkin Trans. 2*, pp. 443–446.
- Popa, N. C. (1998). *J. Appl. Cryst.* **31**, 176–180.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Tafeenko, V. A., Paseshnichenko, K. A. & Schenk, H. (1996). *Z. Kristallogr.* **211**, 457–463.
- Toraya, H. (1986). *J. Appl. Cryst.* **19**, 440–447.
- Visser, J. W. (1969). *J. Appl. Cryst.* **2**, 89–95.
- Visser, J. W. (1986). *Powder Diffr.* **1**, 66–76.
- Zhukov, S. G., Chernyshev, V. V., Babaev, E. V., Sonneveld, E. J. & Schenk, H. (2001). *Z. Kristallogr.* **216**, 5–9.
- Zlokazov, V. B. & Chernyshev, V. V. (1992). *J. Appl. Cryst.* **25**, 447–451.