Sheldrick, G. M. (1997). *SHELXL97. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.
Stoe & Cie (1992*a*). *EMPIR. Empirical Absorption Correction Program.* Version 1.03. Stoe & Cie, Darmstadt, Germany.
Stoe & Cie (1992*b*). *DIF4. Diffractometer Control Program.* Version 7.09. Stoe & Cie, Darmstadt, Germany.
Stoe & Cie (1992*c*). *REDU4. Data Reduction Program.* Version 7.03. Stoe & Cie, Darmstadt, Germany.

Acta Cryst. (1999). C**55**, 1325–1328

2-Aminobenzimidazolium nitrate at 152 K, a triclinic crystal structure with pronounced local pseudo-symmetry

JAN W. BATS,[a] DIRK GÖRDES[b] AND HANS-GÜNTHER SCHMALZ[b]

[a]*Institut für Organische Chemie, Universität Frankfurt, Marie-Curie-Straße 11, D-60439 Frankfurt am Main, Germany, and* [b]*Institut für Organische Chemie der Technischen Universität Berlin, Straße des 17. Juni 135, D-10623 Berlin, Germany. E-mail: bats@indy2.org.chemie.uni-frankfurt.de*

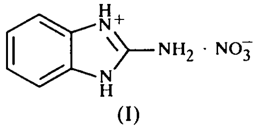
(*Received 11 February 1999; accepted 30 March 1999*)

Abstract

The crystal structure of the title compound, $C_7H_8N_3^+\cdot NO_3^-$, contains four independent molecules. Molecules 1 and 2 are related by local pseudo $2_1/b$ symmetry (*a* axis unique). Molecules 3 and 4 are related by a local pseudo $2_1/a$ symmetry (*b* axis unique). The layer containing molecules 1 and 2 can be transformed to the layer containing molecules 3 and 4 by a rotation of 90° about a local axis perpendicular to the (001) plane plus a translation of *c*/2. The cations and anions are connected by hydrogen bonding to form flat ribbons.

Comment

The structure determination of the title compound, (I), is part of our study of possible hydrogen-bonding arrangements in guanidinium nitrate complexes (Schellhaas *et al.*, 1998). No other crystal structure containing a 2-aminobenzimidazolium group has been reported so far.



(I)

The asymmetric unit of (I) contains four independent molecules. The four aminobenzimidazole groups are almost planar. Individual atoms deviate less than 0.02 Å from the best plane through each group. The four independent nitrate groups are perfectly planar. The C—N_{amino} distances range from 1.309 (2) to 1.314 (2) Å and are slightly shorter than the adjacent C—N bonds in the imidazolium rings which range from 1.342 (2) to 1.348 (2) Å. Each cation donates four hydrogen bonds to three different nitrate groups. Each nitrate group accepts four hydrogen bonds from three different cations. The hydrogen bonding results in flat ribbon structures similar to those found in the crystal structure of *rac*-ptilocaulin nitrate (Schellhaas *et al.*, 1998). The ribbon containing molecules 1 and 2 (Fig. 1) connects these molecules in the crystallographic *a* direction. Adjacent parallel ribbons are related by crystallographic inversion centers to the stacks. Some O···O, O···N, O···C and N···C distances between adjacent ribbons are only 0.1 Å longer than the van der Waals contact distances. There are no short C···C contacts between adjacent ribbons. Thus $\pi\cdots\pi$ interactions in the stacks are not important.

The ribbon containing molecules 3 and 4 (Fig. 2) connects these molecules in the crystallographic *b* direction. Adjacent parallel ribbons are again related by crystallographic inversion centers. Similar stacks are observed as for molecules 1 and 2. Neighboring stacks are connected by benzene···benzene interactions (Fig. 3). These benzene groups show T-shaped arrangements. This has been shown to result in favorable electrostatic interactions (Koch & Egert, 1995).

The crystal structure of the title compound shows very pronounced pseudo-symmetry. A method to locate pseudo-symmetry elements in crystal structures has been described by Kálmán & Argay (1998). The pseudo-symmetry is best visualized using an orthogonal axes system which is approximately obtained by the axes transformation: $\mathbf{a}' = \mathbf{a}$, $\mathbf{b}' = \mathbf{b}$, $\mathbf{c}' = -[(c/a)\cos\beta]\mathbf{a} - [(c/b)\cos\alpha]\mathbf{b} + \mathbf{c}$. Then the fractional coordinates transform according to: $x' = x + [(c/a)\cos\beta]z$, $y' = y + [(c/b)\cos\alpha]z$, $z' = z$. After choosing the appropriate origin, molecule 2 can be transformed to molecule 1 by the pseudo-relation: $x_2 \simeq 0.50 - x_1$, $y_2 \simeq 0.50 + y_1$, $z_2 \simeq z_1$. This is a pseudo-glide plane perpendicular to the *a* axis with a translation of *b*/2 (*b*-glide). If this pseudo-glide plane is combined with the crystallographic inversion center at (0, 0, $\frac{1}{2}$) a new pseudo-symmetry relation is obtained (relation: $x_2 \simeq x_1 + 0.50$, $y_2 \simeq 0.50 - y_1$, $z_2 \simeq 1 - z_1$) which corresponds to a pseudo-screw axis in the crystallographic *a* direction. It is this pseudo-2_1-screw axis which connects the molecules within the hydrogen-bonded ribbon. Thus the layer containing molecules 1 and 2 has a pseudo-monoclinic structure belonging to structural class $P_{\bar{1}(XY)}$ $2_1/b$ $Z = 4(1)$, using the notation of Zorky (1996). Molecule 4 can be transformed to molecule 3 by the pseudo-relation: $x_4 \simeq 0.50 + x_3$, $y_4 \simeq 0.50 - y_3$, $z_4 \simeq z_3$. This is a pseudo-glide plane

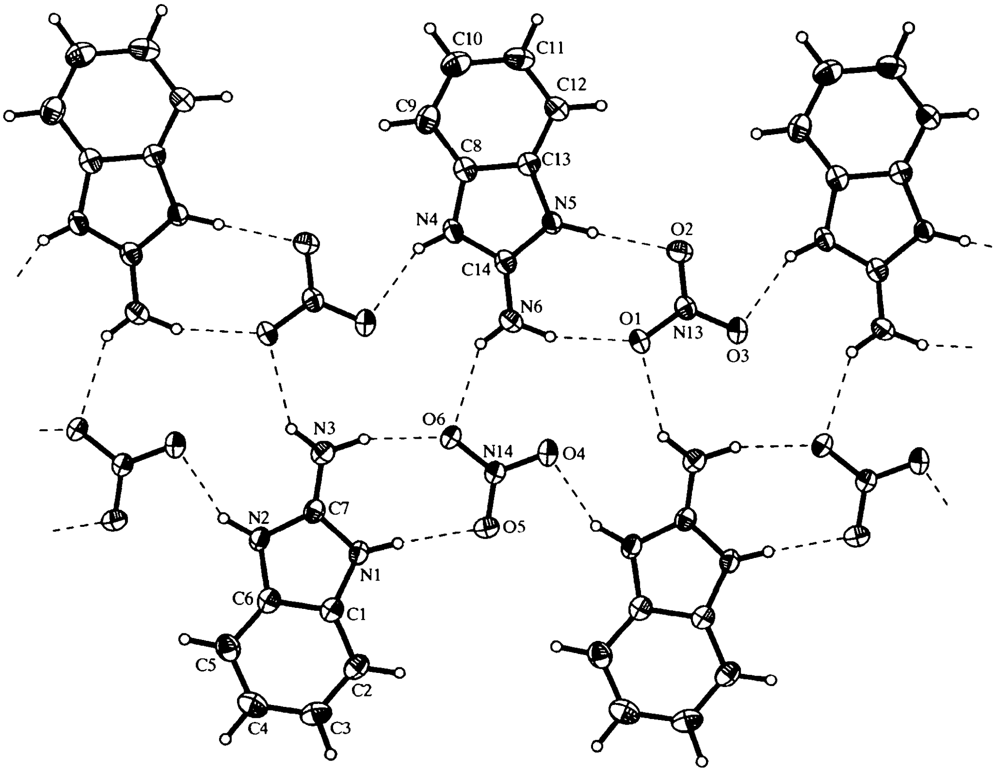


Fig. 1. The hydrogen-bonded ribbon formed by molecules 1 and 2 of (I) with 50% probability displacement ellipsoids.

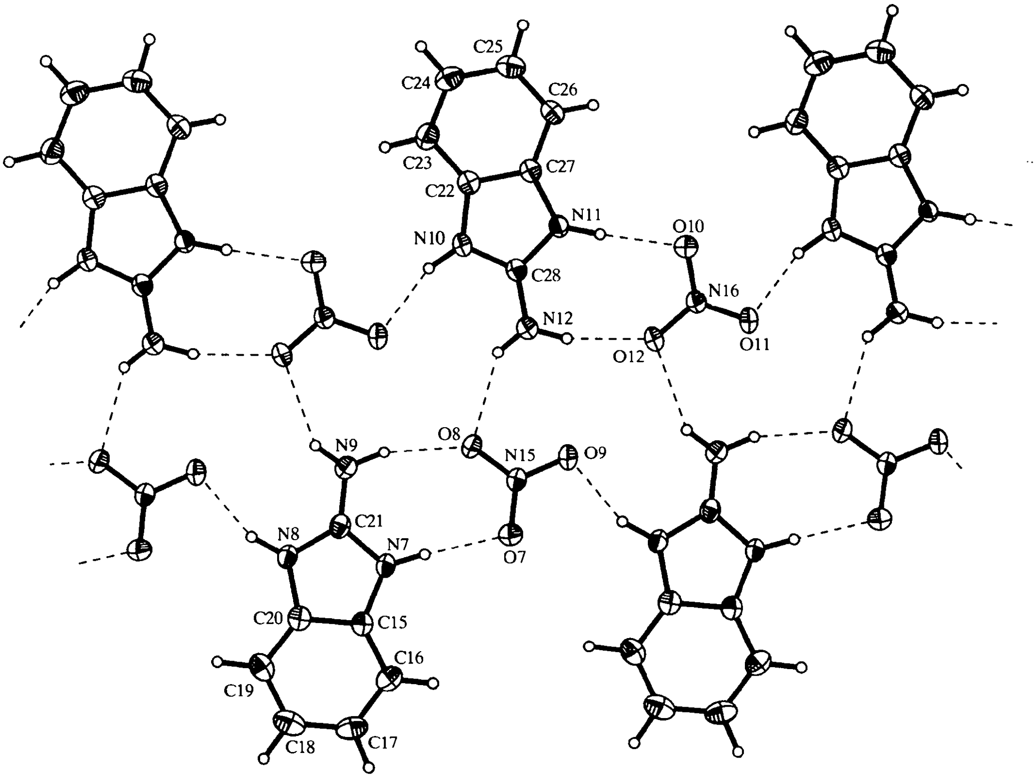


Fig. 2. The hydrogen-bonded ribbon formed by molecules 3 and 4 of (I) with 50% probability displacement ellipsoids.

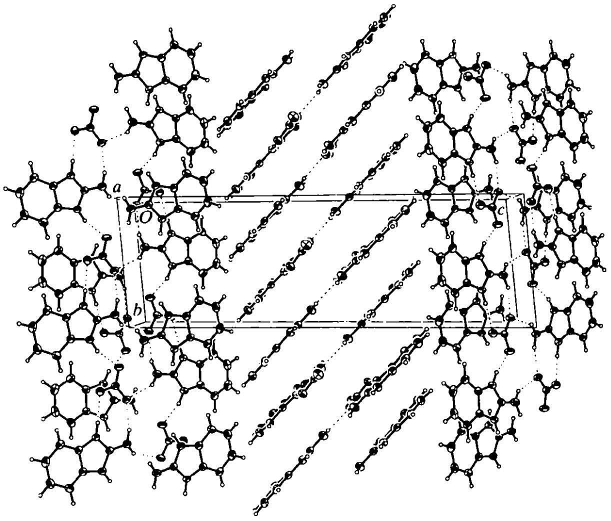


Fig. 3. The crystal packing of (I) shown down the *a* axis.

perpendicular to the *b* axis with a translation of *a*/2 (*a*-glide). Combination of this glide plane with the crystallographic inversion center at (0, 0, 0) results in a pseudo-2_1-screw axis in the crystallographic *b* direction which connects molecules 3 and 4 along the hydrogen-bonded ribbon. Thus the layer containing molecules 3 and 4 has a pseudo-monoclinic structure belonging to structural class $P_{l(XY)}$ $2_1/a$ $Z = 4(1)$.

The molecules in the hydrogen-bonded ribbons found in the crystal structure of *rac*-ptilocaulin nitrate are connected by true crystallographic screw axes. Similar local pseudo-symmetry has also been observed in other layered structures (Bats, Grundl & Hashmi, 1999; Bats, Öhlinger & Mulzer, 1999). In the present case, however, an additional unusual pseudo-transformation is present: molecules 1 and 2 can also be transformed to molecules 3 and 4 by the approximate relation: $x_1 \simeq 0.16 - y_3$, $y_1 \simeq -0.35 + x_3$, $z_1 \simeq 0.50 + z_3$. Thus the layer containing molecules 1 and 2 can be transformed to the layer containing molecules 3 and 4 by a 90° rotation about a local axis perpendicular to the (001) plane followed by a translation about $c'/2$. This rotation axis does not pass through the origin. Thus an offset in the *x* and *y* values ($\Delta x = 0.16$, $\Delta y = 0.15$) is obtained between neighboring layers resulting in the triclinic shape of the unit cell with the angles α and β considerably different from 90°. This pseudo-rotation can further be combined with the pseudo-glide symmetry of the structure to an additional pseudo-relationship: $x_1 \simeq 0.66 + y_4$, $y_1 \simeq 0.15 + x_4$, $z_1 \simeq 0.50 + z_4$. This operation corresponds to a local pseudo-glide plane perpendicular to an axis bisecting the *a* and $-b$ axes with a translation of *c*/2. These latter two pseudo-symmetry relations can be combined with the crystallographic inversions centers to two further local pseudo-symmetry transformations: a local $\bar{4}$ axis ($x_1 \simeq 0.16 + y_3'$, $y_1 \simeq -0.35 - x_3'$, $z_1 \simeq 0.50 - z_3'$) and a local pseudo-twofold rotation axis parallel to an axis bisecting the *a* and $-b$ axes ($x_1 \simeq 0.66 - y_4'$, $y_1 \simeq 0.15 - x_4'$, $z_1 \simeq 0.50 - z_4'$).

The crystals show a tendency to twinning as a result of this pseudo-symmetry. The crystal used for the data collection was found to be untwinned. Two additional crystals which were measured, however, turned out to be twinned about the $(1\bar{1}0)$ plane.

Experimental

To a solution of 2-aminobenzimidazole (133 mg, 1 mmol) (Aldrich, 97%) in anhydrous methanol (5 ml) was added 1 *N* aqueous HNO_3 (1 ml, 1 mmol) (Titrisol, Merck). After stirring for 10 min, the solvent was removed *in vacuo* and the residue was recrystallized three times by dissolving the solid in a small amount of boiling anhydrous ethanol and allowing the mixture to slowly cool to room temperature in an oil bath; m.p. 497 K (decomposition). The compound was recrystallized from ethanol.

Crystal data

$C_7H_8N_3^+ \cdot NO_3^-$
$M_r = 196.17$
Triclinic
$P\bar{1}$
$a = 8.1754(9)$ Å
$b = 8.2776(9)$ Å
$c = 25.696(4)$ Å
$\alpha = 84.509(11)°$
$\beta = 84.279(12)°$
$\gamma = 89.941(9)°$
$V = 1722.3(4)$ Å^3
$Z = 8$
$D_x = 1.513$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 243 reflections
$\theta = 3$–$23°$
$\mu = 0.121$ mm^{-1}
$T = 152(2)$ K
Block
0.42 × 0.40 × 0.35 mm
Pale brown

Data collection

Siemens SMART diffractometer
ω scans
Absorption correction: none
18 822 measured reflections
7592 independent reflections
6227 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.052$
$\theta_{\rm max} = 28.89°$
$h = -10 \rightarrow 10$
$k = -10 \rightarrow 11$
$l = -33 \rightarrow 33$
337 standard reflections
frequency: 540 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.104$
$S = 1.675$
7592 reflections
634 parameters
H atoms refined with isotropic displacement parameters
$w = 1/[\sigma^2(F_o^2) + (0.03P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} = 0.013$
$\Delta\rho_{\rm max} = 0.283$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.244$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0058 (10)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	U_{eq}
O1	0.45345 (11)	0.34734 (11)	0.46771 (4)	0.0295 (2)
O3	0.71802 (11)	0.37425 (12)	0.45992 (4)	0.0360 (3)
N13	0.58101 (13)	0.42137 (13)	0.44737 (5)	0.0259 (3)
O2	0.57188 (12)	0.54138 (11)	0.41409 (4)	0.0318 (3)
N5	0.23471 (14)	0.58389 (13)	0.39398 (5)	0.0241 (3)
N4	−0.03208 (14)	0.55287 (14)	0.39738 (5)	0.0272 (3)
N6	0.11014 (17)	0.38727 (15)	0.45794 (5)	0.0318 (3)
C14	0.10383 (16)	0.50091 (16)	0.41909 (6)	0.0248 (3)
C13	0.18101 (16)	0.69372 (15)	0.35482 (6)	0.0240 (3)
C8	0.01059 (17)	0.67478 (16)	0.35729 (6)	0.0263 (3)
C10	0.0014 (2)	0.88218 (19)	0.28813 (7)	0.0374 (4)
C12	0.26427 (18)	0.80605 (17)	0.31859 (6)	0.0294 (3)
C9	−0.08244 (19)	0.76859 (18)	0.32407 (6)	0.0327 (4)
C11	0.1712 (2)	0.90002 (18)	0.28540 (7)	0.0362 (4)
O6	−0.06934 (11)	0.15155 (11)	0.53324 (4)	0.0305 (3)
O4	0.18970 (12)	0.12266 (12)	0.54138 (5)	0.0363 (3)
O5	0.01333 (12)	−0.04191 (11)	0.58753 (4)	0.0320 (3)
N14	0.04474 (13)	0.07695 (13)	0.55388 (5)	0.0252 (3)
N2	−0.59968 (14)	−0.05858 (14)	0.60191 (5)	0.0267 (3)
N1	−0.33583 (15)	−0.08941 (13)	0.60816 (5)	0.0252 (3)
N3	−0.41634 (17)	0.10871 (15)	0.54349 (5)	0.0325 (3)
C1	−0.41704 (17)	−0.20021 (16)	0.64635 (6)	0.0252 (3)
C7	−0.44900 (16)	−0.00627 (15)	0.58188 (6)	0.0246 (3)
C2	−0.35952 (19)	−0.31213 (17)	0.68367 (6)	0.0306 (3)
C6	−0.58499 (17)	−0.18177 (16)	0.64188 (6)	0.0259 (3)
C5	−0.70145 (19)	−0.27753 (18)	0.67314 (6)	0.0321 (3)
C3	−0.4761 (2)	−0.40767 (19)	0.71519 (7)	0.0354 (4)
C4	−0.6438 (2)	−0.39182 (19)	0.70992 (7)	0.0364 (4)
O8	0.64601 (12)	0.04581 (10)	0.03338 (4)	0.0291 (2)
O7	0.45100 (12)	−0.06507 (11)	0.08886 (4)	0.0313 (2)
O9	0.61867 (13)	−0.21529 (11)	0.04423 (4)	0.0344 (3)
N15	0.57109 (14)	−0.07823 (13)	0.05551 (5)	0.0245 (3)
N7	0.40688 (13)	0.26941 (14)	0.10796 (5)	0.0237 (3)
N8	0.44777 (14)	0.53218 (14)	0.10331 (5)	0.0258 (3)
C21	0.49525 (16)	0.39521 (15)	0.08222 (6)	0.0243 (3)
N9	0.60952 (15)	0.38405 (17)	0.04314 (5)	0.0311 (3)
C20	0.32215 (17)	0.49617 (16)	0.14336 (6)	0.0261 (3)
C16	0.17815 (17)	0.25133 (19)	0.18216 (6)	0.0300 (3)
C15	0.29662 (16)	0.32755 (15)	0.14620 (6)	0.0238 (3)
C19	0.22998 (19)	0.59233 (19)	0.17586 (6)	0.0329 (4)
C17	0.08478 (19)	0.3477 (2)	0.21454 (7)	0.0365 (4)
C18	0.1105 (2)	0.5153 (2)	0.21165 (7)	0.0385 (4)
O12	0.84627 (12)	−0.43551 (11)	−0.03187 (4)	0.0296 (2)
O11	0.87556 (12)	−0.69045 (11)	−0.04162 (4)	0.0342 (3)
O10	1.04316 (12)	−0.51490 (11)	−0.08668 (4)	0.0308 (2)
N10	1.04760 (14)	0.09131 (14)	−0.10002 (5)	0.0254 (3)
N11	1.08726 (13)	−0.16853 (14)	−0.10569 (5)	0.0232 (3)
N16	0.92259 (14)	−0.54671 (13)	−0.05341 (5)	0.0243 (3)
N12	0.88922 (15)	−0.09343 (17)	−0.03927 (5)	0.0291 (3)
C28	1.00137 (16)	−0.05875 (15)	−0.07909 (6)	0.0228 (3)
C22	1.16864 (16)	0.07937 (16)	−0.14123 (6)	0.0253 (3)
C26	1.30451 (17)	−0.14076 (18)	−0.18379 (6)	0.0293 (3)
C27	1.19325 (16)	−0.08653 (16)	−0.14554 (6)	0.0236 (3)
C23	1.25799 (19)	0.19591 (18)	−0.17447 (6)	0.0320 (3)
C24	1.3708 (2)	0.1414 (2)	−0.21231 (7)	0.0360 (4)
C25	1.39270 (19)	−0.0240 (2)	−0.21716 (7)	0.0349 (4)

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H01···O5	0.88 (2)	1.99 (2)	2.871 (2)	176 (2)
N2—H02···O4^{i}	0.91 (2)	1.94 (2)	2.778 (2)	154 (2)
N3—H03*A*···O6	0.95 (2)	1.92 (2)	2.842 (2)	162 (2)
N3—H03*B*···O1^{i}	0.88 (2)	2.17 (2)	2.915 (2)	142 (1)
N4—H04···O3^{i}	0.84 (2)	2.02 (2)	2.800 (2)	153 (2)
N5—H05···O2	0.90 (2)	1.97 (2)	2.870 (2)	178 (2)
N6—H06*A*···O1	0.93 (2)	1.96 (2)	2.859 (2)	160 (2)
N6—H06*B*···O6	0.85 (2)	2.17 (2)	2.902 (2)	144 (2)
N7—H07···O7	0.90 (2)	1.97 (2)	2.874 (2)	176 (2)
N8—H08···O9^{ii}	0.91 (2)	1.89 (2)	2.757 (2)	159 (2)
N9—H09*A*···O8	0.92 (2)	1.97 (2)	2.848 (2)	160 (2)
N9—H09*B*···O12^{ii}	0.85 (2)	2.16 (2)	2.899 (2)	146 (2)
N10—H010···O11^{ii}	0.91 (2)	1.87 (2)	2.754 (2)	162 (2)
N11—H011···O10	0.93 (2)	1.95 (2)	2.879 (2)	177 (2)
N12—H12*A*···O8	0.86 (2)	2.16 (2)	2.904 (2)	144 (2)
N12—H12*B*···O12	0.91 (2)	1.96 (2)	2.839 (2)	164 (2)

Symmetry codes: (i) $x - 1, y, z$; (ii) $x, 1 + y, z$.

Data collection: *SMART* (Siemens, 1995). Cell refinement: *SMART*. Data reduction: *SAINT* (Siemens, 1995). Program(s) used to solve structure: *SHELXS* in *SHELXTL* (Sheldrick, 1996). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *XP* in *SHELXTL*. Software used to prepare material for publication: *CIF* in *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1323). Services for accessing these data are described at the back of the journal.

References

Bats, J. W., Grundl, M. A. & Hashmi, A. S. K. (1999). *Acta Cryst.* C**55**, 689–691.

Bats, J. W., Öhlinger, S. H. & Mulzer, J. (1999). *Acta Cryst.* C**55**, 1158–1160.

Kálmán, A. & Argay, G. (1998). *Acta Cryst.* B**54**, 877–888.

Koch, U. & Egert, E. (1995). *J. Comput. Chem.* **16**, 937–944.

Schellhaas, K., Schmalz, H.-G. & Bats, J. W. (1998). *Chem. Eur. J.* **4**, 57–66.

Sheldrick, G. M. (1996). *SHELXTL. Structure Determination Software Programs*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Sheldrick, G. M. (1997). *SHELXL97. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Siemens (1995). *SMART and SAINT. Area-Detector Control and Integration Software*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Zorky, P. M. (1996). *J. Mol. Struct.* **374**, 9–28

Acta Cryst. (1999). C**55**, 1328–1330

N-(2-Pyridinium)urea nitrate[†]

Velichka Velikova, Snejana Bakardjeva and Olyana Angelova

Bulgarian Academy of Sciences, Central Laboratory of Mineralogy and Crystallography, Rakovski Str. 92, 1000 Sofia, Bulgaria. E-mail: srcic@bgcict.acad.bg

(*Received 24 June 1998; accepted 18 January 1999*)

Abstract

The *N*-(2-pyridinium)urea cation of the title compound, $C_6H_8N_3O^+ \cdot NO_3^-$, is planar within 0.044 (2) Å and adopts an *s-cis–s-cis* conformation with respect to the imino C—N bonds. The hydrogen-bonding network results in layers parallel to the (203) plane.

[†] Alternative name: 2-ureidopyridinium nitrate.