# organic papers

Acta Crystallographica Section E Structure Reports Online

ISSN 1600-5368

## Gregory B. Less, Paul G. Rasmussen\* and Jeff W. Kampf

University of Michigan, Department of Chemistry, 930 N. University, Ann Arbor, MI 48109-1055, USA

Correspondence e-mail: pgrasmsn@umich.edu

#### **Key indicators**

Single-crystal X-ray study T = 158 K Mean  $\sigma$ (C–C) = 0.001 Å R factor = 0.032 wR factor = 0.079 Data-to-parameter ratio = 13.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e. 1H-Imidazole-4-carbonitrile

The title compound,  $C_4H_3N_3$ , was synthesized in three steps from diaminomaleonitrile in an overall yield of 38%. Singlecrystal X-ray analysis reveals that the compound crystallizes exclusively as the 1*H*-imidazole-4-carbonitrile isomer. This heterocycle forms a non-centrosymmetric crystal structure and packs with an appreciable dipole moment, making it a good candidate for non-linear optical applications.

#### Comment

Since the first report of 1H-imidazole-4-carbonitrile (Ferris & Trimmer, 1976), several improvements to the synthesis have been published (Leone-Bay & Glaser, 1987; Matthews et al., 1986; Nippon, 2004). In spite of this, the preparative yields for this simple compound remain low and its crystal structure is previously unreported. The molecule has been the subject of theoretical studies concerning isomerism and tautomerism (Catalan et al., 1983; Kurzepa et al., 2001; Raczynska, 1997), and plays an important role as an agricultural (Schering, 1992), a pharmaceutical (Pfizer, 1977; Shikoku, 1987) and a materials intermediate (Shikoku, 1991). Recently, we have shown that 4cyanoimidazolate can act as both a  $\mu$ -bidentate ligand and a monodentate ligand to late-first-row transition metal cations (Less et al., 2004). We now report the structure of the protonated ligand to be 1H-imidazole-4-carbonitrile, (I), at least in this crystalline form.



The crystal structure is dominated by the formation of an N2-H2···N3 hydrogen-bonded chain and  $\pi$ - $\pi$  stacking between the planar rings. The ring-to-ring distance, as measured between planes defined by the three ring C atoms, is 3.358 Å. The N-H···N bond angle is 142 (4)°, indicating a relatively weak hydrogen bond. Non-linearity of hydrogen bonds has been suggested as a reason for reduced intensity of stretching bands in IR spectra (Hofmeister et al., 1999). Indeed, the IR spectrum of 1H-imidazole-4-carbonitrile shows greatly reduced hydrogen bond stretching intensities relative to those seen in imidazole (Bellocq et al., 1965) and other substituted imidazoles (Densmore et al., 2005). The subject of hydrogen bonding in imidazoles remains a topic of interest due to the important role imidazole plays in the histidine residue, and its potential as an active functionality in proton exchange membranes. Additionally, 1H-imidazole-4-carboReceived 16 March 2005 Accepted 6 May 2005 Online 14 May 2005

C 2005 International Union of Crystallography Printed in Great Britain – all rights reserved

977 reflections with  $I > 2\sigma(I)$ 

 $R_{\rm int} = 0.039$ 

 $\theta_{\rm max} = 36.3^{\circ}$ 

 $h = -9 \rightarrow 9$ 

 $k = -6 \rightarrow 6$ 

 $l = -17 \rightarrow 17$ 



#### Figure 1

A view of the title compound with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.



Figure 2

The crystal packing, showing the net dipole formation along the c axis. All nitrile groups point towards the left, while all H-atom substituents point towards the right of this diagram.

nitrile has the potential to be a frequency doubler, as it forms a non-centrosymmetric crystal structure and packs in such a manner as to give rise to a considerable dipole in the solid state.

## **Experimental**

The title compound was synthesized in three steps according to the combined preparations of Ohtsuka (1976), Kim (1992) and Mitsuhashi et al. (1983). Colorless needles of 1H-imidazole-4-carbonitrile were grown by sublimation at 348 K. Additional details are available as supplementary material. The yields in the first two steps were in accord with those previously reported. The third step, the decarboxylation of 4-cyano-5-imidazole carboxylic acid to 1H-imidazole-4-carbonitrile, however, showed a variable yield, often much lower than that reported by Mitsuhashi and co-workers. Thermogravimetric analysis of the acid shows two weight losses below 483 K, the boiling point of the decarboxylation solvent, and neither corresponds to a clean decarboxylation. We postulate that this is due to the competing mechanism of dehydration. In the mass spectrum of the

carboxylic acid, the largest fragment occurs at m/z = 119.0, corresponding to the loss of water.

Crystal data

C <sub>4</sub> H <sub>3</sub> N <sub>3</sub>	$D_{\rm x} = 1.440 {\rm Mg m}^{-3}$
$M_r = 93.09$	Mo $K\alpha$ radiation
Monoclinic, Pc	Cell parameters from 5074
a = 5.7230 (13)  Å	reflections
b = 3.6965(9)Å	$\theta = 4.0-36.3^{\circ}$
c = 10.244 (2) Å	$\mu = 0.10 \text{ mm}^{-1}$
$\beta = 97.689 \ (7)^{\circ}$	T = 158  K
V = 214.76 (8) Å <sup>3</sup>	Needle, colorless
Z = 2	$0.50\times0.10\times0.10~\rm{mm}$
Data collection	

Bruker SMART 1K CCD areadetector diffractometer  $\varphi$  and  $\omega$  scans Absorption correction: multi-scan (SADABS; Sheldrick, 2003)  $T_{\min} = 0.952, T_{\max} = 0.98$ 9453 measured reflections 1011 independent reflections

## Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0589P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.032$	+ 0.0007P]
$vR(F^2) = 0.079$	where $P = (F_o^2 + 2F_c^2)/3$
S = 1.13	$(\Delta/\sigma)_{\rm max} < 0.001$
011 reflections	$\Delta \rho_{\rm max} = 0.39 \text{ e} \text{ Å}^{-3}$
76 parameters	$\Delta \rho_{\rm min} = -0.19 \text{ e } \text{\AA}^{-3}$
All H-atom parameters refined	

## Table 1

Hydrogen-bonding geometry (Å, °).

$D-H\cdots A$	D-H	$H \cdots A$	$D \cdots A$	$D - \mathbf{H} \cdot \cdot \cdot A$
$N2-H2\cdots N3^{i}$	0.828 (19)	2.21 (3)	2.9080 (12)	142 (4)

Symmetry code: (i)  $x, -y, \frac{1}{2} + z$ .

In the absence of significant anomalous scattering effects, Friedel pairs were merged during the refinement. H atoms were located in a difference map and allowed to refine isotropically.

Data collection: SMART (Bruker, 2001); cell refinement: SAINT-Plus (Bruker, 2001); data reduction: SAINT-Plus; program(s) used to solve structure: SHELXTL (Sheldrick, 1997); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

### References

- Bellocq, A. M., Perchard, C., Novak, A. & Josien, M. L. (1965). J. Chim. Phys. 62, 1334-1342.
- Bruker (2001). SMART (Version 5.054) and SAINT-Plus (Version 6.29). Bruker AXS Inc., Madison, Wisconsin, USA.
- Catalan, J., Perez, P. & Elguero, J. (1983). Heterocycles, 20, 1717-1720.
- Densmore, C. G., Rasmussen, P. G. & Goward, G. R. (2005). Macromolecules, 38, 416-421.
- Ferris, J. P. & Trimmer, R. W. (1976). J. Org. Chem. 41, 19-24.
- Hofmeister, A. M., Cynn, H., Burnley, P. C. & Meade, C. (1999). Am. Mineral. 84, 454-464.
- Kim, Y.-K. (1992). PhD thesis, Macromolecular Science and Engineering, The University of Michigan, Ann Arbor, MI, USA.
- Kurzepa, M., Dobrowolski, J. C. & Mazurek, A. P. (2001). J. Mol. Struct. 565, 107-113.
- Leone-Bay, A. & Glaser, L. (1987). Synth. Commun. 17, 1409-1412.
- Less, G. B., Kampf, J. W. & Rasmussen, P. G. (2004). Inorg. Chem. 43, 4897-4902
- Matthews, D. P., Whitten, J. P. & McCarthy, J. R. (1986). J. Org. Chem. 51, 3228-3231.

- Mitsuhashi, K., Itho, E., Kawahara, T. & Tanaka, K. (1983). J. Heterocycl. Chem. 20, 1103–1105.
- Nippon (2004). *Preparation of 4(5)-Cyanoimidazoles*. Patent JP 2004131404 A2, April 30, 2004. Nippon Soda Co. Ltd, Tokyo, Japan. (URL: http://www.Nippon-soda.co.jp.)
- Ohtsuka, Y. (1976). J. Org. Chem. 41, 713–714.
- Pfizer (1977). US Patent 4 025 504, May 24, 1977, Pfizer Inc., New York, NY, USA. (URL: http://www.pfizer.com/main.html.)
- Raczynska, E. D. (1997). Anal. Chim. Acta, 348, 431-441.
- Schering (1992). Preparation of cyaoimidazole agrochemical fungicides. Patent WO9207835, May 14, 1992. Schering AG, Berlin, Germany. (URL: http:// www.schering.de/scripts/en/index.php.)
- Sheldrick, G. M. (1997). *SHELXTL*. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (2003). SADABS. Version 2.10. University of Göttingen, Germany.
- Shikoku (1987). 2-Substituted-4-cyanoimidazoles and a process for their preparation as reagents in biochemical and pharmaceutical research. Patent JP62175471, 1987. Shikoku Chemical Corporation, Kagawa, Japan. (URL: http://www.shikoku.co.jp/Eng/.)
- Shikoku (1991). Preparation of 4(5)-(2,4-diamino-5-triazin-6-yl)imidazole Derivatives as Epoxy Hardening Agents or Hardening Promoters. Patent JP3284675, 1991. Shikoku Chemical Corporation, Kagawa, Japan. (URL: http://www.shikoku.co.jp/Eng/.)