

1*H*-Imidazole-4-carbonitrileGregory B. Less, Paul G.
Rasmussen* and Jeff W. KampfUniversity of Michigan, Department of
Chemistry, 930 N. University, Ann Arbor,
MI 48109-1055, USA

Correspondence e-mail: pgrasmsn@umich.edu

The title compound, C₄H₃N₃, was synthesized in three steps from diaminomaleonitrile in an overall yield of 38%. Single-crystal 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.

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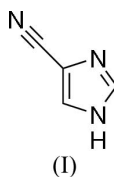
Key indicators

Single-crystal X-ray study
T = 158 K
Mean σ (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>.

Comment

Since the first report of 1*H*-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 4-cyanoimidazolate can act as both a μ -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 1*H*-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 π – π 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 1*H*-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, 1*H*-imidazole-4-carbo-

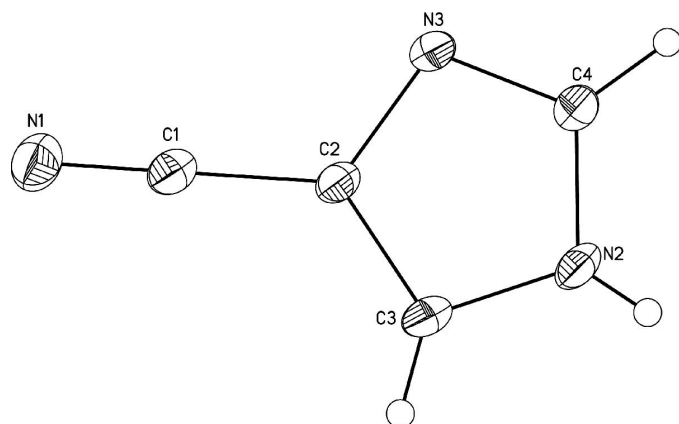


Figure 1
A view of the title compound with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

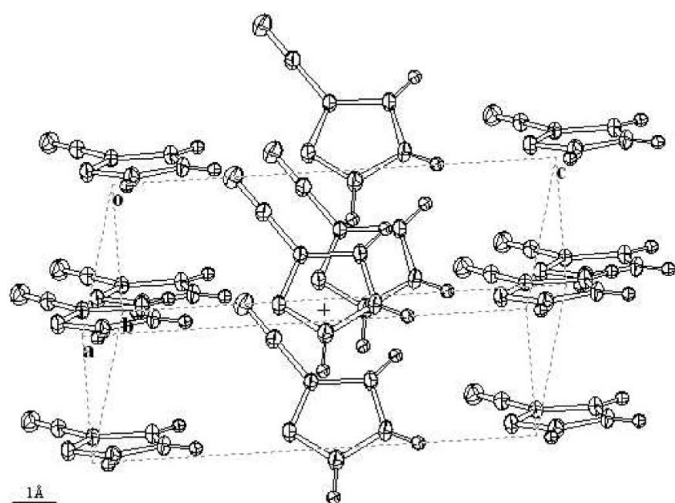


Figure 2
The crystal packing, showing the net dipole formation along the *c* axis. All nitrile groups point towards the left, while all H-atom substituents point towards the right of this diagram.

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 1*H*-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 1*H*-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

$C_4H_3N_3$
 $M_r = 93.09$
Monoclinic, *Pc*
 $a = 5.7230$ (13) Å
 $b = 3.6965$ (9) Å
 $c = 10.244$ (2) Å
 $\beta = 97.689$ (7)°
 $V = 214.76$ (8) Å³
 $Z = 2$

$D_x = 1.440$ Mg m⁻³
Mo $K\alpha$ radiation
Cell parameters from 5074 reflections
 $\theta = 4.0$ – 36.3 °
 $\mu = 0.10$ mm⁻¹
 $T = 158$ K
Needle, colorless
 $0.50 \times 0.10 \times 0.10$ mm

Data collection

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

977 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.039$
 $\theta_{\text{max}} = 36.3$ °
 $h = -9 \rightarrow 9$
 $k = -6 \rightarrow 6$
 $l = -17 \rightarrow 17$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.032$
 $wR(F^2) = 0.079$
 $S = 1.13$
1011 reflections
76 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0589P)^2 + 0.0007P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.39$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.19$ e Å⁻³

Table 1

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N2—H2...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.

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