



A long symmetric N···H···N hydrogen bond in bis(4-aminopyridinium)(1+) azide(1−): redetermination from the original data

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Received 22 July 2017

Accepted 4 August 2017

Edited by W. T. A. Harrison, University of Aberdeen, Scotland

Keywords: crystal structure; redetermination; hydrogen bonding; symmetric hydrogen bonds; refinement constraints; refinement restraints; Cambridge Structural Database.

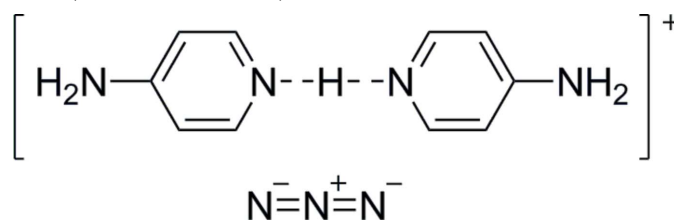
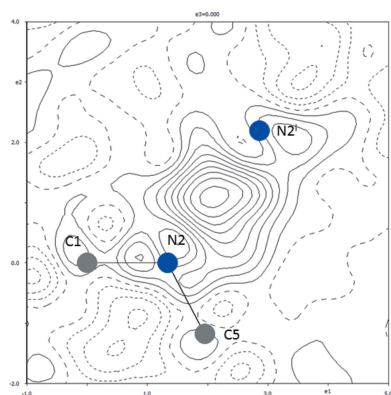
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The structure of the title molecular salt, $C_{10}H_{13}N_4^+ \cdot N_3^-$, has been redetermined from the data published by Qian & Huang [*Acta Cryst.* (2010), E66, o3086; refcode WACMIY (Groom *et al.*, 2016)]. The improvement of the present redetermination consists in a correction of the site-occupancy parameter of the bridging H atom between the pyridine rings, as well as of its position. The present study has shown that the bridging H atom (site symmetry 2) is involved in a symmetric N···H···N hydrogen bond, which is one of the longest ever observed [N···N = 2.678 (3) Å]. In addition, there are also present weaker $N_{am}-H \cdots N_{az}$ hydrogen bonds (am = amine and az = azide) of moderate strength and π -electron pyridine··· π -electron interactions in the structure. All the azide N atoms also lie on a twofold axis.

1. Chemical context

Structures that contain hydroxyl and secondary and primary amine groups are sometimes determined incorrectly because of an assumed geometry of these groups from which the applied constraints or restraints were inferred. In such cases, the correct geometry is missed as it is not verified by inspection of the difference electron-density maps. Thus, a considerable number of structures could have been determined more accurately – *cf.* Figs. 1 and 2 in Fábry *et al.* (2014). The inclusion of such erroneous structures causes bias in crystallographic databases such as the Cambridge Structural Database (Groom *et al.*, 2016).



In the course of recalculation of suspect structures that were retrieved from the Cambridge Structural Database (Groom *et al.*, 2016), the structure determination of the title structure by Qian & Huang (2010) with the pertinent CSD refcode WACMIY became a candidate for a checking recalculation. The reason was that both the primary and secondary amine groups were constrained with distance constraints equal to 0.86 Å, with planar conformation and $U_{iso}(\text{H}) = 1.2U_{eq}(\text{N})$.

Inspection of the publication of the title structure by Qian & Huang (2010) has revealed that the bridging hydrogen atom H2a, lying between two symmetry-equivalent nitrogen atoms

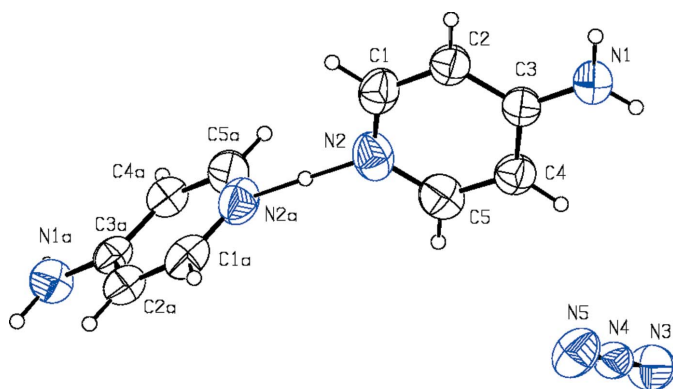


Figure 1
View of the constituent molecules of the title structure after the improved refinement. The displacement ellipsoids are depicted at the 30% probability level (Spek, 2009).

related by a crystallographic twofold axis, was modelled by two (undisordered) H atoms both with occupational parameters equal to 1: such a structural motif is impossible. The present article describes the redetermination of bis(4-aminopyridinium)(1+) azide(1−), which was reported by Qian & Huang (2010).

2. Structural commentary

The components of the title molecular salt are shown in Fig. 1. It is seen that the bridging hydrogen atom (H2a) interconnects symmetry-related 4-aminopyridine molecules; the symmetry operation for atoms with the suffix 'a' is the same as symmetry

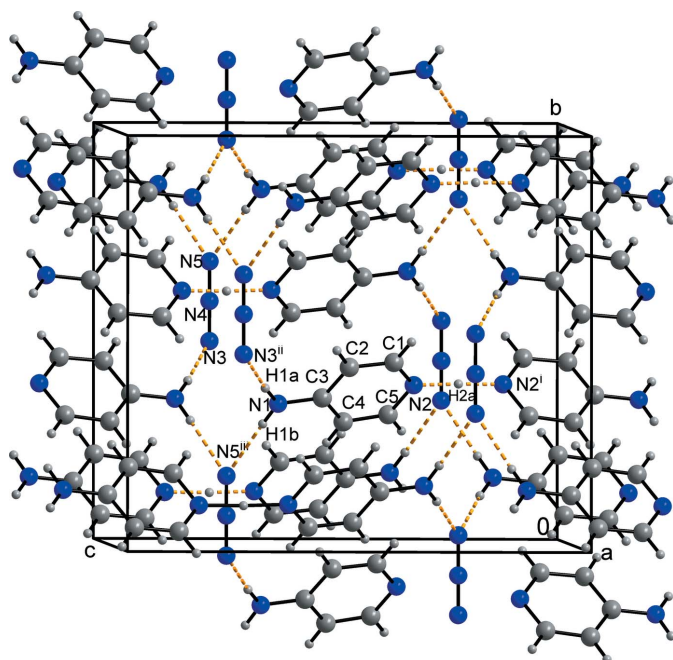


Figure 2
A view of the title structure along the unit-cell axis *a*. Symmetry codes: (i) $-x + 1, y, -z + \frac{1}{2}$; (ii) $x + 1, y, z$; (iii) $x + \frac{1}{2}, y - \frac{1}{2}, z$. Applied colours for atoms: grey = C and H, blue = N; applied colours for bonds: black = covalent bonds, dashed orange = $H \cdots$ hydrogen bonds acceptor (Brandenburg & Putz, 2005).

Table 1
Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$N2-H2a \cdots N2^i$	1.3391 (16)	1.3391 (16)	2.678 (3)	178 (2)
$N1-H1a \cdots N3^{ii}$	0.927 (14)	2.067 (14)	2.990 (2)	173.6 (13)
$N1-H1b \cdots N5^{iii}$	0.857 (16)	2.154 (16)	3.010 (2)	177.9 (14)

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

code (i) in Table 1 and Fig. 2, *viz.* $-x + 1, y, -z + \frac{1}{2}$. The interplanar angle between the pyridine rings $N2/C1-C5$ and $N2^i/C1^i-C5^i$ is $87.90 (7)^\circ$.

Table 1 lists the hydrogen bonds in the structure. The packing of the ions in the unit cell is shown in Fig. 2. Fig. 3 shows the difference electron-density map calculated without the bridging hydrogen atom H2a in the region $N2 \cdots (H2a) \cdots N2^i$. A well-defined, single peak in this map indicates that H2a is situated on a twofold axis, *i.e.* it is involved in a symmetric hydrogen bond while not being disordered. This hydrogen bond is the strongest hydrogen bond in the structure and is one of the family of long symmetric hydrogen bonds $N \cdots H \cdots N$ as listed in Table 1. As Tables 1 and 2 show, the title structure contains the second longest known truly symmetric $N \cdots H \cdots N$ hydrogen bond after CAFHAT01.

The remaining $N-H_{am} \cdots N_{az}$ (*am* = primary amine, *az* = azide) hydrogen bonds are considerably weaker, though still

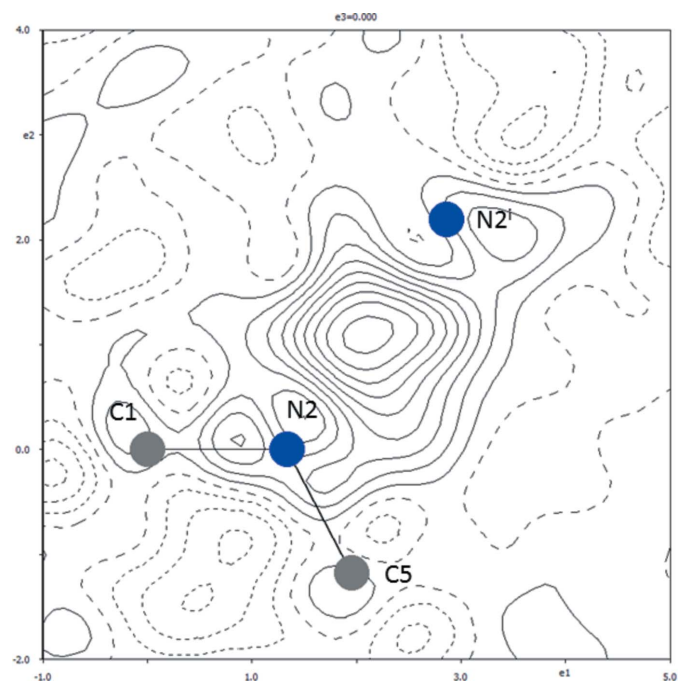


Figure 3
A section of the difference electron-density map for the present redetermined title structure, which shows the build up of the electron density between the atoms N and N^i [symmetry code: (i) $-x + 1, y, -z + \frac{1}{2}$]. Positive and negative electron densities are indicated by continuous and dashed lines, respectively. The increment of electron density between the neighbouring contours is $0.02 e \text{ \AA}^{-3}$ (Petříček *et al.*, 2014).

Table 2

Structures with long N···H···N hydrogen bonds (Å, °) with a centred hydrogen.

For the search in the Cambridge Structural Database (Groom *et al.*, 2016), the D—H distance was set in the interval 1.30–1.45 Å and the non-bonding distance between the donor and acceptor nitrogen atoms was set in the interval 2.6–3.0 Å.

Refcode	D—H	H···A	D···A	D—H···A
BOTXEO ^a	1.322 (3)	1.515 (3)	2.829 (4)	171.09 (16)
CAFHAT01 ^b	1.34	1.37	2.7018	169.8
CAFHAT01 ^b	1.35	1.35	2.7009	175.3
COFMUF10 ^c	1.35 (10)	1.50 (10)	2.844 (7)	171 (11)
DAHGUO01 ^d	1.33 (6)	1.38 (6)	2.690 (8)	168 (6)
EFAZOB ^e	1.32 (5)	1.38 (5)	2.692 (5)	176 (4)
EPIWUX ^f	1.33 (3)	1.33 (2)	2.657 (9)	172 (8)
FISROP ^g	1.45 (4)	1.51 (4)	2.963 (3)	173 (2)
FOGKAP ^h	1.31 (4)	1.34 (4)	2.652 (5)	175 (4)
HUJNUW ⁱ	1.341 (15)	1.414 (16)	2.68 (2)	152.7 (8)
IYEVOX ^j	1.33 (7)	1.37 (7)	2.691 (6)	174 (6)
MIJMUN ^k	1.27 (7)	1.56 (7)	2.812 (7)	165 (5)
MIJMUN ^k	1.34 (9)	1.52 (10)	2.808 (7)	159 (8)
OBUCOE ^l	1.33 (3)	1.43 (3)	2.736 (2)	165 (3)
QUHFEG ^m	1.39 (4)	1.40 (4)	2.792 (10)	176 (5)
SIZSUQ ⁿ	1.317 (14)	1.319 (14)	2.63 (2)	176.8 (9)
WOFGII ^o	1.33 (4)	1.39 (4)	2.706 (4)	167 (3)
XICRIM ^p	1.31 (4)	1.52 (4)	2.826 (3)	164 (3)
ZEYLIA ^q	1.32 (4)	1.51 (4)	2.833 (4)	175 (3)

Notes: (a) 2-(1,3-Benzoxazol-2-yl)-1-phenylvinyl benzoate (Orozco *et al.*, 2009); (b) hydrogen bis[bis(2-[[[imidazol-4-yl]methylene]amino]ethyl)[2-[[imidazolato]methylene]amino]ethyl]amine]cobalt(III) triperchlorate heptahydrate (Marsh & Clemente, 2007); (c) 2,1,3-benzoselenadiazole 2,1,3-benzoselenadiazolium pentaiodide (Gieren *et al.*, 1985); (d) bis[[1,4-diazoniabicyclo(2.2.2)octane][1-aza-4-azoniabicyclo(2.2.2)octane]] tetrakis(tribromide) dibromide (Heravi *et al.*, 2005); (e) bis[[3,5-dimethylpyrazole](3,5-dimethylpyrazolyl)]platinium(II) (Umakoshi *et al.*, 2008); (f) 4-[2-(pyridin-4-yl)oxy]-1,2-bis(2,3,5,6-tetrafluoro-4-iodophenyl)ethoxy]pyridin-1-ium iodide bis(nitrobenzene) (Martí-Rujas *et al.*, 2012); (g) 5,6:14,15-dibenzo-1,4-dioxo-8-azonia-12-azacyclopentadeca-5,14-diene 5,6:14,15-dibenzo-1,4-dioxo-8,12-diazacyclopentadeca-5,14-diene perchlorate (Tušić-Božić *et al.*, 2005); (h) dioxidotetrakis(4-methylpyridine)rhenium(V) 4-methylpyridinium 4-methylpyridine diiodide (Krawczyk *et al.*, 2014); (i) 4-methylpyridinium *trans*-bis(γ -picoline)tetrakis(thiocyanato)molybdenum 4-methylpyridine (Kitanovski *et al.*, 2009); (j) bis(4,4'-bipyridinium) hexakis(μ_2 -sulfido)tetra-germaniumtetrasulfide 4,4'-bipyridine heptahydrate (Wang *et al.*, 2003); (k) 4,4'-bipyridinium 4-(pyrid-4-yl)pyridinium 4,4'-bipyridine hexakis(isothiocyanato-*N*)-iron (Wei *et al.*, 2002); (l) tris(2-benzimidazolylmethyl)ammonium 3,5-dinitrobenzoate 3,5-dinitrobenzoic acid clathrate (Ji *et al.*, 2004); (m) (2*R*,4*S*,5*R*)-9-(hydroxyimino)-6'-methoxycinchonan-1-ium (2*R*,4*S*,5*R*)-*N*-hydroxy-6'-methoxycinchonan-9-imine chloride methanol solvate (Zohri *et al.*, 2015); (n) *catena*-[bis(μ_2 -aqua)-(5-cyano-2*H*-1,2,3-triazole-4-carboxamide)(4-cyano-1,2,3-triazole-5-carboxamide)sodium] (Al-Azmi *et al.*, 2007); (o) (1,1'-hydrogenbis[4-[1'-(4-pyridyl)ferrocen-1-yl]pyridine]) 4-[1'-(4-pyridyl)ferrocen-1-yl]pyridinium tris(5-carboxy-2-thienylcarboxylate) bis(thiophene-2,5-dicarboxylic acid) (Braga *et al.*, 2008); (p) cytosinium 4-amino-2-hydroxybenzoate cytosine monohydrate (Cherukuvada *et al.*, 2013); (q) cytosinium acetylenedicarboxylate cytosine monohydrate (Perumalla *et al.*, 2013).

of moderate strength (Gilli & Gilli, 2009). Atom H1*a* forms a link to the terminal azide nitrogen atom N3 while H1*b* bonds to the other terminal azide atom N5. The graph-set motif is described in the *Supramolecular features* section. In addition to the hydrogen-bonding interactions, there are also π -electron ring··· π -electron pyridine interactions in the structure. The distance between the ring centroids N2/C1–C5 and N2^{iv}/C1^{iv}–C5^{iv} is 3.7145 (17) Å [symmetry code: (iv) $-x + 1, -y + 1, -z + 1$].

The primary amine group centered on N1 is almost planar [C3–N1–H1*a* = 120.0 (9), C3–N1–H1*b* = 119.1 (9), H1*a*–N1–H1*b* = 120.6 (13)°] despite the somewhat lengthened C3–N1 bond [1.345 (2) Å]. The reason may be found in the hydrogen bonds formed by the group with N–H···N bond angles being close to 180°.

Table 3

Experimental details.

Crystal data	
Chemical formula	C ₁₀ H ₁₃ N ₄ ⁺ ·N ₃ [−]
<i>M_r</i>	231.27
Crystal system, space group	Monoclinic, C2/c
Temperature (K)	291
<i>a</i> , <i>b</i> , <i>c</i> (Å)	7.507 (3), 12.247 (5), 13.634 (5)
β (°)	99.278 (5)
<i>V</i> (Å ³)	1237.1 (8)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
μ (mm ^{−1})	0.08
Crystal size (mm)	0.14 × 0.11 × 0.10
Data collection	
Diffractometer	Bruker SMART 1K CCD area-detector
Absorption correction	Multi-scan (SADABS; Bruker, 2000)
<i>T_{min}</i> , <i>T_{max}</i>	0.988, 0.992
No. of measured, independent and observed [<i>I</i> > 3 σ (<i>I</i>)] reflections	3027, 1096, 787
<i>R_{int}</i>	0.072
(sin θ / λ) _{max} (Å ^{−1})	0.595
Refinement	
<i>R</i> [<i>F</i> > 3 σ (<i>F</i>)], <i>wR</i> (<i>F</i>), <i>S</i>	0.034, 0.085, 1.48
No. of reflections	1096
No. of parameters	87
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ^{−3})	0.08, −0.07

Computer programs: SMART and SAINT (Bruker, 2000), SHELXTL (Sheldrick, 2008), PLATON (Spek, 2009), DIAMOND (Brandenburg & Putz, 2005) and JANA2006 (Petříček *et al.*, 2014).

Once again, the present redetermination emphasizes the importance of careful examination of the difference electron-density maps during a structure determination.

3. Supramolecular features

In addition to the above-mentioned symmetric hydrogen bond N2···H2*a*···N2ⁱ [symmetry code: (i) $-x + 1, y, -z + \frac{1}{2}$] for which the graph-set motif notation is missing (the donors act simultaneously as acceptors in the title structure; Etter *et al.*, 1990) the principal graph-set motif in which the primary amine group as well as the azide atoms are involved is *R*₄⁶(20).

In a detail, the atoms involved in this graph-set motif are as follows (Fig. 2): N3^v–H1*a*^{vi}–N1^{vi}–H1*b*^{vi}–N5ⁱⁱ–N4ⁱⁱ–N3ⁱⁱ–H1*a*–N1–H1*b*–N5ⁱⁱⁱ–H1*b*^{vii}–N1^{vii}–H1*a*^{vii}–N3–N4–N5–H1*b*^{viii}–N1^{viii}–H1*a*^{viii} [symmetry codes: (ii) $x + 1, y, z$; (iii) $x + \frac{1}{2}, y - \frac{1}{2}, z$; (v) $x + \frac{1}{2}, y + \frac{1}{2}, z$; (vi) $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$; (vii) $-x + 1, y, -z + \frac{3}{2}$; (viii) $x - \frac{1}{2}, y + \frac{1}{2}, z$].

The hydrogen bonds in this graph set motif are directed along the unit-cell parameter *b*.

4. Synthesis and crystallization

The preparation of the title compound was described by Qian & Huang *et al.* (2010) in the supporting information of their article.

5. Database survey

The structure determination by Qian & Huang (2010) has been included into the Cambridge Structural Database (Groom *et al.*, 2016) under the refcode WACMIY.

6. Refinement

Table 3 lists the details regarding the crystal data, data collection and the refinement. The starting structural model was taken from the determination by Qian & Huang (2010). All hydrogen atoms were discernible in the difference electron-density map. The aryl hydrogen atoms were constrained by $C_{\text{aryl}}-H_{\text{aryl}} = 0.93 \text{ \AA}$ and $U_{\text{iso}}(H_{\text{aryl}}) = 1.2U_{\text{eq}}(C_{\text{aryl}})$. The positional parameters of the primary amine hydrogen atoms were refined freely while their displacement parameters were constrained by $U_{\text{iso}}(H_{\text{N2}}) = 1.2U_{\text{eq}}(\text{N2})$. The bridging hydrogen atom H2a involved in the symmetric hydrogen bond $\text{N2} \cdots \text{H2a} \cdots \text{N2}^i$ was refined freely. Refinements using JANA2006 and SHELXL (Sheldrick, 2008) with the threshold for observed diffractions $I = 2\sigma(I)$ led to the same result of the bridging hydrogen atom being located on the twofold axis.

Acknowledgements

The support by the grant of the Czech Science Foundation 15-12653S is gratefully acknowledged.

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supporting information

Acta Cryst. (2017). E73, 1344-1347 [https://doi.org/10.1107/S2056989017011537]

A long symmetric N \cdots H \cdots N hydrogen bond in bis(4-aminopyridinium)(1+) azide(1-): redetermination from the original data

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Computing details

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINTE* (Bruker, 2000); data reduction: *SAINTE* (Bruker, 2000); program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *JANA2006* (Petříček *et al.*, 2014); molecular graphics: *PLATON* (Spek, 2009), *DIAMOND* (Brandenburg & Putz, 2005) and *JANA2006* (Petříček *et al.*, 2014); software used to prepare material for publication: *JANA2006* (Petříček *et al.*, 2014).

μ -Hydrido-bis(4-aminopyridinium) azide

Crystal data

C₁₀H₁₃N₄⁺·N₃⁻

$M_r = 231.27$

Monoclinic, *C2/c*

Hall symbol: -C 2yc

$a = 7.507$ (3) Å

$b = 12.247$ (5) Å

$c = 13.634$ (5) Å

$\beta = 99.278$ (5)°

$V = 1237.1$ (8) Å³

$Z = 4$

$F(000) = 488$

$D_x = 1.242$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 1359 reflections

$\theta = 3.0$ – 25.4 °

$\mu = 0.08$ mm⁻¹

$T = 291$ K

Block, colourless

$0.14 \times 0.11 \times 0.10$ mm

Data collection

Bruker SMART 1K CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

φ and ω scans

Absorption correction: multi-scan (*SADABS*; Bruker, 2000)

$T_{\min} = 0.988$, $T_{\max} = 0.992$

3027 measured reflections

1096 independent reflections

787 reflections with $I > 3\sigma(I)$

$R_{\text{int}} = 0.072$

$\theta_{\max} = 25.0$ °, $\theta_{\min} = 3.0$ °

$h = -8 \rightarrow 8$

$k = -12 \rightarrow 14$

$l = -16 \rightarrow 15$

Refinement

Refinement on F^2

$R[F > 3\sigma(F)] = 0.034$

$wR(F) = 0.085$

$S = 1.48$

1096 reflections

87 parameters

0 restraints

18 constraints

H atoms treated by a mixture of independent and constrained refinement

Weighting scheme based on measured s.u.'s $w = 1/(\sigma^2(I) + 0.0004I^2)$

$(\Delta/\sigma)_{\max} = 0.004$

$\Delta\rho_{\max} = 0.08$ e Å⁻³

$\Delta\rho_{\min} = -0.07$ e Å⁻³

Special details

Experimental. The structure was solved by direct methods (Bruker, 2000) and successive difference Fourier syntheses.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.6719 (2)	0.44584 (12)	0.40174 (12)	0.0889 (6)
H1	0.732036	0.496631	0.368331	0.1067*
C2	0.72245 (17)	0.43524 (10)	0.50154 (11)	0.0778 (5)
H2	0.814514	0.478469	0.535055	0.0934*
C3	0.63529 (16)	0.35896 (9)	0.55351 (10)	0.0702 (5)
C4	0.49858 (17)	0.29730 (11)	0.49826 (11)	0.0793 (5)
H4	0.436698	0.245345	0.529429	0.0952*
C5	0.4560 (2)	0.31347 (12)	0.39842 (12)	0.0936 (6)
H5	0.364461	0.271568	0.362714	0.1123*
N1	0.68183 (18)	0.34619 (10)	0.65226 (9)	0.0859 (5)
H1a	0.776 (2)	0.3866 (12)	0.6868 (10)	0.1031*
H1b	0.631 (2)	0.2960 (12)	0.6815 (11)	0.1031*
N2	0.54018 (19)	0.38706 (11)	0.34930 (8)	0.0943 (5)
N3	0	0.47492 (16)	0.75	0.1020 (8)
N4	0	0.57130 (18)	0.75	0.0768 (6)
N5	0	0.66663 (17)	0.75	0.1074 (8)
H2a	0.5	0.389 (2)	0.25	0.160 (9)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0946 (10)	0.0866 (10)	0.0930 (11)	0.0183 (8)	0.0376 (9)	0.0120 (8)
C2	0.0752 (8)	0.0760 (8)	0.0853 (10)	0.0109 (6)	0.0224 (7)	0.0054 (7)
C3	0.0685 (7)	0.0688 (7)	0.0762 (9)	0.0166 (6)	0.0205 (6)	0.0039 (6)
C4	0.0762 (8)	0.0795 (8)	0.0847 (10)	0.0065 (6)	0.0205 (7)	0.0007 (7)
C5	0.0948 (10)	0.0999 (10)	0.0854 (11)	0.0105 (8)	0.0125 (8)	-0.0094 (8)
N1	0.0909 (8)	0.0865 (8)	0.0804 (9)	-0.0012 (5)	0.0144 (6)	0.0093 (6)
N2	0.1093 (9)	0.1039 (9)	0.0725 (8)	0.0233 (7)	0.0229 (7)	0.0027 (7)
N3	0.0983 (12)	0.0857 (11)	0.1212 (15)	0	0.0154 (10)	0
N4	0.0625 (8)	0.1024 (13)	0.0667 (9)	0	0.0143 (6)	0
N5	0.1140 (14)	0.0918 (12)	0.1263 (15)	0	0.0495 (12)	0

Geometric parameters (\AA , $^\circ$)

C1—H1	0.93	C5—H5	0.93
C1—C2	1.359 (2)	C5—N2	1.340 (2)
C1—N2	1.334 (2)	N1—H1a	0.927 (14)
C2—H2	0.93	N1—H1b	0.857 (16)
C2—C3	1.397 (2)	H1a—H1b	1.55 (2)
C3—C4	1.3935 (19)	N2—H2a	1.3391 (16)
C3—N1	1.345 (2)	N3—N4	1.180 (3)
C4—H4	0.93	N4—N5	1.168 (3)

C4—C5	1.362 (2)		
H1—C1—C2	118.36	C4—C5—H5	118.53
H1—C1—N2	118.36	C4—C5—N2	122.95 (13)
C2—C1—N2	123.27 (14)	H5—C5—N2	118.53
C1—C2—H2	120.21	C3—N1—H1a	120.0 (9)
C1—C2—C3	119.58 (12)	C3—N1—H1b	119.1 (9)
H2—C2—C3	120.21	H1a—N1—H1b	120.6 (13)
C2—C3—C4	116.91 (12)	C1—N2—C5	117.61 (13)
C2—C3—N1	121.21 (11)	C1—N2—H2a	123.9 (8)
C4—C3—N1	121.88 (12)	C5—N2—H2a	118.2 (9)
C3—C4—H4	120.16	N3—N4—N5	180.0 (5)
C3—C4—C5	119.68 (13)	N2—H2a—N2 ⁱ	178 (2)
H4—C4—C5	120.16		

Symmetry code: (i) $-x+1, y, -z+1/2$.

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N2—H2a \cdots N2 ⁱ	1.3391 (16)	1.3391 (16)	2.678 (3)	178 (2)
N1—H1a \cdots N3 ⁱⁱ	0.927 (14)	2.067 (14)	2.990 (2)	173.6 (13)
N1—H1b \cdots N5 ⁱⁱⁱ	0.857 (16)	2.154 (16)	3.010 (2)	177.9 (14)

Symmetry codes: (i) $-x+1, y, -z+1/2$; (ii) $x+1, y, z$; (iii) $x+1/2, y-1/2, z$.