

# 1,1'-Diethyl-4,4'-bipyridine-1,1'-dium bis(1,1,3,3-tetracyano-2-ethoxypropenide): multiple C—H···N hydrogen bonds form a complex sheet structure

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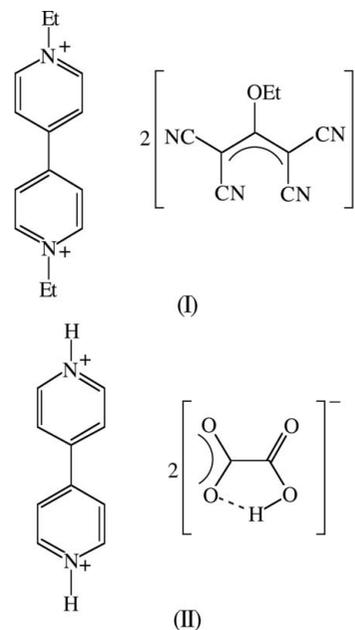
In the title salt,  $C_{14}H_{18}N_2^{2+} \cdot 2C_9H_5N_4O^-$ , the 1,1'-diethyl-4,4'-bipyridine-1,1'-dium dication lies across a centre of inversion in the space group  $P2_1/c$ . In the 1,1,3,3-tetracyano-2-ethoxypropenide anion, the two independent  $-C(CN)_2$  units are rotated, in conrotatory fashion, out of the plane of the central propenide unit, making dihedral angles with the central unit of 16.0 (2) and 23.0 (2)°. The ionic components are linked by C—H···N hydrogen bonds to form a complex sheet structure, within which each cation acts as a sixfold donor of hydrogen bonds and each anion acts as a threefold acceptor of hydrogen bonds.

**Keywords:** crystal structure; hydrogen-bonded sheets; polynitrile anions; 4,4'-bipyridine-1,1'-dium; 1,1,3,3-tetracyano-2-ethoxypropenide.

## 1. Introduction

Polynitrile anions have recently received considerable attention in the fields of coordination chemistry and molecular materials (Benmansour *et al.*, 2010). These organic anions are of interest for their ability to adopt various coordination modes with metal centres and for their high degree of electronic delocalization (Thétiot *et al.*, 2003; Benmansour *et al.*, 2007, 2009; Atmani *et al.*, 2008; Setifi *et al.*, 2007, 2009, 2010). We are interested in using these anionic ligands in combination with other neutral bridging co-ligands to explore their structural features and properties relevant to the field of molecular materials exhibiting the spin crossover (SCO)

phenomenon (Dupouy *et al.*, 2008, 2009). In an attempt to prepare an iron(II) complex of this type using hydrothermal synthesis, the unexpected title salt, 1,1'-diethyl-4,4'-bipyridine-1,1'-dium bis(1,1,3,3-tetracyano-2-ethoxypropenide), (I) (Fig. 1), has been obtained and its structure is reported here.



## 2. Experimental

### 2.1. Synthesis and crystallization

The salt K(tcnoet) was prepared according to the published method of Middleton *et al.* (1958). The title compound, (I), was synthesized hydrothermally from a mixture of iron(II) sulfate heptahydrate (56 mg, 0.2 mmol), 4,4'-bipyridine (16 mg, 0.1 mmol) and K(tcnoet) (90 mg, 0.4 mmol) in water-ethanol (4:1 v/v, 15 ml). The mixture was transferred to a Teflon-lined autoclave and heated at 393 K for 2 d. The autoclave was then allowed to cool to ambient temperature. Pale-yellow crystals of (I) were collected by filtration, washed with water and dried in air (yield 65%).

### 2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. All H atoms were located in difference maps and then treated as riding atoms in geometrically idealized positions, with C—H = 0.95 (aromatic), 0.98 (CH<sub>3</sub>) or 0.99 Å (CH<sub>2</sub>) and with  $U_{iso}(H) = kU_{eq}(C)$ , where  $k = 1.5$  for methyl groups, which were permitted to rotate but not to tilt, and 1.2 for all other H atoms.

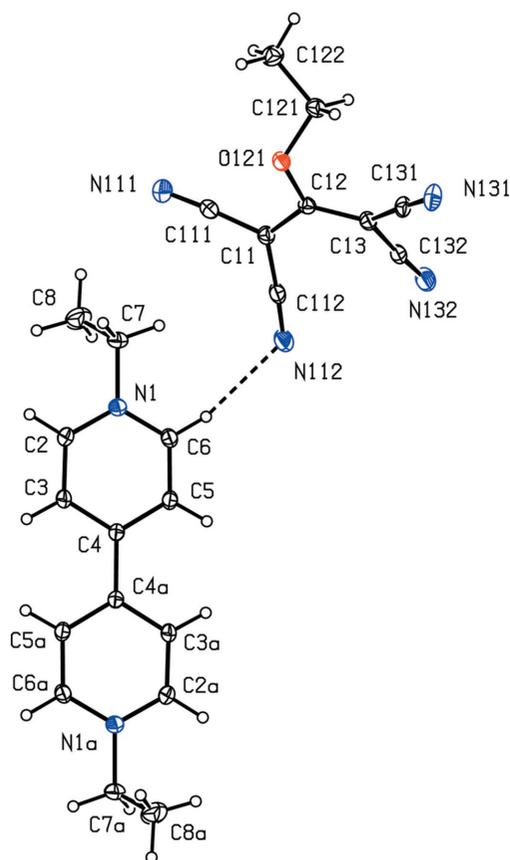
## 3. Results and discussion

The title salt consists of 1,1'-diethyl-4,4'-bipyridine-1,1'-dium dications lying across centres of inversion in the space group  $P2_1/c$  and 1,1,3,3-tetracyano-2-ethoxypropenide (tcnoet) anions occupying general positions; the reference cation was selected as that lying across  $(\frac{1}{2}, \frac{1}{2}, 0)$ . The formation of the cation presumably arises as a result of nucleophilic attack by

**Table 1**  
Experimental details.

Crystal data	
Chemical formula	$C_{14}H_{18}N_2^{2+} \cdot 2C_9H_5N_4O^-$
$M_r$	584.64
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	150
$a, b, c$ (Å)	10.6881 (7), 15.2125 (8), 10.2455 (6)
$\beta$ (°)	110.391 (7)
$V$ (Å <sup>3</sup> )	1561.46 (16)
$Z$	2
Radiation type	Mo $K\alpha$
$\mu$ (mm <sup>-1</sup> )	0.08
Crystal size (mm)	0.32 × 0.20 × 0.10
Data collection	
Diffractometer	Bruker APEXII CCD diffractometer
Absorption correction	Multi-scan (SADABS; Sheldrick, 2003)
$T_{min}, T_{max}$	0.967, 0.992
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	10001, 3578, 2876
$R_{int}$	0.035
$(\sin \theta/\lambda)_{max}$ (Å <sup>-1</sup> )	0.650
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.054, 0.121, 1.12
No. of reflections	3578
No. of parameters	201
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å <sup>-3</sup> )	0.21, -0.21

Computer programs: APEX2 (Bruker, 2009), SAINT (Bruker, 2009), SHELXS97 (Sheldrick, 2008), SHELXL97 (Sheldrick, 2008) and PLATON (Spek, 2009).



**Figure 1**  
The ionic components of compound (I), showing the atom-labelling scheme and the C—H...N hydrogen bond within the selected asymmetric unit. Displacement ellipsoids are drawn at the 30% probability level and the atoms marked 'a' are at the symmetry position ( $-x + 1, -y + 1, -z$ ).

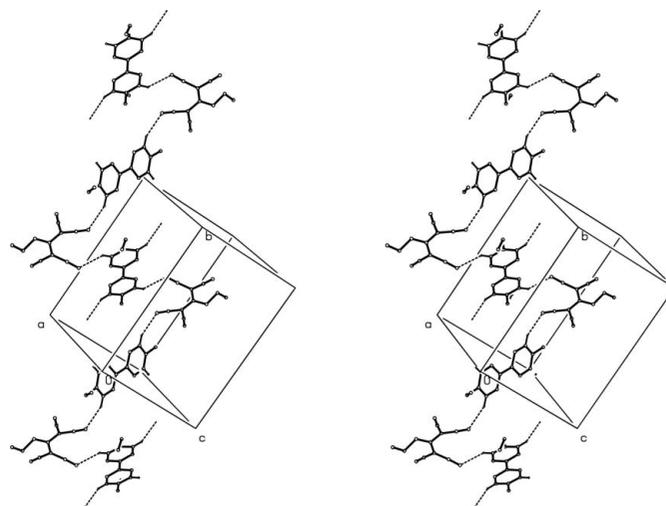
**Table 2**  
Selected geometric parameters (Å, °).

C11—C12	1.404 (2)	C12—C13	1.409 (2)
C11—C111	1.429 (2)	C13—C131	1.421 (2)
C11—C112	1.419 (2)	C13—C132	1.423 (2)
C111—N111	1.151 (2)	C131—N131	1.154 (2)
C112—N112	1.150 (2)	C132—N132	1.152 (2)
C13—C12—C11—C111	-165.22 (16)	C11—C12—C13—C131	-156.34 (16)
C13—C12—C11—C112	16.9 (3)	C11—C12—C13—C132	21.0 (3)

the 4,4'-bipyridine starting material on the 1,1,3,3-tetracyano-2-ethoxypropene anion, with transfer of ethyl groups from oxygen to nitrogen.

The two pyridine rings in the cation are constrained to be parallel but, in the anion, the two independent  $-C(CN)_2$  units are rotated, in conrotatory fashion, out of the plane of the central propene unit. The dihedral angles between the central  $C_3$  unit and the  $-C(CN)_2$  units containing atoms C11 and C13 are 16.0 (2) and 23.0 (2)°, respectively; these values, and the sense of the rotations, are typical of those observed in other systems containing this anion (Setifi *et al.*, 2013, 2014). Within the anion, the two central C—C distances (Table 2) are very similar, while the four independent C—N distances are all the same within experimental uncertainty, and they are long for their type [mean value (Allen *et al.*, 1987) = 1.136 Å, upper quartile value = 1.142 Å]. The peripheral C—CN distances span a very narrow range, *ca* 0.01 Å, and all are short for their type [mean value (Allen *et al.*, 1987) = 1.427 Å, lower quartile value = 1.420 Å], consistent with extensive delocalization of the negative charge, as discussed recently (Setifi *et al.*, 2014).

Three independent hydrogen bonds, all of the C—H...N type, are present in the structure (Table 3); the components of the asymmetric unit were selected so that the most nearly linear of the hydrogen bonds falls within the selected asymmetric unit. The hydrogen bond involving atom C2 has a C—



**Figure 2**  
A stereoview of part of the crystal structure of compound (I), showing the formation of a one-dimensional substructure in the form of a  $C_2^2(15)$  chain parallel to the  $[01\bar{1}]$  direction formed using only atoms C2 and C6 as the hydrogen-bond donors. For the sake of clarity, H atoms not involved in the motif shown have been omitted.

**Table 3**

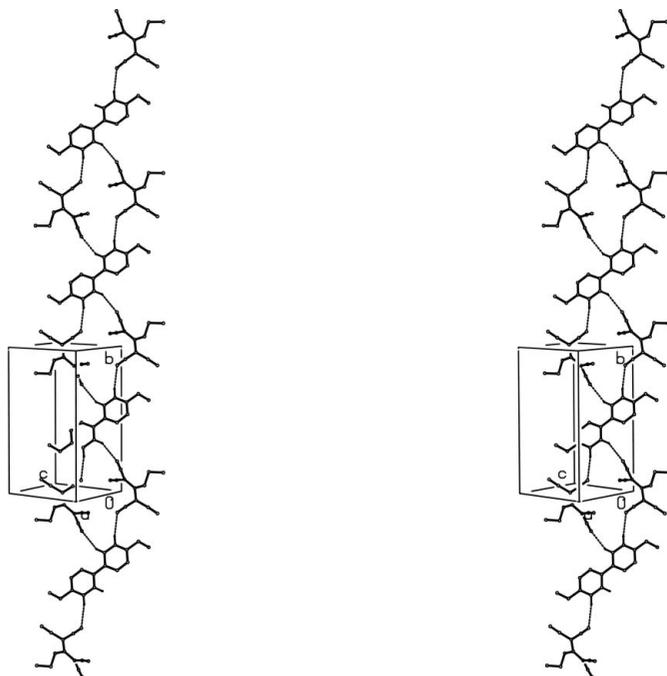
Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$C2-H2\cdots N132^i$	0.95	2.37	3.131 (2)	136
$C5-H5\cdots N131^{ii}$	0.95	2.41	3.270 (2)	150
$C6-H6\cdots N112$	0.95	2.47	3.366 (2)	157

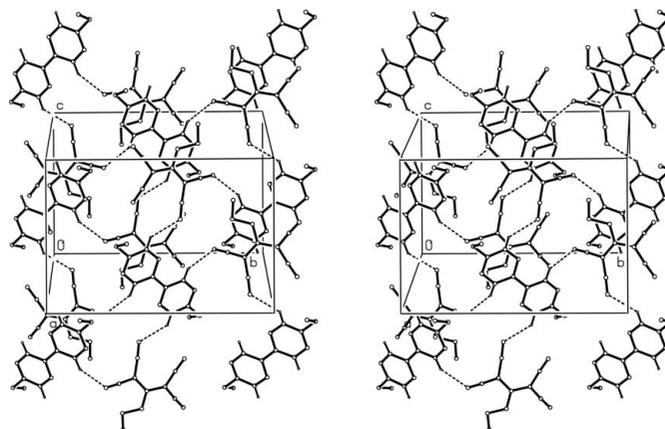
 Symmetry codes: (i)  $x, -y + \frac{1}{2}, z + \frac{1}{2}$ ; (ii)  $-x + 1, -y, -z$ .

$H\cdots N$  angle of only  $136^\circ$  (*cf.* Wood *et al.*, 2009), but this interaction is nonetheless regarded as structurally significant since it is a charge-assisted hydrogen bond (Gilli *et al.*, 1994) between a donor which is a component of a dication and an acceptor which is a component of an anion. Moreover, the donor atom concerned, C2, is immediately adjacent to the quaternary N atom, while there is delocalization of the negative charge of the anion onto the terminal N atoms, as noted above.

Because of the inversion symmetry of the cation, this ion acts as a sixfold donor of hydrogen bonds, such that the reference cation centred across  $(\frac{1}{2}, \frac{1}{2}, 0)$  is directly linked to the six anions at  $(x, y, z)$ ,  $(-x + 1, -y + 1, -z)$ ,  $(x, y + 1, z)$ ,  $(-x + 1, -y, -z)$ ,  $(x, -y + \frac{1}{2}, z + \frac{1}{2})$  and  $(-x + 1, y + \frac{1}{2}, -z - \frac{1}{2})$ . Consistent with the overall stoichiometry, the reference anion at  $(x, y, z)$  is linked directly to the three cations centred at  $(\frac{1}{2}, \frac{1}{2}, 0)$ ,  $(\frac{1}{2}, -\frac{1}{2}, 0)$  and  $(\frac{1}{2}, 0, -\frac{1}{2})$ , so generating a form of 6:3 coordination, albeit only in two dimensions, as discussed below. Atom N111 is the only N atom in the anion not to participate in the hydrogen bonding; the shortest inter-


**Figure 3**

A stereoview of part of the crystal structure of compound (I), showing the formation of a one-dimensional substructure in the form of a chain of  $R_2^2(22)$  rings parallel to the  $[010]$  direction formed using only atoms C5 and C6 as the hydrogen-bond donors. For the sake of clarity, H atoms not involved in the motif shown have been omitted.


**Figure 4**

A stereoview of part of the crystal structure of compound (I), showing the formation of a two-dimensional substructure in the form of a sheet parallel to  $(100)$  formed using only atoms C2 and C5 as the hydrogen-bond donors. For the sake of clarity, H atoms not involved in the motif shown have been omitted.

molecular  $N\cdots H$  distance involving atom N111 is  $2.90 \text{ \AA}$ , to atom H8A at  $(x, -y + \frac{1}{2}, z + \frac{1}{2})$ , far too long to be structurally significant. Despite the large number of hydrogen bonds formed by the cation, the supramolecular assembly is only two-dimensional, in the form of a sheet lying parallel to  $(100)$ . However, the sheet is of considerable complexity, and the supramolecular assembly can most readily be analysed in terms of the three substructures (Ferguson *et al.*, 1998*a,b*; Gregson *et al.*, 2000) which are formed by the three different combinations of just two of the three hydrogen bonds.

The simplest of the three substructures involves atoms C2 and C6 as the hydrogen-bond donors. Here, the cations centred at  $(\frac{1}{2}, \frac{1}{2}, 0)$  and  $(\frac{1}{2}, 0, \frac{1}{2})$  provide hydrogen-bond donors, using atoms C2 and C6, respectively, to the anion at  $(x, -y + \frac{1}{2}, z + \frac{1}{2})$ , and propagation by inversion of these two interactions leads to the formation of a  $C_2^2(15)$  (Bernstein *et al.*, 1995) chain running parallel to the  $[01\bar{1}]$  direction (Fig. 2). A more complex but still one-dimensional substructure is generated by the two hydrogen bonds having atoms C5 and C6 as the donors, producing a chain of centrosymmetric  $R_2^2(22)$  rings running parallel to the  $[010]$  direction, in which the cations centred at  $(\frac{1}{2}, n + \frac{1}{2}, 0)$  alternate with  $R_2^2(22)$  rings centred at  $(\frac{1}{2}, n, 0)$ , where  $n$  represents an integer in each case (Fig. 3). The final possible combination of two hydrogen bonds involves atoms C2 and C5 as the donors, thus excluding the hydrogen bond within the selected asymmetric unit. This combination generates a two-dimensional substructure in the form of a sheet lying parallel to  $(100)$  (Fig. 4), but this, of course, does not represent the full complexity of the overall supramolecular assembly, as it does not include all of the possible hydrogen bonds. The full complexity of the sheet results from the combination of all three substructural motifs.

The supramolecular assembly of salt (I) may be compared with that of the somewhat similar salt (II) (Androš *et al.*, 2011), as salts (I) and (II) show some interesting similarities as well as differences (see Scheme). In salt (II), as in salt (I), the cation lies across a centre of inversion, although here in the space

group  $P\bar{1}$  rather than  $P2_1/c$ , and the mono-negative anion occupies a general position; the cation in (II) acts as a sixfold donor of hydrogen bonds, while the anion contains four potential hydrogen-bond acceptors. However, whereas the cation in salt (I) only forms C—H $\cdots$ N hydrogen bonds, that in (II) forms both N—H $\cdots$ O and C—H $\cdots$ O hydrogen bonds; in addition, the anion, as well as containing an intra-anion O—H $\cdots$ O hydrogen bond, can also act as a donor in inter-ion hydrogen bonds. Accordingly, the supramolecular assembly in (II) is different from that in (I), and indeed it is rather simpler; an important building block in the supramolecular assembly of compound (II) is a centrosymmetric hydrogen-bonded dimer containing two anions, in which an overall  $R_2^2(10)$  motif is subdivided into a central  $R_2^2(4)$  ring flanked by two inversion-related  $S(5)$  rings. These dimeric units are linked to the cations by three-centre N—H $\cdots$ (O) $_2$  hydrogen bonds, forming a chain containing  $S(5)$ ,  $R_2^2(4)$  and  $R_1^1(5)$  rings running parallel to the [321] direction [not the  $[\bar{1}\bar{2}1]$  direction as stated in the original report of Androš *et al.* (2011)]. Chains related by translation along [111] are linked by two independent C—H $\cdots$ O hydrogen bonds to form an almost planar sheet lying parallel to  $(\bar{1}\bar{2}1)$ , which contains, in addition to the ring types within the [321] chains, rings of  $R_4^2(10)$ ,  $R_3^3(12)$  and  $R_4^4(16)$  types between these chains. Finally, the sheets in salt (II) are linked by  $\pi$ – $\pi$  stacking interactions, whereas such interactions are absent from the structure of salt (I), possibly precluded on steric grounds by the presence of the *N*-ethyl substituent.

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Supporting information for this paper is available from the IUCr electronic archives (Reference: SK3538).

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## supplementary materials

*Acta Cryst.* (2014). **C70**, 338–341 [doi:10.1107/S2053229614004379]

## 1,1'-Diethyl-4,4'-bipyridine-1,1'-dium bis(1,1,3,3-tetracyano-2-ethoxypropenide): multiple C—H···N hydrogen bonds form a complex sheet structure

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### Computing details

Data collection: *APEX2* (Bruker, 2009); cell refinement: *APEX2* and *SAINT* (Bruker, 2009); data reduction: *SAINT* (Bruker, 2009); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL97* (Sheldrick, 2008) and *PLATON* (Spek, 2009).

### 1,1'-Diethyl-4,4'-bipyridine-1,1'-dium bis(1,1,3,3-tetracyano-2-ethoxypropenide)

#### Crystal data

$C_{14}H_{18}N_2^{2+} \cdot 2C_9H_5N_4O^-$

$M_r = 584.64$

Monoclinic,  $P2_1/c$

Hall symbol: -P 2ybc

$a = 10.6881$  (7) Å

$b = 15.2125$  (8) Å

$c = 10.2455$  (6) Å

$\beta = 110.391$  (7)°

$V = 1561.46$  (16) Å<sup>3</sup>

$Z = 2$

$F(000) = 612$

$D_x = 1.243$  Mg m<sup>-3</sup>

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

Cell parameters from 6245 reflections

$\theta = 2.0$ – $34.8^\circ$

$\mu = 0.08$  mm<sup>-1</sup>

$T = 150$  K

Block, pale yellow

$0.32 \times 0.20 \times 0.10$  mm

#### Data collection

Bruker APEXII CCD

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

$\omega$ - $2\theta$  scans

Absorption correction: multi-scan

(*SADABS*; Sheldrick, 2003)

$T_{\min} = 0.967$ ,  $T_{\max} = 0.992$

10001 measured reflections

3578 independent reflections

2876 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.035$

$\theta_{\max} = 27.5^\circ$ ,  $\theta_{\min} = 2.4^\circ$

$h = -13 \rightarrow 13$

$k = -19 \rightarrow 17$

$l = -13 \rightarrow 13$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.054$

$wR(F^2) = 0.121$

$S = 1.12$

3578 reflections

201 parameters

0 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0432P)^2 + 0.5424P]$$

where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$

$$\Delta\rho_{\max} = 0.21 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.21 \text{ e } \text{\AA}^{-3}$$

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	0.71639 (14)	0.36359 (9)	0.25561 (14)	0.0279 (3)
C2	0.68195 (18)	0.44238 (11)	0.29166 (17)	0.0326 (4)
H2	0.7171	0.4607	0.3862	0.039*
C3	0.59660 (17)	0.49695 (11)	0.19394 (16)	0.0295 (4)
H3	0.5732	0.5525	0.2210	0.035*
C4	0.54419 (15)	0.47065 (10)	0.05454 (15)	0.0216 (3)
C5	0.57855 (17)	0.38725 (10)	0.02190 (17)	0.0268 (3)
H5	0.5428	0.3664	-0.0712	0.032*
C6	0.66381 (17)	0.33512 (11)	0.12366 (17)	0.0289 (4)
H6	0.6859	0.2782	0.1004	0.035*
C7	0.8126 (2)	0.30753 (13)	0.36364 (19)	0.0419 (5)
H7A	0.8272	0.2520	0.3205	0.050*
H7B	0.7747	0.2926	0.4363	0.050*
C8	0.9434 (2)	0.35362 (18)	0.4293 (2)	0.0611 (7)
H8A	0.9794	0.3704	0.3570	0.092*
H8B	1.0064	0.3142	0.4961	0.092*
H8C	0.9301	0.4064	0.4777	0.092*
C11	0.78557 (17)	0.02696 (10)	0.34610 (17)	0.0272 (3)
C12	0.74379 (15)	-0.05961 (10)	0.35496 (16)	0.0244 (3)
C13	0.68960 (17)	-0.11623 (10)	0.24024 (17)	0.0278 (4)
C111	0.86714 (17)	0.07327 (11)	0.46718 (18)	0.0296 (4)
N111	0.93116 (16)	0.11456 (10)	0.56078 (17)	0.0404 (4)
C112	0.74700 (19)	0.07493 (11)	0.21941 (18)	0.0329 (4)
N112	0.7174 (2)	0.11723 (10)	0.12027 (18)	0.0493 (5)
O121	0.75622 (12)	-0.08330 (7)	0.48549 (11)	0.0291 (3)
C121	0.78374 (19)	-0.17461 (11)	0.53058 (18)	0.0333 (4)
H12A	0.8336	-0.2043	0.4778	0.040*
H12B	0.6993	-0.2068	0.5148	0.040*
C122	0.8659 (2)	-0.17263 (13)	0.68351 (19)	0.0389 (4)
H12C	0.9484	-0.1397	0.6977	0.058*
H12D	0.8879	-0.2329	0.7177	0.058*
H12E	0.8148	-0.1440	0.7346	0.058*
N131	0.53505 (17)	-0.24711 (11)	0.23439 (17)	0.0419 (4)
C131	0.60543 (18)	-0.18855 (11)	0.24026 (17)	0.0307 (4)
N132	0.7310 (2)	-0.09459 (10)	0.00947 (17)	0.0474 (4)
C132	0.71189 (19)	-0.10195 (11)	0.11281 (18)	0.0323 (4)

Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
N1	0.0345 (8)	0.0254 (7)	0.0236 (7)	0.0027 (6)	0.0099 (6)	0.0024 (5)
C2	0.0447 (10)	0.0299 (9)	0.0209 (8)	0.0042 (7)	0.0082 (7)	-0.0033 (6)
C3	0.0411 (10)	0.0246 (9)	0.0224 (8)	0.0048 (7)	0.0105 (7)	-0.0038 (6)

C4	0.0238 (8)	0.0215 (8)	0.0209 (7)	-0.0028 (6)	0.0097 (6)	-0.0008 (6)
C5	0.0342 (9)	0.0233 (8)	0.0222 (8)	-0.0031 (6)	0.0090 (7)	-0.0039 (6)
C6	0.0384 (10)	0.0226 (8)	0.0273 (9)	0.0022 (7)	0.0136 (7)	-0.0015 (6)
C7	0.0586 (13)	0.0344 (10)	0.0267 (9)	0.0167 (9)	0.0074 (9)	0.0067 (7)
C8	0.0474 (13)	0.0751 (17)	0.0455 (13)	0.0225 (12)	-0.0029 (10)	-0.0035 (11)
C11	0.0321 (9)	0.0250 (8)	0.0260 (8)	0.0012 (7)	0.0118 (7)	-0.0011 (6)
C12	0.0248 (8)	0.0257 (8)	0.0254 (8)	0.0048 (6)	0.0122 (6)	0.0011 (6)
C13	0.0343 (9)	0.0230 (8)	0.0283 (8)	0.0019 (6)	0.0136 (7)	-0.0008 (6)
C111	0.0334 (9)	0.0241 (8)	0.0336 (9)	0.0032 (7)	0.0146 (8)	0.0017 (7)
N111	0.0432 (9)	0.0366 (9)	0.0392 (9)	-0.0039 (7)	0.0115 (8)	-0.0057 (7)
C112	0.0474 (11)	0.0209 (8)	0.0324 (9)	0.0006 (7)	0.0166 (8)	-0.0035 (7)
N112	0.0854 (14)	0.0266 (9)	0.0366 (9)	0.0050 (8)	0.0222 (9)	0.0014 (7)
O121	0.0408 (7)	0.0244 (6)	0.0265 (6)	0.0020 (5)	0.0170 (5)	0.0013 (4)
C121	0.0424 (10)	0.0268 (9)	0.0318 (9)	0.0008 (7)	0.0145 (8)	0.0046 (7)
C122	0.0436 (11)	0.0410 (11)	0.0312 (10)	-0.0011 (8)	0.0120 (8)	0.0048 (8)
N131	0.0503 (10)	0.0410 (10)	0.0369 (9)	-0.0149 (8)	0.0184 (8)	-0.0141 (7)
C131	0.0359 (9)	0.0315 (9)	0.0260 (8)	0.0009 (7)	0.0124 (7)	-0.0076 (7)
N132	0.0815 (13)	0.0317 (9)	0.0365 (9)	0.0048 (8)	0.0301 (9)	0.0021 (7)
C132	0.0467 (11)	0.0213 (8)	0.0293 (9)	0.0035 (7)	0.0138 (8)	-0.0016 (6)

*Geometric parameters (Å, °)*

N1—C6	1.342 (2)	C11—C12	1.404 (2)
N1—C2	1.343 (2)	C11—C111	1.429 (2)
N1—C7	1.489 (2)	C11—C112	1.419 (2)
C2—C3	1.374 (2)	C111—N111	1.151 (2)
C2—H2	0.9500	C112—N112	1.150 (2)
C3—C4	1.399 (2)	C12—O121	1.3462 (18)
C3—H3	0.9500	C12—C13	1.409 (2)
C4—C5	1.394 (2)	C13—C131	1.421 (2)
C4—C4 <sup>i</sup>	1.484 (3)	C13—C132	1.423 (2)
C5—C6	1.373 (2)	O121—C121	1.461 (2)
C5—H5	0.9500	C121—C122	1.506 (2)
C6—H6	0.9500	C121—H12A	0.9900
C7—C8	1.498 (3)	C121—H12B	0.9900
C7—H7A	0.9900	C122—H12C	0.9800
C7—H7B	0.9900	C122—H12D	0.9800
C8—H8A	0.9800	C122—H12E	0.9800
C8—H8B	0.9800	C131—N131	1.154 (2)
C8—H8C	0.9800	C132—N132	1.152 (2)
C6—N1—C2	120.42 (14)	H8A—C8—H8C	109.5
C6—N1—C7	120.15 (14)	H8B—C8—H8C	109.5
C2—N1—C7	119.43 (14)	C12—C11—C112	122.95 (15)
N1—C2—C3	121.00 (15)	C12—C11—C111	121.20 (15)
N1—C2—H2	119.5	C112—C11—C111	115.82 (14)
C3—C2—H2	119.5	O121—C12—C11	113.07 (14)
C2—C3—C4	119.95 (14)	O121—C12—C13	122.33 (14)
C2—C3—H3	120.0	C11—C12—C13	124.56 (14)
C4—C3—H3	120.0	C12—C13—C131	123.33 (15)

C5—C4—C3	117.40 (14)	C12—C13—C132	121.37 (15)
C5—C4—C4 <sup>i</sup>	121.25 (17)	C131—C13—C132	115.26 (15)
C3—C4—C4 <sup>i</sup>	121.35 (17)	N111—C111—C11	176.44 (18)
C6—C5—C4	120.29 (15)	N112—C112—C11	176.89 (19)
C6—C5—H5	119.9	C12—O121—C121	120.53 (12)
C4—C5—H5	119.9	O121—C121—C122	106.87 (14)
N1—C6—C5	120.85 (15)	O121—C121—H12A	110.3
N1—C6—H6	119.6	C122—C121—H12A	110.3
C5—C6—H6	119.6	O121—C121—H12B	110.3
N1—C7—C8	111.15 (17)	C122—C121—H12B	110.3
N1—C7—H7A	109.4	H12A—C121—H12B	108.6
C8—C7—H7A	109.4	C121—C122—H12C	109.5
N1—C7—H7B	109.4	C121—C122—H12D	109.5
C8—C7—H7B	109.4	H12C—C122—H12D	109.5
H7A—C7—H7B	108.0	C121—C122—H12E	109.5
C7—C8—H8A	109.5	H12C—C122—H12E	109.5
C7—C8—H8B	109.5	H12D—C122—H12E	109.5
H8A—C8—H8B	109.5	N131—C131—C13	177.19 (19)
C7—C8—H8C	109.5	N132—C132—C13	176.76 (18)
C6—N1—C2—C3	-2.6 (3)	C112—C11—C12—O121	-160.94 (15)
C7—N1—C2—C3	178.00 (17)	C111—C11—C12—O121	17.0 (2)
N1—C2—C3—C4	0.0 (3)	C13—C12—C11—C111	-165.22 (16)
C2—C3—C4—C5	2.1 (2)	C13—C12—C11—C112	16.9 (3)
C2—C3—C4—C4 <sup>i</sup>	-177.66 (18)	O121—C12—C13—C131	21.3 (2)
C3—C4—C5—C6	-1.9 (2)	C11—C12—C13—C131	-156.34 (16)
C4 <sup>i</sup> —C4—C5—C6	177.93 (17)	O121—C12—C13—C132	-161.40 (15)
C2—N1—C6—C5	2.8 (2)	C11—C12—C13—C132	21.0 (3)
C7—N1—C6—C5	-177.73 (16)	C11—C12—O121—C121	-149.08 (15)
C4—C5—C6—N1	-0.6 (2)	C13—C12—O121—C121	33.0 (2)
C6—N1—C7—C8	121.38 (19)	C12—O121—C121—C122	148.22 (15)
C2—N1—C7—C8	-59.2 (2)		

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C2—H2 $\cdots$ N132 <sup>ii</sup>	0.95	2.37	3.131 (2)	136
C5—H5 $\cdots$ N131 <sup>iii</sup>	0.95	2.41	3.270 (2)	150
C6—H6 $\cdots$ N112	0.95	2.47	3.366 (2)	157

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