Hydrogen-bonding landscape of the carbamoylcyanonitrosomethanide anion in the crystal structure of its ammonium salt

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The structure of the title salt, ammonium carbamoylcyanonitrosomethanide, NH4+C3H2N3O2−, features the co-existence of different hydrogen-bonding patterns, which are specific to each of the three functional groups (nitroso, carbamoyl and cyano) of the methanide anion. The nitroso O-atoms accept as many as three N—H/O/C/C/C/C/O bonds from the ammonium cations [N—O = 2.688 (3)–3.000 (3) Å] to form chains of fused rhombs [(NH4)(O)2]. The most prominent bonds of the carbamoyl groups are mutual and they yield 21 helices [N—O = 2.903 (2) Å], whereas the cyano N-atoms accept hydrogen bonds from sterically less accessible carbamoyl H-atoms [N—N = 3.004 (3) Å]. Two weaker NH4+C3H2N3O2−O/C bonds [N—O = 3.021 (2), 3.017 (2) Å] complete the hydrogen-bonded environment of the carbamoyl groups. A Hirshfeld surface analysis indicates that the most important interactions are overwhelmingly O/H—H···O and N—H/H···N, in total accounting for 64.1% of the contacts for the individual anions. The relatively simple scheme of these interactions allows the delineation of the supramolecular synthons, which may be applicable to crystal engineering of hydrogen-bonded solids containing polyfunctional methanide anions.

1. Chemical context

Resonance-stabilized methanide-type anions are excellent ligands in metal–organic chemistry, which reveal a variety of coordination modes toward metal ions (Gerasimchuk, 2019; Turner et al., 2011). The rich molecular functionality of such species, as is exemplified by different nitrile-, nitroso- and carbamoyl-substituted derivatives, also predetermines their special properties as potent acceptors of conventional hydrogen bonds. These kinds of interactions are important for the solvation and solvatochromism of cyanoanions (Gerasimchuk et al., 2010) and intermolecular bonding in the crystal structures of metal complexes (Gerasimchuk et al., 2015), but it could also influence the specific targeting of cyanoanions in biomedical systems (Gerasimchuk et al., 2007) and their behavior as anionic components for ionic liquids (Janikowski et al., 2013). It is worth noting that extensive conjugation and charge delocalization within the molecular frameworks support higher electron densities at all three functional sites (Chesman et al., 2014), which is beneficial for stronger and more directional interactions. Therefore, methanide-type anions are well suited for the crystal engineering of hydrogen-bonded solids with cationic H-atom donors (Turner et al., 2009).
The specific hydrogen-bonding preferences associated with each of the different functional groups at the methanide core could result in a variety of predictable patterns, as well as providing a degree of selectivity for the interactions with hydrogen-bond donors. In this view, structurally similar methanides possess a distinct potential for crystal design. For example, either nitroso or carbamoyl groups equally well complement the cyano groups in methanide systems, but the chemical outputs of such functionalization, represented by closely related \([\text{ONC} (\text{CN})_2]^-\) and \([\text{C} (\text{CN})_3(\text{CONH}_2)]^-\) anions, are rather different with regard to their hydrogen-bonding behavior. The nitroso groups favor direct interactions with hydrogen-bond-donor cations and the assembly of cation/anion pairs (Arulsamy et al., 1999), while the crystal chemistry of carbamoyldicyanomethanide is dominated by mutual amide/amide and amide/cyano interactions with the generation of less-common anion–anion networks (Turner & Batten, 2010). The particular combination of nitrile, nitroso and carbamoyl groups in carbamoylcyanonitrosomethanide \([\text{ONC} (\text{CN}) (\text{CONH}_2)]^-\), which is a well known product of the nucleophilic addition of water to \([\text{ONC} (\text{CN})_2]^-\) (Arulsamy & Bohle, 2000), presumably allows one to unite the individual structural trends for the two kinds of anions. One can anticipate the assembly of such hybrid hydrogen-bonded structures in a predictable fashion, while taking into account the hierarchy of homo- and heterosynthons formed by each of the functional groups and appropriate hydrogen-bond donors.

In the present contribution, we report the construction of a three-dimensional hydrogen-bonded framework in ammonium carbamoylcyanonitrosomethanide \(\text{NH}_4(\text{nccm})\), which features the co-existence and interplay of the abovementioned anion–cation and mutual anion–anion interactions.

2. Structural commentary

The molecular structure of the title compound is shown in Fig. 1. This salt is isomorphous with the previously examined Cs analog (Domasevskaya et al., 1989), which is slightly unusual when considering the very different nature and ionic radii of the cations.

The main geometries of the (nccm)~(−) (or \(\text{C}_2\text{H}_2\text{N}_2\text{O}_2\)~(−)) anion reveal a highly conjugated structure. The nitrosocyano-methanide O1/N1/C1/C2/N2 fragment itself is planar within 0.004 Å, being almost coplanar also with the C3/N3/O2 amide fragment \([\text{dihedral angle } = 3.93 (14) ^\circ]\). The nitroso group adopts a trans–anti configuration with respect to the carbamoyl C=O group, which is the most favorable either for neutral or anionic ONC–COR species (Ponomareva et al., 1997; Ponomarova & Domasevitch, 2012). When compared with the parameters for neutral H(nccm) (Arulsamy & Bohle, 2000), the deprotonation results in a perceptible lengthening of the double bonds. For example, the carbonyl O2—C3 bond in the title compound is 1.252 (2) Å versus 1.228 (3) Å for H(nccm), but the same elongation is relevant also to the N1—C1 bond [1.303 (2) Å], which is significantly longer than in the latter case [1.275 (3) Å].

This is accompanied by a shortening of the N1—O1 bonds, which are particularly sensitive to the protolytic effects. These effects can be precisely traced by gradual shortening of the nitroso bonds for the series H(nccm) [1.356 (2) Å; Arulsamy & Bohle, 2000] > H(nccm)_2~(−) in the Rb(18-crown-6)~(+) salt [1.322 (3) Å; Domasevitch et al., 1998] > (nccm)~(−) in the title salt [1.3117 (19) Å] > (nccm) in the NMe_4~(+) salt [1.293 (2) Å; Izgorodina et al., 2010], in line with the strength of the N—O—H bonding. Thus, with relatively strong multiple hydrogen bonds sustained by the nitroso O atoms, the N—O bond order in the title compound is still greater than for the symmetrical hydrogen dioximate anion H(nccm)_2~(−) [which is structurally similar to more common hydrogen carboxylates (Speakman, 1972)], but is lower than in NMe_4(nccm) (one N—H—O bond) and also Cs(nccm) [1.297 (8) Å; Domasevskaya et al., 1989] showing only distal ion–dipole interactions of the nitroso group. Such an evolution is clearly reflected in the positions of the ν(NO) bands in the IR spectra (cm⁻¹): they are 1098 for H(nccm); 1140 for H(nccm)_2~(−); 1212 for the title compound; 1253 for NMe_4(nccm) and 1290 for Cs(nccm), demonstrating the systematic blue shift as the N—O bond order increases.

3. Supramolecular features

Beyond Coulombic attraction forces, the primary kinds of interactions for the assembly of the present three-dimensional framework are relatively strong and directional N—H···O and N—H···N hydrogen bonds (Table 1). In spite of the high number of hydrogen-bond donors and their multiple inter-
actions with a set of closely separated acceptors of different nature, this directional and well-defined bonding facilitates the identification of supramolecular synthons. This is reminiscent of the behavior of the methanide analogs in NH₄[C(CN)₂(CONH₂)] and NH₄[ONC(CN)₂] (Arulsamy et al., 1999), but is contrary to the structures of comparable nitrosoalonoamides. For example, ammonium violurate exhibits rather weak and bifurcated hydrogen bonding (Nichol & Clegg, 2007). Also, the cationic ammine in the salt [Ag(NH₃)₂]⁺(nccm) (Gerasimchuk et al., 2010) supports only a few weaker and less directional hydrogen bonds.

Both types of O atoms, i.e., the nitroso (O1) and carbamoyl (O2) groups, accept three N—H O bonds. However, their bonding preferences are markedly different. All the bonds with the O1 acceptor are sustained with the NH₄⁺ cations (Fig. 1), but the principal interactions with O2 correspond to the mutual amide/amide type. They represent the strongest bonds accepted by O2 [N3—O2 = 2.903 (2) Å; N3—H1—O² = 161 (2)°; symmetry code (v) −x, −y + 1, z + 1/2] as compared with two weaker bonds arising from the distal NH₄⁺ cations [N4—O2 = 3.017 (2), 3.021 (2) Å, Fig. 2, Table 1].

An important result from the multiple NH₄⁺—ON interactions is the assembly of infinite chains running along the c-axis direction. Stacking interactions [e.g., N2—C1°] are indicated with thin lines [symmetry codes: (v) −x, −y + 1, z + 1/2; (vii) −x, −y + 1, z + 1/2; (viii) x, y, z − 1].

One can suppose that the incorporation of tetrahedral NH₄⁺ donors itself favors the generation of three-dimensional structures. This is reflected by the formation of one-dimensional helicate motifs as a result of the mutual bonding of the carbamoyl groups (Figs. 3 and 4), instead of the more common amide dimers (McMahon et al., 2005) seen in the NMe₄⁺ salt

| Table 1 | Hydrogen-bond geometry (Å, °). |
| --- | --- | --- | --- | --- |
| D—H···A | D—H | H···A | D···A | D—H···A |
| N4—H3—O1 | 0.89 (2) | 2.07 (2) | 2.848 (2) | 145 (2) |
| N4—H4—O1° | 0.92 (2) | 1.78 (2) | 2.688 (3) | 167 (2) |
| N4—H5—O1° | 0.89 (2) | 2.35 (3) | 3.000 (3) | 129 (3) |
| N4—H5—O2° | 0.89 (2) | 2.46 (3) | 3.021 (2) | 122 (3) |
| N4—H6—O2° | 0.93 (2) | 2.19 (2) | 3.017 (2) | 148 (2) |
| N3—H1—O2° | 0.92 (3) | 2.02 (3) | 2.903 (2) | 161 (2) |
| N3—H2—N2° | 0.85 (3) | 2.24 (3) | 3.004 (3) | 149 (3) |

Symmetry codes: (i) −x, −y, z + 1/2; (ii) −x, −y, z + 1/2; (iii) −x + 1, y − 1/2, z + 1/2; (iv) −x + 1, y − 1/2, z − 1/2; (v) −x, −y + 1, z + 1/2; (vi) x − 1/2, −y + 1/2, z + 1.

Figure 2
Fragment of the crystal structure showing chains, propagating down the c-axis direction, of ammonium/nitroso rhombs sharing opposite edges [symmetry codes: (i) −x, −y, z + 1/2; (ii) −x, −y, z + 1/2; (viii) x, y, z − 1].

Figure 3
Mutual bonding of CONH₃ groups, which yields 2, helices propagating along the c-axis direction. Stacking interactions [e.g., N2—C1°] are indicated with thin lines [symmetry codes: (v) −x, −y + 1, z + 1/2; (vii) −x, −y + 1, z + 1/2; (viii) x, y, z − 1].
ammonium salts. With fewer N—H donors [NH$_4^+$] the compound could also be applicable to a series of substituted interactions: ammonium/nitroso chain (a single rhomb of [(NH$_4$)$_2$(O)$_2$]). In this view, the hydrogen-bonding capacity of the (nccm) skeleton is a primary anion–anion interaction for carbamoyl-substituted methanides (Chesman et al., 2014).

Izgorodina et al., 2010) and metal complexes of (nccm)$^-$ (Domasevitch et al., 1996). As well, because of the abundance of hydrogen-bond donors, the nitroso O atoms accept auxiliary weaker bonds [i.e., N4 · · · O1$^\text{H} = 3.000 (3)$ Å], which deliver an extension of the anticipated discrete pattern based upon single rhombs of [(NH$_4$)$_2$(O)$_2$)]. In this view, the hydrogen-bonding preferences of the (nccm)$^-$ anion in the title compound could also be applicable to a series of substituted ammonium salts. With fewer N—H donors [NH$_4^+$ > RNH$_5^+$ > R$_2$NH$_2^+$], the possible thinning of the hydrogen-bond shell may result in the elimination of the weakest of the present interactions, such as both NH$_4^+$ · · · O2 bonds and one of the NH$_4^+$ · · · O1 bonds. Therefore, three kinds of supramolecular synthons, in the form of centrosymmetric amide/amide and ammonium/nitroso dimers as well as the nitrile/amide bonding may be particularly prevalent for crystal engineering with the (nccm)$^-$ anion (Fig. 5).

The columnar packing of (nccm)$^-$ anions yields slipped stacks down the c-axis direction, with an interplanar distance of 3.32 Å (Figs. 2 and 3). This feature is similar to the structures of cyanomethanide species examined by Chesman et al. (2014), which typically support stacks at 3.15–3.30 Å. However, the overlaps of the (nccm)$^-$ skeletons are minor [as indicated by a large slippage angle of 54.9 (2)] and actually only the nitrile fragment is involved in the stacking with the methanide fragment. The shortest contact between translation-related anions is N2 · · · C1$^\text{viii} = 3.357 (2)$ Å [symmetry code: (viii) x, y, z − 1]. This stacking is less significant for (nccm)$^-$ salts due to the prevalent role of hydrogen bonding, which is a primary anion–anion interaction for carbamoyl-substituted methanides (Chesman et al., 2014).

4. Hirshfeld analysis

The supramolecular interactions in the title structure were further investigated by Hirshfeld surface analysis (Spackman & Byrom, 1997; McKinnon et al., 2004; Hirshfeld, 1977; Spackman & McKinnon, 2002) performed with Crystal-Explorer17 (Turner et al., 2017). The Hirshfeld surface of the individual (nccm)$^-$ anion mapped over d$_\text{norm}$, using a fixed color scale of −0.71 (red) to 1.05 a.u. (blue), reveals a set of red spots associated with the interaction sites (Fig. 6). The most intense spot (−0.708 a.u.) reflects the very short NH$_4^+$ · · · O-nitroso bond, whereas a group of six almost equally prominent spots (−0.393 to −0.519 a.u.) correspond to the mutual amide/amide, amide/nitrile, one NH$_4^+$ · · · O-nitroso and one NH$_4^+$ · · · O-carbamoyl bonds. A third spot in the region of the nitroso-O acceptor is less intense (−0.288 a.u.), while the additional NH$_4^+$ · · · O-carbamoyl bond has only a minor indication of −0.081 a.u.

The two-dimensional fingerprint plots (Fig. 7) are consistent with the prevalence of hydrogen bonding in the structure. For the individual NH$_4^+$ cations, as much as 57.3% of their surface are H···O contacts. The H···N contacts account for only 20.1% (H···H and H···C are 20.1% and 2.5%, respectively), which suggests a rather high selectivity in the bonding of NH$_4^+$ cations to the O-acceptor sites. The plots for the anion are even more informative. The short separations are overwhelmingly hydrogen-bond contacts, accounting for 64.1% of the surface. The O···H/H···O fraction of 34.5% appears on the plot as a pair of sharp spikes pointing to the lower left, with the upper spike representing entirely H···O of the amide/amide synthon (the shortest contact is 2.0 Å), while the more intense and longer lower spike is due to a reciprocal O···H bond superimposed with points from stronger and more numerous O···H (NH$_4^+$) contacts (the shortest is 1.7 Å). In the case of N···H/H···N type (29.6%), two spikes are shorter...
contacts (2.8 Å), which has a complementary donor part at the plot for individual NH₄⁺ cations (not shown here). This very distal interaction may be rationalized as an NH⋅⋅⋅π(C≡N) bond, with the distances N4⋅⋅⋅Cg(C2≡N2) = 3.584 (3); H⋅⋅⋅Cg(C2≡N2) = 2.89 (3) Å and N4H⋅⋅⋅Cg(C2≡N2) = 136 (3)° (Cg is the mid-point of the C2—N2 bond). A similar contact was observed for NH₄[ONC(CN)₂] (Arulsamy et al., 1999). Stacking interactions in the title compound are also important. They contribute in total 18.8% of the contacts represented by the N⋅⋅⋅Cc/N, N⋅⋅⋅C, C⋅⋅⋅C and N⋅⋅⋅O/O⋅⋅⋅N types, all of which have a very similar nature and metrics (the shortest is N⋅⋅⋅C = 3.3 Å). In summary, the results of Hirshfeld surface analysis effectively illustrate the predominant roles of multiple ammonium/nitroso, mutual amide/amide and amide-nitrile interactions as the main supramolecular synthons.

5. Synthesis and crystallization

The 2-cyano-2-isonitrosoacetamide H(nccm) was prepared by nitrosation of cyanoacetamide (Gerasimchuk et al., 2010). It is a relatively weak acid (pKₐ = 5.03; Klaus et al., 2015) and therefore the compound NH₄(nccm) is unstable, readily losing ammonia in air within a period of several days. When slowly evaporated, its aqueous or methanolic solutions lose ammonia first and then H(nccm) crystallizes.

For the preparation of the title compound, 0.339 g of H(nccm) (3 mmol) was dissolved in 10 ml of methanol at 303–313 K and 0.6 ml of 25% aqueous ammonia (8 mmol) were added to form a clear pale-yellow solution. It was placed, in an open vial, inside the larger stoppered flask containing mixture of 50 ml of 2-propanol and 1 ml of 25% aqueous ammonia. Slow interdiffusion of the solvents through the gaseous phase resulted in the precipitation of large pale-yellow NH₄(nccm) crystals over a period of 30 d. The yield was 0.250 g (64%). Analysis (%) calculated for C₃H₆N₄O₂: C 27.69, H 4.65, N 43.07; found: C 28.01, H 4.85, N 42.68. IR (KBr, cm⁻¹): 500 w, 668 s, 766 m, 1022 s, 1092 s, 1144 s, 1172 s, 1212 s, 1402 s, 1600 s, 1686 vs, 2218 m, 3170 br, 3302 br, 3450 s.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All hydrogen atoms were located and then refined isotropically. Soft similarity restraints were applied to four N—H bond lengths and six H—N—H bond angles of the ammonium cations.

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Table 2

| Crystal data | Chemical formula | NH₄⁺·C₂H₄N₃O₂⁻ |
|--------------|------------------|----------------|
| Crystal system, space group | Orthorhombic, Pnma, | |
| Temperature (K) | 173 |
| a, b, c (Å) | 10.7174 (5), 13.8944 (7), 4.0643 (2) |
| V (Å³) | 605.22 (5) |
| Z | 4 |
| Radiation type | Mo Kα |
| μ (mm⁻¹) | 0.12 |
| Crystal size (mm) | 0.37 × 0.30 × 0.21 |

Data collection

| Diffractometer | Bruker APEX II CCD |
|----------------|-------------------|
| No. of measured, independent and observed | 7798, 1420, 1504 |
| | |
| 1 > 2σ(F²) reflections | 0.031 |
| | 0.663 |
| R[F² > 2σ(F²)], wR(F²), S | 0.032, 0.081, 1.10 |
| No. of reflections | 1420 |
| No. of parameters | 106 |
| No. of restraints | 22 |
| H-atom treatment | All H-atom parameters refined |
| Δρmax, Δρmin (e Å⁻³) | 0.19, −0.14 |

Computer programs: SMART-NT (Bruker, 1998). SAINT-NT (Bruker, 1999). SHELXS97 (Sheldrick, 2008). SHELXL2014 (Sheldrick, 2015). DIAMOND (Brandenburg, 1999) and WinGX (Farrugia, 2012).
Ammonium carbamoyl(cyano)(nitroso)methanide

Crystal data

\[
\begin{align*}
\text{NH}_4^+\cdot\text{C}_3\text{H}_2\text{N}_3\text{O}_2^- \\
M_r &= 130.12 \\
\text{Orthorhombic, } &Pna_2_1 \\
a &= 10.7174 (5) \text{ Å} \\
b &= 13.8944 (7) \text{ Å} \\
c &= 4.0643 (2) \text{ Å} \\
V &= 605.22 (5) \text{ Å}^3 \\
Z &= 4 \\
F(000) &= 272 \\
\end{align*}
\]

Data collection

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
\( \varphi \) and \( \omega \) scans
7798 measured reflections
1420 independent reflections

Refinement

Refinement on \( F^2 \)
Least-squares matrix: full
\( R[F^2 > 2\sigma(F^2)] = 0.032 \)
\( wR(F^2) = 0.081 \)
\( S = 1.10 \)
1420 reflections
106 parameters
22 restraints

Secondary atom site location: difference Fourier map
Hydrogen site location: difference Fourier map
All H-atom parameters refined
\( w = 1/[\sigma^2(F_c^2) + (0.0439P)^2 + 0.0604P] \)
where \( P = (F_c^2 + 2F_s^2)/3 \)
\( (\Delta/\sigma)_{\text{max}} < 0.001 \)
\( \Delta\rho_{\text{max}} = 0.19 \text{ e Å}^{-3} \)
\( \Delta\rho_{\text{min}} = -0.14 \text{ e Å}^{-3} \)
Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

|   | x         | y         | z         | Uiso/Upq |
|---|-----------|-----------|-----------|----------|
| O1| −0.01669 (13) | 0.10947 (9) | 0.7570 (4) | 0.0365 (4) |
| O2| 0.12729 (11) | 0.42081 (9) | 0.7040 (4) | 0.0306 (3) |
| N1| −0.02966 (14) | 0.20089 (10) | 0.8299 (5) | 0.0285 (4) |
| N2| 0.23276 (19) | 0.19606 (15) | 0.3518 (6) | 0.0472 (5) |
| N3| −0.05305 (16) | 0.38965 (12) | 0.9758 (5) | 0.0319 (4) |
| N4| 0.17308 (17) | −0.03313 (12) | 0.7032 (5) | 0.0367 (4) |
| C1| 0.05333 (15) | 0.25999 (12) | 0.7110 (5) | 0.0242 (4) |
| C2| 0.15514 (18) | 0.22726 (14) | 0.5109 (6) | 0.0301 (4) |
| C3| 0.04438 (16) | 0.36355 (12) | 0.7975 (5) | 0.0243 (4) |
| H1| −0.057 (2) | 0.4525 (18) | 1.043 (8) | 0.045 (7)* |
| H2| −0.104 (3) | 0.346 (2) | 1.039 (8) | 0.054 (8)* |
| H3| 0.1437 (19) | 0.0263 (14) | 0.727 (7) | 0.046 (7)* |
| H4| 0.125 (2) | −0.0681 (17) | 0.557 (6) | 0.052 (8)* |
| H5| 0.177 (3) | −0.066 (2) | 0.891 (7) | 0.15 (2)* |
| H6| 0.251 (2) | −0.0308 (18) | 0.605 (7) | 0.068 (10)* |

Atomic displacement parameters (Å²)

|       | U₁₁ | U₂₂ | U₃₃ | U₁₂ | U₁₃ | U₂₃ |
|-------|-----|-----|-----|-----|-----|-----|
| O1    | 0.0414 (8) | 0.0202 (6) | 0.0479 (11) | −0.0014 (5) | 0.0053 (8) | −0.0033 (6) |
| O2    | 0.0263 (6) | 0.0245 (6) | 0.0410 (8) | −0.0038 (5) | 0.0026 (6) | 0.0051 (6) |
| N1    | 0.0318 (8) | 0.0209 (7) | 0.0329 (9) | −0.0005 (6) | 0.0012 (7) | −0.0016 (7) |
| N2    | 0.0415 (10) | 0.0541 (11) | 0.0459 (13) | 0.0128 (8) | 0.0116 (10) | −0.0012 (9) |
| N3    | 0.0315 (8) | 0.0215 (8) | 0.0427 (11) | −0.0039 (6) | 0.0089 (8) | −0.0041 (7) |
| N4    | 0.0406 (9) | 0.0299 (8) | 0.0396 (10) | 0.0044 (7) | −0.0045 (10) | −0.0042 (9) |
| C1    | 0.0248 (8) | 0.0222 (8) | 0.0256 (8) | 0.0024 (6) | −0.0012 (8) | 0.0010 (7) |
| C2    | 0.0298 (9) | 0.0287 (9) | 0.0318 (10) | 0.0030 (7) | 0.0013 (9) | 0.0043 (8) |
| C3    | 0.0234 (8) | 0.0224 (8) | 0.0270 (10) | −0.0008 (6) | −0.0034 (7) | 0.0027 (7) |

Geometric parameters (Å, °)

|       | O1—N1 | N4—H3 | O2—C3 | N4—H4 | N1—C1 | N4—H5 | N2—C2 | N4—H6 | N3—C3 | C1—C2 | N3—H1 | C1—C3 | N3—H2 |  |
|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| O1—N1| 1.3117 (19) |     | 1.252 (2) |     | 1.303 (2) |     | 1.140 (3) |     | 1.322 (3) |     | 0.92 (3) |     | 0.85 (3) |     |  |
| O2—C3| 1.3117 (19) |     | 1.252 (2) |     | 1.303 (2) |     | 1.140 (3) |     | 1.322 (3) |     | 0.92 (3) |     | 0.85 (3) |     |  |
| N1—C1| 1.3117 (19) |     | 1.252 (2) |     | 1.303 (2) |     | 1.140 (3) |     | 1.322 (3) |     | 0.92 (3) |     | 0.85 (3) |     |  |
C1—N1—O1  
C3—N3—H1  
C3—N3—H2  
H1—N3—H2  
H3—N4—H4  
H3—N4—H5  
H4—N4—H5  
H3—N4—H6  
H4—N4—H6  
O1—N1—C1—C2  
O1—N1—C1—C3  
N1—C1—C3—O2  
Hydrogen-bond geometry (Å, °)

| D—H···A | D—H | H···A | D···A | D—H···A |
|---------|------|-------|-------|---------|
| N4—H3···O1 | 0.89 (2) | 2.07 (2) | 2.848 (2) | 145 (2) |
| N4—H4···O1i | 0.92 (2) | 1.78 (2) | 2.688 (3) | 167 (2) |
| N4—H5···O1ii | 0.89 (2) | 2.35 (3) | 3.000 (3) | 129 (3) |
| N4—H5···O2iii | 0.89 (2) | 2.46 (3) | 3.021 (2) | 122 (3) |
| N4—H6···O2iv | 0.93 (2) | 2.19 (2) | 3.017 (2) | 148 (2) |
| N3—H1···O2v | 0.92 (3) | 2.02 (3) | 2.903 (2) | 161 (2) |
| N3—H2···N2vi | 0.85 (3) | 2.24 (3) | 3.004 (3) | 149 (3) |

Symmetry codes: (i) −x, −y, z+1/2; (ii) −x, −y, z+1/2; (iii) −x+1/2, y−1/2, z+1/2; (iv) −x+1/2, y−1/2, z−1/2; (v) −x, −y+1, z+1/2; (vi) x−1/2, −y+1/2, z+1.