

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

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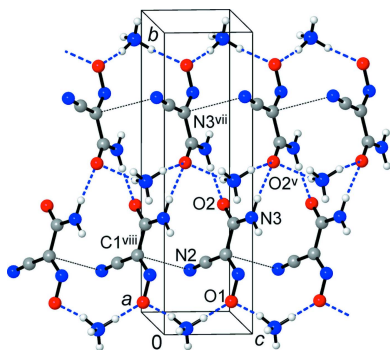
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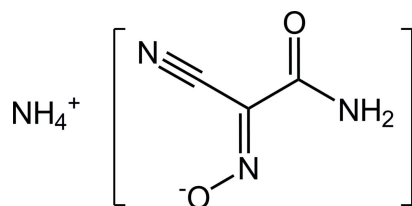
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The structure of the title salt, ammonium carbamoylcyano-nitrosomethanide, $\text{NH}_4^+\cdot\text{C}_3\text{H}_2\text{N}_3\text{O}_2^-$, features the co-existence of different hydrogen-bonding patterns, which are specific to each of the three functional groups (nitroso, carbamoyl and cyano) of the methanide anion. The nitroso O-atoms accept as many as three $\text{N}-\text{H}\cdots\text{O}$ bonds from the ammonium cations [$\text{N}\cdots\text{O} = 2.688(3)\text{--}3.000(3)\text{ \AA}$] to form chains of fused rhombs $[(\text{NH}_4)(\text{O})_2]$. The most prominent bonds of the carbamoyl groups are mutual and they yield 2_1 helices [$\text{N}\cdots\text{O} = 2.903(2)\text{ \AA}$], whereas the cyano N-atoms accept hydrogen bonds from sterically less accessible carbamoyl H-atoms [$\text{N}\cdots\text{N} = 3.004(3)\text{ \AA}$]. Two weaker $\text{NH}_4^+\cdots\text{O}=\text{C}$ bonds [$\text{N}\cdots\text{O} = 3.021(2), 3.017(2)\text{ \AA}$] complete the hydrogen-bonded environment of the carbamoyl groups. A Hirshfeld surface analysis indicates that the most important interactions are overwhelmingly $\text{O}\cdots\text{H}/\text{H}\cdots\text{O}$ and $\text{N}\cdots\text{H}/\text{H}\cdots\text{N}$, 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 $[\text{C}(\text{CN})_2(\text{CONH}_2)]^-$ 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 carbamoylcyano nitrosomethanide $[\text{ONC}(\text{CN})(\text{CONH}_2)]^-$, 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 carbamoylcyano nitrosomethanide $\text{NH}_4(\text{nccm})$, which features the co-existence and interplay of the above-mentioned 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 (Domashevskaya *et al.*, 1989), which is slightly unusual when considering the very different nature and ionic radii of the cations.

The main geometries of the $(\text{nccm})^-$ (or $\text{C}_3\text{H}_2\text{N}_3\text{O}_2^-$) anion reveal a highly conjugated structure. The nitrosocyanomethanide O1/N1/C1/C2/N2 fragment itself is planar within 0.004 Å, being almost coplanar also with the C3/N3/O2 amide fragment [dihedral angle = 3.93 (14)°]. 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 $\text{ONC}(\text{CN})-\text{COR}$ species (Ponomareva *et*

al., 1997; Ponomarova & Domasevitch, 2012). When compared with the parameters for neutral $\text{H}(\text{nccm})$ (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 $\text{H}(\text{nccm})$, 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 $\text{H}(\text{nccm})$ [1.356 (2) Å; Arulsamy & Bohle, 2000] > $\text{H}(\text{nccm})_2^-$ in the $\text{Rb}(18\text{-crown-6})^+$ salt [1.322 (3) Å; Domasevitch *et al.*, 1998] > $(\text{nccm})^-$ in the title salt [1.3117 (19) Å] > $(\text{nccm})^-$ 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 $\text{H}(\text{nccm})_2^-$ [which is structurally similar to more common hydrogen carboxylates (Speakman, 1972)], but is lower than in $\text{NMe}_4(\text{nccm})$ (one N–H···O bond) and also $\text{Cs}(\text{nccm})$ [1.297 (8) Å; Domashevskaya *et al.*, 1989] showing only distal ion–dipole interactions of the nitroso group. Such an evolution is clearly reflected in the positions of the $\nu(\text{NO})$ bands in the IR spectra (cm^{-1}): they are 1098 for $\text{H}(\text{nccm})$; 1140 for $\text{H}(\text{nccm})_2^-$; 1212 for the title compound; 1253 for $\text{NMe}_4(\text{nccm})$ and 1290 for $\text{Cs}(\text{nccm})$, 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-

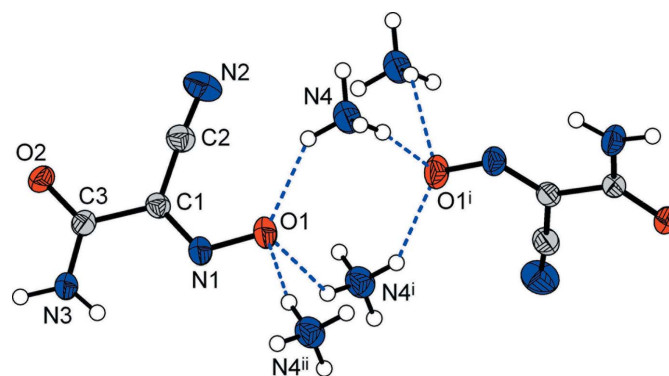


Figure 1
The molecular structure of the title compound with displacement ellipsoids drawn at the 50% probability level. Dotted blue lines indicate N–H···O hydrogen bonds [symmetry codes: (i) $-x, -y, z - \frac{1}{2}$; (ii) $-x, -y, z + \frac{1}{2}$].

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N4—H3 \cdots O1	0.89 (2)	2.07 (2)	2.848 (2)	145 (2)
N4—H4 \cdots O1 ⁱ	0.92 (2)	1.78 (2)	2.688 (3)	167 (2)
N4—H5 \cdots O1 ⁱⁱ	0.89 (2)	2.35 (3)	3.000 (3)	129 (3)
N4—H5 \cdots O2 ⁱⁱⁱ	0.89 (2)	2.46 (3)	3.021 (2)	122 (3)
N4—H6 \cdots O2 ^{iv}	0.93 (2)	2.19 (2)	3.017 (2)	148 (2)
N3—H1 \cdots O2 ^v	0.92 (3)	2.02 (3)	2.903 (2)	161 (2)
N3—H2 \cdots N2 ^{vi}	0.85 (3)	2.24 (3)	3.004 (3)	149 (3)

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

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 $\text{NH}_4[\text{C}(\text{CN})_2(\text{CONH}_2)]$ and $\text{NH}_4[\text{ONC}(\text{CN})_2]$ (Arulsamy *et al.*, 1999), but is contrary to the structures of comparable nitrosomalonoamides. For example, ammonium violurate exhibits rather weak and bifurcated hydrogen bonding (Nichol & Clegg, 2007). Also, the cationic ammine in the salt $[\text{Ag}(\text{NH}_3)_2](\text{nccm})$ (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 $\text{N}-\text{H}\cdots\text{O}$ bonds. However, their bonding preferences are markedly different. All the bonds with the O1 acceptor are sustained with the NH_4^+ cations (Fig. 1), but the principal interactions with O2 correspond to the mutual amide/amide type. They represent the strongest bond accepted by O2 [$\text{N3}\cdots\text{O2}^{\text{v}} = 2.903$ (2) Å; $\text{N3}-\text{H1}\cdots\text{O}^{\text{v}}$

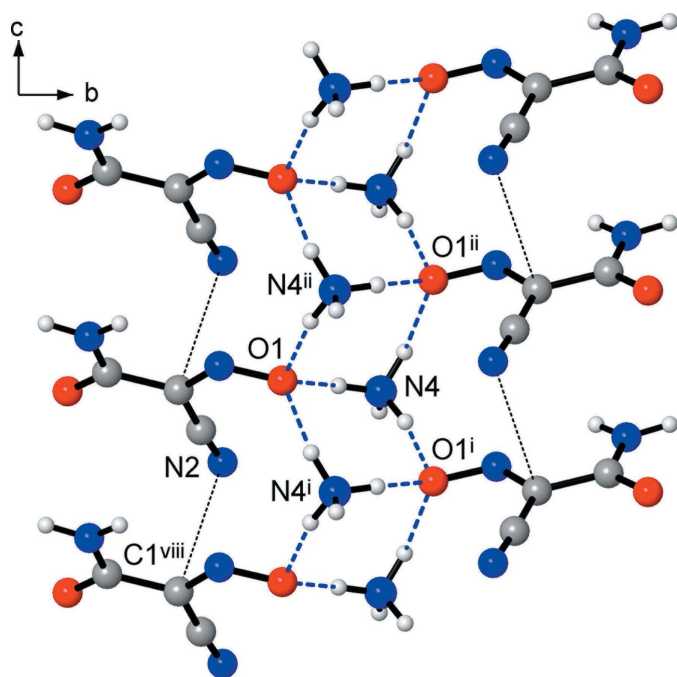


Figure 2
 Fragment of the crystal structure showing chains, propagating down the c -axis direction, of ammonium/nitroso rhombs sharing opposite edges [symmetry codes: (i) $-x, -y, z - \frac{1}{2}$; (ii) $-x, -y, z + \frac{1}{2}$; (viii) $x, y, z - 1$].

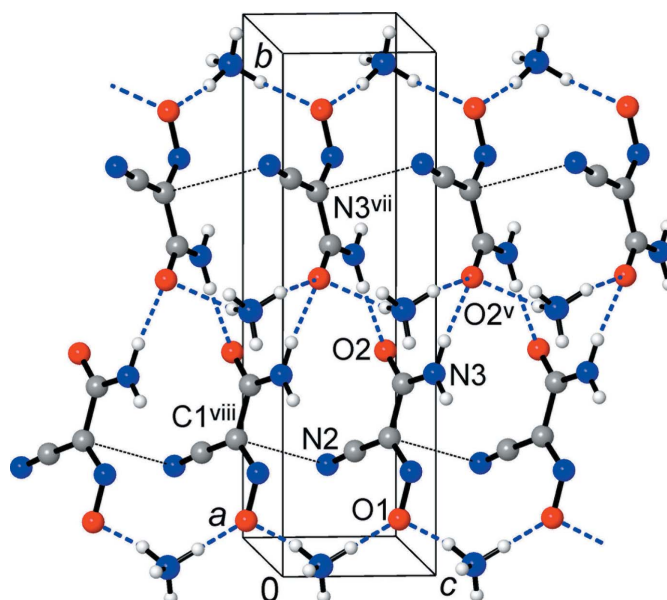


Figure 3
 Mutual bonding of CONH_2 groups, which yields 2_1 helices propagating along the c -axis direction. Stacking interactions [e.g. $\text{N2}\cdots\text{C1}^{\text{viii}}$] are indicated with thin lines [symmetry codes: (v) $-x, -y + 1, z + \frac{1}{2}$; (vii) $-x, -y + 1, -\frac{1}{2} + z$; (viii) $x, y, z - 1$].

$= 161$ (2)°; symmetry code (v) $-x, -y + 1, z + \frac{1}{2}$], as compared with two weaker bonds arising from the distal NH_4^+ cations [$\text{N4}\cdots\text{O2} = 3.017$ (2), 3.021 (2) Å, Fig. 2, Table 1].

An important result from the multiple $\text{NH}_4^+\cdots\text{ON}$ interactions is the assembly of infinite chains running along the c -axis direction in the crystal, with the $[(\text{NH}_4)_2(\text{O})_2]$ rhombs sharing their opposite edges (Fig. 2). Two such $\text{N}-\text{H}\cdots\text{O}$ bonds are relatively strong [$\text{N}\cdots\text{O} = 2.688$ (3) and 2.848 (2) Å, Table 1], whereas $\text{N4}\cdots\text{O1}^{\text{ii}}$ [3.000 (3) Å, symmetry code (ii) $-x, -y, x + \frac{1}{2}$] exists as a branch of a weaker bifurcated $\text{N4}-\text{H5}\cdots(\text{O1}, \text{O2})$ interaction with the nitroso and carbamoyl acceptors. The present motif is noticeably different from the bonding of NH_4^+ cations and nitrosodicyanomethanide, with the ionic pairs assembled *via* both the O and N atoms of the nitroso groups and only two $\text{N}-\text{H}\cdots\text{O}$ interactions retained at $\text{N}\cdots\text{O}$ distances of 2.822 (2), 2.881 (2) Å, which are comparable to the two strongest bonds in the title salt (Arulsamy *et al.*, 1999). Such a discrimination of the nitroso N atom in $(\text{nccm})^-$ may be attributed to its lower accessibility, which is in line with the higher steric demands of the carbamoyl group. At the same time, one of the carbamoyl H atoms (which is *trans*-positioned to the $\text{C}=\text{O}$ bond) is also less accessible and it selectively maintains weaker $\text{N}-\text{H}\cdots\text{N}$ bonding to the nitrile acceptor [$\text{N3}\cdots\text{N2}^{\text{vi}} = 3.004$ (3) Å; symmetry code (vi) $x - \frac{1}{2}, -y + \frac{1}{2}, z + 1$], very similar to the structure of parent $\text{H}(\text{nccm})$ (Arulsamy & Bohle, 2000).

One can suppose that the incorporation of tetrahedral NH_4^+ 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 NMe_4^+ salt

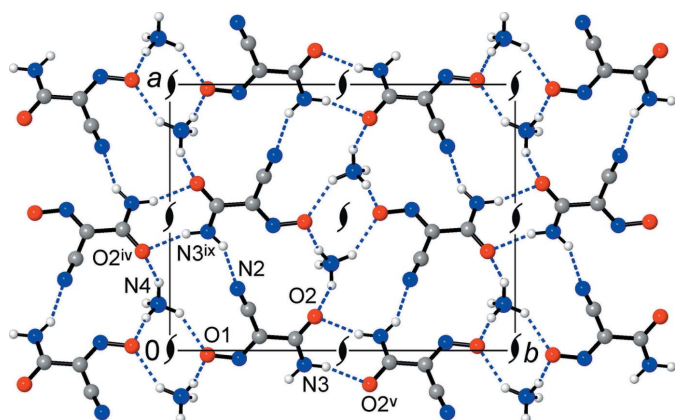


Figure 4
Structure of the title compound, viewed in a projection onto the *ab* plane, showing the co-existence and interplay of the three main supramolecular motifs in the form of ammonium/nitroso chains, amide/amide chains (both of which are situated across 2_1 axes and are orthogonal to the drawing plane) and amide–nitrile mutual bonding [symmetry codes: (iv) $-x + \frac{1}{2}, y - \frac{1}{2}, z - \frac{1}{2}$; (v) $-x, -y + 1, z + \frac{1}{2}$; (ix) $x + \frac{1}{2}, -y + \frac{1}{2}, z$].

(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.*, $N4 \cdots O1^{ii} = 3.000(3) \text{ \AA}$], 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 [$NH_4^+ > RNH_3^+ > R_2NH_2^+$], the possible thinning of the hydrogen-bond shell

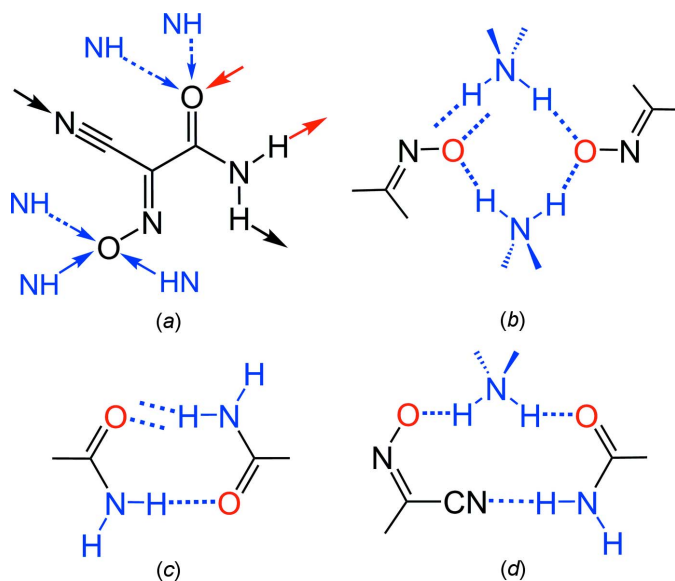


Figure 5
The hydrogen-bonding capacity of the $(nccm)^-$ anion. (a) Two kinds of mutual interactions marked in black and red and bonding with NH_4^+ cations marked in blue; (b–d) three types of supramolecular synthons identified for the title compound taking into account a set of strongest interactions: ammonium/nitroso chain (b), amide/amide chains (c) and mutual amide/nitrile bonding (d).

may result in the elimination of the weakest of the present interactions, such as both $NH_4^+ \cdots O2$ bonds and one of the $NH_4^+ \cdots O1$ 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 \AA (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 $3.15\text{--}3.30 \text{ \AA}$. However, the overlaps of the $(nccm)^-$ skeletons are minor [as indicated by a large slippage angle of $54.9(2)^\circ$] and actually only the nitrile fragment is involved in the stacking with the methanide fragment. The shortest contact between translation-related anions is $N2 \cdots C1^{viii} = 3.357(2) \text{ \AA}$ [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_{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 $H \cdots O$ contacts. The $H \cdots N$ contacts account for only 20.1% ($H \cdots H$ and $H \cdots C$ 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 $O \cdots H/H \cdots O$ 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 $H \cdots O$ of the amide/amide synthon (the shortest contact is 2.0 \AA), while the more intense and longer lower spike is due to a reciprocal $O \cdots H$ bond superimposed with points from stronger and more numerous $O \cdots H$ (NH_4^+) contacts (the shortest is 1.7 \AA). In the case of $N \cdots H/H \cdots N$ type (29.6%), two spikes are shorter

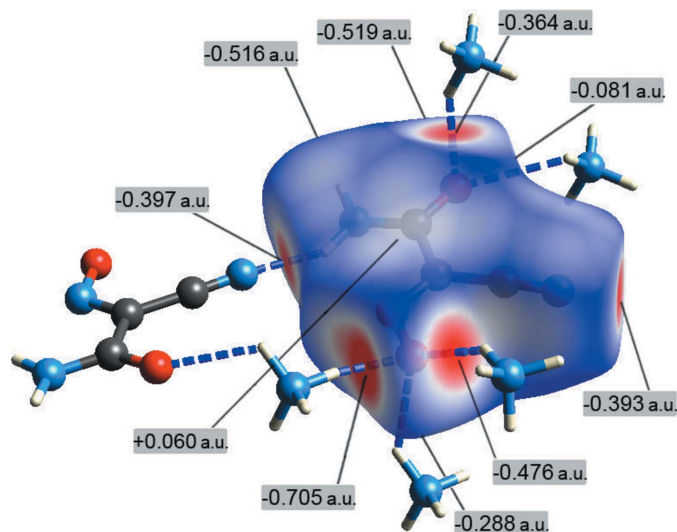


Figure 6
The Hirshfeld surface of the $(\text{nccm})^-$ anion mapped over d_{norm} in the color range -0.71 (red) to 1.05 a.u. (blue), in the environment of the hydrogen-bonded ammonium cations and one (out of three) $(\text{nccm})^-$ anion.

(2.2 \AA) and nearly symmetrical, indicating the mutual character of this weaker bonding. Although the $\text{C}\cdots\text{H}/\text{H}\cdots\text{C}$ contacts of the anion (9.0%) are mostly mutual, the plot also features a small but relatively sharp spike from $\text{C}\cdots\text{NH}_4^+$

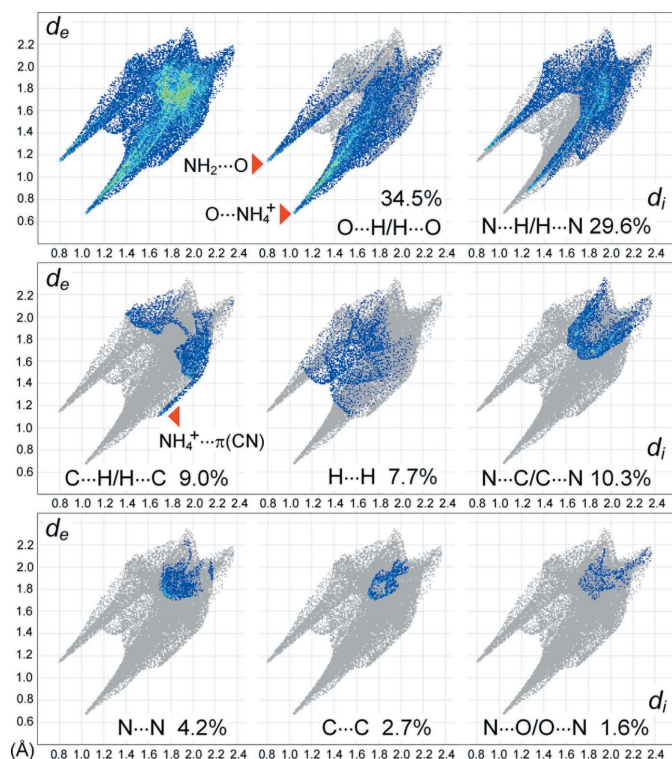


Figure 7
Two-dimensional fingerprint plots for the anions of the title compound, and delineated into the principal contributions of $\text{O}\cdots\text{H}/\text{H}\cdots\text{O}$, $\text{N}\cdots\text{H}/\text{H}\cdots\text{N}$, $\text{C}\cdots\text{H}/\text{H}\cdots\text{C}$, $\text{H}\cdots\text{H}$, $\text{N}\cdots\text{C}/\text{C}\cdots\text{N}$, $\text{N}\cdots\text{N}$, $\text{C}\cdots\text{C}$ and $\text{N}\cdots\text{O}/\text{O}\cdots\text{N}$ contacts. Other minor contributors are $\text{C}\cdots\text{O}/\text{O}\cdots\text{C}$ contacts (0.3%).

contacts (2.8 \AA), which has a complementary donor part at the plot for individual NH_4^+ cations (not shown here). This very distal interaction may be rationalized as an $\text{NH}\cdots\pi(\text{C}\equiv\text{N})$ bond, with the distances $\text{N4}\cdots\text{Cg}(\text{C}\equiv\text{N}2) = 3.584(3)$; $\text{H}\cdots\text{Cg}(\text{C}\equiv\text{N}2) = 2.89(3) \text{ \AA}$ and $\text{N4H}\cdots\text{Cg}(\text{C}\equiv\text{N}2) = 136(3)^\circ$ (Cg is the mid-point of the $\text{C}2-\text{N}2$ bond). A similar contact was observed for $\text{NH}_4[\text{ONC}(\text{CN})_2]$ (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 $\text{N}\cdots\text{C}/\text{C}\cdots\text{N}$, $\text{N}\cdots\text{N}$, $\text{C}\cdots\text{C}$ and $\text{N}\cdots\text{O}/\text{O}\cdots\text{N}$ types, all of which have a very similar nature and metrics (the shortest is $\text{N}\cdots\text{C} = 3.3 \text{ \AA}$). 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 $\text{H}(\text{nccm})$ was prepared by nitrosation of cyanoacetamide (Gerasimchuk *et al.*, 2010). It is a relatively weak acid ($\text{p}K_a = 5.03$; Klaus *et al.*, 2015) and therefore the compound $\text{NH}_4(\text{nccm})$ 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 $\text{H}(\text{nccm})$ crystallizes.

For the preparation of the title compound, 0.339 g of $\text{H}(\text{nccm})$ (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 $\text{NH}_4(\text{nccm})$ crystals over a period of 30 d. The yield was 0.250 g (64%). Analysis (%) calculated for $\text{C}_3\text{H}_6\text{N}_4\text{O}_2$: 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

Experimental details.

Crystal data	
Chemical formula	NH ₄ ⁺ ·C ₃ H ₂ N ₃ O ₂ [−]
<i>M_r</i>	130.12
Crystal system, space group	Orthorhombic, <i>Pna</i> 2 ₁
Temperature (K)	173
<i>a</i> , <i>b</i> , <i>c</i> (Å)	10.7174 (5), 13.8944 (7), 4.0643 (2)
<i>V</i> (Å ³)	605.22 (5)
<i>Z</i>	4
Radiation type	Mo Kα
μ (mm ^{−1})	0.12
Crystal size (mm)	0.37 × 0.30 × 0.21
Data collection	
Diffractionmeter	Bruker APEXII CCD
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	7798, 1420, 1304
<i>R</i> _{int}	0.031
(sin θ/λ) _{max} (Å ^{−1})	0.663
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	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
Δρ _{max} , Δρ _{min} (e Å ^{−3})	0.19, −0.14

Computer programs: *SMART-NT* (Bruker, 1998), *SAINT-NT* (Bruker, 1999), *SHELXS97* (Sheldrick, 2008), *SHELXL2014/7* (Sheldrick, 2015), *DIAMOND* (Brandenburg, 1999) and *WinGX* (Farrugia, 2012).

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supporting information

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

Kostiantyn V. Domasevitch, Ganna A. Senchyk, Andrey B. Lysenko and Eduard B. Rusanov

Computing details

Data collection: *SMART-NT* (Bruker, 1998); cell refinement: *SAINT-NT* (Bruker, 1999); data reduction: *SAINT-NT* (Bruker, 1999); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014/7* (Sheldrick, 2015); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *WinGX* (Farrugia, 2012).

Ammonium carbamoyl(cyano)(nitroso)methanide

Crystal data

$\text{NH}_4^+\cdot\text{C}_3\text{H}_2\text{N}_3\text{O}_2^-$

$M_r = 130.12$

Orthorhombic, *Pna*2₁

$a = 10.7174$ (5) Å

$b = 13.8944$ (7) Å

$c = 4.0643$ (2) Å

$V = 605.22$ (5) Å³

$Z = 4$

$F(000) = 272$

$D_x = 1.428$ Mg m⁻³

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

Cell parameters from 2828 reflections

$\theta = 2.4\text{--}25.3^\circ$

$\mu = 0.12$ mm⁻¹

$T = 173$ K

Prism, yellow

$0.37 \times 0.30 \times 0.21$ mm

Data collection

Bruker APEXII CCD
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

φ and ω scans

7798 measured reflections

1420 independent reflections

1304 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.031$

$\theta_{\text{max}} = 28.1^\circ$, $\theta_{\text{min}} = 2.4^\circ$

$h = -14 \rightarrow 14$

$k = -18 \rightarrow 18$

$l = -5 \rightarrow 5$

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

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: difference Fourier map

All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0439P)^2 + 0.0604P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} < 0.001$

$\Delta\rho_{\text{max}} = 0.19$ e Å⁻³

$\Delta\rho_{\text{min}} = -0.14$ 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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
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 (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
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 (\AA , $^\circ$)

O1—N1	1.3117 (19)	N4—H3	0.89 (2)
O2—C3	1.252 (2)	N4—H4	0.924 (19)
N1—C1	1.303 (2)	N4—H5	0.89 (2)
N2—C2	1.140 (3)	N4—H6	0.93 (2)
N3—C3	1.322 (3)	C1—C2	1.435 (3)
N3—H1	0.92 (3)	C1—C3	1.484 (2)
N3—H2	0.85 (3)		

C1—N1—O1	117.00 (15)	H5—N4—H6	110 (2)
C3—N3—H1	117.6 (17)	N1—C1—C2	121.97 (16)
C3—N3—H2	118 (2)	N1—C1—C3	118.61 (16)
H1—N3—H2	124 (3)	C2—C1—C3	119.38 (15)
H3—N4—H4	111.2 (17)	N2—C2—C1	176.0 (2)
H3—N4—H5	114 (2)	O2—C3—N3	123.56 (17)
H4—N4—H5	108 (2)	O2—C3—C1	119.90 (16)
H3—N4—H6	109.6 (18)	N3—C3—C1	116.54 (15)
H4—N4—H6	104.0 (17)		
O1—N1—C1—C2	-0.4 (3)	C2—C1—C3—O2	-2.1 (3)
O1—N1—C1—C3	-177.92 (16)	N1—C1—C3—N3	-4.0 (3)
N1—C1—C3—O2	175.4 (2)	C2—C1—C3—N3	178.45 (19)

Hydrogen-bond 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>
N4—H3...O1	0.89 (2)	2.07 (2)	2.848 (2)	145 (2)
N4—H4...O1 ⁱ	0.92 (2)	1.78 (2)	2.688 (3)	167 (2)
N4—H5...O1 ⁱⁱ	0.89 (2)	2.35 (3)	3.000 (3)	129 (3)
N4—H5...O2 ⁱⁱⁱ	0.89 (2)	2.46 (3)	3.021 (2)	122 (3)
N4—H6...O2 ^{iv}	0.93 (2)	2.19 (2)	3.017 (2)	148 (2)
N3—H1...O2 ^v	0.92 (3)	2.02 (3)	2.903 (2)	161 (2)
N3—H2...N2 ^{vi}	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) $x-1/2, -y+1/2, z+1$.