Tetramethylammonium (Z)-N′-cyanocarbamimidate

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In the structure of the tetramethyl ammonium salt of cyanourea, $C_4H_{12}N^+ \cdot C_2H_2N_3O^-$, the N—C and O—C bond distances in the cyano and keto groups are in the normal range for such a moieties at 1.1641 (18) and 1.2550 (16) Å. However, the bonds about the central C and N atoms are much shorter than would be expected for single bonds and indicate that there is considerable electron delocalization in the anion as was also found in the silver salt. The NH_2 group is coplanar with the central N_2CO core, in contrast with the nitrile group where the dihedral angle between the N—C—N and N_2CO planes is 36.5 (3)°. The packing of the cations and anions in the unit cell involves N—H···O hydrogen bonds between anions characterized by an $R_2^2(8)$ motif, as well as N—H···O hydrogen bonds between anions and C—H···O interactions between both cations and anions, forming an $R_3^3(14)$ pattern.

3D view

Chemical scheme
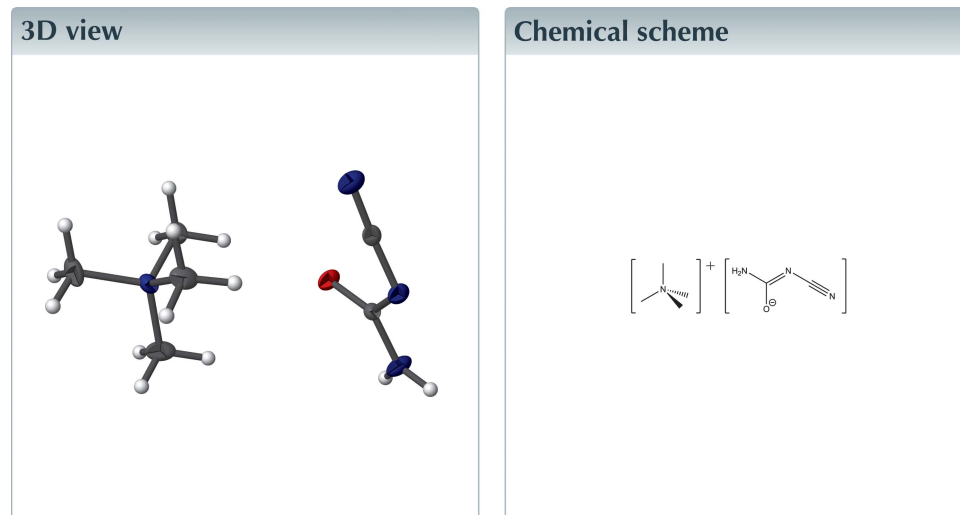
Structure description

Cyanourea and its salts have been the subject of much interest including the use of its derivatives in the study of solid state reaction mechanisms (Lotsch & Schnick, 2004), as substituents in manipulating the conformation of calix[4]arenes (Ling *et al.*, 2014), in the synthesis of amide-acid chloride adducts in organic synthesis (Harris, 1981), and in modulating the magnetic properties of Mn_6 clusters (Yang *et al.*, 2009). In spite of this interest there has been very little structural characterization of this moiety and only structures of its ammonium (Lotsch & Schnick, 2004), silver (Britton, 1987), and potassium salts (Magomedova & Zvonkova, 1974) have been reported.

In the title compound, $[C_4H_{12}N]^+[C_2H_2N_3O]^-$, **1**, the tetramethyl ammonium salt of cyanourea is reported and shown in Fig. 1. The N—C and O—C bond distances in the cyano and keto groups [1.1641 (18) and 1.2550 (16) Å, respective] are in the normal range for such a moieties and similar to the values found for the silver salt [1.149 (6) and

Table 1
Selected geometric parameters (Å, °).

O1—C5	1.2550 (16)	N3—C5	1.3703 (17)
N2—C5	1.3464 (18)	N4—C6	1.1641 (18)
N3—C6	1.3155 (19)		
C6—N3—C5	114.79 (12)	N2—C5—N3	114.95 (12)
O1—C5—N2	120.31 (12)	N4—C6—N3	174.73 (15)
O1—C5—N3	124.73 (13)		

Table 2
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C1—H1$C\cdots$O1^i	0.98	2.63	3.487 (2)	147
C2—H2$A\cdots$O1^i	0.98	2.57	3.447 (2)	149
C3—H3$B\cdots$O1^i	0.98	2.62	3.484 (2)	147
C3—H3$C\cdots$O1	0.98	2.30	3.253 (2)	164
C4—H4$A\cdots$N3^{ii}	0.98	2.54	3.450 (2)	155
C4—H4$C\cdots$N3^{iii}	0.98	2.59	3.536 (2)	162
N2—H2$D\cdots$O1^{iv}	0.88	2.03	2.9084 (16)	174
N2—H2$E\cdots$N4^v	0.88	2.18	3.0126 (19)	158

Symmetry codes: (i) $-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{3}{2}$; (ii) $x+\frac{1}{2}, -y+\frac{3}{2}, z+\frac{1}{2}$; (iii) $-x+1, -y+1, -z+1$; (iv) $-x, -y+1, -z+1$; (v) $x-\frac{1}{2}, -y+\frac{3}{2}, z-\frac{1}{2}$.

1.248 (5) Å, respectively]. However, the bonds about C5 and N3 are much shorter than would be expected for single bonds (Table 1) and indicate that there is considerable electron delocalization in the anion, as was also found in the silver salt. In **1**, the NH$_2$ group is coplanar with the central N$_2$CO core [dihedral angle between NH$_2$ and N$_2$CO planes of only 0.54 (8)°] in contrast with the nitrile group where the dihedral angle between the N—C—N and N$_2$CO planes is 36.5 (3)°. These values are different to those found in the silver salt where the corresponding angles are 23 (6) and 4.5 (3)°.

The packing of the cations and anions in the unit cell involves N—H$\cdots$O hydrogen bonds (Table 2) between anions characterized by an $R_2^2(8)$ motif as well as N—H$\cdots$O hydrogen bonds between anions and C—H$\cdots$O interactions between both cations and anions forming an $R_3^3(14)$ pattern as shown in Fig. 2.
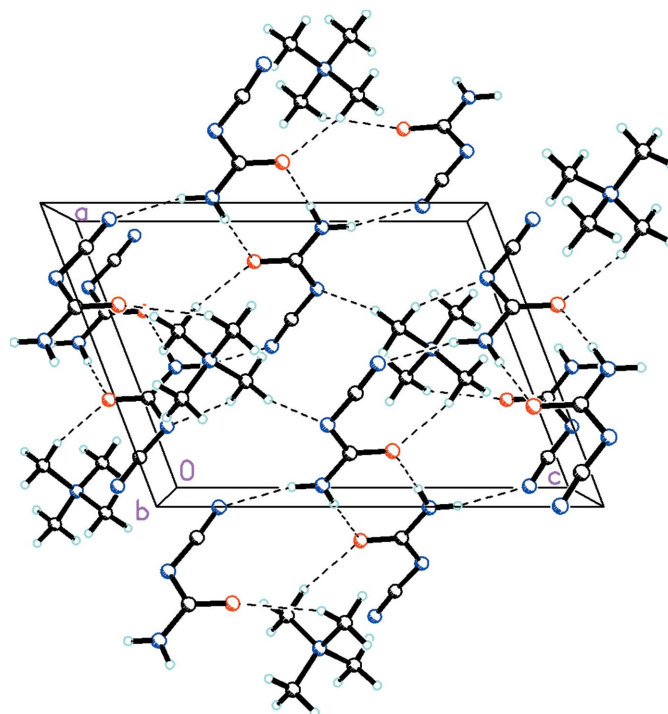
Table 3
Experimental details.

Crystal data	
Chemical formula	$C_4H_{12}N^+\cdot C_2H_2N_3O^-$
M_r	158.21
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	100
a, b, c (Å)	8.8120 (4), 8.7561 (4), 12.1093 (6)
β (°)	110.897 (2)
V (Å^3)	872.88 (7)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.09
Crystal size (mm)	$0.25 \times 0.12 \times 0.05$
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2016)
T_{min}, T_{max}	0.651, 0.747
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	17548, 4340, 2752
R_{int}	0.156
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.836
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.081, 0.174, 1.04
No. of reflections	4340
No. of parameters	105
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	0.44, −0.27

Computer programs: *APEX2* and *SAINT* (Bruker, 2016), *SHELXT* (Sheldrick 2015a), *SHELXL2018/3* (Sheldrick, 2015b), and *SHELXTL* (Sheldrick 2008).

Figure 1
Diagram showing the [C$_4$H$_{12}$N]$^+$ cation and [C$_2$H$_2$N$_3$O$_3$]$^-$ anion linked by a C—H$\cdots$O interaction (shown as a dashed line). Atomic displacement parameters are drawn at the 30% probability level.

Figure 2
Diagram showing the packing of the cations and anions in the unit cell, which involves N—H$\cdots$O hydrogen bonds between anions characterized by an $R_2^2(8)$ motif as well as N—H$\cdots$O hydrogen bonds between anions and C—H$\cdots$O interactions between both cations and anions forming an $R_3^3(14)$ pattern (all interactions shown with dashed lines).

Synthesis and crystallization

An ion-exchange column packed with Dowex HCR-W2 resin was regenerated with $3M$ HCl and washed with water. A solution of 5.00 g of $NaN(CN)_2$ was run through the column and the product was neutralized with Me_4NOH until alkaline. The solution was roto-vapped to dryness, recrystallized from EtOH, washed with MeOH and recrystallized from EtOH again, and pumped to dryness to afford about 1 g of product. Apparently the dicyanamide was partially hydrolyzed to form cyanourea when in free acid form.

NMR of Me_4N^+ $H_2NC(O)NCN^-$ (D_2O) ^1H: $\delta3.06$; ^{13}C (DSS ref): $\delta58.0$ (Me_4N, $^1J_{C-N} = 4$ Hz), 127.0($C\equiv N$), 171.1 (C=O); ^{15}N(NH_4NO_3 ref): $\delta22.5$ (Me_4N), 62.22 (m, NH_2), 72.18 (N), 150.45 ($C\equiv N$).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. The structure was refined as a two-component twin with a fractional contribution of 0.0409 (11) for the minor domain.

Funding information

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full crystallographic data

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Crystal data

$C_4H_{12}N^+ \cdot C_2H_2N_3O^-$	$F(000) = 344$
$M_r = 158.21$	$D_x = 1.204$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 8.8120 (4)$ Å	Cell parameters from 3088 reflections
$b = 8.7561 (4)$ Å	$\theta = 2.9$–$36.0°$
$c = 12.1093 (6)$ Å	$\mu = 0.09$ mm^{-1}
$\beta = 110.897 (2)°$	$T = 100$ K
$V = 872.88 (7)$ Å^3	Prism, colourless
$Z = 4$	$0.25 \times 0.12 \times 0.05$ mm

Data collection

Bruker APEXII CCD diffractometer	4340 independent reflections
φ and ω scans	2752 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (Sadabs; Bruker, 2016)	$R_{int} = 0.156$
	$\theta_{max} = 36.4°$, $\theta_{min} = 2.9°$
$T_{min} = 0.651$, $T_{max} = 0.747$	$h = -14 \rightarrow 14$
17548 measured reflections	$k = -14 \rightarrow 14$
	$l = -20 \rightarrow 20$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.081$	$w = 1/[\sigma^2(F_o^2) + (0.064P)^2 + 0.1366P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.174$	
$S = 1.04$	$(\Delta/\sigma)_{max} < 0.001$
4340 reflections	$\Delta\rho_{max} = 0.44$ e Å^{-3}
105 parameters	$\Delta\rho_{min} = -0.27$ e Å^{-3}
0 restraints	

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.

Refinement. Refined as a 2-component twin. The structure was solved using *SHELXT* (Sheldrick, 2015*a*) and refined with *SHELXL2018* (Sheldrick, 2015*b*). The locations of all hydrogen atoms for the major component were located in difference Fourier maps and refined in idealized position using a riding model with atomic displacement parameters of $U_{iso}(H) = 1.2U_{eq}(C, N)$ [$1.5U_{eq}(C)$ for CH$_3$], with N—H distance of 0.88 Å and C—H distances ranging from 0.95 to 0.99 Å, respectively.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
N1	0.52001 (13)	0.39529 (14)	0.77065 (11)	0.0155 (2)
C1	0.65132 (18)	0.3158 (2)	0.86761 (18)	0.0271 (3)
H1A	0.717795	0.391510	0.923711	0.041*
H1B	0.719731	0.257919	0.834033	0.041*
H1C	0.602538	0.245780	0.908689	0.041*
C2	0.4173 (2)	0.2805 (2)	0.68548 (17)	0.0289 (3)
H2A	0.367659	0.211613	0.726730	0.043*
H2B	0.484911	0.221365	0.651990	0.043*
H2C	0.331794	0.333191	0.621804	0.043*
C3	0.41712 (17)	0.4843 (2)	0.82257 (14)	0.0215 (3)
H3A	0.484635	0.559198	0.878912	0.032*
H3B	0.367829	0.414567	0.863515	0.032*
H3C	0.331387	0.537379	0.759369	0.032*
C4	0.5940 (2)	0.5019 (2)	0.70750 (15)	0.0238 (3)
H4A	0.666165	0.573678	0.764306	0.036*
H4B	0.507855	0.558664	0.647290	0.036*
H4C	0.656586	0.443175	0.669525	0.036*
O1	0.16653 (13)	0.63130 (14)	0.57913 (9)	0.0193 (2)
N2	0.04603 (16)	0.59992 (17)	0.38199 (11)	0.0232 (3)
H2D	−0.024142	0.534851	0.391904	0.028*
H2E	0.041806	0.623148	0.310245	0.028*
N3	0.26105 (14)	0.76503 (15)	0.45058 (11)	0.0172 (2)
N4	0.46972 (16)	0.89392 (18)	0.61890 (12)	0.0230 (3)
C5	0.15986 (15)	0.66395 (15)	0.47658 (12)	0.0139 (2)
C6	0.36986 (15)	0.82986 (16)	0.54310 (12)	0.0150 (2)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0151 (4)	0.0119 (4)	0.0204 (5)	−0.0002 (4)	0.0074 (4)	0.0002 (4)
C1	0.0182 (6)	0.0206 (7)	0.0386 (9)	0.0056 (5)	0.0053 (6)	0.0070 (7)
C2	0.0337 (7)	0.0235 (7)	0.0285 (8)	−0.0118 (6)	0.0099 (7)	−0.0097 (7)
C3	0.0202 (5)	0.0247 (7)	0.0223 (6)	0.0058 (5)	0.0109 (5)	0.0006 (5)
C4	0.0322 (7)	0.0196 (7)	0.0257 (7)	−0.0061 (5)	0.0179 (6)	−0.0015 (5)
O1	0.0229 (4)	0.0226 (5)	0.0125 (4)	−0.0056 (4)	0.0062 (4)	0.0014 (4)
N2	0.0280 (5)	0.0266 (6)	0.0124 (5)	−0.0125 (5)	0.0040 (4)	−0.0013 (5)
N3	0.0199 (5)	0.0182 (5)	0.0130 (4)	−0.0040 (4)	0.0052 (4)	0.0008 (4)
N4	0.0232 (5)	0.0280 (7)	0.0167 (5)	−0.0061 (5)	0.0058 (4)	−0.0017 (5)
C5	0.0156 (5)	0.0121 (5)	0.0137 (5)	0.0006 (4)	0.0047 (4)	0.0002 (4)
C6	0.0160 (5)	0.0155 (5)	0.0148 (5)	0.0013 (4)	0.0069 (4)	0.0022 (4)

Geometric parameters (Å, º)

N1—C2	1.492 (2)	C3—H3C	0.9800
N1—C3	1.4937 (17)	C4—H4A	0.9800

N1—C1	1.494 (2)	C4—H4B	0.9800
N1—C4	1.4958 (19)	C4—H4C	0.9800
C1—H1A	0.9800	O1—C5	1.2550 (16)
C1—H1B	0.9800	N2—C5	1.3464 (18)
C1—H1C	0.9800	N2—H2D	0.8800
C2—H2A	0.9800	N2—H2E	0.8800
C2—H2B	0.9800	N3—C6	1.3155 (19)
C2—H2C	0.9800	N3—C5	1.3703 (17)
C3—H3A	0.9800	N4—C6	1.1641 (18)
C3—H3B	0.9800		

C2—N1—C3	109.42 (12)	N1—C3—H3B	109.5
C2—N1—C1	109.76 (14)	H3A—C3—H3B	109.5
C3—N1—C1	109.17 (12)	N1—C3—H3C	109.5
C2—N1—C4	109.55 (13)	H3A—C3—H3C	109.5
C3—N1—C4	109.31 (12)	H3B—C3—H3C	109.5
C1—N1—C4	109.62 (12)	N1—C4—H4A	109.5
N1—C1—H1A	109.5	N1—C4—H4B	109.5
N1—C1—H1B	109.5	H4A—C4—H4B	109.5
H1A—C1—H1B	109.5	N1—C4—H4C	109.5
N1—C1—H1C	109.5	H4A—C4—H4C	109.5
H1A—C1—H1C	109.5	H4B—C4—H4C	109.5
H1B—C1—H1C	109.5	C5—N2—H2D	120.0
N1—C2—H2A	109.5	C5—N2—H2E	120.0
N1—C2—H2B	109.5	H2D—N2—H2E	120.0
H2A—C2—H2B	109.5	C6—N3—C5	114.79 (12)
N1—C2—H2C	109.5	O1—C5—N2	120.31 (12)
H2A—C2—H2C	109.5	O1—C5—N3	124.73 (13)
H2B—C2—H2C	109.5	N2—C5—N3	114.95 (12)
N1—C3—H3A	109.5	N4—C6—N3	174.73 (15)

C6—N3—C5—O1	−0.5 (2)	C6—N3—C5—N2	178.60 (13)

Hydrogen-bond geometry (Å, °)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
C1—H1C⋯O1[i]	0.98	2.63	3.487 (2)	147
C2—H2A⋯O1[i]	0.98	2.57	3.447 (2)	149
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C3—H3C⋯O1	0.98	2.30	3.253 (2)	164
C4—H4A⋯N3[ii]	0.98	2.54	3.450 (2)	155
C4—H4C⋯N3[iii]	0.98	2.59	3.536 (2)	162
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N2—H2E⋯N4[v]	0.88	2.18	3.0126 (19)	158

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