Tetramethylammonium (Z)-N′-cyanocarbamimidate

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In the structure of the tetramethyl ammonium salt of cyanourea, C₄H₁₂N⁺·C₂H₂N₃O⁻, the N—C and O—C bond distances in the cyano and keto groups are in the normal range for such a moiety 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 NH₂ group is coplanar with the central N₂CO core, in contrast with the nitrile group where the dihedral angle between the N—C—N and N₂CO 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 R₂(8) motif, as well as N—H···O hydrogen bonds between anions and C—H···O interactions between both cations and anions, forming an R₃(14) pattern.

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 Mn₆ 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, [C₄H₁₂N⁺][C₂H₂N₃O⁻], 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, respectively] are in the normal range for such a moiety and similar to the values found for the silver salt [1.149 (6) and
Table 1
Selected geometric parameters (Å, °).

|                | Dist. (Å) | Angle (°) |
|----------------|-----------|-----------|
| O1—C5         | 1.2550 (16) | 1.3703 (17) |
| N2—C5         | 1.3464 (18) | 1.2614 (18) |
| C3—C6         | 1.3155 (19) |           |
| C6—N3—C5     | 114.79 (12) | N2—C5—N3 114.95 (12) |
| O1—C5—N3     | 124.73 (13) |

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

| D—H···A        | D—H    | H···A    | D···A    | D—H···A |
|----------------|--------|---------|----------|---------|
| C1—H1C···O1    | 0.98   | 2.63    | 3.487 (2) | 147     |
| C2—H2A···O1    | 0.98   | 2.57    | 3.447 (2) | 149     |
| C3—H3B···O1    | 0.98   | 2.62    | 3.484 (2) | 147     |
| C3—H3C···O1    | 0.98   | 2.30    | 3.253 (2) | 164     |
| C4—H4A···N3    | 0.98   | 2.54    | 3.450 (2) | 155     |
| C4—H4C···N3    | 0.98   | 2.59    | 3.536 (2) | 162     |
| N2—H2D···O    | 0.88   | 2.03    | 2.9084 (16) | 174     |
| N2—H2E···N4   | 0.88   | 2.18    | 3.0126 (19) | 158     |

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

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 NH2 group is coplanar with the central N2CO core [dihedral angle between NH2 and N2CO planes of only 0.54 (8)°] in contrast with the nitrile group where the dihedral angle between the N—C—N and N2CO planes is 36.5 (3)°. These values are different to those found in the silver salt.

The packing of the cations and anions in the unit cell involves N—H···O hydrogen bonds (Table 2) between anions characterized by an R21(8) motif as well as N—H···O hydrogen bonds between anions and C—H···O interactions between both cations and anions forming an R21(14) pattern as shown in Fig. 2.

![Diagram showing the packing of the cations and anions in the unit cell, which involves N—H···O hydrogen bonds between anions characterized by an R21(8) motif as well as N—H···O hydrogen bonds between anions and C—H···O interactions between both cations and anions forming an R21(14) pattern (all interactions shown with dashed lines).](image)

Table 3
Experimental details.

| Property               | Value |
|------------------------|-------|
| Crystal data           |       |
| Chemical formula       | C6H12N+·C2H2N3O− |
| Mw                     | 158.21 |
| Crystal system, space group | Monoclinic, P21/n |
| Temperature (K)        | 100   |
| a, b, c (Å)            | 8.8120 (4), 8.7561 (4), 12.1093 (6) |
| V (Å3)                 | 872.88 (7) |
| Z                      | 4     |
| Radiation type         | Mo Kα |
| μ (mm−1)               | 0.09  |
| Crystal size (mm)      | 0.25 × 0.12 × 0.05 |

Data collection

Diffractometer: Bruker APEXII CCD
Absorption correction: Multi-scan (SADABS; Bruker, 2016)

Tmin, Tmax: 0.651, 0.747
No. of measured, independent and observed [I > 2σ(I)] reflections: 17548, 4340, 2752
Rint: 0.156
(sin θ/λ)max (Å−1): 0.836

Refinement

R2(F2 > 2σ(F2)), wR2(F2), S: 0.081, 0.174, 1.04
No. of reflections: 4340
No. of parameters: 105
H-atom treatment: H-atoms parameters constrained
Δρmax, Δρmin (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).
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 Me₄NOH 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 Me₄N⁺ H₂NC(O)NCN⁻ (D₂O) ¹H: δ 3.06; ¹³C (DSS ref): δ 58.0 (Me₄N, ¹J_C—N = 4 Hz), 127.0 (C≡N), 171.1 (C=O); ¹⁵N(NH₄NO₃ ref): δ 22.5 (Me₄N), 62.22 (m, NH₂), 72.18 (N), 150.45 (C≡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.

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full crystallographic data

*IUCrData* (2021). 6, x211098  [https://doi.org/10.1107/S2414314621010981]

**Tetramethylammonium (Z)-N’-cyanocarbamimidate**

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**Crystal data**

C4H12N+·C2H2N3O−

\[ F(000) = 344 \]

\[ D_\text{c} = 1.204 \text{ Mg m}^{-3} \]

Monoclinic, \( P2_1/n \)

\[ a = 8.8120 (4) \text{ Å} \]

\[ b = 8.7561 (4) \text{ Å} \]

\[ c = 12.1093 (6) \text{ Å} \]

\[ \beta = 110.897 (2)^\circ \]

\[ V = 872.88 (7) \text{ Å}^3 \]

\[ Z = 4 \]

\[ F_{\text{max}} = 0.09 \text{ mm}^{-1} \]

\[ T = 100 \text{ K} \]

Prism, colourless

\[ 0.25 \times 0.12 \times 0.05 \text{ mm} \]

**Data collection**

Bruker APEXII CCD
diffractometer

\[ 4340 \text{ independent reflections} \]

\[ 2752 \text{ reflections with } I > 2\sigma(I) \]

\[ R_{\text{int}} = 0.156 \]

\[ R = 0.081 \]

\[ wR = 0.174 \]

\[ S = 1.04 \]

4340 reflections

105 parameters

0 restraints

\[ \theta_{\text{max}} = 36.4^\circ, \theta_{\text{min}} = 2.9^\circ \]

\[ h = -14 \rightarrow 14 \]

\[ k = -14 \rightarrow 14 \]

\[ l = -20 \rightarrow 20 \]

**Refinement**

Refinement on \( F^2 \)

Least-squares matrix: full

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

\[ w = 1/\left( \sigma(F_o^2) + (0.064P)^2 + 0.1366P \right) \]

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

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

\[ \Delta\rho_{\text{max}} = 0.44 \text{ e Å}^{-3} \]

\[ \Delta\rho_{\text{min}} = -0.27 \text{ e Å}^{-3} \]

**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, 2015a) and refined with *SHELXL2018* (Sheldrick, 2015b). 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 \( U_{\text{iso}}(H) = 1.2U_{	ext{eq}}(C, N) \) [1.5\( U_{	ext{eq}}(C) \) for CH3], 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)

| Atom | x      | y      | z      | Uiso * / Ueq |
|------|--------|--------|--------|-------------|
| N1   | 0.5200 (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) | 0.82527 (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 | 0.764360 | 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)

| Atom | U11 | U22 | U33 | U12 | U13 | U23 |
|------|-----|-----|-----|-----|-----|-----|
| 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, °)

| Bond | Distance | Angle |
|------|----------|-------|
| N1—C2 | 1.492 (2) | | C3—H3C | 0.9800 |
| N1—C3 | 1.4937 (17) | | C4—H4A | 0.9800 |
| Bond | Length (Å) | Bond | Length (Å) |
|------|-----------|------|-----------|
| 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 | |

| Angle | Value (°) |
|-------|-----------|
| C2—N1—C3 | 109.42 (12) |
| N1—C3—H3B | 109.5 |
| H3A—C3—H3B | 109.5 |
| N1—C3—H3C | 109.5 |
| C2—N1—C3 | 109.17 (12) |
| N1—C1—H1A | 109.5 |
| N1—C1—H1B | 109.5 |
| H1A—C1—H1B | 109.5 |
| C2—N1—C3 | 109.55 (13) |
| H1A—C1—H1B | 109.5 |
| H1A—C1—H1C | 109.5 |
| N1—C1—H1C | 109.5 |
| H1B—C1—H1C | 109.5 |
| N1—C2—H2A | 109.5 |
| N1—C2—H2B | 109.5 |
| H2A—C2—H2B | 109.5 |
| H2A—C2—H2C | 109.5 |
| H2B—C2—H2C | 109.5 |
| N1—C3—H3A | 109.5 |
| N1—C3—H3B | 109.5 |
| C6—N3—C5 | 109.5 |
| C6—N3—C5 | 109.5 |
| N1—C1—H1A | 109.5 |
| N1—C1—H1B | 109.5 |
| H1A—C1—H1B | 109.5 |
| C2—N1—C3 | 109.17 (12) |
| N1—C1—H1A | 109.5 |
| N1—C1—H1B | 109.5 |
| H1A—C1—H1B | 109.5 |
| C2—N1—C3 | 109.55 (13) |
| H1A—C1—H1B | 109.5 |
| H1A—C1—H1C | 109.5 |
| N1—C1—H1C | 109.5 |
| H1B—C1—H1C | 109.5 |
| N1—C2—H2A | 109.5 |
| N1—C2—H2B | 109.5 |
| H2A—C2—H2B | 109.5 |
| H2A—C2—H2C | 109.5 |
| H2B—C2—H2C | 109.5 |
| N1—C3—H3A | 109.5 |
| N1—C3—H3B | 109.5 |
| C6—N3—C5 | 109.5 |
| C6—N3—C5 | 109.5 |
| C6—N3—C5—O1 | 109.5 |
| 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···O1i | 0.98 | 2.63 | 3.487 (2) | 147 |
| C2—H2A···O1i | 0.98 | 2.57 | 3.447 (2) | 149 |
| C3—H3B···O1i | 0.98 | 2.62 | 3.484 (2) | 147 |
| C4—H4A···O1 | 0.98 | 2.54 | 3.450 (2) | 155 |
| C4—H4C···N3ii | 0.98 | 2.59 | 3.536 (2) | 162 |
| N2—H2D···O1iv | 0.88 | 2.03 | 2.9084 (16) | 174 |
| N2—H2E···N4v | 0.88 | 2.18 | 3.0126 (19) | 158 |

Symmetry codes: (i) −x+1/2, y−1/2, −z+3/2; (ii) x+1/2, −y+3/2, z+1/2; (iii) −x+1, −y+1, −z+1; (iv) −x, −y+1, −z+1; (v) x−1/2, −y+3/2, z−1/2.