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Key indicators

Single-crystal X-ray study
T = 298 K
Mean $\sigma(\text{C}-\text{C}) = 0.003 \text{ \AA}$
R factor = 0.067
wR factor = 0.142
Data-to-parameter ratio = 16.6

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Ammonium dicyano(cyanoacetyl)methanide: one condensation product of malononitrile

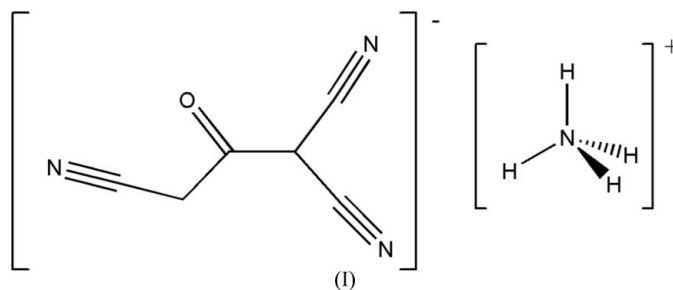
The title compound, $\text{NH}_4^+\cdot\text{C}_6\text{H}_2\text{N}_3\text{O}^-$, was obtained as a secondary product in a reaction of squaric acid and excess malononitrile (1:20). The crystal packing displays a wave-like arrangement of molecules parallel to *b*, in which anion layers are linked by medium–weak hydrogen bonds to the ammonium cation, giving rise to a three-dimensional network. The average $\text{N}\cdots\text{O}$ and $\text{N}\cdots\text{N}$ distances are 2.843 (2) and 3.025 (3) \AA , respectively.

Received 5 July 2006

Accepted 8 July 2006

Comment

The weak cyanocarbon acid malononitrile is a versatile compound and very reactive. It is used as a reactant or reaction intermediate, since the methylene group and cyano groups can take part in condensation reactions to give a variety of addition products and heterocyclic compounds (Freeman, 1969). This compound has been used in substitution reactions with oxocarbon species, especially with the croconate ion ($\text{C}_5\text{O}_5^{2-}$), giving rise to the class of compounds denoted as croconate dyes, mainly the di-substituted product which is known as croconate violet, 3,5-bis(dicyanomethylene)cyclopentane-1,2,4-trionate (Fatiadi, 1980; Diniz *et al.*, 2006). Some crystal structures of self-condensation products of malononitrile have been described by Klewe, *viz.* potassium salts of 2-cyanomethyl-1,1,3,3-tetracyanopropene (Klewe, 1971*a*) and 1,1,3-tricyanopropanone (Klewe, 1971*b*), and 2-amino-1,1,3-tricyanopropene (Klewe, 1971*c*).



The title compound, (I), is isostructural to the potassium salt of 1,1,3-tricyanopropanone (Klewe, 1971*b*). The structure of (I) is illustrated in Fig. 1. The anion is almost planar except for one cyano group (C1/N1), which lies out of the molecular plane, with a torsion angle of 10 (1)°. The molecular plane is approximately perpendicular to the *c* axis, its normal subtending angles of 87.6 and 66.7° with the *b* and *a* axes, respectively. The C–C bond distances [average 1.415 (3) \AA], except C2–C3 [1.522 (3) \AA], are smaller than standard C–C single bonds, which is indicative of delocalization of the anion negative charge. The CO and CN bonds are similar to those

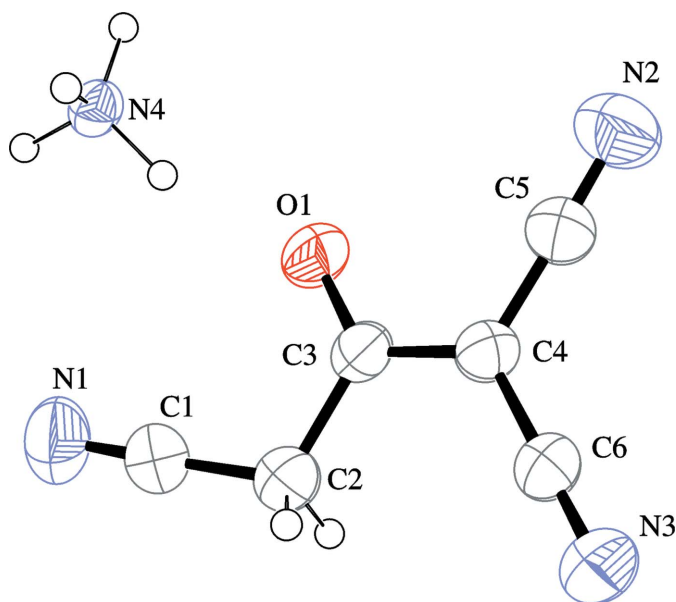


Figure 1
The asymmetric unit of (I), showing 50% probability displacement ellipsoids and the atomic numbering.

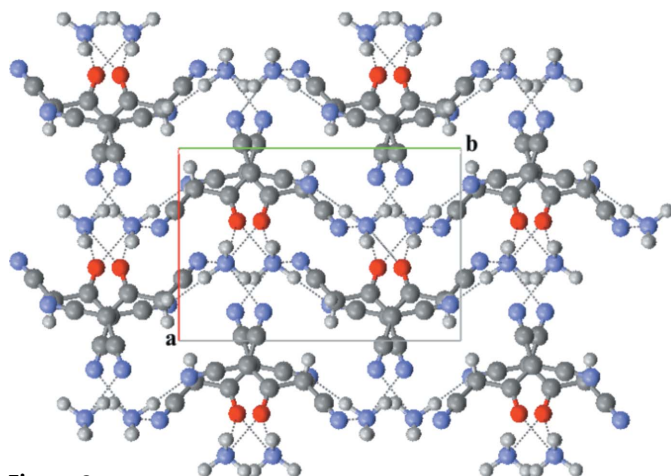


Figure 2
Crystal packing of (I), viewed along the *c* axis. Broken lines indicate hydrogen bonds.

observed in other condensation products of malononitrile (Klewe, 1971*a,b,c*), and C–C–N angles are near to 180° as expected (Table 1).

The ammonium cations are involved in two types of intermolecular hydrogen bonds to the anions (Table 2), and the average N···O and N···N distances are, respectively, 2.843 (2) and 3.025 (3) Å. The crystal packing displays a wave-like arrangement of molecules parallel to *b*, in which anion layers are linked by medium–weak hydrogen bonds, giving rise to a three-dimensional network (Fig. 2).

Experimental

The title compound, which is a self-condensation product of malononitrile, was obtained as a secondary product of squaric acid and

excess malononitrile (1:20) in ethanol solution. The reaction was stirred under reflux at 363 K for two days. The solvent was removed at reduced pressure and the solid was chromatographed on silica gel 60 G (ethyl acetate/methanol 8:2). After slow solvent evaporation at room temperature of the first fraction, yellow single crystals suitable for X-ray diffraction analysis were obtained.

Crystal data

$\text{H}_4\text{N}^+\cdot\text{C}_6\text{H}_2\text{N}_3\text{O}^-$
 $M_r = 150.15$
 Monoclinic, $P2_1/c$
 $a = 8.3642$ (6) Å
 $b = 12.0104$ (9) Å
 $c = 7.6033$ (4) Å
 $\beta = 101.790$ (4)°
 $V = 747.69$ (9) Å³

$Z = 4$
 $D_x = 1.334$ Mg m⁻³
 Mo $K\alpha$ radiation
 $\mu = 0.10$ mm⁻¹
 $T = 298$ (2) K
 Prism, yellow
 $0.30 \times 0.08 \times 0.08$ mm

Data collection

Nonius KappaCCD diffractometer
 φ and ω scans
 Absorption correction: none
 8956 measured reflections

1707 independent reflections
 1164 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.083$
 $\theta_{\text{max}} = 27.6^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.067$
 $wR(F^2) = 0.142$
 $S = 0.94$
 1707 reflections
 103 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.091P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.31$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.17$ e Å⁻³
 Extinction correction: *SHELXL97*
 Extinction coefficient: 0.063 (16)

Table 1

Selected geometric parameters (Å, °).

| | | | |
|----------|-------------|----------|-----------|
| O1–C3 | 1.249 (2) | N2–C5 | 1.148 (3) |
| N1–C1 | 1.139 (3) | N3–C6 | 1.149 (3) |
| N1–C1–C2 | 178.7 (3) | N2–C5–C4 | 178.4 (2) |
| O1–C3–C2 | 119.54 (18) | N3–C6–C4 | 179.3 (2) |
| O1–C3–C4 | 122.83 (18) | | |

Table 2

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–H4A···N2 ⁱ | 1.10 | 1.93 | 3.017 (3) | 174 |
| N4–H4B···O1 ⁱⁱ | 1.02 | 2.05 | 2.869 (2) | 135 |
| N4–H4C···O1 | 1.01 | 1.84 | 2.817 (2) | 163 |
| N4–H4D···N3 ⁱⁱⁱ | 1.03 | 2.19 | 3.033 (2) | 138 |

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

C-bound H atoms were included in the riding-model approximation with C–H = 0.97 Å, and a single $U_{\text{iso}}(\text{H})$ was refined for this group. H atoms of the ammonium cation were located in a difference map, fixed in these positions and assigned the same isotropic displacement parameters for all H atoms; see Table 2 for bond distances.

Data collection: *COLLECT* (Hooft, 1999); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *SCALEPACK* and *DENZO* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997);

molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *PLATON* (Spek, 2003).

The authors thank CNPq, CAPES, FAPESP and FAPEMIG (Brazilian agencies) for financial support.

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