Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

N-Methylpyridinium 3-cyano-4-(dicyanomethylene)-5-oxo-4,5-dihydro-1*H*-pyrrol-2-olate

Viktor A. Tafeenko,[a]* Aleksander N. Nikolaev,[b] Rene Peschar,[c] Olga V. Kaukova,[b] Henk Schenk[c] and Leonid A. Aslanov[a]

[a]Chemistry Department, Moscow State University, 119899 Moscow, Russia, [b]Department of Chemistry, Chuvash State University, 428015 Cheboksary, Russia, and [c]Laboratory for Crystallography, Institute of Molecular Chemistry, University of Amsterdam, Nieuwe Achtergracht 166, Amsterdam 1018WV, The Netherlands
Correspondence e-mail: tafeenko@biocryst.phys.msu.su

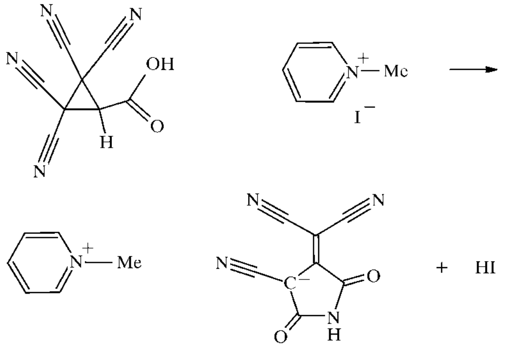
Received 12 February 2004
Accepted 8 March 2004
Online 31 March 2004

The crystal structure of the title compound, $C_6H_8N^+\cdot C_8HN_4O_2^-$, is characterized by three independent ion pairs (*A*, *B* and *C*) in the asymmetric unit. Each ion pair consists of an anion and a cation, and the three ion pairs have similar geometric parameters. All the anions are arranged as dianion dimers *via* two N—H···O hydrogen bonds and the dimers form one-dimensional columns parallel to the *b* axis as a result of π–π interactions. The cations are also stacked, in two different ways: one type of stacking consists of alternating *A* and *B* cations, while the other type consists of *C* cations only. Each dianion dimer stack is surrounded by eight stacks of cations and is not connected directly to other dianion stacks.

Comment

The synthesis and structure of the potassium salt of the title anion have recently been reported for the first time (Tafeenko *et al.*, 2003). Organic salts containing this anion are of interest, from both a theoretical and an experimental point of view, because of their π–π interactions, which are due to the planarity of the organic moieties, and their tendency to form stacks. In *N*,*N*-dimethylanilinium 3-cyano-4-(dicyanomethylene)-5-oxo-4,5-dihydro-1*H*-pyrrol-2-olate, (I) (Tafeenko *et al.*, 2004), the distance between the anion and the cation composing one stack is larger than expected (3.5 Å) and it was conjectured that a smaller distance might be possible if the methyl groups located between the anion and the cation were absent.

To investigate this hypothesis and to determine the 'minimum' anion–cation distance for the system in question, the title salt, (II), was synthesized. *N*-Methylpyridinium was selected as the cation because its characteristics seemed appropriate: it contains a π system and its dimensions are similar to those of the *N*,*N*-dimethylanilinium moiety if the two methyl groups are omitted. Therefore, it was expected that the packing of (II) and (I) would be the same.



(II)

Surprisingly, the crystal structure determination of the selected orange crystal of (II) [the crystal of (I) is yellow] revealed a drastically different packing geometry. The crystal structure of (II) has three independent ion pairs, *viz*. *A*, *B* and *C*, in the asymmetric unit (Fig. 1). Anions *A*, *B* and *C* have similar geometric parameters.

Each of the anions is linked by two N1—H···O1 hydrogen bonds into a dimer (Fig. 2 and Table 1). Anions *A* and B^i [symmetry code: (i) $-x, 1-y, 1-z$], *B* and A^i, and *C* and C^{ii} [symmetry code: (ii) $-x, -y, 1-z$] are held together in approximately parallel planes (the dihedral angle between the C/C^{ii} and A/B^i planes is ~4°) and, as a result of π–π interactions, form dianion stacks parallel to the *b* axis. The distances between adjacent planes composing one stack are 3.3, 3.3 and

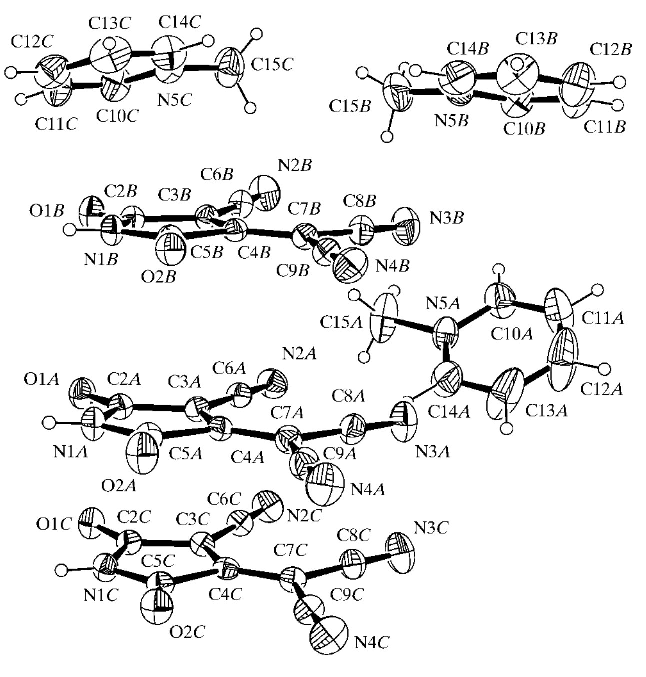


Figure 1
A view of the three independent ion pairs in the title salt, with the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

DOI: 10.1107/S0108270104005372

3.2 Å for C/C^{ii} and A/B^{i}, A/B^{i} and B/A^{i}, and B/A^{i} and $C^{\text{i}}/C^{\text{iii}}$ [symmetry code: (iii) x, $1 + y$, z], respectively. The shortest intermolecular distances between atoms of the anions in adjacent planes are presented in Table 2. Each dianion stack is surrounded by eight cation stacks and is not connected directly to any other dianion stacks (see Figs. 3 and 4). Six of the eight cation stacks consist of alternating *A* and *B* cations, the angle between the *A* and *B* cations composing one stack being ~60° (see Fig. 4). The second type of cation stack consists of *C* cations only and the dihedral angle between two neighboring *C* cations in this stack is ~52°. Other differences also exist between the *A*/*B* and *C*/*C* cation stacks (Fig. 3). In contrast to the *A*/*B* cation stacks, each *C*/*C* cation stack adjoins two dianion stacks only. Moreover, in each *C*/*C* cation stack parallel to the *b* axis, the methyl groups point in opposite directions, whereas the methyl groups of the *A*/*B* stacks are oriented in the same direction as one another (Fig. 3).

The crystal packing of the title compound resembles a 'multiple-conductor cable', in which the stacks of cations are the 'insulator' part (Figs. 3 and 4).

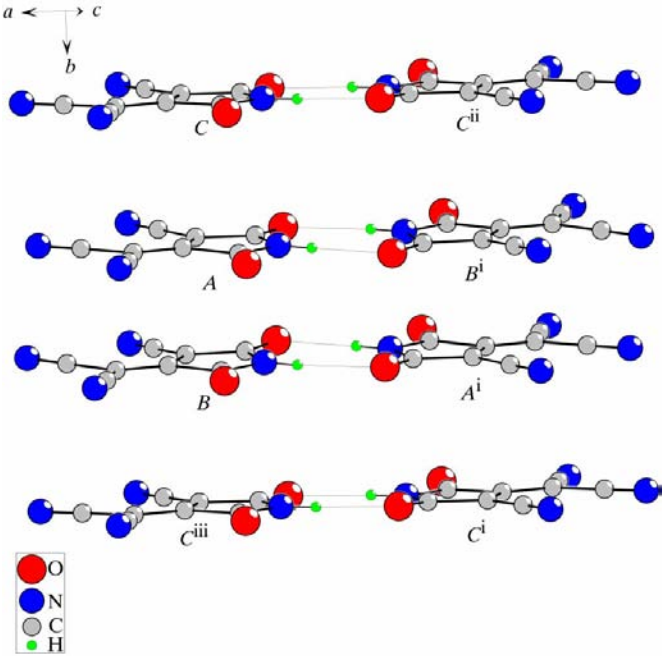


Figure 2
Part of the crystal structure of (II), showing how the three independent anions (*A*, *B* and *C*) form π–π stacks along the *b* axis and dimers *via* strong hydrogen bonds (N—H$\cdots$O). [Symmetry codes: (i) $-x$, $1 - y$, $1 - z$; (ii) $-x$, $-y$, $1 - z$; (iii) x, $1 + y$, z.]

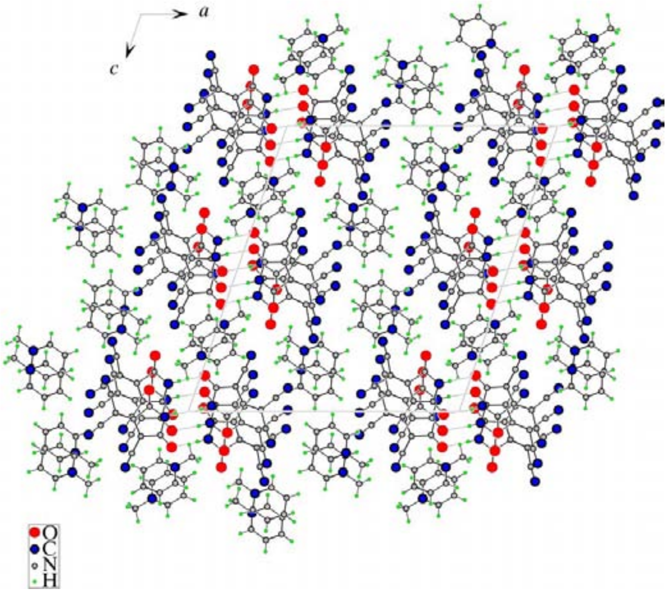


Figure 3
A packing diagram, viewed along the *b* axis, showing the eight cation stacks around every dianion stack.

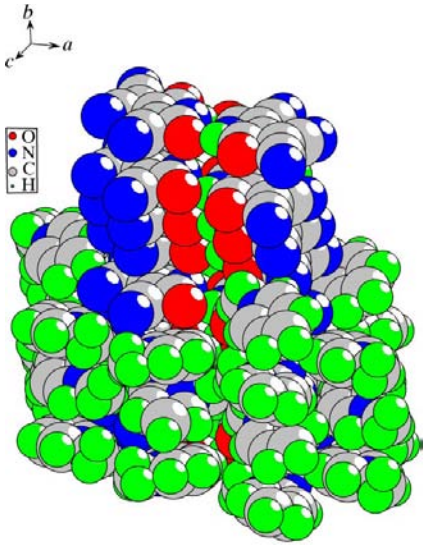


Figure 4
Part of the crystal structure of (II), showing the ladder configuration of an individual stack and how the dianion stacks are surrounded by cations. Cations have been omitted from the top of the figure.

In conclusion, the crystal structure investigation has revealed novel packing characteristics of the title anion; the anions form dimers *via* paired hydrogen bonds and adjacent dianions are linked by π–π stacking interactions, forming one-dimensional columns. With respect to the original goal, a reduction of the cation–anion interstack distance, it is concluded that the anion–cation hydrogen bonding is more important than initially estimated. This topic will be considered in more detail in subsequent investigations.

Experimental

2,2,3,3-Tetracyanocyclopropanecarboxylic acid was synthesized from α-chloroketone and TCNE (ethylene-1,1,2,2-tetracarbonitrile). The title compound, (II), was obtained by mixing *N*-methylpyridinium iodide with 2,2,3,3-tetracyanocyclopropanecarboxylic acid. The reaction was carried out in water/propan-2-ol (1:1) at room temperature. Orange crystals were collected from the reaction mixture by filtration and drying.

Crystal data

$C_6H_8N^+\cdot C_8HN_4O_2^-$
$M_r = 279.26$
Monoclinic, $P2_1/c$
$a = 19.854$ (2) Å
$b = 9.8278$ (11) Å
$c = 22.198$ (2) Å
$\beta = 109.006$ (10)°
$V = 4095.1$ (7) Å^3
$Z = 12$
$D_x = 1.359$ Mg m^{-3}

Cu $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 28$–41°
$\mu = 0.80$ mm^{-1}
$T = 293$ (2) K
Prism, orange
$0.10 \times 0.07 \times 0.05$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Non-profiled ω scans
8264 measured reflections
8037 independent reflections
4686 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.023$
$\theta_{\rm max} = 72.0°$

$h = -24 \rightarrow 23$
$k = 0 \rightarrow 12$
$l = 0 \rightarrow 27$
2 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.057$
$wR(F^2) = 0.153$
$S = 1.01$
8037 reflections
583 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0627P)^2 + 0.7078P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.007$
$\Delta\rho_{\rm max} = 0.21$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.24$ e Å^{-3}

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1A—H1$A\cdots$O1$B^{\rm i}$	0.82 (3)	1.95 (3)	2.769 (3)	178 (3)
N1B—H1$B\cdots$O1$A^{\rm i}$	0.82 (3)	2.11 (3)	2.930 (3)	171 (2)
N1C—H1$C\cdots$O1$C^{\rm ii}$	0.86 (3)	2.00 (3)	2.851 (3)	175 (3)

Symmetry codes: (i) $-x, 1-y, 1-z$; (ii) $-x, -y, 1-z$.

Table 2
Selected distances (Å) between atoms of the anions composing one stack.

Interaction	Distance
N1$C\cdots$C2A	3.309 (4)
C2$A\cdots$N1B	3.305 (3)
N1$B\cdots$C2$C^{\rm iii}$	3.336 (4)
O2$B\cdots$C5$C^{\rm iii}$	3.193 (3)
C3$A\cdots$C5B	3.320 (4)
C3$C\cdots$C6A	3.299 (4)
C4$C\cdots$C3A	3.337 (4)
N4$B\cdots$C9$C^{\rm iii}$	3.297 (4)
C9$B\cdots$C7$C^{\rm iii}$	3.297 (4)

Symmetry code: (iii) $x, 1+y, z$.

Methyl and pyridinium H atoms were placed in idealized positions and constrained to ride on their parent atoms. The positions of the H atoms on the N1 atoms were determined from a Fourier difference map and the coordinates were refined freely with isotropic displacement parameters.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *XCAD*4 (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2000) and *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1438). Services for accessing these data are described at the back of the journal.

References

Brandenburg, K. (2000). *DIAMOND*. Release 2.1d. Crystal Impact GbR, Bonn, Germany.
Enraf–Nonius (1989). *CAD*-4 *Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Harms, K. & Wocadlo, S. (1995). *XCAD*4. University of Marburg, Germany.
Sheldrick, G. M. (1997). *SHELXL*97 and *SHELXS*97. University of Göttingen, Germany.
Tafeenko, V. A., Kaukova, O. V., Peschar, R., Petrov, A. V. & Aslanov, L. A. (2003). *Acta Cryst.* C**59**, m421–m423.
Tafeenko, V. A., Peschar, R., Kaukova, O. V., Schenk, H. & Aslanov, L. A. (2004). *Acta Cryst.* C**60**, o62–o64.