Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

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

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

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

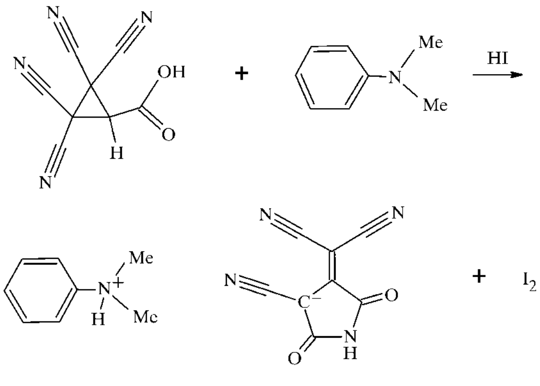
Received 14 October 2003
Accepted 10 November 2003
Online 13 December 2003

In the title compound, $C_8H_{12}N^+\cdot C_8HN_4O_2^-$, the anion and cation lie on a crystallographic mirror plane and form planar ribbons *via* N—H···O [N···O = 2.933 (4) Å, H···O = 2.01 Å and N—H···O = 170°] and N—H···N [N···N = 3.016 (5) Å, H···N = 2.15 Å and N—H···N = 169°] hydrogen bonds. The ribbons are further linked *via* weak C—H···O and C—H···N hydrogen bonds. In adjacent planes, anions lie opposite cations; π–π interactions (separation $a/2 = 3.520$ Å) exist between the anions and the cations, and stacks are formed, running along the *a* axis. The cations are disordered over two interpenetrating sites, with occupancies of 0.833 (5) and 0.167 (5).

Comment

We have recently reported the synthesis and structure of the potassium salt of the title anion (Tafeenko *et al.*, 2003). On the basis of the structural data and the calculated charge distribution on the atoms of the anion, the following types of anion–cation interaction can be postulated: (*a*) 'isotropic' interactions, with each outer heteroatom of the anion taking part in the formation of a polyhedron enclosing the cation (Li, K, Na and Cs); (*b*) π–π stacking interactions, involving planar cations (*e.g.* pyridinium); (*c*) a transition metal–anion π-system interaction (*e.g.* ferrocene); and (*d*) interaction of the heteroatoms of the anion and the transition metal to form a coordination compound or chelate complex. An example of type *a* was described by Tafeenko *et al.* (2003). Interactions of type *b* were expected in the title compound, (I). Interactions of types *c* and *d* are the subject of further investigations.

The synthesis of (I) was carried out as shown in the scheme above. The most remarkable features of this reaction are the main roles that are played by the two elementary particles (proton and electron) supplied by hydrogen iodide. The H atom interacts with the lone pair of the N atom of the *N*,*N*-dimethyl-*N*-phenylamine molecule to form a cation (see scheme), whereas the electron induces the rearrangement of the three-membered ring of 2,2,3,3-tetracyanocyclopropanecarboxylic acid to give an anion.



(I)

In (I) (Fig. 1), all the atoms of the anion and the cation lie on a crystallographic mirror plane, with the exception of the methyl groups of the cation, which are located between planes and have an essential impact on the specific packing geometry. The bond lengths and angles in the anion are similar to those in the corresponding potassium salt (Tafeenko *et al.*, 2003). The unique cation is disordered over two interpenetrating sites, with occupancies of 0.833 (5) and 0.167 (5) (see *Experimental*). The methyl groups enlarge the distances (half of the *a* axis) between the molecular planes and also prevent the formation of a more symmetrical anion–cation stacking. The shortest distance between an anion and a cation that form a stack and lie in adjacent mirror planes is 2.45 Å [H16*B*···N4($\frac{1}{2} - x$, $1 - y$, $z - \frac{1}{2}$); Fig. 2(*a*) and Table 1; atom H16*B* belongs to the C16 methyl group]. Although π–π interactions exist between anions and cations, these interactions might have been stronger if the methyl atoms located

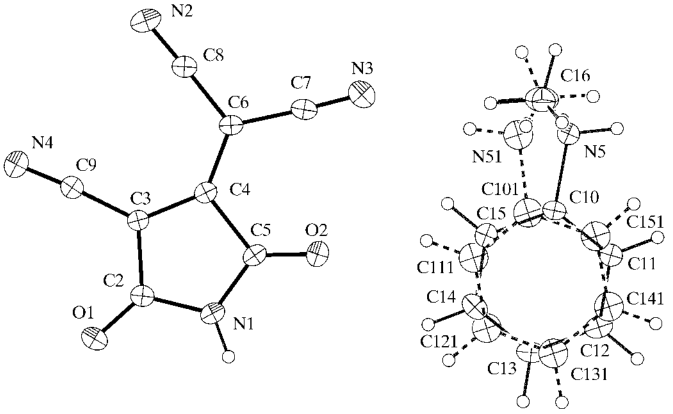


Figure 1
A view of the title salt, with the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. The cations are disordered over two interpenetrating sites, with occupancies of 0.833 (5) and 0.167 (5).

DOI: 10.1107/S0108270103025940

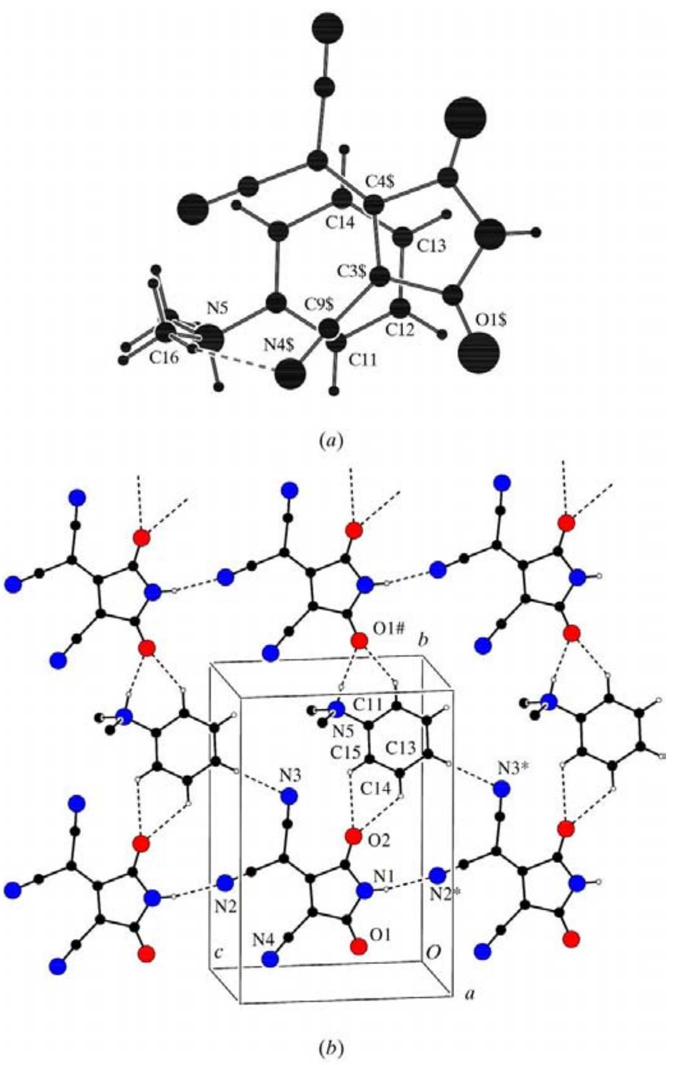


Figure 2
(*a*) A view almost normal to the molecular planes, showing how the cations and anions overlap to form π–π stacks along the *a* axis. Atoms marked with a dollar symbol ($) are at the equivalent position ($\frac{1}{2} - x$, $1 - y$, $z - \frac{1}{2}$). (*b*) Part of the crystal structure of (I), showing the formation *via* strong hydrogen bonds (N—H···N and N—H···O) of ribbons of anions and cations along the *c* axis. The ribbons are connected by weak C—H···O and C—H···N hydrogen bonds. Atoms marked with an asterisk (*) or hash (#) are at the equivalent positions ($x, y, z - 1$) and ($x, y + 1, z$), respectively.

between the planes had been absent. The tendency of the anion–cation distances in the stack to decrease is reflected by the atomic displacement tensors of the atoms of the anion. The principal axes of the ellipsoids of these atoms are orthogonal to the mirror plane, but the values for those atoms that are not involved in the π–π interaction are noticeably larger. Another explanation of the enlarged atomic displacement ellipsoids of the anion is steric hindrance of the exocyclic cyano groups (Tafeenko *et al.*, 2003).

In the mirror plane, adjacent anions are linked *via* N—H···N hydrogen bonds (Table 1 and Fig. 2*b*); cations are linked to the resulting anion chain by N—H···O hydrogen bonds. The ribbons so formed extend in the *c* direction, and adjacent ribbons are linked *via* weak (Steiner, 1996) C—H···O and C—H···N hydrogen bonds (Table 1 and Fig. 2*b*).

Experimental

2,2,3,3-Tetracyanocyclopropanecarboxylic acid was synthesized from α-chloroketone and TCNE (ethylene-1,1,2,2-tetracarbonitrile). Compound (I) was obtained by mixing *N*,*N*-dimethyl-*N*-phenylamine and hydrogen iodide and then adding 2,2,3,3-tetracyanocyclopropanecarboxylic acid. The reaction was carried out in water–1,4-dioxane (1:1) at room temperature. Yellow crystals were collected from the reaction mixture by filtration and drying.

Crystal data

$C_8H_{12}N^+\cdot C_8HN_4O_2^-$
$M_r = 307.31$
Orthorhombic, $Pmn2_1$
$a = 7.0399$ (7) Å
$b = 12.5636$ (12) Å
$c = 8.6695$ (8) Å
$V = 766.79$ (13) Å^3
$Z = 2$
$D_x = 1.331$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 925 reflections
$\theta = 3$–$30°$
$\mu = 0.09$ mm^{-1}
$T = 110$ (2) K
Prism, yellow
0.30 × 0.10 × 0.10 mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer
φ and ω scans
5974 measured reflections
1283 independent reflections
936 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.034$
$\theta_{\rm max} = 30.1°$
$h = -9 \rightarrow 9$
$k = -16 \rightarrow 17$
$l = -11 \rightarrow 12$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.112$
$S = 1.01$
1282 reflections
153 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0684P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.19$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.35$ e Å^{-3}

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···N2$^{\rm i}$	0.88	2.15	3.016 (5)	169
N5—H5···O1$^{\rm ii}$	0.93	2.01	2.933 (4)	170
N51—H51···N3	0.93	2.16	3.07 (2)	169
C11—H11···O1$^{\rm ii}$	0.95	2.31	3.125 (5)	143
C13—H13···N3$^{\rm i}$	0.95	2.42	3.374 (6)	180
C14—H14···O2	0.95	2.50	3.156 (6)	126
C15—H15···O2	0.95	2.65	3.226 (5)	119
C16—H16*B*···N4$^{\rm iii}$	0.98	2.45	3.394 (3)	161

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

Four different diffraction experiments were carried out using three different crystals of the title compound, with both room-temperature and 110 K data sets. (For full details see the _exptl_special_details section of the archived CIF.) All data sets led to the same structure and only the results from the 110 K data set are described here. All H atoms were refined as riding, with N—H distances of 0.88 and 0.93 Å, and C—H distances of 0.95 and 0.98 Å. During refinement, difference maps showed peaks consistent with atoms N5 and C10–C15 in the cation being unequally disordered over two interpenetrating sites.

This disorder was allowed for by the use of appropriate *SHELXL*97 (Sheldrick, 1997) SAME and DFIX restraints. At convergence, the cation disorder was modelled with occupancies of 0.833 (5) and 0.167 (5). The minor-occupancy cation orientation also leads to an N51—H51···N3 hydrogen bond (Table 1). The minor-occupancy methyl C atom (C161) was constrained to have the same coordinates and anisotropic displacement parameters as the major-occupancy (C16) site.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT-Plus* (Bruker, 1998); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); 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: FG1710). 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.
Bruker (1998). *SAINT-Plus* (Version 6.01) and *SMART* (Version 5.059). Bruker AXS Inc., Madison, Wisconsin, USA.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.
Steiner, T. (1996). *Crystallogr. Rev.* **6**, 1–57.
Tafeenko, V. A., Kaukova, O. V., Peschar, R., Petrov, A. V. & Aslanov, A. L. (2003). *Acta Cryst.* C**59**, m421–m423.