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

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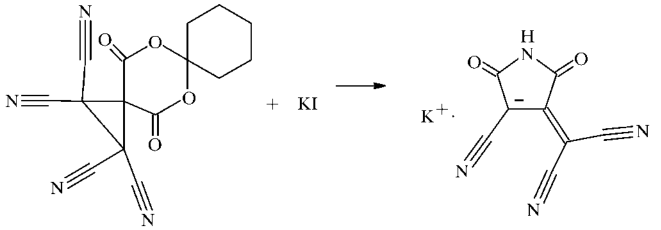
The crystal structure of the title potassium salt, $K^+\cdot C_8HN_4O_2^-$, of the organic anion 3-cyano-4-(dicyanomethylene)-5-oxo-4,5-dihydro-1*H*-pyrrol-2-olate shows that the dicyanomethylene moiety is able to accept an electron in the same way as does tetracyanoethylene, to yield the novel product. The organic anion is nearly planar, with deviations caused by steric crowding among the exocyclic cyano groups. The K^+ cations lie within tricapped trigonal prisms that stack to form channels. The three-dimensional structure is completed by the formation of hydrogen-bonded chains by the anions.

Comment

Tetracyanoethylene (TCNE) is widely used for preparing photochromic materials (Huffman *et al.*, 1967), and anticancer (Nasakin *et al.*, 2000) and biologically active compounds (Abdel-Rahman, 1989; Tacconi *et al.*, 1976), and is the basic reagent for the synthesis of new hetero- and carbocyclic compounds with specific physical and chemical properties (Nasakin *et al.*, 1992, 1994, 1997; Sheverdov *et al.*, 2001). One of the most remarkable features of TCNE is its ability to accept an electron easily, transforming it into an anion or radical anion (Lemenovskiy *et al.*, 1981; Zheludev *et al.*, 1994). Hence, we hypothesize that the same ability could be an intrinsic property of substances or intermediates that contain a fragment of TCNE, specifically dicyanomethylene. This article reports on the positive realisation of this idea. We propose that hetero- and carbocyclic compounds containing two, three or four cyano groups are promising starting reagents for transformations to anions or radical anions. An iodide anion was used as the reducing agent in the present reaction with 4,13-dioxo-5,12-dioxadispiro[2.2.5.2]tridecane-1,1,2,2-tetracarbonitrile (see scheme).

The X-ray analysis of the product isolated from a water–dioxane solution showed that a salt, (I), with a new organic anion, namely potassium 3-cyano-4-(dicyanomethylene)-5-oxo-4,5-dihydro-1*H*-pyrrol-2-olate, had been synthesized. Although the mechanism of this reaction needs further clarification, we can formulate two aspects of the reaction on the basis of the resulting molecular structure; firstly electron transport from the iodide anion into the organic moiety and, secondly, recyclization as a consequence of $(NC)_2C-C(CN)_2$ C—C bond breaking. Note that the negative charge on one C atom (see scheme) only partly reflects the real charge distribution. The charges on the atoms of the anion and on the corresponding radical were calculated by quantum-chemical methods using the semi-empirical AM1 Hamiltonian (Dewar *et al.*, 1985). The results of these calculations are presented in Table 2 (see also Fig. 1), which shows the charge distribution in the anion and the difference in charge distribution between anion and radical. Going from the radical to the anion noticeably increases the negative charge on the external heteroatoms and atoms C3 and C7.



(I)

All external heteroatoms of (I) are involved in the formation of a practically ideal tricapped trigonal prism that encloses a cation (Figs. 2 and 3). There is good indirect evidence that all external heteroatoms bear negative charge. The K$\cdots$*A* distances (where *A* is O or N) range from 2.833 (1) Å for K$\cdots$O1^{i} to 3.174 (2) Å for K$\cdots$N3^{vi} [Table 1; symmetry codes: (i) $x-1, y, z$; (vi) $1-x, 2-y, 1-z$]. Each prism is joined to two neighbouring prisms through a common

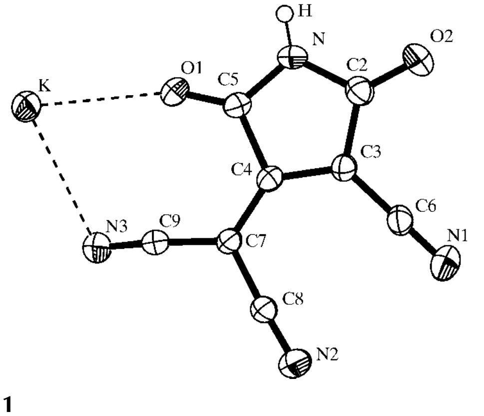


Figure 1
A view of (I) with the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and the H atom is shown as a small sphere of arbitrary radius.

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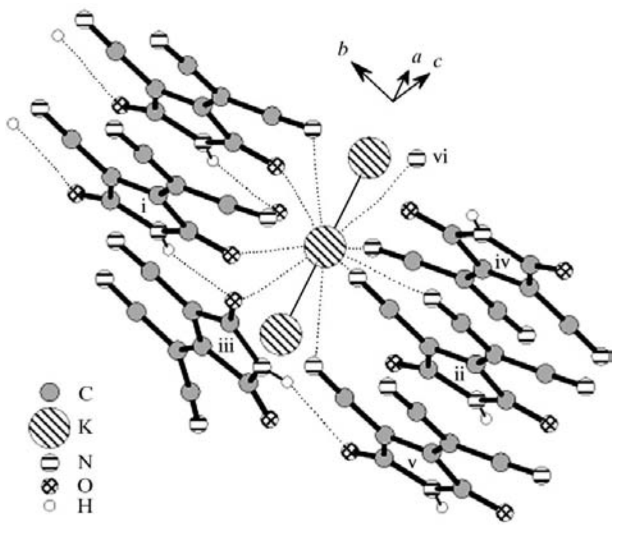

Figure 2
Part of the crystal structure of (I), showing the hydrogen-bonded chain of anions along the *b* axis (dotted lines), the cation arrangement along the *a* axis (solid lines) and the cation–anion interaction (dotted lines) [symmetry codes: (i) $x-1, y, z$; (ii) $x, y-1, z$; (iii) $1-x, y-\frac{1}{2}, \frac{1}{2}-z$; (iv) $-x, 2-y, 1-z$; (v) $x-1, y-1, z$; (vi) $1-x, 2-y, 1-z$].

base and, in this way, a channel is formed along the *a* axis in which the K^+ cations are located (Figs. 2 and 3). The shortest K···K distance is 4.161 (1) Å.

The anions in (I) are connected by an N—H···O2^{vii} interaction to form extended chains which run along the *b* axis, with N—H = 0.82 (2), H···O2^{vii} = 2.31 (2) and N···O2^{vii} = 3.056 (2) Å, and N—H···O2^{vii} = 151 (2)° [symmetry code: (vii) $2-x, y-\frac{1}{2}, \frac{1}{2}-z$].

The five-membered ring of (I) is planar, with a maximum deviation (for N) of 0.011 (1) Å. Atoms O1 [deviation 0.025 (1) Å] and O2 [deviation 0.015 (1) Å] lie in this plane. Atom C7 [deviation 0.0095 (16) Å] also lies nearly exactly in this plane, while atoms C6 [deviation −0.116 (2) Å] and N1 [deviation −0.230 (2) Å] are displaced as a result of steric hindrance and repulsion by the neighbouring cyano groups (Fig. 1). The angle which the –C(CN)$_2$ group makes with the five-membered ring is 4.1 (1)°, demonstrating a small twist from planarity about the C4—C7 bond.

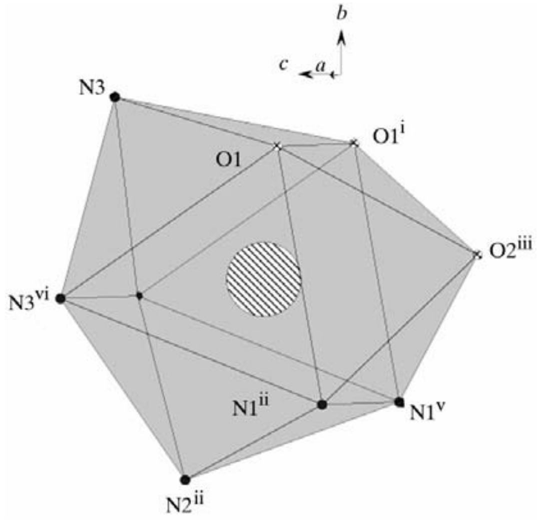

Figure 3
The tricapped trigonal prism surrounding a cation of (I). The unlabelled vertex is N3^{iv}. Symmetry codes are as given in Fig. 2.

Experimental

The starting compound was synthesized from α-chloroketone and tetracyanoethylene. Potassium 3-cyano-4-(dicyanomethylene)-5-oxo-4,5-dihydro-1*H*-pyrrol-2-olate, (I), was obtained by mixing 4,13-dioxo-5,12-dioxadispiro[2.2.5.2]tridecane-1,1,2,2-tetracarbonitrile with potassium iodide in water–1,4-dioxane (1:1, see scheme), followed by refluxing of the resulting solution for 1 h. Yellow crystals of (I) were collected from the reaction mixture by filtration and drying.

Crystal data

$K^+\cdot C_8HN_4O_2^-$
$M_r = 224.23$
Monoclinic, $P2_1/c$
$a = 4.1614$ (10) Å
$b = 9.391$ (2) Å
$c = 21.571$ (3) Å
$\beta = 95.020$ (10)°
$V = 839.7$ (3) Å^3
$Z = 4$
$D_x = 1.773$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 23 reflections
$\theta = 14$–24°
$\mu = 0.61$ mm^{-1}
$T = 293$ (2) K
Prism, yellow
0.20 × 0.15 × 0.10 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Non-profiled ω scan
2434 measured reflections
2434 independent reflections
1935 reflections with $I > 2\sigma(I)$
$\theta_{max} = 30.0°$
$h = -5 \rightarrow 5$
$k = 0 \rightarrow 13$
$l = 0 \rightarrow 30$
2 standard reflections
frequency: 60 min
intensity decay: none

Table 1
Selected geometric parameters (Å, °).

K—O1^{i}	2.8329 (14)	N—C2	1.407 (2)
K—O1	2.8805 (14)	N—H	0.82 (2)
K—N2^{ii}	2.9218 (16)	N1—C6	1.141 (2)
K—N1^{ii}	2.9584 (18)	N2—C8	1.142 (2)
K—O2^{iii}	2.9716 (14)	N3—C9	1.145 (2)
K—N3^{iv}	2.9787 (17)	C4—C5	1.508 (2)
K—N1^{v}	3.0195 (19)	C4—C7	1.383 (2)
K—N3	3.1730 (19)	C3—C4	1.392 (2)
K—N3^{vi}	3.174 (2)	C3—C6	1.412 (2)
O1—C5	1.2109 (19)	C2—C3	1.443 (2)
O2—C2	1.216 (2)	C7—C8	1.424 (2)
N—C5	1.364 (2)	C7—C9	1.424 (2)
C2—N—C5	111.84 (14)	O2—C2—N	124.92 (16)
O1—C5—N	126.86 (15)	O2—C2—C3	128.99 (17)
O1—C5—C4	126.74 (14)	N—C2—C3	106.07 (14)
N—C5—C4	106.41 (13)	N1—C6—C3	178.7 (2)
C7—C4—C3	131.35 (15)	C4—C7—C8	118.99 (14)
C7—C4—C5	122.67 (14)	C4—C7—C9	124.03 (14)
C3—C4—C5	105.97 (13)	C8—C7—C9	116.97 (14)
C4—C3—C6	128.29 (15)	N2—C8—C7	176.43 (17)
C4—C3—C2	109.67 (14)	N3—C9—C7	175.85 (18)
C6—C3—C2	121.87 (15)		

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

Table 2
Charge distribution on the atoms of the anion and neutral radical (e).

Atom	Charge on radical	Charge on anion
O1	−0.257	−0.333
O2	−0.251	−0.374
N1	0.057	−0.142
N2	0.057	−0.114
N3	0.063	−0.112
N	−0.390	−0.420
C2	0.344	0.389
C3	−0.003	−0.340
C4	−0.055	0.122
C5	0.345	0.330
C6	−0.107	−0.011
C7	0.176	−0.145
C8	−0.133	−0.042
C9	−0.124	−0.039
H	0.278	0.237

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.095$
$S = 1.04$
2434 reflections
141 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0469P)^2 + 0.203P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.29$ e Å^{-3}
$\Delta\rho_{\min} = -0.33$ e Å^{-3}

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, 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: FA1025). Services for accessing these data are described at the back of the journal.

References

Abdel-Rahman (1989). *Synth. Commun.* **19**, 1987–1996.

Brandenburg, K. (2000). *DIAMOND*. Release 2.1d. Crystal Impact GbR, Bonn, Germany.

Dewar, M. J. S., Zoebisch, E. F., Healy, E. F. & Stewart, J. J. P. (1985). *J. Am. Chem. Soc.* **107**, 3902–3909.

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.

Huffman, K. R., Loy, M., Henderson, Wm. A. Jr & Ullman, E. F. (1967). *Tetrahedron Lett.* **10**, 931–934.

Lemenovskiy, D. A., Stupan, R. A., Tarasevich, B. N., Slovohotov, Yu. L., Antipin, M. Yu., Kalinin, A. E. & Struchkov, Yu. T. (1981). *Koord. Khim.* **7**, 240–249. (In Russian.)

Nasakin, O. E., Lyshchikov, A. N., Kayukov, Ya. S. & Sheverdov, V. P. (2000). *Khim. Farm. Zh.* **34**, 11–16. (In Russian.)

Nasakin, O. E., Sheverdov, V. P., Lukin, P. M., Tafeenko, V. A. & Bulay, A. Kh. (1992). *Zh. Org. Khim.* **28**, 1841–1849. (In Russian.)

Nasakin, O. E., Sheverdov, V. P., Moiseeva, I. V., Lyschikov, A. N., Ershov, O. V. & Nesterov, V. N. (1997). *Tetrahedron Lett.* **38**, 4455–4456.

Nasakin, O. E., Sheverdov, V. P. & Tafeenko, V. A. (1994). *Dokl. Akad. Nauk*, **334**, 187–189. (In Russian.)

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick G. M. (1997). *SHELXL*97. University of Göttingen, Germany.

Sheverdov, V. P., Ershov, O. E., Nasakin, O. E., Chernushkin, A. N., Tafeenko, V. A. & Firgang, S. I. (2001). *Tetrahedron*, **57**, 5815–5824.

Tacconi, G. I., Invernizzi, A. G. & Desimoni, G. J. (1976). *J. Chem. Soc. Perkin Trans.* 2, pp. 1872–1879.

Zheludev, A., Grand, A., Ressouche, E., Schweizer, J., Morin, B. G., Epstein, A. J., Dixon, D. A. & Miller, J. S. (1994). *J. Am. Chem. Soc.* **116**, 7243–7249.