

Structure of Pyridinium 1,1,3,3-Tetracyano-2-azapropenide

BY J. KOŽÍŠEK AND M. DUNAJ-JURČO

Department of Inorganic Chemistry, Slovak Technical University, CS-812 37 Bratislava, Czechoslovakia

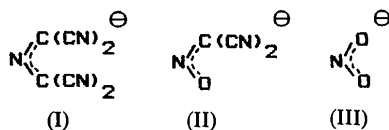
AND U. GROBE AND H. KÖHLER

Chemistry Section, Martin-Luther-University, Halle-Wittenberg, Halle 4010, German Democratic Republic

(Received 31 August 1989; accepted 19 March 1990)

Abstract. $C_5H_6N^+ \cdot C_6N_5^-$, $M_r = 222.21$, monoclinic, $P2_1$, $a = 3.830$ (2), $b = 14.187$ (10), $c = 10.454$ (5) Å, $\beta = 98.58$ (4)°, $V = 561.7$ (5) Å³, $Z = 2$, $D_x = 1.32$, $D_x = 1.31$ Mg m⁻³, $Cu K\alpha$, $\lambda = 1.54178$ Å, $\mu = 0.64$ mm⁻¹, $F(000) = 228$, room temperature, $R = 0.038$ for 585 unique reflections with $F > 4\sigma(F)$. The structure consists of a pyridinium cation and a tetracyanoazapropenide anion, which are both planar and make a dihedral angle of 3.8 (6)°. There is a high degree of π -electron delocalization in the tetracyanoazapropenide anion. The structure is stabilized by hydrogen bonds and interionic contacts, with the shortest contacts involving N atoms which do not take part in the conjugation.

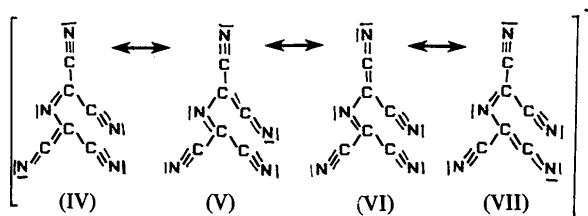
Introduction. In connection with general investigations of the chemistry of pseudochalconide-modified anions (Köhler, 1985), we were interested in the structure and tendency to form complexes, of the tetracyano-2-azapropenide anion (I) (Perchais & Fleury, 1972). On the basis of the pseudo-oxo character of the $C(CN)_2$ group anion (I), it may, together with the nitrosodicyanomethanide anion (II), be considered as a nitrite (III) analogue.



Nitrosodicyanomethanide (II), like nitrite (III), represents an ambivalent ligand. It forms coordination bonds with *d* metals and shows a clear preference for ligation *via* the nitroso N atom, whereas with *f* metals or in organometal derivatives, the nitroso O atom is the preferred donor. Complexes of (II) thus resemble nitro and nitrito complexes respectively (Köhler & Seifert, 1968; Köhler, Lange & Eichler, 1972; Köhler, Jeschke & Kolbe, 1988; Skopenko, Zub, Bolelij & Köhler, 1984).

Early infrared investigations led us to conclude (Kolbe & Köhler, 1970) that (II) has a planar structure. This was later confirmed by X-ray structure investigations: ONC and CCC bond angles were shown to be near 120° for $K[NOC(CN)_2]$: 115.9, 119.8° (Skopenko, Zub, Poray-Koshitz & Sadikov, 1979); $AgNOC(CN)_2$: 112, 123° (Chow & Britton, 1974). At the same time the C—C and C—N distances within the $C(CN)_2$ group are nearly equidistant in $K[NOC(CN)_2]$: 1.43, 1.42; 1.135, 1.143 Å.

Taking into consideration the far reaching oxygen equivalency of the $C(CN)_2$ group (Köhler, 1985) we were interested in whether the tetracyano-2-azapropenide anion (I), formally obtainable from nitrite by an exchange of both O atoms by $C(CN)_2$ groups, is likewise characterized by planarity, with CNC, NCC and CCC bond angles near to 120°. This seems to be indicated by parallels in the infrared and Raman spectra of the homologous anions: $[NOC(CN)_2]^-$, $\nu(CN) = 2220, 2230$; $[pyH][N\{C(CN)_2\}_2]$ 2190, 2200 cm⁻¹ (Kolbe & Köhler, 1970; Kolbe, Grobe & Köhler, 1990; Köhler, Grobe & Hvastijová, 1990). Thus it should be possible to describe the structure of the tetracyano-2-azapropenide anion by the canonical formulae (IV–VII). We now report the X-ray structure of the pyridinium salt of (I).



Experimental. $[C_5H_5NH][N\{C(CN)_2\}_2]$ was obtained (Perchais & Fleury, 1972) from sodium nitrosodicyanomethanide, $Na[NOC(CN)_2]$, *via* its *p*-toluenesulfonyl derivative, $(NC)_2CNOSO_2C_6H_4CH_3$, followed by further reaction with malononitrile in the presence of pyridine. Crystal system and approxi-

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^3$)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
N(1)	6612 (20)	8573*	1742 (8)	84 (3)
C(2)	7597 (12)	7795 (10)	2376 (5)	70 (2)
C(3)	6930 (27)	7003 (7)	1932 (10)	107 (5)
C(4)	4803 (33)	6903 (10)	601 (11)	97 (5)
C(5)	3812 (11)	7718 (9)	13 (4)	79 (2)
C(6)	4725 (29)	8557 (10)	648 (14)	83 (5)
N(7)	2585 (7)	2748 (8)	2793 (3)	58 (1)
C(8)	3457 (20)	3577 (8)	3253 (8)	58 (4)
C(9)	2096 (27)	4342 (8)	2511 (10)	68 (4)
N(10)	876 (26)	4973 (8)	1915 (9)	104 (5)
C(11)	5583 (25)	3772 (9)	4525 (10)	81 (4)
N(12)	7274 (29)	3936 (7)	5460 (9)	97 (5)
C(13)	3474 (23)	1911 (7)	3304 (8)	60 (4)
C(14)	2116 (31)	1100 (9)	2526 (9)	79 (4)
N(15)	987 (29)	516 (8)	1848 (10)	108 (5)
C(16)	5557 (30)	1726 (12)	4481 (10)	63 (4)
N(17)	7313 (23)	1617 (8)	5467 (8)	111 (5)

*Parameter fixed.

Table 2. Selected bond lengths (\AA) and angles ($^\circ$) with their e.s.d.'s

N(1)—C(2)	1.313 (13)	C(8)—C(9)	1.388 (14)
C(2)—C(3)	1.227 (17)	C(9)—N(10)	1.150 (15)
C(3)—C(4)	1.510 (15)	C(8)—C(11)	1.479 (13)
C(4)—C(5)	1.337 (14)	C(11)—N(12)	1.114 (14)
C(5)—C(6)	1.382 (14)	C(13)—C(14)	1.458 (15)
C(6)—N(1)	1.258 (15)	C(14)—N(15)	1.133 (15)
C(13)—N(7)	1.325 (15)	C(13)—C(16)	1.393 (12)
N(7)—C(8)	1.295 (15)	C(16)—N(17)	1.150 (12)
C(2)—N(1)—C(6)	121.8 (8)	C(9)—C(8)—C(11)	117.9 (10)
N(1)—C(2)—C(3)	123.3 (7)	N(10)—C(9)—C(8)	177.9 (12)
C(2)—C(3)—C(4)	119.2 (10)	N(12)—C(11)—C(8)	177.3 (12)
C(3)—C(4)—C(5)	114.8 (10)	N(7)—C(13)—C(14)	115.6 (7)
C(4)—C(5)—C(6)	119.3 (8)	N(7)—C(13)—C(16)	127.7 (9)
N(1)—C(6)—C(5)	121.4 (10)	C(14)—C(13)—C(16)	116.7 (9)
C(8)—N(7)—C(13)	128.8 (6)	C(13)—C(14)—N(15)	174.8 (11)
N(7)—C(8)—C(9)	116.5 (7)	N(13)—C(16)—N(17)	175.9 (12)
N(7)—C(8)—C(11)	125.5 (9)		
X—H...Y	X...Y	H...Y	X—H...Y
N(1)—H(1)...N(15 ⁱ)	3.22 (2)	2.38 (1)	131.0 (6)
C(2)—H(2)...N(12 ⁱⁱ)	3.20 (2)	2.33 (1)	146.3 (6)
C(2)—H(2)...N(17 ⁱⁱⁱ)	3.22 (2)	2.62 (2)	119.3 (8)
C(3)—H(3)...N(10 ⁱⁱⁱ)	3.27 (3)	2.63 (2)	130.3 (8)
C(3)—H(3)...N(17 ⁱⁱⁱ)	3.28 (2)	2.73 (1)	121.4 (9)
C(4)—H(4)...N(10)	3.50 (2)	2.91 (1)	114.5 (8)

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

mate cell dimensions determined from Weissenberg and oscillation photographs; density measured by flotation in a mixture of CHBr_3 and *n*-octane; crystal specimen $0.2 \times 0.3 \times 0.5$ mm; Syntex $P2_1$ four-circle diffractometer, graphite-monochromated $\text{Cu K}\alpha$ radiation, θ - 2θ scan mode with a variable scan rate ranging from 4.88 to $29.30^\circ \text{ min}^{-1}$; accurate cell parameters refined from setting angles of 11 reflections with $12 < 2\theta < 28^\circ$; maximum $(\sin\theta/\lambda) = 0.56 \text{ \AA}^{-1}$; index range $h - 4/4, k 0/14, l 0/11$; two check reflections measured every 98 reflections, no

significant variation; 801 unique reflections measured, 605 considered observed [$F > 3\sigma(F)$], $R_{int} = 0.046$ for 282 reflections, Lp correction, empirical absorption correction based on reflection intensity measurements at different azimuthal angles, transmission range 0.161 – 1.000 . Structure solved by a combination of direct methods and Fourier synthesis techniques (Sheldrick, 1976, 1986). H atoms located from a difference map in positions consistent with the expected locations calculated on geometrical grounds (C—H 1.080 \AA , sp^2 hybridization). Full-matrix least-squares refinement on F , $w^{-1} = k[\sigma^2(F) + gF^2]$, $k = 0.24$, $g = 0.00211$, anisotropic thermal parameters for all non-H atoms, isotropic for H of 0.07 \AA^2 with fixed coordinates. Two of the strongest reflections (020, 068) were considered to be affected by extinction and were excluded from refinement. 153 parameters, $R = 0.0382$, $wR = 0.0429$, maximum $\Delta/\sigma = 0.97$, mean $= 0.20$, maximum $\Delta\rho = +0.13$, minimum $\Delta\rho = -0.10 \text{ e \AA}^{-3}$, slope of normal probability plot $= 1.21$. Scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974, Vol. IV).

Discussion. The atomic coordinates and equivalent isotropic temperature factors are listed in Table 1, and bond lengths and angles in Table 2.* An ORTEP plot of the molecule and the atom numbering is shown in Fig. 1 (Johnson, 1971).

The structure consists of a pyridinium cation and a tetracyanoazapropenide anion. Distances in the pyridinium ring are in the range 1.22 (3)– 1.50 (2) \AA and angles 115 (1)– 123 (1) $^\circ$. The atoms of tetracyanoazapropenide anion are coplanar within the

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53155 (7 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

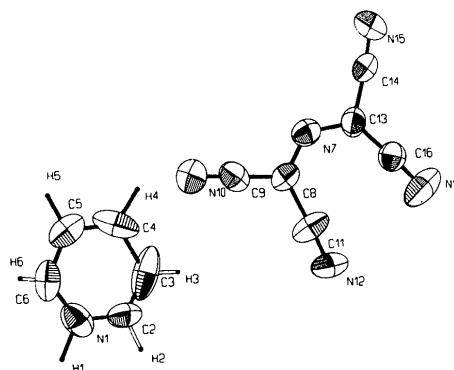


Fig. 1. The molecular structure of pyridinium 1,1,3,3-tetracyano-2-azapropenide showing the atomic numbering scheme.

limits of experimental error. The observed propenide N(7)—C(8) and N(7)—C(13) bond lengths of 1.30 (2) and 1.32 (2) Å indicate partial double-bond character. All cyanide C≡N bonds range from 1.11 (2) to 1.16 (2) Å and are typical triple bonds. The distances C(8)—C(11) and C(13)—C(14) at 1.48 (2) and 1.47 (2) Å are only a little shorter than for a pure single bond, but C(8)—C(9) and C(13)—C(16) at 1.38 (2) and 1.39 (1) Å are significantly shorter. There is a high degree of π -electron delocalization in the tetracyanoazapropenide anion which may be satisfactorily expressed by (VIII).

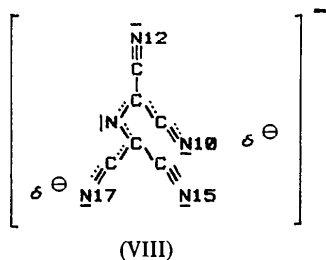


Table 2 shows possible hydrogen bonds and close interionic C—H...N contacts. The shortest H...N

distances involve N(17) and N(19) which do not take part in the conjugation.

References

- CHOW, Y. M. & BRITTON, D. (1974). *Acta Cryst.* **B30**, 1117–1118.
 JOHNSON, C. K. (1971). *ORTEPII*. Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee, USA.
 KÖHLER, H. (1985). *Nova Acta Leopold.* **59**, 259.
 KÖHLER, H., GROBE, U. & HVASTIJOVÁ, M. (1990). In preparation.
 KÖHLER, H., JESCHKE, M. & KOLBE, A. (1988). *Z. Anorg. Allg. Chem.* **559**, 131–134.
 KÖHLER, H., LANGE, U. & EICHLER, B. (1972). *J. Organomet. Chem.* **35**, C17–C19.
 KÖHLER, H. & SEIFERT, B. (1968). *Z. Anorg. Allg. Chem.* **360**, 137–142.
 KOLBE, A., GROBE, U. & KÖHLER, H. (1990). In preparation.
 KOLBE, A. & KÖHLER, H. (1970). *Z. Anorg. Allg. Chem.* **373**, 230–236.
 PERCHAI, J. & FLEURY, J. P. (1972). *Tetrahedron*, **28**, 2267–2283.
 SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
 SHELDRICK, G. M. (1986). *SHELXS86*. In *Crystallographic Computing 3*, edited by G. M. SHELDRICK, C. KRÜGER & R. GODDARD, pp. 175–189. Oxford Univ. Press.
 SKOPENKO, V. V., ZUB, YU. L., BOLELLI, V. F. & KÖHLER, H. (1984). *Koord. Chem. (Moskau)*, **10**, 1317–1331.
 SKOPENKO, V. V., ZUB, YU. L., PORAY-KOSHITZ, M. A. & SADIKOV, G. G. (1979). *Ukr. Khim. Zh.* **45**, 811–816.

Acta Cryst. (1990). **C46**, 2424–2426

Structure of the *N,N'*-Dimethyl Diimine of 3-[3-(2-Hydroxyphenyl)-3-oxo-1-phenylpropyl]flavanone, the Adduct of Flavanone and 2'-Hydroxychalcone

BY CHRISTOPHER J. ADAMS, LYNDISAY MAIN* AND BRIAN K. NICHOLSON

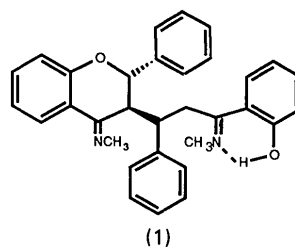
School of Science, University of Waikato, Hamilton, New Zealand

(Received 2 January 1990; accepted 13 March 1990)

Abstract. 2-[3-(2,3-Dihydro-4-methylimino-2-phenyl-4*H*-1-benzopyran-3-yl)-1-methylimino-3-phenylpropyl]phenol, $C_{32}H_{29}N_2O_2$, (1), $M_r = 473.60$, monoclinic, $P2_1/c$, $a = 10.090$ (4), $b = 16.662$ (9), $c = 16.478$ (9) Å, $\beta = 114.68$ (3)°, $V = 2517$ (2) Å³, $Z = 4$, $D_x = 1.251$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 0.43$ cm⁻¹, $F(000) = 1004$, $T = 123$ K, $R = 0.0423$ for 3482 unique observed reflections with $I > 3\sigma(I)$. The structure consists of a flavanone unit linked by its α -carbon [C(3)] to the β -carbon [C(3)] of a 2'-hydroxydihydrochalcone unit, with both carbonyl groups present as their methylimino derivatives. The hydroxy hydrogen is intramolecularly hydrogen bonded to the adjacent imino nitrogen.

Introduction. During the course of imine preparations involving reaction of 2'-hydroxychalcone with

amines, we found in the methylamine case that leaving the reaction solution for a long period resulted in the formation of a byproduct in which two chalcone units are linked, one as a flavanone to the other as a dihydrochalcone. Although such structures are not known to us in natural product chemistry, the potential simplicity of their formation through the conjugate addition of a flavanone to a chalcone makes the current structure of more than novel interest.



* To whom correspondence should be addressed.