

## PSEUDO-CROSS-CONJUGATED MESOMERIC BETAINES.

### 2.\* X-RAY CRYSTALLOGRAPHIC INVESTIGATION OF BETAINES BASED ON QUINOXALINE DERIVATIVES

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*An x-ray crystallographic investigation of 3-methyl-5-cyanoimidazolio[1',2':1,6]pyrido[2,3-b]quinoxalin-4-olate, which is a representative of a previously unknown type of polynuclear heterocyclic pseudo-cross-conjugated mesomeric betaine, was undertaken.*

Earlier we described a general experimental approach to polycyclic pseudo-cross-conjugated mesomeric betaines, involving the reaction of 1,4-dielectrophilic  $\alpha$ -ethoxycarbonyl-3-chloro-2-quinoxalylacetonitrile with azoles [1]. Such polynuclear heterocyclic pseudo-cross-conjugated mesomeric betaines have not been described before. It was therefore of interest to undertake an x-ray crystallographic investigation of the synthesized compounds. In the present work we set out the results from x-ray crystallographic analysis of 3-methyl-5-cyanoimidazolio[1',2':1,6]pyrido[2,3-b]quinoxalin-4-olate (I).

The crystal of compound (I) contains two symmetrically independent molecules A and B. Since their geometry differs little, only one of them (IA) is shown in Fig. 1. The bond lengths and bond angles are given in Tables 1 and 2.

The cyclic system in both molecules is approximately planar — the departures of the atoms from the mean-square plane do not exceed 0.032(2) Å in (IA) and 0.072(2) Å in (IB). The O<sub>(7)</sub>, C<sub>(4)</sub>, and C<sub>(9)</sub> atoms project from this plane by 0.034(2), 0.070(1), and -0.066(2) Å in (IA) and by 0.169(2), 0.104(1), and 0.053(2) Å in (IB). The averaged length of the C—N bond in the pyrazine ring N<sub>(12)</sub>N<sub>(19)</sub>C<sub>(11)</sub>C<sub>(13)</sub>C<sub>(18)</sub>C<sub>(20)</sub> is 1.341(2) and 1.343(2) Å in the two independent molecules and coincides within 3 $\sigma$  with the value obtained for the C—N bond in the molecule of tetramethylpyrazine [2]. The geometric parameters of the five-membered ring N<sub>(3)</sub>N<sub>(21)</sub>C<sub>(1)</sub>C<sub>(2)</sub>C<sub>(5)</sub> are normal for imidazoline systems [3]. At the same time it should be noted that there is some nonequivalence between the C—C bonds in these rings in molecules (IA) and (IB). Thus, in the pyrazine

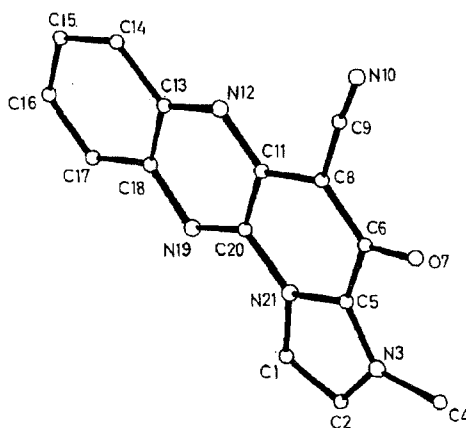


Fig. 1. General appearance of the molecule of (I). (The H atoms are not shown.)

\*For Communication I, see [1].

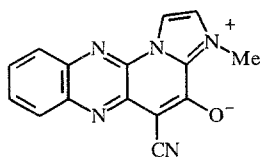
TABLE 1. Bond Lengths  $d(\text{\AA})$  in Molecules (IA) and (IB)

Bond	$d(\text{\AA})$		Bond	$d(\text{\AA})$	
	I A	I B		I A	I B
O(7)—C(6)	1,242(2)	1,250(2)	C(1)—C(2)	1,338(2)	1,334(2)
N(3)—C(2)	1,378(2)	1,379(2)	C(5)—C(6)	1,466(2)	1,468(2)
N(3)—C(4)	1,477(3)	1,473(2)	C(6)—C(8)	1,412(2)	1,408(2)
N(3)—C(5)	1,339(2)	1,339(2)	C(8)—C(9)	1,425(2)	1,422(2)
N(10)—C(9)	1,144(2)	1,143(2)	C(8)—C(11)	1,428(2)	1,427(2)
N(12)—C(11)	1,334(2)	1,335(2)	C(11)—C(20)	1,432(2)	1,431(2)
N(12)—C(13)	1,363(2)	1,366(2)	C(13)—C(14)	1,417(3)	1,412(2)
N(19)—C(18)	1,369(2)	1,367(2)	C(13)—C(18)	1,412(2)	1,419(3)
N(19)—C(20)	1,299(2)	1,304(2)	C(14)—C(15)	1,363(2)	1,360(2)
N(21)—C(1)	1,383(2)	1,390(2)	C(16)—C(15)	1,403(2)	1,411(3)
N(21)—C(5)	1,354(2)	1,357(2)	C(16)—C(17)	1,361(2)	1,353(2)
N(21)—C(20)	1,412(2)	1,410(2)	C(17)—C(18)	1,417(3)	1,415(3)

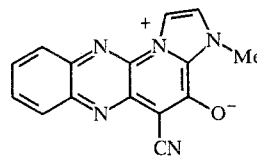
TABLE 2. Bond Angles  $\omega$  (deg) in Molecules (IA) and (IB)

Angle	$\omega$ (°)		Angle	$w$ (°)	
	I A	I B		I A	I B
C(2)N(3)C(4)	124,3 (1)	123,6 (1)	C(9)C(8)C(11)	120,5 (1)	119,3 (1)
C(2)N(3)C(5)	108,8 (1)	108,7 (1)	N(10)C(9)C(8)	176,5 (2)	178,9 (2)
C(4)N(3)C(5)	127,0 (1)	127,6 (1)	N(12)C(11)C(8)	121,6 (1)	120,6 (1)
C(11)N(12)C(13)	117,2 (1)	117,4 (1)	N(12)C(11)C(20)	118,7 (1)	118,9 (1)
C(18)N(19)C(20)	115,3 (1)	115,8 (1)	C(8)C(11)C(20)	119,7 (1)	120,4 (1)
C(1)N(21)C(5)	109,0 (1)	109,0 (1)	N(12)C(13)C(14)	119,6 (1)	119,3 (1)
C(1)N(21)C(20)	128,4 (1)	128,5 (1)	N(12)C(13)C(18)	122,3 (1)	121,9 (1)
C(5)N(21)C(20)	122,7 (2)	122,5 (2)	C(14)C(13)C(18)	118,1 (1)	118,8 (1)
N(21)C(1)C(2)	106,7 (1)	106,5 (1)	C(13)C(14)C(15)	120,3 (2)	120,4 (2)
N(3)C(2)C(1)	108,4 (1)	108,7 (1)	C(14)C(15)C(16)	121,4 (2)	120,5 (2)
N(3)C(5)N(21)	107,3 (1)	107,1 (1)	C(15)C(16)C(17)	120,1 (2)	121,0 (2)
N(3)C(5)C(6)	129,9 (1)	129,4 (1)	C(16)C(17)C(18)	119,9 (2)	119,9 (2)
N(21)C(5)C(6)	122,8 (1)	123,5 (1)	N(19)C(18)C(13)	120,6 (1)	120,6 (1)
O(7)C(6)C(5)	119,1 (1)	119,2 (1)	N(19)C(18)C(17)	119,1 (1)	120,0 (1)
O(7)C(6)C(8)	126,5 (1)	127,2 (1)	C(13)C(18)C(17)	120,3 (1)	119,5 (1)
C(5)C(6)C(8)	114,3 (1)	113,7 (1)	N(19)C(20)C(21)	116,9 (1)	117,9 (1)
C(6)C(8)C(9)	116,3 (1)	117,6 (1)	N(19)C(20)C(11)	126,0 (1)	125,5 (1)
C(6)C(8)C(11)	123,1 (1)	123,2 (1)	N(21)C(20)C(11)	117,2 (1)	116,6 (1)

ring the N<sub>(12)</sub>—C<sub>(11)</sub> bond [1.334(2) and 1.385(2) Å] and N<sub>(19)</sub>—C<sub>(20)</sub> bond [1.299(2) and 1.304(2) Å] are noticeably shorter than the N<sub>(12)</sub>—C<sub>(13)</sub> [1.363(2) and 1.366(2) Å] and N<sub>(19)</sub>—C<sub>(18)</sub> [1.369(2) and 1.367(2) Å] bonds. In the imidazoline ring the N<sub>(21)</sub>—C<sub>(5)</sub> bond [1.354(2) and 1.357(2) Å] is elongated compared with the N<sub>(3)</sub>—C<sub>(5)</sub> bond [1.339(2) and 1.339(2) Å]. Such a distribution of bond lengths indicates that form (Ia) makes a substantial contribution to the electronic structure of compound (I):



I a



I b

Some shortening of the N<sub>(21)</sub>—C<sub>(20)</sub> [1.412(2) and 1.410(2) Å], C<sub>(5)</sub>—C<sub>(6)</sub> [1.466(2) and 1.468(2) Å], and C<sub>(8)</sub>—C<sub>(11)</sub> [1.428(2) and 1.427(2) Å] bonds compared with the standard values for N<sub>sp<sup>2</sup></sub>—C<sub>sp<sup>2</sup></sub> (1.45 Å) and C<sub>sp<sup>2</sup></sub>—C<sub>sp<sup>3</sup></sub> (1.48 Å) single bonds [4] indicates that form (Ib) may also make a contribution to the structure of compound (I). This suggestion agrees well

TABLE 3. Coordinates of the Nonhydrogen Atoms and Their Equivalent Isotropic Temperature Factors  $B_{eq}$  ( $\text{\AA}^2$ )

atom	Molecule (Ia)			Molecule (IB)			B <sub>iso</sub>
	x	y	z	x	y	z	
O(7)	0,8880 (2)	0,53100 (6)	0,37229 (6)	0,1674 (2)	0,15881 (6)	0,59279 (2)	4,30 (3)
N(3)	0,8350 (2)	0,66000 (7)	0,43777 (7)	0,0424 (2)	0,07031 (7)	0,70093 (7)	3,52 (3)
N(10)	0,7982 (2)	0,36688 (7)	0,41468 (9)	0,3192 (2)	0,13230 (8)	0,42056 (8)	4,71 (4)
N(12)	0,6642 (2)	0,43737 (6)	0,57955 (7)	0,2866 (2)	-0,03735 (6)	0,46396 (7)	3,21 (3)
N(19)	0,6374 (2)	0,56834 (6)	0,63141 (6)	0,1742 (2)	-0,11128 (6)	0,57973 (7)	3,34 (3)
N(21)	0,7407 (2)	0,60785 (6)	0,52767 (7)	0,1058 (2)	-0,01264 (6)	0,63468 (7)	3,09 (3)
C(1)	0,7343 (2)	0,67469 (8)	0,54277 (9)	0,0347 (2)	-0,03845 (9)	0,69443 (9)	3,89 (4)
C(2)	0,7925 (2)	0,70641 (8)	0,48701 (9)	-0,0041 (2)	0,01301 (9)	0,73446 (9)	4,08 (4)
C(4)	0,9058 (3)	0,6761 (1)	0,36919 (9)	0,0280 (3)	0,1367 (1)	0,7320 (1)	4,86 (6)
C(5)	0,8025 (2)	0,59973 (8)	0,46292 (8)	0,1090 (2)	0,05430 (8)	0,63961 (8)	2,95 (3)
C(6)	0,8249 (2)	0,53460 (8)	0,43085 (8)	0,1710 (2)	0,09756 (8)	0,58427 (8)	3,07 (3)
C(8)	0,7705 (2)	0,48113 (8)	0,47204 (8)	0,2266 (2)	0,06309 (8)	0,52522 (8)	2,94 (3)
C(9)	0,7849 (2)	0,41690 (8)	0,44201 (9)	0,2794 (2)	0,10114 (8)	0,46719 (9)	3,27 (3)
C(11)	0,7081 (2)	0,48916 (8)	0,54087 (8)	0,2306 (2)	-0,00734 (8)	0,52094 (8)	2,81 (3)
C(13)	0,6065 (2)	0,45020 (8)	0,64465 (8)	0,2899 (2)	-0,10487 (8)	0,46415 (9)	3,28 (3)
C(14)	0,5614 (3)	0,39702 (9)	0,6886 (1)	0,3513 (2)	-0,13869 (9)	0,40550 (9)	4,18 (4)
C(15)	0,5021 (3)	0,4091 (1)	0,7536 (1)	0,3601 (3)	-0,20583 (9)	0,4053 (1)	4,84 (5)
C(16)	0,4812 (2)	0,47381 (9)	0,77825 (9)	0,3054 (3)	-0,24261 (9)	0,4631 (1)	4,87 (5)
C(17)	0,5246 (2)	0,52619 (9)	0,73789 (9)	0,2444 (2)	-0,21206 (8)	0,5201 (1)	4,22 (4)
C(18)	0,5903 (2)	0,51528 (8)	0,67070 (8)	0,2348 (2)	-0,14223 (8)	0,52206 (9)	3,37 (4)
C(20)	0,6931 (2)	0,55413 (7)	0,56994 (8)	0,1721 (2)	-0,04687 (8)	0,57739 (8)	2,82 (3)
O(1)	0,2755 (2)	0,23273 (7)	0,31206 (7)				
O(2)	0,6025 (2)	0,29761 (8)	0,28435 (7)				
O(3)	-0,1024 (2)	0,20798 (7)	0,29524 (8)				

TABLE 4. Coordinates of the H Atoms and Their Isotropic Temperature Factors  $B_{\text{iso}}$  ( $\text{\AA}^2$ )

Atom	Molecule (Ia)				Molecule (Ib)			
	x	y	z	$B_{\text{iso}}$	x	y	z	$B_{\text{iso}}$
H(1)	0,698 (2)	0,6898 (9)	0,5681 (8)	2,4 (4)	0,019 (2)	-0,0870 (8)	0,6992 (8)	1,6 (3)
H(2)	0,806 (2)	0,7544 (8)	0,4754 (9)	2,1 (4)	-0,053 (2)	0,018 (7)	0,7809 (8)	1,5 (3)
H(4.1)	0,937 (3)	0,722 (1)	0,369 (1)	6,0 (6)	-0,022 (3)	0,132 (1)	0,778 (1)	7,4 (7)
H(4.2)	0,827 (3)	0,658 (1)	0,332 (1)	6,5 (6)	-0,029 (4)	0,167 (1)	0,699 (1)	9,2 (8)
H(4.3)	1,018 (4)	0,650 (1)	0,367 (1)	7,6 (7)	0,152 (5)	0,153 (2)	0,752 (2)	11 (1)
H(14)	0,574 (2)	0,3533 (8)	0,6702 (9)	2,1 (4)	0,387 (2)	-0,1107 (8)	0,3666 (8)	1,9 (4)
H(15)	0,475 (2)	0,3729 (8)	0,7831 (8)	2,0 (4)	0,403 (2)	-0,2275 (8)	0,3650 (8)	2,3 (4)
H(16)	0,435 (2)	0,4813 (8)	0,8280 (8)	1,7 (4)	0,317 (2)	-0,2913 (8)	0,4618 (8)	2,4 (4)
H(17)	0,505 (2)	0,5828 (7)	0,7509 (8)	1,2 (3)	0,205 (2)	-0,2366 (8)	0,5622 (8)	2,1 (4)
*H(1.1)	0,124 (3)	0,225 (1)	0,304 (1)	4,7 (5)				
*H(1.2)	0,294 (3)	0,197 (1)	0,349 (1)	7,0 (7)				
*H(2.1)	0,635 (4)	0,319 (1)	0,327 (1)	8,8 (8)				
*H(2.2)	0,476 (4)	0,277 (1)	0,281 (1)	10,8 (9)				
*H(3.1)	-0,201 (4)	0,246 (1)	0,294 (1)	7,5 (7)				
*H(3.2)	-0,130 (6)	0,176 (2)	0,335 (2)	16 (1)				

Note. The H atoms belonging to the solvate water molecules.

with the high degree of flattening of the  $N_{(21)}C_{(20)}C_{(11)}C_{(8)}C_{(6)}$  ring observed in compound (I) — in the independent molecules A and B this ring is planar to within 0.017(2) and 0.026(1)  $\text{\AA}$ . The considerable contribution from forms (Ia) and (Ib) is also confirmed by the alternation of the bonds in the  $C_{(13)}-C_{(18)}$  benzene ring; the  $C_{(14)}-C_{(15)}$  [1.363(2) and 1.360(2)  $\text{\AA}$ ] and  $C_{(16)}-C_{(17)}$  [1.361(2) and 1.353(2)  $\text{\AA}$ ] bonds are noticeably shortened than the other bonds of this ring [1.403-1.419(3)  $\text{\AA}$ ].

We note that the crystal of the investigated compound contains a branched system of intermolecular hydrogen bonds. Thus, in particular, the two independent molecules (IA) and (IB) are linked by H bonds with solvate water molecules, which are in turn linked to each other, forming the  $N_{(10)}^A-H_{(2.1)}-O_{(2)}-H_{(2.2)}\cdots O_{(1)}-H_{(1.2)}\cdots N_{(10)}^B$  chain. The principal geometric parameters of these H bonds are as follows:  $N_{(10)}^A-O_{(2)}$ , 3.050(2)  $\text{\AA}$ ;  $N_{(10)}^A-H_{(2.1)}$ , 2.16(3)  $\text{\AA}$ ;  $N_{(10)}^A H_{(2.1)} O_{(2)}$  angle, 161.2°;  $O_{(1)}\cdots O_{(2)}$ , 2.828(2)  $\text{\AA}$ ;  $O_{(1)}\cdots H_{(2.2)}$ , 1.86(2)  $\text{\AA}$ ;  $O_{(1)} H_{(2.1)} O_{(2)}$  angle, 158.2°;  $O_{(1)}\cdots N_{(10)}^B$ , 2.875(2)  $\text{\AA}$ ;  $N_{(10)}^B\cdots H_{(1.2)}$ , 1.88(3)  $\text{\AA}$ ;  $O_{(1)} H_{(1.2)} N_{(10)}^B$  angle, 176.2°.

## EXPERIMENTAL

The x-ray crystallographic investigation of compound (I) was conducted on an automatic Enraf Nonius CAD-4 four-circle diffractometer at 18°C ( $\lambda\text{Mo-K}\alpha$ , graphite monochromator, 3522 unique reflections, ratio of scan rates  $\omega:\theta = 1.2:1$ ,  $\theta_{\text{max}} = 22^\circ$ ). The crystals, representing the solvate (I)·3H<sub>2</sub>O, were monoclinic with  $a = 7.326(3)$ ,  $b = 20.228(2)$ ,  $c = 18.827(3)$   $\text{\AA}$ ,  $\beta = 96.00(2)^\circ$ ,  $V = 2774.7$   $\text{\AA}^3$ ,  $z = 8$ ,  $d_{\text{calc}} = 1.32$  g/cm<sup>3</sup>, space group P2<sub>1</sub>/c. In the structure calculations we used 2721 reflections with  $J > 3\sigma$ . The structure was interpreted by the direct method using the MULTAN program and was refined in full-matrix anisotropic approximation. All the H atoms were revealed in the difference synthesis of the electron density and were refined isotropically. The final divergence factors were  $R = 0.030$  and  $R_w = 0.041$ . All the calculations were performed on a PDP-11/23+ computer using the SPP-PLUS software [5].

Compound (I) was synthesized by the method in [1]. The crystal of (I) was formed from a 99:1 mixture of DMFA and water as solvent.

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