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SYNTHESIS AND STRUCTURE OF THE BETAINE SYSTEM OF 2-HYDRAZINO-3,4,6-TRICHLORO-5-CYANOPYRIDINE AND DIAZOMETHANE

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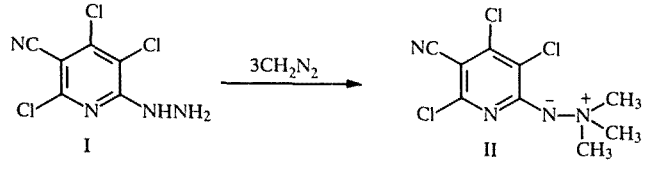
Upon reaction of 2-hydrazino-3,4,6-trichloro-5-cyanopyridine with diazomethane, we obtain a betaine system, 1-trimethyl-2-(3,4,6-trichloro-5-cyanopyrid-2-yl)hydrazin-1-io-2-ide, the structure of which has been established by x-ray diffraction. We calculate the electronic structure of the betaine using the CNDO/3 method.

Earlier we described the synthesis of 2-hydrazino-3,4,6-trichloro-5-cyanopyridine (I) [1]. Within an investigation of its reactivity, in this paper we have studied the reaction of hydrazine I with diazomethane. The possible alternative orientations of the reaction are 1,3-dipolar cycloaddition at the C≡N group, substitution at the C-2 atom, and N-alkylation. Only the last orientation is realized, and it is the terminal NH_2 group which is methylated rather than the (α-NH group of the hydrazine moiety (characterized by the highest acidity). In this case, the trimethylated derivative II is formed, having a betaine structure.



I II

In the IR spectra of both the starting hydrazine I and the methylation product II in the interval 1585-1492 cm^{-1}, we observe intense absorption bands characteristic for stretching vibrations of the C=N and C=C bonds of the pyridine ring, and in the region 2224-2212 cm^{-1} we observe an intense absorption band for the stretching vibrations of the C≡N bond. However, while the spectrum of the starting compound I is characterized by intense absorption bands at 3304-3200 cm^{-1} and 1636 cm^{-1} (belonging, respectively, to the stretching and bending vibrations of the N–H bonds of the hydrazine moiety), the absence of analogous absorption in the spectrum of the reaction product supports the permethylation process.

Analysis of the UV spectra supports similarity between the electronic structure of the starting hydrazine I and the betaine II, but in the spectrum of the second compound we observe a bathochromic (16 nm) and hyperchromic shift of the long-wavelength band of the $\pi-\pi^*$-transition at 304.5 nm (log ε 4.44), and also a bathochromic shift of the shoulder at 330.5 nm (log ε 3.87), probably corresponding to the $n-\pi^*$-transition with participation of electrons of the $N^-N^+(CH_3)_3$ group.

In the ^{13}C NMR spectrum of betaine II in DMSO-d_6, we observe an intense signal from the methyl groups at 54.88 ppm, a signal from the carbon atom of the nitrile group at 111.77 ppm, and characteristic signals from the carbon atoms of the pyridine ring at 99.02 ($C_{(5)}$), 115.51 ($C_{(3)}$), 137.55 ($C_{(4)}$), 148.63 ($C_{(6)}$), and 156.80 ppm ($C_{(2)}$). Assignment of the signals was made in accordance with the data in [2].

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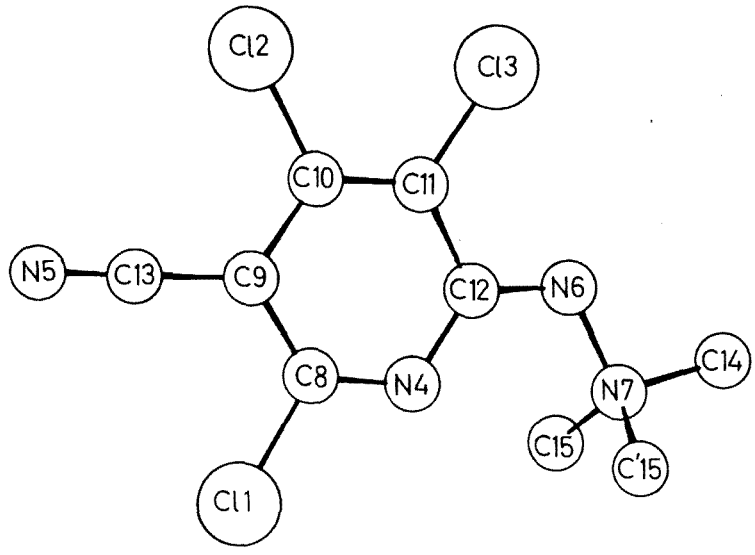


Fig. 1. Structure of the 1-trimethyl-2-(3,4,6-trichloro-5-cyanopyrid-2-yl)hydrazin-1-io-2-ide molecule.

TABLE 1. Bond Lengths in the Betaine II Molecule

Bond	d, Å	Bond	d, Å
$Cl_{(1)}—C_{(8)}$	1,741(6)	$N_{(7)}—C_{(14)}$	1,494(9)
$Cl_{(2)}—C_{(10)}$	1,725(4)	$N_{(7)}—C_{(15)}$	1,526(6)
$Cl_{(3)}—C_{(11)}$	1,729(5)	$C_{(8)}—C_{(9)}$	1,403(5)
$N_{(4)}—C_{(8)}$	1,305(6)	$C_{(9)}—C_{(13)}$	1,424(5)
$N_{(4)}—C_{(12)}$	1,373(6)	$C_{(9)}—C_{(10)}$	1,438(6)
$N_{(5)}—C_{(13)}$	1,138(5)	$C_{(10)}—C_{(11)}$	1,324(5)
$N_{(6)}—C_{(12)}$	1,318(5)	$C_{(11)}—C_{(12)}$	1,468(5)
$N_{(6)}—N_{(7)}$	1,476(5)		

The crystal structure of the betaine system II was investigated by x-ray diffraction. The planar molecules in the crystal are located in special positions on the m symmetry planes. In Fig. 1, we show the structure of the molecule.*

The bond lengths and the bond angles (Tables 1 and 2) in the pyridine ring are markedly different from the corresponding values in other cyanopyridines and in particular in 2-hydrazino-3,4,6-trichlor-5-cyanopyridine [1]. Thus, the $C_{(10)}-C_{(11)}$ and $N_{(4)}-C_{(8)}$ bond lengths (1.324 and 1.305 Å, respectively) are considerably shorter than the analogous bonds in aromatic pyridine rings and have a significant fraction of double-bond character. Furthermore, the exocyclic $N_{(6)}-C_{(12)}$ bond (1.318 Å) is also shortened and has double-bond character. The remaining bonds in the ring are somewhat lengthened compared with the standard values for bonds of order 1.5. The exocyclic $C_{(9)}-C_{(13)}$ bond (1.424 Å) also should be considered shortened. The lengths of analogous bonds in cyanopyridines are usually found within the range 1.44-1.48 Å [3-6].

Thus, from the distribution of bond lengths we can conclude that some contribution to the structure of the molecule comes from the mesomeric bipolar quinoid form (a). The real electronic structure probably corresponds to superposition of the two structures (see top of the following page):

*The numbering of the atoms in the crystal structure (Fig. 1 and Tables 1, 2, and 4) is given independently.

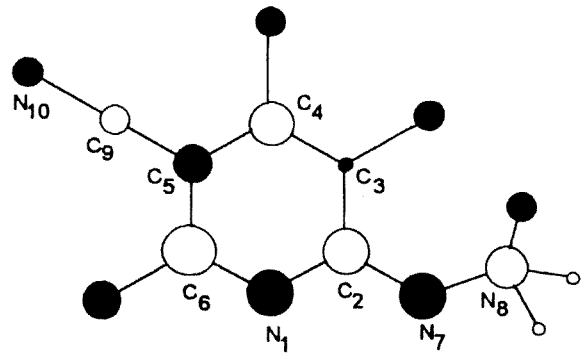


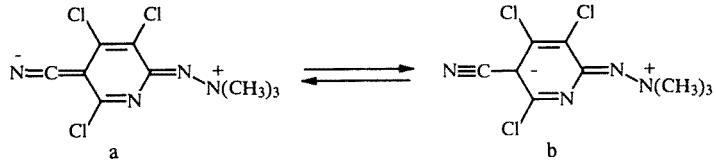
Fig. 2. Diagram of electron density distribution in the betaine II molecule.

TABLE 2. Bond Angles in the Betaine II Molecule

Angle	ω	Angle	ω
$C_{(8)}—N_{(4)}—C_{(12)}$	119,1(1)	$C_{(14)}—N_{(7)}—C_{(15)}$	108,3(3)
$N_{(7)}—N_{(6)}—C_{(12)}$	116,1(3)	$C_{(15)}—N_{(7)}—C_{(15)}$	112,8(5)
$N_{(6)}—N_{(7)}—C_{(14)}$	103,0(3)	$N_{(6)}—N_{(7)}—C_{(15)}$	111,9(3)
$Cl_{(1)}—C_{(8)}—N_{(4)}$	115,5(1)	$Cl_{(1)}—C_{(8)}—C_{(9)}$	117,3(1)
$N_{(4)}—C_{(8)}—C_{(9)}$	127,2(3)	$C_{(10)}—C_{(9)}—C_{(13)}$	122,9(1)
$C_{(8)}—C_{(9)}—C_{(10)}$	113,9(4)	$C_{(8)}—C_{(9)}—C_{(13)}$	123,2(4)
$Cl_{(2)}—C_{(10)}—C_{(9)}$	117,3(2)	$Cl_{(2)}—C_{(10)}—C_{(11)}$	121,6(2)
$C_{(9)}—C_{(10)}—C_{(11)}$	121,1(1)	$C_{(10)}—C_{(11)}—C_{(12)}$	120,9(3)
$Cl_{(3)}—C_{(11)}—C_{(10)}$	121,7(1)	$Cl_{(3)}—C_{(11)}—C_{(12)}$	117,4(1)
$N_{(4)}—C_{(12)}—N_{(6)}$	125,6(1)	$N_{(4)}—C_{(12)}—C_{(11)}$	117,7(3)
$N_{(5)}—C_{(13)}—C_{(9)}$	178,9(2)	$N_{(6)}—C_{(12)}—C_{(11)}$	116,7(2)

TABLE 3. Populations of π-Orbitals and Charges on Atoms in the Betaine II Molecule

Atom	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	$C_{(5)}$	$C_{(6)}$
Population of π-orbital	0,7870	1,2034	0,8948	1,2913	0,8073
Charges on atoms	0,3538	-0,0257	0,3037	-0,2729	0,4278
Atom	$C_{(9)}$	$N_{(1)}$	$N_{(7)}$	$N_{(8)}$	$N_{(10)}$
Population of π-orbital	0,8821	1,4343	1,6258	1,0551	1,1563
Charges on atoms	0,1647	-0,3549	-0,3345	0,3088	-0,1737



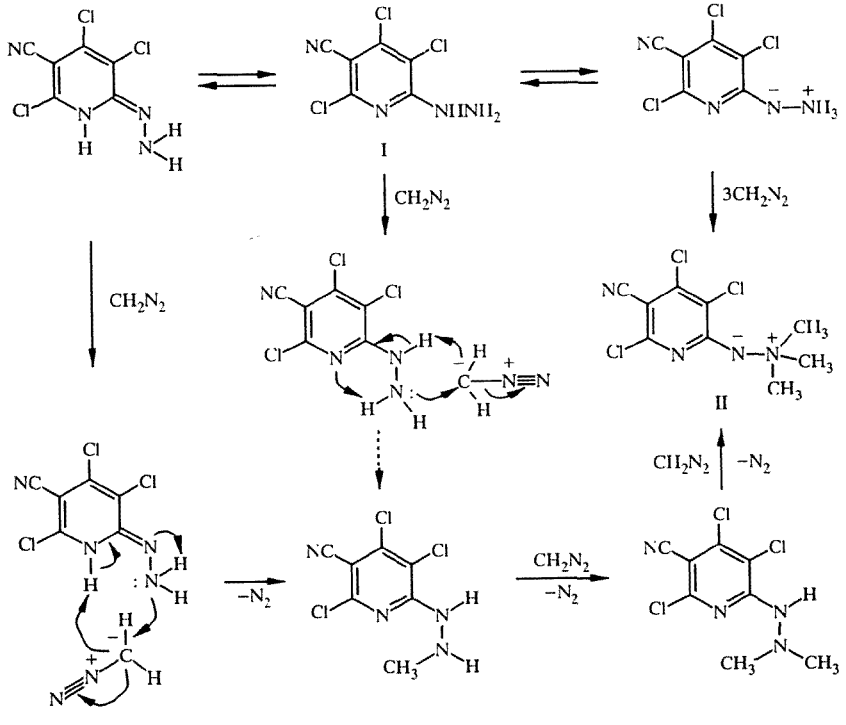
Using the CNDO/3 method, we calculated the electronic structure of the betaine system II. In Table 3, we present the magnitudes of the charges on the atoms and the population of the π orbitals; and in Fig. 2, we present the electron density distribution diagram in molecule II.

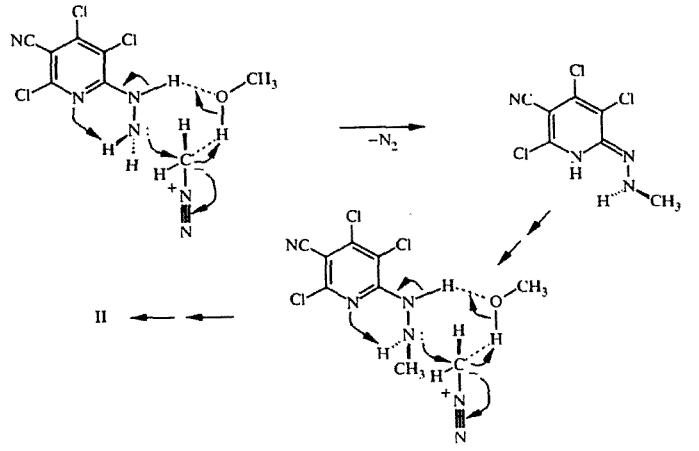
TABLE 4. Coordinates of Atoms ($\times 10^4$) and Isotropic Thermal Vibration Coefficients for Betaine II Molecule

Atom	x	y	z	B_{iso}
$Cl_{(1)}$	5182(1)	2500	3979(3)	3,99
$Cl_{(2)}$	-0653(1)	2500	4922(1)	3,62
$Cl_{(3)}$	1151(1)	2500	8197(3)	4,24
$N_{(4)}$	4813(3)	2500	6492(3)	2,90
$N_{(5)}$	0902(3)	2500	1851(3)	4,16
$N_{(6)}$	4629(3)	2500	8871(3)	3,13
$N_{(7)}$	6417(5)	2500	9388(5)	3,06
$C_{(8)}$	4007(5)	2500	5141(6)	3,15
$C_{(9)}$	2318(5)	2500	4537(3)	3,32
$C_{(10)}$	1434(5)	2500	5565(3)	2,93
$C_{(11)}$	2197(5)	2500	6948(3)	3,25
$C_{(12)}$	3975(5)	2500	7478(3)	2,93
$C_{(13)}$	1544(5)	2500	3042(5)	3,30
$C_{(14)}$	6767(6)	2500	10969(7)	3,85
$C_{(15)}$	7132(7)	4235(5)	8962(8)	4,17

As we see from Table 3 and Fig. 2, the negative charge on the betaine molecule II is delocalized over the $N_{(1)}$, $N_{(7)}$, $N_{(10)}$, and also $C_{(5)}$ atoms. Such delocalization of the negative charge probably is responsible for the stability of betaine II, the formation of which can be represented according to the alternative scheme presented below.

We noted that addition of CH_3OH to the reaction mixture of diazomethane with 2-hydrazino-3,4,6-trichloro-5-cyanopyridine (I) significantly accelerates the process of permethylation, which probably can be explained by the occurrence of a reaction between the energetically more favorable six-membered transition state, including a methanol molecule, with formation of a trimolecular complex.





EXPERIMENTAL

The IR spectra were taken on the Specord M-80. The UV spectra were taken on the Beckman DU-7. The ^{13}C NMR spectra were recorded on the Bruker AC-200 spectrometer (50.32 MHz), internal standard TMS. The mass spectral measurements were made on the Kratos MS-25 (direct injection, ionization energy 70 eV). The course of the reaction and the purity of the material were monitored by TLC on Silufol UV-254 plates in the 1:6 benzene–ethylacetate system.

The elemental analysis data for C, H, and N correspond to the calculated values.

X-Ray Diffraction Analysis of Compound II. Crystals of II belong to monoclinic syngony with the following crystallographic parameters: a = 8.643(1), b = 7.326(1), c = 9.844(1) Å, β = 107.32(1)°, V = 595.1 Å^3, M = 279.5, d_{calc} = 1.56 g/cm^3, Z = 2, space group $P2_1/m$. The intensities of 831 independent reflections were measured on the Syntex-$P2_1$ automatic diffractometer by the $\theta-2\theta$ scanning method; CuKα radiation, graphite monochromator. In the calculations we used 801 reflections with $I > 2\sigma(I)$. The structure was determined and refined in the full-matrix anisotropic approximation to R = 0.049 using the XTLSM program package [7].

The coordinates of the atoms with the isotropic thermal vibration coefficients are presented in Table 4.

2-Hydrazino-3,4,6-trichloro-cyanopyridine (I) was obtained according to the technique in [1].

1-Trimethyl-2-(3,4,6-trichloro-5-cyanopyrid-2-yl)hydrazin-1-io-2-ide (II, $C_9H_9Cl_3N_4$). 200 ml of an ether solution of diazomethane (5-fold excess) was added to a solution of 1.19 g (5 mmoles) compound I in 130 ml methanol with stirring. The reaction mixture was held for 48 h at 20°C. The solution was evaporated under vacuum down to 1/2 volume; the precipitate was filtered off and washed with cold methanol (2 × 30 ml). 0.43 g (31%) compound II was obtained [yellow rhombic crystals, R_f 0.43 (1:6 benzene–ethylacetate), T_{mp} 249-251°C (decomp.)]. IR spectrum (KBr): 2962 (CH_3); 2212 (C≡N); 1580, 1570-1559, 1492 (C=N, C=C); 1456, 1436, 1404 cm^{-1} (CH_3). UV spectrum (CH_3CN), λ_{max} (log ε): 304.5 (4.44); 330.5 nm (3.87 shoulder). ^{13}C NMR spectrum (DMSO-d_6): 54.88 (s, $(CH_3)_3$); 99.02 (s, $C_{(5)}$); 111.77 (s, CN); 115.51 (s, $C_{(3)}$); 137.55 (s, $C_{(4)}$); 148.63 (s, $C_{(6)}$); 156.80 ppm (s, $C_{(2)}$). Mass spectrum, m/z: M^+ 278 (100).

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