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Reaction of 2,2,3,3-Tetracyanocyclopropyl Ketones with Sodium and Potassium Hydroxides

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Abstract—Reaction of 2,2,3,3-tetracyanocyclopropyl ketones with water solution of sodium hydroxide after neutralization with sulfuric acid leads to the formation of 4-amino-1-hydroxy-3,6-dioxo-2,3,5,6-tetrahydro-1*H*-pyrrolo[3,4-*c*]pyridine-7-carbonitriles. Pivaloyltetracyanocyclopropane reacts in another way and is converted into sodium 6a-*tert*-butyl-3,4-dicyano-5-oxo-1,5,6,6a-tetrahydropyrrolo[2,3-*b*]pyrrol-2-olate. 1-Benzoyl-1-methylcyclopropane-2,2,3,3-tetracarbonitrile reacts with the sodium hydroxide with the retention of the three-membered ring and the formation of 11-methyl-4-phenyl-3,5,9-triazatetracyclo[5.3.1.$0^{1,7}$.$0^{4,11}$]undecane-2,6,8,10-tetraone.

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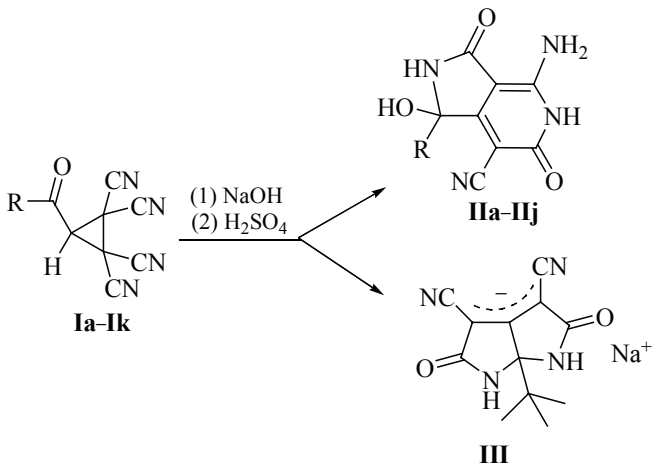
Pyrrolo[3,4-*c*]pyridines attract attention as potential drugs. For instance, substances were found among them that were ligands of serotonin 5-HT_3 receptor [1], caspase inhibitors 3 [2], and anthelminthics [3]. 1-Hydroxy-3-oxo-1-pyridylpyrrolo[3,4-*c*]pyridine fragment is a structural unit of the adduct INH-NAD that forms in vivo from the prodrug isoniazid and NAD, and it inhibits the growth of the infectious agent of tuberculosis [4–8]. Synthetic analogs of INH-NAD containing the pyrrolo[3,4-*c*] pyridine system are tested as potential antitubercular drugs [4–7]. The known synthetic approaches to the synthesis of these compounds proceed from pyridine derivatives and include several stages [4, 6]. We have developed a preparation method of the pyrrolo[3,4-*c*]-pyridine derivatives underlain by a one-step reaction of available tetracyanocyclopropyl ketones with sodium hydroxide [9]. In this paper we report on further research on this reaction.

The reaction of tetracyanocyclopropyl ketones **Ia–Ik** substituted with aromatic, heterocyclic, and aliphatic moieties with the sodium hydroxide after neutralization with sulfuric acid results in substituted 4-amino-1-hydroxy-3,6-dioxo-2,3,5,6-tetrahydro-1*H*-pyrrolo[3,4-*c*]pyridine-7-carbonitriles **IIa–IIj** in 56–77% yields (Scheme 1). The reaction of the sodium hydroxide with cyclopropyl ketone **Ik** proceeds differently. Like in the case of compounds **Ia–Ij** the reaction initially occurred with the ring opening, but the subsequent cyclization gave rise to sodium 6*a*-*tert*-butyl-3,4-dicyano-5-oxo-1,5,6,6*a*-tetrahydropyrrolo[2,3-*b*]pyrrol-2-olate (**III**) that was isolated from the reaction mixture in 92% yield. We failed to obtain the conjugate acid of salt **III** anion since the salt remained practically intact at boiling in H_2SO_4 solutions up to 15% concentration, and in more concentrated solution it suffered slow decomposition with tarring.

The structure of compounds **IIa–IIj** was confirmed by spectral methods. In the ^{1}H NMR spectra the hydroxyl proton appears as a singlet in the region 6.50–7.48 ppm, amino group, as a broadened singlet in the range 7.1–7.6 ppm. The proton of NH group of the pyrrole ring resonates in the region 8.50–9.05 ppm, and NH of the pyridine (pyridone) ring gives rise to a broadened singlet at 11.41–11.49 ppm. The signals of the aromatic substituents appear with their characteristic multiplicity in the range of common values. The structure of pyrrolo-

Scheme 1.



R = Ph (**a**), 4-$MeOC_6H_4$ (**b**), 3-$NO_2C_6H_4$ (**c**), 4-BrC_6H_4 (**d**), 3,4-$(MeO)_2C_6H_3$ (**e**), thien-2-yl (**f**), Me (**g**), naphth-1-yl (**h**), 4-ClC_6H_4 (**i**), 2,4-$Cl_2C_6H_4$ (**j**), $(CH_3)_3C$ (**k**).

pyridines **IId, IIg** is confirmed by the ^{13}C NMR findings whose assignment is given in the table and is consistent with the data for similar compounds [6]. The structure of pyrrolopyridine **IIg** was proved by the data of 2D spectra NOESY and HMBC.

The correlations observed in the HMBC spectrum correspond to the coupling between the carbon atoms and protons of the pyrrole ring and its substituents (Fig. 1). The signals of the protons of the hydroxy group (6.47 ppm) have three cross-peaks: with the carbon atom of the methyl group (24.52 ppm) and atoms C^1 and C^{7a} of the pyrrole ring (92.39 and 151.34 ppm). The proton signals of the methyl group (1.59 ppm) have two cross-peaks, with C^1 and C^{7a}. The proton attached to the nitrogen of the pyrrole ring (8.87 ppm) has cross-peaks with all carbon atoms of the pyrrole ring: C^{7a} (151.34 ppm), C^{3a} (84.51 ppm), C^3 (165.86 ppm), and C^1 (92.39 ppm). The correlation peaks of the amino group signals (7.27 ppm) and NH of pyridone (11.35 ppm) are not observed likely due to the broadening of the signals of these groups.

In the NOESY spectrum the correlations were observed corresponding to the coupling between the protons of the methyl group (1.59 ppm), hydroxy group (6.47 ppm), and NH of the pyrrole (8.48 ppm) (Fig. 2). The proton signal of the amino group (7.27 ppm) correlates with the proton signal of the NH of pyridone (11.35 ppm). Besides the signals of the hydroxy group protons (1.59 ppm) have two cross-peaks: with the proton signals of the amino group (7.27 ppm) and with NH of pyridone (11.35 ppm).

The spectral data did not permit the unambiguous assignment of the positions of the amino and oxo groups in the pyridine ring, therefore the structure was subjected to the XRD. Since the obtained crystals of compounds **II** were unsuitable for XRD study we prepared to this end the potassium salt of compound **IIa**. Potassium salts of this kind anions as a rule are less soluble in water and give better crystals than sodium salts. Potassium 4-amino-7-cyano-1-hydroxy-6-oxo-1-phenyl-2,6-dihydro-1*H*-pyrrolo[3,4-*c*]pyridin-3-olate (**V**) was prepared in two ways: by neutralization of pyrrolopyridine **IIa** with potassium carbonate in water and by the direct reaction of tetracyanocyclopropyl ketone **Ia** with potassium hydroxide (Scheme 2). In the latter case we observed that first precipitated potassium 2-benzoyl-1,1,3,3-tetracyanopropenide (**IV**), which subsequently slowly dissolved with the formation of salt **V**. The structure of salt **V** established by XRD analysis confirms the assumed structure of compounds **IIa–IIj**. Potassium cation (Fig. 3) coordinates three anions through the oxygen atoms of the

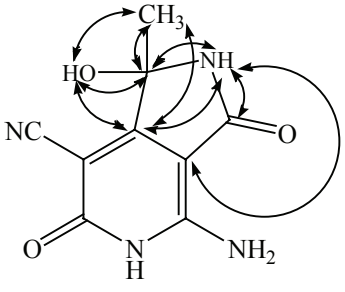


Fig. 1. Spin-spin coupling between the protons of substituents at the pyrrole ring with carbon atoms according to the ^1H-^{13}C HMCC NMR spectrum of compouns **IIg**.

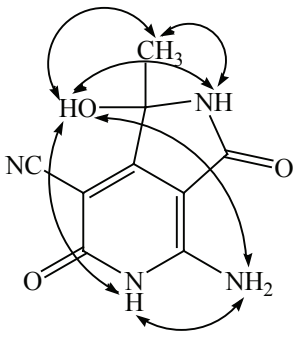
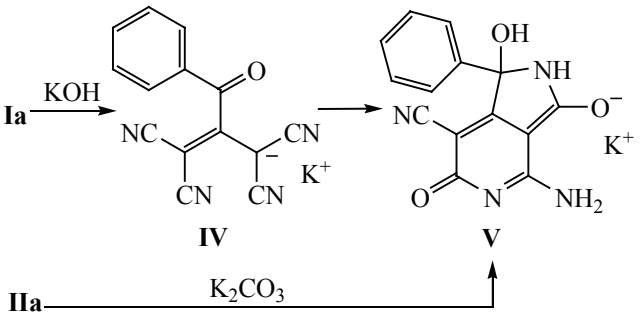


Fig. 2. Correlation of protons according to NOESY spectrum of compound **IIg**.

Scheme 2.



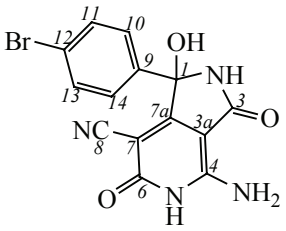
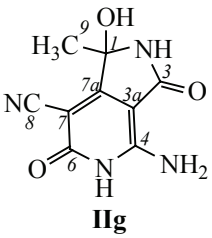
hydroxy and carbonyl groups of the pyrrol fragment and also through the nitrogen atom of the nitrile function. Besides in the coordination sphere of potassium cation four water molecules are present.

The structure of compound **III** was assumed basing on the data of IR and ^{1}H, ^{13}C NMR spectra. The ^{1}H NMR spectrum contains two signals: a singlet at 0.92 ppm corresponding to *tert*-butyl substituent, and a slightly broadened signal at 7.20 ppm, which we assigned to two NH protons. The ^{13}C NMR spectrum also shows the symmetry of the molecule.

We presume that the transformations of tetracyanocyclopropyl ketones **I** under the action of the hydroxide ion proceed along Scheme 3.

In the first stage in the course of acid-base reaction a tetracyanocyclopropyl cation **A** is generated, which suffers an electrocyclic opening giving the corresponding tetracyanopropenide **B.** This assumption is confirmed by the possibility to isolate this intermediate in the reaction with potassium hydroxide. The arising propenide contains two types of electrophilic centers: four cyano groups conjugated with the propenide skeleton, and a carbonyl group cross-conjugated with them. We presume

^{13}C NMR data of compounds **IId, IIg**, δ, ppm

	 **IId**	 **IIg**
C^1	92.08	92.39
C^3	166.66	165.86
C^{3a}	86.16	84.51
C^4	162.10	162.11
C^6	168.04	168.60
C^7	79.86	79.19
C^{7a}	151.37	151.34
C^8	114.68	115.64
C^9	138.77	24.52
C^{10}, C^{14}	128.50	–
C^{11}, C^{13}	130.98	–
C^{12}	121.64	–

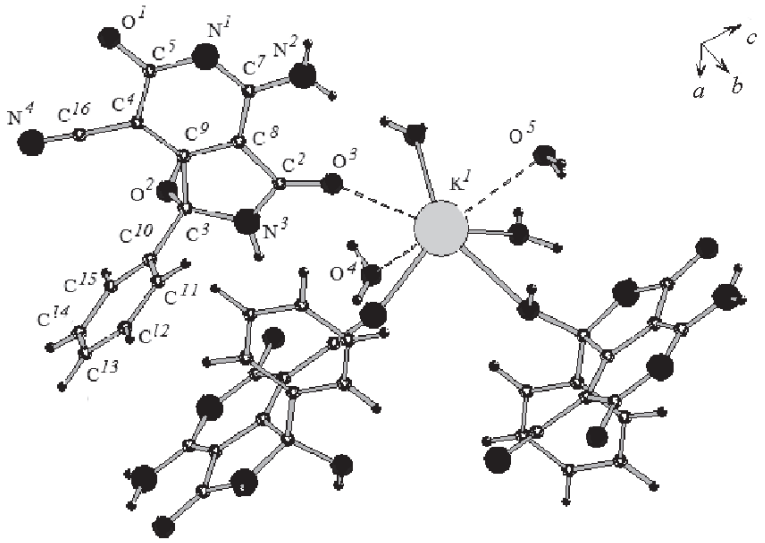
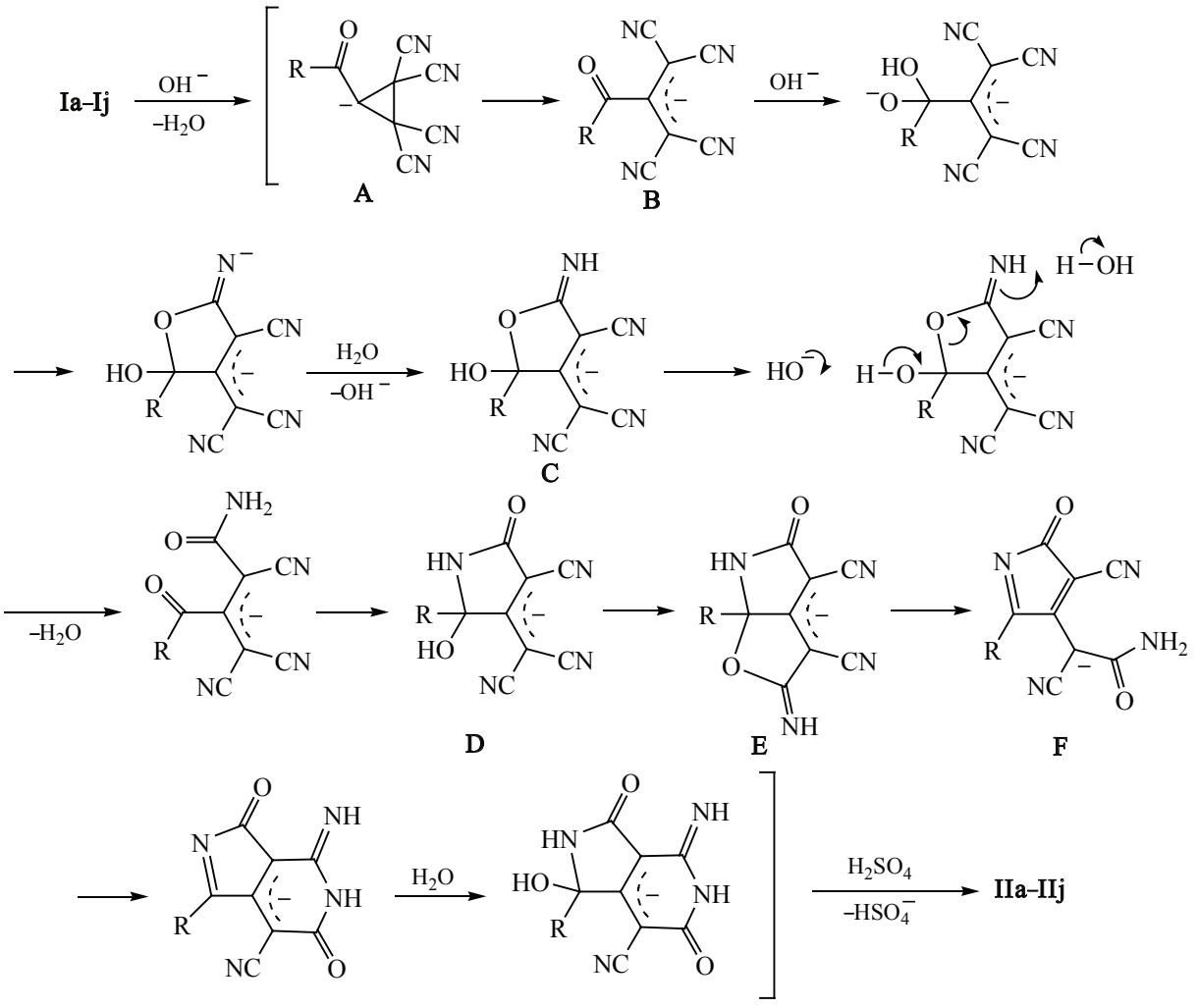


Fig. 3. Molecular structure and a fragment of crystal lattice of potassium 4-amino-7-cyano-1-hydroxy-3-oxo-1-phenyl-2,6-dihydro-1*H*-pyrrolo[3,4-*c*]pyridin-3-olate (**V**) according to XRD analysis.

that the reaction follows by adding a hydroxide ion to the carbonyl group with the subsequent closure of a furan ring and the formation of intermediate **C**. Intermediate **C** contains a furanimine fragment that due to the presence of heteroatom with a mobile hydrogen in the geminal position to the oxygen atom is capable to undergo the iminolactone-lactam rearrangement with the formation of pyrrole intermediate **D**. This type rearrangement was formerly observed in several cases [10–13]. In the formed pyrrole intermediate **D** because of the spatial proximity of a hydroxyl and a cyano group of the dicyanomethylidene fragment a heterocyclization is probable with the formation of furopyrrol intermediate **E.** In this intermediate the oxygen atom also has a geminal NH group, therefore the opening of the furan ring becomes possible. The forming in this process intermediate **F** undergoes the cyclization giving a pyridine ring. The neutralization of the reaction mixture leads to the formation of final products **II**. The alternative mechanism involving the primary attack of the hydroxide ion on the cyano groups cannot explain the reaction regioselectivity and disagrees with the results of the analogous reaction of 2-aroyltetracyanopropenides with alcoholate and oximate ions which due to the impossibility of the iminolactone-lactam rearrangement stops at the stage of the formation of dihydrofurans corresponding to intermediate **C** [14].

The abnormal result of the reaction between the hydroxide ion and cyclopropyl ketone **Ik** may be ascribed to the steric effect of the *tert*-butyl group. It is reasonable to assume that the initial course of the reaction is the same as with the other tetracyanocyclopropyl ketones till the formation of intermediate **F** [R = $(CH_3)_3C$] (Scheme 4). In intermediate **F** two heterocyclization possibilities exist involving the carboxamide group: the cyclization with

Scheme 3.

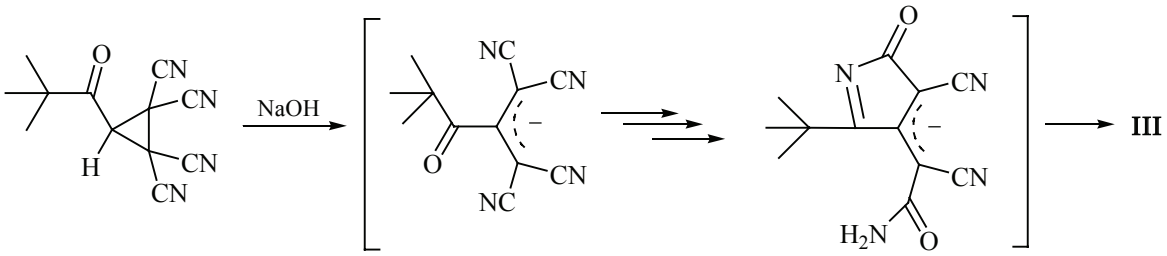


the participation of a cyano group with the formation of the pyrrolopyridine system realized in the case of the most cyclopropyl ketones, and the second way leading to a pyrrolpyrrole system. The formation of the pyridine ring should occur in the conformation where the cyano group should be in the same plane as the hydrocarbon substituent, and this position creates steric hindrances in the case of a bulky substituent like the *tert*-butyl group. In the pyrrolpyrrole derivative the steric hindrances insignificantly differ from those in intermediate **E**, for the place of the oxygen atom at the sp^3-hybridized carbon is occupied by the NH moiety of the pyrrol ring.

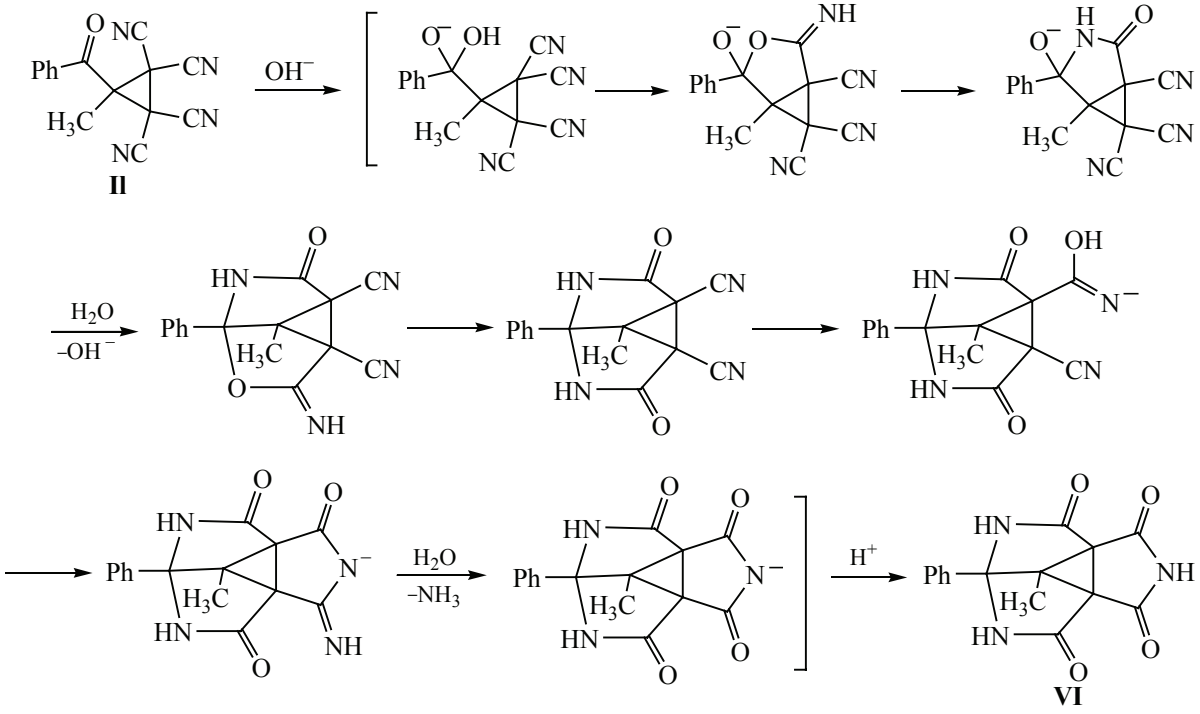
Since the first stage in the reactions of cyclopropanes **Ia–Ik** with the solution of sodium hydroxide is the proton abstraction with the subsequent ring opening, it is expectable that the replacement of the hydrogen by a methyl group should result in another course of the reaction. Actually, in the reaction of 3-benzoyl-3-methylcyclopropane-1,1,2,2-tetracarbonitrile (**II**) with water solution of sodium hydroxide the three-membered ring is conserved, and transformations occur at the functional groups. After the acidifying of the reaction mixture with 5% solution of sulfuric acid we isolated in 74% yield 11-methyl-4-phenyl-3,5,9-triazatetracyclo-[5.3.1.$0^{1,7}$.$0^{4,11}$]undecane-2,6,8,10-tetraone (**VI**) (Scheme 5).

The structure of tetracycle **VI** was established by XRD analysis. The molecular structure and a fragment of crystal packing are shown on Fig. 4. All hydrogen atoms bound to atoms N^1, N^2, N^3take part in hydrogen bonds N^1–$H^1\cdots O^{1i}$, N^2–$H^2\cdots O^{1iii}$, N^3–$H^3\cdots O^{2ii}$. As a result the molecules form chains directed along the crystallographic axis *c*. Among the features of the molecular structure the

Scheme 4.



Scheme 5.



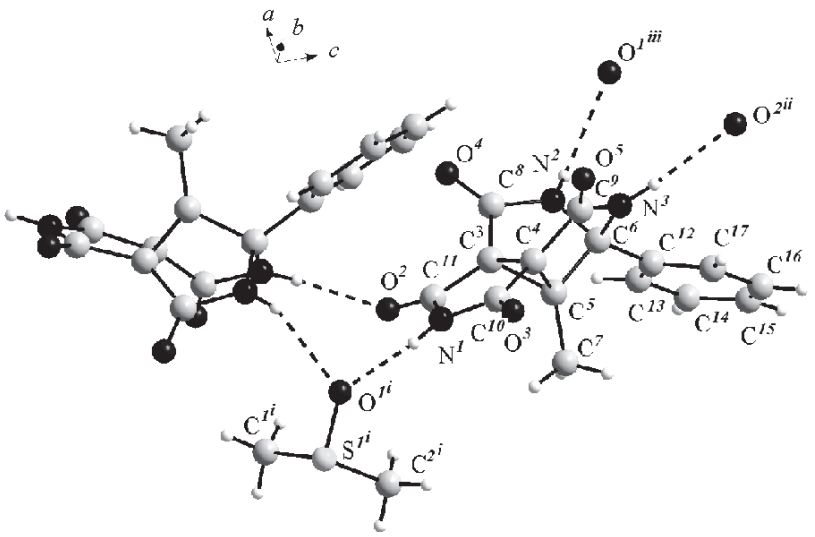


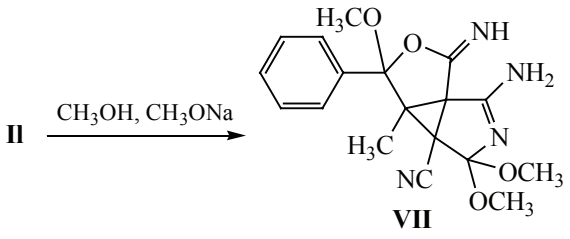
Fig. 4. Molecular structure and a fragment of the crystal lattice of the complex of 11-methyl-4-phenyl-3,5,9-triazatetracyclo[5.3.1.$0^{1,7}$.$0^{4,11}$]-undecane-2,6,8,10-tetraone (**VI**) with dimethyl sulfoxide according to XRD data. The atoms numeration obeys the rules common for XRD analysis.

form of the three-membered ring like isosceles triangle should be mentioned: the bonds C^4–C^5 (1.501 Å) and C^3–C^5 [1.504(3) Å] are shorter than the bond C^3–C^4 [1.553(3) Å]. The C^{11}–O^2 bond of the carbonyl group whose oxygen is involved in the hydrogen bond formation is somewhat extended compared with the other carbonyl groups. The other bond lengths and bond angles are of usual values and do not require a detailed description.

The reactions of alkyltetracyanocyclopropanes with sodium hydroxide are known where all cyano groups are involved resulting in (1*S**,5*S**)-5-carbamoyl-2,4-dioxo-3-azabicyclo[3.1.0]hexane-1-carboxylic acids [15, 16]. An essential distinction of cyclopropane **II** is the presence of a carbonyl group taking part in the reaction. Therewith it is most probable that the transformations start with the addition of a hydroxide ion to the carbonyl group with subsequent cyclization-recyclization processes involving the spatially close cyano groups. The formed intermediate furanimine derivatives undergo recyclization into pyrrole structures, and it occurs twice involving both cyano groups located in the cis-position with respect to the carbonyl. Similar processes were observed in the reaction of cyclopropane **II** with water [17]. The reaction of the trans-cyano groups with the hydroxide ion probably occurs independently and results in the formation of a pyrrole ring. On the whole the reaction results in the formation of a polyheterocyclic structure containing a three-membered carbocycle fused with pyrrole rings. No compounds with this heterocyclic system were described before. The formation of tetracycle **VI** may be described by an alternative scheme where the transformations involving the carbonyl group start with the addition of the hydroxide ion to cyano groups. In order to prove that the reaction proceeded through the furan ring formation we investigated the reaction of cyclopropane **II** with methanol in the presence of sodium methylate.

It was established using the data of mass, ^{1}H NMR, and IR spectra that in this reaction formed 6-amino-1-imino-3,4,4-trimethoxy-3*a*-methyl-3-phenyl-3,3*a*,3*b*,4-tetrahydro-1*H*-furo[3',4':1,3]cyclo-propa[1,2-*c*]pyrrol-3*b*-carbonitrile (**VII**) (Scheme 6). The involvement of the carbonyl group in this process is confirmed by the upfild shift of the *ortho*-proton signals of the phenyl substituent [8.02 ppm (**II**), 7.48 ppm (**VII**)]. The presence of an imine fragment was confirmed by the presence in the IR spectrum of a narrow band at 3382 cm^{-1} and a singlet at 8.33 ppm in the ^{1}H NMR spectrum. The addition of methanol to cyano groups located in the trans-position

Scheme 6.



VII

with respect to benzoyl leads to the formation of the pyrrole ring. On the other hand, the methanol attack is directed on the carbonyl group and results in the formation of iminolactone fragment which does not rearrange into the lactam due to the lack of proton-generating substituent in the β-position to the oxygen atom of the furan ring.

EXPERIMENTAL

Monitoring the reaction progress and checking the purity of compounds was carried out by TLC on Silufol UV-254 plated (spots visualizing by UV irradiation, iodine vapor, or thermal degradation). IR spectra were taken from thin films (mulls in mineral oil) on a Fourier spectrophotometer FSM-1202. ^{1}H and ^{13}C NMR spectra were registered on a spectrometer Bruker DRX-500 at operating frequencies 500.13 and 125 MHz from solutions in DMSO-d_6, internal reference TMS. Mass spectra were measured on an instrument Finnigan MAT INCOS 50 (EI, energy of ionizing electrons 70 eV). Elemental analysis was performed on an instrument Laboratorni Přistroje, Praha. The X-ray diffraction study of single crystals **V, VI** was carried out on a four-circle automatic diffractometer CAD-4 Enraf Nonius, CuK_α-radiation, graphite monochromator, ω-scanning. The structures were solved by the direct method using SHELXS-97 software.The refining of positions and thermal parameters of nonhydrogen atoms was performed in full-matrix anisotropic approximation. The positions of hydrogen atoms were found from the difference Fourier syntheses and freely refined in the isotropic approximation for compound **V**. The positions of hydrogen atoms in structure **VI** were calculated and refined in the rider model.

The crystallographic data are deposited in the Cambridge Crystallographic Data Center [CCDC no. 851386 (**V**), 851385 (**VI**)] and can be obtained free by e-mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk.

4-Amino-1-hydroxy-3,6-dioxo-1-phenyl-2,3,5,6-tetrahydro-1*H*-pyrrolo[3,4-*c*]pyridine-7-carbonitrile (IIa). *a*. In 15 ml of 7% NaOH solution was dissolved at stirring 2.46 g (0.01 mol) of 2,2,3,3-tetracyanocyclopropyl ketone **Ia**, and the mixture was left standing for 24 h. Then the reaction mixture was neutralized with 10% solution of H_2SO_4, the separated precipitate was filtered off and washed with water. Yield 1.89 g (67%), mp 145–147°C (decomp.) {145–147°C (decomp.) [9]}.

b. 0.27 g (0.001 mol) of sodium 1,1,3,3-tetracyano-2-benzoylpropenide was dissolved at stirring in 3 ml of 7% NaOH solution and left standing for 24 h. Then the reaction mixture was neutralized with 10% solution of H_2SO_4, the separated precipitate was filtered off and washed with water. Yield 0.26 g (87%), mp 145–147°C (decomp.).

Compounds **IIb–IIj** were obtained similarly by procedure *a*. **4-Amino-1-hydroxy-1-(4-methoxyphenyl)-3,6-dioxo-2,3,5,6-tetrahydro-1*H*-pyrrolo[3,4-*c*]pyridine-7-carbonitrile (IIb).** Yield 73%, mp 142–144°C (decomp.) {142–144°C (decomp.) [9]}.

4-Amino-1-hydroxy-1-(3-nitrophenyl)-3,6-dioxo-2,3,5,6-tetrahydro-1*H*-pyrrolo[3,4-*c*]pyridine-7-carbonitrile (IIc). Yield 70%, mp 183–184°C (decomp.) {mp 183–184°C (decomp.) [9]}.

4-Amino-1-(4'-bromophenyl)-1-hydroxy-3,6-dioxo-2,3,5,6-tetrahydro-1*H*-pyrrolo[3,4-*c*]pyridine-7-carbonitrile (IId). Yield 70%, mp 136–140°C (decomp.). IR spectrum, ν, cm^{-1}: 3285, 3232 (NH_2), 2219 (C≡N), 1716, 1698 (C=O). ^{1}H NMR spectrum, δ, ppm: 7.10–7.60 br.s (2H, NH_2), 7.33 s (1H, OH), 7.40 d (2H$_{arom}$, *J* 8.5 Hz), 7.51 d (2H$_{arom}$, *J* 8.5 Hz), 8.90 s (1H, NH), 11.41 s (1H, NH). Mass spectrum, *m/z* (I_{rel}, %): 362 (1), 360 (1) $[M]^+$, 344 (8), 342 (8) $[M - 18]^+$, 187 (5), 161 (31), 157 (7), 155 (7) $[C_6H_4Br]^+$, 133 (100). Found, %: C 46.61; H 2.53; N 15.43. $C_{14}H_9BrN_4O_3$. Calculated, %: C 46.56; H 2.51; N 15.51. *M* 359.99.

4-Amino-1-(3',4'-dimethoxyphenyl)-1-hydroxy-3,6-dioxo-2,3,5,6-tetrahydro-1*H*-pyrrolo[3,4-*c*]pyridine-7-carbonitrile (IIe). Yield 69%, mp 132–134°C (decomp.). IR spectrum, ν, cm^{-1}: 3275, 3221 (NH_2), 2220 (C≡N), 1714, 1687 (C=O). ^{1}H NMR spectrum, δ, ppm: 3.745 s (3H, CH_3), 3.75 s (3H, CH_3), 6.86 d.d (1H$_{arom}$, ^3J 8.4, ^4J 2.0 Hz), 6.92 d (1H$_{arom}$, ^3J 8.5 Hz), 7.19 s (1H, OH), 7.23 d (1H$_{arom}$, ^4J 2.1 Hz), 7.38 br.s (2H, NH_2), 8.83 s (1H, NH), 11.41 s (1H, NH). Found, %: C 56.15; H 4.14; N 16.33. $C_{16}H_{14}N_4O_5$. Calculated, %: C 56.14; H 4.12; N 16.37.

4-Amino-1-hydroxy-3,6-dioxo-1-(thien-2-yl)-2,3,5,6-tetrahydro-1*H*-pyrrolo[3,4-*c*]pyridine-7-carbonitrile (IIf). Yield 70%, mp 165–166°C (decomp.). IR spectrum, ν, cm^{-1}: 3289, 3218 (NH_2), 2226 (C≡N), 1718, 1696 (C=O). ^{1}H NMR spectrum, δ, ppm: 7.01 d.d (1H, C_4H_3S, ^3J 5.0, ^3J 3.6 Hz), 7.10 d.d (1H, C_4H_3S, ^3J 3.6, ^4J 1.2 Hz), 7.35 br.s (2H, NH_2), 7.43 s (1H, OH), 7.50 d.d (1H, C_4H_3S, ^3J 5.0, ^4J 1.4 Hz), 9.05 s (1H, NH), 11.41 s (1H, NH). Found, %: C 50.05; H 2.86; N 19.39. $C_{12}H_8N_4O_3S$. Calculated, %: C 50.00; H 2.80; N 19.43.

4-Amino-1-hydroxy-1-methyl-3,6-dioxo-2,3,5,6-

tetrahydro-1*H*-pyrrolo[3,4-*c*]pyridine-7-carbonitrile (IIg). Yield 69%, mp 132–134°C (decomp.). IR spectrum, ν, cm^{-1}: 3271, 3212 (NH_2), 2224 (C≡N), 1707, 1689 (C=O). ^{1}H NMR spectrum, δ, ppm: 1.60 s (3H, CH_3), 6.50 s (1H, OH), 7.34 br.s (2H, NH_2), 8.51 s (1H, NH), 11.42 s (1H, NH). Mass spectrum, *m/z* (I_{rel}, %): 205 (5) [*M* – 15]$^+$, 202 (24) [*M* – 18]$^+$, 187 (3). Found, %: C 49.17; H 3.72; N 25.43. $C_9H_8N_4O_3$. Calculated, %: C 49.09; H 3.66; N 25.45. *M* 220.18.

4-Amino-1-hydroxy-1-(naphth-1-yl)-3,6-dioxo-2,3,5,6-tetrahydro-1*H*-pyrrolo[3,4-*c*]pyridine-7-carbonitrile (IIh). Yield 61%, mp 121–125°C (decomp.). IR spectrum, ν, cm^{-1}: 3282, 3224 (NH_2), 2230 (C≡N), 1705, 1690 (C=O). ^{1}H NMR spectrum, δ, ppm: 7.25–7.75 br.s (2H, NH_2), 7.32 s (1H, OH), 7.42–7.55 m ($5H_{arom}$), 7.94–7.98 m ($2H_{arom}$), 9.01 s (1H, NH), 11.49 s (1H, NH). Mass spectrum, *m/z* (I_{rel}, %): 314 (12) [*M* – 18]$^+$, 127 (6), 126 (6). Found, %: C 65.27; H 3.62; N 16.43. $C_{18}H_{12}N_4O_3$. Calculated, %: C 65.06; H 3.64; N 16.86. *M* 332.09.

4-Amino-1-hydroxy-1-(4-chlorophenyl)-3,6-dioxo-2,3,5,6-tetrahydro-1*H*-pyrrolo[3,4-*c*]pyridine-7-carbonitrile (IIi). Yield 77%, mp 146–148°C (decomp.). IR spectrum, ν, cm^{-1}: 3285, 3230 (NH_2), 2225 (C≡N), 1709, 1685 (C=O). ^{1}H NMR spectrum, δ, ppm: 7.10–7.60 br.s (2H, NH_2), 7.33 (1H, OH), 7.42–7.48 m (*AA′BB′* system, $4H_{arom}$), 8.90 s (1H, NH), 11.41 s (1H, NH). Mass spectrum, *m/z* (I_{rel}, %): 300 (3), 298 (10) [*M* – 18]$^+$, 187 (7), 161 (38), 133 (100). Found, %: C 52.87; H 2.92; N 17.43. $C_{14}H_9ClN_4O_3$. Calculated, %: C 53.09; H 2.86; N 17.69. *M* 316.04.

4-Amino-1-hydroxy-1-(2,4-dichlorophenyl)-3,6-dioxo-2,3,5,6-tetrahydro-1*H*-pyrrolo[3,4-*c*]pyridine-7-carbonitrile (IIj). Yield 56%, mp 137–141°C (decomp.). IR spectrum, ν, cm^{-1}: 3272, 3222 (NH_2), 2225 (C≡N), 1711, 1670 (C=O). ^{1}H NMR spectrum, δ, ppm: 7.10–7.60 br.s (2H, NH_2), 7.48 s (1H, OH), 7.52 d.d ($1H_{arom}$, ^3J 8.6, ^4J 2.0 Hz), 7.56 d ($1H_{arom}$, ^4J 2.0 Hz), 8.11 d ($1H_{arom}$, ^3J 8.6 Hz), 8.78 s (1H, NH), 11.42 s (1H, NH). Mass spectrum, *m/z* (I_{rel}, %): 334 (0.3), 332 (1) [*M* – 18]$^+$, 161 (29), 133 (69). Found, %: C 47.77; H 2. 32; N 15.73. $C_{14}H_8Cl_2N_4O_3$. Calculated, %: C 47.89; H 2.30; N 15.96. *M* 350.00.

Sodium 6*a*-*tert*-butyl-3,4-dicyano-5-oxo-1,5,6,6a-tetrahydropyrrolo[2,3-*b*]pyrrol-2-olate (III). *a*. A mixture of 2.26 g (0.01 mol) of cyclopropane **Ik** with 15 ml of 5% solution of sodium hydroxide was stirred for 10 min; therewith the reagent first completely dissolved and later a precipitate formed. The separated precipitate was filtered off, washed with 5% solution of H_2SO_4 and with water. Yield 2.45 g (92%), mp 164–165°C (decomp.). IR spectrum, ν, cm^{-1}: 3358 (NH), 2209 (C≡N), 1673 (C=O). ^{1}H NMR spectrum, δ, ppm: 0.91 s [9H, $C(CH_3)_3$], 7.20 s (2H, NH). ^{13}C NMR spectrum, δ, ppm: 24.66 [$C(\underline{C}H_3)_3$], 41.73 [$\underline{C}(CH_3)_3$], 72.40 (C^{6a}), 83.96 ($C^{3,4}$), 117.75 (CN), 174.13 ($C^{2,5}$), 176.13 (C^{3a}). Found, %: C 54.05; H 4.35; N 20.98. $C_{12}H_{11}N_4NaO_2$. Calculated, %: C 54.14; H 4.16; N 21.04.

b. The compound was obtained analogously from 2-pivaloyl-1,1,3,3-tetracyanopropenide. Yield 2.50 g (94%).

Potassium 2-benzoyl-1,1,3,3-tetracyanopropenide (IV). A mixture of 0.25 g (0.001 mol) of cyclopropane **Ia** and 0.06 g (0.001 mol) of potassium hydroxide in 3 ml of water was stirred for 10 min; therewith the reagent first completely dissolved and later a precipitate formed. The separated precipitate was filtered off, and washed with water. Yield 0.18 g (64%), mp 230–231°C (decomp.). IR spectrum, ν, cm^{-1}: 2202 (C≡N), 1657 (C=O).

Potassium 4-amino-7-cyano-1-hydroxy-6-oxo-1-phenyl-2,6-dihydro-1*H*-pyrrolo[3,4-*c*]pyridine-3-olate (V). *a*. To 3 ml of 5% solution of potassium hydroxide was added 0.28 g (0.001 mol) of potassium tetracyanopropenide **IV**, and the mixture was stirred till complete dissolution of the reagent. The solution was evaporated. The separated precipitate was filtered off, and washed with a saturated solution of potassium chloride. Yield 0.14 g (45%), mp 112–115°C (decomp.). IR spectrum, ν, cm^{-1}: 3362 (NH), 2209 (C≡N), 1675 (C=O). Found, %: C 52.45; H 2.85; N 17.48. $C_{14}H_9KN_4O_3$. Calculated, %: C 52.49; H 2.83; N 17.49.

b. To a solution of 0.07 g (0.0005 mol) of K_2CO_3 in 5 ml of water was added 0.28 g (0.001 mol) of pyrrolopyridine **IIa**, the solution obtained was evaporated. The separated precipitate was filtered off, and washed with a saturated solution of potassium chloride. Yield 0.18 g (56%).

The molecule of compound **V** crystallized with two water molecules. $C_{14}H_9KN_4O_3 \cdot 2H_2O$. *M* 356.38; $a = b$ = 25.595(3), *c* 9.0761(18) Å; *V* 5945.6(4) Å^3; d_{calc} 1.593 g/cm^3; space group $I4_1/a$, *Z* 16; *R* 0.055.

11-Methyl-4-phenyl-3,5,9-triazatetracyclo[5.3.1.0^{1,7}.0^{4,11}]undecane-2,6,8,10-tetraone (VI). To 10 ml of 5% solution of NaOH was added 2.60 g (0.01 mol) of cyclopropane **II**, and the mixture was stirred till complete dissolution of the reagent. After standing

for 10 h the reaction mixture was neutralized with 5% solution of H_2SO_4. The separated precipitate was filtered off, and washed with water. Yield 2.32 g (78%), mp 227–228°C (decomp.). IR spectrum, ν, cm^{-1}: 3428 (NH), 1710 (C=O). ^1H NMR spectrum, δ, ppm: 0.98 s (3H, CH_3), 7.49–7.53 m ($3H_{arom}$), 7.56 d ($2H_{arom}$, ^3J 7.3 Hz), 9.08 s (2H, NH), 11.59 s (1H, NH). Found, %: C 60.88; H 3.86; N 14.10. $C_{15}H_{11}N_3O_4$. Calculated, %: C 60.61; H 3.73; N 14.14.

The molecule of compound **VI** crystallized with a molecule of dimethyl sulfoxide. $C_{15}H_{11}N_3O_4 \cdot SO(CH_3)_2$, *M* 375.4. *a* 7.879(1), *b* 14.75(2), *c* 15.089(2) Å, *V* 1709.0(4) $Å^3$. Space group $P2_12_12_1$, *Z* 4, d_{calc} 1.459, *R* 0.049.

6-Amino-1-imino-3,4,4-trimethoxy-3a-methyl-3-phenyl-3,3a,3b,4-tetrahydro-1*H*-furo[3',4':1,3]-cyclopropa[1,2-*c*]pyrrol-3b-carbonitrile (VII). In 10 ml of methanol was dissolved 0.046 g (2 mmol) of sodium metal. The solution obtained was added at stirring to a slurry of 2.60 g (0.01 mol) of cyclopropane **II** in 10 ml of methanol. After 5 h the separated precipitate was filtered off and washed with methanol. Yield 2.57 g (72%), mp 216–217°C (decomp.). IR spectrum, ν, cm^{-1}: 3382 (NH), 3265, 3193 (NH_2), 2255 (C≡N), 1712 (C=NH). ^1H NMR spectrum, δ, ppm: 0.76 s (3H, CH_3), 3.15 s (3H, OCH_3), 3.25 s (3H, OCH_3), 3.83 s (3H, OCH_3), 6.75 br.s (2H, NH_2), 7.38 t ($1H_{arom}$, ^3J 7.2 Hz), 7.44 t ($2H_{arom}$, ^3J 7.2 Hz), 7.48 d ($2H_{arom}$, ^3J 7.1 Hz), 8.32 s (1H, NH). Mass spectrum, *m/z* (I_{rel}, %): 356 (1) $[M]^+$. Found, %: C 60.86; H 5.72; N 15.56. $C_{18}H_{20}N_4O_4$. Calculated, %: C 60.66; H 5.66; N 15.72. *M* 356.15.

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