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Domino-Synthesis and Fluorescent Properties of 4-cyano-2-oxo-1,2-dihydropyridine-3-carboxamides and 2-oxo-1,2-dihydropyridine-3,4-dicarbonitriles

O. V. Ershov*, S. V. Fedoseev, M. Yu. Belikov and M. Yu. Ievlev

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Non-catalytic conversion of 4-oxoalkane-1,1,2,2-tetracarbonitriles in presence of water leads to the formation of mixture of fluorescent 4-cyano-2-oxo-1,2-dihydropyridine-3-carboxamides and 2-oxo-1,2-dihydropyridine-3,4-dicarbonitriles in equal proportions. This transformation was explained and spectral-luminescent properties were investigated, fluorescence quantum yield was measured.

Introduction

Organic fluorophores have a wide range of applications, for example, OLED-technology (Organic Light-Emitting Diodes),[1a] photovoltaics,[1b] confocal microscopy,[1c] as fluorescent markers and probes,[1d] as dyes for polymers[1e] and textile[1f]. Several scientific works show that 2-pyridone moiety is fluorophore.[2] Cyano-substituted 1*H*-pyridine-2-ones occupy the special place among compounds of this series. It has been shown that the presence of the carbonitrile group influences positively to the fluorescent properties of these compounds.[2d] Moreover, the synthesis of 2-pyridones has much interest due to the prominent presence of them in biologically active molecules.[3] Examples of such molecule include natural products such as (+)–campothecin (antitumor agent),[3a,b] pyridone L-697,661 (HIV reverse transcriptase inhibitor),[3c] and leporine A (insecticide).[3d] Milirinon and its analogues (amrinone, loprinone etc.), which have 1*H*-pyridine-2-one-3-carbonitrile fragment, are used as cardiotonic drugs for the treatment of heart failure.[3e,d]

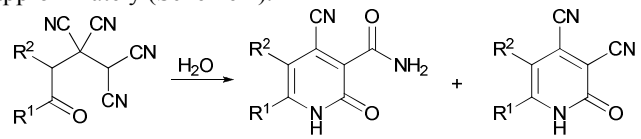
Due to their luminescent properties and biological activity cyano-substituted 2-pyridones are catching much interest in the development of convenient methodologies of the synthesis from simple and available starting materials.[4]

4-Oxoalkane-1,1,2,2-tetracarbonitriles (adducts of tetracyanoethylene and ketones) **1**[5a,b] have a structural predisposition to the directed synthesis of pyridine derivatives. It includes the presence a special moiety containing carbonitrile group and electron deficient carbon atom in the δ-position from it in the molecule. Such characteristic makes them suitable and perspective reagents for the synthesis of pyridine derivatives with the unique frame of functional groups.[5c-i] It was demonstrated in the series of publications about the synthesis of cyano-substituted heterocycles, in particular hydrogenated [5c] and 2-halogen-substituted pyridines.[5d-f] Furthermore, based on compounds **1** luminescent 2-oxo-1,2-dihydropyridine-3,4-dicarbonitriles [5g,h] (also in the form of ammonium salt [5i]) have been previously obtained. It should be noted, that there was not any systematic studies of their fluorescence.

Results and discussion

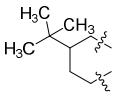
Continuing the investigations we decided to interact 4-oxoalkane-1,1,2,2-tetracarbonitriles **1** with water for the purpose to synthesize new organic fluorophores of the 2-pyridone series and to study the correlation of their structure with optical properties.

It was found, that refluxing of 4-oxoalkane-1,1,2,2-tetracarbonitriles **1** in the mixture of organic solvent and water during 1-5 minutes leads to the obtaining of two compounds 4-cyano-2-oxo-1,2-dihydropyridine-3-carboxamides **2** and 2-oxo-1,2-dihydropyridine-3,4-dicarbonitriles **3** in equal proportions approximately (Scheme 1).



1 2 3

Scheme 1 Conversion of 4-oxoalkane-1,1,2,2-tetracarbonitriles **1** into the two 2-pyridone derivatives **2** and **3**.

Sub-strate	R^1	R^2	Product	Yield (%)[a]	Product	Yield (%)[a]
1a	CH_3	CH_3	**2a**	40	**3a**	39
1b	CH_3	C_2H_5	**2b**	42	**3b**	41
1c	CH_3	C_3H_7	**2c**	45	**3c**	41
1d	$(CH_2)_4$		**2d**	39	**3d**	43
1e	$(CH_2)_5$		**2e**	48	**3e**	44
1f	$(CH_2)_6$		**2f**	47	**3f**	40
1g			**2g**	38	**3g**	41
1h			**2h**	41	**3h**	39

[a] Yield has been reported for isolated crude product.

Compounds **3a, 3c, 3d, 3g, 3h** are known and can be yielded from appropriate 4-oxoalkane-1,1,2,2-tetracarbonitriles **1** under the action of piruvic[5g] or sulfuric[5h] acid. The others are the novel compounds, are not described in the literature earlier.

The feature of transformation described in this paper is the absence of catalysts, in contrast to previously described acid-[5h,6] and base-catalyzed[7] reactions of 4-oxoalkane-1,1,2,2-tetracarbonitriles **1** with water. This fact demonstrates the high reactivity of compounds **1**, caused of their «functional charge» that leads to the easy initiation of domino-processes.

As the solvent for interaction ethyl acetate, 1,4-dioxane, THF, ethanol, propane-2-ol, acetonitrile, acetone, butan-2-one, propane-2-one and cyclohexanone were tested and can be used. The necessity of application a mixture of organic solvent with water explained with the low solubility of starting compounds **1** in water. Separation of the synthesized compounds occurred when ketones had been used as a solvent. 1*H*-Pyridine-2-ones **3** has a good solubility in the mixture of ketone and water, but carboxamides **2** precipitates from the reaction mixture after cooling and requires no further purification. It is noticed, that the temperature conditions of this process strongly influence on its rate – reaction completes after 1-5 minutes under reflux, whereas at room temperature it takes from one to three days. The proportion of the resulting compounds **2** and **3** was found using the integrals of the same signals in ^{1}H NMR spectrum of the mixture obtained by evaporation of the reaction mass.

The structures of the compounds **2** and **3** were proved with IR-, ^{1}H NMR-spectroscopy and mass-spectrometry. IR-spectra of compounds **2** showed no bands of carbonitrile group. The presence of the conjugated system containing cyano group and the possibility to form the intramolecular donor-acceptor complex of carbonitrile group and oxygen of carboxamide presumably explains the absence of it in the IR-spectra. This assumption is consistent with the quantum-chemical calculations carried in the Gaussian 09 W with the Hartree-Fock basis 6-31G.

Heteronuclear multiple-bond correlation spectroscopy (HMBC) was performed for compound **2a** additionally to determine the carboxamide position (Fig. 1). The spectrum showed the correlation peak of the carboxamide proton (7.75 ppm) with the carbon atom C4 (121.37 ppm) of pyridine and the absence of correlation of this proton with the carbon atom C3 (127.40 ppm) of pyridine at the same time. The correlation peaks of protons of alkyl substituents with pyridine ring carbons C1, C2 and C3 also present (Fig. 1). Based on this fact it could be argued that the carboxamide group is in the third position of the pyridine ring.

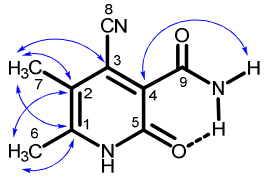
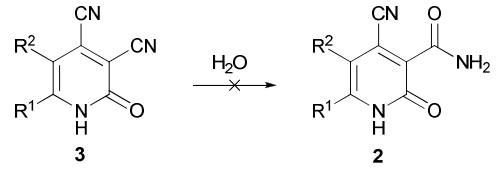


Figure 1 Correlation peaks in HMBC-spectrum of compound **2a**.

Proceeding from the structure of compounds **2** and **3** it can be assumed that carboxamide **2** is the result of the simple hydrolysis of carbonitrile **3** (Scheme 2).

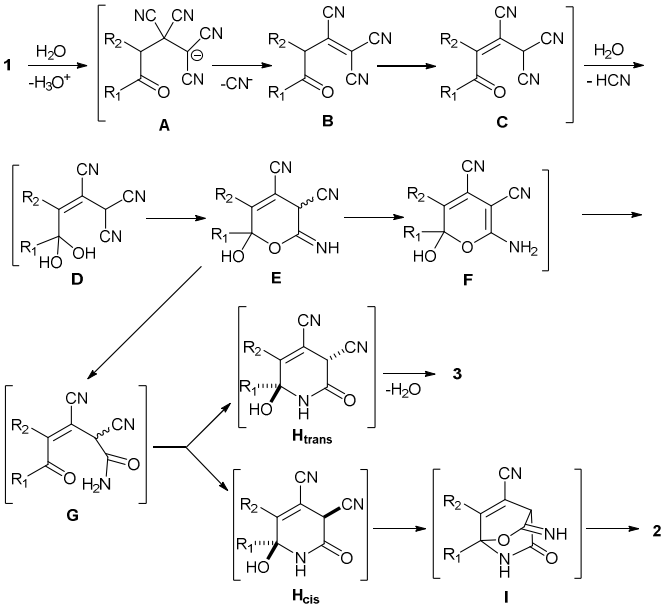
However, our studies shown that carboxamide **2** does not yield even in small amounts after continuous refluxing of carbonitrile **3** under described conditions. The addition of dilute acids also does not lead to the formation of compounds **2**.



Scheme 2 Expected way of formation of 4-cyano-2-oxo-1,2-dihydropyridine-3-carboxamides **2** through the simple hydrolysis of 2-oxo-1,2-dihydropyridine-3,4-dicarbonitriles **3**

The obtained data shows that the stereochemical features of intramolecular processes have much influence on the course of the formation of two compounds. Based on it the following scheme can be suggested (Scheme 3).

At first stage dehydrocyanation of compounds **1** occurs according to the mechanism E1cB presumably. It is possible with the presence of the ionizing solvent (water) and electron-acceptor cyano groups stabilizing the anion **A**. The obtained intermediate **B** isomerizes further in more stable unsaturated ketonitrile **C**. The confirmation of the proposed path **A**→**C** is the obtaining of ammonium salts of 1,1,2-tricyano-4-oxobut-2-ene-1-ide, previously described by us, they have a similar structure with the intermediate **C**.[8] The presence of electron-acceptor groups in the ketonitrile **C** facilitates formation of the geminal diol **D**. Further intramolecular cyclization of hydroxy and cyano group leads to piranimine **E**, that has possibilities to isomerize into piranamine **F**.

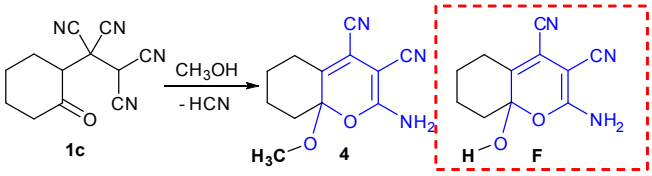


Scheme 3 Estimated way of formation of 4-cyano-2-oxo-1,2-dihydropyridine-3-carboxamides **2** and 2-oxo-1,2-dihydropyridine-3,4-dicarbonitriles **3**

Intermediates **E** and **F** can decyclize to amide **G** as a racemate, that can further cyclize into diastereomeric mixture of tetrahydropyridines $\mathbf{H}_{cis}$ and $\mathbf{H}_{trans}$ with the different spatial position of hydroxy and cyano group. It causes stereospecificity of the further processes. In $\mathbf{H}_{trans}$ interaction between them is impossible, so aromatization through the dehydratation leads to the pyridine-2-one **3**. In $\mathbf{H}_{cis}$ the intramolecular cyclization of hydroxy and cyano group leads to the 2-oxa-6-azabicycle **I**, decyclization of the latter yields pyridine-3-carboxamide **2**.

To prove the transformation sequence **1→E** additional research were carried out. Methanol was used to determine the location of incoming group. It is convenient to use this reagent instead of water for establishing of the reaction path. Intermediates should contain methoxy group instead of the hydroxyl (**E** or **F**), therefore decyclization process does not occur due to stronger carbon-oxygen bond and in some cases the intermediates can be isolated.

It was found that interaction of 1-(2-oxocyclohexyl)ethane-1,1,2,2-tetracarbonitrile **1c** with methanol leads to the analogue of intermediate **F** – 2-amino-8a-methoxy-6,7,8,8a-tetrahydro-5*H*-chromene-3,4-dicarbonitrile **4**.



Scheme 4 Synthesis of the analogue of intermediate **F** – 2-amino-8a-methoxy-6,7,8,8a-tetrahydro-5*H*-chromene-3,4-dicarbonitile **4**.

The formation of chromene **4** indirectly shows that the dehydrocyanation process precedes the formation of the carboxamide **G** (scheme 2). α-Position of methoxy group in the pyran moiety (Fig. 2) confirms that the methanol attacks exactly the carbonyl group, and but not a carbonitrile. Therefore, alternative mechanism with a simple hydrolysis of the cyano group on the way from **C** immediately in **G** is denied.

Thus, in the case of the reaction on the way **C→D→E→F** carbonyl-assisted carbonitrile hydration effect (**CACHE**) is observed. Carbonyl group, due to the formation of hydrate, takes part as acceptor of water, performs the role of transport and enables intramolecular transfer of water to nearly located cyano group.[7,9,10] **CACHE** processes are typical for the chemistry of oxonitriles and often can be the reason of an easy addition of water to the cyano group.[9a-d,g-i]

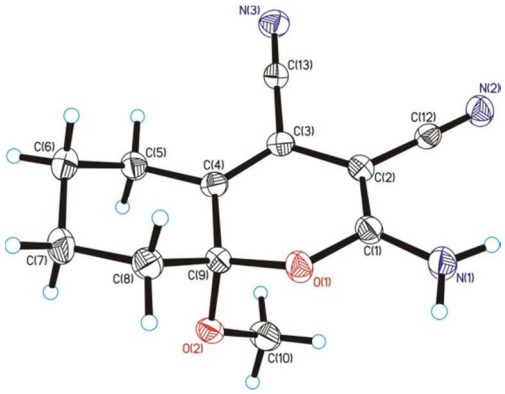


Figure 2 ORTEP diagram of compound **4**.

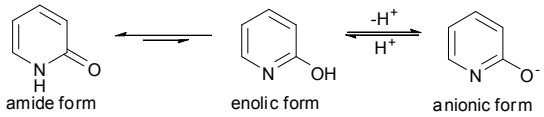
The evidence of transformation along the way **1** → **F** → **3** is the formation of pyridine-2-one **3c** after the hydrolysis of structural analogue of intermediate **F** – compound **4** with aqueous mineral acid.

The absence of carboxamide **2** as a reaction product is caused by fully suppression of intramolecular interaction of hydroxy and cyano groups and easier elimination of water from the intermediate **H** due to acid catalysis. Furthermore, it was found if the reaction described (Scheme 1), is performed using acid, 1% sulfuric acid for example, the formation of the carboxamide **2** also does not occur.[5h] It indirectly confirms the mechanism described in Scheme 2.

In the described transformations in Scheme 2 the iminolactone-lactam rearrangement plays a key role in obtaining of pyrid-2-ones **3** from 4-oxoalkane-1,1,2,2-tetracarbonitriles **1**, specifically stage of transformation of iminolactone **E** into lactam **H**. This rearrangement is often implemented in the chemistry of oxonitriles and definites the formation of one or another heterocyclic ring.[7,10]

Fluorescent properties of synthesized compounds

The uniqueness of the functional frame of synthesized 1*H*-pyridine-2-ones should be noted. On set of physical and chemical properties, including primarily their optical properties, cyano substituted 2-pyridone derivatives can be regarded as potential effective biological labels and fluorescent dyes. Pyridine-2-one moiety is a tautomeric system. It is known, that the amide form of unsubstitute molecule predominates over enolic in neutral solutions in the ratio of about 340:1.[2a] The studies of luminescent properties of these structures show that the majority of pyridine-2-ones have weak fluorescence in most solvents; moreover, the greatest part of its intensity belongs to the predominant amide form.



Scheme 5 Tautomeric forms of 1H-pyridine-2-ones

The relative luminescence quantum yields are low and reach only 0.055 in non-polar organic solvents (using quinine sulfate in 1.0 N H_2SO_4 as a standard).[2b] Unsubstituted molecule shows the greatest fluorescence efficiency in anionic form – quantum yield is 0.072 in 0.1 N solution of sodium hydroxide (using phenol and anisole in cyclohexane as standards).[2c] In the case of cyano substituted pyridine-2-ones situation changes radically, particularly in 3-cyano-1*H*-pyridine-2-ones a significant increase of fluorescence intensity was noted, that mostly influenced by the nitrile group, the removal of latter reduces the emission more than 3 times.[2d]

For 4,6-dimethyl substituted molecule of pyridine-2-one the relative luminescence quantum yield is 0.709 (excitation wavelength is 291 nm, using quinine sulfate in 1.0 N H_2SO_4 as a standard), but the replacement of methyl groups to phenyl leads to the bathochromic shift and increasing of quantum yield till 0.883 (excitation wavelength is 391 nm, using quinine sulfate in 1.0 N H_2SO_4 as a standard), due to increasing of the effective conjugation length.[2e]

It is important to note, in spite of relatively poor solubility in most organic solvents, compounds **2** and **3** have an intense fluorescence even in the strongly diluted solutions including water. To investigate the dependence of fluorescence efficiency from type of acceptor group (carbonitrile and carboxamide), and the influence of alkyl fragments, the spectral-luminescent properties of the synthesized compounds were studied. It was found that compounds **2** and **3** with annelated cyclic moiety possess the highest intensity of fluorescence. It is obvious that in this case a significant role plays a conformational rigidity of the molecule, decreasing the possibility of nonradiative transitions and consumption of the excitation energy to the oscillation and rotation of the individual fragments. In the case

of compound **2h** anchor in the cyclohexane ring also facilitates such fixation of structure.

For the dicarbonitrile derivatives **3** a slight shift of the absorption and fluorescence maxima to longer wavelengths (about 10 nm) was found by comparison with spectra of compounds **2**. Significant influence of the alkyl moiety on position of the maxima does not observed.

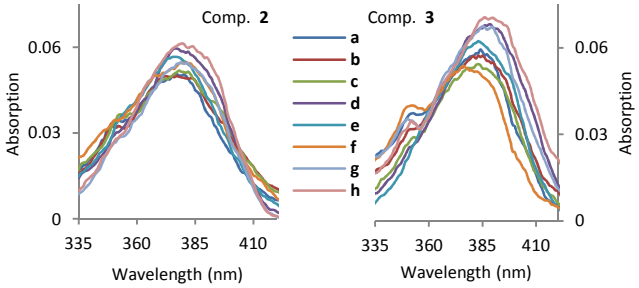


Figure 3 Figure 4

Figure 3, 4 The absorption spectra of compounds **2** (Fig. 3) and **3** (Fig. 4) in ethanol (6×10^{-6} – 1×10^{-5} M).

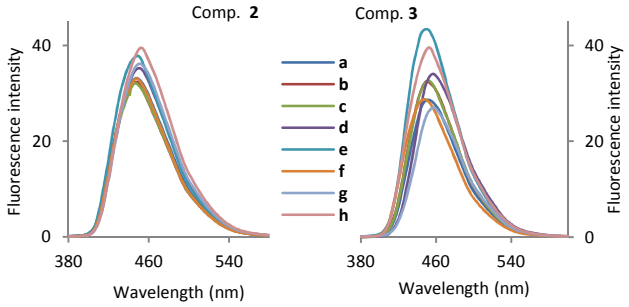


Figure 5 Figure 6

Figure 5, 6 The fluorescence spectra of compounds **2** (Fig. 5) and **3** (Fig. 6) in ethanol (6×10^{-6} – 1×10^{-5} M) at excitation wavelength 365 nm.

Table 1 Fluorescent and UV-absorption properties of synthesized compounds and reference compound, 4-methylumbelliferone in ethanol

Comp.	λ^{abs}_{max} nm	A^{abs}_{max}	ε mol×L^{-1}×cm^{-1}	λ^{flu}_{max} nm	Φ_F
4-Me-umb.	**360**	**0.0459**	**7398**	**448**	**0.63**
2a	376	0.0506	6961	448	0.56
3a	384	0.0594	7238	452	0.48
2b	377	0.0499	7171	449	0.54
3b	383	0.0573	7455	451	0.53
2c	379	0.0514	7301	450	0.54
3c	384	0.0539	7607	453	0.57
2d	377	0.0595	7550	451	0.62
3d	388	0.0681	7683	455	0.59
2e	376	0.0566	6824	448	0.60
3e	383	0.0622	7353	450	0.72
2f	379	0.0545	6893	448	0.51
3f	384	0.0532	7183	451	0.48
2g	378	0.0546	6676	452	0.65
3g	385	0.0674	6965	460	0.42
2h	379	0.0610	7140	454	0.61
3h	386	0.0706	7577	459	0.47

The relative luminescence quantum yields were determined using 4-methylumbelliferone in 0.1 M phosphate buffer at pH 10 as a standard (Φ_F=0.63)[11a] with the excitation wavelength 365 nm and presented in the table 1. It should be noted, that compounds **2d**, **2e**, **2g**, **2h**, **3d** have the same fluorescence efficiency as the standard compound, and the compound **3e** exceeds it.

After analysis of the obtained data, we selected two samples (**2e** and **3e**), with the good fluorescence efficiency. Using them, we investigated the influence of solvent on the absorbance and emission behavior. Unfortunately, due the extremely poor-solubility of synthesized compounds in the several organic solvents, in some cases, quantitative parameters such as the exact concentration of the analyte was not possible to establish reliably. Therefore, the possibility to reliably measure the true molar extinction coefficient of light absorption was absent. In these cases, only the position of the maxima of absorbance and emission, fluorescence quantum yield are presented (table 2).

Table 2 Solvatochromic properties of the compounds **2e** and **3e**.

Comp.	Solvent	λ^{abs}_{max} nm	A^{abs}_{max}	ε_{max} mol×L^{-1}×cm^{-1}	λ^{flu}_{max} nm	Φ_F
2e	**CH_3CN**	382	0.0668	5673	443	0.47
3e	**CH_3CN**	386	0.0660	5410	443	0.41
2e	**AcOH**	383	0.0478	6252	442	0.83
3e	**AcOH**	374	0.0542	5687	444	0.62
2e	**C_6H_6***	394	–	–	442	0.07
3e	**C_6H_6***	391	–	–	443	0.08
2e	**Diox**	383	0.0651	5197	438	0.43
3e	**Diox**	374	0.0642	5901	441	0.25
2e	**DMSO**	385	0.0525	5071	443	0.19
3e	**DMSO**	383	0.0643	5373	444	0.08
2e	***n*-C_6H_{14}***	394	–	–	441	<0.01
3e	***n*-C_6H_{14}***	390	–	–	436	0.01
2e	**C_6H_5N**	404	0.0635	4884	446	0.87
3e	**C_6H_5N**	385	0.0586	5015	445	0.21
2e	**H_2O***	383	–	–	445	0.31
3e	**H_2O***	379	–	–	445	0.47

*cases of the insoluble analyte are marked with star

As a result we observed that the position of the maximum of emission is constant in the most of solvents, while the maxima of absorbance are changeable in narrow range. Also we found that solvents with the pronounced acid or base properties influence on the fluorescence efficiency strongly. Using acetic acid and pyridine we were able to achieve the highest index of fluorescence quantum yields in the case of compound **2e** 0.83 and 0.87 respectively. Compound **3e** has low fluorescent efficiency in the pyridine (0.21) and acceptable in the acetic acid (0.62), but from the standpoint of choosing the best solvent in general ethanol is the most suitable – all of described substances are soluble in it in the required amount, fluorescent quantum yield are acceptable in all cases, and solvent is widely available.

Conclusions

Non-catalytic procedure for preparation of 4-cyano-2-oxo-1,2-dihydropyridine-3-carboxamides and 2-oxo-1,2-dihydropyridine-3,4-dicarbonitriles, having the intense fluorescence was developed. This transformation was explained and spectral-luminescent properties were investigated in the several organic solvents (including water), fluorescence quantum yield was measured.

Experimental

General experimental methods

The progress of reactions and the purity of the products were monitored by TLC on Sorbfil plates (spots were visualized under UV light, by treatment with iodine vapor, or by heating). The IR spectra were recorded on an FSM-1202 spectrometer with Fourier transform from samples dispersed in mineral oil. The NMR spectra were measured in DMSO-d_6 on a Bruker DRX-500 spectrometer using tetramethylsilane as an internal reference. The elemental compositions were determined on a CHN-analyzer vario Micro cube. The mass spectra (electron impact, 70 eV) were obtained on a Finnigan MAT INCOS-50 spectrometer. The UV spectra were recorded from solutions in ethanol on an SF-2000 spectrophotometer. Melting points were determined on the device M-560.

Fluorescence spectra were recorded on a Fluorat-02-Panorama spectrofluorimeter. The relative luminescence quantum yields were determined using solutions of the analyte in ethanol (6×10^{-6} – 1×10^{-5} M, optical density at the excitation wavelength A<0.05). 4-Methylumbelliferone in 0.1 M phosphate buffer at pH 10 was used as a standard (Φ_F=0.63) [11a]. The value of the fluorescence quantum yield was determined by a known method with the excitation wavelength 365 nm [11b].

Starting 4-oxoalkane-1,1,2,2-tetracarbonitriles **1** were prepared according to the general procedure of synthesis β, β, γ, γ-tetracyanoalkanones.[5a,b]

Representative procedure for preparation of 5,6-dimethyl-2-oxo-4-cyano-1,2-dihydropiridine-3-carboxamide 2a and 5,6-dimethyl-2-oxo-1,2-dihydropyridine-3,4-dicarbonitrile 3a.

To the solution of 0.4 g (2 mmol) 3-methyl-4-oxopentane-1,1,2,2-tetracarbonitrile in 5 ml of ethyl acetate 0.5 ml (28 mmol) of water was added. The mixture was left for 5 days, then it was evaporated, precipitated crystals washed with 2 ml of diethyl ether. The residue mixture of compounds **2a** and **3a** was separated. For yield compound **2a** precipitate was refluxed for 2 minutes in 4 ml of acetone, filtered and washed with 1 ml acetone. Yield 0.17 g (45%), m.p. 225-226°C (decomp.). For yield compound **3a** filtrate of acetone was evaporated, precipitated crystals washed with 2 ml of diethyl ether. Yield of **3a** 0.13 g (39%), m.p. 263-265°C (decomp.). After separation the compounds were dried in the vacuum desiccator over $CaCl_2$.

2a. IR: ν_{max}/cm^{-1} 3312, 3163, 1696 cm^{-1}; ^{1}H NMR (500 MHz; DMSO-d_6, TMS) δ_H 2.17 (3H, s, CH_3), 2.34 (3H, s, CH_3), 7.75 (1H, s, $CONH_2$), 9.03 (1H, s, $CONH_2$), 12.98 (1H, br s, NH) ppm; ^{13}C NMR (125 MHz; DMSO-d_6, TMS) δ_C 14.36, 17.67, 114.37, 115.34, 121.37, 127.40, 149.92, 160.60, 163.34 ppm; *m/z* (EI) 191 (M^+, 90); elemental analysis found (%): C, 56.46; H, 4.77; N, 21.99. $C_9H_9N_3O_2$ calculated C, 56.54; H, 4.74; N, 21.98%.

3a. IR: ν_{max}/cm^{-1} 3242, 2224, 1696 cm^{-1}; ^{1}H NMR (500 MHz; DMSO-d_6, TMS) δ_H 2.15 (3H, s, CH_3), 2.35 (3H, s, CH_3), 13.31 (1H, br s, NH) ppm; *m/z* (EI) 173 (M^+, 81); elemental analysis found (%): C, 62.45; H, 4.06; N, 24.25. $C_9H_7N_3O$ requires C, 62.42; H, 4.07; N, 24.27%.

Compounds **2b-h** and **3b-h** were prepared in a similar manner.

2b. Yield 0.18 г (44%). M.p. 231-232°C (dec.). IR: ν_{max}/cm^{-1} 3464, 3372, 3248, 1688 cm^{-1}; ^{1}H NMR (500 MHz; DMSO-d_6, TMS) δ_H 1.06 and 1.11 (3H, m, CH_3), 2.36 and 2.39 (3H, m, CH_3), 2.58 and 2.64 (2H, m, CH_2), 7.75 (1H, d, *J* 2.6 Hz, $CONH_2$), 8.98 (1H, s, $CONH_2$), 12.65 (1H, br s, NH) ppm; *m/z* (EI) 205 (M^+, 16); elemental analysis found (%): C, 58.57; H, 5.38; N, 20.46. $C_{10}H_{11}N_3O_2$ requires C, 58.53; H, 5.40; N, 20.48%.

2c. Yield 0.19 г (46%). M.p. 237-238°C (dec.). IR: ν_{max}/cm^{-1} 3358 and 3161, 1678 cm^{-1}; ^{1}H NMR (500 MHz; DMSO-d_6, TMS) δ_H 0.94 (3H, t, *J* 7.3 Hz, CH_3), 1.48 (2H, m, CH_2), 2.35 (3H, s, CH_3), 2.56 (2H, t, *J* 7.9 Hz, CH_2), 7.75 (1H, s, $CONH_2$), 8.96 (1H, s, $CONH_2$), 12.88 (1H, br s, NH) ppm; *m/z* (EI) 219 (M^+, 59); elemental analysis found (%): C, 60.12; H, 6.01; N, 19.24. $C_{11}H_{13}N_3O_2$ requires C, 60.26; H, 5.98; N, 19.17%.

2d. Yield 0.17 г (39%). M.p. 237-238°C (dec.). IR: ν_{max}/cm^{-1} 3480, 3371, 3190, 1669 cm^{-1}; ^{1}H NMR (500 MHz; DMSO-d_6, TMS) δ_H 1.69 and 1.75 (4H, m, $(CH_2)_2$), 2.56 and 2.59 (2H, m, CH_2), 2.61 and 2.64 (2H, m, CH_2), 7.79 д (1H, d, *J* 2.9 Hz, $CONH_2$), 9.03 с (1H, s, $CONH_2$), 12.85 (1H, br s, NH) ppm; *m/z* (EI) 217 (M^+, 69); elemental analysis found (%): C, 60.95; H, 5.07; N, 19.31. $C_{11}H_{11}N_3O_2$ requires C, 60.82; H, 5.10; N, 19.34%.

2e. Yield 0.22 г (48%). M.p. 250-251°C (dec.). IR: ν_{max}/cm^{-1} 3325, 3180, 1682 cm^{-1}; ^{1}H NMR (500 MHz; DMSO-d_6, TMS) δ_H 1.53 and 1.63 м (4H, m, $(CH_2)_2$), 1.73 and 1.80 (2H, m, CH_2), 2.85 and 2.87 (4H, m, $(CH_2)_2$), 7.73 (1H, s, $CONH_2$), 8.98 (1H, s, $CONH_2$), 12.98 (1H, br s, NH) ppm; *m/z* (EI) 231 (M^+, 40); elemental analysis found (%): C, 62.36; H, 5.68; N, 18.11. $C_{12}H_{13}N_3O_2$ requires C, 62.33; H, 5.67; N, 18.17%.

2f. Yield 0.21 г (44%). M.p. 258-259°C (dec.). IR: ν_{max}/cm^{-1} 3325, 3163, 1677 cm^{-1}; ^{1}H NMR (500 MHz; DMSO-d_6, TMS) δ_H 1.74 and 1.81 (6H, m, $(CH_2)_3$), 2.51 and 2.53 (2H, m, CH_2), 2.83 and 2.87 (4H, m, $(CH_2)_2$), 7.72 (1H, s, $CONH_2$), 8.99 (1H, s, $CONH_2$), 12.98 (1H, br s, NH) ppm; *m/z* (EI) 245 (M^+, 2); elemental analysis found (%): C, 63.59; H, 6.19; N, 17.16. $C_{13}H_{15}N_3O_2$ requires C, 63.66; H, 6.16; N, 17.13%.

2g. Yield 0.19 г (41%). M.p. 244-245°C (dec.). IR: ν_{max}/cm^{-1} 3464, 3372, 3248, 1688 cm^{-1}; ^{1}H NMR (500 MHz; DMSO-d_6, TMS) δ_H 1.04 (3H, d, *J* 6.5 Hz, CH_3), 1.28 and 1.38 (1H, m, C<u>H</u>CH_3), 1.76 and 1.83 (2H, m, CH_2), 2.13 (1H, dd, *J* 16.3 and 10.3 Hz, CHC<u>H</u>$_2$), 2.65 and 2.69 (2H, m, CH_2), 2.73 (1H, dd, *J* 16.3 and 5.1 Hz, CHC<u>H</u>$_2$), 7.77 (1H, d, *J* 2.9 Hz, $CONH_2$), 9.02 (1H, s, $CONH_2$), 12.86 (1H, br s, NH) ppm; *m/z* (EI) 231 (M^+, 9); elemental analysis found (%): C, 62.39; H, 5.63; N, 18.11. $C_{12}H_{13}N_3O_2$ requires C, 62.33; H, 5.67; N, 18.17%.

2h. Yield 0.26 г (44%). M.p. 268-269°C (dec.). IR: ν_{max}/cm^{-1} 3332, 3153, 1686 cm^{-1}; ^{1}H NMR (500 MHz; DMSO-d_6, TMS) δ_H 0.93 (9H, s, *t*-Bu), 1.21 and 1.29 (1H, m, CH_2), 1.37 and 1.45 (1H, m, CH_2), 1.92 and 1.96 (1H, s, *t*-BuC<u>H</u>), 2.19 and 2.28 (1H, m, CH_2), 2.59 and 2.68 (1H, m, CH_2), 2.71 and 2.73 (2H, m, CH_2), 7.76 (1H, d, *J* 2.6 Hz, $CONH_2$), 9.02 (1H, s, $CONH_2$), 12.85 (1H, br s, NH) ppm; *m/z* (EI) 273 (M^+, 16); elemental analysis found (%): C, 65.84; H, 7.05; N, 15.41. $C_{15}H_{19}N_3O_2$ requires C, 65.91; H, 7.01; N, 15.37%.

3b. Yield 0.29 г (84%). M.p. 225-226°C (dec.). IR: ν_{max}/cm^{-1} 3288, 2214, 1655 cm^{-1}; ^{1}H NMR (500 MHz; DMSO-d_6, TMS) δ_H 1.08 (3H, t, *J* 6.5 Hz, CH_3), 2.61 (2H, q, *J* 6.5 Hz, CH_2), 2.36 (3H, s, CH_3), 13.29 (1H, br s, NH) ppm; *m/z* (EI) 187 (M^+, 67); elemental analysis found (%): C 64.12; H 4.84; N 22.48. $C_{10}H_9N_3O$ requires C, 64.16; H, 4.85; N, 22.45%.

3c. Yield 0.28 г (80%). M.p. 238-239°C (dec.). IR: ν_{max}/cm^{-1} 3271, 2223, 1659 cm^{-1}; ^{1}H NMR (500 MHz; DMSO-d_6, TMS) δ_H 0.93 (3H, t, *J* 7.3 Hz, CH_3), 1.50 (2H, h, *J* 7.5 Hz, CH_2), 2.38 (3H, s, CH_3), 2.52 (2H, t, *J* 7.5 Hz, CH_2), 13.28 (1H, br s, NH) ppm; *m/z* (EI) 201 (M^+, 69); elemental analysis found (%): C, 65.59; H, 5.48; N, 20.96. $C_{11}H_{11}N_3O$ requires C, 65.66; H, 5.51; N, 20.88%.

3d. Yield 0.32 г (94%). M.p. 261-263°C (dec.) (266-267°C[4e]). IR: ν_{max}/cm^{-1} 3277, 2211, 1657 cm^{-1}; ^{1}H NMR (500 MHz;

DMSO-d_6, TMS) δ_H 1.69 and 1.73 (4H, m, $2CH_2$), 2.51 and 2.58 (4H, m, $2CH_2$), 13.20 (1H, br s, NH) ppm; *m/z* (EI) 199 (M^+, 100); elemental analysis found (%): C, 66.32; H, 4.54; N, 21.12. $C_{11}H_9N_3O$ requires C, 66.32; H, 4.55; N, 21.09%.

3e. Yield 0.33 г (92%). M.p. 252-254°C (dec.). IR: ν_{max}/cm^{-1} 3214, 2223, 1668 cm^{-1}; ^1H NMR (500 MHz; DMSO-d_6, TMS) δ_H 1.56 and 1.64 (4H, m, CH_2), 1.74 and 1.78 (2H, m, CH_2), 2.69 and 2.73 (2H, m, CH_2), 2.76 and 2.80 (2H, m, CH_2), 13.31 (1H, br s, NH) ppm; *m/z* (EI) 213 (M^+, 100); elemental analysis found (%): C, 67.53; H, 5.22; N, 19.70. $C_{12}H_{11}N_3O$ requires C, 67.59; H, 5.20; N, 19.71%.

3f. Yield 0.31 г (87%). M.p. 289-291°C (dec.). IR: ν_{max}/cm^{-1} 3222, 2226, 1662 cm^{-1}; ^1H NMR (500 MHz; DMSO-d_6, TMS) δ_H 1.34 and 1.42 (4H, m, CH_2), 1.58 and 1.69 (4H, m, CH_2), 2.74 and 2.78 (2H, m, CH_2), 2.83 and 2.87 (2H, m, CH_2), 13.25 (1H, br s, NH) ppm; *m/z* (EI) 227 (M^+, 100); elemental analysis found (%): C, 68.73; H, 5.76; N, 18.47. $C_{13}H_{13}N_3O$ requires C, 68.70; H, 5.77; N, 18.49%.

3g. Yield 0.32 г (93%). M.p. 203-205°C (205-207°C[4f]). IR: ν_{max}/cm^{-1} 3216, 2212, 1653 cm^{-1}; ^1H NMR (500 MHz; DMSO-d_6, TMS) δ_H 1.03 (3H, d, *J* 6.5 Hz, CH_3), 1.28 and 1.37 (1H, m, C<u>H</u>CH_3), 1.76 and 1.83 (2H, m, CH_2), 2.16 (1H, dd, *J* 15.9 and 10.4 Hz, CHC<u>H</u>$_2$), 2.64 and 2.67 (1H, m, H_2), 2.68 and 2.71 (2H, m, CH_2), 13.15 (1H, br s, NH) ppm; *m/z* (EI) 213 (M^+, 22); elemental analysis found (%): C, 67.51; H, 5.22; N, 19.75. $C_{12}H_{11}N_3O$ requires C, 67.59; H, 5.20; N, 19.71%.

3h. Yield 0.32 г (89%). M.p. 150-151°C (153-154°C[4f]). IR: ν_{max}/cm^{-1} 3253, 2215, 1719 cm^{-1}; ^1H NMR (500 MHz; DMSO-d_6, TMS) δ_H 0.92 (9H, s, *t*-Bu), 1.23 and 1.27 (1H, m, CH_2), 1.37 and 1.41 (1H, m, CH_2), 1.93 and 1.97 (1H, m, *t*-BuC<u>H</u>), 2.29 (1H, dd, *J* 15.5 and 12.1 Hz, CH_2), 2.60 and 2.69 (2H, m, CH_2), 2.72 and 2.78 (1H, m, CH_2), 13.10 (1H, br s, NH) ppm; *m/z* (EI) 255 (M^+, 16); elemental analysis found (%): C, 70.50; H, 6.769; N, 16.51. $C_{15}H_{17}N_3O$ requires C, 70.56; H, 6.71; N, 16.46%.

Representative procedure for preparation of 5,6-dimethyl-2-oxo-4-cyano-1,2-dihydropiridine-3-carboxamide 2a. To the solution of 0.4 g (2 mmol) 3-methyl-4-oxopentane-1,1,2,2-tetracarbonitrile in 5 ml of cyclohexanone 0.5 ml (28 mmol) of water was added, then the mixture was refluxed with mixing for 7-10 minutes, cooled, and precipitated product was filtered and washed with hot acetone (3 ml). It was dried in the vacuum desiccator over $CaCl_2$. Yield 0.18 g (47%). Melting point and spectral properties are identical to the substance obtained with described procedure.

Compounds **2b-h** could be prepared in a similar manner.

Representative procedure for preparation of 2-amino-8a-methoxy-6,7,8,8a-tetrahydro-5*H*-chromene-3,4-dicarbonitile 4. The solution of 0.23 g (1 mmol) 1-(2-oxocyclohexyl)ethane-1,1,2,2-tetracarbonitrile **1** in absolute methanol (2 cm^3) was refluxed for 40-60 minutes. After completion of the reaction (TLC) mixture was cooled and evaporated under the room temperature. Precipitated product was filtered и recrystallized from propane-2-ol. It was dried in the vacuum desiccator over $CaCl_2$. Yield 0.22 г (95%). M.p. 173-174°C (dec.). IR: ν_{max}/cm^{-1} 3316 and 3196, 2198 cm^{-1}; ^1H NMR (500 MHz; DMSO-d_6, TMS) δ_H 1.34 and 1.41 (1H, m, CH_2), 1.46 and 1.56 (1H, m, CH_2), 1.67 and 1.74 (2H, m, CH_2), 1.75 and 1.81 (1H, m, CH_2), 2.15 and 2.28 (2H, m, CH_2), 2.60 and 2.65 (1H, m, CH_2), 3.18 (3H, s, OCH_3), 7.81 (2H, s, NH_2) ppm; *m/z* (EI) 231 (M^+, 90); elemental analysis found (%): C, 62.33; H, 5.67; N, 18.17. $C_{12}H_{13}N_3O_2$ requires C, 62.30; H, 5.65; N, 18.19%.

Representative procedure for hydrolysis of 2-amino-8a-methoxy-6,7,8,8a-tetrahydro-5*H*-chromene-3,4-dicarbonitile 4 to 2-oxo-1,2,5,6,7,8-hexahydroquinoline-3,4-dicarbonitrile 3d. The solution of 0.23 g (1 mmol) **4** in 30% hydrochloric or sulfuric acid (3 cm^3) was refluxed with mixing for 10-12 minutes, cooled, and precipitated product was filtered and washed with water (5 cm^3). It was dried in the vacuum desiccator over $CaCl_2$. Melting point and spectral properties are identical to the substance obtained with described procedure.

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Notes and references

Chuvash State University, Moskovskiy pr.15, Cheboksary 428015, Russia
email: oleg.ershov@mail.ru

† Crystallographic data (excluding structure factors) for the structure **4** in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 1040251. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [fax: +44 (0) 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk]

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