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Synthesis, Structure, and Photochemical Properties of Hetarylaldehydes Benzimidazolyl-2-hydrazones

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Abstract—New benzimidazolyl-2-hydrazones of 2-furaldehyde, thiophene-2-carbaldehyde and pyridine-2-carbaldehyde were synthesized and their structure was studied by ^{1}H NMR and X-ray analysis. Photochemical properties of these compounds and of benzothiazolyl-2-hydrazones of 2-furaldehyde, thiophene-2-carbaldehyde and pyridine-2-carbaldehyde in solutions were investigated. The process of phototransformation is determined by the nature of the aldehyde fragment of hydrazones.

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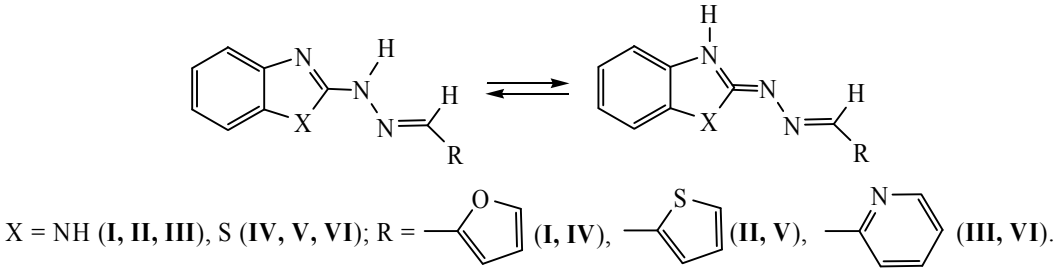
Hydrazones and metal complexes on their basis attract growing attention as important functional materials, in particular, for information technologies [1]. Of special interest are hydrazones containing heterocyclic fragments. Among them, compounds displaying photochrome properties have been found [2, 3]. Hetarylhydrazones are di-, tritopic ligands for synthesis of supramolecular self-assembling polynuclear complexes [4], which can be used for design of photo-sensitive ordered (macro)molecular and multicomponent systems. Mononuclear metal complexes of hydrazones can be used as a recording layer in the range of 350–450 nm (HD DVD) [5, 6].

It was interesting to synthesize new hydrazones having two heterocyclic fragments. In this paper we report on the results of investigation of benzimidazolyl-2- and benzothiazolyl-2-hydrazones of hetaryl-aldehydes **I–VI**.



Benzimidazolylhydrazones **I–III** were synthesized by the reaction of benzimidazolyl-2-hydrazine with heterocyclic aldehydes of a different nature (π-reach thiophene and furan, π-deficient pyridine).

The structure of the synthesized compounds was proved by ^{1}H NMR and XRD methods by the example of benzimidazolyl-2-hydrazone of pyridine-2-carbaldehyde. According to the X-ray analysis data, hydrazone **III** crystallized in the form of hydrate of the *EE*-isomer in the amino tautomeric form (Fig. 1).

The hydrazone has planar structure (deviations of atoms from the mean-square plane do not exceed 0.09 Å), bond lengths and bond angles are close to values normal for these structures. The molecules are packed in the crystal as tilted stacks with interplane distance of 3.363 Å that allows intra-pile contacts of

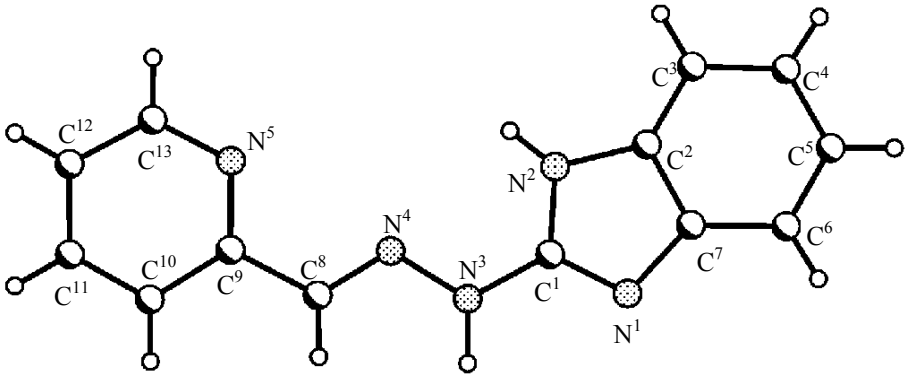


Fig. 1. General view of the molecule of benzimidazolyl-2-hydrazone of pyridine-2-carbaldehyde (**III**).

aromatic systems. The piles are connected with each other by a complex system of intermolecular hydrogen bonds. Firstly, the molecules form planar "dimers" due to hydrogen bonds $N^3–H^{3\cdots}N^1$ [$–x + 1, –y + 1, –z + 1$] between the NH fragment of hydrazone and the imidazole nitrogen atom. The planes of the interacting molecules can be biased with respect to each other by 0.75 Å. Secondly, an important structure-forming factor is water connected by intermolecular hydrogen bonds with the NH group of imidazole and acting as a donor of proton for the bonds with the pyridine and hydrazone nitrogen atoms (Fig. 2a). Finally, the molecules of water are also connected to each other by the system of intermolecular hydrogen bonds forming a zigzag chain at the angle of 50° to the hydrazone plane. As a result, a complex stacking of differently directed piles of "dimers" of hydrazones linked by the system of intermolecular hydrogen bonds with participation of molecules of water is formed (Fig. 2b).

In solution, hydrazones **I–III** can exist in the amino- or the imino-tautomer form. Earlier [7], the structure of a series of benzimidazolylhydrazones of alkyl- and arylaldehydes was studied using the ^1H NMR spectroscopy. It was shown that the signals of the benzene ring protons in benzimidazole resonate at 6.8–7.2 ppm for the imino form, while the shift of the tautomeric equilibrium to the amino form results in a downfield shift to 7.9 ppm.

In the spectrum of hydrazone **II** containing the most electron–donor thienyl substituent the benzene ring protons in benzimidazole resonate at 7.0–7.07 ppm. Introduction of more electron–acceptor substituents (furyl, pyridyl) leads to the downfield shift of these signals (7.0–7.3 ppm for compounds **I, III**). NH protons of benzimidazole appear in the spectrum as a broadened singlet at 11–8.5 ppm, the largest broadening being observed for hydrazone **I**: Whereas for hydrazone **II** it is a two-proton singlet, for compound **III** its intensity corresponds to one proton, and for hydrazone **I** the integral intensity corresponds to 1.7 proton.

From the spectral data it can be concluded that the hydrazone of pyridine-2-carbaldehyde **III** in the solution as well as in the crystal exists in the amino tautomeric form, the hydrazone of thiophene-2-carbaldehyde **II**, in the imino tautomeric form, and hydrazone of 2-furaldehyde **I**, in the equilibrium of the imino and amino forms with predominance of the former.

According to the literature data [2], the photochromism of quinolinylhydrazones of salicyl aldehyde is most evidently displayed when ethanol is used as a solvent. We have studied the behavior of hydrazones **I–III** in ethanol upon the UV irradiation at 230–290 nm wavelength. It turned out that the difference in the structure of hydrazones in solution also affects their photochemical properties. Thus, for compound **I**, upon irradiation of the solutions for 300 s, the photoinduced hypsochromic shift of the absorption band of the initial form and a decrease in its intensity are observed (Fig. 3a). The spectral pattern is characterized by the presence of the isobestic point, which is indicative of the presence of only two forms in the solution: the initial form and a photoinduced one. The initial form of the hydrazones is not recovered either at room temperature in the dark after 72 h or upon heating to 70°C for 2 h meaning that the photoreaction is irreversible. Similar photoinduced spectral changes are observed for the solution of compound **II**. This is consistent with the earlier obtained data [8]. The increased irradiation time to 780–900 s leads to the decrease in the optical density in the absorption spectra

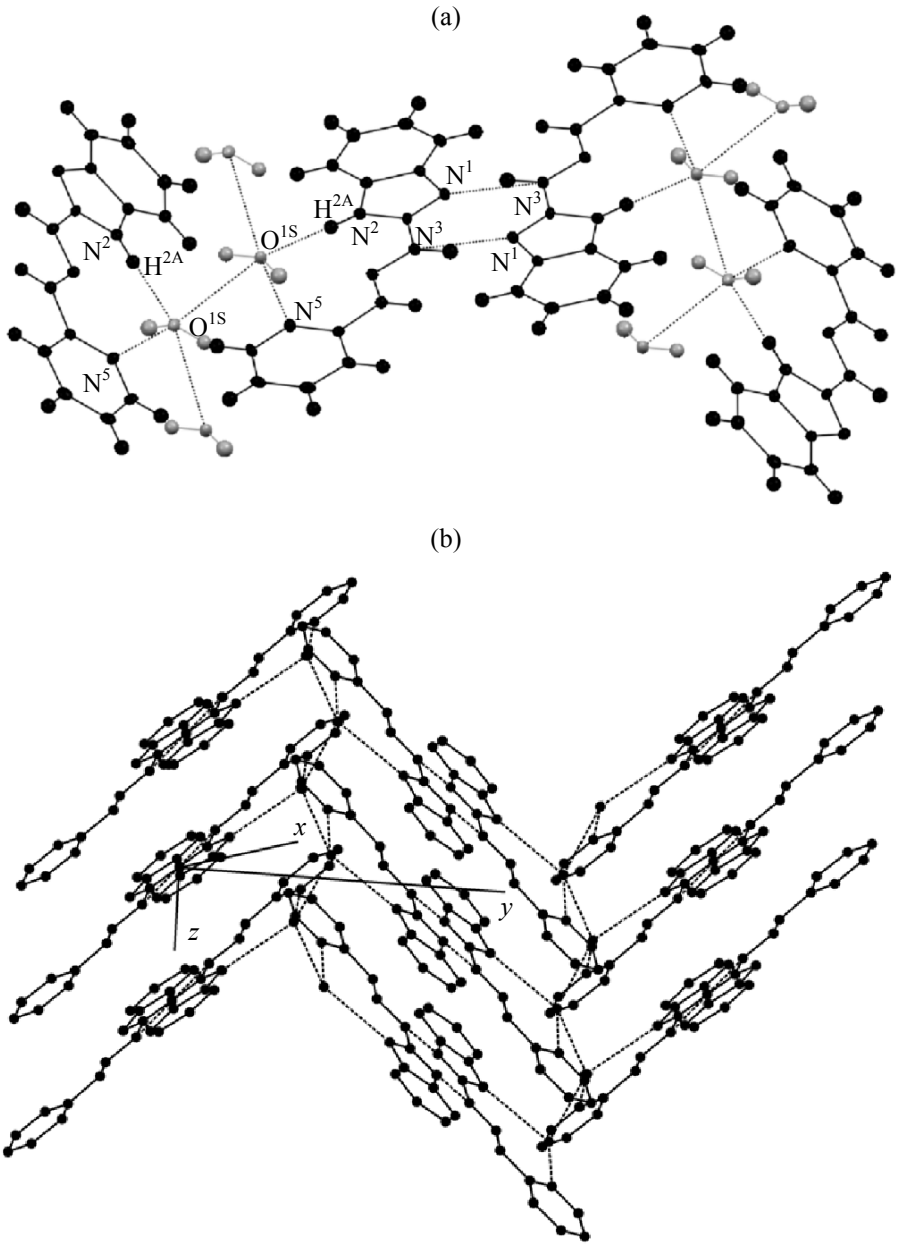


Fig. 2. Structure of (a) pseudodimer and (b) a fragment of packing (B) of molecules of compound **III**.

of the solutions of hydrazones **I, II** in the whole range of the visible part of the spectrum, apparently, due to photodegradation of the compounds.

The irradiation of the ethanol solution of pyridine-containing hydrazone **III** during 30 s results in gradual longwave shift of the absorption maximum by 18 nm followed by small decrease in optical density (Fig. 3c). The obtained colored form of the hydrazone is highly stable: the pattern of the spectrum is not changed either upon further irradiation for 300 s or after staying for 72 h at room temperature in the dark. However, the heating to 70°C for 60 min leads to recovering of the initial form color. The behavior of acetonitrile solutions of hydrazones **I–III** upon irradiation is identical to that in ethanol.

Therefore, the nature of the heterocyclic aldehyde fragment is the factor determining the photochemical properties. This is proved by the results of spectral studies of benzothiazolyl-2-hydrazones of 2-furaldehyde **IV**, thiophene-2-carbaldehyde **V**, pyridine-2-

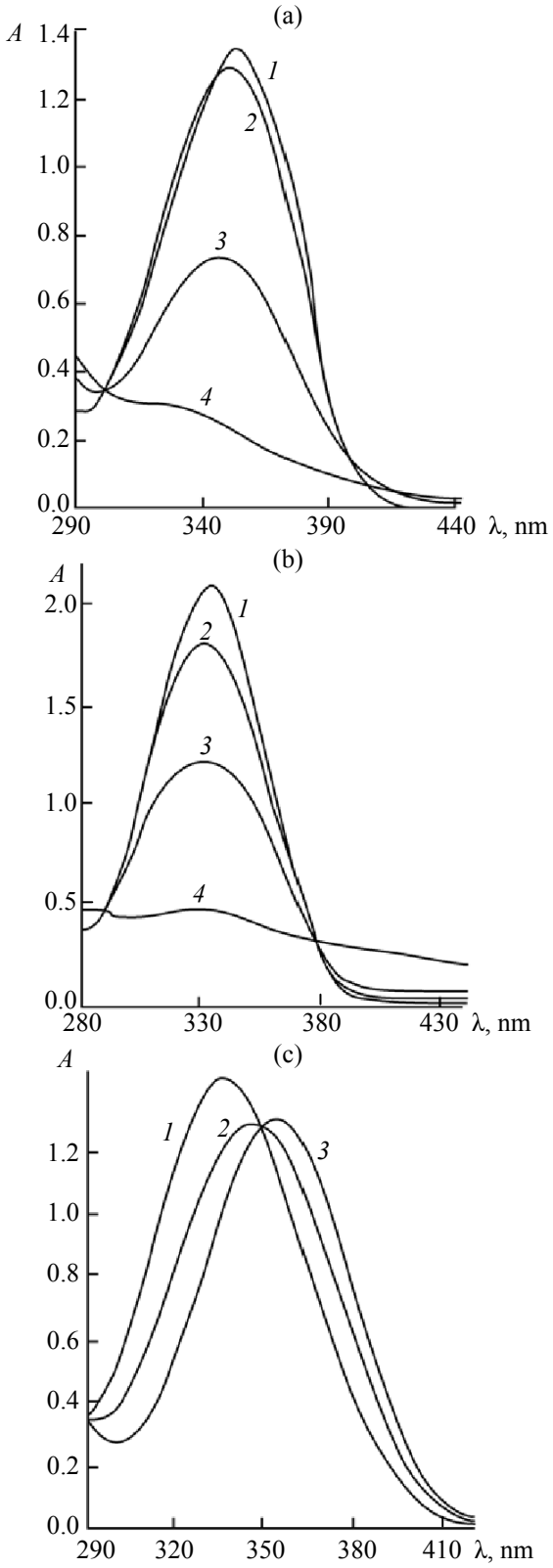


Fig. 3. Absorption spectra of ethanol solutions of hydrazones (a) **I**, (b) **II**, and (c) **III** at 20°C: for **I, II** (*1*) before and (*2*) after irradiation during 10 s, (*3*) 30 s, (*4*) 300 s; for **III** (*1*) before and (*2*) after irradiation during 4 s, (*3*) 30 s.

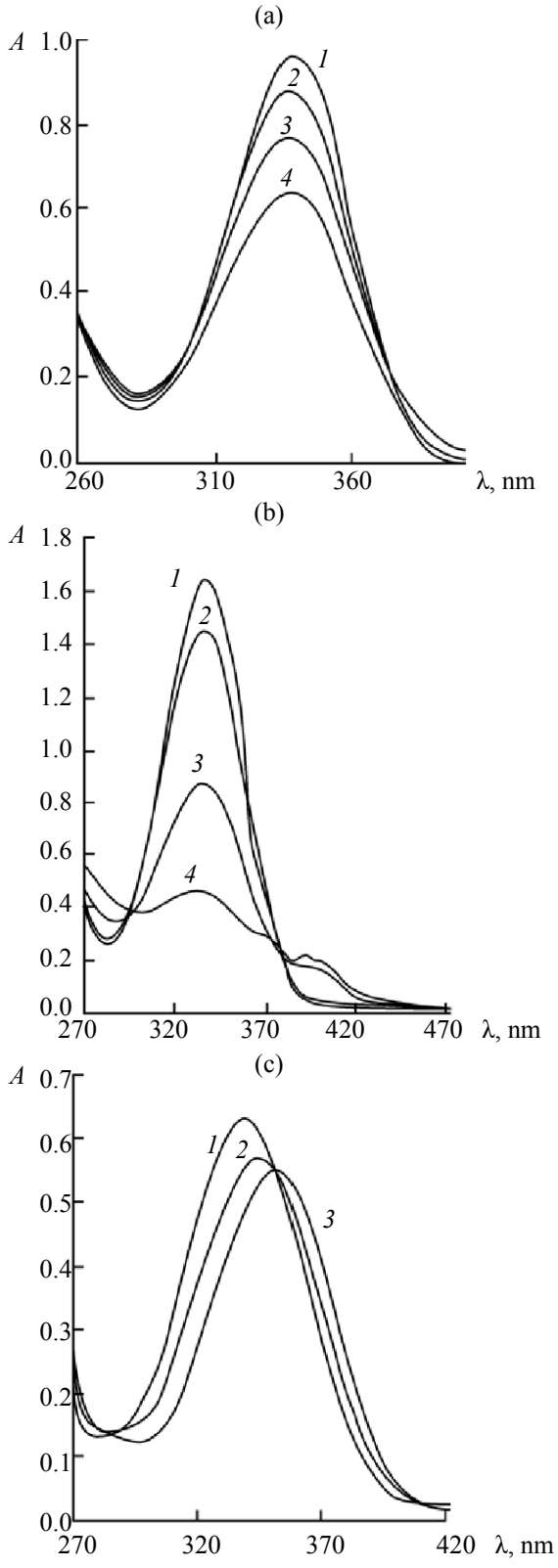
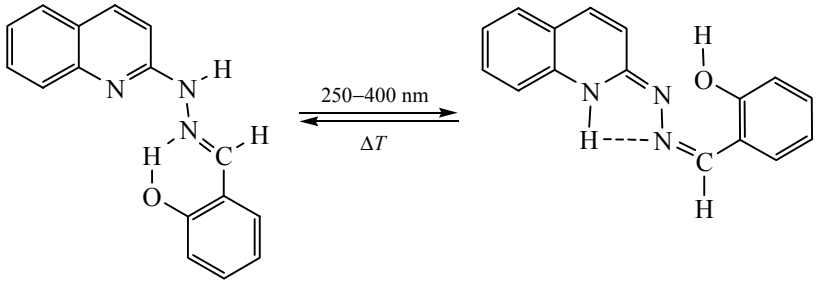


Fig. 4. Absorption spectra of ethanol solutions of hydrazones (a) **IV**, (b) **V**, and (c) **VI** at 20°C: for **IV, V** (*1*) before and (*2*) after irradiation during 10 s, (*3*) 30 s, (*4*) 300 s; for **VI** (*1*) before and (*2*) after irradiation during 4 s, (*3*) 30 s.

carbaldehyde **VI**. Upon irradiation of the ethanol solutions of compounds **IV, V**, as in the case of compounds **I, II**, a blue shift of the absorption band of the initial form is observed and the process is irreversible (Figs. 4a, 4b), while the behavior of compound **VI** upon irradiation is characterized by the same photoinduced spectral changes as those for compound **III** (Fig. 4c). Consequently, photochemical properties of compounds **I–VI** are determined by different processes of phototransformations.

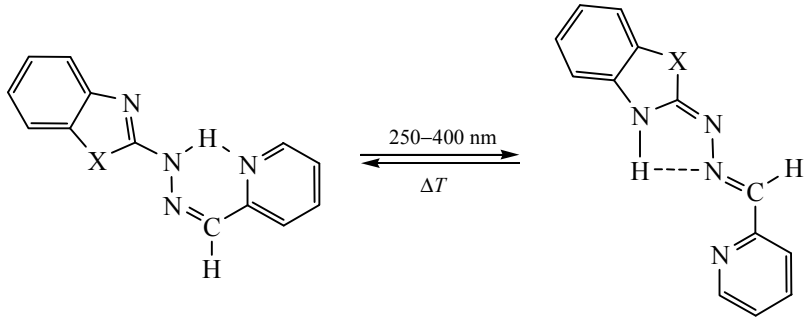
The spectral changes occurring upon irradiation of the hydrazones of pyridine-2-carbaldehyde **III, VI** are similar to those described earlier [2, 9] for the quinoline hydrazone of salicyl aldehyde **VII**. Thus, after UV irradiation (λ = 250–400 nm) of the ethanol solution of compound **VII**, the initial form (λ_{max} = 358 nm) is practically completely (90–93%) converted into a very stable colored form (λ_{max} = 400 nm). The return to the initial state occurs in the dark but slowly ($t_{1/2}$ ≈ 5–6 h in ethanol), or upon heating. The phototransformation of the quinoline hydrazone of salicyl aldehyde **VII** was found to include two photoreactions [2]: the transition from α-amino- into α-iminoquinoline and the *E*→*Z* isomerization at the N=C double bond of the hydrazone chain (Scheme 1).

Scheme 1.



The data on the structure of hydrazones of pyridine-2-carbaldehyde **III, VI** and similar changes occurring in the absorption spectra of these hydrazones and hydrazone **VII** upon irradiation of their solutions allow an assumption that the mechanism of phototransformation of hydrazones **III, VI** also includes the transition of the amino form (with proton transfer) to the imino form and the *E*→*Z* isomerization at the N=C double bond of the hydrazone chain (Scheme 2).

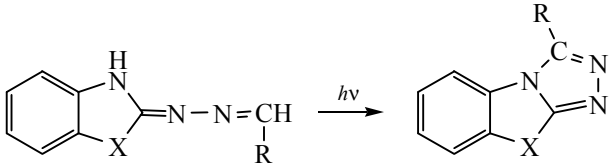
Scheme 2.



X = NH (**III**), S (**VI**).

It can be assumed that the irreversible phototransformations of hydrazones **I, II, IV, V** are due to their photocyclization to fused triazolobenzazoles, similar to the oxidative cyclization readily occurring in a number of hetarylhydrazones [10] (Scheme 3).

Scheme 3.



R = (**I, IV**), (**II, V**).

Therefore, based on the spectral data, it was found that benzazolyl-2-hydrazones of 2-furaldehyde and thiophene-2-carbaldehyde are light sensitive. Hydra-

Table 1. Crystallographic and experimental data for compound **III**

Parameter	Value
Empirical formula	$C_{13}H_{13}N_5O$
Molecular mass	255.28
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell	
a, Å	13.738(4)
b, Å	4.6172(17)
c, Å	18.979(4)
α, deg	90
β, deg	91.25(2)
γ, deg	90
V, Å^{-3}	1203.6(6)
Z	4
ρ_{calc}, g cm^{-3}	1.409
μ, ms^{-1}	0.096
Scanning range, θ/deg	2.97–26.37
Completeness for θ = 26.00°	95.8 %
Number of measured reflections	6107
Independent reflections	2354 (R_{int} = 0.0747)
Number of reflections with $I > 2\sigma(I)$	848
Calculated parameters	184
S on F^2	0.994
R_1; wR_2 [$I > 2\sigma(I)$]	0.0577; 0.1225
R_1; wR_2 (through all reflections)	0.1838; 0.1363
$\delta c_{max/min}$, e/Å^{-3}	0.245 and –0.185

Table 2. Atomic coordinates [×10^4] and isotropic thermal parameters [×10^3 Å] for compound **III**

Atom	x	y	z	U_{eq}
N^4	3576(2)	221(8)	4390(2)	43(1)
N^1	5387(3)	5461(8)	4055(2)	46(1)
N^5	2138(2)	–3764(8)	4157(2)	50(1)
N^2	4424(2)	3047(7)	3313(2)	49(1)
C^9	2475(3)	–3234(9)	4811(2)	41(1)
O^{1S}	2793(2)	–825(7)	2873(2)	59(1)
N^3	4282(3)	2190(8)	4534(2)	45(1)
C^{10}	2107(3)	–4629(9)	5392(2)	48(1)
C^8	3241(3)	–1049(10)	4912(2)	44(1)
C^1	4692(3)	3607(10)	3980(2)	40(1)
C^7	5602(3)	6205(9)	3366(2)	40(1)
C^{11}	1375(3)	–6582(10)	5281(2)	55(1)
C^{12}	1025(3)	–7135(10)	4621(3)	57(1)
C^2	5008(3)	4700(9)	2889(2)	44(1)
C^5	6361(3)	8316(10)	2389(2)	54(1)
C^{13}	1435(3)	–5655(10)	4072(2)	57(1)
C^4	5758(3)	6847(11)	1930(2)	59(1)
C^6	6305(3)	8067(9)	3102(2)	52(1)
C^3	5068(3)	4979(9)	2176(2)	53(1)

zones of pyridine-2-carbaldehyde are photochromes and the mechanism of their phototransformation includes proton transfer and the $E \rightarrow Z$ isomerization at the C=N bond of the hydrazone chain.

EXPERIMENTAL

Electron absorption spectra were registered on a SF-256UVI spectrophotometer (LOMO) in 1.01 cm quartz cells. ^{1}H NMR spectra were recorded on a Tesla BS-587A spectrometer (400 MHz) from 5% solutions in CD_3CN. Elemental analysis was performed on a Vario EL-III Elementar CHN-analyzer, the error of determination was 0.1%. XRD structural analysis was performed on an automatic diffractometer Xcalibur 3 with CCD detector, using the standard procedure (MoK_α irradiation, graphite monochromator, 295 K, ω-scanning, step 1°). The structure was solved and refined using the SHELX program package [11] by full-matrix least-square method on F^2 in the anisotropic approximation for all nonhydrogen atoms. Hydrogen atoms were localized from the peaks of spatial electron density and included into refinement in the isotropic approximation in the *rider* model with dependable thermal parameters. Hydrogen atoms included into the system of hydrogen bonds were refined independently in the isotropic approximation. Principal parameters of X-ray analysis are given in Table 1, atomic coordinates and isotropic thermal parameters, in Table 2, selected bond lengths and bond angles, in Table 3.

As a source of the UV irradiation, a VRM-1 lamp in the range 230–290 nm was used.

Purity of the synthesized hetarylhydrazones was monitored by the TLC method.

Benzimidazolyl-2-hydrazone of 2-furaldehyde I. The solution of 2.9 g (1.96 mmol) of 2-hydrazino-1*H*-benzimidazole and 1.88 g (1.96 mmol) of 2-furaldehyde in 30 ml of isopropanol was refluxed for 5 min.

Table 3. Selected bond lengths (*d*) and bond angles (ω) for compound **III**

Bond	*d*, Å	Angle	ω, deg
N^4–C^8	1.248(4)	$C^8N^4N^3$	115.5(3)
N^4–N^3	1.353(4)	$C^1N^1C^7$	103.5(3)
N^1–C^1	1.287(5)	$N^1C^7C^2$	110.7(4)
N^1–C^7	1.390(4)	$N^1C^7C^6$	130.8(4)
N^5–C^{13}	1.310(5)	$N^1C^1N^2$	114.9(4)
N^5–C^9	1.338(4)	$N^1C^1N^3$	123.4(4)
N^2–C^1	1.337(4)	$N^2C^1N^3$	121.7(4)
N^2–C^2	1.378(5)	$N^5C^9C^8$	118.7(4)
C^9–C^8	1.467(5)	$N^4N^3C^1$	118.1(4)
N^3–C^1	1.370(5)	$C^3C^2N^2$	132.8(4)

Table 4. Hydrogen bonds with parameters H···A < *r*(A) + 2.000 Å and ⟨DHA⟩ 110° for compound **III**

D–H···A bond	Distance, Å			D–H···A angle, deg
	D–H	H···A	D···A	
N^2–H^2···A	0.860	2.114	2.972	176.06
N^3–H^3	0.989	1.959	2.916	162.26
O^{1S}–H^{1S}···A	0.897	2.103	2.946	156.16
O^{1S}–H^{1S}···A	0.897	2.435	3.090	130.03
O^{1S}–H^{2S}···A	0.888	2.248	2.816	121.53

After cooling the crystalline precipitate was filtered off, washed with small amount of cooled ethanol, and dried. Yield 69.93%, mp 202–203°C. ^{1}H NMR (CD_3CN, ppm): 11.5–8.1 br.s (1.7H, N*H*), 7.94 s (1H, N=C*H*), 7.60 m (1H, furan), 7.30 m (2H, benzimidazole), 7.05 m (2H, benzimidazole), 6.75 m (1H, furan), 6.55 m (1H, furan). Found, %: C 59.21, H 5.0, N 22.31. *M* 244.28 $C_{12}H_{10}N_4O\cdot H_2O$. Calculated, %: C 59.0, H 4.96, N 22.41.

Benzimidazolyl-2-hydrazone of thiophene-2-carbaldehyde II was prepared similar to compound **I**. Yield 89.45%, mp 260–262°C. ^{1}H NMR (CD_3CN, ppm), 9.37 br.s (2H, N*H*), 7.73 s (1H, N=C*H*), 7.5 m (1H, thiophene), 7.34 m (1H, thiophene), 7.07–7.00 m (5H, benzimidazole, thiophene). Found, %: C 59 H 4.42, N 23.34. *M* 242.33 $C_{12}H_{10}N_4S$. Calculated, %: C 59.47, H 4.17, N 23.13.

Benzimidazolyl-2-hydrazone of pyridine-2-carbaldehyde III was prepared similar to compound **I**. Yield 90.55%, mp 270–272°C. ^{1}H NMR (CD_3CN, ppm): 10.15 br.s (1H, N*H*), 8.57 m (1H, pyridine), 8.14 m (1H, pyridine), 8.07 s (1H, N=C*H*), 7.81 m (1H, pyridine), 7.30 m (3H, benzimidazole, pyridine), 7.08 m (2H, benzimidazole). Found, %: C 59.27, H 5.17, N 26.31. *M* 264.32 $C_{13}H_{11}N_5\cdot 1.5H_2O$. Calculated, %: C 59.07, H 5.35, N 26.05.

Benzthiazolyl-2-hydrazones of 2-furaldehyde IV, of thiophene-2-carbaldehyde V and of pyridine-2-carbaldehyde VI were synthesized by the procedures described in [12, 13, 14], respectively.

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