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Synthesis and Photochromic Properties of 2-(3-Nitro-2-pyridylmethyl)benzazoles

E. R. Zakhs†, A. I. Ponyaev, M. A. Subbotina, and A. V. El'tsov†

St. Petersburg State Institute of Technology, Petersburg, Russia

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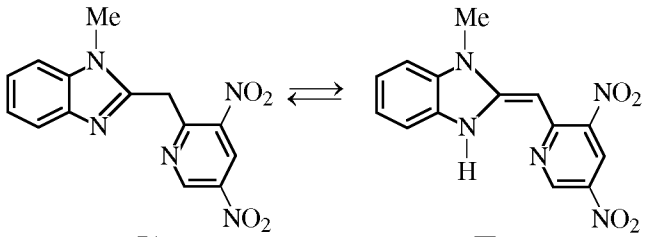
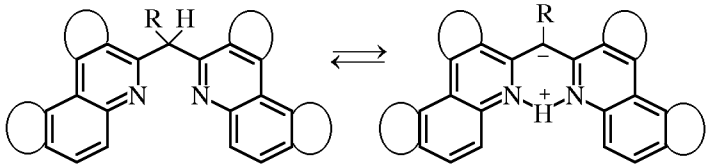
Abstract — 2-(3-Nitro-2-pyridylmethyl)benzazoles were synthesized, and their photochromic properties were studied by flash photolysis. Introduction of a nitropyridyl instead of the nitrophenyl moiety into the 2-methyl group insignificantly increases the basicity of the methylene group. Nitropyridyl-substituted benzazoles give rise to three detectable photoinduced forms: the corresponding anion at pH > 10, azamerocyanine at pH ≈ 4 , and monomethinecyanine at pH ≈ 1. Irradiation of solutions of weakly basic benzoxazole and benzothiazole derivatives at pH ≈ 4 results in formation of neutral chelate structures in which the hydrogen atom is linked simultaneously to two nitrogen atoms: one in the pyridine ring, and the second, in the azole ring.

Photochromic properties of *ortho*-nitroalkylaromatic compounds originate, depending on the acidity of the medium, either from transfer of hydrogen atom from the alkyl to nitro group (as a result, *aci*-nitro isomer is formed) or from ionization of the alkyl group with formation of mesomeric anion [1, 2]. When the molecule contains a basic center, light-induced hydrogen transfer from the alkyl group to such center is possible. In the latter case, the corresponding azamerocyanine is detected as colored isomer. With dinitrobenzyl derivatives of benzimidazole and 2-(2,4-dinitrobenzyl)pyridine as examples we previously showed [3] that these bases, their protonated forms, photochemically generated anion, and azamerocyanine are interrelated through a system of acid–base equilibria. The decoloration process, i.e., the formation of the original *o*-nitroalkyl derivative, is catalyzed by acids, and its rate depends on the nature of the substituents and heteroring [4, 5].

Photochromic compounds of this type are more advantageous than the others due to the lack of reverse photoreaction; theoretically, this provides the possibility for attaining 100% conversion into the colored form and a large contrast in the absorption of the initial and photoinduced forms (Δλ 200–300 nm). All compounds of this type reported up to now contain a nitroaryl moiety as photoactive center. In the present work we have synthesized 2-(3-nitro-2-pyridyl-



IA **IB**



IIA **IIB**

† Deceased.

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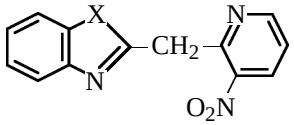
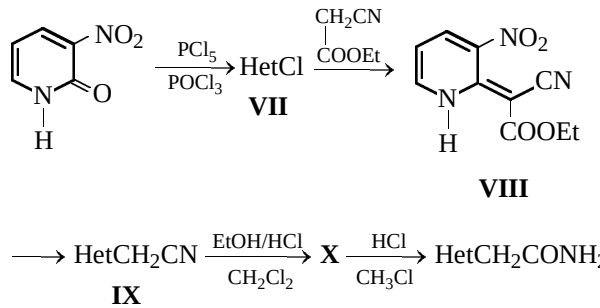
methyl)benzazoles and examined their photochromic properties. Replacement of the 2,4-dinitrobenzyl fragment by 3,5-dinitro-2-pyridylmethyl in the series of benzimidazole derivatives gave strongly colored compounds of the dihydrobenzimidazole series [6].

Heterocyclic fragments in the molecules of (dinitropyridylmethyl)benzimidazole **I** possess strongly different basicities; therefore, protonation of these compounds occurs mainly at the imidazole ring. As follows from the electronic absorption spectra of the model 1,3-dimethyl-2-(3,5-dinitro-2-pyridylmethylene)-2,3-dihydrobenzimidazole, compounds **I** exist as isomers **IB**. This structure is fully consistent with the structure of colored isomers of diquinolylmethanes **II** and their analogs in which two heterocyclic systems are linked through a methylene bridge. Enhanced acidity of the bridging unit in **II** gives rise to displacement of the tautomeric equilibrium from a colorless methane isomer **IIA** to an intensely colored chelate structure like **IIB** or a bis-*cis*-structure with protonated heteroring [7]. In order to reduce the electron-acceptor influence of the dinitropyridine fragment, we made an attempt to synthesize compounds with one nitro group in the pyridine moiety.



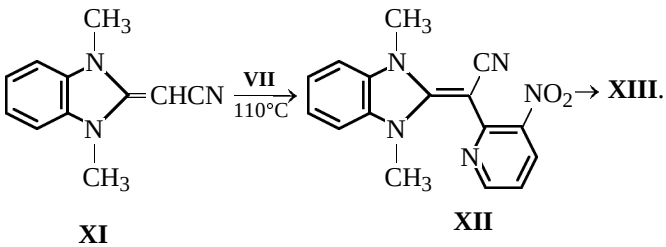
III, X = NMe; **IV**, X = NH; **V**, X = O; **VI**, X = S.

We planned to prepare 2-(3-nitro-2-pyridylmethyl)-benzazoles **III**–**VI** using the imidate technique, but we failed to obtain required amounts of the corresponding imidate. 2-Chloro-3-nitropyridine (**VII**) [8] fairly readily reacted with ethyl cyanoacetate to afford an orange ethyl (3-nitro-1,2-dihydro-2-pyridylidene)-cyanoacetate (**VIII**). Katz and Voyle [9] and Willette [10] reported on their failure to obtain (3-nitro-2-pyridyl)acetonitrile (**IX**) by hydrolysis of **VIII**. Therefore, Katz and Voyle [9] used *tert*-butyl cyanoacetate for the synthesis of nitropyridylacetonitriles. We succeeded in obtaining pyridylacetonitrile **IX** in 70% yield by heating compound **VIII** in boiling 1 M hydrochloric acid. The IR spectrum of product **IX** characteristically contained bands from the CN and NO_2 groups. On dissolution in 0.01 N NaOH ”®-originally colorless compound **IX** gives a colored anion (λ_{max} 560, 590 nm), which absorbs at a longer wavelength than anions derived from the known (2,4-dinitrophenyl)- and (2,4-dinitronaphthyl)acetonitriles (445, 550 and 440, 580 nm, respectively). The ^{1}H NMR spectrum of **IX** in acetone almost coincided with that reported in [9] for deuterochloroform solution, which unambiguously proves its structure. Trifluoroacetic acid protonates the pyridine ring: signals from all protons shift downfield by 0.35 (singlet from the methylene group) and 0.55 ppm (multiplet from 3-H), and the 2-H and 4-H protons give rise to one signal at about δ 9.1 ppm. Our attempt to obtain ethyl (3-nitro-2-pyridyl)acetimidate by addition of ethanol to nitrile **IX** in ether in the presence of HCl was also unsuccessful: The initial compound remained unchanged. The same reaction in methylene chloride gave a color- less intermediate product (compound **X**) with mp 119–120°C. Its ^{1}H NMR spectrum in trifluoroacetic acid lacked signal from ethyl group, a singlet from the CH_2 group was located at δ ~5 ppm, the 3-H signal was observed at δ 8.3 ppm, and the 2-H and 4-H protons gave a multiplet at δ 9.2 ppm; in addition, a one-proton triplet (1 : 1 : 1; J = 52 Hz) was observed at δ 6.7 ppm. Presumably, the latter belongs to the proton on the cyano nitrogen atom. This is consistent with the absence of CN stretching vibration band in the IR spectrum of **X**. Repeated saturation with hydrogen chloride of a solution of **X** and EtOH in chloroform gave (after appropriate workup) (3-nitro-2-pyridyl)acetamide.



Het = 3-nitro-2-pyridyl.

The second version of the synthesis of compounds **III**–**VI** implied introduction of a nitropyridyl fragment into activated methylene group of (benzazolyl)acetonitriles or (benzazolyl)acetates. Preliminarily, we tried to find conditions under which chloronitropyridine **VII** is capable of reacting with 1,3-dimethyl-2-(cyanomethylene)-2,3-dihydrobenzimidazole (**XI**).



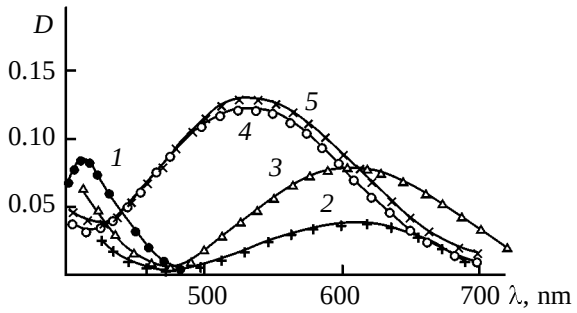
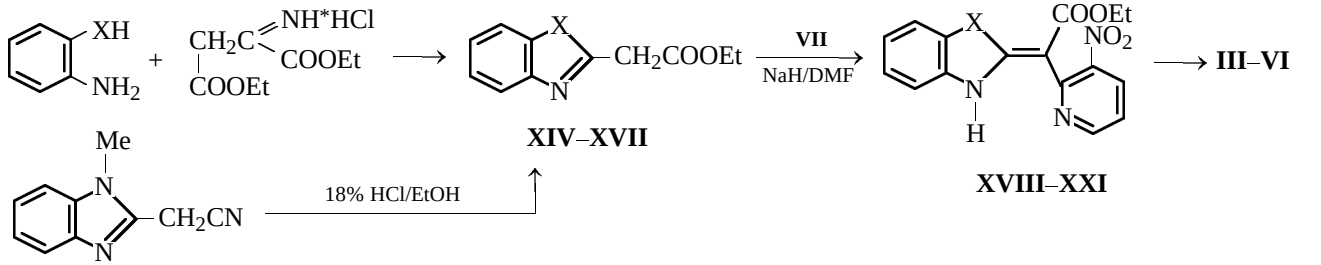


Fig. 1. Electronic absorption spectra of photoinduced forms of (*1*–*4*) 1-methyl-2-(3-nitro-2-pyridylmethyl)-benzimidazole (**III**), $c = 7.2 \times 10^{-5}$ M, and (*5*) its anion, $c = 7.2 \times 10^{-5}$ M, in water containing 1% of ethanol; (*1*) pH 1.04, (*2*) pH 3.15, (*3*) pH 4.3, (*4*) pH 11.75, and (*5*) 2.5 N KOH.

Fusion of the reactants at 110°C in 40 min afforded dark red compound **XII** whose spectral parameters and elemental composition were in agreement with the given formula. However, our attempt to remove the cyano group from **XII** by solvolysis in methanol in the presence of hydrogen chloride resulted in elimination of the pyridyl moiety, yielding product **XIII**.

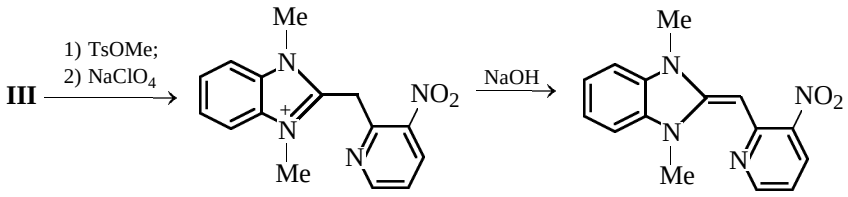
Therefore, in further experiments we took advantage of using not the cyano but the more readily removable ethoxycarbonyl group. By condensation of *ortho*-substituted anilines with ethyl ethoxycarbonylacetimidate hydrochloride [11] we obtained (2-benzazolyl)acetates **XIV**–**XVII**. Compounds **XIV** and **XV** were also prepared from the corresponding 2-(cyanomethyl)benzimidazoles by the action of HCl in alcohol. The reaction of **XIV** with chloronitropyridine **VII** was carried out by melting in DMSO with dimethyl sulfoxide sodium salt as base. The best results were obtained when the reaction was performed in DMF in the presence of sodium hydrides. Unlike the reaction with 2-chloro-3,5-dinitropyridine [6], the arylation at the nitrogen atom almost did not occur. Ester **XVIII** was difficult to purify, but this procedure was unnecessary for the subsequent hydrolysis. Compound **XVIII** was isolated as a dark brown oil which showed in the IR spectrum absorption bands from stretching vibrations of the ester carbonyl and nitro groups (1750 and 1520, 1355 cm^{-1}, respectively). The developed procedure was also suitable for preparation of the other benzazoles. Esters **XVIII**, **XIX**, and **XXI** are red or orange, while the weakly basic benzoxazole derivative **XX** is colorless; i.e., the latter has a structure of bis(heteryl)acetate. Target compounds **III**–**VI** were then synthesized from esters **XVIII**–**XXI** by hydrolysis of the ethoxycarbonyl group in boiling 10% hydrochloric acid:



XIV–**XVII** **XVIII**–**XXI**

XIV, **XVIII**, X = NMe; **XV**, **XIX**, X = NH; **XVI**, **XX**, X = O; **XVII**, **XXI**, X = S.

1,3-Dimethyl-2-(3-nitro-2-pyridylmethyl)benzimidazolium perchlorate **XXII** was obtained by quaternization of benzimidazole derivative **III** with methyl *p*-toluenesulfonate, followed by treatment with sodium perchlorate. Salt **XXII** was converted into deeply colored 1,3-dimethyl-2-(3-nitro-2-pyridylmethylene)-2,3-dihydrobenzimidazole (**XXIII**) by the action of 0.01 N alcoholic potassium hydroxide:



XXII **XXIII**

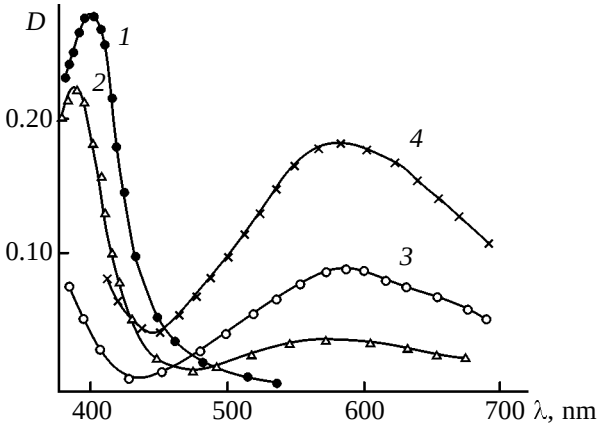


Fig. 2. Electronic absorption spectra of photoinduced forms of (*1–3*) 2-(3-nitro-2-pyridylmethyl)benzoxazole (**V**), $c = 5.85 \times 10^{-5}$ M, and (*4*) its anion, $c = 1.4 \times 10^{-5}$ M, in water containing 1% of ethanol; (*1*) pH 1.06, (*2*) pH 4.2, (*3*) pH 10.75, and (*4*) 2.5 N KOH.

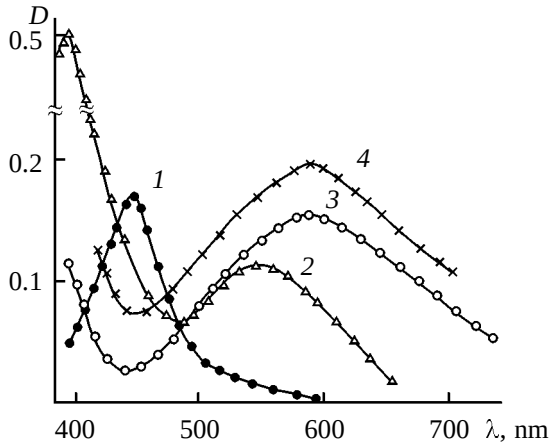
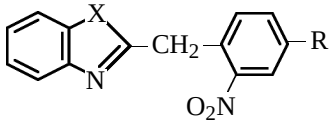


Fig. 3. Electronic absorption spectra of photoinduced forms of (*1–4*) 2-(3-nitro-2-pyridylmethyl)benzothiazole (**VI**), $c = 1.9 \times 10^{-4}$ M, in water containing 1% of ethanol; (*1*) pH 0.75, (*2*) pH 4.15, (*3*) pH 10.7, and (*4*) 2.5 N KOH.

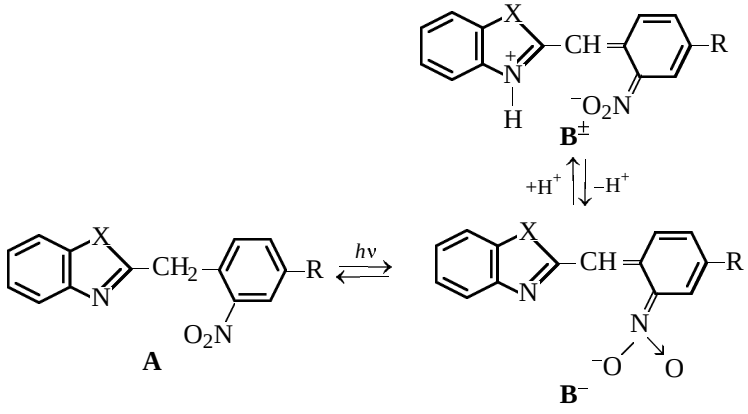
Photochromic properties of nitropyridylmethylbenzazole derivatives **III**–**VI** were studied by flash photolysis and were compared with those found for mononitro- (**XXIV**, **XXV**) and dinitrobenzyl analogs (**XXVI**–**XXIX**):



XXIV, X = NH, R = H; **XXV**, X = O, R = H; **XXVI**, X = NCH_3, R = NO_2; **XXVII**, X = NH, R = NO_2; **XXVIII**, X = S, R = NO_2; **XXIX**, X = O, R = NO_2.

Flash photoexcitation of compounds **III**–**VI** in aqueous and aqueous-ethanolic solutions gives rise to reversible absorption in the visible region (Figs. 1–3). As with compounds **XXIV**–**XXIX**, the rate constants of decoloration and the spectra of photoinduced forms depend on pH.

In the case of mono- (**XXIV**, **XXV**) [12] and dinitrobenzylbenzazoles (**XXVI**–**XXIX**) [5], two colored photoinduced forms are observed (anion $\mathbf{B}^-$ at pH > 8.5 and azamerocyanine $\mathbf{B}^{\pm}$ at pH < 4), whereas for compounds **III**–**VI** we detected three photoinduced forms.

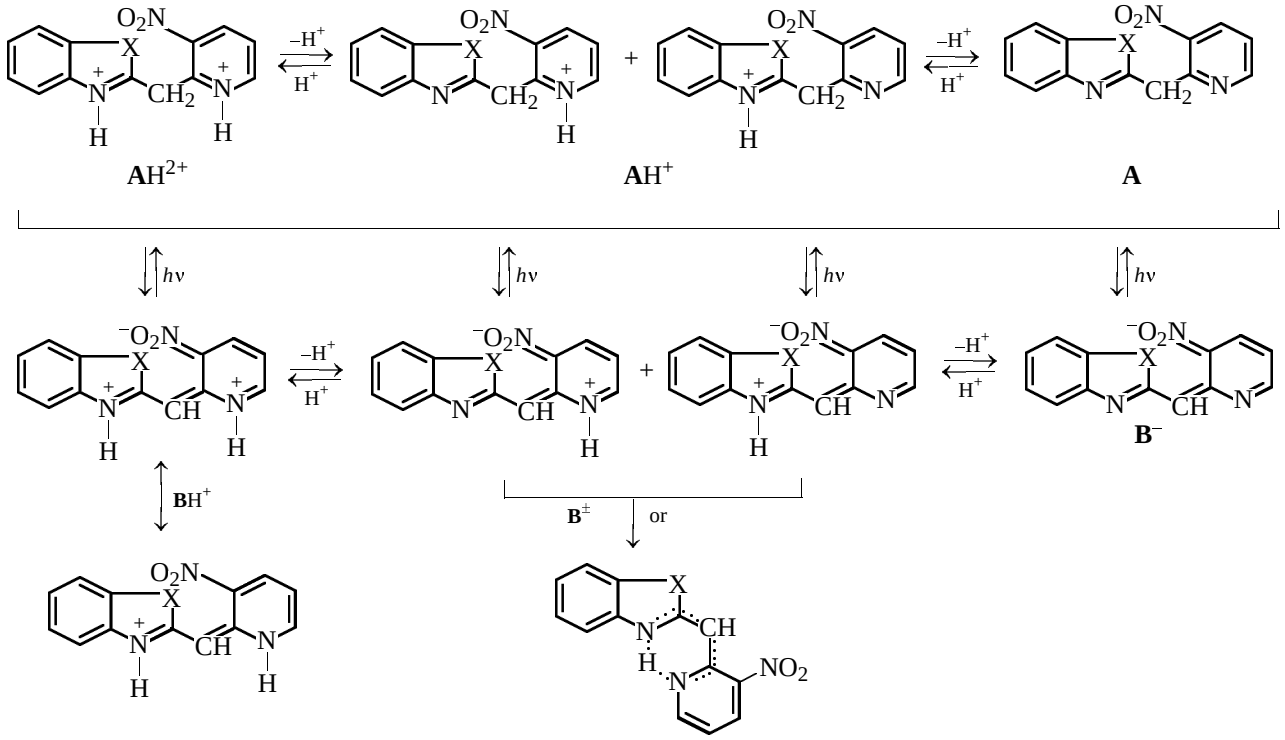


At pH 0–2 the colored forms are characterized by absorption maxima at λ 408 nm for benzimidazoles **III** and **IV** and benzoxazole **V** and λ 450 nm for benzothiazole derivatives **VI**. In less acidic media (pH ~4) the long-wave absorption maxima are λ_{max} 600, 550, and 580 nm for compounds **III**, **VI**, and **V**, respectively. In alkaline medium (pH > 10) we observed colored forms with λ_{max} 540 nm for com-

pounds **III** and **IV** and ~595 nm for benzoxazole and benzothiazole derivatives **V** and **VI**. We believe that mesomeric anions are generated from all three types of compounds in aqueous–alcoholic buffer solutions with pH > 10, for the absorption spectra of their photoinduced forms (the shape and position of the absorption bands) are similar to those observed for the corresponding anions obtained by dark ionization in much more alkaline solutions (Fig. 1–3). The color of the anion depends on the nature of the heteroring which is involved in the chromophore system.

In strongly acidic media (pH 0–1) both initial neutral molecule **A** and its mono- ($\mathbf{A}H^+$) and diprotonated salts ($\mathbf{A}H_2^+$) can undergo photolysis simultaneously. Protonation of both heterocyclic fragments, at least for benzimidazole derivatives **III** and **IV**, is quite probable: the pK_a values of 3-nitropyridine, 2-(2,4-dinitrobenzyl)benzimidazole, and benzothiazole are 0.81 [13], 3.95 [3], and 1.2 [14], respectively. Therefore, the detectable colored species may be monomethinecyanine like $\mathbf{B}H^+$. We previously showed [5] that the basicity of heterocycle in anion is greater than in the original molecule, so that monomethinecyanine $\mathbf{B}H^+$ can be formed not only from dication $\mathbf{A}H_2^+$ but also via protonation of azamerocyanine $\mathbf{B}^{\pm}$ derived from monocation $\mathbf{A}H^+$ (Scheme 1).

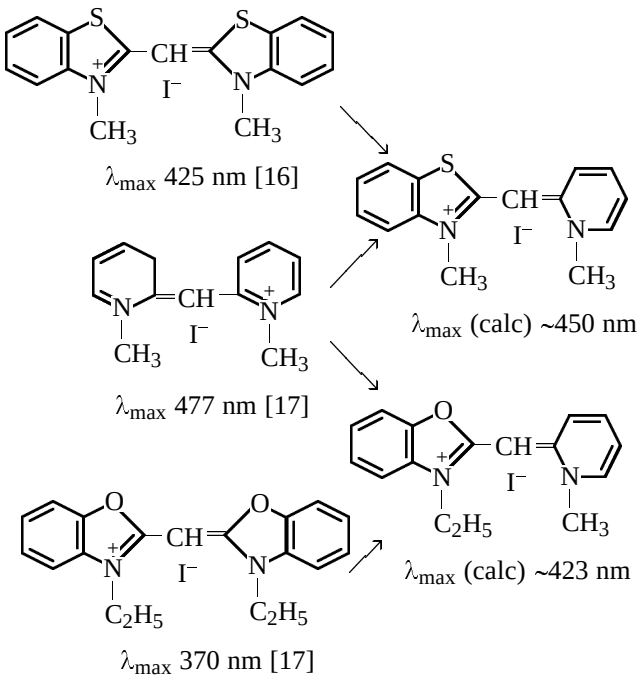
Scheme 1.



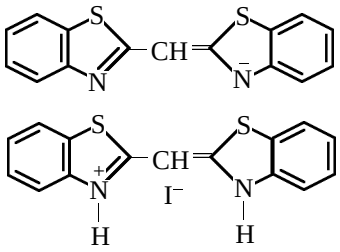
According to Kiprianov [15], the color of an unsymmetric monomethinecyanine dye is determined by addition of colors of the two symmetric parent dyes; here, the deviation from additivity depends on the difference in the basicity of two heterorings involved. Unfortunately, we have found no published data on symmetric monomethinecyanines on the basis of benzimidazole and nitropyridine. From the data for symmetric monomethinecyanines based on benzothiazole (benzoxazole) and pyridine we can estimate absorption maxima of unsymmetric dyes without taking into account the deviation and influence of the nitro groups (Scheme 2).

Such approximation is fairly justified, for the nitro group in the pyridine ring could strongly affect only the color of the anion through delocalization of the negative charge (the anion is thus stabilized). However, it is incapable of delocalizing positive charge and hence of stabilizing cations. These statements are supported, e.g., by the similar in the absorption spectra of bis(benzothiazolyl)methane in acidic and

Scheme 2.



alkaline alcoholic solutions [18] due to the similarity in the chromophoric systems of the cation and anion.



Therefore, the spectra of cations containing a nitro group and lacking it should be similar. The calculated values of λ_{max} of unsymmetric monomethinecyanines approach those found for the colored photoinduced forms of nitropyridylmethyl derivatives of benzoxazole (**V**) and especially of benzothiazole (**VI**) at pH 0–1 (Figs. 1–3). This fact counts in favor of the monomethinecyanine structure of the colored forms of 2-nitropyridylmethylbenzazoles in strongly acidic media. The greater difference in the calculated and experimental values of λ_{max} for benzoxazole **V**, as compared to benzothiazole **VI**, may be attributed to the greater difference in the basicity of these heterocycles, on the one hand, and nitropyridine, on the other.

In moderately acidic media (pH ~4) the absorption maximum of the colored species appreciably shifts to the red region. We showed in [12] that at pH ~4 the photoinduced form of 2-(2-nitrobenzyl)benzimidazole

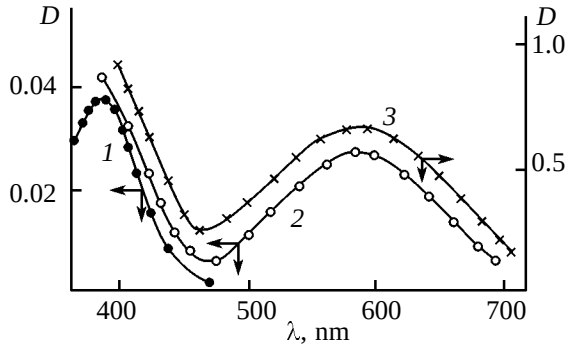
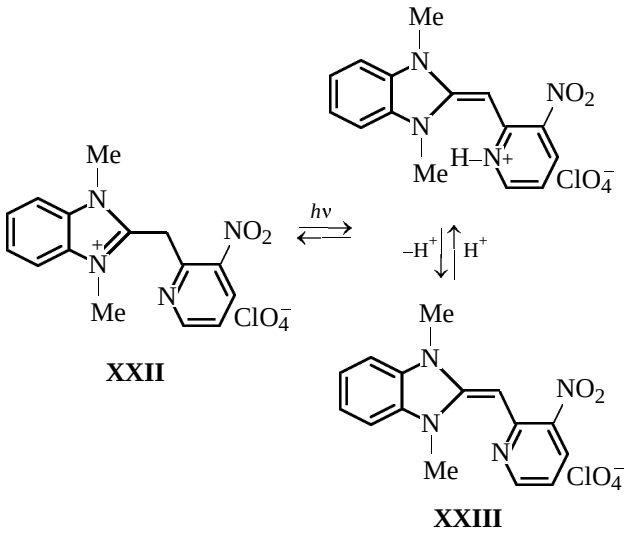


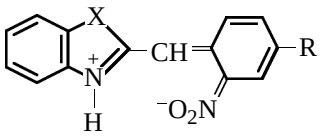
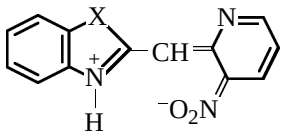
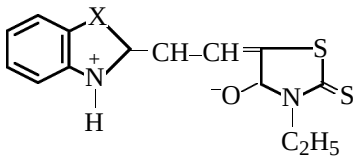
Fig. 4. Electronic absorption spectra of (*1*, *2*) 1,3-dimethyl-2-(3-nitro-2-pyridylmethyl)benzimidazolium perchlorate (**XXIV**), $c = 8.2 \times 10^{-5}$ M, and (*3*) its anion in water containing 1% of ethanol; (*1*) pH 1.07, (*2*) pH 4.4, (*3*) 0.01 N KOH.

has azamerocyanine structure $B^{\pm}$. This conclusion was drawn on the basis of the fact that the absorption spectrum of the colored form coincided with the spectrum of model 2-(2-nitrobenzylidene)-2,3-dihydrobenzimidazole. The spectra of colored species generated from 2-(3-nitro-2-pyridylmethyl)benzimidazoles **III** and **IV** at the same pH values resemble those observed for the nitrophenyl analog; therefore, these species can also be assigned the azamerocyanine structure. This conclusion is proved by the results for a model compound, 1,3-dimethyl-2-(3-nitro-2-pyridylmethyl)benzimidazolium perchlorate (**XXII**). Unlike the carbocyclic analog, flash photoexcitation of compound **XXII** in solutions with various acidities gives rise to two rather than one detectable forms. At pH ~1 the λ_{max} of the photoinduced form is 390 nm, which corresponds to a monomethinecyanine structure; at pH ~4 the long-wave absorption maximum is located at λ 580 nm (Fig. 4). Its shape and position resemble



XXII **XXIII**

Absorption maxima (nm) of photoinduced forms of compounds **III**, **V**, **VI**, **XXIV**, **XXV**, **XXVI**, **XXVIII**, and **XXIX** in aqueous buffer solutions with pH ~4 and of model azamerocyanines based on ethylrodanin in ethanol

X				
	R = H	R = NO_2	**III, V, VI**	
NCH_3	610	520	600	511
O	515	503	380, 580 sh	492
S	–	535	396, 550 sh	526

those observed for base **XXIII** as a model of the azamerocycanine structure (it was prepared by treatment of perchlorate **XXII** with alkali).

Base **XXIII** shows a strong positive solvatochromism, indicating charge delocalization over the chromophore system and lower polarization of the ground state of **XXII**, in contrast to the dinitrobenzyl analog exhibiting a weak negative solvatochromism. Presumably, this difference is responsible for the deeper color of azamerocyanines derived from pyridylmethyl compounds (λ_{max} 600 nm), as compared to the dinitrobenzyl analogs (λ_{max} 520 nm).

At pH ~4 about a half of molecules **III** and **IV** are protonated, and they exist in solution as salts. Therefore, both neutral molecules and the corresponding cations can absorb light. In the two cases, formation of the same colored species is expected; their chromophoric system is analogous to that in 1,3-dimethyl-2-(3-nitro-2-pyridylmethyl)-2,3-dihydrobenzimidazole (**XXIII**) having an azamerocyanine structure. The common azamerocyanine nature of the colored species generated from nitrobenzyl (**XXIV**) and nitropyridylmethyl derivatives (**III** and **IV**) under the given conditions is also confirmed by similar shifts of their absorption bands relative to the corresponding anions. In all cases, azamerocyanines derived from dihydrobenzimidazoles have a deeper color than their anions. The same pattern in the variation of λ_{max} in going from benzimidazole to benzoxazole and benzothiazole heteroring in the series of mono- and dinitrobenzyl derivatives was observed for model merocyanine dyes based on 3-ethylrodanin [19]; however, this pattern slightly differs from that found for nitropyridylmethyl derivatives (see table).

Protonation of benzoxazole and benzothiazole derivatives **V** and **VI** at the azole ring at pH ~4 is hardly probable because of their low basicity (pK_a of benzothiazole is 1.2 [14], and of benzoxazole, –0.5 [20]). Taking into account that the basicity of the heteroring in the anion is greater than in the original molecule, we may presume an azamerocyanine structure of the photoinduced forms of these dyes. As was shown in [5] for the same series of heterocycles, the lower the basicity of the heteroring, the greater the ΔpK_a value.

Unlike dinitrobenzyl derivatives of benzoxazole and benzothiazole **XXIX** and **XXVIII**, 2-nitropyridyl-substituted compounds have two centers with similar basicities: nitrogen atoms in the azole ring and in the nitropyridine ring. Therefore, protonation of the azole and pyridine nitrogen atoms is equally probable. At pH ~4 photoexcitation could give neutral chelate **Ch** as colored species in which hydrogen atom is linked simultaneously to two nitrogen atoms. The strong short-wave absorption maximum of the photoinduced forms of nitropyridylmethylbenzoxazole and nitropyridylmethylbenzothiazole derivatives **V** and **VI** is most likely to result from the chelate structure which is typical of such compounds [7]. The formation of a colored tautomeric form from nitropyridylmethylbenzazoles is governed not only by the acidity of the methylene bridge but also by the ability of heterocyclic nitrogen atoms to chelation. The compounds under study are just those capable of chelating. As we already noted, replacement of the dinitroaryl fragment in the colorless dinitrobenzylbenzimidazole **XXVI** by dinitropyridyl gives rise to appearance of color. This may be due to stabilization of the colored tautomeric form as chelate structure, as also follows from the absence of NH vibration bands in the IR spectrum. Presumably, the formation of chelate azamerocyanine structures from pyridylbenzoxazole and pyridylbenzothiazole derivatives **V** and **VI** is responsible for the observed specific features in their spectral behavior, which differentiate them from the benzyl derivatives (see table).

Thus, introduction of a basic center into the nitrobenzyl chromophore gives rise to an additional photoinduced form having a chelate structure.

EXPERIMENTAL

The molecular weights were determined by reverse ebullioscopy using a Hewlett–Packard B-302 osmometer. The IR spectra of samples pelleted with KBr were obtained on a UR-20 spectrometer. The electronic absorption spectra were measured on a Specord M-40 spectrophotometer. The ^{1}H NMR spectra of solutions in CCl_4 were recorded on a Bruker WP-200 instrument. Photochromic properties of nitropyridylmethylbenzazoles were studied on a modified flash photolysis setup described in [21]. Solutions of the compounds under study were irradiated with an IFP-5000 flash lamp (full spectrum or through a UFS-2 light filter which transmits in the λ range from 270 to 380 nm). The change in the transmission, induced by light flash, was measured using a KGM-12 halogen lamp (100 W) whose irradiation was passed through a 20-cm quartz cell. The outgoing beam (after a DMR-4 monochromator) was recorded at a selected wavelength with a FEU-84 photoelectron multiplier, and the signal was transferred to an S8-13 recording oscillograph or CAMAC spectral–kinetic unit, where it was processed with an FK71-2 AD converter and was transferred through a KK-111 CAMAC crate (manufactured at the Vilnius factory of electrical-type instruments) to a PC. With the aid of special software we obtained kinetic curve for the outgoing signal from the photoelectron multiplier in the time range from 1 ms–200 s and treated it according to first-, second-, and mixed-order equations. The results were output as the corresponding rate constants and deviations of the experimental data from appropriate approximation. The spectrum of the photoinduced form (referred to any moment of time within the kinetic curve) was derived from the set of kinetic curves obtained at different wavelengths. The setup operating in the mode of compensation for a steady component and RC-shunting of noise ensured registration of as small change in the optical density as 0.0005.

3-Nitropyridin-2-one [22]**.** To a solution of 10 g of 2-pyridinone in 50 g of concentrated sulfuric acid we slowly added while stirring and cooling (with an ice–salt mixture) a mixture of 15 g of HNO_3 (d = 1.5) and 5 g of H_2SO_4 (d = 1.84) at such a rate that the temperature did not exceed 10°C. The mixture was then left to stand for 30 min at room temperature. If the mixture spontaneously warmed up to above 30°C, it should be cooled down to room temperature. The mixture was slowly heated to 70–80°C, left to stand for 1 h at that temperature, cooled, and poured onto 200 g of ice. The yellow precipitate was filtered off to obtain 3 g (22%) of 3-nitropyridin-2-one with mp 222–223°C, which can be used in further syntheses without additional purification. The product can be recrystallized from water (1 : 15) or ethanol (1 : 20).

2-Chloro-3-nitropyridine (VII) [23]**.** A mixture of 4 g of 3-nitropyridin-2-one and 8 g of phosphorus pentachloride wetted with 1.5 ml pf phosphoryl chloride was heated for 1 h on a boiling water bath. The brown melt was poured onto 200 g of ice. The yellow precipitate was filtered off, washed with water to neutral reaction of the washings, and recrystallized from 60 ml of a 1 : 1 benzene–petroleum ether mixture. Yield 2.8 g (62%), colorless needles, mp 100–101°C.

1,3-Dimethyl-2-[(3-nitro-2-pyridyl)cyanomethylene]-2,3-dihydrobenzimidazole (XII). A mixture of 0.5 g 2-chloro-3-nitropyridine **VII** and 1.17 g of 1,3-dimethyl-2-cyanomethylene-2,3-dihydrobenzimidazole (**XI**) was kept for 40 min at 110°C. The mixture first turned red and then it melted and solidifed. The solid product was recrystallized from 80 ml of *n*-butanol. Yield 0.75 g (70%), dark red needles. IR spectrum, ν, cm^{-1}: 1330 and 1530 (NO_2), 2130 (CN). Found, N, %: 22.9. $C_{16}H_{13}N_5O_4$. Calculated N, %: 22.8.

Solvolysis of compound XII. A suspension of 0.3 g of compound **XII** in 20 ml of methanol was saturated on cooling with dry hydrogen chloride until the precipitate dissolved completely. The yellow solution was evaporated, and 3 ml of acetone was added to the oily residue. The yellow precipitate (compound **X**) was filtered off. Yield 0.15 g, mp 230°C. IR spectrum, ν, cm^{-1}: 1400, 1520, 1740, 3000. UV spectrum, λ_{max}, nm: in 50% ethanol (neutral solution and a solution containing 0.01 N H_2SO_4): 273, 280; in 0.01 N NaOH: 270, 336. Found N, %: 12.3.

Ethyl (3-nitro-2-pyridyl)cyanoacetate (VIII). To a suspension of 2.42 g of powdered NaOH in 50 ml of DMF we added 7.4 g of ethyl cyanoacetate. A solution of 5 g of 2-chloro-3-nitropyridine in 15 ml of DMF was then added with stirring at 10–20°C over a period of 30 min. The mixture was stirred for 30 min at 25°C and was poured into 1 l of cold water. The orange precipitate was filtered off, washed with water, and recrystallized from 250 ml of ethanol. Yield 5 g (67%), bright orange plates with mp 135–136°C. IR spectrum, ν, cm^{-1}: 1330 and 1530 (NO_2), 1640 (C=O), 2200 (CN). UV spectrum (ethanol; neutral solution and a 0.01 N solution of H_2SO_4), λ_{max}, nm (log ε): 235 (4.26), 280 (3.97), 342 (3.94), 460 (3.22). Found, %: C 51.0; H 3.8; N 17.8. *M* 230

(in toluene). $C_{10}H_9N_3O_4$. Calculated, %: C 50.9; H 4.1; N 17.8. *M* 235.

(3-Nitro-2-pyridyl)acetonitrile (IX). A solution of 1 g of ester **VIII** in 100 ml of 1 M hydrochloric acid was refluxed for 1 h. After cooling, unreacted ester **VIII** (~0.3 g) was filtered off, and the product was extracted from the filtrate into 120 ml of methylene chloride. The extract was washed with a saturated solution of sodium carbonate (2 × 25 ml), dried over sodium sulfate, and filtered through a layer (3–4 cm) of aluminum oxide. The solvent was distilled off, and the solid residue (0.47 g) was recrystallized from 100 ml of benzene–petroleum ether (1 : 5) to isolate 0.39 g (80%) of compound **IX** as colorless lustrous plates with mp 108–109°C. IR spectrum, ν, cm^{-1}: 1350 and 1540 (NO_2), 2260 (CN). Found, %: C 51.5; H 3.1; N 25.6. *M* 161 (in toluene). $C_7H_5N_3O_2$. Calculated, %: C 51.5; H 3.1; N 25.8. *M* 163.

Compound X. A solution of 0.7 g of pyridylacetonitrile **IX** in 20 ml of methylene chloride containing 0.25 g of anhydrous ethanol was saturated at 0–2°C with dry gaseous hydrogen chloride. After 24 h, the colorless precipitate was filtered off and washed with ether (2 × 3 ml). Yield 0.45 g, mp 119–120°C. ^{1}H NMR spectrum (CF_3COOH), δ, ppm: 5.02 s (CH_2), 9.3 m (α-H, γ-H, pyridine), 8.34 s (β-H, pyridine), 7.35–6.03 (NH, *J* = 52 Hz).

3-Nitro-2-pyridylacetamide. A solution of 0.3 g of compound **XIII** in 20 ml of chloroform was saturated at 0–2°C with dry gaseous HCl. After 24 h, the solution was evaporated to isolate 0.17 g of a colorless product with mp 190–191°C. Recrystallization from 4 ml of ethanol gave 0.08 g (34.8%) of colorless plates with mp 169–170°C. IR spectrum, ν, cm^{-1}: 1350 and 1530 (NO_2), 1680 (C=O), 3330 (NH_2). ^{1}H NMR spectrum (CF_3COOH), δ, ppm: 4.82 s (CH_2), 7.52 s (NH_2), 8.1 m (β-H, $J_{\alpha,\beta}$ = 1, $J_{\beta,\gamma}$ = 2.5 Hz, pyridine), 9.3 s (α-H, γ-H, pyridine). Found, %: C 46.2; H 3.9; N 23.3. $C_7H_8N_3O_3$. Calculated, %: C 46.5; H 3.9; N 23.2.

Ethyl ethoxycarbonylacetimidate hydrochloride [11]**.** A stream of dry gaseous hydrogen chloride was passed over a period of 1 h through a mixture of 18 g of ethyl cyanoacetate and 9.3 ml of anhydrous ethanol in dry diethyl ether. The mixture was kept for 48 h in a refrigerator, and the colorless precipitate was filtered off and washed with dry ether. Yield 29 g (90%), colorless plates, mp 102–103°C.

Ethyl 2-benzimidazolylacetate (XV) [11]**.** *a*. To a solution of 7.8 g of ethyl ethoxycarbonylacetimidate hydrochloride in 100 ml of anhydrous methanol at 0°C we added a solution of 4.3 g of *o*-phenylenediamine in 30 ml of anhydrous methanol. The mixture was kept for 30 min at 0°C and was heated for 45 min under reflux. It was then poured into a cold solution of 3.5 g of sodium hydrogen carbonate in 250 ml of water. The solution turned turbid, and colorless plates gradually separated. Yield 4.2 g (52%), mp 126–127°C.

b. A solution of 5 g of 2-cyanomethylbenzimidazole in 75 ml of 9% ethanolic HCl was refluxed for 1.5 h. The mixture was cooled, filtered from ammonium chloride liberated during the reaction, the filtrate was evaporated, and 150 ml of a saturated solution of sodium hydrogen carbonate was added to the brown oily residue. The precipitate was filtered off and recrystallized from benzene (1 : 10). Yield 2.8 g (45%), colorless lustrous plates, mp 126–127°C (published data [24]: 128.5–129.5°C).

Ethyl 1-methyl-2-benzimidazolylacetate (XIV). A solution of 5.5 g of 1-methyl-2-cyanomethylbenzimidazole in 110 ml of 18% HCl in ethanol was refluxed for 2 h. The mixture was then cooled and filtered, and the filtrate was evaporated to leave an oily residue which was treated with a solution of sodium hydrogen carbonate. The product was extracted with 500 ml of chloroform. The extract was dried with sodium sulfate, the solvent was distilled off, and the oily residue was made crystalline by grinding. After recrystallization from petroleum ether (1 : 40) we obtained 4.2 g (60%) of colorless plates with mp 66–68°C (60–62°C [25]). Found, %: C 66.1; H 6.5; N 13. $C_{12}H_{14}N_2O_2$. Calculated, %: C 66.0; H 6.5; N 12.8.

Ethyl 2-benzoxazolylacetate (XVI). To a solution of 7.8 g of ethyl ethoxycarbonylacetimidate hydrochloride in 100 ml of anhydrous methanol at 0°C we added a solution of 4.3 g of *o*-aminophenol in 50 ml of anhydrous methanol. The mixture was kept for 30 min at 0°C and was heated for 40 min under reflux. It was then cooled and poured into 300 ml of water. The product was extracted with ether (5 × 100 ml). The yellow extract was dried over sodium sulfate. After removal of the solvent, the dark brown oil was ground to obtain light yellow plates which were recrystallized from 300 ml of petroleum ether (bp 70–100°C). Yield 5.8 g (72%), colorless lustrous plates with mp 54–55°C [11].

Ethyl 2-benzothiazolylacetate (XVII) was synthesized from *o*-aminobenzenethiol [26] and ethyl ethoxycarbonylacetimidate hydrochloride, following the procedure described above for ethyl 2-benzoxazolylacetate **XVI**. Removal of the solvent left a yellow liquid which was distilled under reduced pressure, a fraction with bp 150°C (1 mm) being collected;

n_D^{20} 1.5070. Yield 3.5 ml (60%). IR spectrum, ν, cm^{-1}: 1750 (C=O), 2990 (CH_3). Found, %: C 59.5; H 5.0; N 6.5; S 14.3. $C_{11}H_{11}NO_2S$. Calculated, %: C 59.7; H 4.9; N 6.3; S 14.5.

1-Methyl-2-[(3-nitro-2-pyridyl)(ethoxycarbonyl)-methylene]-2,3-dihydrobenzimidazole (XVIII). *a*. A mixture of 1 g of 2-chloro-3-nitropyridine and 2.75 g of ethyl 1-methyl-2-benzimidazolylacetate (**XV**) was heated until melting (70°C), and 0.8 g of finely powdered sodium hydroxide was added under vigorous stirring. The mixture was stirred for 20 min at 70°C, cooled, and dissolved in 150 ml of water. The solution was acidified to pH 6 with concentrated hydrochloric acid, and product **XVIII** was extracted into 500 ml of chloroform. We isolated 2.5 g of a dark brown oil containing some impurities in addition to the main substance. The product was brought into further synthesis to obtain target compound **III**.

b. To a suspension of 0.16 g of sodium hydride in 2 ml of DMF at 25–30°C we added under argon a solution of 1.38 g of ethyl 1-methyl-2-benzimidazolylacetate (**XV**) in 3 ml of DMF. The mixture was kept for 20 min at 40°C, and a solution of 2-chloro-3-nitropyridine in 3 ml of DMF was added. The originally yellow reaction mixture turned violet. It was stirred for 30 min at 50°C and for 1 h at 25°C. The progress of the reaction was monitored by chromatography on Silufol UV-254 plates using ethyl acetate as eluent: 2-chloro-3-nitropyridine, R_f 0.8 (colorless spot in daylight), compound **XVIII**, R_f 0.6 (brown spot). The mixture was poured into 200 ml of water, neutralized with hydrochloric acid to pH 7, and extracted with ether (400 ml). The extract was dried over sodium sulfate and evaporated to obtain 0.98 g of a dark brown oil which was brought into further synthesis of target product **III**. IR spectrum, ν, cm^{-1}: 1355 and 1520 (NO_2), 1750 (C=O).

1-Methyl-2-(3-nitro-2-pyridylmethyl)benzimidazole (III). To 1 g of oily compound **XVIII** we added 40 ml of 10% hydrochloric acid, and the mixture was refluxed for 1 h. The progress of the reaction was monitored by TLC (Silufol UV-254, ethyl acetate): **XVIII**, R_f 0.6; **III**, R_f 0.4. When only traces of **XVIII** remained in the mixture, it was diluted with 100 ml of water and neutralized with a solution of sodium carbonate to pH 6. Product **III** was extracted into 300 ml of ether (the extract turned violet). The extract was dried over sodium sulfate and evaporated. The dark grey precipitate was recrystallized from 150 ml of benzene–petroleum ether (1:10) and then from 100 ml of petroleum ether (bp 70–100°C). Yield 0.33 g (50%, calculated on the chloronitropyridine taken), colorless needles, mp 121–122°C. IR spectrum, ν, cm^{-1}: 1355 and 1520 (NO_2), 2920 (CH_3), 3080 ($C-H_{arom}$). ^1H NMR spectrum (CCl_4), δ, ppm: 3.68 s (CH_3), 4.65 s (CH_2), 7.09 m (α-H, β-H, γ-H, pyridine). Found, %: C 62.9; H 4.5; N 21.0. *M* 273 (in chloroform). $C_{14}H_{12}N_4O_2$. Calculated, %: C 62.7; H 4.5; N 20.9. *M* 268.

Ethyl 2,3-dihydrobenzimidazol-2-ylidene-(3-nitro-2-pyridyl)acetate (XIX). A flask was charged with 5 ml of freshly distilled DMSO and 0.3 g of sodium hydride. The mixture was heated to 60–70°C and was kept at that temperature for 30 min. It was then cooled to room temperature, and a solution of 2.58 g of ethyl 2-benzimidazolylacetate (**XV**) in 8 ml of DMSO was added in small portions. The mixture was kept for 20 min at 25°C, and a solution of 1 g of 2-chloro-3-nitropyridine in 10 ml of DMSO was added. The mixture was stirred for 1 h at room temperature, poured into 100 ml of water, and acidified to pH 4 with concentrated hydrochloric acid. The precipitate was filtered off, washed with a small amount of water, and recrystallized from 20 ml of *n*-butanol. We obtained 0.66 g (32%) of dark cherry crystals. IR spectrum, ν, cm^{-1}: 1350 and 1520 (NO_2), 1650 (C=O), 3275 (NH). Found, %: C 58.9; H 4.4; N 17.2. *M* 273 (in dioxane). $C_{14}H_{14}N_4O_4$. Calculated, %: C 58.9; H 4.3; N 17.2. *M* 326.

2-(3-Nitro-2-pyridylmethyl)benzimidazole (IV). A mixture of 0.15 g of compound **XIX** and 20 ml of 10% hydrochloric acid was heated under reflux for 40 min. The progress of the reaction was monitored by thin-layer chromatography on Silufol UV-254 plates using ethyl acetate as eluent: **XIX**, R_f 0.6 (brown spot); **IV**, R_f 0.16. When only traces of **XIX** remained in the mixture, it was diluted with 60 ml of water and neutralized with a solution of alkali to pH 7. The solution changed from yellow to dark red. The product was extracted into 300 ml of chloroform. The extract was dried over sodium sulfate, and the solvent was distilled off. The oily residue was dissolved in 20 ml of benzene on heating. The benzene solution was treated with charcoal. Colorless needles precipitated from the solution. Yield 0.08 g (68%), mp 157°C. IR spectrum, ν, cm^{-1}: 1350 and 1530 (NO_2). ^1H NMR spectrum (CF_3COOH), δ, ppm: 5.17 s (CH_2), 7.28 s (4H, benzimidazole), 7.7 s (β-H, pyridine), 8.78 m (α-H, γ-H, pyridine). Found, %: C 61.1; H 4.0; N 22.1. *M* 254 (in dioxane). $C_{13}H_{10}N_4O_2$. Calculated, %: C 61.4; H 4.0; N 22.0. *M* 253.

Ethyl 2,3-dihydrobenzothiazol-2-ylidene-(3-nitro-2-pyridyl)acetate (XXI). A solution of 2.3 g of ethyl 2-benzothiazolylacetate (**XVII**) in 10 ml of DMF was added under argon to a suspension of

0.25 g of sodium hydride in 2 ml of DMF. During the addition the mixture spontaneously warmed up to 50°C. When the addition was complete, the mixture was kept for 20 min at 30°C, and a solution of 0.82 g of 2-chloro-3-nitropyridine in 5 ml of DMF was added in portions at such a rate that the temperature was within the range 35–40°C. When only traces of 2-chloro-3-nitropyridine remained in the mixture, it was stirred for 30 min at 25°C, poured into 100 ml of water, and acidified to pH 5 with concentrated hydrochloric acid. A red viscous material separated from the orange solution. It was filtered off, washed with water, and dried. The aqueous solution was extracted with 100 ml of chloroform to recover a small amount of compound **XIX**. The extract was dried over sodium sulfate and evaporated. The product was recrystallized from 60 ml of ethanol to obtain 1.1 g (63%) of **XXI** as orange crystals with mp 156–167°C. R_f 0.7 (ethyl acetate, brown spot). IR spectrum, ν, cm^{-1}: 1355 and 1520 (NO_2), 1660 (C=O). Found, %: C 56.1; H 3.8; N 12.4. *M* 340 (in dioxane). $C_{16}H_{13}N_3O_4S$. Calculated, %: C 56.0; H 3.8; N 12.2. *M* 343.

2-(3-Nitro-2-pyridylmethyl)benzothiazole (VI). A mixture of 0.2 g of compound **XXI** and 10 ml of 18% hydrochloric acid was refluxed for 1 h. The progress of the reaction was monitored by TLC (Silufol UV-254 plates, ethyl acetate): **XXI**, R_f 0.7; **VI**, R_f 0.5. When only traces of initial compound **XXI** remained in the mixture, it was cooled, diluted with equal volume of water, and neutralized with a solution of alkali. The dark brown oil was separated from the aqueos phase and was dissolved in 50 ml of petroleum ether (bp 70–100°C) on heating. The solution was treated with charcoal and evaporated to 1/5 of the initial volume. After cooling and grinding, 0.056 g of a yellow solid was isolated. It was dissolved in 3 ml of alcohol, and hot water was added to the solution until it became turbid. After a long time, a slightly yellowish solid precipitated. Yield 30%, mp 91–92°C. IR spectrum, ν, cm^{-1}: 1360 and 1540 (NO_2). Found, %: C 57.4; H 3.4; N 15.3. *M* 277 (in dioxane). $C_{13}H_9N_3O_2$. Calculated, %: C 57.6; H 3.3; N 15.5. *M* 271.

Ethyl 2,3-dihydrobenzoxazol-2-ylidene(3-nitro-2-pyridyl)acetate (XX). To a suspension of 0.32 g of sodium hydride in 2 ml of DMF we added in portions at 40°C under argon 2.56 g of ethyl 2-benzoxazolylacetate (**XVI**). The dark brown mixture was kept for 20 min at 30°C, and 1 g of 2-chloro-3-nitropyridine was added in small portions. During the addition the mixture spontaneously warmed up to 40°C and turned violet. When the addition was complete, the mixture was stirred for 40 min at room temperature, poured into 100 ml of water, and acidified to pH 4 with concentrated hydrochloric acid (the mixture changed from violet to orange). The product was extracted into 300 ml of chloroform. The extract was dried over sodium sulfate and evaporated to obtain a dark brown oil which was ground with petroleum ether to give light yellow crystals. The product was recrystallized from 50 ml of *n*-butanol. Yield 1.7 g (82.5%), colorless needles, mp 107°C. IR spectrum, ν, cm^{-1}: 1350 and 1530 (NO_2), 1745 (C=O), 2980 (CH_3). Found, %: C 58.9; H 4.1; N 12.7. *M* 318 (in dioxane). $C_{16}H_{13}N_3O_5$. Calculated, %: C 58.7; H 4.0; N 12.8. *M* 327.

2-(3-Nitro-2-pyridylmethyl)benzoxazole (V). To a solution of 0.2 g of compound **XX** in 30 ml of benzene we added 30 ml of a 2 N solution of sodium hydroxide, and the mixture was refluxed for 2 h under vigorous stirring. The aqueous phase gradually changed from violet to brown. The progress of the reaction was monitored by TLC on Silufol UV-254 plates using ethyl acetate as eluent: **XX**, R_f 0.6 (yellow spot); **V**, R_f 0.5. When initial compound **XX** disappeared almost completely, the mixture was cooled, the organic phase was separated, and the aqueous phase was extracted with benzene (3 × 10 ml). The benzene extracts were combined with the organic phase, washed with water until neutral reaction, dried over sodium sulfate, and evaporated. The residue was a dark brown oil which was dissolved in 50 ml of boiling petroleum ether (bp 70–100°C). The solution was treated with charcoal and evaporated to 1/6 of the initial volume. After cooling, an oily product separated and was ground to obtain a light gray powder. The precipitate was filtered off and recrystallized from butanol (1:10). Yield 0.087 g (56%), colorless plates, mp 70°C. IR spectrum, ν, cm^{-1}: 1350 and 1530 (NO_2). Found, %: C 61.0; H 3.6; N 16.3. *M* 250 (dioxane). $C_{13}H_9N_3O_3$. Calculated, %: C 61.2; H 3.6; N 16.5. *M* 255.

1,3-Dimethyl-2-(3-nitro-2-pyridylmethyl)benzimidazolium perchlorate (XXII). Methyl *p*-toluenesulfonate, 0.9 g, was added to 0.1 g of compound **III**. At room temperature the mixture became liquid and turned dark blue. It was kept for 40 min at 50°C. By the end of the reaction, the mixture solidified and lost its color. It was ground with 10 ml of ether, and the precipitate was filtered off, washed with ether (3 × 5 ml) on a filter, and dissolved in 5 ml of ethanol. The solution was poured into 10 ml of a saturated aqueous solution of sodium perchlorate. On standing, plates separated from the solution and were recrystallized from 20 ml of 50% ethanol. Yield 0.07 g (49%), colorless plates with mp 253–254°C. ^1H NMR spectrum (CF_3COOH), δ, ppm: 3.73 s (CH_3), 5.2 s

(CH_2), 7.4 s (4H, benzimidazole), 7.67 m (β-H, pyridine), 8.58 m (α-H, γ-H, pyridine). Found, %: C 47.0; H 3.9; Cl 9.2; N 14.3. $C_{15}H_{15}ClN_4O_6$. Calculated, %: C 47.1; H 3.9; Cl 9.3; N 14.6.

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