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CHEMISTRY OF 2-SUBSTITUTED BENZIMIDAZOLES. 1. 5-AMINO-2-METHYL(ARYL, ARYLALKYL, PYRIDYL)BENZIMIDAZOLES

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A series of 2-substituted benzimidazoles was synthesized. These products were consecutively converted into 5-nitro- and 5-amino-2-substituted benzimidazoles.

Keywords: 2-substituted benzimidazoles, 2-pyridylbenzimidazoles, Schiff bases, antitumor agents derived from CH-acids with fused indenyl and azaindenyl fragments.

In recent work [1-3], we proposed a common mechanism of action of interferon-inducing and antitumor agents derived from CH-acids with fused indenyl and azaindenyl fragments using the model of complexes π-interacting with DNA bases in stacking structures. In this regard, benzimidazoles derivatives hold undoubted interest [4-6]. These compounds occupy an intermediate position in the extent of nitrogen saturation between indole and deazapurines. However, although many such compounds have been reported, there is no information on Schiff bases with an azomethine group bound to a benzimidazole phenylene fragment. Only azomethines obtained from 2-formyl-1-methylbenzimidazole and 1,2,3-trimethylbenzimidazolium iodide have been described [5, 7].

In the present work, we describe the synthesis of a series of benzimidazole derivatives, including new 5-nitro- and 5-aminobenzimidazoles. The latter are proposed to be used for the synthesis of azomethines.

Starting 2-R-benzimidazoles **1** were obtained by two common methods: 1) **1a-d** with R = methyl, phenyl, β- or γ-pyridyl were synthesized by the condensation of *o*-phenylenediamine with suitable acids and 2) benzimidazoles **1e-h** with R = α-pyridyl, 5-nitrofur-2-yl, 3,5-di(*tert*-butyl)-4-hydroxyphenyl, and 3-(4-isopropylphenyl)-2-propyl were obtained by heating *o*-phenylenediamines with suitable aldehydes in nitrobenzene solution. Products **1c** and **1d** were synthesized analogously. However, comparison of the above methods and the availability of the starting components indicated preference of the synthesis of β- or γ-pyridyl-substituted products **1c** and **1d** according to the acid method. Products **1a-g** have already been described [6-10]. Substituted benzimidazole **1g** was obtained by the condensation of the hydrochloride salt of 4-hydroxy-3,5-di(*tert*-butyl)benzimino ethyl ether with *o*-phenylenediamine [11]. Methylation of newly synthesized **1h** by methyl iodide in a solution of sodium hydroxide in aqueous ethanol gave N-methyl derivative **2**. With the exception of 2-methyl- (**1a**) and 2-phenylbenzimidazoles (**1b**), which we selected as model compounds in the present study, the properties of **1c-h** and **2** were not studied extensively. In this regard, considerable attention was given to the ^{1}H NMR, mass, IR, and UV spectra and quantum chemical characteristics of the starting and synthesized benzimidazoles, especially, the pyridyl derivatives.

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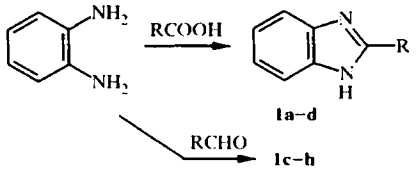
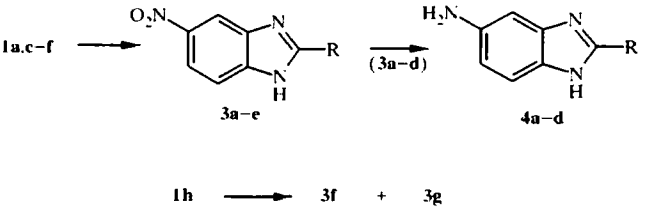


1 a R = CH_3, **b** R = C_6H_5, **c** R = β-C_5H_4N, **d** R = γ-C_5H_4N, **e** R = α-C_5H_4N, **f** R = α-$C_4H_2ONO_2$-5, **g** R = C_6H_2-3,5-[$C(CH_3)_3$]$_2$-OH, **h** R = $CH(CH_3)CH_2C_6H_4CH(CH_3)_2$-4

A characteristic feature of the mass spectra of **1a-g** is existence of highly stable molecular ion peaks with maximum intensity (I_{rel} ~ 100%). The mass spectra of phenyl- and pyridylbenzimidazoles **1b-e** have greatest similarity. In the case of **1b**, **1d**, and **1e**, the intensity of the fragmentation ions peaks do not exceed 22% and the intensity of the $[M-H]^+$ ion peak is 42% only in the mass spectrum of β-pyridylbenzimidazole **1c**. The greater electron density in the β-position of the pyridine ring in comparison with the α- and γ-positions likely accounts for the facile loss of a hydrogen atom from the NH group upon dissociative ionization of **1c**. The spectra of both model 2-phenylbenzimidazole **1b** and isomeric pyridylbenzimidazoles **1c-e** feature peaks for ions arising upon opening of the imidazole ring: $[Ph–C=N]^+$, $[Py–C=N]^+$, $[Ph–C=NH]^+$, and $[Py–C=NH]^+$. Special interest is found in peaks $[M-CN]^+$ and $[M-HCN]^+$, which may arise only as a result of a complex skeletal rearrangement with migration of the aryl or hetaryl substituent and subsequent opening of the imidazole fragment. The intensity of the molecular ion peaks upon electron impact dissociation of **1h** and **2** drops to 69 and 60%, respectively. The formation of characteristic ions $[M-H]^+$ and $[M-CH_3]^+$ is observed in these spectra. The intensity of the peak for $[M-CH_3]^+$ is 100%.

The corresponding 2-R-5-nitrobenzimidazoles **3a-e** were obtained by the nitration of **1a** and **1c-f** by a nitration mixture at 0-20°C in yields from 81 to 100%. Benzimidazoles **3a** and **3e** were synthesized previously from 4-nitro-*o*-phenylenediamine or its N,N-diacetyl derivative [8,12].

The nitration of **1h** gave a mixture of mononitro derivative **3f** and 5-nitro-2-[3-(*p*-isopropyl-*o*-nitrophenyl)prop-2-yl]benzimidazole (**3g**).



3, 4 a R = CH_3, **b** R = β-C_5H_4N, **c** R = γ-C_5H_4N, **d** R = α-C_5H_4N; **3e** R = α-$C_4H_2ONO_2$-5; **3f** R = $CH(CH_3)CH_2C_6H_4CH(CH_3)_2$-4; **3g** R = $CH(CH_3)CH_2C_6H_3(NO_2$-2)$CH(CH_3)_2$-4

The directions of nitration of benzimidazoles **1a,c-f,h** were confirmed by ^1H NMR and IR spectroscopy and mass spectrometry. Furthermore, a PPP quantum chemical calculation was carried out to determine the orientation in the electrophilic substitution of pyridylbenzimidazoles **1c-e** (the molecular diagrams are given in Figs. 1 and 2). The nitration of benzimidazoles occurs at $C_{(5)}$. The results of the quantum chemical prognosis show that the π-electron deficiency of the phenylene ring due to influence of pyridine substituents is greater in **1c-e** than in unsubstituted benzimidazole. The electron density at $C_{(5)}$ and $C_{(6)}$ is considerably diminished, while it is enhanced at $C_{(7)}$ (from 0.029 to from -0.041 to -0.047). An opposite shift is found at $C_{(4)}$ (from -0.024 to 0.001-0.002). However, only $C_{(5)}$ and $C_{(6)}$ undergo electrophilic attack in the phenylene rings studied. This reaction direction is a function of the *para*-orienting effect of the diazole ring imino group and, likely, blocking of negatively charged $C_{(7)}$ by a proton of this group.

The electron impact behavior of nitrobenzimidazoles **3a-e** is typical to aromatic compounds. Strong molecular ion peaks M^+ are the most characteristic in their mass spectra (I_{rel} = 100%). The weak peaks of $[M-O]^+$

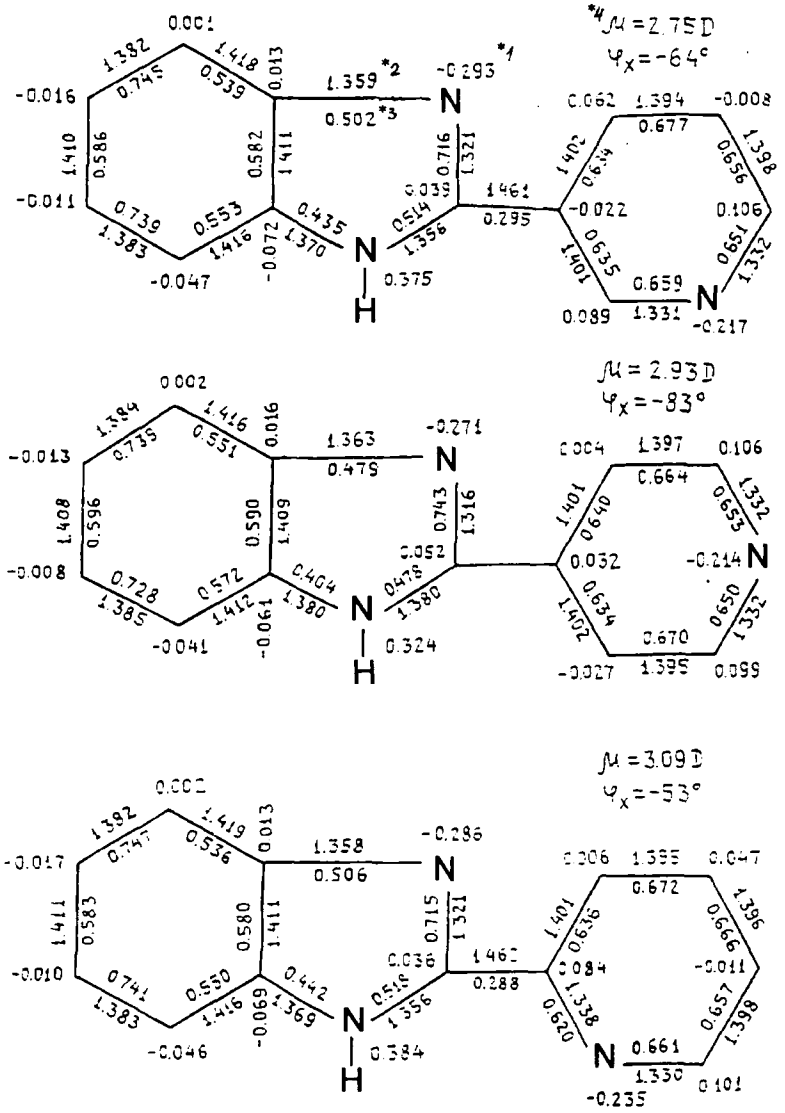


Fig. 1. Molecular diagrams of pyridylbenzimidazoles **1c-e**: *[1] – charges, *[2] – bond lengths, *[3] – bond orders, *[4] – dipole moments.

ions and medium peaks of $[M\text{-}NO]^+$ ions are a consequence of the nitro–nitrite rearrangement. We also find $[M\text{-}NO_2]^+$ ion peaks (I_{rel} = 23-70%). The ^{1}H NMR spectra of **3a-e** feature doublets for 4-H and 7-H coupled with 6-H (J_{46} = 2.00-2.5, J_{67} = 9.0-9.2 Hz). The signal for 6-H is a doublet of doublets.

The mixture of mono and dinitro derivatives **3f** and **3g** obtained in 84% yield could not be separated into individual components. The IR spectrum of this mixture has very strong bands in the NO_2 group stretching band region with maxima at 1553 and 1533 (doublet) and also at 1347 and 1323 cm^{-1} (shoulder). The mass spectrum of this mixture taken at 110-245°C shows molecular ion peaks with *m/z* 323 (**3f**) and 368 (**3g**). The dissociative fragmentation of mononitro derivative **3f** occurs at 200-230°C, while this fragmentation for dinitro derivative **3g** occurs at 245°C. The intensities of the peaks of the M^+, $[M\text{-}CH_3]^+$ (*m/z* 308), and $[M\text{-}NO]^+$ ions (*m/z* 293) are 50, 100, and 30%, respectively. The latter two fragmentation ions are also found in the dissociation of **3g** (*m/z* 353 and 338). The loss of the $[M\text{-}CH_3\text{-}NO]^+$ ion with *m/z* 323 is also characteristic for **3g**. The ratio of the intensities of the peaks of the M^+, $[M\text{-}CH_3]^+$, $[M\text{-}NO]^+$, and $[M\text{-}CH_3\text{-}NO]^+$ ions is ~43:23:14:100, respectively.

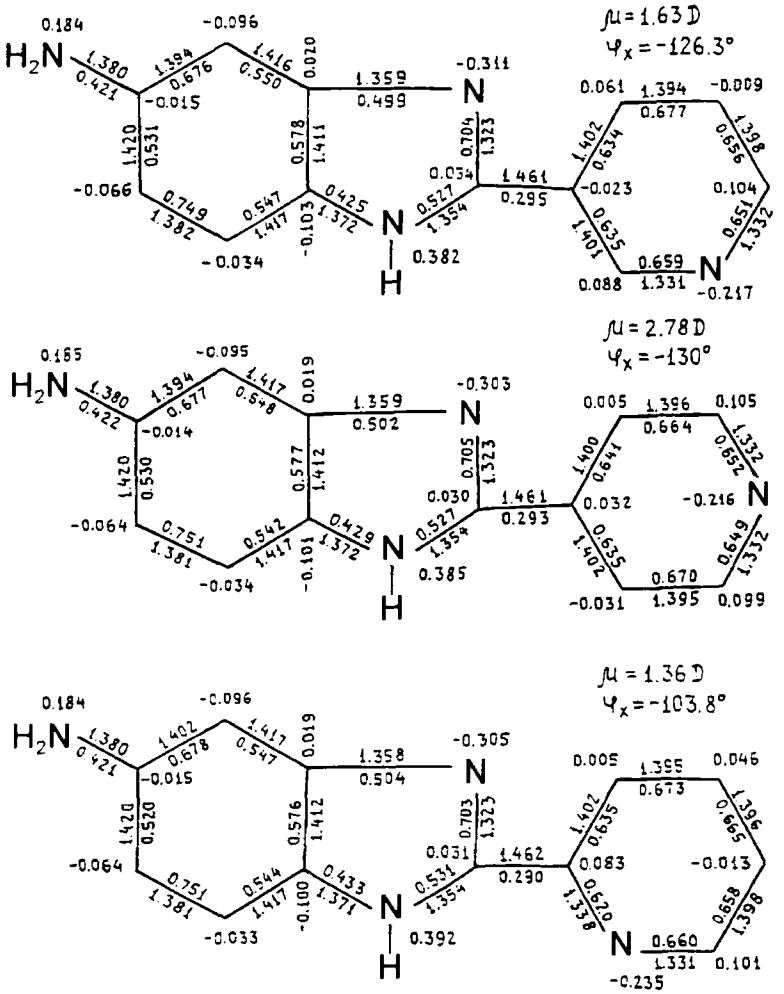


Fig. 2. Molecular diagrams of 5-amino-2-pyridylbenzimidazoles **4b-d**.

TABLE 1. Physical Characteristics of New 5-Nitro-2-pyridyl- and 5-Amino-2-pyridylbenzimidazoles

Compound	Empirical formula	Found, % / Calculated, %			mp, °C*	R_f (ethanol)	Yield, %
		C	H	N			
3b	$C_{12}H_8N_4O_2$	60.02 / 60.00	3.51 / 3.33	23.13 / 23.33	275-277	0.56	81.3
3c	$C_{12}H_8N_4O_2$	59.92 / 60.00	3.32 / 3.33	23.50 / 23.33	282-284	0.65	97.5
3d	$C_{12}H_8N_4O_2$	58.90 / 60.00	3.43 / 3.33	23.21 / 23.33	212-213	0.88	99.6
4b	$C_{12}H_{10}N_4$	68.32 / 68.57	5.03 / 4.76	26.30 / 26.67	248-250	0.57	49.0
4c	$C_{12}H_{10}N_4$	68.20 / 68.57	4.81 / 4.76	26.61 / 26.67	84-88	0.58	71.4
4d	$C_{12}H_{10}N_4$	68.32 / 68.57	4.41 / 4.76	26.51 / 26.67	203-205	0.66	76.2

* Products **3b-d** were recrystallized from acetone, **4b-d** were recrystallized from water.

TABLE 2. Spectral Characteristics of Compounds Synthesized

Compound	IR spectrum, ν_{NH_2} and ν_{NH}, cm^{-1}	UV spectrum, λ_{max}, nm (log ε)*	^1H NMR spectrum, chemical shifts, δ, ppm; coupling constants, J, Hz*[2]
3b	3400-2810	210 (4.46), 215 (4.30), 266 (4.49), 310 sh. (4.30), 322 (4.36)	9.38 (1H, br. dd, 2'-H); 8.68 (1H, br. dd, 6'-H); 8.51 (1H, dd, 4'-H); 8.48 (1H, d, 4-H); 8.13 (1H, dd, 6-H); 7.77 (1H, d, 7-H); 7.50 (1H, dd, 5'-H); $J_{2'6'}$ = 2.0; $J_{4'5'}$ = 7.5; $J_{4'6'}$ = 2.5; $J_{5'6'}$ = 5.0; J_{46} = 2.0; J_{67} = 9.0
3c	3190-2820	213 (4.47), 270 (4.66), 310 sh. (4.44), 326 (4.49), 350 sh. (4.64)	8.82 (2H, m, 2'-H + 6'-H); 8.60 (1H, d, 4-H); 8.23 (1H, dd, 6-H); 8.16 (2H, m, 3'-H + 5'-H); 7.84 (1H, d, 7-H); J_{46} = 2.2; J_{67} = 9.2
3d	3200-2830	215 (4.30), 264 (4.38), 298 (4.40), 315 sh. (4.33), 327 (4.40), 340 sh. (4.30)	8.68 (1H, br. d, 6'-H); 8.46 (1H, d, 4-H); 8.26 (1H, br. d, 3'-H); 8.12 (1H, dd, 6-H); 7.94 (1H, td, 4'-H); 7.65 (1H, d, 7-H); 7.43 (1H, qd, 5'-H); $J_{3'4'}$ = 7.5; $J_{3'5'}$ = 1.0; $J_{4'5'}$ = 7.5; $J_{4'6'}$ = 2.0; $J_{5'6'}$ = 4.5; J_{46} = 2.5 ; J_{67} = 9.0
4b	3400-2870	208 (4.58), 233 (4.38), 250 sh. (4.22), 320 sh. (3.36), 344 (4.36), 390 sh. (3.90)	9.14 (1H, d, 2'-H); 8.54 (1H, dd, 6'-H); 8.36 (1H, ddd, 4'-H); 7.50 (1H, dd, 5'-H); 7.39 (1H, dd, 7-H); 6.90 (1H, d, 4-H); 6.76 (1H, dd, 6-H); $J_{2'6'}$ = 1.8; $J_{4'5'}$ = 8.2; $J_{4'6'}$ = 1.6; $J_{5'6'}$ = 4.7; J_{46} = 2.0; J_{47} = 0.5; J_{67} = 8.5
4c	3390-2800	216 (4.64), 220 (4.46), 275 (4.22), 350 (4.38), 390 sh. (4.20)	8.69 (2H, m, 2'-H and 6'-H); 7.96 (2H, m, 3'- H and 5'-H); 7.38 (1H, dd, 7-H); 6.83 (1H, d, 4-H); 6.73 (1H, dd, 6-H); J_{46} = 2.0; J_{47} = 0.5; J_{67} = 8.5
4d	3400-2800	212 (4.43), 265 (4.16), 320 sh. (4.00), 350 (4.06), 390 sh. (3.94)	8.80-6.58 (6H, m, 3'-, 4'-, 5'-, 6'-, 4-, 7-H); 6.46 (1H, dd, 6-H); J_{67} = 8.5

* Exocyclic bond.

*[2] The spectra of **3b** and **3c** were taken in acetone-d_6, the spectra of **3d**, **4b**, and **4c** were taken in CD_3OD, and the spectrum of **4d** was taken in DMSO-d_6.

Analysis of the ^1H NMR spectrum of this mixture (comparison with the spectrum of starting **1h**, determination of the integral intensity of the signals, and signal position) indicates the position of the nitro group in its components and approximate ratio of these components. Thus, the complex spectrum of this mixture due to the position of some of the signals features signals at 8.39 (d, J = 2.3 Hz), 8.11 (dd, J = 2.3 and 8.8 Hz), and 7.58 ppm (J = 8.8 Hz) assigned to the equivalent protons of the benzimidazole fragment (4-, 6-, and 7-H, respectively) and signals at 7.78 (d, J = 2.0 Hz), 7.42 (br. d, J = 7.9 Hz), and 7.78 ppm assigned to protons of the $C_6H_3NO_2$ fragment (3-, 5-, and 6-H, respectively) of dinitro derivative **3g**. The signals of the methyl groups of the isopropyl moiety at 1.21 ppm (d, J = 7.0 Hz) and protons of the CH and CH_2 groups of the mixture (2.73-3.66 ppm, m) hardly differ from those in starting **1h**. On the other hand, the doublet for the methyl group in the $-CH(CH_3)CH_2-$ fragment (1.50 ppm, d) is downfield relative to the signal of the analogous group in **1h** by 0.05 ppm, while each of its components has additional splitting. We assume that these spectral features are explained by the position of the signals of the mono- and dinitro derivatives **3f** and **3g** as well as the effect of the NO_2 group in the $C_6H_3NO_2$ fragment in **3g**. The intensities of the upfield and downfield components of this signal indicate that the **3g:3f** ratio in the mixture is 1.5:1.

Nitrobenzimidazoles **3a-d** were reduced by heating in aqueous ethanol solutions at reflux with excess zinc powder in the presence of calcium chloride to give the corresponding 2-substituted 5-aminobenzimidazoles

4a-d. The dinitro derivative of furylbenzimidazole **3e** could not be reduced under these conditions. Amines **4a-d** (Tables 1 and 2) were obtained in 49-76% yield. Amine **4a** was first described by Pozharskii et al. [13]. The electron impact dissociation of **4a-d** was analogous to the dissociation of benzimidazoles **1a** and **1c-1e**, which are unsubstituted at $C_{(5)}$. The molecular ion peaks are the strongest (I_{rel} = 100%).

The bioscreening results for **1b,d,h, 3b,c** for pesticide activity indicated promise for 2-β-pyridyl-substituted benzimidazoles **1c** and **3b**. *In vitro* testing of these compounds showed medium antibacterial (Bacteria Xcnt. Maiv.) and fungicide activity (50% for Sol. Sol. and 60% for Vent. In.). Their *in vivo* fungicidal activity was somewhat higher (57%) for powdery cucumber mildew and, in some cases, on tomato phytophthora. All the compounds studied except **1d** showed such activity. The fungicidal activity of **1d** did not exceed 28% under these conditions.

Hydrochloride salts **5a-d** were obtained from benzimidazoles **1c-e,h**. Iodomethylates **6a** and **6b** and 3-allyl-2-β-pyridyl- and 3-allyl-2-γ-pyridylbenzimidazolium bromides **7a** and **7b** were obtained from **1c** and **1d**. The quaternary salts hydrochlorides **5a-c** which are being tested for biological activity were described [6,7].

The quantum chemical calculations for **1c-e** showed that $N_{(3)}$ is the most electronegative nitrogen atom in these molecules and quaternization should occur predominantly at this atom.

EXPERIMENTAL

The IR spectra were recorded on a UR-20 spectrophotometer in KBr pellets. The UV spectra were taken on a UV-Vis spectrophotometer in ethanol solutions. The ^{1}H NMR spectra were measured on a Bruker WP-80 spectrometer at 80 MHz or Super-con-400 spectrometer at 400 MHz in $CDCl_3$, CD_3OD, DMSO-d_6, or acetone-d_6 with TMS as the internal standard. The mass spectra were obtained on MX-1303 or Finnigan MAT-4615 mass spectrometers or on Kratos MS-25RF GC/MS chromato-mass spectrometer at 70 eV. The reaction course and purity of the products were monitored by thin-layer chromatography on Silufol UV-254 plates with ethanol as the eluent.

The physical characteristics of the products are given in Tables 1 and 2. The PPP molecular diagrams for **1c-e** and **1b-d** are given in Figs. 1 and 2.

2-[3-(*p*-Isopropylphenyl)prop-2-yl]benzimidazole (1h). A mixture of *o*-phenylenediamine (3 g, 27 mmol) and γ-(*p*-isopropylphenyl)-α-methylpropanal (5.25 g, 27 mmol) in nitrobenzene (15 ml) were heated at reflux for 15 min. The crystalline precipitate was filtered off and crystallized from aqueous ethanol to give 2.62 g (34%) of compound **1h**; mp 205-207°C, R_f 0.48 (Silufol, ether). Mass spectrum, *m/z* (I_{rel}, %): 278 (69) M^+, 277 (18); 263 (87); 145 (69); 133 (17); 117 (19). ^{1}H NMR spectrum in $CDCl_3$: 1.20 (6H, d, J = 6.8 Hz, $2CH_3$ in *i*-Pr); 1.45 (3H, d, J = 6.8 Hz, CH_3 in Pr); 2.58-3.50 (4H, m, H_{aliph}); 6.90-7.70 ppm (8H, m, H_{arom}). Found, %: C 81.42; H 7.43; N 10.70. $C_{19}H_{22}N_2$. Calculated, %: C 82.01; H 7.91; N 10.07.

2-[3-(*p*-Isopropylphenyl)prop-2-yl]-1-methylbenzimidazole (2). A sample of 50% ethanolic NaOH (0.75 ml) was added to a solution of benzimidazole **1h** (3 g, 10 mmol) in ethanol (50 ml) and then, methyl iodide (0.75 ml, 12 mmol) was added. The reaction mixture was stirred for 24 h at 30-40°C and water (50 ml) was added. The mixture was extracted with chloroform. The extract was dried over sodium sulfate and evaporated to give 2.2 g (69.8%) of compound **2** as a viscous, pinkish brown oily liquid; R_f 0.82. Mass spectrum (*m/z*, I_{rel}, %): 292 (60, M^+), 277 (100). ^{1}H NMR spectrum in $CDCl_3$: 1.16 (6H, d, J = 6.8 Hz, $2CH_3$ in *i*-Pr); 1.45 (3H, d, J = 6.8 Hz, CH_3 in Pr); 2.62-3.45 (8H, m, H_{aliph}); 6.82-7.75 ppm (8H, m, H_{arom}). Found, %: C 82.22; H 8.23; N 9.50. $C_{20}H_{24}N_2$. Calculated, %: C 82.19; H 8.22; N 9.59.

5-Nitro-2-(β-pyridyl)- (3b); 5-Nitro-2-(γ-pyridyl)- (3c); and 5-Nitro-2-(α-pyridyl)benzimidazoles (3d). A sample of **1c-e** (1 g, 5 mmol) in concentrated sulfuric acid (2 ml) was added in portions to a stirred mixture of concentrated nitric acid (4 ml) and sulfuric acid (5 ml) at 0°C. The reaction mixture was stirred for 1 h at 0°C and 1 h at 20°C and then poured onto ice. Aqueous sodium carbonate was added to bring the solution to pH 8. The precipitate formed was crystallized from acetone to give yellow crystals of **3b-d**.

5-Nitro-2-(5-nitrofur-2-yl)benzimidazole (3e) was synthesized analogously to **3b-d** by the nitration of **1f** (3.5 g, 13 mmol) dissolved in concentrated sulfuric acid (20 ml) using a mixture of concentrated nitric acid

(10 ml) and concentrated sulfuric acid (15 ml) to give 3.5 g (97.7%) of compound **3e**; mp 312-314°C (aqueous ethanol) in accord with literature data [8]. ^{1}H NMR spectrum in DMSO-d_6: 8.44 (1H, d, $J_{4,6}$ = 2.0 Hz, 4-H); 8.12 (1H, dd, $J_{6,7}$ = 9.0 Hz, 6-H); 7.82-7.62 (2H, m, 4- and 7-H); 7.52 ppm (1H, d, $J_{3,4}$ = 4.0 Hz, 3-H).

5-Nitro-2-[3-*p*-isopropylphenyl)prop-2-yl]benzimidazole (3f) and 5-Nitro-2-[3-(*p*-isopropyl-*o*-nitrophenyl)prop-2-yl]benzimidazole (3g). A solution of **1h** (2 g, 7.1 mmol) in concentrated sulfuric acid (6 ml) was added gradually to a mixture of concentrated nitric acid (3 ml) and sulfuric acid (4 ml) at 0°C. The reaction mixture was stirred for 1 h at 0°C and 1 h at 25°C and then treated as described for **3b-d** to give 1.95 g of a mixture of **3f** and **3g** as yellow crystals; mp 80-114°C (acetone).

5-Amino-2-(β-pyridyl)- (4b), 5-amino-2-(γ-pyridyl)- (4c), and 5-amino-2-(α-pyridyl)benzimidazoles (4d). A solution of calcium chloride (0.5 g) in water (1 ml) was added to a solution of **3b-d** (2 g, 8.3 mmol) in a mixture of ethanol (35 ml) and water (8 ml) and, then, zinc powder (12.5 g) was added with heating and stirring. The stirred reaction mixture was heated at reflux for 2 h and then filtered. The precipitate on the filter was washed with ethanol, which was then combined with the filtrate. The mixture was evaporated and the precipitate was crystallized from hot distilled water to give **4b-d** as yellow (**4b** and **4c**) or dark brown crystals (**4d**).

Quaternization of 2-[β-Pyridyl]- (1c), 2-[γ-Pyridyl]- (1d), and 2-[α-Pyridyl]benzimidazoles (1e) and 2-[3-(*p*-Isopropylphenyl)prop-2-yl]benzimidazole (1h). Hydrogen chloride was passed through a solution of base **1c-e** in acetone or solution of base **1h** in ether to give hydrochlorides **5a-c** and **5d**, respectively. Hydrochloride **5d** was obtained as an oil in 91% yield. Hydrochloride **5a** was obtained as a powder in 95% yield, mp 298-300°C. Hydrochloride **5b** was obtained as a powder in 98% yield; mp 266-268°C. Hydrochloride **5c** was obtained as a powder in 99% yield; mp 248-249°C. The mp data were in accord with literature values [6, 7].

3-Methyl-2-(β-pyridyl)benzimidazolium Iodide (6a) and 3-Methyl-2-(γ-pyridyl)benzimidazolium Iodide (6b) were obtained by heating solutions of bases **1c** and **1d** in acetone at reflux with excess methyl iodide. Iodomethylate **6a** was obtained in 96.5% yield as brown crystals; mp 237-238°C. Found, %: C 46.91; H 3.42; N 12.5; I 36.92. $C_{11}H_{11}IN_2$. Calculated, %: C 46.29; H 3.56; N 12.46; I 37.69. Iodomethylate **6b** was obtained in 90.7% yield as yellow crystals; mp 265-267°C (dec.). Found, %: C 46.31; H 3.82; N 12.5; I 37.62. $C_{11}H_{11}IN_2$. Calculated, %: C 46.29; H 3.56; N 12.46; I 37.69.

3-Allyl-2-(β-pyridyl)benzimidazolium Bromide (7a). A solution of a mixture of **1c** (1 g, 5.1 mmol) and allyl bromide (0.4 ml) in acetone (50 ml) was heated at reflux for 12 h. The precipitate formed upon cooling was crystallized from acetone to give 0.86 g (53%) beige crystalline salt **7a**; mp 205-207°C (dec.). Found, %: C 55.81; H 4.30; N 13.23; Br 25.21. $C_{15}N_{13}BrN_2$. Calculated, %: C 56.96; H 4.43; N 13.29; Br 25.32.

3-Allyl-2-(γ-pyridylbenzimidazolium Bromide (7b) was obtained by analogy from **1d** (0.7 g, 3.5 mmol) and allyl bromide (0.3 ml) in 58.4% yield as yellow-brown crystals; mp 208-210°C (dec.). Found, %: C 56.51; H 4.60; N 13.11; Br 24.90. $C_{15}H_{13}BrN_2$. Calculated, %: C 56.96; H 4.43; N 13.29; Br 25.32.

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