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^{13}C NMR Spectra and Biological Activity of *N*-(1*H*-Benzimidazol-2-yl)benzamides

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Abstract — Derivatives of 1*H*-benzimidazol-2-amine and halo-, nitro-, methoxy-, and hydroxy-substituted benzoic acids were synthesized, and their fungicide activity against pure *Fusarium culmorum* and *Helminthosporium sativum* cultures and pathogenic microflora of wheat and barley seeds in laboratory and field tests was studied. Some compounds were found to exhibit a strong fungicide activity.
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Benzimidazole derivatives constitute a large and chemically versatile class of compounds. Their biological action is not limited to helminths but extends to pathogenic fungi, viruses, and bacteria [1–25]. An interesting group of benzimidazole derivatives consists of various 1*H*-benzimidazol-2-ylcarbamic acid esters (derivatives of 1*H*-benzimidazol-2-amine) which have found wide application as fungicides. The simplest benzimidazole derivative of this kind is methyl 1*H*-benzimidazol-2-ylcarbamate (**I**, Carbendazim); it is widely used in agriculture as systemic fungicide.

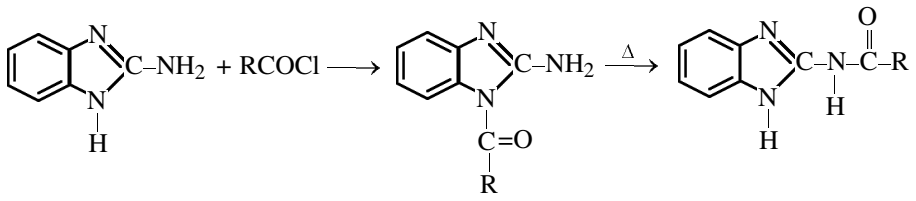
Analysis of available published data shows that many acyl derivatives of 1*H*-benzimidazol-2-amine at the exocyclic amino group in the 2-position exhibit strong biological activity, whereas data on the activity of analogous derivatives at the ring nitrogen atom are considerably fewer in number. The goal of the present study was to develop methods of synthesis of a series of amides derived from substituted 2-hydroxy- and 2-methoxybenzoic acids and 1*H*-benzimidazol-2-amine (**II**) (at the endo- or exocyclic nitrogen atom) and examne their fungicide activity under comparable conditions.

The syntheses of methyl ester **I** used as reference in biological tests, some acyl derivatives of 1*H*-benzimidazol-2-amine, halo- and nitro-substituted salicylic acids, and the corresponding acyl chlorides, as well as the structure of these compounds according to the ^{13}C NMR data, were described by us previously [26]. By acylation of 1*H*-benzimidazol-2-amine with substituted benzoyl chlorides in toluene or acetone we obtained a series of new derivatives at the nitrogen atom in position 1 of the benzimidazole ring or at the exocyclic amino group in position 2 (compounds **III**–**XLI**). It should be noted that the acylation of 1*H*-benzimidazol-2-amine with acid chlorides under mild conditions initially occurs at the N^1 atom. Heating of the reaction mixture (or a solution of preliminarily isolated isomer **A** in an appropriate solvent) promotes migration of the acyl group to the exocyclic nitrogen atom to give isomer **B** (Scheme 1). The rearrangement process was monitored by HPLC and ^{13}C NMR spectroscopy.

The structure of the resulting amides, derivatives of 1*H*-benzimidazol-2-amine and substituted benzoic acids, was confirmed by the ^{13}C NMR spectra (Table 1). The position of the acyl group was determined taking into account that structures with a substituted exocyclic amino group give a simpler spectral pattern due to fast proton exchange between the N^1 and N^3 atoms in the heteroring. The presence of an acyl group at the exocyclic nitrogen atom induces a considerable upfield shift of the C^2 signal (δ_C = 5–8 ppm), while shielding of the C^{3a} and C^{7a} atoms is weaker.

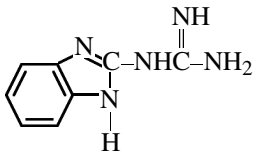
All substituents in the examined compounds exhibit weaker or stronger electron-withdrawing properties (except for 4-aminobenzamide **XXX**, guanidine derivative **XXIII**, and octanamide **XV**) and reduce electron density on the heteroring. On the basis of the NMR data we compared the substituent effects with variations in magnetic shielding on protonation

Scheme 1.

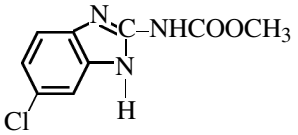


II **A** **B**

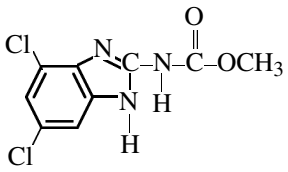
V, VII, X, XXIV, XXXIII, XLI **III, IV, VI, IX, XI–XXII, XXV–XXXII, XXXIV, XXXV**



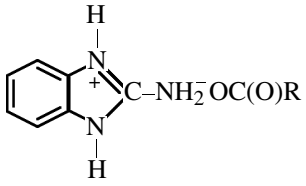
XXIII



XXXVI



XXXVII



XXXVIII–XL

III, R = MeO; **IV**, R = 2-MeO-3,5-$Cl_2C_6H_2$; **V**, R = 2-MeO-3,5,6-Cl_3C_6H; **VI**, R = 2-HO-3,5-$Cl_2C_6H_2$; **VII, XXXV, XXXIX**, R = 2-MeO-3,5-$Cl_2C_6H_2$; **VIII, XL**, R = C_6H_5; **IX**, R = 2-HO-3,5-$Br_2C_6H_2$; **X**, R = 2-MeO-3,6-$Cl_2C_6H_2$; **XI**, R = 2-HO-5-BrC_6H_3; **XII**, R = 2-HO-5-ClC_6H_3; **XIII**, R = 2-HO-5-$O_2NC_6H_3$; **XIV**, R = 2-HO-3,5-$I_2C_6H_3$; **XV**, R = C_7H_{15}; **XVI**, R = 2-MeO-5-ClC_6H_3; **XVII**, R = 2-MeO-5-BrC_6H_3; **XVIII**, R = 3-IC_6H_4; **XIX**, R = 2-Cl-5-$O_2NC_6H_3$; **XX**, R = 4-$O_2NC_6H_4$; **XXI**, R = 3-BrC_6H_4; **XXII**, R = 2-BrC_6H_4; **XXIV**, R = 2-MeO-3,5-$Cl_2C_6H_2$; **XXV**, R = $ClCH_2CH\cdot(OH)CH_2$; **XXVI**, R = 3,5-$(O_2N)_2C_6H_3$; **XXVII**, R = 2,4-$Cl_2C_6H_3$; **XXVIII**, R = 2-Cl-4-$O_2NC_6H_3$; **XXIX**, R = C_6F_5; **XXX**, R = 4-$H_2NC_6H_4$; **XXXI**, R = 3-ClC_6H_4; **XXXII**, R = 2-HOC_6H_4; **XXXIII, XXXIV, XXXVIII**, R = 2-$MeOC_6H_4$; **XLI**, R = 3-BrC_6H_4.

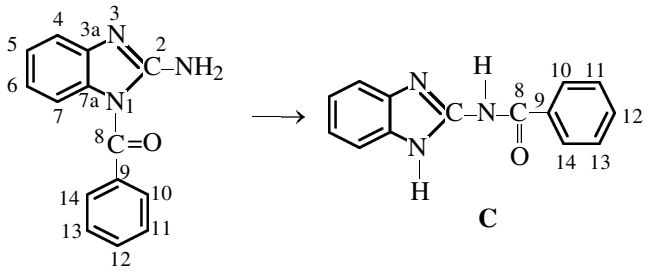
of the heteroring. As follows from the data of [27, 28], protonation of benzimidazole ring leads to an upfield shift of the C^2, C^4, C^7, C^{7a}, and C^{3a} signals by 5–8 ppm. This is consistent with our data for compounds in the protonated form in organic acid solutions. The observed variations of the protonation-induced chemical shifts are comparable with the substituent effects.

Magnetic shielding of the amide carbonyl carbon atom (C^8) in the series of the examined compounds was found to depend on the substitution pattern in the aromatic ring. The chemical shift of C^8 does not exceed δ_C 165.6 ppm (**VII**) for structures containing a methoxy group in the *ortho* position with respect to the carbonyl group. Considerable deshielding of C^8 is produced by the neighboring hydroxy group: the signal shifts downfield to δ_C 171.8 ppm (**XI**). As with substituted benzoic acid, this is the result of formation of an intramolecular hydrogen bond with participation of the hydroxy proton and carbonyl oxygen atom.

The chemical shift of C^2 in benzamide **VIII** is δ_C 149.4 ppm. Introduction of an electron-withdrawing substituent (Cl, NO_2, Br) into the benzene ring leads to displacement of the C^2 signal to δ_C 153.6 ppm (**XVIII**). In the ^{13}C NMR spectra of structures acylated at the endocyclic nitrogen atom (N^1), the C^2 signal is located in the δ_C range from 146.8 (**XXXIII**) to 154.7 ppm (**VII**). As a result of asymmetric substitution of the benzimidazole fragment, a slight difference in the magnetic shielding of the C^7 and C^4 nuclei is observed [$\Delta\delta(C^7, C^4) \approx$ 2–3 ppm].

Fungicide activity of the compounds under study was estimated at a concentration of 0.003% against *Fusarium culmorum* and *Helminthosporium sativum*

Table 1. ^{13}C NMR spectra and yields of 1*H*-benzimidazol-2-amine derivatives



A **C**

Comp. no.	Yield, %	Chemical shifts δ_C, ppm														
		C^2	C^4	C^5	C^6	C^7	C^{7a}	C^{3a}	C^8	C^9	C^{10}	C^{11}	C^{12}	C^{13}	C^{14}	CH_3, O–Alk
I	99	143.5	112.7	125.3	125.3	112.3	127.7	127.7	152.8							54.3
II		150.2	112.1	124.4	124.4	112.1	128.9	128.9								
III	99	144.5	113.0	124.4	124.4	113.0	128.8	128.8	172.0							22.4
IV	90	148.4	114.1	122.3	122.3	114.1	134.8	134.8	152.8	129.0	131.8	134.8	122.3	152.8	128.6	62.5
V	98	153.0	111.5	122.8	126.5	113.9	127.1	128.9	164.2	127.1	153.0	126.6	133.3	129.5	134.2	61.9
VI	48	156.5	112.7	124.1	124.1	112.7	132.9	132.9	170.7	121.6	150.9	122.1	128.4	122.8	129.5	
VII	82	154.7	112.7	120.4	125.3	116.7	127.6	129.3	165.6	132.4	152.0	130.0	133.5	127.0	129.3	62.7
VIII	77	149.4	114.0	122.3	122.3	114.0	134.8	134.8	169.2	132.8	129.0	129.0	134.0	129.0	129.0	
IX	33	150.8	112.6	124.1	124.1	112.6	131.8	131.8	170.5	122.5	157.6	112.6	138.1	109.1	129.4	
X	89	152.9	111.7	123.6	125.6	113.9	127.2	129.0	164.3	133.0	153.8	126.6	134.5	126.7	129.4	62.1
XI	57	151.5	112.6	123.8	123.8	112.6	129.7	129.7	171.8	122.1	160.4	120.2	136.3	109.7	132.4	
XIII	31	150.7	112.7	123.9	123.9	112.7	128.9	128.9	170.5	119.7	167.8	119.1	129.7	138.9	126.6	
XIV	67	150.8	112.6	123.9	123.9	112.6	129.5	129.5	170.3	122.1	160.6	80.6	149.0	89.5	138.6	
XV	55	144.2	114.0	125.7	125.7	114.0	129.2	129.2		152.8						68.0, 31.8, 25.7, 28.9, 28.7, 22.6, 14.7
XVIII	80	153.6	111.8	122.7	122.7	111.8	131.0	131.0	169.2	132.6	138.4	94.8	140.3	132.6	129.1	
XIX	72	150.5	113.4	123.0	123.0	113.4	132.7	132.7	169.1	138.3	138.8	132.3	126.0	146.6	125.3	
XX	87	152.5	112.8	123.9	123.9	112.8	131.4	131.4	170.8	143.8	130.3	123.1	149.7	123.1	130.1	
XXI	79	151.4	113.2	122.8	122.8	113.2	131.7	131.7	169.9	139.0	132.7	122.1	134.8	131.1	128.0	
XXII	61	147.9	114.5	122.5	122.5	114.5	133.5	133.5	168.8	135.8	119.7	132.2	138.5	128.7	129.8	
XXIII	61	159.2	112.5	120.5	120.5	112.5	137.8	137.8	–							159.4
XXVI	89	153.5	112.4	123.7	123.7	112.4	129.9	129.9	165.9	131.7	128.7	148.8	120.9	148.8	128.7	
XXVII	80	148.5	114.2	122.5	122.5	114.2	135.7	135.7	168.0	132.2	131.4	130.5	134.8	127.9	130.0	
XXVIII	91	150.0	113.5	123.0	123.0	113.5	133.0	133.0	169.5	143.9	131.9	125.3	148.7	123.0	131.0	
XXXI	79	152.4	113.5	122.7	122.7	113.5	138.3	138.3	169.5	132.2	139.0	132.2	146.2	132.6	126.8	
XXXIII	34	146.8	112.8	121.9	121.9	112.8	131.0	131.0	165.1	121.4	157.8	114.8	134.2	121.4	137.0	
XXXVI	61	144.3	114.2	125.8	130.5	112.9	128.7	126.8	152.8							54.6

[a] Yields, %: **XII**, 71; **XVI**, 21; **XVII**, 63; **XXIV**, 76; **XXV**, 26; **XXIX**, 25; **XXX**, 32; **XXXII**, 44; **XXXIV**, 32; **XXXV**, 70; **XXXVII**, 35; **XXXVIII**, 95; **XXXIX**, 94; **XL**, 93; **XLI**, 79.

Table 2. Toxicity of 1*H*-benzimidazol-2-amine derivatives at a concentration of 0.003% against pure fungi cultures

Compound no. (**A** : **B** molar ratio)	Inhibition of growth of pathogenic fungi, %		Compound no. (**A** : **B** molar ratio)	Inhibition of growth of pathogenic fungi, %	
	Fusarium culmorum	*Helminthosporium sativum*		*Fusarium culmorum*	*Helminthosporium sativum*
I	**100**	**22.9**	**XXIII**	11.2	12
III	36.3	7.6	**XXIV**	32.8	18.4
IV	28.5	7.7	**XXIV**	15.7	22.7
V	47.5	25.7	**XXV**	35.3	0
VI	**68.5**	**30.5**	**XXV**	36.1	0
VII	12.1	–	**XXVI**	26.4	22.9
VIII	**100**	**73**			
IX	34.0	17.6	**XXVII**	2.8	24.1
X	54.6	23.5	**XXVIII**	5.1	15.6
XI	8.7	0	**XXIX**	19	7
XII	32.1	0	**XXX**	29	1
XIII	**77.3**	**28.7**	**XXXII**	15.9	–
XIV	16.8	20.3	**XXXIII**	**75.8**	**4.6**
XVI	0	19	**XXXIV**	51.4	–
XVII	11.2	25	**XXXV**	12.1	17
XVIII	41.7	6.8	**XXXVI**	**87.3**	**19.8**
XX	28.3	10.9	**XXXVII**	63.5	14.7
XX (50.0 : 50.0)	**86.1**	**20.0**	**XXXVIII**	15.0	–
			XXXIX	31.7	–
XXI	84.7	15.6	**XL**	30.2	–
XXII	17.6	16.2	**XLI**	**90.1**	**34.4**

pathogenic fungi as pure cultures (Table 2) and infected seeds (Tables 3–7).

Primary laboratory tests showed that compounds **VI, VIII, XIII, XX, XXI, XXXIII, XXXVI, XXXVII**, and **XLI** are toxic for phytopathogenic fungi. These compounds were recommended for further testing. As follows from the data in Table 2, their fungicide activity is fairly strong; however, most of them are slightly less toxic than Carbendazim (**I**

Table 3. Fungicide activity of some 1*H*-benzimidazol-2-amine derivatives against pathogenic infections of Voronezhskaya wheat seeds

Compound no.	Dose, kg ton^{-1}	Germination capacity, %	Pathogenic microflora		Weight of 100 germs, g
			affected, %	efficiency with respect to control, %	
Control	–	79	77	–	14.6
I (Carbendazim)	1.0	83	69	10	14.7
III	1.0	87	48	38	13.7
IV	1.0	81	67	13	14.2
V	1.0	82	68	12	14.6
VI	1.0	78	67	13	14.5
VII	1.0	80	68	12	10.8

Table 3. (Contd.)

Compound no.	Dose, kg ton^{-1}	Germination capacity, %	Pathogenic microflora		Weight of 100 germs, g
			affected, %	efficiency with respect to control, %	
VIII	1.0	82	45	42	14.4
IX	1.0	76	78	0	14.6
X	1.0	75	87	0	14.0
XI	1.0	86	42	47	14.5
XII	1.0	84	49	36	14.3
XIII	1.0	84	32	58	15.0
XIV	1.0	80	69	11	14.2
XV	1.0	80	64	19	13.4
XXIII	1.0	81	48	38	13.9
XXXVI	1.0	85	46	40	13.9
XXXVII	1.0	82	51	34	13.4
XLI	1.0	84	49	36	13.8

Table 4. Efficiency of 1*H*-benzimidazol-2-amine derivatives **XXXIII** and **XXXIX**

Compound no.	Dose, kg ton^{-1}	Laboratory germination capacity, %	Affection of seeds by fungi, %	Weight of 100 germs, g
Control	–	87	59	13.7
I (Carbendazim)	0.5	88	37	14.2
	1.0	90	44	14.1
XXXIII	**0.5**	**91**	**9**	**13.5**
	1.0	**93**	**7**	**13.8**
XXXIX	0.5	84	12	13.8
	1.0	86	4	12.2

Table 5. Selective toxicity of 1*H*-benzimidazol-2-amine derivatives toward spring wheat seeds

Compound no.	Dose, l ton^{-1}	Laboratory germination capacity, %	Affection of seeds by root rot, %	Weight of 100 germs, g
Control	–	89	43	14.0
I (Carbendazim)	2.5	94	32	13.7
Raxil	0.5	90	5	13.4
XLI	2.0	93	26	13.8
XXXVI	2.0	95	22	13.7

with respect to *Fusarium culmorum*. Benzamide **VIII** showed the highest activity against both *Fusarium culmorum* and *Helminthosporium sativum* and was superior to Carbendazim (**I**). The above-listed compounds attract interest for studying their toxicity with respect to other fungi species, as well as components of binary fungicide compositions.

The fungicide activity of some compounds was estimated by the reduction of affection of seeds produced

Table 6. Efficiency of 1*H*-benzimidazol-2-amine derivatives against root rot during vegetation of spring wheat

Compound no.	Dose, $1ton^{-1}$	Field germination capacity, %	Root rot	
			affection, %	biological efficiency, %
Control	–	64.8	40.1	–
I (Carbendazim)	2.5	80.2	11.8	70.6
XXXVI	2.0	84.6	11.2	72.1
XLI	2.0	78.0	11.5	71.3

Table 7. Effect of 1*H*-benzimidazol-2-amine derivatives on the crop yield of spring wheat

Compound no.	Dose, $1ton^{-1}$	Number of stems/m^2	Stem length, cm	Ear length, mm	Number of seeds in an ear	Weight of 1000 seeds, g	Crop yield, $g/m^2 \times 10^{-1}$	Gain in crop yield, $g/m^2 \times 10^{-1}$
Control	–	218	81.7	72.3	23.9	7.3	14.2	–
I (Carbendazim)	2.5	270	84.0	76.4	23.6	7.9	17.8	3.6
XXXVI	2.0	295	82.6	75.7	24.2	7.2	19.4	5.2
XLI	2.0	286	79.2	69.1	23.8	7.0	18.4	4.2

by root rot. This procedure ensures estimation of integral fungicide activity, for root rot is caused by a set of pathogenic Fungi imperfecti belonging to different stems (*Helmintosporium*, *Fusarium*, etc.). Infection persists on the seed surface and develops upon germination under moist conditions. The phytotoxicity of compounds can be estimated concurrently by the germination capacity and change in the weight of germs relative to control. From the compounds to be tested we prepared 30% film-forming free-flowing pastes, and seeds were treated with these pastes. The results of treatment of seeds of Voronezhskaya wheat are given in Table 3. It is seen that some compounds exhibit fungicide activity at a dose of 1.0 kg (calculated on the active substance) per ton of seeds, i.e., the effect is higher than or similar to that of widely used Carbendazim (**I**). Specifically, the following compounds must be noted: *N*-(1*H*-benzimidazol-2-yl)-acetamide (**III**), *N*-(1*H*-benzimidazol-2-yl)-3,5-dichloro-2-hydroxybenzamide (**VI**), *N*-(1*H*-benzimidazol-2-yl)benzamide (**VIII**), *N*-(1*H*-benzimidazol-2-yl)-5-chloro-2- hydroxybenzamide (**XII**), *N*-(1*H*-benzimidazol-2-yl)-2-hydroxy-5-nitrobenzamide (**XIII**), *N*-(1*H*-benzimidazol-2-yl)guanidine (**XXIII**), methyl (5-chloro-1*H*-benzimidazol-2-yl)carbamate (**XXXVI**), methyl (5,6-dichloro-1*H*-benzimidazol-2-yl)carbamate (**XXXVII**), and (2-aminobenzimidazol-1-yl)(3-bromophenyl)methanone (**XLI**), whose technical efficiency considerably exceeded that of ester **I**.

Field tests were performed to estimate the efficiency of seed protectants against root rot and their influence on the sowing of seeds and crop yield. The data given in Tables 4–7 indicate that further studies on the above compounds, specifically 1*H*-benzimidazol-2-amine derivatives **XXXVI** and **XLI** (unfortunately, field tests of benzamide **VIII** were not performed), are promising. Moreover, studies on the fungicide activity of compositions for seed treatment should be extended to estimate their toxicity with respect to Ustilaginales and other fungi species inducing plant affections during seed germination and vegetation.

EXPERIMENTAL

The ^{13}C NMR spectra were recorded on a Bruker CXP-100 Fourier-transform spectrometer at a frequency of 22.63 MHz; the spectra were measured both with and without decoupling from protons. Dimethyl sulfoxide was used as solvent, and hexamethyldisiloxane, as reference. Signals were assigned (Table 1) by analyzing the chemical shifts, coupling constants, multiplicities, and signal intensity ratios; the data for model compounds and the results of calculation of magnetic shielding in the benzene ring were taken into account.

Primary tests for fungicide activity were performed by inoculation of a dense nutrient medium with

phytopathogenic fungi in the presence of a compound to be tested. All compounds were tested as a concentration of 0.003%. To ensure uniform distribution over the substrate, compounds were preliminarily dissolved in acetone (1 : 150) or thoroughly powdered. Potato–glucose agar was used as nutrient medium. Compounds to be tested were added to the substrate before its congelation (at 45–50°C), and the medium was transferred onto Petri dishes in a volume of 15 cm^3. *Fusarium culmorum* and *Helminthosporium sativum* mycelia were sown into each Petri dish at three sites simultaneously. In a blank sample, were sown into the same nutrient medium containing no fungicide. Samples were incubated for 72 h at 25–26°C, and average diameters of the fungi colonies were measured. Carbendazim (**I**) (a 30% suspension) was tested under the same conditions for comparison. The fungicide activity was calculated by the known formula [29].

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