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Acyl Derivatives of 2-Aminobenzimidazole and Their Fungicide Activity

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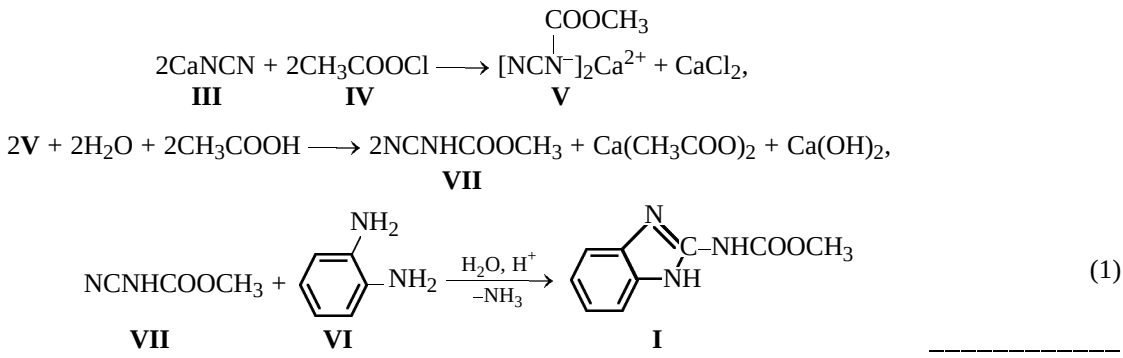
Abstract — Procedures have been developed for the preparation of methyl 2-benzimidazolylcarbamate, 2-acetylaminobenzimidazole, 2-benzoylaminobenzimidazole, 2-(3,5-dibromo-2-hydroxybenzoylamino)benzimidazole, 1-(3,6-dichloro-2-methoxybenzoyl)-2-aminobenzimidazole, 2-(3,5-dichloro-2-hydroxybenzoylamino)benzimidazole, 2-(3,5-dichloro-2-methoxybenzoylamino)benzimidazole, and 1-(3,5,6-trichloro-2-methoxybenzoyl)-2-aminobenzimidazole. The synthesized compounds have been tested for fungicide activity.

Methyl 2-benzimidazolylcarbamate (**I**) is the active component of a series of highly efficient fungicide preparations possessing a wide spectrum of activity, such as Carbendazim, Bavistin, Derosal, etc. In addition, compound **I** is used as a mixture with other fungicides [1–3]. A number of methods for the synthesis of methyl ester **I** have been reported [4]. The goal of the present study was to develop a new, more practical procedure for the preparation of methyl ester **I**, 2-acetylaminobenzimidazole (**II**), and 2-benzoylaminobenzimidazole, as well as to synthesize new acyl derivatives of 2-aminobenzimidazole at the nitrogen atom in position *1* and the amino group from polysubstituted benzoyl chlorides and examine their fungicide activity.

Methyl ester **I** was obtained in [3, 4] by treatment of an aqueous suspension of calcium cyanamide (**III**) with methyl chloroformate (**IV**) and subsequent reaction of methyl cyanocarbamate (**V**) with *o*-phenylenediamine (**VI**) [scheme (1)]. 2-Acetylaminobenzimidazole (**II**) was prepared in a similar way by reaction of acetylcyanamide (**VIII**) with diamine **VI**, and 2-benzoylaminobenzimidazole (**IX**), by reaction of benzoylcyanamide (**X**) with the same diamine.



We have developed a new, more practical procedure for the synthesis of compound **I**, which utilizes no deficient, toxic, and rare starting materials [4]. The developed procedure is also free from an essential disadvantage intrinsic to the cyanamide scheme, namely technical difficulties in the filtration of a solution of calcium salt **V** from a considerable amount of finely dispersed inorganic salts [which are present in an amount of up to 70% in the starting technical grade calcium cyanamide (**III**)] after the reaction of **III** with chloroformate **IV**. The filtration process takes up to 20 h. Our procedure is based on the reaction of thiourea (**XI**) with 4 equiv of sodium hydroxide in melt at 90–100°C. In this case, reactions (2) and (3) occur in 20–30 min.

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$$\underset{\underset{\text{S}}{\|}}{\text{H}_2\text{NCNH}_2} + 2\text{NaOH} \longrightarrow \text{Na}_2\text{S} + 2\text{H}_2\text{O} + \text{H}_2\text{NCN}, \quad (2)$$

XI

$$\text{H}_2\text{NCN} + 2\text{NaOH} \longrightarrow \underset{\textbf{XII}}{\text{Na}_2\text{NCN}} + 2\text{H}_2\text{O}. \quad (3)$$

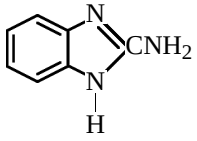
The resulting aqueous suspension of sodium cyanamide (**XII**) was treated with methyl chloroformate (**IV**). Methyl cyanocarbamate sodium salt (**XIII**) thus formed was acidified with hydrochloric acid and was brought into reaction with diamine **VI** to obtain methyl ester **I** [reaction (4) and (5)].

$$\underset{\textbf{XIII}}{\text{NaN}(\text{COOH}_3)\text{CN}} + \text{HCl} \longrightarrow \text{NaCl} + \text{HN}(\text{COOH}_3)\text{CN}, \quad (4)$$

$$\textbf{VI} + \text{NCNHCOOCH}_3 \xrightarrow{\text{HCl}} \textbf{I}. \quad (5)$$

We also developed alternative procedure for the synthesis of ester **I** and its derivatives, which was based on the acylation of 2-aminobenzimidazole (**XIV**) with methyl chloroformate in anhydrous medium. Following this procedure, we obtained new acyl derivatives of 2-aminobenzimidazole, containing polysubstituted benzoic acid moieties. 2-Aminobenzimidazole was prepared as described below. An aqueous suspension of cyanamide **XII** was acidified with hydrochloric acid, and the mixture was vigorously stirred at room temperature (pH 5). Diamine **VI** was then added, and the mixture was adjusted to pH 3 by adding hydrochloric acid, heated to 90–100°C, and stirred for 1.5 h at that temperature. Sodium hydroxide was added, and the mixture was stirred for 3 h at 90–100°C [reaction (6)].

$$\textbf{VI} + \textbf{XIII} \xrightarrow{\text{HCl, NaOH}} \underset{\textbf{XIV}}{\text{2-aminobenzimidazole}} \quad (6)$$



In the synthesis of 2-aminobenzimidazole, the molar ratio thiourea (**XI**) : NaOH : HCl : 1,2-phenylenediamine (**VI**) was 1.0 : 5.04 : 5.0 : 0.91. The mixture was cooled to 20–25°C, and the precipitate of 2-aminobenzimidazole (**XIV**) was filtered off and washed with cold water. After drying, the yield of the crude product was ~80%; it contained more than 80% of the main substance. Crude 2-aminobenzimidazole (**XIV**) was subjected to additional purification prior to acylation. The acylation of 2-aminobenzimidazole with acyl chlorides was carried out in acetone or toluene at 50–55°C in the presence of triethylamine as hydrogen chloride acceptor. The molar ratio 2-aminobenzimidazole : acyl chloride : triethylamine was 1.0 : (1.0–1.07) : (1.0–1.07). The yields of methyl ester **I** and 2-acetylaminobenzimidazole (**II**) were almost quantitative. The products contained more than 99 wt% of the main substance.

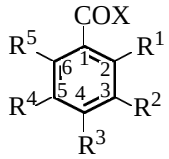
As a rule, halogen-substituted salicylic acids were prepared by halogenation of salicylic acid (**XV**). Chlorination and bromination of acid **XV** in an organic solvent (acetic acid) led to successive formation of 5-halo- and 3,5-dihalo-substituted salicylic acids. Further halogenation under more severe conditions (60–65% oleum, 90°C) afforded 3,5,6-trihalosalicylic acids [5–8].

The structure of halogenated salicylic acids and their derivatives **XVI**–**XXV** was determined on the basis of the ^{13}C NMR spectra. The signals were assigned (Table 1) by analysis of the chemical shifts, spin–spin coupling constants, multiplicities of signals, and their intensity ratios. Also, the available data for model compounds and the results of calculation of magnetic shielding in the aromatic ring were used.

The data in Table 1 show that the difference between the experimental and calculated chemical shifts of aromatic carbon atoms in salicylic acid (**XV**) attains 6 ppm. This is explained by formation of intamolecular hydrogen bond. As a result, the signal from the carboxylic carbon atom shifts downfield (δ_C 171.7 ppm) relative to the corresponding signal of benzoic acid (δ_C 168.5 ppm). Introduction of a halogen atom into the *ortho* position with respect to the hydroxy group (dichloro and dibromo derivatives **XVI**, **XVIII**, and **XIX**), as well as into the *para* position (**XVII**), does not induce an appreciable shift of the COOH signal, indicating that the hydrogen bond is preserved. When a halogen atom is present in position *3* (compounds **XVI**, **XVIII**, and **XIX**), the C^2 signal is displaced strongly upfield. A probable reason is stereoelectronic effect originating from interaction between lone electron pairs on the hydroxy oxygen and halogen atoms. Replacement of hydrogen at C^6 by chlorine (compound **XIX**) leads to shielding of the C^2 atom and shifts the COOH signal downfield by 5–6 ppm. This pattern is likely to result from distortion of coplanarity between the O=C–O– fragment and the benzene ring caused by substituents in positions *1, 2, 3*, and *6*.

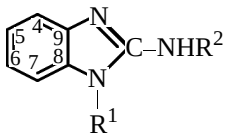
No hydrogen bonding is possible in methylated salicyclic acid derivatives **XX**–**XXV**. The ester carbon signal in the spectra of halogenated compounds **XXI** and **XXII** is displaced upfield relative to the corresponding signal of compounds **XV**–**XVIII**.

Table 1. ^{13}C chemical shifts of salicylic acid derivatives **XV**–**XXV**



Comp. no.	R^1	R^2	R^3	R^4	R^5	δ_C, ppm						
						C^1	C^2	C^3	C^4	C^5	C^6	CO, X
XV	OH	H	H	H	H	112.8	161.1	118.7	135.0	116.9	130.1	171.7
XVI	OH	Br	H	Br	H	115.97	157.6	112.0	140.2	110.3	132.1	171.0
XVII	OH	H	H	Br	H	115.4	160.8	120.0	138.1	110.4	132.6	171.0
XVIII	OH	Cl	H	Cl	H	114.7	155.9	122.2	134.2	127.7	128.0	170.6
XIX	OH	Cl	H	Cl	Cl	121.4	149.7	122.6	130.4	126.8	127.1	165.1
XX	OCH_3	H	H	H	H	121.8	158.6	112.9	131.2	120.6	133.6	167.9, 56.2
XXI	OCH_3	Cl	H	Cl	H	130.0	154.2	125.6	133.1	128.7	129.6	165.7, 62.4
XXII	OCH_3	Br	H	Br	H	129.9	155.8	120.1	138.8	116.8	133.3	165.9, 62.6
XXIII	OCH_3	H	H	Cl	H	123.3	156.8	114.8	129.8	124.3	131.6	168.2, 56.6
XXIV	OCH_3	H	H	Br	H	115.5	157.8	124.7	135.7	111.8	136.7	167.0, 56.7
XXV	OCH_3	Cl	H	H	Cl	128.2	152.6	126.0	131.4	131.7	131.7	164.2, 62.3

Table 2. ^{13}C NMR spectra of 2-aminobenzimidazole derivatives **I, II, IX**, and **XXVI**–**XXXI** in DMSO (δ_C, ppm)

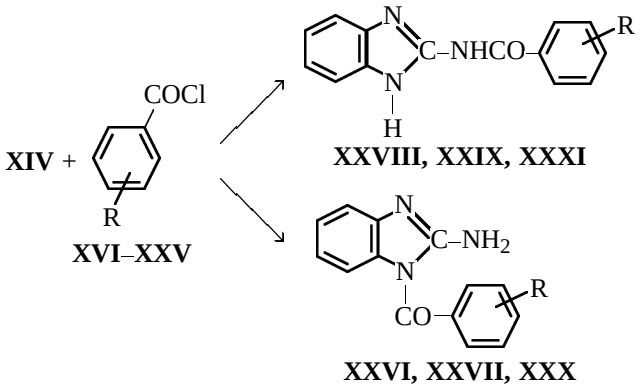


Comp. no.	C^2	C^4	C^5	C^6	C^7	C^8	C^9	C=O	R^1, R^2
I[a]	143.5	112.7	125.3	125.3	112.7	127.7	127.7	152.8	54.3
II	144.5	113.0	124.4	124.4	113.0	128.8	128.8	172.0	22.4
IX	149.4	114.0	122.3	122.3	114.0	134.8	134.8	169.2	134.0, 129.0, 129.0, 129.0, 129.0, 132.8
XXVI[b]	153.0	111.5	122.8	126.2	113.9	127.1	128.9	164.2	61.9, 127.1, 153.0, 126.6, 133.3, 129.5, 134.2
XXVII[b]	152.9	111.7	123.6	125.6	113.9	127.2	129.0	164.3	62.1, 133.0, 153.8, 126.6, 134.5, 126.7, 129.4
XXVIII	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
XXIX	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
XXX	154.7	112.7	120.4	125.3	116.7	127.6	129.3	165.6	62.7, 132.4, 152.0, 130.0, 133.5, 127.0, 129.3
XXXI	148.4	114.1	122.3	122.3	114.1	134.8	134.8	152.8	62.5, 129.0, 131.8, 134.8, 122.3, 152.8, 128.6

[a] In formic acid. [b] In acetic acid.

By acylation of 2-aminobenzimidazole in toluene or acetone with substituted benzoyl chlorides derived from acids **XVI**–**XXV** we obtained a series of new derivatives of 2-aminobenzimidazole at the nitrogen atom in position *1* or at the 2-amino group [scheme (7)]. The yields of compounds **XXVI**–**XXXI** were 98.70, 88.65, 33.48, 47.50, 76.40, and 89.60%, respectively.

Their structure was confirmed by the ^{13}C NMR spectra (Table 2). The site of acylation was established taking into account that structures with a substituted exocyclic amino group are characterized by a simpler spectral pattern of the benzimidazole fragment due to fast proton exchange between the endocyclic nitrogen atoms. The presence of an acyl



(7)

XXVI, R = 2-CH_3CO-3,5,6-Cl_3; **XXVII**, R = 2-CH_3CO-2,6-Cl_2; **XXVIII**, R = 2-OH-3,5-Br_2; **XXIX**, R = 2-OH-3,5-Cl_2; **XXX**, R = 2-CH_3CO-3,5-Cl_2; **XXXI**, R = 2-CH_3CO-3,5-Cl_2.

group at the exocyclic nitrogen atom induces a considerable (δ_C 5–8 ppm) upfield shift of the C^2 signal, while the C^8 and C^9 atoms are shielded to a lesser extent. By contrast, in the N^1-substituted compounds, the C^8 and C^9 atoms are shielded stronger.

All substituents in the compounds under study exhibit stronger or weaker electron-acceptor properties, thus reducing electron density on the heteroring. Using the NMR data, we can compare the substituent effects with variation of magnetic shielding upon protonation of the heteroring. As follows from [9, 10], protonation of the benzimidazole ring leads to an upfield shift of the C^2, C^4, C^7, C^8, and C^9 signals by 5–8 ppm. These results are consistent with our data for compounds that are protonated in organic acid solutions. The changes in chemical shifts observed on protonation are comparable with those induced by the substituents.

It should be noted that the degree of shielding of the amide carbon atom depends on the substitution pattern in the aromatic ring. The chemical shift of that carbon atom does not exceed 166.7 ppm for structures containing a methoxy group *ortho* to C(O)N. When the same position is occupied by a hydroxy group, appreciable deshielding of the amide carbon atom is observed: Its signal shifts to δ 170.5 ppm. As with substituted benzoic acids, the reason is formation of intramolecular hydrogen bond involving the hydroxy proton and carbonyl group of the substituent.

The obtained compounds were tested for fungicide activity by estimating protection of 7-day acrospires from affection with root rots. This procedure gives an integral estimate of fungicide activity, for root rots originate from a combination of pathogenic imperfect fungi belonging to various families (*Helmintosporium*, *Fusarium*, etc.). The infection persists on the seed surface and develops upon germination under moist conditions. The procedure allows simultaneous assessment of phytotoxicity and growth-regulating activity of compounds to be tested by reduction in the affection, increase in the germination capacity, and gain in the weight of acrospires relative to control. Samples were prepared as film-forming flowing pastes containing 30% of a compound to be tested, and Voronezhskaya wheat seeds were treated with these pastes. The results are given in Table 3.

Most of the tested compounds showed an appreciable fungicide activity: at a dose of 5 kg/ton they are superior to widely used Carbendazim. Special comments should be given to 2-acetylaminobenzimidazole (**II**), 2-(3,5-dichloro-2-hydroxybenzoylamino)-benzimidazole (**XXIX**), and 2-benzoylaminobenzimidazole (**IX**), which showed a considerably greater efficiency as compared to Carbendazim at all the applied doses. These compounds are very promising for use in practice.

EXPERIMENTAL

The ^{13}C NMR spectra were recorded on a Bruker CXP-100 Fourier spectrometer operating at 22.63 MHz both with complete decoupling from protons and without it; dimethyl sulfoxide was used as solvent, and hexamethyldisiloxane, as reference.

2-Acetylaminobenzimidazole (II) was synthesized by reaction of an aqueous suspension of calcium cyanamide (**III**) (*c* = 12–15 wt%) with acetic anhydride at a temperature not exceeding 35°C. Solid impurities present in the starting calcium cyanamide (**III**) were separated by filtering the solution of calcium acetylcyanamide. The filtrate was acidified with hydrochloric acid and treated with *o*-phenylenedi-

Table 3. Fungicide activity of 2-aminobenzimidazole derivatives against root rots on Voronezhskaya wheat seeds

Comp. no.	Dose, kg/ton	Germination capacity %	Affection with root rot, %	Technical efficiency, %	Weight of 100 acrospires, g
Control	–	79	77	–	14.6
I	5.0	77	66	14	13.2
	4.0	81	67	13	14.6
	3.0	84	70	9	14.9
II	5.0	78	38	51	12.8
	4.0	83	43	44	13.7
	3.0	89	54	30	13.7
IX	5.0	73	49	38	13.7
	4.0	77	58	26	13.8
	3.0	78	71	8	14.8
XXVI	5.0	76	51	34	14.0
	4.0	78	64	17	14.4
	3.0	86	71	8	15.0
XXVII	5.0	74	61	23	13.7
	4.0	74	82	0	14.0
	3.0	75	95	0	14.1
XXVIII	5.0	78	82	0	14.8
	4.0	74	73	5	14.4
	3.0	78	82	0	14.8
XXIX	5.0	71	66	42	14.1
	4.0	74	67	23	14.2
	3.0	80	70	14	14.7
XXX	5.0	66	43	44	9.7
	4.0	76	60	22	9.8
	3.0	84	70	9	11.5
XXXI	5.0	74	48	38	13.4
	4.0	79	58	25	14.0
	3.0	83	73	5	14.5

amine at 85–95°C, maintaining the acidity at pH 3.0–4.5 by gradual addition of hydrochloric acid to bind liberated ammonia.

2-Benzoylaminobenzimidazole (IX) was synthesized in a similar way from an aqueous suspension of calcium cyanamide (**III**) and benzoyl chloride. The mixture was vigorously stirred for 1.0–1.5 h at 30–40°C. Inorganic salts were removed by filtration, and the resulting aqueous solution of benzoylcyanamide calcium salt (**X**) was acidified with hydrochloric acid to pH ~ 3 and brought into reaction with diamine **VI** at 85–95°C (pH 3.0–4.5; reaction time 1.0–1.5 h). 2-Benzoylaminobenzimidazole (**IX**) was filtered off and thoroughly washed to remove inorganic salts.

In the synthesis of sodium cyanamide (**XII**), solid thiourea (**XI**) and solid sodium hydroxide were stirred in a *Z*-mixer using an endless screw with heating to 90°C. After 20–30 min, the mixture was cooled on stirring. It crystallized below 80°C and was disintegrated with endless screws and additionally ground in a centrifugal blender. The resulting finely powdered mixture of sodium cyanamide (**XII**) and sodium sulfide was forwarded to the synthesis of methyl cyanocarbamate sodium salt **XIII**. For this purpose, sodium cyanamide was dispersed in water to a concentration of 12–15%, and methyl chloroformate was added at 20–30°C under vigorous stirring at such a rate that the temperature did not exceed 30°C. The thiourea–ethyl chloroformate molar ratio was 1 : 1. When the addition of methyl chloroformate was complete, the mixture was vigorously stirred for 15–20 min at 20–30°C and acidified with hydrochloric acid to pH 3.0–4.5. The mixture was filtered, crystalline *o*-phenylenediamine (**VI**) was added to the filtrate containing methyl cyanocarbamate, and the mixture was heated to 85–95°C. At that temperature, the reaction was complete in 90 min. Hydrochloric acid was gradually added to the mixture during the process (binds liberated ammonia), maintaining the pH in the range from 3.0 to 4.5. Methyl 2-benzimidazolylcarbamate (**I**) precipitated and was filtered off, thoroughly washed on a filter to remove inorganic salts, and dried.

3,5-Dibromosalicylic acid. A solution of 51.6 ml of bromine in 50 ml of glacial acetic acid was added under vigorous stirring to a suspension of 55 g of salicylic acid in 350 ml of glacial acetic acid at such a rate that the temperature did not exceed 25°C; if necessary, the mixture was cooled. When ~1/2 of the entire amount of bromine was added, the mixture became a colored transparent solution. After addition of bromine, the solution was dark purple. The solution was cooled to 15–18°C on stirring, and a solid began to separate. Water was added in an amount of ~1/2 of the volume of the mixture, and the mixture was left to stand for 4–5 h. The precipitate of 3,5-dibromosalicylic acid was filtered off, washed on a filter with dilute acetic acid and then with water, and dried. Yield ~114 g (95%); the product contained no less than 95 wt% of 3,5-dibromosalicylic acid. 5-Bromosalicylic acid was identified as by-product. The yield and purity of 3,5-dibromosalicylic acid thus obtained strongly depended on the reactant ratio and temperature. At a bromine-to-salicylic acid molar ratio of ~2.5 : 1.0, the yield of crude 3,5-dibromosalicylic acid attained 99%. Raising the reaction temperature from 20 to 70°C reduced the product yield from 99% to 66%. In this case, the amount of dibromo- and tribromophenol in the filtrate increased.

3,5-Dichlorosalicylic acid. A suspension of 40 g of salicylic acid in 250 ml of glacial acetic acid was heated to 35°C on a water bath (the mixture gradually became homogeneous), and gaseous chlorine was passed through a bubbler over a period of 4–5 h. Bubbling of chlorine was terminated, and the mixture was cooled to room temperature while stirring, purged with air to remove absorbed chlorine, and poured into cold water. The precipitate was filtered off, thoroughly washed on a filter with acetic acid and water (in succession), and dried. Yield of the crude product ~95%; it contained no less than 99% of the main substance.

Methylation of 2-hydroxybenzoic acids. A solution of 8 g of sodium hydroxide in 47 ml of water was cooled to 0°C, and 0.1 mol of the corresponding hydroxybenzoic acid was added under stirring. Dimethyl sulfate, 10 ml, was quickly added on cooling, and the mixture was heated to 35°C and stirred for 20 min at that temperature. An additional 10 ml of dimethyl sulfate was added, the mixture was stirred for 10 min at 45°C, heated to 95–100°C, and stirred for 2 h at 95–100°C, a solution of 3.9 g of NaOH in 13.3 ml of water was added, and the mixture was stirred for 2 h at 95–100°C. The mixture was cooled to room temperature, and 2 ml of concentrated hydrochloric acid was added; the pH value changed from 7 to 1. The mixture turned turbid, and the product was extracted into diethyl ether. Removal of the solvent from the extract gave 76–99% of the corresponding 2-methoxybenzoic acid containing 93–98% of the main substance.

Carboxylic acid chlorides were synthesized by treatment of the corresponding acids in chloroform with 1.5–2.0 equiv of thionyl chloride on heating for 5–8 h under reflux. Several drops of dimethylformamide as catalyst were added. When the reaction was complete, excess thionyl chloride and the solvent were distilled off under reduced pressure. The yields and purity of the crude products were 95–99%.

Acylation of 2-aminobenzimidazole. A mixture of 150 ml of acetone (or toluene), 9.31 g of 2-aminobenzimidazole, and 9.94 ml of triethylamine was heated to 50–55°C, and a solution of 9.31 g of 3,6-dichloro-2-methoxybenzoyl chloride [prepared from technical grade 3,6-dichloro-2-methoxybenzoic acid (from Novartis)] in 50 ml of acetone was added. The mixture was heated for 2 h at 55°C and poured into cold water, and the precipitate was filtered off and dried. Yield 25.6 g. The other acyl derivatives of 2-aminobenzimidazole were synthesized in a similar way.

Seed treatment. A flask was charged with a sample (see above) containing 50 mg of a compound to be tested (this amount corresponds to a dose of 5 kg/ton), and 0.1 ml of water and 10 g of seeds were added. The flask was shaken for 5–8 min until the sample was distributed completely on the seed surface, i.e., until it was removed completely from the flask walls. Laboratory tests were performed with Voronezhskaya wheat seeds. The seeds were treated 3 days prior to germination and were incubated in a moist chamber (Petri dishes) on a filter paper at 24°C. The germination capacity and the degree of affection with root rots were determined in 7 days after germination started. The technical (biological) activity of the fungicides was determined using the known formula [11].

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