Synthesis and spectral properties of derivatives of 3-(benzazolylamino)-2-propenoic acid

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Synthesis of esters and nitriles of *N*-aminobenzimidazole and benzotriazole substituted 2-cyano and 2-ethoxycarbonyl-2-propenoic acid is described. On the basis of infrared, ultraviolet, mass, ^{1}H and ^{13}C NMR spectra the structure and geometrical isomerism of the prepared substitution products is discussed.

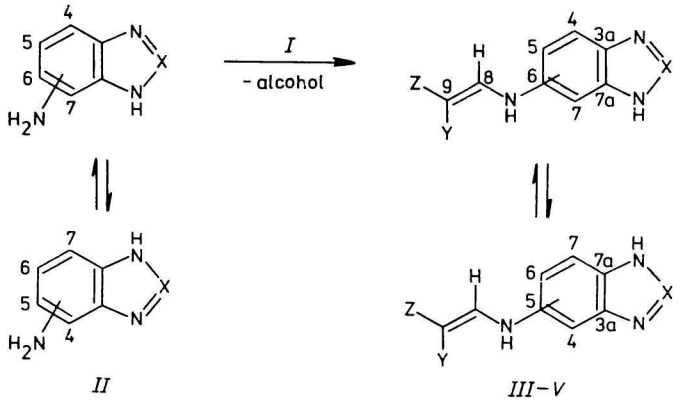
В работе описано получение сложных эфиров и нитрилов *N*-аминобензимидазолов и бензотриазолов 2-циано или 2-этоксикарбонил-2--пропеновой кислоты. На основании ИК-, УФ-, масс-спектрометрических, ^{1}H и ^{13}C ЯМР спектроскопических характеристик обсуждается строение и геометрическая изомерия образовавшихся продуктов замещения.

Derivatives of 3-alkoxy-2-propenoic acid (*I*) undergo easily nucleophilic substitution at the carbon binding the alkoxy group [1]. In the role of nucleophiles were most frequently used aromatic amines [2], heterocyclic amines [3] or heterocycles, containing a nucleophilic nitrogen atom [4].

Now we describe the preparation of substitution products of derivatives *Ia*—*Ic* with aminobenzimidazoles (*IIa*, *IIb*) and aminobenzotriazoles (*IIc*, *IId*), carrying an amino group at the benzene ring. In all attempted reactions substitution products arised and in none cyclization took place (Scheme 1).

Nucleophilic substitutions in which a ring nitrogen atom played the role of nucleophile have already been described [4]. In our reaction conditions no such substitution was observed, even when unsubstituted benzimidazole or 5(6)-nitrobenzimidazole was used. This is in accord with findings [5—8], claiming that an amino group at the benzene ring is more basic than an imino group of an azole ring.

Enamine protons of substitution products can assume either a transoid or a cisoid arrangement. Thus ethyl 3-(2-pyridylamino)-2-cyano-2-propenoate could be separated to *cis* and *trans* conformer, the latter being more stable owing to the intramolecular hydrogen bond [3]. Our substitution products can exist in



			Y	Z
Ia:	EtO–CH=C(COOEt)$_2$	*III*:	COOEt	COOEt
Ib:	MeO–CH=C(CN)COOMe	*IV*:	COOMe	CN
Ic:	EtO–CH=C(CN)$_2$	*V*:	CN	CN

		X	position of the substitution in *III–V*, in *II* position of $-NH_2$
II–V	*a*:	CH	4
	b:	CH	5
	c:	N	4
	d:	N	5

Scheme 1

more conformations as well; derivatives *IV* can form two geometrical isomers.

Electronic spectra of the synthesized compounds *III—V* showed three absorption bands, two of them in the region of $\lambda = 250$—290 nm, the third, most intensive one in the region of $\lambda = 324$—350 nm (Table 1). Introduction of a polar ethylenic group at the aminobenzazole skeleton caused its longwave maximum to shift bathochromically to 350 nm.

^{1}H NMR spectra of the synthesized compounds *III* and *IV* showed doublets with a 14 Hz coupling constant, testifying thus to the antiperiplanar arrangement of the —NH—CH= group, in accord with previous reports [3, 7]. Stabilization of the substituted propenic fragment by an intramolecular hydrogen bond has been assumed based on the presence of a ν(N—H) band at $\tilde{\nu} = 3430\ cm^{-1}$ with a halfwidth of 250—300 cm^{-1} in the infrared spectra of derivatives *III* and *IV*. Derivatives *V*, where such stabilization is not possible, fail to show the band. According to proton NMR spectra, compounds *III*

Table 1

UV[a] and IR[b] spectral data of compounds *III*—*V*

Compound	λ_{max}/nm log (ε/(m^2 mol^{-1}))				$\tilde{\nu}_{max}$/cm^{-1}		
					ν(C=O)	ν(C≡N)	ν(NH)
IIIa	228	252	260	328	1680	—	3445
	3.06	2.89	2.81	3.33	1640		
IIIb	226	252	259	327	1680[d]	—	3435
	3.34	3.22	3.18	3.59	1640		
IIIc	227	259	267	345	1685	—	3425
	3.18	2.83	2.79	3.43	1630		
IIId	225	273	283	330	1680	—	3430
	3.14	3.05	3.08	3.40	1640		
IVa		253	260	335	1680	2215	3420
		2.91	2.88	3.35			
IVb	—	253	262	328	1670	2213	3440
		2.60	2.52	3.09			
IVc	—	264	282	348	1680	2210	3430
		2.75	2.73	3.35			
IVd	—	274	283	328	1670	2207	*c*
		3.06	3.10	3.41			
Va	—	248	259	327	—	2220	—
		2.93	2.83	3.40		2210	
Vb	—	253	260	324	—	2220	—
		2.98	2.94	3.33		2207	
Vc	—	262	288	343	—	2220	—
		2.83	2.80	3.39		2213	
Vd	—	262	283	324	—	2220	—
		2.85	2.79	3.01		2214	

a) In methanol; *b*) in KBr pellets; *c*) unobserved; *d*) Ref. [7]: $\tilde{\nu}$(ν(C=O)) = 1640 and 1680 cm^{-1}.

possessed two nonequivalent ethoxy groups. The same phenomenon (two nonequivalent methoxy groups) in the NMR spectra of derivatives *IV* led us to assume the presence of two geometrical isomers. Consequently, signals of protons at C-4 and C-6 of benzimidazoles came as doubled, whereas those of benzotriazole derivatives were broadened. However, broadened signals of protons at C-8 have been observed even in the spectra of derivatives, that lacked any stabilization by an intramolecular hydrogen bond, *e.g.* derivatives *IVc*, *IVd*, *V*. Proton signals of the studied compounds are given in Table 2.

Inspection of carbon NMR spectra of derivatives *IV* confirmed the existence of two geometrical isomers. Relative intensities of the respective signals allowed us to determine relative content of isomers and based on the coupling constant ^3J(H-8—CO) and ^3J(H-8—CN) the signals could even be assigned to the respective isomers in solution. The *E*/*Z* ratio calculated either from proton or

Table 2

Chemical shifts (δ/ppm) and coupling constants in ^{1}H NMR spectra of compounds *III*–*V*

Compound	H-2	H-4	H-5	H-6	H-7	H-8	NH	OCH_2	$(O)CH_3$
IIIa	8.25 s		———	7.19 m (3H)	———	9.23 d 14 Hz	11.33 d 14 Hz	4.13 q 4.21 q	1.20 t 1.23 t
IIIb	8.24 s	7.58 d 2 Hz		7.16 dd	7.60 d 9 Hz	8.45 d 14 Hz	10.89 d 14 Hz	4.10 q 4.20 q	1.23 t 1.24 t
IIIc			———	7.35 m (3H)	———	9.36 d 14 Hz	10.25 d 14 Hz	4.06 q 4.19 q	1.19 t 1.23 t
IIId		7.79 d 2 Hz		7.41 dd	7.93 d 9 Hz	8.46 d 14 Hz	10.86 d 14 Hz	4.10 q 4.19 q	1.23 t 1.24 t
IVa	8.32 s		———	7.30 m (3H)	———	9.16 d 14 Hz	11.35 d 14 Hz		3.75 s
	8.34 s					10.15 d 14 Hz	10.88 d 14 Hz		3.83 s
IVb	8.24 s	7.73 d 2 Hz		7.38 dd	7.61 d 9 Hz	8.14 d 13.5 Hz	10.85 d 13.5 Hz		3.73 s
		7.88 d 2 Hz		7.43 dd	7.61 d 9 Hz	8.28 d 13.5 Hz	10.79 d 13.5 Hz		3.78 s
IVc			———	7.48 m (3H)	———	9.18 d 14 Hz	11.40 d 14 Hz		3.79 s
						10.0 s			3.85 s
IVd		7.97 d 2 Hz		7.53 dd	8.02 d 9 Hz	8.67 d 12 Hz	10.86 d 12 Hz		3.81 s
		7.96 d 2 Hz		7.58 dd	8.02 d 9 Hz	8.45 s			3.86 s

Table 2 (Continued)

Compound	H-2	H-4	H-5	H-6	H-7	H-8	NH	OCH_2	$(O)CH_3$
Va	8.28 s	—	———	7.43 m (3H)	———	9.66 s	—	—	—
Vb	8.42 s	7.59 d 2 Hz	—	7.09 dd	7.53 d 8.5 Hz	8.16 s	—	—	—
Vc	—	—	———	7.48 m (3H)	———	9.36 s	—	—	—
Vd	—	7.86 d 2 Hz	—	7.49 dd	7.91 d 9 Hz	8.56 s	—		

Table 3

^{13}C NMR spectral data (δ/ppm) of compounds *II*—*V*

Compound	C-2	C-4	C-5	C-6	C-7	C-3a	C-7a	C-8	C-9	CN	CO	OCH_2	$(O)CH_3$
IIa	139.5	144.6	101.5	123.3	104.7	136.3	138.7	—	—	—	—	—	—
IIb	139.5	96.9	144.4	111.6	116.9	137.1	137.8	—	—	—	—	—	—
IIc	—	139.2	97.9	128.0	104.3	134.0	136.2	—	—	—	—	—	—
IId	—	90.4	148.5	116.0	118.2	137.3	136.4	—	—	—	—	—	—
IIIa	141.6	129.4	107.9	123.1	107.3	132.0	134.6	151.8	93.2	—	164.8 167.5	59.3 59.5	14.2
IIIb	143.0	103.8	134.5	113.3	116.4	138.3	136.8	152.0	92.1	—	164.9 167.5	59.3	14.2
IIIc	—	129.3	108.9	126.7	107.5	135.7	137.1	152.3	94.2	—	164.6 167.4	59.4 59.6	14.0
IIId	—	117.3	117.3	137.7	100.3	137.7	137.7	151.1	94.1	—	164.7 167.0	59.3 59.5	14.0
IVa E	142.1	129.7	111.4	122.9	108.6	133.2	134.6	155.8	73.5	116.1	165.4	—	51.8
Z	142.2	128.7	108.6	123.2	107.5	132.5	136.1	153.5	73.4	118.2	167.1	—	51.9
IVb E	143.3	104.8	135.0	113.8	116.4	138.1	136.4	153.4	73.3	116.3	162.1	—	51.8
Z			134.0					154.0	73.4	118.6	165.5	—	52.4
IVc E	—	130.2	111.8	126.6	109.2	135.7	137.7	155.6	74.8	116.0	165.3	—	52.0
Z		128.5			108.8			154.1	74.5	118.5	166.9	—	52.0
IVd E	—	117.5	117.5	137.4	100.8	138.1	136.7	153.2	75.0	115.8	165.0	—	51.8
Z								154.0	74.0	118.1	166.5	—	51.8
Va	142.1 143.1	129.0 114.2	109.3 116.1	123.0 111.5	104.8 117.0	134.7 137.6	135.5 132.9	157.6 156.0	51.1 51.1	114.6 116.6	—	—	—
Vb	143.0	104.8	134.1	113.7	115.8	138.1	136.2	156.0	50.6	114.4 116.6	—	—	—
Vc	—	129.2	112.8	127.5	108.2	136.4	135.8	157.5	52.9	113.4 116.2	—	—	—
Vd	—	117.7	116.7	138.0	101.9	137.9	137.5	156.2	52.4	114.0 116.2	—	—	—

Table 4

Mass spectra of compounds *III*—*V*

Compound	*m/z* (I_r/%)
IIIa	304 (9.4); $M^{+\bullet}$ = 303 (54.9); 258 (16.5); 257 (35.3); 231 (14.1); 230 (100); 229 (21.2); 212 (19.6); 211 (8.2); 201 (14.5); 200 (13.7); 186 (12.2); 185 (43.1); 184 (35.3); 183 (27.4); 158 (31.3); 157 (62.7); 156 (35.3); 144 (37.3); 133 (14.1); 129 (11.4); 118 (29.4); 117 (21.2); 105 (7.8); 103 (9.0); 90 (20); 78 (5.5); 63 (8.6); 44 (9.4); 43 (10.6).
IIIb	$M^{+\bullet}$ = 303 (53.4); 258 (24.1); 257 (100); 256 (5.2); 229 (5.2); 214 (5.9); 213 (16.7); 212 (14.8); 201 (36.2); 185 (11.7); 184 (37.9); 183 (11.4); 167 (13.4); 158 (6.6); 157 (37.9); 156 (15.1); 144 (7.2); 133 (15.9); 129 (8.3); 117 (13.4); 90 (8.6); 71 (7.9); 57 (11.4); 44 (13.1); 43 (7.6).
IIIc	305 (7.9); $M^{+\bullet}$ = 304 (49); 258 (18.1); 257 (37.7); 230 (10.9); 229 (34); 202 (9.4); 186 (20.8); 185 (30.2); 184 (100); 159 (14); 158 (71.7); 157 (13.2); 156 (14.3); 145 (14); 134 (7.9); 131 (9.8); 130 (30.2); 129 (24.9); 128 (11.7); 118 (9.1); 116 (22.6); 106 (14.7); 105 (18.5); 104 (26.4); 103 (21.5); 102 (16.6); 90 (10.9); 78 (18.5); 77 (19.2); 76 (14.3); 63 (11.3); 53 (30.2); 52 (13.2); 51 (14).
IIId	305 (11.8); $M^{+\bullet}$ = 304 (71.4); 276 (22.1); 259 (32.1); 258 (100); 231 (7.1); 230 (39.3); 202 (42.9); 186 (14.6); 185 (53.4); 184 (92.9); 159 (10); 158 (57.1); 157 (28.6); 156 (25); 145 (9.6); 134 (8.9); 131 (10.4); 130 (46.4); 129 (42.9); 128 (13.2); 118 (8.2); 117 (17.9); 116 (85.7); 106 (14.6); 105 (12.5); 104 (17.1); 103 (42.9); 102 (24.6); 101 (8.9); 90 (21.4); 79 (13.9); 78 (17.5); 77 (16.4); 76 (23.6); 75 (8.9); 64 (8.2); 63 (26.8); 62 (7.5); 53 (28.6); 52 (23.2); 51 (18.9); 50 (8.6); 45 (8.2); 44 (8.6); 39 (10); 31 (10); 29 (78.6); 28 (21); 27 (32).
IVa	243 (14); $M^{+\bullet}$ = 242 (100); 211 (14.4); 210 (23.6); 184 (12.4); 183 (96); 182 (88); 181 (9.2); 156 (9.2); 155 (8.4); 144 (52); 118 (32); 117 (25.6); 91 (9.6); 90 (18); 63 (9.2); 44 (25.2); 32 (11.6); 31 (16.4); 28 (44).
IVb	243 (11.6); $M^{+\bullet}$ = 242 (84.4); 211 (23.4); 210 (100); 183 (25); 182 (39.1); 156 (6.6); 155 (7.5); 144 (35.9); 129 (6.25); 128 (6.6); 118 (7.2); 117 (23.4); 105 (6.6); 90 (11.9); 78 (5); 63 (8.8); 52 (6.9); 44 (13.8); 32 (11.9); 31 (18.8); 29 (8.4); 28 (21.9).
IVc	244 (13.8); $M^{+\bullet}$ = 243 (100); 211 (15.6); 184 (34.4); 183 (94); 157 (23.4); 156 (25); 155 (59.4); 154 (16.6); 145 (17.2); 130 (9.4); 129 (40.6); 128 (59.4); 127 (19.7); 117 (8.1); 116 (25); 106 (28.1); 105 (37.5); 104 (34.4); 103 (16.9); 102 (21.9); 101 (18.8); 90 (25); 79 (12.8); 78 (35.9); 77 (39.1); 76 (25); 75 (12.8); 64 (18.7); 63 (31.2); 62 (11.9); 59 (10.6); 53 (19.7); 52 (67.2); 51 (43.8); 50 (18.8); 39 (19.4); 31 (56.3); 29 (50).
IVd	244 (12.6); $M^{+\bullet}$ = 243 (95.6); 215 (30.4); 211 (34.8); 197 (8.30); 185 (9.1); 184 (39.1); 183 (91); 182 (7.8); 158 (10.4); 157 (78.3); 156 (19.1); 155 (41.3); 154 (19.1); 145 (34.8); 130 (13.5); 129 (65.2); 128 (100); 127 (10.9); 118 (10); 117 (20.4); 116 (56.5); 106 (7); 105 (10.4); 104 (16.5); 103 (18.7); 102 (27); 101 (28.7); 100 (7.8); 90 (27.8); 89 (9.6); 79 (11.3); 78 (18.3); 77 (27); 76 (22.6); 75 (13.9); 68 (17.9); 64 (17.4); 63 (56.5); 62 (20.9); 53 (18.3); 52 (76.1); 51 (47.8); 50 (20.4); 44 (11.7); 40 (9.1); 39 (19.6); 38 (17); 37 (7.8); 29 (10.9); 28 (31.3); 27 (10.4).
Va	210 (11); $M^{+\bullet}$ = 209 (83.3); 183 (7.7); 182 (26.7); 181 (6.3); 155 (5.3); 145 (10); 144 (100); 118 (46.7); 117 (30); 91 (9.7); 90 (23.3); 77 (53.3); 63 (14); 52 (7.7).
Vb	210 (13); $M^{+\bullet}$ = 209 (100); 208 (12); 183 (9.7); 182 (43.3); 181 (8.3); 155 (9.7); 154 (9.3); 144 (26.7); 128 (8); 118 (8); 117 (45); 105 (5.3); 90 (24); 78 (7); 77 (9.3); 76 (6.3); 64 (7.7); 63 (24); 62 (9.7); 52 (17.7); 51 (11); 39 (7.7); 38 (7.3); 28 (13.7).
Vc	$M^{+\bullet}$ = 210 (100); 211 (12); 182 (14.7); 181 (13); 156 (7.7); 155 (28.3); 154 (16.3); 149 (9.7); 145 (6.7); 134 (14.3); 129 (7); 128 (26.7); 127 (16.7); 116 (9.3); 106 (7.3); 105 (40); 104 (13.3); 103 (6); 101 (9); 90 (12); 79 (17.6); 78 (19); 77 (21.3); 76 (11); 67 (8.7); 64 (9); 63 (13.7); 62 (7.3); 53 (8); 52 (30); 51 (20.7); 50 (9); 44 (21.7); 39 (9.7); 38 (7.7); 28 (35).
Vd	$M^{+\bullet}$ = 210 (30.6); 182 (7.5); 155 (7.2); 149 (7.5); 128 (9.4); 101 (5.8); 93 (22.2); 86 (6.9); 60 (11.1); 66 (47); 59 (12.2); 58 (19.4); 55 (5.3); 52 (6.1); 51 (7.5); 45 (11.9); 44 (7.7); 43 (72); 42 (100); 41 (72); 40 (16.7); 39 (38.9); 38 (11.9); 29 (19.7); 28 (25); 27 (27.8).

Table 5

3-Benzazolylamino derivatives of 2-propenoic acid *III*—*V*

Compound	Formula M_r	w_i(calc.)/% w_i(found)/%			Yield %	M.p. °C
		C	H	N		
IIIa	$C_{15}H_{17}N_3O_4$	59.40	5.65	13.85	38	166—168
	303.3	59.32	5.78	14.01		
IIIb[a]	$C_{15}H_{17}N_3O_4$				97	186—188
	303.3					
IIIc	$C_{14}H_{16}N_4O_4$	55.26	5.30	18.41	84	218—222
	304.3	55.62	5.08	18.48		
IIId	$C_{14}H_{16}N_4O_4$	55.26	5.30	18.41	58	182—184
	304.3	55.27	5.48	18.31		
IVa	$C_{12}H_{10}N_4O_2$	59.50	4.16	23.13	62	228—231
	242.2	59.38	4.24	23.60		
IVb	$C_{12}H_{10}N_4O_2$	59.50	4.16	23.13	89	218—221
	242.2	59.27	4.15	23.01		
IVc	$C_{11}H_9N_5O_2$	54.32	3.73	28.79	53	213—215
	243.2	54.25	3.75	28.80		
IVd	$C_{11}H_9N_5O_2$	54.32	3.73	28.79	54	203—205
	243.2	54.39	3.70	28.66		
Va	$C_{11}H_7N_5$	63.15	3.37	33.47	72	252—257
	209.2	63.04	3.41	33.22		
Vb	$C_{11}H_7N_5$	63.15	3.37	33.47	51	over 360
	209.2	63.12	2.93	33.41		
Vc	$C_{10}H_6N_6$	57.14	2.88	39.98	52	over 360
	210.2	56.95	2.85	39.91		
Vd	$C_{10}H_6N_6$	57.14	2.88	39.98	57	over 360
	210.2	57.00	2.70	39.54		

a) Ref. [5]: M.p. = 188—189 °C, yield = 83 %.

from carbon NMR spectra was the same. Derivatives *IVa* and *IVd* existed in solution as an equimolar mixture of *E* and *Z* isomer, whereas derivatives *IVb*, *IVc* existed in a 2 : 1 ratio in favour of the energetically preferred isomer. All derivatives displayed a 4—6 Hz ^3J(H-8—C)-*cis* constant and a 10—12 Hz ^3J(H-8—C)-*trans* constant. Nonequivalency of the polar groups attached to the double bond of the propenic fragment asserted itself by doubling of certain carbon signals in ^{13}C NMR spectra (Table 3).

All mass spectra of compounds *III*—*V* showed characteristic molecular ions as well as ions with $m/z = 90$ (C_6H_4N). In the fragmentation of *IV* and *V* a common pattern could be observed, namely splitting of the azole ring under elimination of either HCN or N_2, leading to ions with equal m/z values for both studied heterocyclic derivatives. In addition, benzimidazole derivatives split off

the propenoic acid fragment. Fragmentation of compounds of the type *III* started at the 2-propenic group. The majority of fragmentation processes have been confirmed by the presence of metastable ion peaks. Mass spectra of compounds *III*—*V* are given in Table 4.

Experimental

Starting aminobenzazoles were prepared by catalytic reduction of the corresponding nitro derivatives by hydrogen (catalyst 10 % Pd/active carbon). Alcoholic solutions of all prepared amino derivatives were used directly in subsequent reaction with *I*, according to Ref. [5]. Substitution products were white crystalline compounds, possessing R_f values 0.6 for *III*, 0.5 for *IV*, and 0.35 for *V* (eluant chloroform—methanol, volume ratio = 4 : 1, Silufol 254 UV). Melting points, reaction yields, and results of elemental analyses are given in Table 5.

Infrared and ultraviolet spectra were recorded on a Specord IR 75 and a Specord UV VIS spectrophotometers (Zeiss, Jena), respectively. NMR spectra were taken on a Tesla BS 487 C 80 MHz apparatus and Jeol model FX-100 spectrometer, operating at 25.04 MHz, in dimethyl sulfoxide-d_6 at 25 °C and with hexamethyldisiloxane as internal standard.

Mass spectra were determined on an AEI spectrometer, model MS 902 S, operated at ionizing energy 70 eV, temperature of ionizing chamber 170—180 °C and an ionizing current 100 μA. Only signals having relative intensity greater than 5 % were reproduced.

Derivatives of 3-(benzazolylamino)-2-propenoic acid III—V

To aminobenzazole *II* (0.1 mol), obtained by catalytic reduction of the nitro derivative by hydrogen, in methanol (100 cm^3), *I* (0.1 mol) was added and the reaction mixture was refluxed for 1 h. Then it was evaporated to dryness and separated by chromatography on a silica gel column (graininess 100—140 μm, eluant chloroform—methanol, volume ratio = 10 : 1 for *III*, for *IV* volume ratio = 1 : 1). Substitution products *V* precipitated from the solutions immediately after warm up and 10 min reflux was enough for completion of the reaction. Derivatives *V* were purified in the same manner as *IV*.

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