

## PREPARATION AND NMR SPECTRA OF SUBSTITUTED 2-(4-NITROPHENYL)IMIDAZOLINONES

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A series of 11 substituted 2-(4-nitrophenyl)imidazolinones have been prepared by base catalyzed cyclizations of substituted 2-(4-nitrobenzoylamino)alkanamides. At higher methoxide concentrations the cyclization can be accompanied by reduction of nitro group to azoxy group. All the substances prepared have been identified by <sup>1</sup>H and <sup>13</sup>C NMR spectra.

**Key words:** 2-Benzoylaminocarboxylic acid amides; 2-Phenyl-5-imidazolinones.

Substituted 2-benzoylaminocarboxylic acid amides whose synthesis and NMR spectra were described in a previous paper<sup>1</sup> can be biologically active<sup>2</sup> and can also serve as starting materials for syntheses of substituted imidazolinones, some of which are commercial herbicides<sup>2</sup>.

The aim of the present paper was to prepare substituted imidazolinones **2** by cyclization reactions of 2-(4-nitrobenzoylamino)alkanamides **1** in the presence of sodium methoxide. The starting aminoamides were prepared from the respective nitriles by a known way<sup>1</sup>. The cyclization of substituted 2-benzoylaminocarboxylic acid amides **1** to the substituted 2-phenyl-4-imidazolinones **2** was carried out in methanolic solutions of sodium methoxide. The cyclization of the benzoylaminocarboxylic acid amides **1a–1c**, **1e**, **1h–1j** without any substituent at nitrogen proceeds during a 30 min boiling in 1 M methoxide on water bath. Introduction of a methyl group to the primary nitrogen of the terminal amidic group retards the cyclization to such an extent that the cyclization product of 2-methyl-2-(4-nitrobenzoylamino)propane-*N*-methylamide cannot be isolated in contrast to the cyclization product of 2-methyl-2-(4-nitrobenzoylamino)propanamide (**1c**) which could be isolated in the yield of 82% (Table I). This situation contrasts with the base catalyzed cyclization of substituted amides of hydantoic acid type  $R^1NHCONR^2CH_2CONH_2$ , where – on the contrary – the presence of methyl group at the nitrogen atom attacking the carbonyl group ( $R^1 = H, CH_3$ ) accelerates the cyclization by about one order of magnitude<sup>4</sup>. The reason of this different effects of methyl

group has not been elucidated yet. On the other hand, the replacement of hydrogen by methyl group at the secondary nitrogen atom of benzoylamino group in compounds **1** brings about an acceleration of the cyclization. In contrast to the above-mentioned compounds, the substances **1d**, **1f**, **1g**, **1h** cyclize in 1 M methoxide even at room temperature.

The prepared substituted 2-(4-nitrophenyl)imidazolinones were identified by both their <sup>1</sup>H and <sup>13</sup>C NMR spectra. The chemical shifts of both protons and carbon atoms of compounds **2** are presented in Tables II and III. The character of both <sup>1</sup>H and <sup>13</sup>C NMR spectra of the compounds with NH group is substantially affected by their acid-base behaviour. The relatively highly acidic hydrogen of NH group ( $pK_A$  of compound **2a** is  $12.80 \pm 0.05$  in methanol) is slightly dissociated in dimethyl sulfoxide, and also tautomeric equilibria can become significant which, however, have not been described yet. In the <sup>1</sup>H NMR spectra there is a very broadened half of AA'XX' splitting at higher field, which is adjacent to the heterocyclic part of the molecule. As a rule, the signal of NH group is missing. In the <sup>13</sup>C NMR spectra there are very broadened (or are missing) the signals of carbon atoms involved in the potentially tautomeric system (C-2 and C-4) and adjacent carbon atoms (C-6 and C-5). Similar deformations can be seen also in the <sup>1</sup>H and <sup>13</sup>C NMR spectra of azoxy compounds **3a** and **3b**.

An addition of trifluoroacetic acid (TFA) suppresses the above-described deformations, at the same time, however, we can observe changes in chemical shifts of the previously broadened signals due to partial protonation in the amidine system of the heterocyclic part of the molecule ( $pK_A$ 's of the conjugated acids of compounds **2a** and **2b** in methanol are  $3.70 \pm 0.07$  and  $5.81 \pm 0.016$ , respectively). In dimethyl sulfoxide the respective  $pK_A$  values are higher by 1 to 2 units, and  $pK_A$  of trifluoroacetic acid is 3.45 in the same solvent<sup>5</sup>. Obviously, the protonation takes place at the nitrogen and not at the oxygen, since  $\Delta pK_A$  between the unsubstituted derivative **2b** and the 4-nitro derivative **2a** is 2.1, which corresponds to a  $\rho$  constant about 2.6.

In the imidazolinones **2d**, **2f**, **2g**, **2k** with *N*-methyl group, all the signals in both <sup>1</sup>H and <sup>13</sup>C NMR spectra are sharp when measured in hexadeuteriodimethyl sulfoxide solutions as well as in  $(CD_3)_2SO$ -TFA mixtures.

In the compounds containing isopropyl group, the paired methyl groups are anisochronous due to molecular symmetry. In isobutyl derivative **2g** are anisochronous both the methyl groups and the protons of methylene group (as it is the case in the ethyl derivative **2e**).

The conclusions about acid-base behaviour of compounds **2** deduced from their NMR spectra can be confronted with their electron spectra in DMSO. Figure 1 presents the spectra of compound **2a** in dimethyl sulfoxide with addition of 1% acetic acid, 1% trifluoroacetic acid, or 1% sulfuric acid. The addition of acetic acid to the solution of compound **2a** in DMSO causes practically no change in the spectrum, which means that the concentration of anion of compound **2a** must be very low. The exchange of proton

TABLE I  
Characteristic data of compounds 2

Compound	M.p., °C Yield, %	Formula M.w.	Calculated/Found			
			% C	% H	% N	% Cl
<b>2a</b>	200–202	C <sub>13</sub> H <sub>15</sub> N <sub>3</sub> O <sub>3</sub>	59.76	5.79	16.08	
	69	261.3	60.10	5.84	15.96	
<b>2b<sup>a</sup></b>	176–181 <sup>b</sup>	C <sub>13</sub> H <sub>17</sub> ClN <sub>2</sub> O	61.77	6.78	11.09	14.03
	58	252.7	62.11	6.43	10.95	13.80
<b>2c</b>	213–215	C <sub>11</sub> H <sub>11</sub> N <sub>3</sub> O <sub>3</sub>	56.65	4.76	18.01	
	82	233.2	56.66	4.80	17.82	
<b>2d</b>	153–155	C <sub>12</sub> H <sub>13</sub> N <sub>3</sub> O <sub>3</sub>	58.29	5.30	17.00	
	81	247.2	58.53	5.31	16.90	
<b>2e<sup>a</sup></b>	197–203 <sup>b</sup>	C <sub>12</sub> H <sub>14</sub> ClN <sub>3</sub> O <sub>3</sub>	50.80	4.97	14.81	12.50
	86	283.7	50.65	5.11	14.86	12.44
<b>2f</b>	203–206	C <sub>14</sub> H <sub>17</sub> N <sub>3</sub> O <sub>3</sub>	61.08	6.23	15.26	
	64	275.3	61.03	6.19	15.35	
<b>2g<sup>a</sup></b>	168–179 <sup>b</sup>	C <sub>15</sub> H <sub>20</sub> ClN <sub>3</sub> O <sub>3</sub>	55.30	6.19	12.90	10.88
	49	325.8	55.26	6.18	13.10	10.89
<b>2h</b>	275–277	C <sub>14</sub> H <sub>15</sub> N <sub>3</sub> O <sub>3</sub>	61.53	5.53	15.38	
	55	273.3	61.14	5.52	15.17	
<b>2i</b>	203–205	C <sub>16</sub> H <sub>13</sub> N <sub>3</sub> O <sub>3</sub>	65.08	4.44	14.23	
	74	295.3	65.03	4.46	14.29	
<b>2j</b>	235–238	C <sub>16</sub> H <sub>12</sub> N <sub>4</sub> O <sub>5</sub>	56.45	3.56	16.47	
	77	340.3	56.80	3.80	15.99	
<b>2k</b>	261–262	C <sub>17</sub> H <sub>14</sub> N <sub>4</sub> O <sub>5</sub>	57.62	3.98	15.81	
	83	354.3	57.60	3.88	15.42	

<sup>a</sup> Hydrochloride. <sup>b</sup> M.p. with decomposition.

TABLE II

<sup>1</sup>H NMR spectra of compounds **2** in hexadeuteriodimethyl sulfoxide<sup>a</sup> and in mixture hexadeuteriodimethyl sulfoxide–trifluoroacetic acid<sup>b</sup>

Compound	Arom. <sup>a</sup>	R <sup>2</sup> = H (brs)	R <sup>2</sup> = CH <sub>3</sub> (s)	R <sup>3</sup> = CH <sub>3</sub> (s)	CH (m)	CH(CH <sub>3</sub> ) (d)	Further signals
<b>2a</b> <sup>b</sup>	8.40 8.26	— <sup>c</sup>	—	1.30	1.98	1.02; 0.81 <i>J</i> = 6.79	
<b>2a</b> <sup>d</sup>	8.50 8.34	— <sup>c</sup>	—	1.44	2.09	1.06; 0.89 <i>J</i> = 6.80	
<b>2b</b> <sup>b,e</sup>	8.48 ( <i>o</i> ) 7.93 ( <i>p</i> ) 7.77 ( <i>m</i> )	— <sup>c</sup>	—	1.59	2.22	1.10; 0.97 <i>J</i> = 6.17	
<b>2c</b> <sup>b</sup>	8.42 8.25	11.74	—	1.34	—	—	1.34 (CH <sub>3</sub> )
<b>2c</b> <sup>d</sup>	8.54 8.33	— <sup>c</sup>	—	1.50	—	—	1.50 (CH <sub>3</sub> )
<b>2d</b> <sup>b</sup>	8.42 8.07	—	3.17	1.37	—	—	1.37 (CH <sub>3</sub> )
<b>2d</b> <sup>d</sup>	8.55 8.20	—	3.34	1.59	—	—	1.59 (CH <sub>3</sub> )
<b>2e</b> <sup>b,e</sup>	8.68 8.50	9.2	—	1.57	—	—	1.97 m (CH <sub>2</sub> ); 0.92 t (CH <sub>3</sub> ); <i>J</i> = 7.37
<b>2f</b> <sup>b</sup>	8.44 8.07	—	3.13	1.41	2.12	1.07; 0.87 <i>J</i> = 6.80	
<b>2f</b> <sup>d</sup>	8.57 8.26	—	3.41	1.69	2.41	1.15; 0.95 <i>J</i> = 6.85	
<b>2g</b> <sup>b,e</sup>	8.54 8.26	—	3.38	1.59	1.64	0.92; 0.87 <i>J</i> = 6.60	2.10 and 1.84 (CH <sub>2</sub> ) <sup>f</sup>
<b>2h</b> <sup>b</sup>	8.41 8.27	— <sup>c</sup>	—	—	—	—	1.78–1.60 m (8 H); 1.53–1.45 m (2 H)
<b>2i</b> <sup>b</sup>	8.45 8.36	— <sup>c</sup>	—	1.73	—	—	7.57 ( <i>o</i> ); 7.41 ( <i>m</i> ); 7.34 ( <i>p</i> )
<b>2j</b> <sup>b</sup>	8.45 8.36	— <sup>c</sup>	—	1.76	—	—	8.27 and 7.87 2 × 2 H (arom.) <sup>a</sup>
<b>2k</b> <sup>b</sup>	8.49 8.26	—	3.16	1.93	—	—	8.31 and 7.72 2 × 2 H (arom.) <sup>a</sup>

<sup>a</sup> AA'XX' system except for compound **2b**. <sup>b</sup> In hexadeuteriodimethyl sulfoxide. <sup>c</sup> The signal was not found.

<sup>d</sup> In hexadeuteriodimethyl sulfoxide–trifluoroacetic acid. <sup>e</sup> Hydrochloride. <sup>f</sup> *J*<sub>AB</sub> = 14.87; *J*<sub>AC</sub> = 4.86; *J*<sub>BC</sub> = 7.73.

TABLE III  
 $^{13}\text{C}$  NMR spectra of compounds **2** in hexadeuteriodimethyl sulfoxide or in mixture hexadeuteriodimethyl sulfoxide-trifluoroacetic acid

Compound	C=O	C-2	C-5	Arom.			NCH <sub>3</sub>	CH	C(CH <sub>3</sub> )	CH(CH <sub>3</sub> )	Further signals
				C-6	C-7	C-8					
<b>2a<sup>a</sup></b>	184.50	162.48	72.65	131.50	129.78	124.28	150.38	—	34.60	20.15	16.71
<b>2a<sup>b</sup></b>	187.56	157.06	74.26	134.38	128.31	124.02	149.32	—	34.30	20.98	16.84
<b>2b<sup>b,c</sup></b>	179.94	166.49	70.41	121.99	130.03	129.47	136.18	—	34.81	19.41	16.49
<b>2c<sup>a</sup></b>	185.05	161.75	66.61	131.74	129.87	124.42	150.51	—	—	23.45	—
<b>2d<sup>b</sup></b>	193.89	175.48	65.87	135.22	130.72	123.81	149.25	29.86	—	21.67	—
<b>2d<sup>a</sup></b>	182.29	168.60	68.08	129.43	131.76	124.00	150.40	30.78	—	20.93	—
<b>2e<sup>b,c</sup></b>	180.50	164.46	68.53	128.34	131.37	124.06	151.08	—	—	20.76	—
<b>2f<sup>a</sup></b>	179.53	168.64	74.08	128.41	131.73	124.15	150.64	31.37	33.29	18.18	16.32
<b>2f<sup>b</sup></b>	192.34	176.37	71.05	135.18	130.47	123.78	149.20	30.22	32.91	19.16	16.63
										14.96	15.31

TABLE III  
(Continued)

Compound	C=O	C-2	C-5	Arom.			NCH <sub>3</sub>	CH	C(CH <sub>3</sub> )	CH(CH <sub>3</sub> )	Further signals
				C-6	C-7	C-8					
<b>2g<sup>a,c</sup></b>	180.28	168.30	71.40	128.26	132.05	124.16	150.70	31.39	21.56	23.76	43.24 (CH <sub>2</sub> ) 23.16
<b>2h<sup>b</sup></b>	~188	~ <sup>d</sup> 70	134.63	128.46	123.98	149.30	—	—	—	—	32.97 (C-2,C-2'); 21.38 (C-3,C-3'); 25.02 (C-4)
<b>2h<sup>a</sup></b>	182.91	163.43	69.01	130.64	130.43	124.30	150.72	—	—	—	32.21 (C-2,C-2'); 20.81 (C-3,C-3'); 24.45 (C-4)
<b>2i<sup>a</sup></b>	185.37	160.67	72.07	133.44	129.25	124.30	149.98	—	—	24.92	—
<b>2j<sup>a</sup></b>	185.16	159.97	72.44	134.01	128.94 <sup>e</sup>	124.21 <sup>f</sup>	149.76	—	—	25.74	—
<b>2k<sup>b</sup></b>	190.11	178.19	71.36	134.47	131.03	124.13	149.50	31.02	—	20.15	—
										143.72 (C-i); 127.51 (C-o); 123.77 (C-m); 147.36 (C-p)	

<sup>a</sup> In hexadeuteriodimethyl sulfoxide-trifluoroacetic acid. <sup>b</sup> In hexadeuteriodimethyl sulfoxide. <sup>c</sup> Hydrochloride. <sup>d</sup> The signal was not found. <sup>e,f,g</sup> The assignment may be reversed.

between the presumed anion and neutral compound **2a** is slow in the NMR time scale and affects substantially the width of lines in both the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra. In the presence of trifluoroacetic acid in DMSO, about 20% of compound **2a** is protonated, the proton exchange between compound **2a** and its conjugated acid is very fast in the NMR time scale, hence all the signals in the NMR spectra are sharp. The difference in chemical shifts of both protons and carbon atoms in the neutral compound **2d** (in DMSO) and the partially protonated compound (in 10% TFA in DMSO) can be seen in the spectra of compound **2d** in the two media (Tables II and III).

If after the base-catalyzed cyclization of a substituted 2-(4-nitrobenzoylamino)alkanamide **1** the solution is immediately concentrated (without neutralization), the increasing concentration of the base results in reduction of nitro group and formation of azoxy compounds. The azoxy compounds are practically insoluble in all current solvents,

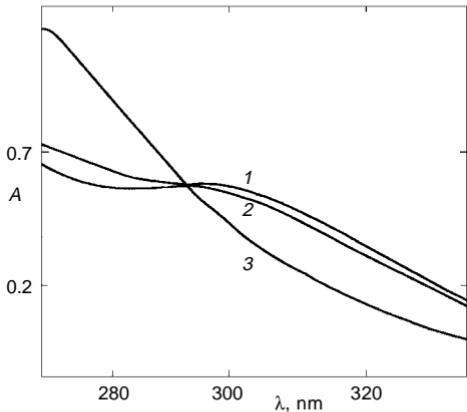


FIG. 1

Electronic spectra of compound **2a** dissolved in dimethyl sulfoxide with addition of 1 vol.% acetic acid (1), trifluoroacetic acid (2), sulfuric acid (3)

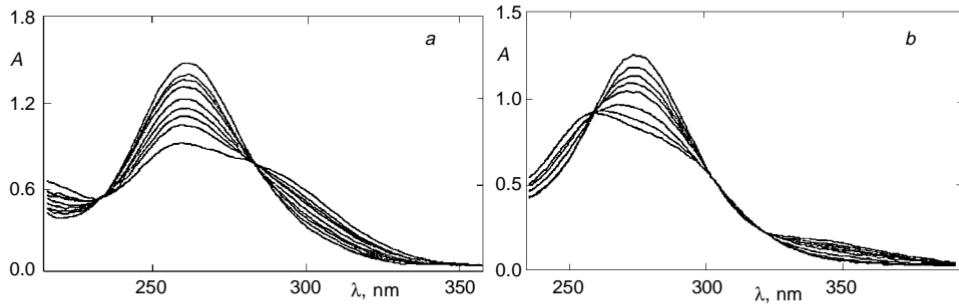
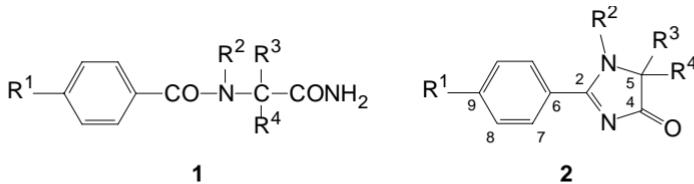


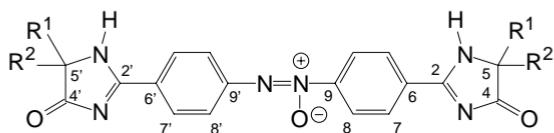
FIG. 2

Electronic spectra of compound **2a** measured in methanolic solutions of: *a*  $0, 1 \cdot 10^{-4}, 1.5 \cdot 10^{-4}, 2 \cdot 10^{-4}, 3 \cdot 10^{-4}, 5 \cdot 10^{-4}, 7 \cdot 10^{-4}, 1 \cdot 10^{-3}$  and  $1 \cdot 10^{-1}$  mol  $\text{l}^{-1}$  HCl (the absorbance decrease with increasing HCl concentration at 262 nm); *b*  $0.4 \cdot 10^{-2}, 7 \cdot 10^{-2}, 1 \cdot 10^{-1}, 1.5 \cdot 10^{-1}, 2 \cdot 10^{-1}$  and  $5 \cdot 10^{-1}$  mol  $\text{l}^{-1}$  sodium acetate (the spectrum of anion of compound **2a** was measured in 0.1 M sodium methoxide; the absorbance decrease with increasing acetate concentration at 280 nm)

being very little soluble even in dimethyl sulfoxide. They cannot be purified by crystallization, do not melt, but above ca 300 °C gradually carbonize. Both azoxy compounds **3** prepared were identified with the help of their <sup>1</sup>H and <sup>13</sup>C NMR spectra, compound **3a** by its mass spectrum, too. The <sup>1</sup>H NMR spectra exhibit obvious doubling of all signals due to the asymmetry of azoxy group. Besides that, both CH groups in CH(CH<sub>3</sub>)<sub>2</sub> are prochiral, hence the spectrum of compound **3a** shows four methyl groups from isopropyl groups. The values of proton chemical shifts depend considerably on concentration of the solutions, temperature, and amount of the trifluoroacetic acid added. The shape



1, 2	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>
<b>a</b>	NO <sub>2</sub>	H	CH <sub>3</sub>	i-C <sub>3</sub> H <sub>7</sub>
<b>b</b>	H	H	CH <sub>3</sub>	i-C <sub>3</sub> H <sub>7</sub>
<b>c</b>	NO <sub>2</sub>	H	CH <sub>3</sub>	CH <sub>3</sub>
<b>d</b>	NO <sub>2</sub>	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>
<b>e</b>	NO <sub>2</sub>	H	CH <sub>3</sub>	CH <sub>2</sub> CH <sub>3</sub>
<b>f</b>	NO <sub>2</sub>	CH <sub>3</sub>	CH <sub>3</sub>	i-C <sub>3</sub> H <sub>7</sub>
<b>g</b>	NO <sub>2</sub>	CH <sub>3</sub>	CH <sub>3</sub>	i-C <sub>4</sub> H <sub>9</sub>
<b>h</b>	NO <sub>2</sub>	H	—	(CH <sub>2</sub> ) <sub>5</sub> —
<b>i</b>	NO <sub>2</sub>	H	CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub>
<b>j</b>	NO <sub>2</sub>	H	CH <sub>3</sub>	4-NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub>
<b>k</b>	NO <sub>2</sub>	CH <sub>3</sub>	CH <sub>3</sub>	4-NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub>

**3**

3	R <sup>1</sup>	R <sup>2</sup>
<b>a</b>	CH <sub>3</sub>	i-C <sub>3</sub> H <sub>7</sub>
<b>b</b>	CH <sub>3</sub>	CH <sub>3</sub>

of multiplet of aromatic protons changes considerably with these parameters, which is obviously connected with the basicity of azoxy group and the ability of forming oriented structures even in solutions<sup>6</sup> which is usual with compounds having extensive planar structures. The mass spectrum of compound **3a** shows a weak signal of  $M^+$  ion with the  $m/z$  value 474.3 ( $C_{26}H_{30}N_6O_3$ ). From among the high-molecular fragments, the highest intensities are observed with the signals  $m/z$  458.3 ( $M - O$ ), documented in the fragmentation of parent azoxybenzene too<sup>7</sup>, and ions 431.2 ( $M - C_3H_7$ ) and 415.2 – base peak ( $M - O - C_3H_7$ ). Attempts at symmetrization of compound **3a** by reductive removal of oxygen from azoxy group (with various reagents, such as  $PCl_3$ ,  $P(OCH_3)_3$ ,  $NaBH_4$  or  $P(C_6H_5)_3$  with  $[(C_2H_5)_2NCS_2]_2MoO_2$  as catalyst<sup>8</sup>) failed due probably to the low solubility.

## EXPERIMENTAL

The  $^1H$  and  $^{13}C$  NMR spectra ( $\delta$ , ppm;  $J$ , Hz) were measured at 400.13 and 100.62 MHz, respectively, using a Bruker AM 400 spectrometer, or at 360.14 and 90.57 MHz, respectively, using a Bruker AMX 360 apparatus, usually at 25 °C. For the measurements the substances were dissolved in hexadeuteriodimethyl sulfoxide or its mixture with 10 vol.% TFA. The chemical shifts are referenced to the middle signal of solvent multiplet ( $\delta(^1H)$  2.55 and  $\delta(^{13}C)$  39.60). The groups CH,  $CH_3$ , and  $C_q, CH_2$  in the  $^{13}C$  NMR spectra were differentiated by the ATP pulse sequence. The assignment of signals in the spectra of compounds **2f**, **2g**, **2h**, **2i**, **2j**, and **2k** was accomplished on the basis of the  $H,C$  COSY and  $H,H$  COSY spectra. The NOE difference spectra were adopted to assign the signals in the  $^1H$  NMR spectrum of compound **2a**. The groups CH and  $CH_3$  in compound **2g** were differentiated by the pulse sequence DEPT-90. The pairs of corresponding signals in the  $^{13}C$  NMR spectra of azoxy compounds **3a**, **3b** were not assigned. The mass spectrum was measured with a spectrometer ZAB-EQ, VG Analytical (Manchester, U.K.) using the EI method with the ionizing voltage of 70 eV. The ion source temperature 200 °C. The elemental composition of selected fragments was determined at the resolution of 10 000. The electron spectra were measured with a HP 8453 Diode Array Spectrometer at 25 °C.

*Measurement of dissociation constants.* The dissociation constants were measured spectrophotometrically at the concentration of  $5 \cdot 10^{-5}$  mol  $l^{-1}$  compound **2a** at 25 °C in a 1 cm cell. The dissociation constant of the protonated form of compound **2a** was measured in methanolic solutions of  $10^{-4}$ – $10^{-3}$  mol  $l^{-1}$  hydrochloric acid at  $\lambda = 262$  nm at the temperature of 25 °C. The ionic strength was not adjusted (Fig. 2a). The dissociation constant of compound **2a** was measured in methanolic solutions of sodium acetate (0.04–0.5 mol  $l^{-1}$ ) at  $\lambda = 272$  nm at the temperature of 25 °C. The ionic strength was not adjusted (Fig. 2b). The  $pK_A$  values were calculated from the relation  $pK_A = pH - \log P$ , where  $P$  is the concentration ratio of conjugated base and acid calculated from the absorbances measured. The dissociation constant of compound **2b** was determined by potentiometric titration of methanolic solution of the substance using an RTS 622 (Radiometer Copenhagen) apparatus with glass and saturated calomel electrode system at 25 °C. The titration was carried out with 0.1 M solution of tetrabutylammonium hydroxide in absolute methanol, and it was repeated three times. Benzoic acid was used as the standard ( $pK_A$  9.41, ref.<sup>3</sup>).

2-(4-Nitrophenyl)-5,5-disubstituted-4-imidazolinones **2**. General Procedure

Compound **1** (7 mmol) (ref.<sup>1</sup>), methanol (20 ml), and 5 M sodium methoxide (1 ml) were placed in a 50 ml flask equipped with a reflux condenser. The mixture was boiled 30 min. After cooling and neutralization with methanolic hydrochloric acid, the solvent was distilled off from a water bath. The dry residue was washed with water and recrystallized from chloroform. This procedure was adopted to prepare compounds **2a–2c**, **2e**, **2h**, **2i**, **2j**.

Compounds **2d**, **2f**, **2g**, **2k** were prepared by cyclization at room temperature – standing overnight. Compounds **2b**, **2e**, **2g** were isolated as hydrochlorides after adding methanolic hydrogen chloride to the extract of evaporation residue in chloroform. The elemental analyses, melting points, and yields of the substances prepared are presented in Table I. The substances prepared were identified with the help of their <sup>1</sup>H and <sup>13</sup>C NMR spectra (Tables II and III).

## Methyl 2-(4-Nitrobenzoylamino)-2-methylpropanoate

2-Amino-2-methylpropanoic acid (15 g, 145 mmol) was dissolved in methanol (250 ml), and gaseous hydrogen chloride was introduced into the solution 1 h, whereupon the mixture was heated to boiling 8 h, 2.5 ml thionyl chloride being added after each hour. The solvent was distilled off from water bath until dry to give 22 g raw methyl 2-amino-2-methylpropanoate hydrochloride.

4-Nitrobenzoyl chloride (3.7 g, 20 mmol) was dissolved in 50 ml dry chloroform, and a mixture of the above-described methyl 2-amino-2-methylpropanoate hydrochloride (3.1 g, 20 mmol) and triethylamine (4.6 g, 46 mmol) in chloroform (50 ml) was added thereto. The reaction mixture was heated at 60 °C 1 h and left to stand overnight. Chloroform was distilled off and the residue in the flask was washed with water and filtered off. Recrystallization from a dichloromethane–hexane mixture gave 3.4 g (75%) title compound, m.p. 164–166 °C. <sup>1</sup>H NMR spectrum ((CD<sub>3</sub>)<sub>2</sub>SO): 9.03 brs, 1 H (NH); 8.36 and 8.14 AA'XX', 2 × 2 H (arom.); 3.65 s, 3 H (OCH<sub>3</sub>); 1.53 s, 6 H (C(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C NMR spectrum ((CD<sub>3</sub>)<sub>2</sub>SO): 174.18 (COOCH<sub>3</sub>), 164.46 (ArCON), 149.23 (C-4), 139.60 (C-1), 129.10 (C-2), 123.51 (C-3), 55.96 (C<sub>q</sub>), 52.04 (OCH<sub>3</sub>), 24.89 (C(CH<sub>3</sub>)<sub>2</sub>).

2-Methyl-2-(4-nitrobenzoylamino)propane-*N*-methylamide

Methyl 2-methyl-2-(4-nitrobenzoylamino)propanoate (2.5 g, 11 mmol) was dissolved in dry benzene (75 ml), and the solution was saturated with gaseous methylamine (9.3 g, 300 mmol) at 0 °C 45 min. The mixture was then heated in a glass ampoule at 100 °C 24 h. The ampoule content was evaporated, and the residue was purified by chromatography (alumina column 30 × 5 cm, CHCl<sub>3</sub>–DMF 30 : 1) to give 0.8 g (32%) product, m.p. 198–200 °C. <sup>1</sup>H NMR spectrum ((CD<sub>3</sub>)<sub>2</sub>SO): 8.64 brs, 1 H (NH); 8.36 and 8.16 AA'XX', 2 × 2 H (arom.); 7.69 brq, 1 H (NHCH<sub>3</sub>); 2.61 d, 3 H, <sup>3</sup>J = 4.50 (NHCH<sub>3</sub>); 1.49 s, 6 H (C(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C NMR spectrum ((CD<sub>3</sub>)<sub>2</sub>SO): 174.15 (CONHCH<sub>3</sub>), 164.32 (ArCON), 149.01 (C-4), 140.59 (C-1), 129.29 (C-2), 123.32 (C-3), 56.79 (C<sub>q</sub>), 26.27 (NHCH<sub>3</sub>), 25.32 (C(CH<sub>3</sub>)<sub>2</sub>).

Attempt at Cyclization of 2-Methyl-2-(4-nitrobenzoylamino)propane-*N*-methylamide

A mixture of 2-methyl-2-(4-nitrobenzoylamino)propane-*N*-methylamide (1.86 g, 7 mmol) and 20 ml 0.2 (or 0.4 or 0.8 or 1.2) M sodium methoxide was refluxed 0.5 (or 1, 2 or 3) h. After cooling, the mixture was neutralized with methanolic hydrochloric acid and the solvent was distilled off until dry from water bath. The evaporation residue was washed with water and recrystallized from chloroform. In all the cases only the starting amide was isolated (m.p. and mixed m.p. 198–200 °C).

Bis-4,4'-(5-methyl-5-isopropyl-4-imidazolinon-2-yl)azoxybenzene (**3a**)

2-(4-Nitrobenzoylamino)-2,3-dimethylbutanamide (**1a**; 2 g, 8 mmol), methanol (20 ml), and 5 M sodium methoxide (1 ml) were placed in a 50 ml flask equipped with a reflux condenser, and the mixture was refluxed 8 h, whereupon the solvent was distilled off until dry from a water bath. The residue was neutralized with methanolic hydrogen chloride, and the substance obtained was collected by suction, washed with water and with acetone. After drying, the product was reprecipitated from dimethylformamide with water to give 1 g (29%) yellow microcrystalline compound **3a**, m.p. 312 °C (dec.). <sup>1</sup>H NMR spectrum ((CD<sub>3</sub>)<sub>2</sub>SO-TFA): 11.70 brs, 1 H (NH); 11.59 brs, 1 H (NH); 8.58 and 8.45 AA'XX', 2 × 2 H (arom.); 8.48 and 8.31 AA'XX', 2 × 2 H (arom.); 2.19 sept, 1 H (CH(CH<sub>3</sub>)<sub>2</sub>); 2.11 sept, 1 H (CH(CH<sub>3</sub>)<sub>2</sub>); 1.56 s, 3 H (CCH<sub>3</sub>); 1.46 s, 3 H (CCH<sub>3</sub>); 1.11 d, 3 H, *J* = 6.99 (CH(CH<sub>3</sub>)); 1.09 d, 3 H, *J* = 6.94 (CH(CH<sub>3</sub>)); 0.97 d, 3 H, *J* = 6.79 (CH(CH<sub>3</sub>)); 0.91 d, 3 H, *J* = 6.76 (CH(CH<sub>3</sub>)). <sup>13</sup>C NMR spectrum ((CD<sub>3</sub>)<sub>2</sub>SO-TFA): 182.32 and 180.26 (CO), 166.28 and 164.92 (C-2,2'), 151.23 and 148.90 (C-9,9'), 130.71 and 130.48 (C-7,7'), 127.82 and 122.59 (C-6,6'), 125.60 and 123.57 (C-8,8'), 71.84 and 70.95 (C-5,5'), 32.02 and 34.88 (CH(CH<sub>3</sub>)<sub>2</sub>), 19.69 and 19.38 (CCH<sub>3</sub>), 16.62, 16.50, 16.44, and 16.33 (CH(CH<sub>3</sub>)<sub>2</sub>).

Bis-4,4'-(5,5-dimethyl-4-imidazolinon-2-yl)azoxybenzene (**3b**)

Compound **3b** was prepared from compound **1c** in the same way as compound **3a**, yield 45%, m.p. 300 °C (dec.). <sup>1</sup>H NMR spectrum ((CD<sub>3</sub>)<sub>2</sub>SO-TFA): 11.65 brs, 1 H (NH); 11.55 brs, 1 H (NH); 8.46 and 8.26 AA'XX', 2 × 2 H (arom.); 8.23 and 8.19 AA'BB', 2 × 2 H (arom.); 1.37 s, 6 H (C(CH<sub>3</sub>)<sub>2</sub>); 1.36 s, 6 H (C(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C NMR spectrum ((CD<sub>3</sub>)<sub>2</sub>SO-TFA): 181.38 and 180.28 (CO), 165.33 and 164.64 (C-2,2'), 151.51 and 148.86 (C-9,9'), 130.71 and 130.65 (C-7,7'), 127.18 and 122.72 (C-6,6'), 125.70 and 123.70 (C-8,8'), 65.04 and 64.31 (C-5,5'), 22.93 and 22.86 (CH<sub>3</sub>).

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