N-(2-METHYL-2-NITROPROPYL) AND *N*-NITROSO DERIVATIVES OF SOME DIAMINES

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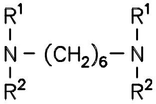
Preparation of ten new derivatives of 1,6-hexanediamine and 1,4-bis(4-aminophenoxy)butane with different combination of *N*-nitroso and/or *N*-(2-methyl-2-nitropropyl) groups is presented. The title compounds are potential improvers of vulcanized rubber dynamic properties.

In last years, some *N*,*N′*-bis(2-methyl-2-nitropropyl) derivatives of aliphatic and aromatic diamines were developed[1–3] as a new non-nitroso type carbon black/rubber coupling agents. The utilization of these compounds in practice is described in many patents, which were reviewed[4].

This paper describes the preparation of two series of compounds. The first of them are derivatives of 1,6-hexanediamine, which are analogues of the most widely used compound[4], *N*,*N′*-bis(2-methyl-2-nitropropyl)-1,6-hexanediamine (*Ia*). They are represented by the formulae *Ib*–*If*. Compounds of the second series (*IIa*–*IIm*) are derivatives of 1,4-bis(4-aminophenoxy)butane.

Diamide *Ib* was prepared from dinitrodiamine *Ia* by acetylation with acetic anhydride. Crude Schiff base, prepared from 1,6-hexanediamine and benzaldehyde, was reduced with sodium borohydride and *N*,*N′*-dibenzyl derivative *Ic* was obtained. This compound yielded *N*,*N′*-bis(2-methyl-2-nitropropyl) derivative *Id* by the Mannich reaction with formaldehyde and 2-nitropropane. *N*,*N′*-Diethyl-1,6-hexanediamine (*Ie*) was prepared by reduction of 1,6-bis(acetamido)hexane with lithium aluminium hydride in ether. The poor yield of this reaction is propably caused by the low solubility of the starting substance. *N*,*N′*-Bis(2-methyl-2-nitropropyl) derivative *If* was obtained by the condensation of diamine *Ie* with 2-methyl-2-nitropropanol.

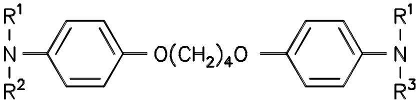
1,4-Bis(4-acetamidophenoxy)butane (*IIa*) and its *N*,*N′*-dimethyl derivative *IIb* were prepared by the reaction of the corresponding sodium phenolates with 1,4-dibromobutane in ethanol. Both acid and alkaline hydrolyses of *IIa* and *IIb* lead to the corre-



$\underset{R^2}{\overset{R^1}{N}}-(CH_2)_6-\underset{R^2}{\overset{R^1}{N}}$

I

I	R^1	R^2
a	H	$CH_2C(CH_3)_2NO_2$
b	$COCH_3$	$CH_2C(CH_3)_2NO_2$
c	CH_2Ph	H
d	CH_2Ph	$CH_2C(CH_3)_2NO_2$
e	C_2H_5	H
f	C_2H_5	$CH_2C(CH_3)_2NO_2$



II

II	R^1	R^2	R^3
a	H	$COCH_3$	$COCH_3$
b	CH_3	$COCH_3$	$COCH_3$
c	H	H	H
d	CH_3	H	H
e	CH_3	$COCH_3$	H
f	CH_3	NO	NO
g	CH_3	$COCH_3$	NO
h	H	$CH_2C(CH_3)_2NO_2$	$CH_2C(CH_3)_2NO_2$
i	CH_3	$CH_2C(CH_3)_2NO_2$	$CH_2C(CH_3)_2NO_2$
j	CH_3	$COCH_3$	$CH_2C(CH_3)_2NO_2$
k	$COCH_3$	$CH_2C(CH_3)_2NO_2$	$CH_2C(CH_3)_2NO_2$
l	NO	$CH_2C(CH_3)_2NO_2$	$CH_2C(CH_3)_2NO_2$
m	CH_3	$CH_2C(CH_3)_2NH_2$	$CH_2C(CH_3)_2NH_2$

sponding diamines *IIc* and *IId*. The alkaline hydrolysis of diamide *IIb* gave *N*-acetyl-1,4-bis(4-methylaminophenoxy)butane (*IIe*) besides the diamine *IId*.

Similar procedures for the preparation of diamide *IIa* and its alkaline hydrolysis to diamine *IIc* were described[5] with somewhat poorer yields, but neither melting points nor spectral evidences of these compounds were given. Analogous preparation of diamide *IIb* was also reported[6], but this compound was hydrolyzed without isolation and dihydrochloride of *IId* was obtained[6]. Diamine *IIc* was prepared earlier both by hydrogenation of the corresponding dinitro derivative[7,8] and in the form of dihydrochloride by reaction of the corresponding Schiff base with benzaldehyde[9]. Preparation of diamide *IIa* by acetylation of diamine *IIc* is known[7].

Nitrosamines *IIf* and *IIg* were prepared in almost quantitative yields by the reaction of compounds *IId* and *IIe* with sodium nitrite in acidic medium. Our experiments on Mannich condensation of diamines *IIc* and *IId* and amine *IIe* with formaldehyde and 2-nitropropane were unsuccessful. However, by condensation of these compounds with 2-methyl-2-nitropropanol under basic catalysis, expected 2-methyl-2-nitropropyl derivatives *IIh*, *IIi* and *IIj* were obtained in good yields. From the compound *IIh*, acetyl derivative *IIk* was prepared by reaction with acetic anhydride. Because of its insolubility in aqueous medium, the nitrosation of diamine *IIh* was carried out in pyridine solution, giving compound *IIl* in quantitative yield. Compound *IIi* was obtained also by alkylation of *IIh* with dimethyl sulfate in 2-butanone in the presence of potassium carbonate. Compound *IIm* was prepared by reduction of *IIi* with zinc in diluted hydrochloric acid.

EXPERIMENTAL

Melting points were determined on a Kofler block and are uncorrected. The purity of substances was checked by thin-layer chromatography on Silufol UV 254 foils (Kavalier, Votice), detection by UV-irradiation and/or by exposure to iodine vapours. Column chromatography was carried out on silica gel Silpearl (Kavalier, Votice). The elemental analyses were carried out at the Department of Organic and Analytical Chemistry, Faculty of Natural Sciences, Palacky University in Olomouc. NMR spectra (δ, ppm; *J*, Hz) were measured on a Varian VXR-400 spectrometer (400 MHz for ^{1}H, 100 MHz for ^{13}C) at 25 °C in deuteriochloroform when no otherwise stated. Signals were referenced to the residual solvent signal (H 7.265, C 77.00). Multiplicity of carbon signals was determined by Attached Proton Test (APT) method. 2D NMR experiments used in some cases for the signal assignment (COSY, HETCOR) were realized using the manufacturer's software. The spectral data of prepared compounds are given in Tables I–IV.

N,*N*′-Diacetyl-*N*,*N*′-bis(2-methyl-2-nitropropyl)-1,6-hexanediamine (*Ib*)

Acetic anhydride (12 ml, 120 mmol) was added dropwise during 15 min to stirred benzene (30 ml) solution of *Ia* (ref.[1], 9.5 g, 29.8 mmol). After 2 h standing at room temperature, the reaction mixture was evaporated in vacuo. By the crystallization from ethanol, compound *Ib* (9.1 g, 76%), m.p. 139–145 °C (143–144 °C after recrystallization from dilute acetic acid), was obtained. For $C_{18}H_{34}N_4O_6$ (402.5) calculated: 53.71% C, 8.51% H, 13.92% N; found: 53.67% C, 8.52% H, 13.99% N.

TABLE I
^{1}H NMR data of compounds *Ib*, *Id*, and *If*

Assignment	*Ib*	*Id*	*If*
$(CH_3)_2C$	1.534 s	1.512 s	1.531 s
CCH_2N	3.927 s	2.971 s	2.862 s
α-CH_2	3.059 m	2.336 m	2.416 m
β-CH_2	1.465 m	1.323 m	1.338 m
γ-CH_2	1.214 m	1.061 m	1.203 m
CH_3CO	2.093 s	–	–
$C\mathbf{H}_3CH_2$	–	–	0.928 t (7.0)
$CH_3C\mathbf{H}_2$	–	–	2.512 q (7.0)
$PhCH_2$	–	3.594 s	–
Ph	–	7.184–7.301 m	–

TABLE II
^{13}C NMR data of compounds *Ib*, *Id*, and *If*

Assignment	*Ib*	*Id*	*If*
$(\mathbf{C}H_3)_2C$	24.10	24.12	24.14
C–NO_2	88.56	88.78	89.12
$C\mathbf{C}H_2N$	51.98	63.33	63.93
α-CH_2	48.78	54.82	54.85
β-CH_2	28.29	26.16	27.14
γ-CH_2	26.16	26.75	27.10
$\mathbf{C}H_3CO$	21.23	–	–
C=O	171.61	–	–
$CH_3\mathbf{C}H_2$	–	–	48.64
$\mathbf{C}H_3CH_2$	–	–	11.50
$Ph\mathbf{C}H_2$	–	59.81	–
ipso	–	139.04	–
ortho	–	128.05	–
meta	–	128.54	–
para	–	126.83	–

N,N′-Dibenzyl-1,6-hexanediamine (Ic)

Benzaldehyde (62.4 g, 600 mmol) was added portionwise at 40 °C to 1,6-hexanediamine (34.8 g, 300 mmol). After 1 h, the oily upper layer was separated, the crude product was dissolved in ethanol (600 ml) and sodium borohydride (22.7 g, 600 mmol) was portionwise added under stirring and cooling to 60–70 °C during 30 min. After 3 h boiling, the reaction mixture was diluted with water (600 ml) and extracted with benzene (3 × 100 ml). From the benzene extract, the oily residue was obtained which was converted to dihydrochloride of diamine *Ic* (80 g, 72%), m.p. 301–304 °C (reported[10] m.p. 295 °C) by addition of concentrated hydrochloric acid (50 ml). Free base *Ic* (51.1 g, 98%), m.p. 26–29 °C, was obtained from dihydrochloride by the usual manner. For $C_{20}H_{28}N_2$ (296.5) calculated: 81.03% C, 9.52% H, 9.45% N; found: 81.13% C, 9.45% H, 9.39% N.

N,*N′*-Dibenzyl-1,6-bis(2-methyl-2-nitropropylamino)hexane (*Id*)

Aqueous formaldehyde (37%, 14.1 g, 175 mmol) was added dropwise within 1 h to a stirred mixture of diamine *Ic* (46.7 g, 158 mmol), 2-nitropropane (27.5 g, 316 mmol), and methanol (30 ml) at 50 °C. After 2 h at the same temperature, the solution was diluted with water (100 ml) and cooled to 0 °C. The aqueous layer was separated from waxy crude product that was dissolved in benzene (300 ml). The solution was extracted with water (2 × 20 ml), dried over Na_2SO_4 and evaporated to give the oily product *Id* (66.5 g, 85%). The crude product (1.5 g) was purified by column chromatography (12 g silica gel, benzene) and gave pure compound *Id* (1.1 g), which was dried over phosphorus pentoxide. For $C_{28}H_{42}N_4O_4$ (498.7) calculated: 67.44% C, 8.49% H, 10.43% N; found: 67.22% C, 8.83% H, 11.17% N.

N,*N′*-Diethyl-1,6-hexanediamine (*Ie*)

The suspension of $LiAlH_4$ (12.8 g, 337 mmol) and 1,6-hexanediacetamide[11] (30.0 g, 150 mmol) in diethyl ether (1 700 ml) was refluxed for 18 h under stirring. After cooling, 1 M NaOH (50 ml) was added, solid phase was filtered off and the ethereal solution was dried over K_2CO_3. Upon solvent removal, the diamine *Ie* (9.1 g, 35%), b.p. 113–115 °C/2.4 kPa (reported[12] b.p. 110 °C/1.6 kPa) was obtained. Acidification of ethanolic solution of diamine *Ie* with concentrated hydrochloric acid provided the corresponding dihydrochloride, m.p. 285–287 °C (reported[13] m.p. 278 °C).

N,*N′*-Diethyl-1,6-bis(2-methyl-2-nitropropylamino)hexane (*If*)

The mixture of diamine *Ie* (5.4 g, 31.3 mmol) and 2-methyl–2-nitropropanol (11.2 g, 94 mmol) was heated 1 h at 120 °C in an open reaction vessel. The oily product was dissolved in petroleum ether (25 ml), the solution was washed with water (4 × 25 ml) and evaporated to give oily product *If* (10.6 g, 90%). The crude product (2.2 g) was further purified by column chromatography (12 g silica gel, benzene). For $C_{18}H_{38}N_4O_4$ (374.5) calculated: 57.73% C, 10.23% H, 14.96% N; found: 57.90% C, 9.96% H, 15.44% N.

1,4-Bis(4-acetamidophenoxy)butane (*IIa*)

To a solution of sodium ethoxide, prepared by dissolving sodium (18.9 g, 822 mmol) in ethanol (700 ml), 4-hydroxyacetanilide (123.6 g, 818 mmol) and 1,4-dibromobutane (84.1 g, 389 mmol) were added and the mixture was refluxed for 4 h under stirring. After cooling, the suspension was diluted with water (360 ml), the precipitate was filtered off, washed with hot water (1 600 ml) and air-dried to give crude compound *IIa* (119.9 g, 86%), m.p. 224–232 °C. On recrystallization from acetic acid,

TABLE III
^{1}H NMR data of compounds *II*

Compound	CH_3N	CH_3CO	NH/NH_2	$(CH_3)_2C$	NCH_2C	Ar[c]	Σ(*J*)[c]	OCH_2	CCH_2C
IIa[a]	–	2.091 s	[b]	–	–	6.818, 7.368	9.0	3.993 m	1.926 m
IIb	3.210 s	1.836 s	–	–	–	6.899, 7.079	8.8	4.043 m	1.998 m
IIc	–	–	3.228 s	–	–	6.642, 6.748	8.9	3.952 m	1.919 m
IId	2.812 s	–	3.123 s	–	–	6.586, 6.812	8.9	3.967 m	1.931 m
IIe	3.226 s	1.852 s	–	–	–	6.905, 7.083	8.9	4.037 m	1.983 m
	2.808 s	–	[b]	–	–	6.581, 6.800	8.9	3.957 m	1.994 m
IIf	3.448 s	–	–	–	–	6.999, 7.435	8.9	4.098 m	2.035 m
IIg	3.222 s	1.847 s	–	–	–	6.911, 7.091	9.1	4.057 m	2.017 m
	3.440 s	–	–	–	–	6.988, 7.421	8.8	5.086 m	2.017 m
IIh	–	–	3.622 s	1.653 s	3.549 s	6.586, 6.768	9.0	3.947 m	1.931 m
IIi	3.210 s	–	–	1.863 s	3.210 s	6.899, 7.080	8.9	4.044 m	1.998 m
IIj	3.227 s	1.853 s	–	–	–	6.700, 6.816	9.1	3.980 t[d]	1.968 m
	2.855 s	–	–	1.609 s	3.769 s	6.905, 7.085	8.9	4.038 t[d]	1.968 m
IIk	–	1.819 s	–	1.606 s	4.287 s	6.841, 6.978	9.0	4.014 m	1.971 m
IIl	–	–	–	1.403 s	4.523 s	6.864, 7.192	9.0	3.980 m	1.919 m
IIm	2.969 s	–	–	1.172 s	3.145 s	6.797, 6.820	9.1	3.963 m	1.923 m

[a] $CDCl_3 + CD_3OD$; [b] not observed; [c] AA′BB′ pattern; [d] *J* = 5.9 Hz.

TABLE IV
^{13}C NMR data of compounds *II*

Compound	CH_3N	$\mathbf{C}H_3CO$	C=O	$(\mathbf{C}H_3)_2C$	$N\mathbf{C}H_2C$	$C–NO_2$	C-1	C-2,6	C-3,5	C-4	OCH_2	$C\mathbf{C}H_2C$
IIa[a]	–	23.86	170.42	–	–	–	156.23	122.45	115.22	131.95	68.37	28.48
IIb	37.22	22.25	170.80	–	–	–	158.14	128.09	115.26	137.45	67.67	25.92
IIc	–	–	–	–	–	–	152.18	116.39	115.67	139.89	68.20	26.12
IId	31.59	–	–	–	–	–	151.40	115.80	113.58	143.67	68.35	26.15
IIe	37.28	22.32	170.94	–	–	–	158.25	128.09	115.31	137.35	67.82	26.00
	31.57	–	–	–	–	–	151.29	115.77	113.57	143.76	68.20	26.08
IIf	32.23	–	–	–	–	–	158.30	121.13	115.12	135.72	67.81	25.93
IIg	32.21	–	–	–	–	–	158.29	121.11	115.10	135.71	67.80	25.95
	37.28	22.32	170.89	–	–	–	158.17	128.14	115.29	137.47	67.69	25.95
IIh	–	–	–	24.21	53.71	88.96	141.63	115.78	114.58	138.04	68.22	26.11
IIi	40.80	–	–	24.39	65.52	89.35	151.62	115.45	114.00	144.37	68.07	26.10
IIj	37.28	22.33	170.12	–	–	–	158.24	115.44	114.59	137.39	67.98	26.00
	40.85	–	–	24.42	62.53	89.34	151.56	128.10	115.32	144.42	67.81	26.07
IIk	–	22.51	172.11	24.20	55.62	87.95	158.49	128.82	115.14	134.86	67.50	25.87
IIl	–	–	–	24.46	49.10	87.18	159.01	123.41	115.17	135.52	67.67	25.86
IIm	41.90	–	–	29.41	65.15	[b]	150.72	115.42	113.79	145.65	68.26	26.15

[a] $CDCl_3 + CD_3OD$; [b] $C–NH_2$, not observed.

m.p. raised to 231–233 °C (reported[7] m.p. 227–228 °C). For $C_{20}H_{24}N_2O_4$ (356.4) calculated: 67.39% C, 6.79% H, 7.86% N; found: 66.97% C, 7.01% H, 7.69% N.

1,4-Bis(*N*-methyl-4-acetamidophenoxy)butane (*IIb*)

Compound *IIb* (54.9 g, 95%), m.p. 140–147 °C (148–151 °C after recrystallization from ethanol) was obtained by analogical procedure as described for compound *IIa*, from 4-hydroxy-*N*-methylacetanilide (50.9 g, 0.308 mol) and 1,4-dibromobutane (32.4 g, 150 mmol). For $C_{22}H_{28}N_2O_4$ (384.5) calculated: 68.73% C, 7.34% H, 7.29% N; found: 68.89% C, 7.39% H, 7.17% N.

1,4-Bis(4-aminophenoxy)butane (*IIc*)

Method A. Diamide *IIa* (60.0 g, 168 mmol) was added to a hot solution of NaOH (67.3 g, 1.68 mol) in ethylene glycol (340 ml) and the mixture was refluxed for 2.5 h. After cooling and addition of water (100 ml), the precipitate was filtered off, suspended in water (100 ml) and acidified by HCl (1 : 1) to kongo red. The hot solution was filtered through charcoal, cooled and the precipitated crystals were filtered off to give *IIc* dihydrochloride (57.5 g, 99%), m.p.220–228 °C (dec.). Dihydrochloride was dissolved in hot water (240 ml), the solution was filtered through charcoal and alcalized with 20% aqueous NaOH. After cooling and filtration, diamine *IIc* (42.2 g, 93%), m.p. 133–135 °C (136–137 °C after recrystallization from ethanol), was obtained (reported[8] m.p. 126 °C). For $C_{16}H_{20}N_2O_2$ (272.4) calculated: 70.56% C, 7.40% H, 10.29% N; found: 70.59% C, 7.74% H, 10.23% N.

Method B. The mixture of diamide *IIa* (35.6 g, 100 mmol) and diluted HCl (1 : 2, 750 ml) was refluxed for 4 h. After cooling, the precipitated crystals of *IIc* dihydrochloride, m.p. 220–230 °C, were isolated (32.8 g, 95%). Its conversion to the free diamine was carried out as described above yielding the diamine *IIc*, (25.3 g, 93%), m.p. 136–137 °C (ethanol).

1,4-Bis(4-methylaminophenoxy)butane (*IId*)

Method A. Diamide *IIb* (15.0 g, 39 mmol) was added to a solution of KOH (9.0 g, 160 mmol) in ethanol (45 ml). The mixture was refluxed for 4 h and evaporated to dryness in vacuo. The residue was washed with water and dissolved in 1 M hydrochloric acid (40 ml). After filtration through charcoal, the solution was evaporated to dryness and extracted with boiling acetone (4 × 50 ml). From the acetone extract, compound *IIe* was isolated (see below). The insoluble portion was converted to a free base by alkalization with 20% NaOH yielding diamine *IId* (7.2 g, 61%), m.p. 128–130 °C (benzene). For $C_{18}H_{24}N_2O_2$ (300.4) calculated: 71.97% C, 8.05% H, 9.33% N; found: 71.67% C, 8.24% H, 9.11% N.

Method B. The mixture of diamide *IIb* (84.1 g, 219 mmol) and diluted HCl (1 : 1, 800 ml) was refluxed for 4 h. After cooling, the precipitated crystals were recrystallized from ethanol to give *IId* dihydrochloride (71.4 g, 87%), m.p. 219–223 °C (ref.[6] gives m.p. 240 °C). For $C_{18}H_{26}N_2O_2Cl_2$ (373.2) calculated: 57.93% C, 7.02% H, 7.51% N; found: 58.15% C, 7.26% H, 7.50% N. The dihydrochloride was converted by usual procedure to diamine *IId* (93%), identical with the compound prepared by method *A*.

N-Acetyl-1,4-bis(4-methylaminophenoxy)butane (*IIe*)

Acetone extract, obtained in the course of isolation of *IId* according to method *A* was evaporated to dryness and the residue was converted to a free base with NaOH solution yielding compound *IIe* (2.1 g, 16%), m.p. 113–115 °C (ethanol). For $C_{20}H_{26}N_2O_3$ (342.4) calculated: 70.15% C, 7.65% H, 8.18% N; found: 70.28% C, 7.87% H, 8.19% N.

1,4-Bis(*N*-nitroso-4-methylaminophenoxy)butane (*IIf*)

Aqueous solution of $NaNO_2$ (25 ml, 5.52 g, 80 mmol) was dropwise added during 30 min to a stirred solution of diamine *IId* (7.46 g, 20 mmol) in diluted hydrochloric acid (8%, 60 ml) at 50–60 °C. After 1 h mixing at the same temperature, precipitated crystals were separated to give compound *IIf* (7.0 g, 98%), m.p 160–161 °C (benzene). For $C_{18}H_{22}N_4O_4$ (358.4) calculated: 60.32% C, 6.19% H, 15.63% N; found: 60.62% C, 6.35% H, 15.58% N.

N-Nitroso-*N*′-acetyl-1,4-bis(4-methylaminophenoxy)butane (*IIg*)

The nitroso compound *IIg* (1.71 g, 97%), m.p. 109–110 °C (ethanol) was prepared by the same procedure as described for compound *IIf* from compound *IIe* (1.63 g, 4.76 mmol). For $C_{20}H_{25}N_3O_4$ (371.4) calculated: 64.67% C, 6.78% H, 11.31% N; found: 65.04% C, 6.95% H, 11.39% N.

1,4-Bis[4-(2-methyl-2-nitropropyl)aminophenoxy]butane (*IIh*)

Compound *IIh* (1.65 g, 73%), m.p. 133–139 °C, was prepared from diamine *IIc* (1.3 g, 4.8 mmol) and 2-methyl-2-nitropropanol (1.2 g, 10 mmol) in the presence of aqueous tetrabutylammonium hydroxide (20%, 0.07 ml) using the same procedure as for *If*. Pure compound *IIh* (1.17 g), m.p. 138–141 °C (benzene), was obtained after column chromatography on silica gel (30 g, chloroform). For $C_{24}H_{34}N_4O_6$ (474.6) calculated: 60.74% C, 7.22% H, 11.81% N; found: 60.88% C, 7.35% H, 11.64% N.

1,4-Bis[*N*-(2-methyl-2-nitropropyl)-4-methylaminophenoxy]butane (*IIi*)

Method A. Compound *IIi* (19.6 g, 78%), m.p. 126–127 °C (benzene) was obtained from diamine *IId* (15.0 g, 50 mmol) and 2-methyl-2-nitropropanol (11.0 g, 92 mmol) in the presence of aqueous tetrabutylammonium hydroxide (20%, 0.7 ml) by the same procedure as in the case of compound *If*. For $C_{26}H_{38}N_4O_6$ (502.6) calculated: 62.13% C, 7.62% H, 11.15% N; found: 62.39% C, 7.83% H, 10.87% N.

Method B. The mixture of *IIh* (11.86 g, 25 mmol), powdered potassium carbonate (9.47 g, 75 mmol), dimethyl sulfate (6.94 g, 55 mmol), and 2-butanone (75 ml) was refluxed for 6.5 h. After cooling and dilution with ice water, the insoluble paste was crystallized from benzene and recrystallized from ethanol to give compound *IIi* (4.06 g, 32%), m.p. 116–121 °C, identical with that prepared according to the method *A*.

N-Acetyl-*N*′-(2-methyl-2-nitropropyl)-1,4-bis(4-methylaminophenoxy)butane (*IIj*)

Compound *IIj* (102 mg), m.p. 74–76 °C (ethanol) was obtained from compound *IIe* (300 mg, 0.876 mmol) and 2-methyl-2-nitropropanol (300 mg, 2.52 mmol) in the presence of aqueous tetrabutylammonium hydroxide (20%, 2 drops) by the same procedure as described for substance *If*. Further portion of *IIj* was obtained by column chromatography of mother liquor on silica gel (5 g, benzene–ethanol 19 : 1). The total yield of *IIj* was 249 mg (64%). For $C_{24}H_{33}N_3O_5$ (443.6) calculated: 64.99% C, 7.50% H, 9.47% N; found: 65.26% C, 7.98% H, 9.32% N.

N,*N*′-Bis(2-methyl-2-nitropropyl)-1,4-bis(4-acetamidophenoxy)butane (*IIk*)

Acetic anhydride (10 ml, 100 mmol) was added to a solution of compound *IIh* (11.86 g, 25 mmol) in pyridine (80 ml) and the reaction mixture was heated 1 h at 80 °C. After evaporation in vacuo, the residue was crystallized from ethanol to give compound *IIk* (10.3 g, 74%), m.p. 135–140 °C. For $C_{28}H_{38}N_4O_8$ (558.64) calculated: 60.20% C, 6.86% H, 10.03% N; found: 59.84% C, 7.26% H, 9.59% N.

N,*N*′-Bis(2-methyl-2-nitropropyl)-1,4-bis(4-nitrosaminophenoxy)butane (*IIl*)

The mixture of pyridine (5 ml) and concentrated HCl (1 ml, 12 mmol) was added to a solution of sodium nitrite (0.552 g, 8 mmol) in water (0.7 ml). To the formed suspension a solution of compound *IIh* (0.949 g, 2 mmol) in pyridine (10 ml) was added and reaction mixture was stirred for 2 h at 80 °C. After cooling and dilution with water (25 ml), the precipitate was collected to give crude product *IIl* (1.05 g, 99%), m.p. 134–141 °C. After recrystallization from benzene, the melting point raised to 146–150 °C. For $C_{24}H_{32}N_6O_8$ (532.56) calculated: 54.13% C, 6.06% H, 15.78% N; found: 54.73% C, 5.98% H, 15.32% N.

N,*N*′-Bis(2-amino-2-methylpropyl)-1,4-bis(4-methylaminophenoxy)butane (*IIm*)

Zinc powder (9.81 g, 150 mmol) was added portionwise during 1 h to a stirred solution of compound *IIi* (5.02 g, 10 mmol) in hydrochloric acid (15%, 130 ml). After another 1 h, the solution was filtered, strongly alkalized with 20% NaOH and extracted with chloroform, dried over Na_2SO_4 and the solvent was removed. The oily residue was crystallized from cyclohexane to give compound *IIm* (2.45 g, 71%), m.p. 71–73 °C. For $C_{26}H_{42}N_4O_2$ (442.6) calculated: 70.55% C, 9.56% H, 12.66% N; found: 70.07% C, 10.11% H, 12.75% N.

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