3,3-Bis(2-nitroxyethyl) derivatives of 1,1′-[methylenebis(oxy)]bis(triaz-1-ene 2-oxides) as a new type of NO donors

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3,3-Bis(2-nitroxyethyl) derivatives of 1,1′-[methylenebis(oxy)]bis(triaz-1-ene 2-oxides) were synthesized by either nucleophilic substitution of the bromine atoms of parent 3,3-bis(2-bromoethyl) compounds or nitration of structurally related 3,3-bis(2-hydroxyethyl) derivatives. The synthesized compounds comprise two different NO donating moieties, namely, oxytriaz-1-ene 2-oxide and nitrate groups, and, therefore, can be regarded as a new type of NO-donating agents.

Key words: NO donors, 1,1′-[methylenebis(oxy)]bis(triaz-1-ene 2-oxides), 2-bromoethyl derivatives, 2-hydroxyethyl derivatives, 2-nitroxyethyl derivatives, alkylation, nitration, nucleophilic substitution.

1-Alkoxytriaz-1-ene 2-oxide derivatives are extensively studied during recent years, manly, as potential NO donors in living organisms.[1—6] Earlier, we have reported on the first syntheses of 1,1′-[methylenebis(oxy)]bis(triaz-1-ene 2-oxides), their *N*-(2-haloethyl) and *N*-(2-hydroxyethyl)-derivatives, and isomeric analogs.[7—13] It also should be noted that 1-oxytriaz-1-ene 2-oxide derivatives have a relatively high enthalpy of formation of the triazene oxide moiety and contain active oxygen and, therefore, can be classified as energetic compounds. Energy content of 1-oxytriaz-1-ene 2-oxides can be enhanced by introducing the additional functional moieties with active oxygen atoms in their structure. For instance, we pioneered in synthesizing compounds with a similar structure bearing the nitrate group, *i.e.*, 3-(2-nitroxyethyl) derivatives of 1,1′-[methylenebis(oxy)]bis(triaz-1-ene 2-oxides).[14] It is also noteworthy that the nitrate group is capable of donating nitric oxide; the living example of such a compound is trinitroglycerin. Therefore, combining two different NO donating moieties in one molecule can provide a new type of hybrid NO donors.

The aim of the present work is the development of synthetic procedures to 1,1′-[methylenebis(oxy)]bis(triaz-1-ene 2-oxides) bearing two 2-nitroxyethyl groups at the same oxytriazene oxide moiety. This type of structure can be constructed by two paths. The first path involves nucleophilic substitution of the bromine atom of the corresponding 2-bromoethyl derivatives with the nitrate group. The second path is nitration of the corresponding 2-(hydroxyethyl) analogs. Earlier, we have demonstrated that most convenient laboratory procedure to the target 2-nitroxyethyl derivatives is nucleophilic substitution of the bromine atom of the corresponding 2-bromoethyl derivatives with nitrate group on treatment with $AgNO_3$.[14] Accomplishment of this synthetic scheme requires to work out first the synthesis of the corresponding intermediates, 3,3-bis(2-bromoethyl) derivatives of methylenebis(oxy) bis(triaz-1-ene 2-oxides) bearing different substituents. We achieved this goal by using synthetic approaches[12] shown on Scheme 1 (methods ***A*** and ***B***).

Synthesis of 3,3-bis(2-bromoethyl) derivatives **3** following method ***A*** involves alkylation of variously substituted sodium salts **1** with earlier described chloromethoxy derivative **2**[15] bearing two 2-bromoethyl groups. Method ***A*** was used to synthesize dibromides **3a—g,j** in the yields of about 20%.

Synthesis of dibromides **3** by method ***B*** (see Scheme 1) started from alkylation of sodium salts **1a**,**f—j** with chloromethoxy derivative **4**[10] bearing two acetoxyethyl groups to give bis-derivatives **5a**,**f—j** in 21—34% yields. On the next step, compounds **5a**,**f—j** were hydrolyzed to the corresponding 3,3-bis(2-hydroxyethyl) derivatives. The synthesis was finalized by bromination of diols **6a**,**f—j** to access dibromides **3a**,**f—j** in 52—95% yields. Despite a three-step procedure, synthesis of dibromides **3** by method ***B*** is advisable in some cases since intermediate diols **6** can also be used as the precursors for the synthesis of the target nitrates.

Bromo derivatives **3a—j** react with $AgNO_3$ in MeCN at room temperature for 2—5 days to give new 3,3-bis(2-nitroxyethyl) derivatives of 1,1′-[methylenebis(oxy)]bis-(triaz-1-ene 2-oxides) **7a—j** in 62—95% yields (Scheme 2). All synthesized nitrates are heavy oils.

Alkali metal nitrates were found low reactive in nitration giving rise to the low yields of the nitration products.

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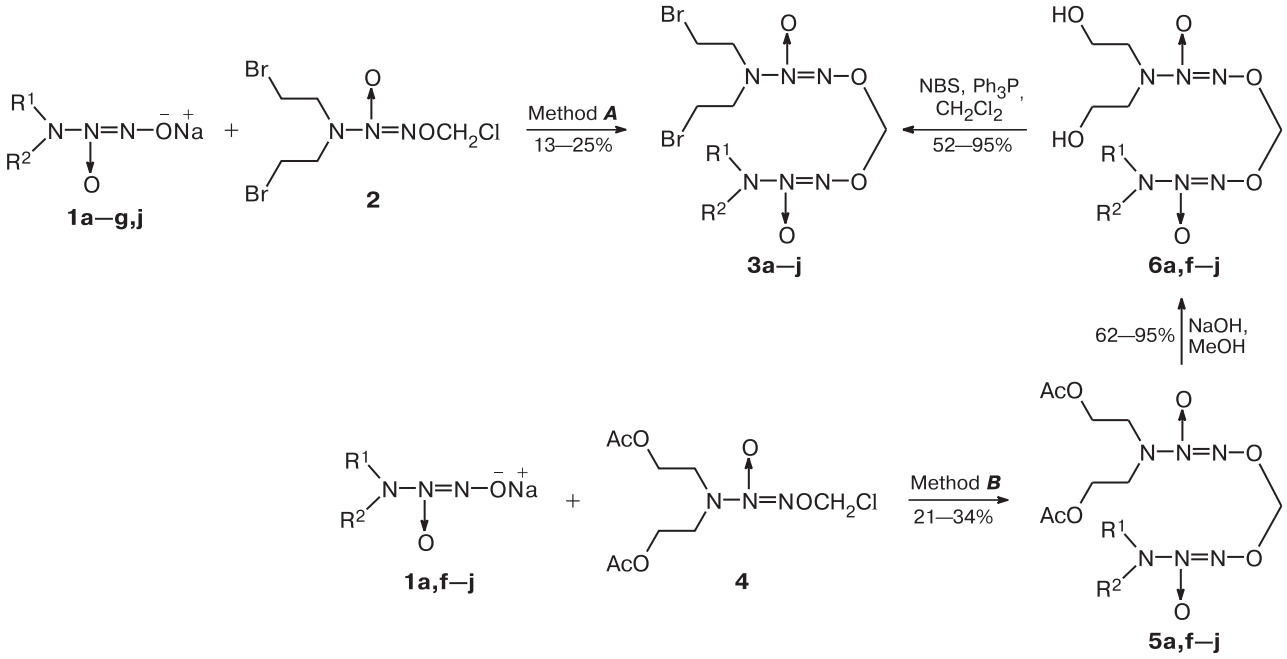
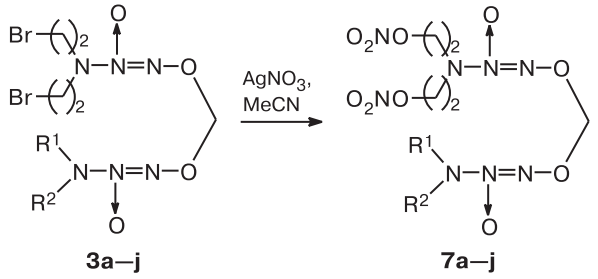
Scheme 1



Compounds **1—6**	R^1	R^2
a	Me	Me
b	Et	Et
c	CH_2CH_2OH	Me
d	CH_2CH_2OH	Et
e	CH_2CH_2OH	Pr^i

Compounds **1—6**	R^1	R^2
f	$-(CH_2)_5-$	
g	$-(CH_2)_4-$	
h	$-(CH_2)_2O(CH_2)_2-$	
i	Bn	Me
j	$CH_2CH=CH_2$	Me

Scheme 2



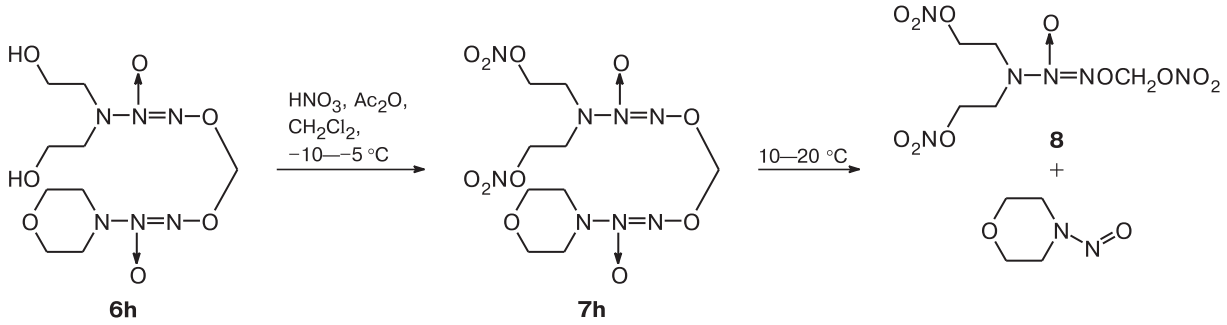
Compounds **3** and **7**	R^1	R^2	Yield of **7** (%)
a	Me	Me	62
b	Et	Et	70
c	CH_2CH_2OH	Me	93
d	CH_2CH_2OH	Et	84
e	CH_2CH_2OH	Pr^i	72
f	$-(CH_2)_5-$		67
g	$-(CH_2)_4-$		43
h	$-(CH_2)_2O(CH_2)_2-$		86
i	Bn	Me	83
j	$CH_2CH=CH_2$	Me	89

This was exemplified by the nitration of dibromide **3i** with $NaNO_3$. This reaction requires more drastic conditions to proceed and gives dinitrate **7i** in significantly lower yield (15%) than nitration of **3i** with $AgNO_3$ (83%).

The second available approach to *N*-(2-nitroxyethyl) derivatives is nitration of the corresponding alcohols. However, the structural features of the molecule and, particularly, susceptibility of the oxytriazene oxide moiety to acids, make this approach unreliable and limit the choice of the nitrating agents. For instance, triazene oxides completely decompose upon treatment with nitrating mixture. Earlier,[14] we used nitration with a nitric acid—acetic anhydride mixture to synthesize mononitroxyethyl derivatives of 1,1′-[methylenebis(oxy)bis(triaz-1-ene 2-oxides). In the present work, we studied the effects of the reaction temperature and the reaction time on the yields of the products of nitration of diol **6h** with nitric acid—acetic anhydride in dichloromethane (Scheme 3).

It was found that the target product **7h** is stable in the reaction mixture at −10÷−5 °C but it decomposes on heating to room temperature to give *N*-nitrosomorpholine and hitherto unknown trinitrate **8**. Compound **8** is apparently a result of further nitrolysis of dinitrate **7h**. The yield of the target dinitrate **7h** after maintaining the reaction mixture at room temperature for 1 h was *ca.* 15% but 3 h after from the reaction onset the reaction mixture contains only *N*-nitrosomorpholine and trinitrate **8**. Later, we optimized the reaction conditions to avoid destructive nitration by carrying out the reaction at lowered temperature (−5 °C). Under these condi-

Scheme 3



tions, the target dinitrate **7h** was obtained in 67% yield (Scheme 4).

Nitration of some other diols was also accomplished at −10÷−5 °C (see Scheme 4). Nitration of diols **6a,f,g,i** gives the corresponding dinitrates **7a,f,g,i** in the yields of 26—65%.

Apparently, the nature of the substituents of dinitrate **7** exerts a certain effect on its stability in the nitrating mixture. Thus, destruction of compound **7i** bearing a good leaving benzylic group starts even on cooling, therefore, the complete isolation of this compound is hindered and its isolated yield was relatively low (less than 30%). Nitration of diols **6a** and **6f** gives products of mononitration, *i.e.*, mononitrates **9a** (48%) and **9f** (25%), along with the target products. To achieve the exhaustive nitration of diol **6a**, we increased the amount of the nitrating agent (from 3 to 6 equiv.) and performed the reaction at lowered temperature. However, even 30 min after the reaction onset the main reaction product was trinitrate **8** (68%) and the yield of the target dinitrate **7a** was only 19%. These data indicate that the nitration of 3,3-bis(2-hydroxyethyl) derivatives of methylenebis(oxy)bis(triazene oxides) must be carried out under conditions carefully chosen for every substrate.

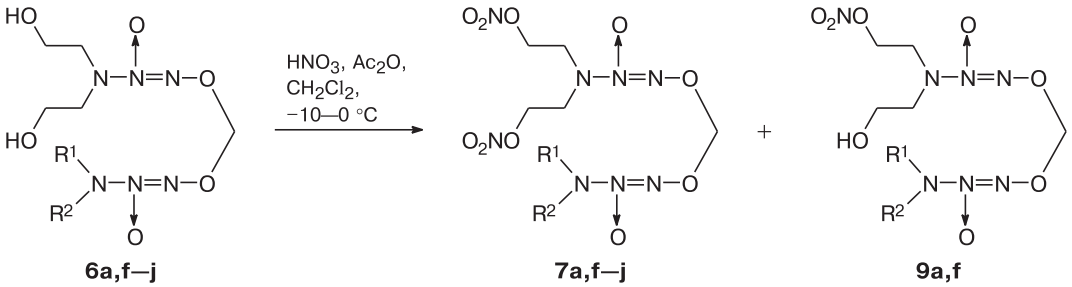
In summary, we developed two different approaches for synthesizing new 3,3-bis(2-nitroxyethyl) derivatives of 1,1′-[methylenebis(oxy)]bis(triaz-1-ene 2-oxides) possessing promising NO donating activity.

Experimental

The reaction course was monitored by TLC on precoated Silufol UV-254 plates. IR spectra were recorded with a Bruker ALPHA-T spectrometer. NMR spectra were run on a Bruker-AM-300 instrument. High resolution electrospray ionization mass spectrometry was performed with a Bruker micrOTOF II instrument. Sodium salts **1a—i**,[7,8,16] chloromethoxy derivatives **2**[15] and **4**,[10] diols **6a**,**f**,**h**,[10] and dibromides **3c,h**[12] were synthesized following known procedures.

3-Allyl-3-methyl-1-hydroxytriaz-1-ene 2-oxide sodium salt (1j). A 1 L three-neck flask equipped with a stirrer, a condenser with a liquid lock, and a gas inlet was charged with allylmethylamine (5.5 g, 0.077 mmol), sodium methoxide (obtained from Na (1.78 g, 0.77 gram atom) and MeOH (20 mL)), and diethyl ether (200 mL). Nitric oxide was passed for through the vigorously stirred mixture for 16—18 h with a rate providing excess pressure of NO of 13—20 Torr. The resulting thick precipitate was collected by filtration, washed with diethyl ether, and dried first on a filter and then under oil pump vacuum to give salt **1j** in

Scheme 4



Compounds **6** and **7**	R^1	R^2	Yield (%)	
			7	**9**
a	Me	Me	35	48
f	$-(CH_2)_5-$		65	25
g	$-(CH_2)_4-$		42	—
h	$-(CH_2)_2O(CH_2)_2-$		67	—
i	Bn	Me	26	—

63% yield. ^{1}H NMR (DMSO-d_6), δ: 2.61 (s, 3 H, CH_3); 3.43 (d, 2 H, CH_2, J = 6.5 Hz); 5.01—5.25 (m, 2 H, CH_2); 5.61—5.89 (m,1 H, CH).

Reaction of chloromethoxy derivative 2 with sodium salts 1a—g (general procedure). To a solution of dibromide **2** (0.104 g, 0.3 mmol) in anhydrous DMSO (2 mL), sodium salt **1a—g** (0.6 mmol) was added portionwise at 12—15 °C. After 1—2 h stirring, the mixture was warmed up to 20 °C, poured onto ice, and extracted with ethyl acetate (2×10 mL). The combined organic layers were washed with water (3×5 mL), dried with $MgSO_4$, and concentrated. Purification of the residue by preparative TLC (development with ethyl acetate—petroleum ether, 1 : 2) afforded target products **3a—g**, oils.

1-Bromo-3-(2-bromoethyl)-11-methyl-6,8-dioxa-3,4,5,9,10,11-hexaazadodeca-4,9-diene 4,10-dioxide (3a). Yield 0.03 g (24%). ^{1}H NMR ($CDCl_3$), δ: 3.09 (s, 6 H, 2 CH_3); 3.54 (t, 4 H, 2 CH_2, J = 6.7 Hz); 3.89 (t, 4 H, 2 CH_2, J = 6.7 Hz); 5.79 (s, 2 H, OCH_2O). The product is identical to the earlier described.[12]

1-Bromo-3-(2-bromoethyl)-11-ethyl-6,8-dioxa-3,4,5,9,10,11-hexaazatrideca-4,9-diene 4,10-dioxide (3b). Yield 0.032 g (25%). ^{1}H NMR ($CDCl_3$), δ: 1.12 (t, 6 H, 2 CH_3C, J = 7.0 Hz); 3.26 (quint, 4 H, 2 CH_2, J = 7.0 Hz); 3.55 (t, 4 H, 2 CH_2, J = 6.7 Hz); 3.89 (t, 4 H, 2 CH_2, J = 6.7 Hz); 5.80 (s, 2 H, OCH_2O). MS (ESI), *m/z*: 456.9809, 458.9789, 460.9775 $[M + Na]^+$, 472.9553, 474.9531, 476.9514 $[M + K]^+$. $C_9H_{20}Br_2N_6O_4$. Calculated: 456.9805, 458.9785, 460.9764 $[M + Na]^+$, 472.9544, 474.9524, 476.9504 $[M + K]^+$.

1-Bromo-3-(2-bromoethyl)-13-hydroxy-11-ethyl-6,8-dioxa-3,4,5,9,10,11-hexaazatrideca-4,9-diene 4,10 dioxide (3d). Yield 0.025 g (19%). ^{1}H NMR ($CDCl_3$), δ: 1.12 (t, 3 H, CH_3C, J = 7.0 Hz); 2.25 (br.s, 1 H, OH); 3.31—3.37 (m, 4 H, 2 CH_2); 3.50—3.54 (m, 4 H, 2 CH_2); 3.72 (t, 2 H, CH_2, J = 6.7 Hz); 3.79—3.91 (m, 4 H, 2 CH_2); 5.79 (s, 2 H, OCH_2O). MS (ESI), *m/z*: 472.9741, 474.9723, 476.9699 $[M + Na]^+$, 488.9479, 490.9457, 492.9434 $[M + K]^+$. $C_9H_{20}Br_2N_6O_5$. Calculated: 472.9754, 474.9734, 476.9714 $[M + Na]^+$, 488.9494, 490.9474, 492.9453 $[M + K]^+$.

1-Bromo-3-(2-bromoethyl)-13-hydroxy-11-isopropyl-6,8-dioxa-3,4,5,9,10,11-hexaazatrideca-4,9-diene 4,10-dioxide (3e). Yield 0.018 g (13%). ^{1}H NMR ($CDCl_3$), δ: 1.18 (d, 6 H, 2 CH_3C, J = 4.7 Hz); 2.20 (br.s, 1 H, OH), 3.32 (t, 2 H, CH_2, J = 5.0 Hz); 3.55 (t, 4 H, 2 CH_2, J = 6.7 Hz); 3.70 (t, 2 H, CH_2, J = 5.0 Hz); 3.79—3.91 (m, 5 H, 2 CH_2 + CH); 5.80 (s, 2 H, OCH_2O). MS (ESI), *m/z*: 486.9919, 488.9895, 490.9879 $[M + Na]^+$, 502.9655, 504.9634, 506.9621 $[M + K]^+$. $C_{10}H_{22}Br_2N_6O_5$. Calculated: 486.9911, 488.9891, 490.9870 $[M + Na]^+$, 502.9650, 504.9630, 506.9610 $[M + K]^+$.

1-Bromo-3-(2-bromoethyl)-10-(piperidin-4-yl)-6,8-dioxa-3,4,5,9,10-pentaazadeca-4,9-diene 4,10-dioxide (3f). Yield 0.027 g (20%). ^{1}H NMR ($CDCl_3$), δ: 1.48—1.54 (m, 2 H, CH_2); 1.70—1.77 (m, 4 H, 2 CH_2); 3.43 (t, 4 H, 2 NCH_2, J = 5.3 Hz); 3.52 (t, 4 H, 2 CH_2, J = 6.7 Hz); 3.88 (t, 4 H, 2 OCH_2, J = 6.7 Hz); 5.78 (s, 2 H, OCH_2O). The product is identical to the earlier described.[12]

1-Bromo-3-(2-bromoethyl)-10-(pyrrolidin-4-yl)-6,8-dioxa-3,4,5,9,10-pentaazadeca-4,9-diene 4,10-dioxide (3g). Yield 0.034 g (26%). ^{1}H NMR ($CDCl_3$), δ: 1.87—1.93 (m, 4 H, 2 CH_2); 3.51—3.54 (m, 8 H, 4 CH_2); 3.77 (t, 4 H, 2 CH_2, J = 6.7 Hz); 5.75 (s, 2 H, OCH_2O). MS (ESI), *m/z*: 432.9836, 434.9815, 436.9797 $[M + H]^+$, 450.0104, 452.0083, 454.0064 $[M + NH_4]^+$, 456.9638, 458.9617 $[M + Na]^+$. $C_9H_{18}Br_2N_6O_4$. Calculated: 432.9829, 434.9809, 436.9789 $[M + H]^+$, 450.0095, 452.0075, 454.0054 $[M + NH_4]^+$, 456.9629, 458.9608 $[M + Na]^+$.

1-Bromo-3-(2-bromoethyl)-11-methyl-12-phenyl-6,8-dioxa-3,4,5,9,10,11-hexaazadodeca-4,9-diene 4,10-dioxide (3i). To a solution of compound **6i** (0.06 g, 0.17 mmol) and Ph_3P (0.13 g, 0.5 mmol) in CH_2Cl_2 (10 mL), *N*-bromosuccinimide (0.09 g, 0.5 mmol) was added at 0—5 °C. Cooling was removed, the reaction mixture was stirred at 20 °C for 16 h, and concentrated *in vacuo*. Purification of the residue by preparative TLC (development with ethyl acetate—petroleum ether, 1 : 2) afforded 0.077 g (95%) of compound **3i**, oil. ^{1}H NMR ($CDCl_3$), δ: 2.96 (s, 3 H, NCH_3); 3.51 (t, 4 H, 2 CH_2, J = 6.7 Hz); 3.86 (t, 4 H, 2 CH_2, J = 6.7 Hz); 4.55 (s, 2 H, $PhCH_2N$); 5.72 (s, 2 H, OCH_2O); 7.26—7.34 (m, 5 H, Ph). IR (neat), ν/cm^{-1}: 1501, 1439, 1229, 1110, 1073, 1026, 943. MS (ESI), *m/z*: 504.9821, 506.9780, 508.9759 $[M + Na]^+$. $C_{13}H_{20}Br_2N_6O_8$. Calculated: 504.9805, 506.9785, 508.9765 $[M + Na]^+$.

1-Bromo-3-(2-bromoethyl)-11-methyl-6,8-dioxa-3,4,5,9,10,11-hexaazatetradeca-4,9,13-triene 4,10-dioxide (3j). Method *A*. To a stirred solution of compound **6j** (0.045 g, 0.15 mmol) in CH_2Cl_2 (10 mL), Ph_3P (0.13 g, 0.5 mmol) was added at room temperature followed by addition of *N*-bromosuccinimide (0.08 g, 0.48 mmol) after 10 min stirring. The reaction mixture was kept at room temperature for 10 h and concentrated *in vacuo*. Purification of the residue by preparative TLC (development with ethyl acetate—petroleum ether, 1 : 2) afforded 0.033 g (52%) of compound **3j**, oil. ^{1}H NMR ($CDCl_3$), δ: 3.02 (s, 3 H, CH_3N); 3.54 (t, 4 H, 2 CH_2N, J = 6.7 Hz); 3.88 (t, 4 H, 2 CH_2Br, J = 6.7 Hz); 3.98 (d, 2 H, CH_2N, J = 6.5 Hz); 5.21—5.30 (m, 2 H, CH_2=CH); 5.77 (s, 2 H, OCH_2O); 5.85 (m, 1 H, CH). IR (neat), ν/cm^{-1}: 2969, 2857, 1644, 1503, 14442, 1390, 1252, 1234, 1172, 1070, 1024, 946, 755, 671. MS (ESI), *m/z*: 454.9644 $[M + Na]^+$, 470.9384 $[M + K]^+$. $C_9H_{18}Br_2N_6O_4$. Calculated: 454.9648 $[M + Na]^+$, 470.9388 $[M + K]^+$.

Method *B*. To a stirred solution of sodium salt **1j** (0.2 g, 1.3 mmol) and K_2CO_3 (0.04 g, 0.29 mmol) in DMSO (10 mL), chloride **2** (0.42 g, 1.24 mmol) was added dropwise under cooling with cold water. Cooling was removed, the reaction mixture was stirred at 20 °C for 10 h, diluted with water (15 mL), and extracted with CH_2Cl_2 (4×10 mL). The combined organic layers were washed with water (3×10 mL), dried with $MgSO_4$, and concentrated *in vacuo*. Purification of the residue by preparative TLC (development with CH_2Cl_2) afforded 0.1 g (18%) of compound **3j** identical to the sample obtained by method *A*.

1-Acetoxy-3-(2-acetoxyethyl)-10-(pyrrolidin-1-yl)-6,8-dioxa-3,4,5,9,10-pentaazadeca-4,9-diene 4,10-dioxide (5g). To a stirred solution of chloride **4** (0.165 g, 0.55 mmol) in anhydrous DMSO (3 mL) cooled to ~15 °C, sodium salt **1g** (0.17 g, 1.1 mmol) was added by portions. The reaction mixture was stirred for 2 h gradually rising the reaction temperature to 20 °C, poured into ice-water (15 mL), and extracted with ethyl acetate (3×7 mL). The combined organic layers were washed with water (5 mL), dried with $MgSO_4$, and concentrated *in vacuo*. Purification of the residue by preparative TLC (development with ethyl acetate—petroleum ether, 2 : 1) afforded 0.046 g (21%) of compound **5g**, oil. ^{1}H NMR ($CDCl_3$), δ: 1.92 (s, 4 H, 2 CCH_2); 2.05 (s, 6 H, 2 CH_3CO); 3.53—3.59 (m, 4 H, 2 CH_2N); 3.68 (t, 4 H, 2 CH_2N, J = 5.3 Hz); 4.25 (t, 4 H, OCH_2, J = 5.3 Hz); 5.72 (s, 2 H, OCH_2O). IR (neat), ν/cm^{-1}: 1738, 1504, 1435, 1219, 1055, 944. MS (ESI), *m/z*: 393.1716 $[M + H]^+$, 410.1982 $[M + NH_4]^+$, 415.1533 $[M + Na]^+$, 431.1272 $[M + K]^+$. $C_{13}H_{24}N_6O_8$. Calculated:

393.1728 $[M + H]^+$, 410.1994 $[M + NH_4]^+$, 415.1548 $[M + Na]^+$, 431.1282 $[M + K]^+$.

1-Acetoxy-3-(2-acetoxyethyl)-11-methyl-12-phenyl-6,8-dioxa-3,4,5,9,10,11-hexaazadodeca-4,9-diene 4,10-dioxide (5i). To a mixture of sodium salt **1i** (0.37 g, 1.8 mmol) and Na_2CO_3 (0.05 g, 0.5 mmol) in DMSO (15 mL), chloromethoxy derivative **5** (0.45 g, 1.5 mmol) was added. The reaction mixture was stirred at 20 °C for 16 h, diluted with water, and extracted with $CHCl_3$ (3×5 mL). The combined organic layers were washed with water, dried with Mg_2SO_4, and concentrated *in vacuo*. Purification of the residue by preparative TLC (development with ethyl acetate—petroleum ether, 1 : 1) afforded 0.23 g (34%) of compound **5i**, oil. ^1H NMR ($CDCl_3$), δ: 1.98 (s, 6 H, 2 CCH_3); 2.89 (s, 3 H, NCH_3); 3.61 (t, 4 H, NCH_2, J = 5.3 Hz); 4.19 (t, 4 H, OCH_2, J = 5.3 Hz); 4.49 (s, 2 H, $PhCH_2N$); 5.66 (s, 2 H, OCH_2O); 7.23—7.32 (m, 5 H, Ph). IR (neat), ν/cm^{-1}: 1740, 1504, 1455, 1371, 1229, 1068, 945. MS (ESI), *m/z*: 443.1880 $[M + H]^+$, 460.2141 $[M + NH_4]^+$, 465.1699 $[M + Na]^+$, 481.1442 $[M + K]^+$. $C_{17}H_{26}N_6O_8$. Calculated: 443.1885 $[M + H]^+$, 460.2150 $[M + NH_4]^+$, 465.1704 $[M + Na]^+$, 481.1444 $[M + K]^+$.

1-Acetoxy-3-(2-acetoxyethyl)-11-methyl-6,8-dioxa-3,4,5,9,10,11-hexaazatetradeca-4,9,13-triene 4,10-dioxide (5j). To a stirred solution of salt **1j** (0.15 g, 0.98 mmol) in DMSO (8 mL), a solution of chloromethoxy derivative **4** (0.2 g, 0.67 mmol) in DMSO (2 mL) was added dropwise at room temperature. The reaction mixture was stirred at 20 °C for 10 h, diluted with water (10 mL), and extracted with CH_2Cl_2 (3×10 mL). The combined organic layers were washed with water (3×5 mL), dried with $MgSO_4$, and concentrated *in vacuo*. Purification of the residue by preparative TLC (development with methanol—$CHCl_3$, 1 : 15) afforded 0.06 g (23%) of compound **5j**, oil. ^1H NMR ($CDCl_3$), δ: 2.02 (s, 6 H, 2 CH_3CO); 2.95 (s, 3 H, CH_3N); 3.65 (t, 4 H, 2 CH_2N, J = 5.3 Hz); 3.93 (d, 2 H, CH_2N, J = 6.5 Hz); 4.21 (t, 4 H, 2 CH_2O, J = 5.3 Hz); 5.16—5.28 (m, 2 H, CH_2=CH); 5.70 (s, 2 H, OCH_2O); 5.75 (m, 1 H, CH). IR (neat), ν/cm^{-1}: 2968, 1742, 1657, 1646, 1504, 1444, 1370, 1232, 1048, 1026, 947, 606. MS (ESI), *m/z*: 415.1544 $[M + Na]^+$, 431.1296 $[M + K]^+$. $C_{13}H_{24}N_6O_8$. Calculated: 415.1548 $[M + Na]^+$, 431.1287 $[M + K]^+$.

1-Hydroxy-3-(2-hydroxyethyl)-10-(pyrrolidin-1-yl)-6,8-dioxa-3,4,5,9,10-pentaazadeca-4,9-diene 4,10-dioxide (6g). To a stirred solution of compound **5g** (0.034 g, 0.086 mmol) in MeOH (0.5 mL), 5% solution of NaOH in MeOH (0.3 mL, 0.014 g of NaOH) was added. The resulting mixture was kept at 20 °C for 10 min and subjected to preparative TLC (development with ethyl acetate—MeOH, 9 : 1) to afford 0.02 g (74%) of compound **6g**, oil. ^1H NMR ($CDCl_3$), δ: 1.95—1.99 (m, 4 H, 2 CH_2); 3.25 (br.s, 2 H, 2 OH); 3.55—3.63 (m, 6 H, 3 CH_2); 3.79—3.82 (m, 4 H, 2 CH_2); 5.72 (s, 2 H, OCH_2). IR (neat), ν/cm^{-1}: 3401 (OH), 2956, 2882, 1488, 1279, 1232, 1169, 1064, 1029. MS (ESI), *m/z*: 309.1519 $[M + H]^+$, 326.1781 $[M + NH_4]^+$, 331.1334 $[M + Na]^+$, 347.1067 $[M + K]^+$. $C_9H_{20}N_6O_6$. Calculated: 309.1517 $[M + H]^+$, 326.1783 $[M + NH_4]^+$, 331.1337 $[M + Na]^+$, 347.1076 $[M + K]^+$.

1-Hydroxy-3-(2-hydroxyethyl)-11-methyl-12-phenyl-6,8-dioxa-3,4,5,9,10,11-hexaazadodeca-4,9-diene 4,10-dioxide (6i). A mixture of diacetate **5i** (0.2 g, 0.45 mmol) in EtOH (5 mL) was treated with a solution of NaOH (0.05 g, 1.25 mmol) in EtOH (5 mL). The reaction mixture was stirred at 20 °C for 1 h and concentrated *in vacuo*. Purification of the residue by preparative TLC (development with methanol—chloroform, 1 : 5) afforded 0.1 g (62%) of compound **6i**, oil. ^1H NMR ($CDCl_3$), δ: 2.92 (s, 3 H, NCH_3); 3.52 (t, 4 H, 2 NCH_2, J = 5.0 Hz); 3.72 (t, 4 H, 2 OCH_2, J = 5.0 Hz); 3,82 (br.s, 2 H, 2 OH); 4.51 (s, 2 H, $PhCH_2N$); 5.69 (s, 2 H, OCH_2O); 7.25—7.35 (m, 5 H, Ph). IR (neat), ν/cm^{-1}: 2924, 2854, 1508, 1438, 1384, 1280, 1106, 949. MS (ESI), *m/z*: 359.1672 $[M + H]^+$; 376.1934 $[M + NH_4]^+$; 381.1488 $[M + Na]^+$, 397.1226 $[M + K]^+$. $C_{13}H_{22}N_6O_6$. Calculated: 359.1674 $[M + H]^+$; 376.1939 $[M + NH_4]^+$; 381.1493 $[M + Na]^+$, 397.1232 $[M + K]^+$.

1-Hydroxy-3-(2-hydroxyethyl)-11-methyl-6,8-dioxa-3,4,5,9,10,11-hexaazatetradeca-4,9,13-triene 4,10-dioxide (6j). To a stirred solution of diacetate **5j** (0.06 g, 0.15 mmol) in MeOH (5 mL), 10% solution of NaOH in MeOH (0.2 mL) was added at room temperature. The reaction mixture was stirred at 20 °C for 1 h and filtered through a silica gel pad. Removal of the solvent *in vacuo* afforded 0.045 g (95%) of compound **6j**, oil. Product **6j** was used in the next step without further purification. ^1H NMR ($CDCl_3$), δ: 2.98 (s, 3 H, CH_3N); 3.46 (br.s, 2 H, 2 OH); 3.57 (t, 4 H, 2 CH_2N, J = 5.0 Hz); 3.75 (t, 4 H, 2 CH_2O, J = 5.0 Hz); 3.97 (d, 2 H, CH_2N, J = 6.5 Hz); 5.20—5.31 (m, 2 H, CH_2=CH); 5.72 (s, 2 H, OCH_2O); 5.68—5.86 (m, 1 H, CH).

Reaction of dibromides 3a—j with $AgNO_3$ (general procedure). A solution of dibromide **3a—j** (0.12 mmol) and $AgNO_3$ (0.1 g, 0.59 mmol) in anhydrous MeCN (1 mL) was stirred at 20 °C for 48—120 h, filtered, and concentrated *in vacuo*. Purification of the residue by preparative TLC (development with ethyl acetate—petroleum ether, 1 : 1) afforded dinitrates **7a—j**, oils.

2-Methyl-12-nitroxy-10-(2-nitroxyethyl)-5,7-dioxa-2,3,4,8,9,10-hexaazadodeca-3,8-diene 3,9-dioxide (7a). Yield 0.029 g (62%). ^1H NMR ($CDCl_3$), δ: 3.10 (s, 6 H, 2 CH_3); 3.82 (t, 4 H, 2 CH_2, J = 5.0 Hz); 4.70 (t, 4 H, 2 CH_2, J = 5.0 Hz); 5.79 (s, 2 H, OCH_2O). ^{13}C NMR ($CDCl_3$), δ: 42.09 (CH_3N); 50.78 (CH_2N); 69.86 (CH_2ONO_2); 95.52 (OCH_2O). ^{14}N NMR ($CDCl_3$), δ: −44.49 (NO_2); −50.89 (NO). IR (neat), ν/cm^{-1}: 2974, 1634 (ONO_2), 1504, 1442, 1280, 1025, 944. MS (ESI), *m/z*: 373.1080 $[M + H]^+$, 390.1319 $[M + NH_4]^+$, 395.0876 $[M + Na]^+$, 411.0615 $[M + K]^+$. $C_7H_{16}N_8O_{10}$. Calculated: 373.1062 $[M + H]^+$, 390.1328 $[M + NH_4]^+$, 395.0882 $[M + Na]^+$, 411.0621 $[M + K]^+$.

11-Ethyl-1-nitroxy-3-(2-nitroxyethyl)-6,8-dioxa-3,4,5,9,10,11-hexaazatrideca-4,9-diene 4,10-dioxide (7b). Yield 0.035 g (70%). ^1H NMR ($CDCl_3$), δ: 1.09 (t, 6 H, 2 CH_3C, J = 7.0 Hz); 3.25 (q, 4 H, 2 CH_2, J = 7.0 Hz); 3.82 (t, 4 H, 2 CH_2, J = 5.0 Hz); 4.68 (t, 4 H, 2 CH_2, J = 5.0 Hz); 5.80 (s, 2 H, OCH_2O). IR (neat), ν/cm^{-1}: 2980, 1638 (ONO_2), 1514, 1448, 1280, 1027, 950. MS (ESI), *m/z*: 423.1202 $[M + Na]^+$, 439.0938 $[M + K]^+$. $C_9H_{20}N_8O_{10}$. Calculated: 423.1195 $[M + Na]^+$, 439.0934 $[M + K]^+$.

1-Hydroxy-3-methyl-13-nitroxy-11-(2-nitroxyethyl)-6,8-dioxa-3,4,5,9,10,11-hexaazatrideca-4,9-diene 4,10-dioxide (7c). Yield 0.047 g (93%). ^1H NMR ($CDCl_3$), δ: 2,18 (br.s, 1 H, OH); 3.12 (s, 6 H, 2 CH_3); 3.55 (t, 2 H, CH_2, J = 5.0 Hz); 3.79—3.85 (m, 6 H, 3 CH_2); 4.70 (m, 4 H, 2 CH_2); 5.78 (s, 2 H, OCH_2O). IR (neat), ν/cm^{-1}: 3468 (OH), 2967, 1637 (ONO_2), 1504, 1441, 1280, 1070, 1025, 948. MS (ESI), *m/z*: 403.1174 $[M + H]^+$, 420.1440 $[M + NH_4]^+$, 425.0996 $[M + Na]^+$, 441.0734 $[M + K]^+$. $C_8H_{18}N_8O_{11}$. Calculated: 403.1168 $[M + H]^+$, 420.1433 $[M + NH_4]^+$, 425.0987 $[M + Na]^+$, 441.0727 $[M + K]^+$.

3-Ethyl-1-hydroxy-13-nitroxy-11-(2-nitroxyethyl)-6,8-dioxa-3,4,5,9,10,11-hexaazatrideca-4,9-diene 4,10-dioxide (7d). Yield 0.044 g (84%). ^1H NMR ($CDCl_3$), δ: 1.12 (t, 3 H, CH_3C, J = 7.0 Hz); 2.12 (br.s, 1 H, OH), 3.30—3.40 (m, 4 H, 2 CH_2); 3.70 (t, 2 H, CH_2, J = 5.1 Hz); 3.80 (t, 4 H, 2 CH_2, J = 5.0 Hz); 3.80 (t, 4 H, 2 CH_2, J = 5.0 Hz); 5.79 (s, 2 H, OCH_2O). IR (neat), ν/cm^{-1}: 3470 (OH), 1637 (ONO_2), 1501, 1441, 1255, 1080, 948.

MS (ESI), *m/z*: 417.1316 $[M + H]^+$, 434.1586 $[M + NH_4]^+$, 439.1137 $[M + Na]^+$, 455.0875 $[M + K]^+$. $C_9H_{20}N_8O_{11}$. Calculated: 417.1324 $[M + H]^+$, 434.1590 $[M + NH_4]^+$, 439.1144 $[M + Na]^+$, 455.0883 $[M + K]^+$.

1-Hydroxy-3-isopropyl-13-nitroxy-11-(2-nitroxyethyl)-6,8-dioxa-3,4,5,9,10,11-hexaazatrideca-4,9-diene 4,10-dioxide (7e). Yield 0.039 g (72%). ^1H NMR ($CDCl_3$), δ: 1.18 (d, 6 H, 2 CH_3C, J = 4.7 Hz); 2.20 (br.s, 1 H, OH), 3.32 (t, 2 H, CH_2, J = 5.0 Hz); 3.67 (t, 2 H, CH_2, J = 5.0 Hz); 3.70 (t, 2 H, CH_2, J = 5.0 Hz); 3.81—3.88 (m, 5 H, 2 CH_2 and CH); 3.69 (t, 4 H, 2 CH_2, J = 5.0 Hz); 5.80 (s, 2 H, OCH_2O). IR (neat), ν/cm^{-1}: 3466 (OH), 1638 (ONO_2), 1501, 1438, 1255, 1079, 944. MS (ESI), *m/z*: 431.1476 $[M + H]^+$, 453.1294 $[M + Na]^+$, 469.1031 $[M + K]^+$. $C_{10}H_{22}N_8O_{11}$. Calculated: 431.1481 $[M + H]^+$, 453.1300 $[M + Na]^+$, 469.1040 $[M + K]^+$.

1-Nitroxy-3-(2-nitroxyethyl)-10-(piperidin-4-yl)-6,8-dioxa-3,4,5,9,10-pentaazadeca-4,9-diene 4,10-dioxide (7f). Yield 0.036 g (67%). ^1H NMR ($CDCl_3$), δ: 1.47—1.55 (m, 2 H, CH_2); 1.70—1.77 (m, 4 H, 2 CH_2); 3.42 (t, 4 H, 2 NCH_2, J = 5.3 Hz); 3.82 (t, 4 H, 2 CH_2, J = 5.0 Hz); 4.69 (t, 4 H, 2 OCH_2, J = 5.0 Hz); 5.80 (s, 2 H, OCH_2O). ^{13}C NMR ($CDCl_3$), δ: 23.41 (CH_2C); 24.62 (CH_2C); 50.93 (CH_2N); 52.15 (CH_2N); 69.62 (CH_2ONO_2); 95.69 (OCH_2O). IR (neat), ν/cm^{-1}: 2948, 2860, 1634, 1504, 1445, 1392, 1280, 1228, 1070, 1021, 851. MS (ESI), *m/z*: 413.1376 $[M + H]^+$, 430.1640 $[M + NH_4]^+$, 435.1193 $[M + Na]^+$, 451.0928 $[M + K]^+$. $C_{10}H_{20}N_8O_{10}$. Calculated: 413.1375 $[M + H]^+$, 430.1641 $[M + NH_4]^+$, 435.1195 $[M + Na]^+$, 451.0934 $[M + K]^+$.

1-Nitroxy-3-(2-nitroxyethyl)-10-(pyrrolidin-4-yl)-6,8-dioxa-3,4,5,9,10-pentaazadeca-4,9-diene 4,10-dioxide (7g). Yield 0.022 g (43%). ^1H NMR ($CDCl_3$), δ: 1.95—2.00 (m, 4 H, 2 CH_2); 3.59—3.63 (m, 4 H, 2 CH_2); 3.83 (t, 4 H, 2 CH_2, J = 5.0 Hz); 4.68 (t, 4 H, 2 NCH_2, J = 5.0 Hz); 5.76 (s, 2 H, OCH_2O). IR (neat), ν/cm^{-1}: 2970, 2886, 1637 (ONO_2), 1491, 1280, 1026, 945. MS (ESI), *m/z*: 399.1213 $[M + H]^+$, 416.1485 $[M + NH_4]^+$, 421.1025 $[M + Na]^+$, 437.0772 $[M + K]^+$. $C_9H_{18}N_8O_{10}$. Calculated: 399.1219 $[M + H]^+$, 416.1484 $[M + NH_4]^+$, 421.1038 $[M + Na]^+$, 437.0777 $[M + K]^+$.

1-(Morpholin-4-yl)-10-nitroxy-8-(2-nitroxyethyl)-3,5-dioxa-1,2,6,7,8-pentaazadeca-1,6-diene 1,7-dioxide (7h). Yield 0.046 g (86%). ^1H NMR ($CDCl_3$), δ: 3.49 (t, 4 H, 2 NCH_2, J = 4.6 Hz); 3.79—3.86 (m, 8 H, 4 CH_2); 4.67 (t, 4 H, 2 OCH_2, J = 5.0 Hz); 5.77 (s, 2 H, OCH_2O). IR (neat), ν/cm^{-1}: 1633, 1504, 1457, 1281, 1230, 1079, 1024, 950. MS (ESI), *m/z*: 415.1167 $[M + H]^+$, 432.1434 $[M + NH_4]^+$, 437.0985 $[M + Na]^+$, 453.0724 $[M + K]^+$. $C_9H_{18}N_8O_{11}$. Calculated: 415.1168 $[M + H]^+$, 432.1433 $[M + NH_4]^+$, 437.0987 $[M + Na]^+$, 453.0727 $[M + K]^+$.

2-Methyl-12-nitroxy-10-(2-nitroxyethyl)-1-phenyl-5,7-dioxa-2,3,4,8,9,10-hexaazadodeca-3,8-diene 3,9-dioxide (7i). Yield 0.045 g (83%). ^1H NMR ($CDCl_3$), δ: 2.98 (s, 3 H, NCH_3); 3.81 (t, 4 H, NCH_2, J = 5.0 Hz); 4.56 (s, 2 H, $PhCH_2N$); 4.67 (t, 4 H, OCH_2, J = 5.0 Hz); 5.73 (s, 2 H, OCH_2O); 7.28—7.37 (m, 5 H, Ph). IR (neat), ν/cm^{-1}: 1635, 1505, 1437, 1279, 1107, 1026, 947. MS (ESI), *m/z*: 449.1370 $[M + H]^+$, 466.1642 $[M + NH_4]^+$, 471.1170 $[M + Na]^+$, 487.0929 $[M + K]^+$. $C_{13}H_{20}N_8O_{10}$. Calculated: 449.1375 $[M + H]^+$, 466.1641 $[M + NH_4]^+$, 471.1195 $[M + Na]^+$, 487.0934 $[M + K]^+$.

11-Methyl-1-nitroxy-3-(2-nitroxyethyl)-6,8-dioxa-3,4,5,9,10,11-hexaazatetradeca-4,9,14-triene 4,10-dioxide (7j). Yield 0.044 g (89%). ^1H NMR ($CDCl_3$), δ: 3.02 (s, 3 H, CH_3N); 3.82 (t, 4 H, 2 CH_2N, J = 5.1 Hz); 4.02 (d, 2 H, CH_2N, J = 6.5 Hz); 4.68 (t, 4 H, 2 CH_2O, J = 5.1 Hz); 5.26—5.32 (m, 2 H, CH_2=CH); 5.77 (s, 2 H, OCH_2O); 5.74—5.84 (m, 1 H, CH). IR (neat), ν/cm^{-1}: 3084, 2975, 2904, 1633, 1504, 1442, 1393, 1280, 1252, 1173, 1068, 949, 852, 757. MS (ESI), *m/z*: 399.1215 $[M + H]^+$, 416.1478 $[M + NH_4]^+$, 421.1035 $[M + Na]^+$, 437.0772 $[M + K]^+$. $C_9H_{18}N_8O_{10}$. Calculated: 399.1219 $[M + H]^+$, 416.1484 $[M + NH_4]^+$, 421.1038 $[M + Na]^+$, 437.0777 $[M + K]^+$.

Reaction of bromide 3i with $NaNO_3$. A mixture of bromide **3i** (0.036 g, 0.07 mmol) and $NaNO_3$ (0.05 g, 0.59 mmol) in DMF (3 mL) was stirred at 60 °C for 48 h, diluted with water, and extracted with $CHCl_3$ (3×3 mL). The combined organic layers were washed with water, dried with Mg_2SO_4, and concentrated *in vacuo*. Purification of the residue by preparative TLC (development with ethyl acetate—petroleum ether, 1 : 1) afforded 0.005 g (15%) of compound **7i** identical to the sample obtained above.

1-(Morpholin-4-yl)-10-nitroxy-8-(2-nitroxyethyl)-3,5-dioxa-1,2,6,7,8-pentaazadeca-1,6-diene 1,7-dioxide (7h). To a solution of Ac_2O (0.1 mL) in anhydrous CH_2Cl_2 (2 mL) cooled to −5 °C, 98% HNO_3 (0.05 mL) was added. After 5 min stirring at −5 °C, a solution of compound **6h** (0.07 g, 0.22 mmol) in CH_2Cl_2 (1 mL) was added dropwise to the nitrating mixture. The reaction mixture was stirred at −10 °C for 10 min and subjected to preparative TLC (development with ethyl acetate—petroleum ether, 1 : 1) to afford 0.06 g (67%) of dinitrate **7h** identical to the sample obtained above.

3,3-Bis(2-nitroxyethyl)-1-(nitroxymethoxy)triaz-1-ene 2-oxide (8). To a solution of Ac_2O (0.1 mL) in anhydrous CH_2Cl_2 (2 mL) cooled to −5 °C, 98% HNO_3 (0.05 mL) was added. After 5 min stirring at −5 °C, a solution of compound **6h** (0.08 g, 0.25 mmol) in CH_2Cl_2 (2 mL) was added to the nitrating mixture. The reaction mixture was stirred at −5 °C for 10 min, cooling was removed and after warming up to 20 °C the mixture was stirred for additional 3 h. Preparative TLC of the reaction mixture (development with ethyl acetate—petroleum ether, 1 : 1) afforded 0.036 g (44%) of compound **8**, oil. ^1H NMR ($CDCl_3$), δ: 3.85 (t, 4 H, 2 CH_2, J = 5.0 Hz); 4.68 (t, 2 H, CH_2, J = 5.0 Hz); 6.04 (s, 2 H, OCH_2O). IR (neat), ν/cm^{-1}: 1638 (ONO_2), 1509, 1452, 1280, 1250, 1075, 1022, 951. MS (ESI), *m/z*: 348.0748 $[M + NH_4]^+$, 353.0301 $[M + Na]^+$, 369.0040 $[M + K]^+$. $C_5H_{10}N_6O_{11}$. Calculated: 348.0746 $[M + NH_4]^+$, 353.0300 $[M + Na]^+$, 369.0039 $[M + K]^+$.

Nitration of 1-hydroxy-3-(2-hydroxyethyl)-11-methyl-6,8-dioxa-3,4,5,9,10,11-hexaazadodeca-4,9-diene 4,10-dioxide (6a). Method *A*. To a stirred solution of Ac_2O (0.10 mL, 0.09 g, 1.0 mmol) in anhydrous CH_2Cl_2 (15 mL) cooled to −5—0 °C, fuming HNO_3 (0.04 mL, 0.065 g, 1.0 mmol) was added dropwise. After 10 min stirring at −5—0 °C, a solution of diol **6a** (0.12 g, 0.43 mmol) in anhydrous CH_2Cl_2 (10 mL) was added dropwise at −3 °C. The reaction mixture was stirred at 18 °C for 17 h and subjected to preparative TLC (development with ethyl acetate—petroleum ether, 2 : 1) to give 0.055 g (35%) of compound **7a** identical to the sample obtained above and 0.067 g (48%) of compound **9a**.

1-Hydroxy-11-methyl-3-(2-nitroxyethyl)-6,8-dioxa-3,4,5,9,10,11-hexaazadodeca-4,9-diene 4,10-dioxide (9a). Oil. ^1H NMR ($CDCl_3$), δ: 2.15 (br.s, 1 H, OH); 3.10 (s, 6 H, 2 CH_3); 3.59 (t, 2 H, CH_2, J = 5.0 Hz); 3.82 (t, 4 H, 2 CH_2, J = 5.0 Hz); 4.69 (t, 2 H, CH_2, J = 5.0 Hz); 5.79 (s, 2 H, OCH_2O). IR (neat), ν/cm^{-1}: 3485 (OH), 2920, 1634 (ONO_2), 1503, 1452, 1281, 1069, 1025, 943. MS (ESI), *m/z*: 328.1218 $[M + H]^+$, 345.1476 $[M + NH_4]^+$, 350.1027 $[M + Na]^+$, 366.0762 $[M + K]^+$.

$C_7H_{17}N_7O_8$. Calculated: 328.1211 $[M + H]^+$, 345.1477 $[M + NH_4]^+$, 350.1031 $[M + Na]^+$, 366.0770 $[M + K]^+$.

Method *B*. To a stirred solution of Ac_2O (0.17 mL, 0.18 g, 1.75 mmol) in anhydrous CH_2Cl_2 (20 mL) cooled to −5—0 °C, fuming HNO_3 (0.08 mL, 0.11 g, 1.75 mmol) was added dropwise. After stirring at −5—0 °C for 5 min, a solution of diol **6a** (0.1 g, 0.35 mmol) in anhydrous CH_2Cl_2 (10 mL) was added dropwise at −3 °C. The reaction mixture was stirred at 20 °C for 30 min and subjected to preparative TLC (development with ethyl acetate—petroleum ether, 2 : 1) to give 0.025 g (19%) of compound **7a** and 0.082 g (68%) of compound **8** identical to the sample obtained above.

Nitration of 1-hydroxy-3-(2-hydroxyethyl)-10-(piperidin-4-yl)-6,8-dioxa-3,4,5,9,10-pentaazadeca-4,9-diene 4,10-dioxide (6f). To a stirred solution of fuming HNO_3 (0.029 g, 0.46 mmol) in anhydrous CH_2Cl_2 (2 mL) cooled to ~0 °C, Ac_2O (0.03 g, 0.46 mmol) was added. After stirring at ~0 °C for 30 min, a solution of compound **6f** (0.048 g, 0.149 mmol) in CH_2Cl_2 (1 mL) was added dropwise. After warming up to 10 °C, the reaction mixture was kept for 4 h and then subjected to preparative TLC (development with ethyl acetate—petroleum ether, 2 : 1) to give 0.04 g (65%) of compound **7f** identical to the sample obtained above and 0.014 g (25%) of compound **9f**.

1-Hydroxy-3-(2-nitroxyethyl)-10-(piperidin-4-yl)-6,8-dioxa-3,4,5,9,10-pentaazadeca-4,9-diene 4,10-dioxide (9f). Oil. ^{1}H NMR ($CDCl_3$), δ: 1.49—1.56 (m, 2 H, CH_2); 1.72—1.79 (m, 4 H, 2 CH_2); 3.40 (t, 4 H, 2 CH_2, J = 5.5 Hz); 3.60 (t, 2 H, CH_2, J = 5.0 Hz); 3.78—3.83 (m, 4 H, 2 CH_2); 4.70 (t, 2 H, CH_2, J = 5.0 Hz); 5.80 (s, 2 H, OCH_2). IR (neat), ν/cm^{-1}: 3470 (OH), 2946, 2858, 1634 (ONO_2), 1504, 1445, 1386, 1280, 1228, 1172, 1069, 1022, 944, 852. MS (ESI), *m/z*: 368.1517 $[M + H]^+$, 385.1779 $[M + NH_4]^+$, 390.1332 $[M + Na]^+$, 406.1067 $[M + K]^+$. $C_{10}H_{21}N_7O_8$. Calculated: 368.1524 $[M + H]^+$, 385.1790 $[M + NH_4]^+$, 390.1344 $[M + Na]^+$, 406.1083 $[M + K]^+$.

Nitration of 1-hydroxy-3-(2-hydroxyethyl)-10-(pyrrolidin-4-yl)-6,8-dioxa-3,4,5,9,10-pentaazadeca-4,9-diene 4,10-dioxide (6g). To a stirred solution of Ac_2O (0.15 mL, 0.16 g, 1.6 mmol) in anhydrous CH_2Cl_2 (10 mL) cooled to −5—0 °C, fuming HNO_3 (0.07 mL, 0.1 g, 1.6 mmol) was added dropwise. After 10 min stirring at −5—0 °C, a solution of diol **6g** (0.11 g, 0.32 mmol) in anhydrous CH_2Cl_2 (5 mL) was added dropwise at −3 °C. The reaction mixture was stirred at 5—7 °C for 2.5 h and subjected to preparative TLC (development with ethyl acetate—petroleum ether, 1 : 1) to afford 0.05 g (42%) of compound **7g** identical to the sample obtained above.

Nitration of 1-hydroxy-3-(2-hydroxyethyl)-11-methyl-12-phenyl-6,8-dioxa-3,4,5,9,10,11-hexaazadodeca-4,9-diene 4,10-dioxide (6i). To a solution of Ac_2O (0.05 mL) in anhydrous CH_2Cl_2 (1 mL) cooled to −5 °C, 98% HNO_3 (0.02 mL) was added followed by dropwise addition of a solution of diol **6i** (0.03 g, 0.08 mmol) in CH_2Cl_2 (1 mL) after 5 min stirring. The reaction mixture was stirred at −10 °C for 10 min and subjected to preparative TLC (development with ethyl acetate—petroleum ether, 1 : 1) to afford 0.01 g (27%) of compound **7i** identical to the sample obtained by nitration of compound **3j** with $AgNO_3$.

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