Synthesis of 3-R-1,5-dinitro-3-azabicyclo[3.3.1]nonanes fused to azoles*

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3-R-1,5-Dinitro-3-azabicyclo[3.3.1]nonanes fused to the pyrazole, thiazole, and triazole rings were synthesized by reductive cyclization of *meta*-dinitrobenzazoles.

Key words: azabicyclo[3.3.1]nonanes, reduction, Mannich reaction, nitro group, azoles.

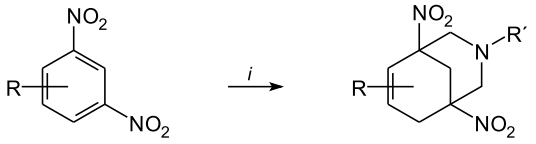
The present study is a continuation of our research on the development of methods for the synthesis of polycyclic fused heterosystems based on five-membered aromatic 4,6-dinitrobenzannulated heterocycles *via* the annulation of additional heterocycles using the ability of the starting dinitrobicyclic compounds to form σ^H adducts with nucleophilic reagents.[1] The aim of the present study was to synthesize 3-R-1,5-dinitro-3-azabicyclo[3.3.1]-nonanes fused at the C(7)—C(8) bond to different azoles.

Heteroanalogs of bicyclo[3.3.1]nonanes are structural fragments of terpene alkaloids and have found use as biologically active compounds.[2] In recent years, 1,5-dinitro-3-azabicyclo[3.3.1]nonane derivatives have found to possess antiarrhythmic activity (see, for example, Ref. 3). Many of these compounds have been synthesized earlier[3—6] based on substituted 1,3-dinitrobenzenes (Scheme 1). The method of synthesis of these compounds involves the reduction of C=C bonds in the benzene ring activated by the *meta*-nitro groups with $NaBH_4$ or KBH_4 followed by the double Mannich reaction with formaldehyde and primary amines.

It should be noted that analogous transformations of *meta*-dinitrobenzannulated heterocycles are virtually unknown. Only two syntheses of these compounds containing the pyridine ring were documented.[6,7] Data on the synthesis of 3-azabicyclo[3.3.1]nonanes fused to five-membered heterocycles are lacking in the literature.

We developed a method for the synthesis of 3-R-1,5-dinitro-3-azabicyclo[3.3.1]nonanes fused to the pyrazole ring.[8] Isomeric 4,6-dinitro-1- and 2-phenylindazoles **1** and **2** can be used as the starting compounds for the synthesis of these compounds. Compounds **1** and **2** can be prepared based on 2,4,6-trinitrotoluene (TNT).[9,10]

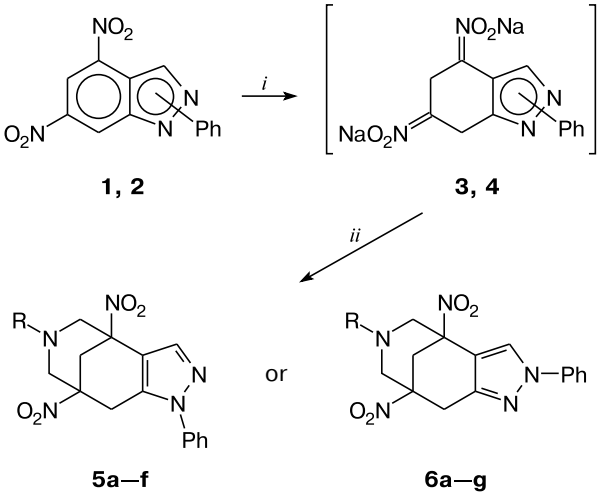
Scheme 1



i. 1) $NaBH_4$, THF—EtOH—$HCONH_2$; 2) HCHO, R´NH_2, AcOH

R = OH, Alk, Hal, OAlk, COOH; R´ = Alk, $(CH_2)_nCOOH$

Scheme 2



i. $NaBH_4$, EtOH—THF—$HCONH_2$; *ii*. CH_2O, RNH_2, AcOH

5, 6	R	5	R	6	R
a	Me	d	$CH(CH_3)COOH$	d	$(CH_2)_3COOH$
b	CH_2COOH	f	$(CH_2)_3COOH$	f	$CH(CH_3)COOH$
c	$(CH_2)_2COOH$			g	$(CH_2)_2Cl$
e	$CHMe_2$				

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Thus, the reaction of dinitroindazoles **1** and **2** with $NaBH_4$ produces hydride adducts **3** and **4**,[11] whose treatment with a formaldehyde solution and a primary amine affords tricyclic derivatives, *viz.*, 1,5-dinitro-3-azabicyclo-[3.3.1]nonanes **5** and **6** fused at the C(7)—C(8) bond to the pyrazole ring (Scheme 2).

We used alkylamines and amino acids as primary amines.

The structures of compounds **5** and **6** were confirmed by NMR and IR spectroscopy and elemental analysis.

The three-dimensional structures of the 1,5-dinitro-3-azabicyclo[3.3.1]nonane derivatives were determined based on the study of compound **5a**. The complete assignment of the signals for the hydrogen and carbon atoms in compound **5a** was based on NMR experiments (^1H, ^{13}C, COSY, 2D-NOESY, HSQC, and HMBC). The conformation of the piperidine ring (chair) was established based on the NOESY spectrum, in which the correlation peaks between the $N—CH_3$ protons and the H(2), H(2′), H(6), and H(6′) protons and between H(4′) and the H(2′) and H(6′) protons indicate that the corresponding protons are closely spaced (Fig. 1).

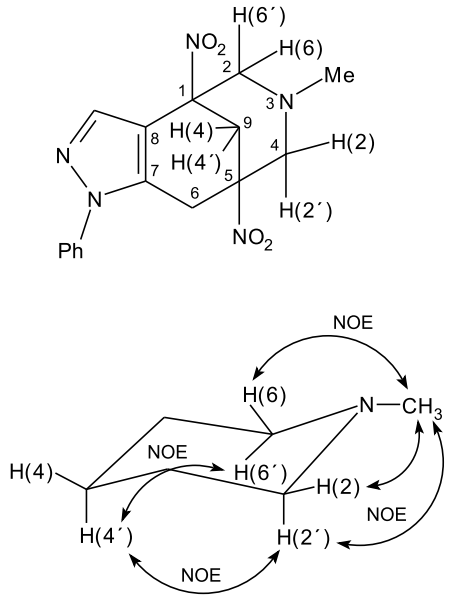
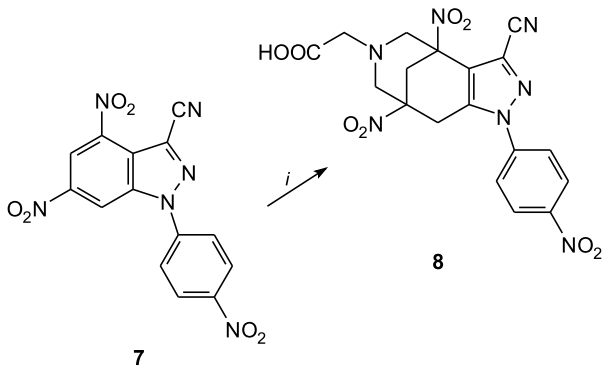


Fig. 1. Structure of compound **5a**.

The cyclohexene ring is nearly planar. These data are similar to those obtained for 7-polyfluoroalkoxy-1,5-dinitro-3-azabicyclo[3.3.1]non-6-enes.[12,13]

In the reaction of 3-cyano-4,6-dinitro-1-(4-nitrophenyl)indazole **7**, which was prepared by the nitration of the corresponding N-phenyl derivative,[14] with $NaBH_4$, the reduction is selective (only at the dinitrophenyl fragment), and the subsequent double Mannich reaction with formaldehyde and glycine affords tricyclic derivative **8** in good yield (Scheme 3).

Scheme 3

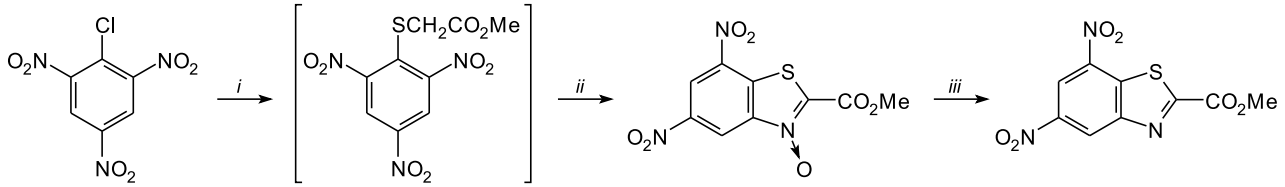


i. $NaBH_4$, EtOH—THF—$HCONH_2$, CH_2O, $NH_2CH_2CO_2H$, AcOH

It was of interest to study the behavior of other readily available dinitrobenzazoles containing two NO_2 groups in the *meta* positions in the transformations under consideration. For this purpose, we chose *meta*-dinitro derivatives of benzothiazole and benzotriazole.

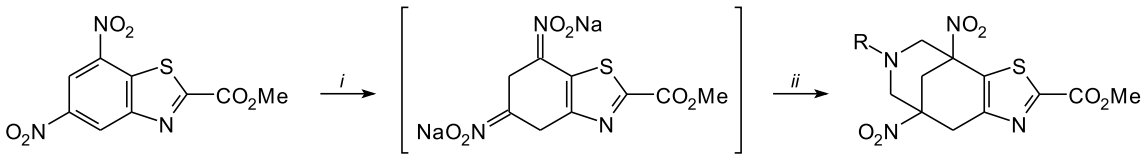
Dinitro-substituted benzothiazole *N*-oxide can easily be synthesized by the treatment of picryl chloride with methyl thioglycolate in the presence of a small excess of a base. In this reaction, the intermediate replacement product of the chlorine atom **10** undergoes *in situ* cyclization *via* the addition of the active methylene group of the SCH_2CO_2Me fragment at the NO_2 group.[15] The *N*-oxide

Scheme 4



i. $HSCH_2CO_2Me$, Et_3N (1 equiv.); *ii*. Et_3N (cat); *iii*. PCl_3, $CHCl_3$, Δ

Scheme 5



i. $NaBH_4$, EtOH—THF—$HCONH_2$; *ii*. CH_2O, RNH_2, AcOH

R = $CHMe_2$ (**a**), Me (**b**), $(CH_2)_2CO_2H$ (**c**)

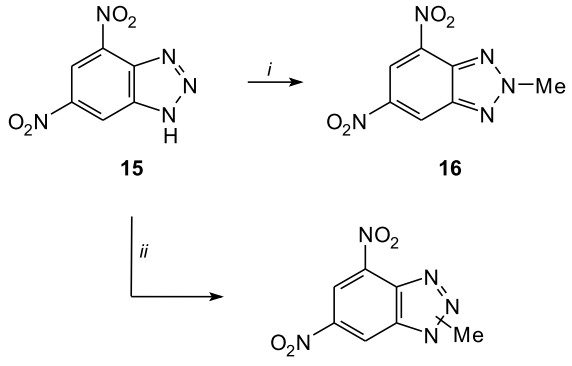
fragment of the thiazole ring in compound **11** is reduced under reflux in $CHCl_3$ in the presence of PCl_3 to form dinitrobenzothiazole **12** (Scheme 4).

Compound **12**, unlike its *N*-oxide analog **11,** reacts with $NaBH_4$ followed by the double Mannich reaction under ambient conditions. This reaction produces dinitro derivatives of 3-azabicyclo[3.3.1]nonane **14** fused to the thiazole ring in good yields (Scheme 5).

In the present study, we also examined *N*-substituted 4,6-dinitrobenzotriazole as a heterocyclic compound because the triazole ring is stable to $NaBH_4$ and it is even a better electron-withdrawing group compared to pyrazole, which should facilitate the formation of hydride adducts.

The methylation of 4,6-dinitrobenzotriazole[16] **15** can theoretically afford three isomeric *N*-methyl derivatives. We found and optimize the reaction conditions, in which one methylation product **16** is predominantly formed (Scheme 6).

Scheme 6

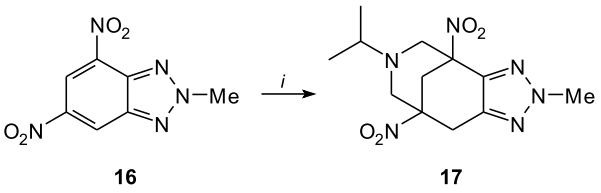


i. MeI, NaOH, MeCN, 20 °C; *ii*. MeI, K_2CO_3, DMF, 20 °C

The structure of the previously unknown compound **16** was determined by ^1H, ^{13}C, ^{14}N, and ^{15}N NMR experiments (NOESY, HCQC, HMBC, *etc.*). The assignment was based on the ^1H—^{13}C and ^1H—^{15}N correlations. The presence of cross-peaks characterizing interactions between the hydrogen atoms of the methyl group and all the three endocyclic nitrogen atoms indicates that the methyl group in compound **16** is attached at position 2.

We performed the reaction of 2-methyl-4,6-dinitrobenzotriazole **16** with $NaBH_4$ followed by the double Mannich reaction under ambient conditions. This reaction produced triazole-containing derivative of 1,5-dinitro-3-azabicyclo[3.3.1]nonane **17**.

Scheme 7



i. (*1*) $NaBH_4$, EtOH—THF—$HCONH_2$, (*2*) CH_2O, $NH_2CH(CH_3)_2$, AcOH

To sum up, we developed a general method for the synthesis of 3-R-1,5-dinitro-3-azabicyclo[3.3.1]nonanes fused with azole (pyrazole, thiazole, and triazole) rings based on a series of *meta*-dinitro-substituted benzazoles.

Experimental

The ^1H and ^{13}C NMR spectra were recorded on a Bruker AM-300 instrument. The ^{14}N and ^{15}N NMR spectra were measured on a Bruker DRX-500 instrument. All experiments were performed with the use of the Bruker software. The chemical shifts are given with respect to $SiMe_4$ (^1H and ^{13}C) and CH_3NO_2 (^{14}N and ^{15}N). The upfield chemical shifts are given with a minus sign. Samples for NMR spectroscopy were prepared in DMSO-d_6 (unless otherwise stated). The IR spectra were recorded on a Specord-M-80 instrument in KBr pellets. The EI mass spectra were obtained on a MS-30 Kratos instrument (70 eV). The course of the reactions was monitored and the purity of the compounds was checked by TLC on Silufol UV-254 plates. Dry DMF and MeCN were used. Other solvents were used without special drying. Compounds **1**, **2**, **7**, **11**, **12**, and **15** were synthesized according to procedures described earlier (see the text).

Synthesis of compounds 5, 6, 8, 14, and 17 (general procedure). Sodium borohydride (0.36 g, 9.5 mmol) was added portionwise to a solution of the corresponding dinitrobenzazole (1.7 mmol) in a mixture of THF (2 mL), EtOH (6 mL), and formamide (4 mL) at a temperature no higher than 10 °C for 20 min. After 30 min, water (7 mL), a mixture of a 30% aqueous RNH_2 solution (2 mL), water (2 mL), a 30% formaldehyde solution (2 mL), and then glacial AcOH (2 mL) were successively added. The reaction mixture was stirred at 20 °C for 30 min and poured into water (150 mL). The precipitate was filtered off and dried in air.

10-Methyl-1,8-dinitro-5-phenyl-4,5,10-triazatricyclo[6.3.1.$0^{2,6}$]dodeca-2(6),3-diene (5a). The yield was 48%, m.p. 152—154 °C (EtOH). Found (%): C, 56.00; H, 4.80; N, 20.20. $C_{16}H_{17}N_5O_4$. Calculated (%): C, 55.97; H, 4.99; N, 20.40 (C=N). ^{1}H NMR, δ: 2.34 (s, 3 H, NMe); 2.55 (d, 1 H, J = 10.2 Hz); 2.60 (d, 1 H, J = 10.9 Hz); 2.80 (d, 1 H, J = 11.8 Hz); 3.09 (d, 1 H, J = 11.8 Hz); 3.27 (d, 1 H, J = 10.2 Hz); 3.31 (d, 1 H, J = 10.9 Hz); 3.41 (d, 1 H, J = 16.6 Hz); 3.47 (d, 1 H, J = 16.7 Hz); 7.43 (m, 1 H, Ph); 7.49—7.51 (m, 4 H, Ph); 7.69 (s, 1 H, Pz). ^{13}C NMR, δ: 33.74, 38.47, 45.03, 62.34, 63.85, 83.80, 85.92, 117.11, 123.46, 128.46, 128.13, 129.51, 135.29, 136.84, 139.11. IR, ν/cm^{-1}: 1352, 1552 (NO_2); 1600 (C=N).

2-(1,8-Dinitro-5-phenyl-4,5,10-triazatricyclo[6.3.1.$0^{2,6}$]dodeca-2(6),3-dien-10-yl)acetic acid (5b). The yield was 70%, m.p. 154—155 °C. Found (%): C, 52.27; H, 4.12; N, 18.08. $C_{17}H_{17}N_5O_6$. Calculated (%): C, 52.71; H, 4.42; N, 17.56. ^{1}H NMR, δ: 2.92 (d, 1 H, J = 12.8 Hz); 3.08 (d, 1 H, J = 12.9 Hz); 3.23—3.57 (m, 7 H); 3.74 (d, 1 H, J = 16.2 Hz); 7.44 (t, 1 H, p-Ph, J = 8.1 Hz); 7.52—7.65 (m, 5 H, Pz, Ph).

3-(1,8-Dinitro-5-phenyl-4,5,10-triazatricyclo[6.3.1.$0^{2,6}$]dodeca-2(6),3-dien-10-yl)propionic acid (5c). The yield was 80%, m.p. 208—210 °C. Found (%): C, 53.86; H, 4.77; N, 17.45. $C_{18}H_{19}N_5O_6$. Calculated (%): C, 54.12; H, 4.57; N, 17.46. ^{1}H NMR, δ: 2.24 (t, 2 H, CH_2, J = 5.1 Hz); 2.60—3.53 (m, 9 H); 3.72 (d, 1 H, J = 16.2 Hz); 7.41—7.64 (m, 6 H, Pz, Ph).

2-(1,8-Dinitro-5-phenyl-4,5,10-triazatricyclo[6.3.1.$0^{2,6}$]dodeca-2(6),3-dien-10-yl)propionic acid (5d). The yield was 68%, m.p. 193—194 °C. Found (%): C, 53.83; H, 4.97; N, 16.65. $C_{18}H_{19}N_5O_6$. Calculated (%): C, 53.86; H, 4.77; N, 17.45. ^{1}H NMR, δ: 0.89 and 1.04 (both d, 3 H, CH_3 (mixture of diastereomers), J = 7.6 Hz); 2.92—3.53 (m, 8 H); 3.73 (d, 1 H, J = 16.1 Hz); 7.43—7.62 (m, 6 H, Pz, Ph).

10-Isopropyl-1,8-dinitro-5-phenyl-4,5,10-triazatricyclo[6.3.1.$0^{2,6}$]dodeca-2(6),3-diene (5e). The yield was 72%, m.p. 96—98 °C. Found (%): C, 58.00; H, 5.80; N, 18.60. $C_{18}H_{21}N_5O_4$. Calculated (%): C, 58.21; H, 5.70; N, 18.86. ^{1}H NMR, δ: 0.88 (d, 3 H, CH_3, J = 8.6 Hz); 1.06 (d, 3 H, CH_3, J = 8.6 Hz); 2.91—3.67 (m, 9 H); 7.38—7.63 (m, 6 H, Pz, Ph).

4-(1,8-Dinitro-5-phenyl-4,5,10-triazatricyclo[6.3.1.$0^{2,6}$]dodeca-2(6),3-dien-10-yl)butyric acid (5f). The yield was 75%, m.p. 79—81 °C. Found (%): C, 54.82; H, 5.30; N, 16.57. $C_{19}H_{21}N_5O_6$. Calculated (%): C, 54.94; H, 5.10; N, 16.86. ^{1}H NMR, δ: 1.46 (m, 2 H, CH_2); 1.78 (m, 2 H, CH_2); 2.41 (m, 2 H, CH_2); 2.68 (d, 1 H, J = 10.7 Hz); 2.75 (d, 1 H, J = 10.7 Hz); 2.94 (d, 1 H, J = 10.7 Hz); 3.10 (t, 2 H, J = 12.9 Hz); 3.32 (d, 2 H, J = 17.5 Hz); 3.79 (d, 1 H, J = 17.5 Hz); 7.42—7.63 (m, 6 H, Pz, Ph).

10-Methyl-1,8-dinitro-4-phenyl-4,5,10-triazatricyclo[6.3.1.$0^{2,6}$]dodeca-2,5-diene (6a). The yield was 29%, m.p. 127—129 °C (EtOH). Found (%): C, 56.45; H, 4.91; N, 20.00. $C_{16}H_{17}N_5O_4$. Calculated (%): C, 55.97; H, 4.99; N, 20.40. ^{1}H NMR, δ: 2.26 (s, 3 H, N—Me); 2.52, 2.60, and 2.72 (all d, 1 H each, J = 10.1 Hz); 2.92 and 3.05 (both d, 1 H each, J = 11.1 Hz); 3.17 (d, 1 H, J = 8.9 Hz); 3.35—3.54 (m, 2 H); 7.31 (t, 1 H, p-H_{Ph}); 7.48 (t, 2 H, m-H_{Ph}, J = 8.1 Hz); 7.85 (d, 2 H, o-H_{Ph}, J = 8.0 Hz); 8.42 (s, 1 H, Pz). IR, ν/cm^{-1}: 1352, 1544 (NO_2); 1600 (C=N).

2-(1,8-Dinitro-4-phenyl-4,5,10-triazatricyclo[6.3.1.$0^{2,6}$]dodeca-2,5-dien-10-yl)acetic acid (6b). The yield was 82%, m.p. 88—90 °C. Found (%): C, 52.63; H, 4.58; N, 17.30. $C_{17}H_{17}N_5O_6$. Calculated (%): C, 52.71; H, 4.42; N, 18.08. ^{1}H NMR, δ: 2.92 (d, 1 H, J = 13.3 Hz); 3.02—3.54 (m, 9 H); 7.28 (t, 1 H, p-H_{Ph}, J = 8.2 Hz); 7.45 (t, 2 H, m-H_{Ph}, J = 8.2 Hz); 7.80 (d, 2 H, o-H_{Ph}, J = 8.3 Hz); 8.43 (s, 1 H, Pz).

3-(1,8-Dinitro-4-phenyl-4,5,10-triazatricyclo[6.3.1.$0^{2,6}$]dodeca-2,5-dien-10-yl)propionic acid (6c). The yield was 76%, m.p. 92—94 °C. Found (%): C, 53.77; H, 4.63. $C_{18}H_{19}N_5O_6$. Calculated (%): C, 53.86; H, 4.77. ^{1}H NMR, δ: 2.25 (t, 2 H, CH_2, J = 6.6 Hz); 2.65—3.62 (m, 10 H); 7.28 (t, 1 H, p-H_{Ph}, J = 8.0 Hz); 7.46 (t, 2 H, m-H_{Ph}, J = 8.1 Hz); 7.82 (d, 2 H, o-H_{Ph}, J = 8.1 Hz); 8.38 (s, 1 H, Pz).

4-(1,8-Dinitro-4-phenyl-4,5,10-triazatricyclo[6.3.1.$0^{2,6}$]dodeca-2,5-dien-10-yl)butyric acid (6d). The yield was 75%, m.p. 75 °C. Found (%): C, 55.11; H, 5.36. $C_{19}H_{21}N_5O_6$. Calculated (%): C, 54.94; H, 5.10. ^{1}H NMR, δ: 1.48 (m, 2 H, CH_2); 1.86 (m, 2 H, CH_2); 2.48 (m, 2 H, CH_2); 2.73—3.30 (m, 5 H); 3.34—3.62 (m, 3 H); 7.29 (t, 1 H, p-H_{Ph}, J = 8.5 Hz); 7.48 (t, 2 H, m-H_{Ph}, J = 8.4 Hz); 7.80 (d, 2 H, o-H_{Ph}, J = 8.6 Hz); 8.35 (s, 1 H, Pz).

10-Isopropyl-1,8-dinitro-4-phenyl-4,5,10-triazatricyclo[6.3.1.$0^{2,6}$]dodeca-2,5-diene (6e). The yield was 83%, m.p. 139—141 °C. Found (%): C, 58.24; H, 5.92; N, 18.28. $C_{18}H_{21}N_5O_4$. Calculated (%): C, 58.21; H, 5.70; N, 18.86. ^{1}H NMR, δ: 0.81 (d, 3 H, CH_3, J = 8.6 Hz); 0.90 (d, 3 H, CH_3, J = 8.6 Hz); 2.80—3.52 (m, 9 H); 7.28 (t, 1 H, p-H_{Ph}, J = 8.1 Hz); 7.47 (t, 2 H, m-H_{Ph}, J = 8.1 Hz); 7.83 (d, 2 H, o-H_{Ph}, J = 8.0 Hz); 8.37 (s, 1 H, Pz).

2-(1,8-Dinitro-4-phenyl-4,5,10-triazatricyclo[6.3.1.$0^{2,6}$]dodeca-2,5-dien-10-yl)propionic acid (6f). The yield was 76%, m.p. 188—190 °C. Found (%): C, 53.60; H, 5.10; N, 16.80. $C_{18}H_{19}N_5O_6$. Calculated (%): C, 53.86; H, 4.77; N, 17.45. ^{1}H NMR, δ: 0.88 and 1.08 (both d, 3 H, CH_3 (for a mixture of diastereomers), J = 8.6 Hz); 2.95—3.58 (m, 9 H); 7.29 (t, 1 H, p-H_{Ph}, J = 8.5 Hz); 7.47 (t, 2 H, m-H_{Ph}, J = 8.6 Hz); 7.83 (d, 2 H, o-H_{Ph}, J = 8.6 Hz); 8.41 (s, 1 H, Pz).

10-(2-Chloroethyl)-1,8-dinitro-4-phenyl-4,5,10-triazatricyclo[6.3.1.$0^{2,6}$]dodeca-2,5-diene (6g). The yield was 16%, m.p. 65—67 °C. Found (%): C, 52.13; H, 4.73; Cl, 9.35. $C_{17}H_{18}ClN_5O_4$. Calculated (%): C, 52.11; H, 4.63; Cl, 9.05. ^{1}H NMR, δ: 2.71—3.10 (m, 6 H); 3.23—3.58 (m, 6 H); 7.30 (t, 1 H, p-H_{Ph}, J = 8.1 Hz); 7.47 (t, 2 H, m-H_{Ph}, J = 8.1 Hz); 7.82 (d, 2 H, o-H_{Ph}, J = 8.2 Hz); 8.42 (s, 1 H, Pz).

2-[3-Cyano-1,8-dinitro-5-(4-nitrophenyl)-4,5,10-triazatricyclo[6.3.1.$0^{2,6}$]dodeca-2(6),3-dien-10-yl]acetic acid (8). The yield was 75%, m.p. 178—180 °C. Found (%): C, 47.34; H, 3.03. $C_{18}H_{15}N_7O_8$. Calculated (%): C, 47.27; H, 3.31. ^{1}H NMR, δ: 2.95—3.45 (m, 8 H); 3.60 (d, 1 H, J = 18.6 Hz); 3.93 (d, 1 H, J = 18.6 Hz); 8.00 (d, 2 H, 4-$NO_2C_6H_4$, J = 9.4 Hz); 8.43 (d, 2 H, 4-$NO_2C_6H_4$, J = 9.4 Hz).

Methyl 10-isopropyl-1,8-dinitro-3-thia-5,10-diazatricyclo[6.3.1.$0^{2,6}$]dodeca-2(6),4-diene-4-carboxylate (14a). The yield

was 0.25 g (40%), m.p. 147—150 °C. Found (%): C, 45.76; H, 5.13; N, 15.04. $C_{14}H_{18}N_4O_6S$. Calculated (%): C, 45.40; H, 4.90; N, 15.13. ^{1}H NMR, δ: 0.72 (d, 3 H, CH_3, J = 6.5 Hz); 0.83 (d, 3 H, CH_3, J = 6.4 Hz); 2.80 (m, 1 H); 2.95 (m, 2 H); 3.12 (m, 2 H); 3.35 (m, 2 H); 3.47 (d, 1 H, J = 16.7 Hz); 3.59 (d, 1 H, J = 16.7 Hz); 3.91 (s, 3 H, Me).

Methyl 10-methyl-1,8-dinitro-3-thia-5,10-diazatricyclo-[6.3.1.0^{2,6}]dodeca-2(6),4-diene-4-carboxylate (14b). The yield was 0.3 g (52%), m.p. 164—168 °C. Found (%): C, 42.21; H, 4.23; N, 16.15. $C_{12}H_{14}N_4O_6S$. Calculated (%): C, 42.10; H, 4.12; N, 16.37. ^{1}H NMR, δ: 2.22 (s, 3 H); 2.68 (d, 1 H, J = 10.5 Hz); 2.75 (d, 1 H, J = 10.5 Hz); 3.17 (m, 3 H); 3.35 (m, 1 H); 3.53 (d, 1 H, J = 16.8 Hz); 3.62 (d, 1 H, J = 16.8 Hz); 3.91 (s, 3 H, Me).

3-[4-(Methoxycarbonyl)-1,8-dinitro-3-thia-5,10-diazatri-cyclo[6.3.1.0^{2,6}]dodeca-2(6),4-dien-10-yl]propionic acid (14c). The yield was 0.14 g (41%), m.p. 202—206 °C. Found (%): C, 42.14; H, 4.07; N, 13.77. $C_{14}H_{16}N_4O_8S$. Calculated (%): C, 42.00; H, 4.03; N, 13.99. ^{1}H NMR, δ: 2.19 (m, 2 H); 2.64—3.72 (m, 10 H); 3.91 (s, 3 H, Me); 12.00 (br.s, 1 H).

10-Isopropyl-4-methyl-1,8-dinitro-3,4,5,10-tetraaza-tricyclo[6.3.1.0^{2,6}]dodeca-2,5-diene (17). The yield was 0.32 g (57%), m.p. 125—128 °C. Found (%): C, 46.41; H, 5.86; N, 27.15. $C_{12}H_{18}N_6O_4$. Calculated (%): C, 46.45; H, 5.85; N, 27.08. ^{1}H NMR, δ: 0.78 (d, 3 H, CH_3, J = 6.4 Hz); 0.86 (d, 3 H, CH_3, J = 6.4 Hz); 2.81 (d, 2 H, J = 10.5 Hz); 2.98 (d, 2 H, J = 10.2 Hz); 3.16 (m, 2 H); 3.35 (m, 2 H); 3.53 (d, 1 H, J = 10.2 Hz); 4.08 (s, 3 H, N—Me).

2-Methyl-4,6-dinitro-2*H*-1,2,3-benzotriazole (16). Sodium hydroxide (0.43 g, 0.0107 mol) was added to a solution of dinitrobenzotriazole **15** (2.25 g, 0.0107 mol) in dry acetonitrile (40 mL). The reaction mixture was cooled to 0 °C, and CH_3I (0.67 mL, 0.0108 mol) was added. Then the reaction mixture was kept at 0 °C for 3 h, CH_3I (1.34 mL, 0.0216 mol) was added, and the mixture was allowed to stand at room temperature for 3 days, poured into water (150 mL), and extracted with ethyl acetate (3×50 mL). The organic layer was washed with water, dried over Na_2SO_4, and concentrated to dryness. The residue was washed with hot ethanol and recrystallized from chloroform. The yield of compound **16** was 0.671 g (28%), m.p. 206—208 °C ($CHCl_3$). Found (%): C, 37.43; H, 2.54; N, 31.73. $C_7H_5N_5O_4$. Calculated (%): C, 37.68; H, 2.26; N, 31.38. ^{1}H NMR ($CDCl_3$), δ: 4.78 (s, 3 H, Me); 9.24 (s, 1 H, H(5)); 9.25 (s, 1 H, H(7)). ^{13}C NMR ($CDCl_3$), δ: 45.0, 119.0, 122.5, 137.8, 139.3, 144.8, 145.4. ^{14}N NMR ($CDCl_3$), δ: −26.5 (NO_2). ^{15}N NMR ($CDCl_3$), δ: −100.9 (N(2)); −59.7 (N(1)); −50.4 (N(3)).

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