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The Synthesis and Complete ^{1}H and ^{13}C NMR Spectral Assignment of 2,2,4,4,6,6-Hexanitroadamantane and its Precursor Nitroketones by 2D NMR Spectroscopy

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ABSTRACT: *The synthesis of 2,2,4,4,6,6-hexanitroadamantane from the precursors, 4,4,6,6-tetranitroadamantan-2-one and 4,4-dinitroadamantane-2,6-dione is reported. The complete ^{1}H and ^{13}C NMR assignment of these compounds by 2D ^{13}C-^{1}H shift correlated spectra, ^{1}H-^{1}H COSY spectra and ^{1}H-^{1}H NOESY spectra is described.*

INTRODUCTION

Polynitropolycyclic cage molecules are central to the current efforts aimed at the development of new energetic materials to meet modern requirements for fuels, propellants and explosives.[1] These systems are particularly attractive because strain energy incorporated in the cage combined with the accumulation of nitro groups tend to bolster energy output, while the molecular compactness produces high density materials favorably increasing the detonation velocity.[2] Simultaneously, high crystal density materials are advantageous in volume-limited applications.

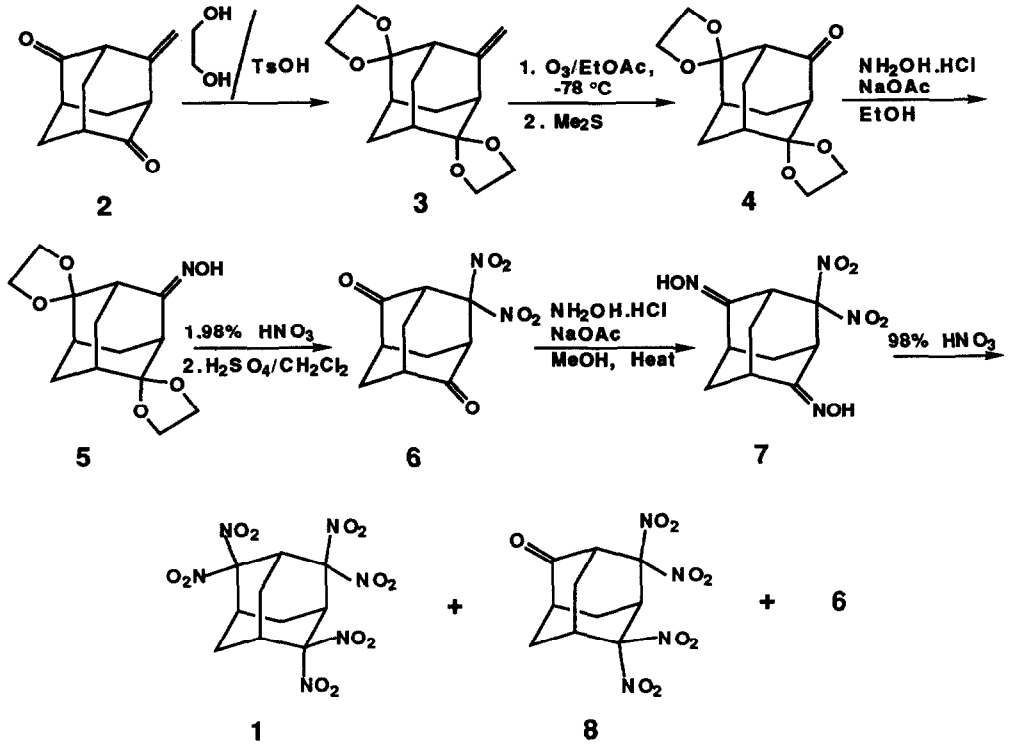
As a class of compounds, polynitroadamantanes have been of interest for more than a decade since Sollott and Gilbert[3] first synthesized and demonstrated that the bridgehead-substituted 1,3,5,7-tetranitroadamantane exhibited very low impact sensitivity.[1] Subsequently, several members of this class of compounds have been reported including 2,2-dinitro- and 2,2,6,6-tetranitroadamantane.[4] More recently, we achieved the synthesis of the isomeric geminally substituted 2,2,4,4-tetranitroadamantane.[5] This report describes the synthesis of 2,2,4,4,6,6-hexanitroadamantane and its complete ^{1}H and ^{13}C NMR characterization as well as those of 4,4,6,6-tetranitroadamantan-2-one and 4,4-dinitroadamantane-2,6-dione, its precursors.

RESULTS AND DISCUSSION

SYNTHESIS

2,2,4,4,6,6-Hexanitroadamantane, **1**, was prepared by the reaction sequence outlined in Scheme 1. This synthetic strategy overcomes problems associated with steric crowding and takes advantage of the ease with which an oxime can be converted to the geminal dinitro function by oxidative nitration with 98% nitric acid.

Scheme 1



The starting material for this synthesis was 4-methyleneadamantane-2,6-dione, **2**, available from bicyclo-[3.3.1]-nonane-2,6-dione[9] by treatment with acetic anhydride and sulfuric acid.[10] The carbonyl groups were protected as ethylene ketals and the exocyclic methylene unit was ozonated to yield 2,2,6,6-bis(ethylenedioxy)adamantan-4-one, **4**. Compound **4** is ideally suited for the synthesis of **1** as it allows for sequential conversion of carbonyl groups that bear a 1,3 relationship as shown to be necessary in the synthesis of 2,2,4,4-tetranitroadamantane.[5] The corresponding bis(methylketal) has been reported.[11] Compound **4** was converted to the corresponding oxime **5**, which was treated with 98% nitric acid in refluxing methylene chloride. The reaction mixture after workup showed the presence of ethylene ketal by NMR, and so was treated with conc. sulfuric acid in methylene chloride to effect deketalization.[12] The resulting mixture was purified by chromatography to afford 4,4-dinitroadamantane-2,6-dione **6** in 37% yield. Reaction of **6** with hydroxylamine hydrochloride in refluxing methanol gave the bis(oxime) **7** which on similar oxidation with 98% nitric acid in refluxing methylene chloride afforded 2,2,4,4,6,6-hexanitroadamantane (21%) and 4,4,6,6-tetranitroadamantan-2-one (34%). A small amount of **6** was also recovered.

ASSIGNMENT OF SPECTRA

The steric configurations were established by ^{13}C-^{1}H shift correlated spectra, ^{1}H-^{1}H COSY spectra and ^{1}H-^{1}H NOESY spectra as well as aromatic solvent-induced shifts.

2,2,4,4,6,6-Hexanitroadamantane, 1.

The ^1H spectrum of 2,2,4,4,6,6-hexanitroadamantane,**1**, along with the corresponding ^{13}C spectrum recorded in benzene-d_6 solution are shown on the axes of the HETCOR spectrum in Figure 1. Table 1 summarizes the chemical shift correlations obtained from HETCOR and DEPT experiments with 2,2,4,4,6,6-hexanitroadamantane, **1**, 4,4,6,6-tetranitroadamantan-2-one, **8**, and 4,4-dinitroadamantane-2,6-dione, **6**, all measured in chloroform-d_1. Table 2 summarizes similar chemical shift correlations for 2,2,4,4,6,6-hexanitroadamantane, **1**, and 4,4-dinitroadamantane-2,6-dione, **6**, measured in benzene-d_6 and acetone-d_6.

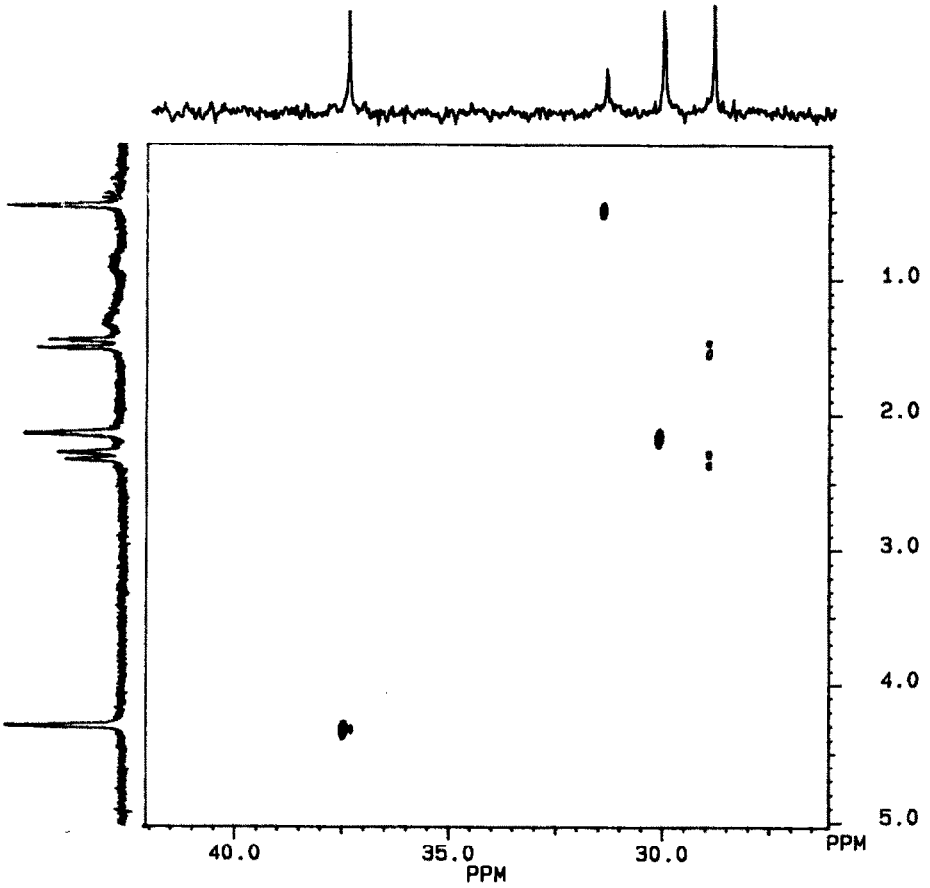


Figure 1. Contour plot of heteronuclear ^{13}C-^1H (75 MHz / 300 MHz) chemical shift correlation spectrum of 2,2,4,4,6,6-hexanitroadamantane, **1**, in benzene-d_6.

The structural assignments in **1** were arrived at in a straight-forward manner. As has previously been observed in the case of 2,2,4,4-tetranitroadamantane,[14] on changing from chloroform to benzene solution, those protons in the molecule most remote from the electron-withdrawing nitro groups experience the greatest upfield shift while, for example, proton H-1 situated between the geminal dinitromethylene groups is essentially unaffected by the solvent. Inspection of the data in Tables 1 and 2 shows that the anisotropic solvent effect is most pronounced with the protons on the distant periphery of the molecule. A substantial diamagnetic shift, especially of H-8 and H-9,9'/H-10,10' is observed in benzene while acetone induces paramagnetic shifts. The

most severe change in the acetone spectrum occurs in the complete collapse of the AB pattern at δ3.06 due to the diastereotopic methylene protons H-9,9'/H-10,10'. Moreover, the chemical shift dispersion is greatest in benzene solution which facilitates the observation and identification of cross-peaks in the COSY and NOESY spectra.

By analogy with 2,2,4,4-tetranitroadamantane,[14] an entrance point was available to begin the proton and ^{13}C NMR chemical shifts assignments. Thus, the absence of any significant solvent effect on the ^{1}H resonance at δ4.32 and its low-field position permit the assignment of this signal as due to the H-3 proton which is flanked by two geminal dinitromethylene carbons. This proton correlates with the equivalent bridgehead carbon atoms, C-3/C-5 at δ37.48. The other upfield methine hydrogen at δ2.15 could then be assigned to C-1/C-7 at δ30.12. While the HETCOR and DEPT spectra identified and distinguished the equivalent geminal protons (δ0.47) at C-8 (δ31.44) from the diastereotopic geminal protons (δ2.34 and δ1.50) attached to C-9/C-10, the spatial disposition of the latter protons remained ambiguous. The assignment of the resonance at δ31.44 as arising from C-8 was reinforced by the observation that the relative intensity of this signal, measured under inverse gated decoupling conditions with long relaxation delays, is half that of the other carbon signals.

Table 1. ^{1}H and ^{13}C Chemical Shift (δ) Correlations for 2,2,4,4,6,6-Hexanitroadamantane, **1**, 4,4,6,6-Tetranitroadamantan-2-one, **8**, and 4,4-Dinitroadamantane-2,6-dione, **6**, in Chloroform-d_1.

	1		**8**		**6**	
carbon/ proton	δ^{13}C, ppm	δ^{1}H, ppm	δ^{13}C, ppm	δ^{1}H, ppm	δ^{13}C, ppm	δ^{1}H, ppm
C-1/H-1	30.28	3.36	40.75	2.66	43.25	2.82
C2/H-2	120.2		201.46		201.90	
C-3/H-3	37.49	4.77	49.20	4.03	51.03	3.83
C-4/H-4	119.5		120.30		124.21	
C-5/H-5	37.49	4.77	38.79	4.81	51.03	3.83
C-6/H-6	120.2		120.30		210.90	
C-7/H-7	30.28	3.36	32.01	3.48	43.25	2.82
C-8/H-8	32.68	2.03	36.92	2.33, 2.04	42.20	2.38
C-9/H-9	29.78	3.10, 2.70	29.46	2.51, 2.12	32.92	2.06, 2.36
C-10/H-10	29.78	3.10, 2.70	32.84	2.98, 2.56	32.92	2.06, 2.36

The assignment of the steric configuration of the H-9.9'/H-10,10' protons was resolved by consideration of the COSY and NOESY spectra measured in benzene-d_6 solution. The ^{1}H resonance at δ4.32(H-3/H-5) in the COSY spectrum shows cross-peaks at δ1.50, δ2.34 due to the adjacent H-9.9'/H-10,10' protons 3-bonds removed, while the δ2.15 cross-peak arises from the 4-bond 'W" coupling to the coplanar H-1/H-7 protons, respectively. Similarly, δ2.34 (H-9 /H-10) correlates with δ1.50 (H-9'/H-10') which clearly is due to geminal AB coupling. The correlation between δ2.34 (H-9 or H-10) and the protons at δ0.47 may be conditionally assigned to that one (H-8 or H-8')) proton with which it has the necessary planar orientation for "W" coupling. Confirmation is supplied by the correlation seen in the NOESY spectrum between H-9' or H-10' (δ1.50) and H-8 (δ0.47) which have a 1,3-diaxial orientation. No correlation is found in the NOESY spectrum between the signals at δ2.34 and δ0.47, which is consistent with the distance between protons H-9 or H-10 and H-8 being too great for mutual spin relaxation to occur. These assignments are summarized for structures **1** and **8** in Figure 2. Table 2 summarizes and compares similar chemical shift correlations for 2,2,4,4,6,6-hexanitroadamantane, **1**, and 4,4-dinitroadamantan-2,6-dione, **6**, measured in acetone-d_6.

An x-ray diffraction examination revealed that 2,2,4,4,6,6-hexanitroadamantane crystallizes in either one of two tetragonal space groups, P4 , or $P4_3$, with four asymmetric groups (with two molecules per asymmetric group) in the unit cell. Based on the observed unit cell parameters [a = b = 11.975 (5) and c = 21.068(6) A°], the x-ray density was calculated to be 1.785 g/cc. The crystal structure, however, could not be determined because of twinning.

4,4-Dinitroadamantan-2,6-dione, 6.

The same combination of homonuclear and heteronuclear correlation spectra provided the information needed to complete the assignments of all the carbons and protons in 4,4-dinitroadamantane-2,6-dione, **6**. The chemical shift correlations from the HETCOR spectra, measured in chloroform-d_1, benzene-d_6 and acetone-d_6, are tabulated in Tables 1 and 2. Of the two methine carbons identified in DEPT and HETCOR experiments, measured in acetone-d_6, the low field resonance at δ52.14 and the proton with which it correlates at δ3.83 could readily be assigned to C-3/C-5 and H-3/H-5, respectively. It follows then that upfield methine carbon resonance at δ44.30 belongs to C-1/C-7 which in turn is bonded to H-1/H-7 at δ2.80. Based on the 2:1 relative intensities observed in an inverse gated decoupling experiment, the methylene carbon at δ42.66 could readily be assigned to C-8 and that at δ33.64 to C-9/C-10. The assignments were reinforced by the HETCOR experiment which showed that the former was attached to two equivalent protons, while the latter was joined to the diastereotopic protons having chemical shifts of δ2.55 and δ2.10.

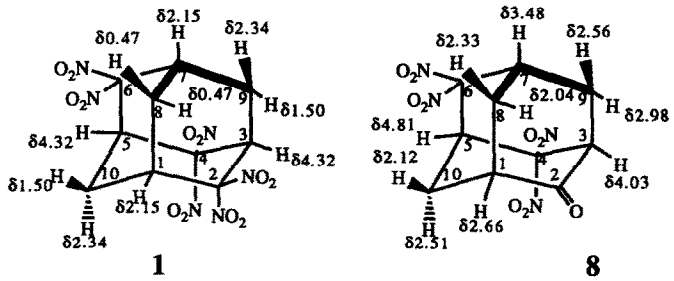


Figure 2. Chemical shift assignments and operative coupling pathways.

Examination of the proton chemical shift data for **6** shown in Tables 1 and 2 reveals that in the various solvents that were examined only very small chemical shift differences exist between the H-9/H-10, H-9'/H-10' and H-8 protons. Thus, observation of the selective Overhauser enhancements crucial to making these assignments was not possible. The assignment of the steric configuration of these geminal methylene protons is provisionally based on the planar geometric dependence of "W" coupling which is typically observed in these rigid adamantanes. The COSY spectrum, in acetone, shows four-bond coupling between the protons of chemical shift δ2.46 (H-8) and δ2.10 and similarly between those at δ2.38 (H-8) and δ2.06 in chloroform. Such four-bond coupling occurs when the coupled nuclei adopt a coplanar "W" arrangement. One may, therefore, infer that the other protons having chemical shifts δ2.38 (H-8') and δ2.36 (H-9'/H-10') in chloroform and δ2.46 (H-8') and δ2.55 (H-9'/H-10') in acetone are 1,3-diaxially oriented to one another.

4,4,6,6-Tetranitroadamantan-2-one, 8.

The ^{13}C spectrum shows the expected four resonances due to the bridgehead methine carbons and three methylene carbons each of which is coupled to two non-equivalent protons. Similarly, the proton spectrum exhibits four signals due to the bridgehead protons in addition to the more complex and overlapping AB patterns at higher field arising from three different methylene groups. The ^1H and ^{13}C chemical shift correlations are tabulated in Table 1.

Of the four methine protons, the lowest field proton at δ4.81 can readily be assigned to H-5 based on the similarity of its chemical shift with that of the comparable proton in 2,2,4,4,6,6-hexanitroadamantane, **1**, which is attached to a carbon flanked by two geminal dinitromethylene groups. Extending this rationale for assigning the methine protons based on their proximity to one or more dinitromethylene or carbonyl groups, it follows that the progressively shielded methine protons at δ4.03, δ3.48 and δ2.66 correspond to H-3, H-7 and H-1, respectively. The HETCOR experiment then identifies the carbons to which these protons are attached. Analysis of the COSY spectrum shows that in addition to the four-bond planar "W" coupling between the methine protons at δ4.81 (H-5) and δ4.03 (H-3), each of these protons is coupled over three bonds to the adjacent non-equivalent methylene protons at δ2.51 (H-9) and 2.12 (H-9') and δ2.56 (H-10) and δ2.98 (H-10'), respectively. The COSY spectrum also shows coupling between δ3.48 (H-7) and the adjacent sets of methylene signals at δ2.98 and δ2.56 (H-9/9') and δ2.33 and δ2.04 (H-8/8'). These assignments are reinforced by the HETCOR data which unambiguously establish the chemical shifts of the pairs of protons attached to each of the different methylene carbon atoms. Similarly, the proton at δ2.66 (H-1) shows cross-peaks denoting three-bond coupling to the adjacent methylene protons at δ2.51, δ2.12 (H-10/10') and δ2.33 and δ2.04 (H-8/8').

Table 2. ^{1}H and ^{13}C Chemical Shift (δ) Correlations for 2,2,4,4,6,6-Hexanitroadamantane, **1**, and 4,4-Dinitroadamantane-2,6-dione, **6**, in Benzene-d_6 and Acetone-d_6.

	1				**6**			
	Benzene-d_6		Acetone-d_6		Benzene-d_6		Acetone-d_6	
carbon / proton	$\delta^{13}C$, ppm	$\delta^{1}H$, ppm	$\delta^{13}C$, ppm	$\delta^{1}H$, ppm	$\delta^{13}C$, ppm	$\delta^{1}H$, ppm	$\delta^{13}C$, ppm	$\delta^{1}H$ ppm
C-1/H-1	30.12	2.15	31.35	3.52	43.11	1.78	44.30	2.80
C-2/H-2		--	121.9		200.84		203.12	
C-3/H-3	37.48	4.32	38.60	4.84	51.08	3.32	52.14	3.83
C-4/H-4		--	121.6			--		--
C-5/H-5	37.48	4.32	38.60	4.84	51.08	3.32	52.14	3.83
C-6/H-6		--	121.9		200.84		203.12	
C-7/H-7	30.12	2.15	31.35	3.52	43.11	1.78	44.30	2.80
C-8/H-8	31.44	0.47	32.58	2.35	41.39	1.18	42.66	2.46
C-9/H-9	28.97	2.34, 1.50	30.42	3.06, 3.06	32.08	1.08, 0.98	33.64	2.55, 2.10
C-10/H-10	28.97	2.34, 1.50	30.42	3.06, 3.06	32.08	1.08, 0.98	33.64	2.55, 2.10

The elucidation of the spatial disposition of the several non-equivalent methylene protons at C-6, C-9 and C-10 is the remaining task necessary for the complete structural and configurational assignment of 4,4,6,6-tetranitroadamantan-2-one, **8**. The most important evidence bearing on these assignments was developed from the NOE enhancements (measured by 1D NOE or 2D NOESY spectra) observed between H-9 (δ2.98) and the protons absorbing at δ2.04 (H-8) indicating that these protons induce mutual spin relaxation and therefore occupy a 1,3-diaxial orientation with respect to each other. This, of course, fixes the orientation of the protons H-8' (δ2.33) and H-9' (δ2.56). Corroboration of these conclusions comes from NOESY evidence showing a correlation between H-8' (δ2.33) and H-10' (δ2.12) which must be similarly 1,3-diaxially oriented. These configurational assignments in **8** are summarized in the Figure 2, which also depicts the coupling pathways and the spatial disposition of nuclei interacting through space:

In conclusion the synthesis of the conformationally-rigid polynitropolycylic cage molecule, 2,2,4,4,6,6-hexanitroadamantane, **1**, has been achieved. and the NMR analysis presented corroborates its structure along

with those of the precursors, 4,4,6,6-tetranitroadamantan-2-one, **8** and 4,4-dinitroadamantane-2,6-dione, **6**.

EXPERIMENTAL

All spectra.were measured in 5-mm tubes at concentrations of approximately 0.3 mol l^{-1} and referenced to TMS Spectra were recorded on a Bruker NR 300 spectrometer using standard Aspect 3000 pulse programs. Elemental analysis were performed by Galbraith Laboratories, Inc., Knoxville, TN.

2,2,6,6-bis(Ethylenedioxy)-4-methyleneadamantane, 3. A mixture of **2** (1 g, 5.7 mmol), ethylene glycol (1.4 g, 22.6 mmol) and p-TsOH (0.1 g) in benzene was heated at reflux in a flask fitted with a Dean Stark tube for 4 hours. The cooled reaction mixture was concentrated in vacuo and the residue was partitioned between water (100 mL) and methylene chloride (100 mL). The organic layer was separated, washed with saturated sodium bicarbonate solution (100 mL), dried ($MgSO_4$), and the filtrate was concentrated under reduced pressure. Recrystallization of the residue from hexanes gave **3** as a colorless microcrystalline solid (1.3 g, 87%), mp 119-20 °C: IR (KBr) 1650 cm^{-1} (m); ^1H NMR ($CDCl_3$) δ1.78-δ2.08 (m, 8H), δ2.39 (bs, 2H), δ3.92-4.04 (m, 8H), δ4.75 (s, 2H); ^{13}C NMR ($CDCl_3$) δ31.27 (t), δ32.22 (t), δ35.02 (d), δ46.39 (d), δ64.36 (2C, t), δ106.89 (t), δ110.30 (s), δ150.45 (s). Anal. calcd. for $C_{15}H_{20}O_4$: C, 68.16; H, 7.63. Found: C, 68.15; H, 7.67.

2,2,6,6-bis(Ethylenedioxy)adamantan-4-one, 4. Ozone was bubbled through a solution of **3** (0.35 g, 1.32 mmol) in ethyl acetate (50 mL) at -78 °C until the blue color of ozone persisted. To the mixture at room temperature was added dimethyl sulfide (5 mL) and stirring was continued for 30 min. Concentration of the reaction mixture in vacuo and chromatography of the residue on silica gel, eluting with a 1:4 mixture of acetone/hexanes gave **4** (0.15 g, 41%), mp 164-6 °C (from acetone/hexane) : IR (KBr) 1720 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ1.85-2.12 (m, 8H), δ2.55 (m, 2H),δ3.9-4.12 (m, 8H); ^{13}C NMR ($CDCl_3$) δ29.47 (t), δ30.90 (t), δ35.18 (d), δ54.66(d) ,δ 64.63 (t),δ 64.84 (t), δ111.12 (s), δ209.21 (s). HRMS m/z calcd. for $C_{14}H_{18}O_5$ M^+ 266.1154. Found 266.1129.

2,2,6,6-bis(Ethylenedioxy)-4-oximidoadamantane, 5. A suspension of **4** (1.0 g, 3.75 mmol) in absolute ethanol (50 mL) containing sodium acetate trihydrate (3.2 g, 23.5 mmol) and hydroxylamine hydrochloride (0.80 g, 11.5 mmol) was stirred overnight at room temperature. The reaction mixture was then concentrated in vacuo and the residue was partitioned between methylene chloride (100 mL) and water (100 mL). The separated organic layer was washed successively with saturated sodium bicarbonate solution and brine, and then dried ($MgSO_4$). The mixture was filtered and the residue obtained by concentration of the filtrate under reduced pressure was recrystallized from methylene chloride/hexanes to give **5** (0.90 g, 86%), mp 219-21 °C: IR (KBr) 3260 (br, s), 1670 cm^{-1} (w). Anal. calcd. for $C_{14}H_{19}NO_5$: C, 59.78; H, 6.81; N, 4.98. Found: C, 59.70; H, 6.81; N, 4.81.

4,4-Dinitroadamantan-2,6-dione, 6. To a refluxing solution of **5** (0.90 g, 3.2 mmol) in methylene chloride (50 mL) under nitrogen was added dropwise a solution of 98% nitric acid (20 mL), urea (0.15 g, 250 mmol) and ammonium nitrate (0.15 g, 200 mmol) in methylene chloride (20 mL). (CAUTION: Urea and ammonium nitrate should be added carefully in small portions to the nitric acid/methylene chloride solution since a slight exotherm occurs and nitrogen oxide fumes are evolved.). The initial blue-green color faded as more nitric acid was added. After the addition was completed, the mixture was heated under reflux for a further 30 min. The mixture was then cooled to room temperature and poured over ice (50 g). After the ice had melted the layers were separated and the organic layer was washed successively with saturated sodium bicarbonate solution (100 mL) and brine (100 mL). The organic phase was dried ($MgSO_4$), filtered, and the filtrate was concentrated in vacuo. To the residual oil in methylene chloride (50 mL) was added conc. sulfuric acid (10 mL) and the mixture was stirred for 3 hours at room temperature. The mixture was poured onto 100 g

of ice water mixture. The layers were separated and the organic phase was washed with saturated sodium bicarbonate solution (100 mL) followed by brine (100 mL), dried ($MgSO_4$), filtered and the filtrate was concentrated in vacuo to yield a solid residue that was recrystallized from acetone/hexane mixed solvent system to give pure **6** as a colorless microcrystalline solid (0.3 g, 37%), mp 244-46 °C: IR (KBr) 1740 (s), 1560 cm^{-1} (s); ^1H NMR (CD_3COCD_3) δ2.04-2.18 (m, 2H), δ2.42-2.58 (m, 4H),δ2.80 (m, 2H),δ3.82 (m, 2H); ^{13}C NMR (CD_3COCD_3) δ 22.70 (d), δ 41.72 (d), δ43.36 (t), δ51.18 (t), δ123.45 (s),δ202.24 (s). HRMS m/z calcd for $C_{10}H_{11}N_2O_6$ $(M+H)^+$ 255.0617. Found 255.0615.

4,4-Dinitro-2,6-dioximidoadamantane, 7. Essentially the same procedure as that described for the preparation of **5** was used. From **6** (0.3 g, 1.18 mmol) in methanol (100 mL) containing sodium acetate trihydrate (2.4 g, 17.65 mmol) and hydroxylamine hydrochloride (0.6 g, 9.30 mmol) which was heated under reflux for 4 hours and then stirred at room temperature overnight., there was obtained **7** (0.25g, 76%) mp 208-10 °C (methylene chloride/hexanes): IR (KBr) 3240 (br, s), 1660 (w), 1580 (s), 1360 cm^{-1} (m). HRMS m/z calcd. for $C_{10}H_{12}N_4O_6$ M^+ 284.0757. Found 284.0747.

2,2,4,4,6,6-Hexanitroadamantane, 1, and 4,4,6,6-Tetranitroadamantan-2-one, 8. The same procedure as that described for the preparation of **6** was followed. From **7** (0.1g, 0.35 mmol) in methylene chloride (25mL), 98% nitric acid (20 mL), urea (0.15 g, 250 mmol) and ammonium nitrate (0.15 g, 200 mmol) in methylene chloride (20 mL). there was obtained a crude product which was chromatographed on silica gel and eluted with an acetone/hexane solvent gradient (5% acetone to 30 % acetone). The first fraction afforded **1** (0.03 g, 21%) as a colorless microcrystalline solid, mp 198-200 °C (acetone/hexanes): IR (KBr) 1580 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ2.1-2.4 (m, 2H), δ2.65-3.15 (m, 4H), δ3.35-3.54 (m,2H), δ4.76-4.80 (m, 2H); ^{13}C NMR ($CDCl_3$) δ29.78 (t), δ30.28 (d), δ32.68 (t), δ37.49 (d), δ119.5 (s), δ120.2 (s).

Continued elution gave **8** as a colorless solid (0.04g, 34%), mp 240-41 °C (acetone/hexanes) : IR (KBr) 1740 (s), 1580 cm^{-1} (s); ^1HNMR ($CDCl_3$) δ2.0-3.08, (m,7H), δ3.45-3.54 (m, 1H), δ4.05-4.06 (m, 1H), δ4.83-4.83 (m,1H); ^{13}C NMR ($CDCl_3$) δ29.46 (t), δ32.01 (d),δ32.84 (t), δ36.92 (t),δ38.79 (d), δ40.75 (d), δ49.20 (d), δ120.3 (2C, s), δ201.46 (s). HRMS m/z calcd. for $C_{10}H_{11}N_4O_9$ $(M+H)^+$ 331.0526. Found 331.0510.

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