H atoms on water molecule O2W were not located and assumed to be disordered. Final $R = 0.066$, $R_w = 0.082$ for 2047 data and 182 variables. Maximum residual electron density is 0.33 e A^{-3}.

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Registry No. 1, 484-11-7; 2, 118896-77-8; 4, 118896-78-9; 5, 118896-79-0; 6, 118896-80-3.

Supplementary Material Available: Tables of atomic coordinates, bond distances and angles, and anisotropic thermal parameters for $2\cdot 2H_2O$ (4 pages). Ordering information is given on any current masthead page.

Synthesis of 4,4,8,8,11,11-Hexanitropentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane

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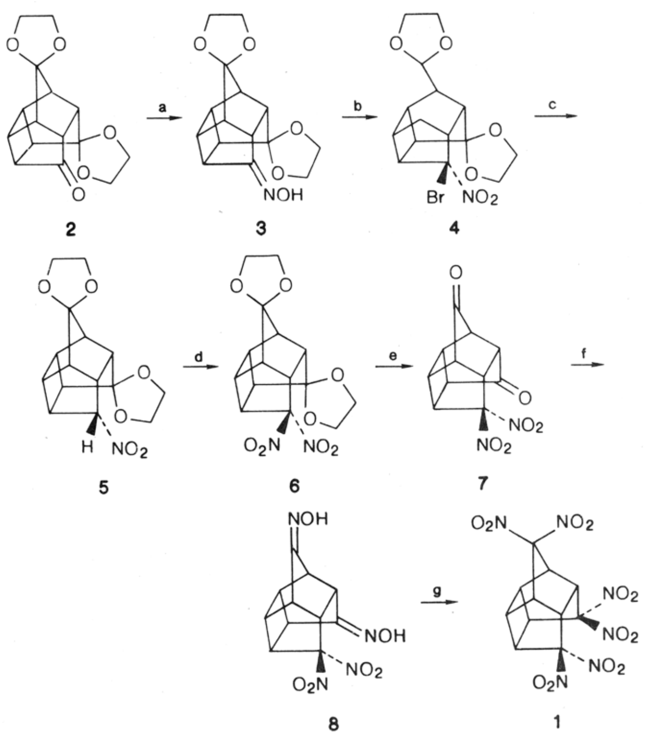
There is considerable current interst in the synthesis and chemistry of polynitropolycyclic "cage" molecules.[1,2] Compounds of this type are of interest as a new class of energetic materials.[2] Additionally, these compounds are of theoretical interest; the cumulative effects of increasing NO_2 substitution upon the structure, thermodynamic stability, and chemical reactivity of carbocyclic cage systems can be probed through studies of the physical and chemical properties of individual compounds in a series of increasingly NO_2 substituted cage molecules.

As part of a continuing effort to synthesize new polynitropolycyclic systems[1] and in accordance with our long-standing interest in the synthesis and chemistry of novel, substituted pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecanes (PCU),[3] we now report our synthesis of the title compound, 1. Compound 1 is isomeric with D_3-hexanitrotrishomocubane, whose synthesis was reported recently.[1i] To our knowledge, 1 is the most highly NO_2 substituted PCU derivative to have been synthesized.[1c,j]

Scheme I[a]



[a] (a) $NH_2OH\cdot HCl$, K_2CO_3, EtOH, reflux 24 h (79%); (b) NBS, dioxane, room temperature, overnight (62%); (c) $NaBH_4$, 60% aqueous EtOH, 0 °C → room temperature, 1 h (84%); (d) $K_3Fe(CN)_6$, $NaNO_2$, aqueous MeOH, room temperature, 2 h (83%); (e) concentrated H_2SO_4, CH_2Cl_2, room temperature, 24 h (50%); (f) $NH_2OH\cdot HCl$, NaOAc, MeOH, reflux 2 h (75%); (g) 98% red nitric acid, NH_4NO_3, urea, dry CH_2Cl_2, reflux 0.5 h, then 30% aqueous H_2O_2, reflux 15 min (19%).

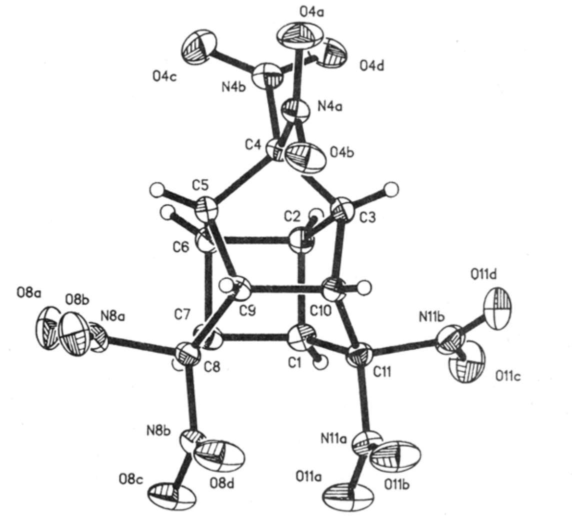


Figure 1. X-ray structure drawing of 1.

Recently, we demonstrated that NO_2 groups could be introduced conveniently into the 8- and 11-positions of the pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane ring system via oxidative nitration of the corresponding 8,11-dioxime.[1j] Hence, our strategy simply was to functionalize the 4-position of the PCU ring system with a masked carbonyl group, which ultimately would be converted into a $C(NO_2)_2$ group.

Our synthesis of 1 that begins with the readily available 4,4:11,11-bis(ethylenedioxy)pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecan-9-one (2)[1i] is shown in Scheme I. Initially, 2 was converted into the corresponding oxime, 3. The oximino

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group in **3** then was subjected to oxidative bromination with *N*-bromosuccinimide,[1j] thereby affording the corresponding *exo*-8-bromo-*endo*-8-nitro derivative, **4**.[1d,e] Reduction of the carbon–bromine bond in **4** afforded **5**, which was converted into the corresponding 8,8-dinitro derivative, **6**, by using the procedure described by Kornblum and co-workers.[4] Hydrolysis of the ethylene ketal functionality in **6** was carried out by stirring with concentrated sulfuric acid at room temperature.[5] The corresponding dinitro diketone, **7**, was thereby obtained. Oxidative nitration of the dioxime, **8**, derived from **7** was carried out by using 98% red fuming nitric acid[6] in refluxing methylene chloride. This reaction afforded **1** in low yield (see Experimental Section).

X-ray Crystallographic Study of 1. The results of the X-ray crystallographic study of **1** are illustrated in Figure 1. The refinement indicates that, while the overall conformation of the two molecules in the asymmetric unit is essentially the same, there are significant differences between the torsions of the nitro groups. The C–C–N–O torsion angles vary by as much as 33.5° between comparable NO_2 groups. In addition, the molecular mirror plane which passes through atoms C(4), N(4a), and N(4b) is distorted significantly in the solid state. Comparison of NO_2 torsion angles that are related by this pseudo mirror plane reveal an average difference of 10.5° in molecule I and 32.8° in molecule II. These results most likely are due to differences in the packing environments among the various NO_2 groups in the molecule. The two molecules in the unit cell are similar in that (i) the geminal nitro groups are all approximately perpendicular to one another and (ii) the two NO_2 groups that occupy axial positions on a boat-shaped six-membered ring [i.e., N(8b) and N(11a)] are mutually parallel. The cage moieties in the two molecules that comprise the asymmetric unit are also very similar structurally. The two bonds in the six-membered ring adjacent to the cyclobutane ring [i.e., C(7)–C(8) and C(1)–C(11)] are abnormally short, averaging 1.494 (5) Å. The cage bond which lies across the cage from the cyclobutane ring [i.e., C(9)–C(10)] is lengthened, averaging 1.587 (6) Å. Similar extremes were noted by Coxon et al.[7] in their study of three cage diketones that are closely related structurally to **1**.

There is another unusual, yet consistent, departure from "normal geometry" in **1**, i.e., the C–NO_2 C–N bond distances for axial nitro groups on the boat-shaped six-membered ring average 1.503 (5) Å, while the average value for the corresponding equatorial NO_2 groups is 1.562 (6) Å. The structure of 8,8,11,11-tetranitropentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane has also been studied by X-ray diffraction,[8] and its conformation agrees with that found in the present study for **1**.

Experimental Section

Melting points are uncorrected.

***exo*-8-Bromo-*endo*-8-nitro-4,4:11,11-bis(ethylenedioxy)pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane (4).** 4,4:11,11-Bis(ethylenedioxy)pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecan-8-one oxime (**3**) was synthesized via reaction of the corresponding ketone, **2**,[1i] with hydroxylamine hydrochloride; the procedure described by Sasaki and co-workers[9] was employed for this purpose. Thus, to a stirred suspension of hydroxylamine hydrochloride (20.0 g, 288 mmol) and potassium carbonate (23.0 g, 166 mmol) in absolute ethanol (300 mL) was added **2** (17.0 g, 61.6 mmol), and the resulting mixture was refluxed for 24 h. The reaction mixture was then cooled to room temperature and concentrated in vacuo. Water (300 mL) was added to the residue, and the resulting mixture was extracted with dichloromethane (4 × 75 mL). The combined organic extracts were washed with water (100 mL), dried (anhydrous sodium sulfate), and filtered. The filtrate was concentrated in vacuo, thereby affording a viscous oil, which solidified upon trituration with ethanol. The resulting solid was recrystallized from ethanol to afford **3** as a colorless microcrystalline solid (mixture of geometric isomers, 14.1 g, 79%): mp 173–174 °C; IR (KBr) 3410 (br s), 1683 (w), 1334 cm^{-1} (m). This material was used without further purification for the ensuing synthesis of **4**.

To a suspension of *N*-bromosuccinimide (NBS, 25.0 g, 140 mmol) and sodium bicarbonate (33.0 g, 393 mmol) in 5% aqueous dioxane solution (800 mL) was added oxime **3** (14.0 g, 48.1 mmol). The reaction mixture was stirred overnight at ambient temperature. Crushed potassium hydroxide pellets (17.0 g, 303 mmol) were added, and the resulting mixture was stirred for an additional 20 min at room temperature. The reaction mixture then was extracted with methylene chloride (3 × 125 mL), and the combined organic extracts were washed with 10% aqueous potassium hydroxide solution (200 mL). The organic layer was dried (anhydrous magnesium sulfate) and filtered, and the filtrate was concentrated in vacuo. Compound **4** (12.3 g, 62%) was thereby obtained as a cream-colored microcrystalline solid. Recrystallization of this material from ethanol afforded pure **4** as colorless prisms: mp 120–121 °C; IR (KBr) 1556 (s), 1347 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 2.43 (m, 1 H), 2.63 (m, 2 H), 2.79 (m, 1 H), 2.98 (m, 1 H), 3.18 (m, 1 H), 3.49 (m, 2 H), 3.7–4.0 (m, 8 H); ^{13}C NMR ($CDCl_3$) δ 36.33 (d), 38.70 (d), 40.89 (d), 44.95 (d), 46.80 (d), 48.58 (d), 50.19 (d), 50.69 (d), 62.78 (t), 65.20 (t), 65.28 (t), 65.89 (t), 97.61 (s), 113.44 (s), 117.44 (s).

Anal. Calcd for $C_{15}H_{16}BrNO_6$: C, 46.45; H, 4.18. Found: C, 46.64; H, 3.99.

***endo*-8-Nitro-4,4:11,11-bis(ethylenedioxy)pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane (5).** A suspension of **4** (12.0 g, 31.0 mmol) in 95% aqueous ethanol (800 mL) was cooled to 0 °C via application of an external ice bath. To this cooled suspension was added dropwise with stirring a solution of sodium borohydride (6.5 g, 172 mmol) in 60% aqueous ethanol (100 mL) during 5 min. The ice bath was removed, and the stirred reaction mixture was allowed to warm gradually to room temperature during 1 h. Dilute acetic acid was added dropwise with stirring until all solid material had dissolved. The resulting clear solution was then concentrated in vacuo. The residue was partitioned between water (300 mL) and methylene chloride (200 mL). The layers were then separated, and the aqueous layer was extracted with methylene chloride (3 × 50 mL). The combined organic layers were washed with water (200 mL), dried (anhydrous magnesium sulfate), and filtered, and the filtrate was concentrated in vacuo. The resulting solid (8.1 g, 84%) was recrystallized from ethanol; pure **5** was thereby obtained as a colorless microcrystalline solid: mp 169–170 °C; IR (KBr) 1547 (s), 1358 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 2.07 (m, 1 H), 2.21 (m, 1 H), 2.57 (m, 2 H), 2.95 (m, 2 H), 3.38 (m, 2 H), 3.7–4.0 (m, 8 H), 4.14 (dd, J_1 = 4.2 Hz, J_2 = 3.2 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 35.68 (d), 37.59 (d), 37.69 (d), 38.71 (d), 41.69 (d), 44.20 (d), 46.91 (d), 46.99 (d), 62.90 (t), 65.03 (t), 65.15 (t), 65.47 (t), 82.39 (d), 114.66 (s), 119.01 (s).

Anal. Calcd for $C_{15}H_{17}NO_6$: C, 58.63; H, 5.58. Found: C, 58.41; H, 5.40.

8,8-Dinitro-4,4:11,11-bis(ethylenedioxy)pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane (6).[5] Compound **5** (7.50 g, 24.4 mmol) was dissolved in a solution of potassium hydroxide (6.00 g, 107 mmol) in 40% aqueous methanol (100 mL). The resulting yellow solution was filtered, and the filtrate was added to another solution, which contained potassium ferricyanide (40.0 g, 121 mmol) and sodium nitrite (24.0 g, 348 mmol) in water (300 mL). The reaction mixture was stirred at room temperature for 2 h, at which time methylene chloride (150 mL) was added, and stirring was

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continued for an additional 1 h. The layers were separated, and the aqueous layer was extracted with methylene chloride (2 × 100 mL). The combined organic extracts were washed with water (2 × 150 mL), dried (anhydrous magnesium sulfate), and filtered, and the filtrate was concentrated in vacuo. Solid **6** (7.1 g, 83%) was thereby obtained. Recrystallization of this material from ethanol afforded pure **6** as colorless prisms: mp 151.0–151.5 °C; IR (KBr) 1572 (vs), 1355 (s), 1339 cm^{-1} (s); ^{1}H NMR (CDCl$_3$) δ 1.98 (m, 1 H), 2.35 (m, 1 H), 2.74 (m, 2 H), 3.01 (m, 1 H), 3.17 (m, 1 H), 3.7–4.0 (m, 10 H); ^{13}C NMR (CDCl$_3$) δ 37.37 (d), 38.89 (d), 39.05 (2 C, d), 45.51 (d), 46.62 (d), 46.70 (d), 47.74 (d), 63.17 (t), 65.27 (t), 65.36 (t), 65.90 (t), 113.79 (s), 118.47 (s), 124.26 (s).

Anal. Calcd for $C_{15}H_{16}N_2O_8$: C, 51.14; H, 4.58. Found: C, 51.02; H, 4.56.

8,8-Dinitropentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-4,11-dione (7). To a solution of **6** (3.0 g, 9.52 mmol) in methylene chloride (30 mL) was added concentrated sulfuric acid (5 mL), and the resulting mixture was stirred at room temperature for 2 h. The reaction mixture then was poured over crushed ice (50 g). Solid sodium bicarbonate was added portionwise with stirring (**CAUTION!**) until evolution of carbon dioxide had ceased. The resulting mixture was diluted with water (30 mL). The layers were separated, and the aqueous layer was extracted with methylene chloride (2 × 25 mL). The combined organic extracts were washed sequentially with 10% aqueous sodium bicarbonate solution (2 × 20 mL) and with water (20 mL). The organic layer was dried (anhydrous magnesium sulfate) and filtered, and the filtrate was concentrated in vacuo, thereby affording **7** (1.1 g, 50%). Recrystallization of this material from ethanol afforded pure **7** as colorless needles: mp 272 °C dec; IR (KBr) 1760 (s), 1725 (s), 1545 (s), 1345 cm^{-1} (m); ^{1}H NMR (CDCl$_3$) δ 2.54–2.70 (m, 2 H), 3.0–3.6 (m, 3 H), 3.75–4.2 (m, 3 H); ^{13}C NMR (CDCl$_3$) δ 29.81 (d), 38.51 (d), 39.98 (d), 41.28 (d), 43.19 (d), 44.36 (d), 44.81 (d), 46.36 (d), 121.90 (s), 203.10 (s), 204.10 (s).

Anal. Calcd for $C_{11}H_8N_2O_6$: C, 50.01; H, 3.01. Found: C, 49.53; H, 3.13.

8,8-Dinitropentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-4,11-dione Dioxime (8).[10] To a solution of **7** (1.00 g, 3.79 mmol) in methanol (50 mL) were added hydroxylamine hydrochloride (1.74 g, 25.0 mmol) and sodium acetate (4.1 g, 50 mmol), and the resulting mixture was refluxed for 2 h. The reaction mixture then was concentrated in vacuo; cold water (30 mL) was added to the residue, and the resulting mixture was extracted with methylene chloride (3 × 20 mL). The combined organic extracts were washed with water (20 mL), dried (anhydrous magnesium sulfate), and filtered. The filtrate was concentrated in vacuo, thereby affording **8** (0.82 g, 75%) as a colorless microcrystalline solid (mixture of geometric isomers): mp 155–160 °C; IR (KBr) 3400 (s), 1685 (w), 1540 (s), 1330 cm^{-1} (m). This material was used without further purification for the ensuing synthesis of **1**.

4,4,8,8,11,11-Hexanitropentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane (1). To a refluxing solution of **8** (950 mg, 3.28 mmol) in dry methylene chloride (50 mL) under nitrogen was added a solution of red nitric acid (98%)[1j] (20 mL, excess), urea (200 mg, 3.33 mmol), and ammonium nitrate (200 mg, 2.67 mmol) in methylene chloride (30 mL). A deep blue-green color developed initially; the color of the reaction mixture changed to brown as more nitric acid was added. After the addition of nitric acid had been completed, the reaction mixture was refluxed for 30 min, at which time 30% aqueous hydrogen peroxide solution (5 mL) was added cautiously to the refluxing mixture. The reaction mixture was thereby rendered colorless. After the addition of hydrogen peroxide had been completed, refluxing was continued for an additional 15 min. The reaction mixture then was allowed to cool to room temperature. The cooled reaction mixture was washed with ice–water (3 × 75 mL), dried (anhydrous magnesium sulfate), and filtered, and the filtrate was concentrated in vacuo. The residue was purified via column chromatography (silica gel stationary phase, 3:2 methylene chloride–hexane mixed solvent as eluent). The first fraction thereby collected afforded pure **1** (240 mg, 19%) as colorless microcrystalline solid: mp 199–200 °C; IR (KBr) 1565 (s), 1535 cm^{-1} (m); ^{1}H NMR (acetone-d_6) δ 3.85 (m, 4 H), 4.50 (m, 2 H), 4.70 (m, 2 H); ^{13}C NMR (acetone-d_6) δ 37.88 (d), 39.45 (d), 47.57 (d), 49.41 (d), 120.20 (s), 121.83 (s).

Anal. Calcd for $C_{11}H_8N_6O_{12}$: C, 31.70; H, 1.94. Found: C, 31.76; H, 1.94.

Single-crystal X-ray structural analysis of 1: $C_{11}H_8N_6O_{12}$, molecular weight 416.25, monoclinic, space group $P2_1/c$, a = 13.080 (3) Å, b = 17.842 (2) Å, c = 13.530 (3) Å, β = 106.67°, D_{calcd} = 1.83 g cm^{-3}, μ = 1.44 mm^{-1}, Z = 8 (two molecules per asymmetric unit). A total of 4094 independent reflections were measured out to $2\theta_{\max}$ = 112° with a Nicolet R3MV diffractometer by using CuKα radiation (λ = 1.5418 Å) with an incident beam graphite monochromator. The data were collected at 295 K from a colorless crystal by using the $\theta/2\theta$ scan technique with a variable 2θ scan rate depending upon the intensity of a reflection (10°/min minimum to 30°/min maximum). An empirical absorption correction was applied. The minimum and maximum transmission factors were found to be 0.675 and 0.752, respectively. The structure was solved by direct methods as implemented by the SHELXTL system of programs.[11] Least-squares refinement was performed on 588 parameters (coordinates for all atoms, anisotropic thermal parameters for non-hydrogen atoms, isotropic thermal parameters for hydrogen atoms) by using the 3601 reflections for which $|F_o| > 3\sigma|F_o|$ gave a final R factor of 0.060 (Rw = 0.077). The goodness of fit parameter was 3.20, and the final difference map was featureless.

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Registry No. **1**, 119183-92-5; **2**, 110243-30-6; (*E*)-**3**, 119183-93-6; (*Z*)-**3**, 119183-98-1; **4**, 119183-94-7; **5**, 119183-95-8; **6**, 119183-96-9; **7**, 119183-97-0; **8**, 119207-88-4.

Supplementary Material Available: A list of atomic coordinates and equivalent isotropic displacement parameters, bond lengths, bond angles, and H-atom coordinates and isotropic displacement parameters for 1 (5 pages). Ordering information is given on any current masthead page.

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Cyclopropanation of 2-Ylideneoxazol-5-one with Diphenyldiazomethane: Stereospecific Synthesis of Novel *gem*-Diphenylcyclopropyl Amino Acid Derivatives[†]

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Aminocyclopropanecarboxylic acid derivatives are known to possess a wide spectrum of biological action.[1-4] Introduction of a *gem*-diphenyl group into the cyclopropane system leads to compounds that have shown pronounced action as plant growth regulatory, insecticidal, and anticancer activity. In our attempts to prepare cyclopropyl amino alcohol and acid derivatives for biological screening, we have achieved a stereospecific synthesis of

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