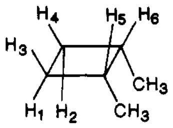
between protons at carbons 1 and 3 and 2 and 3. This allowed us to set the sum of $J_{1,5} + J_{1,6}$ to 4.7 Hz for the cis-anti-cis compound and $J_{3,5} + J_{3,6}$ to 9.4 Hz for the cis-syn-cis compound. Values for the other coupling constants (in Hz) used in the simulations include the following: $J_{1,2} = 8.9$, $J_{1,5} = 5.5$, $J_{1,6} = -0.8$, $J_{5,6} = 9.4$ for the cis-anti-cis isomer; $J_{3,4} = 8.0$, $J_{3,5} = 8.0$, $J_{3,6} = 1.4$ for the cis-syn-cis isomer. The use of values for $J_{1,6}$ and $J_{3,6}$ outside the range of uncertainty quoted in the text, resulted in spectra which were different from experiment; variations in the other J values were not sufficient to produce acceptable simulations. The chemical shifts used for the protons in *cis*-1,2-dimethylcyclobutane were δ 1.64, 2.14, and 2.47 ($CDCl_3$). The methyl resonances at δ 1.0 were not used in the simulations.



A

Acknowledgment. We would like to thank Dr. Jordon Bloomfield for a generous sample of 3-cyclobutene-1,2-carboxylic anhydride, the NSF (for purchase of the JEOL FX 100 NMR spectrometer (CHE77-02068) used in this work and for additional support (CHE84-05386)), and the office of Research at UM—St. Louis for financial support.

Registry No. *cis*-1,2-Dimethyl-*anti*-3,4-dideuteriocyclobutane, 39768-31-5; *trans*-1,2-dimethyl-*cis*-3,4-dideuteriocyclobutane, 110221-72-2.

Notes

Synthesis of Nitro-Substituted 2,3,4,8-Tetraphenylpentacyclo$[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]$decanes

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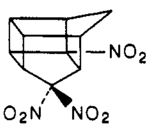
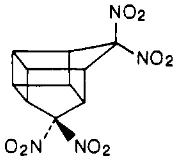
There is considerable current interest in the synthesis and chemistry of energetic polycyclic "cage" compounds.[1-5] The title compounds are novel, strained energetic materials that have been prepared as part of an ongoing program involved with the synthesis of new polynitro-1,3-bishomocubanes. Two such systems, a trinitro- and a tetranitro-1,3-bishomocubane (1[3] and 2[4], respectively) have been prepared in our laboratory, and their respective structures have been determined via single-crystal X-ray crystallography.[6,7]

Three compounds, a dinitro- (3), a trinitro- (4), and a tetranitro-2,3,4,8-tetraphenylpentacyclo$[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]$decane (5), have been prepared in the present study. The route employed for synthesizing 3–5 is shown in Scheme I. The starting material for this reaction sequence is the known[8,9] 2,3,4,8-tetraphenylpentacyclo$[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]$decane-6,10-dione 6 (Scheme I). Subsequent conversion of the ketone functionalities in 6 into $CHNO_2$ and into $C(NO_2)_2$ groups was accomplished by using previously published procedures.[3,4]



1



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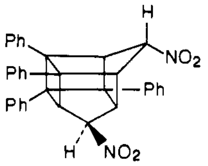

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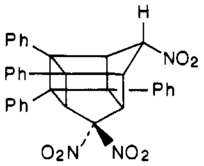

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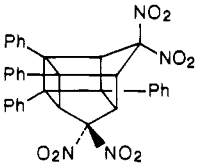

5

Trifluoroperacetic acid oxidation of bis(oxime) 7 (derived[10] from cage dione 6) afforded a gross mixture of isomeric 2,3,4,8-tetraphenyl-6,10-dinitropentacyclo$[5.4.0.0^{2,5}.0^{3,9}.0^{4,8}]$decanes. Careful fractional recrystallization of this mixture from methanol afforded a single isomer, 3. Analysis of the proton and carbon-13 NMR spectra of 3 suggests that it contains a twofold symmetry element. While this result rules out the syn-6, anti-10 isomer, it is consistent with either of two possible structures for 3, i.e., the syn-6, syn-10 or the anti-6, anti-10 isomer. Careful fractional recrystallization of this material from methanol afforded only a poor quality single crystal for use in single-crystal X-ray structural analysis. The quality of refinement of the crystallographic data obtained for this crystal was correspondingly poor (see Experimental Section). Nevertheless, the results thereby obtained

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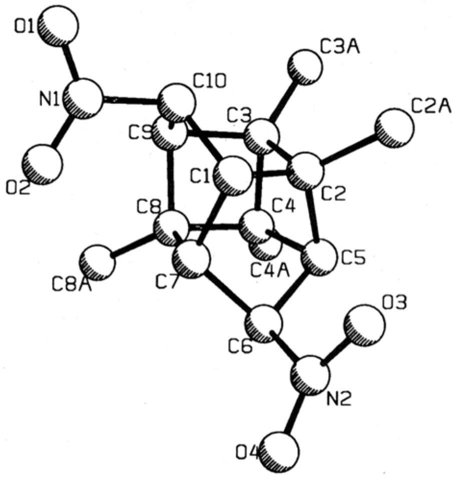
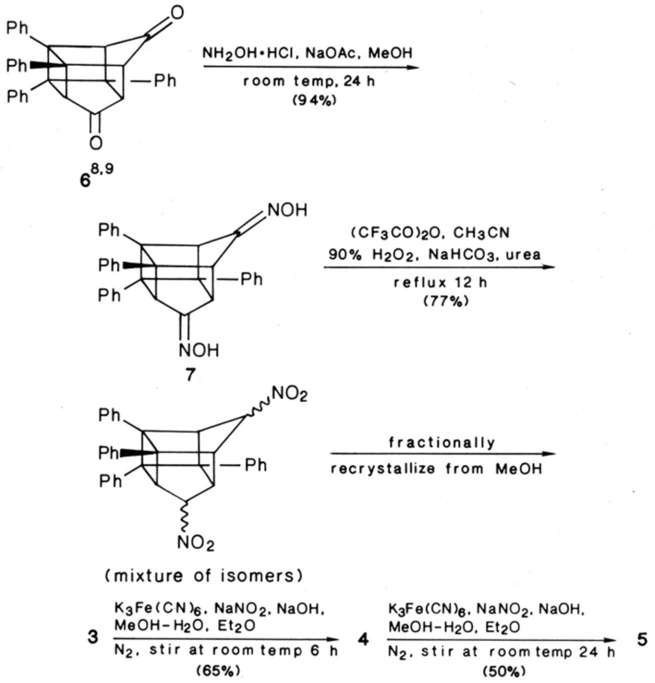


Figure 1. Results of the X-ray study on **3**. For clarity, the phenyl groups on C-2, C-3, C-4, and C-8 are represented as single atoms (C-2a, C-3a, C-4a, and C-8a).

Scheme I



(shown in Figure 1) permit our making unequivocal configurational assignments; our conclusion, i.e., that the two C–NO_2 bonds in **3** possess the anti-6, anti-10 configuration, received independent confirmation via X-ray crystallographic examination of the product of mononitration of **3**, (vide infra).

Reaction of **3** with potassium ferricyanide–sodium nitrite[11] could be controlled to afford a single mononitration product, (i.e., the corresponding 6,6,10-trinitro compound, **4**). The X-ray structure of **4** (vide infra) was obtained on a single crystal prepared via careful fractional recrystallization of this material from ethyl acetate–hexane. The fact that the C–NO_2 bond in the 10-position is anti to the 2,3-Ph groups in **4**, together with the fact that **3** contains a twofold symmetry element, confirms our previous configurational assignment of the C–NO_2 bonds in **3**.

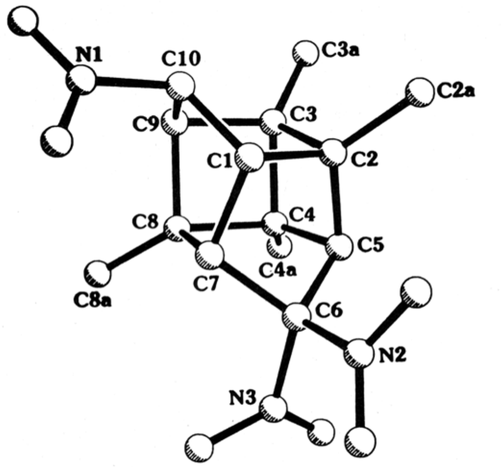


Figure 2. Results of the X-ray study on **4**. For clarity, the phenyl groups on C-2, C-3, C-4, and C-8 are represented as single atoms (C-2a, C-3a, C-4a, and C-8a).

Compound **4** ($C_{34}H_{25}N_3O_6$, shown in Figure 2) crystallizes in the monoclinic space group $P2_1/c$ with unit cell dimensions a = 10.869 (4), b = 15.667 (8), and c = 17.084 (8) Å, β = 108.36°, and Z = 4. The volume of the cell is 2760.9 (2) Å^3, the molecular formula weight is 571.59, and the calculated crystal density is 1.37 g cm^{-3}. The presence of the phenyl groups does not appear to have a major effect upon the overall configuration of the bishomocubane skeleton. For the most part, the structural parameters agree quite well with those found for **1**[6] and for **2**.[7] The interior C–C–C angles average 89.4 (2)° in the four-membered rings and 102.4 (2)° in the five-membered rings. Carbon–carbon bonds to the bridge carbons that bear NO_2 substituents average 1.516 (3) Å in **4**, 1.517 (13) Å in **2**, and 1.513 Å in **1**. However, the average for the remaining C–C cage bonds in **4** is 1.572 (3) Å while these cage bonds average only 1.554 (13) Å in **2** and 1.550 Å in **1**. The C–C bond elongation noted in **4** might result from the presence of the phenyl groups at C-2, C-3, C-4, and C-8.

Further nitration of **4**, performed by using a modification of the procedure described above,[11] afforded the corresponding 6,6,10,10-tetranitro derivative **5**. We were unable to obtain a crystal of sufficient quality to permit determination of the structure of **5** by single-crystal X-ray crystallographic analysis. Nevertheless, its structure is not in doubt; its proton and carbon-13 NMR spectra are fully consistent with the suggested structure (see Experimental Section).

Experimental Section

Melting points are uncorrected.

2,3,4,8-Tetraphenyl-*anti*-6,*anti*-10-dinitropentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decane (3). Bis(oxime) **7** was synthesized from cage dione **6**[8,9] by using the method described by Corey and co-workers.[10] To a refluxing mixture of **7** (6.0 g, 12 mmol), sodium bicarbonate (15.12 g, 180 mmol), and urea (2.4 g, 40 mmol) in acetonitrile (200 mL) was added dropwise with vigorous stirring during 1 h a solution of 90% hydrogen peroxide (1.68 mL, 61 mmol) and trifluoroacetic anhydride (9.6 mL, 68 mmol) in acetonitrile (40 mL). The temperature of the reaction mixture was maintained at 75–90 °C during the time of addition of the oxidizing agent. The resulting mixture was refluxed for 12 h. The reaction mixture was then cooled to ambient temperature and concentrated in vacuo. The residue was poured over crushed ice (ca. 300 g) and allowed to stand for 3 h. The resulting mixture was then filtered, thereby affording crude **3** (4.9 g, 77%) as a mixture of isomeric dinitro compounds. This mixture was purified via careful fractional recrystallization from methanol. A single isomer, shown subsequently to be the anti-6, anti-10 isomer (see text and results of X-ray structural analysis, shown below), was thereby isolated as a colorless microcrystalline solid: mp 216–218 °C; IR (KBr) 1540 (vs), 1350 cm^{-1} (vs); ^{1}H NMR ($CDCl_3$) δ 3.78

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(bs, 2 H), 4.51 (bs, 2 H), 5.69 (bs, 2 H), 6.52–7.60 (m, 20 H); ^{13}C NMR(CDCl$_3$) δ 49.62 (d), 56.91 (d), 58.21 (s), 60.09 (s), 91.57 (d), 126.42 (d), 126.75 (d, 2 H), 127.85 (d), 128.11 (d, 2 H), 134.16 (s), 137.28 (s).

Anal. Calcd for $C_{35}H_{26}N_2O4$: C, 77.56; H, 5.06; N, 5.32. Found: C, 77.97; H, 4.94; N, 5.25.

X-ray Analysis of 3. Compound **3** crystallized from methanol as triangular plates. Crystals separated from the mother liquor and allowed to dry rapidly deteriorated; within 1–2 min, a perfectly clear single crystal became opaque and fractured. A specimen for X-ray analysis (crystal dimensions 0.2 × 0.4 × 0.5 mm) was transferred by pipet from the crystallization solution to 1-pentanol, which served to clean away the mother liquor and to provide an alcohol environment less volatile than methanol. The crystal was transferred into a 0.7 mm thin-walled capillary in a manner similar to that used for mounting protein crystals for X-ray analysis. A small amount of pentanol served to attach the crystal to the capillary wall. Pentanol plugs were placed at both ends of the capillary, and the capillary ends were then sealed with wax.

X-ray data were collected on an Enraf-Nonius CAD4 diffractometer with Mo radiation (incident beam graphite monochromator, $\lambda K\alpha = 0.71069$ Å). Cell parameters were determined from 25 reflections. Space groups is $C2/c$, $a = 23.761$ (6), $b = 14.581$ (3), and $c = 17.539$ (4) Å, $\beta = 91.31$ (2)°, ρ(X-ray) = 1.151 g cm^{-3} for $Z = 8$; $C_{34}H_{26}N_2O_4$, M_r 526.6; 3186 total data collected in the range $2° < \theta < 20°$; 96 step scan; θ range = 1.0 + 0.35 tan θ; θ scan speed from 5.49–0.97 deg per min; 9 standard reflections measured every 2 h of X-ray exposure; crystal reoriented every 500 reflections; reflection intensities derived with a local profile-processing program based upon the Lehmann–Larsen algorithm;[12] 2964 unique data; 1257 data with $I > 3\sigma(I)$. No absorption correction was applied. All subsequent crystallographic calculations were performed with the TEXSAN system[13] on a D. E. C. MicroVAX I computer. Structure was solved via the direct methods program MITHRIL.[14] Refinement was carried out by full-matrix least-squares calculations with individual isotropic temperature factors and with minimization of $\Sigma w(F_o - F_c)^2$, $w = 1/\sigma(F)$. Refinement with anisotropic temperature factors was unsuccessful, leading to nonpositive definite temperature factors for many atoms. The model includes two extra atoms, O(11) and O(12), that may correspond to adventitious water. The maximum and minimum values in the final difference map were 1.03 and –0.63 e Å^{-3}. The final $R = 0.173$; $R_w = 0.098$.[15]

2,3,4,8-Tetraphenyl-6,6,*anti*-10-trinitropentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decane (4).[11] To a rapidly stirred solution of sodium hydroxide (40 mg, 1.0 mmol) in water (1 mL) under nitrogen was added **3** (132 mg, 0.25 mmol). The resulting clear, light yellow solution was stirred at room temperature for 4 h. This solution was then added to a flask which contained under nitrogen a mixture of potassium ferricyanide (825 mg, 2.5 mmol), sodium nitrite (350 mg, 5.0 mmol), water (2 mL), and ether (4 mL). The resulting mixture was stirred under nitrogen at room temperature for 6 h. The organic layer was then separated, and the aqueous layer was washed with ether (15 mL). The combined organic layers were dried (anhydrous magnesium sulfate) and filtered, and the filtrate was concentrated in vacuo. The residue was recrystallized from 1:4 ethyl acetate–hexane mixed solvent, thereby affording pure **4** (93 mg, 65%) as a colorless microcrystalline solid: mp 248 °C dec; IR (KBr) 1559 (s), 1534 (s), 1362 (m), 1319 (m), 694 cm^{-1} (s); ^{1}H NMR (CDCl$_3$) δ 3.80 (m, 1 H), 4.30 (t, J = 3 Hz, 1 H), 4.45 (t, J = 2 Hz, 1 H), 5.10 (d, J = 2 Hz, 1 H), 5.70 (br s, 1 H), 6.4–7.20 (m, 20 H, aryl ring protons); ^{13}C NMR (CDCl$_3$) δ 49.74 (d), 54.36 (d), 57.92 (s), 58.19 (d), 59.14 (s), 59.36 (s), 61.03 (d), 63.92 (s), 91.05 (d), 125.94–128.51 (d, 20 C), 128.13 (s), 133.86 (s), 134.29 (s), 135.55 (s), 136.08 (s).

Anal. Calcd for $C_{34}H_{25}N_3O_6$: C, 71.45; H, 4.37. Found: C, 71.14; H, 4.45.

X-ray Analysis of 4. Cell dimensions were obtained from a least-squares fit of the coordinates of 25 centered reflections with 2θ between 30° and 35° using Mo Kα radiation ($\lambda = 0.81069$ Å). The 4899 independent reflections were collected out to $2\theta_{max}$ = 50° on a Nicolet R3M automatic diffractometer with an incident beam graphite monochromator. The structure was solved by direct methods at the Naval Research Laboratory and refined by full-matrix least-squares[15] in which the function minimized was $\Sigma w(|F_o| - |F_c|)^2$ where $w = 1/(\sigma^2|F_o| + g(F_o)^2)$ and $g(F_o)^2$ is included to account for random instrumental errors (g is estimated to be 0.00023). There were 388 parameters refined, including atomic coordinates and anisotropic thermal parameters for all non-hydrogen atoms. For hydrogen atoms (originally located in difference maps), coordinates were allowed to ride (C–H distance held at 0.96 Å) on covalently bonded atoms, and thermal parameters were set to the final isotropic values of their covalently bonded atoms. The final residual for the 1331 observed data ($|F_o| > 3\sigma|F_o|$) used in the refinement was $R = 0.052$ and $R_w = 0.054$. In the final Fourier difference map, the ripple density ranged from –0.23 to +0.23 e Å^{-3}. All programs used were part of the MicroVAX versions of the SHELXTL[16] system.

2,3,4,8-Tetraphenyl-6,6,10,10-tetranitropentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decane (5). To a rapidly stirred solution of sodium hydroxide (20 mg, 0.5 mmol) and methanol (1 mL) in water (1 mL) under nitrogen was added **4** (140 mg, 0.25 mmol). The resulting clear, light yellow solution was stirred at room temperature for 24 h. This solution was then added to a flask which contained under nitrogen potassium ferricyanide (825 mg, 2.5 mmol), sodium nitrite (350 mg, 5.1 mmol), water (3 mL), and ether (4 mL). The resulting mixture was stirred under nitrogen at room temperature for 24 h. Workup was performed in the manner described above for the preparation of **4**. The crude product was recrystallized from ethyle acetate–hexane mixed solvent, thereby affording pure **5** (72 mg, 50%) as a colorless microcrystalline solid: mp 278 °C dec; IR (KBr) 1574 (s), 704 cm^{-1} (m); ^{1}H NMR (CDCl$_3$) δ 4.30 (s, 2 H), 4.95 (s, 2 H), 6.45 (m, 4 H, aryl ring protons), 6.75 (m, 4 H, aryl ring protons), 6.90 (m, 6 H, aryl ring protons), 7.10 (m, 6 H, aryl ring protons); ^{13}C NMR (CDCl$_3$) δ 52.74 (d), 59.05 (s), 59.64 (s), 60.16 (d), 126.42 (d), 127.20 (d), 127.40 (d), 127.81 (s), 128.31 (d), 128.50 (d), 128.76 (d), 131.37 (s), 134.23 (s).

Anal. Calcd for $C_{34}H_{24}N_4O_8$: C, 66.26; H, 4.18; Found: C, 66.23; H, 3.92.

Acknowledgment. A.P.M. gratefully acknowledged financial support of this study by the U.S. Army Armament Research and Development Center, Dover, NJ (Contract DAAA21-86-C-0091), the Air Force Office of Scientific Research (Grant AFOSR-84-0085), the Robert A. Welch Foundation (Grant B-963), and the North Texas State University Facutly Research Committee. The X-ray crystallographic structure determination of **3** was supported in part by a grant (to H.L.A.) from the National Science Foundation (CHE-84-02155, for purchase of the X-ray diffractometer and MicroVAX system). The X-ray crystallographic structure determination of **4** was supported in part by the Office of Naval Research Mechanics Division.

Registry No. **3**, 110243-36-2; **4**, 110243-37-3; **5**, 110243-38-4; **6**, 38932-12-6; **7**, 110243-39-5.

Supplementary Material Available: A list of positional parameters and B(eq), intramolecular distances, and intramolecular bond angles for **3** and a list of atomic coordinates and equivalent isotropic displacement parameters, bond lengths, bond angles, anisotropic displacement parameters, and H-atom coordinates for **4** (9 pages); a table of $10|F|_o$ vs. $10|F|_c$ for **3** (10 pages). Ordering information is given on any current masthead page.

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(14) Gilmore, C. J. *J. Appl. Crystallogr.* **1984**, *17*, 42. MITHRIL is one of the subprogram links in the TEXSAN[13] system.

(15) Tables of atomic coordinates, bond lengths, and bond angles for **4** have been deposited as supplementary material.

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