to give **18b** (2.15 g, 68%) as a colorless solid: $[\alpha]_D$ -30.7° (*c* 0.90, $CHCl_3$); TLC $R_f$ 0.4 (silica; hexanes-$Et_2O$, 4:1); IR (neat) 1717, 1545, 1455, 1310, 1210, 1115 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 8.41 (d, 1 H, $J$ = 8.4 Hz) 7.65-7.50 and 7.40-7.17 (2 m, 14 H), 6.55 (d, 1 H, $J$ = 4.0 Hz), 5.20 (d, 1 H, $J$ = 6.0 Hz), 4.69 (dd, 1 H, $J$ = 6.0 and 6.6 Hz), 4.63-4.50 (m, 1 H), 3.41 (dd, 1 H, $J$ = 4.8 and 10.6 Hz), 3.34 (dd, 1 H, $J$ = 2.6 and 10.6 Hz), 2.88 (s, 3 H), 1.51 (s, 3 H), 1.44 (s, 3 H), 0.82 (s, 9 H); $^{13}C$ NMR (101 MHz, $CDCl_3$) $\delta$ 167.0, 135.9, 135.8, 135.7, 134.0, 133.3, 130.3, 129.5, 129.4, 127.4, 127.2, 125.1, 124.4, 123.9, 120.7, 117.0, 111.1, 109.6, 78.9, 74.8, 73.4, 70.8, 58.0, 26.7, 26.7, 25.6, 19.1; mass spectrum (EI) *m/e* 542, ($M^+$ - Me), 500, 410, 368, 332, 304, 255, 213, 199, 184, 158, 153, 144, 135, 117. Anal. Calcd for $C_{33}H_{39}NO_5Si$: C, 71.06; H, 7.05; N, 2.56. Found: C, 70.88; H, 7.18; N, 2.54.

**2,3-*O*-Isopropylidene-5-*O*-methyl-4-*O*-(*tert*-butyldiphenylsilyl)-D-ribonic Acid (18c).** A solution of LiOH (170 mg) in $H_2O$ (3 mL) was added to a stirred solution of the indole derivative **18b** (570 mg) in THF (40 mL), and the mixture was refluxed for 3.5 h. The reaction mixture was poured into $H_2O$ (100 mL), acidified to pH 4 by the careful addition of orthophosphoric acid, and extracted with EtOAc (4 × 50 mL). The combined extracts were dried ($Na_2SO_4$), and the EtOAc was removed under reduced pressure. Chromatography on silica gave (eluant $Et_2O$-hexanes, 1:4) indole and (eluant $Et_2O$-hexanes, 4:1) **18c** (380 mg, 81%) as a white solid: mp 168-170 °C (from $Me_2CO$/hexanes); $[\alpha]_D$ -22.5° (*c* 1.43, $CHCl_3$); TLC $R_f$ 0.2 (silica; hexanes-$Et_2O$, 1:4); IR (KBr) 3500-2700, 1756, 1210, 1105, 710 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.80-7.70 and 7.46-7.35 (m, 10 H), 4.56 (d, 1 H, $J$ = 7.2 Hz), 4.38 (dd, 1 H, $J$ = 2.6 and 7.2 Hz), 4.30-4.20 (m, 1 H), 3.48 (dd, 1 H, $J$ = 5.0 and 10.2 Hz), 3.26 (dd, 1 H, $J$ = 3.8 and 10.2 Hz), 3.46 (s, 3 H), 1.70 (s, 3 H), 1.37 (s, 3 H), 1.06 (s, 9 H); $^{13}C$ NMR (101 MHz, $CDCl_3$) $\delta$ 172.2, 136.3, 136.0, 135.8, 134.0, 132.7, 129.8, 129.7, 127.6, 127.5, 109.8, 79.7, 74.7, 73.6, 70.2, 58.7, 26.7, 26.5, 26.1, 19.3; mass spectrum (EI) *m/e* 443 ($M^+$ - Me), 401, 369, 343, 311, 281, 269, 265, 255, 241, 237, 221, 213, 205, 199, 195, 189, 163, 153, 139, 129. Anal. Calcd for $C_{25}H_{34}O_6Si$: C, 65.47; H, 7.47. Found: C, 65.34; H, 7.41.

**Acknowledgment.** We thank the National Institutes of Health and G. D. Searle and Co. for support of our research; G. D. Searle and Co. for granting study leave to A.F.G.; FRD CSIR, Pretoria, for financial support to B.C.B.B.; the Midwest Center for Mass Spectrometry, an NSF Regional Instrument facility (CHE-8211164), for obtaining mass spectral data; and the National Institutes of Health (RR-02314) for the purchase of a 400-MHz NMR spectrometer used in these studies. We additionally thank Martin J. Wythes for the preparation of **2a** and **2b**.

**Registry No.** **1**, 492-30-8; **2a**, 120927-76-6; **2b**, 114877-78-0; **3a**, 53657-41-3; **3b**, 16740-98-0; **3b** (triacetyl analogue), 2873-29-2; **3b** (triol), 13265-84-4; α-**4a**, 120964-47-8; β-**4a**, 120964-48-9; **4b**, 120927-77-7; α-**5a**, 120927-78-8; β-**5a**, 120927-79-9; **5b**, 51224-22-7; **6**, 96845-45-3; **7**, 114877-77-9; **8**, 92512-25-9; **9**, 14233-64-8; **10**, 71671-16-4; **11**, 56119-03-0; **12a**, 114877-74-6; **12b**, 114877-90-6; **12c**, 120927-80-2; **12d**, 114877-75-7; **12e**, 120927-88-0; **12f**, 114877-76-8; **12g**, 118715-16-5; **13a**, 114877-79-1; **13b**, 120927-81-3; **13c**, 120927-82-4; **13d**, 120927-89-1; **13e**, 87729-39-3; **13f**, 118715-27-8; **14a**, 120927-83-5; **14b**, 120927-90-4; **14c**, 118715-38-1; **15a**, 114877-80-4; **15b**, 114904-27-7; **15c**, 114877-87-1; **16a**, 114904-26-6; **16b**, 114877-83-7; **16c**, 114877-86-0; **17a**, 114877-82-6; **17b**, 114877-85-9; **17c**, 120927-73-3; **17d**, 114877-89-3; **18a**, 120942-48-5; **18a** (deprotected alcohol), 120927-74-4; **18b**, 120927-75-5; **18c**, 118715-10-9; **19a**, 120927-84-6; **19b**, 120927-91-5; **19c**, 120927-94-8; **20a**, 114877-81-5; **20b**, 114877-84-8; **20c**, 114877-88-2; **21a**, 120927-86-8; **21a** (alcohol), 120927-85-7; **21b**, 120927-92-6; **21c**, 118715-53-0; **22a**, 120927-87-9; **22b**, 120927-93-7; **22c**, 120927-95-9; $Me_2AlCl$, 1184-58-3; *o*-allylaniline, 32704-22-6; rhamnal, 53657-42-4; γ-butyrolactone, 96-48-0; δ-valerolactone, 542-28-9.

**Supplementary Material Available:** Full experimental details for the preparation and authentication of all new compounds described in this paper (30 pages). Ordering information is given on any current masthead page.

# Impact of a Basal Nitro Group on the Density Characteristics of Select [4]Peristylane Derivatives

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Several [4]peristylanes have been prepared that share in common a nitro group at C-9 of the basal cyclobutane ring. The synthetic entry of this class of molecules begins by Diels-Alder addition of nitro(trimethylsilyl)acetylene to tricyclo[5.2.1.$0^{2,6}$]deca-2,5,8-triene. This cycloaddition proceeds stereospecifically from below-plane to deliver a functionalized *syn*-sesquinorbornatriene. In characteristic fashion, this adduct can be cleanly epoxidized at its central double bond from the exo direction and subsequently irradiated to give the cage compound **10**. Periodate cleavage prior to or following desilylation delivers the required 9-nitro[4]peristylane-2,6-diones, the carbonyl functionalities in which have been transformed in stepwise fashion into *gem*-dinitro groups. Density measurements performed on four key compounds have disclosed that the 9-nitro group does not exert in general an effect that increases crystal density relative to the parent system.

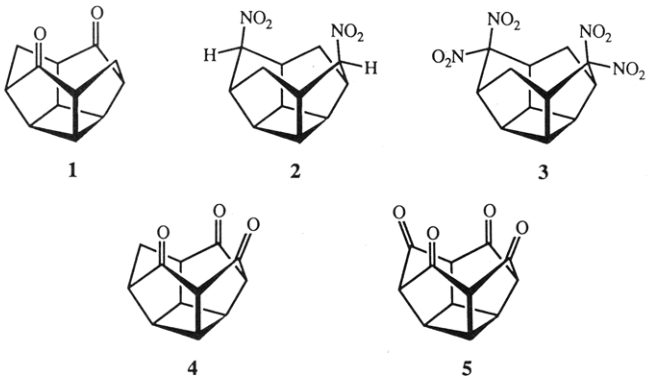
Although the [4]peristylane framework was first prepared only a short while ago,[1] its rigid structural network consisting of four mutually fused cyclopentane rings surrounding a cyclobutane base is recognized to allow close molecular packing within crystalline derivatives. Particularly dramatic are the notable increases in density that accompany the conversion of diketone **1** ($\rho$ = 1.42 g/$cm^3$)[2] to the *endo,endo*-dinitro compound **2** ($\rho$ = 1.54 g/$cm^3$)[3] and ultimately to the tetranitro system **3** ($\rho$ = 1.70 g/$cm^3$).[3] In an attempt to develop properties more closely approaching the $\rho$ = 2 plateau so highly desirable for high density

(1) (a) Paquette, L. A.; Browne, A. R.; Doecke, C. W.; Williams, R. V. *J. Am. Chem. Soc.* **1983**, *105*, 4113. (b) Paquette, L. A.; Fischer, J. W.; Browne, A. R.; Doecke, C. W. *Ibid.* **1985**, *107*, 686.

(2) Engel, P.; Fischer, J. W.; Paquette, L. A. *Z. Kristallogr.* **1984**, *166*, 225.

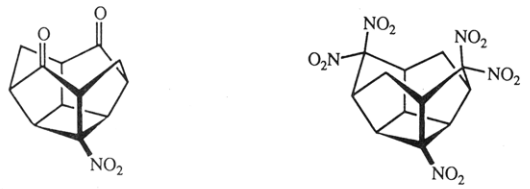
(3) Waykole, L. M.; Shen, C.-C.; Paquette, L. A. *J. Org. Chem.* **1988**, *53*, 4969.

0022-3263/89/1954-3324$01.50/0 



1 2 3 4 5

propellants,[4] we have accomplished extended functionalization of the fluted [4]peristylane perimeter as in **4** and **5** recently.[5] Their transformation into polynitro derivatives remains to be accomplished. Additionally, we have sought to assess the impact of a basal nitro group on density. To this end, we describe herein the synthesis of **6** and **7** and report on the impact of substitution in this



6 7

manner on select physical characteristics of these and related molecules. Contrary to popular notion, the density values are not enhanced in direct proportion to the number of nitro groups present, but depend instead on the efficiency of molecular packing.

## Synthetic Methodology

In light of the established proclivity of tricyclo-[5.2.1.$0^{2,6}$]deca-2,5,8-triene (**8**) for engaging in kinetically controlled Diels–Alder cycloadditions from below-plane,[6] this diene was treated with nitro(trimethylsilyl)acetylene[7] in dichloromethane solution at room temperature. The condensation was judged to be complete after 18 h (TLC analysis). As expected,[8] the resulting adduct proved to be air-sensitive and therefore it was directly epoxidized to give **9** (Scheme I). The relative stereochemistry of **9**, a molecule that is not particularly stable to chromatography, was apparent initially on the basis of the chemical shifts of select protons (see Experimental Section). Independent chemical confirmation of the syn double-bond arrangement was provided by intramolecular [2 + 2] photocyclization. When attempts to purify **9** are avoided, an overall 19% yield of **10** from **8** can be realized reproducibly.

Contrary to experience,[9] all attempts to cleave the oxirane ring in **10** with periodic acid in tetrahydrofuran at

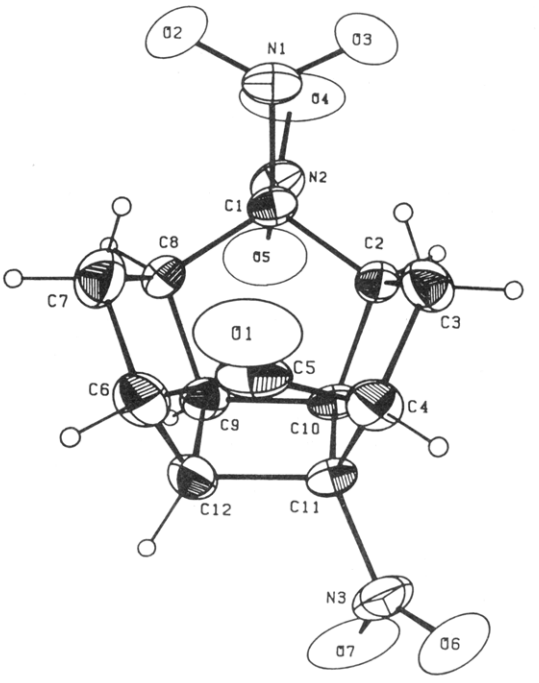



**Figure 1.** Computer-generated perspective drawing of **15** as determined by X-ray crystallography. The atom numbering is arbitrary.

**Table I. Crystal Data and Summary of Intensity Data Collection and Structure Refinement for 15**

| | |
|---|---|
| color/shape | colorless/parallelepiped |
| form. wt. | 309.24 |
| space group | $P2_1$ |
| temp, °C | 20 |
| cell constants[a] | |
| $a$, Å | 7.225 (1) |
| $b$, Å | 11.735 (2) |
| $c$, Å | 7.770 (1) |
| $\beta$, deg | 112.07 (1) |
| cell vol, Å$^3$ | 610.5 |
| formula units/unit cell | 2 |
| $D_{calc}$, g cm$^{-3}$ | 1.68 |
| $\mu_{calc}$, cm$^{-1}$ | 0.92 |
| diffractometer/scan | Enraf-Nonius CAD-4/$\theta$–2$\theta$ |
| radiatn, graphite monochromator | Mo K$\alpha$ ($\lambda$ = 0.71073) |
| max crystal dimensns, mm | 0.08 × 0.10 × 0.18 |
| scan width | 0.80 + 0.35 tan $\theta$ |
| standard reflctns | 004; 0$\bar{6}$0; 500 |
| decay of standrds | ±3% |
| reflctns measd | 1216 |
| 2$\theta$ range, deg | 2 ≤ 2$\theta$ ≤ 50 |
| range of $h$, $k$, $l$ | +8, −13, ±9 |
| reflctns obsd [$F_o \geq 5\sigma(F_o)$][b] | 857 |
| computer programs[c] | SHELX[13] |
| structure solutn | MULTAN[14] |
| no. of parameters varied | 198 |
| weights | $[\sigma(F_o)^2 + 0.00004F_o^2]^{-1}$ |
| GOF | 1.80 |
| $R = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$ | 0.040 |
| $R_w$ | 0.040 |
| largest feature final diff map | 0.2 e Å$^{-3}$ |

[a] Least-squares refinement of $((\sin\theta)/\lambda)^2$ values for 25 reflections $\theta > 20°$. [b] Corrections: Lorentz and polarization. [c] Neutral scattering factors and anomalous dispersion corrections from ref 15.

(4) (a) Cady, H. H. "Estimation of the Density of Organic Explosives from their Structural Formulas", Los Alamos Scientific Laboratory, Report LA-7760-MS, 1979. (b) Stine, J. R. "Prediction of Crystal Densities of Organic Explosives by Group Additivity", Los Alamos National Laboratory, Report LA-8920, 1981.

(5) (a) Paquette, L. A.; Shen, C.-C. *Tetrahedron Lett.* **1988**, *29*, 4069. (b) Paquette, L. A.; Shen, C.-C.; Engel, P. *J. Org. Chem.*, following paper in this issue.

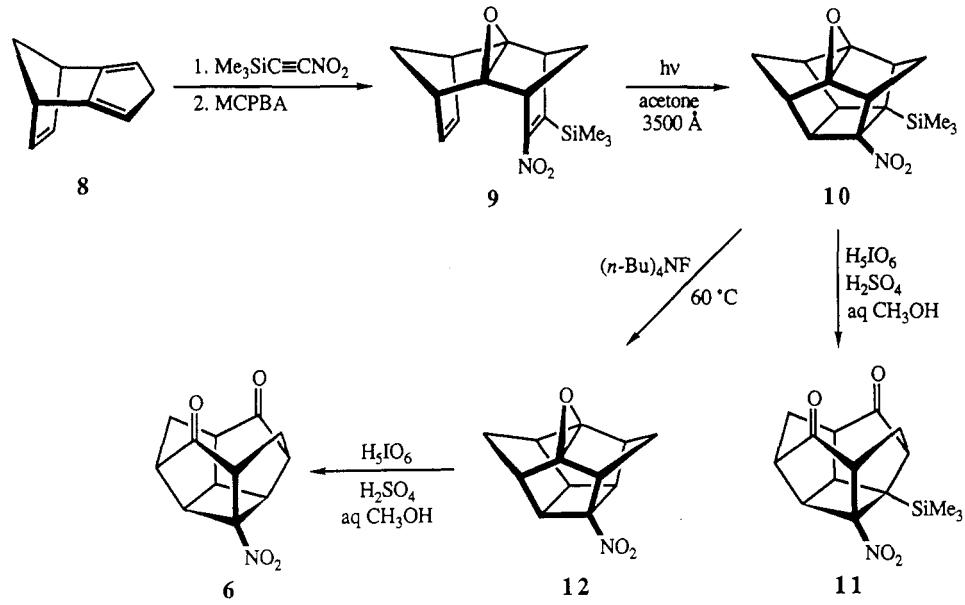
(6) (a) Böhm, M. C.; Carr, R. V. C.; Gleiter, R.; Paquette, L. A. *J. Am. Chem. Soc.* **1980**, *102*, 7218. (b) Paquette, L. A. in *Stereochemistry and Reactivity of Pi Systems*; Watson, W. H., Ed.; Verlag Chemie International: Deerfield Beach, FL, 1983; pp 41–73. (c) Gleiter, R.; Paquette, L. A. *Acc. Chem. Res.* **1983**, *16*, 328.

(7) (a) Schmitt, R. J.; Bedford, C. D. *Synthesis* **1986**, 132. (b) Schmitt, R. J.; Bottaro, J. C.; Malhotra, R.; Bedford, C. D. *J. Org. Chem.* **1987**, *52*, 2294.

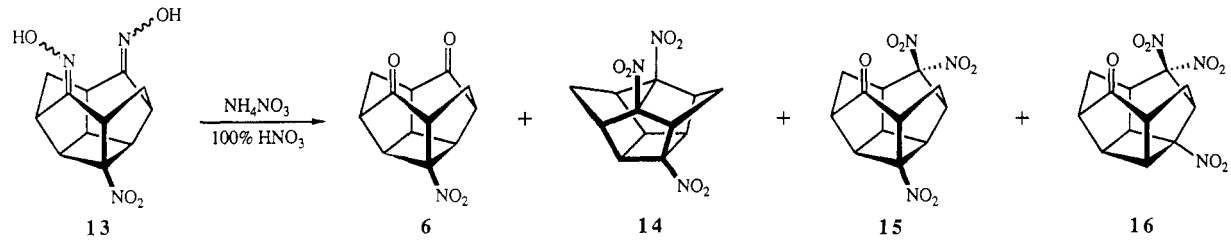
(8) Paquette, L. A.; Künzer, H.; Green, K. E.; De Lucchi, O.; Licini, G.; Pasquato, L.; Valle, G. *J. Am. Chem. Soc.* **1986**, *108*, 3453 and relevant references cited therein.

(9) (a) Paquette, L. A.; Browne, A. R.; Doecke, C. W.; Williams, R. V. *J. Am. Chem. Soc.* **1983**, *105*, 4113. (b) Paquette, L. A.; Fischer, J. W.; Browne, A. R.; Doecke, C. W. *Ibid.* **1985**, *107*, 686.

**Scheme I**




**Scheme II**

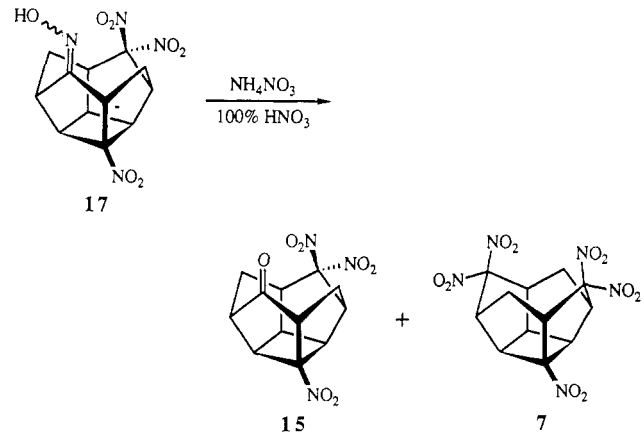



25 °C or in hot aqueous methanol failed. However, addition of sulfuric acid as a catalyst allowed conversion to **11** to proceed smoothly (89%). This diketone was noted to undergo decomposition when fused with tetra-*n*-butylammonium fluoride.[10] Application of these conditions to **10**, on the other hand, produced **12**, which served as a convenient precursor to **6**.

Oximation of this nitro diketone made **13** available as a mixture of *E*/*Z* isomers (Scheme II). Oxidation of this intermediate with 100% nitric acid in the presence of ammonium nitrate[11] at 20 °C resulted in a modest level of hydrolytic conversion back to **6** (32%). In addition, the trinitro cage compound **14** was formed (20%) as a direct consequence of transannular bond formation. Functionalized [4]peristylanes are recognized to be particularly prone to ring closure in this fashion.[3,9,11] The isomeric trinitro ketones **15** (12%) and **16** (15%) were also isolated, with **15** proving significantly less polar than **16**. Detailed NMR spectroscopic analysis did not provide the desired rigor for defining the specific locus of the basal nitro substituent in these isomers. Accordingly, an X-ray crystallographic study of **15** was undertaken (Figure 1, Table I). The nearly equal distribution of **15** and **16** suggests that the cyclobutyl-bound nitro group exerts little control over the regiochemistry of the geminal nitration reaction.

Formation of **7** was realized by exposure of **15** to hydroxylamine and submission of **17** to the Ungnade–Kissinger conditions.[3,11] Although the major product was trinitro ketone **15** (68%), the desired pentanitro[4]-peristylane was formed to the extent of 32% (Scheme III).

**Scheme III**




By recycling **15**, efficient throughput to **7** is feasible.

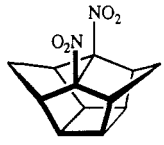
## Crystal Density Measurements

Density measurements were made on the nitro ketones **6** and **15**, the trinitro cage compound **14**, and the pentanitro derivative **7**. In each instance, densities were available for the particular structural counterpart lacking the basal nitro group. Consequently, experimental definition of the role played by this pendant substituent on the ability of these molecules to pack in their respective crystal lattices was at hand. In each instance, the density value is based on a unit cell determination.

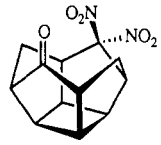
The density of **6**, found to be 1.52 g/cm$^3$, is higher than the value of 1.42 g/cm$^3$ previously recorded for **1**.[2] Clearly, the added nitro group has a positive effect in this case. At 1.62 g/cm$^3$, the density of trinitro bishomopentaprismane **14** is enhanced relative to that of **6**. However, the value

(10) Sugimura, T.; Paquette, L. A. *J. Am. Chem. Soc.* **1987**, *109*, 3017.
(11) Ungnade, H. E.; Kissinger, L. W. *J. Org. Chem.* **1959**, *24*, 666.

is essentially identical with that exhibited by **18** (1.63 g/cm$^3$).[12] As a result, the higher $\rho$ seen for **6** is lost in **14**.



**18**



**19**

Peristylane **15** was determined to have a density of 1.68 g/cm$^3$, essentially equivalent to that of **19** (1.67 g/cm$^3$).[3] Significantly, the trend noted for **14** and **15** persists where **7** is concerned. The density of 1.72 g/cm$^3$ for this pentanitro compound is indistinguishable from that of **3** (1.70 g/cm$^3$).[3]

As a consequence, the attachment of a nitro group to the cyclobutane base of the [4]peristylane ring system does not enhance the density of these molecules, a finding that goes contrary to the common belief that $\rho$ should increase with cumulative attachment of nitro groups to a carbocyclic framework. It remains to assess the role of additional nitro groups on the fluted perimeter of **3** as a means of surpassing the 1.7 g/cm$^3$ "barrier".

## Experimental Section

**Cycloaddition of Tricyclo[5.2.1.0$^{2,6}$]deca-2,5,8-triene with Nitro(trimethylsilyl)acetylene.** Nitronium tetrafluoroborate was washed thoroughly with anhydrous dichloromethane before use. To a suspension of $NO_2BF_4$ (12.0 g, 90.4 mmol) in 75 mL of dichloromethane was added 15.4 g (90.4 mmol) of bis(trimethylsilyl)acetylene at 0 °C under an atmosphere of argon. The reaction mixture was stirred at this temperature for 2 h, quickly passed through a short silica gel column (elution with chloroform), and evaporated. There was obtained 9.27 g of crude nitro(trimethylsilyl)acetylene as an orange liquid, which was stirred with 8.50 g (64.5 mmol) of **8** in 150 mL of dichloromethane at room temperature under an argon atmosphere for 18 h. The solvent was evaporated and the residue was rapidly chromatographed (silica gel, elution with 4:1 petroleum ether–dichloromethane) to furnish 8.95 g of orange-colored adduct.

This material was immediately dissolved in dichloromethane (200 mL) and a solution of *m*-chloroperbenzoic acid (6.60 g of 80–85% purity) in the same solvent (100 mL) was added dropwise at −10 °C. After 6 h of stirring at 0 °C, the solid was filtered off and the filtrate was washed with 10% sodium bisulfite solution and water, dried, and concentrated in vacuo. Chromatography of the residue on silica gel (elution with 2:1 petroleum ether–dichloromethane) gave 3.13 g (17%) of **9** as a yellowish solid, mp 104–105.5 °C: IR (KBr, cm$^{-1}$) 3035, 3010, 2990, 2965, 1495, 1340, 1260, 1250, 1235, 845, 730; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 6.30 (dd, $J$ = 5.5, 3.1 Hz, 1 H), 6.07 (dd, $J$ = 5.5, 3.1 Hz, 1 H), 3.52 (d, $J$ = 1.1 Hz, 1 H), 3.48 (d, $J$ = 1.1 Hz, 1 H), 3.12 (m, 2 H), 2.25 (dt, $J$ = 8.4, 1.6 Hz, 1 H), 2.18 (dt, $J$ = 7.8, 1.6 Hz, 1 H), 1.55 (ddd, $J$ = 8.4, 2.7, 1.3 Hz, 1 H), 1.46 (dd, $J$ = 7.8, 1.3 Hz, 1 H), 0.24 (s, 9 H); $^{13}$C NMR (75 MHz, $CDCl_3$) ppm 170.46, 167.23, 143.45, 139.97, 76.13, 73.20, 52.85, 51.86, 50.80, 47.11, 45.90, 45.49, −1.74; MS $m/z$ ($M^+ - CH_3$) calcd 274.0900, obsd 274.0906.

**Photocyclization of 9.** A solution of **9** (607 mg, 2.10 mmol) in 145 mL of acetone was divided among several Pyrex test tubes and irradiated in a Rayonet reactor equipped with a full bank of 3500-Å lamps for 22 h. After evaporation of the solvent, the residue was chromatographed on silica gel (elution with 2:1 petroleum ether–dichloromethane) to afford 452 mg (74%) of **10** as colorless crystals, mp 137–137.5 °C: IR (KBr, cm$^{-1}$) 3020, 2995, 2965, 2875, 1525, 1450, 1365, 1350, 1285, 1275, 1260, 1255, 995, 845; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 3.38 (dd, $J$ = 8, 5 Hz, 1 H), 2.70 (d, $J$ = 1 Hz, 1 H), 2.61 (dd, $J$ = 5, 1 Hz, 1 H), 2.52 (dd, $J$ = 8, 4 Hz, 1 H), 2.36 (d, $J$ = 1 Hz, 1 H), 2.31 (dd, $J$ = 5, 1 Hz, 1 H), 2.01 (dd, $J$ = 11, 1 Hz, 1 H), 1.75 (d, $J$ = 11 Hz, 1 H), 1.70 (d, $J$ = 11 Hz, 1 H), 1.49 (dd, $J$ = 11, 1 Hz, 1 H), 0.04 (s, 9 H); $^{13}$C NMR (75 MHz, $CDCl_3$) ppm 93.61, 64.71, 61.59, 50.19, 47.68, 45.49, 42.68, 39.27, 38.47, 33.96, 33.86, −3.72 (1 C not observed); MS $m/z$ ($M^+ - CH_3$) calcd 274.0899, obsd 274.0884.

Anal. Calcd for $C_{15}H_{19}NO_3Si$: C, 62.25; H, 6.62. Found: C, 62.09; H, 6.65.

**Oxidative Cleavage of 10.** A magnetically stirred solution of **10** (99.0 mg, 0.342 mmol), periodic acid (160 mg, 0.702 mmol), and concentrated sulfuric acid (0.2 mL) in 11 mL of 10% aqueous methanol was heated at reflux for 15.5 h. After removal of the volatiles under reduced pressure, the product was extracted into dichloromethane. The combined organic extracts were washed with 20% sodium bisulfite solution and brine, dried, and concentrated. After silica gel chromatography (elution with 5:1 petroleum ether–ethyl acetate), 93.1 mg (89%) of **11** was obtained as a white solid, mp 123–125 °C: IR (KBr, cm$^{-1}$) 3005, 2970, 2945, 1745, 1725, 1535, 1445, 1370, 1255, 1240, 1150, 850; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 4.22 (t, $J$ = 8.8 Hz, 1 H), 3.34 (t, $J$ = 8.5 Hz, 1 H), 3.12–3.00 (m, 2 H), 2.70 (m, 2 H), 2.52–2.16 (m, 4 H); $^{13}$C NMR (20 MHz, $CDCl_3$) ppm 225.28, 220.21, 98.33, 60.87, 57.24, 53.95, 52.37, 50.80, 47.18, 41.80, 41.19, 40.72 −4.31; MS $m/z$ ($M^+ - CH_3$) calcd 290.0849, obsd 290.0880.

**Desilylation of 10.** Tetra-*n*-butylammonium fluoride trihydrate (1.00 g) was heated at 90 °C and 2 Torr for 3 h. A solution of **10** (119 mg, 0.411 mmol) in 3 mL of tetrahydrofuran was added, the solvent was carefully evaporated in vacuo, and the residue was heated at 60 °C under a pressure of 2 Torr for 24 h. After cooling, the product was extracted into dichloromethane and washed with water and brine. After drying and solvent evaporation, the residue was purified by silica gel chromatography (elution with 1:1 petroleum ether–dichloromethane). There was isolated 52.8 mg (59%) of **12** as a white solid, mp 48–49 °C: IR (KBr, cm$^{-1}$) 2985, 2875, 1525, 1445, 1370, 1350, 1290, 980, 795; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 3.31 (m, 1 H), 3.24 (m, 1 H), 2.83 (t, $J$ = 1.4 Hz, 1 H), 2.78 (dd, $J$ = 7, 5 Hz, 1 H), 2.61 (m, 1 H), 2.50 (m, 1 H), 2.41 (m, 1 H), 1.91 (dd, $J$ = 12, 1.1 Hz, 1 H), 1.74 (d, $J$ = 12 Hz, 1 H), 1.69 (d, $J$ = 12 Hz, 1 H), 1.47 (dt, $J$ = 12, 1.2 Hz, 1 H); $^{13}$C NMR (75 MHz, $CDCl_3$) ppm 91.00, 63,71, 61.19, 49.00, 47.09, 45.63, 39.41, 39.33, 38.28, 37.19, 33.95, 33.69; MS $m/z$ ($M^+$) calcd 217.0739, obsd 217.0778.

**Oxidative Cleavage of 12.** A magnetically stirred solution of **12** (410 mg, 1.89 mmol), periodic acid (930 mg, 4.1 mmol), and concentrated sulfuric acid (0.4 mL) in 25 mL of 10% aqueous methanol was heated at reflux for 11.5 h. Workup in the predescribed manner afforded 302 mg (68%) of **6** as colorless crystals, mp 280–280.5 °C (from dichloromethane–hexanes): IR (KBr, cm$^{-1}$) 3010, 2960, 2940, 2870, 1745, 1730, 1535, 1380, 1365, 1245, 1230, 1150, 875, 820; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 4.11 (m, 2 H), 3.69 (q, $J$ = 8.8 Hz, 1 H), 3.30 (d, $J$ = 8.0 Hz, 1 H), 3.05 (td, $J$ = 8.6, 2.4 Hz, 1 H), 2.92 (td, $J$ = 8.3, 2.3 Hz, 1 H), 2.79 (td, $J$ = 8.6, 2.2 Hz, 1 H), 2.54–2.19 (m, 4 H); $^{13}$C NMR (75 MHz, $CDCl_3$) ppm 224.68, 220.29, 95.66, 58.18, 54.05, 53.37, 52.07, 50.08, 48.89, 41.90, 40.56, 39.17; MS $m/z$ ($M^+$) calcd 233.0688, obsd 233.0700.

Anal. Calcd for $C_{12}H_{11}NO_4$: C, 61.80; H, 4.75. Found: C, 61.81; H, 4.88.

**9-Nitro[4]peristylane-2,6-dione Dioxime (13).** A mixture of **6** (267 mg, 1.14 mmol), hydroxylamine hydrochloride (790 mg, 11.4 mmol), sodium acetate (1.88 g, 2.29 mmol), and methanol (20 mL) was stirred magnetically at room temperature for 47.5 h. After evaporation of the volatiles, water was added and the insoluble solid was collected by filtration and air-dried. There was obtained 256 mg (85%) of **13** as colorless crystals, mp 263 °C dec (from ethanol): MS $m/z$ ($M^+$) calcd 263.0906, obsd 263.0913.

**Oxidative Nitration of 13.** Ammonium nitrate (2.88 g) was added with stirring to 1.5 mL of 100% nitric acid at room temperature. After 30 min, 414 mg (1.57 mmol) of **13** was introduced portionwise. The reaction mixture was stirred for 3 h, poured

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onto ice, and extracted with dichloromethane. The combined organic extracts were washed with water and brine, dried, and concentrated. After MPLC on silica gel (elution with 1:1 petroleum ether–ethyl acetate), three fractions were obtained. The first fraction contained a mixture of two products. The second fraction consisted of **6** (117 mg, 32%). The third fraction was composed of the more polar trinitro ketone **16** (71.8 mg, 15%). The first fraction was rechromatographed (MPLC, silica gel, elution with dichloromethane) and gave 90.7 mg (20%) of **14** and 58.7 mg (12%) of the less polar trinitro ketone **15**.

For **14**: colorless crystals, mp >300 °C (from dichloromethane–hexanes); IR (KBr, $cm^{-1}$) 3005, 2975, 2890, 1555, 1460, 1365, 820; $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 3.78 (s, 1 H), 3.59–3.39 (m, 5 H), 3.14–3.03 (m, 3 H), 2.35 (d, $J$ = 12 Hz, 1 H), 1.96 (d, $J$ = 12 Hz, 1 H); $^{13}C$ NMR (75 MHz, acetone-$d_6$) ppm 109.69, 108.26, 92.04, 56.21, 53.90, 52.56, 51.37, 51.12, 46.67, 41.98, 41.74, 38.73; MS $m/z$ ($M^+ - NO_2$) calcd 247.0719, obsd 247.0722.

Anal. Calcd for $C_{12}H_{11}N_3O_6$: C, 49.15; H, 3.78. Found: C, 48.99; H, 3.84.

For **15**: colorless crystals, mp 210 °C dec (from dichloromethane–hexanes); IR (KBr, $cm^{-1}$) 3010, 2960, 2885, 1745, 1570, 1540, 1460, 1370, 1325, 1195, 800; $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 4.25 (td, $J$ = 8.7, 2.5 Hz, 1 H), 4.05 (td, $J$ = 8.6, 2.5 Hz, 1 H), 3.90–3.78 (m, 2 H), 3.63 (m, 1 H), 3.43 (d, $J$ = 12 Hz, 1 H), 3.15 (m, 1 H), 2.95 (dt, $J$ = 16, 11 Hz, 1 H), 2.73 (dt, $J$ = 16, 11 Hz, 1 H), 2.60 (d, $J$ = 16 Hz, 1 H), 2.56 (d, $J$ = 16 Hz, 1 H); $^{13}C$ NMR (75 MHz, acetone-$d_6$) ppm 219.72, 133.42, 96.26, 58.17, 55.32, 55.21, 54.84, 54.26, 50.23, 45.55, 40.55, 39.33; MS $m/z$ ($M^+$) calcd 309.0597, obsd 309.0562.

For **16**: colorless crystals, mp 221 °C dec (from acetone–ethyl acetate); IR (KBr, $cm^{-1}$) 3035, 3000, 1740, 1575, 1535, 1465, 1370, 1325, 1195, 845; $^1H$ NMR (300 MHz, acetone-$d_6$) $\delta$ 4.44 (dd, $J$ = 9.9, 2.1 Hz, 1 H), 4.37 (td, $J$ = 8.6, 2.5 Hz, 1 H), 4.07–3.97 (m, 2 H), 3.78 (q, $J$ = 8.6 Hz, 1 H), 3.71 (s, 1 H), 3.21–3.03 (m, 1 H), 2.96–2.56 (m, 2 H), 2.51 (d, $J$ = 15 Hz, 1 H), 2.38 (d, $J$ = 15 Hz, 1 H); $^{13}C$ NMR (75 MHz, DMSO-$d_6$) ppm 223.51, 130.07, 99.11, 56.63, 53.56, 52.83, 52.76, 51.99, 49.84, 38.67, 38.32 (1 C not observed); MS $m/z$ ($M^+$) calcd 309.0597, obsd 309.0643.

**X-ray Crystallographic Analysis of 15.** A transparent single crystal of **15** was mounted on a pin, transferred to the goniometer, and cooled to −150 °C during data collection using a stream of cold nitrogen gas. The space group was determined to be either the centric $P2_1/n$ or acentric $P2_1$ from the systematic absences. Symmetry considerations indicated that the space group was acentric and the subsequent solution and successful refinement of the structure in the space group $P2_1$ confirmed this. A summary of data collection parameters is given in Table I.

Least-squares refinement with isotropic thermal parameters led to $R$ = 0.113. The geometrically constrained hydrogen atoms were placed in calculated positions 0.95 Å from the bonded carbon atom and allowed to ride on that atom with $B$ fixed at 5.5 $Å^2$. Refinement of the non-hydrogen atoms with anisotropic temperature factors led to the final values of $R$ = 0.040 and $R_w$ = 0.040. The final values of the positional parameters are given in Table II (supplementary material).

**6,6,9-Trinitro[4]peristylan-2-one Oxime (17).** A mixture of **15** (78.9 mg, 0.255 mmol), hydroxylamine hydrochloride (180 mg, 2.59 mmol), sodium acetate (420 mg, 5.12 mmol), and methanol (7 mL) was stirred magnetically at room temperature for 58 h. After evaporation of the volatiles, water was added and the insoluble solid was collected by filtration, washed with water, and air-dried. There was obtained 51.8 mg (63%) of **17** as colorless crystals, mp 195 °C dec (from ethanol): MS $m/z$ ($M^+$) calcd 324.0706, obsd 324.0729.

**2,2,6,6,9-Pentanitro[4]peristylane (7).** Ammonium nitrate (380 mg) was added to 0.20 mL of 100% nitric acid and the solution was stirred at room temperature for 30 min. Trinitro oxime **17** (48.0 mg, 0.148 mmol) was added in small portions and the resulting mixture was stirred at room temperature for 3 h before being quenched with ice. The products were extracted into dichloromethane and washed with water and brine. After drying and solvent removal, two products were separated by MPLC on silica gel (elution with dichloromethane): 18.1 mg (32%) of **7** and 31.0 mg (68%) of **15**.

For **7**: colorless crystals, mp 222 °C dec (from dichloromethane–hexanes); IR (KBr, $cm^{-1}$) 3005, 1570, 1550, 1465, 1370, 1325, 1220, 1165, 1125, 790; $^1H$ NMR (300 MHz, acetone-$d_6$) $\delta$ 4.58 (dt, $J$ = 12, 2,6 Hz, 1 H), 4.33–4.07 (m, 4 H), 4.01–3.89 (m, 2 H), 3.56 (dt, $J$ = 18, 12 Hz, 1 H), 3.22 (dt, $J$ = 18, 11 Hz, 1 H), 2.58 (dt, $J$ = 18, 2.6 Hz, 1 H), 2.38 (dt, $J$ = 18, 2.5 Hz, 1 H); $^{13}C$ NMR (75 MHz, acetone-$d_6$) ppm 132.52, 130.82, 98.06, 56.30, 54.22, 53.58, 52.94, 52.78, 52.54, 42.58, 36.13, 35.90; MS $m/z$ ($M^+ - 2NO_2$) calcd 293.0647, obsd 293.0610.

Anal. Calcd for $C_{12}H_{11}N_5O_{10}$: C, 37.41; H, 2.88. Found: C, 37.48; H, 3.14.

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**Supplementary Material Available:** Tables of bond distances and angles, least-squares planes, final fractional coordinates, and thermal parameters for **15** (7 pages); observed and calculated structure factors for **15** (2 pages). Ordering information can be found on any current masthead page.