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Reactivity of [1(2,3)4]Pentamantane (T_d-Pentamantane): A Nanoscale Model of Diamond†

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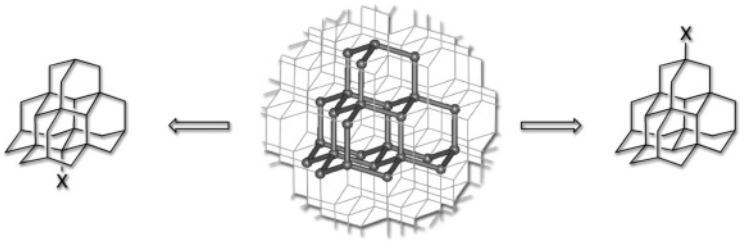

To model the chemical properties of the hydrogen-terminated nanodiamond {111} and {110} surfaces, the functionalizations of the higher diamondoid [1(2,3)4]pentamantane were studied. [1(2,3)4]Pentamantane reacts selectively with neat bromine to give the medial 2-mono- and 2,4-disubstitution products. In contrast, oxidation with nitric acid as well as single-electron-transfer oxidation involving the [1(2,3)4]pentamantane radical cation results in apical C^7-substitutions. This substitution pattern dominates in the free-radical bromination under phase-transfer catalytic conditions that gives a mixture of 7- and 2-bromo[1(2,3)4]-pentamantane in a 95:5 ratio. Replacement of the functional groups in [1(2,3)4]pentamantane occurs without isomerization. This was demonstrated for the interconversions of the bromo and hydroxy derivatives as well as for the preparation of [1(2,3)4]pentamantyl-7-thiol from 7-hydroxy[1(2,3)4]-pentamantane. Thus, the selective functionalization of hydrogen-terminated nanodiamonds is possible by means of reactions with common electrophiles−oxidizers.

Introduction

The combination of strength, hardness,[1] high-temperature semiconductance, electron as well as field emission,[2] and unique optical properties make diamond-based materials especially attractive. Increasing attention has been paid to nanometer-sized diamonds (nanodiamonds and diamondoids) because the relative stability of carbon-rich compounds strongly depends on their size; at the 2−5 nm scale sp^3-carbon materials are more stable than graphite particles composed of sp^2 carbon.[3] Thus, future nanotechnological developments may be based on diamond-like species as well as on combinations[4] of sp^3 and sp^2 carbon nanoparticles,[1,5] rather than on pure nanotubes or fullerenoids. Moreover, it has been noted that it is desirable to reduce a nanodiamond in size to less than 2 nm in order to increase, for instance, its optical gap[6,7] for applications in nano-optical devices. Diamond particles of slightly larger size are available

† Functionalized nanodiamonds. 4. For part 3, see ref 46.
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(1) Shenderova, O. A.; Zhirnov, V. V.; Brenner, D. W. *Crit. Rev. Solid State Mater. Sci.* **2002**, *27*, 227−356.
(2) Kang, W. P.; Davidson, J. L.; Wong, Y. M.; Holmes, K. *Diam. Relat. Mater.* **2004**, *13*, 975−981.
(3) Badziag, P.; Verwoerd, W. S.; Ellis, W. P.; Greiner, N. R. *Nature* **1990**, *343*, 244−245.
(4) Barnard, A. S.; Russo, S. P.; Snook, I. K. *J. Chem. Phys.* **2003**, *118*, 5094−5097.
(5) Kuznetsov, V. L.; Chuvilin, A. L.; Butenko, Yu. V.; Malkov, I. Y.; Titov, V. M. *Chem. Phys. Lett.* **1994**, *222*, 343−348.
(6) Raty, J.-Y.; Galli, G.; Bostedt, C.; van Buuren, T. W.; Terminello, L. J. *Phys. Rev. Lett.* **2003**, *90*, 037401/1−037401/4. McIntosh, G. C.; Yoon, M.; Berber, S.; Tománek, D. *Phys. Rev. B* **2004**, *70*, 045401/1−045401/8.

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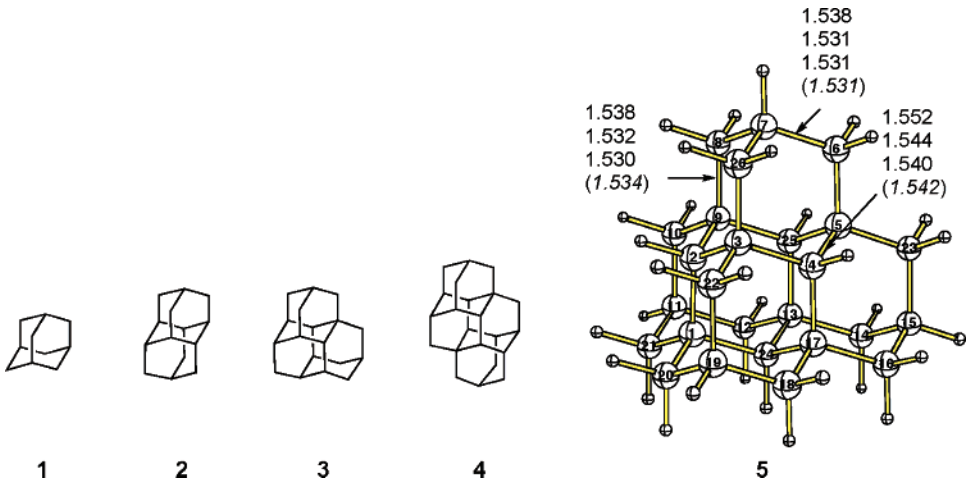


FIGURE 1. Structures of adamantane (**1**), diamantane (**2**), triamantane (**3**), [121]tetramantane (**4**), and [1(2,3)4]pentamantane (**5**). Computed bond distances in Å (B3LYP/6-311+G*, B3PW91/6-311+G*, and MP2/6-31G*); experimental bond lengths[19,20] in italics.

synthetically through plasma-enhanced CVD techniques (3−5 nm films)[8] and detonation (2−5 nm),[9] but as exceedingly complex dispersions. In addition, 1−3 nm diamonds are also believed to be present in interstellar space.[10] Although knowledge about the chemical properties of such species would enhance the development of the nanodiamond field toward technological applications, owing to inseparable, inhomogeneous size distributions, CVD and detonation nanodiamonds are not well characterized from a chemical point of view (geometries, reactivities).[11]

Diamondoid hydrocarbons[12] can serve as models for hydrogen-terminated nanodiamonds in theoretical and experimental studies.[7,13] The simplest nanodiamonds are represented (Figure 1) by adamantane (**1**)[14] as well as higher members diamantane (**2**),[15] triamantane (**3**),[16] [121]tetramantane (C_{2h}-tetramantane, **4**), and [1(2,3)4]pentamantane (**5**).[17,18] The big advantage of these substances is that they are, in contrast to detonation and CVD nanodiamonds "knowable," that is, they are physically well characterized and are all structurally homogeneous.

The chemical properties of adamantane and diamantane are well documented. Adamantane derivatives are already found in numerous applications in pharmacology and the material sciences.[12] The basic chemistry of triamantane (**3**) and, especially, the higher diamondoid [121]tetramantane (**4**), both of which are also available from petroleum, is much less developed, and the preparations of functional derivatives of **4** were described only very recently.[21]

Strictly speaking, diamondoids **1**−**4** do not include hydrogen-terminated moieties present in hexagonal nanodiamonds and nanodiamond films,[1,8] which contain repeating C−H units on their surfaces. The simplest centrosymmetric hydrocarbon that represents the {111}[22] face of a diamond surface with two different types of C−H bonds is indeed [1(2,3)4]pentamantane (**5**) (Figures 1 and 2). Thus, the 0.7−0.8 nm dimensions of hydrocarbon **5** make it the smallest possible topological representative of hydrogen-terminated diamond. This most basic nanodiamond model has escaped its synthetic preparation because thermodynamically controlled Lewis acid catalyzed rearrangements of suitable precursor hydrocarbons[14,15] fail in the preparation of higher diamondois.[23] At the same time, fullerenoids become increasingly more stable than nanodiamonds at particle sizes above a few nm.[4] Despite numerous

(7) Drummond, N. D.; Williamson, A. J.; Needs, R. J.; Galli, G. *Phys. Rev. Lett.* **2005**, *95*, 096801/1−096801/4.
(8) Gruen, D. M. *Annu. Rev. Mater. Sci.* **1999**, *29*, 211−259.
(9) Kuznetsov, V. L.; Chuvilin, A. L.; Moroz, E. M.; Kolomiichuk, V. N.; Shaikhutdinov, Sh. K.; Butenko, Yu. V.; Mal'kov, I. Y. *Carbon* **1994**, *32*, 873−882.
(10) Daulton, T. L.; Eisenhour, D. D.; Bernatowicz, T. J.; Lewis, R. S.; Buseck, P. R. *Geochim. Cosmochim. Acta* **1996**, *60*, 4853−4872. Chen, C.-F.; Wu, C.-C.; Cheng, C.-L.; Sheu, S.-Y.; Chang, H.-C. *J. Chem. Phys.* **2002**, *116*, 1211−1214.
(11) Liu, Y.; Gu, Z.; Margrave, J. L.; Khabashesku, V. N. *Chem. Mater.* **2004**, *16*, 3924−3930. Ando, T.; Tanaka, J.; Ishii, M.; Kamo, M.; Sato, Y.; Ohashi, N.; Shimosaki, S. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 3105−3109. Nichols, B. M.; Butler, J. E.; Russell, J. N., Jr.; Hamers, R. J. *J. Phys. Chem. B* **2005**, *109*, 20938−20947. Strother, T.; Knickerbocker, T.; Russell, J. N., Jr.; Butler, J. E.; Smith, L. M.; Hamers, R. J. *Langmuir* **2002**, *18*, 968−971.
(12) Olah, G. A. *The Chemistry of Cage Compounds*;, 1990. Fort, R. C. *Adamantane: The Chemistry of Diamondoid Molecules*; Dekker: New York, 1976. Schleyer, P. v. R. In *Cage Hydrocarbons*; Olah, G. A., Ed.; Wiley: New York, 1990; pp 1−38.
(13) Shen, M.; Schaefer, H. F., III; Liang, C.; Lii, J.-H.; Allinger, N. L.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1992**, *114*, 497−505.
(14) Schleyer, P. v. R. *J. Am. Chem. Soc.* **1957**, *79*, 3292.
(15) Cupas, C.; Schleyer, P. v. R.; Trecker, D. J. *J. Am. Chem. Soc.* **1965**, *87*, 917−918.
(16) Williams, V. Z., Jr.; Schleyer, P. v. R.; Gleicher, G. J.; Rodewald, L. B. *J. Am. Chem. Soc.* **1966**, *88*, 3862−3863. Hollowood, F. S.; McKervey, M. A.; Hamilton, R.; Rooney, J. J. *J. Org. Chem.* **1980**, *45*, 4954−4958.
(17) Burns, W.; Mitchell, T. R. B.; McKervey, M. A.; Rooney, J. J.; Ferguson, G.; Roberts, P. *J. Chem. Soc., Chem. Commun.* **1976**, 893−895.
(18) [1(2,3)4]Pentamantane is available from MolecularDiamond Technologies. For further information, see: http://www.chevron.com/moleculardiamond/.
(19) Dahl, J. E.; Liu, S. G.; Carlson, R. M. K. *Science* **2003**, *299*, 96−99.
(20) Dahl, J. E. P.; Moldowan, J. M.; Peakman, T. M.; Clardy, J. C.; Lobkovsky, E.; Olmstead, M. M.; May, P. W.; Davis, T. J.; Steeds, J. W.; Peters, K. E.; Pepper, A.; Ekuan, A.; Carlson, R. M. K. *Angew. Chem., Int. Ed.* **2003**, *42*, 2040−2044.
(21) Schreiner, P. R.; Fokina, N. A.; Tkachenko, B. A.; Hausmann, H.; Serafin, M.; Dahl, J. E. P.; Liu, S.; Carlson, R. M. K.; Fokin, A. A. *J. Org. Chem.* **2006**, *71*, 6709−6720.
(22) Chang, Y. K.; Hsieh, H. H.; Pong, W. F.; Tsai, M.-H.; Chien, F. Z.; Tseng, P. K.; Chen, L. C.; Wang, T. Y.; Chen, K. H.; Bhusari, D. M.; Yang, J. R.; Lin, S. T. *Phys. Rev. Lett.* **1999**, *82*, 5377−5380.
(23) Burns, W.; McKervey, M. A.; Mitchell, T. R. B.; Rooney, J. J. *J. Am. Chem. Soc.* **1978**, *100*, 906−911.

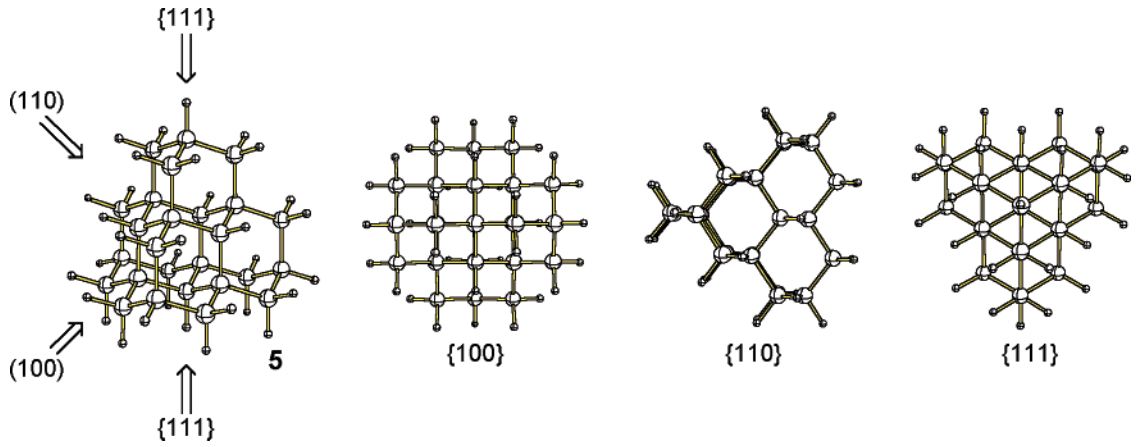


FIGURE 2. [1(2,3)4]Pentamantane (**5**) representing the C−H bonds of the hydrogen-terminated {110} and {111} faces of diamond.

attempted syntheses aimed at preparing **5**, Nature is the only viable source for higher diamondoids such as **5**.[19,20,24]

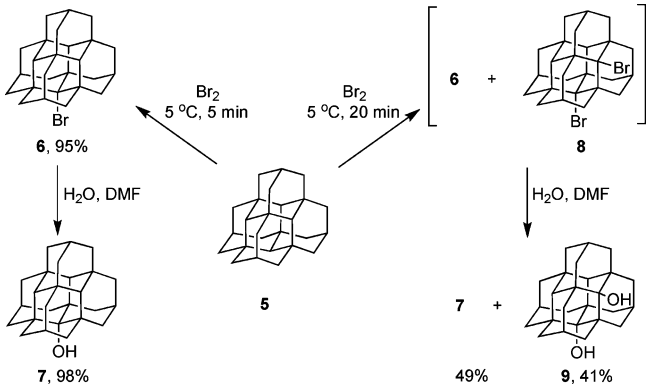
The selective functionalization of large diamondoids was considered to be extremely difficult because of the large number of similarly reactive C−H bonds. However, in our earlier assessment,[25] we predicted computationally and recently confirmed experimentally[21] that the *opposite* is true. For instance, the functionalizations of [121]tetramantane **4** are more selective than those of triamantane **3**.[21] Thus, the selectivities of the functionalizations of nanodiamonds are likely to increase with increasing size. The reactions of higher diamondoid **5**, which also displays a number of similarly reactive C−H bonds, are presented in the following.

Herein we describe a combined experimental/computational examination of the reactivities of nanodiamond **5** toward C−H activating reagents. This reveals the behavior of this unusual molecule in a variety of synthetic sequences for the first time. We show that selective C−H functionalizations can be achieved with various electrophilic, radical, and oxidative reagents leading to mono- and disubstituted products in high yields. Possible uses of functionalized nanodiamonds include not only traditional applications in pharmacology and material sciences, but also the construction of nanoelectronic devices, diamond growth on surfaces that requires a well-defined nucleation step,[26] design of nanoelectromechanical systems,[27] and many others.[28]

Results and Discussion

Hydrocarbon **5** displays a relatively low melting point[19] and, in contrast to **4**, high solubility in common organic solvents. We first tested the "classical" bromination, which is most widely used in the chemistry of cage compounds.[29] As **5** readily reacts with neat bromine at room temperature to produce polybromides, we reduced the amount of bromine and conducted the reaction

SCHEME 1. Bromination of [1(2,3)4]Pentamantane (5) with Subsequent Hydrolysis (All Yields Are Preparative)



in CH_2Cl_2 at 5 °C for short times. This gave the substitution product of the most sterically hindered tertiary C−H position (for numbering, see Figure 1), i.e., 2-bromo[1(2,3)4]pentamantane (**6**) in high preparative yield (Scheme 1). The bromination of **5** is kinetically controlled, as the medial bromide **6** is thermodynamically less stable ($\Delta\Delta G_{298} = 2.7$ kcal/mol, B3LYP/6-31G*) than its apical 7-isomer **12** (Figure 3, bottom).

The ^{1}H NMR spectrum of bromide **6** (Figure 3) is characterized by two double doublet-like signals at 2.22 and 1.16 ppm (six protons each), which could be assigned on the basis of HETCOR experiments for the nonequivalent methylene protons F and E, respectively. From the integral values and the correlations observed in the DQF-COSY spectrum the multiplet at 1.88 ppm is due to the methine protons D and that at 1.84 ppm corresponds to the methine proton A. The doublets at 1.41 and 1.31 ppm belong to the methylene hydrogens C and B, respectively. The methine hydrogens G appear as a singlet at 1.39 ppm.

The hydrolysis of **6** in DMF/H_2O at 90 °C gave 2-hydroxy-[1(2,3)4]pentamantane (**7**) selectively (Scheme 1). The X-ray crystal structure of **7** is shown in Figure 4. Despite the presence of hydroxy group in the structure the crystal packing of **7** is similar to that of hydrocarbon **5**,[19] in which the molecules are held together only through van der Waals forces. Thus, apparently due to steric hindrance, the OH groups do not interact in the crystal lattice of **7**.

Upon increasing the amount of bromine, 2,4-dibromo[1(2,3)4]-pentamantane (**8**) forms together with **6**. Hydrolysis of the reaction mixture followed by column chromatography gave pure

(24) Lin, R.; Wilk, Z. A. *Fuel* **1995**, *74*, 1512−1521.
(25) Fokin, A. A.; Tkachenko, B. A.; Gunchenko, P. A.; Gusev, D. V.; Schreiner, P. R. *Chem. Eur. J.* **2005**, *11*, 7091−7101.
(26) Lifshitz, Y.; Köhler, Th.; Frauenheim, Th.; Guzmann, I.; Hoffman, A.; Zhang, R. Q.; Zhou, X. T.; Lee, S. T. *Science* **2002**, *297*, 1531−1533.
(27) Auciello, O.; Birrell, J.; Carlisle, J. A.; Gerbi, J. E.; Xiao, X.; Peng, B.; Espinosa, H. D. *J. Phys.: Condens. Matter* **2004**, *16*, R539−R552.
(28) Zimmermann, T.; Kubovic, M.; Denisenko, A.; Janischowsky, K.; Williams, O. A.; Gruen, D. M.; Kohn, E. *Diam. Relat. Mater.* **2005**, *14*, 416−420. Sumant, A. V.; Grierson, D. S.; Gerbi, J. E.; Birrell, J.; Lanke, U. D.; Auciello, O.; Carlisle, J. A.; Carpick, R. W. *Adv. Mater.* **2005**, *17*, 1039−1045.
(29) Stetter, H.; Schwarz, M.; Hirschhorn, A. *Chem. Ber.* **1959**, *92*, 1629−1635.

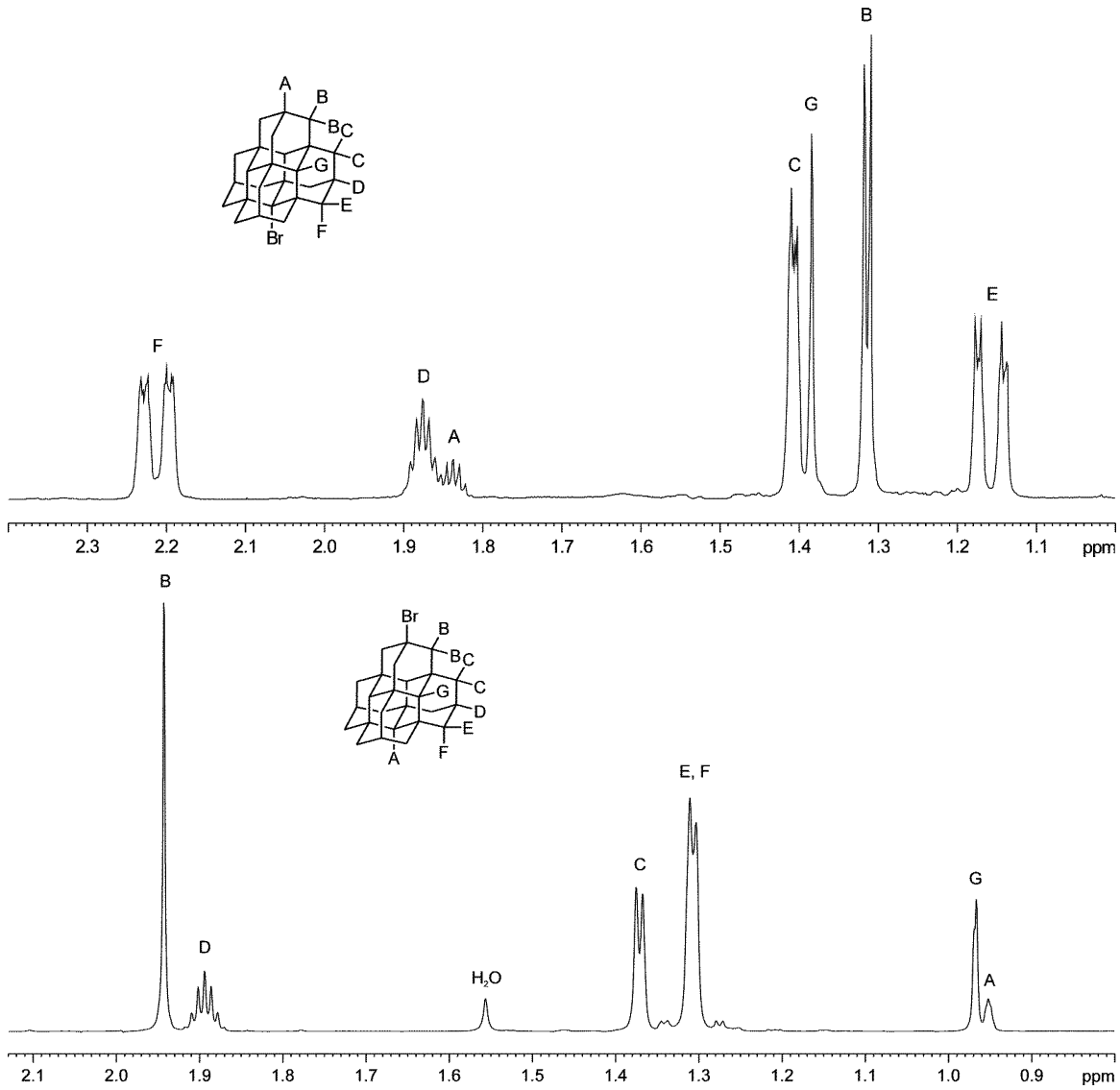


FIGURE 3. 400 MHz ^{1}H NMR spectra assignments for isomeric [1(2,3)4]pentamantyl bromides. Top, **6**, bottom, **12**.

2,4-dihydroxy derivative (**9**), whose C_{2v} structure was also confirmed by ^{13}C NMR.

In contrast to the bromination, the nitroxylation of **5** with 100% nitric acid, which was previously used for the oxidations of a variety of cage hydrocarbons,[30] followed by hydrolysis of the reaction mixture, gave 7-hydroxy[1(2,3)4]pentamantane (**10**) exclusively (Scheme 2). We were not able to isolate the hydrolytically unstable intermediate mononitrate **11** (vide infra) in this transformation. The exchange of the hydroxy group in **10** for bromine with $SOBr_2$/pyridine gave 7-bromo[1(2,3)4]-pentamantane (**12**), whose ^{1}H NMR spectrum is clearly different from that of 2-bromide **6** as it contains six well separated and easily assigned resonances (Figure 3). The singlet at 1.94 ppm is assigned to the methylene hydrogens B. The multiplet at 1.89 ppm belongs to the methine hydrogens D and the doublet at 1.37 to the methylene groups C. The protons F and E of the methylene groups are observed as a partially resolved AB-system in the 1.30−1.32 ppm region. The high-field singlets of nonequivalent protons G and A appear at 0.97 and 0.95 ppm, respectively; G and A in the bottom spectrum appear broadened, i.e., G and A show "w" couplings. The complete ^{1}H assignments of the CH and CH_2 hydrogens were verified by an analysis of the connectivities in the COSY spectrum and the HSQC correlation peaks.

Increasing the amount of HNO_3 gave dinitroxy derivative **13**, which is stable enough to be isolated and characterized. In addition to NMR spectral data for **13**, the characteristic bands of the ONO_2 group vibrations were observed in the IR spectrum (see the Experimental Section). Hydrolysis of **13** gave 7,11-dihydroxy[1(2,3)4]pentamantane (**14**) and 7,11-dibromide (**15**) after the reaction of **14** with $SOBr_2$/pyridine. Thus, we have found preparative methods for the selective mono- as well as disubstitutions of the medial and apical C−H bonds of **5**. This paves the way for the preparation of numerous pentamantane derivatives because the C−H functionalizations are more

(30) Moiseev, I. K.; Belyaev, P. G.; Barabanova, N. V.; Bardyug, O. P.; Vishnevskii, E. H.; Novatskaya, N. I.; Golod, E. L.; Gidaspov, B. V. *Zh. Org. Khim.* **1975**, *11*, 214−215. Schreiner, P. R.; Fokin, A. A. Patent Application 10 2005 058 357.1, 2005.

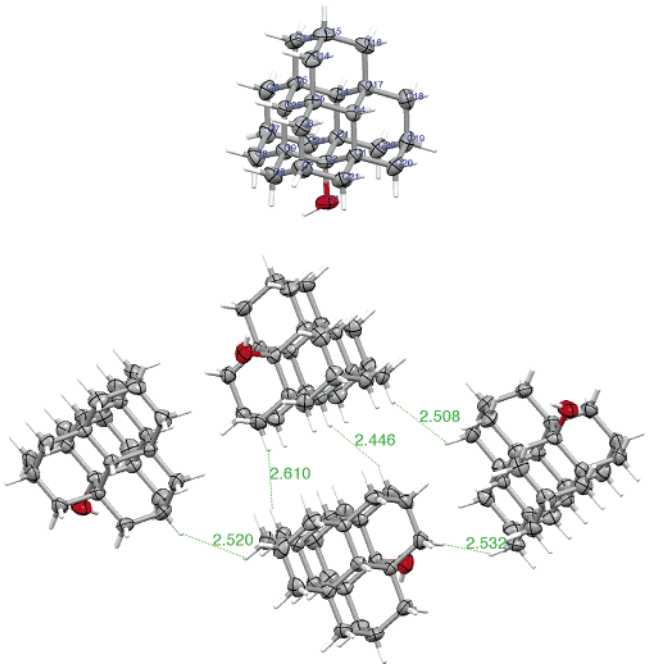


FIGURE 4. X-ray structure of 2-hydroxy[1(2,3)4]pentamantane (**7**) and its packing in the crystal.

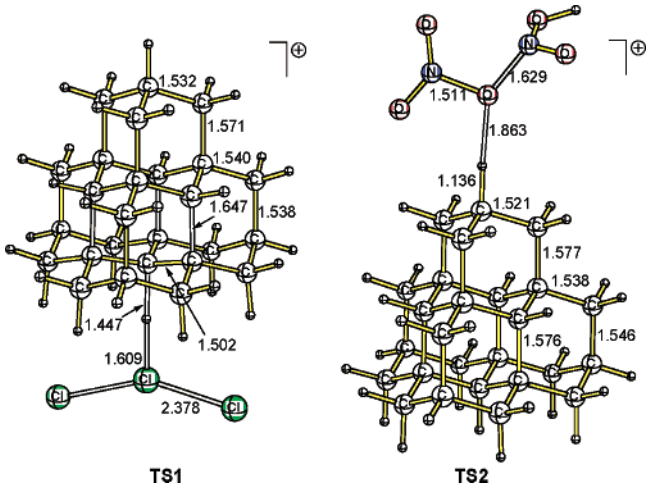


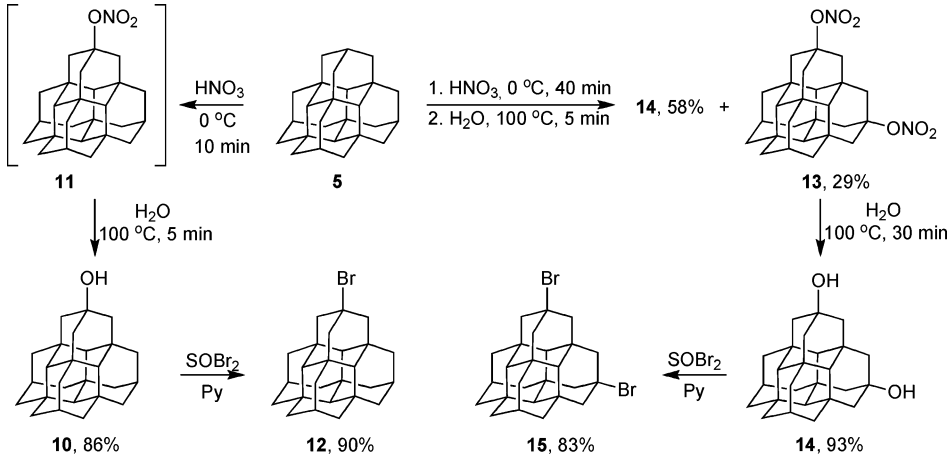
FIGURE 5. H-coupled electron-transfer transition structures for the halogenation of the C^2-H (**TS1**) and nitroxylation of the C^7-H (**TS2**) bonds of [1(2,3)4]pentamantane (**5**) with the model electrophiles—oxidizers Cl_3^+ and $(NO_2\cdots HNO_3)^+$, respectively (B3LYP/6-31G*, bond distances in Å).

difficult in diamondoid chemistry than subsequent functional group exchanges.

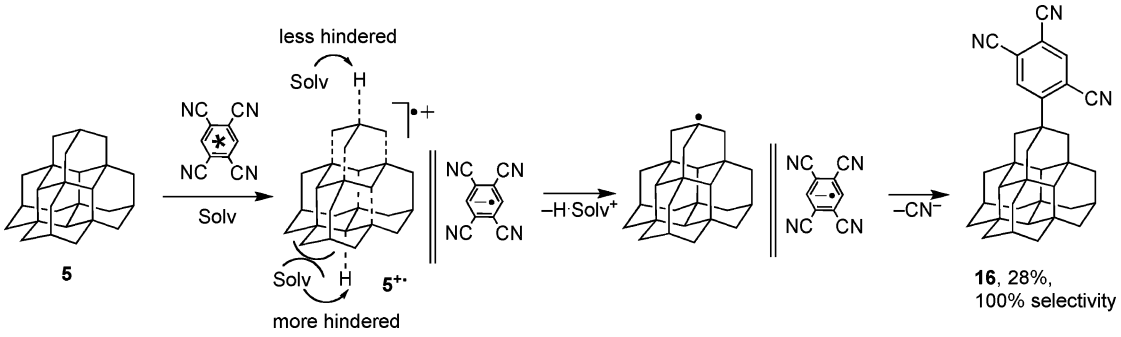
It is rather unusual that entirely different positional selectivities in the reactions of **5** with bromine and 100% HNO_3 were observed. For hydrocarbons **2**−**4** previously we found an increase in the apical substitution products with HNO_3 relative to Br_2.[21] To the best of our knowledge, however, **5** represents the first example for which the nitroxylation and bromination reactions show *inverse* selectivities. We had previously suggested that the halogenations of saturated hydrocarbons occur through hydrogen abstractions by positively polarized halogens through highly polarized transition structures (H-coupled electron transfer, ET).[31] In accordance to previous computations[25] the tertiary carbocation in the 2-position (medial) of **5** with the positive charge located closer to the geometrical center of the molecule is 0.9 kcal/mol (ΔG^{298}, B3LYP/6-31G*) more stable than the one at the apical 7-position (for numbering see Figure 1). Since the transition structures for H-coupled ET halogenations are carbocation-like, the polarization of the cage through the medial C^2-H position is more favorable than that through the apical position C^7-H. The transition structure **TS1** ($\Delta G_{298}^{\ddagger}$ = 9.5 kcal/mol, B3LYP/6-31G*) for the hydrogen abstraction with model electrophile[32] Cl_3^+ from the C^2-H position from the pentamantane cage is shown in Figure 5. As the crucial C^2-H distance in **TS1** is quite long (1.447 Å), the hydrocarbon cage, to a large extent, resembles the structure of the carbocation. Therefore, steric factors affect the direct halogenation only slightly.

The transition structures for the reaction of **5** with HNO_3 (modeled with the $NO_2^+\cdots HNO_3$ complex)[25] are earlier than those for the reaction with positively polarized halogens. We found that **TS2** ($\Delta G_{298}^{\ddagger}$ = 20.6 kcal/mol, B3LYP/6-31G*) describes the H-abstraction for the pentamantane C^7-H position (Figure 5), whereas the transition structure **(**see the Supporting Information) for the C^2-H position displays the migration of the reagent from one H-bonding position to another in the cluster. These results show that the hydrogen abstraction with halogens is more sensitive to electronic effects, whereas the activation with HNO_3 is largely sterically controlled. This is

SCHEME 2. Oxidations of [1(2,3)4]Pentamantane (5) with 100% Nitric Acid, Subsequent Hydrolysis, and Brominations (All Yields Are Preparative)



SCHEME 3. Single-Electron Oxidation of [1(2,3)4]Pentamantane (5)



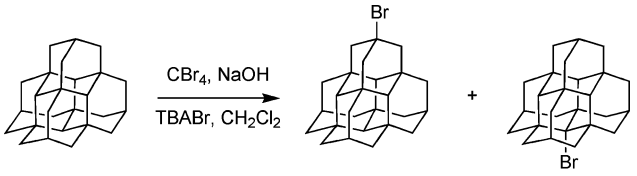
the reason halogenation of **5** gives medial derivatives, while nitroxylation results in apical substitution. It should be pointed out that we did not find any secondary C−H substitution products with these reagents. This is typical for diamondoids in the reactions with electrophiles−oxidizers for which H-coupled transfer to the electrophile-oxidizers through the tertiary C−H positions dominates.[21,25] This is in marked contrast to free-radical substitutions that give substantial amounts of CH_2-substitution products.[33]

As we have shown previously,[31,34−36] the transition structures for the reactions with oxidizing electrophiles are characteristic for inner-sphere ET and thus resemble the structures of the respective hydrocarbon radical cations.[34,35,37,38] Since Jahn−Teller-active[39] [1(2,3)4]pentamantane **5** distorts upon single ET ionization to the C_{3v}-form $\mathbf{5}^{\bullet+}$ (Scheme 3),[25] with two axial tertiary C−H bonds in hyperconjugation with parallel C−C bonds, it is not surprising that two different substitution products form in reactions with electrophiles−oxidizers.

Photoexcited 1,2,4,5-tetracyanobenzene (TCB) is among the most powerful organic single electron acceptors and is often used[21,38,40] for the generation of hydrocarbon radical cations via an outer sphere ET. Oxidation of **5** with TCB in acetonitrile gave a single oxidation product **16** with the aromatic substituent at the apical position of the cage. To avoid overoxidation, we performed this reaction at ca. 30% conversion and did not detect other isomers of **16** in the NMR spectrum of the reaction mixture. Thus, proton loss from the radical cation to the solvent occurs exclusively from the sterically less hindered position of the [1(2,3)4]pentamantane radical cation $\mathbf{5}^{\bullet+}$ (Scheme 3). The unique structure of the radical cation $\mathbf{5}^{\bullet+}$ determines the reactivity of **5** with ET acceptors.

As we suggested earlier,[25] the free-radical functionalizations of diamondoids are not expected to be very selective because the differences in the C−H bond energies in diamondoids vary only within 1−2 kcal/mol.[41,42] For instance, the energies of the 1- and 2-adamantyl radicals are virtually identical,[42] and the same is true for all isomeric radicals derived from **5**. However, because the hydrogen abstractions with radicals[35] are mostly sterically controlled, we used tertiary carbon-centered radicals (e.g., $Br_3C^{\bullet}$) for the C−H substitutions of **5**.

SCHEME 4. Bromination of [1(2,3)4]Pentamantane (5) under Phase-Transfer-Catalytic-Conditions (TBABr = Tetra-*n*-butylammonium Bromide)



For the generation of $Br_3C^{\bullet}$ we employed our phase-transfer catalytic (PTC) protocol, previously used for the C−H halogenations of various hydrocarbons.[43] The PTC bromination of **5** with CBr_4 in the $NaOH/H_2O/CH_2Cl_2$/TBABr system predominantly gave the C^7-bromide **12** (Scheme 4). The substitution mostly occurs at the sterically less hindered apical position of **5**, and it shows an inverse selectivity relative to the reaction with neat bromine (vide supra). Substantial steric hindrance at the 2-position of **5** is seen from the geometries of the respective transition structures (**TS5** and **TS6**, Figure 6): The crucial Br···H···C distances as well as intramolecular Br···H contacts vary substantially. These interactions decrease the barrier for **TS5**, which is 5.1 kcal/mol ($\Delta\Delta G_{298}$, B3LYP/6-31G*) lower than that of **TS6**.

(31) Fokin, A. A.; Shubina, T. E.; Gunchenko, P. A.; Isaev, S. D.; Yurchenko, A. G.; Schreiner, P. R. *J. Am. Chem. Soc.* **2002**, *124*, 10718−10727.
(32) Cacace, F.; de Petris, G.; Pepi, F.; Rosi, M.; Troiani, A. *Chem. Eur. J.* **1999**, *5*, 2750−2756.
(33) Fokin, A. A.; Schreiner, P. R. *Adv. Synth. Catal.* **2003**, *345*, 1035−1052.
(34) Schreiner, P. R.; Fokin, A. A. *Chem. Rec.* **2004**, *3*, 247−257.
(35) Fokin, A. A.; Schreiner, P. R. *Chem. Rev.* **2002**, *102*, 1551−1593.
(36) Schreiner, P. R.; Fokin, A. A.; Schleyer, P. v. R.; Schaefer H. F., III. In *Fundamental World in Quantum Chemistry*; Kryachko, E., Ed.; Kluwer Academic Publishers: Dordrecht, 2003; Vol. II, pp 349−375.
(37) Fokin, A. A.; Gunchenko, P. A.; Peleshanko, S. A.; Schleyer, P. v. R.; Schreiner, P. R. *Eur. J. Org. Chem.* **1999**, 855−860. Fokin, A. A.; Schreiner, P. R.; Gunchenko, P. A.; Peleshanko, S. A.; Shubina, T. E.; Isaev, S. D.; Tarasenko, P. V.; Kulik, N. I.; Schiebel, H.-M.; Yurchenko, A. G. *J. Am. Chem. Soc.* **2000**, *122*, 7317−7326. Shubina, T. E.; Gunchenko, P. A.; Yurchenko, A. G.; Schreiner, P. R.; Butova, E. D.; Fokin, A. A. *Theor. Exp. Chem.* **2002**, *38*, 8−14.
(38) Fokin, A. A.; Tkachenko, B. A.; Shubina, T. E.; Gunchenko, P. A.; Gusev, D. V.; Vohs, J. K.; Robinson, G. H.; Yurchenko, A. G.; Schreiner, P. R. *Eur. J. Org. Chem.* **2002**, 3844−3849.
(39) Bersuker, I. B. *Chem. Rev.* **2001**, *101*, 1067−1114.
(40) Mella, M.; Freccero, M.; Albini, A. *Tetrahedron* **1996**, *52*, 5533−5548. Mella, M.; Freccero, M.; Soldi, T.; Fasani, E.; Albini, A. *J. Org. Chem.* **1996**, *61*, 1413−1422.
(41) Kruppa, G. H.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1986**, *108*, 2162−2169.
(42) Aubry, C.; Holmes, J. L.; Walton, J. C. *J. Phys. Chem. A* **1998**, *102*, 1389−1393.
(43) Schreiner, P. R.; Lauenstein, O.; Butova, E. D.; Fokin, A. A. *Angew. Chem., Int. Ed.* **1999**, *38*, 2786−2788. Lauenstein, O.; Fokin, A. A.; Schreiner, P. R. *Org. Lett.* **2000**, *2*, 2201−2204. Fokin, A. A.; Lauenstein, O.; Gunchenko, P. A.; Schreiner, P. R. *J. Am. Chem. Soc.* **2001**, *123*, 1842−1847. Schreiner, P. R.; Lauenstein, O.; Butova, E. D.; Gunchenko, P. A.; Kolomitsin, I. V.; Wittkopp, A.; Feder, G.; Fokin, A. A. *Chem. Eur. J.* **2001**, *7*, 4996−5003.

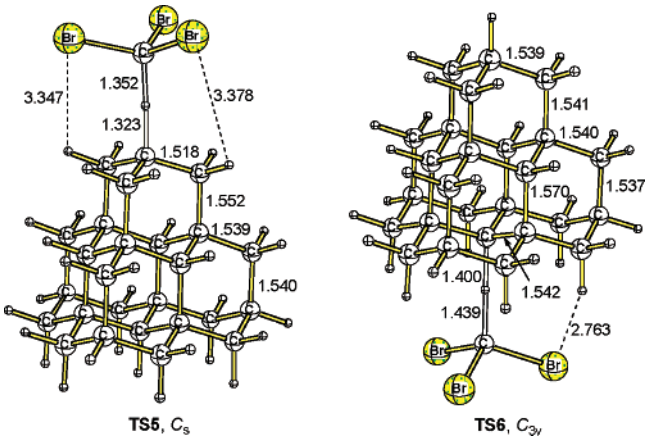
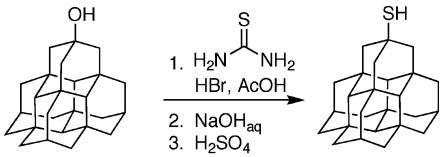


FIGURE 6. Transition structures for the H-abstraction from the C^7-(**TS5**) and C^2-(**TS6**) positions of [1(2,3)4]pentamantane (**5**) with the CBr_3-radical (B3LYP/6-31G*; selected bond distances in Å).

SCHEME 5. Thiolation of 7-Hydroxy[1(2,3)4]pentamantane (10)



Further development of pentamantane chemistry may follow several directions. One of these is the preparation of hydrocarbon self-assembled monolayers (SAMs)[44] on gold surfaces, which may facilitate the nucleation step in preparations of CVD diamond films.[1] Recently, the deposition of adamantyl-1-thiol on gold surfaces resulted in highly ordered hexagonally close-packed layer structures.[45] Further improvements of this strategy may be made by the deposition of higher diamondoid thiols prepared recently by us.[46] Owing to their high symmetry, thiols derived from [1(2,3)4]pentamantane are particularly attractive. While the preparation of tertiary thiols is usually quite difficult, our recently developed protocol[46] also allows the preparation of [1(2,3)4]pentamantyl-7-thiol (**17**) from 7-hydroxy-[1(2,3)4]pentamantane (**10**) in 38% preparative yield (Scheme 5).

Conclusions

The higher diamondoid [1(2,3)4]pentamantane (**5**), the smallest structural model of macroscopic diamond, readily reacts with electrophiles and these reactions are more selective than for triamantane and [121]tetramantane. This is in line with our earlier observations that the functionalization selectivities *increase* when going from lower to higher diamondoids. Both the 2- as well as the 7-derivatives of **5** can be prepared selectively using different electrophilic and/or oxidizing reagents. Based on these findings, one can envisage that the selective functionalizations of the C−H bonds on the hydrogen-terminated {111} nanodiamond surfaces also may be achieved under mild reaction conditions with strong electrophiles−oxidizers.

Experimental Section

Bromination of [1(2,3)4]Pentamantane (5) and Hydrolysis of 2-Bromo[1(2,3)4]pentamantane (6). To a stirred mixture (0 °C) of 30 mg (0.09 mmol) of [1(2,3)4]pentamantane (**5**) and 0.02 mL of $CHCl_3$, 0.1 mL (0.31 g, 1.9 mmol) of bromine was added in one portion. The reaction mixture was stirred for 5 min at 5 °C, quenched with saturated $NaHSO_3$ solution, and extracted with 4 × 1 mL of chloroform. The combined extracts were washed with brine, dried over Na_2SO_4, and evaporated to give 33 mg (95%) of 2-bromo[1(2,3)4]pentamantane (**6**) as a colorless solid: mp > 310 °C dec; ^{1}H NMR 2.22 (dd, $^2J \approx 14$ Hz, $^3J \approx 3$ Hz, 6H), 1.88 (m, 3H), 1.84 (m, 1H), 1.41 (m, 6H), 1.39 (s, 3H), 1.31 (d, $^3J \approx 3$ Hz, 6H), 1.16 (dd, $^2J \approx 14$ Hz, $^3J \approx 3$ Hz, 6H); ^{13}C NMR 58.0 (CH), 46.7 (CH_2), 44.1 (CH_2), 41.5 (CH_2), 39.8 (C), 32.9 (C), 28.0 (CH), 27.1 (CH); MS (*m*/*z*) 343 (100), 203 (2), 181 (5), 171 (19), 141 (7), 129 (4), 91 (13), 79 (9), 55 (4); HR-MS (*m*/*z*) found 421.1528, calcd for $C_{26}H_{31}Br$ 422.1609.

A mixture of 32 mg of 2-bromo[1(2,3)4]pentamantane (**6**), 0.6 mL of dimethylformamide, and 0.2 mL of water was heated at 90 °C under stirring for 5 h. The solvents were evaporated in vacuo. The residue was purified by column chromatography on silica gel (pentane/ether 3:1) giving 26 mg (98%) of 2-hydroxy[1(2,3)4]-pentamantane (**7**) as a colorless solid: mp > 310 °C dec; ^{1}H NMR 1.87−1.85 m (4H), 1.82 (dd, $^2J \approx 14$ Hz, $^3J \approx 3$ Hz, 6H), 1.44 bs (1H), 1.36 m (6H), 1.32 (d, $^3J \approx 3$ Hz, 6H), 1.21 (s, 3H), 1.03 (dd, $^2J \approx 14$ Hz, $^3J \approx 3$ Hz, 6H); ^{13}C NMR 75.5 (C), 57.6 (CH), 45.3 (CH_2), 44.6 (CH_2), 39.4 (CH_2), 36.0 (C), 32.8 (C), 28.2 (CH), 28.1 (CH); MS (*m*/*z*) 360 (32), 342 (100), 299 (2), 249 (3), 193 (4), 181 (7), 179 (7), 171 (58), 150 (15), 129 (9), 91 (7); HR-MS (*m*/*z*) found 360.2423, calcd for $C_{26}H_{32}O$ 360.2453.

Dibromination of [1(2,3)4]Pentamantane (5) Followed by Hydrolysis. Bromine (0.25 mL, 0.62 g, 3.8 mmol) was added in one portion to a stirred mixture (0 °C) of 60 mg (0.18 mmol) of [1(2,3)4]pentamantane (**5**) and 0.04 mL of $CHCl_3$. The reaction mixture was stirred for 20 min at 5 °C, quenched with saturated $NaHSO_3$ solution, and extracted with chloroform (4 × 2 mL). Combined extracts were washed with brine, dried over Na_2SO_4, and evaporated. Dimethylformamide (1.8 mL) and water (0.6 mL) were added to the residue, and the reaction mixture was heated at 90 °C under stirring for 5 h. After evaporation in vacuo, the residue was purified by column chromatography on silica gel (pentane/ether 3:1) to give 31 mg (49%) of 2-hydroxy[1(2,3)4]pentamantane (**7**). Changing the eluent for ether/ethyl acetate (1:1) gave 27 mg (41%) of 2,4-dihydroxy[1(2,3)4]pentamantane (**9**) as a colorless solid: mp > 310 °C dec; ^{1}H NMR 1.81 (m, 12H), 1.59 (m, 2H), 1.54 (m, 4H), 1.35 (m, 6H), 1.07 (m, 2H), 1.04 (m, 2H), 1.03 (m, 2H), 1.00 (m, 2H); ^{13}C NMR 76.4 (C), 58.9 (CH), 45.0 (CH_2), 40.1 (C), 39.4 (CH_2), 39.2 (CH_2), 36.0 (C), 33.0 (CH_2), 32.6 (C), 27.8 (CH), 27.6 (CH); MS (*m*/*z*) 376 (28), 358 (100), 329 (2), 217 (1), 193 (2), 179 (8), 141 (4), 128 (3), 91 (5); HR-MS (*m*/*z*) found 376.2398, calcd for $C_{26}H_{32}O_2$ 376.2402.

Hydroxylation of [1(2,3)4]Pentamantane (5) with Nitric Acid. Nitric acid (100%, 0.03 mL, 0.7 mmol) was added in one portion to a stirred (0 °C) mixture of 30 mg (0.09 mmol) of [1(2,3)4]-pentamantane (**5**) and 0.4 mL of CH_2Cl_2. The reaction mixture was stirred for 10 min at 0 °C and quenched with 2 mL of 30% HNO_3. CH_2Cl_2 was distilled off, and the reaction mixture was refluxed for 5 min. Nitric acid was evaporated in vacuo, and the residue was separated by column chromatography on silica gel (pentane/ether 3:1) to give 27 mg (86%) of 7-hydroxy[1(2,3)4]pentamantane (**10**) as a colorless solid: mp > 310 °C dec; ^{1}H NMR 1.82 (m,

(44) Ulman, A. *Chem. Rev.* **1996**, *96*, 1533−1554.
(45) Dameron, A. A.; Charles, L. F.; Weiss, P. S. *J. Am. Chem. Soc.* **2005**, *127*, 8697−8704.
(46) Tkachenko, B. A.; Fokina, N. A.; Chernish, L. V.; Dahl, J. E. P.; Liu, S.; Carlson, R. M. K.; Fokin, A. A.; Schreiner, P. R. *Org. Lett.* **2006**, *8*, 1767−1770.

3H), 1.31 (d, $J = 3$ Hz, 6H), 1.23 (m, 12H), 1.23 (m, 6H), 0.88 (m, 1H), 0.79 (d, $^4J = 1.4$ Hz, 3H); ^{13}C NMR: 68.1 (C), 53.3 (CH), 52.4 (CH), 52.1 (CH_2), 44.8 (CH_2), 44.5 (CH_2), 36.3 (C), 33.1(C), 28.4 (CH); MS (*m*/*z*) 360 (100), 343 (30), 209 (1), 193 (2), 180 (7), 153 (4), 128 (2), 105 (2), 91 (4); HR-MS (*m*/*z*) found 360.2479, calcd for $C_{26}H_{32}O$ 360.2453.

Dihydroxylation of [1(2,3)4]Pentamantane (5) with Nitric Acid. Nitric acid (100%, 0.08 mL, 1.9 mmol) was added in one portion to a stirred (0 °C) mixture of 50 mg (0.14 mmol) of [1(2,3)4]-pentamantane (**5**) and 0.3 mL of CH_2Cl_2. The reaction mixture was stirred for 40 min at 0 °C and quenched with 0.7 mL of 30% HNO_3, CH_2Cl_2 was distilled off, and the reaction mixture was refluxed for 5 min. Nitric acid was evaporated in vacuo at a temperature lower than 40 °C, and column chromatography of the residue on silica gel (pentane/ether 3:1) gave 20 mg (29%) of 7,11-dinitroxy-[1(2,3)4]pentamantane (**13**): ^{1}H NMR 1.99 (m, 2H), 1.84 (s, 4H), 1.76 (s, 8H), 1.46 (m, 8H), 1.36 (d, $J = 4$ Hz, 4H), 1.02 (s, 4H); ^{13}C NMR 88.6 (C), 51.5 (CH), 50.8 (CH), 45.8 (CH_2), 45.5 (CH_2), 43.9 (CH_2), 43.7 (CH_2), 40.3 (C), 36.7 (C), 33.3 (C), 28.0 (CH); IR (cm^{-1}) 2907−2845 (ν_{CH}), 1618 (ν_{NO}), 1291 (ν_{NO}), 864 (δ_{NO2}). Separately, 32 mg (58%) of 7,11-dihydroxy[1(2,3)4]pentamantane (**14**) was obtained (ether/ethyl acetate 1:1): mp > 310 °C dec; ^{1}H NMR 1.92 (m, 2H), 1.51 (m, 6H), 1.39 (m, 10H), 1.33 (m, 10H), 0.88 (s, 2H), 0.81 (s, 2H); ^{13}C NMR 68.1 (C), 52.0 (CH), 51.9 (CH_2), 51.7 (CH_2), 51.1 (CH), 44.5 (CH_2), 44.1 (CH_2), 36.2 (C), 33.0 (C), 30.1 (C), 28.2 (CH); MS (*m*/*z*) 376 (100), 359 (45), 195 (2), 188 (6), 152 (3), 128 (2), 105 (3), 91 (4); HR-MS (*m*/*z*) found 376.2418, calcd for $C_{26}H_{32}O_2$ 376.2402. 7,11-Dinitroxy[1(2,3)4]-pentamantane (**13**) was refluxed with 30% nitric acid for 30 min, and after evaporation of the solvent, pure 7,11-dihydroxy[1(2,3)4]-pentamantane (**14**) was obtained in 93% yield.

7-Bromo[1(2,3)4]pentamantane (12). To a mixture of 20 mg (0.06 mmol) of 7-hydroxy[1(2,3)4]pentamantane (**10**), 2 mL of CH_2Cl_2, and 0.05 mL (0.64 mmol) pyridine was added $SOBr_2$ (0.05 mL, 0.64 mmol) at 0 °C under stirring. The reaction mixture was stirred at room temperature for 3 h, quenched with water, and extracted with chloroform (3 × 2 mL). The combined extracts were washed with water (1.5 mL), 3% HCl (1 mL), and brine (1 mL) and dried over Na_2SO_4. The residue after evaporation of the solvents was filtered through the silica gel (pentane) to give 22 mg (90%) of 7-bromo[1(2,3)4]pentamantane (**12**): mp = 222−225 °C; ^{1}H NMR 1.94 (s, 6H), 1.89 (m, 3H), 1.37 (d, $^3J = 3$ Hz, 6H), 1.30 (d, 12H), 0.97 (bs, 3H), 0.95 (bs, $^4J = 1$ Hz, 1H); ^{13}C NMR 65.4 (C), 55.9 (CH_2), 53.0 (CH), 51.9 (CH), 44.5 (CH_2), 44.1 (CH_2), 38.2 (C), 33.1(C), 28.4 (CH); MS (*m*/*z*) 421 (<1), 378 (<1), 360 (1), 343 (100), 179 (1), 171 (5), 150 (1), 141 (1), 115 (1), 91 (2); HR-MS (*m*/*z*) found 422.1555, calcd for $C_{26}H_{31}Br$ 422.1609.

7,11-Dibromo[1(2,3)4]pentamantane (15). A solution of 10 mg (0.03 mmol) of 7,11-dihydroxy[1(2,3)4]pentamantane (**14**) in 2 mL of CH_2Cl_2 was treated as above with 0.05 mL of bromine to give 11 mg (83%) of 7,11-dibromo[1(2,3)4]pentamantane (**15**) as a colorless solid: mp = 233−234 °C; ^{1}H NMR 1.99 (s, 4H), 1.95 (s, 10H), 1.39 (m, 8H), 1.32 (d, $J = 4$ Hz, 4H), 1.01 (s, 2H), 0.99 (m, 2H); ^{13}C NMR 63.2 (C), 55.4 (CH_2), 54.8 (CH_2), 51.2 (CH), 50.1 (CH), 44.0 (CH_2), 43.6 (CH_2), 42.6 (C), 38.0 (C), 33.3 (C), 28.1 (CH); HR-MS (*m*/*z*) found 500.0678, calcd for $C_{26}H_{30}Br_2$ 500.0714.

Photooxidation of [1(2,3)4]Pentamantane (5) with TCB. A solution of 30 mg (0.09 mmol) of [1(2,3)4]pentamantane (**5**) and 36 mg (0.11 mmol) of 1,2,4,5-tetracyanobenzene in 45 mL of CH_3CN was irradiated with a low-pressure 300 W Hg lamp for 15 min under argon. The reaction mixture was evaporated. Column chromatography of the residue on silica gel (cyclohexane) gave 18 mg of unreacted **5**; changing the eluent for cyclohexane/EtOAc (10:1.5) gave 12 mg (28%) of a slightly brownish product, which after recrystallization from hexane gave 7-(2,4,5-tricyanobenzyl[1(2,3)4]-pentamantane (**16**) as a colorless solid: mp = 257−259 °C (dec); ^{1}H NMR 8.03 (s, 1H), 7.85 (s, 1H), 1.95 (m, 3H), 1.71 (s, 6H), 1.42 (d, $J \approx 3$ Hz, 6H), 1.37 (m, 6H), 1.27 (m, 6H), 1.03 (bs, 3H), 0.96 (bs, 1H); ^{13}C NMR 159.6 (C), 139.5 (CH), 132.3 (CH), 119.3 (C), 116.7 (C), 115.9 (C), 114.5 (C), 113.8 (C), 113.7 (C), 53.1 (C), 52.3 (CH), 47.5 (CH_2), 44.5 (CH_2), 44.4 (CH_2), 34.0 (C), 32.8 (C), 28.0 (CH), 27.6 (CH); HR-MS (*m*/*z*) found 495.2670, calcd for $C_{35}H_{33}N_3$ 495.2674.

Halogenation of [1(2,3)4]Pentamantane (5) under Phase-Transfer Catalytic Conditions. A mixture of 14 mg (0.04 mmol) of [1(2,3)4]pentamantane (**5**), 60 mg (0.19 mmol) of CBr_4, 0.3 mL of CH_2Cl_2, 0.3 mL of 50% aqueous NaOH, and 1 mg of tetra-*n*-butylammonium bromide was stirred at room temperature for 23 h. The reaction mixture was evaporated in a vacuum (0.05 mm) at 30 °C. The residue, which in accordance with 400 MHz ^{1}H NMR spectra contained 7-bromo[1(2,3)4]pentamantane (**12**) and unreacted **5**, was stirred with 2.4 mL of dimethylformamide and 0.8 mL of water at 90 °C for 3 h. The reaction mixture was evaporated, and the residue was separated by column chromatography on silica gel (pentane) to give 4 mg of unreacted **5**. Separately, 8 mg (55%) of a mixture (GC/MS and NMR) of 95% of 7-hydroxy[1(2,3)4]-pentamantane (**10**) and 5% of 2-hydroxy[1(2,3)4]pentamantane (**7**) was obtained (pentane/ether 3:1).

[1(2,3)4]Pentamantanyl-7-thiol (17). To a stirred solution of thiourea (633 mg, 8.321 mmol) in glacial acetic acid (2.8 mL) and 48% aqueous HBr (1.4 mL) was added 7-hydroxy[1(2,3)4]-pentamantane (**10**) (20 mg, 0.056 mmol). The mixture was refluxed under argon for 3 h. The hot reaction mixture was poured in small portions into a cold (ice bath) 15% aqueous NaOH solution (16 mL) and was stirred for 2 h at room temperature. The resultant mixture was cooled (ice bath) and acidified with 50% aqueous H_2SO_4 to pH ≈ 2−3 maintaining the temperature below 10 °C. The crude product was extracted with chloroform (4 × 4 mL), and the combined extracts were washed with aqueous $NaHCO_3$, and brine and dried over Na_2SO_4. Solvent removal gave the crude thiol which was purified by column chromatography on silica gel (CCl_4) to give 8 mg (38%) of [1(2,3)4]pentamantane-7-thiol (**17**): mp = 199−202 °C; ^{1}H NMR 1.88 (m, 3H), 1.63 (s, 1H), 1.50 (s, 6H), 1.33 (d, $J = 2.9$ Hz, 6H), 1.30 (d, $J = 2.9$ Hz, 12H), 0.95 (s, 1H), 0.89 (s, 3H); ^{13}C NMR 54.5 (CH_2), 53.2 (CH), 52.1 (CH), 44.7 (CH_2), 44.3 (CH_2), 42.8 (C), 35.4 (C), 32.8 (C), 28.3 (CH); MS (*m*/*z*) 376 (2), 375 (3), 360 (2), 343 (100), 171 (8), 165 (2), 150 (2), 143 (2), 105 (2), 91 (2); HR-MS (*m*/*z*) found 376.2195, calcd for $C_{26}H_{32}S$ 376.2225.

Computational Methods. Becke's gradient-corrected exchange functional[47] in conjunction with the Lee−Yang−Parr nonlocal correlation functional (B3LYP)[48] and a 6-31G(d) basis set as implemented in Gaussian03 was utilized for all optimizations.[49] All

(47) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098−3100.
(48) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785−789.
(49) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. Gaussian, B.03 ed., Gaussian, Pittsburgh, 2003.

structures were characterized as stationary points by means of determining harmonic vibrational frequencies (with zero imaginary frequencies for minima and one imaginary frequency for transition structures).

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Supporting Information Available: Absolute energies and *xyz*-coordinates of all computed species and ^{13}C NMR spectra of all [1(2,3)4]pentamantane derivatives. This material is available free of charge via the Internet at http://pubs.acs.org.

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