Structure Elucidation

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# [2](1,3)Adamantano[2](2,7)pyrenophane: A Hydrocarbon with a Large Dipole Moment

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***Abstract:*** *The fusion of the $sp^3$-hybridized parent diamondoid adamantane with the $sp^2$-hybridized pyrene results in a hybrid structure with a very large dipole moment which arises from bending the pyrene moiety. Presented herein is the synthesis, study of the electronic and optical properties, as well as the dynamic behavior of this new hydrocarbon.*

Owing to its electrochemical properties and chemical resistivity, diamond has found, inter alia, application as an electrode,[1] and it is also an excellent electron emitter because of its negative electron affinity (NEA).[2] However, after thermal treatment of natural diamond, $C(sp^2)$–$C(sp^2)$ bonds ("graphitic islands") tend to form in the absence of hydrogen, thus leading to electrical conduction.[2e] The question whether the electrical conduction occurs only within the $sp^2$ system or in combination with the $sp^3$ system is difficult to answer because of a large variety of different $sp^2$ sites,[3] as well as functionality on the diamond surface and inner defects. Hence, it is useful to study diamond's nanometer-sized congeners, the diamondoids, which comprise well-defined hydrogen-terminated nanodiamonds.[4] These fit perfectly into the diamond lattice and can be selectively functionalized,[4,5] thereby providing access to tailored diamondoid building blocks. Indeed, self-assembled monolayers of thiolated diamondoids[6] share diamond's NEA properties.[7] The combination of diamondoids with fullerenes produces a hydrocarbon rectifier (**1**; Figure 1) owing to the electron-acceptor and electron-donor abilities of the fullerene and diamondoid moieties, respectively.[8]

One limitation with the use of **1** as a self-assembled diode material is that there is too much mobility on the metal surface because of the ball-shaped fullerene, which only has a small contact area to the metal. Additionally, the connecting cyclohexenyl bridge slowly undergoes retro-Diels–Alder reaction. The dipole moment vector is also off-center relative to the $C_{60}$ subunit. Hence, we searched for better hydrocarbon models which would ultimately be amenable to rectifying behavior by combining $sp^2$- and $sp^3$-hybridized carbon atoms and reckoned that a bent graphene-diamondoid adduct would be promising.

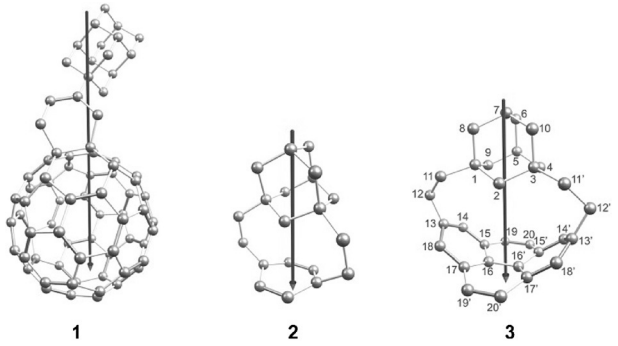


***Figure 1.*** 2-(Diamantan-4-yl)-1,3-butadiene–$C_{60}$ adduct (**1**), [2](1,3)adamantano[2](1,4)benzenophane (**2**), and [2](1,3)adamantano-[2](2,7)pyrenophane (**3**), and their dipole moment vectors in dark gray.

The parent model compound, [2](1,3)adamantano[2]-(1,4)benzenophane (**2**; Figure 1), was synthesized by Lemmerz et al. in search of delineating the stabilities of highly strained cyclophanes,[9] and it does show a much better dipole moment alignment. Hence, we chose [2](1,3)adamantano[2]-(2,7)pyrenophane (**3**; Figure 1), in which the pyrene moiety acts as the electron acceptor and the diamondoid as the electron donor. This molecule would constitute a new hydrocarbon, the carbon allotrope components of which are nonpolar, but where the resulting structure has an appreciable dipole moment which originates predominantly from bending the $sp^2$ moiety and placing an electron donor on its concave side. Herein, we present the synthesis of **3** and a combined experimental and computational examination of its structure, stability, optical properties, and conformational dynamics.

The synthetic approach to **3** (see the Supporting Information for experimental details) derives from the preparation of cyclophanes such as [2](1,4)benzeno[2](2,7)pyrenophane.[10] Coupling of 1,3-di-ethynyladamantane[11] (**4**) with dimethyl 5-bromoisophthalate (**5**) gave **6** in 77% yield (Scheme 1). Hydrogenation of **6**, using 10 wt.% Pd/C, to **7** and subsequent reduction to the tetraalcohol **8** with $LiAlH_4$ proceeded quantitatively. Bromination with 33% HBr/HOAc afforded **9** in 89% yield. For the cyclization step to the dithiacyclophane **10**, it turned out that higher dilution than was used for

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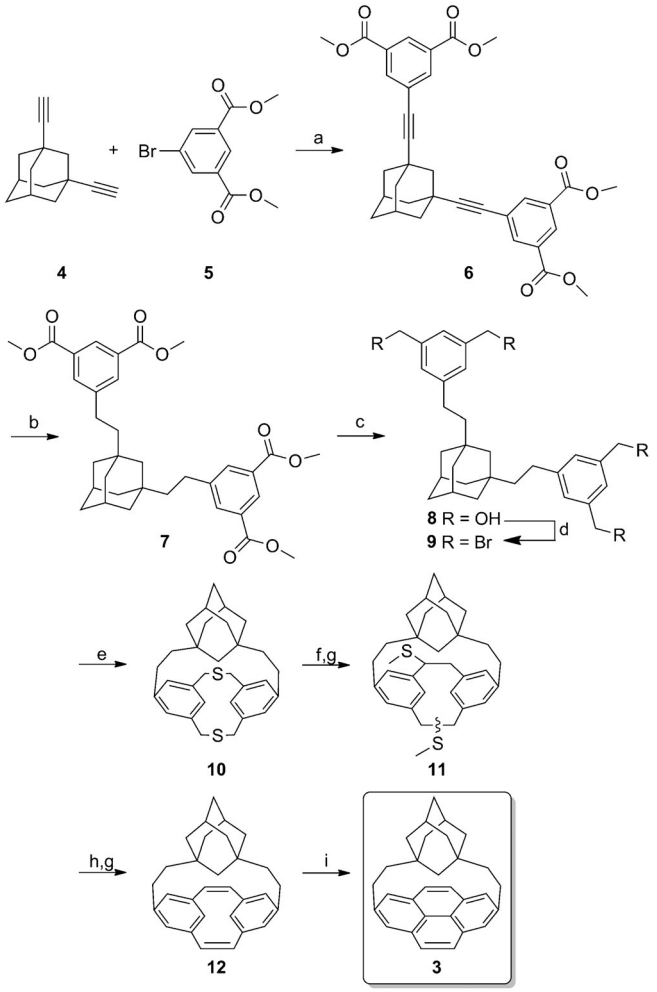


***Scheme 1.*** Total synthesis of **3**: a) $[Pd(PPh_3)_2Cl_2]$, CuI, DBU, toluene, RT, 22 h, 77%; b) $H_2$, 10 wt.% Pd/C, $CH_2Cl_2$, 6 h, RT 99%; c) $LiAlH_4$, THF, 2 h 95 °C, 99%; d) 33 wt.% HBr/HOAc, 60 °C, 1 h, 89%; e) $Na_2S/Al_2O_3$, toluene/EtOH (3:7), 55 °C, 2 h, 91%; f) $CH_2Cl_2$, $Me_3OBF_4$, RT, 3 h; g) KO*t*Bu, DMF, RT, 2 h; h) $CH_2Cl_2$, $Me_3OBF_4$, RT, 3.5 h; i) DDQ, $CH_2Cl_2$, RT, 4 h, 55%. DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene, DMF = *N*,*N*-dimethylformamide, THF = tetrahydrofuran.

similar transformations was necessary (see Table S1 in the Supporting Information).[12] The use of toluene instead of halogenated solvents proved advantageous and vacuum filtration over silica gel afforded 91% of **10**. The synthesis of the cyclophanediene **12** involved a four-step procedure, whereby **10** was S-methylated, and then subjected to a base-induced Stevens rearrangement, followed by a second S-methylation and elimination. For the methylation steps, Meerwein's salt[13] was used instead of the typically employed dimethoxycarbonium tetrafluoroborate[14] to achieve higher yields. Oxidation of **12** with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) afforded **3** in 55% yield after chromatography. The total yield of **3** from **4** is 25% over ten steps.

The crystal structure of **3** reveals $C_s$ symmetry with the adamantyl moiety leaning slightly toward one side of the pyrene (Figure 2; see Figure S1). The large bond and angle deformations in **3** relative to adamantane[15] and pyrene[16] are well reproduced with the three density functional theory

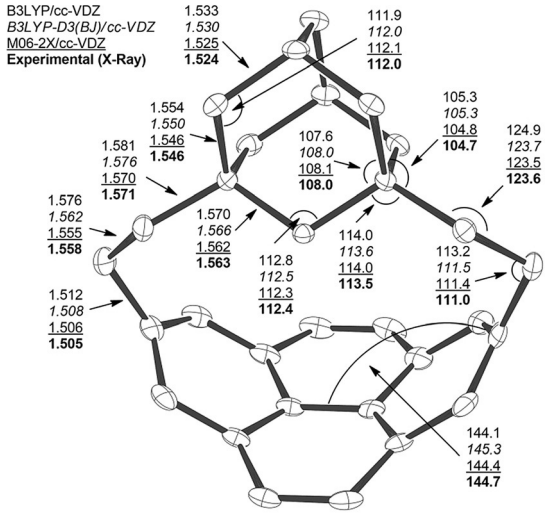


***Figure 2.*** Comparison of bond lengths (in Å) and bond angles (in deg.) for **3** between X-ray crystal structure data (thermal ellipsoids are shown 50% probability) and selected computational data at the levels of theory given. Some XRD values of the bond lengths and bond angles are averages of two values.

(DFT) methods employed here. The M06-2X/cc-pVDZ level provided an excellent match with experiment. The largest deviations from ideal values are observed in the ethano bridge which features C–C bonds at the short (1.51 Å) and long (1.56 Å and 1.57 Å) ends of the typical range. Most remarkable is the 124° C-C-C angle, which is peculiar for an $sp^3$-hybridized carbon atom, and indicates significant strain. To assess the strain of **3**, we determined its heat of formation by homodesmotic equations[17] using pyrene, adamantane, and *trans*-1,4-dimethylcyclohexane, along with *n*-butane and *n*-hexane as reference compounds for which the experimental $\Delta_f H^0$ values are known (see Scheme S1 and Tables S3 and S4). B3LYP was used with (D3-BJ) and without dispersion corrections as well as M06-2X with a cc-pVDZ basis set for geometry optimizations and a cc-pVTZ basis set for single-point energies on these geometries. The $\Delta_f H^0$ value for **3** is in the range of 57–69 kcal mol$^{-1}$, with B3LYP being at the higher and B3LYP-D3(BJ) at the lower end. M06-2X gives a value of 62.7 kcal mol$^{-1}$. Comparison with Benson increments[18] then yields strain energies of 54–66 kcal mol$^{-1}$.

For comparison, we computed a strain energy of 35–44 kcal mol$^{-1}$ for **2** utilizing a comparable set of equations (see the Supporting Information), and it compares well with the 34.7 kcal mol$^{-1}$ for **2** reported by Vögtle et al.[9,19] using semiempirical methods. Thus, **3** is significantly more strained than **2**, as the major deformations in **2** occur for the aryl ring,[9,19] while the ethano bridges are also highly distorted in **3**. The bend angle $\theta$[12b] of the pyrene system in **3** is 104.3°, and is just shy of the highest reported value [$\theta$ = 109.1° for 1,7-dioxa[7](2,7)pyrenophane].[12d] The average bend angle $\alpha$[12d,20] between adjacent planes of carbon atoms over the length of the pyrene unit in **3** is 17.4° (see Figure S3). A similar bend angle of 18.0°[12d] exists in the fullerenes $D_{5h}$-$C_{70}$ and $D_{5h}$-$C_{90}$.[21] The side chain bend angles, $\beta$,[20] in **3** (13.0° and 14.0°) are larger than those observed in 1,7-dioxa[7]-

  

(2,7)pyrenophane (8.2° and 8.7°), but smaller than those in [2]metacyclo[2](2,7)pyrenophane (17.6° and 17.7°), for which $\theta = 96.1°$.[22] Overall, **3** and [2]metacyclo[2](2,7)pyrenophane are tied for the largest sum of $\theta$ and the two $\beta$ angles (131.3° and 131.4°, respectively).

The shapes of the measured UV/Vis and fluorescence spectra of **3** in several solvents (see Figures S4–S13) are similar to those of pyrenophanes with comparable bend angles.[12a,23] The agreement with the TD-B3LYP/cc-pVDZ computed UV/Vis spectrum in cyclohexane is excellent (see Figure S5). We observe a 30 nm and 40 nm red shift in the UV/Vis and fluorescence spectra relative to pyrene, respectively. The relatively featureless fluorescence spectra in various solvents have a $\lambda_{max}$ at around 423 nm and there is no indication of excimer formation or charge transfer. The Stokes shift for **3** (40 nm) is larger than that of pyrene (32 nm) in cyclohexane, but half as large as those of some other pyrenophanes.[23,24] A fluorescence quantum yield $\Phi_f = 0.074$ for **3** in non-degassed cyclohexane (0.15 mM) at $\lambda_{ex} = 360$ nm was measured relative to quinine sulfate (16 μM) in 0.1 N $H_2SO_{4(aq)}$ with $\Phi_f = 0.546$[25] at room temperature. By comparison, a $\Phi_f = 0.185$ was determined for pyrene (2.8 μM) with $\lambda_{ex} = 306$ nm under the same reaction conditions. This compares well with the $\Phi_f$ value of the first organic light-emitting diode (OLED) candidate Alq3[26] ($\Phi_f = 0.15$[27]).

While the chemical shifts of the C(2)-$H_2$ protons (of the adamantane methylene group pointing inside) **10** and **12** at room temperature appear at unusually low field ($\delta =$ 0.57 ppm and 0.40 ppm, respectively), the C(2)-$H_2$ protons of **3** appear as a very broad and hardly discernible signal at $\delta = -2.09$ ppm because of the magnetic anisotropy of the pyrene system. Thus, although the pyrene moiety in **3** is severely bent, it keeps much of its aromatic character. To estimate the extent to which the aromatic character is retained, we computed the nucleus independent chemical shift (NICS)[28] in the benzene rings of **3** and pyrene at M06-2X/cc-pVDZ. The NICS values (see Figure S6) of **3** are reduced by about 30–50% relative to pyrene, that is, still indicating appreciable aromatic character. Cyranski et al. also compared the NICS values of several pyrenophanes with those of pyrene.[12a] Even in the pyrenophane with the most bent pyrene system, it was found that the NICS is reduced only by about 10–20%.

The $^{13}$C-NMR spectra of **3**, **10**, and **12** show broad signals indicating the existence of an intramolecular dynamic process. The X-ray data of **12** provide a hint as to what kind of dynamics are present as it spontaneously crystallizes in two forms, namely as an (*M*)- and (*P*)-$C_2$ racemate as well as an achiral $C_s$-symmetric conformer. The computed relative Gibbs free energy difference ($\Delta G_{298}$) indeed only amounts to 0.7 kcal mol$^{-1}$ with very little variation with the method employed (Figure 3; see Table S2).

Computations on the conformational potential energy hypersurface of **3** show behavior comparable to that of **12**: there is a $C_s$ structure and a pair of chiral $C_2$ conformers, with an interconnecting transition state (**TS3**; see Figure S1). However, the energy difference of the two types of symmetries is much larger (6.3 kcal mol$^{-1}$) for **3** than for **12** (0.7 kcal mol$^{-1}$), and this explains why **3** crystallizes exclusively in its $C_s$-symmetric form, whereas **12** does so in two almost equally stable crystal forms. The appearance of different conformers of the same molecule equally distributed in the same crystal is termed conformational isomorphism,[29] which is not common.[30] In principle, crystallization of conformers should be widespread, as even toluene crystallizes in two rotameric forms.[31] We found 486 hits in the Cambridge Structural Database of pure hydrocarbons which crystallize with more than one molecule in the asymmetric unit ($Z' > 1$). In most cases the conformers differ from each other through the rotation of functional groups such as phenyl rings or through a slightly different position of methyl or ethyl groups. This behavior is also often the case for cyclophanes, where the different conformations of the alkane bridges crystallize concomitantly.[22,32] To the best of our knowledge, **12** is the first example of conformational isomorphism of a pure hydrocarbon, where two optomers and a *meso*-conformer crystallize individually.

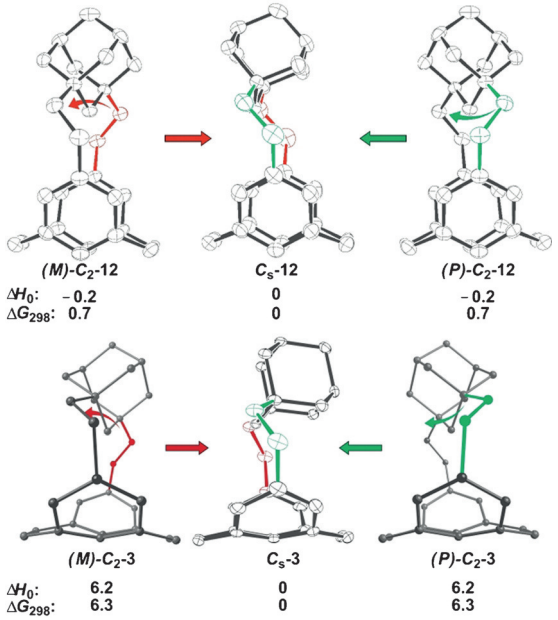


***Figure 3.*** XRD structures of the cyclophanediene **12** (top) and adamantanopyrenophane **3** (bottom center). **12** crystallizes in two conformers: as a racemate with (*M*)-$C_2$-**12** (left), as well as (*P*)-$C_2$-**12** (right) and with $C_s$-**12** symmetry (middle). **3** crystallizes only with $C_s$-symmetry. The $C_2$ conformers of **3** are computed. For clarity the hydrogen atoms are omitted. The relative Gibbs free energies ($\Delta G_{298}$) and the enthalpies at 0 K ($\Delta H_0$) in kcal mol$^{-1}$ computed at M06-2X/cc-pVTZ(PCM:$CH_2Cl_2$)//M06-2X/cc-pVDZ(PCM:$CH_2Cl_2$) are given.

We surmised that the dynamic process indicated in the NMR spectra is related to the conformational changes as the barrier for the flipping of the ethano bridges in **3** was consistently computed to be about 11–12 kcal mol$^{-1}$, depending on the level of theory employed (see Figure S1). Inclusion of solvation by polarized continuum model (PCM) computations in dichloromethane change the relative free energies by as little as 0.1 kcal mol$^{-1}$.

The computed activation barrier should readily be measurable by temperature-dependent $^1$H NMR spectroscopy utilizing line-shape analysis. This method provided a free

  

energy barrier of $\Delta G_{298} = 11.1 \pm 0.6$ kcal mol$^{-1}$, and is in excellent agreement with the computed value (12.2 kcal mol$^{-1}$) at M06-2X/cc-pVTZ (PCM: $CH_2Cl_2$) and, as expected, is larger than that of **2** [$(9.6 \pm 2.4)$ kcal mol$^{-1}$; 9.9 kcal mol$^{-1}$ at the same level; see Figure S2]. At 30 °C, the C(2)-$H_2$ signal for both protons is very broad and of low intensity. At 60 °C, the rate of flipping becomes faster and the C(2)-$H_2$ signal becomes sharper. At −30 °C, the exchange is slow enough to split the H2 signal into two, with the signals becoming sharper and slightly shifted to higher field at lower *T*. We also computed the $^1$H NMR spectrum of $C_s$-**3**, which should prevail at low temperatures, and **TS3**, the averaged spectrum of which should provide an excellent approximation of the experimental NMR spectra at room temperature and higher temperatures (Figure 4).

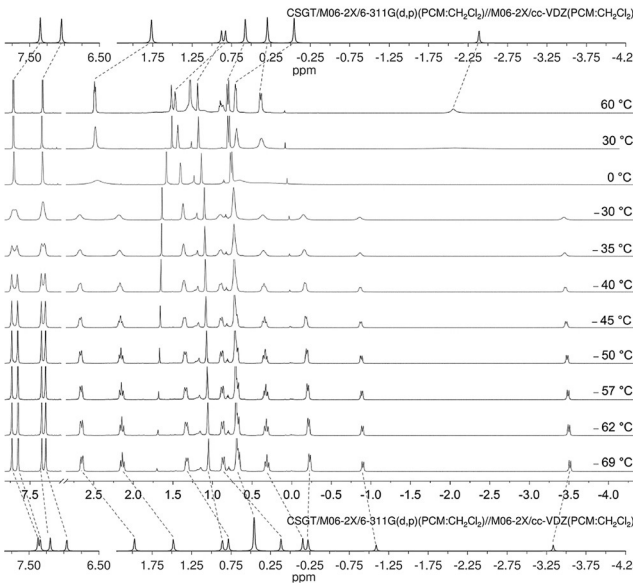


***Figure 4.*** Temperature-dependent $^1$H NMR spectra in $CD_2Cl_2$ (except at 60 °C in $C_2D_2Cl_4$) of **3** and computed averaged $^1$H NMR spectra of $C_s$-**3** (bottom) and **TS3** (top, as an approximation of the spectrum to be expected from fast exchange), at the level indicated, including solvation in reference to tetramethylsilane.

Finally, we found that the M06-2X/cc-pVDZ computed dipole moment of **3** is indeed rather large (2.3 D) and is even larger than that of a common dipolar hydrocarbon, azulene (computed 1.2 D, expt. 0.8–1.1 D).[33] the computed value for **2** is 0.7 D. The dipole moment of **1** is still much larger (5.5 D) owing to its molecular size. One can simply derive the approximate charge separation through the relationship with the dipole moment $\mu = q \times r$, which gives hypothetical charge separations of 1.0, 0.3, and 0.9 e for **1**, **2**, and **3**, respectively (with *r* measured from midpoint-to-midpoint of the $sp^2$ and $sp^3$ moieties). The adamantyl and pyrene units in **3** carry partial charges of about +0.45 and −0.45 e, which is quite remarkable for a hydrocarbon. For comparison, the same considerations give charges of +0.3 in the cycloheptatrienyl and −0.3 in the cyclopentadienyl moiety of azulene. The large polarization of **3**, which is comparable to that of **1**, implies that it indeed may be a similarly good candidate for a hydrocarbon molecular rectifier,[8] with a more ideal dipole moment orientation and significantly higher thermodynamic stability.

In conclusion, we presented the first synthesis and characterization of [2](1,3)adamantano[2](2,7)pyrenophane (**3**) as a dipolar hydrocarbon. The activation barrier for the flipping of the ethano bridges in **3** was determined both experimentally and computationally to be in the range of 11–12 kcal mol$^{-1}$ and the strain energy was estimated by homodesmotic equations to be around 66 kcal mol$^{-1}$. The new structure displays a large dipole moment vector which is ideally aligned orthogonally to the basal plane of the pyrene system.

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