JACS JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
COMMUNICATION
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σ/σ- and π/π-Interactions Are Equally Important: Multilayered Graphanes

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S *Supporting Information*

ABSTRACT: The properties of single-sheet [*n*]graphanes, their double-layered forms (diamondoids), and their van der Waals (vdW) complexes (multilayered [*n*]graphanes) were studied for n = 10−97 at the dispersion-corrected density functional theory (DFT) level utilizing B97D with a 6-31G(d,p) basis set; for comparison, we also computed a series of structures at M06-2X/6-31G(d,p) as well as B3LYP-D3/6-31G(d,p) and evaluated SCS-MP2/cc-pVDZ single-point energies. The association energies for the vdW complexes reach 120 kcal mol^{-1} already at 2 nm particle size ([97]graphane dimer), and graphanes adopt layered structures similar to that of graphenes. The association energies of multilayered graphanes per carbon atom are rather similar and independent of the number of layers (ca. 1.2 kcal mol^{-1}). Graphanes show quantum confinement effects as the HOMO−LUMO gaps decrease from 8.2 eV for [10]graphane to 5.7 eV for [97]graphane, asymptotically approaching 5.4 eV previously obtained for bulk graphane. Similar trends were found for layered graphanes, where the differences in the electronic properties of double-sheet CH/σ vdW and double-layered CC/σ diamondoids vanish at particles sizes of 1 nm. For comparison, we studied the parent CC/π systems, i.e., the single- and double-sheet [*n*]graphenes (n = 10−130) for which the association energies demonstrate the same trends as in the case of [*n*]graphanes; in both cases the band gaps decrease with an increase in system size. The [112]graphene dimer (HOMO−LUMO gap = 0.5 eV) already approaches the 2D metallic properties of graphite.

Acting at larger distances than conventional covalent bonding, van der Waals (vdW) forces are decisive for molecular recognition. This was first stated by Newton regarding light dispersion: "*Have not the small Particles of Bodies certain Powers, Virtues or Forces, by which they act at a distance...upon one another for producing a great Part of the Phaenomena of Nature?*"[1] Noncovalent interactions traditionally have been associated with biomolecules, highly ordered supramolecular and polymer structures, and molecular fluids as well as solids. It is being recognized that the accurate description of small molecules also necessitates the quantitative inclusion of weak interactions. The attraction between neutral atoms or uncharged molecules is mostly attributed to attractive dispersion (London) forces. Due to the absence of (polar) functional groups, dispersion dominates intermolecular interactions between hydrocarbon moieties and is characteristic for CH/σ and CC/π as well as for various other σ/π-mixed clusters, as exemplified by the benzene and methane complexes (Figure 1). While the association energies for the methane and benzene dimers are only 0.5 and 2.7 kcal mol^{-1}, respectively,[2] the contributions of noncovalent interactions may increase significantly with increasing size of the interacting molecules due to cooperativity[3] and/or additivity[4] effects. Examples involve the energetic preference for branched over linear alkanes (protobranching),[5] alkyl group recognition through encapsulation,[6] high thermal stability of proteins,[7] stabilization of alkanes with very long C−C bonds achieved through steric crowding[8] ("dispersion energy donors"[9]),[10] existence of stable CH/π[11] and CH/σ[12] crystals, and many others.

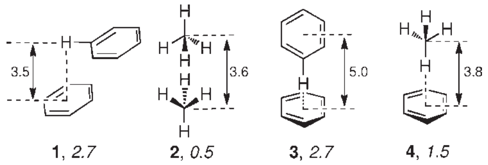

Figure 1. Prototypical hydrocarbon π/π- (**1**), σ/σ- (**2**), and σ/π-dimers (**3** and **4**) {CCSD(T)/CBS(Δha(TQ)Z), bond distances in Å, interaction energies (italics) in kcal mol^{-1}}.[2a]

Very recently we reported the preparation and characterization of alkanes with the longest C−C bonds observed to date (up to 1.704 Å), whose surprisingly high thermal stabilities are due to a favorable balance of repulsive and attractive vdW interactions between the CH surfaces.[8a] Graphanes representing a new class of extended two-dimensional hydrocarbon material were first predicted theoretically[13] and then realized by hydrogenation of graphene.[14] Only little is known about the properties of graphanes, primarily because their topologically reproducible preparation is rather challenging. In a formal sense, the simplest graphane is perhydrophenalene ($C_{13}H_{22}$, [13]graphane, **5**, Figure 2), which has been known for a long time;[15] some larger representatives were also isolated, e. g., perhydrocoronene ([24]graphane).[16] Interest in graphanes arises from their potential use in nanoelectronics since this material perfectly resembles the {111} surface of hydrogen-terminated (HT) diamond, which is the only organic material that displays a negative electron affinity (NEA) both in bulk[17] and as thin layers.[18] In contrast to chemical vapor deposition (CVD) and detonation nanodiamond, diamondoids are available in well-defined shapes and sizes.[19] We have shown that diamondoids can be selectively functionalized[20] and, when attached to metal surfaces, reproduce the diamond NEA properties with much higher quantum yields (up to 70%).[21] From an alternative perspective, nanodiamond **6** (for convenience named cyclohexamantane[20f]) structurally

Received: July 26, 2011
Published: November 07, 2011

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Figure 2. Large alkanes viewed as prototypical graphanes: single-layered [13]graphane (**5**), naturally occurring diamondoid cyclohexamantane (**6**) (a double-layered CC/σ [13]graphane), and CH/σ double-sheet [13]graphane (**7**).

represents the simplest CC/σ bilayered [13]graphane. HT nanodiamond materials, diamondoids, and graphanes (single and layered) all belong to the σ-carbon (sp^3) family.[22]

To examine the properties of σ-carbon nanomaterials, we report here computations[23] on single-layered graphanes, prism-shaped diamondoids (viewed as two-layered CC/σ graphanes), concentrating specifically on the potential of such materials for self-association through the formation of vdW multilayered CH/σ-nanoclusters. For comparison we also include single- and double-layered graphenes in our study, since these materials may be interconverted (see SI).

The choice of the computational method for the correct description of such rather large structures is challenging. Earlier studies demonstrated that conventional DFT approaches are not able to describe vdW clusters correctly,[24] mostly due to exchange functional failure,[25] PW91 being somewhat of an exception.[26] This triggered the successful development of DFT methods that are corrected for dispersion[25,27] and heavily parametrized meta-generalized-gradient approximated functionals such as the M0*n* series (n = 5, 6, ...)[28] that account for medium-range correlation.[29] We utilized the B97D[27e] approach (D stands for dispersion), which demonstrates overall good performance in the description of both CH/σ and CC/π clusters.[29,30] As the C−C interlayer distances in layered graphanes (ca. 4.1 Å) and layered graphenes (ca. 3.3 Å) lie in a region where the difference between the D2[27b] and D3[27e] dispersion energy correction through the (different) C^6 dispersion coefficients is small,[31] we assume that graphanes and graphenes are treated similarly well at B97D/6-31G(d,p). For comparison, we include B3LYP-D3/6-31G(d,p) computations as well as spin-component-scaled SCS-MP2[32]/cc-pVDZ energies on M06-2X[28]/6-31G(d,p)-optimized geometries. However, the system sizes that can be handled at the SCS-MP2 level are quickly limited by the typical computational ressources.

As found for nanodiamonds,[33] the HOMO−LUMO gap (Δ_{HL}) of graphanes monotonically decreases (Figure 3) with increasing size and asymptotically approaches the band gap of bulk diamond (5.5 eV)[34] at about 2 nm ([97]graphane). This is close to the value of 5.4 eV obtained for graphane computed with Green's functions with screened Coulomb interactions;[35] however, it is substantially higher than the 4.7 eV obtained with the PW91 functional with a plane-wave basis set for [240]graphane[36] and the 3.5 eV determined from plane-wave DFT PBE.[22a] Very recently the properties of the vdW dimers of graphane were studied with a plane-wave vdW DFT method estimating the band gap of 4 eV.[37] Thus, we predict quantum confinement effects for single-sheet graphanes only up to 2 nm particle size. This is very similar to the trends in the behavior of hydrogen-terminated nanodiamond[38] and diamondoids.[39] The graphane sheets strongly associate due to a large number of additive dispersion attractions. We optimized several dimers (Figure 4) and found that the B97D functional satisfactorily reproduces the intermolecular vdW contacts (H···H = 2.2 and C···C = 4.1 Å) described previously in the crystal structure unit cells of diamondoids[40] and other organic crystals.[41]

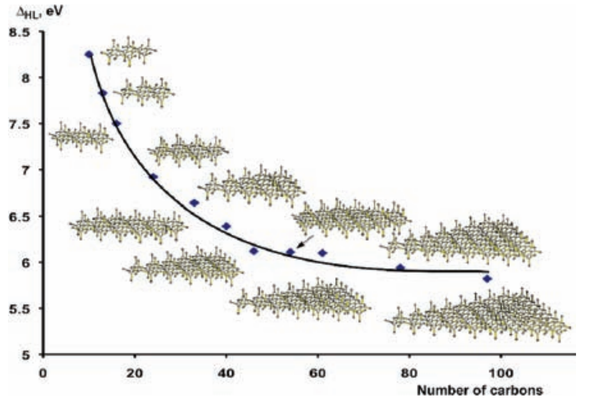

Figure 3. B97D/6-31(d,p) HOMO−LUMO gap (Δ_{HL}) for single-sheet [10]−[97]graphanes.

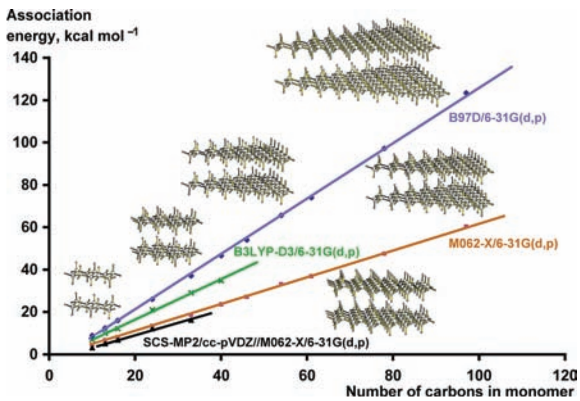

Figure 4. B97D/6-31G(d,p) (blue), M06-2X/6-31G(d,p) (red), B3LYP-D3/6-31G(d,p) (green), and SCS-MP2/cc-pVDZ (black) dimerization energies for [10]−[97]graphane.

The SCS-MP2 and M06-2X results are similar to each other but reduce the association energies by about 50% (Figure 4). B3LYP-D3 lies between these two and our reference level. Hence, B97D is very likely to be at the upper end for computing the association energies discussed here, but we have to leave it to more accurate approaches to gauge the performance of these and related methods for these rather large structures.

We found a continuous increase in the dimerization exothermicites en route from the small particles ([10]graphane, −8.9 kcal mol^{-1}) to the medium-sized dimers (−54.0 and −65.6 kcal mol^{-1} for [46]- and [54]graphanes, respectively). The [97]graphane dimer has a complexation energy of 123 kcal mol^{-1} (Figure 4), exceeding values of covalent C−C bonding. The linear size−energy correlation gives ca. 1.2 kcal mol^{-1} per carbon complexation energy for all clusters studied.

We also computed a series of multilayered graphanes up to the [33]graphane pentamer, the [46]graphane tetramer, and the [61]graphane trimer (Figure 5). We found no decrease in the association trends with a growing number of layers since the associations energies per carbon and interface stay constant for all molecules (1.1−1.2 kcal mol^{-1}), practically identical to the experimental interaction energy of aromatic CC/π dimers

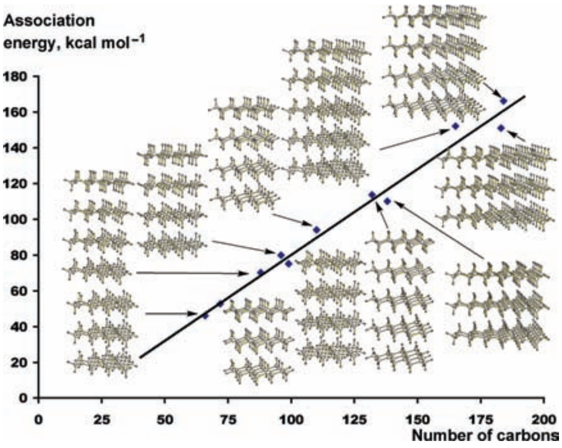

Figure 5. B97D/6-31G(d,p) total association energies for multilayered [22]−[61]graphanes.

(1.20 ± 0.1 kcal mol^{-1} per carbon).[42] We estimated these values at the B97D/6-31(d,p) level of theory for the [10]−[112] graphene dimers and also found an association energy of ca. 1.2 kcal mol^{-1} per carbon (Figure S1). This value agrees well with the interlayer binding in graphite computed with vdW-corrected DFT methods[43] and nicely matches the experimental value for graphite (1.4 ± 0.1 kcal mol^{-1} per carbon).[42] The band gaps decrease with increasing system sizes both for the monomeric (Figure S2) and the dimeric (Figure S3) forms: The [112]graphene dimer (Δ_{HL} = 0.5 eV) already approaches that of graphite.

The dimer dispersion attractions reveal that graphanes prefer CH/σ-layered structures with strong interlayer bonding comparable to that of graphite, in contrast to flexible linear[44] and branched[45] alkanes. Our findings are therefore at variance with the earlier statement that "*The graphane bonds are fully saturated and there is no opportunity for hydrogen bonding between the sheets.*"[13] While we discourage using the term "hydrogen bonding" for the interlayer vdW attractions, our data suggest that the opposite is true!

The trends in the change in Δ_{HL} for the graphane monomers (Figure 3) and double-sheet structures (Figure S4) are quite similar. The most interesting situation arises from a comparison of double-sheet CH/σ and double-layered CC/σ graphanes. While the difference in the Δ_{HL} values of the [13]graphane dimer and the corresponding C_{26} nanodiamond is ca. 0.8 eV (Figure 6), it reduces to 0.25 eV for [27]graphane dimer vs its corresponding diamondoid and vanishes for particles larger than C_{150}.

Astonishingly, this implies that from particle sizes larger than ca. 1 nm the electronic properties of vdW graphane dimers and fully covalent nanodiamonds are very similar. This suggests that only the total number of carbon atoms (or electrons) in the sp^3 systems matter as these grow larger.

Finally, the question arises of mixed graphene−graphane particles and what their electronic properties would be. The situation is somewhat complicated by the fact that only some combinations of graphenes and graphanes with the proper symmetry fit well together. For such systems, as depicted in Figure S5, the vdW interaction energies also are around 1 kcal mol^{-1} per carbon, as found for the pure graphane and graphene dimers.

Graphanes form CH/σ-multilayered structures similar to graphene due to strong attractive interlayer dispersion interactions that grow with size. While the band gap of the [112]graphene dimer (Δ_{HL} = 0.5 eV) already approaches that of graphite, increasingly larger graphanes change from being insulators to becoming semiconductors as Δ_{HL} decreases with increasing system size up to a limiting value, which matches that of diamond. The differences in the electronic properties between double-layered CC/σ graphanes (diamondoids) and double-sheet CH/σ graphanes vanish above 1 nm, offering many opportunities for the exploitation of novel CC/π, CH/σ, and CC/σ carbon materials.

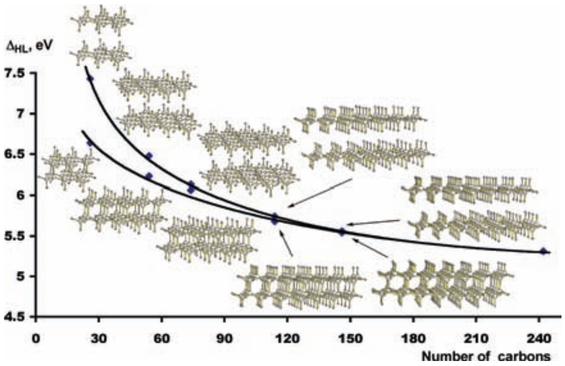

Figure 6. B97D/6-31G(d,p) Δ_{HL} values for double-sheet CH/σ and double-layered CC/σ (diamondoid) as well as [13]-, [27]-, [46]-, [57]-, and [73]graphane dimers.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Complete refs 21a and 23; additional figures and tables; XYZ-coordinates and energies of all computed species. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

This work was supported through German Academic Exchange Service and the Ministry of Science and Education of Ukraine.

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