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# Carbon chains and the (5,5) single-walled nanotube: Structure and energetics versus length

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Reliable thermochemistry is computed for infinite stretches of pure-carbon materials including acetylenic and cumulenic carbon chains, graphene sheet, and single-walled carbon nanotubes (SWCNTs) by connection to the properties of finite size molecules that grow into the infinitely long systems. Using *ab initio* G3 theory, the infinite cumulenic chain ($:C{=}C{=}C{=}C:$) is found to be $1.9 \pm 0.4$ kcal/mol per carbon less stable in free energy at room temperature than the acetylenic chain ($\dot{C}{\equiv}C{-}C{\equiv}\dot{C}$) which is 24.0 kcal/mol less stable than graphite. The difference between carbon-carbon triple, double, and single bond lengths (1.257, 1.279, and 1.333 Å, respectively) in infinite chains is evident but much less than with small hydrocarbon molecules. These results are used to evaluate the efficacy of similar calculations with the less rigorous PM3 semiempirical method on the (5,5) SWCNT, which is too large to be studied with high-level *ab initio* methods. The equilibrium electronic energy change for $C(g) \rightarrow C$[infinite (5,5) SWCNT] is $-166.7$ kcal/mol, while the corresponding free energy change at room temperature is $-153.3$ kcal/mol (6.7 kcal/mol less stable than graphite). A threefold alternation (6.866, 6.866, and 6.823 Å) in the ring diameter of the equilibrium structure of infinitely long (5,5) SWCNT is apparent, although the stability of this structure over the constant diameter structure is small compared to the zero point energy of the nanotube. In general, different $(n,m)$ SWCNTs have different infinite tube energetics, as well as very different energetic trends that vary significantly with length, diameter, and capping. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2397680]

## INTRODUCTION

Properties, such as the length of a carbon-carbon triple bond or the stability of a finite carbon cluster, change significantly with molecular length. From an experimental perspective, the connection of small molecule properties to infinite length can be established by mapping such properties versus length. Theoretically, this approach is called the finite-cluster method.[1] This activity can provide a fundamental basis for understanding properties in the nanosize regime. As chemists pursue reactions incorporating new allotropes of carbon into nanotech materials, it is important to establish the thermodynamic stability versus size with as much rigor as possible. The goals of this work are (1) to compute reliable enthalpy and free energy changes upon creation of infinite lengths of carbon chains and single-walled carbon nanotubes (SWCNTs), (2) to present the thermochemical results in a general way for comparison to any carbon structures, not just ones with similar bonds, i.e., to check the isodesmic assumption for curved versus flat carbon regions, and (3) to provide input which will aid in the construction of carbon energetics versus size. In the course of pursuing these goals, interesting structural results were also obtained.

Individual *ab initio* and density functional theory (DFT) techniques that work very well for structure and relative energetics do not generally yield reasonable accuracy regarding thermochemistry (such as heats of formation) of small gas phase molecules. To address this issue, we have used the *ab-initio*-based G3 theory (sequences of individual approaches) when size permits and the PM3 semiempirical method otherwise. Structure and thermochemistry were computed with optimizations and normal mode analyses of sequences of finite size molecules which grow into infinite stretches of pure-carbon materials including acetylenic and cumulenic carbon chains, graphene sheet, and SWCNTs.

This work is distinguished by its free energy assessments, as well as and in contrast to the equilibrium electronic energy differences that might be obtained from *ab initio* electronic structure methods. If the reaction C(graphene) → C(SWCNT) is isodesmic, i.e., has the same bonds on each side, then the calculated change in equilibrium electronic energy can be taken as the enthalpy change for the reaction.[2] This would be a good first step towards thermochemistry, but it does not provide free energy changes. The question also arises as to whether the bonds of a curved carbon surface are the same as those of a flat surface. In our work, we have determined equilibrium electronic energy, enthalpy, and free energy changes so that our results can be compared to any other carbon structures, not just to ones with similar bonds.

### Background

Single-walled carbon nanotubes (SWCNTs) are a relatively new $sp^2$ allotrope of carbon.[3–5] They are labeled by an $(n,m)$ system[4,6] which defines a wrap-around point for mak-

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TABLE I. Electronic equilibrium energies, enthalpies of formation, zero point energies, thermal enthalpic correction from equilibrium, and thermal free energy correction from equilibrium for test molecules.

| Species | Method | $E^{\text{eq}}$ (hartree) | $\Delta H_f^{298\text{ K}}$ (kcal/mol) | ZPE (kcal/mol) | $\Delta H^{\text{eq}\rightarrow 298\text{ K}}$ (kcal/mol) | $\Delta G^{\text{eq}\rightarrow 298\text{ K}}$ (kcal/mol) |
|---|---|---|---|---|---|---|
| $CH_4$ | G3 | −40.500 3[a] | −18.0 | 26.77 | 29.16 | 15.09 |
| | HF/6-31G* | −40.195 17 | +77.5 | 29.98 | 32.36 | 17.65 |
| (methane) | MP2/aug-cc-pVDZ | −40.367 727 | +23.1 | 28.25 | 30.64 | 16.55 |
| | B3LYP/6-31G* | −40.518 38 | −17.95 | 28.39 | 30.77 | 16.04 |
| | PM3 | | −13.1 | 28.39 | 30.78 | 16.71 |
| | Expt. | | −17.89 | | | |
| $C_2H_2$ | G3 | −77.302 2[a] | 55.1 | 16.50 | 18.81 | 4.63 |
| | HF/6-31G* | −76.817 83 | 173.16 | 18.48 | 20.72 | 6.64 |
| (acetylene) | MP2/aug-cc-pVDZ | −77.092 997 | 63.14 | 15.91 | 18.48 | 3.85 |
| | B3LYP/6-31G* | −77.325 646 | 63.11 | 16.71 | 19.14 | 4.77 |
| | PM3 | | 50.7 | 17.50 | 19.74 | 5.66 |
| | Expt. | | 54.19 | | | |

[a]Estimated with harmonic approximation for vibrations, scaling factor of 0.8929.

ing a tube from graphene sheet. The (5,5) SWCNT studied in this work is an armchair tube with the same diameter as the $C_{60}$ fullerene molecule. SWCNTs are of great interest as nanowires.[7] They are metallic or semiconducting depending on whether $n-m$ is an integer multiple of 3.[8] They have many unusual electronic properties[5] such as the capacity to carry large amounts of current ballistically (without heat). Capped forms of SWCNTs have been implicated in some growth mechanisms,[9] particularly on catalytic metal particles. There is a paucity of experimental information on the thermodynamics of the growth processes.[10] There is also interest in other forms of carbon, such as the *sp*-hybridized allotrope of carbon,[11] which in cluster work is a reference point important in understanding the trends of small carbon chains[12] towards bulk. The existence of long carbon chains in samples[13] was suggested as early as 1967. When gas phase fullerene production is altered with capping groups,[14,15] fullerenes are no longer produced and evidence suggests the presence of linear carbon chains with hundreds of carbon atoms. Stable acetylenic carbon chains of ∼30 atoms have been synthesized[15,16] by capping the chains with unreactive terminal groups. Additionally, H and CN capped carbon chains (cyanopolyynes) have been observed in the interstellar medium[17] and in the laboratory.[18] There are a few *ab initio* calculations on infinite linear carbon chains,[19–21] but none that are thermochemically reliable. Hartree-Fock (HF) theory[19,21] predicts that the acetylenic chain is more stable than the cumulenic chain (by ∼3.9 kcal/mol per carbon in electronic equilibrium energy) in accordance with Peierls theorem,[22] but HF theory does not accurately predict $\Delta H_f^{298\text{ K}}$ (the HF value for $CH_4$ is +77.5 kcal/mol, while the experimental value is −17.89 kcal/mol, see Table I). This prediction is in contrast to small molecule, average local bond, enthalpic expectations[23] [an acetylenic carbon shares a single bond (83.2 kcal/mol) and a triple bond (200.5 kcal/mol) for a stability of 141.9 kcal/mol per carbon, while a cumulenic carbon shares two double bonds (146.7 kcal/mol) for a greater stability of 146.7 kcal/mol per carbon]. Clearly, a G3 theory prediction would be illuminating.

## COMPUTATIONAL APPROACH

Most of these calculations were performed on a desktop personal computer (PC) [Pentium 4, 2 Gbyte random access memory (RAM)], and 2.40 GHz processing speed] and all of them could have been.

### Details of quantum mechanical methods

Quantum chemical composite methods,[24–28] such as G3 theory,[27] are now capable of providing accurate predictions of thermochemical properties of small molecules. The equilibrium geometries of G3 theory correspond to the MP2(full)/6-31G* level and the zero point energies (ZPEs) are computed at the HF/6-31G* level with a 0.8929 scaling factor. The enthalpy and free energy changes associated with thermal effects are calculated using ideal gas partition functions.[29] The method amounts to sequences of calculations at different levels of configuration interaction treatment and with different basis sets enabling extrapolation to the full electron configuration interaction [including MP4 and QCISD(T) calculations], the full basis set result (G3large), and other detailed effects including spin orbit effects. The final electron equilibrium energies might be denoted as QCISD(T,FULL)/G3large. G3 theory has obtained an average deviation from experiment of 0.94 kcal/mol in calculations of the enthalpies of formation ($\Delta H_f^{298\text{ K}}$) of 148 molecules contained in its test set. A subset of 20 hydrocarbons from the G3 set exhibits an average deviation of 0.62 kcal/mol. Such energetic results will herein be divided by the number of carbon atoms in the finite cluster, so accuracies of better than 0.2 kcal/mol can be expected (as judged by extrapolating the error in calculated $\Delta H_f^{298\text{ K}}$ per carbon atom versus the reciprocal of the number of carbons to infinite length).

Stewart's semiempirical PM3 method[30] [third parametrization of modified neglect of diatomic overlap (MNDO)] is surprisingly good at absolute energetics, although not as good as G3 theory. Calculation of $\Delta H_f^{298\text{ K}}$ of the same 20 hydrocarbon subset mentioned above gives an average deviation of 3.1 kcal/mol that is vastly better than one obtains with Hartree-Fock (HF) or second order Moller-Plesset (MP2) theory. This is perhaps not surprising since PM3 was developed on a training set of molecular properties including $\Delta H_f^{298\ \mathrm{K}}$. However, PM3 is not as good at just about any other molecular property, so care must be exercised in interpreting the geometrical results. The PM3 results in our calculations will be divided by the number of carbons, so the results may be considerably better than 3.1 kcal/mol. In this work, the accuracy of the PM3 results is ultimately judged by comparison to comparable calculations on infinite acetylenic and cumulenic chains by G3 theory. Accuracy can also be gauged by the enthalpy change for constructing an infinite graphene sheet which can be experimentally placed relative to NIST webbook[31] values for graphite. With these calibrations in hand, the thermochemical and electronic equilibrium energy changes were determined for the construction of the armchair (5,5) SWCNT, with and without fullerene caps. In the course of pursuing absolute energetics, several interesting discoveries were revealed concerning the corresponding geometries of these systems.

To place the current approach in a broader context, we have also included the popular B3LYP (Refs. 25 and 32) hybrid density functional theory method in our initial examples. The B3LYP method obtains the electron density from a Hartree-Fock wave-function-like treatment that is augmented with a parametrized exchange-correlation functional that obtains [generally slightly overestimates (compare $E^{\mathrm{eq}}$ in Table I for B3LYP and the G3 estimate)] the electron correlation energy. The standard deviations of the difference between $\Delta H_f^{298\ \mathrm{K}}$ and experiment using a test set of four molecules ($CH_4$, $CH_3F$, $CH_3Cl$, and $C_2H_2$) for the G3, PM3, B3LYP/6-31G$^*$, and MP2/aug-cc-pVDZ methods were 0.7, 4.4, 5.5, and 35 kcal/mol, respectively. Calculation of $\Delta H_f^{298\ \mathrm{K}}$ with the same 20 hydrocarbon subset mentioned above[33] gives an average deviation of 3.2 kcal/mol which is again not as good as G3, comparable to the PM3 result, and better than most individual *ab initio* methods. The B3LYP method is roughly a factor of 2 more computationally intensive than Hartree-Fock theory, but it is considerably more computationally intensive than PM3; so the SWCNT work has been pursued with PM3. If a sequence of clusters was amenable to B3LYP computations, it would be desirable over PM3 because the electronic structure and geometry are likely to be better. Interest in other properties or access to a bit more computational power might favor the use of B3LYP.

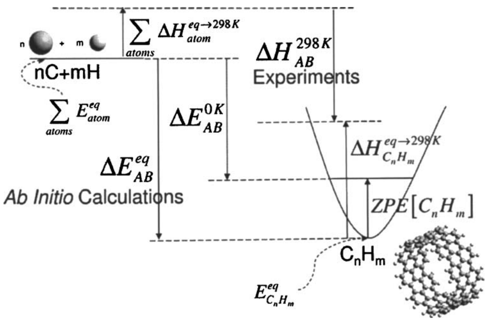

FIG. 1. Energetics for constructing a molecule by the atomic binding reaction $n\mathrm{C(g)}+m\mathrm{H(g)}\rightarrow \mathrm{C}_n\mathrm{H}_m\mathrm{(g)}$. Arrows indicate the signs of the quantities. A similar diagram could be constructed for free energy changes by substituting '*G*'s for the enthalpic '*H*'s. Normal mode analysis enables one to go between the *ab initio* and experimental quantities.

## Basic thermochemical definitions

In order to facilitate comparisons across disparate structures, the energetics in this work are eventually presented in terms of the incorporation of a gas phase carbon atom into the structure of interest, i.e., for the reaction C(g) → C(structure of interest). We present the energetics in terms of electronic equilibrium energy changes (for direct comparison to *ab initio* work) and as thermochemical quantities (such as enthalpy change at 298 K, free energy change at 298 K, and energy change at 0 K) for use in experimental situations. Experiment and certain semiempirical methods commonly give energetics in terms of the enthalpy of formation of a molecule. For example, the generalized hydrocarbon molecule $C_nH_m$ is formed from the elements in their standard states as

$$n\mathrm{C(graphite)} + \frac{m}{2}\mathrm{H_2(g)} \rightarrow \mathrm{C}_n\mathrm{H}_m\mathrm{(g)}, \quad \Delta H_f^{298\ \mathrm{K}}[\mathrm{C}_n\mathrm{H}_m]. \tag{1}$$

On the other hand, *ab initio* computations commonly determine equilibrium electronic energies for the molecule ($E_{\mathrm{C}_n\mathrm{H}_m}^{\mathrm{eq}}$) and each of the atoms ($E_{\mathrm{atom}}^{\mathrm{eq}}$) at infinite separation to determine the equilibrium electronic energy change ($\Delta E_{AB}^{\mathrm{eq}}$) for binding the separate atoms into a molecule as

$$\begin{gathered} nC(\mathrm{g}) + mH(\mathrm{g}) \rightarrow \mathrm{C}_n\mathrm{H}_m(\mathrm{g}), \\ \Delta E_{AB}^{\mathrm{eq}} = -\Sigma D_e = E_{\mathrm{C}_n\mathrm{H}_m}^{\mathrm{eq}} - \sum_{\mathrm{atoms}} E_{\mathrm{atom}}^{\mathrm{eq}}. \end{gathered} \tag{2}$$

This reaction is the reverse of atomization (the equilibrium atomization energy is often denoted as $\Sigma D_e$). Accepted atomic values (NIST webbook[31]) enable the conversion of $\Delta H_f^{298\ \mathrm{K}}$ to $\Delta H_{AB}^{298\ \mathrm{K}}$, where *AB* indicates the atomic binding reaction of Eq. (2). The relationships between (and signs of) $\Delta H_{AB}^{298\ \mathrm{K}}$, $\Delta E_{AB}^{0\ \mathrm{K}}$, and $\Delta E_{AB}^{\mathrm{eq}}$ are presented graphically in Fig. 1, and the details of the conversions are available in the M.S. thesis of Rodriguez.[34] The equilibrium electronic energy change ($\Delta E_{AB}^{\mathrm{eq}}$) is corrected to the energy change at a temperature of 0 K ($\Delta E_{AB}^{0\ \mathrm{K}}$) by adding the zero point energy (ZPE[$\mathrm{C}_n\mathrm{H}_m\mathrm{(g)}$]) of the molecule. The enthalpy change at 298 K for the atomic binding enthalpy reaction of Eq. (2) is obtained from $\Delta E_{AB}^{\mathrm{eq}}$ by adding $\Delta H_{\mathrm{species}}^{\mathrm{eq}\rightarrow 298\ \mathrm{K}}$ [the enthalpic contribution for both taking the molecular species from equilibrium to 0 K (ZPE) and heating the species from 0 to 298 K] and by subtracting the sum of the thermal corrections for each atom. Similar expressions for the standard free energy change for the atomic binding reaction ($\Delta G_{AB}^{298\ \mathrm{K}}$) are obtained by replacing the *H*'s of Fig. 1 with *G*'s. The ZPE, $\Delta H_{\mathrm{species}}^{\mathrm{eq}\rightarrow 298\ \mathrm{K}}$, and $\Delta G_{\mathrm{species}}^{\mathrm{eq}\rightarrow 298\ \mathrm{K}}$ quantities are routinely obtained with the GAUSSIAN98 or GAUSSIAN03 (Ref. 35) software package by vibrational mode analysis. The $\Delta H_{\mathrm{species}}^{\mathrm{eq}\rightarrow 298\ \mathrm{K}}$ and $\Delta G_{\mathrm{species}}^{\mathrm{eq}\rightarrow 298\ \mathrm{K}}$ terms derive from statistical mechanics expressions of ideal gas partition functions[29] which basically require the fundamental vibrational frequencies and the rotational constants of the molecule as input. As we require intensive properties for the infinitely long structures, these properties are extrapolated as $\Delta E_{AB}^{\mathrm{eq}}/n_{\mathrm{C}}$, $\Delta E_{AB}^{0\ \mathrm{K}}/n_{\mathrm{C}}$, $\Delta H_{AB}^{298\ \mathrm{K}}/n_{\mathrm{C}}$, and $\Delta G_{AB}^{298\ \mathrm{K}}/n_{\mathrm{C}}$, where $n_c$ is the number of carbon atoms in the structure.

### An illustration for the uninitiated

Test calculations are presented on the $CH_4$ and $HC\equiv CH$ molecules in Table I concerning the conversion between electron equilibrium energies and enthalpies of formation. Since G3 theory is in excellent accord with experimental enthalpies of formation, we can take the G3 theory estimate of the total electronic equilibrium energy as a best estimate of the total electronic equilibrium energies of these molecules. No single *ab initio* calculation that one might carry out with GAUSSIAN98 or GAUSSIAN03 (Ref. 35) (such as HF/6-31G$^*$ or MP2/aug-cc-pVDZ) gives enthalpies of formation in acceptable agreement with experiment. For example with $CH_4$, the HF/6-31G$^*$ (lowest level of *ab initio* theory with no electron correlation and a small basis set) and MP2/aug-cc-pVDZ (some electron correlation and a bigger basis set) results are missing 0.30 and 0.13 hartree (188 and 82 kcal/mol) of the total electronic energy, respectively. Clearly, the unaccounted portions of the equilibrium electronic energy are large compared to thermochemical values of interest. Note that spin orbit and other effects in the atoms are not always treated as well as possible making the deviations worse. *Ab-initio*-based recipes [G2,[24] G3,[27] and W2 (Refs. 28 and 36)] have been developed to take into account the deficiency of individual calculations. These methods involve sequences of calculations with small, medium, and large basis sets to estimate an infinite basis set result and sequences with increasingly sophisticated treatments of electron correlation to estimate the full amount of electron correlation.

Stewart's semiempirical PM3 method[30] does better on enthalpies of formation than single *ab initio* methods, such as HF/6-31G$^*$ or MP2/aug-cc-pVDZ, because it was "trained" to reproduce such numbers. The energies calculated with the PM3 method are enthalpies of formation, but beware—the GAUSSIAN98W or GAUSSIAN03W software package reports them as if they were the electronic equilibrium energies of *ab initio* calculations. It is up to the user to account for this "quirk" when converting between enthalpy changes, equilibrium energies, and free energies. These conversions are not very sensitive to the level of theory involved (as supported by the similarity of the last three columns in Table I), so it is concluded that PM3 will do pretty well at electronic equilibrium energy changes for C(g) → C(structure of interest) by comparison to an individual *ab initio* method such as MP2/aug-cc-pVDZ. While a method such as MP2/aug-cc-pVDZ might be desirable for many molecular properties (geometries or electronic properties), the atomic binding energetics should not be counted among them. The PM3 method displays an average deviation of 3.1 kcal/mol for enthalpies of formation over a set of 20 hydrocarbons which is quite acceptable because the error of a cluster's enthalpy of formation gets divided by the number of carbon atoms in the molecule. Consequently, we can apply these strategies with PM3 to more complex and larger carbon molecules, such as the (5,5) armchair SWCNTs.

There are fewer calibration points for free energies than for enthalpies. Literature entropies[37] were used for acetylene ($C_2H_2$) to calculate $\Delta G_{AB}^{298\ \mathrm{K}} n_{\mathrm{C}} - \Delta H_{AB}^{298\ \mathrm{K}}/n_{\mathrm{C}} = 6.141\ \mathrm{kcal/mol}$. We obtain values of 5.84 and 5.80 kcal/mol with the G3 and PM3 methods, respectively. Our values seem to be in reasonable accord with each other and the literature.

### Finite-cluster approach

Kirtman *et al.*[38] made early observations that ionization potentials, band gaps, and bandwidths show fast convergence with length using a fit of polynomial type in the reciprocal of the number of unit cells. The finite-cluster approach has been formalized[1,39] by Cioslowski (with discussion of other early work therein). The finite-cluster method enables rigorous treatment of electron correlation effects (rare with crystal orbital methods), permits the use of terminal groups on the clusters controlling desired structures[39] (nonglobal minima can be difficult with crystal calculations), and avoids the parametrization associated with the number of unit cells needed for proper sampling of $k$ space with periodic boundary calculations. Finite-cluster methods have been applied to a number of systems[39–41] including cumulenic chains with various terminations.[39] To use this approach with hydrocarbons consisting of carbon clusters with hydrogen termination, we have found the reciprocal of the number of carbon atoms ($n_{\mathrm{C}}$) to be an excellent parameter for extrapolation, i.e., it is similar to the reciprocal of the number of unit cells[1,41] in the limit as $n_{\mathrm{C}} \to \infty$. In this limit, the hydrogens make a negligible contribution to the stability per carbon because they become infinitely dilute. Similarly, a plot of a thermochemical property per carbon atom or a structural property of polyynes or polyenes versus the reciprocal of the number of carbon atoms in a series will linearly extrapolate to the value of the property in an infinite structure of pure carbon as shown in this work. Fits have been performed to the form

$$X = \sum_{i=0}^{i_{\max}} \alpha_i (n_c^{-k})^i, \tag{3}$$

where $X$ could be any intensive property, such as $\Delta H_{AB}^{298\ \mathrm{K}}/n_{\mathrm{C}}$, $\Delta G_{AB}^{298\ \mathrm{K}}/n_{\mathrm{C}}$, $\Delta E_{AB}^{0\ \mathrm{K}}/n_{\mathrm{C}}$, and $\Delta E_{AB}^{\mathrm{eq}}/n_{\mathrm{C}}$ for the atomic binding reaction of Eq. (2), or geometry such as the internal carbon-carbon triple, double, or single bond lengths in the molecules. The parameter $k$ is the dimension of the growth ($k=1$ for chains, $k=2$ for sheets, and $k=3$ for graphitic or diamond clusters). Metallic character can lead to oscillations of such properties[1,42] making extrapolations to infinite length more difficult. This aspect was particularly evident in the structures of the (5,5) SWCNTs and $C=C$ bond lengths of the chains.

## POLYYNES AND POLYENES EXTRAPOLATED TO INFINITE PURE-CARBON CHAINS

The most stable small-pure-carbon chains are cumulenic and the most stable infinite chain will be shown to be acetylenic, so chains of some finite length will have almost identical stabilities for the cumulenic and acetylenic forms. This can present optimization difficulties[11,43] which the finite-cluster approach with hydrogen or other caps[39] avoids. The hydrogen end caps (two at each end for cumulenic and one at the end of an even chain for acetylenic) enforce the expected structures in all of the polyyne and polyene structures studied [as gauged by the MP2(full)/6-31G$^*$ optimized structures], although the triple, double, and single carbon-carbon bond lengths become much more similar in infinite chains. We obtain the properties of pure-carbon chains by extrapolating the calculated properties of polyynes and polyenes to infinite length. The effect of terminal hydrogen atoms on the thermochemical properties of linear polyynes ($\mathrm{HC}_{2n}\mathrm{H}$) and linear polyenes ($\mathrm{H}_2\mathrm{C}_{2n}\mathrm{H}_2$) becomes diluted as these molecules grow to infinite length. As the number of carbon atoms ($n_\mathrm{C}$) goes to infinity, the effect of terminating hydrogens becomes infinitely dilute and therefore has no effect on the infinite-length thermochemistry, i.e., we obtain the thermochemistry and geometry of pure acetylenic ($^{\cdot}\mathrm{C}{\equiv}\mathrm{C}{-}\mathrm{C}{\equiv}\mathrm{C}^{\cdot}$) or cumulenic ($:\mathrm{C}{=}\mathrm{C}{=}\mathrm{C}{=}\mathrm{C}:$) carbon chains by extrapolating the properties of polyynes and polyenes to $n_\mathrm{C}=\infty$. The basic thermochemical calculations of linear polyynes and polyenes are summarized in Table II. The $\Delta G_{AB}^{298\ \mathrm{K}}/n_\mathrm{C}$ quantity is given versus $n_\mathrm{C}^{-1}$ for polyynes and polyenes ($k=1$) in Fig. 2 for both the G3 and PM3 methods. Each of these properties has been fitted to the polynomial expression of Eq. (3) with $i_\mathrm{max}=2$ (see Table III), as well as B3LYP results not shown in Fig. 2. These plots are very linear and readily extrapolate to well-defined values at $n_\mathrm{C}=\infty$ ($1/n_\mathrm{C}=0$). The $\alpha_2$ quadratic term is barely required for these fits in contrast to the behavior of finite, pure-carbon chains (which are open-shell species) to be presented in future work. The parameter $\alpha_0$ represents the value for a carbon atom in an infinite chain. A carbon atom in an infinite acetylenic chain has a G3 stability of $\Delta H_{AB}^{298\ \mathrm{K}}/n_\mathrm{C}=-145.0\pm0.4$, $\Delta G_{AB}^{298\ \mathrm{K}}/n_\mathrm{C}=-136.0\pm0.4$, $\Delta E_{AB}^{0\ \mathrm{K}}/n_\mathrm{C}=-144.3\pm0.3$, and $\Delta E_{AB}^{\mathrm{eq}}/n_\mathrm{C}=-147.4\pm0.4$ kcal/mol. A carbon atom in an infinite cumulenic chain has G3 stability of $\Delta H_{AB}^{298\ \mathrm{K}}/n_\mathrm{C}=-143.0\pm0.1$, $\Delta G_{AB}^{298\ \mathrm{K}}/n_\mathrm{C}=-134.1\pm0.1$, $\Delta E_{AB}^{0\ \mathrm{K}}/n_\mathrm{C}=-142.1\pm0.1$, and $\Delta E_{AB}^{\mathrm{eq}}/n_\mathrm{C}=-145.0\pm0.1$ kcal/mol. The errors represent the random errors of extrapolation to which one must add the systematic error inherent in the theory (perhaps $<0.2$ kcal/mol). The infinite acetylenic chain is $1.9\pm0.4$ kcal/mol more stable than the infinite cumulenic chain in free energy at room temperature. The G3 theory optimized structures [using the MP2(full)/6-31G$^*$ level of theory] have been analyzed regarding the progression of the most internal carbon-carbon bond lengths in order to determine the geometry of the infinite pure-carbon chains (see Fig. 3). The most internal triple bonds of the polyynes get longer as the chains grow longer giving a fit (in angstroms) of $1.2569(10)-0.142(4)n_\mathrm{C}^{-1}$. The single bonds get shorter giving a fit (in angstroms) of $1.333(4)+0.165(25)n_\mathrm{C}^{-1}$. Uncertainties (estimated standard deviations) are given in parentheses as the least significant digits. The infinite, pure-carbon results come from the intercepts, so the infinite acetylenic carbon chain triple bond and single bond lengths are $1.2569\pm0.0010$ and $1.333\pm0.004$ Å, respectively. The internal, polyene double bonds show two different values depending on whether $n_\mathrm{C}/2$ is even or odd. Both groups of double bonds were fitted with a common intercept. When odd, the double bond length (in angstroms) is $1.2788(26)+0.111(9)n_\mathrm{C}^{-1}$ and when even $1.2788(26)-0.154n_\mathrm{C}^{-1}$. The double bond length in an infinite cumulenic chain is $1.2788\pm0.0026$ Å. Clearly, both the energetic and geometric distinctions between triple, double, and single carbon-carbon bonds get smaller (but are not gone) at infinite length.

Similar calculations were performed with the semiempirical PM3 and B3LYP/6-31G$^*$ methods to see how well they do by comparison to G3 theory. For the four absolute bulk values ($\alpha_0$, from Table III), the PM3 values are within 2 kcal/mol of G3, while the B3LYP values are within 1 kcal/mol of G3, i.e., both are quite good. In terms of the room temperature, free energy difference in stability of the cumulenic chain from the acetylenic chain, the G3, PM3, and B3LYP methods all agree qualitatively and obtain 1.9, 4.1, and 0.6 kcal/mol, respectively. The optimized geometries of the PM3 polyyne calculations resulted in an internal C≡C bond length (in angstroms) of $1.2014(3)-0.0238(17)n_\mathrm{C}^{-1}$ and a C–C bond length (in angstroms) of $1.3618(5)+0.149(36)n_\mathrm{C}^{-2}$. The PM3 internal double bonds show a length (in angstroms) of $1.2726(3)+0.017(3)n_\mathrm{C}^{-1}-0.0069(57)n_\mathrm{C}^{-2}$ when $n_\mathrm{C}/2$ is odd and $1.2726(3)-0.066(21)n_\mathrm{C}^{-1}$ when $n_\mathrm{C}/2$ is even. The optimized geometries of the B3LYP/6-31G$^*$ polyyne calculations resulted in an internal C≡C bond length (in angstroms) of $1.2280(18)-0.050(7)n_\mathrm{C}^{-1}$ and a C–C bond length (in angstroms) of $1.3371(11)+0.130(7)n_\mathrm{C}^{-2}$. The internal B3LYP double bonds show a length (in angstroms) of $1.2762(23)+0.107(8)n_\mathrm{C}^{-1}$ when $n_\mathrm{C}/2$ is odd and $1.2762(23)-0.014(16)n_\mathrm{C}^{-1}$ when $n_\mathrm{C}/2$ is even. Both the B3LYP and PM3 methods show qualitatively similar trends to the G3 results with length; however, the B3LYP results quantitatively follow the *ab initio* geometry towards bulk better than the PM3. Since the B3LYP method was not currently viable for the SWCNT clusters with our PCs, we note the reasonable agreement of the lesser PM3 method with the more rigorous G3 method suggesting that PM3 will be useful for characterizing the thermochemistry (and to a lesser extent geometry) of large carbon clusters for which G3 theory becomes infeasible.

## INFINITE GRAPHENE SHEET

Infinite graphene sheet is an important calibrating point for those interested in SWCNTs as it can be considered a SWCNT with infinite diameter. Since curvature destabilizes a graphitic sheet, graphene will be a lower limit on the range of stabilities of infinitely long SWCNTs. Enthalpy of wetting data (energies of cohesion)[44] suggests that graphene is $2.0\pm0.2$ kcal/mol per carbon less stable than graphite in enthalpy (in agreement with empirical estimates[44,45] of 1.5–2.0 kcal/mol). Combined with accepted values for

TABLE II. Electronic equilibrium energies, enthalpies of formation, zero point energies, thermal enthalpic correction from equilibrium, and thermal free energy correction from equilibrium for linear polyynes and polyenes.

| Species | Method | $E^{\mathrm{eq}}$ (hartree) | $\Delta H_f^{298\ \mathrm{K}}$ (kcal/mol) | ZPE (kcal/mol) | $\Delta H^{\mathrm{eq}\rightarrow 298\ \mathrm{K}}$ (kcal/mol) | $\Delta G^{\mathrm{eq}\rightarrow 298\ \mathrm{K}}$ (kcal/mol) |
|---|---|---|---|---|---|---|
| $C_2H_2$ | G3 | −77.302 3[a] | 55.07 | 16.50 | 18.81 | 4.63 |
| | PM3 | | 50.7 | 17.50 | 19.74 | 5.66 |
| | B3LYP/631G* | −77.325 646 | 63.11 | 16.71 | 19.14 | 4.77 |
| | Expt. | | 54.19 | | | |
| $C_4H_2$ | G3 | −153.422 8[a] | 110.7 | 23.53 | 26.68 | 8.94 |
| | PM3 | | 102.4 | 25.13 | 28.07 | 10.72 |
| | B3LYP/631G* | −153.481 644 | 119.9 | 23.91 | 27.11 | 9.72 |
| | Expt. | | 111 | | | |
| $C_6H_2$ | G3 | −229.544 8[a] | 164.8 | 29.55 | 33.93 | 13.18 |
| | PM3 | | 153.6 | 32.44 | 36.31 | 16.36 |
| | B3LYP/631G* | −229.639 718 | 174.7 | 29.89 | 34.36 | 13.37 |
| $C_8H_2$ | G3 | −305.667 5[a] | 219.1 | 36.22 | 41.74 | 17.78 |
| | PM3 | | 204.8 | 39.65 | 44.52 | 22.04 |
| | B3LYP/631G* | −305.799 445 | 229.0 | 36.66 | 42.24 | 18.32 |
| $C_{10}H_2$ | G3 | −381.790 1[a] | 269.3 | 43.01 | 49.66 | 22.51 |
| | PM3 | | 255.9 | 46.85 | 52.73 | 27.81 |
| | B3LYP/631G* | −381.959 546 | 283.0 | 43.36 | 50.08 | 23.02 |
| $C_{12}H_2$ | PM3 | | 307.0 | 54.04 | 60.96 | 33.60 |
| | B3LYP/631G* | −458.119 837 | 337.1 | 50.19 | 58.03 | 27.85 |
| $C_{14}H_2$ | PM3 | | 358.1 | 61.20 | 69.16 | 39.40 |
| $C_{16}H_2$ | PM3 | | 409.2 | 68.42 | 77.39 | 45.36 |
| $C_{18}H_2$ | PM3 | | 460.4 | 75.60 | 85.62 | 51.69 |
| $C_{20}H_2$ | PM3 | | 511.5 | 81.26 | 93.12 | 54.95 |
| $C_{40}H_2$ | PM3 | | 1023 | 153.90 | 174.61 | 117.34 |
| $C_{50}H_2$ | PM3 | | 1279 | 189.74 | 215.68 | 147.54 |
| $C_{80}H_2$ | PM3 | | 2046 | — | — | — |
| $C_2H_4$ | G3 | −78.556 32[a] | 12.54 | 30.68 | 33.19 | 17.60 |
| | PM3 | | 16.6 | 31.25 | 33.78 | 17.34 |
| | B3LYP/631G* | −78.587 4583 | 15.88 | 32.15 | 34.65 | 19.05 |
| $C_4H_4$ | G3 | −154.661 09[a] | 77.0 | 36.39 | 39.97 | 20.94 |
| | PM3 | | 78.6 | 37.61 | 41.14 | 21.37 |
| | B3LYP/631G* | −154.730 7 | 79.6 | 38.04 | 41.54 | 22.64 |
| $C_6H_4$ | G3 | −230.774 21[a] | 136.5 | 42.20 | 47.04 | 24.57 |
| | PM3 | | 140.1 | 44.27 | 48.96 | 25.90 |
| | B3LYP/631G* | −230.882 82 | 138.0 | 43.91 | 48.66 | 26.37 |
| $C_8H_4$ | G3 | −306.889 89[a] | 194.4 | 48.00 | 54.14 | 28.21 |
| | PM3 | | 200.8 | 50.94 | 56.82 | 30.50 |
| | B3LYP/631G* | −307.038 54 | 194.4 | 50.13 | 56.08 | 30.57 |
| $C_{10}H_4$ | G3 | −383.006 5[a] | 251.7 | 53.69 | 61.18 | 31.73 |
| | PM3 | | 261.3 | 57.61 | 64.68 | 35.11 |
| | B3LYP/631G* | −383.195 5 | 250.2 | 56.46 | 63.58 | 34.89 |
| $C_{12}H_4$ | PM3 | | 321.7 | 64.29 | 72.54 | 39.72 |
| | B3LYP/631G* | −459.353 13 | 305.52 | 62.81 | 71.12 | 39.24 |
| $C_{14}H_4$ | PM3 | | 382.1 | 70.95 | 80.40 | 44.35 |
| $C_{16}H_4$ | PM3 | | 442.4 | 77.62 | 88.26 | 48.97 |
| $C_{18}H_4$ | PM3 | | 502.8 | 84.28 | 96.12 | 53.57 |
| $C_{20}H_4$ | PM3 | | 563.2 | 90.94 | 103.97 | 58.21 |
| $C_{40}H_4$ | PM3 | | 1166.8 | 157.60 | 182.52 | 104.64 |
| $C_{60}H_4$ | PM3 | | 1770.6 | 224.32 | 261.11 | 151.18 |

[a] Estimated with harmonic approximation for vibrations.

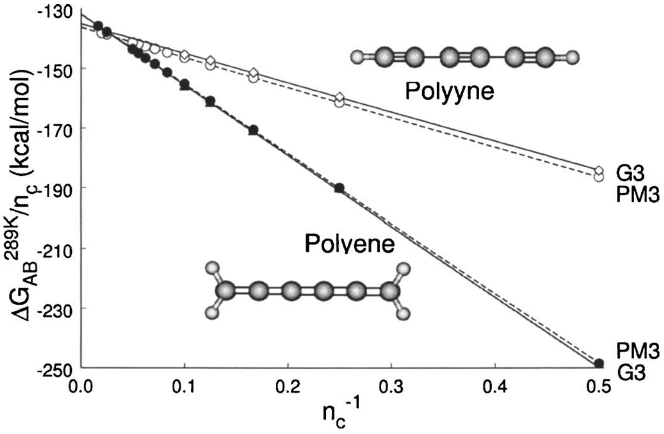

FIG. 2. Free energy change for the atomic binding reaction $n_C C(g) + mH(g) \rightarrow C_{n_C}H_m(g)$ on a per carbon basis, i.e., $\Delta G_{AB}^{298\ K}/n_C$, where $n_C$ is the number of carbon atoms in polyyne or polyene molecules. The effect of the hydrogen atoms is infinitely diluted at $n_C=\infty$ ($n_C^{-1}=0$) indicating the stability of an infinite pure-carbon chain. The semiempirical (PM3) method does reasonably well compared to the G3 theory [QCISD(T,full)/G3large energies] which is a composite of well-defined *ab initio* electronic structure calculations providing agreement with experimental thermochemistry.

graphite (NIST webbook[31]), an experimental value for the enthalpy change of C(g)→C(graphene sheet) is −169.3±0.2 kcal/mol. An MNDO cluster-extrapolation study[46] (same semiempirical model as PM3 but trained on a smaller set of molecules) found that graphene was 3.0±0.2 less stable than graphite in enthalpy by extrapolating a sequence of polyaromatic hydrocarbons (PAHs) built of six-member rings growing in radial steps about a central carbon ring. Other work has also looked at PAHs and fullerenes[44,47] and is useful for gauging reliability, but again only for enthalpies. Our work is distinguished by normal mode analysis which enables free energy changes, enthalpy changes, energetics at 0 K, and electronic equilibrium energy changes to be calculated. Furthermore, in order to make the extrapolations to infinite area more reliable, we have extrapolated the results of four different families of finite structures that share the same infinite intercept. Calculations were performed on pure-carbon triangulenes (high spin, non-Kekule structures which curve upon optimization), pure-carbon triangulene forced to be flat with symmetry constraints, triangulene PAHs (lower optimal multiplicities than their pure-carbon counterparts that remain flat), and parallelulene PAHs (which have singlet ground states and are also flat). The enthalpies of formation, ZPEs, and enthalpic and free energy corrections are presented in Table IV. The structures of these families are represented in Fig. 4 which shows a plot of the free energy change on a per carbon basis versus $n_C^{-1/2}$. The PAHs approach their infinite area energies from below, while the

TABLE III. Fits of cluster thermochemical values on a per carbon basis vs the reciprocal of the number of carbon atoms as given in Eq. (3). The parameter $\alpha_0$ is the bulk value for an infinite length. Uncertainties are just the random errors and are given in parentheses as the least significant digits.

| Family | Method | Thermochemical quantity (kcal/mol) | $\alpha_0$ (kcal/mol) ∞ length | $\alpha_1$ (kcal/mol) $n_C^{-1}$ slope | $\alpha_2$ (kcal/mol) | s.d. of fit (kcal/mol) |
|---|---|---|---|---|---|---|
| Linear polyyne $HC_nH$ | G3 | $\Delta E_{AB}^{eq}/n_C$ | −147.4(4) | −104(4) | −13(6) | 0.19 |
| | PM3 | | −148.36(2) | −112.01(24) | −2.5(5) | 0.03 |
| | B3LYP/6-31G* | | −146.73(7) | −97.7(7) | −11.3(11) | 0.04 |
| Linear polyyne $HC_nH$ | G3 | $\Delta E_{AB}^{0\ K}/n_C$ | −144.3(3) | −91.2(29) | −17(5) | 0.15 |
| | PM3 | | −144.77(2) | −101.14(25) | −3.4(5) | 0.03 |
| | B3LYP/6-31G* | | −143.57(4) | −85.8(4) | −14.6(7) | 0.03 |
| Linear polyyne $HC_nH$ | G3 | $\Delta H_{AB}^{298\ K}/n_C$ | −145.0(4) | −96(4) | −13(6) | 0.19 |
| | PM3 | | −145.73(2) | −103.59(28) | −1.9(5) | 0.03 |
| | B3LYP/6-31G* | | −144.38(6) | −89.1(6) | −11.6(9) | 0.04 |
| Linear polyyne $HC_nH$ | G3 | $\Delta G_{AB}^{298\ K}/n_C$ | −136.0(4) | −90(4) | −13(6) | 0.18 |
| | PM3 | | −136.24(3) | −101.7(4) | −3.2(8) | 0.05 |
| | B3LYP/6-31G* | | −135.42(8) | −83.2(8) | −13.2(13) | 0.05 |
| Linear polyene $H_2C_nH_2$ | G3 | $\Delta E_{AB}^{eq}/n_C$ | −145.02(13) | −256.4(11) | −32.7(18) | 0.06 |
| | PM3 | | −143.56(3) | −267.7(4) | −8.9(7) | 0.04 |
| | B3LYP/6-31G* | | −146.07(11) | −249.6(10) | −38.2(17) | 0.06 |
| Linear polyene $H_2C_nH_2$ | G3 | $\Delta E_{AB}^{0\ K}/n_C$ | −142.05(9) | −232.3(8) | −31.2(12) | 0.04 |
| | PM3 | | −140.21(3) | −243.8(4) | −7.7(7) | 0.04 |
| | B3LYP/6-31G* | | −142.94(3) | −224.8(3) | −36.4(5) | 0.02 |
| Linear polyene $H_2C_nH_2$ | G3 | $\Delta H_{AB}^{298\ K}/n_C$ | −143.02(10) | −236.2(9) | −32.3(14) | 0.04 |
| | PM3 | | −141.13(3) | −248.0(4) | −8.3(7) | 0.04 |
| | B3LYP/6-31G* | | −143.75(10) | −229.8(10) | −35.7(16) | 0.06 |
| Linear polyene $H_2C_nH_2$ | G3 | $\Delta G_{AB}^{298\ K}/n_C$ | −134.07(2) | −216.23(19) | −31.7(3) | 0.01 |
| | PM3 | | −132.13(3) | −229.1(4) | −7.4(7) | 0.04 |
| | B3LYP/6-31G* | | −134.77(4) | −209.7(3) | −35.1(6) | 0.02 |

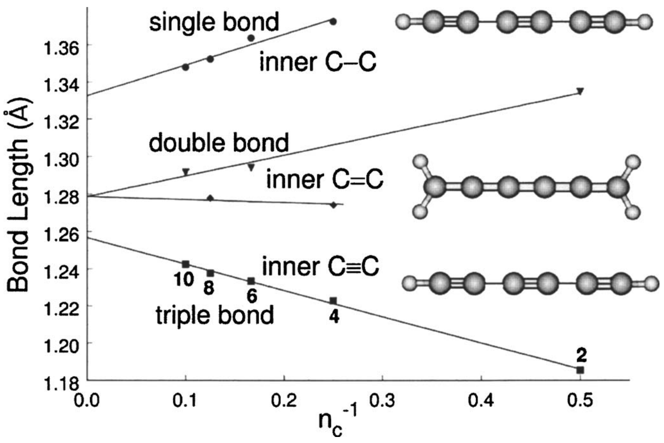

FIG. 3. Internal carbon-carbon bond lengths from G3 theory [MP2(full)/6-31G$^*$ optimized structures] of polyynes and polyenes growing in length plotted vs the reciprocal of the number of carbon atoms in each structure. The infinite, pure-carbon results come from the intercepts at $n_C^{-1}=0$. There is less distinction between triple, double, and single carbon-carbon bonds as the carbon chains become infinite.

pure-carbon species approach from above. Each family is fitted to a form similar to Eq. (3) except that the independent variable is $n_C^{-1/2}$ because the growth is two dimensional ($k=2$ because we are extrapolating to infinite area rather than length). Multiple linear regression analyses were simultaneously performed on each family constraining them to share a common infinite area intercept. When fitted together with a common intercept, these four families produce a value with smaller statistical uncertainty than any family by itself. A summary of the fits for the various energetic quantities on a per carbon basis is given in Table V. We obtain −169.4±0.7 kcal/mol for the enthalpy change of C(g)→C (graphene sheet), which is in excellent agreement with the experimental value of −169.3±0.2 kcal/mol. A simultaneous fit of the most internal carbon-carbon bond lengths of each of these families with a common intercept gives an infinite sheet, PM3 bond length of 1.408±.009 Å. are −109(5), −114(3), 123(3), and 122(3) for the paralleluThere is a small but detectable shrinking of the most internal carbon-carbon bond distances as the two-dimensional structures grow. The experimental carbon-carbon bond distance is 1.421 Å,[48] the periodic boundary condition density functional theory[49] (PBC-PBE/3-21G level) value is 1.431 Å, and the MNDO estimate from the family of PAHs growing in rings[46] is 1.437(3) Å.

## STRUCTURE AND ENERGETICS OF THE (5,5) SWCNT

Semiempirical PM3 optimizations and normal mode analyses were performed on the (5,5) armchair SWCNT with open ends, with a half-fullerene cap on one end and with half-fullerene caps on both ends (all as singlets, presented in Table VI). The atomic binding energetics on a per carbon basis were determined from the data in Table VI. The $\Delta G_{AB}^{298\ \mathrm{K}}/n_C$ quantity is plotted in Fig. 5 versus $n_C^{-1}$ for the various capping options. All three groups (open, half capped, and capped at each end) extrapolate to very similar values (within a few kcal/mol) at infinite length when fitted by Eq. (3) ($k=1$), providing support for the assertion that all three groups must extrapolate to the same value at infinity. This is a strategy similar to that employed with the polyenes and polynes; however, in this case, the effect of the ends (and

TABLE IV. PM3 calculations of the enthalpies of formation, zero point energies, thermal enthalpic correction from equilibrium, and thermal free energy correction from equilibrium for a series of parallelulene PAHs (flat, closed-shell molecules where six-member rings grow equally at two adjacent edges producing parallelagrams), triangulene PAHs (non-Kekule, high spin molecules which are flat and one edge of the triangle grows with each step), pure-carbon triangulenes (which are open-shell and curve upon optimization), and pure-carbon triangulene (constrained by symmetry to be flat). The multiplicities displayed are the ones that had the lowest energies upon optimization.

| Species | Multiplicity $2S+1$ | $\Delta H_i^{298\ \mathrm{K}}$ (kcal/mol) | ZPE (kcal/mol) | $\Delta H^{\mathrm{eq}\rightarrow 298\ \mathrm{K}}$ (kcal/mol) | $\Delta G^{\mathrm{eq}\rightarrow 298\ \mathrm{K}}$ (kcal/mol) |
|---|---|---|---|---|---|
| Parallelogram $C_{16}H_{10}$ | 1 | 63.9 | 130.6 | 137.6 | 108.2 |
| Parrallelogram $C_{30}H_{14}$ | 1 | 129.7 | 216.4 | 228.2 | 188.5 |
| Parallelogram $C_{48}H_{18}$ | 1 | 219.7 | 319.6 | 337.3 | 285.6 |
| Parallelogram $C_{70}H_{22}$ | 1 | 331.6 | 440.0 | 464.5 | 399.3 |
| Triangular $C_6H_6$ (benzene) | 1 | 23.4 | 62.0 | 65.4 | 44.7 |
| Triangular $C_{13}H_9$ | 2 | 50.8 | 108.6 | 114.9 | 87.0 |
| Triangular $C_{22}H_{12}$ | 3 | 79.7 | 164.6 | 174.2 | 138.6 |
| Triangular $C_{33}H_{15}$ | 4 | 112.0 | 229.1 | 242.7 | 198.7 |
| Triangular $C_{46}H_{18}$ | 5 | 148.0 | 302.2 | 320.1 | 266.9 |
| Triangular $C_{61}H_{21}$ | 6 | 187.7 | 383.7 | 406.6 | 343.3 |
| Triangular $C_6$ curved | 3 | 334.3 | 16.8 | 19.8 | −0.7 |
| Triangular $C_{13}$ curved | 5 | 473.6 | 36.3 | 41.3 | 14.9 |
| Triangular $C_{22}$ curved | 11 | 716.1 | 79.1 | 87.5 | 53.4 |
| Triangular $C_{33}$ curved | 13 | 716.1 | 79.1 | 87.5 | 53.4 |
| Triangular $C_6$ flat | 3 | 334.3 | 16.4 | 19.3 | −1.1 |
| Triangular $C_{13}$ flat | 7 | 503.0 | 43.4 | 48.9 | 21.5 |
| Triangular $C_{22}$ flat | 11 | 673.9 | 77.8 | 86.5 | 58.0 |
| Triangular $C_{33}$ flat | 13 | 819.0 | 120.4 | 132.8 | 90.2 |

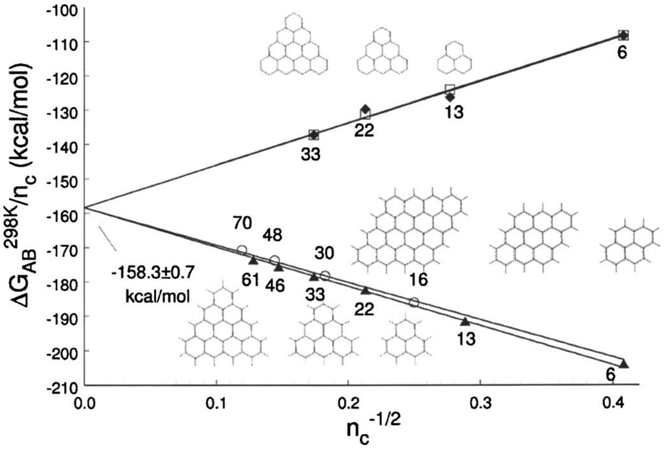

FIG. 4. Determining the PM3 value for $\Delta G_{AB}^{298\ \mathrm{K}}/n_{\mathrm{C}}$, the free energy change for C(g)→C(graphene). The four families that share a common graphene intercept include pure-carbon triangulenes (high spin, non-Kekule structures which curve upon optimization), pure-carbon triangulene transition states (forced to be flat with symmetry constraints), triangulene polyaromatic hydrocarbons (PAHs with lower optimal multiplicities than their pure-carbon counterparts, but which remain flat), and paralleulene PAHs (which have singlet ground states and are also flat) all share the same intercept, $-158.3\pm0.7$ kcal/mol. The enthalpic intercept obtained with this procedure is in excellent agreement with experiment.

their open shell or curved nature) becomes infinitely dilute at infinite length. All three groups were simultaneously fitted with a multiple linear regression procedure that forced all three sets to share a common infinite-length intercept. The results are presented in Table VII. The parameter $\alpha_0$ is the stability on a per carbon basis for the infinite (5,5) SWCNT giving PM3 values for C(g) →C(infinite(5,5)SWCNT) of $\Delta H_{AB}^{298\ \mathrm{K}}/n_{\mathrm{C}}=-163.5\pm0.2$, $\Delta G_{AB}^{298\ \mathrm{K}}/n_{\mathrm{C}}=-153.3\pm0.2$, $\Delta E_{AB}^{0\ \mathrm{K}}/n_{\mathrm{C}}=-162.3\pm0.2$, and $\Delta E_{AB}^{\mathrm{eq}}/n_{\mathrm{C}}=-166.7\pm0.2$ kcal/mol, where the uncertainties are the random errors of the statistical fitting process. An absolute error of $<3$ kcal/mol must be added, but differences within families are better determined (perhaps to ~0.3 kcal/mol). A carbon atom in an infinite (5,5) SWCNT is 5.1 kcal/mol less stable in free energy than graphene sheet and 6.7 kcal/mol less stable than graphite. There have been some DFT periodic calculations[49] on SWCNTs (periodic boundary condition PBE/3-21G*), but no quantities are presented that are directly comparable to the broad set of absolute energetics of this work. However, they do give a strain energy of 3.8 kcal/mol per carbon for the (5,5) SWCNT which is the energy penalty for curving this structure from an infinite graphene sheet. Assuming that this energy is obtained from the equilibrium energy differences of their calculations, we can compare our finding that the (5,5) SWCNT is 5.8 kcal/mol less stable than infinite graphene sheet in electronic equilibrium energy. The methods agree within 2.0 kcal/mol per carbon which is as good as can be expected based upon the previously determined limitations of PM3 and the comparable thermochemical limitations of DFT.[50] Noting that several investigators[49,51] have observed linearity in the strain energy with the reciprocal of diameter squared, we offer a crude (two point) PM3 estimate of the strain free energy in kcal/mol for armchair SWCNTs of $239/[d(\text{Å})]^2$ where $d$ is the diameter of the tube.

The smallest double capped (5,5) SWCNT is just the $C_{60}$ fullerene molecule. This molecule serves as an additional test of the quality of the PM3 results at small size because there is an experimental value for the heat of formation of $C_{60}(g)$ based on heat of combustion experiments on $C_{60}(s)$ and heat

TABLE V. PM3 calculations of paralleluene PAHs, triangulene PAHs, pure-carbon triangulene, and pure-carbon triangulene transition states (constrained to be flat) growing into graphene sheet. Fits of cluster thermochemical values on a per carbon basis vs $n_{\mathrm{C}}^{-1/2}$ (for two dimensional growth). The parameter $\alpha_0$ is the bulk intercept corresponding to infinite area. The parameter $\alpha_1$ is the $n_{\mathrm{C}}^{-1/2}$ slope (in contrast to the one dimensional fits that employ $n_{\mathrm{C}}^{-1}$). Uncertainties are just the random errors and are given in parentheses as the least significant digits.

| Family | Thermochemical quantity (kcal/mol) | $\alpha_0$ (kcal/mol) infinite area | $\alpha_1$ (kcal/mol) $n_{\mathrm{C}}^{-1/2}$ slope | s.d. of fit (kcal/mol) |
|---|---|---|---|---|
| Paralleluene PAH | | | −132(5) | |
| Triangulene PAH | $\Delta E_{AB}^{\mathrm{eq}}/n_{\mathrm{C}}$ | −172.5(7) | −137(3) | 1.0 |
| Triangulene $\mathrm{C}_n$ flat | | | 136(3) | |
| Triangulene $\mathrm{C}_n$ curved | | | 135(3) | |
| Parallelulene PAH | | | −117(5) | |
| Triangulene PAH | $\Delta E_{AB}^{0\ \mathrm{K}}/n_{\mathrm{C}}$ | −168.1(7) | −122(3) | 1.1 |
| Triangulene $\mathrm{C}_n$ flat | | | 132(3) | |
| Triangulene $\mathrm{C}_n$ curved | | | 131(3) | |
| Parallelulene PAH | | | −120(5) | |
| Triangulene PAH | $\Delta H_{AB}^{298\ \mathrm{K}}/n_{\mathrm{C}}$ | −169.4(7) | −125(3) | 1.1 |
| Triangulene $\mathrm{C}_n$ flat | | | 132(3) | |
| Triangulene $\mathrm{C}_n$ curved | | | 132(3) | |
| Parallelulene PAH | | | −109(5) | |
| Triangulene PAH | $\Delta G_{AB}^{298\ \mathrm{K}}/n_{\mathrm{C}}$ | −158.3(7) | −114(3) | 1.0 |
| Triangulene $\mathrm{C}_n$ flat | | | 123(3) | |
| Triangulene $\mathrm{C}_n$ curved | | | 122(3) | |

TABLE VI. PM3 calculations of the enthalpies of formation, zero point energies, thermal enthalpic correction from equilibrium, and thermal free energy correction from equilibrium for (5,5) SWCNTs. All species in this table were calculated as singlets, which are the ground state for the double capped but not for tubes with open edges.

| Species | $\Delta H_f^{298\text{ K}}$ (kcal/mol) | ZPE (kcal/mol) | $\Delta H^{\text{eq}\rightarrow 298\text{ K}}$ (kcal/mol) | $\Delta G^{\text{eq}\rightarrow 298\text{ K}}$ (kcal/mol) |
|---|---|---|---|---|
| (5,5) SWCNT open $C_{30}$ | 1284.8 | 110.7 | 123.0 | 81.1 |
| (5,5) SWCNT open $C_{40}$ | 1306.0 | 153.3 | 167.5 | 123.5 |
| (5,5) SWCNT open $C_{50}$ | 1387.1 | 196.8 | 213.2 | 165.3 |
| (5,5) SWCNT open $C_{60}$ | 1459.4 | 240.8 | 259.3 | 207.9 |
| (5,5) SWCNT open $C_{70}$ | 1515.0 | 285.2 | 305.8 | 250.8 |
| (5,5) SWCNT open $C_{80}$ | 1586.0 | 328.2 | 3512 | 292.3 |
| (5,5) SWCNT open $C_{90}$ | 1662.5 | 372.2 | 397.2 | 334.7 |
| (5,5) SWCNT open $C_{100}$ | 1720.2 | 416.4 | 443.7 | 377.5 |
| (5,5) SWCNT open $C_{110}$ | 1820.1 | 459.5 | 489.2 | 419.0 |
| (5,5) SWCNT one cap $C_{30}$ | 1005.1 | 117.2 | 127.0 | 91.7 |
| (5,5) SWCNT one cap $C_{40}$ | 959.0 | 162.9 | 174.2 | 136.3 |
| (5,5) SWCNT one cap $C_{50}$ | 1043.1 | 207.7 | 220.9 | 179.6 |
| (5,5) SWCNT one cap $C_{60}$ | 1129.1 | 250.8 | 266.3 | 221.0 |
| (5,5) SWCNT one cap $C_{70}$ | 1222.2 | 294.3 | 311.9 | 263.1 |
| (5,5) SWCNT one cap $C_{80}$ | 1264.6 | 338.7 | 358.5 | 305.9 |
| (5,5) SWCNT one cap $C_{90}$ | 1336.6 | 381.9 | 404.1 | 347.6 |
| (5,5) SWCNT one cap $C_{100}$ | 1413.0 | 425.6 | 449.9 | 389.7 |
| (5,5) SWCNT one cap $C_{110}$ | 1469.3 | 470.0 | 496.5 | 432.6 |
| (5,5) SWCNT one cap $C_{120}$ | 1539.9 | ⋯ | ⋯ | ⋯ |
| (5,5) SWCNT one cap $C_{130}$ | 1617.9 | ⋯ | ⋯ | ⋯ |
| (5,5) SWCNT double capped $C_{60}$ | 810.8 | 260.7 | 273.1 | 234.0 |
| (5,5) SWCNT double capped $C_{70}$ | 883.0 | 303.9 | 318.6 | 275.7 |
| (5,5) SWCNT double capped $C_{80}$ | 956.9 | 347.6 | 364.5 | 317.9 |
| (5,5) SWCNT double capped $C_{90}$ | 1012.0 | 392.2 | 411.3 | 361.0 |
| (5,5) SWCNT double capped $C_{100}$ | 1087.7 | 435.6 | 456.9 | 402.8 |
| (5,5) SWCNT double capped $C_{110}$ | 1164.6 | 479.0 | 502.6 | 444.6 |
| (5,5) SWCNT double capped $C_{120}$ | 1218.8 | 523.5 | 549.3 | 487.6 |
| (5,5) SWCNT double capped $C_{130}$ | 1289.9 | 566.9 | 595.0 | 529.4 |
| (5,5) SWCNT double capped $C_{140}$ | 1370.1 | ⋯ | ⋯ | ⋯ |
| (5,5) SWCNT double capped $C_{160}$ | 1493.5 | ⋯ | ⋯ | ⋯ |
| (5,5) SWCNT double capped $C_{180}$ | 1653.7 | ⋯ | ⋯ | ⋯ |

of sublimation values. The current NIST webbook[31] value of $\Delta H_f^{298\text{ K}}[C_{60}(g)]$ is 635(6) kcal/mol as compared to earlier experiments that obtained significantly lower values before it was known how tightly fullerene holds onto solvent. Presumably, more accurate measurements will be made when larger amounts of highly purified fullerenes are available for combustion. Our value of 810.8 kcal/mol is high by comparison. Note also that unrestricted Hartree-Fock (UHF) calculations on $C_{60}$ fullerene[47] obtain $\Delta H_f^{298\text{ K}}[C_{60}(g)] = 799.2(6)$ kcal/mol. The PM3 difference from experiment corresponds to an error of 2.7 kcal/mol on a per carbon basis which is not as good as our results at infinite length. More caution should be exercised in discussing small cluster energetics. Absolute energetics may be no better than 3 kcal/mol for the smallest molecules, although relative differences may be considerably better.

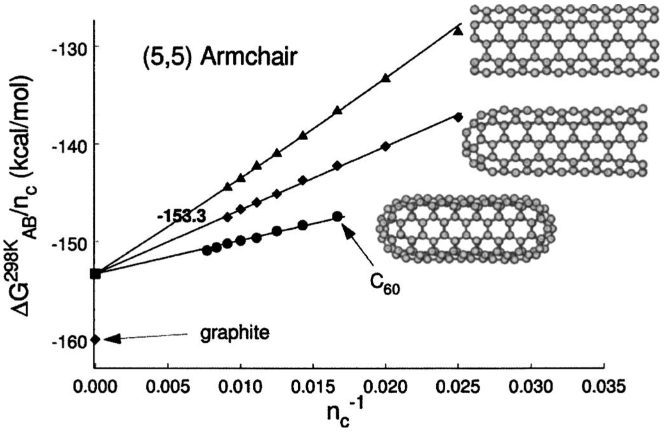

FIG. 5. Free energy change on a per carbon basis, $\Delta G_{AB}^{298\text{ K}}/n_C$, for $C(g) \rightarrow C[(5,5)\text{ SWCNT}]$, where $n_C$ is the number of carbon atoms in a (5,5) SWCNT with open ends, one fullerene capped end, or fullerene caps on both ends. All three groups must extrapolate to the same value at infinite length giving a more reliable determination of the infinite-length value. Also shown are the values for graphite and the $C_{60}$ fullerene molecule.

Connecting the geometry of (5,5) SWCNT finite-length molecules to the infinitely long tube was much more difficult than the energetics. The bonding in finite molecules is considerably perturbed by the caps and there is symmetry of the tube diameter about the center along the tube axis (a symmetry that the infinitely long tube does not have). A (5,5) SWCNT is constructed of rings of ten carbon atoms each and three adjacent rings are displayed in the inset of Fig. 6 giving

TABLE VII. Fits of (5,5) SWCNT cluster thermochemical values on a per carbon basis vs the reciprocal of the number of carbon atoms. The parameter $\alpha_0$ is the bulk value for an infinite length. Uncertainties are just the random errors and are given in parentheses as the least significant digits.

| Family | Method | Thermochemical quantity (kcal/mol) | $\alpha_0$ (kcal/mol) bulk value | $\alpha_1$ (kcal/mol) | $\alpha_2$ (kcal/mol) | s.d. of fit (kcal/mol) |
|---|---|---|---|---|---|---|
| Open (5,5) SWCNT singlet | PM3 | $\Delta E_{AB}^{\mathrm{eq}}/n_{\mathrm{C}}$ | −166.69(16) | 1006(20) | 2400(600) | 0.20 |
| Half-capped (5,5) SWCNT singlet | | | | 687(11) | | |
| Both capped (5,5) SWCNT | | | | 368(15) | | |
| Open (5,5) SWCNT singlet | PM3 | $\Delta E_{AB}^{0\ \mathrm{K}}/n_{\mathrm{C}}$ | −162.25(17) | 1006(22) | 2000(600) | 0.21 |
| Half-capped (5,5) SWCNT singlet | | | | 673(11) | | |
| Both capped (5,5) SWCNT | | | | 360(16) | | |
| Open (5,5) SWCNT singlet | PM3 | $\Delta H_{AB}^{298\ \mathrm{K}}/n_{\mathrm{C}}$ | −163.54(15) | 958(18) | 3000(500) | 0.18 |
| Half-capped (5,5) SWCNT singlet | | | | 677(10) | | |
| Both capped (5,5) SWCNT | | | | 361(13) | | |
| Open (5,5) SWCNT singlet | PM3 | $\Delta G_{AB}^{298\ \mathrm{K}}/n_{\mathrm{C}}$ | −153.29(16) | 954(20) | 2600(600) | 0.20 |
| Half-capped (5,5) SWCNT singlet | | | | 654(11) | | |

the bond variable definitions for the case where there could be different diameters. The diameter ($d_{\mathrm{ring}}$) of any ring has a simple relationship to the distance ($R$) between a carbon atom and the similar atom in the ring upon rotating by 72° about the tube axis, i.e., $d_{\mathrm{ring}}=R/\sin(36°)$. Diameters were determined from atom distances in the optimized structures in this manner. If one assumes that the rings of an infinitely long tube all have the same diameter, as Bettinger *et al.*[49] (PBC-PBE/3-21G) and Sun *et al.*[52] (PBC-PW91/GGA UltraVTP) have with periodic DFT calculations, then there will be two types of C–C bond distances: $R1$'s are perpendicular to the tube axis (with a PBC-PBE/3-21G value of 1.438 Å) and $R2$'s are not perpendicular (with a PBC-PBE/3-21G value of 1.435 Å). This turns out to be a good representation of the zero point energy structure, but the equilibrium structures can be more complicated. If all diameters are the same, then the inner ring diameters of finite molecules should converge towards such values as the molecules get larger. However, we observed oscillations in the inner ring diameters that did not subside with increased molecule size. The oscillations were three fold in diameter (six fold if one considers that each ring is rotated by 36° from its adjacent ring) if the mirror symmetry at the center of the tube was avoided. Note that only certain length molecules can maintain a three fold oscillation pattern across the center mirror of symmetry for diameters. To sort this out, periodic PM3 calculations were performed using the MOPAC2000 program[53] and the $k$-space integration method with the "Γ point only" option. Use of this option requires a repeating cell longer than ~10 Å, so cells consisting of many unit cells were used. Many different size cells were tried; however, only cells with an integral multiple of six rings gave satisfactory results. For example, a histogram of the ring diameters obtained with cells of 240 and 200 carbon atoms is given in Fig. 6. The 240 C atom cell (24 rings) shows only two different diameters (the larger having twice the frequency of the smaller), whereas the 200 carbon atom cell (20 rings which is not integrally divisible by 6) shows a wide distribution of diameters. Cells that are not multiples of six ring units do not match the inherent repeating unit of the infinitely long tube and give disparate results. The 240 carbon atom, (5,5) SWCNT cell had 16 large ring diameters ($d_{\mathrm{H1}}$ and $d_{\mathrm{H2}}$) giving an average value of 6.8663(6) Å and eight smaller ring diameters ($d_L$) with a value of 6.8227(5) Å using the variables defined in Fig. 6. This infinite structure gives rise to two different values of C–C bond distances, but they have a different distribution than the equal diameter case. For instance, the bonds perpendicular to the tube axis no longer have just one value. We find that $R2_{\mathrm{H2H1}}=R1_{\mathrm{H1}}=1.4054(8)$ Å and $R2_{\mathrm{LH2}}=R2_{\mathrm{H1L}}=R1_{\mathrm{H2}}=R1_{\mathrm{L}}=1.4334(3)$. These periodic calculations were performed on sequences of cells in length, both constrained to equal diameters (at $n_{\mathrm{C}}=80$, 100, 120, 140, 160, 180, 200, 220, 280, and 320) and unconstrained but with the number of rings being a multiple of 6 (at $n_{\mathrm{C}}=60$, 120, 180, 240, and 300). The value of $\Delta H_{AB}^{298\ \mathrm{K}}/n_{\mathrm{C}}$ for $\mathrm{C(g)} \rightarrow \mathrm{C(infinite(5,5)SWCNT)}$ extrapolated to infinite length from PBC-PM3 (5,5) SWCNT is −164.0±0.1 kcal/mol for

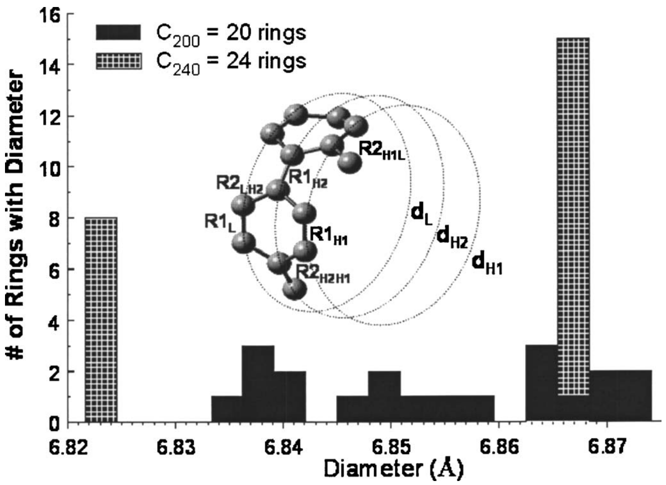

FIG. 6. Histogram of the ring diameters for PM3 periodic boundary condition calculations on (5,5) SWCNT cells with 240 and 200 carbon atoms. Cells that are multiples of 60 carbon atoms give distinctly two different diameters (in a low-high-high pattern) rather than a distribution. The schematic of three adjacent rings at the center defines the geometry variables for the case when the diameters are not necessarily the same.

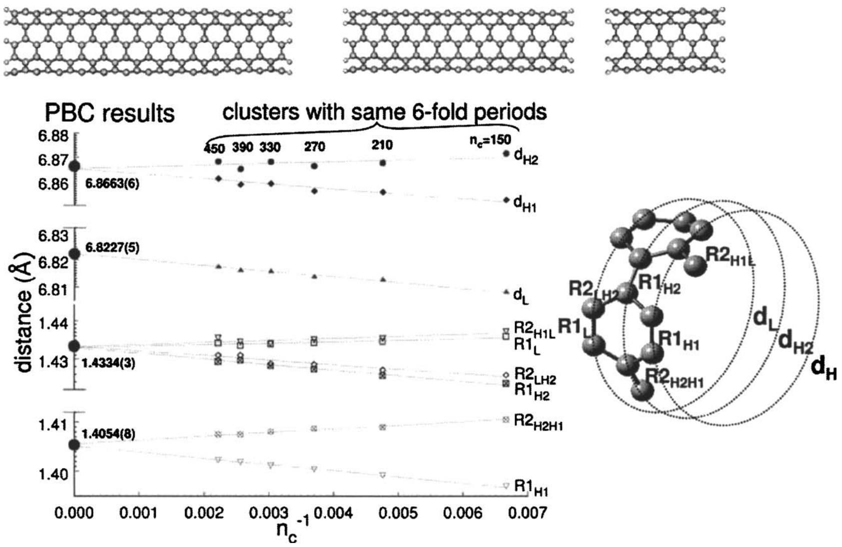

FIG. 7. The inner geometric parameters (ring diameter and C–C bond distance) of a special sequence of open-ended, hydrogen-atom-terminated (5,5) SWCNT molecules vs reciprocal of the number of carbon atoms. The sequence was chosen such that the threefold oscillation of diameters was not interrupted by the mirroring of diameters about the center of the cluster. This sequence connects smoothly to the infinitely long (5,5) SWCNT as defined by the periodic boundary calculations in a manner similar to the simpler systems described earlier.

the high-high-low diameter structure and $-163.7 \pm 0.1$ kcal/mol for the equal diameter structure. These values compare well to the value of $-163.5 \pm 0.2$ kcal/mol obtained by the finite-cluster extrapolation method. The high-high-low diameter structure is slightly more stable, but the difference is small compared to the zero point energy ($4.4 \pm 0.2$ kcal/mol per carbon atom as extracted from Table VII). Therefore, the equal diameter structure is reasonable as a ZPE-averaged structure, but one may have to consider nonequal diameter structures when searching for the equilibrium minimum.

Arguments in this paper are based on the smooth progress of molecular properties to infinite length, so it is fair to require that a legitimate structure for infinitely long (5,5) nanotube should be smoothly connected to finite molecule structures. This became possible with the PBC-PM3 results and awareness of the issue of diameter mirroring about the center. A sequence of open-ended, H-atom-terminated (5,5) SWCNT molecules containing 150, 210, 270, 330, 390, and 450 carbon atoms was chosen because these sizes enable the three fold diameter oscillating pattern to propagate across the molecule without being interrupted by the mirroring at the center (they need a smaller diameter at the center). In fact, all of the bond distances in these molecules can be smoothly correlated to infinite length, as shown in the M.S. thesis of Rodriguez;[34] however, for simplicity only the inner diameter and associated C–C bond distances are plotted in Fig. 7 as a function of size (versus $1/n_C$). The larger of the two diameters in infinitely long tubes breaks into two different diameters in finite molecules and the two C–C bond distances of infinitely long tubes break into four such distances in the molecules.

The smooth connection of molecules to infinite chains reinforces the high-high-low diameter structure of the infinitely long (5,5) SWCNT; however, PM3 is not as good as *ab initio* or DFT methods for investigating structure. Higher level calculations were sought that might provide more confidence in our structural conclusions. B3LYP/6-311G$^*$ calculations have been reported by Cioslowski *et al.*[42] on the $C_{210}$ doubly capped (5,5) SWCNT. Taking the 30 carbon fullerene caps off of each end, the double capped $C_{210}$ cluster has 15 rings with a smaller diameter in the middle, just like the smallest member of the special sequence described in the preceding paragraph. Cioslowski's results (as graphically extracted from a figure) are overlaid with our PM3 calculations in Fig. 8 showing similar trends. This is taken as strong evidence in favor of the high-high-low diameter structure of the infinitely long (5,5) SWCNT. It is possible that the effect is a bit less pronounced in the B3LYP result (0.03 versus 0.05 Å), but it could be easily discerned by higher level calculations upon relaxing the similar diameter constraint. It would appear that the results of Bettinger *et al.*[49] and Sun *et al.*[52] are averages of high-high-low structures.

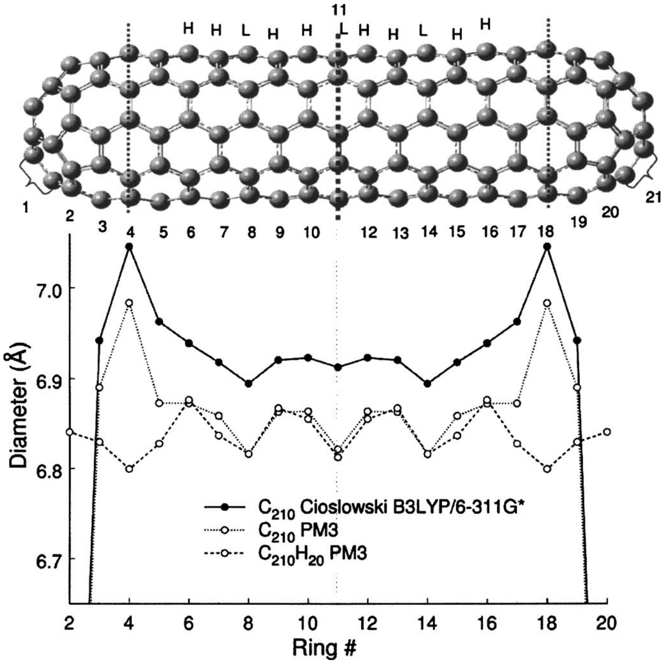

FIG. 8. The ring diameters of the double capped $C_{210}$ cluster as calculated with the hybrid DFT method (B3LYP/6-311G$^*$, filled symbols) by Cioslowski and co-workers as compared to semiempirical PM3 calculations of this work (open symbols). The rings are numbered in the drawing above the plot as by Cioslowski.

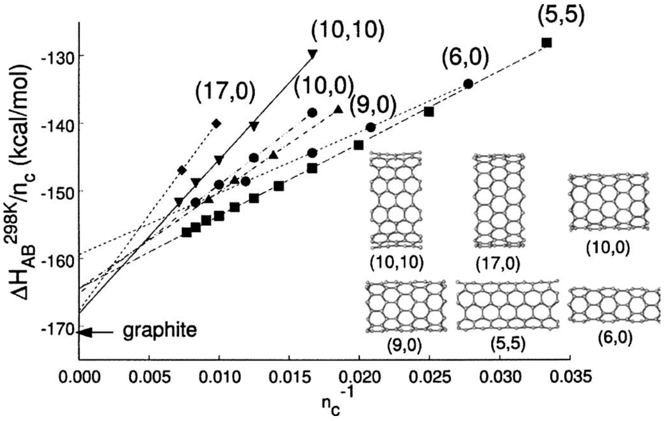

FIG. 9. Enthalpy change on a per carbon basis, $\Delta H_{AB}^{298\ \mathrm{K}}/n_C$, for C(g) $\rightarrow$C[$(n,m)$ SWCNT] where for various open-ended $(n,m)$ SWCNTs. Each tube has a different infinite-length value and different slopes vs $n_C^{-1}$.

## OTHER SWCNTs

Preliminary enthalpic PM3 calculations on (10,10), (17,0), (10,0), (9,0), (5,5), and (6,0) SWCNTs are presented in Fig. 9. Different SWCNTs have significantly different bulk values and $n_C^{-1}$ slopes, so future efforts will involve characterizing the thermochemistry of different $(n,m)$ SWCNTs. It would be interesting to see if data such as that on the (5,5) SWCNT could be generated for a large set of $(n,m)$ SWCNTs to see if it could be parametrized by $n$ and $m$. The variations in slopes and intercepts between SWCNTs suggest that different strategies in particular length regimes may be useful with regard to optimizing specific SWCNTs in the synthesis process. Only the open tubes had a determinable quadratic term $(\alpha_2)$ and it was barely determined, so the fits were dominated by the $n_C^{-1}$ linear term $(\alpha_1)$. The $\alpha_1$ and $\alpha_2$ terms determine the effect of size on the energetics of the (5,5) SWCNTs. The current techniques allow one to characterize these energetics in different $(n,m)$ SWCNTs in the finite size regimes of increasing importance in nanotechnology work.

## DISCUSSION AND CONCLUSIONS

Each carbon atom in a cumulenic chain shares two C$=$C bonds with its neighbors, so the quantity $-\Delta H_{AB}^{298\ \mathrm{K}}/n_C$ for an infinite cumulenic chain is equivalent to the enthalpic strength of a C$=$C bond. Use of local bond averages[23] [2(146.6)/2 kcal/mol] suggests an estimate of 146.6 kcal/mol from small molecules, while the more definitive G3 theory finds 143.0±0.3 kcal/mol for the enthalpic strength of the double bond in an infinite cumulenic chain. Similarly, each carbon atom in an acetylenic chain shares a C$\equiv$C bond and C–C bond with its neighbors, so the quantity $-\Delta H_{AB}^{298\ \mathrm{K}}/n_C$ for an infinite acetylenic chain is the average of the enthalpic strength of a C$\equiv$C and a C–C bond. Use of local bond averages[23] [(200.5+83.2)/2 kcal/mol] suggests an estimate of 141.9 kcal/mol, while the more definitive G3 theory finds 145.0±0.4 kcal/mol for the average of the enthalpic strength of a C$\equiv$C and a C–C bond in an infinite acetylenic chain. Even though local bond averages suggest that a carbon atom will be more stabilized in a cumulenic rather than acetylenic chain, G3 theory finds the infinite acetylenic chain to be more stable in enthalpy than the cumulenic chain by 2.0±0.5 kcal/mol in accordance with Hartree-Fock predictions[21] and the Peierls theorem.[22] In the future, we will use the thermochemistry of the infinite carbon chains determined in this work as a constraint on the energetic trends towards bulk of various small carbon chains which exhibit extensive deviations from linearity in $n_C^{-1}$.

Each carbon atom in the infinite graphene sheet shares two C–C bonds and one C$=$C bond with its neighbors, so the quantity $-\Delta H_{AB}^{298\ \mathrm{K}}/n_C$ for an infinite sheet is an average of the enthalpic bond strength of two C–C bonds and one C$=$C bond in infinite sheet. Local bond averages[23] [{2(83.2)+146.6}/2] suggest an estimate of 156.5 kcal/mol, while the PM3 method finds 169.4 kcal/mol. Clearly there is an enhancement of ~12.9 kcal/mol per carbon due to conjugation or resonance (as is well known with benzene). Each carbon atom in the infinite length (5,5) SWCNT shares the same type of bonds as in infinite sheet, except that they are curved which is destabilizing. Our PM3 calculated enthalpic average of two C–C bonds and one C$=$C bond in (5,5) SWCNT tube (163.5±2.0 kcal/mol) is greater than expected without conjugation (156.5 kcal/mol) but not as strong as in flat infinite sheet (169.4 kcal/mol). The infinite (5,5) SWCNT is 7.8 kcal/mol less stable in enthalpy than graphite.

The extrapolation of polyyne and polyene properties gives *ab initio* (G3 theory) values of infinite acetylenic and cumulenic pure-carbon chains. An infinite carbon chain has (G3 theory) bond lengths of 1.333, 1.279, and 1.257 Å for single, double, and triple bonds, respectively. These bond lengths correspond to the MP2(full)/6-31G$^*$ level of theory. The differences between the single, double, and triple bonds are less pronounced in infinite chains than they are in small hydrocarbon molecules. The infinite acetylenic chain is 1.9±0.4 kcal/mol per carbon more stable in free energy at room temperature than the cumulenic chain and this difference corresponds to the QCISD(T,full)/G3 large level of theory (state of the art energetics). The infinite acetylenic chain has +24 kcal/mol of chemical potential relative to graphite. Semiempirical PM3 calculations were also performed showing reasonable agreement of the energetics with the G3 theory results.

The PM3 method was applied to the (5,5) SWCNT showing 7 kcal/mol chemical potential relative to graphite. Graphene sheet shows 1.9 kcal/mol of chemical potential relative to graphite with the PM3 method. The ZPE/$n_C$ of a (5,5) SWCNT has been determined to be 4.4 kcal/mol (without the ~0.9 correction often applied to such evaluations). A three fold alternation in ring diameter has been detected in the equilibrium structure of the infinitely long (5,5) SWCNT which involves a high-high-low pattern and changes of about 0.044 Å in diameter. The high-high-low diameter structure is only slightly more stable than the equal diameter structure, and the difference is small compared to the zero point energy. These observations may indicate larger deviations from equilibrium than expected in the zero point energy structure.

Regarding our original goals, first, the absolute thermochemical properties (changes in equilibrium electronic energy, internal energy at 0 K, enthalpy at 298 K, and free energy at 298 K) have been presented as the parameter $\alpha_0$ in Tables III, V, and VII for carbon chains, graphene sheet, and the (5,5) SWCNT, respectively. Secondly, taking differences from the PM3 values in Tables V and VII, an equilibrium electronic energy difference of $5.8 \pm 0.7$ kcal/mol and an enthalpic difference of $5.9 \pm 0.7$ kcal/mol are found for C(graphene) → C(SWCNT). These are essentially the same number, so the curving of the carbon surface on the product side of this reaction does not invalidate the isodesmic approach. Note that rather than making the isodesmic assumption, we have determined that it is good. For instance, it would be reasonable to take the "strain energy" of the periodic boundary condition-PBE/3-21G$^*$ calculations[49] (3.8 kcal/mol) as the enthalpic change for this reaction at that level of theory. One big advantage of our method is the determination of free energy changes which are largely unavailable from other methods at this point in time. Our energetic presentation enables comparison to any other forms of carbon, not just those related by isodesmic reactions. Finally, these results provide some important initial inputs needed for the construction of the thermochemical energetics of carbon versus size. The bulk values ($\alpha_0$ in Tables III, V, and VII) provide valuable reference points to which the properties of certain pure-carbon clusters must evolve. Since the small clusters are often open-shell systems with oscillating properties, the trends with size are not always easy to deduce. Likewise, the slopes of pure-carbon clusters ($\alpha_1$ in Tables V and VII) provide the size dependence of the clusters. Different $(n,m)$ SWCNTs show very different finite size energetics (see Fig. 9). Future work will be directed at establishing the critical sizes where different finite carbon clusters become most stable in free energy.

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[1] J. Cioslowski and M. B. Lepetit, J. Chem. Phys. **95**, 3536 (1991).

[2] C. J. Cramer, *Essentials of Computational Chemistry, Theories and Models*, 2002 ed. (John Wiley, Chichester, 2002).

[3] T. W. Ebbesen, in *Physics and Chemistry of the Fullerenes*, NATO Advanced Studies Institute, Series C: Mathematical and Physical Sciences Vol. 443, edited by K. Prassides (Springer, New York, 1994), p. 11. H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, and R. E. Smalley, Nature (London) **318**, 162 (1985).

[4] S. Iijima, MRS Bull. **198**, 43 (1994).

[5] A. Thess, R. Lee, P. Nikovaev *et al.*, Science **273**, 483 (1996).

[6] D. S. Bethune, C. H. Kiang, M. DeVries, G. Gorman, R. Savoy, J. Vazquez, and R. Beyers, Nature (London) **363**, 605 (1993).

[7] C. Guerret-Plecourt, Y. Le Bouar, A. Loiseau, and H. Pascard, Nature (London) **372**, 761 (1994).

[8] J. W. G. Wilder, L. C. Venema, A. G. Rinzler, R. E. Smalley, and C. Dekker, Nature (London) **391**, 59 (1998).

[9] P. M. Ajayan and T. W. Ebbesen, Rep. Prog. Phys. **60**, 1025 (1997); C. H. Kiang, W. A. Goddard, R. Beyers, J. R. Salem, and D. Bethune, J. Phys. Chem. Solids **57**, 35 (1996).

[10] L. M. Wagg, G. L. Hornyak, L. Grigorian, A. C. Dillon, K. M. Jones, J. Blackburn, P. A. Parilla, and M. J. Heben, J. Phys. Chem. B **109**, 10435 (2005).

[11] R. Hoffmann, Tetrahedron **22**, 521 (1966).

[12] W. Weltner and R. J. Vanzee, Chem. Rev. (Washington, D.C.) **89**, 1713 (1989); A. Van Orden and R. J. Saykally, *ibid.* **98**, 2313 (1998).

[13] V. I. Kasatochin, A. M. Sladkov, Y. P. Kudryatsev, N. M. Popov, and V. V. Korshak, Dokl. Akad. Nauk SSSR **177**, 358 (1967).

[14] J. R. Heath, Q. Zhang, S. C. O'Brien, R. F. Curl, H. W. Kroto, and R. E. Smalley, J. Am. Chem. Soc. **109**, 359 (1987).

[15] R. J. Lagow, J. J. Kampa, H.-C. Wei *et al.*, Science **267**, 362 (1995).

[16] R. Eastmond, T. R. Johnson, and D. R. M. Walton, Tetrahedron **28**(17), 4601 (1972).

[17] H. W. Kroto and D. R. M. Walton, Philos. Trans. R. Soc. London, Ser. A **343**, 103 (1993).

[18] E. A. Rohlfing, D. M. Cox, and A. Kaldor, J. Chem. Phys. **81**, 3322 (1984).

[19] M. Kertesz, J. Koller, and A. Azman, J. Chem. Phys. **68**, 2779 (1978).

[20] M. Kertesz, J. Koller, and A. Azman, Phys. Rev. B **19**, 2034 (1979); M. Springborg, J. Phys. C **19**, 4473 (1986); T. D. Poulsen, K. V. Mikkelsen, J. G. Fripiat, D. Jacquemin, and B. Champagne, J. Chem. Phys. **114**, 5917 (2001).

[21] A. Karpfen, J. Phys. C **12**, 3227 (1979).

[22] R. Peierls, *Quantum Theory of Solids* (OUP, New York, 1955).

[23] T. L. Brown, H. E. LeMay, and B. E. Bursten, *Chemistry: The Central Science* (Prentice-Hall, Upper Saddle River, NJ, 2000).

[24] L. A. Curtiss, K. Raghavachari, G. W. Trucks, and J. A. Pople, J. Chem. Phys. **94**, 7221 (1991).

[25] A. D. Becke, J. Chem. Phys. **98**, 5648 (1993).

[26] L. A. Curtiss, K. Raghavachari, and J. A. Pople, J. Chem. Phys. **98**, 1293 (1993); L. A. Curtiss, K. Raghavachari, P. C. Redfern, and J. A. Pople, *ibid.* **106**, 1063 (1997); L. A. Curtiss, K. Raghavachari, P. C. Redfern, and B. B. Stefanov, *ibid.* **108**, 692 (1998).

[27] L. A. Curtiss, K. Raghavachari, P. C. Redfern, V. Rassolov, and J. A. Pople, J. Chem. Phys. **109**, 7764 (1998).

[28] S. Parthiban, J. M. L. Martin, and J. F. Liebman, Los Alamos National Laboratory, Preprint Archive, Physics 1, 2001.

[29] D. A. McQuarrie, *Statistical Mechanics* (Harper & Row, New York, 1976).

[30] J. J. P. Stewart, J. Comput. Chem. **10**, 221 (1989); **10**, 209 (1989).

[31] H. Y. Afeefy, J. F. Liebman, and S. E. Stein, in *NIST Chemistry WebBook, NIST Standard Reference Database Number 69*, edited by P. J. Linstrom and W. G. Mallard (National Institute of Standards and Technology, Gaithersburg, MD, 2005), http://webbook.nist.gov

[32] A. D. Becke, J. Chem. Phys. **96**, 2155 (1992); **97**, 9173 (1992).

[33] S. J. Mole, X. Zhou, and R. Liu, J. Phys. Chem. **100**, 14665 (1996).

[34] K. R. Rodriguez, M.S. thesis, The Ohio State University, 2005.

[35] M. J. Frisch, G. W. Trucks, H. B. Schlegel *et al.*, GAUSSIAN98, Revision A.11.2, Gaussian, Inc., Pittsburgh, PA, 2001.

[36] J. M. L. Martin and G. d. Oliveira, J. Chem. Phys. **111**, 1843 (1999).

[37] J. D. Cox, D. D. Wagman, and V. A. Medvedev, *CODATA Key Values for Thermodynamics* (Hemisphere, New York, 1989).

[38] B. Kirtman, W. B. Nilsson, and W. E. Palke, Solid State Commun. **46**, 791 (1983); B. Kirtman, Chem. Phys. Lett. **143**, 81 (1988).

[39] J. Cioslowski, Chem. Phys. Lett. **153**, 446 (1988).

[40] J. Cioslowski, J. Chem. Phys. **98**, 473 (1993).

[41] J. Cioslowski and E. J. Weniger, J. Comput. Chem. **14**, 1468 (1993); J. Cioslowski, Theor. Chim. Acta **77**, 253 (1990).

[42] J. Cioslowski, N. Rao, and D. Moncrieff, J. Am. Chem. Soc. **124**, 8485 (2002).

[43] J. J. Belbruno, Z. Tang, R. Smith, and S. Hobday, Mol. Phys. **99**, 957 (2001); M. Feyereisen, M. Gutowski, J. Simons, and J. Almlof, J. Chem. Phys. **96**, 29262932 (1992); J. R. Heath, Q. Zhang, S. C. O'Brien, R. F. Curl, H. W. Kroto, and R. E. Smalley, J. Am. Chem. Soc. **109**, 359 (1987); A. V. Orden and R. J. Saykally, Chem. Rev. (Washington, D.C.) **98**, 2313 (1998); D. E. Woon, Chem. Phys. Lett. **244**, 45 (1995).

[44] M. D. Newton and R. E. Stanton, J. Am. Chem. Soc. **108**, 2469 (1986).

[45] J. M. Schulman, R. C. Peck, R. L. Disch, J. Am. Chem. Soc. **115**, 5675 (1989).

[46] D. Bakowies and W. Thiel, J. Am. Chem. Soc. **113**, 3704 (1991).

[47] C. J. Pope and J. B. Howard, J. Phys. Chem. **99**, 4306 (1995).
[48] M. D. Newton and R. E. Stanton, J. Am. Chem. Soc. **108**, 2469 (1986); J. B. Nelson and D. P. Riley, Proc. Phys. Soc. London **57**, 477 (1945).
[49] H. F. Bettinger, K. N. Kudin, and G. E. Scuseria, J. Am. Chem. Soc. **123**, 12849 (2001).
[50] K. Raghavachari, B. B. Stefanov, and L. A. Curtiss, Mol. Phys. **91**, 555 (1997).
[51] E. Hernandez, C. Goze, P. Bernier, and A. Rubio, Appl. Phys. A: Mater. Sci. Process. **68**, 287 (1999); J. W. Mintmire and C. T. White, in *Carbon Nanotubes: Preparation and Properties*, edited by T. W. Ebbesen (CRC, Boca Raton, FL, 1997).
[52] G. Sun, J. Kurti, M. Kertesz, and R. H. Baughman, J. Phys. Chem. B **107**, 6924 (2003).
[53] J. J. P. Stewart, MOPAC2000 Fujitsu Limited, Tokyo, Japan, 1999.