Chiral Adsorption Conformations of Long Chain n-Alkanes Induced by Lattice Mismatch

Lander Verstraete,^a Tamara Rinkovec,^a Hai Cao,^b Hywel I. Reeves,^a Jeremy N. Harvey,^a and Steven De Feyter^{a*}

a. Department of Chemistry, Division of Molecular Imaging and Photonics, KU Leuven-University of Leuven, Celestijnenlaan 200F, B-3001 Leuven, Belgium.

b. State Key Laboratory of Materials-Oriented Chemical Engineering, College of Chemical Engineering, Nanjing Tech University, Nanjing 211816, China.

ABSTRACT: The adsorption and self-assembly of n-alkanes on graphite finds value in applications related to lubrication and surface passivation, but is also of fundamental importance in the study of molecule/substrate interactions. Their adsorption is classically described by Groszek's model of commensurate registry, which is confirmed by high-resolution scanning tunneling microscopy studies. Nonetheless, the role of the chain length-dependent lattice mismatch between n-alkanes and graphite has not been considered. Here, a systematic study of various length n-alkanes at the liquid/graphite interface reveals the existence of a stability limit for the classical straight chain conformation postulated by Groszek's model. Once the critical length is reached, the increasing lattice mismatch induces a swerved chain conformation that is chiral. Experimentally, as well as computationally, the crossover from a straight to a swerved chain conformation is determined to be between 40 and 50 carbon atoms.

INTRODUCTION

Non-covalent surface functionalization has become an essential strategy for building useful interfaces in the field of nanotechnology.¹⁻² Physisorbed monolayers allow to modulate the substrate properties in a predefined manner,³⁻⁵ and at the same time, allow to change the interaction of the surface with its surroundings.⁶ Utilizing molecular self-assembly principles, highly ordered networks exhibiting varying degrees of structural complexity can be formed.⁷ These self-assembled molecular networks rely on stabilizing forces arising from molecule/molecule interactions within the adsorbed layer, as well as molecule/substrate interactions. In addition, interactions of the adsorbed molecules with their environment, *e.g.* a liquid, might play an important role in the overall network stability.⁸⁻¹⁰

On highly oriented pyrolytic graphite (HOPG) and graphene, molecules used for non-covalent surface functionalization are often designed with (long) alkyl chains.¹¹⁻¹⁵ Alkyl chains help to stabilize on-surface assemblies, and can be used to tailor the network morphology.¹⁵⁻¹⁸ Given the importance of alkyl chains as stabilizing motifs in many self-assembled networks, the precise packing arrangement of n-alkanes, the most basic alkylated compounds, on HOPG constitutes an interesting topic in surface science. Furthermore, the adsorption characteristics of n-alkanes may serve as a model system for more complex long chain molecules such as polymers and biomolecules. Finally, self-as-

Figure 1. n-C₁₀H₂₂ adsorbed on HOPG according to Groszek's model. The alkane chains are fully extended in the all-*trans* conformation and take a flat-on adsorption geometry. The interchain spacing, 4.26 Å, is commensurate with the graphite lattice. The distance between alternate CH₂ units along the carbon zigzag backbone, 2.58 Å, is slightly larger than the corresponding distance in the graphite lattice, 2.46 Å.

sembled n-alkane layers find important applications in lubrication,¹⁹⁻²⁰ surface passivation,²¹⁻²² and molecular templating.²³⁻²⁶

Scanning tunneling microscopy (STM) is particularly well suited to study the adsorption patterns of n-alkanes on solid surfaces. Early STM images of various n-alkanes at

the liquid/HOPG interface showed densely packed monolayers of *n*-alkanes organized in lamellae of fully extended chains lying side-to-side, and being oriented orthogonal to the interlamellar troughs.²⁷⁻²⁹ From the absence of a Moiré pattern along the lamellar direction, it was furthermore concluded that the interchain spacing along the lamellae is commensurate with the HOPG substrate.²⁸ These observations are in line with an earlier model postulated by Groszek,³⁰ which is illustrated in Figure 1. This model assumes that the alkyl chains are oriented with the carbon backbone plane parallel to the surface, *i.e.* flat-on adsorption. Whereas most STM studies indeed claim flat-on adsorption, edge-on adsorption²⁸ (*i.e.* carbon backbone plane orthogonal to the surface) as well as mixed adsorption orientations have also been reported.^{29, 31-32} Theoretical calculations indicate that the flat-on adsorption geometry is energetically preferred over edge-on adsorption, although the energy difference is small.³³⁻³⁴

Owing to a lower degree of orbital hybridization, the carbon zigzag backbone of graphite exhibits a slightly shorter periodicity (2.46 Å) than that of an *n*-alkane in the all-*trans* conformation (2.58 Å, value taken from ref.³³). Consequently, not every CH₂ unit of the alkane chain can be adsorbed on top of its preferred lattice site, *i.e.* the center of a graphite hexagon. In fact, the molecule/substrate interaction will depend on this lattice mismatch, leading to a lower average stabilization per CH₂ unit for increasing alkane chain lengths. Deviant adsorption behavior might thus be expected for sufficiently long alkane chains.

Deviant adsorption behavior of *n*-alkanes due to the lattice mismatch has been observed on several substrates. For instance, on Au(111), with a lattice constant of 2.88 Å, the periodicity mismatch with *n*-alkanes leads to the absence of ordered structures for $18 \leq n_C \leq 26$, with n_C the number of carbon atoms.³⁵ In this chain length range, the average stabilization per CH₂ unit reaches a minimum.³⁶ Moreover, the mismatch on Au(111) is observed to induce a periodic alternation between tilted and rectangular lamellae.³⁷ In another example, adsorption of tetratetracontane (*n*-C₄₄H₉₀) on graphene supported by mica (with intercalated water) is shown to induce a curvature in the graphene layer in order to mitigate the unfavorable lattice mismatch, and thus increase the overall molecule/substrate interaction.³⁸ At the liquid/HOPG interface, however, no manifestations of such deviant adsorption behavior have been reported despite a large number of STM studies on various length *n*-alkanes going from tridecane (*n*-C₁₃H₂₈)³⁹ to hexacontane (*n*-C₆₀H₁₂₂).⁴⁰

Here, we systematically investigate the adsorption of a homologous series of *n*-alkanes, with $30 \leq n_C \leq 60$, at the liquid/HOPG interface using STM. High resolution images of *n*-C₅₀H₁₀₂ and *n*-C₆₀H₁₂₂ reveal a slight deviation from the generally accepted adsorption model. That is, the alkane chains appear not completely straight, but make a subtle “swerve” in the direction orthogonal to the molecular axis. Depending on the directionality of the swerve, two chiral adsorption conformations thus emerge. Images of *n*-C₃₀H₆₂ and *n*-C₄₀H₈₂ do not exhibit such effect, pointing out its critical dependence on alkane chain length. This deviant

adsorption behavior for *n*-C₅₀H₁₀₂ and *n*-C₆₀H₁₂₂ is attributed to the increased lattice mismatch of longer chain *n*-alkanes on HOPG, and is supported by density functional theory (DFT) and molecular mechanics (MM) calculations.

METHODS

STM experiments. The following solutions were prepared by dissolving the appropriate amounts of solid: 10^{-3} M *n*-C₃₀H₆₂ (Sigma-Aldrich, 99%) in 1-phenyloctane; 10^{-3} M *n*-C₄₀H₈₂ (Acros, 98%) in 1-phenyloctane; 10^{-3} M *n*-C₄₀H₈₂ in tetradecane; 10^{-4} M *n*-C₅₀H₁₀₂ (Sigma-Aldrich, $\geq 97\%$) in 1-phenyloctane; 10^{-4} M *n*-C₅₀H₁₀₂ in tetradecane; 10^{-4} M *n*-C₆₀H₁₂₂ (Sigma-Aldrich, $\geq 99\%$) in tetradecane. 1-phenyloctane (J&K Scientific, 99%) and tetradecane (Acros, 99%) were used without further purification. For each experiment, the HOPG (grade ZYB, Advanced Ceramics Inc., Cleveland, OH, U.S.A.) surface was freshly cleaved using scotch tape, and a solution of *n*-alkanes was immediately dropcasted on top. STM imaging was subsequently performed at the liquid/graphite interface using a PicoLE (Keysight) setup operating in constant current mode. STM tips were prepared by mechanical cutting from a Pt/Ir wire (Advent Research Materials, 80%/20%, diameter 0.25 mm). The imaging conditions are indicated in the figure captions, and are denoted as I_t for tunneling current, and V_s for sample bias. When indicated in the figure caption, the image was corrected for drift using a reference image of the graphite lattice obtained under the same conditions, except $I_t = 200$ pA, $V_s = -0.001$ V. All image processing was done using the SPIP software.

DFT Calculations. DFT calculations were performed under periodic boundary conditions with the CASTEP module available in Material Studio in a generalized gradient approximation, using the PBE exchange-correlation functional, a plane-wave basis set with an energy cutoff of 400 eV and $1 \times 3 \times 1$ k-points. The van der Waals interactions were described by a semi-empirical Grimme DFT-D2 approach, the ionic core was represented by ultrasoft pseudopotentials and a dipole correction is applied. All the results were based on non-spin polarization calculations with density mixing scheme. The periodic slab models include a graphene layer, alkanes which are adsorbed on one side of the graphene and a 20 Å vacuum layer. Graphene supercells of $\sqrt{3} \times 10$, $\sqrt{3} \times 15$, $\sqrt{3} \times 20$, $\sqrt{3} \times 25$ and $\sqrt{3} \times 30$ are used for the adsorption of *n*-C₁₀H₂₂, *n*-C₂₀H₄₂, *n*-C₃₀H₆₂, *n*-C₄₀H₈₂ and *n*-C₅₀H₁₀₂, respectively. The alkanes are oriented along the main symmetry axis of graphite and the interchain distance is fixed at 4.26 Å. The possible adsorption configurations of alkanes on surface were firstly searched by a simulated quench method at 400 K in 30 ps with 1 fs time steps, using the Compass-II force field in Forcite module of Material Studio, and then further optimized by DFT calculations. The graphene layer was frozen in the optimization process while the alkanes were fully relaxed until the convergence criteria reach 2×10^{-6} eV for SCF, 2×10^{-5} eV/atom for electronic structure, and 5×10^{-3} eV/Å for forces.

MM calculations. Molecular mechanics (MM) geometry minimization calculations were performed under periodic boundary conditions using the Tinker package (version 6.3.3)⁴¹ with an RMS gradient threshold of 0.001 kcal mol⁻¹ Å⁻¹. Periodic boundary conditions were applied to supercells containing the alkane monolayer and a single-layer graphite substrate. The graphite substrate was assigned an aromatic carbon atom type, modified to have a charge of zero. Furthermore, the graphite substrate atoms were kept frozen throughout the minimization. For benchmarking studies, intramolecular and nonbonding intermolecular interactions for all atoms were modelled by the MM3-2000 force field, modified by changing the vdW parameters for carbon and hydrogen atoms to reduce the observed discrepancies between relative potential energies obtained by MM and explicitly correlated (F12) coupled-cluster with singles and doubles and perturbative triples (CCSD(T)) calculations⁴² with the cc-pVDZ-F12 basis set.⁴³ Here, a butane dimer was used as a test system and the relative energy was calculated as a function of distance between two butane molecules. Reference used for the parametrization were butane molecules at a distance of 20 Å. The CCSD(T)-F12 calculations were performed in Molpro (Version 2015.1).⁴⁴ The initial structures of adsorbed monolayers were generated using in-house Python code, with the alkane molecules oriented along the main symmetry axis of the graphite and an alkane interchain distance of 4.7925 Å. The size of the supercell in the direction orthogonal to the graphite substrate ('z direction') was put at 25 Å to avoid interactions between periodic images in this direction. In the direction orthogonal to the alkane chains, the supercell size was chosen based on the above interchain separation, giving 8 alkanes per 9 lattice positions. In the remaining direction, the supercell size was chosen so as to avoid close contact between respective alkane chain ends. Both 'straight' and 'swerved' initial structures were constructed for n-C₄₀H₈₂, n-C₅₀H₁₀₂, and n-C₆₀H₁₂₂; the 'swerved' structures involve a shift in the middle of the alkane by roughly one lattice unit (2.46 Å).

RESULTS AND DISCUSSION

n-Alkanes exhibiting four different chain lengths, *i.e.* n-C₃₀H₆₂, n-C₄₀H₈₂, n-C₅₀H₁₀₂, n-C₆₀H₁₂₂, were applied from solution to the basal plane of graphite and were subsequently characterized using STM. For all investigated systems, a monolayer of densely packed lamellae is formed (Figure 2). High-resolution imaging allows to discern the individual alkane chains, revealing a side-to-side packing along the lamellar direction. The interchain spacing and lamellar width are given in Table 1. While the interchain spacing values are not accurate enough to be a criterion, the absence of a Moiré pattern along the lamellar direction suggests that all systems are commensurate in this direction. However, a subtle, yet important, difference is observed when comparing the adsorption of n-C₃₀H₆₂ and n-C₄₀H₈₂ (Figure 2b,d) to that of the longer n-C₅₀H₁₀₂ and n-C₆₀H₁₂₂ (Figure 2f,h). For both n-C₃₀H₆₂ and n-C₄₀H₈₂, the chains appear straight, and are strictly aligned along the high-symmetry axes of HOPG (green axis) in accordance with

Groszek's model. In comparison, a close inspection of n-C₅₀H₁₀₂ and n-C₆₀H₁₂₂ monolayers reveals that one end of the chain is displaced with respect to the other in the direction orthogonal to the high-symmetry axes. As a result, n-C₅₀H₁₀₂ and n-C₆₀H₁₂₂ chains adopt a "swerved" (*i.e.* S-shaped), rather than a straight conformation. This swerved conformation is chiral, and we will be referring to the two chiralities as "S" or "-S" as shown by respectively the red and blue overlays in Figure 2f,h. It is also clear that all chains within a single lamella exhibit the same swerve chirality. It should be noted that the swerved chain conformation bears many similarities to an early report by Rabe and coworkers who described a communal tilting of n-C₅₀H₁₀₂ lamellae at the 1-phenyloctane/HOPG interface.⁴⁵ Nonetheless, to the best of our knowledge, no further attention was given to this phenomenon.

Table 1. Interchain spacing and lamellar width of n-alkanes at the liquid/HOPG interface.^a

	Interchain spacing (Å)	Lamellar width (nm)
n-C ₃₀ H ₆₂ ^b	4.28 ± 0.03	4.03 ± 0.03
n-C ₄₀ H ₈₂ ^b	4.28 ± 0.02	5.30 ± 0.04
n-C ₅₀ H ₁₀₂ ^b	4.26 ± 0.04	6.55 ± 0.05
n-C ₆₀ H ₁₂₂ ^c	4.29 ± 0.03	7.88 ± 0.04

a. All measurements were performed on at least five calibrated high resolution images.

b. 1-Phenyloctane/HOPG interface.

c. Tetradecane/HOPG interface.

A second striking difference between n-C₃₀H₆₂ and n-C₄₀H₈₂ compared to n-C₅₀H₁₀₂ and n-C₆₀H₁₂₂ is the observed STM contrast (Figure 2). All lamellae of n-C₃₀H₆₂ and n-C₄₀H₈₂ display a similar contrast, whereas lamellae of n-C₅₀H₁₀₂ and n-C₆₀H₁₂₂ tend to appear with alternating bright and dark contrast. The intensity and appearance of this contrast alternation for n-C₅₀H₁₀₂ and n-C₆₀H₁₂₂ lamellae differs substantially on the condition of the STM tip (Figure S1) and is often more apparent on a larger scan size (Figure 2e,g vs. Figure 2f,h). Nevertheless, this contrast alternation is not purely a scanning artefact, but is believed to find its origin in the swerved conformation of alkane chains. First, high resolution images, such as the one shown in Figure 3a, clearly show that "S" appears dark, whereas "-S" is bright. It should be noted, though, that the inverse contrast, *i.e.* "S" is bright and "-S" is dark, also occurs (Figure S2). This seems reasonable given that both conformations are related via mirror symmetry. Second, the alternating contrast was never observed for n-C₃₀H₆₂ and n-C₄₀H₈₂ chains, in accordance with the fact that these chains do not adopt the swerved conformation. At this point, we attribute the observed STM contrast to the registry between the alkane chain and the graphite. Admittedly, it remains puzzling how in certain images the whole chain appears bright(dark), rather than displaying a more gradual contrast change as expected from a Moiré pattern.

Figure 2. STM images showing self-assembled networks formed by (a, b) $n\text{-C}_{30}\text{H}_{62}$, (c, d) $n\text{-C}_{40}\text{H}_{82}$, (e, f) $n\text{-C}_{50}\text{H}_{102}$, and (g, h) $n\text{-C}_{60}\text{H}_{122}$ at the 1-phenyloctane/HOPG ($n\text{-C}_{30}\text{H}_{62}$, $n\text{-C}_{40}\text{H}_{82}$, $n\text{-C}_{50}\text{H}_{102}$), or tetradecane/HOPG ($n\text{-C}_{60}\text{H}_{122}$) interface. A straight chain conformation is found for $n\text{-C}_{30}\text{H}_{62}$ and $n\text{-C}_{40}\text{H}_{82}$, whereas $n\text{-C}_{50}\text{H}_{102}$ and $n\text{-C}_{60}\text{H}_{122}$ chains display a subtle swerve with respect to the graphite high-symmetry axis (green axis). This swerved conformation can occur with an S or -S type chirality as illustrated by the red and blue overlays, respectively. Images (b), (d), (f), and (h) were corrected for drift. Imaging conditions: (a, c, g) $I_t = 120$ pA, $V_s = -0.8$ V; (b) $I_t = 200$ pA, $V_s = -0.8$ V; (d, h) $I_t = 180$ pA, $V_s = -0.8$ V; (e, f) $I_t = 140$ pA, $V_s = -0.8$ V.

For $n\text{-C}_{50}\text{H}_{102}$ and $n\text{-C}_{60}\text{H}_{122}$, a clear preference for an alternating lamellae contrast over long distances can be observed in Figure 2e,g. Occasionally, two neighboring lamellae exhibit the same contrast, such as the dark-dark feature shown in Figure 3b. Such features are often source of increased dynamics indicating their instability with respect to alternating contrasts. For instance, during the scan in Figure 3b, the dark-dark “defect” is observed to hop randomly across the domain (purple arrows). Each hopping event is witnessed as a switching of the contrast between a pair of neighboring lamellae. Switching of the contrast of a single lamella (green dashed line), as well as simultaneous switching of multiple lamellae (≥ 8 , purple dashed line) has also been observed as illustrated in Figure 3c. Importantly, given the correlation between contrast and swerve chirality as pointed out above, and based on high resolution images such as the one shown in Figure 3d, we conclude that the observed contrast switching corresponds to actual changes in the swerve chirality of the chains. While a change in tip state might also cause differences to the observed contrast, this effect is excluded here since the contrast switches occur only for particular lamellae rather than

across the entire width of the image. Hence, our observations imply the existence of a driving force towards alternating swerve chiralities in neighboring lamellae. An interesting characteristic of these dynamics is that all molecules along the entire length of a lamella switch concertedly within the time required for a single line scan, *i.e.* switching of the swerve chirality within a lamella occurs on a time scale ≤ 115 ms. Taking a subsequent STM image after a switching event confirms that the change of swerve chirality affects the entire lamella, rather than part of it (Figure S3).

To verify the thermodynamic stability of the swerved chain conformation for long n -alkanes, a sample containing an $n\text{-C}_{50}\text{H}_{102}$ monolayer was heated at 70°C for 5 min following room temperature deposition. Again, the swerved conformation and characteristic contrast alternation were observed (Figure S4). This result provides strong evidence that the swerved chain conformation corresponds to an energetic minimum state. Noteworthy, despite the annealing treatment, the alternation of swerve chirality between neighboring lamellae was not yet perfect,

Figure 3. STM images of $n\text{-C}_{50}\text{H}_{102}$ at the 1-phenyloctane/HOPG interface. (a) High resolution image showing that the observed contrast variation corresponds to an alternating swerve chirality. The image was corrected for drift. (b) Hopping of a dark-dark defect across the domain. Five hopping events are witnessed whereby neighboring lamellae exchange contrast as indicated by the purple arrows. The scan direction is given by the arrow in the top right corner. (c) At the position of the purple dashed line, the contrast of ≥ 8 lamellae switches concertedly, whereas the contrast of only one lamella switches at the location indicated by the green dashed line. (d) Zoomed image near a contrast switching event (purple dashed line) showing the change in swerve chirality. Imaging conditions: (a,d) $I_t = 180$ pA, $V_s = -0.8$ V; (b) $I_t = 140$ pA, $V_s = -0.8$ V; (c) $I_t = 120$ pA, $V_s = -0.8$ V.

and dynamics were still observed (Figure S4). Often, a perfect alternation of the swerve chirality can only be reached when defects (*i.e.* neighboring lamellae with the same swerve chirality) propagate throughout the whole domain. Therefore, it is not surprising that mild heating does not suffice to reach complete equilibrium. Similarly, heating a sample of $n\text{-C}_{40}\text{H}_{82}$ on HOPG to 70°C for 5 min does not alter the straight adsorption conformation of the chains (Figure S4). Therefore, it seems that the observed conformational differences between the shorter and longer chain analogues are thermodynamically driven. Also, no solvent dependency of the adsorption behavior was observed when comparing solutions in 1-phenyloctane and tetradecane (Figure S5).

To understand what causes the swerved chain conformation for $n\text{-C}_{50}\text{H}_{102}$ and $n\text{-C}_{60}\text{H}_{122}$, but not for $n\text{-C}_{30}\text{H}_{62}$ and $n\text{-C}_{40}\text{H}_{82}$, we recall that the carbon zigzag backbone of the graphite has a slightly shorter periodicity than that of an n -alkane in the all-*trans* conformation. Superposition of the two lattice periods generates a new period (T) equal to:

$$T = \frac{T_a \cdot T_g}{|T_a - T_g|} = 52.9 \text{ \AA},$$

with $T_a = 2.58 \text{ \AA}$, and $T_g = 2.46 \text{ \AA}$, the periods of the alkane and graphite substrate, respectively. Hence, for an alkane chain of length T (which corresponds to $n_c = 42$) and longer, one CH_2 unit will necessarily be located above a

Figure 4. DFT optimized structures of different length n -alkanes on a single sheet of graphite. From $n\text{-C}_{10}\text{H}_{22}$ to $n\text{-C}_{40}\text{H}_{82}$, the straight chain conformation is most stable, whereas the swerved chain conformation is favored for $n\text{-C}_{50}\text{H}_{102}$. $\Delta E = E_{\text{straight}} - E_{\text{swerved}}$.

substrate atom, leading to a minimum average stabilization per CH_2 unit. Note that $n_c = 42$ is only a rough estimate for the critical chain length, and that the actual crossover point will depend on the precise periodicity values. Nonetheless, from this simple description it can thus be understood that n -alkanes longer than the critical length adopt a different adsorption conformation, *i.e.* the swerved conformation, to mitigate the unfavorable lattice mismatch.

To confirm this hypothesis, DFT calculations were performed on the adsorption of n -alkanes ranging from $n\text{-C}_{10}\text{H}_{22}$ to $n\text{-C}_{50}\text{H}_{102}$ on a single sheet of graphite. In accordance with our experiments, the chains were assumed to be commensurate along the lamellar direction, *i.e.* the inter-chain distance was fixed at $4.26 \text{ \AA}$. Furthermore, the period between alternating CH_2 units along the alkane chain was initially set to $2.58 \text{ \AA}$, as taken from ref.³³ Further details are provided in the methods section. DFT optimized structures for all investigated n -alkanes are shown in Figure 4. For the shorter chain analogues, *i.e.* $n\text{-C}_{10}\text{H}_{22}$ to $n\text{-C}_{40}\text{H}_{82}$, DFT optimization yields the straight chain conformation. For $n\text{-C}_{40}\text{H}_{82}$, the straight chain conformation is calculated to be more stable than the swerved conformation by 6.3 kJ/mol . In contrast thereto, for $n\text{-C}_{50}\text{H}_{102}$, the swerved chain conformation is preferred by 12.0 kJ/mol . The calculated stability crossover from straight to swerved adsorption conformations between $n\text{-C}_{40}\text{H}_{82}$ and $n\text{-C}_{50}\text{H}_{102}$ agrees remarkably well with the experimental observations. Overall, these calculations strongly support that the observed conformational differences are driven by a chain length dependent molecule-substrate interaction.

Figure 3. Conformational energy difference (modified MM3, kcal mol⁻¹) as a function of a) van der Waals well-depth and b) equilibrium carbon-carbon bond length for n-C₅₀H₁₀₂ monolayer on a single sheet of graphite. $\Delta E = E_{\text{straight}} - E_{\text{swerved}}$. ■ calculated; — linear fit.

Additional insight can be obtained from molecular mechanics (MM) calculations in which the key parameters for the above-suggested model are varied. Here, a unit cell consisting of eight alkane molecules spaced across nine lattice positions of the graphite sublayer was used, making the model slightly incommensurate. The MM calculations were performed on the adsorption of n-alkanes ranging from n-C₄₀H₈₂ to n-C₆₀H₁₂₂ using a reparametrized MM3 force field based on CCSD(T)-F12 calculations for a butane dimer. Minimization yields a preference for a swerved conformation for both n-C₅₀H₁₀₂ and n-C₆₀H₁₂₂, which is in good agreement with both experiments and DFT calculation (Supporting information). Furthermore, in the case of n-C₄₀H₈₂, MM only yields the straight chain conformation as in the case of shorter chain analogues in DFT.

Furthermore, one of the parameters that is assumed in our hypothesis to play an important role in determining the crossover to swerved structures is the strength of the molecule-substrate interactions. We varied this by modifying the Lennard-Jones well-depth parameter ϵ for the graphite atoms. Increasing this parameter led to a linear increase in the calculated preference for a swerved conformation of the alkane (Figure 5a). Moreover, in the MM approach, there is the possibility to ‘alchemically’ create alkanes with a different mismatch in periodicity to the graphite by varying the parameter r_0 specifying the equilibrium carbon-carbon bond length. Here, the results yield a

more complex, but still very strong dependence of conformational energy difference on the periodicity mismatch between monolayer and graphite (Figure 5b). Together, these results corroborate the qualitative model and show high susceptibility of the relative stability of the swerved alkane chain conformation to the details of the graphite/alkane interaction.

CONCLUSIONS

In conclusion, it is shown, for the first time, that an adsorbate/substrate lattice mismatch can induce a chiral adsorption conformation in an otherwise achiral system. This behavior is observed for the self-assembly of n-alkanes on HOPG with a chain length of 50 or 60 carbon atoms, but not for chains with 30 or 40 carbons. For the longer chain molecules, the mismatch between the alkane backbone and the HOPG surface becomes significant, and, as a result, the longer analogues energetically prefer a chiral swerved chain conformation rather than the classical straight conformation. Overall, the results presented here add to the fundamental understanding of a long studied system, and underscore the importance of subtle details in the molecule/substrate interaction.

ASSOCIATED CONTENT

Supporting Information. Additional STM data, computational details. “This material is available free of charge via the Internet at <http://pubs.acs.org>.”

AUTHOR INFORMATION

Corresponding Author

* steven.defeyter@kuleuven.be

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