

# The Physicochemical Origins of Coincident Epitaxy in Molecular Overlayers: Lattice Modeling vs Potential Energy Calculations

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The physicochemical basis for epitaxial stabilization of coincident molecular overlayers is illustrated by comparison of optimum overlayer–substrate configurations calculated with potential energy (PE) methods and a simple geometric lattice misfit modeling algorithm (EpiCalc) that neglects molecular orientations and intermolecular potentials. Using  $\beta$ -bis(ethylenedithio)tetrathiafulvalene triiodide ( $\beta$ -ET<sub>2</sub>I<sub>3</sub>), perylenetetracarboxylic diimide (PTCDI), and perylenetetracarboxylic dianhydride (PTCDA) overlayers on a graphite substrate as examples, both methods predict identical optimum azimuthal overlayer orientations for each overlayer that also agree with experimental observations. PE calculations for three hypothetical PTCDA overlayers, with identical lattice parameters but different molecular orientations, predict coincidence at the same azimuthal orientation for all overlayers. Identical results are achieved for PE calculations performed with this lattice when it is occupied by naphthalenetetracarboxylic dianhydride (NTCDA) molecules or argon atoms. These results demonstrate that the epitaxial orientation of coincident overlayers is governed more by geometric lattice matching than specific molecule–substrate interactions and that unambiguous determination of the optimum azimuthal orientation relies on establishing the phase relationship between several overlayer supercells and the substrate. In the case of PE methods, calculations with large overlayer sizes are computationally prohibitive and the energy differences between alternative orientations typically are smaller than the confidence limits of the method. In contrast, the calculation time required by EpiCalc is independent of overlayer size, providing a significant advantage over PE methods with respect to computational speed while enabling unambiguous assignment of the optimum coincident configuration. The reliability of EpiCalc in predicting observed epitaxial overlayer orientations indicates that geometric lattice misfit modeling can be used to screen efficiently for the most favorable epitaxial configuration (overlayer lattice parameters and azimuthal angle), which can then be used in subsequent PE calculations that allow for other degrees of freedom such as molecular orientation.

## Introduction

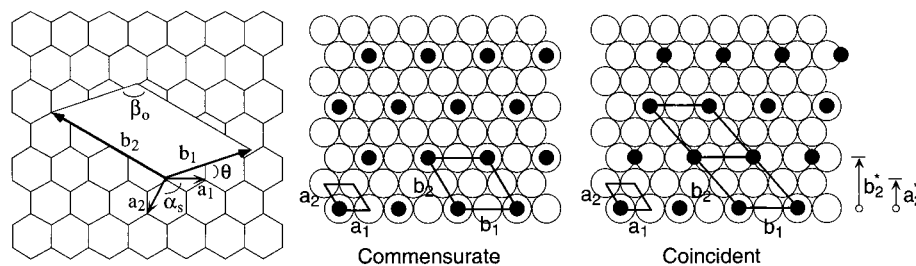
Molecular films offer unique opportunities as components in electronic devices, sensors, displays, and logic elements<sup>1</sup> because their optical and electronic properties can be systematically manipulated at the molecular level. Indeed, recent reports of light emitting diodes,<sup>2,3,4,5</sup> field effect transistors,<sup>6,7,8,9,10,11</sup> and photovoltaic devices<sup>12,13</sup> with molecular films illustrate a growing interest in such materials. The properties of molecular films depend strongly upon their structure and their orientation with respect to the substrate upon which they are deposited. Therefore, their design and synthesis require careful attention to the interface between the primary molecular overlayer and the substrate. In the case of crystalline films grown on ordered substrates, elucidating the role of epitaxy at the overlayer–substrate interface is crucial for the fabrication of high quality films. While the influence of epitaxial interactions at the overlayer–substrate interface on film structure and orientation has been firmly established for inorganic and elemental systems,<sup>14</sup> epitaxial principles for molecular films are just beginning to emerge.

Epitaxial principles for molecular overlayers merit special attention because overlayer structures depend on a delicate energetic balance of noncovalent interactions between the molecules comprising the overlayer and between the overlayer and substrate. The “soft” nature of these noncovalent interactions, which stems from shallow potential functions (i.e., small elastic constants), makes the structure of molecular films and the mode of epitaxy very sensitive to the competition between intralayer and overlayer–substrate interactions. Additionally, the size and symmetry of the unit cells of molecular overlayers typically differ from those of common substrates, arguing against commensurate lattices in the absence of severe distortions of a “native” close-packed overlayer structure. Consequently, native molecular overlayers will tend to be stabilized by coincidence, a condition in which the corners of a supercell, comprising several overlayer unit cells, coincide with substrate lattice points at periodic intervals, while overlayer lattice points within the supercell do not coincide with substrate lattice points.

In principle, the existence of an epitaxial relationship between a given overlayer and substrate can be predicted by potential energy (PE) calculations. However, PE calculations consider the interaction of every overlayer atom with every substrate atom and can be computationally intensive for the large overlayer

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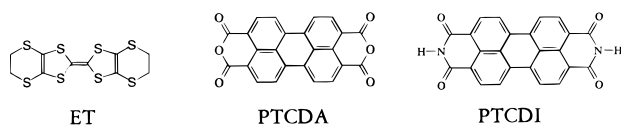


**Figure 1.** (left) Schematic representation of a generic molecular overlayer on a rigid substrate. The substrate and overlayer lattices are defined by two-dimensional cells with lattice constants  $a_1$ ,  $a_2$ ,  $\alpha_s$  and  $b_1$ ,  $b_2$ ,  $\beta_o$ , respectively. The angle  $\theta$  between the vectors  $\mathbf{a}_1$  and  $\mathbf{b}_1$  defines the azimuthal orientation of the overlayer with respect to the substrate. (right) Schematic representations of specific commensurate and point-on-line coincident overlayer lattices (filled circles) on a hexagonal substrate lattice (open circles). In this example of coincidence,  $\mathbf{b}_2^* = 2\mathbf{a}_2^*$  and the supercell has dimensions of  $1 \times 2$  ( $\mathbf{b}_1 \times \mathbf{b}_2$ ). For clarity we depicted coincidence with  $\theta = 0^\circ$  and  $\mathbf{b}_1 = 2\mathbf{a}_1$ . However, it should be noted that this condition is not required for coincidence. Molecules at the corners of the supercells need not coincide precisely with substrate lattice atoms as coincidence only requires an integer periodicity in one direction of the lattices in direct space. However, the supercell is illustrated in this manner for conceptual simplicity.

sizes needed to establish coincident epitaxy. We recently reported a computationally efficient geometric lattice misfit algorithm, EpiCalc, that enables reliable and rapid prediction of the mode of epitaxy (i.e., incommensurism, commensurism, or coincidence) and the optimum azimuthal orientation for a given overlayer–substrate combination, using only the lattice parameters of the overlayer and substrate as input.<sup>15</sup>

EpiCalc has verified the existence of coincidence and the experimentally observed azimuthal orientations of several molecular overlayer–substrate combinations, including overlayers of ionic charge-transfer salts based on bis(ethylenedithio)-tetrathiafulvalene (ET) and neutral overlayers of perylenetetracarboxylic diimide (PTCDI) and perylenetetracarboxylic dianhydride (PTCDA).<sup>16,17,18</sup> While the existence of coincident epitaxy has been noted for some PTCDA overlayers,<sup>16d,16e</sup> others have been described as “quasi-epitaxial”.<sup>17,18</sup> Our analysis of these overlayers with EpiCalc and a limited number of PE calculations suggested that coincident epitaxy was responsible for the quasiepitaxial configurations as well, with the phase coherence between the overlayer supercell and the substrate providing the physiochemical driving force for overlayer formation.

We describe herein more extensive comparisons of epitaxial configurations determined by geometric lattice misfit modeling and PE methods with coincident  $\beta$ -ET<sub>2</sub>I<sub>3</sub>, PTCDI, and PTCDA overlayers. These studies establish that, at least for van der Waals overlayers, the overlayer orientations are governed more by the phase relationship between the overlayer and the substrate than by specific molecule–substrate interactions. Geometric lattice misfit modeling routines such as EpiCalc can reliably predict epitaxial configurations while offering significant practical advantages with respect to computational efficiency.



## Overview

A two-dimensional interface consisting of a substrate and an overlayer can be defined by seven independent parameters, the substrate by lattice constants  $a_1$ ,  $a_2$ , and angle  $\alpha_s$ , the overlayer by  $b_1$ ,  $b_2$ , and angle  $\beta_o$ , and the azimuthal orientation by the angle between  $\mathbf{a}_1$  and  $\mathbf{b}_1$  (Figure 1). Commensurism exists when the periodicities of the overlayer and substrate are related by integral multiples along two lattice vectors such

that each overlayer molecule can be placed on equivalent substrate lattice points. The elastic constants are determined by the second derivative of the potential energy function, representing the curvature of the potential energy at the minimum energy position. If the in-plane overlayer–substrate elastic constants exceed the intralayer elastic constants of the overlayer, expansion or contraction of the overlayer to a commensurate structure will be preferred over a noncommensurate form in which some molecules do not sit on minimum energy substrate sites.<sup>19</sup>

In contrast, intralayer elastic constants exceeding the in-plane overlayer–substrate elastic constants will tend to favor a given “native” overlayer structure and adopt a coincident epitaxial configuration if possible. The special case of point-on-line coincidence describes the condition in which rows of overlayer lattice points coincide with uniformly spaced rows of substrate lattice points corresponding to a specific lattice direction; that is, every lattice point of the overlayer coincides with a lattice vector of the primitive unit cell of the substrate. By definition, the direction of one of the overlayer reciprocal lattice vectors coincides with the direction of the reciprocal lattice vector defined by the substrate rows. The magnitudes of these reciprocal lattice vectors are related by an integral multiple.

An important consequence of coincidence is the existence of an overlayer supercell with molecules on its corners that coincide periodically with substrate lattice points, but with molecules within the supercell that do not coincide with substrate lattice points. The existence of a real-space supercell has been largely unrecognized, yet it is highly instructive and facilitates an understanding of coincidence. Contrary to assertions in ref 18 that coincidence models lack a compelling physical foundation, the registry of the supercell corners with the substrate provides a physicochemical basis for coincidence that is conceptually identical to true commensurism. The two modes of epitaxy differ only with respect to their “degree of commensurability”. It should be noted that the molecules at the corners of the supercells need not coincide precisely with substrate lattice atoms as coincidence only requires an integer periodicity in one direction of the lattices in direct space. However, the supercell in Figure 1 is illustrated in this manner for conceptual simplicity.

If the coinciding lattice points at the supercell corners are the most energetically favorable, by inference the noncoinciding lattice positions are less favorable. However, small in-plane overlayer–substrate elastic constants, expected for van der Waals interfaces, diminish the energetic penalty and stress

associated with the noncoinciding lattice positions of a coincident overlayer, reducing the driving force for the overlayer to adopt a true commensurate structure. The favorable interactions between the substrate and the molecules at the supercell corners can stabilize a specific coincident configuration. The existence of less favorable noncoinciding overlayer lattice points within the supercell implies that the overlayer stability of a given rigid overlayer will decrease with the fraction of noncoinciding sites, that is, with increasing size of the supercell, as demonstrated recently in our laboratory.<sup>20</sup> As the number of noncoincident overlayer lattice points increases, the overlayer will tend to adopt a more stable alternative coincident configuration or a truly commensurate structure.

The general lack of awareness of coincident epitaxy probably can be attributed to the difficulty in predicting, and even visualizing, coincident lattices, particularly for organic overlayers with oblique symmetries. In fact, it has even been suggested that epitaxy cannot be important for organic films.<sup>21</sup> Nonetheless, the observation of numerous molecular overlayers with azimuthal orientations and lattice parameters that reflect coincidence<sup>15</sup> argues that this mode of epitaxy is governed by the thermodynamics, not kinetics,<sup>18</sup> of the overlayer–substrate interface.

Advances in the design and fabrication of coincident (and commensurate) molecular overlayers hinge on the ability to predict (i) the optimum configuration with respect to the orientation of molecules within the overlayer, (ii) the size and symmetry of the overlayer, and (iii) the azimuthal orientation of the overlayer with respect to the substrate. The most direct approach for predicting epitaxial configurations involves total potential energy (PE) calculations, typically based on semiempirical Buckingham or Lennard–Jones 6-12 potential functions. However, PE methods tend to be computationally intensive, requiring  $r \times s$  calculations for each azimuthal orientation of a given overlayer, where  $r$  and  $s$  represent the number of overlayer and substrate atoms, respectively. Calculations that allow additional degrees of freedom, such as permitting molecules to translate and rotate within the unit cell, become computationally prohibitive, particularly for the large basis of a typical coincident supercell. This limitation is further exacerbated by the need to establish the phase relationship between a coincident overlayer and the substrate, which may require calculations based on numerous supercells (*vide infra*). Consequently, PE calculations of large coincident overlayers can be unreasonable unless the positions of the molecules and the lattice parameters are fixed, leaving the azimuthal orientation as the only degree of freedom. Furthermore, the accuracy of semiempirical PE calculations, which do not account for Coulomb, dipolar, and multipolar forces, may not be sufficient for unambiguous assignment of an optimum structure among polymorphic alternatives.

In contrast, methods based solely on geometric lattice misfit models can predict optimum epitaxial configurations for a specific overlayer in a fraction of the time required for PE methods. Although lattice matching routines neglect intermolecular potentials and therefore cannot predict detailed overlayer structure, they can simplify subsequent PE calculations by first identifying the optimum coincident configuration (*i.e.*, lattice parameters and azimuthal angle) for an overlayer. However, it first must be demonstrated that lattice matching routines predict epitaxial configurations that are identical to those predicted by PE calculations. Under these conditions, the surface potentials of the substrate and overlayer would correspond to their respective lattice periodicities. Such agreement would signal that

overlayer configurations are influenced primarily by lattice matching rather than the detailed supramolecular organization within the overlayer.

A geometric lattice model adapted from Bollmann's coincident-site lattice method for describing grain and phase boundaries has been used by Reeves and Evans to identify preferred epitaxial orientations<sup>22</sup> based on the number density of coinciding lattice sites in the 2-D overlayer–substrate interface. The analytical function used in this method typically produces numerous orientations with similar coinciding site densities, thereby complicating assignment of a single optimum orientation. Another method based on numerical iteration has been used by Hoshino to surmise the best degree of fit between the overlayer and substrate,<sup>23</sup> but this procedure is computationally intensive. EpiCalc, a program devised in our laboratory that relies on a direct analytical function, is computationally efficient. The time required for calculations with EpiCalc is independent of overlayer size, enabling analysis of systems with large bases (such as coincident lattice supercells) and examination of numerous different overlayer–substrate lattice combinations in a timely manner.

## Methods

Potential energy calculations were performed on a Hewlett-Packard 710 workstation using universal force field<sup>24</sup> parameters and the Lennard–Jones 6-12 potential function. These calculations were combined with a FORTRAN code that allowed approach, translation, and rotation of an overlayer with respect to a substrate. Calculations were performed with the chosen overlayer lattice plane parallel to the HOPG substrate surface (*vide infra*). The minimum energy overlayer–substrate separation was determined by positioning the origin of the overlayer unit cell (taken as the origin of its crystallographic analog) over the crystallographic origin of the HOPG substrate and calculating energy as a function of distance. The overlayer was then fixed at this separation and the energy calculated at 1° increments of azimuthal angle  $\theta$ . All PE calculations considered only overlayer–substrate interatomic potentials such that intermolecular interactions within an overlayer were neglected.

Determination of the mode of epitaxy and optimum overlayer orientation was accomplished using EpiCalc, a program developed in our laboratory that has been designed for operation in the Windows 95 environment. EpiCalc relies on an analytical function devised in our laboratory that enables calculation of  $V/V_0$ , which we termed a “dimensionless potential” (eq 1).<sup>15</sup>

$$\frac{V}{V_0} = \left\{ 2MN - \frac{\sin(M\pi p_x)\sin(N\pi q_x)}{\sin(\pi p_x)\sin(\pi q_x)} - \frac{\sin(M\pi q_y)\sin(N\pi p_y)}{\sin(\pi q_y)\sin(\pi p_y)} \right\} \left( \frac{1}{2MN} \right) \quad (1)$$

where  $1/(MN)$  is a normalization constant and  $M$  and  $N$  define the size of the overlayer. The values of  $p_x$ ,  $q_x$ ,  $p_y$ , and  $q_y$  are defined by a transformation matrix that relates the overlayer lattice vectors to the lattice vectors of the substrate (eqs 2–6).

$$\begin{bmatrix} b_1 \\ b_2 \end{bmatrix} = [\mathbf{C}] \begin{bmatrix} a_1 \\ a_2 \end{bmatrix} = \begin{bmatrix} p_x & q_x \\ q_x & p_y \end{bmatrix} \begin{bmatrix} a_1 \\ a_2 \end{bmatrix} \quad (2)$$

and



$$p_x = \frac{b_1 \sin(\alpha - \theta)}{a_1 \sin(\alpha)} \quad (3)$$

$$q_y = \frac{b_1 \sin(\theta)}{a_2 \sin(\alpha)} \quad (4)$$

$$q_x = \frac{b_2 \sin(\alpha - \theta - \beta)}{a_1 \sin(\alpha)} \quad (5)$$

$$p_y = \frac{b_2 \sin(\theta + \beta)}{a_2 \sin(\alpha)} \quad (6)$$

The function defined by  $V/V_0$  evaluates the misfit between the periodic overlayer and substrate lattices. Even though  $V/V_0$  does not provide an actual energy, the correspondence between the periodicity of these lattices and their respective potential surfaces argues that  $V/V_0$  represents the goodness-of-fit between the periodic overlayer and substrate potential surfaces. The value of  $V/V_0$ , which must lie in the range  $-0.5 \leq V/V_0 \leq 1$ , depends on the degree of commensurism of the interface at the azimuthal angle  $\theta$ . Specific modes of epitaxy produce discrete values of  $V/V_0$ , with  $V/V_0 = 1$  for incommensurism,  $V/V_0 = 0.5$  for point-on-line coincidence,  $V/V_0 = 0$  for commensurism on a nonhexagonal substrate, and for commensurism on a hexagonal substrate  $V/V_0 = -0.5$ .

In principle, the lattice misfit should be independent of overlayer size if the specified values of  $M$  and  $N$  reflect an integral number of supercells. However, because of the inherent inexactness in the near-coincident lattice parameters chosen for the calculation, values of  $M$  and  $N$  must exceed 40 in order to establish an unambiguous minimum that signifies coincidence (see Appendix).

EpiCalc requires as input the 2-D lattice parameters for both substrate and overlayer and the range and increment of azimuthal angles ( $\theta$ ) at which calculations are to be performed. The calculation also requires the user to input the size of the overlayer as  $m$  and  $n$ , where  $M = 2m + 1$  and  $N = 2n + 1$ . This is to ensure that  $M$  and  $N$  are odd numbers, as required to achieve the aforementioned discrete values of  $V/V_0$ . The output of the program includes the calculated value of  $V/V_0$  over the specified range of  $\theta$  and the transformation matrix elements that describe the overlayer orientation in terms of the substrate lattice vectors. All calculations reported here were performed with an increment of  $\Delta\theta = 0.25^\circ$ . EpiCalc also contains a subroutine EpiSearch, which searches for epitaxial configurations for a user-defined range of overlayer lattice parameters  $b_1$ ,  $b_2$ , and  $\beta_0$ , reporting  $V/V_0$  values and  $\theta$  for each set of lattice parameters. This subroutine is useful for finding exact fits between the overlayer and substrate that can be achieved by minor adjustments to a selected set of overlayer lattice parameters. EpiCalc is available on the World Wide Web at [www.wardgroup.umn.edu](http://www.wardgroup.umn.edu).

The overlayer structures examined here were based on layers in the corresponding bulk crystal structures (Figure 2). Lattice parameters for the bulk crystal planes and the coincident overlayers are summarized in Table 1. For PE calculations, the coincident overlayers were derived from the bulk layer structures, but were modified in the Cerius<sup>2</sup> v.2.0 molecular modeling environment (Molecular Simulations Inc., San Diego). The  $\beta$ -ET<sub>2</sub>I<sub>3</sub> overlayer was based on the (001) layer of bulk  $\beta$ -ET<sub>2</sub>I<sub>3</sub>.<sup>25</sup> PE calculations were performed with the triiodide layer removed so that only the interactions between the ET molecules and the HOPG substrate were considered. The PTCDI overlayer examined here was generated by flattening the (102)

layer of bulk PTCDI<sup>26</sup> so that the PTDCI planes were confined to the lattice plane. The lattice parameters were then expanded to the values reported in ref 16e and the molecules repositioned within the expanded unit cell to the original fractional coordinates. The overlayer was verified as coincident with EpiCalc.

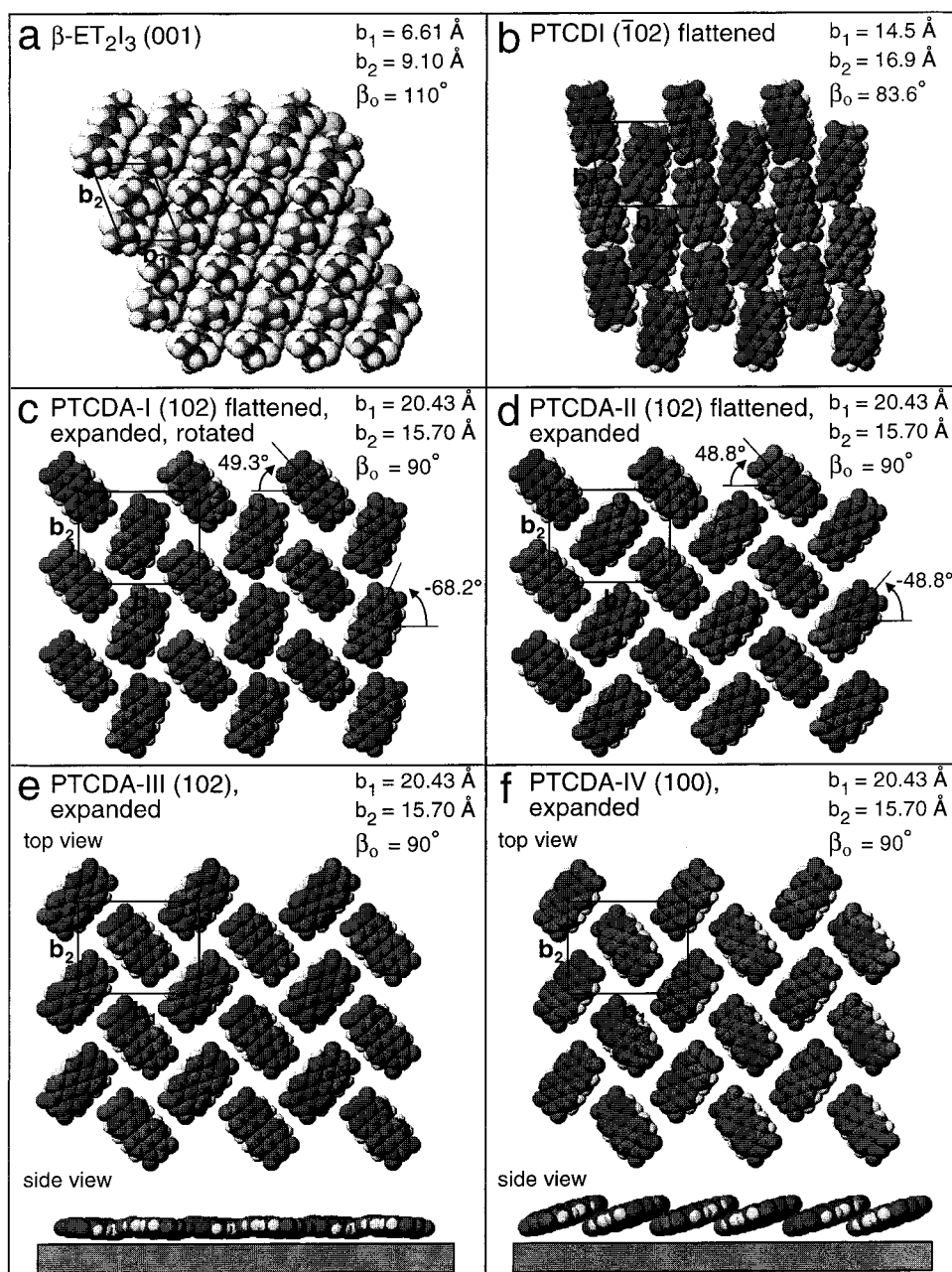
The PTCDI overlayers examined here were modified forms of the bulk (100) and (102) layers. PTCDI overlayers I–IV were based on the overlayer structure reported in ref 17. **PTCDA-I** (Figure 2c) was generated by flattening the (102) layer of the bulk crystal so that the PTCDA planes were confined to the lattice plane, expanding the lattice parameters to the coincident values determined by EpiCalc, and repositioning the molecules to the original fractional coordinates. The PTCDA molecules were then rotated in-plane so that the in-plane orientations of the molecules at 0,0,0 and 1/2,1/2,1/2 are  $+49.3^\circ$  (clockwise) and  $-68.2^\circ$  (counterclockwise) from **b**<sub>1</sub>, respectively, generating the structure that was previously reported as the minimum energy configuration.<sup>17,18</sup> **PTCDA-II** (Figure 2d) was generated by flattening the (102) layer so that the PTCDA planes were confined to the lattice plane, expanding the lattice parameters to the coincident values determined by EpiCalc, and repositioning the molecules to the original fractional coordinates. The in-plane orientations of the molecules at 0,0,0 and 1/2,1/2,1/2 are  $+48.8^\circ$  (clockwise) and  $-48.8^\circ$  from **b**<sub>1</sub>, respectively. **PTCDA-III** (Figure 2e) was generated by expanding the unflattened (102) layer to the coincident values determined by EpiCalc and repositioning the molecules to the original fractional coordinates. **PTCDA-IV** (Figure 2f) was generated by expanding the unflattened bulk (100) layer to the coincident lattice parameters and repositioning the PTCDA molecules within the unit cell to the original fractional coordinates. Both **PTCDA-III** and **PTCDA-IV** were *not* flattened. A hypothetical overlayer, constructed by replacing PTCDA molecules in a flattened (102) layer with naphthalenetetracarboxylic dianhydride (NTCDA), also was examined.

A PTCDA overlayer (on HOPG) with lattice parameters nearer those of the bulk (102) plane than the PTCDA overlayers above has also been reported.<sup>16e,22</sup> This overlayer structure, **PTCDA-V** (Figure 8), was generated by adjusting the unflattened (102) layer to the coincident values found by EpiSearch, nearest the reported values. The molecules were repositioned to their respective original fractional coordinates after the unit cell was adjusted.

## Results

**$\beta$ -(ET)<sub>2</sub>I<sub>3</sub> Overlayer.** Using in situ atomic force microscopy, we previously observed the formation of a 15.5 Å thick ET<sub>2</sub>I<sub>3</sub> overlayer on HOPG at an azimuthal orientation of  $\theta = 18^\circ$  with lattice parameters  $b_1 = 6.2 \pm 0.5$  Å,  $b_2 = 9.4 \pm 0.8$  Å, and  $\beta_0 = 107 \pm 4^\circ$ .<sup>19</sup> These lattice parameters were nominally identical to the values for the (001) plane of bulk  $\beta$ -(ET)<sub>2</sub>I<sub>3</sub> ( $a = 6.6$  Å,  $b = 9.1$  Å,  $\gamma = 110^\circ$  and (001) layer thickness = 15.5 Å). The ET molecules in the (001) orientation are tilted  $38^\circ$  from a normal to the HOPG surface. The value of  $\theta$  in this case (and in all following examples) is based on the angle between **b**<sub>1</sub> and **a**<sub>1</sub>, the latter assigned to the conventionally accepted lattice vector for HOPG (this is emphasized here as some reports<sup>17,18</sup> have used a lattice vector rotated  $30^\circ$  from **a**<sub>1</sub> to measure  $\theta$ ). EpiCalc produced  $V/V_0 = 0.5$  at  $\theta = 19.8^\circ$  for a  $51 \times 51$  overlayer, verifying the existence of coincidence for these lattice parameters (Figure 3a). This azimuthal angle is identical, within experimental error, to the observed value.

A comparison of PE calculations with EpiCalc for the (001)  $\beta$ -ET<sub>2</sub>I<sub>3</sub> overlayer reveals the importance of overlayer size when



**Figure 2.** Schematic representations of (a)  $\beta$ -ET<sub>2</sub>I<sub>3</sub>, (b) PTCDI, (c) PTCDA-I, (d) PTCDA-II, (e) PTCDA-III, and (f) PTCDA-IV coincident overlayers. A detailed description of the construction of these overlayers can be found in the text.

attempting to determine the optimum azimuthal angle (Figure 4). PE calculations performed with a  $3 \times 3$  ( $3b_1 \times 3b_2$ ) overlayer produces multiple, broad minima. A  $10 \times 10$  overlayer affords five minima at  $\theta = 18^\circ$ ,  $\theta = 21^\circ$ ,  $\theta = 24^\circ$ ,  $\theta = 38^\circ$ , and  $\theta = 60^\circ$  (Figure 4). The two minima at  $\theta = 18^\circ$  and  $\theta = 21^\circ$  converge with increasing overlayer size to  $\theta = 20^\circ$  for a  $15 \times 15$  overlayer.

The azimuthal angle predicted by PE methods is nominally identical to the coincident value of  $\theta = 19.8^\circ$  determined by EpiCalc and observed experimentally (the slight difference is simply a consequence of the  $1^\circ$  increments used in the PE calculation). The minima at  $\theta = 38^\circ$  and  $\theta = 60^\circ$  remain for the  $15 \times 15$  overlayer, although these orientations were never observed experimentally. We note that at small overlayer sizes the energy at and near the coincident orientation of  $\theta = 20^\circ$  is less negative than the energy for other, noncoincident orientations. This is due to the contribution of local interactions that predominate at small overlayer sizes, wherein the energy is

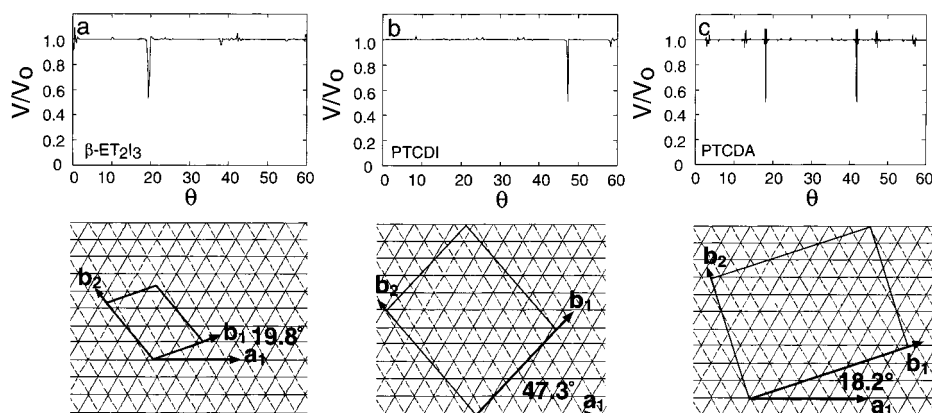
sensitive to molecular structures and orientations within the unit cell as well as overlayer translational positioning on the substrate. A similar trend with overlayer size was observed with EpiCalc. Small overlayer sizes exhibited multiple and broader minima, but the single coincident value of  $\theta = 19.8^\circ$  is clearly evident for overlayer dimensions exceeding  $15 \times 15$ .

**PTCDI Overlayer.** The lattice parameters of epitaxial PTCDI overlayers on HOPG, as determined by scanning tunneling microscopy,<sup>16e</sup> are  $b_1 = 14.5$  Å,  $b_2 = 16.9$  Å, and  $\beta_0 = 83.6^\circ$ , with an azimuthal orientation of  $\theta = 12.7^\circ$ . EpiCalc for a  $51 \times 51$  overlayer indicates that an overlayer with these lattice parameters is coincident at  $\theta = 47.3^\circ$  (Figure 3b). This is identical to the reported value of  $12.7^\circ$  (the convention used for lattice parameter assignment in ref 16e differs from that used here;  $47.3^\circ$  is simply the  $60^\circ$  complement of  $12.7^\circ$ ).<sup>27</sup> PE calculations for this overlayer were performed on a PTCDI layer structure (Figure 2b) generated by flattening the bulk  $(\bar{1} 02)$  layer so that the PTCDI planes would lay flat on the HOPG

**TABLE 1: Comparison of Bulk, Experimental, and Calculated Lattice Parameters and Azimuthal Orientations for Coincident Overlayers on a HOPG Substrate**

overlayer	$b_1$ (Å)	$b_2$ (Å)	$\beta_o$	$\theta$	$\theta$ (PE) <sup>a</sup>	supercell size <sup>b</sup> ( $b_1 \times b_2$ )
$\beta$ -ET <sub>2</sub> I <sub>3</sub>						
bulk (001) <sup>28</sup>	6.61	9.10	109.8°	—		
experimental <sup>c,24</sup>	6.2 ± 0.5	9.4 ± 0.8	107 ± 4°	18°		
coincident <sup>d</sup>	6.6	9.1	110°	19.8°	20°	1 × 3
PTCDI						
bulk (102) <sup>e</sup>	14.42	14.73	90°	—		
experimental <sup>f,16e</sup>	14.5	16.9	83.6°	12.7°		
coincident <sup>d</sup>	14.5	16.9	83.6°	47.3°	47°	2 × 1
PTCDA						
bulk (100) <sup>f</sup>	17.34	11.96	90°	—		
bulk (102) <sup>f</sup>	19.89	11.96	90°	—		
experimental <sup>g,17,18</sup>	20.5 ± 1.2	14.2 ± 1.5	90°	21.6 ± 4°		
PE <sup>h,17,18</sup>	20.0 ± 0.5	15.7 ± 0.5	90°	19°		incommensurate
coincident <sup>d</sup>	20.43	15.7	90°	18.2°	18°	1 × 3
bulk (102) <sup>f</sup>	11.96	19.89	90°	—		
experimental <sup>16e</sup>	12.7	19.2	89.5°	3.2°		
experimental <sup>22</sup>	12.69	19.22	89.5°	3.1°		
coincident	12.72	19.20	89.5°	56.8°	57°	3 × 1
NTCDA <sup>i</sup>						
coincident <sup>d</sup>	20.43	15.7	90°	18.2°	18°	

<sup>a</sup> This work. <sup>b</sup> Determined by EpiCalc from the matrix coefficients that define the coincident configuration. <sup>c</sup> Lattice parameters determined by in situ atomic force microscopy. <sup>d</sup> Coincident lattice parameters were determined with EpiCalc. <sup>e</sup> Cambridge Structural Database entry LENPEZ, G. Klebe, private communication, 1994. <sup>f</sup> Private communication, R. Pascal. <sup>g</sup> Lattice parameters determined by scanning tunneling microscopy. <sup>h</sup> PE calculations were used to determine the minimum energy structure and lattice parameters for a single unit cell on the HOPG substrate. The optimum value of  $\theta$  was subsequently determined by PE methods for a 10 × 10 overlayer with the structure and lattice parameters locked (refs 17, 18). <sup>i</sup> Hypothetical structure.



**Figure 3.** Calculated dependence of  $V/V_0$  on azimuthal angle  $\theta$  and schematic representations of the optimum overlayer orientations for the coincident overlayer–substrate systems: (a)  $\beta$ -ET<sub>2</sub>I<sub>3</sub>/HOPG ( $b_1 = 6.6$  Å,  $b_2 = 9.1$  Å,  $\beta_o = 109.8^\circ$ ); (b) PTCDI/HOPG ( $b_1 = 14.5$  Å,  $b_2 = 16.9$  Å,  $\beta_o = 83.6^\circ$ ); and (c) PTCDA/HOPG ( $b_1 = 20.43$  Å,  $b_2 = 15.7$  Å,  $\beta_o = 90^\circ$ ). The calculations were performed with 51 × 51 overlayers.

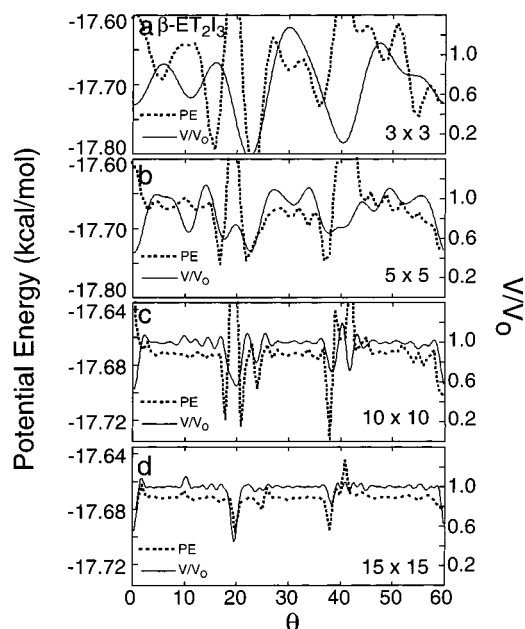
surface, followed by expanding the lattice parameters to the values reported in ref 16e, which was verified as coincident by EpiCalc. The PE calculation for a 3 × 3 overlayer produces a pronounced minimum at  $\theta = 22^\circ$  (Figure 5). However, as the overlayer size is increased several others emerge, including a deep minimum at  $\theta = 47^\circ$ . Eventually, for a 15 × 15 overlayer the PE minimum at  $\theta = 22^\circ$  broadens and becomes less prominent and the sharp minimum at  $\theta = 47^\circ$  remains. This result agrees with EpiCalc, which produces  $V/V_0 = 0.5$  at  $\theta = 47.3^\circ$  for overlayer sizes exceeding 15 × 15.

**PTCDA Overlayers.** Several groups have reported PTCDA overlayers on HOPG, with Forrest et al. describing overlayer growth as “quasiepitaxial”.<sup>17,18</sup> However, the experimental data reported by Forrest et al. indicated a single azimuthal orientation of  $\theta = 21.6 \pm 4^\circ$  with lattice parameters  $b_1 = 20.5 \pm 1.2$  Å,  $b_2 = 14.2 \pm 1.5$  Å, and  $\beta_o = 90^\circ$  (Table 1).<sup>17,18,28</sup> A second structure, reported by two other groups as epitaxial, is described below. Previous PE calculations<sup>17,18</sup> for the “quasiepitaxial” structure, with the PTCDA molecular planes parallel to the HOPG substrate, predicted a minimum energy unit cell structure

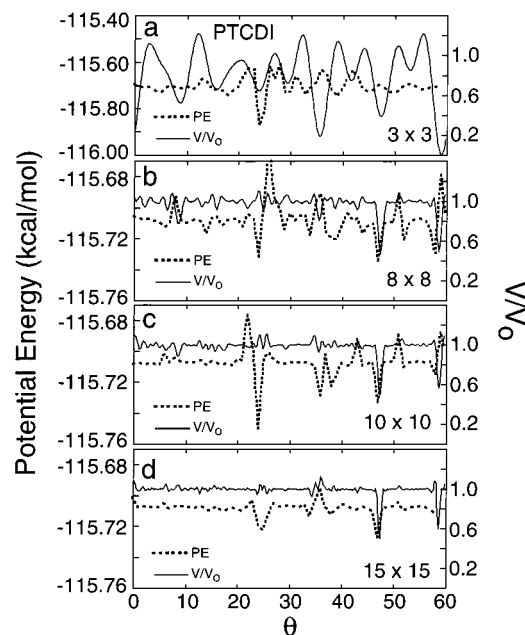
with lattice constants  $b_1 = 20.0 \pm 0.5$  Å,  $b_2 = 15.7 \pm 0.5$  Å, and  $\beta_o = 90^\circ$ . These calculations were performed with a Buckingham potential and a single PTCDA unit cell on HOPG. The energy minimization resulted in PTCDA molecules adopting specific in-plane orientations, with the long axes of the two independent molecules in the unit cell rotated by +49.3° and −68.2° from  $b_1$ . Subsequent PE calculations performed for a 10 × 10 PTCDA overlayer constructed from this unit cell, with the molecules in fixed positions, predicted an optimum azimuthal angle of  $19^\circ$ .<sup>17,18</sup>

The availability of structural data and PE calculations for this overlayer prompted us to examine its epitaxial relationship with HOPG using EpiCalc and compare these results with PE calculations. EpiCalc returns  $V/V_0 = 1$  for all values of  $\theta$  with these lattice parameters, indicating that this overlayer is incommensurate. However, EpiSearch finds  $V/V_0 = 0.5$  for a 51 × 51 overlayer on HOPG at  $\theta = 18.2^\circ$  for  $b_1 = 20.43$  Å,  $b_2 = 15.70$  Å, and  $\beta_o = 90^\circ$  (Figure 3c). Notably, these values are within the errors for the experimental data and PE computations in ref 17. PE calculations performed in our laboratory (not



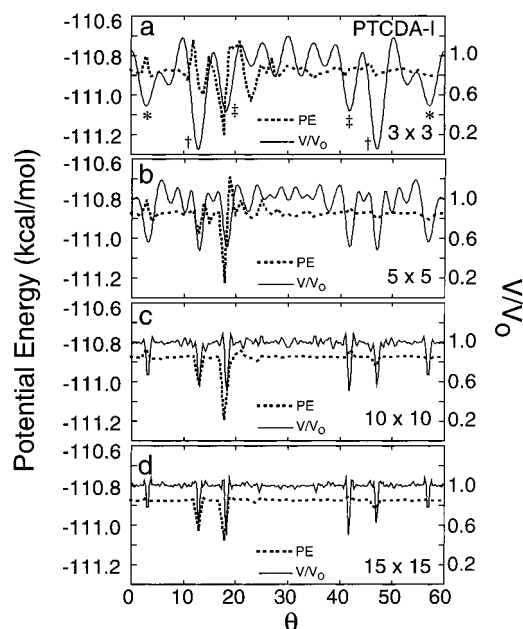


**Figure 4.** Dependence of the total PE (---) and  $V/V_0$  (—) on overlayer size for the (001)  $\beta$ -ET<sub>2</sub>I<sub>3</sub> overlayer in Figure 3a with  $b_1 = 6.6$  Å,  $b_2 = 9.1$  Å,  $\beta_0 = 109.8^\circ$  and a HOPG substrate with  $a_1 = 2.46$  Å,  $a_2 = 2.46$  Å,  $\alpha_s = 120^\circ$ . Overlayer sizes are indicated on each plot. However, for (c) the overlayer size for the  $V/V_0$  calculation is  $11 \times 11$  (even  $M$  and  $N$  values cannot be used as inputs for EpiCalc). The PE calculations were performed with the ET layer in contact with the HOPG substrate; the triiodide layer was not included in the calculations.



**Figure 5.** Dependence of the total PE (---) and  $V/V_0$  (—) on overlayer size for the PTCDA overlayer in Figure 3b with  $b_1 = 14.5$  Å,  $b_2 = 16.9$  Å,  $\beta_0 = 83.6^\circ$  and a HOPG substrate with  $a_1 = 2.46$  Å,  $a_2 = 2.46$  Å,  $\alpha_s = 120^\circ$ . Overlayer sizes for the PE calculations are indicated on each plot. Overlayer sizes for the  $V/V_0$  calculations of a–d are  $3 \times 3$ ,  $9 \times 9$ ,  $11 \times 11$ , and  $15 \times 15$ , respectively (even  $M$  and  $N$  values cannot be used as inputs for EpiCalc).

shown here) on a  $10 \times 10$  overlayer, having the same structure and lattice parameters calculated in ref 17, produce minima at  $\theta = 14^\circ$  and  $\theta = 17^\circ$ . We observe that even at large ( $15 \times 15$ ) overlayer sizes these minima are shallow and not well defined. To further explore the importance of using coincident lattice parameters when performing PE calculations, we examined the overlayer identified as **PTCDA-I** (Figure 2c), which is identical

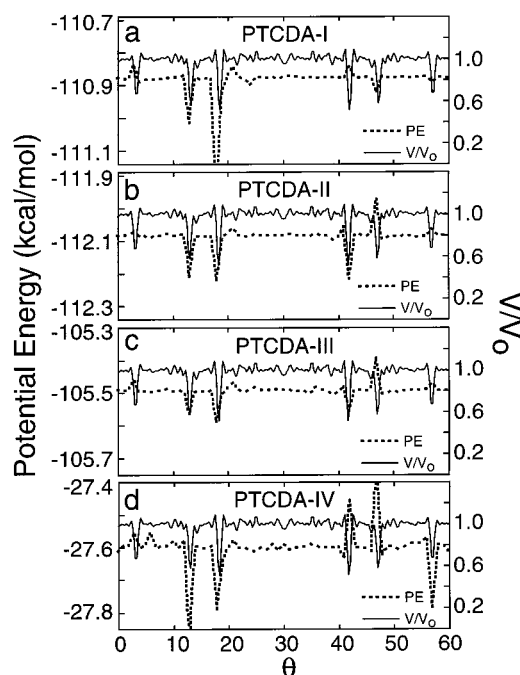


**Figure 6.** Dependence of the total PE (---) and  $V/V_0$  (—) on overlayer size for the PTCDA-I overlayer with  $b_1 = 20.43$  Å,  $b_2 = 15.7$  Å,  $\beta_0 = 90^\circ$  and an HOPG substrate with  $a_1 = 2.46$  Å,  $a_2 = 2.46$  Å,  $\alpha_s = 120^\circ$ . Overlayer sizes are indicated on each plot. However, the  $V/V_0$  calculation for (c) was performed with an  $11 \times 11$  overlayer (even  $M$  and  $N$  values cannot be used as inputs for EpiCalc).

to the overlayer described in ref 17 but has lattice parameters expanded to the exact coincident values determined by EpiCalc. Three minima at  $\theta = 14^\circ$ ,  $18^\circ$ , and  $23^\circ$  are observed for a  $3 \times 3$  overlayer, but as the overlayer size is increased the minimum at  $\theta = 23^\circ$  vanishes, the minimum at  $14^\circ$  shifts to  $13^\circ$ , and the peak at  $18^\circ$  remains (Figure 6). Calculations performed for a  $15 \times 15$  overlayer reveal that the energy minimum at  $\theta = 18^\circ$  is approximately 0.1 kcal/mol less than that at  $\theta = 13^\circ$ .

In contrast, EpiCalc produces six minima at  $\theta = 3.2^\circ$ ,  $13.0^\circ$ ,  $18.2^\circ$ ,  $41.8^\circ$ ,  $47.0^\circ$ , and  $56.8^\circ$  for a  $15 \times 15$  **PTCDA-I** overlayer. The first three values are simply the complements of the last three owing to symmetry considerations associated with the rectangular overlayer unit cell and the hexagonal symmetry of the HOPG substrate (Figure 6, minima at complementary angles are denoted by the symbols \*, †, or ‡). This symmetry equivalence is absent in the PE calculations because the asymmetric orientation of the two PTCDA molecules in **PTCDA-I** reduces the overlayer symmetry. The minima at  $\theta = 3.2^\circ$ ,  $13.0^\circ$ ,  $47.0^\circ$ , and  $56.8^\circ$  become less prominent with increasing overlayer size until only the single coincident orientation at  $\theta = 18.2^\circ$  (and its complementary angle of  $\theta = 41.8^\circ$ ) was observed for the  $51 \times 51$  overlayer (Figure 3c). The coincident lattice parameters agree with the measured values, arguing that the observed PTCDA overlayer is *coincident* rather than incommensurate. The convergence toward a clearly identifiable and unambiguous minimum in both EpiCalc and PE calculations with increasing overlayer size illustrates the importance of using large overlayers in calculations.

The observation of the same minimum at  $\theta = 18^\circ$  for EpiCalc and PE calculations for the **PTCDA-I** overlayer argues convincingly that the lattice registry associated with coincidence is primarily responsible for the observed epitaxial configuration. This prompted us to examine if the arrangement of molecules in the overlayer, for a given set of lattice parameters, affected the optimum  $\theta$  value produced by PE calculations. PE calculations were performed on various PTCDA lattices derived from bulk (102) and (100) layers (Figures 2d–2f), with lattice



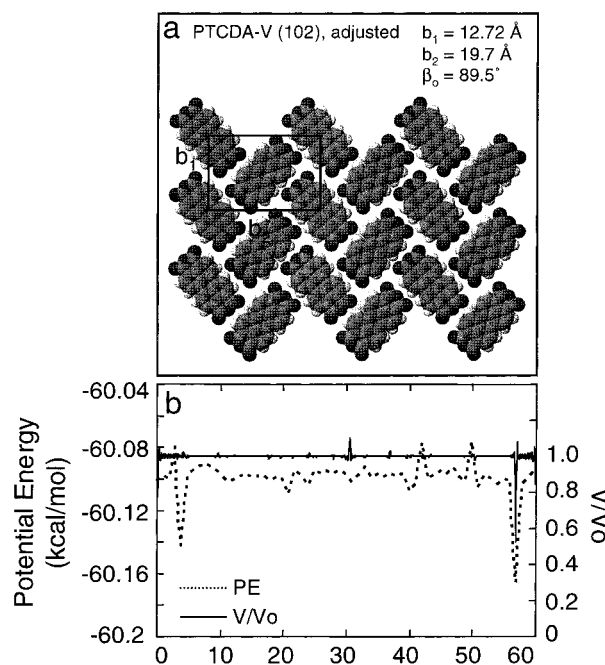
**Figure 7.** Dependence of total interaction PE (---) and  $V/V_o$  (—) on molecular orientation for the PTCDA overlayers: (a) PTCDA-I, (b) PTCDA-II, (c) PTCDA-III, and (d) PTCDA-IV. The overlayer size was  $10 \times 10$  for each PE calculation and  $11 \times 11$  for each  $V/V_o$  calculation.

parameters fixed at the coincident values of  $b_1 = 20.43 \text{ \AA}$ ,  $b_2 = 15.7 \text{ \AA}$ , and  $\beta_o = 90^\circ$ .

Overlayer **PTCDA-II** is a (102) layer, flattened and expanded, with the PTCDA molecules retained in their bulk in-plane orientations (the long molecular axes of the two independent molecules are oriented  $48.8^\circ$  and  $-48.8^\circ$  with respect to  $b_1$ ). PE calculations and EpiCalc produce two minima at  $\theta = 13^\circ$  and  $\theta = 18^\circ$  for a  $10 \times 10$  overlayer of **PTCDA-II** (Figure 7). These angles are identical to those obtained for **PTCDA-I**, although the actual energy values from the PE calculations differ slightly ( $\approx 1 \text{ kcal/mol}$ ,  $< 1\%$  of total energy). Two peaks were also observed at the complementary angles of  $\theta = 42^\circ$  and  $\theta = 47^\circ$ . The observation of an energy maximum at  $\theta = 47^\circ$ , instead of a minimum, has been noted previously for other systems.<sup>29</sup> The observation of this maximum, which also is a consequence of the phase coherence of the substrate and overlayer, is due to the sensitivity of the energy to overlayer translations on the substrate.

The remaining two overlayers, **PTCDA-III** and **PTCDA-IV**, correspond to unflattened versions of the (102) and (100) planes, respectively, expanded to the coincident parameters. The out-of-plane tilts of the PTCDA molecules are  $3^\circ$  and  $20^\circ$  for **PTCDA-III** and **PTCDA-IV**, respectively. Even though the arrangements of PTCDA molecules in these overlayers differ substantially, PE calculations for both produce the same azimuthal orientations predicted for **PTCDA-I** and **PTCDA-II** at  $\theta = 13^\circ$  and  $\theta = 18^\circ$  (and two minima at the complementary angles of  $\theta = 42^\circ$  and  $\theta = 47^\circ$ ). The energies of the PE minima for **PTCDA-III** are approximately four times that of **PTCDA-IV**. This can be attributed to the nominally parallel orientation of the molecules in **PTCDA-III**, which has more atoms in contact with the HOPG substrate.

In contrast to the other three overlayers, **PTCDA-IV** exhibits the deeper minimum at  $\theta = 13^\circ$ . However, the energy difference between the two minima for **PTCDA-IV** is only  $0.1 \text{ kcal/mol}$ , less than  $0.4\%$  of the total energy. Small differences in the energy of the two minima are evident for the other three



**Figure 8.** (a) Schematic representation of the PTCDA-V coincident overlayer. (b) Calculation of PE (---) and  $V/V_o$  (—) for the PTCDA-V overlayer with  $b_1 = 12.72 \text{ \AA}$ ,  $b_2 = 19.7 \text{ \AA}$ ,  $\beta_o = 89.5^\circ$  and a HOPG substrate with  $a_1 = 2.46 \text{ \AA}$ ,  $a_2 = 2.46 \text{ \AA}$ ,  $\alpha_s = 120^\circ$ . The overlayer size was  $10 \times 10$  for the PE calculations and  $71 \times 71$  for  $V/V_o$ .

overlayers as well. The data in Figure 7 indicate that  $[E(\theta = 18^\circ) - E(\theta = 13^\circ)]$  for **PTCDA-I** is only  $-0.2 \text{ kcal/mol}$  ( $< 0.2\%$  of total energy), while for **PTCDA-II** and **PTCDA-III** this quantity is  $< 0.05\%$  of the total energy. These same two minima are also evident in the EpiCalc results, their  $V/V_o$  values indicating near coincidence at  $\theta = 13^\circ$  and coincidence at  $\theta = 18^\circ$ . The peak at  $\theta = 13^\circ$  vanishes completely for overlayer sizes exceeding  $31 \times 31$  when using EpiCalc, while the peak at  $\theta = 18^\circ$  remains.

A PTCDA overlayer with a structure differing from **PTCDA-I**, **II**, **III**, and **IV**, but having lattice parameters nearer those of the (102) layer of the bulk crystal structure, has also been reported (Table 1).<sup>16e,22</sup> Using the reported lattice parameters as a starting point for EpiSearch, we found a precisely coincident lattice with lattice parameters  $b_1 = 12.72 \text{ \AA}$ ,  $b_2 = 19.2 \text{ \AA}$ , and  $\beta_o = 89.5^\circ$  (**PTCDA-V**, Figure 8a) and  $\theta = 56.8^\circ$ . PE calculations for **PTCDA-V** revealed a minimum at  $\theta = 57^\circ$  (Figure 8b), identical to the experimentally observed values reported as  $\theta = 3.1^\circ$  and  $\theta = 3.2^\circ$  ( $57^\circ$  is simply the  $60^\circ$  complement of  $3^\circ$ ; the small difference between the calculated and observed values can be attributed to the  $1^\circ$  increment used in the PE calculations).

## Discussion

The observed trends described above demonstrate that the determination of the optimum azimuthal angle by either method is ambiguous for overlayers with dimensions of  $15 \times 15$  or less. However, the lattice modeling calculations with large overlayers return a single optimum azimuthal angle that reflects a coincident overlayer. In all cases, the orientations determined with EpiCalc agree with the corresponding experimentally observed values and one of the minima predicted by PE methods. This agreement argues that the overriding factor governing epitaxy for these van der Waals interfaces is phase coherence between the overlayer and substrate.

The observation of multiple and false minima has been attributed to "edge effects" that are only eliminated upon



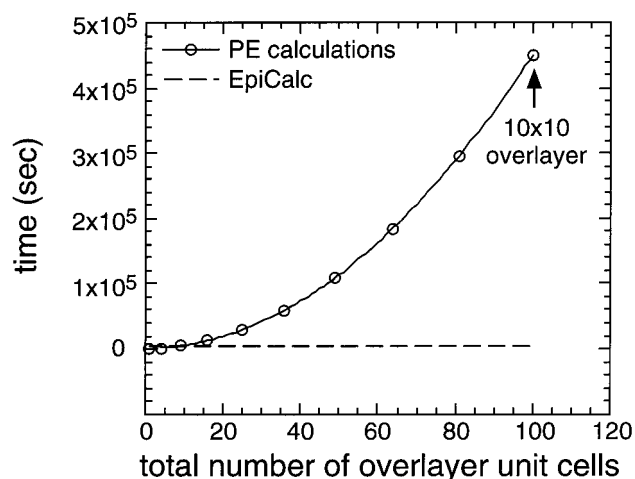
reducing the edge-to-area ratio, which is achieved by increasing the overlayer size.<sup>17,18</sup> However, edge effects do not contribute to the PE calculations reported here because a 15 Å cutoff is used for each atom–atom pair. In addition, EpiCalc, which only considers the periodicity of the overlayer and substrate lattices, also exhibits multiple and broad minima at small overlayer sizes.

In order to establish the coincident orientation the overlayer size must be at least equal to the size of the commensurate supercell. The results described above demonstrate that the determination of this orientation becomes less ambiguous with increasing overlayer size. In principle, the lattice misfit should be independent of overlayer size if the specified values of  $M$  and  $N$  reflect an integral number of supercells. However, because of the inherent inexactness in the near-coincident lattice parameters chosen for the calculation, values of  $M$  and  $N$  must exceed 40 in order to establish an unambiguous minimum that signifies coincidence (see Appendix).

The origin of the overlayer size dependence in PE calculations can be attributed to the error associated with the 15 Å cutoff distance for each atom–atom pair in the Lennard–Jones calculation. If exact coincident lattice parameters were used for the overlayer (to at least several decimal places), two crystallographically equivalent overlayer lattice points separated by many unit cells would reside on identical substrate positions and would encounter the same number of substrate atoms within the 15 Å cutoff. However, if the lattice parameters are inexact, overlayer molecules in different unit cells can encounter a different number of substrate atoms within this cutoff. The total error in the calculations due to these inexact parameters increases as the overlayer size increases. The total error for the false minima, which represent greater misfit than the minimum for the exact coincident configuration, accumulates faster than the error for the coincident minimum as the overlayer size is increased.<sup>30</sup> Consequently, the energy of the false minimum increases faster than the optimum minimum, eventually disappearing while the optimum minimum only decreases slightly. The same principle applies to the energy values in the immediate vicinity of the optimum minimum, resulting in a narrowing of this peak.

PE calculations and EpiCalc also produce different values of  $\theta$  at small overlayer sizes. This difference can be attributed to local, nonperiodic molecule–substrate interactions that appear in PE calculations and contribute more at small overlayer sizes. Such effects are not germane to EpiCalc, which relies solely on lattice registry. However, the agreement between these methods (with respect to  $\theta$ ) when large overlayer sizes are used, and the agreement of these values with experimentally observed values of  $\theta$ , corroborates the existence of coincidence and its importance in determining epitaxial configurations.

The reliability of EpiCalc with respect to predicting the correct azimuthal orientation for a coincident overlayer is fortunate in two respects. The precision of semiempirical PE calculations is not sufficient for confident assignment of a global thermodynamic minimum when multiple minima are observed. Additionally, the computational time required for EpiCalc is significantly less than for PE methods so that EpiCalc can be reasonably performed with large overlayer sizes at which a single optimum azimuthal orientation can be observed. PE calculations rely on calculating the interaction of every atom of the overlayer with every atom of the substrate. Consequently, the computational time increases exponentially with increasing overlayer area, quickly becoming prohibitive. This is exacerbated by the numerous atoms per lattice site in molecular films and the need to perform calculations with large overlayer sizes



**Figure 9.** Dependence of calculation time as a function of the number of overlayer unit cells for PE (○) and EpiCalc (---) calculations, based on the hypothetical NTCDA overlayer with 48 atoms per unit cell and an HOPG substrate with two atoms per unit cell. The calculations for each method were performed by rotating the overlayer over a 60° range by 1° increments.

to establish the phase coherence that is necessary for accurate calculations. In contrast, computational time for EpiCalc is independent of overlayer size and, for a single set of user-defined lattice parameters, requires less than one second per calculation at each azimuthal angle.

An illustrative comparison of computation times for the two methods is depicted in Figure 9. Calculation of the total PE over the range  $0^\circ \leq \theta \leq 60^\circ$  for a  $10 \times 10$  overlayer with a fixed set of lattice parameters and 48 atoms per unit cell (the hypothetical NTCDA overlayer) requires approximately 12.5 h, while the corresponding calculation with EpiCalc requires only seconds. This time for PE calculations is actually a conservative estimate as molecular overlayers typically contain more than 48 atoms per unit cell, for example, 55 and 76 atoms in the unit cells of  $\beta$ -ET<sub>2</sub>I<sub>3</sub> and PTCDA, respectively.

## Conclusions

The results described above demonstrate that geometric lattice matching routines such as EpiCalc can be used reliably to detect the existence of coincidence and predict the optimum azimuthal orientation for a given set of overlayer and substrate lattice parameters. EpiCalc is unique among geometric models with respect to its capacity to search for lattice parameters that are coincident with a chosen substrate. Because of the analytical nature of the EpiCalc algorithm, searching for coincident configurations is rapid even though the calculations involve four degrees of freedom ( $b_1$ ,  $b_2$ ,  $\beta_0$ , and  $\theta$ ). Such calculations with PE methods are computationally prohibitive, particularly for large overlayer sizes that are required for unambiguous assignment of optimum configurations.

The agreement of experimental data and PE calculations with the configurations predicted by EpiCalc demonstrates the validity of using this geometric lattice misfit model to predict and visualize epitaxial configurations, particularly coincident overlayers that are difficult to predict and visualize owing to their oblique symmetry, large size, and reduced commensurability with the substrate. EpiCalc is a convenient method for rapid screening of optimum coincident configurations ( $b_1$ ,  $b_2$ ,  $\beta_0$ , and  $\theta$ ) that can be used in subsequent PE calculations that allow relaxation of the molecular orientation to a minimum energy structure within the overlayer. The ability to reduce the degrees

of freedom in the PE calculation by first determining the coincident lattice parameters and  $\theta$  makes the calculation of overlayer structures more feasible for large overlayers. Furthermore, the agreement between experiment, semiempirical calculations, and a modeling routine based solely on lattice geometry demonstrates that molecular overlayer orientations are commonly governed by coincident epitaxy. More important, these results confirm that coincidence has a fundamental physicochemical foundation that is identical to that used to explain the occurrence of strictly commensurate lattices.

We note that phenomenological arguments based on Moiré patterns have been advanced to explain the orientation of apparently noncommensurate, simple inorganic lattices, which also were shown to be energetically favorable by numerical simulations.<sup>31,32</sup> Interestingly, the results of these simulations do not depend strongly on the form of the potential function used in the calculation.<sup>33</sup> Other analyses have demonstrated that these systems are actually coincident and have concluded that the phase coherence resulting from coincidence is responsible for overlayer stabilization.<sup>34,35</sup> Notably, the minima observed for PE calculations of the **PTCDA-I** overlayer are reproduced when the PTCDA molecules are replaced with smaller NTCDA molecules or argon atoms. This further substantiates that the phase coherence between the substrate and overlayer lattices governs the optimum azimuthal angle, not the specific arrangements or structures of the molecules within the unit cell. We anticipate that the recognition of the importance of coincidence to molecular overlayers and the use of convenient methods such as EpiCalc will significantly facilitate the design and fabrication of complex functional molecular films.

**Acknowledgment.** The authors are grateful to the Office of Naval Research for financial support.

## Appendix

Determination of the mode of epitaxy and optimum overlayer orientation can be accomplished using EpiCalc, a geometric lattice misfit algorithm developed in our laboratory. EpiCalc relies on an analytical function devised in our laboratory that enables calculation of  $V/V_o$ , which we termed a “dimensionless potential” (eq A1).

$$\frac{V}{V_o} = \left\{ 2MN - \frac{\sin(M\pi p_x)\sin(N\pi q_x)}{\sin(\pi p_x)\sin(\pi q_x)} - \frac{\sin(M\pi q_y)\sin(N\pi p_y)}{\sin(\pi q_y)\sin(\pi p_y)} \right\} \left( \frac{1}{2MN} \right) \quad (\text{A1})$$

term A:  $2MN$

$$\text{term B: } \frac{\sin(M\pi p_x)\sin(N\pi q_x)}{\sin(\pi p_x)\sin(\pi q_x)}$$

$$\text{term C: } \frac{\sin(M\pi q_y)\sin(N\pi p_y)}{\sin(\pi q_y)\sin(\pi p_y)}$$

term D:  $1/(2MN)$

Note:  $M = 2m + 1$  and  $N = 2n + 1$ ;  $m$  and  $n$  are the values input into EpiCalc, resulting in  $M$  and  $N$  always being odd. This is required to achieve nonzero values for numerators in terms B and C in (A1) so that the discrete values of  $V/V_o$  (1, 0.5, and 0), which are necessary to distinguish the different modes of epitaxy, can be realized. The function in (A1) behaves as follows for the different modes of epitaxy.

**1. Commensurism.** Every matrix element is an integer. In this case, terms B and C are both equal to 0/0 ( $\sin(\text{integer} \cdot \pi) = 0$ ). Therefore, L'Hopitals rule (eq A2) must be invoked.

$$\lim_{x \rightarrow a} \frac{f(x)}{g(x)} = \frac{f'(a)}{g'(a)} \quad (\text{A2})$$

Then, the numerator of term B becomes

$$\frac{d}{dq_x dp_x} = M\pi \cos(M\pi p_x) N\pi \cos(N\pi q_x)$$

and the denominator becomes

$$\frac{d}{dq_x dp_x} = \pi \cos(\pi p_x) \pi \cos(\pi q_x)$$

Therefore,

$$\text{term B} = \frac{M\pi \cos(M\pi p_x) N\pi \cos(N\pi q_x)}{\pi \cos(\pi p_x) \pi \cos(\pi q_x)}$$

Similarly,

$$\text{term C} = \frac{M\pi \cos(M\pi q_y) N\pi \cos(N\pi p_y)}{\pi \cos(\pi q_y) \pi \cos(\pi p_y)}$$

For the case of two identical, square lattices,  $p_x = p_y = 1$  and  $q_x = q_y = 0$ . Then,

$$\frac{V}{V_o} = \frac{2MN - MN - MN}{2MN} = 0$$

**2. Coincidence.** Here,  $p_x$  and  $q_x$  or  $p_y$  and  $q_y$  must be integers. This will result in either term A or term B being indeterminate with a value of 0/0. Therefore, L'Hopitals rule must be used to solve the indeterminate term. For example, if only  $p_y$  and  $q_y$  are integers,

$$\text{term C} = \frac{M\pi \cos(M\pi q_y) N\pi \cos(N\pi p_y)}{\pi \cos(\pi q_y) \pi \cos(\pi p_y)} = MN$$

However,

$$\text{term B} = \frac{\sin(M\pi p_x)\sin(N\pi q_x)}{\sin(\pi p_x)\sin(\pi q_x)}$$

A property of coincidence is that  $p_x$  and  $q_x$  are fractions with values such that the products  $Mp_x$  and  $Nq_x$  will be integers if  $M$  and  $N$  are integer multiples of the supercell dimensions. If  $M$  and  $N$  are not integer multiples of the supercell,  $Mp_x$  and  $Nq_x$  are not integers and term B =  $\pm 1$ . Therefore,

$$\frac{V}{V_o} = \frac{2MN \pm 1 - MN}{2MN}$$

As  $MN$  becomes large compared to 1, the  $\pm 1$  term becomes negligible and  $V/V_o \rightarrow 0.5$ . Therefore, large values of  $M$  and  $N$  will enable convergence toward an unambiguous minimum for coincidence. Conversely, if  $M$  and  $N$  are integer multiples of the supercell,  $Mp_x$  and  $Nq_x$  will be integers and term B = 0. However, this condition requires that the lattice parameters be *exactly* the coincident values so that the matrix elements assume values that ensure that  $Mp_x$  and  $Nq_x$  are integers. It is improbable that the user will select lattice parameters for the calculation

that are the exact values required for coincidence. Consequently, in most calculations  $Mp_x$  and  $Nq_x$  can be slightly nonintegral and term B (or term C if  $p_x$  and  $q_x$  are the pair of integral matrix coefficients) will be slightly nonzero. Therefore, EpiCalc is most reliable when  $M$  and  $N$  are large values.

**3. Incommensurism.** Here  $p_x$ ,  $q_x$ ,  $p_y$ , and  $q_y$  are not integers. Therefore,  $Mp_x$ ,  $Nq_x$ ,  $Mq_y$ , and  $Np_y$  will not be integers and terms B and C will be equal to  $\pm 1$ . Then,

$$\frac{V}{V_o} = \frac{2MN \pm 1 \pm 1}{2MN}$$

As  $MN$  becomes large, the  $\pm 1$  terms become negligible and  $V/V_o \rightarrow 1$ .

## References and Notes

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