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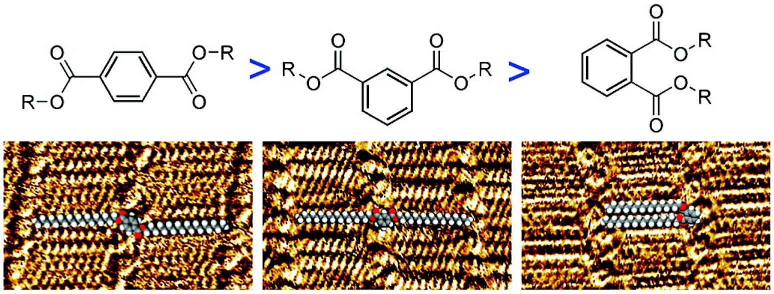

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Contrasting Two- and Three-Dimensional Crystal Properties of Isomeric Dialkyl Phthalates

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Abstract: Competitive adsorption occurs whenever a solution containing multiple components is in contact with a surface, and the relative adsorption strengths affect both the properties of the interface and the solution. To investigate this phenomenon, the factors influencing relative adsorption strengths of a series of isomeric dialkyl phthalates were determined from their competitive adsorption behavior and interpreted in the context of the thermodynamic properties of the bulk crystals and the structural features of the monolayers. The order of stabilities of the two-dimensional crystals paralleled that of the three-dimensional crystals, as determined by the trends in melting point, enthalpy of melting, and solubility. The magnitude of the stability differences, however, could only be understood through examination of the structures of the monolayers. Thus, the important process of adsorption of solutes from solution must be viewed as a microscopic phenomenon; adsorption strengths are influenced not only by molecular and macroscopic properties but also by the distinct assembly mode of the adsorbed layer.

Introduction

Whenever solutions containing multiple solutes are in contact with a surface, as is the case in most industrial, biological, and environmental processes, competitive adsorption takes place. When these solutes adsorb into ordered monolayers, they can be directly imaged at the liquid/solid interface on metal, mineral, and carbon substrates.[1−4] The monolayers that result at the solid interface from a mixed solution either consist of one preferentially adsorbed component that completely displaces the others or consist of different coexisting components. Which component is preferentially adsorbed depends upon the strength of the intermolecular interactions between the adsorbed molecules and the interactions of these molecules with the surface, as well as the relative amounts of each component and their concentrations in solution. The composition of the adsorbed film affects its properties as well as those of the solution when preferential depletion occurs; therefore, the prediction of competitive adsorption behavior based on easily obtainable bulk crystal properties of the components is an appealing approach that could prove valuable in designing purification and surface-coating processes, particularly where in-depth characterization of adsorption processes is not feasible. The viability of such an approach was suggested by the parallels between the two- and three-dimensional crystals of a series of dicarbamate molecules,[5] where both systems exhibited an odd−even effect; those dicarbamates with an even number of methylene groups separating the functional groups had higher melting points and greater adsorption strengths than similarly sized compounds with an odd number of methylenes. Comparisons of two-dimensional and three-dimensional crystal properties have been few and are primarily limited to structural comparisons. Here we present a detailed comparison of two- and three-dimensional crystal stabilities which is essential to understanding adsorption processes at a molecular level and establishing a unified framework for self-assembly phenomena across dimensions.

A particularly challenging situation, for which the outcome is important in a variety of industrial processes, is the competitive adsorption of positional isomers. These compounds have the same elemental constitution but vary, for example, in the substitution about an aromatic ring. Such isomers are produced as a mixture through reactions such as Friedel−Crafts alkylation or acylation and are found as components in petroleum products. The competitive adsorption behavior determines whether these isomers can be separated via chromatographic methods based on their differing affinities for a solid stationary phase. Examination of the competitive adsorption of disubstituted benzene isomers not only offers an opportunity to examine the effect of geometry on two-dimensional crystal packing stability controlled for the effect of molecular size and functionality, but also enables comparison between the relative adsorption strengths and the well-established melting point trend in this class of materials. For the disubstituted benzenes in general, the para compounds melt at higher temperature than the meta and ortho compounds.[6−8]

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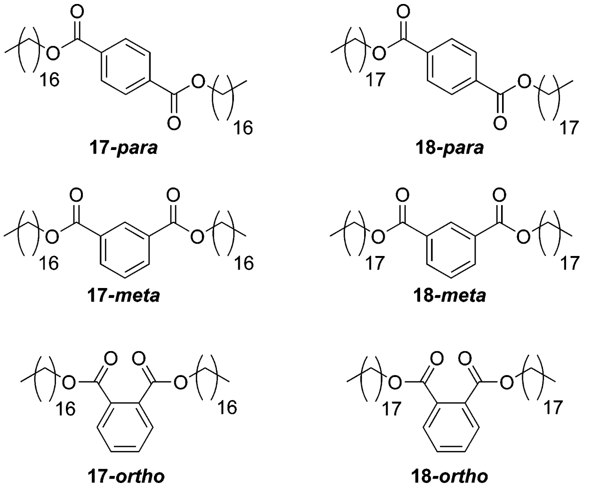

Figure 1. Compounds belonging to both isomeric series for which two- and three-dimensional crystal stabilities were compared and two-dimensional crystal structures determined. The isomers of diheptadecyl phthalate, which have 17 carbons in each alkyl chain, are termed the "odd isomers", and the isomers of dioctadecyl phthalate, which have one more methylene in each alkyl chain, are the "even isomers".

The adsorption properties of a series of alkyl-substituted phthalate isomers (Figure 1) were examined, and the results were interpreted by comparison of their bulk properties and monolayer structural features. The self-assembly of these compounds has implications for their use as surfactants, lubricants, and polymer additives. This class of molecules is also a valuable model for understanding various alkyl phthalate-based polyesters. The monolayer structures of these compounds at the solution-graphite interface were examined, as was the competitive adsorption between ortho, meta, and para isomers. Graphite is a particularly relevant substrate because it is a model for important carbonaceous adsorbents, such as activated carbon and carbon black. Furthermore, the solution−graphite interface is an excellent system for studying competitive adsorption processes because the molecules that make up the physisorbed monolayer are in dynamic equilibrium with molecules in solution and the structure of the adsorbed phase can be examined with high-resolution using scanning tunneling microscopy (STM). The stabilities of the two-dimensional crystals of these compounds are determined by competitive adsorption experiments. In order to establish a relationship with three-dimensional crystal properties, the melting points, the change in enthalpy upon melting, the change in entropy upon melting, and solubilities were compared among isomers and with the two-dimensional crystal data.

Results and Discussion

The surface-adsorbed and bulk crystalline properties of the ortho, meta, and para isomers of dioctadecyl phthalate (termed the even isomers: **18-*ortho***, **18-*meta***, and **18-*para***) and diheptadecyl phthalate (termed the odd isomers: **17-*ortho***, **17-*meta***, and **17-*para***), were examined (Figure 1). These names describe the number of carbons in each alkyl chain and the ring-substitution pattern.

Two-Dimensional Crystal Structures. The variation in the two-dimensional structures formed by isomers offers an opportunity to explore the effects of molecular symmetry and structure on packing.[9−15] In the dialkyl phthalate isomers examined here, the packing motif depends both on the ring-substitution geometry and the length of the alkyl chains (Table 1). The patterns adopted by meta- and para-substituted molecules (Figures 2 and 3) are related; both are close-packed, interdigitated structures wherein molecules adopt a flat conformation retaining the maximal molecular symmetry.[16−18] Thus, meta isomers sit on mirror planes, in the plane groups *cm* or *p*2*mg*, while para isomers sit on two-fold rotation axes in *p*2 or *p*2*gg* (Table 1). Such retention of two-fold molecular symmetry is very common in monolayers formed at the liquid/graphite interface, but retention of molecular mirror planes is not.[18] In fact, mirror planes are not generally incorporated into two-dimensional crystal symmetry in any case; thus, the meta isomers represent an unusual class of compounds that form symmetric, achiral monolayers. Selection between the two possible plane groups for a given substitution position is based on the parity of the number of carbons in the alkyl chain—an "odd/even" effect.[5,16,19,20] In the meta series, the odd isomer forms in *cm*, while the even isomer forms in *p*2*mg*. This is a result of a two-fold rotation between adjacent columns that allows the densest packing. The extra methylene group present in each chain in the even isomers would induce either steric crowding or empty space if they adopted the same packing motif as the odd isomers, depending on the respective shift of the methylenes. The flipping of adjacent columns in the even isomers structure enables a packing density comparable to that of the odd isomer structure. Evidence for this arrangement is seen in the contrast difference between adjacent columns of aromatic rings observed for **18-*meta*** monolayers, but not for **17-*meta*** monolayers.[16,17] The same phenomenon is seen in the para isomers, but it is the odd isomer

Table 1. Two-Dimensional Crystal Structure Parameters, Both Observed by STM and Calculated by Computational Modeling, for All Observed Phases

			experimental			computed		
molecule	*Z'*	plane group	*a* (nm)	*b* (nm)	α (deg)	*a* (nm)	*b* (nm)	α (deg)
17-*meta*	0.5	*cm*	6.1(1)	0.84(1)	90(3)	5.99	0.88	90.0
18-*meta*	0.5	*p*2*mg*	6.7(2)	0.80(5)	87(3)	6.25	0.88	90.0
17-*ortho*	1.0	*p*2	3.1(2)	1.9(2)	110(5)	2.86	1.78	100.4
18-*ortho*	1.0	*p*2	3.2(2)	2.0(2)	98(5)	2.95	1.77	98.2
17-*para*	0.5	*p*2*gg*	5.6(1)	0.9(1)	99(5)	5.90	0.88	89.9
18-*para* phase I	0.5	*p*2	3.3(2)	0.9(1)	86(3)	3.09	0.88	87.7
18-*para* phase II	1.0	*p*2	2.4(2)	2.4(3)	89(2)	2.42	2.34	83.2

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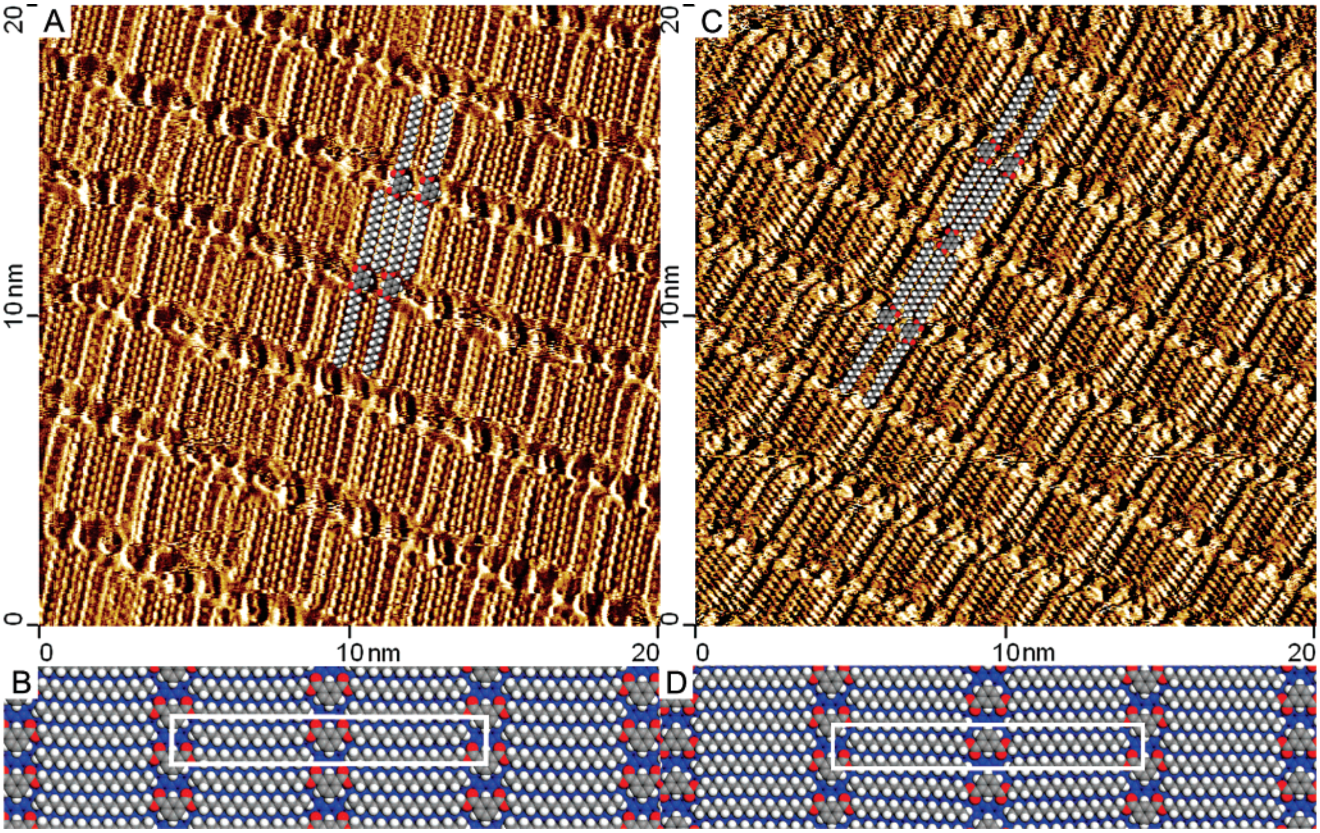

Figure 2. Two-dimensional crystals of the meta isomers, **17-*meta*** (A,B) and **18-*meta*** (C,D). (A,C) STM images with overlaid molecular models and (B,D) computed packing patterns with unit cell. These two packing motifs, formed by molecules that have a one methylene difference in both the attached alkyl chains, are distinguished by the relative orientation of adjacent columns.

that exhibits differently oriented adjacent columns, adopting a *p*2*gg* symmetry rather than *p*2 (Table 1). The difference in ring-substitution geometry allows a slightly denser packing for the para isomers than for the meta, as indicated by the computational models. Both sets of structures can be understood on the basis of the tendency toward close-packing, given that the lowest-energy conformation for these molecules is an all-trans carbon backbone with the ester functionality at 0° torsion angle with respect to the benzene ring.[16]

In addition to this packing motif, **18-*para*** has a pseudopolymorph, phase II (Supporting Information). This alternate packing is characterized by the interdigitation of dimers. Both packing structures often coexist, but as the solutions are diluted, phase II ceases to form, and only phase I is observed. When the solution ratios approach the transition from adsorption of **18-*para*** to adsorption of either **18-*ortho*** or **18-*meta***, it is phase I that is in competition with the phases formed by the other isomers, and therefore, it is the relative stability of this more stable form that is measured in competitive adsorption experiments.

The two-dimensional crystals of the ortho isomers differ significantly from those of the meta or para isomers due to the constraints on the molecular conformation set by the ring-substitution geometry.[17] The ortho isomers, unlike the meta or para compounds, cannot lie flat on the surface due to the proximity of the substituents, thus reducing the interaction between the molecules and the substrate. The steric interaction of the ester functionalities on adjacent carbons prevents them from both adopting the energetically preferred 0° torsion angle with respect to the benzene ring. Furthermore, the proximity of the alkyl chains enables extensive intramolecular contacts. This results in a hairpin conformation, similar to that seen with other ortho-substituted molecules,[17,21] that precludes interdigitation with the alkyl chains of neighboring molecules. Instead, these monolayers are characterized by dimers of molecules forming angled columns. The partially desorbed benzene rings can overlap slightly with the methyl group from a neighboring molecule, providing a stabilizing $\mathrm{C-H}\cdots\pi$ interaction. The model and STM images are given in Figure 4. In contrast to the meta and para structures, no marked differences were observed between monolayers consisting of ortho-substituted molecules with 17 or 18 carbons in the alkyl chains.

Competitive Adsorption. The para isomers preferentially adsorbed to the surface when in competition with an equal number of the corresponding ortho isomers, forming a monolayer indistinguishable from that obtained from pure compound. Thus, the para isomers form more stable two-dimensional crystals on the graphite substrate with more negative free energies of adsorption.[22] As the ratio of ortho to para in solution was increased, there was a sharp transition from adsorption of solely the para isomer to solely the ortho isomer, such that co-adsorption was not observed. Only upon increase of the solution ratio of ortho:para (80:1 for the even isomers and 99:1 for the odd isomers) was the ortho monolayer observed. From the solute

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[22] The phase observed to form at the surface from multicomponent solutions during the competitive adsorption experiments were not metastable, kinetically favored phases. This was determined by displacement experiments, where a monolayer was formed from pure solution and then rapidly displaced by addition of another isomer.

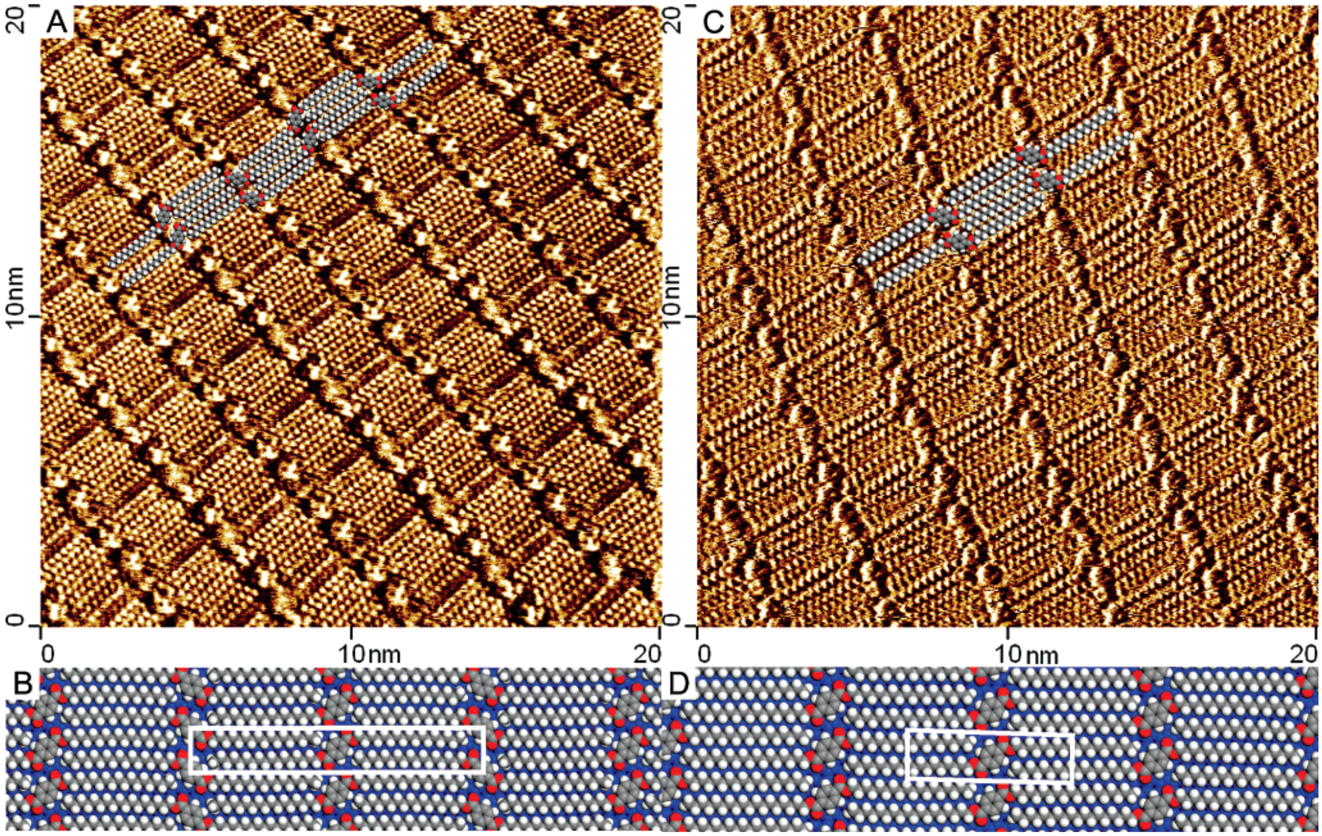

Figure 3. Two-dimensional crystals of the para isomers, **17-*para*** (A,B) and **18-*para*** (C,D). (A,C) STM images with overlaid molecular models and (B,D) computed packing patterns with unit cell. The para compounds pack very similarly to their meta isomers, with the same molecular conformations and contact with the surface; however, the odd−even effect is reversed.

ratios at which pure monolayers form,[5,23,24] it was calculated that the ortho monolayers are less stable than the para monolayers by greater than 2.5 kcal mol^{-1} (Table 2).

When in competition with an equal concentration of meta isomers, the ortho isomers are displaced, just as they were when competing with para isomers; thus, the meta isomers are preferentially adsorbed. For the odd isomers, coadsorption was not observed because of the sharp transition from one phase to the other as the solution ratios were increased. For the even isomers, however, cocrystallization was observed in a narrow solute ratio range (ratios of 40:1 and 50:1 **18-*ortho***:**18-*meta***).[17] This 1:1 cocrystal exhibits a very unusual structure, with a much larger periodicity than the crystals formed by either of the pure compounds. The cocrystal results from an energetic compromise wherein the changing solution composition is accommodated by formation of a phase that is of intermediate stability to either pure form. Solution ratios of ortho:meta of 80:1 (odd isomers) and 60:1 (even isomers) were required in order for the ortho monolayer to adsorb. Therefore, the meta monolayers are between 2.2 and 2.5 kcal mol^{-1} more stable than those of the ortho isomers (Table 2).

Monitoring the competitive adsorption between the para and meta isomers was more difficult than for the ortho/para and ortho/meta mixtures due to the similarity in the two-dimensional crystal structures. Very high-resolution STM images were required to distinguish one phase from another based on the contrast difference between the columns, and random mixing was difficult to rule out due to the similarities in shape and conformation. High-resolution images obtained for 1:1 solutions (Supporting Information) confirmed that the para isomers are preferentially adsorbed and hence constitute the more stable monolayer. This is in agreement with the observation that it requires more ortho molecules to displace the para isomers than it does to displace meta isomers. Approximate values of the free energy difference between para and meta are obtained by subtracting the results obtained from the competition between para/ortho and ortho/meta. Thus, the two-dimensional crystals of the meta isomers are less stable than those of the para isomers by no more than 0.5 kcal mol^{-1} (Table 2).

Overall, the ortho isomers of both alkyl chain lengths formed the least stable two-dimensional crystals, and those formed by the para isomers were the most stable. It is well-known that molecules with larger molecular weights often displace smaller molecules,[25] and that molecules with stronger intermolecular interactions will adsorb preferentially to those without.[5] The differences in the free energies of adsorption for the various isomers are, therefore, particularly significant because of the identical molecular functionality and molecular weights. The origin of this behavior will be discussed below in the context of the bulk properties and two-dimensional structure.

Bulk Properties. The substitution geometries of disubstituted benzene isomers have been observed to affect melting points,

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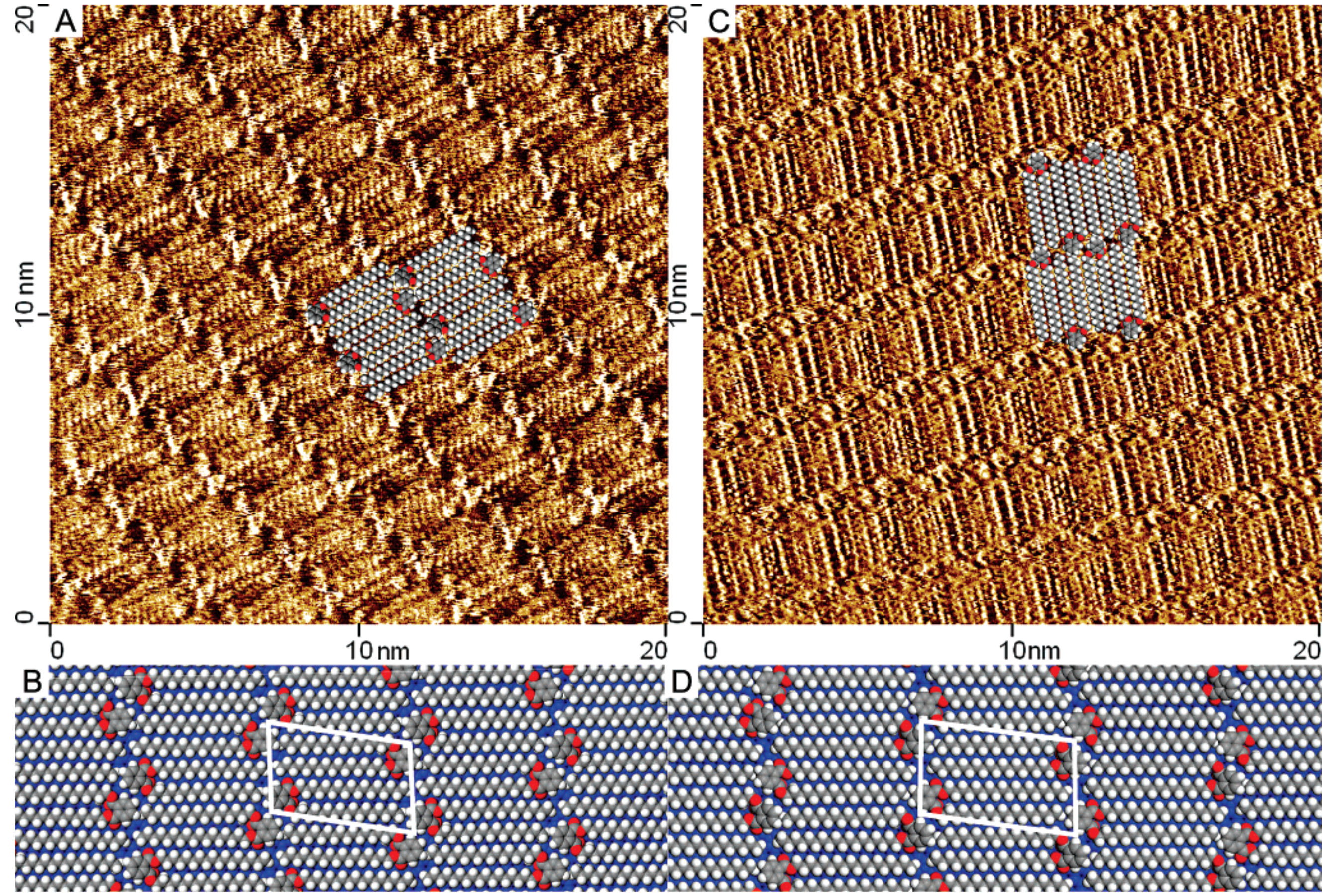

Figure 4. Two-dimensional crystals of the ortho isomers, **17-*ortho*** (A,B) and **18-*ortho*** (C,D). (A,C) STM images with overlaid molecular models and (B,D) computed packing patterns with unit cell. The packing motifs adopted by the ortho compounds are very different than those of the meta and para isomers, with increased intramolecular contact and decreased contact between the molecules in the monolayer and partial desorption from the graphite surface.

Table 2. Calculated Free Energy of Adsorption Differences between the Two-Dimensional Crystals of Different Isomers

		differences in the free energy of adsorption (kcal mol^{-1})	
more stable isomer	less stable isomer	odd isomers	even isomers
para	ortho	2.7 ± 0.1	2.5 ± 0.1
meta	ortho	2.5 ± 0.1	2.2 ± 0.3
para	meta	~0.2	~0.3

melting enthalpies, melting entropies, and solubilities.[6−8,26−30] For the general class, the para isomers have the highest melting points, greatest enthalpies of melting, smallest entropies of melting, and lowest solubilities compared to the ortho and meta isomers, all suggesting that the para isomers have the lowest free energy of crystallization and therefore form more stable crystals. This behavior is attributed to both the smaller difference in entropy between a symmetric molecule in the solid and liquid states, which is indicated by the entropy of melting,[8,29] and greater crystal cohesion for more symmetric molecules, indicated by the enthalpy of melting.[28] These factors affect both the melting points and the solubilities.[8,30] While the relationship between meta and ortho isomers is variable, depending on the chemical composition,[6] examination of the melting points of the short-chain phthalate esters (Supporting Information) reveals that for these compounds, para has the highest melting point, and ortho generally has the lowest, although the melting points of the ortho and meta isomers become similar as the alkyl chain length increases.

Table 3. Solubilities, Melting Points, Heats of Melting (ΔH_m), and Entropies of Melting (ΔS_m) for Both the Odd and Even Isomers[a]

	solubility in phenyloctane (mg mL^{-1})	onset temperature of the melting curve (°C)[b]	ΔH_m (kcal mol^{-1})	ΔS_m (kcal mol^{-1} K^{-1})
17-*ortho*	160 (20)	50.1	22.2	0.072
17-*meta* (form I)	87 (3)	54.0	24.3	0.074
17-*para*	5.8 (8)	76.9	27.9	0.080
order for odd isomers	$o > m > p$	$o < m < p$	$o < m < p$	$o < m < p$
18-*ortho*	122 (6)	54.2	23.4	0.071
18-*meta*	60 (15)	54.5	31.3	0.096
18-*para*	2.4 (4)	85.5	33.2	0.089
order for even isomers	$o > m > p$	$o \approx m < p$	$o < m < p$	$o < p < m$

[a] The orders of solubility, melting points, and heats of melting are in accordance with the trends for shorter-chain dialkyl phthalate isomers, whereas the entropies of melting exhibit no consistent trend. [b] Measured by DSC at 10 °C min^{-1}

The melting points, melting enthalpies, melting entropies, and solubilities of the even and odd isomers (Table 3) were compared to determine if they conform to the established trends. For these properties, the relationships among the various isomers were similar to the shorter chain analogues. Among the even

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isomers, the **18-*para*** crystal was most stable, having the lowest solubility, highest melting point, and greatest enthalpy of melting, as anticipated from the behavior of this general class. The solubilities and enthalpies of melting indicated that **18-*ortho*** was the least stable, but the melting points of **18-*ortho*** and **18-*meta*** were essentially identical. In the odd isomer series, **17-*meta*** exists in two different bulk crystalline forms. Because it is the more stable polymorph, the properties of form I were compared to those of the other isomers.[31] The solubilities, melting points, and melting enthalpies followed the trend expected from the melting points of the small molecules and the even isomers: **17-*para*** had the lowest solubility, the highest melting point, and the greatest melting enthalpy, while the **17-*ortho*** properties were the reverse. For both the odd and even isomers, the bulk properties of these isomers indicate that the para isomers form the most stable crystals and the ortho isomers form the least stable crystals.

As stated above, the melting point trend of the disubstituted benzene isomers has been related to the effect of molecular symmetry on the entropy in the solid and liquid states,[8,29] and greater crystal cohesion for more symmetric molecules.[28] From the data gathered in this case, however, the entropy does not contribute to the trend in three-dimensional crystal stability. Generally, it is reported that the most symmetric isomer has the smallest change in entropy upon melting, but that is not the case here. Instead, entropy of melting was lowest for the ortho isomers. This small entropy change in the ortho isomers may be due to intramolecular contact of the alkyl chains in both the bulk and in solution, which would minimize the conformational entropy change between the solid and liquid, the increase of which is a contributing factor to the behavior of other isomer sets. This smaller entropy difference would also explain the decrease in the melting point difference between ortho and meta isomers as the alkyl chain length increases.

Comparison between Two- and Three-Dimensional Crystalline Properties. The possibility of using bulk crystal properties to predict adsorption behavior of the isomeric dialkyl phthalates investigated can be assessed on the basis of the relative stabilities of two- and three-dimensional crystals determined here. The general stability trend for these isomers, wherein para compounds form the most stable crystals and ortho compounds form the least stable crystals, is retained during surface adsorption: para molecules are most strongly adsorbed while ortho molecules are least strongly adsorbed. Despite the persistence of this trend, the magnitudes of the two-dimensional crystal stability differences can only be interpreted by examination of the structural features of the monolayers, such as the contact area, molecular conformations, and densities of the monolayers. This is an important caveat when attempting to predict adsorption behavior. The small energy difference between the meta and para isomers on the surface, for example, would not have been predicted from their disparate properties in the bulk. The melting points and solubilities of the meta and ortho isomers are much closer to each other than to those of the para isomer. The two-dimensional crystalline structures of **17-*meta***, **18-*meta***, **17-*para***, and **18-*para*** in phase I were analogous; all consist of flat molecules with oppositely extended interdigitated all-*trans* alkyl chains. The molecular conformations, intermolecular interactions, and interactions with the surface are quite similar for both isomers. This is not the case with the bulk structures. Powder X-ray diffraction data indicate that among a set of isomers, none of the three-dimensional crystal structures is isomorphous. The failure of bulk properties to predict the adsorption strengths can be attributed to the lack of structural similarity between the meta and para isomers in the bulk. This underscores the necessity of studying two-dimensional structural properties and developing the means to predict and control this packing. In comparison to the meta and para isomer packing motifs, the two-dimensional crystal structures of the ortho isomers exhibit several features that make them much less stable than both the meta and para crystals. The ortho isomer has conformational barriers to lying flat on the surface, resulting in a hairpin conformation where the benzene ring is partially desorbed. Thus, the interaction with the substrate is not as stabilizing for the ortho monolayers as it is with the other isomers. The contact area with the surface is decreased, and the possible $\pi\cdots\pi$ interactions between the benzene ring and the graphite are attenuated. The two-dimensional structures generated by the ortho isomers are also less stable because a molecular conformation is adopted that is strained relative to the energy-minimized gas-phase conformation and because intermolecular contacts are greatly reduced due to the hairpin conformation.[32] Taking this two-dimensional structural information into account, the small difference in the stabilities of the monolayers of para and meta isomers and the great reduction in stability of the ortho isomers monolayers can be rationalized.

Three-dimensional crystal properties can now be compared with the relative adsorption strengths for two different systems, the phthalate isomers and the previously reported series of dicarbamates.[5,33] In the dicarbamate system, the order of stability of the two-dimensional crystals parallels the orders of the melting points and the enthalpies of melting, but unlike in the dialkyl phthalate isomer system, the solubilities are not related to the monolayer stabilities. No single bulk property could reliably predict the magnitudes of the adsorption strengths in both systems. The universality of any parallels between two- and three-dimensional crystal stabilities is dubious and will likely depend more on structural similarities between the packing patterns in both systems.

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(31) Two polymorphs of **17-*meta*** were discovered: form II was obtained from recrystallization from methyl ethyl ketone, and cooling from the melt of form II produced form I. The relative stabilities were determined by allowing saturated solutions of the two polymorphs of **17-*meta*** in phenyloctane to equilibrate. These solutions were filtered, and the precipitates were compared by optical microscopy and powder X-ray diffraction, which indicated that both solids were form I. The same process was monitored in acetone using optical microscopy. The transformation of form II to form I indicates that form I is the more stable polymorph of **17-*meta***.

(32) See ref 5 and (a) Eichhorst-Gerner, K.; Stabel, A.; Moessner, G.; Declerq, D.; Valiyaveettil, S.; Enkelmann, V.; Müllen, K.; Rabe, J. P. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1492−1495. (b) Mena-Osteritz, E. *Adv. Mater.* **2002**, *14*, 609−616. (c) Mu, Z.-C.; Kong, J.-F.; Wang, Y.; Ye, L.; Yang, G.-D.; Zhang, X. *ChemPhysChem* **2004**, *5*, 202−208. (d) Constable, E. C.; Guntherodt, H. J.; Housecroft, C. E.; Merz, L.; Neuburger, M.; Schaffner, S.; Tao, Y. Q. *New J. Chem.* **2006**, *30*, 1470−1479 for comparisons of the two- and three-dimensional crystal packing of various compounds.

(33) The solubilities and enthalpies of melting for dicarbamates were compared to the previously reported relative adsorption strengths and melting points. 1,12-Diyl-bis(octylcarbamate)dodecane, (mp = 111 °C, ΔH_m = 22.5 kcal mol^{-1}, solubility = 0.3(1) mg mL^{-1}) was the most strongly adsorbed dicarbamate, forming a two-dimensional crystal 0.16(3) kcal mol^{-1} more stable than that formed by 1,8-diyl-bis(octylcarbamate)octane (mp = 109 °C, ΔH_m = 17.9 kcal mol^{-1}, solubility = 1.1(1) mg mL^{-1}) and 0.21(3) kcal mol^{-1} more stable than that formed by 1,10-diyl-bis(octylcarbamate)-decane (mp = 98 °C, ΔH_m = 11.9 kcal mol^{-1}, solubility = 0.9(1) mg mL^{-1}).

Conclusion

The substitution position of isomeric dialkyl phthalates affected the structure and stabilities of the two-dimensional crystals formed at the liquid–solid interface, as well as the bulk solubility and melting temperature, enthalpy, and entropy. The stability ordering of isomeric dialkyl phthalate crystals is the same in two- and three-dimensions, indicating that similar factors may be influencing crystal stabilities. Isomers with higher melting points and enthalpies of melting and lower solubilities formed more strongly adsorbed monolayers. However, detailed knowledge of the packing structure at the liquid/solid interface and examination of the structural features that affect stability was requisite for interpreting the magnitudes of the stability differences. Only through comparison of the intermolecular interactions, the interaction with the surface, and the density of packing could the nearly equivalent adsorption strengths of the para and meta isomers and the much lower adsorption strengths of the ortho isomers be rationalized; none of the bulk thermodynamic properties suggested this result. Thus, the properties of two-dimensional crystals are specifically dependent on monolayer structure, and a general extrapolation of bulk properties to these systems is not valid, making adsorption strength prediction from bulk properties inadvisable. While these findings make apparent a disconnect between two- and three-dimensional properties of the same compounds, they provide a unified context for understanding crystallization phenomena based on structural analysis. The broad applicability of this paradigm can be seen in the aspects of molecular structure, in addition to the molecular weight and functionality, that affect adsorption strengths revealed here, which must be employed to predict selective removal from solution, a ubiquitous purification technique.

Experimental Methods

Competitive Adsorption. For the competitive adsorption experiments, solutions in phenyloctane containing two solutes of the same alkyl chain length were prepared. For each set of compounds, the ratios of the solutes were varied, while the total concentration was held constant. Table S1 (Supporting Information) contains all of the ratios of ortho:meta and ortho:para examined and the identity of the resulting monolayer. The total concentration was 20.0 mg/mL in phenyloctane for the ortho/meta comparisons, 1.0 mg/mL for the meta/para comparisons, 1.0 mg/mL for **18-*ortho***/**18-*para***, and 5.0 mg/mL for **17-*ortho***/**17-*para***. Different concentrations were used, depending upon the pair of isomers examined to ensure that monolayers of each compound would be observable in the absence of the other component.

Differential Scanning Calorimetry. Thermograms of all samples were measured on a TA Instruments DSC Q10 with Universal Analysis 2000 software (version 4.0C). Samples were weighed to the nearest microgram and enclosed in a hermetically sealed aluminum pan (TA Instruments). Thermal behavior of the samples was studied under a nitrogen purge at a rate of 10 °C min^{-1} while heating in the range of 30–120 °C. The melting temperature was obtained from the peak of these curves, and the enthalpy of melting was derived from the peak area. Entropies of melting were calculated by dividing the enthalpies of melting by the peak temperature of the melting curve. Melting entropy calculations assume that the free energy difference is zero when the liquid and solid are in equilibrium, and the melting peak is the best estimate of the temperature at which this equilibrium occurs.

Solubility. Saturated solutions in phenyloctane containing two isomers of the same alkyl chain length were allowed to sit for several weeks to ensure equilibrium. These solutions were then filtered, and 15.0 μL was combined with 15.0 μL of a 1,2,4,5-tetramethylbenzene solution in phenyloctane (9.00 mg/mL). The proton NMR spectra of these solutions diluted in $CDCl_3$ were obtained using a 400 MHz spectrometer. The relative solubilities were confirmed by comparing the areas of peaks due to the aromatic hydrogens, and the absolute solubilities were measured with respect to the internal standard, correcting for the different number of protons contributing to each peak. The solubility of the para isomers were sufficiently low that detection by NMR was difficult; thus, the volume of phenyloctane required to dissolve a known mass of material was measured instead to obtain the solubility.

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Supporting Information Available: Synthesis and characterization of compounds, experimental details, STM image of the two-dimensional crystal of **18-*para*** in phase II, table of the solution ratios examined by STM and the identity of the resulting monolayers, STM images of 1:1 meta:para solution mixtures, melting points of various alkyl phthalate esters, table of the bulk properties of the less stable polymorph of **17-*meta***, DSC curves of **17-*meta*** polymorphs, and DSC curves of all reported compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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