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Inequivalent Molecules in a Two-Dimensional Crystal

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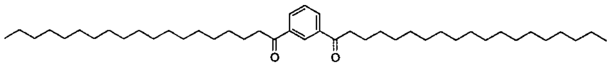
Received May 3, 2002

The prediction and design of crystal structures of organic compounds is one of the greatest outstanding scientific challenges. The fact that crystal packing is often governed by nondirectional weak forces, and that such a myriad of possible arrangements in three dimensions can be conceived, hampers efforts at prediction.[1,2] One of the most promising platforms for studying the crystallization problem is physisorbed monolayers spontaneously self-assembled at the solution−solid interface. These organized assemblies can be regarded as two-dimensional (2D) crystals in that they have periodic structure and, as in the case of three-dimensional (3D) crystals, their structure is often determined by weak forces. Hundreds of physisorbed monolayers have been characterized by scanning tunneling microscopy (STM) to elucidate their 2D packing including functionalized *n*-alkanes,[3−5] phthalocyanines,[6,7] liquid crystals,[8−10] conducting oligomers,[11] and polymers.[12,13] The advantage of studying the structure of physisorbed monolayers is that, by using STM, one can achieve submolecular resolution with nonspace averaged molecular information leading to a detailed understanding of both periodic and nonperiodic (i.e., domains and defects) packing.

Although packing motifs[14] and reactivity[15,16] have been observed to be similar in 2D and in 3D crystals,[14,17] the analogy is not perfect. For example, the unit cells of ordered monolayers have been observed to contain one or fewer unique molecules ($Z' \leq 1$).[18] By contrast, 3D crystals often display multiple inequivalent molecules in the unit cell ($Z' > 1$). In fact the incidence of $Z' > 1$ is 13% in the Cambridge Structural Database (CSD) for organic crystals.[19,20] We report herein the structure of a self-assembled monolayer of an aromatic diketone which demonstrates that multiple inequivalent molecules are also possible in 2D packing. This is the first example, to our knowledge, of a physisorbed monolayer of this type with more than one inequivalent molecule in the asymmetric unit, and this observation serves as an important bridge between two- and three-dimensional crystallization.



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Compound **1**, 1,3-dinonadecanoylbenzene, spontaneously forms a self-assembled monolayer at the solution−solid interface by placing a drop of a nearly saturated solution in phenyl octane onto a freshly cleaved highly oriented pyrolytic graphite (HOPG) surface. Imaging of this monolayer is achieved with the STM tip submerged in a liquid droplet under ambient conditions. Figure 1 shows submolecularly resolved STM images of the monolayer of **1** acquired during two separate imaging sessions.

The monolayer of **1** (Figure 1) features lines of large bright spots designated columns A and B, and smaller spots arranged in rows

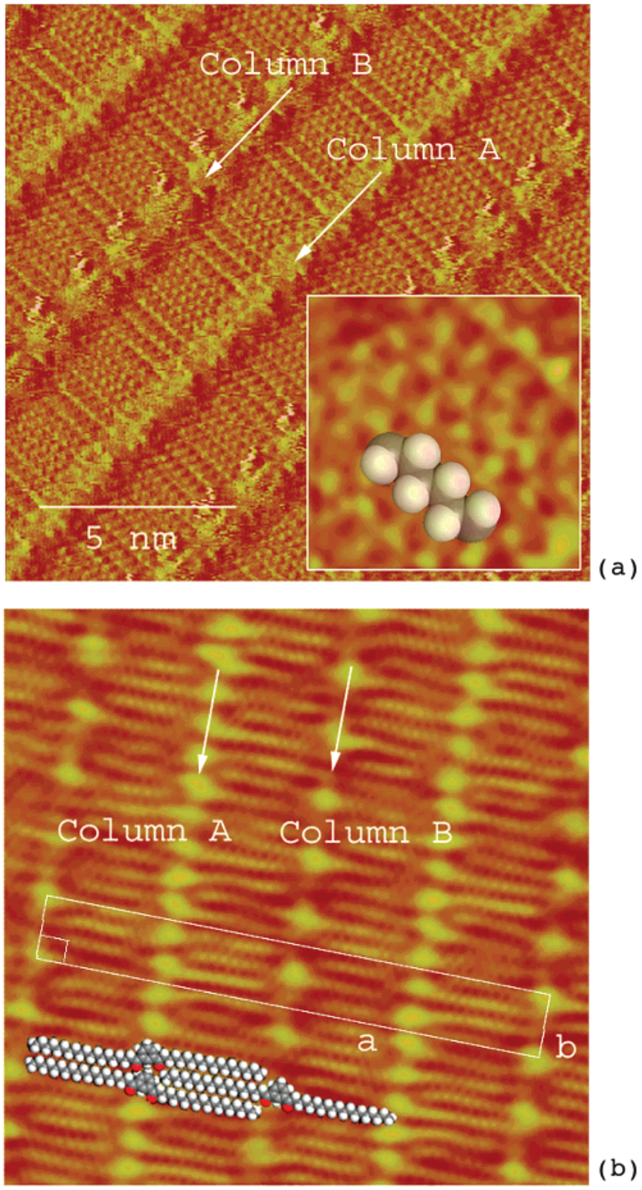

Figure 1. STM images (15×15 nm^2) of a monolayer of **1**. Images were obtained under constant current conditions. Both images were obtained with current = 300 pA and bias = 800 mV (sample positive). (a) Close packing of alkyl chains on HOPG surface. (Inset) Magnified and filtered image of the alkyl chains of the monolayer with a spacefilling model overlaid. This zigzag spot pattern confirms horizontal configuration of alkyl backbone relative to the HOPG surface. (b) Connectivity between each alkyl chain and each aromatic group as well as the number of molecules in a given unit cell. The white box drawn in b represents one unit cell containing six molecules. Overlaid on b is a molecular model of **1**.

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10.1021/ja026786d CCC: $22.00 © 2002 American Chemical Society

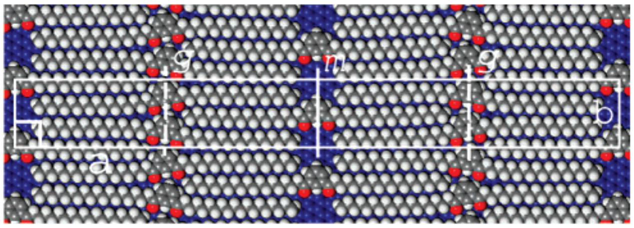

Figure 2. Molecular model of the monolayer of **1** on HOPG generated by Cerius^2 with the COMPASS force field. The white box drawn on this model shows a 2D unit cell containing six molecules. The mirror plane and a glide plane are designated as m and g. The computed unit cell parameters are $a = 123.5$ Å and $b = 14.0$ Å which show reasonable agreement with the measured unit cell parameters of $a = 128.1 \pm 1.0$ Å and $b = 14.3 \pm 0.3$ Å.

connecting these columns. Because aromatic rings appear bright in the STM image relative to alkyl chains,[21,22] the large bright spots in columns A and B can be assigned to the aromatic core of this molecule. Accordingly, the small spots filling up the space between aromatic cores are ascribed to hydrogens attached to alkyl chains.[5] Close inspection of Figure 1a clearly shows that the molecules are lying flat on the surface with their alkyl backbones parallel to the HOPG surface. This “horizontal” configuration of the alkyl chains is confirmed by the zigzag pattern of small bright spots originating from hydrogen atoms attached to the carbon backbone.[3,23] This pattern is more easily identified in the zoomed and filtered image inset in Figure 1a. Connectivity between each alkyl chain and each aromatic core is not clear from Figure 1a. However, that information is easily obtained from the image in Figure 1b where individual molecules are clearly visible. Another feature of this image is the difference between the orientation of the aromatic groups in column A and column B. The aromatic cores in column B appear as ovals with their long axis parallel to the alkyl chain direction of **1**. However, the aromatic cores in column A have their long axis tilted from alkyl chain direction, and the tilt angle alternates along the column. In Figure 1b a proposed arrangement of three molecules of **1** is overlaid corresponding to their position in the monolayer. This model is extracted from the computed molecular model proposed in Figure 2. Figure 1b also shows that the number of aromatic cores in each column of large bright spots are not the same. Column A has twice the number of large bright spots compared to column B, indicating that there are twice as many molecules in column A as in column B.

The above analysis of STM images provides the 2D crystal structure of this molecule and, accordingly, its unit cell. The white box in Figure 1b shows the unit cell of this monolayer containing six molecules. The unit cell has a mirror plane and a glide plane along the column direction uniquely determining the 2D space group to be *cm*. Thus, this monolayer has a unit cell with 1.5 inequivalent molecules ($Z' = 1.5$). A molecular model based on the STM images of **1** is presented in Figure 2. This model represents an energy-minimized ensemble of **1** (45 molecules) on a single sheet of graphite predicted by molecular mechanics.[24]

Consistent with the experimental images, this model has twice the number of molecules in column A as in column B and shows the horizontal configuration of the alkyl backbones relative to the HOPG surface. The coplanarity of the ketones with the aromatic ring is also found for 1,3-diacetyl benzene at the B3LYP/6-31G** level. Column A of this model has the aromatic cores tilted away from the alkyl chain direction in an alternating fashion as in Figure 1b. The unit cell drawn on this model contains six molecules and has a mirror plane and a glide plane as shown.

In summary, a monolayer of **1** adopts a novel packing arrangement with more than one molecule in its 2D asymmetric unit. Thus, this monolayer can serve as a platform to test theories on the factors leading $Z' > 1$. The question of why this phenomenon is so much more prevalent in 3D crystallization will be explored through the synthesis and imaging of other 1,3-disubstituted aromatic compounds. In addition we are continuing our effort to grow suitable crystals to determine if a similar motif is present in the single-crystal structure of **1**.

Acknowledgment. This work was supported by the University of Michigan and a 3M Non-Tenured Faculty Grant. K.K. thanks the College of Engineering for a Dean’s Fellowship.

Supporting Information Available: Experimental details of synthesis of compound **1** and STM imaging (PDF). This material is available free of charge via the Internet at http://pubs.acs.org

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(24) The monolayer of **1** was generated and minimized under periodic boundary conditions, and a nonperiodic superstructure made of 45 molecules of **1** was minimized over a slab of graphite with Cerius^2 using the COMPASS force field from Accelrys Inc.

JA026786D