

Self-Assembly of Benzene–Dicarboxylic Acid Isomers at the Liquid Solid Interface: Steric Aspects of Hydrogen Bonding

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We compare the self-assembly of the various isomers of benzene–dicarboxylic acids at the interface between solution and graphite substrate. In the case of planar benzene–dicarboxylic acids it was possible to observe long-range ordered monolayers by STM. However, no ordered adsorption was observed for the nonplanar 1,2-benzene–dicarboxylic acid. By means of a control experiment with 1,2,4,5-benzene-tetracarboxylic acid, it was possible to demonstrate that the nonplanar structure is not the decisive reason for the absence of self-assembly. In fact, the direct neighborhood of the two carboxylic groups in 1,2-benzene–dicarboxylic acid does not allow for extended hydrogen-bound aggregations. Thus, the stabilization due to intermolecular hydrogen bonding is too weak for STM investigations, at least at room temperature. It has been shown that a periodic, infinitely extendable hydrogen-bonding scheme is a requirement.

Introduction

Spontaneous molecular self-assembly on surfaces is believed to be an appropriate approach for the efficient preparation of long-range ordered highly uniform molecular films, creating possibly important novel materials for sensing, catalysis, and molecular electronics. To deliberately design molecular architectures a fundamental knowledge of intermolecular interactions and their interplay with adsorbate–substrate interactions is highly desirable. Although the principal interactions are well understood, it is still challenging to predict the two- or three-dimensional structure of a molecular crystal just from the knowledge of the building block. Therefore, a combination of STM measurements and subsequent molecular mechanics is helpful for a comprehensive investigation of self-assembled molecular structures.^{1,2}

Both in the nature and in the design of supramolecular architectures, the selectivity and directivity of hydrogen bonds is an important aspect concerning molecular self-assembly.^{3–8} For many noncovalently bound molecular architectures hydrogen bonds are the strongest, hence the most important interaction, which in some cases governs the molecular ordering.^{9–11} Among hydrogen bonds the bond between two carboxylic groups can be classified as intermediately strong,¹² and a bonding angle of 180° is ideal.

For two-dimensional supramolecular architectures, STM is shown to be an ideal tool to investigate the crystallographic and electronic properties of molecular monolayers in real space.¹³ Moreover, the tunneling microscope's unique capability to manipulate single molecules can be applied to intentionally alter the adsorbate arrangement in a defined manner.^{14–16} A further major advantage of STM is its applicability to different environments. It is also particularly valuable for gaining insight

into equilibrium adsorption structures at the liquid–solid interface.^{17–20}

In this paper, the self-assembly of various isomers of benzene–dicarboxylic acids at a graphite surface is compared. It will be demonstrated that the relative positions of the two carboxylic groups at the benzene core determine whether long-range ordered structures can be observed.

Experimental Section

A home-built, low-current, pocket-size STM equipped with a commercial RHK STM-100 control system was used for the studies at the liquid–solid interface under ambient conditions. For sample preparation a small droplet of solution of the benzene–dicarboxylic acids was placed on the basal plane of freshly cleaved HOPG. A suitable solvent is heptanoic acid, which is an electrically nonconductive liquid with a room-temperature vapor pressure low enough to allow for STM experiments in the order of 1 h. By choosing a solvent with the same functional group as the solute, the benzene–dicarboxylic acid solubility apparently becomes sufficiently large to provide enough molecules for the self-assembly of closed monolayers. Best imaging results were obtained with mechanically cut PtIr tips, which were conditioned by short voltage pulses. Tunneling voltages between +0.3 V and +1.5 V with respect to the tip and reference currents around 0.1 nA were used. All STM images shown were recorded in the constant current mode of operation. For noise reduction the represented STM images were processed by leveling and application of a 3 × 3 G filter.

Results and Discussion

Terephthalic acid, isophthalic acid, and phthalic acid are the three possible isomers of benzene–dicarboxylic acid (C₈H₆O₄). Their molecular structures are shown in Figures 1a–c. Terephthalic and isophthalic acid are planar molecules, whereas phthalic acid is not. The close proximity of the two carboxylic groups leads to steric hindering and results in a tilt of the

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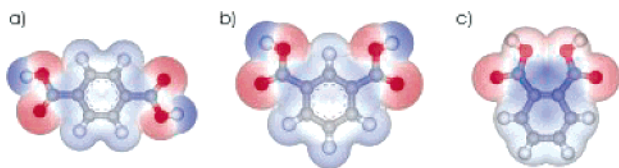


Figure 1. Molecular structures of (a) terephthalic acid (1,4-benzene–dicarboxylic acid), (b) isophthalic acid (1,3-benzene–dicarboxylic acid), and (c) phthalic acid (1,2-benzene–dicarboxylic acid); the surface is given by the van der Waals radii of the atoms.

carboxylic groups out of the plane of the benzene core. Because of its nonplanar structure, the interaction between phthalic acid and the substrate is expected to be reduced compared to terephthalic and isophthalic acid.

For terephthalic and isophthalic acid it was possible to routinely observe ordered monolayers, whereas for phthalic acid no indications of adsorption were noticed. The first two molecules were found to adsorb with their molecular plane parallel to the substrate. This adsorption geometry is well known from planar molecules with an aromatic system on various substrates^{21–23} and is consistent with the apparent size and shape of the molecules in the STM topographs. To obtain the crystallographic relation between adsorbate and substrate for terephthalic acid and isophthalic acid, respectively, both lattices were recorded within one frame. In the first half of the image the adsorbate layer was imaged with at least molecular resolution. In the second half, graphite was atomically resolved by applying appropriate tunneling parameters. By using the substrate lattice as an intrinsic ruler, the measured adsorbate lattice parameters are not falsified by drift and do not depend on the calibration of the scanner.

In the case of terephthalic acid a commensurate superstructure was deduced within the experimental error of ± 0.2 :

$$\begin{pmatrix} \vec{A} \\ \vec{B} \end{pmatrix} = \begin{pmatrix} 3 & 0 \\ 3 & 4 \end{pmatrix} \begin{pmatrix} \vec{a} \\ \vec{b} \end{pmatrix}$$

These values suggest a commensurate unit cell. However, the thorough theoretical study of Mannsfeld and Fritz²⁴ on finite adsorbate islands showed that point-on-line structures (i.e., the adsorbate vectors end on primitive lines of the substrate) are also a very common epitaxial relation for weak interacting substrates.

For the superstructure matrix the lattice of the graphite B-atoms, as visible in the STM, was used as a base. This result was obtained by means of Figure 2a, which shows both the adsorbate and substrate lattice. Figure 2b was scanned with constant tunneling parameters and depicts a densely packed terephthalic acid monolayer. Since all molecules in the STM images appear with similar height, orientation, and shape, the assumption of one molecule per primitive unit cell is justified. The experimentally determined adsorbate unit cell was used as a constraint for molecular mechanics simulations using a Dreiding II force field,²⁵ which includes a specific term for hydrogen bonding and applying periodic boundary conditions to determine the orientation of the molecules. The graphite substrate was simulated using two graphene sheets, the lower one being fixed. Although the experimental accuracy is not sufficient to unambiguously prove commensurability of the unit cell, a reasonably rapid convergence was achieved in the molecular mechanics calculations, and the layer remained planar. Slight variations in the matrix elements led to small changes of the total energy on the order of a few percent, but the orientation of the molecules within the unit cell was unaffected. Since substrate effects, for example, mirror charges in the semimetal

graphite, are not taken into account, it is difficult to specify absolute values for the binding energy. Although a clear discrimination between true commensurability or point-on-line coincidence cannot be given, the results of the simulation are in good agreement with the experimental data and well reproduce the orientation of the molecules. A model of the energy-minimized structure is depicted in Figure 3a. As anticipated, the molecules are arranged in one-dimensional hydrogen-bound straight chains. In this configuration, all hydrogen bonds are saturated under an ideal bonding angle of 180° . These chains interact via van der Waals attraction, resulting in a densely packed two-dimensional structure.

The same combination of STM calibration and subsequent molecular-mechanics simulation was also applied to the isophthalic acid monolayer. A STM topograph and the corresponding energy-minimized structure are shown in Figure 4 and Figure 3b, respectively. The superstructure matrix is given by

$$\begin{pmatrix} \vec{A} \\ \vec{B} \end{pmatrix} = \begin{pmatrix} 8 & 3 \\ 2 & 4 \end{pmatrix} \begin{pmatrix} \vec{a} \\ \vec{b} \end{pmatrix}$$

The same experimental errors and considerations for molecular-mechanics simulation apply respectively in this case. Again, the molecules are organized in chainlike configurations. In contrast to terephthalic acid these chains are not straight, but run along zigzag lines with angles of 108° . This angle is mainly caused by the molecular structure, but significantly deviates from the ideal bonding angle of 120° given by the 1,3 positions of the carboxylic groups. The physical reason for this deviation is the complex interplay of interactions between the chains and with the graphite substrate. It is noteworthy that both the stabilization due to van der Waals attraction among the chains and the interaction with the graphite substrate are necessary to stabilize the isophthalic acid monolayers. Molecular mechanics simulations of unsupported monolayers result in a buckling of the molecules out of plane in contradiction to the experimental observation, thereby proving the stabilizing influence of the substrate. On the other hand, unsupported, two-dimensional hydrogen-bound trimesic acid (1,3,5-benzene-tricarboxylic acid) networks remain planar in molecular-mechanics simulations. Likewise, a single zigzag chain of isophthalic acid, adsorbed on a graphine sheet, is not stable according to simple force-field simulations. In the STM topograph reproduced in Figure 4, two types of molecules with different contrast are evident. In accordance with molecular mechanics, the primitive unit cell is comprised of two molecules differing in their azimuthal orientation and adsorption site. Equivalent molecules are aligned along rows.

In contrast to these two isomers, and despite many attempts, it was not possible to image ordered structures of phthalic acid at the liquid–solid interface by STM. Although all tips were checked for their capability to image the graphite substrate with atomic resolution before and after the solution was applied, there was no evidence of phthalic acid adsorption, even though very small reference currents were applied. To provide further evidence that neither tip nor device performance was responsible, trimesic acid solution was added to the liquid phase comprised of phthalic acid in heptanoic acid solution. After doing so, ordered structures of trimesic acid were observed with the same tip without any need for additional tip treatment, proving that both the tip and the STM were capable of resolving ordered adsorbate structures. This experimental finding supports the prediction that no ordered structures of phthalic acid stable enough for STM investigations at room temperature evolve at the liquid–solid interface. It cannot be distinguished whether

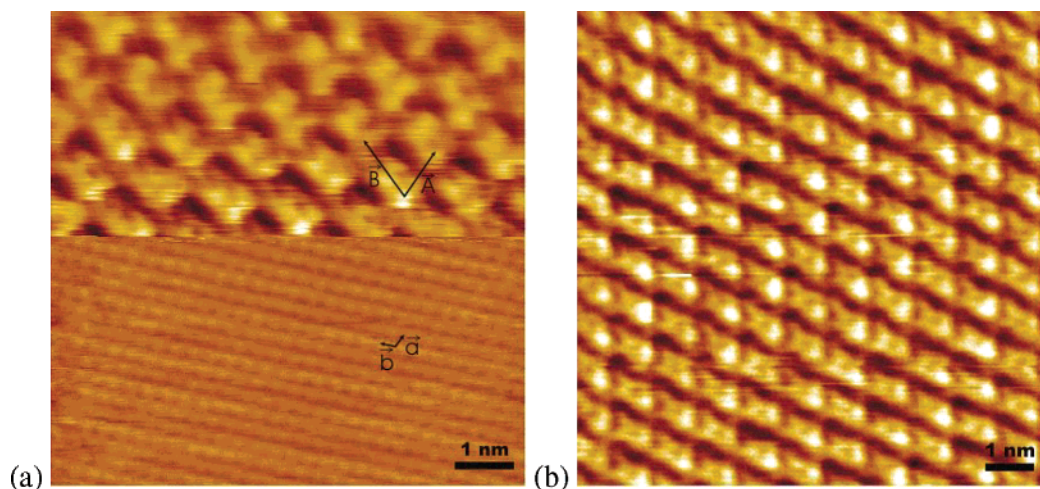


Figure 2. STM topographs of a terephthalic acid monolayer at HOPG(0001): (a) the lower half was scanned with tunneling parameters appropriate for the atomic resolution of graphite; from this image the relation between substrate and adsorbate lattice was deduced, (b) whole image scanned with parameters suitable for terephthalic acid; the monolayer is comprised of a dense packing of hydrogen-bound linear chains.

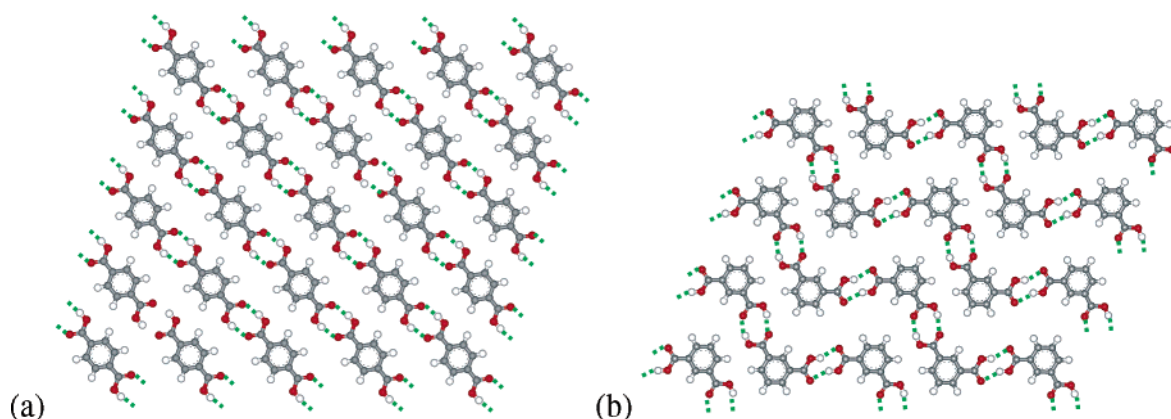


Figure 3. Molecular mechanics simulation of (a) terephthalic acid and (b) isophthalic acid monolayers on HOPG(0001), respectively. For clarity, the substrate atoms are not shown in these images, but were taken into account for the calculation. H-bonds are indicated by dashed lines. In both cases the commensurate superstructure matrix, as revealed by calibration of the STM data with the substrate, was used as a constraint. As expected, terephthalic acid arranges itself in linear chains with the molecules interconnected by hydrogen bonds between adjacent carboxylic groups. In contrast, isophthalic acid arranges in hydrogen-bound zigzag chains under an angle of 108° . This deviation from the ideal angle of 120° is caused by interactions of the chains with their neighbors and the substrate.

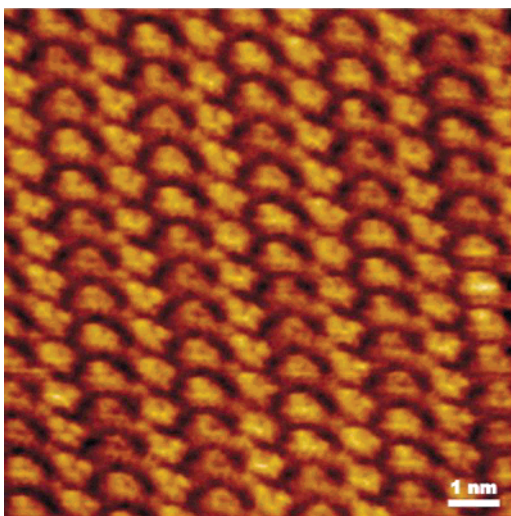


Figure 4. STM topograph of isophthalic acid monolayers on HOPG; the zigzag arrangement of hydrogen bound molecules is visible.

no ordered layer adsorbs or if the interface is not sufficiently stable for STM. Nevertheless, it can be stated that the adsorption energy of phthalic acid would be substantially lower than for

the other two isomers, in the case of an adsorption from the liquid phase.

What is the physical reason for this considerably lower stabilization energy? An important difference is the nonplanar structure of phthalic acid, hence reducing the interaction of the benzene core with the graphite. This nonplanar structure can already be revealed by simple molecular mechanical simulations of isolated molecules, with more sophisticated methods such as DFT leading to qualitatively similar results.

To check whether the nonplanar structure is responsible for the experimental observation, a control experiment was performed with pyromellitic acid (1,2,4,5-benzene-tetracarboxylic acid). This molecule contains two pairs of adjacent carboxylic groups that sterically hinder each other in a way similar to those of phthalic acid. Likewise, this molecule is nonplanar, but in contrast it was possible to observe self-assembled monolayers with heptanoic acid solutions (to be published elsewhere). Thus, it can be stated that the nonplanar structure is not the main reason for the lack of STM results on self-assembly of phthalic acid. In principle, when looking at the order structures of terephthalic and isophthalic acid, the molecules build infinite, periodic straight and zigzag hydrogen-bound chains, respectively. Hence, a large number of molecules are interconnected via hydrogen bonds and stabilize each other. In contrast to

previously investigated two-dimensional hydrogen bound trimetric acid networks,⁹ the hydrogen-bond stabilization occurs only in one dimension. These agglomerations lead to molecular structures that are sufficiently stable for STM investigations. Because of the close proximity of the two carboxylic groups in phthalic acid, a comparable, infinitely extendable configuration is not conceivable. For steric reasons only two, or a maximum of three, molecules can be interconnected in a circular bonding scheme, thus saturating all the carboxylic groups of the molecules involved. Apparently, this agglomerate size is not large enough for either stable adsorption or imaging. Yet the experimental observation of close-packed, highly ordered pyromellitic acid monolayers can also be explained within that framework. The reason is that its molecular structure allows for periodic hydrogen-bound structures and the tilt of the carboxylic groups does not inhibit the intermolecular hydrogen bonding. Therefore, a larger number of hydrogen-bound molecules is stabilized, although the interaction with the substrate is not as pronounced as for planar molecules of similar size.

Summary and Conclusion

By comparison of the various isomers of benzene–dicarboxylic acids it was shown that intermolecular stabilization is important for the self-assembly process. If the molecular structure allows for periodic, hydrogen-bound arrangements it is possible to routinely observe stable monolayers. It has also been shown that using precise, that is, substrate calibrated, structural data from STM measurements as a constraint for subsequent molecular mechanics simulations is very effective for revealing molecular structures. Although in many cases the hydrogen bonding dominates the molecular ordering, there is also marked influence from other interactions among molecules and with the substrate. A further interesting aspect, also accessible by STM, is the anisotropy of the force needed to displace a single molecule within the layer due to the directivity of the H-bonds. Studies such as the one presented here may eventually contribute to a refinement of simulation methods as an important step toward designing supramolecular architectures on the drawing board.

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