Scanning Tunneling Microscopy of 1,5-Dioxyoctylanthracene

Ian Pilgrim, Matthew Pokrifchak

Dr. K. W. Hipp

Department of Chemistry & Materials Science Program, Washington State University, Pullman, WA

Introduction and Background

In order to fully recognize and utilize the practical potential of chemical compounds in applications in our macroscopic world, it is necessary to understand the behavior of such compounds at the sub-microscopic level. On the scale of atoms and molecules, particles no longer interact in the classical manners we are familiar with. Instead, they follow the laws of quantum mechanics, so we must probe materials at this scale using quantum mechanical phenomena. Scanning Tunneling Microscopy is a powerful tool with which we may obtain a clear understanding of the inter- and intra-molecular structure of a compound via the principle of quantum tunneling.

Purpose and Summary of Research

In this research, scanning tunneling microscopy was used to investigate the inter- and intra-molecular structures of 1,5-dioxyoctylanthracene (empirical formula C_{26}H_{18}O_2). Organic molecules such as this are of interest in the field of nanotechnology for their potential use as two-dimensional matrices upon which nanostructures may be self-assembled -- a scaffolding of sorts for the nanoscale world. In particular, such compounds could be the foundations for -- or in and of themselves act as -- such tools as photosensors, sensors, biocompatible interfaces, molecular severs, molecular electronics, and catalysis. We are thus concerned with the structures of the individual molecules and the spacing between molecules in a monolayer, as well as the solvents in which and the substrates upon which such monolayers may be formed.

In this research we determined that 1,5-dioxyoctylanthracene may be imaged with scanning tunneling microscopy in air using either dichloromethane or octane as a solvent, or in solution when n-octylbenzene is used as a solvent. In all cases, graphite serves as the substrate. In each solvent, molecules of 1,5-dioxyoctylanthracene assemble into rows with a spacing of approximately 17 to 18 angstroms between rows, and the carbon atoms in each molecule’s alkane chains seem to assume an alternating trans/gauche configuration as opposed to an all-trans configuration.

Sample Preparation

Solutions prepared using dichloromethane or octane as solvents were applied to freshly cleaved pieces of Highly Oriented Pyrolytic Graphite (HOPG) and immediately spun at high speed for several seconds, a process known as spin doping, so as to ensure even coverage on the graphite. Due to the relatively low vapor pressure of n-octylbenzene, we were able to scan samples made with this solvent through the solution itself. That is, 1.3 drops of the solution were applied to the surface of the graphite and the sample was imaged until visibly dry spots emerged on the graphite or the surface of the graphite no longer appeared smooth in the STM image, typically several hours after the initial application.

Tips and Substrates

1,5-Dioxyoctylanthracene was successfully imaged on a graphite substrate using both electrochemically etched and hand-cut platinum-iridium tips as well as electrochemically etched tungsten tips. All images presented here were produced using Pt(111) Tips -- electrochemically etched tips in images from dichloromethane and octane solutions, and cut tips in images from n-octylbenzene solutions. All scans were performed with the Digital Instruments STM (see Figure 7) and Digital Instruments NanoScope IV E SPM Controller. Attempts were also made to scan through a solution of 1,5-dioxyoctylanthracene on an Au(111) surface; however, molecules were never successfully imaged on this substrate, even when doubling the concentration of the solution that produced consistent images on graphite.

Experimental Procedures and Results

Conclusions

• 1,5-Dioxyoctylanthracene may be imaged with scanning tunneling microscopy as a solute in dichloromethane or octane forming a monolayer on graphite, as a solute in n-octylbenzene scanned in-situ on graphite.

• Owing to the lack of the steric template effect of adsorption which makes graphite an ideal substrate, gold does not permit the assembly of 1,5-dioxyoctylanthracene onto Au(111).

• 1,5-Dioxyoctylanthracene likely assumes an internal structure in which the carbon atoms in its octane chains form an all-trans configuration much better than that of the all-trans configuration (see Figures 3 and 4).

• The images obtained during this research provide a good understanding of the inter- and intra-molecular structures of 1,5-dioxyoctylanthracene.

Discussion

The images obtained during this research provide a good understanding of the inter- and intra-molecular structures of 1,5-dioxyoctylanthracene. Prior to this research, it was unknown whether this compound would self-assemble into monolayers, and if so, whether the individual molecules assumed a structure in which the octane chains assembled in an all-trans configuration. In Figure 1, where 1 is the molecule in which the carbon atoms in the chain are staggered and in an alternating trans/gauche configuration as in Figure 2, Given that the observed obtuse angle of the unit cell -- approximately 103.5° -- matches that of the ‘staggered’ configuration much better than that of the all-trans configuration (see Figures 3 and 4). It appears that the molecular structure represented in Figure 2 accurately describes the structure of 1,5-dioxyoctylanthracene.

In nano-structured thin film and other surface science experiments solution concentration plays a key role; however, in our research with 1,5-dioxyoctylanthracene, the substrate choice had an even greater effect. Our research demonstrated that graphite provides a superior substrate to Au(111) for this particular compound. Due to the similar spacing between the carbon atoms in the compound’s two long alkane chains, the graphite lattice and the lattice of the graphite substrate, the compound easily adsorbs onto the graphite’s surface -- a phenomenon known as the steric template effect of adsorption. In other words, the graphite lattice served as an ideal scaffolding for the adsorption of the alkane chains of the compound. In trials involving the gold substrate, however, no adsorption occurred since the spacing between gold atoms is more than twice that of graphite, and any adsorption of the molecule and gold would be as a result of relatively weak van der Waals forces.

Due to fruitful initial trials, undoubtedly due to the steric template effect of adsorption, graphite was chosen as the substrate used to obtain the STM images shown. As one studies these images an interesting point arises: holes in the 1,5-dioxyoctylanthracene monolayer are observed in the octane and dichloromethane spun doped samples, while in the in-situ (solution) image using n-octylbenzene no holes in the monolayer are observable. This point clearly demonstrates an advantage of in-situ versus dry adsorbed monolayers. While spin doped effectively produces a monolayer free of large numbers of excess molecules floating on top of the adsorbed layer, it also eliminates the source of extra compound molecules that can be fixed defects (holes) in the monolayer.

When scanning in-situ, excess molecules are free to adsorb from the solution and repair a defect caused by thermal drift, physical deformation from the STM tip, or another source if given enough time.

Acknowledgements

We would like to thank Dr. Martin Johnston of the School of Chemistry, Physics, and Earth Sciences, Flinders University, Adelaide, Australia, for providing our samples of 1,5-dioxyoctylanthracene. We would also like to thank Dr. K. W. Hipp and Dr. Ursula Mazur for their assistance in this research.

The REU work was supported through the National Science Foundation: Division of Materials Research REU site program under grant number 0453554 and by the Washington State University Center for Integrated Biotechnology.