SELF-ORGANIZATION OF HEXADECYL BORON ACID MOLECULES ON ATOMICALLY FLAT SURFACE OF GRAPHITE

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It has been shown that highly ordered monolayer films of hexadecyl boron acid CH_3–$(CH_2)_{15}$–$B(OH)_2$ can be obtained on the basal plane of highly oriented pyrolytic graphite by the deposition from a solution of the acid in n-tetradecane n-$C_{14}H_{30}$. Using the scanning tunneling microscopy, it has been found that the ordered monolayers have a lamella-like structure. In this structure, each lamella is composed of pairs (dimers) of molecules of the acid. The association of molecules in each pair is implemented through the interaction between $B(OH)_2$-groups. It has been also found that molecules of solvent n-$C_{14}H_{30}$, being at a temperature sufficiently higher than the surface crystallization temperature can be coadsorbed with molecules of the acid. The coadsorption is explained by the geometric factor due to a specific size of the dimers of hexadecyl boron acid.

1. Introduction

Superthin organic films deposited on the surface of a solid substrate are an object of intense experimental and theoretical studies [1-4]. The interest in organic films is explained by their wide use in modern molecular electronics [5–6], in particular, in optoelectronic [7–8] and memory [9] units, in the development of solar cells [10], organic light diodes and field transistors [11–12]. In addition, the ordered organic films are important model objects, whose study allows one to improve the idea of the processes of self-organization of more complicated biological molecules and polymers [13]. The physical characteristics of superthin organic films depend on the degree of their ordering and are determined to a significant extent by the monolayers closest to the substrate. Therefore, the enhanced attention is paid namely to the investigation of a structure and properties of the first monolayer.

A particular role in nanotechnologies of the future will be played by the phenomena of self-organization (self-assembling) of molecules on atomically flat surfaces [14]. The processes of molecular self-assembling are considered as one of the key technological stages in the production of the two-dimensional memory matrices of molecular integrated nanoschemes. It is foreseen that the role of separate elements (diodes, transistors, switches) in such nanoschemes will be played by isolated molecules or their small ensembles. The transition of microelectronics onto the molecular level becomes more real with the creation of the method of scanning tunneling microscopy (STM), which allows one to obtain the structural and spectroscopic information on the molecular and submolecular level in the direct space [15].

For the last decade, the adsorption of long-chain aliphatic compounds on atomically flat substrates such as graphite and Au(111) was most intensively studied with the help of STM [16, 17]. The enhanced attention to the adsorption of aliphatic compounds is caused by their importance for modern chemical technologies. In addition, the molecules with aliphatic chain

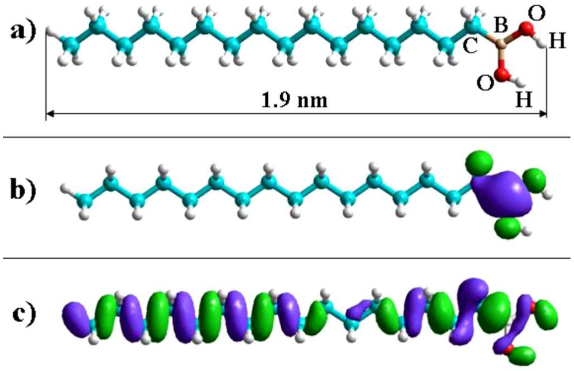

Fig. 1. (a) – Structure of a free neutral molecule of hexadecyl boron acid optimized by the density functional method. (b) and (c) – profiles of the first empty (LUMO+1) and filled (HOMO-1) molecular orbitals close to the Fermi level for a free neutral molecule of hexadecyl boron acid, which are calculated within the method DFT/B3LYP/6-31G*. The energies $E = 1.79$ eV (b) and $E = -8.01$ eV (c)

are convenient model objects, whose study allows one to better understand the general mechanisms of adsorption, especially those of adsorption of large molecules. The results of STM-observations of normal alkanes and their derivatives revealed that the packing structures for molecules of this class, kinetics of their adsorption, and STM-contrast are determined by the length of an alkyl chain, type of a functional group, and type of a substrate. Despite the intense research in this direction, the processes of self-assembling and properties of monolayers of aliphatic compounds are insufficiently clarified yet. In particular, this concerns the important questions related to the mechanisms of charge transport through isolated molecules and to the physics of the formation of STM-contrasts at the study of monolayers.

In the present work, we present the results of STM-studies of monolayer films of hexadecyl boron acid CH_3–$(CH_2)_{15}$–$B(OH)_2$ adsorbed on the atomically flat surface of graphite. A molecule of hexadecyl boron acid belongs to the class of alkyl boron acids and includes the saturated alkyl chain $–C_{16}H_{33}$ (≈ 1.7 nm in length) and the polar group $–B(OH)_2$ (Fig. 1). The length of a molecule determined by the rigid frame is ≈ 1.9 nm. Alkyl boron acids are widely used in the synthesis of substances-protectors in the chemistry of hydrocarbons and play the role of precursors in the synthesis of clathrochelates [18]. By data in the literature, the STM-studies of the adsorption of boron-containing aliphatic compounds have not been performed till now.

2. Experiment

As a substrate, we took the atomically flat surface of highly ordered pyrolytic graphite, which was obtained by shearing of a graphite monocrystal. Hard granules of hexadecyl boron acid were dissolved in normal tetradecane n-$C_{14}H_{30}$ (Aldrich) to concentrations of $\sim$ 0.1 mg/ml. A drop of the solution was deposited on the substrate in air at room temperature. The structure of films was studied with the help of a scanning tunneling microscope (NT MDT, Russia) adapted to the measurements in a liquid medium. The STM-tips were fabricated of a Pt/Ir (80:20) wire 0.25 mm in diameter by means of the mechanical sharpening. The STM-measurements were carried out in the mode of steady current. The tunnel current and the electric voltage on the tunnel gap were 10–500 pA and 100–1000 mV, respectively. In the process of STM-measurements, the tip was immersed in a drop of the solution deposited on the substrate. The temperature drift in STM-measurements was at most 0.1 nm/min. The relative error of the determination of distances in the lateral direction was in the limits of 9%. The calibration of STM piezoelements was realized on the basis of STM-observations of the atomic structure of the graphite substrate. The obtained STM-images were not subjected to the procedure of filtration, except for the correction of a slope of the plane of a specimen, and were reproduced many times with different tips on different areas of the substrate.

For the interpretation of STM-images, we performed the quantum-mechanical calculations of the spatial and electronic structure of a free molecule of hexadecyl boron acid in the neutral state. The calculations were executed by the density functional theory (DFT) with hybrid functional B3LYP, which is composed from the three-parameter Becke functional (B3) [19] and the Lee–Yang–Parr (LYP) functional [20]. Thus, we took the local and nonlocal correlations. All calculations were performed in the basis 631G*, which is standard for molecular calculations, wih the help of the commercial program package GAUSSIAN'03 with a convergence parameter of 10^{-4} eV.

3. Results and Discussion

After the deposition of a solution, the large-scale STM-images revealed the domain structure, in which each domain was formed by densely packed parallel lamellae (Fig. 2). The angle between lamellae in neighboring domains is equal to $\approx 120°$, i.e., it corresponds to the angle between equivalent crystallographic directions of a graphite monocrystal. This allows us to assert that

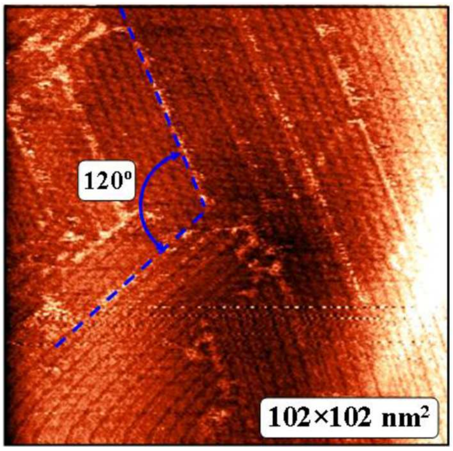

Fig. 2. (*a*) STM-image of a monolayer of hexadecyl boron acid on the *n*-tetradecane/graphite interface. Scanning area: 102×102 nm^2. Tunneling current: I_t=60 pA, voltage on the gap: $U_t = 350$ mV

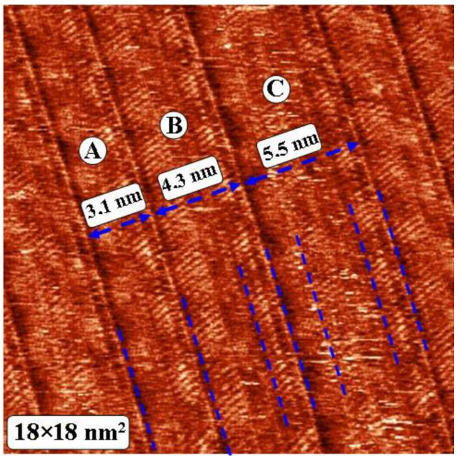

Fig. 3. Lamella-like structure of a monolayer of hexadecyl boron acid on graphite. Three types of lamellae with different widths. Scanning area: 18×18 nm^2. Tunneling current: $I_t = 60$ pA, voltage on the gap: $U_t = 300$ mV

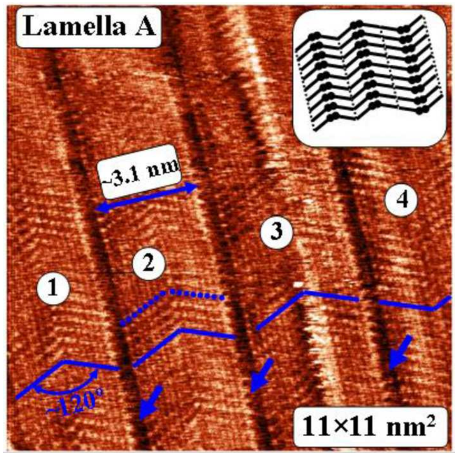

Fig. 4. Intramolecular separation of a monolayer of hexadecyl boron acid on graphite. Lamellae are formed by dimers of molecules of the acid. Polar groups –B(OH)$_2$ are located in the middle of each lamella. Spots denote the positions of –CH$_2$-groups of an alkyl chain. Scanning area: 10×10 nm^2, tunneling current: $I_t = 50$ pA, voltage on the gap: $U_t = 350$ mV. In insert: schematic model of packing

the adsorbed film and the substrate are in the epitaxial relationship.

The STM-images of a decreased scale (Fig. 3) demonstrate significant peculiarities as for the width of lamellae and the contrast of boundaries between them. The estimate of sizes within the measurement error indicates that the width of lamellae can vary by a value multiple to ≈ 1.2 nm. In Fig. 3, three types of strips are clearly seen: with widths of ≈ 3.1 nm, ≈ 4.3 nm, and ≈ 5.5 nm (we denote them conditionally by **A**, **B**, and **C**). It can be noticed that lamella **C** with a width of ≈ 5.5 nm is composed from three narrower sublamellae, and the striae between them have a weaker STM-contrast (they are marked by dotted lines). Lamella **B** is also composed from two sublamellae with different widths. The attempts to attain the molecular resolution simultaneously for three types of lamellae failed. We succeeded to study a molecular structure of the packing only for lamellae with a width of ~ 3.1 nm (type A). The STM-images with molecular resolution (Fig. 4) demonstrate a molecular structure of the packing of A-type lamellae. As is seen from Fig. 4, each of four presented lamellae includes densely packed "Λ"-like objects, for which the angle between their edges is close to $\sim 120°$ (the so-called "parquet" or "herringbone" structure). Similar "herringbone" structures of the packing were observed in monolayers of organic alcohols adsorbed on graphite [21]. It is worth noting that lamella 4 is antiparallel to lamellae 1–3. It can be noticed that each of the edges of the observed "Λ"-objects is a row of 8 linearly arranged bright spots (marked in lamella *2*). It is basically important that the distance between neighboring spots coincides with the period of the alkyl chain (≈ 0.25 nm), and the number of spots is exactly twice less than the number of CH$_2$-groups in the alkyl chain of a molecule of hexadecyl boron acid. We recall that it is known from the STM-studies of monolayer films of normal alkanes that only each second CH$_2$-group of the chain appears on the STM-images of alkyl chains [22]. This is related to the nonequivalence of neighboring carbon atoms of the graphite substrate and, respectively, to the nonequiva-

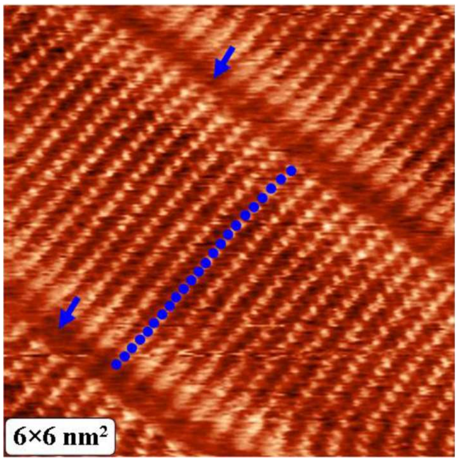

Fig. 5. Intramolecular separation of a monolayer of alkane n-$C_{46}H_{94}$ on graphite. The number of $-CH_2$-groups visible on the STM-image is equal to 23 (marked by spots), which is twice less than that in a molecule of $C_{46}H_{94}$. Scanning area: 6×6 nm^2, tunneling current: $I_t = 50$ pA, voltage on the gap: $U_t = 350$ mV

lence of the atomic surroundings of each second CH_2-group of an alkyl chain adsorbed on graphite. As a result, the contributions of even and odd CH_2-groups to the STM-contrast are essentially different. Therefore, the STM-images present only a half of CH_2-groups of the chain. For example, on the STM-image of a monolayer of alkane n-$C_{46}H_{94}$ (Fig. 5), each molecule has the form of 23 linearly arranged light spots instead of 46 expected ones. With regard for this fact, we interpret each row of 8 bright spots on the STM-image (Fig. 4) as the alkyl tail of a molecule of hexadecyl boron acid. The "Λ"-objects are considered as a pair of associated molecules (dimer). The phenomenon of dimerization is characteristic of some long-chain molecules with a certain polar group. For example, we observed earlier the dimerization in monolayers of arachic acid (polar group $-COOH$). It was experimentally proved in [23] that the pairing of molecules of fatty acids is realized due to the interaction of carboxyl groups. We consider that, in the case of hexadecyl boron acid, the dimerization occurs due to the interaction of boron groups $-B(OH)_2$. The question concerning the positions of boron groups remains open. In view of the results of our DFT-calculations of empty (LUMO+1) orbitals close to the Fermi level (Fig. 1,*b*), we can expect the increase in the STM-contrast of boron groups and, thus, perform their identification. However, we failed to register a significant increase in the STM-contrast of boron groups, except for the anomalies observed in the middle part of lamella *3* (see below).

In order to clarify the position of boron groups, we carried out the comparative experiments studying the sensitivity of the STM-contrast in monolayers of alkane n-$C_{46}H_{94}$ (Fig. 5) and hexadecyl boron acid, which were obtained under the same conditions. We established that, under a change of tunneling parameters (tunneling current, voltage on the gap), the behaviors of the STM-contrast of dark striae between acid lamellae in Fig. 4 and striae between lamellae of alkane n-$C_{46}H_{94}$ (Fig. 5) did not significantly differ from each other. This allows us to assert that the dark striae in Fig. 4 (marked by arrows) correspond to the positions of end CH_3-groups of alkyl chains like the striae between lamellae of n-$C_{46}H_{94}$ in Fig. 5. This implies that the molecules of hexadecyl boron acid form a structure, where the boron groups are placed in the middle of each lamella. Such a character of the packing is corroborated also by our calculations of the optimum geometric conformation of a molecule, which corresponds to the total energy minimum (Fig. 1,*a*). It is a flat configuration, where the plane with atoms of boron and oxygen coincides with that of the carbon frame of a molecule. Namely such a configuration agrees well with the observed packing.

Returning to the STM-image in Fig. 4, we pay attention to two basic peculiarities concerning the size of lamellae and the anomaly of the STM-contrast in the middle of lamella *3*. The more thorough analysis of distances indicates that the width of lamella 3 exceeds the widths of lamellae *1*, *2*, and *4* approximately by 10%. In addition, the STM-contrast in the middle part of lamella *3* is anomalously increased as compared with that of lamellae *1*, *2*, and *4*. Since the width of a lamella is determined by the size of dimers, the differences in the sizes of lamellae indicate the differences in the sizes of dimers, which form these lamellae. The observed differences in the sizes can be explained by specific features of the association of molecules of boron acid. It is known that alkyl boron acids can form dimers, being in two possible states: hydrated and dehydrated ones (Fig. 6). The transition in the dehydrated state is accompanied by the removal of one oxygen atom and two hydrogen atoms from each pair of molecules with the formation of a free water molecule. Since the energy barrier of dehydration does not exceed 0.1 eV, the probability of such a process is rather high under conditions of our experiments. It is obvious that the sizes of dimers in these two states must be different. Hence, the differences in the widths of lamellae on the STM-image (Fig. 4), as well as the anomalous enhancement of the STM-contrast in lamella *3*, can be explained by different states of molecules in pairs: the dehydrated state in lamellae *1*, *2*, and 4 and the hydrated one in lamella *3*.

In conclusion, we discuss the nature of narrow lamellae in Fig. 3. We note that their width is equal to ~ 1.2 nm and agrees well with the value of $l \cdot \sin 60°$, where l is the length of a molecule of n-tetradecane$n$-$C_{14}H_{30}$ (≈ 1.6 nm). In view of this fact, we interpret them as the lamellae of molecules of the solvent, which are included in the monolayer of hexadecyl boron acid. In fact, this means the formation of a monolayer nanocomposite, which is composed of lamellae of the dissolved substance (acid) and the solvent (tetradecane). The principal axes of n-tetradecane molecules in narrow lamellae form an angle of $\sim 60°$ with the direction of lamellae. It is worth noting that the coadsorption of n-tetradecane molecules with molecules of hexadecyl boron acid is observed at a temperature significantly higher than the temperature of crystallization of a monolayer of this substance on graphite [22]. This can be explained by the following. Under the formation of monolayer lamellae of hexadecyl boron acid, the free areas can remain on the surface, whose width allows their dense filling by n-tetradecane molecules at a certain orientation of these molecules relative to the surface of graphite. In other words, the unique conditions for a spatial confinement of the mobility of n-tetradecane molecules are created on the surface: a distinctive molecular template stimulating the ordered adsorption of the solvent is formed. The uniqueness of these conditions is demonstrated by that the phenomenon of coadsorption of n-tetradecane is not observed at the deposition of similar aliphatic molecules (normal alcohols, fatty acids [24]) on the surface of graphite. This allows us to consider boron-containing aliphatic compounds as a promising class of substances for the development of two-dimensional nanocomposites.

4. Conclusions

Thus, we have shown that the highly ordered monolayer films of hexadecyl boron acid $CH_3–(CH_2)_{15}–B(OH)_2$ can be obtained on the base plane of highly oriented pyrolytic graphite at room temperature by the deposition of a solution of the acid in n-tetradecane n-$C_{14}H_{30}$. With the help of STM, we have established that the monolayers are formed by dimers of molecules of hexadecyl boron acid. We assume that the association of molecules in pairs is realized due to the interaction between $B(OH)_2$-groups. It is experimentally found that molecules of the solvent n-$C_{14}H_{30}$ can be adsorbed on the graphite substrate together with molecules of the acid at a temperature significantly higher than the temperature of crystallization of a monolayer of tetradecane on graphite. The coadsorption of molecules of n-tetradecane and hexadecyl boron acid can be caused by the favorable conditions for the confinement of n-tetradecane molecules.

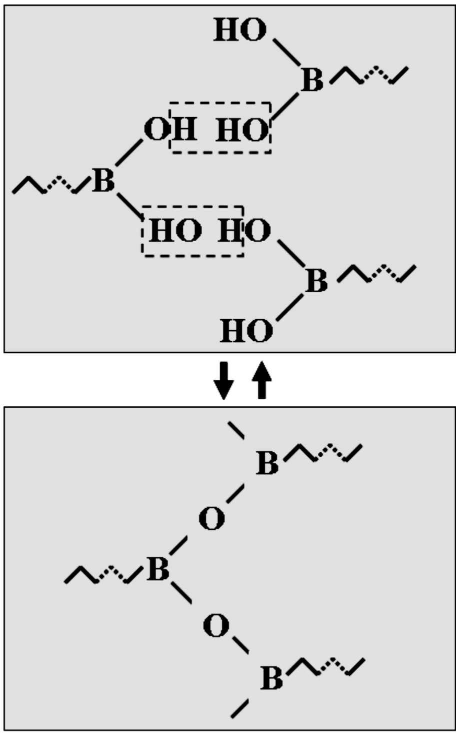

Fig. 6. Schematic model of association of molecules of alkyl boron acids in the hydrated (above) and dehydrated (below) states. Dotted rectangles denote the atoms, which are removed from molecules in the process of dehydration

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САМООРГАНIЗАЦIЯ МОЛЕКУЛ ГЕКСАДЕЦИЛБОРНОЇ КИСЛОТИ НА АТОМНО-ГЛАДКIЙ ПОВЕРХНI ГРАФIТУ

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Резюме

Показано, що високовпорядковані моношарові плівки гексадецилборної кислоти CH_3–$(CH_2)_{15}$–$B(OH)_2$ можуть бути отримані на базисній площині високоорієнтованого піролітичного графіту шляхом нанесення розчину кислоти в n-тетрадекані n-$C_{14}H_{30}$ при кімнатній температурі. За допомогою скануючого тунельного мікроскопа (СТМ) встановлено, що моношари мають ламелеподібну структуру, в якій кожна ламель сформована парами (димерами) молекул гексадецилборної кислоти. Асоціація молекул у димери здійснюється завдяки взаємодії між $B(OH)_2$-групами. Виявлено також, що молекули розчинника n-$C_{14}H_{30}$, перебуваючи при температурі, значно вищій, ніж температура поверхневої кристалізації моношару тетрадекану на графіті, можуть адсорбуватись спільно з молекулами кислоти. Співадсорбцію молекул розчинника можна пояснити специфікою взаємної геометрії поверхні підкладки і димерів гексадецилборної кислоти.