

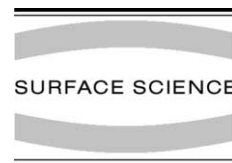


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Coexisting superstructures of iodobenzene on Cu(1 1 1) near saturation coverage

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Abstract

Low-temperature scanning tunnelling microscopy reveals seven coexisting structures of iodobenzene (IC₆H₅) adsorbed on Cu(1 1 1) at ≈55 K. Only the least dense structure reflects the threefold symmetry of the surface. The other structures show p2-symmetry. In the densest structure molecules adsorb with their π system perpendicular to the surface. We identify as a common driving force for ordering the tendency of the phenyl rings (C₆H₅) to encapsulate the iodine.

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1. Introduction

The current interest in nanostructures is motivated by their potential use in the mass fabrication of nanoscale devices [1–3]. At present, modern integrated circuits contain structures with a lateral extension of 0.1 μm that are only a few atoms thick. Both building parts and memory units for information devices are decreasing in size. However, many of the nanoscale structures formed from atoms during nucleation and growth experiments are only meta-stable, and their stability is

often a limiting factor for the scientists' ability to synthesise new structures from atoms. In contrast, molecules can be tailored to exhibit controllable and highly specific interactions. A promising way forward is therefore to self-assemble thermodynamically stable nanostructures from appropriately designed molecules [1,2,4]. The additional degrees of freedom introduced by a non-spherical molecular shape result in rich ordering phenomena [5,6]. Molecules adsorbed on surfaces are particularly appealing because their arrangement is directly observable with scanning tunnelling microscopy (STM) [7–9]. For physisorbed molecules, molecule–molecule interactions can be stronger than surface–molecule interactions. Beyond the constraint of planar assembly, the substrate is then a relevant, but not the dominating factor in the assembly process. A first step towards nanoscale

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molecular devices is to characterise superstructures and to identify driving forces for the particular structuring.

In this article, we characterise nanostructures of the molecule iodobenzene (IC_6H_5) physisorbed on $\text{Cu}(111)$. We extract as common driving force for the rich variety of superstructures upon small differences in *local* concentration the high energy to form an iodine step on the surface (called 1D boundary energy) as compared to the energy to form a phenyl step.

2. Experimental

The measurements have been performed with a home-built STM of the beetle type, placed within cryogenic shields for low-temperature operation. The ultra-high vacuum chamber described else-

where [10] is equipped with standard facilities for sample preparation and characterisation. The sample has been cleaned by repeated cycles of 20 min Ne^+ sputtering and annealing at 800 K. Iodobenzene is deposited through a leak valve directly onto the sample held at 50–60 K. The background pressure reaches 10^{-8} mbar and the deposition time is 30 s. The sample is then transferred back into the precooled STM. Measurements are performed at 12 K.

The distances given are based on calibration of atomic resolution images and monatomic steps of $\text{Cu}(111)$ for in-plane (x, y) and out-of-plane (h) values, respectively. Due to drift, creep, and temperature uncertainties, the values might have an error up to 10% within the plane (x and y). All heights stated refer to apparent heights, which for molecules usually greatly underestimates the real height. However, these values have a high precision

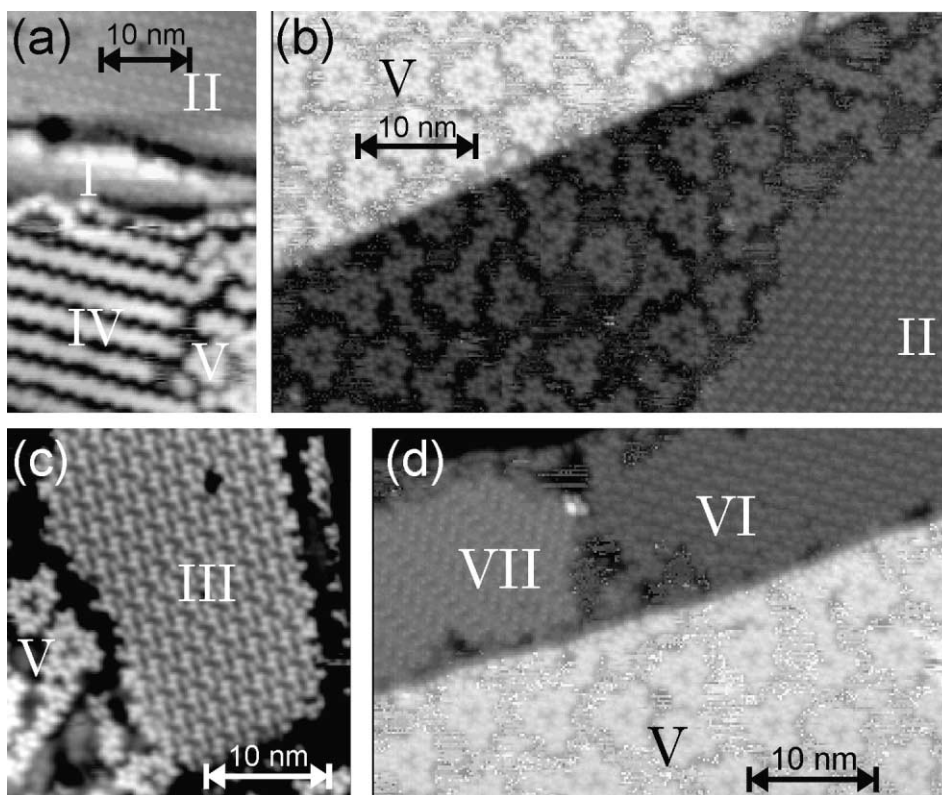


Fig. 1. Large-scale STM images of IC_6H_5 on $\text{Cu}(111)$ near saturation coverage revealing seven coexisting superstructures: (a) 0.8 V, (b) 0.65 V, (c) 0.6 V, (d) 0.6 V.

and relative heights in different structures as well as within a structure give reliable information.

3. Results and discussion

3.1. Overview

Fig. 1 shows several large-scale images that demonstrate seven coexisting structures formed at

or near saturation coverage. The local molecular densities differ between one molecule per 0.54 nm^2 in structure V and one molecule per 1.8 nm^2 in structure I, i.e., by more than a factor of 3. The density in the less well-resolvable structures VI and VII is presumably even higher. Remarkable are continuation of the same structure on both sides of a preexisting copper step, on the one hand, and sharp phase boundaries, on the other hand (Fig. 1b). Furthermore, structure free regions exist in

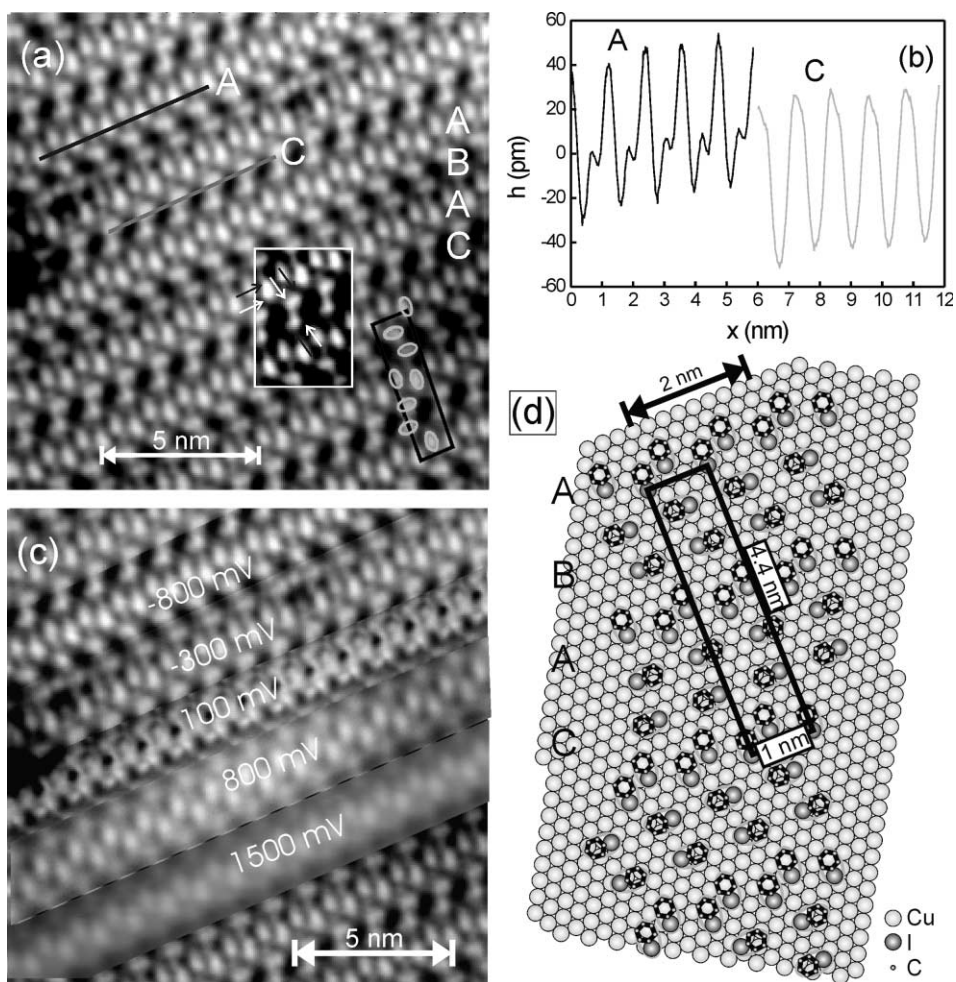


Fig. 2. Structure I: (a) STM image (-0.3 V) with sub-molecular resolution, black quadrangle indicates unit cell each containing eight molecules, ellipsoids mark these eight molecules, contrast is enhanced within the white rectangle, white and black arrow point to the brighter and the darker end of the molecules, respectively. Contrast is enhanced within white rectangle; black and white arrows point to darker and brighter end of the molecule. (b) Line scans as indicated in (a). (c) Collage of images taken at the same spot with different bias voltages as indicated. (d) Structural model, scales to (a) as 2:1, the crystallographic directions of Cu(1 1 1) have been deduced from atomic resolution images and are identical in all images.

between the densest structures VI and VII. The white stripes there and between the star like structures in the least dense structure V are indicative of a molecular gas still existing even at these low temperatures [11]. Most structures, with the exception of structure V have p2-symmetry, however with different unit cells. In Section 3.2 we describe the two-dimensional structures I–V in detail and identify the orientation of the molecules within the structure. We give a structural model supposing that the iodine of the molecule is adsorbed in the energetically preferable threefold hollow site [12]. Common features of the structures are summarised in Section 3.3. The three-dimensional structures are discussed in Section 3.4.

3.2. Structures

Within structure I (Fig. 2), the molecules are arranged in three types of chains, A, B, and C, following a sequence ABACABAC... (Fig. 2a and d). Type A chains consist of ellipsoidal protrusions perpendicular to the direction of the chain. Each protrusion has a darker and a brighter end (marked by respective arrows in the contrast enhanced rectangle). We have shown before that iodobenzene is usually imaged as an asymmetric ellipsoidal protrusion with the long axis of the ellipsoid corresponding to the molecular axis [12]. Sometimes, the phenyl ring and the iodine have been imaged as two distinguishable circles of different intensity

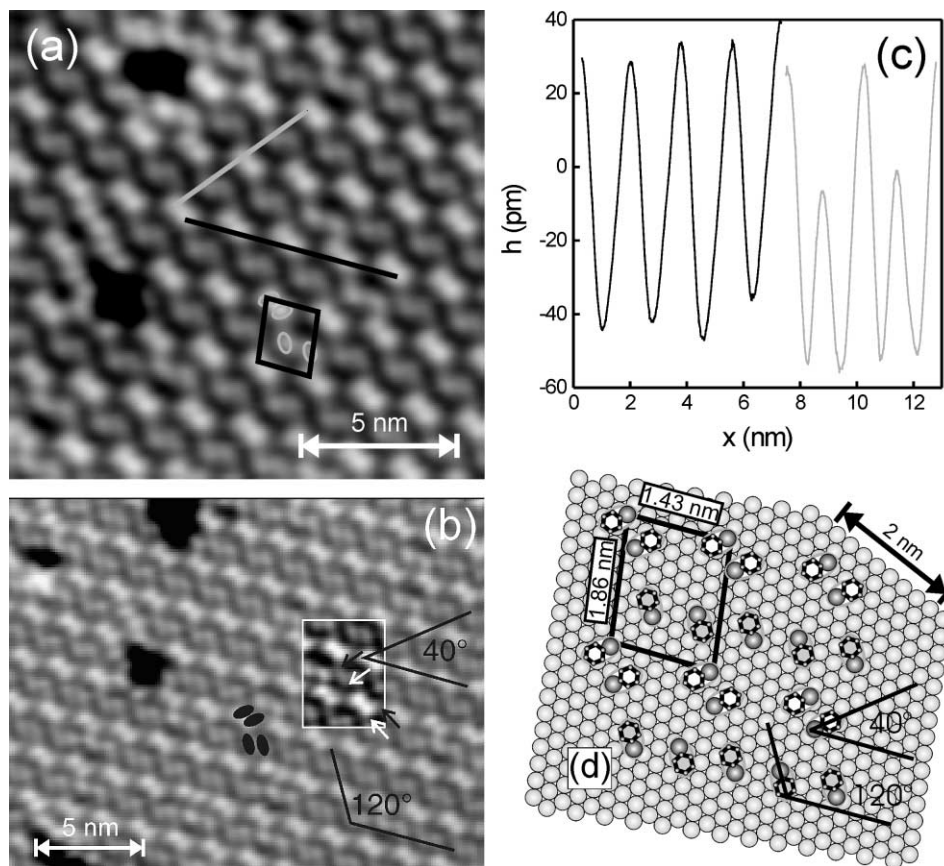


Fig. 3. Structure II: (a) STM image (0.1 V), quadrangle indicates unit cell each containing four molecules indicated by the ellipsoids. (b) Molecular resolution (0.8 V), ellipsoids mark the four molecules contained in a unit cell, contrast is enhanced within the white rectangle; white and black arrow point to the brighter and the darker end of the molecules, respectively. (c) Line scans as indicated in (a). (d) Structural model scales to (b) as 2:1.

[13]. By tip-induced dissociation of the molecule, we have identified the brighter ring as well as the brighter end of the asymmetric ellipsoid to be the iodine [13]. This knowledge is used throughout this article to identify the molecular arrangement within the superstructure.

In structure I, the molecules in chain A are parallel to each other with the iodine atoms pointing into the same direction (see model in Fig. 2d). The molecules are displaced by half their molecular axis to one another reminiscent of zippers formed by 1-nitronaphthalene on Au(111) due to electrostatic interaction [7]. In type B and type C chains the molecules are arranged in par-

allel to the chains. Within the chains they form pairs. The distance between the molecules within a pair is (0.07 ± 0.01) nm. In the upper and lower rows of chain B the iodine is to the right and to the left of the phenyl ring, respectively. B and C are mirror images to each other. Thus, in the upper and lower rows of type C the iodine is to the left and to the right of the phenyl ring, respectively. This leads to the two different angles of the pairs with respect to the unit cell and thus to the herringbone impression of the structure. The overall structure leads to a large unit cell of $4.4 \text{ nm} \times 1.0 \text{ nm}$, each containing eight molecules, i.e., to a density of $1.82 \text{ molecules/nm}^2$. Molecules in type

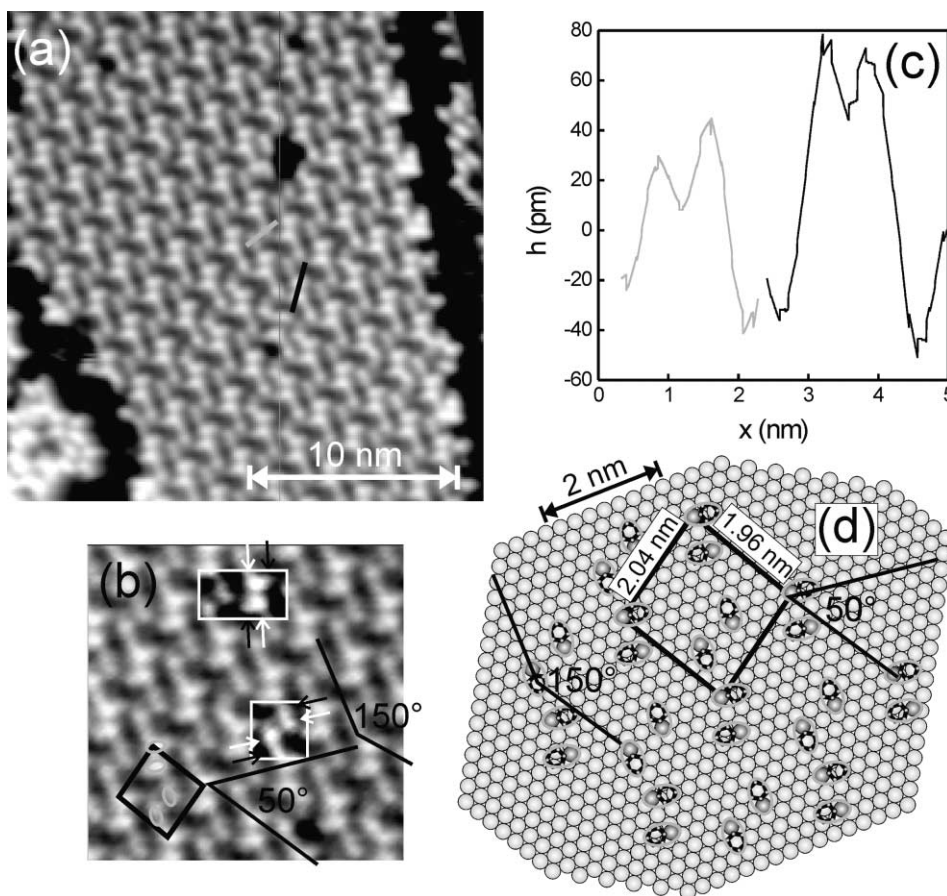


Fig. 4. Structure III: (a) STM image (0.6 V). (b) Close-up of (a) showing molecular and sub-molecular resolution; quadrangle indicates unit cell; ellipsoids mark the four molecules within a unit cell, contrast is enhanced within the white rectangle; white and black arrow point to the brighter and the darker end of the molecules, respectively. (c) Line scans as indicated in (a). (d) Structural model (b);(d) = 1:2.

A-chain are imaged higher by about 20 pm than molecules in type B-chain and type C-chain (Fig. 2b).

At different bias voltages, the chains are imaged differently (Fig. 2c). At 0.1 V, the imaging also influences the molecules in the type A rows, i.e., the molecules are temporarily displaced under the influence of the tip. At this voltage, resolution is best in the other two types of rows. Therefore, imaging at different voltages is helpful (and is used) to identify the structures and develop the models presented below in Figs. 2d, 3d, 4d and 5c.

Structure II (Fig. 3) is with 1.5 molecules/nm² 20% less dense than structure I. Each rhomboidal unit cell (Fig. 3a) of 1.4 nm × 1.9 nm contains four molecules. The two molecules in the centre of the unit cell are imaged lower by 30 pm than the other two molecules (Fig. 3c). Equivalently imaged molecules form pairs. The distance between the molecules in a pair (Fig. 3c) is measured to

(0.7 ± 0.1) nm. Again the molecular axes within pairs are parallel to each other with the iodine atoms pairing up (Fig. 3a and d). The molecular axes of the pairs are 120° and 40° to the principal axis of the unit cell (Fig. 3b and d).

The unit cell of structure III (Fig. 4) is almost quadratic with 2.0 nm width and 2.0 nm length. The base consists again of four molecules (Fig. 4b and d) giving an overall density of ≈1 molecules/nm². Two of the molecules have an apparent height of ≈(45 ± 20) pm lower than the other two molecules (Fig. 4c). The intermolecular distance between the protrusions of same apparent height is (0.7 ± 0.1) nm (Fig. 4b). The molecular axes in a pair are parallel to each other. The molecular axes of the two pairs have an angle of 100° to each other and the brighter pair an angle of 50° to the principal axis of the unit cell. Contrast enhancement (Fig. 4b) reveals that the apparent structure of the molecules in the two kinds of pairs is different. The

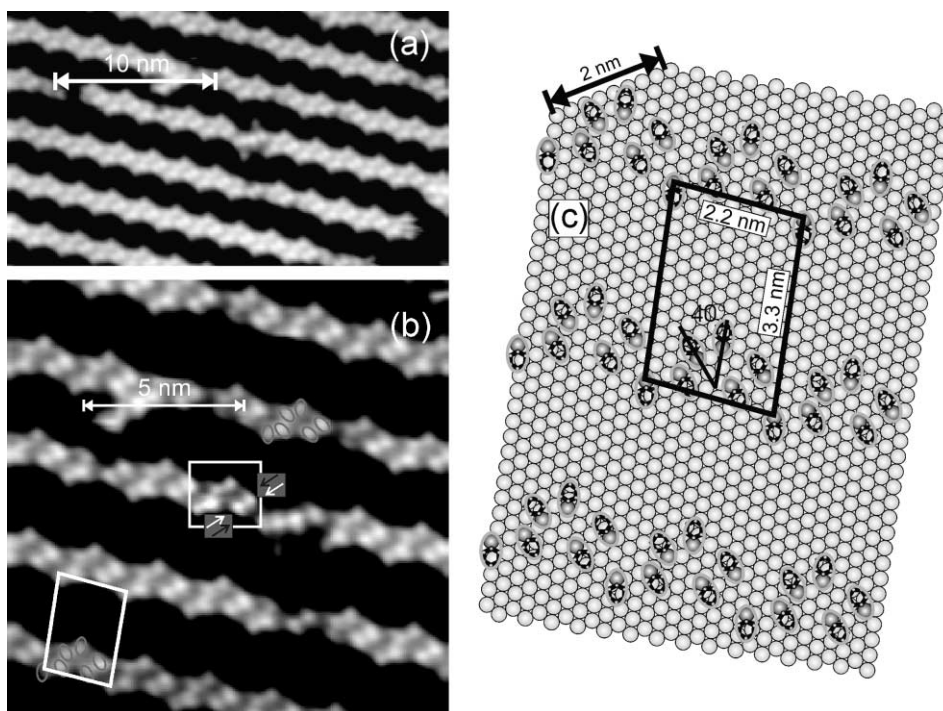


Fig. 5. Structure IV: (a) STM image (0.8 V). (b) Close-up (0.8 V), quadrangle indicates unit cell each containing six molecules, ellipsoids mark the six molecules contained in a unit cell, contrast is enhanced within the white rectangle, white and black arrows point to the brighter and the darker end of the molecules, respectively. (c) Structural model scaling to (b) as 2:1.

less bright pair appears as two circular protrusions, the brighter one as only one ellipsoidal protrusion.

Structure IV (Fig. 5) is with $0.85 \text{ molecules/nm}^2$ the least dense of the striped p2-structures. One unit cell (Fig. 5b and c) of $2.2 \text{ nm} \times 3.3 \text{ nm}$ contains only six molecules. The structure consists of molecular sinusoidal chains. Despite the large distance of $\approx 1 \text{ nm}$ between the molecular chains a correlation is seen between them (Fig. 5a; zipper like feature). Also, the molecules in these chains form pairs (Fig. 5b). The distance of the molecules within a pair is $(0.6 \pm 0.1) \text{ nm}$. Two features differ from the structures discussed so far. First, all molecules are imaged as ellipsoids and with the same apparent height. Second, the molecular axes are not parallel to one another in the pairs on the border of the molecular chains, but they have an angle of 40° to each other. We point out a higher density of defects in this structure than in the denser structures I–III, which is partly due to efforts to achieve high-resolution imaging (cf. to the less well-resolved image in Fig. 1a).

Short portions of these molecular chains are sometimes merged in the least dense structure V (Fig. 6, one molecule per 1.8 nm^2). Despite some non-regularity, triangular structures consisting of exactly 24 molecules are frequent. This is the only structure reflecting the threefold symmetry of the surface. Also in this structure, the molecules form pairs of ≈ 0.6 and 0.7 nm distance and with the iodines pairing up (Fig. 6b). On an inner circle, there are six pairs with the phenyl rings pointing in opposite directions, and the molecular axes being parallel. On an outer circle, there are six pairs with the phenyls pointing to the same side with an intermolecular angle of $(60 \pm 10)^\circ$. Further details and applications of this structure will be addressed in a separate publication [16].

3.3. Common features

Table 1 summarises the data presented in the previous section. The densities should be compared to the surface density of copper of 18 atoms/nm^2 . Thus, the distance between the molecules is on the average between 3 and 5 atomic distances (see ball models presented in Figs. 2–6). The distance between the pairs is three atomic distances.

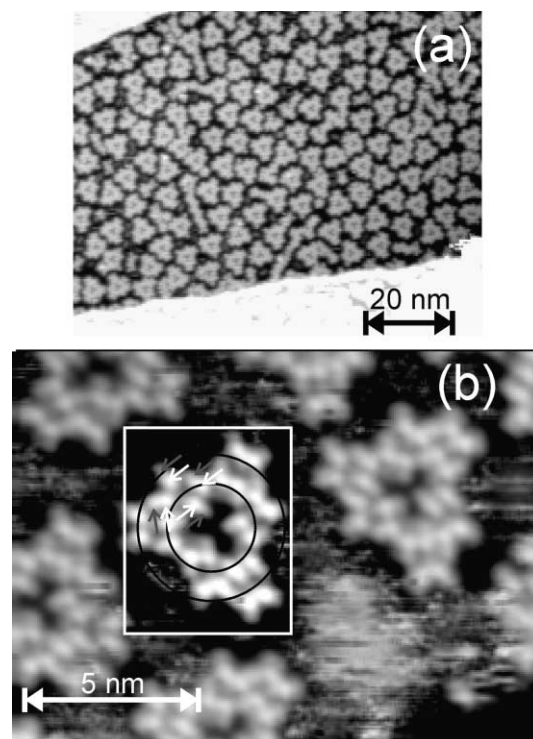


Fig. 6. Structure V: (a) Large-scale STM image (0.6 V). (b) Close-up (0.6 V), contrast is enhanced within the white rectangle; circles mark inner and outer circle discussed in the text; white and black arrow point to the brighter and the darker end of the molecules, respectively.

Some general features can be extracted. In the dense structures iodobenzene likes to align in parallel pairs with the iodine molecules close to one another in the centre of the pairs and the phenyls pointing in opposite directions away from the iodine pair. In structures with free surface regions the phenyls align at the outer edge of the molecular structure, i.e., phenyls encapsulate the iodine atoms. This leads to pairs with the phenyls pointing to the same side but with angles between the molecular axis of either 40° or 60° again maintaining a phenyl distance of $\approx 3a_{\text{Cu}}$. These distinct angles show the influence of the substrate on the structures.

For the molecular axis angles of 30° towards the main axis of the structure are preferred. This is the angle between the $[110]$ and $[\bar{1}\bar{1}2]$ surface directions.

Table 1
Structural properties

Structure	D (molecules/nm ²)	U (nm × nm)	N	d_{in} (nm)	Δh (nm)	Appearance	
I	1.82	4.4 × 1.0	8	0.7	0.03	1 Ellipsoid	2 Circles
II	1.50	1.9 × 1.4	4	0.7	0.05	1 Ellipsoid	2 Circles
III	1.00	2.0 × 2.0	4	0.7	0.03	1 Ellipsoid	2 Circles
IV	0.83	3.3 × 2.2	6	0.6	≤ 0.02	1 Ellipsoid	1 Ellipsoid
V	0.56			0.6		1 Ellipsoid	1 Ellipsoid
VI	≥ 1.85	2.4 × 1.7	≥ 6	0.7	0.03	1 Ellipsoid	2 Circles
VII	0.76 (second layer)	4.4 × 1.2	4	0.6			

D : local density; U : size of unit cell; N : number of molecules in a unit cell; d_{in} : distance between molecules within a pair (± 0.1 nm); Δh : difference in apparent height of the molecules (± 0.02 nm); appearance in brighter and in less bright pair.

Furthermore, in the denser structures half of the molecules display different apparent heights and are imaged differently (one asymmetric ellipsoid as opposed to two circular protrusions of different intensities). This can be explained by different adsorption geometries as indicated in the ball models. It is known from STM measurements [17,18] and theoretical calculations [19,20] of CO and benzene on Pt(1 1 1) that different binding sites of adsorbates might be discriminated by their different contrast in STM images. The dense structures thus support that half of the molecules are displaced from their most favourable adsorption site in order to better match the superstructure. This demonstrates the importance of intermolecular interactions. While the iodine is expected to adsorb in a threefold hollow site, the phenyl ring might adapt several different adsorption geometries.

It was shown before that for the polar molecule 1-nitronaphthalene [7,8], the driving force for structuring is electrostatic interaction. Despite the dipole moment of iodobenzene this is not the case here. Driving force is the tendency of iodine to form pairs and of the phenyls (C₆H₅) to surround these cores, i.e., the tendency of the iodine atoms to avoid the outer edges of the structures. In a two-dimensional equivalent to the free surface energy, we propose that the 1D boundary energy of the iodine is higher than that of the phenyls. In a simplistic energy consideration, one would expect that benzene only interacting via van-der-Waals interaction is indeed less prone to gaining energy by step formation than iodine.

In conclusion, there is interplay between different interactions. First, molecule surface interaction

is strong enough to determine the adsorption site, but not to impose the surface symmetry (except in the least dense structure). Second, molecule–molecule interaction leads to iodine pairing.

While kinetic limitations might be considered responsible for the different structures, we think that the following two aspects contradict this supposition: Very distinct regular structures with low defect densities are separated by sharp phase boundaries; a molecular gas coexists with the densest structure far below the deposition temperature. The defect density in the structure reflects the impurity density of the surface.

3.4. 3D structures

Structure VII looks very different from the structures discussed so far. On top of a close packed first layer we see circular (as opposed to ellipsoidal) protrusions and a density of 0.758 protrusions per nm² (Fig. 7). The diameter of 0.6 nm of the circles corresponds to the width of the ellipsoids that are usually seen for a molecule. The distance between the maxima is 0.6 and 0.7 nm in the straight and in the tilted pairs, respectively. The second difference is the apparent height. For instance structure III (Fig. 4) is imaged with an apparent height of ≈ 0.14 nm. This height is quite typical for planar molecules with their π -system parallel to the surface [7,14,15]. In contrast, the apparent height of the protrusions on structure VII is ≈ 0.25 nm.

The different shape and the different apparent height are an indication for seeing only one of the molecular groups, i.e., either the phenyl or the

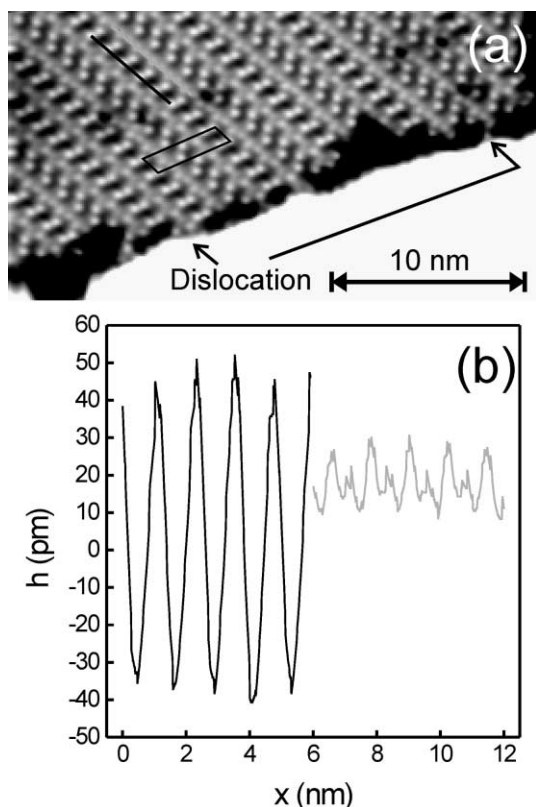


Fig. 7. Structure VII: (a) STM image (0.6 V); quadrangle indicates unit cell. (b) Line scans as indicated in (a).

iodine, of the molecules being adsorbed along the surface normal. The discussion above of the tendency of the phenyls to encapsulate the iodine atoms suggests that the phenyl is pointing away from the surface while the iodine is buried within the first layer which is represented by a poorly resolved background with an apparent height of ≈ 0.15 nm (Fig. 7b). Also in their perpendicular adsorption geometry, molecular pairing persists.

Finally, we mention the less well-resolved structure VI (Fig. 8). Also in this structure the molecules pair up with a distance between the pairs of (0.7 ± 0.1) nm and a height difference between the molecules of 30 pm. Again the lower imaged molecules seem to consist of two bumps while the higher imaged molecules are imaged as a single ellipsoid. The apparent height of this structure (Fig. 8b) (centre molecules 0.3 nm; 0.15 nm) is

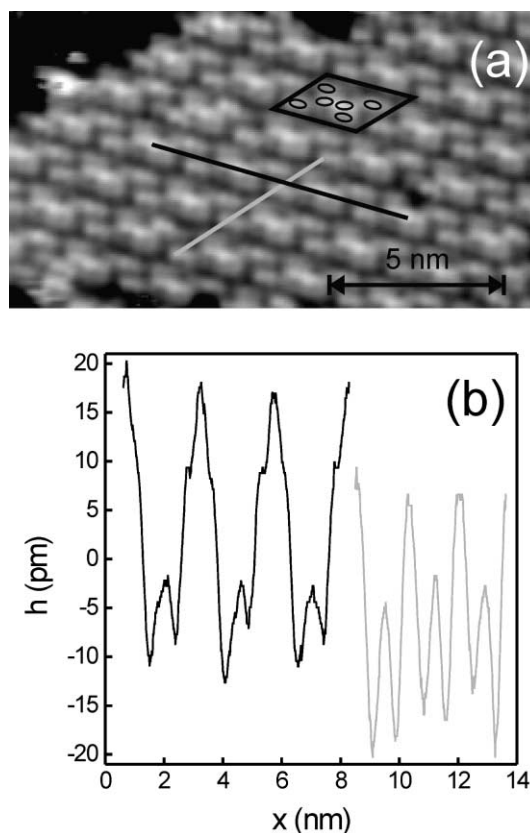


Fig. 8. Structure VI: (a) STM image (1.0 V); quadrangle indicates unit cell; ellipsoids mark visible molecules within a unit cell. (b) Line scans as indicated in (a).

an indication for adsorption of two of the molecules on top of other molecules, possibly in a tilted geometry. Here, STM does not allow to gain enough information to propose a structural model.

4. Conclusion

Iodobenzene on Cu(111) near saturation coverage separates into different structures with different molecular densities. Slight differences in local molecule density lead to a rich variety of structures driven by the tendency to pair molecules and to form structures with the phenyls encapsulating the iodine atoms. Indications of upright adsorption geometry are found in the densest structure. Phase separation between structures of different dimensionality is remarkably sharp.

Acknowledgement

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