Adsorption-induced chirality in highly symmetric hydrocarbon molecules: lattice matching to substrates of lower symmetry

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Abstract. For molecules of high symmetry and lateral interactions dominated by van der Waals’ interactions, such as some planar aromatic hydrocarbons, there is a preference for hexagonal close packing on adsorption. Optimization of packing by minimization of the interadsorbate spacing may favour correlated rotations of the molecules, which reduces the symmetry and leads to chiral properties in the two-dimensional overlayer. Independently, mapping of the preferred hexagonal packing on to lower symmetry substrates, which provide pseudo-hexagonal lattices, can lead to alternative mirror image lattices. The interaction of these independent chiral phenomena gives rise to diastereoisomerism in the adsorbed array. Coronene and its substituted, larger derivative hexa-tert-butyl hexabenzocoronene adsorbed on copper surfaces provide examples of these phenomena. A new structure is proposed for coronene on Cu(100) while new STM and LEED data are presented for this molecule adsorbed on Cu(110). Finally, the adsorption of hexa-tert-butyl hexabenzocoronene on Cu(110) is re-examined and the implications of the competition between two, closely related, pseudo-hexagonal lattices are considered.
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### 1. Introduction

The adsorption of planar aromatic hydrocarbons on single crystal surfaces has received considerable attention both because of their potential technological significance, in areas such as molecular electronics or light emitting devices, but also because of their structural and chemical simplicity as model systems for the study of adsorption and other fundamental surface processes [1]. Included within this family are the highly symmetrical molecules coronene, hexabenzocoronene and their symmetrically substituted derivatives such as 2,5,8,11,14,17-hexa-tert-butylhexabenzo[bc,ef,hi,kl,no,qr]coronene (HtB-HBC). The adsorption of coronene has been characterized on a particularly wide variety of single crystal surfaces including Cu\{100\} [2], Ag\{110\} [3], Ag\{111\} [4, 5], Au\{110\}-1 × 2 [3], Ag\{111\} [3], [6–8], highly oriented pyrolytic graphite (HOPG) [5, 9], MoS$_2$ [9, 10] and Si\{100\} [11]. The adsorption of the much larger molecule HtB-HBC on Cu\{110\} has recently been investigated by Schöck et al [12]. With the exception of Si\{100\}-2 × 1 [11], where strong Si–C bonds are formed, the adsorption of such molecules is considered to involve a major contribution from the van der Waals’ (vdW) interactions. These and the π–d interactions, which may also play a role in the case of adsorption on d-band metals, both favour a geometry in which the molecular plane lies parallel to a flat single crystal surface. Lateral interactions, also dominated by the vdW terms, result in close-packed two-dimensional (2D) structures, although crucially the corrugation of the lateral adsorption potential is sufficiently strong in most cases to favour commensurate overlayers. The importance of vdW interactions to the adsorption properties of these hydrocarbon molecules causes severe difficulties for a quantitative description using methods of density functional theory [13] but means that geometric arguments based on molecular size can be useful in describing and rationalizing their structural properties on well-defined surfaces. For molecules of high symmetry, such as coronene or benzocoronene (D$_{6h}$ symmetry), hexagonal close-packing is found on Ag\{111\} [4, 5], Ag\{111\} [3, 6, 7], HOPG [8, 9] surfaces. A pseudo-hexagonal 2D arrangement is observed for hexabenzocoronene on GeS [9] and for coronene, on Cu\{110\} [14], Ag\{110\} [3] and Cu\{100\} [2] as well as for HtB-HBC adsorbed on Cu\{110\} [12]. The role of lattice matching between overlayers, which have a preference for hexagonal close packing, and the substrate, particularly if this does not have three-fold symmetry, can give rise to interesting structural properties. In a similar fashion, the epitaxial growth of atomic adsorbates on hexagonal substrates,
focusing on matching of lattice sizes rather than shape and symmetry, has previously been described in detail by Bauer et al [15].

A subtle structural aspect of molecular adsorption is the emergence of chiral properties due to the loss of mirror symmetry in the adsorbate–substrate system. This can be further distinguished as being local and/or array chirality within the 2D layer according to whether the local site symmetry of the molecule lacks a mirror plane or whether this symmetry element is only lost as a consequence of the long range order within the 2D array [16]. Mapping of the 2D array on to a low symmetry substrate introduces other aspects of chirality depending on whether the array unit cell vectors are aligned with a high symmetry direction of the substrate lattice and whether an individual molecule occupies a high symmetry local site on the substrate. The inherently chiral but non-planar hydrocarbons helicene and rubrene show interesting 2D chiral phenomena, involving respectively, chiral amplification [17] and supramolecular chiral cluster formation [18]. At first sight, however, it might seem improbable that molecules of high symmetry, such as coronene, benzocoronene or HtB-HBC would give rise to chiral molecular arrays, albeit with the occurrence of racemic mixtures of the two enantiomeric arrays, if a large enough area of the surface is considered. For such molecules to display chirality requires a substrate of the appropriate (low?) symmetry and a judicious balance between molecule–substrate and molecule–molecule lateral interactions. The former, if strong enough, favour specific adsorption sites, a commensurate overlayer and a particular molecular orientation (polar and azimuthal) while the latter also play a role in molecular orientation and the shape and size of the 2D array, although not its orientation with respect to the substrate lattice.

In the following, a description and classification of pseudo-hexagonal layers on fcc\{100\} and \{110\} surfaces is given. The cases of coronene adsorption on Cu\{100\} and Cu\{110\} surfaces are considered within this description, leading to an alternative suggestion for the structure for coronene on Cu\{100\}. We also build on the investigation by Schöck et al [12] of HtB-HBC adsorption on Cu\{110\} and show that the preference for the observed structure, rather than an alternative with very close structural similarities, is probably related to the ability of the lattice to accommodate adsorbate-induced strain.

2. Lattice matching to fcc\{110\} and \{100\} surfaces

While it is reasonable to expect that atoms or molecules with a high degree of rotational symmetry would adopt hexagonal close packing within an isolated 2D layer, a perfectly commensurate hexagonal lattice is not present on an fcc\{100\} or \{110\} surface so a compromise is required either by sacrificing the commensurability or, alternatively, if the preference for a specific adsorption site is strong, by relaxing the constraint of perfect hexagonality. With increasing dimensions of the hexagonal overlayer unit cell, relative to the fcc\{100\} or \{110\} surface unit cells, there is an increasing probability of defining overlayer lattices, which closely approximate to a hexagonal lattice and which are therefore likely to be favoured for close-packing of adsorbates with 2D isotropic or at least highly symmetric, interaction potentials. Large molecules requiring relatively large unit-cells are more likely to fit the criteria for matching to such a pseudo-hexagonal lattice than small molecules.
2.1. Pseudo-hexagonal lattices on fcc\{110\} surfaces

If we begin by defining the orthogonal unit vectors $0,1$ and $1,0$ for the fcc unit cell, where $0,1$ corresponds to the close-packed direction with length $a$, and $1,0$ has length $\sqrt{2}a$, then a lattice vector $m,n$ has a length $\sqrt{(m^2+2n^2)a}$, where $m$ and $n$ are both integers. If we then define, somewhat arbitrarily, an acceptable pseudo-hexagonal coincident lattice as one in which the defining vectors differ in length by less than 10% and where the included angle is $120^\circ \pm 3^\circ$, then there are families of lattices, which conform to these criteria. Within a given family, the members are related by the length of the vectors, which follow a sequence $l, 1, 2, \sqrt{3}, \sqrt{5}, \sqrt{7}, \ldots$, where $l$ is an integer obeying $p^2+2q^2 = r^2$ with $p$ and $q$ both integers. Within the family, the unit vectors, which define one lattice, have the same length ratio and the same included angle as all other members of the family. If we restrict ourselves to those lattices with unit cell vectors shorter than $\sqrt{120a}$, then a limited number of families are possible. These are shown, with their constituent members and their interrelationship in table 1 and the early members of one such family are shown in figure 1. We note that higher members of any family can be generated from the smallest member by the transformations shown in table 2. It is also particularly significant that for certain lengths relative to the initial member, i.e. $\sqrt{3}, \sqrt{6}$ and 3, there are multiple solutions and different pseudo-hexagonal lattices exist with exactly the same dimensions but differently aligned with the substrate lattice (see an example in figure 1).

Table 1. The families of pseudo-hexagonal lattices on an fcc\{110\} substrate defined by the lattice vectors defining the nearest neighbour positions.

| Lattice vectors | Length/a | Relative length | Comment |
|-----------------|----------|-----------------|---------|
| 1st Family      |          |                 |         |
| 1,3             | $-4, -1$ | $3, -2$        | $\sqrt{19}$ | $\sqrt{18}$ | $\sqrt{17}$ | 1 | Chiral |
| 6,1             | $-2, -4$ | $-4, 3$        | $\sqrt{38}$ | $\sqrt{36}$ | $\sqrt{34}$ | $\sqrt{2}$ | Chiral |
| 7, $-2$         | $-6, -3$ | $-1, 5$        | $\sqrt{57}$ | $\sqrt{54}$ | $\sqrt{51}$ | $\sqrt{3}$ | Chiral |
| 5, $-4$         | $2, 5$   | $-7, -1$       | $\sqrt{57}$ | $\sqrt{54}$ | $\sqrt{51}$ | $\sqrt{3}$ | Chiral |
| 2,6             | $-8, -2$ | $6, -4$        | $\sqrt{76}$ | $\sqrt{72}$ | $\sqrt{68}$ | 2 | Chiral |
| $-4, 7$         | $-6, -6$ | $10, -1$       | $\sqrt{114}$ | $\sqrt{108}$ | $\sqrt{102}$ | $\sqrt{6}$ | Chiral |
| 8, $-5$         | $-10, -2$| $2, 7$         | $\sqrt{114}$ | $\sqrt{108}$ | $\sqrt{102}$ | $\sqrt{6}$ | Chiral (A) |

| 2nd Family      |          |                 |         |
| 0,4             | $5, -2$  | $-5, -2$       | $\sqrt{32}$ | $\sqrt{33}$ | $\sqrt{33}$ | 1 | Achiral |
| 8,0             | $-4, 5$  | $-4, -5$       | $\sqrt{64}$ | $\sqrt{66}$ | $\sqrt{66}$ | $\sqrt{2}$ | Achiral |
| 8, $-4$         | $1, 7$   | $-9, -3$       | $\sqrt{96}$ | $\sqrt{99}$ | $\sqrt{99}$ | $\sqrt{3}$ | Chiral, two $\sqrt{3}$ transformations produce same lattice |

| Others          |          |                 |         |
| 0,6             | $7, -3$  | $-7, -3$       | $\sqrt{72}$ | $\sqrt{67}$ | $\sqrt{67}$ | Achiral |
| 3,6             | $9, -1$  | $6, -5$        | $\sqrt{81}$ | $\sqrt{83}$ | $\sqrt{86}$ | Chiral |
| $-5, 6$         | $10, 0$  | $-5, -6$       | $\sqrt{97}$ | $\sqrt{100}$ | $\sqrt{97}$ | Achiral |
| $-7, 5$         | $10, 2$  | $-3, -7$       | $\sqrt{99}$ | $\sqrt{108}$ | $\sqrt{107}$ | Chiral, variation on A |

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Figure 1. Members of a family of pseudo-hexagonal lattices found on fcc{110} surfaces. (a) The two enantiomers associated with the smallest member of the family, (b) one enantiomer of the second member, larger by $\sqrt{2}$, (c) and (d) are alternative lattices, not enantiomers, which are $\sqrt{3}$ larger than those in (a). In each case, the shortest (longest) vector is indicated in blue (green). In all members of the family, the angular separations between vectors are the same as those given in (a).

Considering the families in more detail, we find that the smallest is defined by the three vectors $1, 3; -4, -1; 3, -2$, which have lengths $\sqrt{(m^2 + 2n^2)}a$, namely $\sqrt{19}a$, $\sqrt{18}a$, $\sqrt{17}a$ and angular separations clockwise from $1, 3$ of 122.7°, 117.2° and 120.1°. This set is appropriate for the consideration of coronene/Cu{110}. The next member of this family, with vectors $\sqrt{2}$ longer hence $\sqrt{38}a$, $\sqrt{36}a$ and $\sqrt{34}a$, is $6, 1; -2, -4, 3$. The two alternative lattices, which are $\sqrt{3}$ times longer hence $\sqrt{57}a$, $\sqrt{54}a$, $\sqrt{51}a$, are then $7, -2; -6, -3; -1, 5$ and $-5, 4; -2, -5; -1, 7$. These two alternative lattices are relevant to the case of HtB-HBC/Cu{110} [12] vide infra. It should be noted that some lattices give rise to chiral arrays but this is not the case if one of the vectors lies parallel to a principal substrate axis $1, 0$ or $0, 1$ and the other pair are related by reflection across this axis.

All three vectors, which define the nearest neighbours in the pseudo-hexagonal structure, are indicated, although only two such vectors are required to define the unit cell, since this more clearly shows the relationship between family members and the distortion from perfect hexagonality.
Table 2. The transformations, which permit larger members of a family of pseudo-hexagonal lattices to be generated from the smallest member \( m,n \).

| Vector transformation | Length/\( a \sqrt{(p^2 + 2q^2)} \) |
|-----------------------|-----------------------------------|
| \( m,n \)            | 1                                 |
| \( 2n,m \)           | \( \sqrt{2} \)                     |
| \( m + 2n, m - n \)  | \( \sqrt{3} \)                     |
| \( m - 2n, m + n \)  |                                    |
| \( 2m,2n \)          | \( \sqrt{4} = 2 \)                 |
| \( 2(m - n), m + 2n \)| \( \sqrt{6} \)                     |
| \( 2(m + n), m - 2n \)|                                    |
| \( 4n,2m \)          | \( \sqrt{8} = 2\sqrt{2} \)        |
| \( 3m,3n \)          | \( \sqrt{9} = 3 \)                 |
| \( -m + 4n, 2m + n \)|                                    |
| \( -m - 4n, 2m - n \)|                                    |

Table 3. The families of pseudo-hexagonal lattices on an fcc\{100\} substrate defined by the lattice vectors defining the nearest neighbour positions.

| Lattice vectors | Length/\( a \) | Relative length | Comment |
|-----------------|---------------|----------------|---------|
| 1st Family | | | |
| 1,4 | -4, -1 | 3, -3 | \( \sqrt{17} \) | \( \sqrt{17} \) | \( \sqrt{18} \) | 1 | Achiral |
| -3, 5 | -3, -5 | 6,0 | \( \sqrt{34} \) | \( \sqrt{34} \) | \( \sqrt{36} \) | \( \sqrt{2} \) | Achiral |
| 2,8 | -8, -2 | 6, -6 | \( \sqrt{68} \) | \( \sqrt{68} \) | \( \sqrt{72} \) | \( \sqrt{4} = 2 \) | Achiral |
| -2, 9 | 7, -6 | 9,3 | \( \sqrt{85} \) | \( \sqrt{85} \) | \( \sqrt{90} \) | \( \sqrt{5} \) | Chiral |
| 2nd Family | | | |
| 1,6 | -6, -2 | 5, -4 | \( \sqrt{37} \) | \( \sqrt{40} \) | \( \sqrt{41} \) | 1 | Chiral |
| -5, 7 | -4, -8 | 9,1 | \( \sqrt{74} \) | \( \sqrt{80} \) | \( \sqrt{82} \) | \( \sqrt{2} \) | Chiral |
| 3rd Family | | | |
| 5, -5 | -7, -2 | 2,7 | \( \sqrt{50} \) | \( \sqrt{53} \) | \( \sqrt{53} \) | 1 | Achiral |
| 10,0 | -5, -9 | -5, 9 | \( \sqrt{100} \) | \( \sqrt{106} \) | \( \sqrt{106} \) | \( \sqrt{2} \) | Achiral |
| Others | | | |
| 0,8 | -7, -4 | 7, -4 | \( \sqrt{64} \) | \( \sqrt{65} \) | \( \sqrt{65} \) | 1 | Achiral |
| 3,7 | 5, -6 | -8, -1 | \( \sqrt{58} \) | \( \sqrt{61} \) | \( \sqrt{65} \) | 1 | Chiral |
| 4,8 | -9, 0 | 5, -8 | \( \sqrt{80} \) | \( \sqrt{81} \) | \( \sqrt{89} \) | Chiral |
| 7,7 | -10, 3 | 3, -10 | \( \sqrt{98} \) | \( \sqrt{109} \) | \( \sqrt{109} \) | Chiral |
| 7,8 | -10, 2 | 3, -10 | \( \sqrt{113} \) | \( \sqrt{104} \) | \( \sqrt{109} \) | Chiral |

2.2. Pseudo-hexagonal lattices on fcc\{100\} surfaces

A similar situation arises for the \{100\} surfaces except that the substrate unit cell vectors both have length \( a \), such that the lattice vectors \( m,n \) now have lengths \( \sqrt{(m^2 + n^2)a} \). Family members then follow a sequence \( 1, \sqrt{2}, \sqrt{4}, \sqrt{5}, \sqrt{8}, \sqrt{9} \ldots \sqrt{r} \ldots \), where \( r \) is now an integer obeying \( p^2 + q^2 = r^2 \). Again, within the same arbitrary constraints of length and angle on the definition of pseudo-hexagonality, families of lattices appear as indicated in table 3, although in this case, the
Table 4. The transformations, which permit larger members of a family of pseudo-hexagonal lattices to be generated from the smallest member \( m, n \).

| Vector transformation | Length \( /a\sqrt{(p^2 + q^2)} \) |
|-----------------------|----------------------------------|
| \( m,n \)             | 1                                |
| \( m - n, m + n \)     | \( \sqrt{2} \)                  |
| \( 2m,2n \)            | \( \sqrt{4} = 2 \)              |
| \( m - 2n, m + 2n \)   | \( \sqrt{5} \)                  |
| \( 2(m - n), 2(m + n) \)| \( \sqrt{8} = 2\sqrt{2} \)      |

Figure 2. Structure of coronene showing the molecular size including the vdW radii (1 Å) of the peripheral hydrogen atoms for comparison with the unit cell of a Cu\{110\} substrate. The diameter of the encompassing circle is 11.6 Å and the width of the hexagon 11.26 Å.

higher symmetry of the \{100\} surface relative to the \{110\} surface limits the number of chiral arrays, since those symmetrical with respect to the 1,1 as well as 1,0 and 0,1 directions are excluded. The transformations, which link members of increasing lattice size within any family, are given in table 4. The smallest member of the first family, i.e. with vectors 1, 4; \(-4, -1\) and 3, \(-3\) is relevant to the case of coronene on Cu\{100\} [2] as briefly discussed below.

3. Coronene adsorption on Cu\{100\} and Cu\{110\}

Coronene, C\(_{24}\)H\(_{12}\), considered as circular has a vdW diameter of 11.6 Å or as a hexagon with a width of 11.26 Å, implying areas per molecule of 105.7 and 109.8 Å\(^2\), respectively (figure 2). More relevant is that hexagonal close-packing of circular or hexagonal objects requires unit cells of 116.1 and 109.8 Å\(^2\), respectively, the latter being substantially less than the former by being space filling. This describes well the behaviour of coronene adsorption on hexagonal substrates. On graphite, coronene forms a \((\sqrt{21} \times \sqrt{21}) \pm R10.9^\circ\) structure corresponding to an intermolecular spacing of 11.27 Å and a unit cell of 110.1 Å\(^2\) [5, 9]. On MoS\(_2\), the corresponding length is 11.18 Å and a \((\sqrt{13} \times \sqrt{13})R \pm 13.9^\circ\) unit cell of 108.2 Å\(^2\) [9, 10]. On Ag\{111\} the intermolecular spacing is 11.54 Å in a \((4 \times 4)\) superstructure and a unit cell of 115.3 Å\(^2\) [4, 5]. Coronene on Au\{111\} behaves similarly also forming a \((4 \times 4)\) superstructure at
monolayer saturation coverage and therefore a similar area per unit cell of 114.8 Å² [3], [6]–[8].

In the case of adsorption on Cu{100}, Schuerlein et al [2] report, on the basis of LEED measurements, a \( p(4 \times 7) \) structure containing two molecules per unit cell with two rotational domains. Although the structure is commensurate, the molecules are proposed to occupy both four-fold hollow and bridge sites. This structure provides an area per molecule of only 91.4 Å², markedly less than found in the hexagonal systems with no evidence that the molecules adopt other than a flat-lying geometry. Before proposing an alternative structure for this system, it should be noted that there is some opportunity to reduce the intermolecular spacing by interdigitation of the peripheral C–H bonds on adjacent molecules. Although coronene formally has \( D_{6h} \) symmetry, the H atoms are almost equally spaced around the molecular periphery suggesting that the lateral, vdW interaction potential has almost 12-fold symmetry. The scope for interdigitation is small but a concerted rotation of all molecules by 8.4° allows a reduction of the intermolecular spacing to 10.90 Å and a unit cell of 102.9 Å². However, this is still almost 13% larger than that provided by the proposed \( p(4 \times 7) \) structure.

Consideration of table 3 shows that the smallest pseudo-hexagonal unit cell on an fcc{100} surface corresponds to nearest neighbour lattice vectors of 1, 4, –4, –1 and 3, –3, which have relative lengths of \( \sqrt{17}a \), \( \sqrt{17}a \) and \( \sqrt{18}a \) corresponding for copper, where \( a = 2.555 \) Å, to 10.53, 10.53 and 10.84 Å respectively. The unit cell area corresponds to 15 substrate unit cells as opposed to 14 in the \( p(4 \times 7) \) structure that is to an enlarged unit cell of 97.9 Å² reducing the discrepancy to 5%. A comparison of the first order diffraction spots in the LEED patterns arising from the two structures is given in figure 3. Although the difference between the two structures

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**Figure 3.** Comparison of the measured and simulated LEED pattern (red spots) arising from the \( p(4 \times 7) \) unit cell of coronene on Cu{100}, with two molecules per unit cell in different adsorption sites, as proposed by Schuerlein et al [2] with that (blue spots) from the alternative \( \{ 4,1; -1,-4 \} \) structure based on a pseudo-hexagonal commensurate lattice with all molecules occupying equivalent sites. See text for further details.
in the separation of the spots from the 0,0 beam is only \(~3\%\), the angular position of the beams is clearly different. Unfortunately, it is not possible to resolve the discrepancy from the published LEED pattern since its precise orientation, relative to the high-symmetry directions of the substrate, is not given but it is to be noted that the orientation of the measured pattern is at odds with the LEED simulation for the \((p(4 \times 7))\) structure shown by Schuerlein et al [2]. It is suggested that the molecules adopt this alternative structure in which all molecules occupy the same adsorption site with pseudo-hexagonal close packing and rotation of the molecules within the 2D layer to allow interdigitation of the C–H bonds.

The LEED pattern and an STM image arising from the adsorption of a saturated monolayer of coronene on Cu\((110)\) are shown in figure 4 [14]. The results are consistent with the formation of a \((3,–2;\ 1,3)\) structure and its mirror image \((3,2;\ 1,–3)\). The area of these unit cells, which corresponds to 11 substrate unit cells, is \(101.6\ \text{Å}^2\). The structure is the smallest pseudo-hexagonal lattice for an fcc\((110)\) surface as shown in table 1. The nearest neighbour lattice vectors are \(3,–2,–4,–1\) and \(1,3\) with lengths \(\sqrt{17}a\), \(\sqrt{18}a\) and \(\sqrt{19}a\) i.e. 10.53, 10.84 and 11.14 Å. These dimensions and the area of the molecular unit cell fit very well with those of the close-packed molecular layer, if interdigitation of the C–H bonds is again invoked.

The concerted rotation required to achieve this interdigitation reduces the site symmetry of the molecules even within the 2D layer from C\(_6\) to C\(_3\) and this introduces local chirality depending on whether rotation is clockwise or anticlockwise with respect to the unit cell of the 2D array. The distortion of the hexagonal lattice needed to fit to a \(\{110\}\) substrate additionally introduces the element of array chirality depending on whether the \(\sqrt{17}a\), \(\sqrt{18}a\) and \(\sqrt{19}a\) form a clockwise or anticlockwise sequence. The two distinct aspects of chirality lead to four diastereoisomers in two energetically distinct enantiomer pairs. Since the sequence depends on the choice of sub-lattice \((3,–2;\ 1,3)\) or its mirror image \((3,2;\ 1,–3)\), this will favour a correlation between the direction of molecular rotation and the choice of sub-lattice with the more energetically favourable pair determined by the better interdigitation along the shortest \((\sqrt{17}a)\) lattice vector. This effect is illustrated in figure 5. A similar effect has been recognized.
Figure 5. Structure of coronene on Cu{110} showing the correlation between the site chirality defined by the rotation ($8.4^\circ$) of the molecule with respect to the 2D unit cell vectors and the choice of enantiomeric array defined by the unit cell orientation with respect to the substrate lattice. The preferred choice of array $(3,-2; 1,3)$, for molecules rotated anticlockwise, is shown by the continuous outline. The alternative shown as the dashed outline leads to steric hindrance between H atoms on neighbouring molecules.

by Schöck et al [12] in the case HtB-HBC on Cu{110}, a system which we consider next in some detail.

4. HtB-HBC adsorption on Cu{110}

Here, we develop further some ideas presented in a recent paper by Schöck et al [12], who drew attention to the unlikely case of chirality in the highly symmetric molecule, HtB-HBC, shown in figure 6, when adsorbed to monolayer coverage on a Cu{110} surface. Focus is placed particularly on the key role played by the substrate lattice with consideration of crucial aspects of the adsorbate–adsorbate and adsorbate–substrate interactions, whose subtle balance is the key to understanding the observed structure and its chirality. Attention is then drawn to an alternative, energetically very similar structure for this adsorbate system, the consideration of which could allow information on the nature of the adsorbate-induced strains on the copper lattice to be obtained.

The key observations by Schöck et al [12] were that the molecules order in two, mirror equivalent domains characterized by the structure \( \{7,2;-1,-5\} \) termed the L lattice and \( \{7,-2;-1,5\} \) the R lattice\(^2\), individual molecules exhibit point chirality by being rotated either \( \alpha = +5^\circ \) (anticlockwise) or \( \alpha = -5^\circ \) (clockwise) with respect to the substrate, high symmetry 1, 0 direction and crucially the clockwise (anticlockwise) rotation is exclusively associated with

\(^2\) Schöck et al [12] choose, perfectly correctly, to describe the R lattice as \( \{6,-3; 1,5\} \) while we prefer an alternative description, which emphasizes the mirror relationship to the L lattice across the 1,0 axis.
Figure 6. The HtB-HBC molecule is shown above a four-fold hollow site and twisted by an angle $-\alpha$ with respect to the close-packed direction of a Cu[110] lattice. Key lattice vectors, relevant to the ordered structures observed in this adsorption system \cite{12} are defined.

The L (R) lattice (figure 6). They show, on the basis of MM2 force field calculations, that the single molecules have a preference to rotate by $\pm 5^\circ$ and that the correlation between the direction of rotation and the lattice ensures that the steric hindrance of the peripheral $t$-butyl groups on the adjacent molecules is avoided. We fully accept these conclusions but believe further interesting conclusions can be drawn from this fascinating example of adsorption-induced chirality in a highly symmetric molecule and the mapping of hexagonal symmetry on to an fcc{110} surface.

Schöck et al \cite{12} appropriately chose to discuss the adsorption behaviour as that of a six-pointed, star shaped molecule with rotations being defined by reference to a line joining the points of the star, i.e. the peripheral $t$-butyl groups. We continue this analogy and their notation for the rotation and then extend their L,R notation for the ordered lattices.

If the structure of HtB-HBC is initially further simplified and treated as a hexagon enclosing the star at its vdW periphery then such molecules would be expected to form a simple, hexagonally close-packed array as indicated in figure 7. In this arrangement, we define the molecular centre-to-centre separation as having unit length and the unit cell basis vectors of the hexagonal array, which link the neighbouring molecular centres, as rotated $\theta = 30^\circ$ from the direction from centre-to-point of star, as shown in figure 7. As noted by Schöck et al \cite{12}, this is not the closest packed structure, however, for six-pointed stars.

Figure 8 shows how the nearest neighbour, centre-to-centre separation varies with rotation of the molecules with respect to the unit cell vectors of the array, which remains hexagonal, with molecules allowed to touch at their vdW envelope but not to overlap. The greatest separation (1.16) is found at $0^\circ$ rotation when adjacent stars touch at a single point. The ‘hexagonal’ star, which has neighbours with two touching points and defined as the separation of 1, is found at a rotation of $30^\circ$ but the optimum, closest packed arrangement is found at a rotation, $\theta = 10.9^\circ$, when the separation is reduced to 0.88. An immediate consequence of this rotation is a loss of site symmetry of the molecule. The site symmetry of the molecule at a rotation of $0^\circ$ or
Figure 7. The star and hexagon, which enclose the HtB-HBC molecule, of width 18.7 Å, are shown together with close-packing of the hexagons, defining a centre-to-centre separation of unity at a rotation of $\theta = 30^\circ$, defined in terms of the twist of the points of the star relative to the unit cell vectors of the 2D array.

30° is $C_{6v}$, while at all other angles it is only $C_6$ and crucially there are no mirror planes. This introduces chirality into the system and mirror equivalent lattices exist corresponding to clockwise or anticlockwise rotation of the molecule with respect to the unit cell vectors of the 2D hexagonal Bravais lattice. Note that this chirality is introduced regardless of the underlying structure of the substrate and derives solely from the site symmetry within the 2D layer.

The HtB-HBC molecule has a width, including the vdW radii of the peripheral hydrogen atoms, of $\sim 18.7$ Å across the hexagon (figure 7) and this would therefore be the centre-to-centre separation at 30° rotation. Optimal packing as six-pointed stars, at a rotation of 10.9°, would allow this separation to be reduced to 16.5 Å. At this stage, it is useful to consider the available, pseudo-hexagonal lattices of an fcc{110} substrate. The lattice observed by Schöck et al [12] for HtB-HBC/Cu{110} has nearest neighbour separations of $\sqrt{51}a$, $\sqrt{54}a$ and $\sqrt{57}a$, i.e. 18.2, 18.7 and 19.3 Å, corresponding to the unit cell vectors $-1,5; -6,-3; 7,-2$. This particular lattice belongs to a family of equivalently distorted, pseudo-hexagonal lattices on fcc{110} surfaces (see table 1), of which the smallest member is observed for the adsorption of coronene on Cu{110}. Since the adsorbate–substrate interaction is dominant enough to enforce a commensurate overlayer, clearly congestion of the $t$-butyl groups will occur along the $-1,5$ direction, unless there is some appropriate concerted rotation of all molecules. To avoid overlap of the stars at the separation of the shortest vector, 18.2 Å, a rotation-induced reduction of the hexagonal lattice to at least $0.97 = 18.2/18.7$ is necessary, shown by the blue horizontal line cutting the curve of figure 8. This can be achieved by rotations, $\theta$, between 6.5° and 27° (black axis in figure 8), relative to the 2D array unit cell vectors. This is equivalent to rotations, $\alpha$, between $-15.5^\circ$ and $+5^\circ$ (red axis in figure 8) relative to the substrate 1,0.

The choice is made from the ten point groups, which are relevant to 2D arrays of adsorbed molecules rather than those of isolated 2D molecular arrays.

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Figure 8. The minimum centre-to-centre separation of six-pointed stars, avoiding overlap, as a function of the rotation $\theta$, defined as the angle between the line joining the centre of the two stars and the line joining the points of a star as shown in figure 2. We define unit separation as that which occurs at $\theta = 30^\circ$. Alternative $x$ axes are shown, which allow the rotation angle $\theta$ to be converted to a rotation angle, $\alpha$, with respect to the substrate lattice for two alternative lattices, based on nearest neighbour vectors $7, -2$ (A lattice) and $7, -1$ (B lattice) as discussed in the text. The horizontal line at a separation of 0.97 is the condition below which the overlap of star-shaped, HtB-HBC molecules, in a pseudo-hexagonal lattice on Cu{110}, is avoided. The vertical red and blue arrows indicate points on the curve corresponding to $\pm 5^\circ$ rotation with respect to the substrate 1,0 direction for lattices A and B, respectively. The insert shows the chiral arrays arising from clockwise or anticlockwise rotation of the molecules, with respect to the 2D unit cell.

direction, if the molecules are arranged on the L lattice noted by Schöck et al [12], based on the $7, -2$ unit cell vector, which itself has a clockwise rotation of $22^\circ$ from the 1,0 direction (figure 6). For this particular molecule and the nature of the bulky t-butyl groups, which form the points of the star, it is likely that a greater reduction in lattice size to $< 0.97$ will be required and, therefore, to an even narrower range of angles around the optimal packing angle of $\theta = 10.9^\circ$ ($\alpha = -11.1^\circ$). Nevertheless, even without this further likely constraint, we note that, since the $7, -2$ vector makes a $22^\circ$ angle to the substrate 1,0 direction, an $\alpha = +5^\circ$ rotation of the molecule anticlockwise ($+5^\circ$, L in the notation used by Schöck et al [12]) with respect to this 1,0 direction, i.e. $\theta = 27^\circ$ (right-hand red arrow in figure 8) relative to the 2D array unit vector aligned along $7, -2$ is already at the limits for avoiding t-butyl steric overlap, as shown in their supporting modelling. Clockwise rotation ($-5^\circ$, L), on the other hand, allows better interdigitation of the star points and would permit, even for a perfect star-shaped molecule, a reduced separation of 0.91 (left-hand red arrow in figure 8), i.e. down to 17.0 Å, which is well inside the commensurate lattice distance along $-1, 5$ of 18.2 Å.
Schöck et al [12] have argued that the anticlockwise rotation of $\alpha = -5^\circ$ is required to optimize the interaction of individual molecules with respect to the substrate lattice and have supported this with appropriate calculations of a single molecule on the Cu[110] surface. However, it is also the case that the optimal molecular rotation is that at which the molecules just touch thereby maximizing the vdW interadsorbate interactions within the 2D adsorbate lattice, at the separation enforced by the need for a commensurate relationship with the substrate lattice. Allowing for the more complex shape because of the $t$-butyl substituents, it seems that both these contributions may be satisfied by the observed structure of HtB-HBC on Cu[110].

There is a further important aspect of this chemisorption system, which has not yet been described. A consideration of pseudo-hexagonal lattices on fcc[110] surfaces indicates that, when the nearest neighbour separations are $\sqrt{57}a$, $\sqrt{54}a$ and $\sqrt{51}a$, where $a$ is the length of the substrate $1,0$ unit vector, there are two distinct, but exactly equivalent lattices, in the sense of the lengths of their unit vectors and their included angles, as seen from tables 2 and 3. Schöck et al recognized one of these, namely $7, -2; -6, -3; -1, 5$; the alternative is $-5, -4; -2, 5; 7, -1$. There are therefore eight networks, rather than the four previously identified, which need to be considered, when discussing the chirality of this system. We refer to these distinct lattices as the A and B structures respectively. Of course, each has a mirror equivalent, e.g. $A_L$ and $A_R$ and molecules can be rotated clockwise or anticlockwise within the lattice. In the new $B_L$ structure, the $7, -1$ vector, rather than the $-1, 5$ of the $A_L$ structure, is now the shortest, (18.2 Å), and at $11.4^\circ$ closest to the $1, 0$ substrate unit vector in angular separation. If packing of HtB-HBC on this alternative B lattice is considered then rotations between $\theta = 6.5^\circ$ and $\theta = 27^\circ$, with respect to the adsorbate array unit cell vectors, now correspond to rotations between $\alpha = -4.9^\circ$ and $\alpha = 15.6^\circ$ relative to the substrate $1,0$ direction as shown by the blue axis in figure 8. Again this range may well be reduced further by the more complex structure of the molecule. The blue vertical arrows in figure 8 identify the conditions for $\pm 5^\circ$ rotation with respect to the substrate. The $-5^\circ$ rotation clearly gives rise to steric hindrance in the $t$-butyl groups but, with $+5^\circ$ rotation, this is avoided. It is particularly intriguing that a $\alpha = +5.3^\circ$ rotation, with respect to the substrate for the $B_L$ lattice, is almost equivalent to a $\alpha = -5.3^\circ$ rotation with respect to the $A_L$ lattice (figure 9). Molecules occupy the same site; have the same azimuthal orientation ($5.3^\circ$) with respect to the substrate lattice; the adsorbate lattices are both commensurate and of exactly the same pseudo-hexagonal dimensions and the interdigitating rotation of the molecules with respect to the adsorbate lattice unit cell is the same at $\alpha = 16.7^\circ$ from the point to point direction, i.e. $5.8^\circ$ beyond the optimal packing rotation for both A and B lattices. Indeed it is not easy at first to see at what level of subtle interactions these two lattice systems do differ.

Before focusing more carefully on the distinction between these A and B lattices, it is worth digressing to consider first the chirality of a system with a distorted, 2D hexagonal array of star-shaped molecules. There is a sense of rotation associated with the sequence of the vectors linking the three nearest neighbours in that, moving from shortest through to the longest, can be either clockwise or anticlockwise and importantly this is independent of the direction of rotation of the individual molecules required to allow denser packing. The breaking of the hexagonal Bravais lattice symmetry, by the substrate imposed distortion, coupled with the molecular rotation to achieve closer packing, leads to four possibilities, in two diastereomeric pairs, which, even in the absence of a substrate, would have slightly different energies. The preference for one pair over the other pair has a contribution from the 2D adsorbate interactions but this can be substantially enhanced by the preference of the substrate for a particular, e.g. $\pm 5^\circ$ rotation of the molecule with respect to the substrate 1,0 direction. However, this is not the origin
Figure 9. A comparison of the key parameters describing the very closely related $-5.3^\circ$, $A_L$ and $-5.3^\circ$, $B_L$ lattices. Full line curved arrows refer to the rotation of the star with respect to the adsorbate unit cell vectors while the curved dotted arrows identify the sense of the hexagonal lattice distortion, denoting the direction of increasing nearest neighbour distance.

of the preference for the $A$ lattice over the $B$ lattice for HtB-HBC/Cu[110], since the 2D array required to produce the $-5^\circ$, $A_L$ structure observed by Schöck et al [12] is exactly the same in this regard as that of the alternative $+5^\circ$, $B_L$ structure (figure 9). It is clear therefore that the observed lattice, $A$, is preferred, not because of diastereomeric interactions within the 2D array, as might have been the possibility, but is related rather to the orientation of the pseudo-hexagonal array vectors with respect to the substrate lattice. It implies that the strain associated with fitting the distorted adsorbate hexagon on the substrate lattice is more easily accommodated for the $A$ arrangement than for the $B$ arrangement. Forcing molecules on to substrate lattice sites with a $\sqrt{57}a$ spacing, one which is significantly larger than the molecules would adopt in the absence of the substrate and likely to produce a compressive strain on the substrate lattice. For the $A$ arrangement this direction corresponds to the $7,-2$, direction, which is $22^\circ$ from the substrate 1,0 direction, whereas for the $B$ arrangement, the long direction is 5,4, and $48.5^\circ$ from the 1,0 substrate direction. These quite different orientations with respect to the substrate determine the relative ease with which this strain can be accommodated, and in turn the preference for the $A$ lattice. A detailed, accurate calculation will be necessary to reveal the deeper origin of this effect.

5. Conclusions

The lattice matching of highly symmetric planar hydrocarbons, which favour hexagonal close-packing, to substrates of lower symmetry is described in terms of pseudo-hexagonal lattices on fcc{100} and {100} surfaces. It is shown that this lattice matching may give rise to chiral effects both at the local and array level and consequently to diastereoisomerism. An alternative structure is proposed for coronene adsorption on Cu[100] and new results have been presented for the structure of this molecule adsorbed on Cu[110]. By considering in detail the pseudo-hexagonal lattices, which can arise on an fcc{110} surface, it is shown that alternative lattices are available for HtB-HBC on Cu[110] and the preference for one over the other is probably linked to the accommodation of strain in the substrate lattice.
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