

# Unconventional adsorption of alkane substituted naphthalene diimides on highly ordered pyrolytic graphite

## Introduction

Two dimensional self-assembled structures at the solution-solid interface are being evaluated for their application in the design of nanoscale materials and molecular devices. Scanning Tunneling Microscopy (STM) is valuable in the analysis of these structures. Many factors influence self-assembly such as intermolecular interactions, molecule-solvent interactions and molecule-substrate interactions. Understanding the factors that lead to a particular surface structure is critical for designing better materials and devices.

In this research, we investigate the self-assembled structure of  $N,N'$ -Dialkyl-1,8:4,5-naphthalenediimides ( $C_n$ -diimide) with alkane chains of varying length (C6, C8, and C12). Many alkane substituted systems exhibit linear lamellar structures due to the energetically favored Van der Waals interactions between the alkane chains (see Figure 1.) However, alkane substituted naphthalene diimides exhibit an unconventional structure.

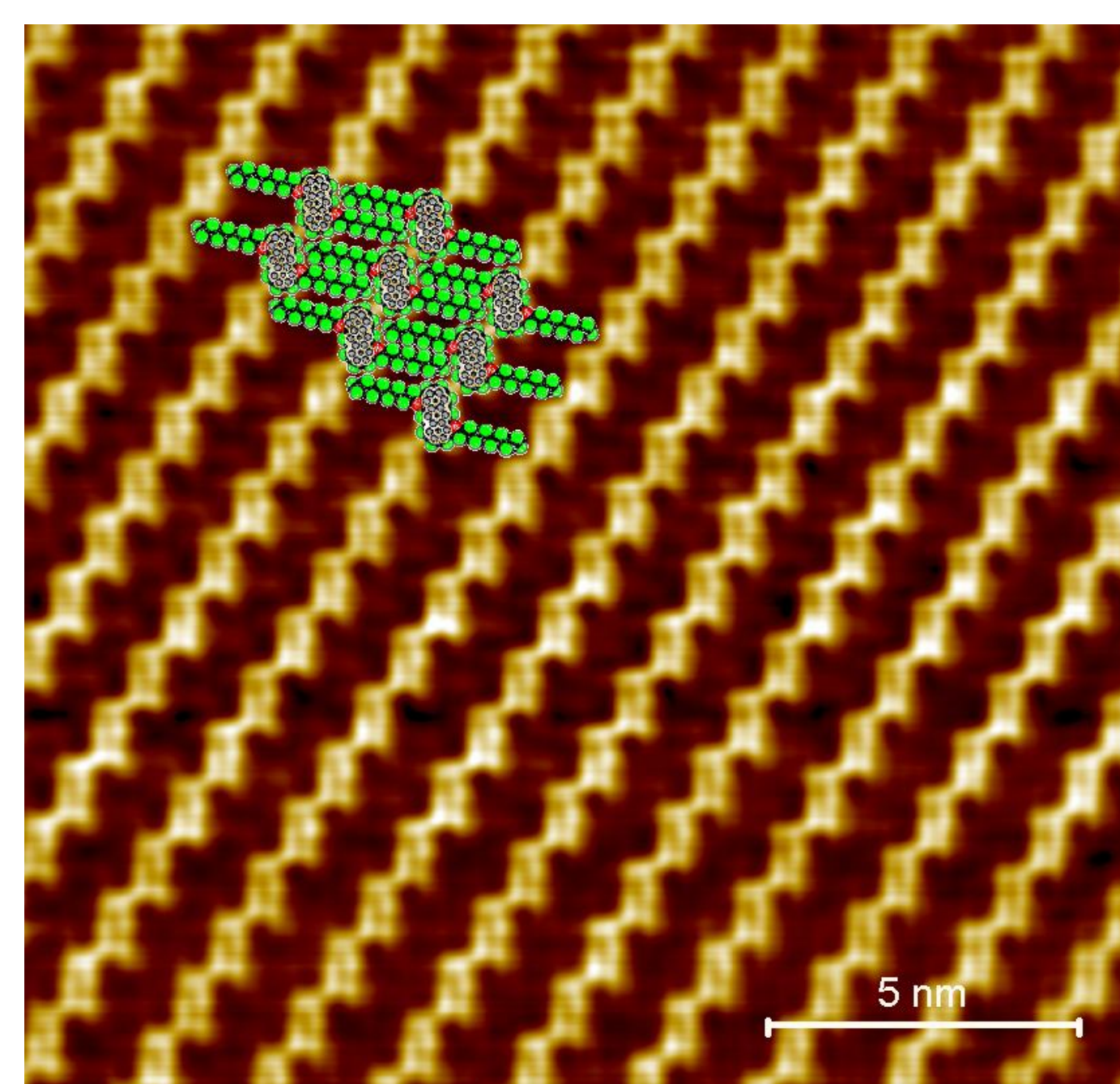


Figure 1. STM image of 1,5-di(octyloxy)anthracene in octylbenzene solution adsorbed on HOPG<sup>1</sup>.

## Experimental

Solutions of C6-diimide and C8-diimide in a solvent of *n*-octylbenzene were made at concentrations of  $1.04 \times 10^{-4}$  M and  $4 \times 10^{-4}$  M respectively. The solution of C12-diimide in a solvent of 1:1 toluene/*n*-octylbenzene was made at a concentration of  $3.32 \times 10^{-4}$  M. A few drops of solution were placed on a cleaved highly ordered pyrolytic graphite (HOPG) surface and left overnight before imaging with Digital Instruments Nanoscope E controller (now Veeco)<sup>2</sup>, software version 4, using electrochemically etched W tips. Imaging of the surface structure occurred with the tip penetrating the solution. SPIP version 4.6.4<sup>3</sup> was used for image analysis.

### Diagram of the STM Apparatus

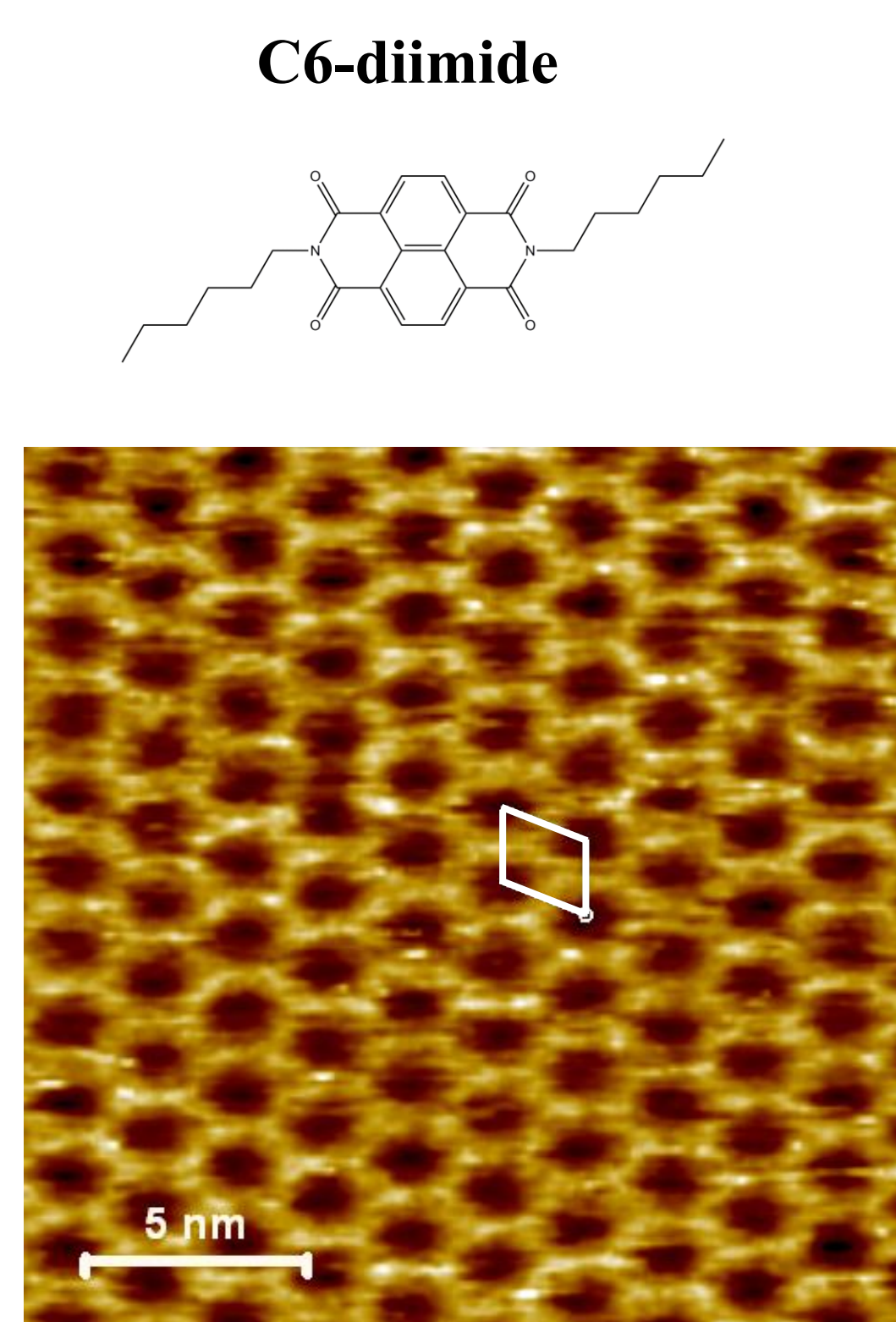
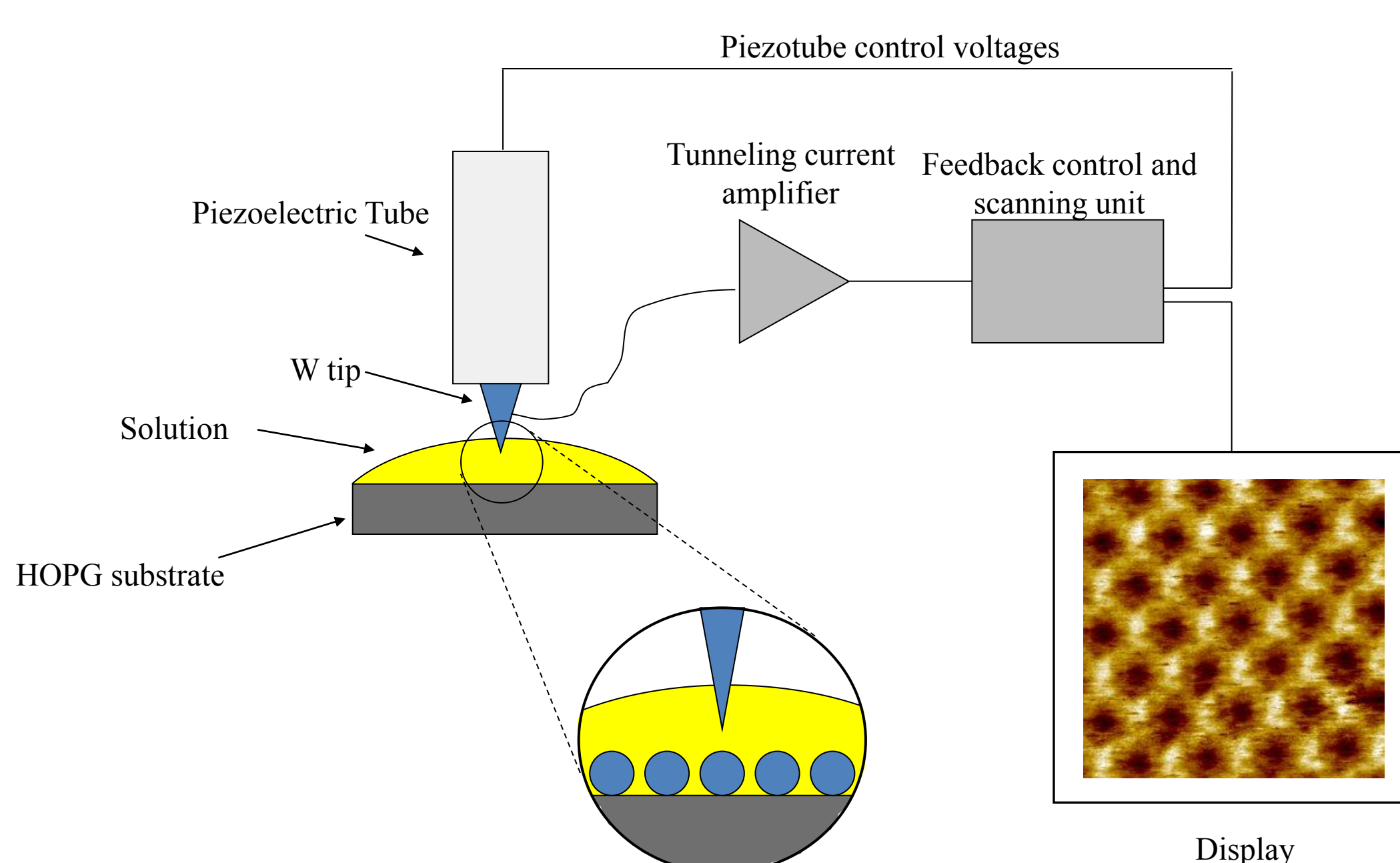


Figure 2. STM image of C6-diimide in *n*-octylbenzene solution adsorbed on HOPG with unit cell.

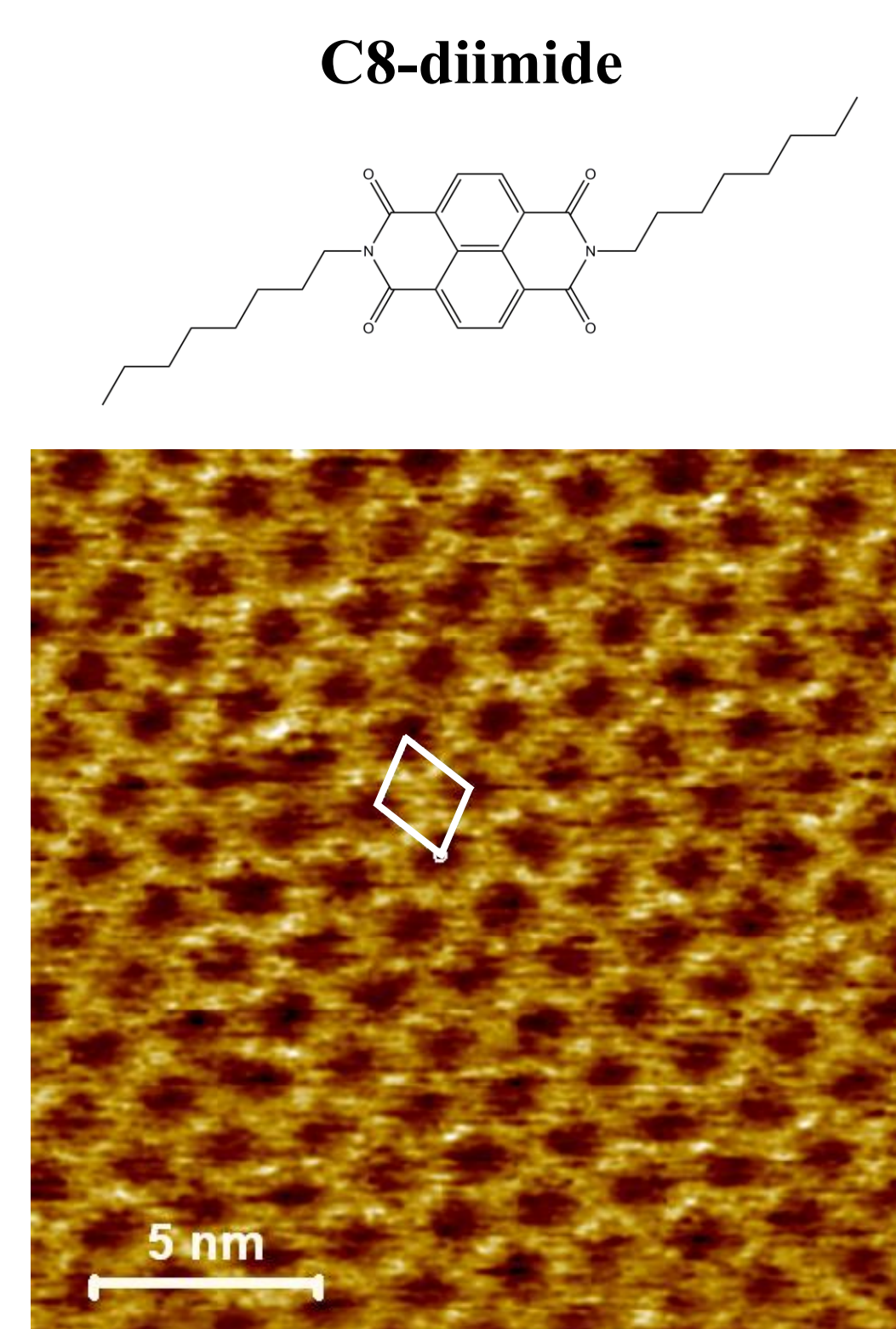


Figure 3. STM image of C8-diimide in *n*-octylbenzene solution adsorbed on HOPG with unit cell.

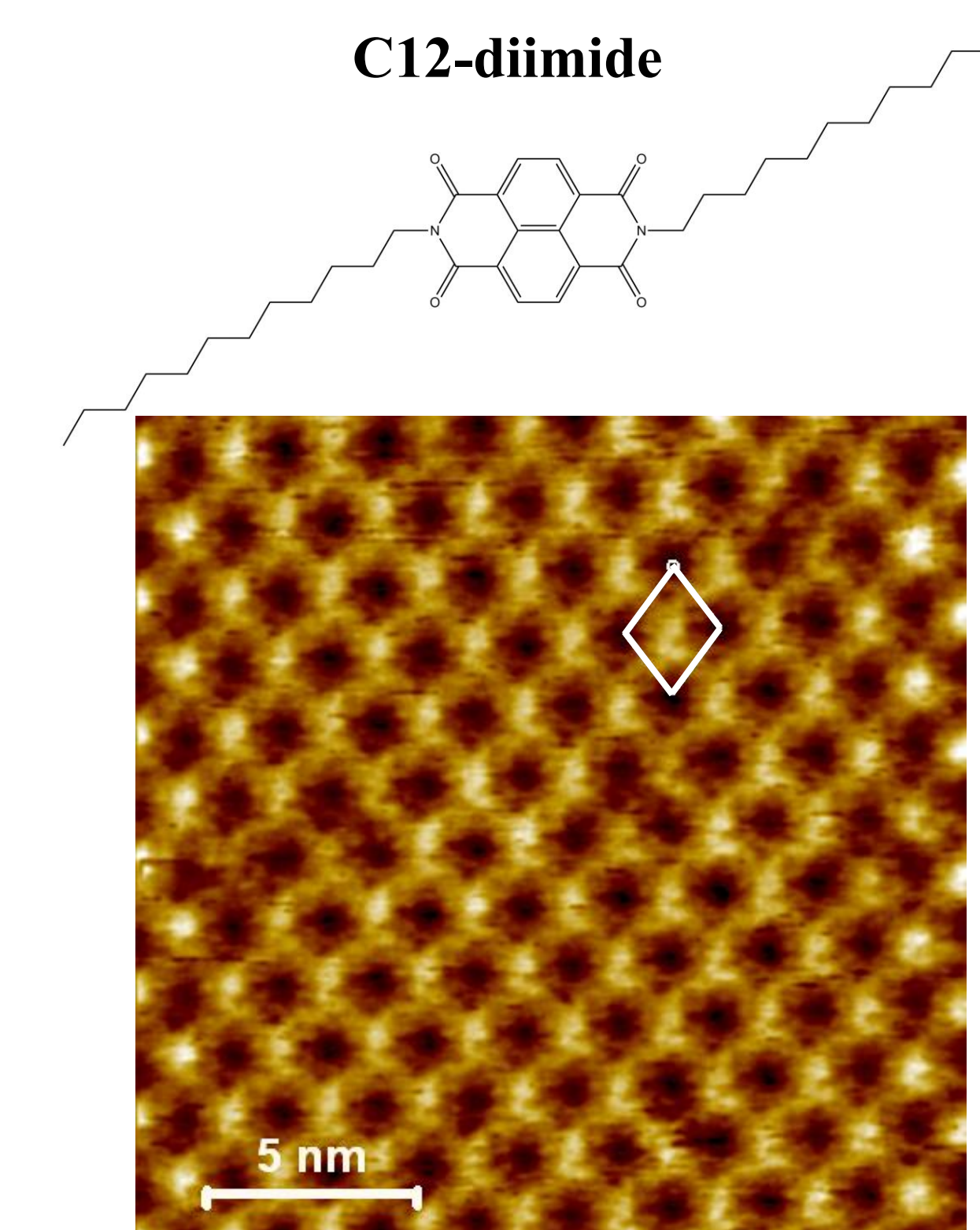


Figure 4. STM image of C12-diimide in toluene/*n*-octylbenzene solution adsorbed on HOPG with unit cell.

Sample	a	b	Angle
C6-diimide	$2.11 \pm 0.04$ nm	$1.75 \pm 0.14$ nm	$67 \pm 2^\circ$
C8-diimide	$1.98 \pm 0.25$ nm	$1.73 \pm 0.25$ nm	$68 \pm 2^\circ$
C12-diimide	$1.97 \pm 0.08$ nm	$1.92 \pm 0.08$ nm	$72 \pm 2^\circ$
C12-diimide from graphite structure	1.95	1.92	$71^\circ$

Table 1. Unit cell parameters

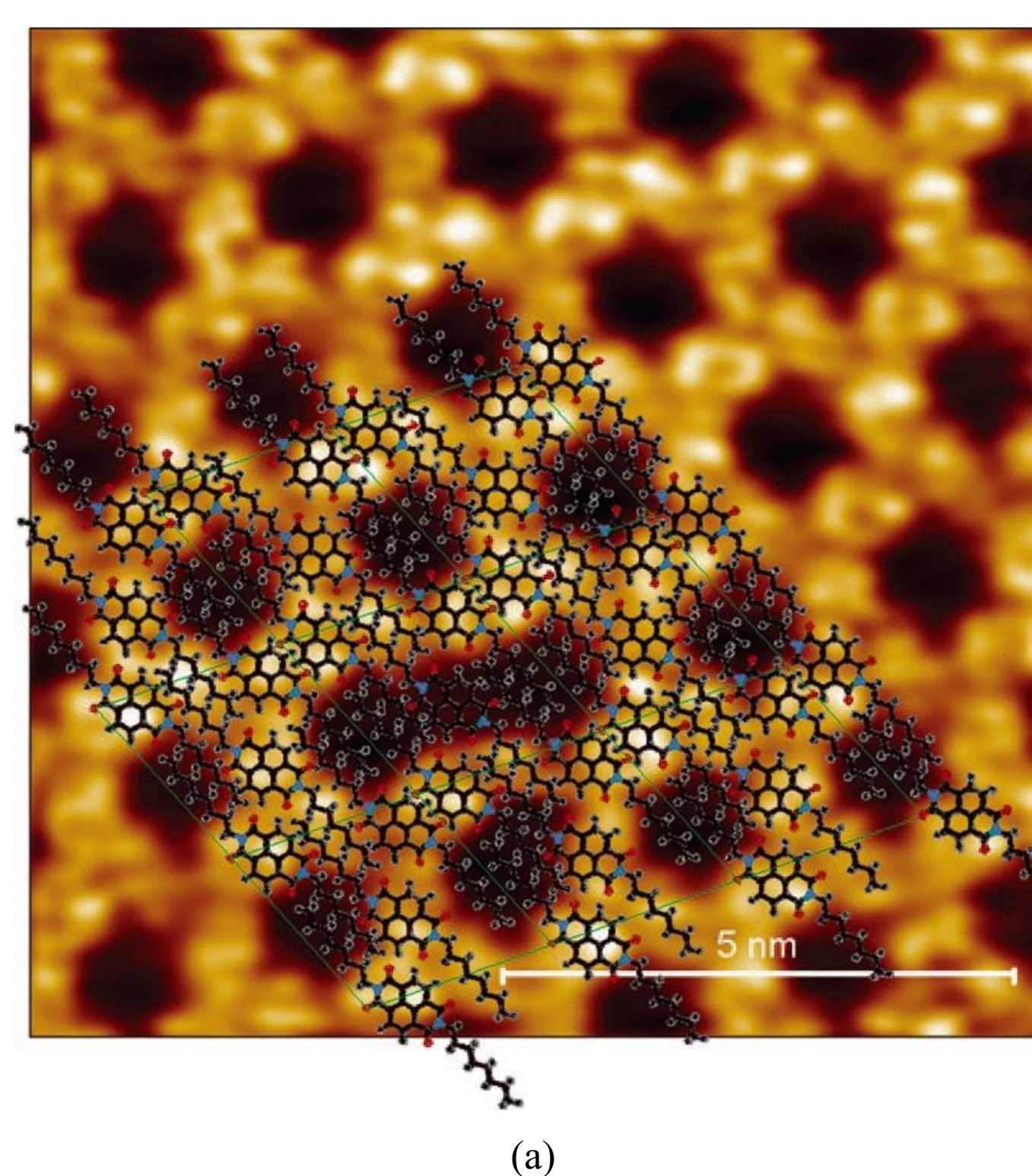


Figure 5. UHV STM image of C8-diimide with conceptual models (a) with flat alkane chains<sup>4</sup> and (b) CPK models with no alkane chains.

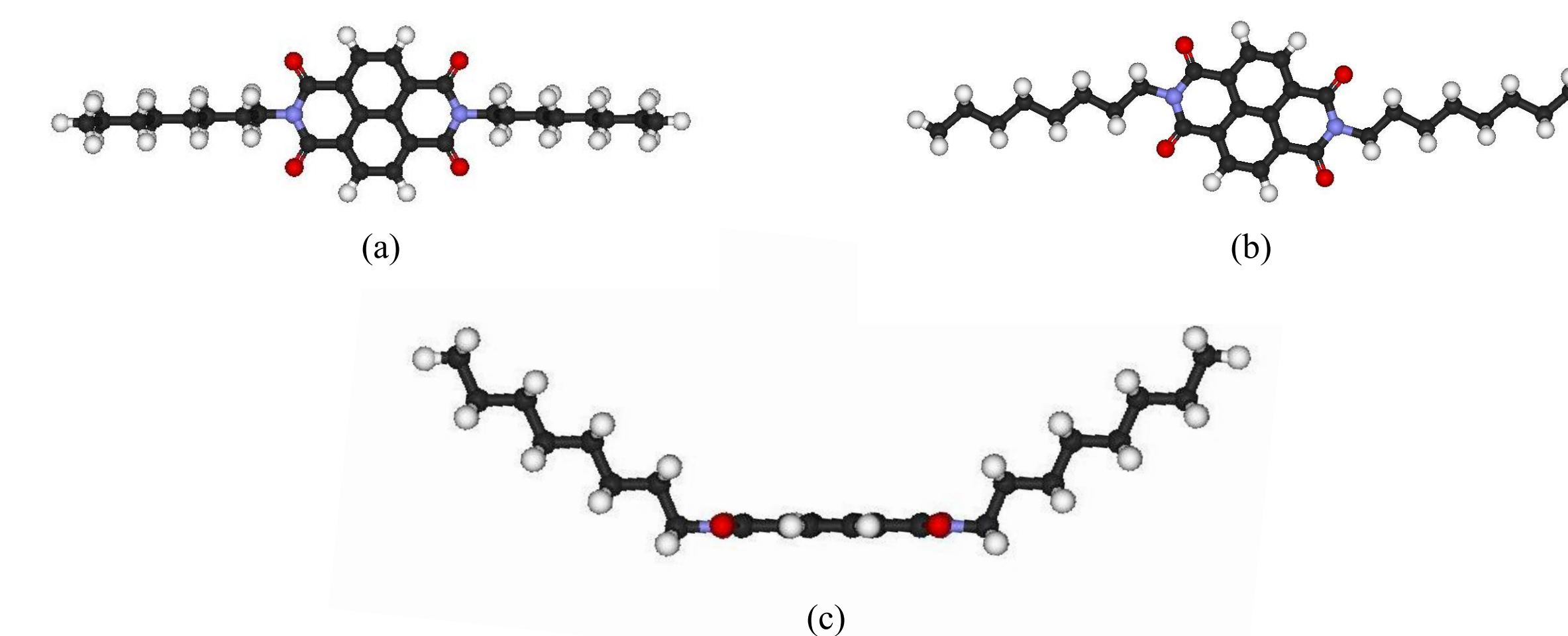
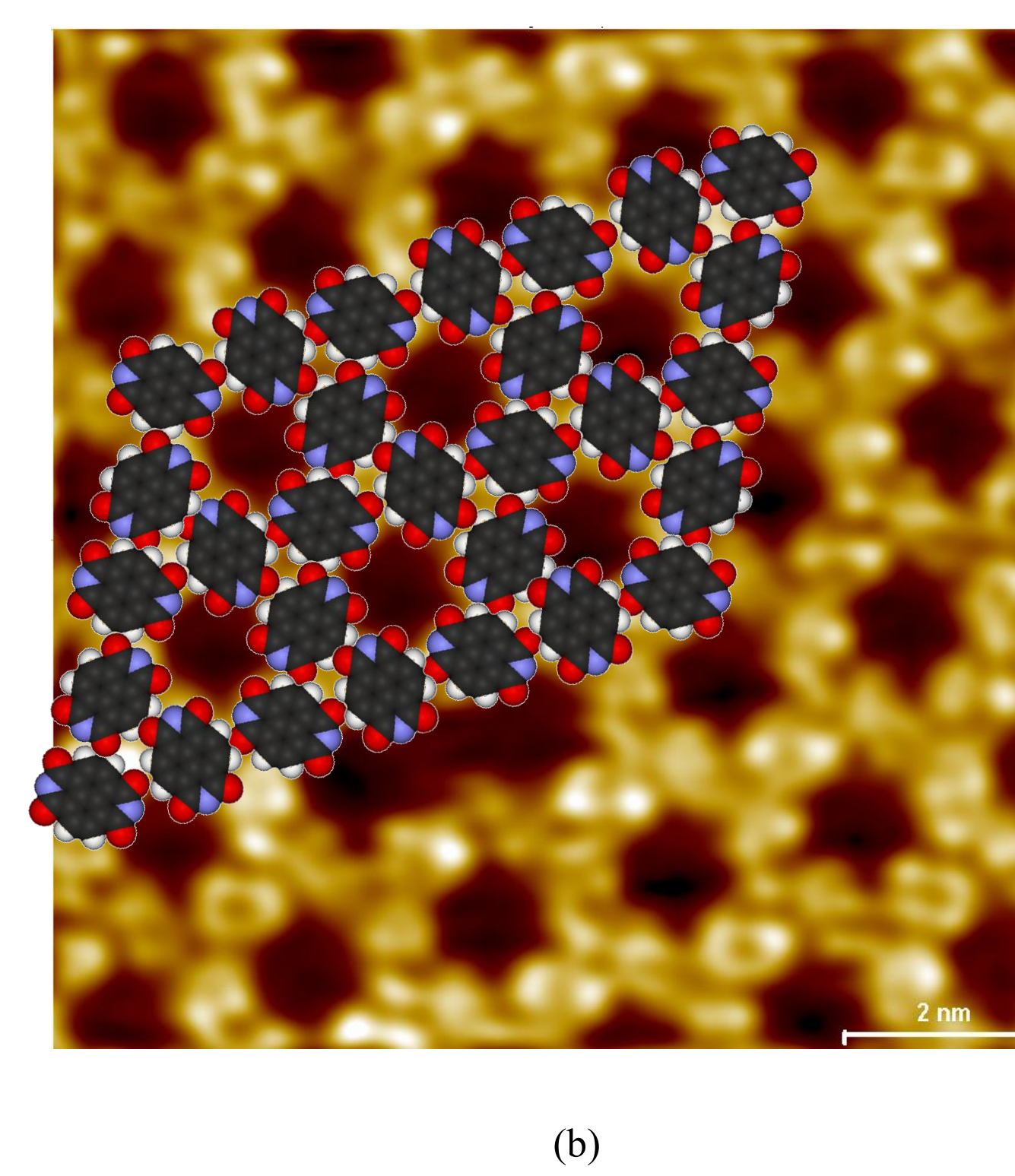


Figure 9. Ball and stick models of C8-diimide. (a) Top view with arms bent, (b) Top view with arms flat, and (c) side view with arms bent

## Conclusions

In alkane substituted diimide systems, core-core and core-substrate interactions govern the self-assembly. The structure of C8-diimide can be conceptually reconstructed with the alkane chains lying flat, but is overcrowded (see Figure 5a). In order to generate a similar conceptual reproduction of the structure found for C12-diimide, the alkane chains of the diimide molecule must be raised off of the substrate into the solvent. Since the C6, C8 and C12-diimide molecules exhibit the same structure, we can conclude that the alkane chains are not on the graphite for any of the  $C_n$ -diimides (see Figure 2-4). Conceptual reproductions using CPK models illustrate the importance of core-core interactions (see Figure 5b). The close proximity of the aromatic cores suggests hydrogen bonding has an important role in the structure. In Figure 5b the red atoms are oxygen and the white are hydrogen.

The C12-diimide structure has been found to be commensurate with the underlying graphite lattice (see Figures 6 & 7). The unit cell parameters derived from the graphite structure are in excellent agreement with the unit cell parameters found experimentally (see Table 1).

## References

- 1) Pokrifchak, M.; Turner, T.; Pilgrim, I.; Johnston, M.; Hipps, K.W.; *J. Phys. Chem.*; 2007; 111(21); 7735-7740.
- 2) Veeco Instruments Inc., Plainview, NY
- 3) Image Metrology A/S, Hørsholm, Denmark.
- 4) Kleiner-Shuhler, L.; Johnston, M.R.; Hipps, K.W.; *J. Phys. Chem. C*; 2008; 112; 14907

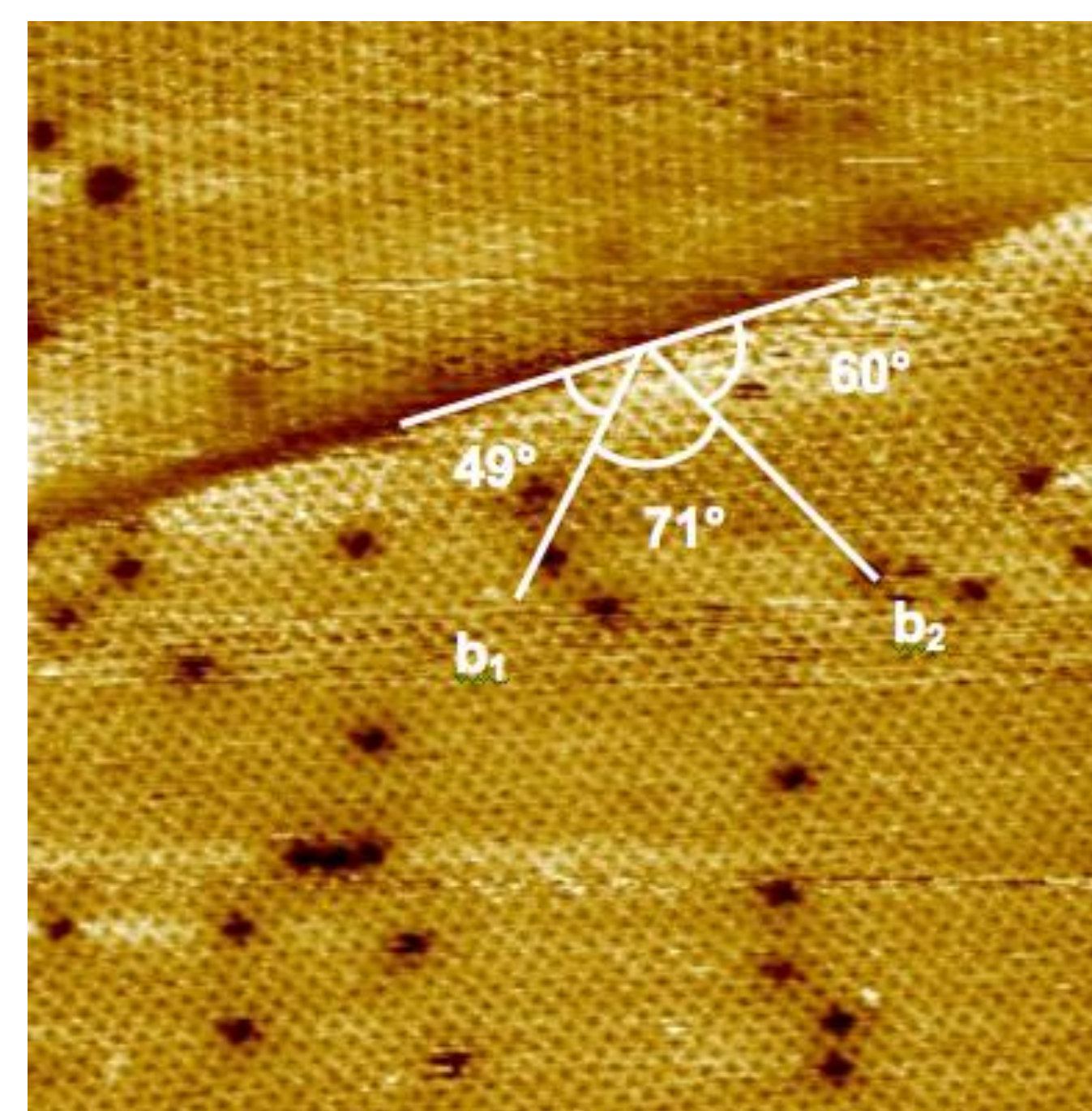


Figure 6. STM image of C12-diimide monolayer with step edge.

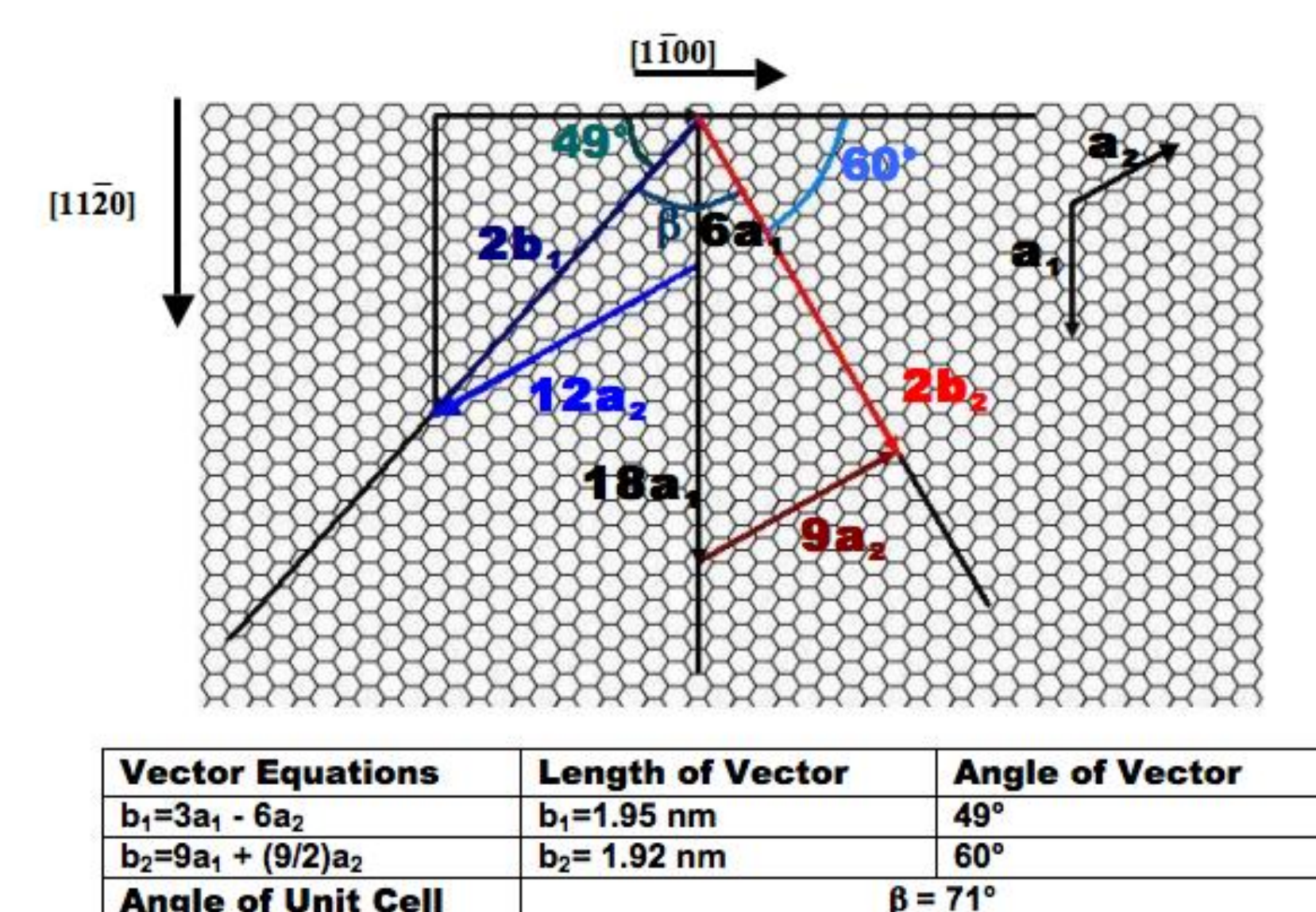


Figure 7. Unit cell calculation from graphite lattice

