Adsorption of supramolecular building blocks on graphite: A force field and density functional theory study

Daniela Künzel,[†] Katrin Tonigold,[†] Jan Kučera,[†] Michael Roos,[‡] Harry E. Hoster,[‡,¶] R. Jürgen Behm,[‡] and Axel Groß[*,†]

Institute of Theoretical Chemistry, Ulm University, D-89069 Ulm, Germany, and Institute of Surface Chemistry and Catalysis, Ulm University, D-89069 Ulm, Germany

Received March 21, 2011; E-mail: axel.gross@uni-ulm.de

The adsorption of the oligopyridine isomers 2,4'-BTP and 3,3'-BTP on graphite is studied using both force-field methods and the DFT-D approach based on density functional theory together with an C_6R^{-6}-type dispersion correction, and the calculated adsorption energies are compared to the results of thermal desorption experiments. Whereas the used force fields yield different adsorption geometries and strongly varying adsorption energies which all overestimate the experimental value by more than 1 eV, the adsorption energy obtained in the DFT-D approach is in a rather good agreement with the experiment. This indicates that the DFT-D approach is able to reliably reproduce adsorption energies of supramolecular building blocks on graphite surfaces. Furthermore, the DFT-D calculations show that these organic molecules are almost entirely bound via the nominally weak van der Waals interaction with the strong bonding caused by the large size of the molecules.

There is a growing interest in the study of supramolecular architectures on surfaces as they can serve as building blocks in molecular electronics [1] or as template structures for functionalized particles in the form of host-guest networks. [2] For a better understanding of the principles underlying the structure formation and the function of such networks, a reliable theoretical description of such systems is desirable. However, density functional theory (DFT) calculations which have been so successful in describing complex surface structures [3] face two problems for these particular systems. First, the molecules which form building blocks of supramolecular structures are typically so large that the calculation of their adsorption properties becomes prohibitively expensive. Second and even more important, for an accurate description of the adsorption of these molecules, the London dispersion interaction needs to be taken into account since these molecules often do not form any true chemical bonds with the surface. However, this kind of interaction is only poorly described in standard DFT methods. [4–7]

As a computationally inexpensive alternative, empirical force field methods are available. Yet, we have recently shown that both adsorption energies as well as adsorption geometries of organic molecules on graphite determined with force fields strongly depend on the particular force field chosen. [8] Recently, the DFT-D approach that adds a C_6R^{-6}-type dispersion correction to the Kohn-Sham Hamiltonian has been proposed as a further alternative. [5,6] Still, for the adsorption of molecules on metal surfaces it is not fully clear yet how screening effects in the metal should be properly treated. [9–11] Furthermore, there are only few experimental studies in which the adsorption energies of supramolecular building blocks are measured. [12] This hampers the assessment of the reliability of the different theoretical approaches. Here we show, based on a combined theoretical and experimental work, that for the adsorption of large organic molecules on *graphite* the DFT-D approach [5,6] can yield rather accurate results and thus opens the way for a reliable theoretical description of this important class of chemical systems.

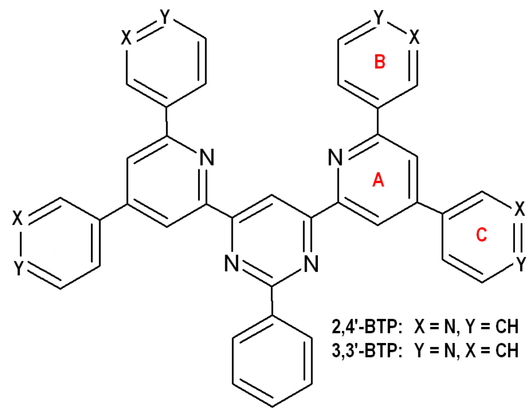

Figure 1. Illustration of the general structure of the bis(terpyridine)-derived isomers 2,4'-BTP and 3,3'-BTP.

As a model system, we consider the adsorption of oligopyridines, namely the bis(terpyridine)-derived isomers 2,4'-BTP and 3,3'-BTP, as depicted in Figure 1, on graphene and graphite. Recently, experimental data have become available for this system. [12] For the force field calculations, Universal (UFF), [13] Dreiding, [14] Compass [15] and CVFF [16] were used as implemented in the Accelrys' Materials Studio program package. Gasteiger charging was used with the UFF and Dreiding force fields. [17] Corresponding DFT results were obtained using the Vienna ab initio simulation package (VASP) [18] using the Perdew-Burke-Ernzerhof functional [19] to describe the exchange-correlation effects. The ionic cores were represented by projector augmented wave (PAW) potentials [20] as constructed by Kresse and Joubert. [21] For the k-point sampling, the Gamma point turned out to be sufficient for the rather large considered systems. Furthermore, Gaussian smearing with a plane wave energy cut-off of 400 eV was used.

The adsorption energies of 3,3'-BTP and 2,4'-BTP on a 3-layer graphite model obtained with various force fields for optimized binding geometries are shown in Figure 2 as the white and dark grey columns, respectively. Both isomers yield very similar adsorption energies which is not surprising regarding the structural similarity of both isomers. However, the results are strongly depending on the employed force field. Furthermore, compared to the desorption energy of -2.54 eV for 3,3'-BTP on highly ordered pyrolytic graphite (HOPG, solid red line in Figure 2) derived from

[†] Institute of Theoretical Chemistry, Ulm University

[‡] Institute of Surface Chemistry and Catalysis, Ulm University

[¶] New address: Technical University of Munich, TUM CREATE Centre for Electromobility, Singapore 637459

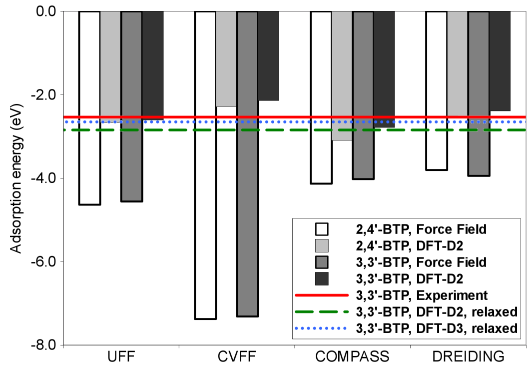

Figure 2. Adsorption energies in eV of 3,3'-BTP and 2,4'-BTP on a 3-layer graphite model, force field and DFT-D data with the 2006 set of Grimme parameters.[5] The red line denotes the experimental desorption energy of 3,3'-BTP. The green dashed line and the blue dotted line symbolize adsorption energies of 3,3'-BTP in a relaxed geometry obtained using the DFT-D2[5] and the DFT-D3 method,[6] respectively.

thermal desorption experiments as described in Ref.,[12] the force fields significantly overestimate the interaction between the 3-layer graphite model and BTP yielding binding energies that are in all cases more than 1 eV too large, with CVFF overestimating the adsorption energy by even more than 4 eV.

Note that the various force fields not only give different adsorption energies but also varying adsorption geometries. The average distance between BTP and a single graphene layer changes from 3.4 Å with Compass to 3.6 Å with CVFF. There is also a difference in the internal flexibility of the molecule depending on the force field: CVFF and Compass clearly favor planar BTP molecules, dihedral angles between rings A and B as well as between rings A and C are below 5° (for the definition of the rings, see Figure 1). For UFF and Dreiding, the torsion between A and C ist between 24 and 30°, with slightly larger values for Dreiding. The dihedral angle between A and B is somewhat smaller and less uniform. For both isomers, it is not above 10° and in some cases, this part of the molecule is nearly planar.

In contrast, the DFT-D results for the BTP adsorption in the optimum geometry within the DFT-D2[5] and the DFT-D3[6] parametrization are in rather good agreement with the experiment. In these calculations, due to computational limitations, each of the 3 carbon layers of the model substrate had to be treated separately. Model calculations of benzene on graphite showed that this procedure does only introduce a negligible error of less than 4 meV per benzene ring.

DFT-D relaxation of 3,3'-BTP on graphene and graphite modeled by three carbon layers resulted in a molecule adsorbed in a nearly planar geometry, as illustrated in Figure 3. The deviation from planarity is less than 1° for dihedral angles between rings A and B and rings A and C. Using the DFT-D2 parameters, the average distance between graphene and adsorbate is 3.35 Å, the adsorption energy on graphite is -2.84 eV (dashed line in Figure 2). For the newer set of Grimme parameters (DFT-D3[6]) the average substrate-adsorbate distance is slightly increased by 3 % to 3.44 Å and the adsorption energy is reduced to -2.65 eV (dotted line in Figure 2) yielding an even better agreement with the experiment.

Using DFT without any dispersion correction, the BTP molecule is bound to graphene with an adsorption energy of only -0.12 eV at an average distance to the surface of 4.38 Å. Interestingly enough, the BTP molecule does not stay planar for such a weak bonding. The torsion between rings A and B is 18° on one and 26° on the other half of the molecule. Between rings A and C, dihedral angles of 34 and 36° have been found corresponding to the gas-phase structure of the BTP molecule.[8] Hence the consideration of dispersive forces does also lead to structural changes of the adsorbed molecule. Furthermore, it is important to note that the comparison of the DFT results with and without dispersion corrections demonstrates without ambiguity that the strong bonding of BTP is almost entirely due to the van der Waals interaction and is not caused by any chemical interaction, as it is usually associated with sizable adsorption energies. The strong interaction here is just a consequence of the large size of the molecule leading to the dominant contribution of the van der Waals interaction to the bonding which keeps the molecule adsorbed at the surface up to temperatures above 500 K.[12] Furthermore, because of the non-directional nature of the van der Waals interaction, the adsorption energy of BTP on graphite exhibits only a small corrugation, i.e., it depends very weakly on the lateral position of the molecule. Hence the particular arrangement of BTP molecules in an ordered supramolecular structure on graphite[2,22] is almost entirely determined by the formation of intermolecular hydrogen-bonds.[8]

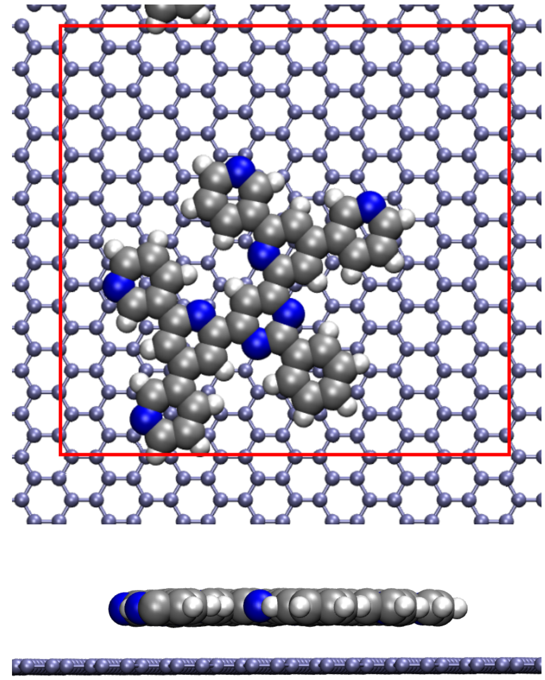

Figure 3. Geometry of 3,3'-BTP on graphene after DFT-D relaxation, top and side view. The unit cell is highlighted in red.

In order to trace back the reason for the large discrepancy between force field calculations and experiment, we used the optimized geometry obtained from each force field for so-called single-point DFT-D2[5] energy calculations, i.e. without any further structure optimization. The corresponding results for 3,3'-BTP and 2,4'-BTP are depicted as the light grey and black columns, respectively, in Figure 2. In spite of the fact that the optimum geometries according to the different force fields vary to some extent, the DFT-D adsorption energies of all these different structures are rather similar, ranging from about -2.1 (3,3'-BTP) and -2.3 eV (2,4'-BTP) for the CVFF geometries, up to -2.8 and -3.1 eV for the Compass results. Again, using different BTP isomers does not change adsorption energies significantly, the difference between 2,4'-BTP and 3,3'-BTP is about 300 meV for the Compass geometry and considerably smaller for the other structures. This clearly indicates that the differences in force field adsorption energies have to be attributed mainly to differences in parametrization of the force fields. The slightly different structures are rather close in energy, hence they are not the main reason for the large discrepancies in the force-field adsorption energies.

In conclusion, we showed that dispersion-corrected density functional theory is able to reliably yield adsorption energies of van der Waals bonded molecules on graphite surfaces. This opens the way to a reliable first-principles treatment of these important type of systems which constitute building blocks in molecular electronics. Force field methods, on the other hand, yield a broad variety of different adsorption geometries and energies which indicates that their reliability in the modeling of the adsorption of organic molecules is limited.

Acknowledgement

Financial support by the Deutsche Forschungsgemeinschaft (DFG) within SFB 569 is gratefully acknowledged. We thank the bwGRiD project for the computational resources.

References

(1) Ma, C.-Q.; Mena-Osteritz, E.; Debaerdemaeker, T.; Wienk, M. M.; Janssen, R. A. J.; Bäuerle, P. *Angew. Chem. Int. Ed.* **2007**, *46*, 1679–1683.
(2) Meier, C.; Landfester, K.; Künzel, D.; Markert, T.; Groß, A.; Ziener, U. *Angew. Chem. Int. Ed.* **2008**, *47*, 3821–3825.
(3) Kresse, G.; Schmid, M.; Napetschnig, E.; Shishkin, M.; Köhler, L.; Varga, P. *Science* **2005**, *308*, 1440.
(4) Andersson, Y.; Langreth, D. C.; Lundqvist, B. I. *Phys. Rev. Lett.* **1996**, *76*, 102.
(5) Grimme, S. *J. Comput. Chem.* **2006**, *27*, 1787.
(6) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. *J. Chem. Phys.* **2010**, *132*, 154104.
(7) Ortmann, F.; Schmidt, W. G.; Bechstedt, F. *Phys. Rev. Lett.* **2005**, *95*, 186101.
(8) Künzel, D.; Markert, T.; Groß, A.; Benoit, D. *Phys. Chem. Chem. Phys.* **2009**, *11*, 8867.
(9) Tkatchenko, A.; Scheffler, M. *Phys. Rev. Lett.* **2009**, *102*, 073005.
(10) McNellis, E. R.; Meyer, J.; Reuter, K. *Phys. Rev. B* **2009**, *80*, 205414.
(11) Tonigold, K.; Groß, A. *J. Chem. Phys.* **2010**, *132*, 224701.
(12) Roos, M.; Breitruck, A.; Hoster, H. E.; Behm, R. J. *Phys. Chem. Chem. Phys.* **2010**, *12*, 818.
(13) Rappé, A. K.; Casewit, C. J.; Colwell, K. S.; Goddard, W. A.; Skiff, W. M. *J. Am. Chem. Soc.* **1992**, *114*, 10024.
(14) Mayo, S. L.; Olafson, B. D.; Goddard, W. A. *J. Phys. Chem.* **1990**, *94*, 8897.
(15) Sun, H. *J. Phys. Chem. B* **1998**, *102*, 7338.
(16) Dauber-Osguthorpe, P.; Roberts, V. A.; Osguthorpe, D. J.; Wolff, J.; Genest, M.; Hagler, A. T. *PROTEINS: Structure, Function, and Genetics* **1988**, *4*, 31.
(17) Gasteiger, J.; Masili, M. *Tetrahedron* **1980**, *36*, 3219.
(18) Kresse, G.; Furthmüller, J. *Phys. Rev. B* **1996**, *54*, 11169.
(19) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865.
(20) Blöchl, P. E. *Phys. Rev. B* **1994**, *50*, 17953.
(21) Kresse, G.; Joubert, D. *Phys. Rev. B* **1999**, *59*, 1758.
(22) Meier, C.; Roos, M.; Künzel, D.; Breitruck, A.; Hoster, H. E.; Landfester, K.; Gross, A.; Behm, R. J.; Ziener, U. *J. Phys. Chem. C* **2010**, *114*, 1268–1277.