

**Orientation of OH terminal groups
 in oligo(ethylene glycol)-terminated self-assemblies:
 results of *ab initio* modeling**

Lyuba Malysheva¹, Alexander Onipko², and Bo Liedberg²

¹ Bogolyubov Institute for Theoretical Physics, 03143 Kiev, Ukraine

² Division of Molecular Physics, Department of Physics, Chemistry and Biology, Linköping University, 581 83 Linköping, Sweden

Received 20 April 2006, revised 15 May 2006, accepted 1 August 2006

Published online 19 September 2006

PACS 31.15.Ar, 73.61.Ph, 87.15.-v

Ab initio optimization of periodic arrays of HS(CH₂)₅CONH-EG₃ [EG_{*n*} = (CH₂CH₂O)_{*n*}H], which are used to model real self-assembled monolayers (SAMs) terminated by oligomers of ethylene glycol (OEGs), favors a molecular geometry with a strong distortion of the OH tail group. The distortion effect is conformation dependent and appears exclusively in assemblies of helical OEGs. Helical SAM structures with the O–H bond directed towards the substrate surface exhibits a lower energy than the corresponding all trans SAMs with OH group oriented towards the vacuum interface. In view of strict limitations in molecular complexity and basis set for this kind of calculations, we tested the obtained molecular geometry as the starting point for performing optimization of the HS(CH₂)₁₅CONH-EG₆ molecule with the use of BP86/6-31G* method/basis set provided by Gaussian03. It is found that the observed trend in OH tail group orientation survives and is consistent with a wealth of experimental data available for this type of SAMs.

phys. stat. sol. (b) **243**, No. 13, 3489–3493 (2006) / DOI 10.1002/pssb.200669158

Orientation of OH terminal groups in oligo(ethylene glycol)-terminated self-assemblies: results of *ab initio* modeling

Lyuba Malysheva^{*1}, Alexander Onipko², and Bo Liedberg²

¹ Bogolyubov Institute for Theoretical Physics, 03143 Kiev, Ukraine

² Division of Molecular Physics, Department of Physics, Chemistry and Biology, Linköping University, 581 83 Linköping, Sweden

Received 20 April 2006, revised 15 May 2006, accepted 1 August 2006

Published online 19 September 2006

PACS 31.15.Ar, 73.61.Ph, 87.15.-v

Ab initio optimization of periodic arrays of HS(CH₂)₅CONH-EG₃ [EG_{*n*} = (CH₂CH₂O)_{*n*}H], which are used to model real self-assembled monolayers (SAMs) terminated by oligomers of ethylene glycol (OEGs), favors a molecular geometry with a strong distortion of the OH tail group. The distortion effect is conformation dependent and appears exclusively in assemblies of helical OEGs. Helical SAM structures with the O–H bond directed towards the substrate surface exhibits a lower energy than the corresponding all trans SAMs with OH group oriented towards the vacuum interface. In view of strict limitations in molecular complexity and basis set for this kind of calculations, we tested the obtained molecular geometry as the starting point for performing optimization of the HS(CH₂)₁₅CONH-EG₆ molecule with the use of BP86/6-31G^{*} method/basis set provided by Gaussian03. It is found that the observed trend in OH tail group orientation survives and is consistent with a wealth of experimental data available for this type of SAMs.

© 2006 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

1 Introduction

Stimulated by variety of promising biomedical and bioanalytical applications, self-assemblies of (OEG)-terminated alkanethiols have been under extensive experimental [1–3] and theoretical [4–6] investigation during last decade. For example, it has been firmly established that the OEG part can adopt different conformations (all trans and helical) depending on nature of the supporting lattice (gold or silver) and OEG chain length [1, 2]. Conformational transitions, helical to all trans and all trans to helical, driven by moderate heating/cooling of OEG-terminated and amide containing SAMs, have been demonstrated to occur [1]. Protein repellency, wetting, and other surface properties also have proven to be strongly dependent on the OEG conformational state [2–5].

In general, structure-function relationships have been thoroughly discussed for OEG-SAMs and the related poly(ethylene glycols). However, details of how the SAM building blocks are structured, oriented and stabilized within the assembly have not been investigated to the same extent. Only recently, the likely orientation of the alkyl and OEG components was reported in concrete numbers for the respective Euler angles [6]. This set of data were based on the first principle calculations of molecular geometry and vibrational spectra of isolated HS(CH₂)_{*m*}CONH-EG_{*n*} molecules. It is evident though that more extensive studies are required to evaluate the role of intermolecular interactions on the molecular structure and orientation of the SAM constituents. Here we present the first *ab initio* study of (OEG)-terminated alkanethiols arranged in periodic arrays.

* Corresponding author; e-mail: malysh@bitp.kiev.ua

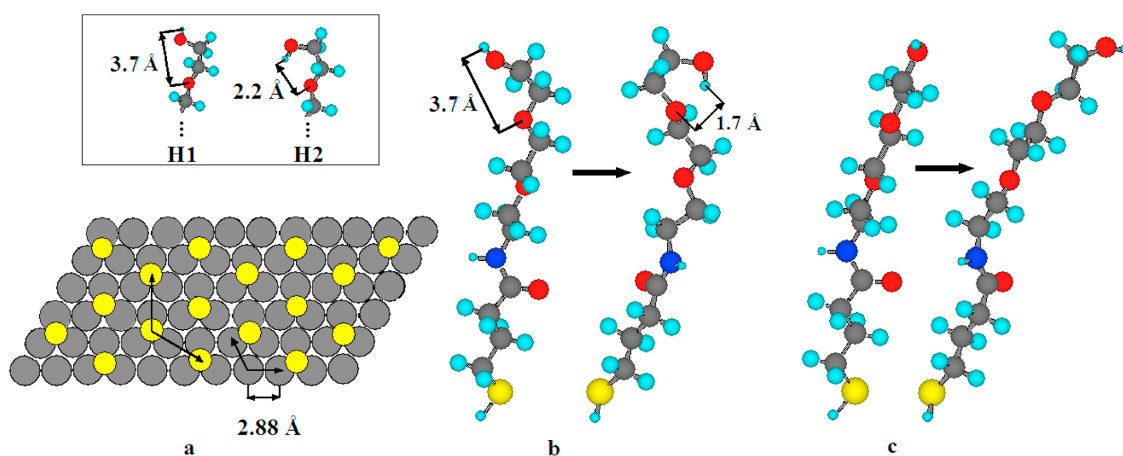


Fig. 1 (online colour at: www.pss-b.com) (a) Au(111) substrate surface: dark circles represent gold atoms, Au–Au = 2.88 Å; hexagonal overlayer of sulphur atoms is indicated by lighter and smaller circles, S–S = $2.88 \times \sqrt{3} \text{ Å} \sim 5 \text{ Å}$. (b) HS(CH₂)₃CONH-EG₃ molecule with the OEG terminus in the helical conformation before (left) and after (right) optimization with PBC/pseudo potential. (c) Same structures as in (b) but with the OEG terminus in the all trans state. The termini with exposed (**H1**) and inverted (**H2**) O–H bond in equilibrium configurations of helical HS(CH₂)₁₅CONH-EG₆ molecule obtained with BP86/6-31G* are shown in the inset.

2 Computational strategy

Ab initio optimization of periodic 2D structures, which are build up of long molecules (such as those used in real OEG SAMs) demands a huge amount of time and memory. To reduce required computational resources, somewhat simplified procedures of calculations have been accepted. First, we found optimized molecular geometry in periodic arrays of molecules HS(CH₂)₃CONH-EG₃ having shorter alkyl and OEG components. The initial internal coordinates (bond lengths, bending and dihedral angles), as well as initial molecular orientation with respect to the substrate surface, were taken from [6]. It was assumed that the molecules are arranged in a hexagonal overlayer ($\sqrt{3} \times \sqrt{3}$) R30°, where the sulphur atoms are separated from each other by $\sim 5 \text{ Å}$, see Fig. 1a. This structure was kept fixed during optimization process. For the helical and all trans conformational states of the OEG, which are shown in Fig. 1(b) and (c), calculations have been performed by density functional theory (DFT) method with periodical boundary conditions (PBC). Specifically, LSDA exchange-correlation functional (3–21 G* basis set) for valence electrons and pseudo-potential for core electrons (effective core potential LP-31G) were borrowed from Gaussian03 suit of programs. The internal coordinates obtained for the OEG part were then used as the starting parameters in the optimization of an isolated HS(CH₂)₁₅CONH-EG₆ molecule, carried out with BP86 exchange-correlation potential and 6–31 G* basis set.

3 Results

The geometries of HS(CH₂)₃CONH-EG₃ in the periodic array before and after optimization are shown in Fig. 1. A striking difference in the orientation of OH terminal group is observed in the case of the helical OEG conformation, Fig. 1b. Being initially exposed to the vacuum, the OH bond is nearly inverted in the equilibrium configuration, a conformation change that decreases the distance between the OH hydrogen and the nearest oxygen by, at least, a factor of two. These changes can be rationalized in terms of dihedral angles $\tau^{\perp}(\text{OCCO})$ and $\tau(\text{CCOH})$ which determine rotation angles of the nearby C–C and C–O bonds. These angles are changing under optimization from 72° and –170° to 41° and –30°, respectively. Before optimization, total energy of the molecule is higher for the helical than for the all trans conforma-

Table 1 Orientation and characteristic dihedral angles calculated for optimized geometries of molecules **H1** and **H2**. Relative orientation of OEG part ($\theta_E^0, \psi_E^0, \varphi_E^0$) and amide CONH group ($\theta_N^0, \psi_N^0, \varphi_N^0$) is determined with respect to alkyl CCC plane [6]. Notations of dihedrals imply rotation about the bond connecting two central atoms: (from left to right) C–C, N–C, C–C, and C–O; $\tau^L(\text{OCCO})$ and $\tau(\text{CCOH})$ represent the OEG terminus.

	θ_E^0	ψ_E^0	φ_E^0	θ_N^0	ψ_N^0	φ_N^0	$\tau(\text{CCCN})$	$\tau(\text{CNCC})$	$\tau^L(\text{OCCO})$	$\tau(\text{CCOH})$
H1	28°	87°	–69°	–41°	36°	103°	133°	–105°	72°	–170°
H2	26°	72°	–33°	–41°	34°	115°	137°	–94°	59°	–49°

tion, but after optimization, the former exhibits a lower energy than the latter by 0.8 kcal/mol. It should be stressed that the same optimization of the isolated $\text{HS}(\text{CH}_2)_3\text{CONH-EG}_3$ molecule, does not lead to any significant changes in the initial geometry and the energy difference between the all trans and helical states. Thus the reorientation of O–H bond and accompanying changes of nearest dihedrals has to be attributed to intermolecular interaction effects.

Earlier, we have studied equilibrium geometries of $\text{HS}(\text{CH}_2)_{15}\text{CONH-EG}_6$ and deduced the orientation of these molecules within corresponding SAMs by comparing model calculations with experimental data [6]. Table 1 shows a few principal dihedral angles of SAM constituents (abbreviated below as **H1**). In fact, all dihedral angles, $\tau(\text{OCCO})$, in the canonical helical conformation of ethylene glycols equal 72°. Assuming that the structure adopted by OEG-SAMs consisting of shorter and longer OEGs is similar, and that the equilibrium geometry of SAM constituents is influenced by intermolecular interactions, we have performed geometry optimization of **H1** with the initial values $\tau^L(\text{OCCO}) = 41^\circ$ and $\tau(\text{CCOH}) = -30^\circ$ as obtained from PBC/pseudo potential calculations described above. As a result, a new equilibrium geometry of $\text{HS}(\text{CH}_2)_{15}\text{CONH-EG}_6$ (**H2**) is found, and the structural parameters of **H1** and **H2** are compared in Table 1.

Similar to the result obtained for the shorter molecule, the **H2** conformation appears to be energetically more favorable in the helical than the all trans state. The energy difference between the helical **H2** state and the same molecule in the all trans state, with the OH group pointing outwards, is about 3.3 kcal/mol. This is in contrast to the **H1** state which has a higher energy than its all trans counterpart.

The most systematic experimental investigation of the SAMs in focus has been carried out by means of infrared reflection-absorption (RA) spectroscopy [1]. To a large extent, the spectral appearance of SAMs is determined by the molecular orientation with respect to the substrate surface. To check the consistency of the new geometry with experimental RA spectra, the most favorable orientation of **H2** within SAMs was found by using the same routine of model calculations as described in [6].

The mutual orientations of the alkyl, amide, and OEG parts, as well as the orientation of the entire molecule with respect to the substrate surface, is determined by the corresponding sets of Euler angles. For the alkyl CCC plane, these are θ_A – tilt angle of alkyl axis z_A relatively to the substrate normal; ψ_A – the angle of rotation of x_A, z_A -plane about z_A -axis; and azimuthal angle φ_A . Axes x_A, y_A , and z_A are defined in the work by Parikh and Allara [7]. The other sets of angles have similar meaning and are denoted by subscripts N and E for amide and OEG, respectively. Table 1 represents relative orientation of molecular structural components which corresponds to the frame of reference coinciding with x_A, y_A, z_A , i.e., $\theta_A = \psi_A = \varphi_A = 0$.

Table 2 Likely orientation adopted by molecules **H1** and **H2** and their structural components within SAMs.

	θ_A	ψ_A	φ_A	θ_E	ψ_E	φ_E	θ_N	ψ_N	φ_N	$\gamma_{\text{C=O}}$
H1	26°	–62°	–77°	22°	25°	–151°	–27°	–4°	–3°	96°
H2	26°	–72°	–71°	31°	17°	–127°	–27°	–6°	6°	95°

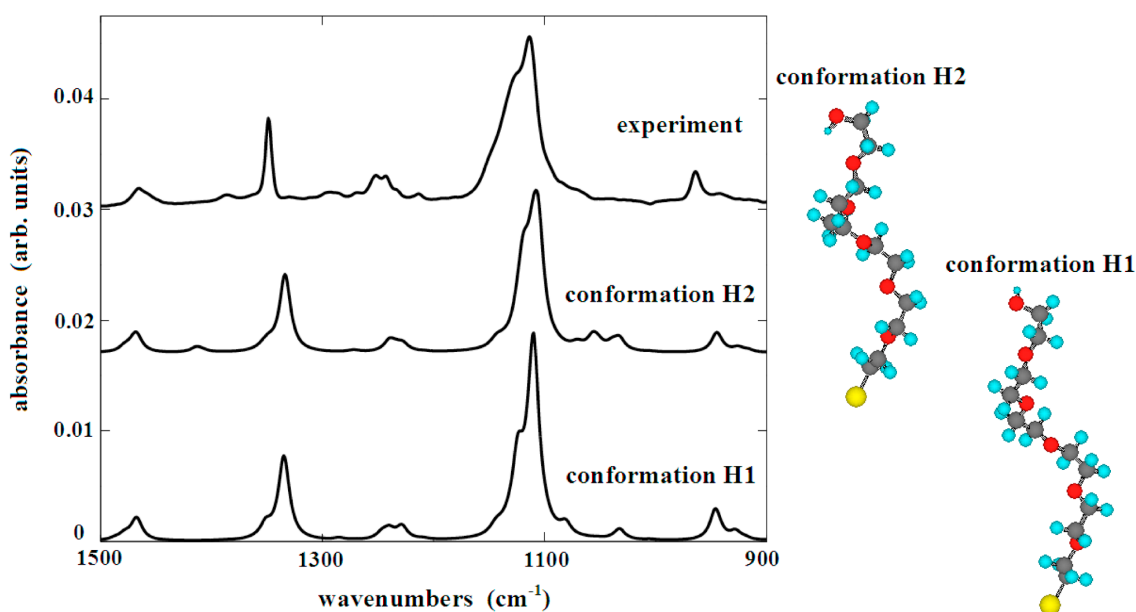


Fig. 2 (online colour at: www.pss-b.com) Infrared RA spectra in the fingerprint frequency region: upper curve – spectrum measured for self-assemblies of HS(CH₂)₁₅CONH-EG₆ [1]; lower curves – spectra calculated for HS-EG₆ molecules with the OEG part having the same structure as in **H1** (lower curve) and **H2** (mid curve). Orientation of HS-EG₆ shown to the right is specified in Table 2 by the angles θ_E and ψ_E . No frequency scaling is used. For computation details see [6].

Characteristic angles summarized above are dictated by the molecular geometry. For interpretation of experimental data, it is often necessary to know how SAM molecules are oriented with respect to the substrate surface. As mentioned above, to get an access to this information, a special procedure has been developed [6]. Here, we use it to compare orientation angles θ_A , ψ_A , and φ_A for molecules in the **H1** and **H2** states. The values of the angles that provide the best possible reproduction of observed RA spectra in the fingerprint region, see Fig. 2, are shown in Table 2. The data are complemented by the C=O bond orientation with respect to the substrate normal (angle $\gamma_{C=O}$) and by angles θ_E , ψ_E , φ_E , θ_N , ψ_N , and φ_N . The model RA spectra of **H1** and **H2** are approximated by using HS-EG₆ instead of HS(CH₂)₁₅CONH-EG₆ with the OEG part in the same configurations as those calculated for **H1** and **H2**. In view of the fact that OEG contribution into the RA spectra is dominating in the fingerprint region, the choice of shortened molecule for modeling seems to be justified. Other details of calculations can be found in [6].

4 Summary

It is observed that a perfect helical structure, as in crystalline poly(ethylene glycols), with equal dihedrals $\tau(\text{OCCO})$, may be not the case in OEG-terminated SAMs. We found a new optimized geometry with substantially different dihedral angle $\tau^L(\text{OCCO})$ of the terminal ethylene glycol and, as a consequence, an inverted orientation of the O–H bond. An inverted configuration is expected to influence the wetting and hydrogen bond accepting/donating properties of the outermost SAM surface as well as the overall reactivity of the OH group. It is, however, too early to conclusively state that the inverted **H2**-like configuration dominates in helical OEG-SAMs. Answer to this question requires more extensive theoretical and experimental work which currently is in progress.

Acknowledgements This work was supported by the Swedish Institute (SI) through Visby Programme. We also thank the Swedish Foundation for Strategic Research (SFF) and the Swedish Research Council (VR) for financial support.

References

- [1] R. Valiokas, M. Östblom, S. Svedhem, S. C. T. Svensson, and B. Liedberg, *J. Phys. Chem. B* **105**, 5459 (2001).
- [2] P. Harder, M. Grunze, R. Dahint, G. M. Whitesides, and P. E. Laibinis, *J. Phys. Chem. B* **102**, 426 (1998).
- [3] D. J. Vanderah, G. Valincius, and C. W. Meuse, *Langmuir* **18**, 4674 (2002).
- [4] A. J. Pertsin and M. Grunze, *Langmuir* **10**, 3668 (1994).
A. J. Pertsin, M. Grunze, and I. A. Garbuzova, *J. Phys. Chem. B* **102**, 4918 (1997).
- [5] R. L. C. Wang, H. J. Kreuzer, and M. Grunze, *Phys. Chem. Chem. Phys.* **2**, 3613 (2000).
- [6] L. Malysheva, A. Onipko, R. Valiokas, and B. Liedberg, *J. Phys. Chem. A* **109**, 7788 (2005).
- [7] A. N. Parikh and D. L. Allara, *J. Chem. Phys.* **96**, 927 (1992).