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Theoretical study of the interaction between phenyl diacetylenes and the solvent for the formation of Langmuir–Blodgett films

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Abstract

A theoretical thermodynamical study was carried out on the formation of Langmuir–Blodgett films of phenyl diacetylene carboxylic acid derivatives containing a lateral chain. Two cases were computed: one for the isolated molecule and another one for the same structure immersed in water with an acid pH. The result of this process shows that the formation of the film under the latter conditions is favoured by the moiety of the carboxylic group. An analysis of the frontier orbitals and the dipole moment in both situations is also presented.

Keywords: Langmuir–Blodgett films; Gaussian 94 calculations; Aromatic diacetylenes

1. Introduction

Langmuir–Blodgett (LB) films have recently received attention in the form of functional ultrathin films. LB films are built up from condensed monolayers on a water–air interface by multiple deposition onto a solid support. The LB technique can provide organized molecular assemblies with a well-defined molecular orientation and an ordered layer structure. The functionality and properties of the organized monolayer assemblies can be designed from a molecular level by selecting the corresponding monolayer and building up different monolayers.

The polymerization of diacetylenes was first studied in the solid state by Wagner [1,2], as well as their polymerization mechanism. It was found that the polymerization is a topochemical reaction and proceeds by a radical stepwise 1,4-addition to the conjugated triple bond (Fig. 1) [3]. According to Fig. 1, starting from suitable substituted diacetylenes (polymers with double and triple bonds in conjugated chains) [2,4], the reaction can be activated by a variety of methods, such as thermal, UV light, or by high-energy radiations when using carbenes as active intermediates [5].

Tieke and Wegner's group [6–9] have extensively studied polymerization in LB films. They have especially discussed the influence of the chemical structure on polymerizability, stability of the LB films, orientation of the molecules and packing of the long chains.

Photopolymerizations of *n*-alkyl diacetylenic carboxylic acids in LB films have been extensively

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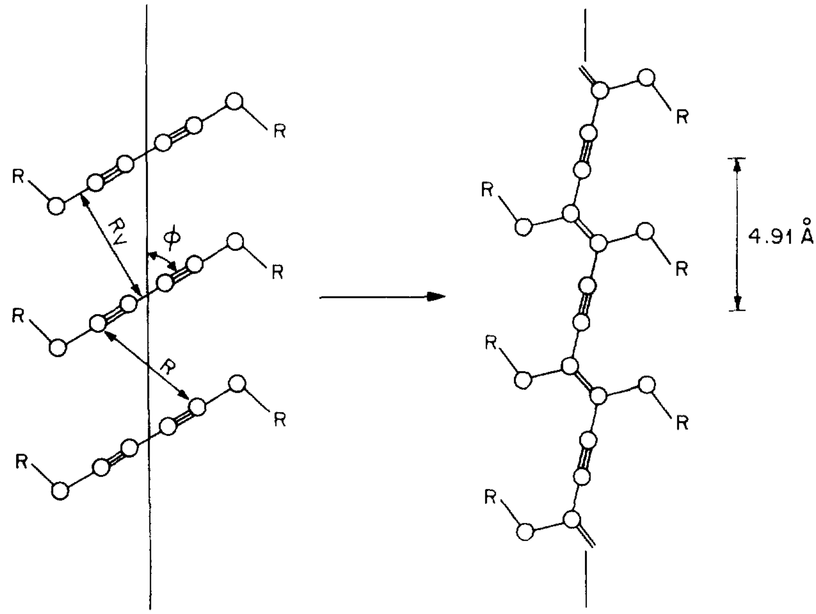

Fig. 1. Chemical process for the topochemical formation of polydiacetylenes.

studied over the last decade [10–15]. It has been suggested that the LB films of polydiacetylenes have great potential for many applications in electronics, optoelectronics and optics. The polydiacetylenes have large third-order susceptibilities [16]. The polymerized LB films of $CH_3(CH_2)_{17}C{\equiv}C{-}C{\equiv}CCOOH$ and $CH_3(CH_2)_{15}C{\equiv}C{-}C{\equiv}C(CH_2)_8COOH$ generate the third harmonic by transmitting Nd:YAG laser light in a normal direction to the layers [17]. It is well known that these effects arise from the delocalization of π-electrons of the polydiacetylene backbone. In addition to the diacetylene group, the incorporation of a phenyl ring into the LB films provides a primary structure for practical applications. However, publications on mono- and multilayers containing phenyl and diacetylene simultaneously are very rare [18].

It was shown in a recent publication that a series of aromatic diacetylenes can be spread at the air–water interphase and multilayers can be built up by the LB technique, and subsequently polymerized by exposure to UV light [19].

However, it is not clear what happen when these benzoic acid molecules are anchored in an acidic water surface, what kind of changes occur on the diacetylene molecule, which region of the same molecule enables or allows the interaction, and what thermodynamic effects favour the formation of the film. In order to find answers for these questions, a theoretical study on these molecules was carried out and the results are described in this report.

2. Methodology

The quantum chemical calculations were carried out using the GAUSSIAN94 program [20] included in the CERIUS package [21], the initial geometries were optimized by Universal 1.01 Molecular Mechanics [22] included in the same software. The calculations of molecule **1** without interactions with optimization of geometry were carried out at the HF/3-21G level. The calculation of the molecular interaction in the presence of water (**2**) was carried out with full optimization of geometry using the Onsanger model [23,24] at the HF/3-21G level. The solute radius was computed from the molecular volume of the optimized (gas phase) compound using a Monte-Carlo integration [20].

3. Results and discussion

The model molecule is shown in Fig. 2.

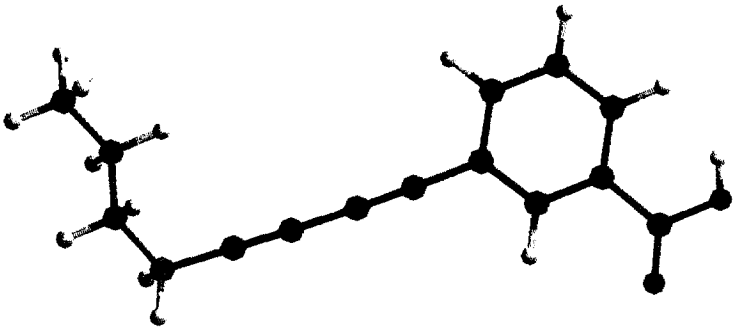

Fig. 2. Model molecule calculated (molecule **1**).

There is a lot of controversy about the role played by the chain joined at the end of the diacetylenic monomers [6,13,25]. For this reason we searched for evidence of this influence in many of the results that we obtained.

The frontier orbitals (HOMO and LUMO) for **2** are shown in Fig. 3.

The same wave functions are present for **1**. An important feature observed on these orbitals is that, as in the case of the HOMO the wave function is concentrated mainly in the electronic resonance region, i.e. both triple bonds and some part of the ring. There is no symmetry for the molecule, so it is not possible to label the orbitals. However, in the absence of the lateral chains, it could belong to an a_1 irreducible representation of a C_{2v} point group.

This orbital should be the one that donates electrons in an orbital interaction of a reaction, so it could be a good target for a nucleophilic process which we need for a polymerization.

The LUMO has no symmetry and is weaker than the HOMO. It is also concentrated in the electronic delocalization region, but here the new main feature is that the carboxylic group has a very important role. Since the molecule was calculated without dissociation of the acid group (considering a solution with

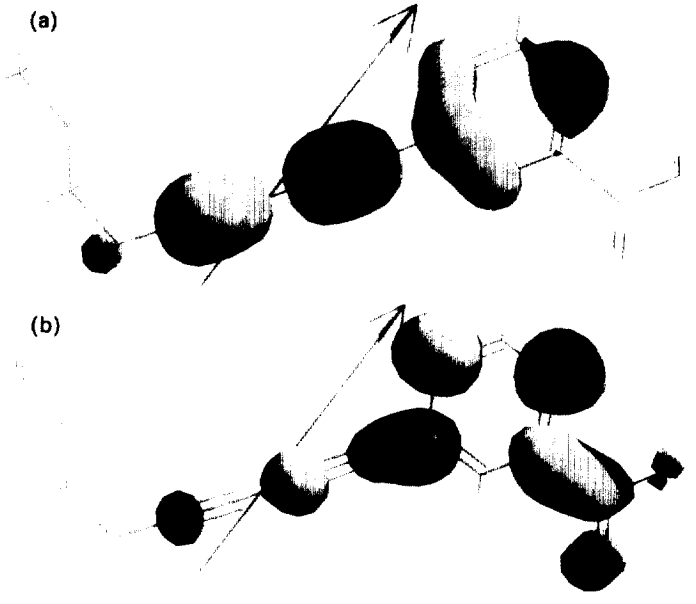

Fig. 3. (a) HOMO; (b) LUMO.

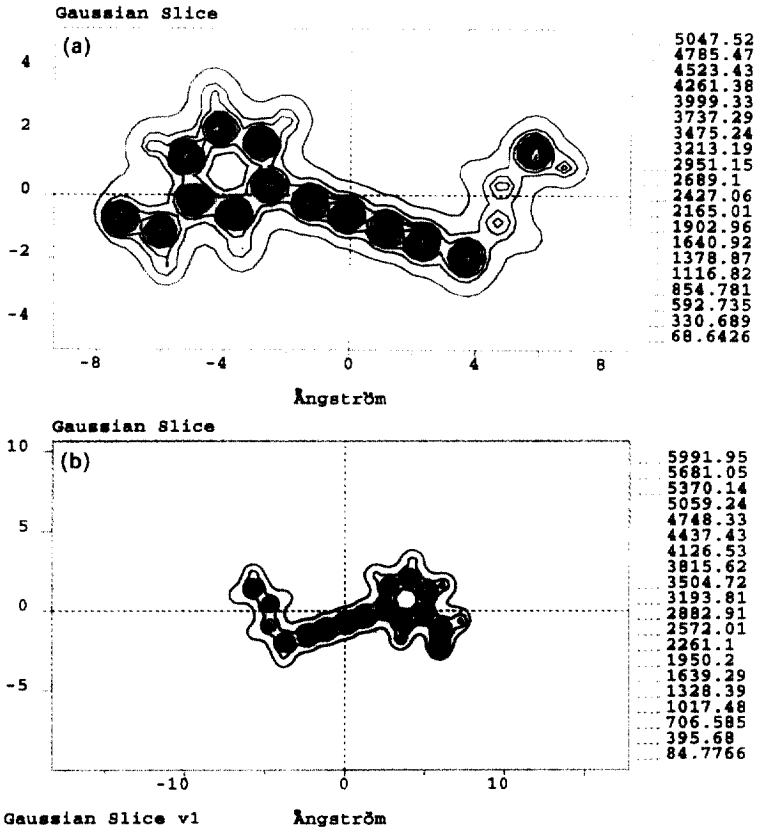

Fig. 4. Electrostatic potential shields for (a) **1** and (b) **2**. The black point indicates the highest charge center in each case.

acid pH), this orbital can receive electrons, which is the kind of interaction that we expect in this process for the formation of the Langmuir–Blodgett film. In this way the solvent can polarize as is the case of water.

The last interpretation is very useful for our calculations. There is no real chemical interaction in this process and the shape and nature of the orbital have not changed on passing from a neutral and isolated molecule to one immersed in the solvent. Therefore, it is necessary to analyze other features in order to establish if the process is favoured.

With this in mind, a thermodynamic analysis was carried out considering that the formation of the LB film has the same behavior as that in the formation of a solution, since the carboxylic group can easily interact with water. However, the interesting point is that the chain at the end of the diacetylene group seems to be hydrophobic and does not play any role in the formation of the film. Consequently, the solvation phenomenon should occur only at the carboxylic end.

The total energy of both species was computed and is shown in Table 1. It can be seen that there is a difference of $\Delta U = -2.0727$ kcal mol^{-1}. This result indicates that the process is thermodynamically favoured to form the LB film because, in the present case, there is only one process that can change the value of the energy and it is the formation of a mixture. Then we can consider that this value corresponds to the free energy of the mixture.

The dipole moment changes on going from the isolate item to the film. The corresponding values are also shown in Table 1 and there is a net increase of 1.428 Db. The direction of the corresponding resultant vector originally has a perpendicular direction to the axis formed by the diacetylene fragment in the same plane than the ring, and finally we have a resultant in a 45° angle in the direction of the aromatic ring on the

Table 1

	Total energy/kcal mol^{-1}	μ/Db
1	−452921.0562	5.641
2	−452923.1289	7.070

opposite side to the carboxylic group. This indicates that the molecule changes to a polarized form with a net positive density of charge near the hydrogen atoms of the ring. This effect is a consequence of the interaction of the carboxylic group with the solvent surface.

The electrostatic potential maps were computed in order to probe the last proposition. It is possible to see a center of charge well defined on the oxygen atom of the hydroxylic group in molecule **1**; this center of charge is lost in **2**. This phenomenon indicates that the charge density is satisfied by solvation on the formation of the film (see Fig. 4).

There is experimental evidence about the stability of the monolayer which increases as the length of the lateral chain increases; however, some recent results of our group [19] indicate that it is possible to obtain stable monolayers in the case of a monomer with a chain of four carbon atoms like the model compounds calculated in this paper, However, the process of polymerization is poor for this case. Therefore, it seems that the size of the chain is only relevant for the topochemical polymerization process and not for the formation of the film as was mentioned by Tieke and Wegner's group [6]. Our results confirm this interpretation, and allow us to establish that the formation of the film is a thermodynamic process in which the chain does not play any role.

4. Conclusions

Langmuir–Blodgett films represent a very important topic of research. Theoretical studies contribute to the understanding of the formation of these chemical items [26]. In this work we demonstrated that there is a thermodynamical preference for the formation of the film when the model molecule interacts with water at an acid pH. Also we found evidence that the chain at the end of the diacetylene group is not important for the formation of the stable layers although it can play an important role for a further polymerization.

References

[1] G. Wegner, Z. Naturforsch., Teil B 24 (1969) 824.
[2] G. Wegner, Pure Appl. Chem. 49 (1977) 443.
[3] R. Salcedo, L.E. Sansores, A.A. Valladares, D. Likhatchev. L. Alexandrova, T. Ogawa, Polymer 37 (1996) 1703.
[4] G. Wegner, Makromol. Chem. 154 (1972) 35.
[5] H. Eichele, M. Schwoerer, R. Huber, D. Bloor, Chem. Phys. Lett. 42 (1976) 342.
[6] B. Tieke, G. Lieser, J. Colloid Interface Sci. 88 (1982) 471.
[7] G. Lieser, B. Tieke, H. Wegner, Thin Solid Films 68 (1980) 77.
[8] C. Bubeck, B. Tieke, G. Wegner, Ber. Bunsenges. Phys. Chem. 86 (1982) 495.
[9] B. Tieke, G. Lieser, Macromolecules 18 (1985) 327.
[10] H.J. Cantow (Ed.), Polydiacetylenes, in: Advances in Polymer Science, vol. 63, Springer, New York, 1984.
[11] G. Wegner, Recent progress in the chemistry and physics of poly(diacetylenes), in: W.E. Holtfield (Ed.), Molecular Metals, Plenum, New York, 1979, p. 209.
[12] M. Brenton, J. Macromol. Sci., Rev. Macromol. Chem. 21 (1981) 61.
[13] B. Tieke, G. Lieser, G. Wegner, J. Polym. Sci. Polym. Chem. Ed. 17 (1979) 1631.
[14] B. Tieke, V. Enkelmann, H. Kapp, G. Lieser, G. Wegner, J. Macromol. Sci., Chem. 15 (1981) 1045.
[15] J. Olmsted III, M. Strand, J. Phys. Chem. 87 (1983) 4790.
[16] C.W. Pitt, L.M. Walpita, Thin Solid Films 68 (1980) 101.
[17] G.M. Carter, Y.K. Chen, S.K. Tripathy, Appl. Phys. Lett. 43 (1983) 891.
[18] F. Kajzar, J. Messier, Thin Solid Films 99 (1983) 109.
[19] M.P. Carreón, G. Burillo, V. Agabekov, T. Ogawa, Polymer Journal 29 (1997) 103.
[20] M.J. Frisch, G.W. Trucks, H.B. Schlegel, P.M.W. Gill, B.G. Johnson, M.A. Robb, J.R. Cheeseman, T.A. Keith, G.A. Peterson, J.A. Montgomery, K. Raghavachari, M.A. Al-Laham, V.G. Zakrzewski, J.V. Ortiz, J.B. Foresman, J. Ciolslowski, B.B. Stefanov, A. Nanayakkara, M. Challacombe, C.Y. Peng, P.Y. Ayala, W. Chen, M.W. Wong, J.L. Andres, E.S. Replogle, R. Gomperts, R.L. Martin, D.J. Fox, J.S. Binkley, D.J. Defrees, J. Baker, J.P. Stewart, M. Head-Gordon, C. Gonzalez, J.A. Pople, GAUSSIAN 94 (Revision B.1), Gaussian Inc., Pittsburg, PA, 1995.
[21] The program Cerius2™ was developed by Molecular Simulations Incorporated.
[22] A.K. Rappé, C.J. Casewit, K.S. Colwell, W.A. Goddard, W.M. Skiff, J. Am. Chem. Soc. 114 (1992) 10024.
[23] M.W. Wong, M.J. Frisch, K.B. Wiberg, J. Am. Chem. Soc. 113 (1991) 4776.
[24] M.W. Wong, K.B. Wiberg, M.J. Frisch, J. Chem. Phys. 95 (1991) 8991.
[25] B. Tieke, G. Wegner, in: E. Kay, P.S. Bagus (Eds.), Topics in Surface Chemistry, Plenum, New York, 1978, p. 121.
[26] M.J. Callaway, D.J. Tidesley, N. Quirke, Molecular Simulations 18 (1996) 277.