Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 24 Sep 2006.

To cite this article: Gerard Pepe , Didier Siri , André Samat , Eliane Pottier & Robert Guglielmetti (1994): Modeling of Spiropyran Aggregates with the Help of Genmol Program, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 246:1, 247-250

To link to this article: http://dx.doi.org/10.1080/10587259408037821

Mol. Cryst. Liq. Cryst. 1994, Vol. 246, pp. 247–250
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Printed in the United States of America

MODELING OF SPIROPYRAN AGGREGATES WITH THE HELP OF GENMOL PROGRAM

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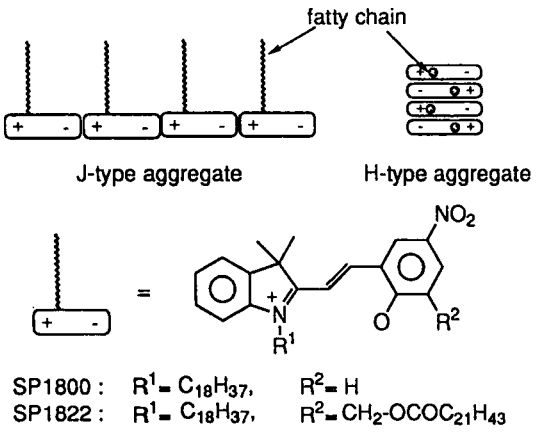
Abstract J-and H-aggregates of spiro [indoline-pyranes] were modeled using GenMol molecular mechanic software. The highest stability of J-aggregates was confirmed, particularly when aggregates interact with a water surface.

INTRODUCTION

Photochromic spiropyrans have been extensively studied [1,2] essentially because of their potential usefulness for several applications [1b]. One of the most interesting application is the design of high density optical memories [3]. The formation of high order structure of reactive molecules has been investigated in a monomolecular layer or multilayers prepared by the Langmuir Blodgett technique [4]. The aggregation type [5], i.e J-type ("head to tail") or H-type ("side by side") , particularly depends on the structure of the photochromic compounds used. In order to better understand the aggregates formation mechanism and their interaction with a water phase (like in LB film formation) we decided to use molecular modeling through GenMol [6] software.

This software based on molecular mechanic calculations is designed to build molecule (it can treat 45 types of atoms, free radicals, carbenes, ions, metallic cations, etc...) and to find the preferred conformation of a molecule in a given medium. It also allows to model molecular interactions and to find the energy minimum of complex molecular systems as photochromic aggregates.

Two photomerocyanines coming from spiro[indoline-pyranes] , bearing one (SP1800) or two fatty chains (SP1822) are chosen, because the ability of these photochromic substances to give aggregates.[7]



SP1800 : $R^1 = C_{18}H_{37}$, $R^2 = H$
SP1822 : $R^1 = C_{18}H_{37}$, $R^2 = CH_2\text{-}OCOC_{21}H_{43}$

METHODOLOGY

- The single molecules are built and optimized in their preferred conformations, thus they are gathered to form aggregates.
- Molecules are associated side to side and head to tail in order to obtain molecule pair and then optimized in the dimer.
- Two dimers so obtained are thus associated in a way leading to the most stable aggregation of the four molecules.
- The tetramer so built is placed next to a water molecule surface and optimized subsequently.

In order to find the best molecular association only the non-bonded interactions between molecules (van der Waals, coulombic and hydrogen bonds) are considered.

RESULTS AND DISCUSSION

In table 1 the interaction energy between two pairs of photochromic molecules, which expresses the complex stability with and without a water molecule surface are reported. The association energies of molecule pairs are generally weak, but greater for J-aggregates than for H-aggregates: -4.45 kcal /mol instead of -3.10 kcal /mol respectively for compound SP1800, and -9.40 kcal /mol instead of -3.40 kcal /mol for compound SP1822. The water surface stabilizes the aggregates and more the J-aggregates than H-aggregates which is in agreement with experimental data, showing that only J-aggregates are obtained during the formation of Langmuir Blodgett films of these compounds.

TABLE I Association energies in kcal /mol of pairs of photochromic molecules, alone and on a water wall.

Compound		J -aggregates	H -aggregates
SP1800	alone	-4.45	-3.10
	with H_2O	-13.70	-9.20
SP1822	alone	-9.40	-3.40
	with H_2O	-15.00	-13.90

The figure 1 displays the most stable system of the J-aggregates for SP1800 placed on a water wall, strong hydrophilic interactions between the molecule polar groups and the water can be observed. It is interesting to notice that molecules are not really juxtaposed, but there is a light overlap between the negative part of one and the positive part of the other leading to a tile like structure.

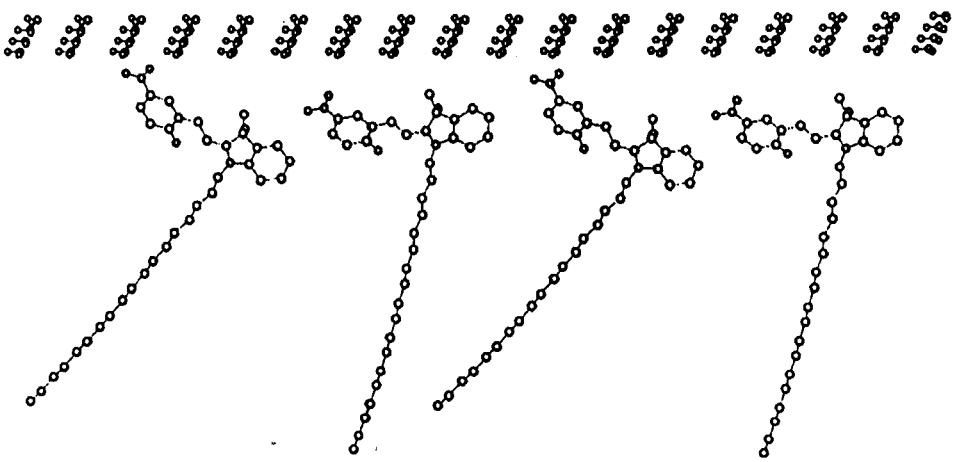
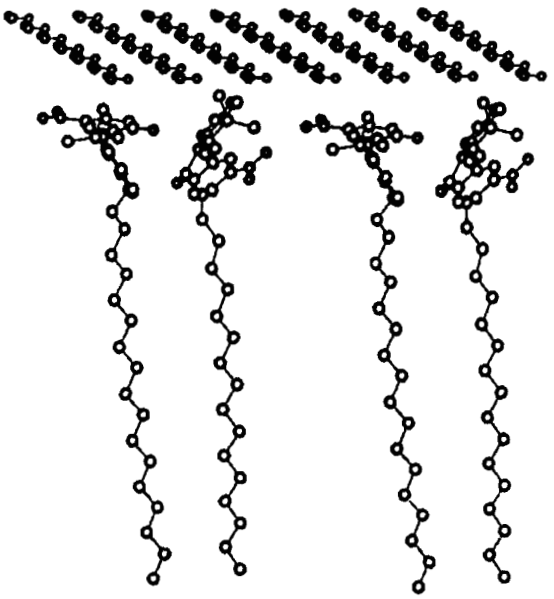


FIGURE 1 Modeling of J-aggregates for SP1800

The figure 2 shows H-aggregates of SP1800 compound, the polar interaction with the water wall are weaker.



FIGUE 2 Modeling of H-aggregates for 1822

This kind of preliminary approach using molecular modeling is encouraging and can be used to design original molecules able to lead to very stable aggregates.

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