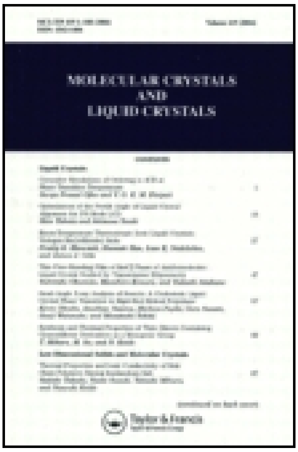

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Influence of *Meso*-Substituted Porphyrins Molecular Structure on Their Self-Organization in Floating Layers

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The influence of molecular structure peculiarities on the supramolecular organization in the bulk and thin layers was studied by the example of two new meso-*substituted ligands of tetraphenylporphyrin with substitution in alkoxygroups (-OC_4H_9) in* para- *or* ortho-*positions of phenyl rings. It is established that* meso-*alkyloxysubstituted tetraphenylporphyrin with substituents (-OC_4H_9) in the* ortho-*position (compound* ***I****) shows thermotropic monotropic mesomorphism, whereas the substitution in* para-*position (compound* ***II****) leads to the mesophase disappearance. The influence of substituent position on supramolecular organization of* meso-*substituted porphyrins in thin films was shown.*

Keywords Floating layers; liquid crystal; porphyrin; structure

1. Introduction

Obtaining structures with regular molecular definition [1,2] (the co-called "molecular architecture") is a relevant question of realization of new generation of molecular devices. Langmuir-Blodgett (LB) technique seems to be the best method to get such structures [1]. It helps us to obtain not only monopropellant layers with molecular thickness control, but to create more complicated structures with the required combination of different materials. However, LB-films' structure depends on the self-organization of the molecules in floating layers, being the basis for obtaining these films. So, in this work we turned to the analysis of the influence of discotic compounds' molecular structure on their liquid crystalline properties and supramolecular organization in floating layers.

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Structure of the derived supramolecular systems depends to a large extent on chemical structure peculiarities of forming compounds. Although phthalocyanine derivatives as the objects of thin-film technologies are studied in detail, we have only few data on their supramolecular organization dependence in thin films on the structure of particular ligands and their metal complexes for porphyrin derivatives. The urgency of floating layers and LB-films of porphyrin derivatives study is caused by the following: their supramolecular organization study makes a large contribution to the understanding of supramolecular ensembles forming dependence on the structure of this widespread in the nature compounds; that is very important for understanding of the living systems' functioning. Along with fundamental value, such researches make a large contribution to the practical application of porphyrin derivatives as sensors, sorbents and other elements of thin-film technologies.

2. Results and Discussion

Two new compounds with *meso*-substitution in the molecule were studied. Their synthesis was carried out by the earlier described method [3].

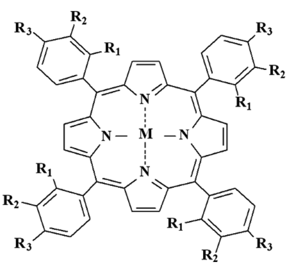
Phase state of compounds was investigated by polarizing optical microscopy method (Leitz Laborlux 12 Pol with a hot stage Mettler FP 82).

Modeling of compounds **I** ($R_1 = -OC_4H_9$) and **II** ($R_3 = -OC_4H_9$) as well as calculation of their geometric characteristics (Figs. 2, 3) were made in the HyperChem program version 7.5 (MM+ method).

Langmuir layers were formed on a FSUE «SRC «NIOPIK» Langmuir trough (Moscow, Russia). The solutions of compound **I** ($C = 0.0245\%$) and **II** ($C = 0.0445\%$) in chloroform were spread on deionized water at $20 \pm 1°C$. The compression rate was $55\,sm^2/min$. Initial extents of surface coating were **c** = 19, 24, 30, 37, 45, 50, 63% and c = 45, 49, 59, 74, 83% correspondingly.

Quantitative analysis of the isotherms was carried out using πA-π graphs. Every linear section corresponded with stable condition of the layer. Space per molecule ($\mathbf{A_{mol}}$) was equal to tangent of this linear section angle of slope. The layer structure was characterized by the molecules' angle of slope in the stack relative to air-water interface (ψ).

Volume samples investigation made us establish that alkoxysubstituted ligand of tetraphenylporphyrin **I** (with substitution in *ortho*-position of phenyl rings, Figure 1) possesses mesomorphic properties (Table 1). Such behavior is atypical for related analogues of phthalocyanine. Probably, short peripheral substituent packs optimally in the free space between phenyl fragments, creating the prerequisites for good microsegregation of supramolecular ensemble at the same time.



I M = 2H $R_1 = -OC_4H_9$ $R_2 = H$ $R_3 = H$

II M = 2H $R_1 = H$ $R_2 = H$ $R_3 = -OC_4H_9$

Figure 1. Chemical structure of *meso*-substituted tetraphenylporphyrin.

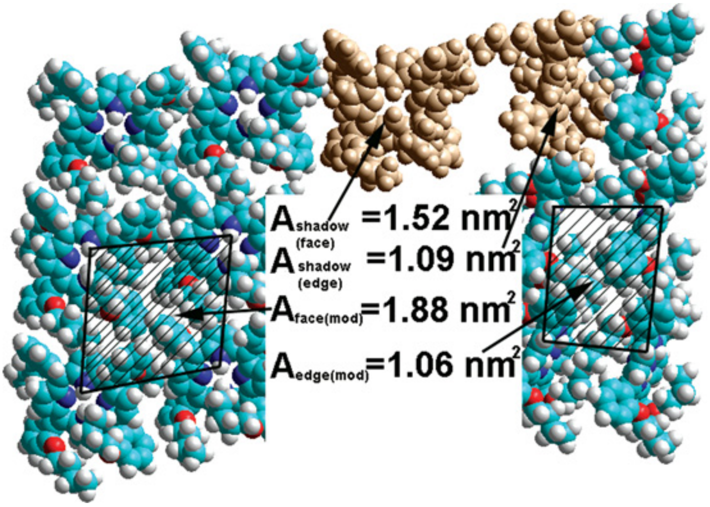


Figure 2. Types of mounting and geometry characteristics of the molecules **I**. (Figure appears in color online.)

The substitution in the *para*-position (compound **II**) leads to the mesophase disappearance (Table 1) [4,5].

Supramolecular organization in thin films of compounds **I** and **II** was investigated by Langmuir method. Analysis of Langmuir layers' isotherms of the investigated porphyrin derivatives allows to point out several linear sections on the related πA-π graphs corresponding to the stable state of the layers (Figs. 4, and 5). Area related to the molecule ($\mathbf{A_{mol}}$) and pressure zone in which the current stable state is carried out are marked by dots on the graphs.

Layer properties of the studied compounds for all analyzed coverage are shown in the Table 2.

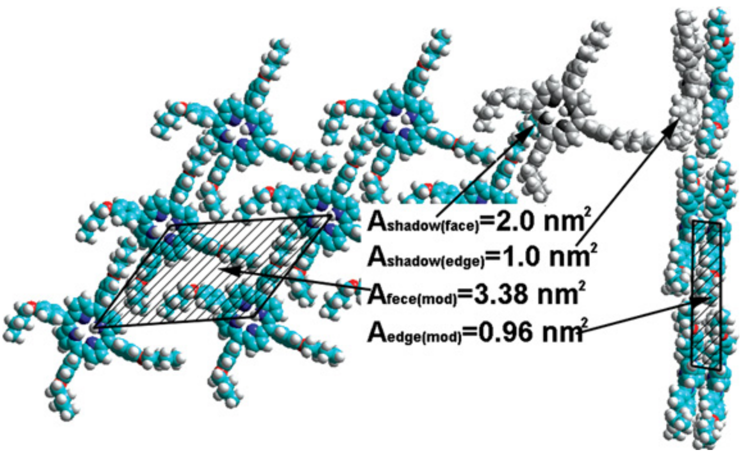


Figure 3. Types of mounting and geometry characteristics of the molecules **II**. (Figure appears in color online.)

Table 1. Phase transitions of the porphyrin derivatives

No of compound	Thermotropic mesomorphism
I	Cr · 237,7°C Iso (Iso · 176,8°C Mes · 60,2°C G) Forms the glass state with the mesophase texture conservation
II	Cr · 283,8°C Iso

(Phase transition during the cooling process) Iso – isotropic;.
Cr – crystalline phase; Mes – liquid crystal phase.

For *meso*-alkyloxysubstituted tetraphenylporphyrin **I** with substituent in *ortho*-position in all stable states $\mathbf{A_{mol}}$ is less than area related to the molecule in the densest package corresponding to the face-on molecular arrangement (even in the zone of low pressure at $\mathbf{c} = 19\%$) (Table 2). So, the structure with face-on arrangement in the studied range of coverage is not shown.

Comparison of $\mathbf{A_{mol}}$ and $\mathbf{A_{edge}}$ in the densest package for given compound (Figs. 2, and 3) shows that the stable monolayer is formed only at $\mathbf{c} = 19\%$ for the studied coverage range in the mentioned pressure zone (Table 2). Pressure increase (at $c = 19\%$) is entailed by transfer of monolayer with tilt angle $\psi = 50^o$ (according to our calculations) into bilayer ($\psi = 79^o$), and for the larger coverage – by transfer of bilayer into polylayer.

Meso-alkyloxysubstituted tetraphenylporphine **II** shows 3D-aggregation in floating layers. Homogeneous layers start to form only at $\mathbf{c} = 45\%$. In all stable states $\mathbf{A_{mol}}$ is less than area related to the molecule in the densest package corresponding to the edge-on molecular arrangement (even in the zone of low pressure at $\mathbf{c} = 45\%$) (Table 2). So, the studied compound does not form monolayer structures.

Comparison of $\mathbf{A_{mol}}$ and $\mathbf{A_{edge}}$ in the densest package of the compound **II** shows that only bilayers are formed in the mentioned pressure zone (Table 2) for the studied **c**. Coverage increase is entailed by increasing of the molecules tilt angle concerning the water – air interface from $\psi = 48^o$ ($\mathbf{c} = 45\%$) to $\psi = 90^o$ ($\mathbf{c} = 83\%$).

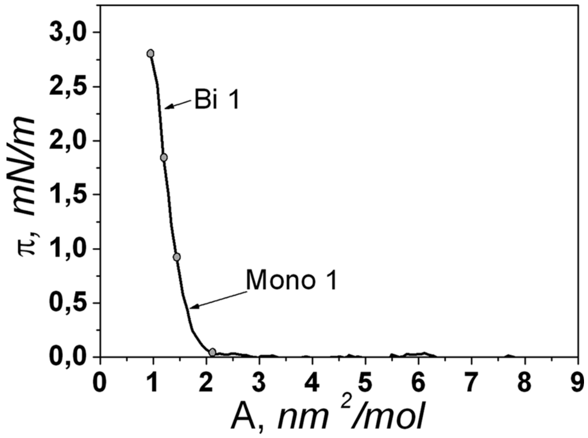


Figure 4. π-A isotherm of compound **I** ($c = 19\%$).

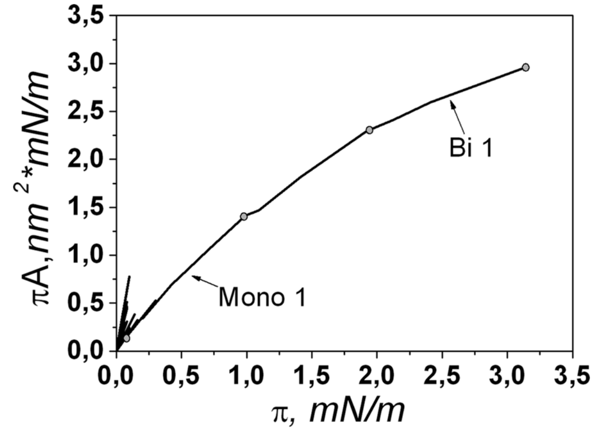


Figure 5. πA-π plot for compound **I** (c = 19%).

It is established (Fig. 6a) that area $\mathbf{A_{mol}}$ related to the molecule of compound **I** is decreasing exponentially with the coverage increase according to the expression $\mathbf{A_{mol}} = 0.62 + 513 \cdot \exp(-\mathbf{c}/2.63) + 1.36 \cdot \exp(-\mathbf{c}/15.3)$ and works for the value of $0.62\,\mathrm{nm}^2$ (Fig. 6a). Thus, minimally possible area related to the molecule under the given experiment conditions is equal to $0.62\,\mathrm{nm}^2$. The given dependence for compound **II** (in the range of the investigation) is expressed by the straight line (Fig. 6b) $\mathbf{A_{mol}} = 0.85 - 0.004 \cdot \mathbf{c}$.

Table 2. Characteristics of floating layers of studied compounds

Compound	$\mathbf{c}_{\mathrm{face}}$, %	π_i-π_f, mN/m	$\mathbf{A_{mol}}$, nm^2	State layer	ψ, deg
I	19	0,06–0,99	1,39	Mono 1	50
		1,92–3,16	0,54	Bi 1	79
	24	0,02–0,44	0,96	Bi 1	34
	30	0,04–0,70	0,82	Bi 1	40
	37	0,1–1,16	0,77	Bi 1	44
		2,18–3,5	0,40	Poly	–
	45	0–1,03	0,68	Bi 1	51
		1,79–3,04	0,36	Poly	–
	50	0–1,15	0,66	Bi 1	53
		2,14–3,24	0,33	Poly	–
	63	0–1,23	0,66	Bi 1	53
		3,04–4,75	0,19	Poly	–
II	45	0,14–0,48	0,65	Bi 1	48
	49	0,02–0,54	0,62	Bi 1	51
	59	0,06–0,66	0,61	Bi 1	52
	74	0,04–1,6	0,52	Bi 1	67
	83	0,08–3,03	0,48	Bi 1	90

ψ – molecules' tilt angle in the layer; $\mathbf{c}_{\mathrm{face}}$ – face-on coverage; π_i–π_f – stable state pressure zone, mN/m.

$\mathrm{A_{mol}}$ – area related to a molecule, nm^2.

Mono 1 – monolayer 1; Bi 1 – bilayer 1; Poly – Polylayer.

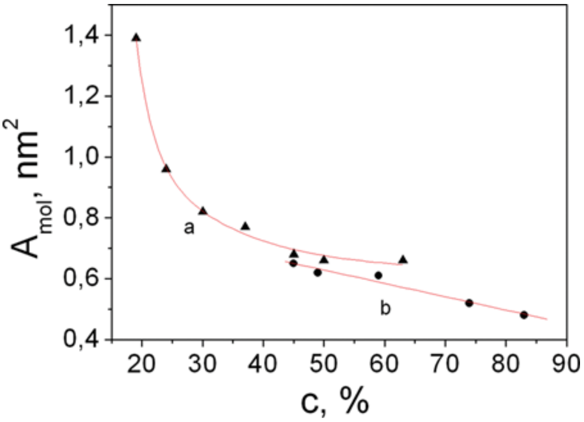


Figure 6. A_{mol} dependence on the initial coverage (a – for compound **I**, b – for compound **II**). (Figure appears in color online.)

So, mesogenic *meso*-alkyloxysubstituted tetraphenylporphyrin with substituent in *ortho*-position (compound **I**) forms homogeneous stable layers already at the initial coverage of 19%. In this case tilt angle concerning the water – air interface in the first stable state is equal to $\psi = 50°$. Non-mesogenic *meso*-alkyloxysubstituted tetraphenylporphyrin with substituent in *para*-position (compound **II**) forms stable layers only from $\mathbf{c} = 45\%$ and is more inclined to 3D aggregation than mesogenic compound **I**.

In the range of large initial coverage both compounds form stacks in which molecules take up positions of close tilt angles to the surface: at $\mathbf{c} = 45\%$ $\psi = 51°$ and $\psi = 48°$ for compounds **I** and **II** correspondingly.

3. Conclusion

The influence of molecular structure peculiarities on the supramolecular organization in the bulk and thin layers was studied by the example of two new *meso*-substituted ligands of tetraphenylporphyrin with substitution by alkoxygroups ($-OC_4H_9$) in *para*- or *ortho*-positions of phenyl rings. It is established that *meso*-alkyloxysubstituted tetraphenylporphyrin with substituents ($-OC_4H_9$) in the *ortho*-position (compound **I**) shows thermotropic monotropic mesomorphism, whereas the substitution in *para*-position (compound **II**) leads to the mesophase disappearance.

It is shown that mesogenic *ortho*-alkyloxysubstituted tetraphenylporphyrin (compound **I**) in floating layers forms homogeneous stable layers at the initial coverage of 19% and is more inclined to 3D aggregation than non-mesogenic *meso*-alkyloxysubstituted tetraphenylporphyrin with substituents ($-OC_4H_9$) in *para*-position (compound **II**).

It is also established that at the coverage of $\mathbf{c} = 45\%$ both compounds form stacks with close tilt angles to the surface.

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