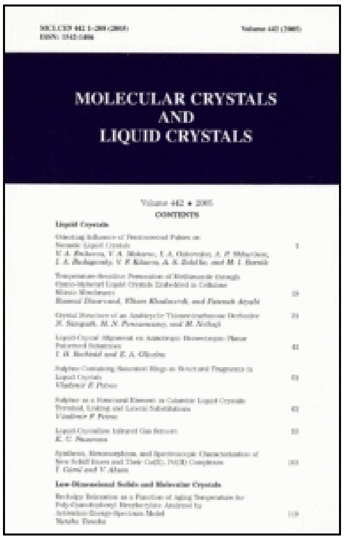


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644168

Influence of *Meso*-Substituted Porphyrins Molecular Structure on Their Mesogenity

N. Usol'tseva[a]; V. Bykova[a]; N. Zharnikova[a]; A. Alexandrov[a]; A. Semeikin[a]; A. Kazak[a]
[a] Ivanovo State University, Ivanovo, Russia

To cite this Article Usol'tseva, N. , Bykova, V. , Zharnikova, N. , Alexandrov, A. , Semeikin, A. and Kazak, A.(2010) 'Influence of *Meso*-Substituted Porphyrins Molecular Structure on Their Mesogenity', Molecular Crystals and Liquid Crystals, 525: 1, 184 — 193

To link to this Article: DOI: 10.1080/15421401003799557

URL: http://dx.doi.org/10.1080/15421401003799557

Mol. Cryst. Liq. Cryst., Vol. 525: pp. 184–193, 2010
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421401003799557

Influence of *Meso*-Substituted Porphyrins Molecular Structure on Their Mesogenity

N. USOL'TSEVA, V. BYKOVA, N. ZHARNIKOVA,
A. ALEXANDROV, A. SEMEIKIN, AND A. KAZAK

Ivanovo State University, Ivanovo, Russia

The study of 27 new meso-*substituted free-base and metal complexes of tetraphenylporphyrins with substitution by alkoxygroups (from -OC_4H_9 to -$OC_{16}H_{33}$) in* para-, meta-, *or* ortho-*position has been carried out. Out of 11 synthesized free-base alkoxysubstituted tetraphenylporphyrins – 4 possess mesomorphic state of columnar type and 1 – lyotropic mesomorphism in binary systems with toluene, benzene or chloroform. The important role of substituents position in phenyl rings of porphyrins was determined. It was established, that metal complexes (Cu, Ni, Zn, Ag, Pd, $SnCl_2$, ZnOAc, VO) of mesogenic free-base porphyrins does not display liquid crystal properties.*

Keywords Liquid crystal properties; metallomesogens; porphyrin derivatives

Introduction

Unique supramolecular structures of disc-like mesogens (columnar three dimensional, columnar lamellar and nematic) show potential in many technologies, such as photovoltaic cells, semiconductors, gas sensors, etc. [1]. Compared to disc-like phthalocyanine mesogens porphyrin derivatives are less investigated, probably because of their more complicated synthesis process. After J. Goodby, systematic work in this area was carried out by B. Gregg, M. Fox and A. Bard, who described the synthesis and physical properties of octasubstituted free-base porphyrins as well as metal complexes containing a variety of metals [2,3]. D. Bruce established, that 5,15-disubstituted metal porphyrins are able to show smectic A and N-phase [4,5]. Shimizu *et al.* [6] examined mesomorphic phase transition of tetraphenylporphyrins with four long aliphatic chains in *para*-position and their metal complexes. They determined non-mesogenity of alkoxyderivatives. These data came up against Kugimiya *et al.* [7] work. According to this work some alkoxyderivatives were mesogenic. From the theoretical view point and from the directional synthesis of new mesogens the study of connection between molecular structure and ability to form liquid crystal phases by these discotic compounds related to phthalocyanine is very important.

This manuscript has not been published elsewhere and it has not been submitted simultaneously for publication elsewhere.

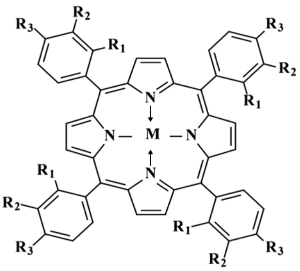
Address correspondence to N. Usol'tseva, Ivanovo State University, Ivanovo 153025, Russia. Tel.: +7(4932)370808; Fax: +7(4932)324677; E-mail: nv_usoltseva@mail.ru

That's why we think it was important to spread the research of porphyrin derivatives and their metal complexes mesomorphism to the compounds with alkoxygroups in *ortho*- or *meta*-positions. Taking into consideration the contradiction between data in publications [6,7], we also studied mesomorphism of some porphyrin alkoxyderivatives with substitution in *para*-position (-OC_nH_{2n+1}, n = 3–10, 12, 16).

Experimental

With the purpose to research the relationship between porphyrin derivatives molecular structure, their supramolecular packing and properties, the synthesis and study of 27 new compounds with *meso*-substitution in the molecule have been carried out. The synthetic details of the derivatives mentioned in this report (Fig. 1) are described

INFLUENCE OF *MESO*-SUBSTITUTED PORPHYRINS MOLECULAR STRUCTURE ON THEIR MESOGENITY



I	M = 2H	$R_1 = H$	$R_2 = H$	$R_3 = OCH_2CH = CH_2$
II	M = 2H	$R_1 = H$	$R_2 = H$	$R_3 = OC_4H_9$
III	M = 2H	$R_1 = H$	$R_2 = H$	$R_3 = OC_7H_{15}$
IV	M = 2H	$R_1 = H$	$R_2 = H$	$R_3 = OC_8H_{17}$
V	M = 2H	$R_1 = H$	$R_2 = H$	$R_3 = OC_{10}H_{21}$
VI	M = 2H	$R_1 = H$	$R_2 = H$	$R_3 = OC_{12}H_{25}$
VII	M = 2H	$R_1 = H$	$R_2 = H$	$R_3 = OC_{16}H_{33}$
VIII	M = 2H	$R_1 = H$	$R_2 = OC_4H_9$	$R_3 = H$
IX	M = 2H	$R_1 = OC_4H_9$	$R_2 = H$	$R_3 = H$
X	M = 2H	$R_1 = OC_{10}H_{21}$	$R_2 = H$	$R_3 = H$
XI	M = 2H	$R_1 = OC_{16}H_{33}$	$R_2 = H$	$R_3 = H$
XII	M = Cu	$R_1 = H$	$R_2 = H$	$R_3 = OC_{16}H_{33}$
XIII	M = Cu	$R_1 = OC_{16}H_{33}$	$R_2 = H$	$R_3 = H$
XIV	M = Ni	$R_1 = H$	$R_2 = H$	$R_3 = OC_{16}H_{33}$
XV	M = Ni	$R_1 = OC_{16}H_{33}$	$R_2 = H$	$R_3 = H$
XVI	M = Zn	$R_1 = H$	$R_2 = H$	$R_3 = OC_{16}H_{33}$
XVII	M = Zn	$R_1 = OC_{16}H_{33}$	$R_2 = H$	$R_3 = H$
XVIII	M = Ag	$R_1 = H$	$R_2 = H$	$R_3 = OC_{16}H_{33}$
XIX	M = Ag	$R_1 = OC_{16}H_{33}$	$R_2 = H$	$R_3 = H$
XX	M = Pd	$R_1 = H$	$R_2 = H$	$R_3 = OC_{16}H_{33}$
XXI	M = Pd	$R_1 = OC_{16}H_{33}$	$R_2 = H$	$R_3 = H$
XXII	M = $SnCl_2$	$R_1 = H$	$R_2 = H$	$R_3 = OC_{16}H_{33}$
XXIII	M = $SnCl_2$	$R_1 = OC_{16}H_{33}$	$R_2 = H$	$R_3 = H$
XXIV	M = InOAc	$R_1 = H$	$R_2 = H$	$R_3 = OC_{16}H_{33}$
XXV	M = InOAc	$R_1 = OC_{16}H_{33}$	$R_2 = H$	$R_3 = H$
XXVI	M = VO	$R_1 = H$	$R_2 = H$	$R_3 = OC_{16}H_{33}$
XXVII	M = VO	$R_1 = OC_{16}H_{33}$	$R_2 = H$	$R_3 = H$

Figure 1. Chemical structure of compounds **I** – **XXVII**.

elsewhere [8]. The phase behavior of free-base and metal-complexes of porphyrins was investigated by polarizing optical microscopy (Leitz LaborLux 12 Pol with a hot stage Mettler FP 82), differential scanning calorimetry (using a Netzsch DSC 200 PC Phox calorimeter) and X-ray diffraction method (Cu K_α-irradiation, X-ray powder patterns were indexed by Ito's method [9]).

Four out of the eleven synthesized alkoxysubstituted free-base tetraphenylporphyrins (with substituents in *para*-, *meta*- or *ortho*-positions of phenyl rings) possess mesomorphic properties: the **VI** and **VII** homologues in *para*-position of substituents in phenyl rings, and also the **IX** and the **XI** – in *ortho*-position of substituents (Fig. 1, Table 1).

It was surprising, that compound **IX** with short substituent in *ortho*-position displays mesomorphic properties. Such behavior is not typical for related phthalocyanine compounds with non-peripheral substituents (-OC_5H_{11} and -OC_8H_{17}) [10,11]. Probably, short peripheral substituent (-OC_4H_9) is likely to pack optimally in vacant space between phenyl fragments, simultaneously creating prerequisites for good microsegregation of supramolecular ensemble. Below we prove it by X-ray method.

On Figure 2 the textures of thermotropic columnar phases of the studied compounds and lyomesophases (Fig. 3) are represented. The transition temperatures of the thermotropic phases were drastically reduced in binary systems with organic solvents.

The analysis of phase transitions temperature crystal – isotropic phase shows that at the transition from *para*- to *meta*- and *ortho*-substitution ($R = -OC_4H_9$) of porphyrin derivatives the decrease of phase transition temperature Cr – I in more than 2 times is observed. For all tetrasubstituted porphyrin homologues with *para*-position of alkoxygroups the increase of carbon atoms number in the substituent also leads to the decrease of phase transition temperature Cr – I.

The thermotropic 2D columnar phase formation by the representatives of this series of compounds (**VI**, **IX**, **XI**) is observed monotropically. For *para*-substituted

Table 1. Temperature of phase transitions of free-base compounds **I** – **XI**

Number of compound	Phase transitions (polarizing microscopy)	Lyotropic mesomorphism
I	Cr · 253.3°C Iso	–
II	Cr · 283.8°C Iso	–
III	Cr · 253.3°C Iso	–
IV	Cr · 214.1°C Iso	–
V	Cr · 136.6°C Iso	–
VI	Cr · 124.1°C Iso (Iso · 88.7°C Mes · 44.6°C G) glassing with mesophase texture retention	–
VII	Cr · 112.3°C Iso (Iso · 93.1°C Mes · 59.0°C G) glassing with mesophase texture retention	+ (toluene, benzene, chloroform)
VIII	Cr · 125.7°C Iso	–
IX	Cr · 237.7°C Iso (Iso · 176.8°C Mes · 60.2°C G) glassing with mesophase texture retention	–
X	Cr · 149.0°C Iso	–
XI	Cr · 79.9°C Iso (Iso · 53.3°C Mes · 25.0°C Cr)	–

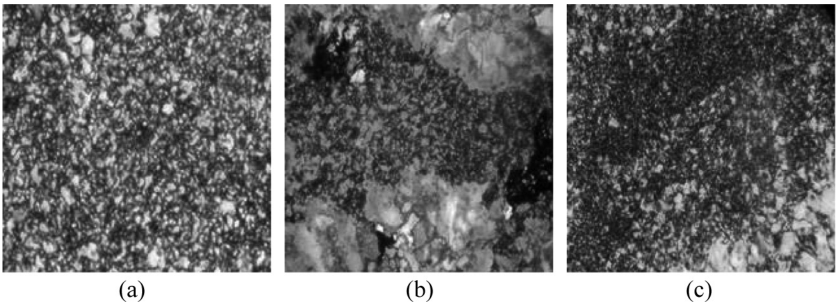

(a) (b) (c)

Figure 2. Textures of the thermotropic mesophase of compounds: (a) – **VI** on cooling, temperature 74.0°C; (b) – **VII** on cooling, temperature 93.1°C; (c) – **XI** on cooling, T = 53.3°C; ×250.

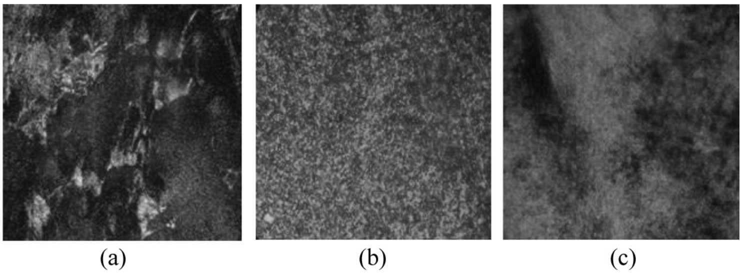

(a) (b) (c)

Figure 3. Textures of contact preparations of compound **VII**: (a) – with toluene, (b) – with benzene, (c) – with chloroform. T = 22.0°C, ×250.

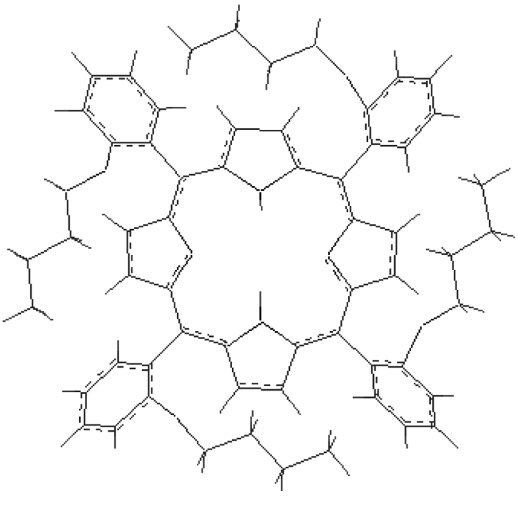


Figure 4. The optimized geometry of porphyrin derivative **IX**.

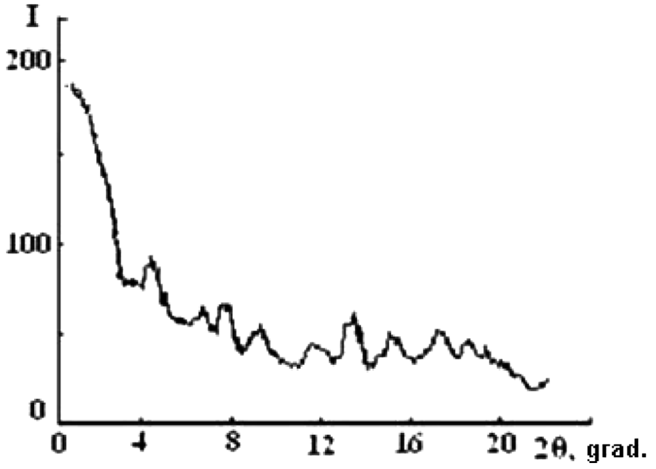


Figure 5. X-ray reflectivity data for compound **IX**, on heating (T = 200°C).

derivatives mesogenity is revealed only starting from the 12th homologue (**VI**), but for *ortho*-substituted ones even the fourth homologue (**IX**) is mesomorphic. According to the X-ray data compound **VII** displays nematic-like behavior enantiotropically (see below), though neither by means of polarizing microscopy nor by DSC method phase transition into nematic phase could be established on heating.

Probably it is connected with the presence of considerable vacant spaces in tetrasubstituted porphyrin derivatives with *para*-position of substituents that hinders successful microsegregation with columnar supramolecular packing formation.

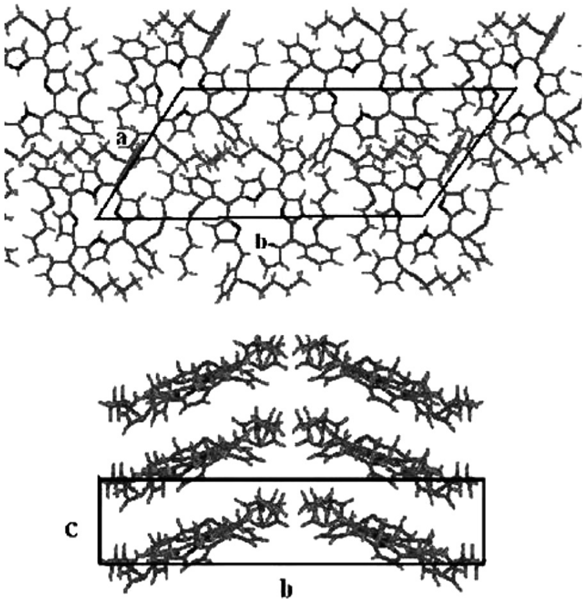


Figure 6. Possible molecular arrangements of compound **IX** in low-level cell lattice (High-temperature phase, T = 200°C).

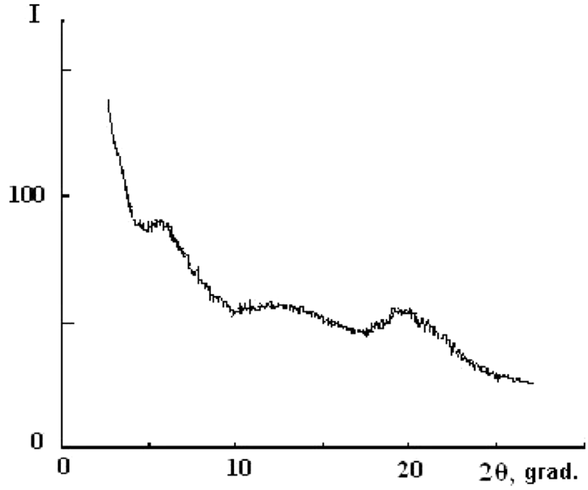


Figure 7. X-ray reflectivity data for the mesophase of compound **IX** on cooling from isotropic state (T = 170°C).

On the contrary, in *ortho*-substitution an alkoxy group is optimally packed into vacant spaces between phenyl molecule fragments that promotes microsegregation of hydrophobic periphery and central macrocycle. Namely this supports the supramolecular ensemble of columnar mesophase.

To clarify this question we compared the above mentioned data with the data of X-ray investigation. Here is the optimized geometry of porphyrin derivative **IX** (AM-1 HyperChem.).

The phases on heating seem to be crystal ones. Crystal lattice of low-temperature phase is monoclinic with parameters of low-level cell equals to $a = 1.356$ nm, $b = 2.774$ nm, $c = 0.89$ nm, $\alpha = \gamma = 90$°C, $\beta = 125.5$°C. In low-level cell there are 2 molecules of the compound.

Crystal lattice of high-temperature phase is also monoclinic but with other parameters of low-level cell as follows: $a = 1.370$ nm, $b = 2.407$ nm, $c = 0.945$ nm,

Table 2. Structural parameters of mesophase of compound **IX**

T, °C	N	d_{exp},[a] nm	g_l,[b] %
203	1	1.333	10.9
	2	0.664	
	3	0.444	
170	1	1.342	10.8
	2	0.670	
	3	0.435	
23	1	1.382	10.1
	2	1.284	
	3	0.665	
	4	0.463	

[a] d = interplanar distance.

[b] $g_l = (\Delta d/d$ – imperfection parameter of second order.

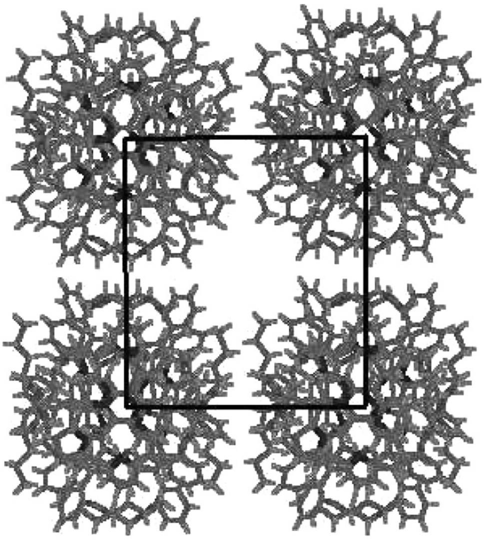


Figure 8. The probable scheme of stacking of compound **IX** molecules in mesophase (the cross section is perpendicular to the columnar axis, T = 70°C).

$\alpha = \gamma = 90°C$, $\beta = 128.2°C$. In low-level cell 2 molecules of the compound are presented (Figs. 5 and 6).

In contrast to it, on cooling mesomorphic state could be observed (Fig. 7, Table 2). Here the probable scheme of stacking of molecules in mesophases is represented (Fig. 8). Molecules form a tilted columnar structure with rectangular lattice. At higher temperatures rectangular type of lattice transforms into the square one due to azimuth disorientation of columns.

Compound **VII** with *para*-substitution ($R = OC_{16}H_{33}$) has the crystal monoclinic lattice of symmetry $P2_1/m$ with the parameters of an elementary cell: $a = 3.31$ nm,

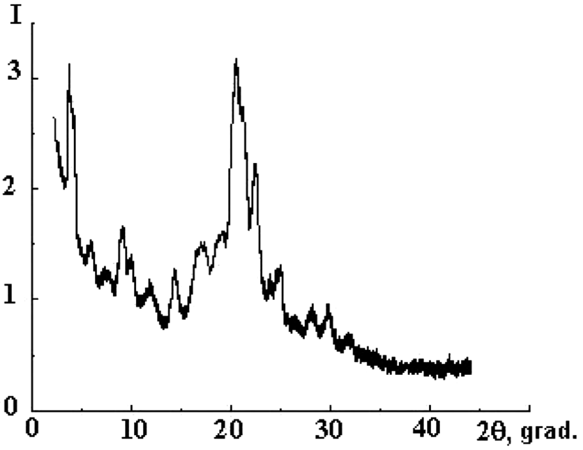


Figure 9. X-ray reflectivity data for the non-oriented sample crystal phase of compound **VII** (T = 22°C).

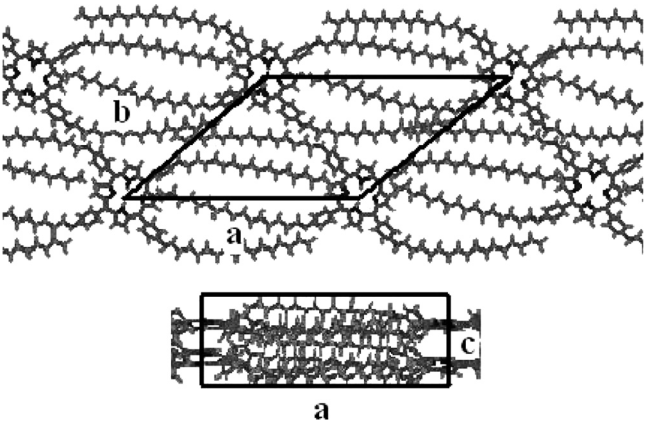


Figure 10. The scheme of the probable packing of the porphyrin **VII** molecules in the elementary cell of the crystal lattice.

$b = 2.087$ nm, $c = 0.900$ nm, $\alpha = \beta = 90°$, $\gamma = 134.2°$. There are two molecules per unit cell. The calculated density of the crystal phase is 1.17 gr/sm^3.

The probable packing of the porphyrin molecules in the elementary cell is represented on Fig. 10. The structure is nematogenic as it has overlapping of the adjoining molecules' substituents (in the *ab* plane).

X-ray received at the temperature of 125°C contains low-angled and wide-angled maximums of diffusive type that is typical for nematic phase, Figure 11.

The periods corresponding to the low-angled and wide-angled maximums are 3.33 nm and 0.462 nm accordingly. The correlation of the paracrystal dislocations values in the longitudinal $g_{1/l} = 17.2\%$ and side $g_{1\perp} = 13.6\%$ molecules packing valued from the radial width of the diffractive maximums [12] corresponds to the classical nematic phase.

Porphyrin **VII** nematic phase is enantiomorphic. But there is no clear phase transition *nematic phase* ↔ *isotropic liquid.* On the heating cycle there is a slow

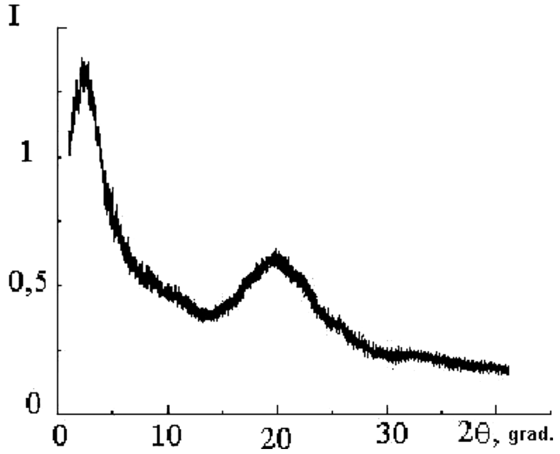


Figure 11. X-ray reflectivity data for the porphyrin **VII** liquid crystal phase (T = 125°C).

weakening of the diffusive low-angled maximum and its transformation to the diffusive halo. At the temperature of 172°C (when only the diffusive halo is observed in the low-angled field) the violation parameter in the side molecule packing $g_{1\perp} = 21\%$.

The cause of the extended phase transition lies evidently in the fact that molecular associates with the nematic structure are formed in the isotropic phase. In these phases the circular maximums of the diffusive type can be observed in low angles. This high temperature field is revealed as an isotropic phase in the polarizing microscope.

With the purpose to study the liquid crystal properties of metal complexes the *ortho*- and *para*-subsituted porphyrin derivatives, analogues of mesomorphic compounds **VII** and **XI** were synthesized (Fig. 1, **XII** – **XXVII**). It was established that all the synthesized metal complexes lost their mesomorphic properties peculiar to the free-base analogues.

Conclusion

The study of 27 new *meso*-substituted free-base and metal complexes of tetraphenylporphyrins with substitution by alkoxygroups (from -OC_4H_9 to -$OC_{16}H_{33}$) in *para*-, *meta*-, or *ortho*-position has been carried out. Out of 11 synthesized free-base alkoxysubstituted tetraphenylporphyrins – 4 possess mesomorphic state of columnar type and 1 – lyotropic mesomorphism in binary systems with toluene, benzene or chloroform. The important role of substituents position in phenyl rings of porphyrins was determined. Molecule modification due to structural isomerization from *para*-position of alkoxygroups in phenyl rings to their *meta*- or *ortho*-positions leads to the decrease of Cr – I phase transition temperature. In the homologous series of *ortho*-substituted porphyrin derivatives mesogenity is revealed with lower number of carbon atoms in alkoxygroups in comparison with *para*-substituted analogues. The increase of the carbon atom number in alkoxygroup in *para*-position of phenyl rings leads to the decrease of the temperature of Cr – I phase transition.

It was established, that metal complexes (Cu, Ni, Zn, Ag, Pd, $SnCl_2$, ZnOAc, VO) of mesogenic free-base porphyrins does not display liquid crystal properties.

Acknowledgments

The work is carried out with the financial support of the RFBR (grant No. 07-03-00427).

References

[1] Usol'tseva, N. V., Akopova, O. B., Bykova, V. V. *et al.* (2004). *Liquid Crystals: Disc-Like Mesogens*, Ivanovo, Russia, 546 (Rus.).

[2] Gregg, B. A., Fox, M. A., & Bard, A. J. (1989). *J. Am. Chem. Soc.*, *111*, 3024.

[3] Gregg, B. A., Fox, M. A., & Bard, A. J. (1987). *J. Chem. Soc. Chem. Commun.*, *1134*.

[4] Bruce, D. W. (1996). In: *Inorganic Materials*, 2nd edn., Ducan W. Bruce & Dermot, O'Hare (Eds.), John Wiley and Sons: Chichester, New York, Brisbane, Toronto, Singapore, 429.

[5] Bruce, D. W., Dunmur, D. A., Santa, L. S., & Wali, M. A. (1992). *J. Mater. Chem.*, *2*, 363.

[6] Shimizu, Y., Miya, M., Nagata, A., Ohta, K., Matsumura, A., Yamamoto, I., & Kusabayashi, S. (1991). *Chem. Lett.*, *20*, 25.

[7] Kugimiya, S., & Takemura, M. (1990). *Tetrahedron Lett.*, *31*, 3160.

[8] Bykova, V., Usol'tseva, N., & Semeikin, A. *et al*. (2007). *J. Liquid Crystals and their Application*, *4*, 67 (Rus.).

[9] Ito, T. (1950). *X-ray Studies on Polymorphism*, Marűzen Gj. Ltd.: Tokyo, 187.

[10] Cook, M. J., Daniel, M. F., Harrison, J. K., McKeown, N. B., & Tomson, A. (1987). *J. Chem. Soc. Chem. Commun.*, *208*, 1086.

[11] Cherodian, A. S., Davies, A. N., Richardson, R. M., Cook, M. J., McKeown, N. B., Thomson, A. J., Feijoo, J., Ungar, G., & Harrison, J. (1991). *Mol. Cryst. Liq. Cryst.*, *196*, 103.

[12] Alexandrov, A. I. (1976). *Zhidkie Kristally i ih Prakticheskoe Primenenie*, Mezhvuzovskii sbornik: Ivanovo, IGU, 14 (Rus.).