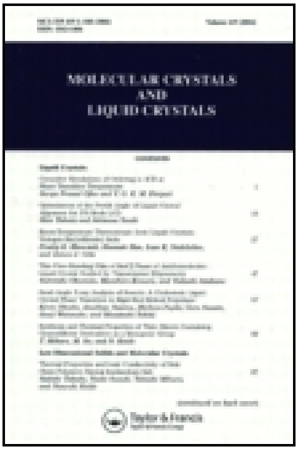

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The Prognosis of Columnar Mesomorphism and Experimental Data for a New Series of Porphin Derivatives

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The Prognosis of Columnar Mesomorphism and Experimental Data for a New Series of Porphin Derivatives

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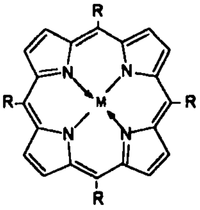
The results of the columnar mesomorphism (CM) prognosis and experimental data for the verification of a new series porphyrine derivatives (**I a, b**) are represented here. The calculation of molecular parameters (MP) for a known series porphyrins (**I a** – M = 2H, n=12, 16, 18; M = Zn or Cu, n = 16, 18) and others hypothetical structures is carried out on two algorithms. Some of hypothetical structures have been synthesized and their lyotropic and thermotropic mesomorphism has been investigated. The better correlation of the CM prognosis with experimental data has been found in case of new algorithm use, when all atoms of oxygen of near ester groups are included in the central part of a molecule.

Keywords: columnar mesomorphism; mesogenic compounds; porphin derivatives; prognosis synthesis

INTRODUCTION

We already reported about the prognosis of columnar mesophases (CM) for tetra- octa- and deca- substituted phthalocyanine and porphyrins with different hydrophobic substituents [1-5]. It was shown, that while prognosing the mesomorphism for tetrasubstituted phthalocyanine it is necessary to take into account the possible pairing of molecules in the mesophase [3]. It is necessary to enter the additional molecular parameters (MP) for tetrasubstituted porphyrins, with the aim of increasing the probability of CM prognosis [5].

As a development of these previous investigations [1-5] a new series of compounds **I a, b** (only five kinds of these materials were known before [6]) are discussed here. The peculiarity of all these samples is the number of substitutents on a periphery of the molecules: no more than 4. The aim of our work is to reveal the influence of a reduced number of peripheral substituents of compounds series I on MP and to develop the prognosis of columnar mesomorphism in this case. In particular, to study the influence of the different algorithms of MP calculation on the precision of prognosis. We have also synthesized some of these compounds for the prognosis verification and for their mesomorphic properties investigation.



M = 2H, Cu, Co, Zn

I **a)** R = C_6H_4-O (O)CC_nH_{2n+1}, n = 1-18;

b) R = C_6H_4-O (O)CC_6H_4-C_nH_{2n+1}, n = 1-12;

METHODS AND MATERIALS

The research method is a calculation and analysis of molecular parameters (MP) values. The calculation technique does not differ from the one-proposed earlier [1-7]. Structures of molecules were optimized by a molecular-mechanic method (force field MM+). Optimization of geometry was finished at a gradient 0.01 kcal/mol.

Three types of parameters were calculated: i) parameters connected which anisometric properties of a molecule or its moieties ($K = L_{max} / s$, L_{max} – maximum length of the molecule, s – thickness of the molecule in the stable conformation; $K_c = l_c / b_{c_1}$, l_c – length of the centre, b_c - width of the centre including with adjoining heteroatoms; $K_p = l_c / 2l_p$, where $2l_p$ – length of the periphery, hydrocarbon moieties being at trans- conformation.); ii) parameter based on the ratio of the real number of peripheral substituents in the molecule to the maximum possible number of substituents ($K_s = N / N_{max}$, N - number of the substituents in the molecule, N_{max}- the maximum possible number of substituents); iii) parameters based on the ratio of the central fragment weights to the weights of peripheral substituents ($M_m = M_c / M_p$, where M_c – molecular mass of the central fragment, including heteroatoms, adjoining to it, M_p – molecular mass of the periphery; $M_r = M_m \cdot K_s$ - transformed molecular-mass parameter considering the degree of central fragment substitution by peripheral substituents).

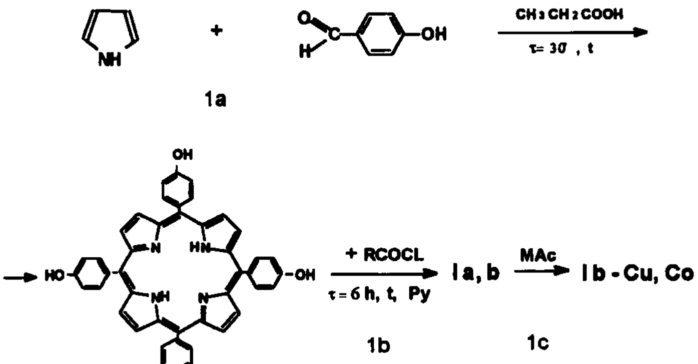
Besides, another parameter K_{ar} was introduced [1]. It made it possible to estimate the density of the peripheral substituents packing mesogenic or non mesogenic compounds. It was calculated by using the following formula: $K_{ax} = N_p / \pi (l_p^2 + l_p * l_c)$, N_p – number of carbon, hydrogen and other atoms surrounding the central fragment.

The numera series received earlier [1, 7] in the MP analysis of more than 600 non-mesogenic or mesogenic compounds serve as a mesogenic (disc-like compounds) criterion for the tested molecules. This series is as follows: $K = 2.00 - 8.50$, $K_c = 1.00 - 2.60$, $K_s = 0.25 - 1.00$, $K_p = 0.25$ -

0.70, M_m = 0.30 - 0.80, M_r = 0.15 - 0.80 [7], K_{ar} = 0.080 - 0.300 [1]. The structures, which have the parameters values in the above mentioned range are potentially discotic mesogens. It is necessary to emphasize the closer the boundaries of the ranges are, the lesser the reliability of mesophase prediction is. It has been revealed that in case one of the parameters falls outside the limits of this series, the probability of CM existence for such structures is very small.

The synthesis of the porphin derivatives was also used for the prognosis results verification. Compounds I **a**, **b** were synthesized as shown in scheme 1.

Scheme 1



1a

1b

1c

a) R = C_nH_{2n+1}, n=5, 7
b) R = C_6H_4-OC_nH_{2n+1}, n= 3, 7, 8, 12

The detailed methods of separate stages of reaction synthesis are listed below.

Organic solvents, e.g. benzene, toluene, xylene, linear alkanes, are commercially available and were used without further purification.

RESULTS AND DISCUSSION

We calculated molecular parameters (MP) of 5 known and 25 hypothetic structures series I using two different algorithms (See Tables 1, 2). In the first case (1) the central part of a molecule included four directly linked oxygen atoms (See the upper sublines in the Tables 1, 2).

TABLE 1 Calculated values of molecular parameters of known and hypothetical structures series I a and their metal complexes

n	K	K_p	K_{ar}	M_m	M_r	P	E	T,°C
Ia-1	4.15	0.586	0.123	0.567	0.189	+		
	«—»	1.93'	0.131	3.92'	1.31'	–		
2	4.59	0.440	0.131	0.513	0.171	+		
	«—»	1.55'	0.161	2.96'	0.99'	–		
3	4.38	0.406	0.133	0.462	0.156	+		
	«—»	1.09'	0.136	2.37'	0.79'	–		
4	5.38	0.347	0.118	0.432	0.144'	+, –		
	«—»	0.90'	0.128	1.98'	0.660	–		
5	5.87«	0.317	0.114	0.400	0.134'	–	–	subl.
	—»	0.80'	0.122	1.70'	0.567	–		
7	6.88	0.268	0.104	0.349	0.116'	–	–	300, destr.
	«—»	0.594	0.114	1.33'	0.442	–		
8	6.69	0.249	0.099	0.329	0.110'	–		
	«—»	0.532	0.107	1.20'	0.340	–		
12	8.61'	0.205'	0.095	0.265'	0.088'	–	–	143.8
	«—»	0.377	0.093	0.855'	0.285	–		[6]
16	11.0'	0.161'	0.075'	0.222'	0.074'	–	–	123.4
	«—»	0.297	0.084	0.666	0.222	–		[6]
18	9.77'	0.145'	0.085	0.205'	0.068'	–	–	117.3
	«—»	0.258	0.075'	0.599	0.200	–		[6]
16-Zn	10.8'	0.156'	0.077'	0.268'	0.089'	–	–	138.2
	«—»	0.294	0.082	0.728	0.243	–		[6]
16-Cu	10.8'	0.156'	0.077'	0.266'	0.089'	–	–	132.9
	«—»	0.294	0.082	0.726	0.242	–		[6]

Note: ' – indication of parameters, falling outside the limits of established boundary values; K_c = 1.01, K_s = 0.33 – for the entire series; P- the prognosis of CM; E – experimental data; T – transition temperatures; subl.- sublimate; destr.- destruction.

In the second case (2) all eight oxygen atoms of ester groups belonged to the central part (See the lower sublines in the Tables 1, 2).

The negative prognosis was established for compounds **I a (M= 2H, n= 12, 16, 18) & (M= Zn or Cu, n= 16, 18)** with the help algorithms (See Table 1). It is well correlated with the data of the previous research [6], where it was shown, that these materials do not form any columnar mesophases, but the appearance of smectic phases is possible. The clearing temperatures are presented in the table 1.

Other compounds (See tables 1, 2) were hypothetical. Some of them were synthesized: **I a** (M=2H, n =5, 7), **I b** (M=2H, n =3, 7, 8, 12 and M =Co, Cu, n=12) aiming at verification of our prognosis the results using algorithms (1) and (2). All the synthesized products possess spectroscopic properties (UV-VIS spectroscopy, NMR) and elemental analysis in accordance with the proposed structures (See Tables 3, 4).

Afterwards their thermo- and lyo- mesomorphism was investigated. Using the method of polarizing microscopy it has been established, that **I a-5, 7** are non-mesomorphic mesogens. Thermodestruction of the samples **I a-7** takes place at the temperature above 300 °C without transition to isotropic state. The absence of mesomorphism of samples **I a 5, 7** (See Table 1) is well correlated with the results of the prognosis biased on both algorithms.

Compounds **I b** (M=2H, n=7, 8) and **I b** (Co, n=12) soften at heating and spread under pressure without wetting the slides. They show nongeometrical texture. However mesophases with digitizer contours are observed at shift deformation (Figure 1 illustrates), which is characteristic of columnar mesophases with hexagonal packing [11,12]. The temperature being reduced the samples strongly overcool, some of them displaying glass transition (**Ib-8**).

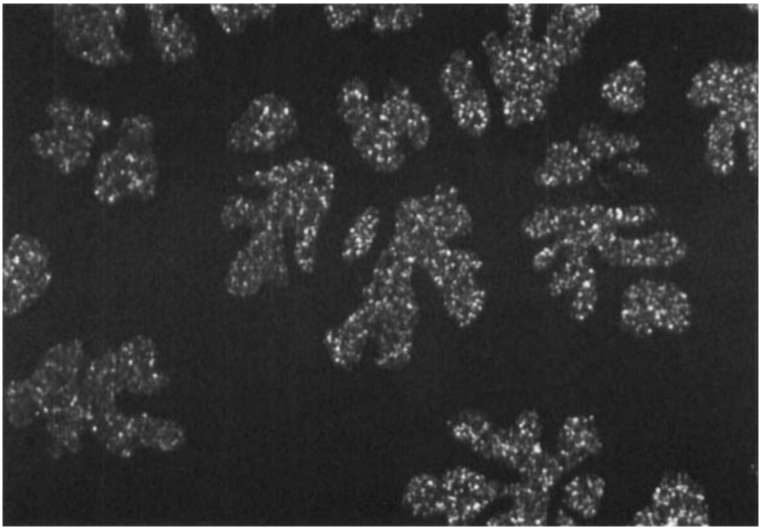


FIGURE 1 Photomicrograph of texture with digit-like contours of **I b-7** at 159 °C on heating, crossed polarizers, (160 x), shift deformation. See Color Plate XXII at the back of this issue.

The transition temperatures are presented in the table 2. It seems noteworthy, that for these compounds the second algorithm gives the best correlation of experiment results with the data of the prognosis, except for of cobalt complex porphyrine. In this case the second algorithm gives the equiprobable prognosis for CM existence (See Table 2).

Table 2 Calculated values of molecular parameters of hypothetical structures **I b** and their metal complexes

n	K	K_p	K_{ar}	M_m	M_r	P	E	T,°C
Ib –1	5.84	0.309	0.105	0.337	0.112'	–		
	«---»	0.738'	0.113	1.25'	0.416	–		
2	6.07	0.285	0.102	0.317	0.106'	–		
	«---»	0.638	0.109	1.13'	0.377	–		
3	6.33	0.263	0.098	0.300	0.100'	–		
	«---»	0.572	0.106	1.03'	0.344	–	–	365
4	6.81	0.246'	0.095	0.284'	0.095'	–		
	«---»	0.562	0.127	0.952'	0.317	–		
5	7.08	0.229'	0.091	0.270'	0.090'	–		
	«---»	0.467	0.099	0.882'	0.294	–,+		
6	7.44	0.215'	0.089	0.258'	0.086'	–		
	«---»	0.429	0.096	0.822'	0.274	–,+		
7	7,73	0.203'	0.086	0.246'	0.082'	–		146-
	«---»	0.407	0.095	0.769	0.256	+	+	172
8	8.13	0.192'	0.083	0.235'	0.078'	–		76-
	«---»	0.368	0.089	0.723	0.241	+	+	168
9	8.38	0.182'	0.080	0.226'	0.075'	–		
	«---»	0.347	0.089	0.682	0.227	+		
10	8.72'	0.173'	0.078'	0.217'	0.072'	–		
	«---»	0.324	0.086	0.645	0.215	–,+		
11	8.71'	0.165'	0.075'	0.208'	0.069'	–		
	«---»	0.304	0.083	0.612	0.204	–,+		
12	9.20'	0.158'	0.073'	0.201'	0.067'	–		
	«---»	0.286	0.078'	0.583	0.194	–	–	146
12-Cu	9.08'	0.160'	0.075'	0.241'	0.080'	–		
	«---»	0.291	0.080	0.636	0.212	–,+	–	165
12-Zn	9.02'	0.161'	0.074'	0.242'	0.081'	–		
	«---»	0.293	0.080	0.638	0.212	–,+		
12-Co	9.04'	0.161'	0.075'	0.238'	0.079'	–		190-
	«---»	0.292	0.080	0.632	0.211	–,+	+	220

Note: ' indication of parameters, falling outside the limits of established boundary values. K_c = 1.01, K_s = 0.33 – for whole series; P- the prognosis of CM; E – experimental data; T – transition temperatures.

Thus, the second algorithm when all atoms of ester group are included into the central fragment, is more preferable while prognosing CM of the porphyrine derivatives using molecular parameters.

One of the ways of forming mesophases of non-mesogenic compounds is creation of binary mixtures with solvents. Lyomesomorphic behavior was investigated by contact preparations method [8-10] using the following apolar organic solvents: linear alkanes (hexane, decane, pentadecane, isooctane), cyclic hydrocarbons (cyclodecane, cyclooctane, cyclohexene), chloroform, ethylacetate, isoprpopylacetate, benzene and its derivatives (ethyl-, butyl-, hexyl-, tretbutyl-). It was impossible to induce lyomesophase in each of the specified solvents. The dissolution of samples was observed only in benzene derivatives and cyclic hydrocarbons at heating, whereas at cooling needle-shaped or plate-like solid crystals dropped out. Compounds **I b-7, 8** displaying a thermotropic columnar mesophases, are non-lyomesomorphic in mixtures with the above mentioned solvents.

Such behaviour of thermotropic liquid crystal samples in the presence was recently in mixtures of their columnar mesogens, possessing disordered type of columnar packing with organic solvents [13]. In the same paper it is shown, that only the members of the series with an ordered columnar array, Col_{ho}, exhibit lyotropic phases in mixtures with linear alkanes. Probably, the above mentioned observation is a general principle of lyomesophase formation for compounds creations Col_{ho} and Col_{hd} phases. These facts allow us to conclude that the columnar phase of disordered type created in case of **I-b 7, 8** compounds in thermotropic state.

EXPERIMENTAL

The thermal behavior of compounds I **a**, b and their lyotropic compositions were investigated by the polarizing microscopy, using a MIN-8 or a Leitz Laborlux 12 microscopes, equipped with a Mettler FP hot stage. The electronic absorption spectra (Table. 4) were recorded on " Specord UV VIS " spectrophotometer.

TABLE 3 Data of the elemental analysis of compounds I **a**, b

Compound	Brutto formula	MM	Calculated, (found) % C	H	N
I-a,5	$C_{68}H_{70}O_8N_4$	1071.33	76.23 (76.01)	6.60 (6.06)	5.23 (5.03)
I-a,7	$C_{76}H_{86}O_8N_4$	1183.58	77.12 (76.57)	7.34 (7,99)	4.73 (4.82)
I-b,3	$C_{84}H_{70}O_{12}N_4$	1327.49	76.00 (76.19)	5.33 (5.70)	4.22 (4.34)
I-b,7	$C_{100}H_{92}O_{12}N_4$	1541.92	77.09 (77.19)	6.03 (6.70)	3.63 (3.40)
I-b,8	$C_{104}H_{100}O_{12}N_4$	1598.04	78.16 (78.25)	6.32 (6.50)	3.50 (3.70)
I-b,12	$C_{120}H_{142}O_{12}N_4$	1832.47	78.65 (79.92)	7.83 (8.37)	3.06 (3.20)
I-b,12-Co	$C_{120}H_{140}O_{12}N_4Co$	1889.38	76.28 (75.20)	7.48 (7.89)	2.97 (3.15)
I-b, 12-Cu	$C_{120}H_{140}O_{12}N_4Cu$	1894.00	76.09 (74.89)	7.47 (7.52)	2.96 (2.79)

TABLE 4 Electronic absorption spectra of compounds I **a**, b

Compound	λ_1, / lg ε_1	λ_2, / lg ε_2	λ_3, / lg ε_3	λ_4, / lg ε_4	Solvent
I-a,5	694/4.07	610/4.21	562/4.40	521/4.83	CH_2Cl_2
I-a,7	667/4.28	606/4.22	562/4.55	524/4.74	"-----"
I-b,3	653/3.70	599/3.80	563/4.03	524/4.37	"-----"
I-b,7	649/3.82	595/3.94	551/4.14	518/4.43	Benzene
I-b,8	648/3.54	593/3.76	552/3.98	517/4.35	"-----"
I-b,12	645/3.32	595/3.47	556/3.69	519/3.99	"-----"
I-b,12-Co	-	549/4.28	439/5.11	418/5.16	"-----"
I-b,12-Cu	-	549/3.79	-	417/4.97	"-----"

5,10,15,20-tetra(*p*-oxyphenyl)porphin (Scheme 1, stage 1) was obtained by adding of p-oxyphenylbehzaldehyd (0.072 mol) and pyrrol 5 ml to 250 ml boiling propionic acid. The melange boiled for 0.5 hours; it was also cooled. Then the product was filtered off, washed out by methanol and dried up. The product was then purified by chromatography on silica gel with chloroform, isolated yields of 15-20 %.

Tetra (*p*'-dodecyloxybenzoat-*p*-oxyphenyl) porphin–I b-12 (Scheme 1, stage 2) was obtained by adding dropwise of chloranhydride *p*-dodecyloxybenzoic acid (0.60 g, 1.8 mmol) in pyridine (50 ml) to a solution of 5,10,15,20-tetra (*p*-oxyphenyl) porphin (0.1g, 0.3 mmol) in pyridine (30 ml) within 0.5 hours and stirring the mixture at heating for 6 h; then the mixture was cooled, diluted into 150 ml of water and left for 12 h. The dropped out residue was collected, washed out by water and dried up, then it was washed several times with hot ethanol to remove the acid. The rest of the product was then purified by column chromatography using aluminium oxide (neutral) and chloroform as the eluent, isolated yields of 80%. The crude product was recrystallized from melange ethanol and benzene (yield 85 %). H' (NMR) – 300 MHz, $CDCl_3$, TMS: δ 8.94-8.90 (d, 8H pyrrol); 7.99-7.06 (m, 16H, arom.); 5.29 (S, H, NH); 4.38-4.24 (m, 16H, arom.); 4.13-4.02 (q, 8H, OCH_2); 3.99-3.87 (t, 8H, OCH_2 CH_2); 2.84-2.75 (q, 8H, CH_2-CH_3); 1.90-1.81 (q, 8H CH_2- CH_2-CH_3), 1.79-1.36 (m, 28H, CH_2); 0.90-0.85 (t, 12H, CH_3).

Tetra (*p*'-dodecyloxybenzoat-*p*-oxyphenyl) porphin metal complexes: I b-12Cu and I b-12Co were obtained by refluxing of waterless $CuCl_2$ or $Co(CH_3COO)_2$ with corresponding compounds I b-12 in chloroform within 1-2 h. The end of reaction was defined by spectroscopy based on disappearance of absorption bands of metal-free porphyrine. Then the product was filtered, the filtrate was steamed and purified by column chromatography using aluminium oxide (neutral) with chloroform as the eluent. At column rechromatography the mixture hexane-chloroform was used, isolated yields of 60%. All the possible fraction were collected. Desired product was identified by using spectroscopy data.

CONCLUSION

The calculation of the MP for a new series of porphyrine derivatives was carried out using two algorithms. Three new tetrasubstituted porphyrins with predicted columnar mesomorphism type were synthesised. The second algorithm shows the better correlation between calculated and experimental data. Hence, the proposed method of columnar mesophases prognosis based on calculation of MP could be applied for compounds of porphyrine nature with a small number of substituents.

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