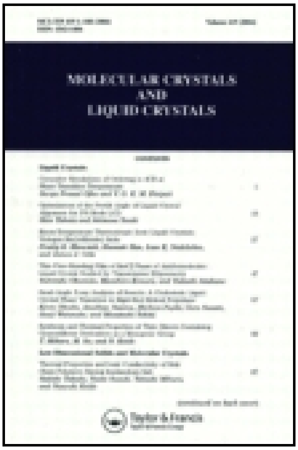

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Lyomesomorphism of Carboxyl- and Alkoxycarbonyl Substituted Phthalocyanine Copper Complexes

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Lyomesomorphism of Carboxyl- and Alkoxycarbonyl Substituted Phthalocyanine Copper Complexes

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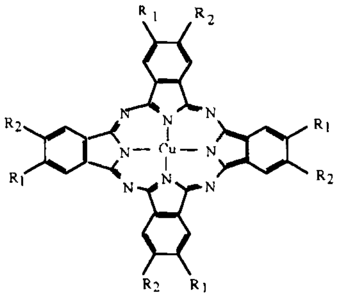
The copper complexes of tetra-4-[(*n*-alkoxy)carbonyl] phthalocyanines **1** and tetra-[(4,4',4",4"'-carboxyl),(5,5',5",5"'-alkoxycarbonyl)] phthalocyanines **2** have been synthesized and the influence of the variation of the number, polarity or the length of the lateral substituents on their thermotropic and lyotropic mesomorphism has been studied. For the first time it has been shown that the homologous of both series can display lyotropic and thermotropic mesophases, i. e. amphotropy. The structure – properties relationship of these two mesomorphic series has been discussed as a consequence of the micro-segregation in the thermotropic as well as in the lyotropic state.

Keywords: amphotropics; columnar phases; copper phthalocyanine derivatives; chromonics; micro-segregation; lyotropy

INTRODUCTION

Already many years ago it was established that hydrophilic *non*-mesomorphic tetra- [1,2] and octacarboxylated phthalocyanine copper complexes exhibit *lyotropic* columnar mesomorphism of the M- and N-chromonic type [2,3] in aqueous solutions. Besides that, numerous of thermotropic phthalocyanine (Pc) derivatives with eight chains display a lyotropic phase behaviour in binary systems with organic solvents [3]. It is commonly accepted [4] that more than four paraffin side chains of definite length are necessary to stabilize the columnar mesomorphic structure of disc-like compounds. In spite of this opinion, an amphotropic phase behaviour has been found also for tetra-substituted Pc derivatives in aqueous solutions [5] as well as in organic solvents [6]. In order to study the structure – properties relationship of disc-like compounds we undertook further variations of the molecular structure of Pc derivatives: copper complexes of (hydrophobic) tetra(alkoxycarbonyl) Pc **1a-j** and tetra[(carboxyl),(alkoxycarbonyl)] Pc **2 a-c** (Figure 1) have been synthesized and their amphotropic properties have been investigated.



1: $R_1 = H$
$R_2 = COOC_nH_{2n+1}$
1a: n=1; **1f**: n=7;
1b: n=2; **1g**: n=9;
1c: n=3; **1h**: n=10;
1d: n=4; **1i**: n=11;
1e: n=6; **1j**: n=16

2: $R_1 = COOH$ **2a**: n=4
$R_2 = COOC_nH_{2n+1}$ **2b**: n=9
2c: n=11

FIGURE 1 Structural formulas of copper complexes of tetra(alkoxycarbonyl) Pc **1a-j** and tetra[(carboxyl),(alkoxycarbonyl)] Pc **2a-c**.

It should be mentioned that some homologues of **1** were used recently for the investigation of Langmuir-Blodgett films [7], but their mesomorphism has not been studied before.

MATERIALS AND METHODS

The synthesis of tetra-4-[(*n*-alkoxy)carbonyl] copper phthalocyanines **1** and of tetra[(4,4',4'',4'''-carboxyl),(5,5',5'',5'''-alkoxycarbonyl)] copper phthalocyanines **2** has been performed as described previously [8]. The structure of the compounds **1** and **2** was confirmed by the data of elemental analysis, thin layer chromatography, ^{1}H NMR, IR, FAB-MS and UV-VIS spectroscopy. The mesomorphic behaviour of these compounds and their mixtures with organic solvents (nonane, pentadecane, chloroform, benzene, DMFA) was investigated by polarizing microscopy using a «Leitz Laborlux 12 Pol» microscope equipped with a «Mettler FP 82» hot stage, heating rate of 2 ^{0}C/min. The photographs of the textures were taken with a 24 x 36 mm microscope camera and a Photoautomat «Wild MPS 51». Besides that, in order to obtain the temperatures and enthalpies of some of phase transition differential scanning calorimetry measurements were carried out with a «Mettler TA 3000/DSC 30S», at heating rates of 5 and 10 ^{0}C/min. X-ray diffraction patterns were obtained using an «IRIS-3» diffractometer.

RESULTS AND DISCUSSION

Thermotropic mesomorphism.

The thermotropic data for the compounds **1** are presented in Table 1.

TABLE 1 Transition temperatures for tetra[(*n*-alkoxy)carbonyl] copper phthalocyanines **1** [$CuPc(COOR)_4$]

1	**R**	$T_{Cr\rightarrow Iso}$, ^{0}C	$T_{Cr\rightarrow Col}$, ^{0}C	$T_{Col\rightarrow Iso}$, ^{0}C
A	$COOCH_3$	> 300	-	-
B	$COOC_2H_5$	> 300	-	-
C	$COOC_3H_7$	-	160.0	> 300
D	$COOC_4H_9$	-	50.0*	> 300
E	$COOC_6H_{13}$	-	37.5	> 300
▨ **F**	$COOC_7H_{15}$	-	26.6	> 300
▨ **G**	$COOC_9H_{19}$	-	-4.0*	> 300
▨ **H**	$COOC_{10}H_{21}$	-	21.5	> 300
▨ **I**	$COOC_{11}H_{23}$	-	30.5	> 300
J	$COOC_{16}H_{33}$	-	80.0	> 300

*from the data of DSC measurements;

▨ viscous at room temperature.

Compounds **1a** and **b** are *non*-mesomorphic and keep a crystalline state even at T > 300 ^{0}C. On heating, the compounds **1c-j** form a mesophase with a non-geometrical texture (Figure 2). Such a texture is typical of the columnar two-dimensional ordered phases. Thermotropic mesomorphism of the compounds **1** is strongly dependent on the length of lateral substituents. When the paraffin chains become longer (**1c-g**), the melting points decrease firstly; further extension of the lateral substituents (**1h-j**) leads to an increase of the transitions temperatures into the mesophase.

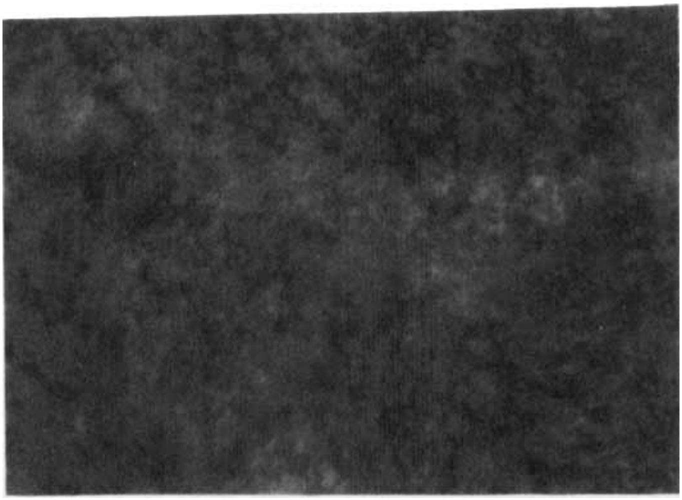
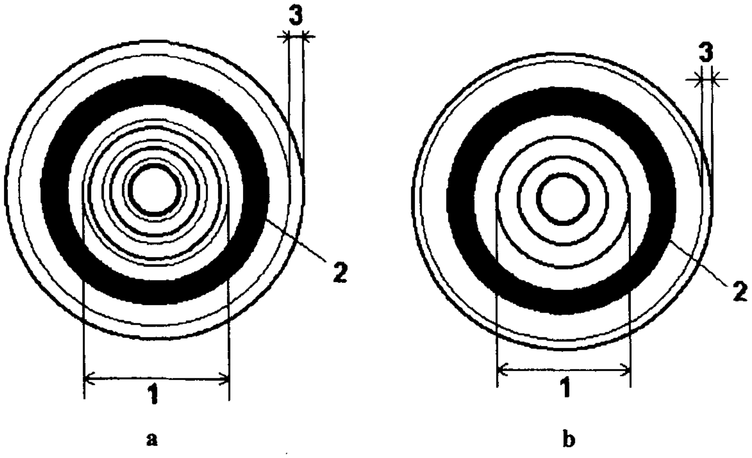


Figure 2 Non-geometrical texture of compound **1g** on heating, crossed polarizers, T = 120 °C, x 320. See Color Plate I at the back of this issue.

The length of the lateral substituents also affects the 2D columnar order in the mesophase. To identify the supramolecular structure of the compounds **1d**, **e**, **g**, **i**, and **j**, the X-ray measurements were carried out at temperatures of 20, 50, 70, 90, 120 and 150 ^{0}C. Typical diffraction patterns are schematically shown in Figure 3. While compound **1f** (n = 4) displays diffraction patterns with a Bragg spacing ratio equal to 1:0.71:0.45 (typical of two-dimensional square lattice), the higher homologues (**1i**, n = 11 and **1j**, n = 16) show patterns that are characte-



FUGURE 3 The scheme of the X-ray diffraction patterns of compounds: a) **1d** (n = 4), 90°C, b) **1i** (n = 11), 90 °C; 1, 2 and 3 are the small-, middle- and wide-angle regions, respectively.

ristic for a hexagonal order (1:0.578:0.49:0.379 and 1:0.57:0.52:0.3, respectively). In wide angles a weak diffraction ring (3,33 Å) and a sharp one (3,69 Å) corresponding to a basic repeat distance and its reflection have been observed. X-ray diffraction patterns of compound **1g** (n=9) have only four diffraction rings in the small-angle region at 20, 50 and 90 ^{0}C. The Bragg spacing ratio for these rings (1:0.72:0.52:0.46) is very similar to that of a two-dimensional square lattice. However, at a temperature of 90 ^{0}C we have obtained an «intermediate» ratio (1:0.61:0.52:0.38) which shows reflections typical of a square lattice as well as for a hexagonal one. This change is in good agreement with the DSC-data; around 80 ^{0}C a small peak was observed, that can be attributed to the transition between two mesophases with closely related structures. The polarizing microscopy shows that this transition is not accompanied by any texture change.

The thermotropic properties of the compounds **2** are summarized in Table 2. In comparison to analogs of series **1** (n = 4, 9 or 11), the introduction of four COOH-groups besides four alkoxycarbonyl groups into the Pc molecule diminished the thermotropic mesomorphism of these compounds.

TABLE 2 Transition temperatures for the tetra[(4,4',4'',4'''-carboxyl), (5,5',5'',5'''-alkoxycarbonyl)] copper phthalocyanines **2** CuPc[(COOH)(COOR)]$_4$

2	**R**	$T_{Cr\rightarrow Iso}$, ^0C	$T_{Cr\rightarrow Col}$, ^0C	$T_{Col\rightarrow Iso}$, ^0C
A	R_1=COOH R_2=$COOC_4H_9$	-	-	> 300 decomp.
B	R_1=COOH R_2=$COOC_9H_{19}$	-	130	> 300
C	R_1=COOH R_2=$COOC_{11}H_{23}$	-	100	> 300

Lyotropic mesomorphism.

For the compounds of series **1** lyotropic behaviour was found only for **1d-j** in the solvents mentioned above (Table 3). The lyotropic systems show a schlieren-texture in addition to a non-geometrical one (Figure 4). This first lyomesophase with a schlieren-texture was characterized as a nematic columnar phase proceeding from the supramolecular columnar structure of **1** in the thermotropic state and a strong association of these compounds in solution. On the basis of the molecular structure, the typical textures and phase diagrams (e.g. Figure 5), the lyotropic mesophases of **1** can be determined as M- and N-chromonic-like phases: N means a columnar nematic and M - a columnar two-dimensionally ordered phase. A boundary between these two lyo-mesophases cannot be confirmed unambiguously (Figure 4). J. Lydon [9] calls such a system a P-phase. As can be clearly seen from Table 3, the lyotropic polymorphism depends on the number of carbon atoms in Pc substituents and on the character of the solvent. In mixtures with chloroform or benzene both the lyomesophases exist at room temperature. In the case of linear alkanes, lyotropic behaviour depends on the ratio of the number of carbon atoms in the alkane molecule and in the hydrocarbon moiety of series **1** [10]. Probably, this fact can be explained by the difference in the possible packing of the paraffin periphery of the mesogens and of the linear solvents [11].

The data on lyotropic mesomorphism of the compounds **2** with organic solvents are shown in Table 4. The *non*-mesomorphic compound **2a** does not display any lyomesophase in binary systems with nonane, chloroform or benzene. However, the mixture of **2a** with DMFA shows lyomesophase of the M-chromonic type (*induced* type). A similar situation was described recently [12] for tetrasubstituted ($R=SO_2NHC_3H_7$) copper phthalocyanine.

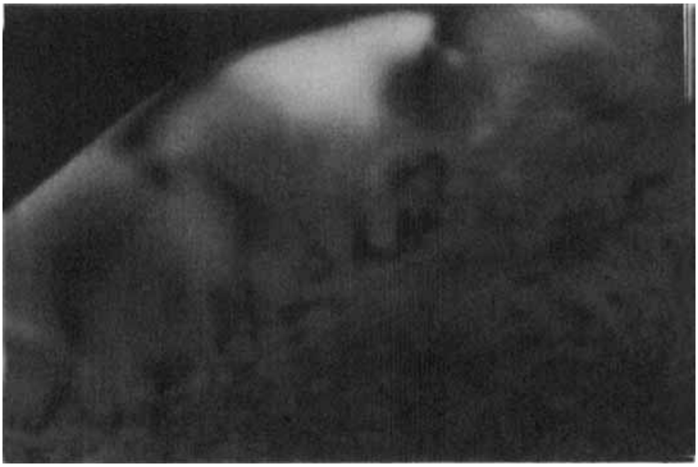


FIGURE 4 Contact preparation of **1f** with CCl_4 on heating, crossed polarizers (T=25 ^{0}C), x 320. From top to bottom: isotropic liquid, schlieren-texture, non-geometrical texture.

See Color Plate II at the back of this issue.

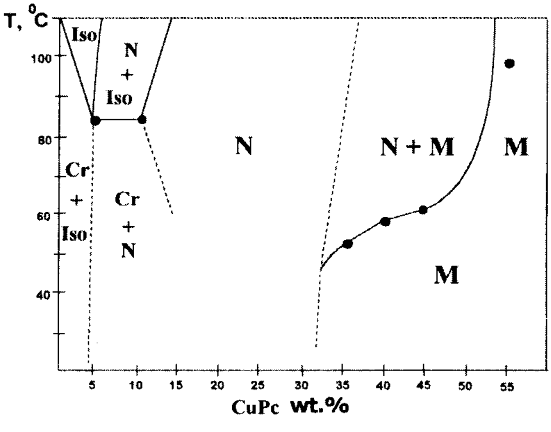


FIGURE 5 Section of the simplified phase diagram of the **1f**/nonane system, on heating; Cr - crystal phase, N – columnar nematic chromonic-like phase, M – columnar 2D ordered chromonic-like phase, Iso - isotropic phase.

TABLE 3 Lyotropic phase behaviour of CuPc(COOR)$_4$ derivatives **1**

1	**R**	**Solvents, 23 ^{0}C**		
		Nonane	**Chlorof.**	**Benzene**
D	COOC$_4$H$_9$	$\boxed{N}$	$\boxed{N}$ **M**	$\boxed{N}$ **M**
F	COOC$_7$H$_{15}$	$\boxed{N}$	$\boxed{N}$ **M**	$\boxed{N}$ **M**
G	COOC$_9$H$_{19}$	$\boxed{N}$	$\boxed{N}$ **M**	$\boxed{N}$ **M**
J	COOC$_{16}$H$_{33}$	$\boxed{N}$	$\boxed{N}$ **M**	$\boxed{N}$ **M**

N - columnar nematic chromonic-like N-phase;
M- columnar two-dimensional ordered chromonic-like M-phase.
□ the *induced* status of the **N** phase.

TABLE 4 Lyomesophases of CuPc[(COOH)(COOR)]$_4$ derivatives **2**

2	**R**	**Solvents, 23 ^{0}C**			
		Nonane	**Chlorof.**	**Benzene**	**DMFA**
a	R$_1$=COOH R$_2$=COOC$_4$H$_9$	-	-	-	$\boxed{M}$
b	R$_1$=COOH R$_2$=COOC$_9$H$_{19}$	**M**	$\boxed{N}$ **M**	-	-
c	R$_1$=COOH R$_2$=COOC$_{11}$H$_{23}$	-	$\boxed{N}$ **M**	$\boxed{N}$ **M**	-

Thus, the mesomorphism of tetra(alkoxycarbonyl) CuPc **1** is **a new rare case of amphotropic behaviour** shown by tetrasubstituted disc-like mesogens. It is very important, that the preservation of mesomorphic properties even at four alkanoyl substituents clearly proves the contribution of the polarity of the linking groups and of a space-filling effect in the micro-segregation within the columns and, consequently, in the mesomorphic behaviour of these disc-like mesogens.

Further increase of the polarity (the replacement of four H-atoms by four COOH-groups) expands the polar core, but the steric effect of these polar groups diminishes the density of the hydrophobic area. These factors lead to an increase of thermostability of the crystalline phase and to a decrease of thermotropic properties as well as (with organic solvents) lyotropic ones of the samples of series **2**, because the alternation of carboxyl and alkoxycarbonyl groups is not favourable for the space filling in the paraffin area and, therefore, increases the micto-segregation within the columns.

CONCLUSIONS

The copper complexes of tetraalkyl esters of tetracarboxylated Pc **1** and of tetra[(carboxyl),(alkoxycarbonyl)] Pc **2** were synthesized and amphotropic properties for a number of homologues were established for the first time. It has been found that the compounds of both series **1c-j** and **2a-c** display a thermotropic mesomorphism of the columnar type. The length of the lateral substituents of **1** affects not only the temperature of the crystal → liquid crystal phase transition, but also the type of supramolecular packing in the mesophase.

In the *binary systems* with numerous linear alkanes (e.g., nonane, pentadecane), benzene, CCl_4 or chloroform the *hydrophobic* compounds **1d-j**, containing four ester groups with aliphatic substituents of various length, form columnar *lyotropic* phases of the N- and M-chromonic-like type (at definite concentrations and temperatures).

The introduction of four alkoxycarbonyl and four carboxyl groups into the phthalocyanine molecule diminishes both the thermotropic and the lyotropic mesomorphism of **2** caused by decrease of the micro-segregation forces.

The induction of mesomorphic behaviour has been observed in a binary mixture composed of the non-mesomorphic **2a** with DMFA.

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