Organometallic Chemistry

Synthesis and liquid crystalline properties of copper tetra-4-(*n*-alkoxycarbonyl)phthalocyanines

A. I. Smirnova,[a] V. E. Maizlish,[b]* N. V. Usol'tseva,[a] V. V. Bykova,[a] G. A. Anan'eva,[a] E. V. Kudrik,[b] A. V. Shirokov,[b] and G. P. Shaposhnikov[b]*

[a]*Ivanovo State University,*
39 ul. Ermaka, 153025 Ivanovo, Russian Federation.
Fax: +7 (093 2) 32 6600. E-mail: usol@ivgu.ivanovo.su
[b]*Ivanovo State University of Chemistry and Technology,*
7 prosp. F. Engel'sa, 153460 Ivanovo, Russian Federation.
Fax: +7 (093 2) 32 9502. E-mail: isl@icti.ivanovo.su

Copper tetra-4-(*n*-alkoxycarbonyl)phthalocyanines were synthesized, and their thermotropic and lyotropic mesomorphism at different lengths of lateral substituents was studied. Their possibility of forming both thermotropic and lyophilic mesophases (amphotropy) was found. The length of lateral substituents affects the type of supramolecular packing in the mesophase rather than the temperature of the crystal → mesophase phase transition. A rare case of the mesogeneity of disk-like compounds of the same chemical nature possessing only four substituents is discussed.

Key words: copper phthalocyanine, mesophase, phase diagram, mesogen, columnar liquid crystalline phases.

Phthalocyanines (Pc) have been under systematic study for more than 60 years; however, researchers are still interested in this class of compounds.[1] It has recently been found[2—11] that numerous phthalocyanine derivatives exhibit thermotropic or lyotropic mesomorphism. The liquid crystalline properties of these compounds depend on the number, position, and character of peripheral substituents and the nature of the central complex-forming ion.

It was earlier accepted that phthalocyanine derivatives possessed columnar mesomorphism if their molecules contained from six to eight lateral substituents. Nevertheless, several compounds of this class with only four substituents and exhibiting mesomorphism have been found,[4—7,11] and only two of them are amphotropic,[5] *i.e.*, possess both thermo- and lyomesomorphism.

For the purpose of searching for other tetrasubstituted mesomorphic Pc, we considered copper tetra-4-(*n*-alkoxycarbonyl)phthalocyanines (**1a—k**).*

Some homologs of this series (n = 4, 6, 8, 10) were used for the formation of Langmuir—Blodgett films,[8—10] but their mesomorphism was not studied.

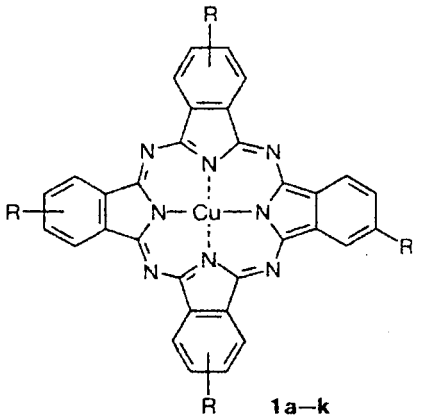
Experimental

The phase state of samples was studied by polarization microscopy on a Leitz Laborlux 12 Pol microscope with crossed polarizers and a Mettler FP 82 heating plate (heating rate

* Compounds **1a—k** represent mixtures of all possible positional isomers (see formula where only one immobilized substituent is shown).

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 1, pp. 129—136, January, 2000.

1066-5285/00/4901-0132 $25.00



1a—k

R = $COOC_nH_{2n-1}$;
n = 1 (**a**), 2 (**b**), 3 (**c**), 4 (**d**), 6 (**e**), 7 (**f**), 9 (**g**), 10 (**h**), 11 (**i**), 16 (**k**)

2 °C min^{-1}). Photographs of textures were obtained with an inserted chamber (24 × 36 mm), a Wild MPS 51 camera (amplification ×320), and a MIN-8 microscope with a thermoplate and a Zorkii photoattachment. Lyotropic mesomorphism was studied by contact preparations[12] and on the basis of phase diagrams of binary systems with a specific content of the solvent. For plotting phase diagrams, a calculated amount of the solvent was added to weighed samples of the substances under study. The obtained mixtures were evacuated, sealed, and homogenized for 120 min in an ultrasound bath in the 60—80 °C temperature range, depending on the temperature of the phase transition of the mesogen and the melting point of the solvent. Then the mixtures were placed in planar capillaries and sealed with Plus endfest 300 resin or EPD universal epoxide glue.

Differential scanning calorimetry (DSC) was performed on a Mettler TA 3000/DSC 30S instrument with a Graph Wave TA 72 graph plotter, and the heating rate was 5 and 10 °C min^{-1}. The temperatures and enthalpies of phase transitions of the substances under study were characterized by DSC.

X-ray diffraction studies were carried out by the small-angle scattering method on a small-angle X-ray diffractometer with a coordinate detector (Cu-Kα radiation, a Ni filter). X-ray diffraction patterns were photometered on an MF-4 microphotometer.

IR spectra were recorded on Specord M-80 and IR-Beckmann 9 instruments in the 400—4000 cm^{-1} region in KBr. ^1H NMR spectra were recorded on a Bruker WH 400 instrument in $CDCl_3$ using Me_4Si as the internal standard. Mass spectra (FAB) were recorded on a VG ZAB-HF-2F/AMO604 instrument. Electronic absorption spectra were measured on a Specord M-40 spectrophotometer at ~23 °C in the 400—900 nm wavelength region.

Resistance of compounds to thermooxidative destruction in air was determined on a Derivatograph-1500 derivatograph (Paulik—Paulik—Erdey system) in the 20—700 °C temperature range with a heating rate of 5 °C min^{-1} and weighed samples of 90—100 mg.

Copper tetra-4-(*n*-alkoxycarbonyl)phthalocyanines (1a—k) (general procedure). Copper tetra-4-carboxyphthalocyanine tetrachloride (0.5 g) (obtained by a known procedure[13]; its structure was confirmed by elemental analysis and comparison of its electronic absorption and IR spectra with the published data[13]) and anhydrous alcohol (10 mL) were placed in a one-necked flask with a stirrer and a reflux condenser. The mixture was refluxed with stirring for 10 h. The solution obtained was diluted with acetonitrile (50 mL), and a dark-blue precipitate that formed was filtered off and washed with MeCN in a Soxhlet apparatus. The residue was dried at 40 °C, dissolved in 10 mL of benzene or CCl_4 (for compounds **1i—k**), and chromatographed on a column packed with Al_2O_3. The first bright-blue fraction was collected and evaporated to dryness. The elemental analysis data and yields of final products are presented in Table 1.

Results and Discussion

The high solubility of compounds **1a—k** synthesized by us in nonpolar organic solvents (chloroform, benzene, CCl_4) made it possible to purify them by column chromatography.

The complexes are either dark-blue powders (**1a—d, k**) or waxy masses. They are highly soluble in nonpolar organic solvents and concentrated H_2SO_4, but insoluble in water, aqueous alkalis, methanol, and acetonitrile. Unlike other compounds, compounds **1a—d** are soluble in DMF and DMSO, and upon prolonged storage (>24 h) their solutions are decolorized due to coagulation.

The individual character and structure of the complexes were confirmed by elemental analysis, thin layer chromatography, and electron and vibrational spectroscopy, and compounds **1d** and **1g** were also studied by ^1H NMR and mass spectroscopy.

The absorption bands characteristic of phthalocyanines[14,15] were observed in the IR spectra of the synthesized complexes (Fig. 1): at 1612—1624, 1505—1524, 1342—1360, 1246—1288, 1170—1188, 1140—1150,

Table 1. Yields and elemental analysis data for copper tetra-4-(*n*-alkoxycarbonyl)phthalocyanines

Compound	Yield (%)	Found / Calculated (%)			Molecular formula
		C	H	N	
1a	54	59.2 59.4	2.9 2.9	13.8 13.9	$C_{40}H_{24}CuN_8O_8$
1b	62	61.0 61.1	3.8 3.7	13.1 13.0	$C_{44}H_{32}CuN_8O_8$
1c	61	62.4 62.6	4.4 4.4	12.3 12.2	$C_{48}H_{40}CuN_8O_8$
1d	52	64.1 64.0	5.1 5.0	11.4 11.5	$C_{52}H_{48}CuN_8O_8$
1e	48	66.0 66.2	5.9 5.9	10.2 10.3	$C_{60}H_{64}CuN_8O_8$
1f	48	67.0 67.1	6.5 6.4	9.7 9.8	$C_{64}H_{72}CuN_8O_8$
1g	42	68.6 68.8	7.2 7.1	8.8 8.9	$C_{72}H_{88}CuN_8O_8$
1h	38	69.4 69.5	7.5 7.4	8.4 8.5	$C_{76}H_{96}CuN_8O_8$
1i	32	70.0 70.2	7.8 7.7	8.1 8.2	$C_{80}H_{104}CuN_8O_8$
1k	21	72.6 72.8	8.9 8.8	6.7 6.8	$C_{100}H_{144}CuN_8O_8$

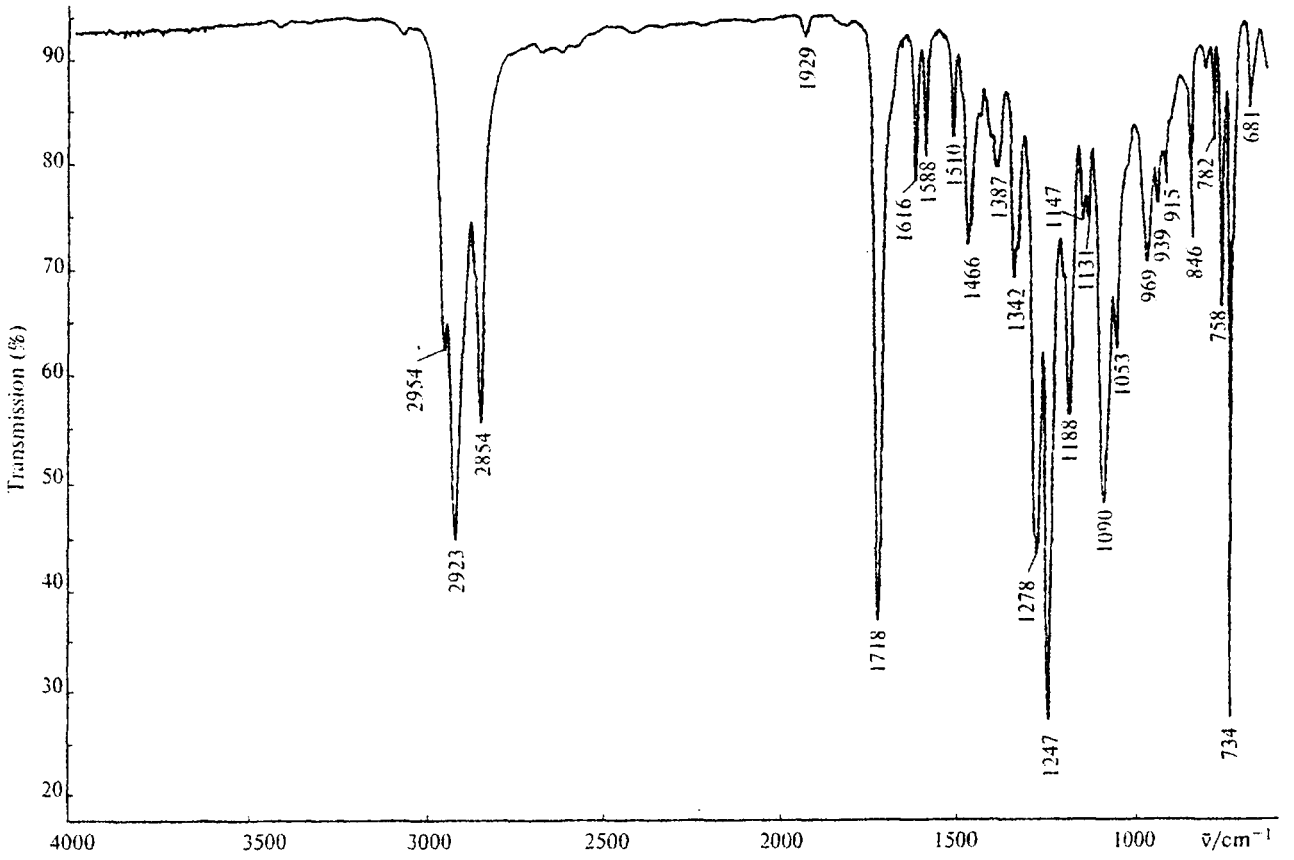


Fig. 1. IR spectrum of compound **1g** (pellets with KBr).

1116—1130, 1080—1092, 1048—1060, 910—950, 850—880, 770—780, and 734—736 cm^{-1}. In addition, the bands corresponding to stretching asymmetrical and symmetrical vibrations of the C—H bonds of the methyl and methylene groups are observed in the 2848—2960 cm^{-1} interval. The bands that characterize asymmetrical and symmetrical bending vibrations of these groups are presented in the 1460—1480 and 1384—1391 cm^{-1} regions, and the intensity of these bands, as should be expected, increases with increase in the alkyl chain length of the substituent. Comparison of the spectral curves of the complexes obtained and copper tetra-4-carboxyphthalocyanine showed the absence (in the first case) of the absorption band at 1700 cm^{-1} and the appearance of a new band at 1716—1728 cm^{-1} characteristic of stretching vibrations of C=O of esters, which indicates the absence of products of incomplete esterification as admixtures.

^{1}H NMR spectra of compounds **1d** and **1g** confirm the structure suggested for them. Three groups of signals are observed in the spectra. Three signals of protons of alkyl substituents are observed in the spectra. For example, for complex **1g**, the singlet with δ 1.0 (12 H) corresponds to protons of the methyl groups. The singlet with δ 1.18 (48 H) can be attributed to absorption of the $C(3)H_2$—$C(8)H_2$ methylene groups of the alkyl residues of the compound. The doublet with δ 1.62 and 1.66 (8 H) corresponds to the signals of protons of $C(2)H_2$.

$$-O-\overset{1}{C}H_2-\overset{2}{C}H_2-(\overset{3-8}{C}H_2)_6-CH_3$$

The downfield shift of signals belonging to the $C(2)H_2$ methylene groups is explained by the pronounced negative induction effect of the carboxyl oxygen atom of the ester group, and it decreases rapidly when the methylene groups are removed from an acceptor. In our opinion, splitting of this band is due to the fact that compound **1g**, perhaps, is a mixture of regioisomers. In addition, the absence of splitting of signals from protons of the methyl and methylene $C(3)H_2$—$C(8)H_2$ groups and their broadening is, probably, the result of association of the compounds under study in solutions. The spectra of both compounds in the 3.5—4.2 ppm region exhibit broadened singlets (8 H) corresponding to protons of the methylene groups directly bound to the carboxyl oxygen atom, unlike the ^{1}H NMR spectrum presented previously[2] for 4,5-octa-(*n*-alkoxycarbonyl)-phthalocyanines, in which this absorption is well resolved and presented as a doublet. This is most likely

caused by the effect of the paramagnetic complex-forming ion Cu^{II} and the affinity of the synthesized compounds to association, which impedes interpretation of signals in the region of 7—10 ppm that correspond to protons of the isoindole fragments. A similar situation is observed for the ^1H NMR spectra of tetrasubstituted copper phthalocyanines containing octadecylamino groups as substituents.[16]

The FAB mass spectra of compounds **1d** and **1g** exhibit peaks of their molecular ions. In addition, the spectra exhibit no peaks corresponding to molecular ions of the starting copper tetracarboxyphthalocyanine and products containing one, two, or three free carboxyl groups.

The study of resistance of the synthesized complexes toward thermooxidative destruction in air shows that they are stable on heating to 290—340 °C, and their intense decomposition begins at 390—415 °C.

The electronic absorption spectra (EAS) of the compounds synthesized (Fig. 2, Table 2) are characterized by a two-band spectrum with maxima at 598—617 and 674—685 nm. The shape of the absorption bands and the ratio of their intensities indicate the affinity of complexes **1a—k** to association in solutions. It is noteworthy that the positions of these bands only insignificantly depend on the concentration of the compounds, the solvent nature, and the alkyl chain length. When the concentration increases, the relative intensity of the short-wave absorption band increases, whereas an increase in the temperature results in the opposite effect. Associative processes also have another consequence: the Bouguer—Lambert—Beer law is not fulfilled at concentrations up to 10^{-7} mol L^{-1}.

Since compounds **1** were not studied earlier as mesogens, we aimed at studying their thermotropic and lyotropic mesomorphism.

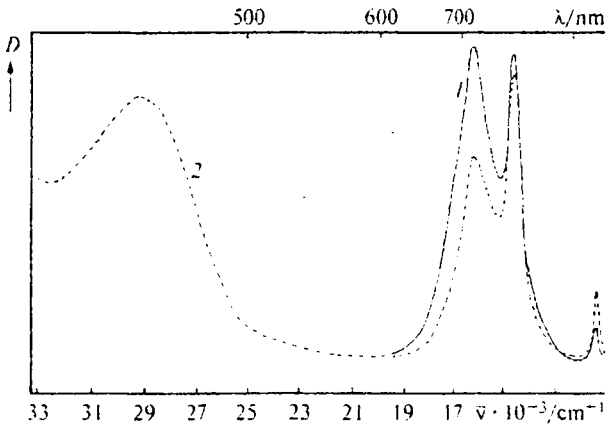


Fig. 2. Electronic absorption spectra of compound **1d** in benzene: [**1d**]/mol L^{-1} = $1.13 \cdot 10^{-5}$ (*1*) and $4.02 \cdot 10^{-6}$ (*2*).

Table 2. Bands in electronic absorption spectra of copper tetra-4-(*n*-alkoxycarbonyl)phthalocyanines

Compound	λ_{max}/nm			
	DMF	Benzene	Chloroform	CCl_4
1a	610, 676			
1b	611, 676	608, 681		
1c	604, 676	617, 685	615, 683	598, 687
1d	605, 674	614, 683	614, 683	600, 683
1e		604, 681		
1f		614, 683	615, 683	608, 685
1g		614, 685	615, 683	612, 682
1h		616, 681	617, 683	606, 681
1i		613, 681	618, 683	612, 682
1k		617, 685	618, 683	614, 682

Thermotropic mesomorphism

It was established by polarization microscopy that the first two compounds of this series (**1a,b**) are not thermotropic mesogens and remain in the crystalline state even at $T > 300$ °C. Under standard conditions, compounds **1c—e** and **1k** are crystalline substances. On heating they form a mesophase with a non-geometric or granular texture (Fig. 3). The substances thermally decompose at temperatures above 300 °C; therefore, the transition to the isotropic state is not achieved. Homologs **1f—i** are highly viscous masses forming no crystals even on deep cooling. On heating they become more mobile, and their non-geometric or granular texture (see Fig. 3), which is retained up to 300 °C, can be observed in polarized light. Columnar two-dimensionally ordered phases are characterized by a similar texture. The temperatures of phase transitions of the compounds of series **1** were established from the data of polarization microscopy and DSC (Table 3).

DSC curves were obtained for compounds **1d** and **1g**. The measurements were performed in a wide tem-

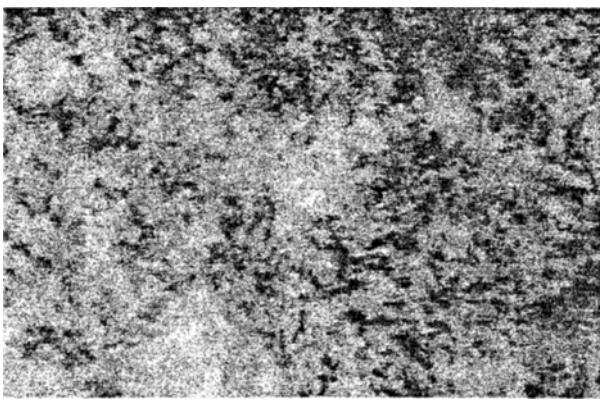


Fig. 3. Photomicrograph of the nongeometric texture of the thermotropic two-dimensionally ordered columnar phase of compound **1g** at 150 °C (crossed polarizers, amplification ×320).

Table 3. Temperatures of phase transitions[a] of copper phthalocyanines **1**

Compound	R	$T_{Cr\rightarrow Iso}$	$T_{Cr\rightarrow Col}$	$T_{Col\rightarrow Iso}$
		°C		
1a	COOMe	>300	—	—
1b	COOEt	>300	—	—
1c	$COOPr^n$	—	160.0	>300
1d	$COOBu^n$	—	50.0[c]	>300
1e	$COOC_6H_{13}$	—	37.5	>300
1f[b]	$COOC_7H_{15}$	—	26.6	>300
1g[b]	$COOC_9H_{19}$	—	−4.0[c]	>300
1h[b]	$COOC_{10}H_{21}$	—	21.5	>300
1i[b]	$COOC_{11}H_{23}$	—	30.5	>300
1k	$COOC_{16}H_{33}$	—	80.0	>300

[a] Cr is the crystalline phase, Col is the columnar phase, and Iso is the isotropic phase.
[b] Viscous at room temperature.
[c] DSC data; the other values are the polarization microscopic data.

perature range (from −50 to +300 °C) with a heating rate of 10 °C min^{-1}. Several heating—cooling cycles were carried out for each sample. The curves obtained were well reproducible. Some shift of the peaks over the temperature scale was observed for the last heating cycles, which indicates a partial thermal decomposition of the samples. The DSC curve for compound **1g** is presented in Fig. 4 as an example and distinctly exhibits two small broad peaks. The first peak at T = −4.0 °C (ΔH = 0.3 J g^{-1}) is sufficiently broad and characterized by a small change in enthalpy, which suggests that structural rearrangements are insignificant and the mesophase possesses high ordering compared to crystal packing. In our opinion, this peak can be attributed to the crystal → mesophase transition. The second peak appears at T = 75.5 °C (ΔH = 0.4 J g^{-1}). No texture changes were visually detected in this temperature region by optical microscopy. Since the change in enthalpy is also small, this peak probably belongs to the transition between two mesophases whose internal structures are very close.

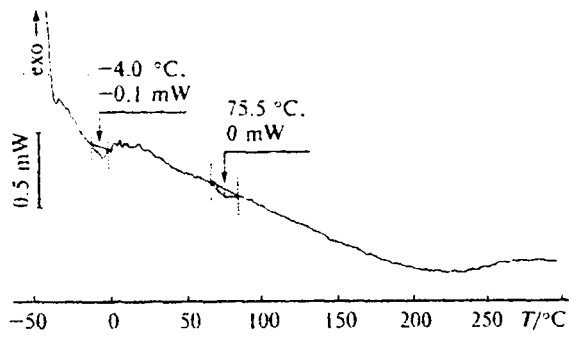


Fig. 4. DSC curve for compound **1g** on heating (heating rate 10 °C min^{-1}).

It follows from the data in Fig. 3 that thermotropic mesomorphism of these homologs is rigorously related to the length of lateral substituents. It is important that the temperature of crystal → mesophase phase transition first decreases accompanied by the corresponding broadening of the region of existence of the mesophase for compounds **1c—g**. However, when the chains elongate (**1h—k**), the temperature of the phase transition to the mesomorphic state increases. This run of the curve of the temperature of crystal → mesophase phase transition in the homologic series of tetrasubstituted carboxy derivatives of the copper phthalocyanine complex agrees well with the data on octasubstituted esters of the phthalocyanine ligand[2] but contradicts the data for other octasubstituted mesomorphic discotic phthalocyanines.[17]

To identify the supramolecular structure and confirm the assumed columnar packing of the observed thermotropic mesophase, we performed X-ray diffraction studies of compounds **1d,e,g,h,k** in the temperature range from 20 to 150 °C.

The X-ray diffraction patterns of compound **1d** (n = 4) (Fig. 5) exhibit a set of Bragg reflections typical of the rectangular lattice,[19] whereas the X-ray patterns of higher homologs **1i,k** (n = 11, 16) (Fig. 6) have a ratio of reflections which corresponds, according to the published data,[17] to hexagonal packing. In the case of compound **1g** (n = 9), when the temperature increases, the ratio of Bragg reflections changes from 1 : 0.72 : 0.52 : 0.46 (close to that characteristic of a rectangular lattice) to 1 : 0.61 : 0.52 : 0.38 (being "intermediate," because it contains reflections inherent in both rectan-

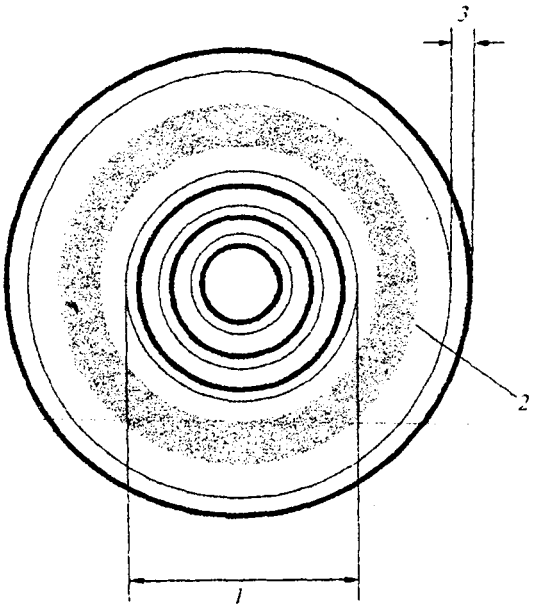


Fig. 5. Scheme of arrangement of diffraction reflections on the X-ray diffraction pattern of compound **1d**. Three regions are conventionally distinguished here and in Fig. 6: small-angle (*1*), broad diffuse (*2*), and large-angle (*3*).

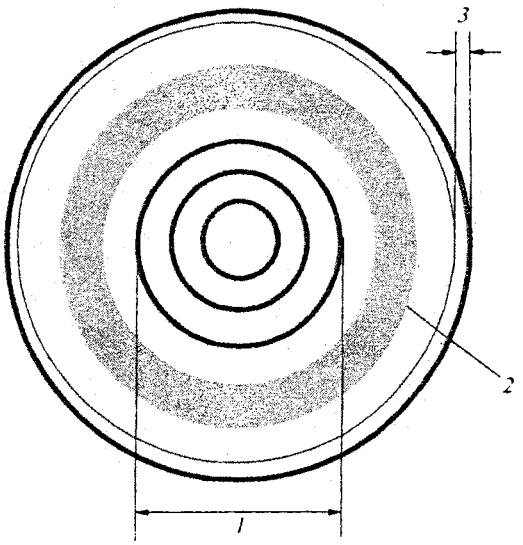


Fig. 6. Scheme of arrangement of diffraction reflections on the X-ray diffraction patterns of compounds **1i,k**.

gular and hexagonal lattices). Note that the changes observed for this homolog with temperature increase to 90 °C agree with the data of differential scanning calorimetry. This is precisely the region of $T = 80$ °C on the DSC curve in which the peak appears attributed by us to the phase transition between two mesophases close in structure, because this transition was not accompanied by texture changes. The X-ray analysis data show that this peak on the DSC curve is most likely due to the transition from a rectangular to a hexagonal phase.

Since the X-ray diffraction patterns of the homologs under study at all temperatures contain in the large-angle region the broad reflection of ~3.3 Å, which is the characteristic van der Waals distance for aromatic compounds and can be assigned to the formation of phthalocyanine columns, all mesophases observed can be attributed to the columnar type.

Thus, the X-ray structural studies showed that copper phthalocyanine complexes **1** form columnar ordered phases: rectangular for lower (n = 4, 6) and hexagonal for higher (n = 11, 16) homologs. Compound **1g** (n = 9), depending on the temperature, has tetra- or hexagonal supramolecular packing of columnar aggregates.

Lyotropic mesomorphism

Lyotropic mesomorphism of complexes **1** in systems with linear alkanes, chloroform, benzene, and CCl_4 was studied by the methods of contact preparations and plotting of phase diagrams. Of all studied compounds of series **1** with the solvents indicated above, lyotropic mesomorphism was observed only for homologs **1d—k**. The specific features of lyomesomorphism were studied for four homologs in different solvents (Table 4).

Table 4. Lyotropic mesomorphism of several compounds **1** with some organic solvents at ~23 °C

Compound	R	Nonane	Chloroform	Benzene
1d	$COOC_4H_9$	N[a]	N, M	N, M
1f	$COOC_7H_{15}$	N, M[b]	N, M	N, M
1g	$COOC_9H_{19}$	N, M	N, M	N, M
1k	$COOC_{16}H_{33}$	N	N, M	N, M

[a] N is the columnar chromonic N phase.
[b] M is the two-dimensionally ordered chromonic M phase.

We established by the method of contact preparations that an additional schlieren texture, which is typical of the nematic phase, appears in lyotropic systems along with the non-geometric texture characteristic of the thermotropic state (Fig. 7). Based on the columnar structure of the thermotropic mesophase and affinity of these compounds to association in solutions, we assumed that this nematic phase is also columnar, *i.e.*, the mesophases that appear in this case can be assigned to the chromonic type and designated as N for the nematic columnar phase and M for the two-dimensionally ordered columnar phase. The boundary between these two lyomesophases is not distinct, and the region of existence of the biphase system N + M (see Fig. 7) is sufficiently broad. In similar cases, the region of coexistence of the N and M phases is designated as the P phase.[20] It has been assumed that the difference between the N/M and P phases is related to the difference in geometry of the transversal cross section of columnar/supramolecular aggregates. For the appearance of the P phase, the shape of this cross section should be closer to a circumference.

As can be seen from the data in Table 4, lyotropic polymorphism depends on the number of carbon atoms in the homolog and the solvent nature. In chloroform

Fig. 7. Schlieren texture of the nematic phase in the contact preparation of compound **1g** with CCl_4 at 22 °C (the polarizers were crossed, amplification ×320).

and benzene at ~23 °C all complexes under study (n = 4, 7, 9, 16) form both types of phases, whereas in a linear alkane (nonane) homologs with a shorter (than the hydrocarbon chain of the solvent) paraffinic part or, *vice versa*, with a much longer hydrocarbon fragment form only the N phase (**1d,i**). If the lengths of the hydrophobic regions of the mesogen and alkane molecules are comparable (**1f,g**), both types of lyomesophases appear. This difference in the lyotropic behavior can probably be explained by different mutual packings of the paraffinic lipophilic periphery of mesogen molecules with hydrophobic molecules of the solvent.

For the purpose of determining the temperature-concentration regions of existence of the mesophases, we studied the binary **1f**—nonane system. A fragment of the phase diagram of this system is presented in Fig. 8. As can be seen in Fig. 8, the lyomesophases exist in wide concentration (from 4.8 wt.% mesogen) and temperature (from ~23 to 110 °C) ranges. The value of 110 °C was chosen as the upper temperature boundary of observation for this phase diagram due to its closeness to the boiling temperature of nonane (128.26 °C). The biphase nematic-isotropic region is localized in the left part of the diagram, beginning from a very low mesogen content (~4.8 wt.%) and at T > 84 °C. The broad region of the nematic phase (from 15 to 35 wt.% mesogen) is present in the center of the phase diagram and occupies the whole temperature range under study (from ~23 °C to the boiling temperature of nonane). When the mesogen concentration further increases (from 35 to 50 wt.%), the region of pure N phase is superseded by the broad region of coexistence of N and M phases. This biphase region exists at T > 60 °C. The region of M phase is arranged in the right part of the phase diagram. At low temperatures, it is already observed at concentrations of **1f** of about 33 wt.%, but on heating to T > 60 °C, it is transformed into the above mentioned biphase (N + M) region. At a higher mesogen content (50 wt.% and higher), the M phase is retained on heating up to the boiling temperature of the solvent.

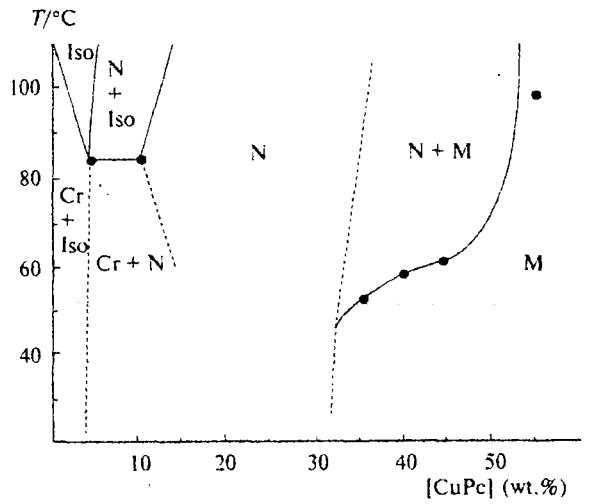


Fig. 8. Fragment of the simplified phase diagram of the **1f**—nonane system on heating: Cr is the crystalline phase; N is the columnar chromonic N phase; M is the two-dimensional chromonic M phase; and Iso is the isotropic phase.

Analysis of the sequence of arrangement of the phases on the phase diagram of the **1f**—nonane binary system shows that it agrees with the typical phase diagram of chromonic mesogens.[20]

Thus, we assumed the chromonic type of supramolecular packing of these compounds in the lyotropic state on the basis of the spectroscopic data in the visible region, the shape of the phase diagrams, X-ray analysis data of the substances in the thermotropic state, and their texture parameters.

The results of studying mesomorphism of copper tetra-4-(n-alkoxycarbonyl)phthalocyanines **1a—k** suggest the following: these compounds form both thermotropic and lyotropic mesophases (amphotropy), and the amphotropic properties depend on the lengths of lateral substituents. Lower homologs (**1a,b**) do not exhibit mesomorphic properties. Homologs **1c—k** exhibit thermotropic mesomorphism. For the series of copper complexes synthesized, similarly to octa-4,5-(n-alkoxycarbonyl)phthalocyanine, first a decrease and then an increase (after compound **1g**) in the melting temperature are observed when the number of carbon atoms in the lateral chain increases. The tetrasubstituted copper phthalocyanines under study exhibit the mesomorphic properties in a relatively more narrow temperature interval than that for octa-4,5-(n-alkoxycarbonyl)-phthalocyanine at equal thermostabilities of the mesophase. The length of the lateral substituent affects the type of the supramolecular packing in the mesophase rather than the temperature of the crystal → mesophase phase transition.

In binary systems with nonpolar organic solvents, compounds **1d—k** exhibit lyotropic polymorphism of the chromonic type. Thus, complex **1c** is only a thermotropic mesogen, and complexes **1d—k** are amphotropic mesogens.

As shown above, octasubstituted esters of phthalocyanine $H_2Pc(4,5\text{-}COOC_nH_{2n+1})_8$ (n = 5—12)[2] exhibit thermotropic mesomorphism. The retention of mesomorphic properties even at four similar substituents proves clearly the contribution of polarity to the microsegregation of fragments of columnar aggregates and stabilization of the mesomorphic properties of discotic mesogens, because tetrasubstituted alkyl and alkoxy derivatives of phthalocyanine do not form mesophases.[17,21] We cannot rule out the contribution of the bulky group (—COO—) to the process of filling the space around the macrocyclic core, which also favors microsegregation.

A. I. Smirnova thanks the Ministry of Education of the Russian Federation for the scholarship for work at

Berlin Technical University (Germany) and L. S. Shabyshev (Ivanovo State University) for help in X-ray structural studies.

This work was financially supported by the Program "Universities of Russia — Basic Research" (Project No. 4007).

References

1. *Phthalocyanines: Properties and Applications*, Eds. C. C. Leznoff and A. B. P. Lever, VCH, New York, 1989, **1**, 436; 1993, **2**, 436; 1993, **3**, 303; 1996, **4**, 524.
2. L. Dulog and A. Gittinger, *Mol. Cryst. Liq. Cryst.*, 1992, **213**, 31.
3. P. G. Shoten, J. F. van der Pol, E. Neelman, and J. W. Zvikker, *Recl. Trav. Chim. Pays-Bas*, 1988, **107**, 615.
4. N. V. Usol'tseva, *Liotropnye zhidkie kristally: khimicheskaya i nadmolekulyarnaya struktura* [*Lyotropic Liquid Crystals: Chemical and Supramolecular Structure*], Izd. Ivanovskogo Gos. Univ., Ivanovo, 1994, 220 pp. (in Russian).
5. N. B. McKeown and J. Painter, *J. Mater. Chem.*, 1994, **4**, 1153.
6. P. Humberstone, G. J. Clarkson, N. B. McKeown, and K. E. Treacher, *J. Mater. Chem.*, 1996, **6**, 315.
7. K. E. Treacher, G. J. Clarkson, and N. B. McKeown, *Liq. Cryst.*, 1995, **19**, 887.
8. P. A. Albouy, *J. Phys. Chem.*, 1994, **98**, 8543.
9. K. Ogawa, H. Yonehara, T. Shoji, S. I. Kinoshita, E. Maekava, H. Nakahara, and K. Fukuda, *Thin Solid Films*, 1989, **178**, 8543.
10. K. Ogawa, H. Yonehara, and E. Maekava, *Thin Solid Films*, 1992, **210—211**, 535.
11. V. V. Bykova, N. V. Usol'tseva, G. A. Anan'eva, G. P. Shaposhnikov, and V. E. Maizlish, *Izv. Akad. Nauk, Ser. Fiz.*, 1998, **62**, 1647 [*Bull. Russ. Acad. Sci. Physics*, 1998, **62** (Engl. Transl.)].
12. K. Praefcke, B. Bilgin, N. Usol'tseva, B. Heinrich, and D. Guillon, *J. Mater. Chem.*, 1995, **5**, 2257.
13. K. Ogawa, S. I. Kinoshita, H. Yonehara, H. Nakahara, and K. Fukuda, *J. Chem. Soc., Chem. Comm.*, 1989, 477.
14. A. N. Sidorov and I. P. Kotlyar, *Opt. Spektrosk.*, 1961, **11**, 175 [*Opt. Spectrosc.*, 1961, **11** (Engl. Transl.)].
15. B. N. Achar, G. M. Fohlen, J. A. Parker, and J. Keshavaya, *Polyhedron*, 1987, **6**, 1463.
16. M. Fujiki, H. Tabei, and T. Kurihara, *J. Phys. Chem.*, 1988, **92**, 1281.
17. J. Barbera, *Metallomesogens. Synthesis, Properties and Applications*, Ed. J. L. Serrano, VCH, Weinheim—New York—Basel—Cambridge—Tokyo, 1996, 325.
18. N. Kobayashi, Y. Nishijama, T. Ohys, and M. Sato, *J. Chem. Soc., Chem. Comm.*, 1987, 390.
19. V. K. Vainshtein, *Sovremennaya Kristallografiya* [*Modern Crystallography*], Nauka, Moscow, 1979, **1**, 384 pp. (in Russian).
20. J. Lydon, *Handbook of Liquid Crystals*, Eds. D. Demus, J. Goodby, G. W. Gray, H.-W. Spiess, and V. Vill, Wiley—VCH, Weinheim—New York—Chichester, 1998, **2B**, 981.
21. C. Tschierske, *J. Mater. Chem.*, 1998, **8**, 1485.

Received March 30, 1999;
in revised form July 21, 1999