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THE INFLUENCE OF THE STRUCTURE OF TETRA(4-SULPHOPHENYL)PORPHIN DERIVATIVES ON THEIR LYOTROPIC MESOMORPHISM

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Abstract Tetra(4-sulphophenyl)-β-octamethyl-porphin has been synthesized with the object of studying how the structure of the macrocycle, the type and position of the substitutes, and the character of the metal-complex generator influences the lyotropic mesomorphism. Its spectral properties and lyotropic mesomorphism in water-ammonia and water-NaOH systems have been studied.

INTRODUCTION

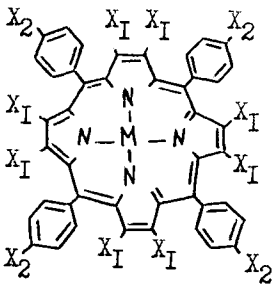
The experiments carried out in the past few years have demonstrated that the lyotropic liquid crystalline state is a characteristic feature of organic compounds with disc-like or rod-like molecules.[1-6] To date several lyotropic mesogenes of discotic type have been discribed as manifesting the mesophase in aqueous solutions, namely, phthalocyanine[1,2], triphenylene[4], tetrabenzocyclododecatriene[6] and porphin derivatives.[7-9]

Earlier a number of investigations was undertaken with the aim of establishing how the lyotropic mesomorphism is influenced by the structure of the macrocycle, the type and position of the substitutes and the character of the metal complex generator in phthalocyanine[7] and porphin derivatives.[8,9]

Following this line of research, we now report on the results obtained earlier on the lyomesomorphism of tetra(4-sulphophenyl)porphin (I),its sodium salt (II) and their metal complexes (Table 1) and present the data on

the synthesis, spectral characteristics and lyomesomorphism of tetra(4-sulphophenyl)-β-octamethylporphine (Ⅲ).

TABLE 1 Potential mesogens of porphin derivatives.

Structural formula	N	Metal	Substitutes X_1	Substitutes X_2	Mesogenic properties
	1	$(2H^+)$	H	SO_3H	+
	1a	Ni^{2+}	H	SO_3H	+
	1b	Cu^{2+}	H	SO_3H	+
	1v	Co^{3+}	H	SO_3H	-
	II	$(2H^+)$	H	SO_3Na	+
	IIa	Ni^{2+}	H	SO_3Na	+
	IIb	Co^{3+}	H	SO_3Na	-
	III	$(2H^+)$	CH_3	SO_3H	+

MATERIALS AND METHODS

Tetra(4-sulphophenyl)-β-octamethylporphin was obtained by heating in a soldered ampoule 150 ml (0,2 mmol) of tetra(4-phenyl)-β-octamethylporphin with 3 ml of concentrated H_2SO_4 at 100°C for 4 hours. The reaction mixture was cooled, diluted with 12 ml of water, the pricipitate was centrifuged, washed with acetone several tymes, and dried off at 80°C in a vacuum till a constant weight was obtained. We obtained 172 mg (82%) of compound III. The purity of compound III was proved using the method of thin-layer chromatography on siluphol and the elementary analysis confirmed it.

Estimated, % : C 59.67 ; H 4.40 ; N 5.35 ; S 12.25.
Obtained, % : C 59.52 ; H 4.31 ; N 5.29 ; S 12.17.

Spectral characteristics were studied on a "Specord UV VIS" spectrometer. Solvents: water-ammonia system (pH 8.0; 10.0; 12.0), water-NaOH (pH 8.0; 10.0; 12.0), dimethylsulphoxide (DMSO). The lyotropic mesomorphism of compound III was investigated using the penet-

ration method on a MIN-8 polarization microscope with a thermotable.

RESULTS AND DISCUSSION

Along with the stydy of lyomesomorphism carried out using the method of contact preparations the present research includes the analysis of the spectral characteristics of compound III since the characteristic feature of the lyotropic liquid crystalline state is the presence of thermodynamically stable supramolecular ensembles as elements of its structure. Formation of such particles is caused by the processes of association in diluted solutions.

Absorption spectra of compound III in DMSO, in water-NaOH (pH 8.0; 10.0; 12.0), or water-ammonia (pH 8.0; 10.0; 12.0) systems are represented in Figures 1 and 2. Absorption spectrum of compound III in water-NaOH system with pH from 8.0 to 12.0 reveals a one-band (weak splitting) spectrum, which is attributed to a monocation. When transition to a system with pH 12.0 takes place compound III aquires a 4-band spectrum characteristic of a free porphin[10] (Fig.1). Absorption spectrum of compound III in water-ammonia system with pH 8.0 and 10.0 reveals a one-band spectrum which is attributed to a dication (Fig.2). When transition to a system with pH 12.0 takes place compound III reveals a one-band (weak splitting) spectrum which is attributed to a monoanion.

Thus transition from dication to monoanion was observed when pH of the system for compound III was changed. The polarized microscopy method showed that in a contact preparation compound III in water-ammonia solutions (pH 12.0) and water-alkali solutions (pH 8.0 and 10.0) form the lyomesophase (Fig.3), compound III existing as a monication in a solution with these pH. At room temperature compound III revealed shlieren texture in water-alkili solutions with pH 8.0 or 10.0 which is characteristic of the lyotropic liquid crystalline state.

Similar textures were observed by us earlier with other compounds of this row: 1; 1a,b; II,IIa (Table 1)[8,9] and were referred to N- and M-phases of chromonic type

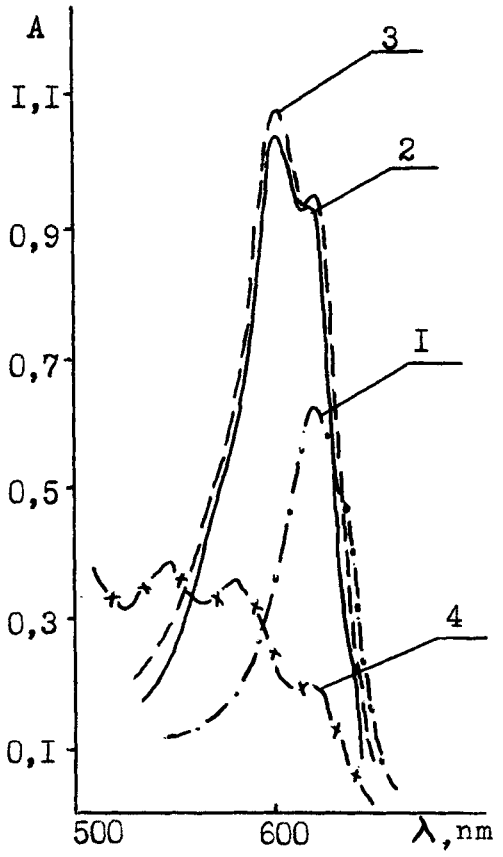


FIGURE 1 Absorption spectra of compound III (long-wave region); c = 1.65 10^{-4} mol/l:
1- in dimethylsulphoxide, cuv. 0.5 cm;
2- in NaOH-water system (pH 8.0), cuv. 0.1 cm;
3- in NaOH-water system (pH 10.0), cuv. 0.1 cm;
4- in NaOH-water system (pH 12.0), cuv. 0.1 cm.

formed by these macroheterocyclic compounds in water-ammonia systems due to plane-plane interaction of their molecules.

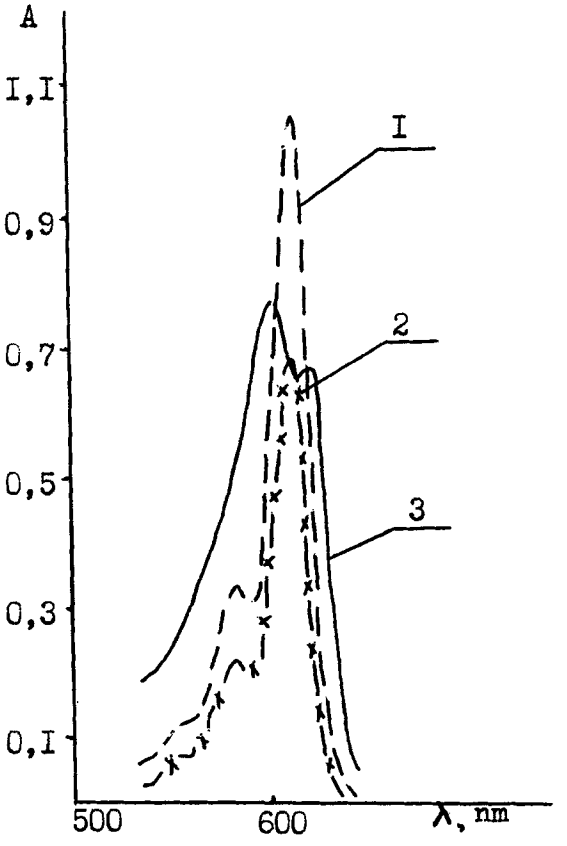
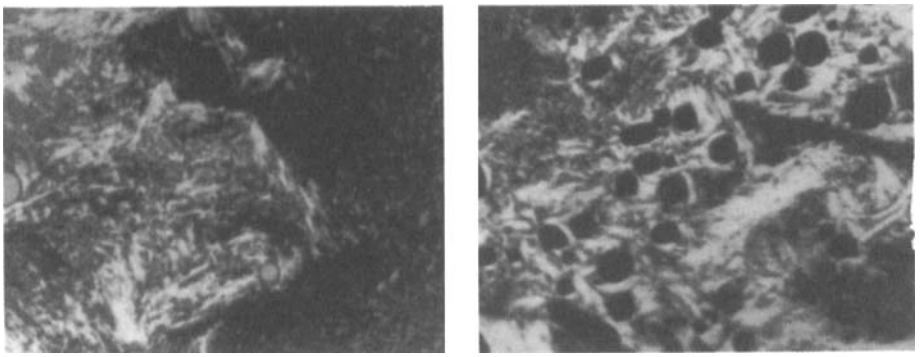


FIGURE 2 Absorption spectra of compound III (long-wave region):
1- in water-ammonia system (pH 8.0), c = 1.65 10^{-4} mol/l, cuv. 0.1 cm;
2- in water-ammonia system (pH 10.0), c = 5.5 10^{-5} mol/l, cuv. 0.1 cm;
3- in water-ammonis system (pH 12.0), c = 8.25 10^{-5} mol/l, cuv. 0.1 cm.

Compounds I,II,III are closely related to phthalocyanines as their molecular structure is concerned.[10]

The molecules of porphin derivatives similarly have a 16-member macrocycle, the rigidity of which is caused



a b

FIGURE 3 Microphotography of the texture of the lyotropic liquid crystalline phase, formed by compound III in a) water-ammonia system (pH 12.0), contact preparation, b) water-NaOH system (pH 8.0). Nicols crossed, x 90.

by a strong π-electronic interaction within the hole of the closed circuit.

This similarity in the structure of the central parts of phthalocyanine and porphin derivatives suggests that the reason why compound III forms the lyomesophase in a water-ammonia system (pH 12.0) lies in the formation of stacked aggregates due to plane-plane interaction of their molecules. Evidently, the introduction of 8 methyl groups contributes considerably to the ability to form mesophase.

We believe that the differences between compound II and compound I are caused by the influence of electronic donor methyl groups on the central part of the molecular structure due to steric factors.

The character of the metal complex generator influ-

ences the formation of the lyomesophase. In compounds Iv and IIb, in which a trivalent metal (Co^{3+}) acts as a complex generator such stacking is not possible due to extracoordination of the solvent, hence these compounds do not form the lyomesophase.

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