

Influence of meso-substituted porphyrines molecular structure on their mesogeneity

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The influence of molecular structure on mesophase formation was analysed on the basis of 64 new meso-substituted porphyrine derivatives [1, 2].

It was established that:

1. The substitution of tetraphenylporphyrine meso-positions with alkyl chains (from $-\text{CH}_3$ to $-\text{C}_{16}\text{H}_{33}$) does not lead to the mesophase formation.

2. Tetraphenylporphyrine meso-substitution with four alkoxy groups (from $-\text{OC}_4\text{H}_9$ to $-\text{OC}_{16}\text{H}_{33}$) in *para*-, *meta*- or *ortho*-positions of phenyl rings allowed to establish that four of eleven synthesized compounds possess thermotropic monotropic mesomorphism of columnar type, including one possessing lyotropic mesomorphism in binary systems with toluol, benzene or chloroform.

The important role of substituents' position in phenyl rings of porphyrines is determined. The modification of molecules at structural isomerization (from *para*-positions of alkoxy groups in phenyl rings into their *meta*- or *ortho*-positions) leads to the decrease of phase transition temperature "Cr – Iso". Mesogeneity with lower number of carbon atoms in alkoxy groups compared to *para*-substituted analogues is observed in the homologues series of *ortho*-substituted porphyrine derivatives. Supramolecular packing type and elementary cell parameters of the representative of this series of mesogenic compounds in crystal phase and mesophase under different temperatures are established.

The introduction of metal-complex formation (Zn or Co) into tetra-substituted non-mesogenic homologues did not induce the mesophase formation. Moreover, mesogenic ligand ($-\text{OC}_{16}\text{H}_{33}$) in metal complexes (Ni or Zn) becomes non-mesogenic.

3. The decreasing of the alkoxy substituents number from four to two leads to the thermotropic enantiotropic mesophase formation in homologues $-\text{OC}_{14}\text{H}_{29}$ and $-\text{OC}_{16}\text{H}_{33}$ and to mesomorphism of these di-substituted compounds in binary systems with toluol, benzene, chloroform. Thermotropic mesophase glasses on cooling. The introduction of metal-complex formation (Zn, Co) induces mesomorphism in the lower homologue ($-\text{OC}_8\text{H}_{17}$). Zinc complex possesses lower mesophase thermostability than cobalt complex, but broader temperature interval of its existence. On cooling the glassing of these complexes is observed.

4. The studied tetra-substituted esters of tetraphenylporphyrine with meso-substitution ($-\text{OCOC}_{13}\text{H}_{27}$ and $-\text{OCOC}_{15}\text{H}_{31}$) reveal enantiotropic thermotropic properties with glassing on cooling. The decrease of carbon atom number leads to the loss of mesogeneity.

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References

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