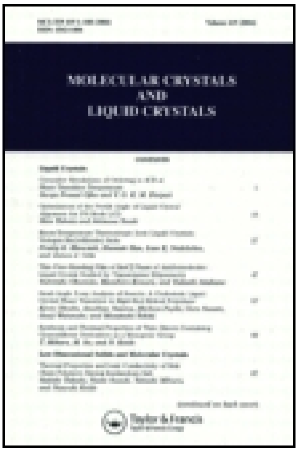

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Synthesis and Mesomorphic Properties of Substituted Pyrazinoporphyrazines

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Tert-*butylsubstituted pyrazinoporphyrazines (**Ia–Id**) and octacarboxypyrazinoporphyrazine (**II**) were synthesized. The structure of these compounds was determined using elemental analysis, IR and UV-Vis absorption spectroscopy. All synthesized compounds do not exhibit thermotropic mesomorphism. In this work we induced an enantiotropic mesophase due to charge transfer (CT) interactions in mixtures of compounds **Ia–Id** with a strong electron acceptor 2,4,7-trinitrofluorenone (**TNF**). The computer simulation of water systems of polar octacarboxypyrazinoporphyrazine (**II**) was carried out. The simulation shows that compound **II** does not possess mesomorphic properties in binary systems (lyotropic mesomorphism).*

Keywords substituted pyrazinoporphyrazines; synthesis; mesomorphic properties; CT-complex; computer simulation

1. Introduction

The history of study of phthalocyanine and its metal complexes spans several dozen years. Nevertheless, their ability to form thermotropic and lyotropic liquid crystals was discovered not long ago [1–3].

On the contrary, heteroarenoporphyrazines, that is the porphyrazines annulated by heterocycles, are less studied. It was shown that octa(dodecyl)etrapyrazinoporphyrazine and its metal complexes are the π-acceptor of the columnar-type [4], and triphenylene-based porphyrazine complexes bearing sixteen decyloxy side-chains possess thermotropic mesomorphism [5]. It aimed us to synthesize tetraheteroarenoporphyrazines soluble in water and organic solvents and to investigate their mesomorphic properties.

2. Results and Discussion

To study the influence of the substituted pyrazinoporphyrazine structure peculiarities the *tert*-butylsubstituted pyrazinoporphyrazines (**Ia–Id**) and octacarboxypyrazinoporphyrazine (**II**) were synthesized (Fig. 1).

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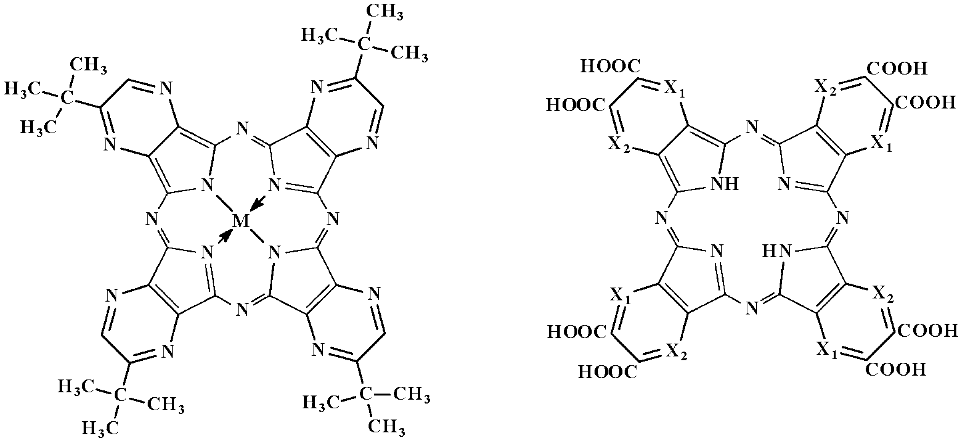


M = 2H (Ia), Cu (Ib), Zn (Ic), Co (Id)

II. $X_1 = X_2 = N$

III. $X_1 = X_2 = CH$

Figure 1. Chemical structure of **I–III** compounds.

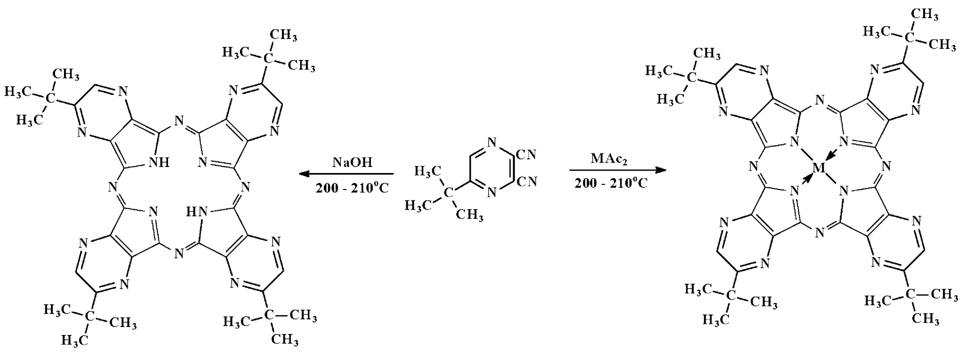
Tert-butylsubstituted pyrazinoporphyrazines (**Ia–Id**) were synthesized by the template cyclotetramerization from *tert*-butylsubstituted nitrile pyrazine-2,3-dicarboxylic acid with the metal salt. Metal free (**Ia**) registered by our method [6] was obtained by annealing of nitrile and alkali with 90% yield (Fig. 2).

The compound **II** was obtained according to the previously described method [7, 8].

The high solubility of compound **I** in the acetone, alcohols, chloroform allows carrying out of all the compounds purification by the columnar chromatography. The synthesized pyrazinoporphyrazines were characterized by elemental analysis, IR and UV-Vis absorption spectroscopy.

IR spectra in a KBr pellets were recorded on a spectrophotometer AVATAR 360 FT-IR in the range of 400–4000 cm^{-1}.

The UV-Vis absorption spectra of the studied compounds were recorded with a HITACHI U-2001 spectrophotometer (Fig. 3).



M = Cu (Ib), Zn (Ic), Co (Id)

M = 2H (Ia)

Figure 2. Synthetic scheme of the *tert*-butylsubstituted pyrazinoporphyrazine (**Ia–Id**).

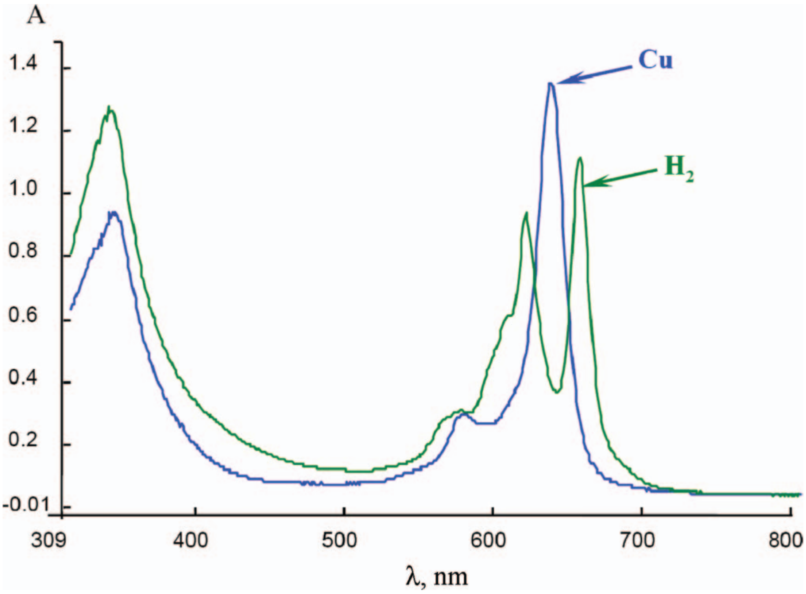


Figure 3. UV-visible absorption spectra in chloroform: H_2–**Ia**, Cu–**Ib.**

The mesomorphic properties were investigated by polarizing optical microscopy. The thermotropic mesomorphism of the individual samples and their CT-complexes was studied by means of a polarizing optical microscope (Leitz Laborlux 12 Pol") equipped with a hot stage (Mettler Toledo FP82). The lyotropic properties were studied using contact preparations with a number of the organic solvents (toluene, chloroform).

Tetra-(5-*tert*-butylpyrazino)porphyrazines (**Ia**–**Id**) do not possess thermotropic mesomorphism. The compound **Ic** possesses lyotropic mesomorphism in the binary systems with toluene and chloroform (Fig. 4).

Compound **II** exhibits neither lyotropic mesomorphism, nor the thermotropic one.

Nowadays, the modification of liquid crystal properties is being actively investigated to the point of liquid crystalline state induction of the non-mesogenic compounds by

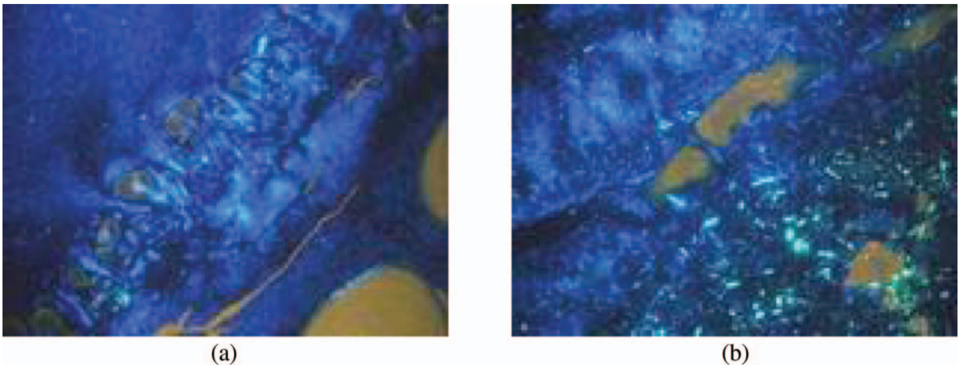

(a) (b)

Figure 4. Optical textures of lyotropic mesophases obtained in contact preparations of the systems **Ic**–solvent: (a)–chloroform, (b)–toluene. T = 25°C, crossed polarizers.

forming the binary and multi-component systems. The mesomorphic state can be induced or modified by the formation of charge-transfer complexes (CT-complexes) between the electron donor and strong electron acceptor [9, 10].

This approach was applied to induce the mesomorphic state of non-mesomorphic **Ia**–**Id** with 2,4,7-trinitrofluorenone (**TNF**). The first stage of the contact preparation was melting of the investigated substituted porphyrazines with **TNF** on the hot stage. It was established that all compounds (**Ia**–**Id**) with **TNF** in the contact preparations after the annealing form the CT-complex zone possessing mesomorphic properties in the temperature range of 44.0–66.4°C. The CT-complex zone of all the mentioned compounds is marked with the change of color from dark-blue to green. Probably the given compounds (**Ia**–**Id**) are the weak donor molecules in contact with strong electron acceptor **TNF**.

It is important that octacarboxypyrazinoporphyrazine (**II**) does not possess lyotropic mesomorphism in aqueous systems in contrast to octacarboxyphthalocyanine (**III**) [3]. To understand the mechanism of this difference the computer simulation was carried out in the work by the molecular dynamics method with the parameters of molecular mechanics.

The potential system energy was described as:

$$\mathrm{U(r)} = \mathrm{U_b} + \mathrm{U_v} + \mathrm{U}_\varphi + \mathrm{U_{VdW}} + \mathrm{U_{el}},$$

where the items respond to the following types of interactions: $\mathrm{U_b}$–valence bonds; U_ν–valence angles; U_φ–torsion angles; $\mathrm{U_{VdW}}$–Van der Waals interactions; $\mathrm{U_{el}}$–electrostatic interactions of uncompensated charges on the atoms [11]. The force field AMBER [12] was used to describe the molecular system. However, only the static description of the system was not enough. To obtain the phase structure and its thermodynamic properties it was necessary to use the method allowing description of the system evolution. As the great number of differential equations is solved at the modeling, the method to solve this task using the graphic processing unit (GPU) was developed. It allowed enlarging of the simulated systems' size.

The following systems of disc-like molecules such as porphyrine derivatives were chosen as the research objects:

- binary system of octacarboxypyrazinoporphyrazine (**II**) with water: 60 compound molecules and 16440 water molecules;
- binary system of octacarboxyphthalocyanine (**III**) with water: 72 compound molecules and 16440 water molecules.

The choice of the molecules' correlation in the binary systems was determined by the previously established data [3] of lyotropic mesomorphism of octacarboxyphthalocyanine (**III**). Similar to the last one, we used such ration of solvent molecules with compound **II**.

The distribution functions for molecule mass centers g(r) at the different temperatures representing the probability of a molecule being at the definite positions about each other were built with the results of the numerical experiments.

The simulation shows that compound **II** does not possess mesomorphic properties in binary systems (lyotropic mesomorphism). It is completely dissolved forming a few spherical shape associates. It does not lead to the lyomesophase formation.

According to the computer simulation data in the presence of water on the diagrams of the distribution functions (Fig. 5), octacarboxyphthalocyanine (**III**) shows two pronounced picks.

The first one (r ≈ 3.8 Å) is the distance between the two next molecules in the column. The second one (r ≈ 7.4 Å) is the distance between the next nearest molecules. As a whole

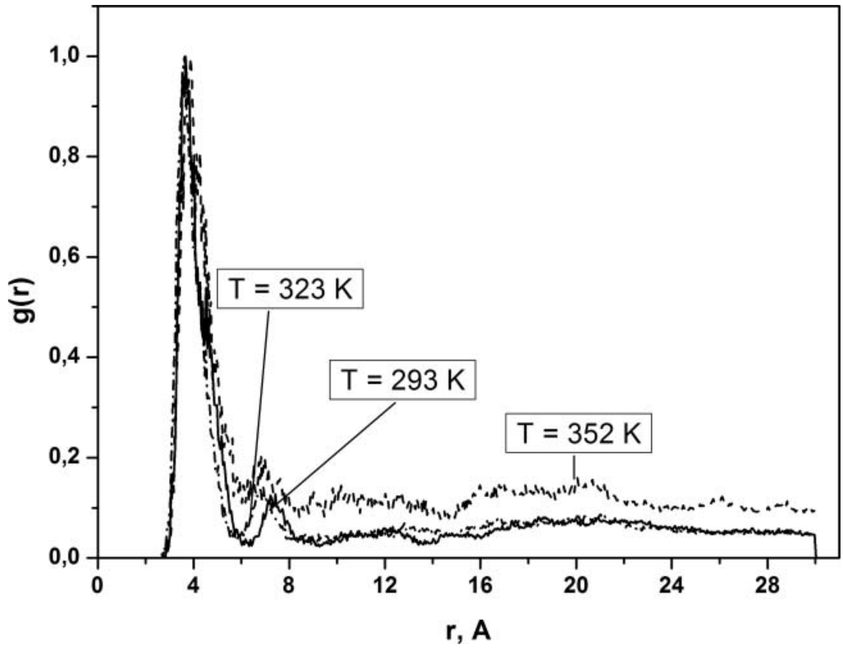


Figure 5. Distribution functions for compound **III** in binary system with water at different temperatures.

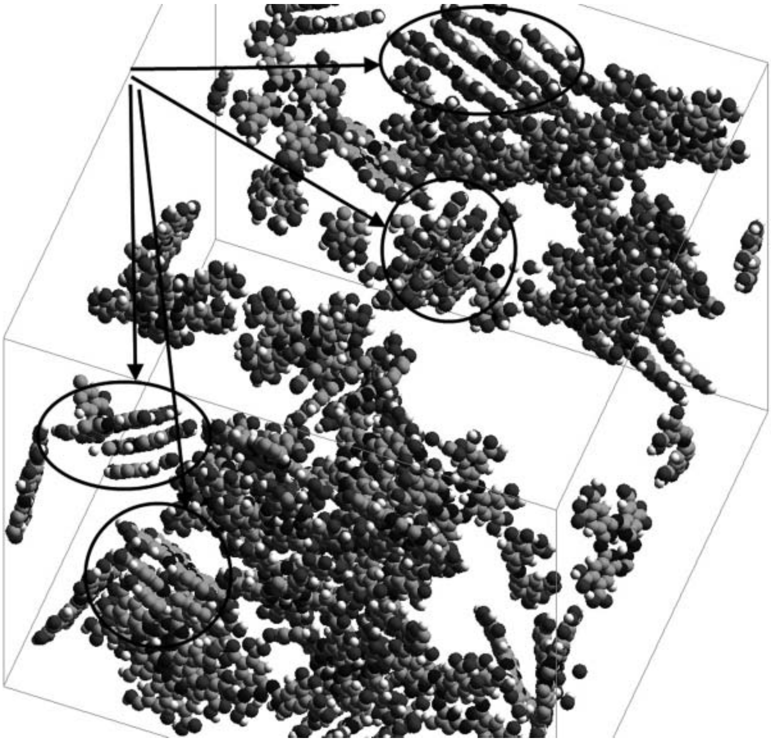


Figure 6. Packing model of compound **II** in binary system with water (the water molecules are not shown).

with the visual analysis it can be concluded that compound **III** molecules form the columnar associates (Fig. 6).

The computer simulation helps to determine the structure peculiarities of lyotropic mesophase in binary system octacarboxyphthalocyanine–water. The obtained data confirm the chromonic lyomesophase type with columnar supramolecular packing of disc-like compound **III** [3].

3. Conclusion

Five new disc-like compounds: *tert*-butylsubstituted pyrazinoporphyrazines (**Ia**–**Id**) and octacarboxypyrazinoporphyrazine (**II**) were synthesized. All synthesized compounds do not exhibit thermotropic mesomorphism. We induced an enantiotropic mesophase due to CT interactions in mixtures of compounds **Ia**–**Id** with a strong electron acceptor **TNF**, and also in contact preparation of the **Ic–**solvents (chloroform, toluene).

Compound **II** exhibits neither lyotropic mesomorphism, nor the thermotropic one. The computer simulation shows the structure peculiarities of binary system compound **II**–water. In contrast to octacarboxyphthalocyanine derivative (**III**), compound **II** doesn’t form any columnar associates in aqueous solutions.

Acknowledgments

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References

[1] Goodby, J. W., Robinson, P. S., Teo, B. K., & Cladi, P. E. (1980). *Mol. Cryst. Liq. Cryst.*, *56*, 303.

[2] Bruce, D. W. (1992). *Inorganic Materials*, J. Willey and Sons Ltd., 610 p.

[3] Usol’tseva, N. V., Akopova, O. B., Bykova, V. V., Smirnova, A. I., Pikin, S. A., & Liquid Crystals: Discotic Mesogens. (2004). *Ivanovo*, Publishing House “IvSU”, 504 p. (in Russ.)

[4] Ohta, K., Watanabe, T., Hasebe H., Morizumi, Y., Fujimoto, T., Yamamoto, I., Lelièvre, D., & Simon J. (1991). *Mol. Cryst. Liq. Cryst.*, *196*, 13.

[5] Mohr, B., Wegner, G., & Ohta, K. (1995). *J. Chem. Soc., Chem. Commun.*, 995.

[6] Belozerova, Yu. I., Efimova, S. V., Korzhenevskii, A. B., & Koifman, O. I. (2009). *Russian Journal of General Chemistry*, *79*, 2678.

[7] Galpern, E. G., Lukyanets, E. A., & Galpern, M. G. (1973). *Izv. Akad. Nauk SSSR, Ser. Khim.*, *9*, 1976 (in Russ.).

[8] Efimova, S. V., Korzhenevskii, A. B., & Koifman, O. I. (2006). Patent RF No 2 269 532, I.B. No 4 of 10.02.06.

[9] Ringsdorf, H., Bengs, H., Karthaus, O., Wüstefeld, R., Ebert, M., Wendorff, J. H., Kohne, B., & Praefcke, K. (1990). *Adv. Mater.*, *2*, 141.

[10] Praefcke, K., & Singer, D. (1998). In: D. Demus, J. Goodby, G. W. Gray, H.-W. Spies, & V. Vill (Eds.), *Handbook of liquid crystals*, Vol. 2B, Chapter 7, Wiley-VCH, 945.

[11] Wilson, M. R. (1998). In: D. Demus, J. Goodby, G. W. Gray, H.-W. Spies, & V. Vill (Eds.), *Handbook of Liquid Crystals,* Vol. 1, Wiley-VCH, 950 p.

[12] Cornell, W. D., Cieplak, P., Bayly, Ch. I., Gould, I. R., Merz, K. M., Ferguson, D. M., Spellmeyer, D. C., Fox, T., Caldwell, J. W., & Kollman, P. A. (1995). *J. Am. Chem. Soc.*, *117*, 5179.