Russian Journal of General Chemistry, Vol. 72, No. 9, 2002, pp. 1463–1467. Translated from Zhurnal Obshchei Khimii, Vol. 72, No. 9, 2002, pp. 1552–1556.

Nucleophilic Substitution in 4-Bromo-5-nitrophthalodinitrile: VI.[1] 4-Dimethylphenoxy-5-nitrophenoxyphthalodinitrile and the Copper Phthalocyanine Derived from It

V. E. Maizlish, S. A. Ivanovskii, G. P. Shaposhnikov, I. G. Abramov, A. V. Smirnov, V. V. Bykova, and N. V. Usol'tseva

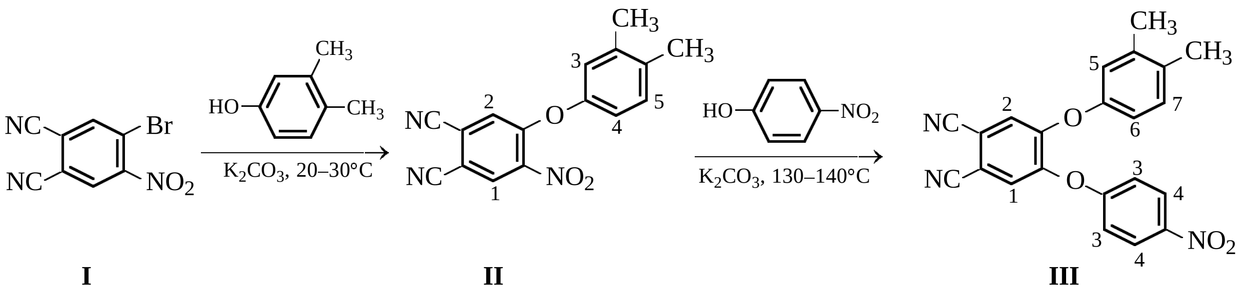
Ivanovo State University of Chemical Engineering, Ivanovo, Russia
Yaroslavl State Technical University, Yaroslavl, Russia
Ivanovo State University, Ivanovo, Russia

Received December 28, 2000

Abstract—4-(3,4-Dimethylphenoxy)-5-(4-nitrophenoxy)phthalodinitrile was prepared by stepwise nucleophilic substitution of bromine and then the nitro group in 4-bromo-5-nitrophthalodinitrile by the substituted phenoxy groups and was converted to the corresponding octasubstituted copper phthalocyanine by the reaction with copper acetate. The spectroscopic and mesomorphic properties of the resulting complex were studied. It exhibits thermotropic mesomorphism and forms an M phase in the range 85–155°C.

Unsubstituted and substituted phthalocyanines (Pc) are widely used as pigments and dyes [2, 3]. Active study of this class of compounds showed that they can also be successfully used as catalysts, chemical sensors, and liquid crystals, and also as materials for photoelectric cells, optical discs, photodynamic cancer therapy, Langmuir–Blodgett films, thin-film electronics, etc. [3–11]. Synthesis of new substituted Pc, in particular, of those containing various substituents is limited by the lack of required precursors, e.g., of the corresponding phthalodinitriles. One of the routes to new substituted phthalodinitriles is replacement of an existing substituent by another group. We have already reported on the high reactivity of 4-bromo-5-nitrophthalodinitrile in nucleophilic substitutions [1, 2, 12–17]. The presence of labile leaving groups (Br, NO_2) makes this phthalodinitrile a unique synthon for preparing new substituted phthalodinitriles. We found that the bromine substituent is more reactive and is relatively readily substituted under mild conditions with O-, S- and N-nucleophiles, whereas the second leaving group, NO_2, is substituted under more rigorous conditions. Previous reports concerned either nucleophilic substitution of bromine only [1, 12–17] or substitution of both bromine and nitro group with the same nucleophiles [17]. Some of the resulting phthalodinitriles were converted into the corresponding octasubstituted metal phthalocyanines [15, 18, 19].

Here we report on synthesis of a phthalodinitrile containing two differently substituted phenoxy groups and of the copper phthalocyanine derived from it.



---

[1] For communication V, see [1].

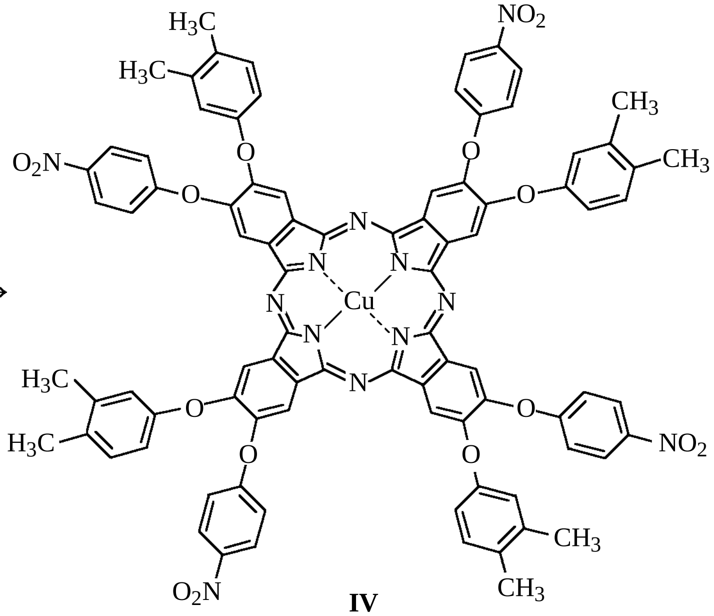
4-(3,4-Dimethylphenoxy)-5-(4-nitrophenoxy)-phthalodinitrile (**III**) was prepared by stepwise nucleophilic substitution, first of bromine in 4-bromo-5-nitrophthalodinitrile (**I**) under mild conditions and then of the nitro group in the intermediate dinitrile **II** under more rigorous conditions, as shown above.

The stepwise synthesis was performed by the previously developed procedures [16, 17] with isolation and identification of each reaction product.

4-(3,4-Dimethylphenoxy)-5-nitrophthalodinitrile **II** was prepared by the reaction of dinitrile **I** with 3,4-dimethylphenol in DMF in the presence of aqueous K_2CO_3 solution at room temperature. After isolation and purification, compound **II** was treated with *p*-nitrophenol in DMF in the presence of anhydrous K_2CO_3 at elevated temperature (130–140°C). Under these conditions, the nitro group is nucleophilically substituted to form the desired 4-(3,4-dimethylphenoxy)-5-(4-nitrophenoxy)phthalodinitrile (**III**).

The phthalodinitriles were identified by elemental analysis and by H NMR and IR spectroscopy. The IR spectrum of **III** is largely similar to those of other substituted phthalodinitriles [20]. The C≡N vibration bands are manifested at 2240 cm^{-1}, and the C–O (ether) bands, at 1260 cm^{-1}. The bands at 1340 and 1560 cm^{-1} confirm the presence of nitro groups, and the bands at 2860 and 2970 cm^{-1}, the presence of methyl groups [21]. By the template reaction of phthalodinitrile **III** with copper acetate at 180–185°C, we prepared copper tetra-4-(3,4-dimethylphenoxy)-5-(4-nitrophenoxy)phthalocyanine **IV** (one of positional isomers is shown):

III $\xrightarrow{Cu(Ac)_2}$



IV

The target product was extracted with chloroform and, after removing the solvent, purified by reprecipitation from concentrated H_2SO_4 and extraction of the residual organic impurities with acetone. Final purification was performed by liquid chromatography (Al_2O_3, eluent chloroform). The resulting compound **IV** is soluble in chloroform, DMF, and concentrated sulfuric acid, sparingly soluble in benzene, and insoluble in acetone.

The electronic absorption spectra of **IV** in organic solvents are poorly sensitive to the nature of the solvent. The spectra in chloroform, benzene, and DMF are similar and suggest association of the complex (Fig. 1): The monomer and dimer give bands with maxima at 682 and 629–631 nm, respectively [22–24]. The association is proved by the concentration dependence of the spectrum. When the solution is diluted threefold, the intensity ratio of the dimer and monomer bands changes from 1 : 1.25 to 1 : 1.71 (Fig. 1, curves *1* and *2*).

The relationship between the structures of phthalocyanine molecules and their properties (in particular, mesomorphic) is a subject of active research [11, 25–30]. Substituted phthalocyanines and their metal complexes exhibit both thermotropic and lyotropic mesomorphism in binary mixtures with aqueous and nonaqueous solvents. The mesomorphic properties of these compounds depend on the number, position, and nature of peripheral substituents, and also on the nature of the central ion [11, 25–30]. Therefore, it was interesting to study the mesomorphic properties of **IV**, as this complex contains differently substituted peripheral phenoxy groups. Polarization microscopic examination showed that the compound exhibits thermotropic mesomorphism, forming an enantiotropic columnar phase in the temperature range 85–155°C (Fig. 2). This fact suggests that the columnar mesophase belongs to the disordered type, because disordered columnar phases exhibiting weak microsegregation do not tend to preserve the column packing and transform into the isotropic state in solution [31]. No lyotropic properties were found in binary systems of **IV** with organic solvents (dimethyl sulfoxide, chloroform, benzene, etc.).

EXPERIMENTAL

The IR spectra were taken on a Specord M-80 spectrophotometer in the range 4000–400 cm^{-1}, using KBr pellets. The ^1H NMR spectra (5% solutions in DMSO, internal reference TMS) were taken on a Bruker AC-200P spectrometer (Institute of Organic Chemistry, Russian Academy of Sciences, Moscow). The electronic absorption spectra were recorded in DMF, chloroform, or benzene on Specord M-40 UV/Vis and Perkin–Elmer Lambda-20 spectrophotometers at room temperature in the range 300–900 nm.

The phase state of copper tetra-4-(3,4-dimethylphenoxy)-5-(4-nitrophenoxy)phthalocyanine was examined by polarization microscopy with an MIN-8 microscope equipped with a heating stage and a Zorkii camera; the heating rate was 2 deg min^{-1}.

The texture was photographed with a built-in camera (24 × 36 mm) and a Wild MPS-51 camera (×320 magnification).

Lyotropic mesomorphism was studied using contact samples.

4-(3,4-Dimethylphenoxy)-5-nitrophthalodinitrile (II). A 0.01-mol portion of dinitrile **I** and equimolar amount of 3,4-dimethylphenol were added with stirring to 30 ml of DMF. After dissolution of the reactants, a solution of 0.01 mol of K_2CO_3 in 10 ml of water was added at 20–30°C with vigorous stirring. The resulting mixture was stirred at 20–30°C for 0.5 h. The precipitated target product was filtered off, washed with 10 ml of ethanol and 50 ml of water, and recrystallized from 2-propanol–DMF. Yield 74%, mp 176–178°C. ^1H NMR spectrum, δ, ppm: 8.82 s (1H, H^1), 7.60 s (1H, H^2), 7.26 d (1H, H^4, J 8 Hz), 7.01 d (1H, H^3, J 2 Hz), 6.93 d (1H, H^5, J 8 Hz), 2.30 s (6H, CH_3).

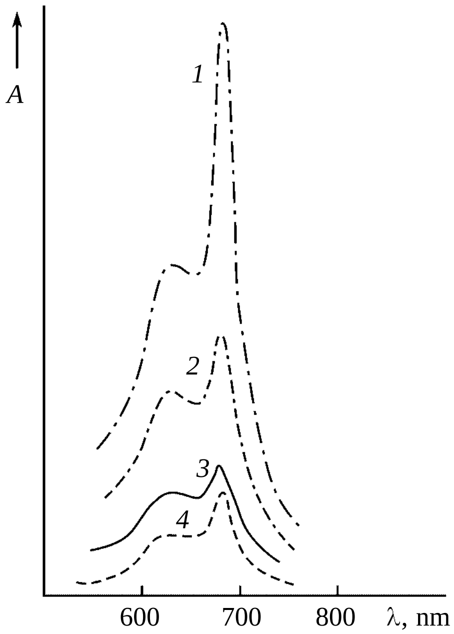


Fig. 1. Electronic absorption spectra of **IV** in various organic solvents: (*1*) chloroform, *c* 1.5 × 10^{-5} M; (*2*) chloroform, *c* 4.5 × 10^{-5} M; (*3*) DMF; and (*4*) benzene.

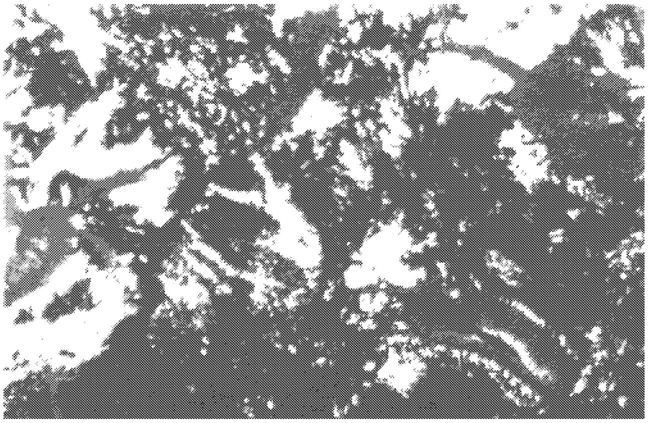


Fig. 2. Nongeometric texture of **IV** at 150°C. Crossed nicols; ×100.

4-(3,4-Dimethylphenoxy)-5-(4-nitrophenoxy)phthalodinitrile (III). Dinitrile **II** (0.01 mol), anhydrous K_2CO_3 (0.01 mol), and 4-nitrophenol (0.01 mol) were added with stirring to 30 ml of DMF. The resulting mixture was vigorously stirred at 130–140°C for 3 h, cooled, and poured into 100 ml of water. The precipitated target product was filtered off, washed with water, and recrystallized from 2-propanol–DMF. Yield 56%, mp 151–153°C. IR spectrum (KBr), ν, cm^{-1}: 2240 (CN); 1260 (C–O); 1560, 1340 (NO_2); 2970, 2860 (CH_3). ^{1}H NMR spectrum, δ, ppm: 8.28 s (1H, H^1), 8.23 s (1H, H^2), 7.37 d (2H, H^4, *J* 8 Hz), 7.25 d (2H, H^3, *J* 8 Hz), 6.88–6.75 m (3H, H^5, H^6, H^7), 2.27 s (3H, CH_3), 2.24 s (3H, CH_3). Found, %: C 68.55; H 3.95; N 10.84. $C_{22}H_{15}N_3O_5$. Calculated, %: C 68.57; H 3.92; N 10.90.

Copper tetra-4-(3,4-dimethylphenoxy)-5-(4-nitrophenoxy)phthalocyanine. A quartz ampule was charged with 1 mmol of dinitrile **III** and 0.3 mmol of copper acetate; the mixture was fused at 180–185°C for 0.5 h. The target product was extracted with chloroform. The complex was reprecipitated from concentrated sulfuric acid, and the impurities were extracted with acetone. The compound was finally purified by column chromatography (Al_2O_3, eluent chloroform). The phthalocyanine was vacuum-dried at 60°C; yield 40%. Electronic absorption spectrum, λ_{max}, nm: 631, 682 (chloroform); 631, 682 (DMF); 631, 682 (benzene). Found, %: C 72.16; H 4.35; N 11.22. $C_{88}H_{60}\cdot CuN_{12}O_8$. Calculated, %: C 71.55; H 4.10; N 11.38.

ACKNOWLEDGMENTS

The study was financially supported by the Ministry of Education of the Russian Federation (project no. 97-0-9.4-381 in the field of basic natural science) and Russian Foundation for Basic Research (project no. 98-03-32 084).

REFERENCES

1. Balakirev, A.E., Maizlish, V.E., and Shaposhnikov, G.P., *Zh. Obshch. Khim.*, 2002, vol. 72, no. 2, p. 332.
2. Stepanov, B.I., *Vvedenie v khimiyu i tekhnologiyu organicheskikh krasitelei* (Introduction to Chemistry and Technology of Organic Dyes), Moscow: Khimiya, 1984.
3. Booth, G., *The Chemistry of Synthetic Dyes,* Venkataraman, K., Ed., New York: Academic, 1971, vol. 5. Translated under the title *Khimiya sinteticheskikh krasitelei,* Leningrad: Khimiya, 1977, vol. 5, ch. 4, p. 211.
4. Moser, F.H. and Thomas, A.L., *The Phthalocyanines,* Boca Raton: CRC, 1983, vols. 1, 2.
5. *Phthalocyanines: Properties and Applications,* Lezmoff, C.C. and Lever, A.B.P., Eds., New York: VCH, 1989, vol. 1; 1993, vol. 2; 1993, vol. 3; 1996, vol. 4.
6. Maizlish, V.E. and Borodkin, V.F., *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.,* 1984, vol. 27, no. 9, p. 1003.
7. Velichko, A.V., Maizlish, V.E., Shaposhnikov, G.P., and Smirnov, R.P., *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, 1993, vol. 36, no. 2, p. 47.
8. Simon, J. and Andre, J.J., *Molecular Semiconductors. Photoelectrical Properties and Solar Cells*, Berlin: Springer, 1985.
9. Loutfy, R.O., Hor, A.-M., Hsiao, C.-K., Baranyi, G., and Kazmaier, P., *Pure Appl. Chem.*, 1988, vol. 60, no. 7, p. 1047.
10. *Porfiriny: Spektroskopiya, elektrokhimiya, primenenie* (Porphyrins: Spectroscopy, Electrochemistry, and Applications), Enikolopyan, N.S., Ed., Moscow: Nauka, 1987.
11. Usol'tseva, N.V., *Liotropnye zhidkie kristally: Khimicheskaya i nadmolekulyarnaya struktura* (Lyotropic Liquid Crystals: Chemical and Supramolecular Structure), Ivanovo: Ivanov. Gos. Univ., 1994.
12. Shishkina, O.V., Maizlish, V.E., Kudrik, E.V., Shaposhnikov, G.P., and Smirnov, R.P., *Zh. Obshch. Khim.,* 1999, vol. 69, no. 10, p. 1712.
13. Zharnikova, M.A., Balakirev, A.E., Maizlish, V.E., Kudrik, E.V., and Shaposhnikov, G.P., *Zh. Obshch. Khim.,* 1999, vol. 69, no. 11, p. 1870.
14. Shishkina, O.V., Maizlish, V.E., Kudrik, E.V., Shaposhnikov, G.P., and Smirnov, R.P., *Zh. Obshch. Khim.,* 2000, vol. 70, no. 5, p. 815.
15. Shishkina, O.V., Maizlish, V.E., and Shaposhnikov, G.P., *Zh. Obshch. Khim.,* 2001, vol. 71, no. 2, p. 271.
16. Abramov, I.G., Ivanovskii, S.A., Smirnov, A.V., and Dorogov, M.V., *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.,* 2000, vol. 43, no. 1, p. 120.
17. Abramov, I.G., Dorogov, M.V., Ivanovskii, S.A., Smirnov, A.V., and Abramova, M.B., *Mendeleev Commun.,* 2000, no. 1, p. 78.
18. Shishkina, O.V., Maizlish, V.E., Shaposhnikov, G.P., and Smirnov, R.P., *Zh. Obshch. Khim.,* 2000, vol. 70, no. 1, p. 137.
19. Maizlish, V.E., Balakirev, A.E., Shishkina, O.V., and Shaposhnikov, G.P., *Zh. Obshch. Khim.*, 2001, vol. 71, no. 2, p. 274.
20. Rodionova, G.N., Boglaenkova, G.V., Mikhalenko, S.A., and Luk'yanets, E.A., in *Khimiya i tekhnologiya promezhutochnykh produktov i krasitelei, tekstil'no-vspomogatel'nykh veshchestv i drugikh produktov organicheskogo sinteza* (Chemistry and Technology of Intermediate and Dyes, Auxiliary Substances of Textile Industry, and Other Products of Organic Synthesis), Moscow: NIITEKhim, 1974, p. 3.
21. Nakanishi, K., *Infrared Absorption Spectroscopy,* San Francisco: Holden-Day, 1962.
22. Maizlish, V.E., Mochalova, N.L., Snegireva, F.P., and

Borodkin, V.F., *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, 1986, vol. 29, no. 1, p. 3.

23. Kimura, M., Yamaguchi, Y., Muto, T., Hanabusa, K., and Shirai, H., *J. Porphyrins Phthalocyanines*, 2000, vol. 4, no. 1, p. 123.
24. Schutte, W.J., Sluyters-Rehbach, M., and Sluyters, J.H., *J. Phys. Chem.*, 1993, vol. 97, no. 22, p. 6069.
25. Usol'tseva, N.V., Bykova, V.V., Anan'eva, G.A., and Maizlish, V.E., *Izv. Ross. Akad. Nauk, Ser. Fiz.*, 1995, vol. 59, no. 3, p. 49.
26. Bykova, V.V., Usol'tseva, N.V., Anan'eva, G.A., Smirnova, A.I., Shaposhnikov, G.P., and Maizlish, V.E., *Zh. Obshch. Khim.*, 2000, vol. 70, no. 1, p. 153.
27. Bykova, V.V., Usol'tseva, N.V., Anan'eva, G.A., Shaposhnikov, G.P., and Maizlish, V.E., *Izv. Ross. Akad. Nauk, Ser. Fiz.*, 1998, vol. 62, no. 8, p. 1647.
28. Smirnova, A.I., Maizlish, V.E., Usol'tseva, N.V., Bykova, V.V., Anan'eva, G.A., Kudrik, E.V., Shirokov, A.V., and Shaposhnikov, G.P., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 2000, no. 1, p. 129.
29. Usol'tseva, N.V., in *Uspekhi khimii porfirinov* (Advances in Porphyrin Chemistry), St. Petersburg: Nauchno-Issled. Inst. Khimii S.-Peterb. Gos. Univ., 1999, vol. 2, p. 142.
30. *Metallomesogens: Synthesis, Properties and Applications*, Serrano, J.L., Ed., New York: VCH, 1996, p. 160.
31. Cammidge, A.N. and Bushby, J.R., Jr., in *Handbook of Liquid Crystals,* Weinheim: Wiley, 1998, vol. 2B, ch. 16, p. 739.