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Organic Chemistry

3,6-Didecyloxyphthalonitrile as a starting compound for the selective synthesis of phthalocyanines of the ABAB type

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Reactions of 3,6-dipentyloxy- and 3,6-didecyloxyphthalonitriles with lithium pentoxide in pentan-1-ol were studied. 3,6-Didecyloxyphthalonitrile can be used for the preparation of both the corresponding octasubstituted phthalocyanines and phthalocyanines of the ABAB type.

Key words: phthalocyanine, asymmetrical substitution, selectivity, isoindole derivatives, phthalonitrile.

Due to the presence of the unique two-circuit conjugation macrosystem and the high chemical and thermal stability, phthalocyanines (Pc) find wide use as organic dyes,[1] materials for sensors[2] and microelectronics,[3] and thermotropic and lyotropic liquid crystals.[4]

Recently, owing primarily to the discovery of the nonlinear-optical effect,[5] the synthesis and the nonlinear-optical properties of unsymmetrically substituted phthalocyanines containing simultaneously electron-donating and electron-withdrawing substituents have been extensively studied.[6—8] It has also been found[9] that some compounds of this type are very convenient for the formation of Langmuir—Blodgett films.

The major procedure for the preparation of unsymmetrically substituted phthalocyanines involves statistical condensation of two phthalonitriles or 1,3-diiminoisoindolines containing different substituents. However, this procedure has a number of serious drawbacks the major of which are the difficulties in the separation of isomers and the difference in the reactivities of phthalogens introduced into condensation.

The synthesis in which one of the phthalogens introduced into condensation is sterically hindered, *i.e.*, cannot undergo tetramerization to form the phthalocyanine ring, seems to be a very promising procedure because it substantially facilitates the separation of isomers. Previously, tetraphenylphthalonitrile[10] and 2,3-dicyano-1,4-diphenylnaphthalene[11] have been used as sterically hindered compounds.

With the aim of developing procedures for the selective synthesis of phthalocyanines of the ABAB type, we studied the reactions of 3,6-dipentyloxy- and 3,6-didecyloxyphthalonitriles (**1** and **2**, respectively) with lithium pentoxide in pentan-1-ol.

3,6-Dialkoxyphthalonitriles have for a rather long time been known as the starting compounds in the synthesis of the corresponding octasubstituted phthalocyanines soluble in organic solvents.[12] This synthesis is carried out by adding metallic lithium to boiling alcoholic solutions of the dinitriles. Due to steric hindrances caused by the presence of substituents at positions 3 and 6, the pronounced *trans* effect would be expected to

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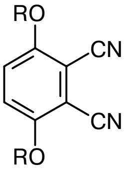
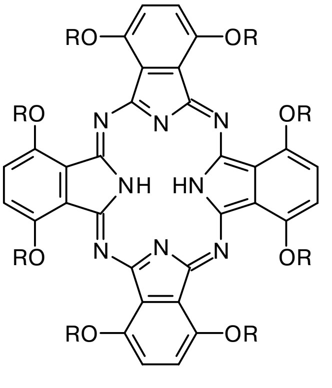
occur in the synthesis of mixed phthalocyanines resulting in the predominant formation of compounds of the ABAB type. Actually, it was demonstrated that the selective synthesis of porphyrazines of the ABAB type with the use of 4,7-diisopropoxy-1,3-diiminoisoindoline as the starting compound sometimes afforded the *trans* isomer in a yield several times higher than that of the *cis* isomer (porphyrazine of the AABB type) depending on the nature of the second component.[13]

Results and Discussion

Refluxing of phthalonitrile **1** with a solution of *n*-$C_5H_{11}OLi$ in pentan-1-ol afforded octasubstituted phthalocyanine (**3**). Under analogous conditions, phthalonitrile **2** did not produce even traces of phthalocyanine. At the same time, the IR spectrum of the reaction mixture did not have bands corresponding to C≡N stretching vibrations of the nitrile groups, which is indicative of their conversion with the possible formation of the isoindole ring. The addition of a new portion of metallic Li to a boiling solution of compound **2** in pentan-1-ol containing $C_5H_{11}OLi$ rapidly yielded 1,4,1′,4′,1″,4″,1‴,4‴-octakis(decyloxy)phthalocyanine **4**, which is identical with that described previously.[12]



1, **2**



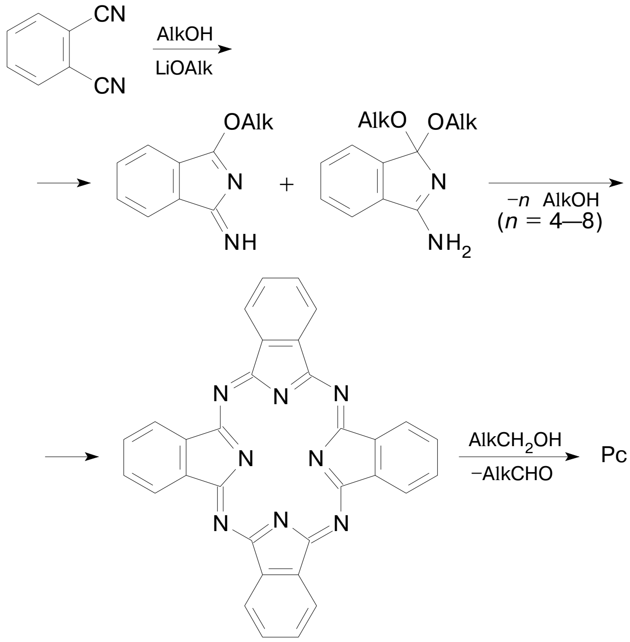
3, **4**

R = C_5H_{11} (**1**, **3**); $C_{10}H_{21}$ (**2**, **4**)

We believe that the above-mentioned differences in the chemical behavior of compounds **1** and **2** result from the following fact. It is known[14] that the first stage of the reaction of phthalonitrile with alcohols catalyzed by alkali metal alkoxides affords monoalkoxy and dialkoxy derivatives, which then undergo tetramerization to form dehydrophthalocyanine (Scheme 1).

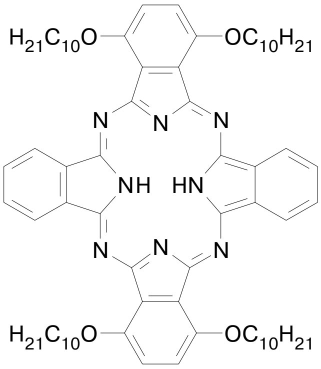
The transformation into phthalocyanine requires the participation of a reducing agent. Either alcohol, which is converted into the corresponding aldehyde, or alkali metal can act as such a reducing agent. Thus it was demonstrated[14] that dehydrophthalocyanine could be isolated from the reaction mixture in the absence of protic solvents (lithium in anhydrous benzene). Subsequent treatment with protic solvents (alcohols or H_2O) afforded phthalocyanine.

Scheme 1



Phthalonitrile **1** in the $C_5H_{11}OLi$—$C_5H_{11}OH$ system underwent cyclization to form dehydrophthalocyanine, which was reduced yielding octapentyloxyphthalocyanine **3**. Under analogous conditions, compound **2** cannot be converted into the corresponding dehydrophthalocyanine due to steric hindrances caused by "twisting" of the decyl chains; instead, it formed only mono- and dialkoxy derivatives. Apparently, the repeated addition of Li to the reaction mixture caused reduction of the above-mentioned alkoxy derivatives, giving rise to octakis(decyloxy)phthalocyanine **4**.

The addition of a 10-fold excess of phthalonitrile to a boiling solution of compound **2** in pentan-1-ol containing $C_5H_{11}OLi$ afforded a mixture of unsubstituted phthalocyanine and an isomer of the ABAB type (**5**). The mass spectrum (FAB-MS) of phthalocyanine **5** has two major groups of peaks. The first group containing the major peak at *m/z* 1139.7 corresponds to the molecular ion (M = 1138.77). The second group is characterized by an intense peak at *m/z* 577.2 [M + H^+ − 4 $C_{10}H_{21}$].



5

The formation of octakis(decyloxy)phthalocyanine **4** and isomers of the AB_3 and AABB types was not observed and the A_3B isomer was obtained only as an admixture. An unexpectedly high selectivity of the process is attributed to the fact that compound **2** cannot undergo tetramerization under conditions used for the synthesis.

Under conditions of statistical condensation of a mixture of two dinitriles, mixtures of all six possible isomers are always formed except for rare cases in which one of dinitriles is sterically hindered.[15] Steric hindrances in one of the starting dinitriles result in the formation of mixtures of only three isomers, *viz*., A_4, A_3B, and ABAB,[10] where A is the non-hindered unit. Therefore, the fact that the mass spectra do not have signals corresponding to molecular ions of the AB_3 and B_4 isomers allows one to conclude with a fair degree of assurance that the mixture does not contain an isomer of the AABB type whose spectrum is analogous to the mass spectrum of the target product **5** and also supports the previous suggestion that 3,6-didecyloxyphthalonitrile can be used as a sterically hindered dinitrile for the synthesis of phthalocyanines of the ABAB type. The structure of compound **5** was also confirmed by the ^{1}H NMR spectral data. The ^{1}H NMR spectrum of phthalocyanine **5** has only one triplet corresponding to eight protons of the α-CH_2 groups, which is indicative of the equivalence of all four α-methylene groups.

The presence of the low-intensity signals with m/z [M − 70] and [M − 140] in the mass spectrum is attributable to the fact that the synthesis of phthalocyanine **5** can be accompanied by transetherification and one or two decyloxy fragments are replaced by the pentyloxy groups.

The electronic absorption spectrum of phthalocyanine **5** (Fig. 1) has two groups of signals. The Soret band (a_{2u}—b^*_{1g}, π—π^*-transition) for this compound is shifted bathochromically by 6 nm compared to its position in the spectrum of phthalocyanine **3** (337.7 and 331.5 nm, respectively). The replacement affects only slightly the position of this band because the a_{2u} orbital is localized primarily on the nitrogen atoms of the phthalocyanine ring and the introduction of substituents at the periphery of the molecule exerts only an insignificant perturbing effect. The position of the Q band (a_{1u}—b^*_{1g}, π—π^*-transition) depends on the nature of the substituents to a substantially greater extent due to localization of the a_{1u} orbital on the carbon atoms of the isoindole fragments. This band is split into two components with approximately equal intensities, which is also characteristic of unsubstituted phthalocyanine. It should be noted that the long-wavelength component of the Q band for compound **5** is hypsochromically shifted by 33 nm compared to its position in the spectrum of compound **3** (737.1 and 770.0 nm, respectively). It is known that the introduction of the electron-donating substituents into the phthalocyanine molecule leads to an increase in the electron density in the single conjugation macrosystem of the molecule resulting in a substantial bathochromic shift of the Q band. From comparison of the electronic absorption spectra of phthalocyanines **5** and **3**, it may be concluded that the electron density redistribution takes place in molecule **5**. In this case the fragments containing the decyloxy groups act as electron donors, whereas the fragments without these groups act as electron acceptors. The UV spectral data also confirm the proposed structure of phthalocyanine **5**, which follows from comparison of its spectra with the spectra of the structurally very similar phthalocyanine of the ABAB type prepared based on compound **1** and tetraphenylphthalonitrile.[15]

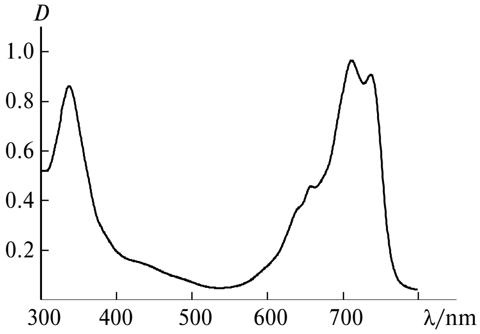


Fig. 1. UV spectrum of compound **5** (solution in $CHCl_3$).

Therefore, we demonstrated that the use of 3,6-didecyloxyphthalonitrile as a sterically hindered dinitrile allows one to perform the selective synthesis of phthalocyanines of the ABAB type and of the corresponding octasubstituted phthalocyanine.

Experimental

The electronic absorption spectra were measured on a Hitachi UV-2000 instrument in $CHCl_3$. The ^{1}H NMR spectra were recorded on a Bruker AM-200 spectrometer.

The IR spectra of compound **2**, which has been refluxed in the pentan-1-ol—lithium 1-pentoxide mixture for 2 h, were measured on a Specord M-60 instrument in the frequency region of 2400—2100 cm^{-1} at ~20 °C.

Compounds **1** and **2** were synthesized according to a procedure reported previously,[13] which was insignificantly modified, *viz*., the temperature of the process was increased to 100 °C. The resulting compounds were purified by double recrystallization successively from light petroleum and DMF. The compounds were identified based on the data of elemental analysis and comparison of the melting points of the resulting compounds with the published data.[12]

1,4,1′,4′,1″,4″,1‴,4‴-Octapentyloxyphthalocyanine (3). 3,6-Dipentyloxyphthalonitrile (**1**) (2 g, 0.67 mmol) was added to a solution of $C_5H_{11}OLi$ (prepared from Li (0.15 g, 2.14 mg-at.)) in pentan-1-ol (50 mL). The resulting solution was refluxed with stirring for 30 min and cooled. Then AcOH (5 mL) and acetone (100 mL) were added. The precipitate that formed was filtered off, dissolved in $CHCl_3$, and chromatographed on a column with Al_2O_3 (the 20 : 1 $CHCl_3$—acetone mixture as the eluent). The eluate was concentrated. The target product was recrystallized from DMF, washed with acetone, and dried at 60 °C. Phthalocyanine **3** was obtained as a crystalline bright-green powder in a yield of 1.13 g (56%). Found (%):

C, 71.73; H, 8.28; N, 9.37. $C_{72}H_{98}N_8O_8$. Calculated (%): C, 71.85; H, 8.21; N, 9.31. UV, λ_{max}/nm (log ε): 770.0 (5.16), 694.0 (4.58), 458.0 (4.19), 419.0 (4.24), 331.5 (4.78). FAB-MS (*m*-nitrobenzyl alcohol), *m/z*: 1203.9 $[M + H]^+$.

1,4,1′,4′,1″,4″,1‴,4‴-Octakis(decyloxy)phthalocyanine (4). 3,6-Didecyloxyphthalonitrile (**2**) (1 g, 0.23 mmol) was added to a solution of $C_5H_{11}OLi$ (prepared from Li (0.075 g, 1.07 mg-at.)) in pentan-1-ol (20 mL) and the reaction mixture was refluxed with stirring for 2 h. The solution remained colorless. Then an additional amount of lithium (0.075 g) was added and the mixture was refluxed for 20 min. After cooling, AcOH (5 mL) and acetone (100 mL) were added to the bright-green solution. The precipitate that formed was filtered off, dissolved in benzene, and chromatographed on a column with Al_2O_3 (C_6H_6 as the eluent). The eluate was concentrated. The residue was washed with acetone and dried at 60 °C. Phthalocyanine **4** was obtained as a waxy bright-green substance in a yield of 0.43 g (43%), m.p. 47—49 °C. Found (%): C, 75.94; H, 10.48; N, 6.83. $C_{112}H_{178}N_8O_8$. Calculated (%): C, 76.23; H, 10.92; N, 6.35. UV, λ_{max}/nm (*D*): 775.0 (1.579), 331.0 (1.397).

1,4,1″,4″-Tetrakis(decyloxy)phthalocyanine (5). 3,6-Didecyloxyphthalonitrile (**2**) (1 g, 0.23 mmol) was added to a solution of $C_5H_{11}OLi$ (prepared from Li (0.15 g, 2.14 mg-at.)) in pentan-1-ol (50 mL). The reaction mixture was refluxed for 2 h. Then phthalonitrile (2.6 g, 2.03 mmol) was added and the mixture was refluxed for 4 h. The resulting suspension was cooled, AcOH (5 mL) was added, and the mixture was diluted with MeCN (200 mL). The precipitate that formed was filtered off, the products were extracted with CCl_4 using a Soxhlet apparatus, and the extract was chromatographed on a column with Al_2O_3 (benzene as the eluent). The eluate was concentrated and the residue was washed with acetone and dried at 40 °C. Tetrasubstituted phthalocyanine **5** was obtained as a blue powder in a yield of 0.091 g (7%). Found (%): C, 74.92; H, 8.48; N, 10.02. $C_{72}H_{98}N_8O_4$. Calculated (%): C, 75.88; H, 8.67; N, 9.83. UV, λ_{max}/nm (log ε): 337.7 (4.82), 434.4 (4.08), 644.5 (4.48), 712.3 (4.87), 737.1 (4.84). ^{1}H NMR ($CDCl_3$), δ: 0.72—0.85 (m, 12 H, CH_3); 1.10—1.23 (m, 56 H, CH_2); 1.55—1.65 (m, 8 H, β-CH_2); 4.02 (t, 8 H, α-CH_2). FAB-MS (*m*-nitrobenzyl alcohol), *m/z*: 1139.7 $[M + H]^+$, 577.2 $[M + H - 4\ C_{10}H_{21}]^+$.

After completion of extraction, the residue was withdrawn from the Soxhlet apparatus and reprecipitated from concentrated H_2SO_4 (50 mL) by pouring into ice water. Then the precipitate was filtered off, washed with water, and dried at 120 °C. Unsubstituted phthalocyanine was obtained in a yield of 1.82 g (62%). The UV spectra of the resulting compound are identical with those reported previously.[16]

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