Novel Synthesis of Liquid Crystalline Phthalocyanines

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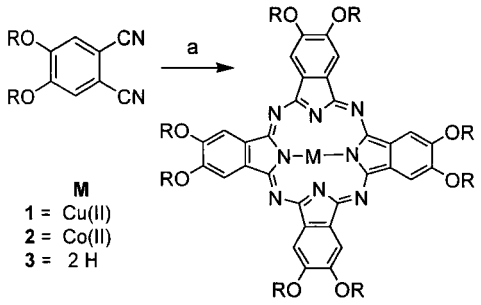
Received December 16, 1999

Introduction

The physical and chemical properties of phthalocyanines (Pc) have long attracted considerable interest due to their applications as dyes, organoelectronics, liquid crystals, ultrathin films, and in photodynamic therapy.[1] A particularly attractive feature of Pc is the dependence of the properties of the molecule on the nature of the peripheral functional groups, as well as the electronic properties of the central metal cations in the phthalocyanine ring.[2] Unsubstituted phthalocyanines are not very soluble and tend to aggregate in solution; however, the addition of peripheral chains can increase solubility, processibility, and facilitate the formation of discotic mesophases.[3] Indeed we recently reported copper(II) 2,3,9,10,16,17,23,24-octakis(2-benzyoxyethoxy)phthalocyanine (**1**) (see Scheme 1) exhibits an exceptionally stable discotic mesophases.[4] Moreover, the unusual degree of cofacial association of this Pc favors the formation of coherent self-associated rodlike structures at the air−water interface and after transfer onto solid supports.[5] The highly ordered thin films of **1** exhibit large electrical and optical anisotropies.[6] Consequently we have developed an improved synthetic method to prepare this class of Pc.

Despite the active research on substituted Pc, the methods of synthesis have changed relatively little in the last 90 years.[7,8] Metal-free and non-copper metallo-Pc are typically prepared from the corresponding phthalonitriles (Scheme 1), which are often synthesized from the corresponding substituted 1,2-dibromo benzenes, utilizing copper(I) cyanide in the Rosenmund−von Braun reaction. The reaction involves refluxing the dibromobenzene with the CuCN in dimethylformamide, substituting nitriles for the bromides via a complex mechanism.[9] The conditions of the Rosenmund−von Braun reaction are a suitable route to copper-substituted phthalocyanines, since the phthalonitrile tetramerizes directly to the phthalocyanine under the reaction conditions. However if non-copper metallo-Pc are desired, the formation of copper phthalocyanine results in undesirable low yields of the desired phthalonitrile and complex product mixtures, which can be difficult to purify.[10] Accordingly a more general synthetic approach to the phthalonitrile precursors were sought that would allow the ready synthesis of extremely pure phthalocyanines with diverse functionality and substitution. We have developed a new synthetic method for the synthesis of substituted phthalonitriles from readily available starting materials with an excellent overall yield of 45% after eight steps. In addition this method is suitable for scale-up to produce multigram quantities, because purification required only one chromatography step.

Scheme 1. Synthesis of Alkoxy Phthalocyanines[a]



[a] Key: (a) pentanol, DBU, heat, and MX_2 in the case of **1** and **2** (MX_2 = $CuBr_2$ for **1**/$CoBr_2$ for **2**).

Results and Discussion

Synthetic Design. The production of substituted phthalocyanines for various areas of research is controlled by the synthesis of the corresponding phthalonitrile precursors. We turned to the well characterized Diels−Alder reaction to produce the key intermediate for subsequent conversion to the desired phthalonitrile. The Diels−Alder approach provides maximum flexibility in a general synthetic approach to Pc, because it is possible to place a variety of substituents on the phthalonitrile, without the possibility of side products that can occur in the Rosenmund−von Braun reaction.[11]

Synthesis of the Aromatic Core. Synthesis of 4,5-bis(benzyloxyethoxy)phthalic acid dimethyl ester (**10**) began with the commercially available 2,3-butadione (**4**), which was converted by the method of Hansson[12] to 2,3-bis(trimethylsilyloxy)-1,3-butadiene (**5**) using LiBr, trimethyl silyl chloride (TMS-Cl), and triethylamine (Scheme 2). The desired substituted butadiene **5** was collected by vacuum distillation (86%). A Diels−Alder cycloaddition between the commercially available dimethylacetylene dicarboxylate (**6**) and the butadiene **5** was performed neat at 90 °C for 24 h.[13] The desired cyclohexadiene (**7**) was purified by vacuum distillation (83%). The cyclohexadiene **7** was aromatized with cleavage of the TMS groups by treatment with bromine in CCl_4, and the desired product (**8**) precipitated and was collected by filtration with excellent yield (94%). The alkoxy "arms" were attached

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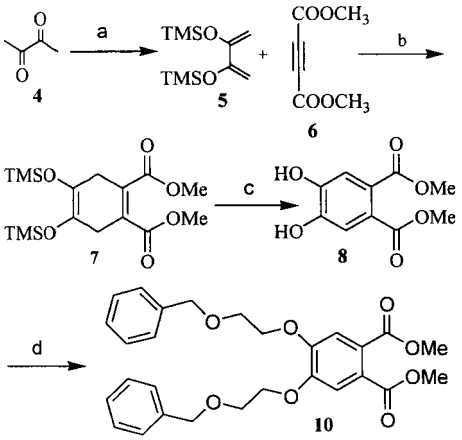
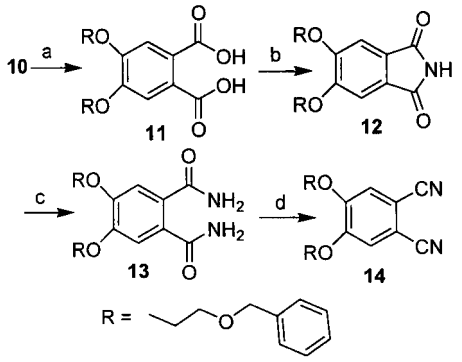
10.1021/jo9919254 CCC: $19.00
Published on Web 03/08/2000

Scheme 2. Synthesis of Aromatic Core[a]



[a] Key: (a) TMSCl, LiBr, triethylamine, THF; (b) 90 °C; (c) 5% Br_2/CCl_4; (d) benzyloxyethoxy bromide (**9**), K_2CO_3, acetone.

Scheme 3. Conversion to Phthalonitrile[a]



[a] Key: (a) (1) 10% NaOH, EtOH, (2) 10% HCl (b) urea; (c) 30% NH_4OH; (d) oxalyl chloride/DMF, pyridine.

using a Williamson ether synthesis between the commercially available 2-benzyloxy-1-ethyl bromide (**9**) and the catechol phthalic acid dimethyl ester (**8**) by refluxing in acetone with K_2CO_3 as the base. The reaction was purified by gravity filtration to remove insoluble salts, and the solvent was removed in vacuo to yield a pale yellow oil. The oil was purified by column chromatography to yield the desired ether (**10**) as a white solid upon removal of the solvent (90%).

Conversion of the Diester to Phthalonitrile. Conversion of the alkoxy-substituted phthalic ester (**10**) (Scheme 3) into the phthalonitrile began with the saponification of the ester by heating in aqueous sodium hydroxide/methanol for 12 h, upon which the solution was concentrated in vacuo to remove methanol. The pH of the solution was lowered to 3.0 using 10% HCl, and a white precipitate formed. The sample was cooled to 5 °C, and the resulting solid was filtered to yield the desired phthalic acid (**11**) as white crystals (99%). The conversion of the phthalic acid (**11**) to the corresponding phthalimide (**12**) was achieved by heating **11** and urea to 180 °C with evolution of ammonia and water as side products. The reaction progress was monitored with pH paper and upon cessation of ammonia generation the reaction was cooled to room temperature. The resulting solid was isolated by an aqueous workup yielding the desired phthalimide (**12**) as a white solid (85%). The phthalimide (**12**) was converted to the phthalamide (**13**) by stirring vigorously with concentrated aqueous ammonia for 24 h. The resulting white precipitate was collected by vacuum filtration, washed with DI water, and dried in a vacuum desiccator for 12 h, yielding a light tan solid (96%). The phthalamide (**13**) was dehydrated to the phthalonitrile (**14**) using an oxalyl chloride/DMF complex at 0 °C in 45 min. The phthalonitrile was collected nearly quantitatively (93%) by extraction into ethyl ether and concentration in vacuo. The slightly yellow liquid crystallized without further need for purification, to yield the desired product as white crystalline needles that showed no contaminants by NMR or TLC.

The Diels−Alder route to the phthalonitrile is more efficient and flexible than previous methods. We have shown that the Diels−Alder method for the synthesis of an alkoxy-substituted phthalonitrile occurs in 45% overall yield, compared to 24% yield[14] when using the Rosenmund−von Braun reaction. Typical yields of other alkoxy-substituted phthalonitriles when synthesized using the Cu(I)CN reagent are 22−33%.[15,16] Moreover, this new method allows the synthesis of very pure phthalonitrile precursors without the possibility of metal contamination or rearrangements.

The potential generality of the Diels−Alder method is illustrated by consideration of other dienes that are known to react with the dimethylacetylene dicarboxylate (DMAD) dieneophile. These reports indicate that a phthalonitrile precursor to Pc could be prepared with alkyl groups,[17,18] alkyl halides,[19] alkyl nitro compounds,[20] alkyl carboxylic acids,[21] amines,[22] silyl compounds,[23−26] alkenes,[27] thioethers,[28] unsymmetrically substituted systems,[29,30] and external ring systems.[31] It has been shown that DMAD will also under go cycloaddition with the appropriate dienes to offer a possible synthetic route to substituted naphthalocyanines[32] and azaphthalocyanines.[33−35] In theory this chemistry could be modified to incorporate electron-withdrawing substituents on the

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diene utilizing an "inverse demand" Diels−Alder reaction; however, this subject will be left for future investigations.

Experimental Section

General Information. All nonaqueous reactions were carried out under an argon atmosphere unless otherwise specified. Reagents and solvents were purchased from Aldrich Chemical and used as received unless otherwise specified. THF was distilled from Na/benzophenone. LiBr was dried for 24 h in a vacuum oven at 200 °C. 2,3-bis(trimethylsilyloxy)-1,3-butadiene (**5**) was prepared as described by Hansson[12] in 86% yield.

1,2-Bis(trimethylsilyloxy)-1,4-cyclohexadiene-4,5-dicarboxylic Acid Dimethyl Ester (7).[13] A mixture of bis(trimethylsilyloxy)-1,3-butadiene (**5**) (15.62 g, 67.8 mmol) and acetylenedicarboxylic acid dimethyl ester (**6**) (10.60 g, 74.6 mmol) was stirred 24 h at 90 °C. Vacuum distillation of the mixture gave 20.87 g of the product, bp 133−138 °C, 0.1 mmHg (82.6% yield). ^{1}H NMR ($CDCl_3$): δ 3.72 (s, 6H), 3.05 (s, 4H), 0.18 (s, 18H). ^{13}C NMR ($CDCl_3$): δ 167.52, 132.07, 127.48, 52.28, 32.82, 0.75. Mass spectral analysis (GC/MS): MI peak = 372 (M^+), 339, 251, 193, 73, 45.

4,5-Bis(hydroxy)phthalic Acid Dimethyl Ester (8). A 5% (wt/wt) solution of Br_2 in carbon tetrachloride was slowly added to a solution of dimethyl ester catechol **7** (20.87 g, 56.0 mmol) in 60 mL of CCl_4 cooled to 0 °C, and it was stirred until the reaction color remained orange. The reaction mixture was then heated to 60 °C for 2 h, and it was then removed from heat and cooled to 5 °C to precipitate the product. The crystals were vacuum collected, washed with cold CCl_4, and allowed to dry. The resulting solid weighed 11.96 g (94.4% yield). The product was identified by ^{1}H NMR (acetone-d_6): δ 3.78 (s, 6H), 7.18 (s, 2H), 8.18 (b, 2H). ^{13}C NMR (acetone-d_6): δ 168.16, 147.95, 125.55, 116.66, 52.43. Mass spectral analysis (DIP-EI): m/z = 226 (M^+), 195, 179, 165,152, 136, 108, 82, 62.

4,5-Bis(benzyloxyethoxy)phthalic Acid Dimethyl Ester (10). A solution of dimethyl ester **8** (1.50 g, 6.63 mmol), 2-bromoethylbenzyl ether (**9**) (5.00 g, 23.2 mmol), and anhydrous K_2CO_3 (6.00 g, 43.4 mmol) in 50 mL of acetone was refluxed for 48 h and then gravity filtered to remove unreacted K_2CO_3 and KBr. The filtrate was concentrated in vacuo and purified by flash chromatography on SiO_2 eluting with hexanes/ethyl acetate (70:30), giving the desired diether **10** (2.94 g 90%) as a white solid upon removal of solvent: mp = 44−46 °C, R_{xa6} = 0.42 (70:30 Hex/EtOAc), IR (KBr) 1732 cm^{-1}, ^{1}H NMR (acetone-d_6) δ 7.38−7.17 (m, 12H), 4.57 (s, 4H), 4.29 (t, J = 4.6 Hz, 4H), 3.88−3.75 (singlet on triplet, J = 4.6 Hz, 10H), ^{13}C NMR (acetone-d_6) δ 168.0, 151.5, 139.6, 129.0, 128.3, 128.1, 126.4, 114.7, 73.5, 69.9, 69.2, 52.6, mass spectral analysis (FAB) MI 495.15 (theoretical mass for $C_{28}H_{31}O_8$ = 495.20).

4,5-Bis(benzyloxyethoxy)phthalic Acid (11). A solution of dimethyl ester **10** (2.75 g, 5.6 mmol) in 50 mL of 10% NaOH and 50 mL methanol was heated to reflux for 24 h and then allowed to cool to room temperature. The solution was then concentrated in vacuo removing the methanol and a majority of the water. A 20 mL portion of DI water was added, and the pH of the solution was slowly adjusted to 3.0 using 10% HCl. The solution was cooled to 5 °C, and the desired phthalic acid **11** was collected by vacuum filtration and dried for 12 h in a vacuum oven at 60 °C. The white crystalline solid collected weighed 2.55 g (99%). mp = 97−99 °C, IR (KBr) 2612 and 1714 cm^{-1}, ^{1}H NMR (CD_2Cl_2) δ 12.4−11.7 (broad, 2 H), 7.55−7.14 (m, 12H), 4.57 (s, 4H), 4.12 (t, J = 4.6 Hz, 4H) 3.74 (t, J = 4.6 Hz, 4H), ^{13}C NMR (d_6 DMSO) δ 168.3, 149.4, 138.4, 128.3, 127.54, 127.48, 127.11, 114.7, 72.2, 68.41, 68.12, mass spectral analysis (ESI+) MI 466.8 (theoretical mass for $C_{26}H_{26}O_8$ = 466.2).

4,5-Bis(benzyloxyethoxy)phthalimide (12). The procedure for phthalimide formation was modified from a literature method,[36] and it should be noted that when the reaction in the literature was followed using ethylene glycol as the solvent, the n-ethanol-substituted phthalimide, not the phthalimide, was obtained as the major product as shown by NMR and mass spectrometry. Phthalic acid **11** (2.53 g, 4.93 mmol) was heated to 180 °C with constant stirring in a 50 mL beaker containing urea (0.65 g, 10.8 mmol). The reaction was removed from the oil bath when the evolution of ammonia gas ceased, as monitored using moistened pH paper. The resulting solid was dissolved in CH_2Cl_2/DI water, and the organic layer was separated and dried over $MgSO_4$. Removal of the CH_2Cl_2 in vacuo afforded 1.87 g of the desired phthalimide (**12**) (85%) as a white solid: mp 129−130 °C, R_{xa6} = 0.92 (90:10 $CHCl_3$/MeOH), IR (KBr) 3250, 1767, and 1711 cm^{-1}, ^{1}H NMR (CD_2Cl_2) δ 7.55−7.39 (broad, 1H), 7.35−7.12 (m, 12H), 4.54 (s, 4H), 4.22 (t, J = 4.6 Hz, 4H) and 3.83 (t, J = 4.6 Hz, 4H), ^{13}C NMR (CD_2Cl_2) δ 168.2, 154.1, 138.5, 128.7, 128.03, 127.96, 126.5, 107.2, 73.6, 69.6, and 68.5, Mass Spectral Analysis (ESI) MI 448.2 (MH^+).

4,5-Bis(benzyloxyethoxy)phthalamide (13). The conversion of the phthalimide (**12**) to the phthalamide (**13**) was achieved by modification of a literature procedure.[37] A mixture of phthalimide **12** (1.53 g, 3.4 mmol) and 40 mL of 25% (wt %) aqueous ammonia in a 50 mL round-bottom flask was sealed with a rubber septum and stirred vigorously for 24 h at room temperature. The mixture was then gravity filtered and washed with DI water. The solid collected was dried in a vacuum desiccator for 12 h, affording 1.53 g of the desired phthalamide **13** (96%) as a light tan solid. mp = 161−163 °C, R_{xa6} = 0.30 (90:10 $CHCl_3$/MeOH), IR (KBr) 3387, 3195, 1653, 1597 cm^{-1}, ^{1}H (DMSO-d_6) δ 7.85−7.72 (broad, 4H), 7.44−7.22 (m, 12H), 4.63 (s, 4H), 4.29 (t, J = 4.6 Hz, 4H), 3.86 (t, J = 4.6 Hz, 4H), ^{13}C NMR (d_6-DMSO) δ 169.7, 149.5, 138.4, 129.1, 129.1, 128.2, 127.51, 127.48, 113.5, 72.1, 68.4, 68.0, mass spectral analysis (FAB) MI 465.11 (MH^+).

4,5-Bis(benzyloxyethoxy)phthalonitrile (14). The phthalamide was converted to the phthalonitrile functionality by using an oxalyl chloride/DMF complex.[38] Anhydrous DMF (1.20 mL, 15.5 mmol) was added via syringe to 25 mL of acetonitrile cooled to 0 °C, and then oxalyl chloride (1.25 mL, 14.2 mmol) was slowly added with formation of a white precipitate and gas evolution. When the evolution of gas ceased, phthalamide **13** (1.50 g, 3.23 mmol) was added as a suspension in 5 mL of acetonitrile. Within a few minutes the reaction solution became homogeneous. Pyridine (2.30 mL, 28.4 mmol) was then added, and the reaction was stirred for an additional 45 min at 0 °C. The reaction was then quenched by the addition of 50 mL of ethyl ether and 50 mL of 10% HCl. The aqueous layer was extracted and washed with 50 mL of ethyl ether. The combined ether layers were then extracted with saturated NaCl and dried over Na_2SO_4. The ether was removed in vacuo to yield a pale yellow oil, which solidified into white needle crystals. The resulting crystals were washed with 5 mL portions of cold pentane and dried in a vacuum desiccator. The desired phthalonitrile **14** weighed 1.30 g (93%): mp = 77−79 °C, R_{xa6} = 0.92 (90:10 $CHCl_3$/MeOH), IR (KBr) 2228 cm^{-1}, ^{1}H NMR (acetone-d_6) δ 7.64−7.58 (s, 2H), 7.41−7.17 (m, 10H), 4.63 (s, 4H), 4.44 (t, J = 4.5 Hz, 4H) 3.92 (t, J = 4.5 Hz, 4H), ^{13}C NMR (acetone-d_6) δ 153.2, 139.4, 129.0, 128.3, 128.2, 117.9, 116.7, 109.0, 73.5, 70.2, 68.9, mass spectral analysis (FAB) MI 429.2 (MH^+).

Synthesis of 2,3,9,10,16,17,23,24-Octa(2-benzyloxyethoxy)phthalocyanines (1−3). A solution of phthalonitrile **14** (1.00 mmol) and 1,8-diazabicyclo(5.4.0)undec-7-ene (DBU) (1.00 mmol) in 20 mL of 1-pentanol was heated to reflux for 22 h. In the case of the cobalt Pc (**2**) and copper Pc (**1**), 0.25 mmol of corresponding metal(II) bromide was added as well. The resulting dark green solution was placed in a freezer to precipitate the desired phthalocyanine. The solid was collected by vacuum filtration through a medium sintered glass crucible and washed with DI water. The solid was purified by flash chromatography on SiO_2 eluting with chloroform/methanol (99:1). Phthalocyanine **3** was obtained as a green solid (28% yield) after removal of solvent in vacuo. R_{xa6} = 0.82 (95:5 $CHCl_3$/MeOH), IR (KBr) 3465, 2870, 1279, 1190, 1100, 1026, and 741 cm^{-1}, UV−vis ($CHCl_3$) 699.2, 661.3, and 598.9 nm, high-resolution mass spectral analysis (FAB) MI 1715.71 (calcd mass for $C_{104}H_{99}N_8O_{16}$ =1715.72). Cobalt phthalocyanine **2** was obtained as a green-

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blue solid (43% yield). $R_{xa6} = 0.82$ (95:5 $CHCl_3$/MeOH), UV−vis ($CHCl_3$) 669.6, and 607.6 nm, high-resolution mass spectral analysis (FAB) MI 1772.64 (calcd mass for $C_{104}H_{97}N_8O_{16}Co$ = 1772.64). Copper phthalocyanine **1** was obtained as a green solid (48% yield). $R_{xa6} = 0.82$ (95:5 $CHCl_3$/MeOH), UV−vis ($CHCl_3$) 676.6 and 610.2 nm, high-resolution mass spectral analysis (FAB) MI 1776.61 (calcd mass for $C_{104}H_{97}N_8O_{16}Cu$ = 1776.64).

Acknowledgment. This research was supported by a grant from the National Science Foundation.

Supporting Information Available: ^1H NMR spectrum of **13**; ^{13}C NMR spectra of **10**−**12** and **14**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO9919254