Synthesis and Liquid-Crystal Behavior of Metal-Free and Metal-Containing Phthalocyanines Substituted with Long-Chain Amide Groups

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The synthesis and characterization (by optical microscopy, differential scanning calorimetry (DSC), X-ray diffraction) of two series of octasubstituted lipophilic phthalocyanines **1**−**3** and **4**−**7**, bearing amide functions in the peripheral chains, are reported. Compounds **1**−**3**, **6**, and **7** exhibit a liquid-crystal phase, for which a hexagonal columnar structure is proposed on the basis of the X-ray studies. The number of peripheral hydrocarbon chains and the possibility of hydrogen bonding is shown to have a critical influence on mesomorphism in these compounds.

Introduction

Phthalocyanines exhibit a number of unique properties that make them of great interest in different scientific and technological areas.[1] These compounds and related analogues are presently being investigated mainly as part of efforts to engineer new molecular materials with improved electrical[2] and nonlinear optical properties.[3] Phthalocyanines have usually constituted a group of crystalline or polycrystalline compounds, whose insolubility in organic solvents is a very common characteristic.[1,4] However, in the past few years the introduction of long−chain lipophilic substituents on the periphery of the phthalocyanine ring has drastically improved their solubility in nonpolar solvents[1] and in some cases has provided these compounds with thermotropic behavior.[5,6] Thus, for example, octaalkyl-,[7] octaalkoxy-,[8] octaalkoxymethyl-,[9] or even "crowned"-phthalocyanines[10] give rise to discotic liquid crystals.[6] The interest in bringing the phthalocyanine ring to the field of liquid crystals arises from the tendency of this macrocycle to stack up to give columnar structures, as well as its ability to form stable complexes with a wide variety of metal ions. Discotic mesomorphism makes this kind of compound potentially interesting as one-dimensional conductors,[8e,11] in which the conducting chains would be formed by the spine of the columnar structure, which consists of a central conjugated system surrounded by an insulating region of hydrocarbon chains.

We have recently described the synthesis and aggregation properties of the octasubstituted copper phthalocyanine **2**[12] (Figure 1) and the third-order nonlinear optical response of this and related compounds.[13] In the present paper we report on the preparation,

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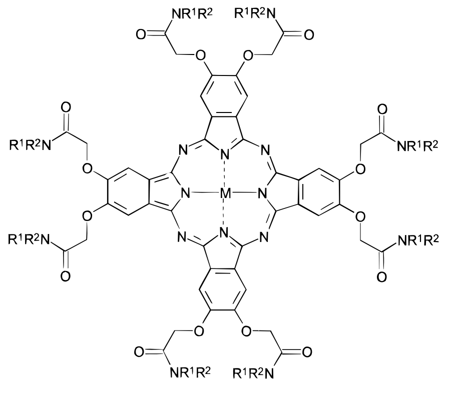

1 M = H_2, $R^1 = R^2$ = Octyl
2 M = Cu, $R^1 = R^2$ = Octyl
3 M = Ni, $R^1 = R^2$ = Octyl
4 M = Cu, R^1 = Dodecyl, R^2 = H
5 M = H_2, R^1 = Octyl, R^2 = H
6 M = Cu, R^1 = Octyl, R^2 = H
7 M = Ni, R^1 = Octyl, R^2 = H

Figure 1. Octasubstituted phthalocyanines.

characterization, and mesogenic properties of two families of octasubstituted lipophilic phthalocyanines **1**−**3** and **4**−**7** containing dialkylated and monoalkylated amide functions, respectively. The NHCO moieties present in compounds **4**−**7** could play an important role in promoting aggregation of the metallomacrocycles by intermolecular hydrogen bonding interactions.[14,15]

Experimental section

Techniques. The compounds were characterized by elemental analysis, IR and UV−visible spectroscopies, fast atom bombardment (FAB) mass spectrometry, and nuclear magnetic resonance. UV−visible and infrared measurements were carried out respectively on Perkin-Elmer Model Lambda 6 and PU 9716 Philips spectrometers. FAB-MS spectra were determined on a MAT 900 (Finnigan MAT, GmbH, Bremen) instrument. Proton NMR spectra were recorded with a Bruker WM-200-SY, 200 MHz spectrometer. The optical textures of the mesophases were studied with a Meiji polarizing microscope equipped with a Mettler FP8 hot stage and an FP80 central processor. The transition temperatures and enthalpies were measured by differential scanning calorimetry with a Perkin-Elmer DSC-7 instrument operated at a scanning rate of 10 °C/min on heating. The apparatus was calibrated with indium (156.6 °C; 28.4 J g^{-1}) as a standard. X-ray diffraction experiments were carried out on powder samples in a Guinier diffractometer (Huber 644) operating with a Cu Kα_1 beam issued from a germanium monochromator and in a Pinhole camera (Anton-Paar) operating with a Ni-filtered Cu Kα beam. The samples were held in Lindemann glass capillaries (0.7 mm diameter) and heated with a variable-temperature attachment.

Synthesis. Compounds **10**,[14] **11**,[12] **13**,[13] **15**,[13] and phthalocyaninatocopper(II) complexes **2**[12] and **4**[14] were described in detail recently.

*4,5-Dibromo-1,2-bis[(ethoxycarbonyl)methoxy]benzene (***8***).* A mixture of 4,5-dibromo-1,2-dihydroxybenzene[16] (3.00 g, 11.2 mmol), ethyl bromoacetate (4.86 g, 29.1 mmol), K_2CO_3 (12.2 g, 88.3 mmol), and tetrabutylammonium bisulfate (1.90 g, 5.60 mmol) in 90 mL of CH_3CN was vigorously stirred at 35−40 °C for 1.5 h. After cooling, the mixture was filtered and the solvent removed. The crude product was purified by column chromatography on silica gel (CH_2Cl_2) and then recrystallized from toluene/hexane to yield a crystalline colorless solid (3.50 g, 71%), mp 97−99 °C. Anal. Found: C, 38.30; H, 3.49. Calcd for $C_{14}H_{16}Br_2O_6$: C, 38.21; H, 3.66. IR (KBr) (cm^{-1}): 1750−1710 (C═O), 1280−1200 (C−O−C), 1180−1020 (C−O−C). EI-MS (70 eV) (*m/z*): 442 (49), 440 (97), 438 (49) (M^+). ^1H NMR ($CDCl_3$) δ 1.30 (6H, t, $J = 7.2$ Hz, CH_3), 4.27 (4H, q, $J = 7.2$ Hz, CH_2CH_3), 4.68 (4H, s, CH_2C═O), 7.11 (2H, s, arom H). ^{13}C NMR ($CDCl_3$) δ 14.1 (CH_3), 61.5 (CH_2CH_3), 66.6 (CH_2C═O), 116.5 (CBr), 119.9 (arom CH), 147.7 (arom C−O), 168.1 (C═O).

*4,5-Dibromo-1,2-bis[(octylaminocarbonyl)methoxy]benzene (***9***).* A mixture of compound **8** (1.00 g, 2.30 mmol) and octylamine (0.77 g, 5.98 mmol) was refluxed in 23 mL of MeOH overnight. The solid was isolated by filtration in analytical pure grade (1.30 g, 98%), mp 129−30 °C. Anal. Found: C, 51.23; H, 6.81; N, 4.60. Calcd for $C_{26}H_{42}Br_2N_2O_4$: C, 51.49; H, 6.98; N, 4.62. IR (KBr, cm^{-1}): 3360, 3280 (NH), 1650 (C═O), 1260−1240 (C−O−C), 1180−1050 (C−O−C). FAB-MS (*m*-NBA) (*m/z*): 609 (24), 607 (46), 605 (26) (M + H^+). ^1H NMR ($CDCl_3$) δ 0.88 (6H, t, $J = 6.4$ Hz, CH_3), 1.26 (20H, broad s, CH_2), 1.5 (4H, m, CH_2CH_2N), 3.3 (4H, m, CH_2N), 4.51 (4H, s, CH_2O), 6.5 (2H, m, NH), 7.14 (2H, s, arom H). ^{13}C NMR ($CDCl_3$) δ 14.0 (CH_3), 22.6, 26.8, 29.2, 29.5, 31.7 (CH_2), 39.2 (CH_2N), 68.9 (CH_2O), 117.1 (CBr), 119.4 (arom CH), 147.0 (arom C−O), 166.9 (C═O).

*1,2-Dicyano-4,5-bis[(octylaminocarbonyl)methoxy]benzene (***12***).* A mixture of dibromo derivative **9** (2.00 g, 3.30 mmol), CuCN (0.90 g, 10.0 mmol) and DMF (34 mL) was heated at reflux temperature under argon for 7 h. After cooling at room temperature, NH_4OH (30%, 60 mL) was added, and air was bubbled for 24 h. Then, the mixture was filtered over Celite and washed with additional amounts of NH_4OH (30%) until no blue color appears, and finally with water. Afterward, the solid residue was extracted with EtOH by means of a Soxhlet for 48 h. The product was then purified by column chromatography on silica gel (CH_2Cl_2/acetone = 10/1), and recrystallized from MeOH giving a white solid (0.6 g, 36%), mp 194−6 °C. Anal. Found: C, 66.27; H, 8.58; N, 10.97. Calcd for $C_{28}H_{42}N_4O_4 \cdot 0.5H_2O$: C, 66.24; H, 8.54; N, 11.04. IR (KBr, cm^{-1}): 3220−3070 (NH), 2220 (C≡N), 1650 (C═O), 1290−1220 (C−O−C), 1090 (C−O−C). FAB-MS (*m*-NBA, *m/z*): 499 (100) ($M + H^+$). ^1H NMR (DMSO-d_6) δ 0.8 (6H, m, CH_3), 1.21 (20H, br s, CH_2), 1.4 (4H, m, CH_2CH_2N), 3.1 (4H, m, CH_2N), 4.73 (4H, s, CH_2O), 7.71 (2H, s, arom H), 8.1 (2H, m, NH). ^{13}C NMR (DMSO-d_6) δ 14.0 (CH_3), 22.1, 26.4, 28.7, 29.0, 31.3 (CH_2), 48.7 (CH_2N), 67.9 (CH_2O), 107.9 (CCN), 115.9 (CN), 118.3 (arom CH), 151.2 (arom C−O), 166.3 (C═O).

*1,3-Diimino-5,6-bis[(octylaminocarbonyl)methoxy]isoindoline (***14***).* Through a mixture of the dicyano derivative **12** (0.40 g, 0.80 mmol) and NaOMe (32 mg, 0.6 mmol) in 20 mL of MeOH kept at reflux temperature, NH_3 was bubbled for 6 h. After cooling at room temperature the greenish solid was isolated by filtration (0.41 g, 99%), mp 223 °C (dec). IR (KBr, cm^{-1}): 3400−3000 (NH), 1660 (C═O), 1610 (C═N), 1290−1200 (C−O−C), 1060 (C−O−C). FAB-MS (*m*-NBA) (*m/z*): 516 (100) ($M + H^+$). ^1H NMR (TFA-d_1) δ 0.9 (6H, m, CH_3), 1.4 (20H, m, CH_2), 1.7 (4H, m, CH_2CH_2N), 3.6 (4H, m, CH_2N), 5.10 (4H, s, CH_2O), 8.22 (2H, s, arom H). The compound was used in the next synthetic step without any further purification.

*2,3,9,10,16,17,23,24-Octakis[(dioctylaminocarbonyl)methoxy] phthalocyanine (***1***).* The diiminoisoindoline **15**[13] (0.82 mmol) obtained from the dicyano derivative **13**[13] (0.60 g, 0.82 mmol) was refluxed in (dimethylamino)ethanol (0.6 mL) under argon for 7 h. After cooling at room temperature the mixture was partitioned into H_2O/hexane (50:50). The organic solvent was removed and the residue was recrystallized from CH_3CN/HCl (37%), 50:1. The green-black product obtained was dried at 150 °C under vacuum (0.19 g, 31%). Anal. Found: C, 70.66; H, 9.95; N, 7.89. Calcd for $C_{176}H_{298}N_{16}O_{16} \cdot 5H_2O$: C, 70.83; H, 10.40; N, 7.51. IR ($CHCl_3$) (cm^{-1}): 1650 (s, C═O), 1280 (C−O−C), 1100 (C−O−C). UV−vis λ_{max}/nm (log ϵ/dm^3 mol^{-1} cm^{-1}) ($CHCl_3$) 293 (4.8), 346 (4.9), 395 (4.6), 602 (4.5), 642 (4.7), 661 (5.0), 698 (5.1). FAB-MS (*m*-NBA) (*m/z*): 2894 (25), 2893 (24), 2892 (17), (M^+, $M + H^+$). ^1H NMR ($CDCl_3$) δ 0.7, 0.8 (48H, 2 × m, CH_3), 1.0−1.5 (160H, m, CH_2), 1.7, 1.8 (32H, 2 × m, CH_2CH_2N), 3.3, 3.6 (32H, 2 × m, CH_2N), 5.35 (16H, s, CH_2O), 9.03 (8H, s, arom H). ^{13}C NMR ($CDCl_3$) δ 13.9, 14.0 (CH_3), 22.5, 22.6, 27.1, 27.6, 29.2, 29.3, 29.4, 31.8 (CH_2), 46.2, 47.6 (CH_2N),

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68.8 (CH_2O), 107.9 (CCN), 131.4 (arom CH), 149.7 (C=N), 151.2 (arom C−O), 166.9 (C=O).

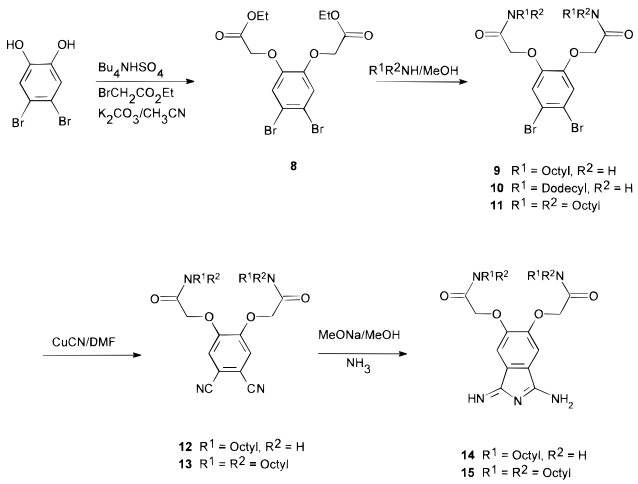
2,3,9,10,16,17,23,24-Octakis[(dioctylaminocarbonyl)methoxy]-phthalocyaninatonickel(II) (**3**). A mixture of the dicyano derivative **13**[13] (0.50 g, 0.68 mmol) and $Ni(AcO)_2 \cdot 4H_2O$ (43 mg, 0.17 mmol) was heated in ethylene glycol (0.8 mL) under argon at reflux temperature for 6 h. After cooling at room temperature, the mixture was partitioned into H_2O/hexane (50:50) and the organic phase washed with CH_3CN. The solvent was then removed and the residue was recrystallized from acetone/HCl (37%) 40:1, giving a green-black product which was dried at 150 °C under vacuum (0.15 g, 31%). Anal. Found: C, 69.65; H, 10.11; N, 7.47. Calcd for $C_{176}H_{296}N_{16}NiO_{16} \cdot 4H_2O$: C, 69.92; H, 10.14; N, 7.41. IR ($CHCl_3$) (cm^{-1}): 1640 (s, C=O), 1280 (C−O−C), 1110 (C−O−C). UV−vis λ_{max}/nm (log ϵ/dm^3 mol^{-1} cm^{-1}) ($CHCl_3$) 287 (4.9), 305 (4.9), 327 (4.7), 391 (4.5), 602 (4.5), 640 (4.6), 667 (5.3). FAB-MS (*m*-NBA) (*m/z*): 2969 (16), 2967 (24), 2966 (24), 2965 (45), 2964 (20), ($[M + H_2O]^+$, $[M^+ + H_2O - H]$), 2954 (22), 2953 (37), 2952 (43), 2951 (85), 2950 (100), 2949 (69), (M^+, $M + H^+$). ^1H NMR ($CDCl_3$) δ 0.71, 0.81 (48H, 2 × t, $J = 6.5$ Hz, CH_3), 1.0−1.5 (160H, m, CH_2), 1.7, 1.8 (32H, 2 × m, CH_2CH_2N), 3.5, 3.6 (32H, 2 × m, CH_2N), 5.30 (16H, s, CH_2O), 8.93 (8H, s, arom H). ^{13}C NMR ($CDCl_3$) δ 13.9 (CH_3), 22.5, 22.6, 27.0, 27.1, 27.6, 29.2, 29.3, 29.4, 31.8 (CH_2), 46.1, 47.6 (CH_2N), 68.8 (CH_2O), 107.1 (CCN), 132.0 (arom CH), 145.7 (C=N), 151.0 (arom C−O), 166.9 (C=O).

2,3,9,10,16,17,23,24-Octakis[(octylaminocarbonyl)methoxy]-phthalocyanine (**5**). The diiminoisoindoline **14** (0.41 g, 0.79 mmol) was heated at reflux temperature in (dimethylamino)-ethanol (0.55 mL) under argon for 7 h. After cooling at room temperature, EtOH (10 mL) was added and the mixture centrifuged. The green solid was recrystallized from DMF, centrifuged and washed with EtOH and ether (0.10 g, 25%). IR (KBr, cm^{-1}): 3400−3280 (NH), 1690 (C=O), 1280−1250 (C−O−C), 1090 (C−O−C). UV−vis λ_{max}/nm (log ϵ/dm^3 mol^{-1} cm^{-1}) ($CHCl_3$) 264 (4.7), 302 (5.0), 352 (5.1), 411 (4.7), 611 (4.7), 648 (4.9), 672 (5.3), 708 (5.4). ^1H NMR (TFA-d_1) δ 0.9 (24H, m, CH_3), 1.4 (80H, m, CH_2), 1.8 (16H, m, CH_2CH_2N), 3.7 (16H, m, CH_2N), 5.5 (16H, m, CH_2O), 9.3 (8H, broad s, arom H).

2,3,9,10,16,17,23,24-Octakis[(octylaminocarbonyl)methoxy]-phthalocyaninatocopper(II) (**6**). A mixture of the dibromo derivative **9** (2.00 g, 3.30 mmol) and CuCN (0.78 g, 8.73 mmol) in DMF (4.3 mL) was heated at reflux temperature for 10 h. After cooling at room temperature, NH_4OH (30%) saturated with NaCl was added and then extracted with several portions of $CHCl_3$. The organic phase was washed with water and the solvent removed. The green solid was washed at room temperature with a mixture of EtOH/HCl (37%) (10:1), filtered, and recrystallized from toluene/EtOH giving a green solid (0.47 g, 28%). Anal. Found: C, 64.93; H, 8.06; N, 10.54. Calcd for $C_{112}H_{168}CuN_{16}O_{16}$: C, 65.36; H, 8.23; N, 10.89. IR (KBr, cm^{-1}): 3100−3080 (NH), 1650 (C=O), 1280−1200 (C−O−C), 1120−1070 (C−O−C). UV−vis λ_{max}/nm (log ϵ/dm^3 mol^{-1} cm^{-1}) (TFA) 291 (4.9), 325 (4.7), 396 (4.6), 439−443 (sh), 635−639 (sh), 665−668 (sh), 695 (5.0), 727 (5.2). UV−vis λ_{max}/nm ($CHCl_3$) 290, 335, 395, 610, 675. The low solubility of the compound in this solvent prevented the quantitative determination of the ϵ values.

2,3,9,10,16,17,23,24-Octakis[(octylaminocarbonyl)methoxy]-phthalocyaninatonickel(II) (**7**). A mixture of the dicyano derivative **12** (0.35 g, 0.70 mmol) and $Ni(AcO)_2 \cdot 4H_2O$ (43 mg, 0.17 mmol) in ethylene glycol (0.8 mL) was heated at 185 °C for 5 h. After cooling at room temperature, EtOH (10 mL) was added and the mixture was filtered. The residue was washed with EtOH until the mother liquors remained colorless. The solid was recrystallized from toluene/EtOH giving a blue-greenish product (0.12 g, 33%). Anal. Found: C, 63.95; H, 8.27; N, 10.51. Calcd for $C_{112}H_{168}N_{16}NiO_{16} \cdot 3H_2O$: C, 63.83; H, 8.32; N, 10.63. IR (KBr, cm^{-1}): 3280−3080 (NH), 1660 (C=O), 1270−1200 (C−O−C), 1100 (C−O−C). UV−vis λ_{max}/nm (log ϵ/dm^3 mol^{-1} cm^{-1}) ($CHCl_3$) 257 (5.0), 294 (4.8), 616 (4.2), 658−665 (sh). FAB-MS (*m*-NBA) (*m/z*): 2072 (17), 2071 (28), 2070 (51), 2069 (59), 2068 (19) ($[M + H_2O]^+$, $[M + H_2O + H^+]$). ^1H NMR (TFA-d_1) δ 0.9 (24H, m, CH_3), 1.4 (80H, m, CH_2), 1.7 (16H, m, CH_2CH_2N), 3.6 (16H, m, CH_2N), 5.1 (16H, m, CH_2O), 7.69, 7.76, 8.05, 8.22 (8H, 4 × m, arom H).

Scheme 1



Results and Discussion

Synthesis and Characterization. Substituted phthalocyanines are frequently synthesized by cyclotetramerization of the corresponding *o*-dicyanobenzene or diiminoisoindoline derivatives.[1,17] In particular cases (copper(II) complexes), the dibromobenzene derivatives are also used. The preparation of phthalocyanines **1**−**7** (Figure 1) was carried out by standard procedures, starting from precursors **9**−**15**, whose synthesis is depicted in Scheme 1.

Alkylation of 4,5-dibromo-1,2-dihydroxybenzene[16] with ethyl bromoacetate under phase-transfer catalysis (PTC) conditions afforded the diester **8**, which by condensation with octylamine in boiling MeOH yielded the amide **9** in quantitative yield. The synthesis of **11** was achieved by a different method than was previously described.[12] To obtain the dicyano compounds **12** and **13**,[13] the dibromo derivatives **9** and **11**[12] were reacted with copper(I) cyanide in DMF. Compounds **12** and **13**[13] were then reacted with methanolic NH_3 in the presence of a catalytic amount of NaOMe to give the diiminoisoindoline derivatives **14** and **15**.[13]

Copper phthalocyanines **2**,[12] **4**,[14] and **6** were obtained from the reaction of the corresponding dibromo derivative **9**−**11** with an excess of copper(I) cyanide in boiling DMF. Phthalocyanines **4**[14] and **6** are green-black powders at room temperature while the dioctylamino derivative **2**[12] is a highly viscous mass. On the other hand, the solubility of these compounds in common organic solvents follows the order **6** < **4** < < **2**, thus indicating the importance of the NH function in the properties of these phthalocyanines, which gives rise to strong intermolecular hydrogen bonding.

Diiminoisoindolines **14**, **15**[13] were used for the preparation of the free phthalocyanines **1** and **5**. In these cases, the cyclization reaction was carried out in a concentrated solution of (dimethylamino)ethanol at reflux temperature. As in the previous case, the dioctylamino derivative **1** is a viscous mass highly soluble in organic solvents and the octylamino derivative **5** is a powder which is only slightly soluble.

Nickel(II) complexes **3** and **7** were prepared from the dicyano derivatives **12**, **13**,[13] and nickel(II) acetate tetrahydrate in ethylene glycol. Nickel phthalocyanines

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(17) Pawlowski, G.; Hanack, M. *Synthesis* **1980**, 287.

3 and **7** exhibit also different characteristics, with complex **3** much more soluble than its analogue **7**.

The compounds were characterized by elemental analysis, IR and UV−visible spectroscopies, fast atom bombardment mass spectrometry (FAB-MS), and ^{1}H and ^{13}C NMR (in the case of precursors and diamagnetic complexes). The presence of crystallization water in some compounds (**1, 3, 7, 12**) was detected by elemental analysis and confirmed by ^{1}H NMR experiments.

Metal-free phthalocyanines **1** and **5** show in their ^{1}H NMR spectra characteristic singlets at 9.03 and 9.30 respectively, corresponding to the deshielded aromatic protons. The electronic spectra of **1** and **5** in chloroform are typical of monomeric species with Q bands at 661 and 698 nm and 672 and 708 nm, respectively. Nickel complex **3** presents the same behavior in terms of its ^{1}H NMR and UV−visible spectra. In this case a single Q-band, as it is usual for the metal complexes of phthalocyanines, is observed at 667 nm corresponding to the monomeric form. In the FAB-MS spectrum of **3**, the isotopic clusters at m/z 2954−2949 correspond to species M^+ and $M + H^+$. Association with a water molecule could be also observed in the spectrum.

Copper and nickel compounds **6** and **7** are only slightly soluble in chloroform. The shape of the bands in the UV−visible spectra of both compounds clearly indicate the presence of several oligomeric species in the chloroform solution.[18] This aggregation phenomenon does not take place in TFA. Thus, the UV−visible spectrum of **6** in this solvent shows only monomeric species. A detailed study of the aggregation properties of compounds **1**−**7** has been recently reported.[14]

Compound **7** was the only one of the family **4**−**7**, with NHCO moieties, that could be identified by FAB-MS and shows an isotopic cluster at m/z 2072−2068, corresponding to the protonated molecular peak asociated with a water molecule.

Microscopy Study. When observed through a polarizing microscope, phthalocyanines **1**−**3** show similar behavior. At room temperature the three compounds are waxy materials, which do not display any characteristic texture under polarized light. On heating, each of these waxy compounds becomes more fluid and finally clears into an isotropic liquid at temperatures slightly below 100 °C. On cooling, a sharp transition to an anisotropic phase is not observed. Instead, the appearance of birrefringent texture is slow and takes place only after several minutes or even hours of keeping the sample below the clearing temperature observed on heating. The observed textures can be described either as fanlike or mosaiclike (Figure 2). No further changes are observed on further cooling, and the samples can be kept at room temperature for months without any detectable texture change.

Phthalocyanines **4**−**7** have a very different thermal behavior from that of compounds **1**−**3**. These compounds are powders at room temperature. On heating each of these products undergoes a slow transition, difficult to observe in some cases, to another anisotropic phase at around 200 °C. Although the change is very subtle, above this temperature the sample acquires a certain mobility, and some fluidity is detected under stress. However, the high-temperature phase is highly viscous and does not show any characteristic texture. No further transitions are observed in the temperature range of the microscope (<350 °C), although gradual decomposition of the samples is detected after prolonged heating.

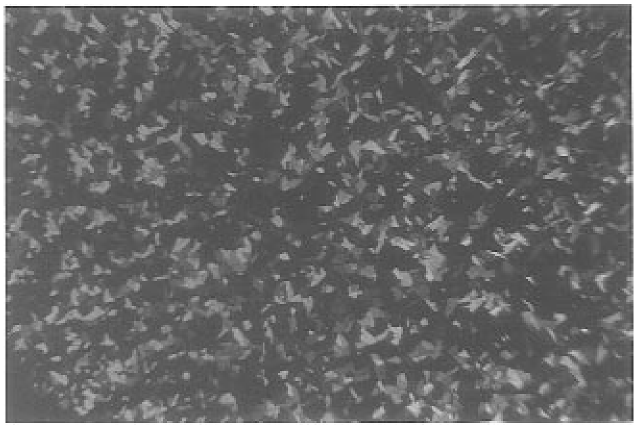

Figure 2. Micrograph of the optical texture of the mesophase of compound **3** at 70 °C observed under polarized light (magnification: 1 cm ≈ 100 μm).

Table 1. Transition Temperatures Measured by DSC

compound	transition temp/°C	transition enthalpies/J g^{-1}
1	91	0.3
2	21	1.0
	83	0.14
	95	1.1
3	21	0.2
	81	0.6
4	191	18.4
	223	1.3
5	212	0.3
6		
7	104	3.9
	190	23.3

DSC Study. In Table 1 the transition temperatures extracted from the DSC thermograms of the compounds are gathered. By comparing the DSC results with the microscope observations, a view of the thermal behavior of these compounds can be drawn.

For metal-free phthalocyanine **1** a single maximum appears at 91 °C, which approximately corresponds to the transition to the isotropic liquid observed by microscopy. For nickel complex **3** maxima at 21 and 81 °C are observed; the 81 °C peak agrees well with the clearing temperature detected in the microscope. For copper(II) phthalocyanine **2** the behavior is more complex. Peaks at 21, 83, and 95 °C are observed, the latter corresponds to the transition to the isotropic liquid. The transition at 21 °C and 83 °C for this compound as well as the transition at 21 °C for compound **3** are not detected in the microscope. For the three compounds **1**−**3** the measured enthalpy for the high-temperature transition is small, which is in agreement with a mesophase−isotropic liquid transition.

The DSC curves of the family **4**−**7** yield a variable number of peaks, some of which correspond well with the temperature transitions observed in the microscope. However, the curves are not reproduced in subsequent scans, probably due to decomposition at high temperatures (∼250 °C). The transition enthalpies strongly depend on each particular compound, and it is difficult to draw any conclusion about the nature of the involved transition only on the basis of their values. The peak

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(18) Duro, J. A. Ph.D. Thesis, Universidad Autónoma de Madrid, 1993.

at 223 °C in compound **4** and the peak at 104 °C in compound **7** are not detected in the microscope. Copper complex **6** does not exhibit any DSC peak between room temperature and 250 °C.

X-ray Diffraction Study. Powder X-ray diffraction experiments were carried out on the seven compounds at different temperatures (Table 2).

*Compounds **1**−**3**.* The diffraction patterns obtained at room temperature from dialkylamide derivatives **1**−**3** are very similar. They consist of a set of sharp peaks at small angles (long distances) corresponding to reciprocal spacings in the ratio 1:$\sqrt{7}$:$\sqrt{9}$, and two diffuse maxima at wide angles (short distances) corresponding approximately in the three cases to 4.5 and 3.5 Å. This kind of pattern, as well as the optical textures, are unambiguously characteristic of a mesomorphic phase. The ratio 1:$\sqrt{7}$:$\sqrt{9}$ is consistent with a columnar hexagonal structure. Indeed, these maxima can be assigned, respectively, to the (100), (210), and (300) reflections of a hexagonal network, for which a lattice constant *a* (shortest distance between neighboring column axes) of 31.0 Å for **1** and **2**, and 30.7 Å for **3** is calculated (see Table 2). The diffuse maximum at about 3.5 Å corresponds to the short-range correlation between stacked molecules. Indeed, an interdisk distance in the range 3.3−3.6 Å has been typically observed in columnar mesophases of phthalocyanines and corresponds roughly to the molecule thickness.[5] The diffuse maximum found at about 4.5 Å is generally observed on the X-ray patterns of discotic mesophases[19] and corresponds to interferences between the conformationally disordered aliphatic chains.

X-ray patterns were also taken on compounds **1**−**3** at temperatures slightly below the clearing point. These patterns are practically identical to those obtained at room temperature. The only differences are a slight broadening of the peaks at small angles and the flattening of the maximum at 3.5 Å, which becomes difficult to observe. These slight differences are not inconsistent with a same type of mesophase at both temperatures but suggest that the correlation length both in the plane of the two-dimensional hexagonal lattice and along the column axis decreases on increasing the temperature.

As the employed X-ray instruments are not provided with a low-temperature device, the phase below 21 °C for compounds **2** and **3** could not be identified. This transition is not detected by microscopy and might correspond either to crystallization or to a reorganization of the mesophase.

*Compounds **4**−**7**.* The X-ray patterns of monoalkylamide-substituted phthalocyanines **4**−**7** are different from those of **1**−**3**. At room temperature (solid phase) numerous sharp reflections are found both at small and wide angles (see Table 2). The exception to this behavior is found for the octylamide-substituted copper complex **6**, for which a set of sharp peaks are found at small angles, corresponding to reciprocal spacings in the ratio 1:$\sqrt{3}$:$\sqrt{4}$:$\sqrt{7}$:$\sqrt{9}$; in addition, at wide angles a diffuse maximum centered at 4.4 Å and a sharp reflection at 3.32 Å are found in this compound.

Table 2. Powder X-ray Diffraction Results

compound	temp (°C)	measd dist (*d*/Å)	hexagonal lattice constant (*a*/Å)
1	25	26.8	31.0
		10.2	
		4.5 (diffuse)	
		3.5 (diffuse)	
2	25	26.8	31.0
		10.3	
		8.9	
		4.6 (diffuse)	
		3.5 (diffuse)	
3	25	26.3	30.7
		10.1	
		8.9	
		4.5 (diffuse)	
		3.5 (diffuse)	
4	25	33.0	
		18.5	
		9.9	
		4.31	
		4.10	
		3.36	
	225	33.2	
		19.1	
		16.6	
		12.4	
		4.32	
		4.11	
		3.89	
		3.33	
5	25	20.9	
		10.4	
		6.9	
		5.6	
		5.0	
		4.5	
		3.49	
	225	21.3	
		10.6	
		7.1	
		5.7	
		5.1	
		3.57	
6	25	29.3	32.9
		16.6	
		14.2	
		10.6	
		9.3	
		4.4 (diffuse)	
		3.32	
	225	29.8	33.7
		16.8	
		14.6	
		10.9	
		9.7	
		4.5 (diffuse)	
		3.37	
7	25	34.3	
		17.8	
		11.5	
		8.5	
		4.28	
		4.07	
		3.32	
	225	31.0	35.6
		17.8	
		15.6	
		11.7	
		10.3	
		4.6 (diffuse)	
		3.37	

The powdered appearance and the diffraction patterns taken for compounds **4**, **5**, and **7** indicate that these complexes are crystalline solids at room temperature. On the other hand, for compound **6** the presence at wide angles of only a diffuse maximum and a Bragg peak is consistent with a liquid-crystal phase. The small-angle peaks in this compound correspond to a reciprocal spacing ratio of 1:$\sqrt{3}$:$\sqrt{4}$:$\sqrt{7}$:$\sqrt{9}$ and can be indexed, respectively, as the (100), (110), (200), (210), and (300)

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(19) Levelut, A. M. *J. Chim. Phys.* **1983**, *80*, 149.

reflections of a hexagonal network. Thus, in contrast with compounds **4**, **5**, and **7**, copper complex **6** adopts a hexagonal columnar structure at room temperature, with a constant lattice $a = 32.9$ Å (see Table 2). The reflection at 3.32 Å corresponds to the interdisk distance, and its sharpness indicates that the stacking correlation extends to long distances.

On increasing the temperature to 225 °C, i.e., above the transition temperature observed in the microscope, the diffraction pattern of compound **6** does not change significantly, and only a weak shifting of the peaks to smaller angles (longer distances) is observed. This pattern is also assigned to a hexagonal columnar mesophase, with a hexagonal lattice constant of 33.7 Å and a stacking distance of 3.37 Å. The fact that the low- and high-temperature phases in this compound are of the same nature agrees well with the absence of peaks in the DSC curves (see Table 1).

For nickel complex **7**, the high-temperature pattern significantly changes from that obtained at room temperature and becomes similar to those of compound **6**. The pattern consists of a set of small-angle peaks corresponding to reciprocal spacings in the ratio $1:\sqrt{3}:\sqrt{4}:\sqrt{7}:\sqrt{9}$, and a wide-angle peak at 3.37 Å, together with a broad band centered at 4.4 Å. This kind of pattern is characteristic of a hexagonal columnar mesophase with a hexagonal lattice constant of 35.6 Å and a stacking periodicity of 3.37 Å (see Table 2).

On the other hand, for compounds **4** and **5**, although the high-temperature patterns differ from those obtained at room temperature, numerous small and wide-angle reflections are still observed. This indicates that the high-temperature phase of these compounds is crystalline. For these two compounds, X-ray patterns have also been registered at 250 °C, the upper limit of the variable-temperature attachment of our instrument. However, no differences with the patterns taken at 225 °C were observed for compound **5**, and a gradual decreasing of the diffracted intensities, indicating decomposition, was observed for compound **4**.

Conclusions

Dialkylamide-substituted metal-free and metal-containing phthalocyanines **1**−**3** are mesomorphic at room temperature and show a hexagonal columnar mesophase up to the transition to the isotropic liquid at around 90 °C. The disk stacking along the column axis is short range, a situation which corresponds to a disordered hexagonal columnar (D_{hd}) structure.

Monoalkylamide-substituted metal-free and metal-containing phthalocyanines **4**−**7** are crystalline at room temperature, except for the octylamide-substituted copper complex **6** which exhibits a hexagonal columnar mesophase both at low and high temperature. The analogous nickel complex **7** undergoes a transition from the room-temperature crystalline phase to a high-temperature hexagonal columnar mesophase. The disk stacking is long range, and thus the mesophase of compounds **6** and **7** is ordered hexagonal columnar (D_{ho}). The dodecylamide-substituted copper complex **4** and the octylamide-substituted metal-free phthalocyanine **5** are not mesogenic in the temperature range investigated (<250 °C).

The different mesomorphic behavior in the family **4**−**7** compared to the family **1**−**3** is probably due to two main reasons: (i) First, the number of aliphatic chains in these compounds is 8, contrary to compounds **1**−**3**, in which the nitrogen of the amide group bears two octyl chains, thus giving a total number of 16 identical chains. The lower number of aliphatic chains in **4**−**7** and the characteristic rigidity of the amide function could make difficult their symmetrical arrangement in the periphery of the disk and the effective filling of the space around the central core. Eventually, with sufficient conformational disorder the aliphatic chains are able to efficiently fill this space (compounds **6** and **7**). (ii) Second, the hydrogen atom bonded to the nitrogen of the amide group makes the occurrence of inter- and intramolecular hydrogen bonding possible. This phenomenon, not present in phthalocyanines **1**−**3**, is known to noticeably increase the transition temperatures. The transition to the high-temperature phase involves most probably a reorganization of the hydrogen bonds. Indeed, the importance of hydrogen bonding on the aggregation behavior of this kind of system has recently been shown by UV−visible spectroscopy.[14]

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