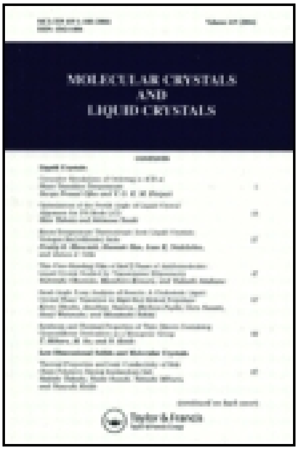

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Synthesis and Characterization of Novel Tetra- and Octa-Triethyleneoxysulfanyl Substituted Phthalocyanines Forming Lyotropic Mesophases

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Synthesis and Characterization of Novel Tetra- and Octa-Triethyleneoxysulfanyl Substituted Phthalocyanines Forming Lyotropic Mesophases*

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Metal-free phthalocyanines and nickel phthalocyanines carrying four or eight oligo(ethyleneoxy)thia groups on peripheral positions have been synthesized from new phthalonitrile derivatives. These phthalocyanine derivatives were characterized both thermotropic and lyotropic mesophases by DSC and X-ray.

Keywords: Phthalocyanines; soluble; Oligo(ethyleneoxy)thia; Liquid crystal; thermotropic and lyotropic mesophases

INTRODUCTION

In addition to their comprehensive use as dyes and pigments, phthalocyanines (pcs) have found wide applications in catalysis, optical recording, photoconductive materials, photodynamic therapy of cancer, chemical sensors and liquid crystals[1]. The attractive characteristics of phthalocyanines are their great variety, chemical stability, the relative ease with which they can be prepared and purified

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* Dedicated to Professor Dr. Özer Bekaroğlu on the occasion of his 65th birthday (May 3, 1998) with our best wishes.

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and the strong dependence of their properties on peripheral and axial substitution patterns[2]. For example pcs, when peripherally substituted with alkyl-,[3,4] alkoxy-,[4,5] alkoxymethyl-[4,6] or oligo(ethyleneoxy)[7] groups form thermotropic discotic liquid crystals.

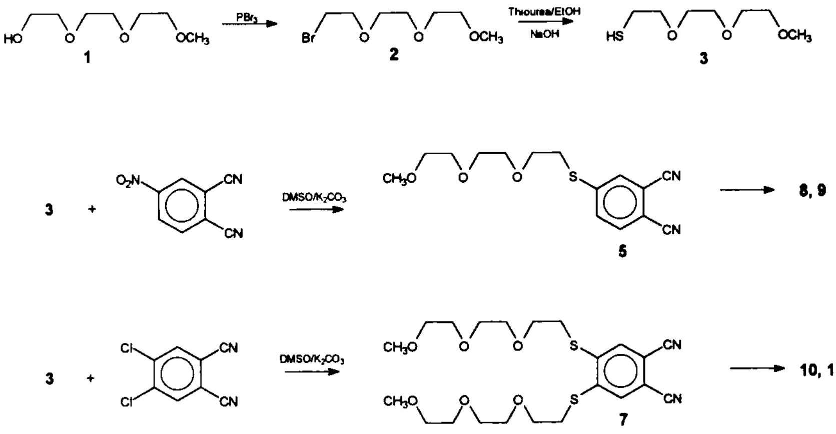
Similar behaviour is demonstrated by derivatives with eight alkyl[3,8] or alkoxymethyl[9] substitution at the nonperipheral sites. In addition, a number of benzo-15-crown-5 substituted pcs have been shown to form discotic mesophases.[10]

Novel synthetic modifications on the pc formation which have been accomplished due to the efficient synthetic methodology developed in the last 20 years for symmetrical and unsymmetrical pcs,[1] can be exemplified in recent reports of unsymmetrically substituted[11] derivatives and symmetrically substituted ones with active peripheral substituents such as crown ethers,[12] tetraaza[13]- and tetrathia[14]- macrocycles which are capable of binding to alkali and transition metals. The crucial consequences of these substituents is enhanced solubility in common organic solvents and additional donor sites for alkali or transition metal ions.

Recently, it has been reported that pc derivatives substituted by four or eight oligo(ethyleneoxy) chains display both thermotropic and lyotropic columnar mesophases.[4,15,16] In contrast to the relatively high number of *O* donor substituted phthalocyanine derivatives reported in the literature, those with S donors on the periphery are relatively few.[8,17,18] Also there is a small number of recent patents and proceedings describing the use of these types of compounds as IR absorbers.[19,20] The shift of the high-intensity Q bands to longer wavelengths is a common feature of these compounds. In the present article we report the synthesis and basic lyotropic mesophase properties of pcs substituted by four and eight tri(ethyleneoxy) side-chains through S donors.

RESULTS AND DISCUSSION

The synthesis of the tetrakis(4,7,10-trioxaundecan-1-sulfanyl)phthalocyanines (**8, 9**) and octakis(4,7,10-trioxaundecan-1-sulfanyl)phthalocyanines (**10, 11**) are shown in the Scheme 1. 1-Mercapto-4,7,10-trioxaundecane that was produced from triethyleneglycol-monomethylether was used in synthesis of mono- and disubstituted phthalonitriles. The first step in the synthetic procedure triethyleneglycol monomethylether was bromination with PBr_3 and then the bromo derivative was treated with an excess of thiourea in ethanol to obtain the sulfanyl compounds. The starting material for both of the precursors are 4-nitrophthalonitrile[21] and 1,2-dichloro-4,5-dicyanobenzene.[19b,22] They are converted by nucleophilic displacement reaction of the nitro group and chloro groups with 1-mercapto-4,7,10-trioxaundecane (**3**) into 4-(4,7, 10-trioxaundecan 1-sulfanyl)-phthalonitrile (**5**) and 4,5-bis(4,7,10-trioxaundecan-1-sulfanyl)-phthalonitrile (**7**). The reaction was carried out in dimethyl sulfoxide at room temperature with sodium carbonate which was used as the base. The reaction of phthalonitrile in 2-(dimethylamino)ethanol yields the metal-free phthalocyanines **8**, **10**. In the case of Nipcs **9**, **11**, cyclotetramerization was carried out in quinoline in the presence of a nickel(II) salt.



SCHEME 1 Synthetic route to tetra- and octa substituted phthalocyanines **8–11**

Column chromatography with silica gel was used to obtain the pure product from the reaction mixture. The solubility of pcs in apolar and polar solvents such as dichloromethane, chloroform, benzene, diethylether, tetrachloromethane, N,N-dimethylformamide, acetone, methanol and ethanol is extremely high. The octasubstituted pcs (**10**, **11**) are water soluble and tetrasubstituted pcs (**8**, **9**) are insoluble in anhydrous ethanol and water.

Elemental-analysis results and the spectral data (^{1}H NMR, ^{13}C NMR, IR, UV-Vis and MS) for all the new products were consistent with the assigned formulations. The relatively weak absorption at 570 cm^{-1} in the IR spectrum of **2** can be assigned to C-Br bond. These bands disappeared after conversion of **2** to sulfanyl **3** which shows absorption at 2560 cm^{-1} for the SH group. Characteristic intense absorptions of CN groups at 2240 cm^{-1} in the spectra of phthalonitrile derivatives **5** and **7** disappear after pc formation. IR spectra of the phthalocyanines **8–11** are very similar with the exception of the metal-free **8** and **10** showing an NH stretching band at 3300 cm^{-1} due to the inner hydrogens.

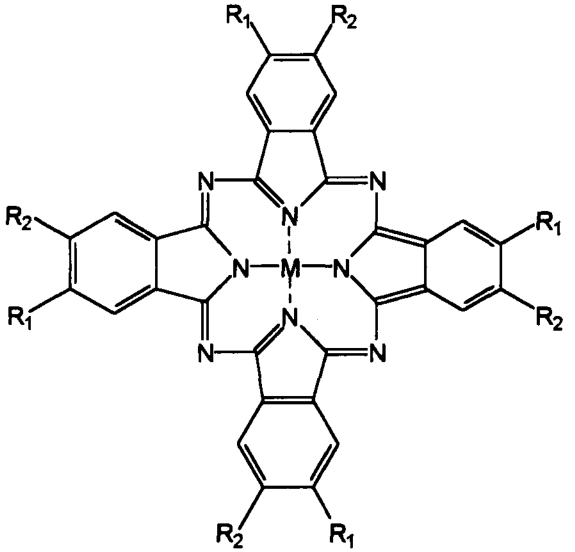
NMR investigation of the compounds **2**, **3**, **5**, **7**, **8–11** have provided the characteristic chemical shifts for the structures as expected (Table I and II). The ^1H NMR spectra of **5** and **7** exhibited the aromatic protons around 7.76–8.07 ppm as multiplets and at 7.64 ppm as a singlet; SCH_2, OCH_3, and OCH_2 protons are appeared around 3.25 ppm as triplet, 3.38 ppm as a singlet and 3.53–3.80 ppm as multiplet respectively. The ^1H NMR spectra of metal-free pcs and Nipcs are almost identical, the only difference being the disappearance of the broad NH protons of **8** and **10** at ca. δ –5.51 and –2.80 ppm in Nipcs. The high solubility of the pcs has enabled us to obtain ^{13}C NMR spectra. The chemical shift values in these spectra closely follow the empirically calculated ones, and the D_{4h} symmetry of the metallo-pcs prevails especially for the octasubstituted ones.[23] In the ^{13}C NMR spectra of the phthalonitrile derivatives **5**, **7** the aromatic carbon in the vicinity of the thia groups are at the lowest field (δ 146.48 and 143.94); the protonated aromatic carbons are at δ 130.46, 130.56 and 133.38 for **5** and at δ 129.39 for **7** while the chemical shifts of the other two aromatic carbons and two nitrile carbons appear at δ 109.58, 115.86, 114.87 and 115.42 for **5** and δ 111.41, and 115.47 for **7**. The ^{13}C NMR spectral data of tetra and octa substituted pcs **8–11** given in Table II are also in accord with the expected structures.

The electronic spectra of the phthalocyanines **8–11** show the characteristic Q band absorptions as a single peak at 690 nm and shoulders at 650 nm in **9**, a single peak at 702 nm and a shoulder at 660 nm in **11**, two intense and two lower intense peaks in metal-free pcs (Table III). Solvent effect is also evident in pcs **8–11** e.g. methanol solution causes drastic changes in the Q band with lowering of intensity and the wavelengths of the peaks (Table III) as a result of aggregation [12(a,b),15] (Figure 2).

A close investigation of the mass spectra of the phthalonitrile derivatives **5**, **7** and phthalocyanines **8-11** confirmed the proposed structures. In the case of phthalonitriles 5 and 7, in addition to the M^+ peaks at m/z = 306 and 486, fragment ions were easily identified by EI technique. The spectra of pcs **8-11** were obtained by the FAB technique using a mnba (*m*-nitrobenzylalcohol) matrix and here we observed the molecular ions at m/z = 1226 $(M-1)^+$, 1284, 1939 $(M-1)^+$ and 1997 $(M-1)^+$ respectively.

Thermotropic phase behaviour

The DSC-measurements (DSC-7, Perkin-Elmer) of all four compounds show no significant sharp peaks from –25 to ~200°C. This is especially true for the tetra-substituted compounds **8** and **9** which contain no peaks representing melting or any other phase transition. The heating cycle was interrupted before reaching any clearing point to avoid decomposition. However, the octa-substituted



8-11

	R_1	R_2	M
8	$S(CH_2CH_2O)_3CH_3$	H	2H
9	$S(CH_2CH_2O)_3CH_3$	H	Ni
10	$S(CH_2CH_2O)_3CH_3$	$S(CH_2CH_2O)_3CH_3$	2H
11	$S(CH_2CH_2O)_3CH_3$	$S(CH_2CH_2O)_3CH_3$	Ni

FIGURE 1 Structure of the phthalocyanines

compounds **10** and **11** show broad peaks at about 140°C (**10**) and 80°C (**11**) for the first heating cycle, respectively, and at about 125°C (**10**) and 60°C (**11**) for the second one. These peaks may be related to the melting. The cooling cycle shows very weak peaks at about 140°C for **10** and 80°C for **11**. In all cases, decomposition of the pcs are around 250–275°C (determined by Thermal Gravimetric Analysis, TGA).

TABLE I Proton NMR spectral data for the starting materials and the phthalocyanines in $CDCl_3$

SH	*OCH$_3$*	*OCH$_2$C*	*S(CH$_2$)*	*OCH$_2$*	*Ar-H*
	3.38(s, 3H)	3.38–3.44(m, 12H)			
2.19(s, 1H)	3.25(s, 3H)	3.43–3.54(m, 10H)	2.61(t, 2H)		
	3.24(s, 3H)	3.32–3.67(m, 8H)	3.24(t, 2H)	3.70(t, 2H)	7.76–8.07(m, 3
	3.38(s, 6H)	3.53–3.66(m, 16H)	3.25(t, 4H)	3.80(t, 4H)	7.64(s, 2H)
	3.39(s, 12H)	3.52–3.86(m, 40H)		4.04(t, 8H)	7.42–7.63(m, 4 7.89–8.18(m, 8
	3.42(s, 12H)	3.41–3.84(m,40H)		4.03(t, 8H)	7.34–7.53(m, 4 7.69–7.99(m, 8
	3.46(s, 24H)	3.46–3.83(m, 80H)		4.08(t, 16H)	8.82(s, 8H)
	3.29(s, 24H)	3.48–3.78(m, 80H)		4.05(t, 16H)	8.64(s, 8H)

TABLE II ^{13}C-NMR spectral data for the starting material and phthalocyanines in $CDCl_3$

	SCH$_2$	*OCH$_3$*	*-CH$_2$-*	*CN*	*Ar-CH*	*Ar-C*
.28		59.03	70.61, 71.23, 71.95			
	23.28	57.88	68.55, 69.32, 69.49, 69.65, 71.17, 72.03			
	30.87	57.87	68.53, 69.45, 69.64, 71.85	114.87	130.46, 130.56, 133.38	109.58, 115.86 1
	32.66	58.95	69.34, 70.55, 70.70, 71.85	115.45	129.38	111.41, 143.3
	32.83 33.15	59.08	69.07, 70.68, 72.00		119.43, 120.21, 121.51, 121.74, 128.04	131.50, 131.77, 1 138.65, 146.3
	32.86 33.19	59.08	69.95, 70.68, 72.02		118.47, 119.42, 120.80 127.54	131.96, 135.08, 1 141.98
	33.97	58.95	69.80, 70.61, 71.91		122.13	133.62, 140.24, 1
	33.97	58.96	69.75, 70.58, 71.90		121.27	133.92, 139.75, 1

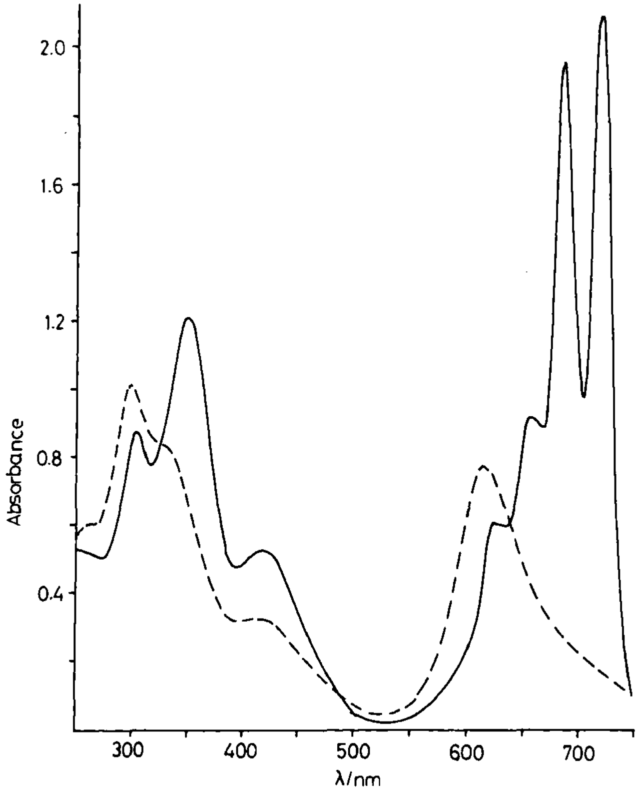


FIGURE 2 UV/Vis spectra of phthalocyanine **8**, (-) in $CHCl_3$and (- - -) in MeOH

TABLE III Electronic spectra of the phthalocyanines in chloroform and methanol

Compound	*Solvent/c ($10^5 mol/dm^3$)*	*λ_{max}/nm ($10^{-4}\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$)*
8	$CHCl_3$/1.32	720(16.67), 685(14.85), 655(6.97), 622(4.55), 418(3.94), 348(9.17), 303(6.67)
	MeOH/1.17	616(6.58), 412(2.91), 325(sh)(7.18), 297(8.63)
9	$CHCl_3$/1.10	690(11.41), 650(sh)(4.73), 405(sh)(2.10), 310(7.45)
	MeOH/1.18	612(4.58), 390(sh)(1.69), 293(6.61)
10	$CHCl_3$/1.10	730(21.45), 700(19.00), 679(6.27), 638(4.64), 438(4.91), 365(10.00), 337(sh)(9.55)
	MeOH/1.15	610(6.26), 438(sh)(2.87), 328(8.00)
11	$CHCl_3$/1.02	702(21.27), 660(sh)(6.18), 425(4.02), 327(13.14)
	MeOH/1.00	650(5.45), 428(2.40), 318(8.70)

It should be noted that no recrystallization is observed at any time which may be suppressed under the conditions applied as in a capillary (for X-ray measurements) or between two glass slides (for optical microscopy). From the investigations performed it can be concluded that the compounds are in a thermotropic liquid crystalline phase between the melting and 250°C.[3a,6,7,15,16]

Optical microscopy of thermotropic mesophases

Optical textures were observed with the polarising microscope Olympus BH-2 equipped with the hot stage and temperature-controller Linkam Pr 600, and pictures were taken with the camera Olympus OM-2n of thin samples.

The textures observed by polarizing optical microscopy for the compounds studied are very similar to those described in literature.[3a,7,24,25] Good textures of the samples were obtained by slowly cooling from the isotropic melt (notice the decomposition). Phase transition from mesophase to isotropic liquid are for **8**, **9**, and **11**>250°C and was observed at 236°C for **10**. They appear flower-like with digitate stars or fan-like with needles (Figure 3). Figure 4 and 5 represent a rare example of an observed crystallization in microscope. The flower-like texture (Figure 4) becomes striated by cooling in a wide temperature range (Figure 5). Therefore, it is not surprising that the transitions detected in DSC are very weak.

In the cases where the isotropic liquid could not be obtained by heating on the hot stage without decomposition, the samples were prepared in chloroform and the solvent evaporated before the microscopic investigation.

Lyotropic mesophase

Similar compounds are reported in the literature[15,16] and possess both thermotropic and lyotropic mesophase behaviour. All compounds investigated form a lyotropic mesophase in 2-propanol, nitromethane, n-butylacetate, diethyleneglycol monomethylether, 95% ethanol and ethyleneglycol monomethyletheracetate (EMMAc) at room temperature. The best schlieren texture was observed in EMMAc. The samples were prepared by dissolving the compounds in one drop of solvent and placed between two cover slide. A partial evaporation of the solvent occurred before investigation so that the concentration cannot exactly be defined. Both compounds **8** and **9** form a lyotropic columnar nematic schlieren texture N_c lying between the isotropic solution and the discotic hexagonal phase D_h which exhibits fans at the concentrated side of the sample (Figure 6). Lyotropic phase are formed by **10** and **11** too. But instead of a nematic schlieren texture, they show a discotic phase in form of a flower-like texture or digitate stars (similar to the thermotropic textures) (Figure 7) between the isotropic solution and the discotic hexagonal, fan shaped phase D_h.

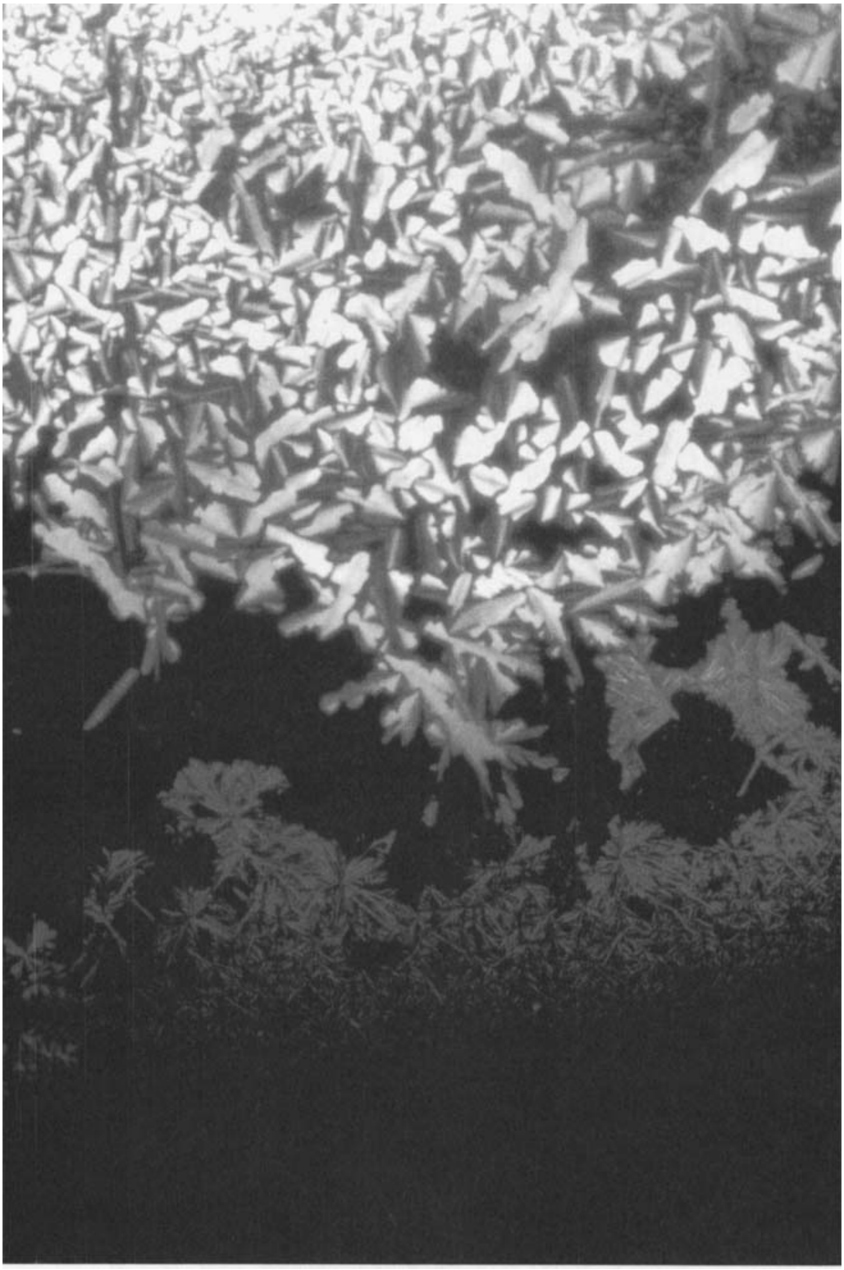


FIGURE 3 Fan-like texture with needles at 40°C of compound **10** (after application of the procedure with chloroform as described in the text) (See Color Plate I at the back of this issue)

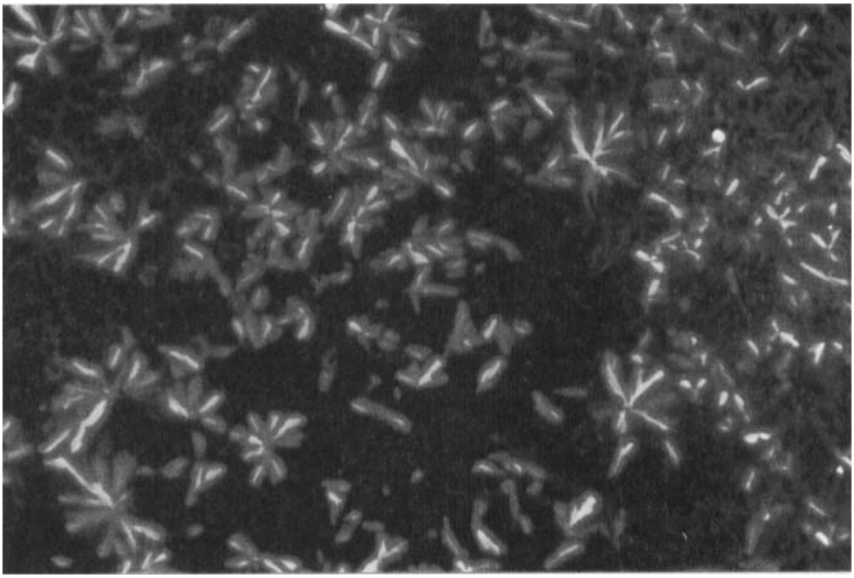


FIGURE 4 Flower-like texture with digitates stars at 190°C of compound **10** (See Color Plate II at the back of this issue)

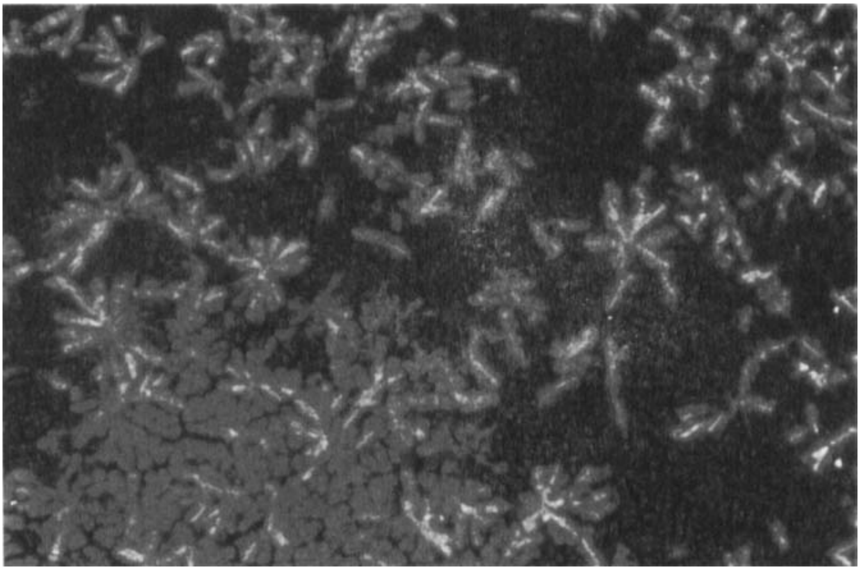


FIGURE 5 Striated flower-like texture at 180°C of compound **10** (See Color Plate III at the back of this issue)

FIGURE 6 Lyotropic mesophase: columnar nematic schlieren texture $N_c$between isotropic liquid and discotic hexagonal phase D_h at room temperature of compound **9** in EMMAc (See Color Plate IV at the back ot this issue)

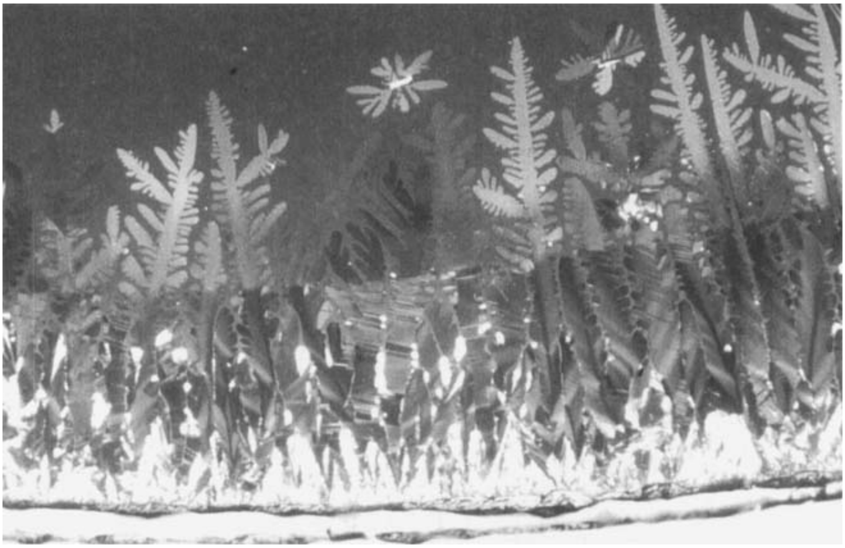


FIGURE 7 Lyotropic mesophase: discotic phase in form of digitated stars between the isotropic solution and the discotic hexagonal phase D_h at room temperature of compound **10** in EMMAc. At the edge the sample seems to crystallize (See Color Plate V at the back of this issue)

The discotic hexagonal phase D_h can be identified by X-ray diffraction (c.f. X-ray investigations on thermotropic mesophases below).

X-ray diffraction

The samples were filled in 0.7 mm capillaries for X-ray investigations of the thermotropic phase by a flat film and a Debye-Scherrer camera. The diffraction diagrams were taken at room temperature at which the samples are already in the liquid crystalline states as discussed above.

The low angle regions of the X-ray diffraction diagrams of the compounds **8, 9, 10, 11** show four sharp Bragg reflections with d-spacing ratios $1:1\ \sqrt{3}:1\ \sqrt{4}:1\sqrt{7}$ (Table IV).[3a,6,7,16,24] This suggests a two-dimensional hexagonal lattice with the disk-like molecules stacked in columns in a hexagonal arrangement. All the X-ray data may be indexed with an orthorhombic symmetry of the planar unit cell. The a- and b-parameter of the cell with $a=b\sqrt{3}$ (Table V) are obtained with the Miller indices hkl from Table IV. The distance between the axes of two neighboring piles of molecules corresponds to the b-dimension in such an arrangement. The diameter of the aromatic core can be estimated to about 15 Å, and the length of the side-chains in the extended all-trans conformation to about 14 Å. With these data the X-ray results are in good agreement with the geometrical parameters of the molecules, although the intercolumnar distance seems to be somewhat shorter than in case of all-trans-side-chains.

TABLE IV X-ray diffraction data of the phthalocyanines

Compound	*d [Å]*					
	8	***9***	***10***	***11***	*ratio*	*hkl*
	20.8 s[a]	20.8 s	23.4 s	23.0 s	1	110, 200
	12.0 w	11.9 m	13.4 md	13.3 m	$\sqrt{3}$	020, 310
	10.5 w	10.8 m		11.4 m	$\sqrt{4}$	220, 400
	9.4 m	9.5 m		9.8 w		
		7.7 w	8.9 w	8.7 m	$\sqrt{7}$	130, 420, 510
				7.7 w	$\sqrt{9}$	330, 600
				6.6 md		
	4.4 md	4.2 md	4.2 sd	4.5 md		
	3.4 m	3.3 m	3.5 md	3.5 md		

[a] s: sharp ; m: middle ; w: weak ; d: diffuse

TABLE V The cell parameters of the phthalocyanines

Compound		*8*	*9*	*10*	*11*
	a [Å]	41.6	41.6	46.8	46.0
	b [Å]	24.0	23.8	26.8	26.6

The distance between adjacent columns is independent of the presence of a metal ion in the phthalocyanine centre. There is no significant difference between the nickel-complexed compounds **9** and **11** and the metal-free **8** and **10** with the same number of side-chains. The tetra-substituted compounds **8** and **9** show shorter distances than the octa-substituted compounds **10** and **11**. This is not surprising, since eight side-chain require more space between the phthalocyanine rings than four side-chains.

In the wide angle region the compounds show a diffuse halo at about 4.2 to 4.5 Å which is compatible with the disorder of the paraffinic tails in the side-chain. An additional reflection at about 3.3 to 3.5 Å is also observed which may be assigned to the packing of macrocyclic subunits in the columns.

The sharpness of this reflection of **8** and **9** suggests good order within the columns and is consistent with the strong intramolecular periodicity associated with the discotic hexagonal ordered D_{ho}-mesophase. The compounds **10** and **11**show a diffuse reflection indicating that there is no long range translational order of the molecules along the axis of the stacks which is associated with the discotic hexagonal disordered D_{hd}-mesophase.

EXPERIMENTAL

IR spectra (KBr cell) were recorded on a Perkin-Elmer 983 spectrophotometer. Optical spectra in the UV-visible region were recorded with a Varian DMS 90 spectrophotometer using 1 cm pathlength cuvettes at room temperature. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 200-MHz spectrometer. Elemental analyses were performed by the Instrumental Analysis Laboratory of TUBITAK, Marmara Research Centre. Mass spectra were recorded on a VG ZAB-SPEC spectrometer. 4-nitrophthalonitrile [21] and 1,2-dichloro-4,5-dicyanobenzene[19b,22] were prepared according to the reported procedures.

1-Bromo-4,7,10-trioxaundecane (2)

In a three-necked flask is placed 50 g (0.3 mol) of triethylene glycol monomethylether. After cooling in an ice bath the stirring is started and 27.5 g (9.5 ml, 0.1 mol) of freshly distilled phosphorus tribromide is added from a dropping funnel over a period of 2 hours under argon. The mixture was stirred at room temperature for 24 h. The product was obtained by fractional distillation B.p. 65°C/3 mbar, yield: 28.74 g (42 %). Found C, 37.58; H, 6.28%; $C_7H_{15}O_3Br$ (227.1); requires C, 37.02; H, 6.66%; IR(Cell) ν_{max}: 2920–2840, 1450, 1360, 1280, 1200, 1150–1100, 570 cm^{-1}; MS (CI), m/z (%): 182 (2) $[M-CH_2OCH_3]^+$, 181 (19) $[(M-1)-CH_2OCH_3]^+$, 151 (47) $[(M-1)-OCH_2CH_2OCH_3]^+$, 137 (38) $[(M-1)-CH_2OC_2H_4OCH_3]^+$, 107 (87) $[(M-1)-(OC_2H_4)_2OCH_3]^+$, 89 (68) $[M-BrC_2H_4OCH_2]^+$.

1-mercapto-4,7,10-trioxaundecane (3)

8.44 g (0.11 mol) thiourea was dissolved under reflux in EtOH (80 ml) and 20 g (0.074 mol) of 2 was added. The mixture was refluxed for 8h and the solvent was evaporated under reduced pressure. To the residue the solution of 4 g of NaOH in degassed water with argon was added. After refluxing for 1h, 6N HCl was added to adjust the pH value to 7 and the product was extracted with diethyl ether (3 × 100 ml). The ether solution was dried with Na_2SO_4, evaporated and the residue was distilled B.p. 70–72°C/5 mbar, yield 9.00 g (67%). Found C, 46.36; H, 8.92%; $C_7H_{16}O_3S$ (180.26); requires C, 46.64; H, 8.95%; IR(Cell) ν_{max}: 2960–2840, 2560(SH), 1460, 1350, 1300, 1250, 1200, 1140–1110 cm^{-1}; MS (CI), m/z (%): 180 (1%) $[M]^+$, 135 (3) $[M-CH_2OCH_3]^+$, 133 (11) $[M-CH_2{=}SH]^+$, 121 (75) $[M- C_2H_4OCH_3]^+$, 89 (58) $[M-CH_2OC_2H_4SH]^+$.

4(4,7,10-trioxaundecan-1-sulfanyl)phthalonitrile (5)

To a solution of 4-nitrophthalonitrile (2 g, 0.011 mol) in anhydrous DMSO (20 ml) 1-mercapto-4,7,10-trioxaundecane (**3**) (1.9 g, 0.011 mol) was added under argon. After stirring for 10 min, finely ground anhydrous potassium carbonate (4 g, 0.029 mol) was added portionwise in 2h with efficient stirring. The reaction mixture was stirred under argon at room temperature for 16h. Then 150 ml water was added and the aqueous phase was extracted with dichloromethane (3 × 50 ml). The combined extracts were dried over sodium sulfate, the solvent was evaporated and the oily product was crystallized from MeOH and dried in vacuum. Yield: 1.75 g (52%), m.p. 45°C; Found C, 58.93; H, 5.44; N, 8.87%; $C_{15}H_{18}N_2O_3S$ (306.37); requires C, 58.81; H, 5.92; N, 9.14%; IR(Cell) ν_{max}: 2820–3000, 2240(C≡N), 1580, 1540, 1480, 1420, 1390, 1300, 1200, 1150–1060, 940, 910, 840 cm^{-1}; MS(CI), m/z (%): 306(13) $[M]^+$, 274 (11) $[(M+1)-OCH_3]^+$, 248 (11) $[(M+1)-C_2H_4OCH_3]^+$, 231 (8) $[M-OCH_2CH_2OCH_3)]^+$, 204 (18) $[(M+1)-(C_2H_4O)_2CH_3]^+$, 187 (100) $[M-(OC_2H_4)_2OCH_3]^+$.

4,5-bis(4,7,10-trioxaundecan-1-sulfanyl)phthalonitrile (7)

7 was prepared according to the same procedure as described for **5** by starting from 1,2-dichloro-4,5-dicyanobenzene (2 g, 0.01 mol) and **3** (4 g, 0.022 mol). The product was purified by column chromatography on silica gel using dichloromethane/methanol (20/1) as the eluent. The product is oily at room temperature. Yield: 2.5 g (52 %). Found C, 54.70; H, 6.64; N, 5.99%; $C_{22}H_{32}N_2O_6S_2$ (484.62); requires C, 54.53; H, 6.66; N, 5.78 %; IR (Cell) ν_{max}: 2940–2840, 2240(C≡N), 1560, 1460, 1350, 1270, 1200, 1150–1110, 1030, 930 cm^{-1}; MS (CI), m/z(%): 484(22) $[M]^+$, 364 (37), $[(M\text{-}1)\text{-}(OCH_2CH_2)_2OCH_3]^+$, 306 (20) $[(M+1)\text{-}S(CH_2CH_2O)_3CH_3]^+$, 275 (5), 262 (39), 244 (70), 216 (82), 203 (80), 190 (76).

Tetrakis(4,7,10-trioxaundecan-1-sulfanyl)phthalocyanine (8)

4-nitrophthalonitrile (1.0 g, $3.26\text{x}10^{-3}$ mol) in dry 2-(dimethylamino)ethanol was refluxed under argon for 6h. After cooling, the mixture was added dropwise into diethylether with stirring to precipitate the solid, which was filtered and washed several times with diethylether. The dark green product was purified by column chromatography on silicagel using dichloromethane/methanol (20/1) as eluent. Yield: 0.31 g (28%); Found C, 58.22; H, 5.76; N, 8.94%; $C_{60}H_{74}N_8O_{12}S_4$ (1227.48); requires C, 58.71; H, 6.08; N, 9.12 %; IR (Cell) ν_{max}: 3300 (NH), 2940–2820, 1600, 1500, 1450, 1300, 1200, 1150–1070 (CH_2OCH_2), 1020, 900, 820, 740 cm^{-1}; MS (FAB), m/z (%): 1226 (100) $[M\text{-}1]^+$, 1080 (22) $[M\text{-}(CH_2CH_2O)CH_3]^+$, 933 (5) $[M\text{-}2x((CH_2CH_2O)_3CH_3)]^+$, 787 (3) $[M\text{-}3x((CH_2CH_2O)_3CH_3)]^+$, 640 (7) $[M\text{-}4x((CH_2CH_2O)_3CH_3)]^+$.

Tetrakis(4,7,10-trioxaundecan-1-sulfanyl)phthalocyaninatonickel (9)

A mixture of **5** (0.5 g, 1.63 mmol), anhydrous $NiCl_2$ (0.065 g, 0.5 mmol) and anhydrous quinoline (1.5 ml) was heated and stirred at 170°C for 8h under argon in a round-bottomed flask. The resulting green suspension was cooled and the product was precipitated by addition of diethylether. The crude green product was purified by column chromatography (Silicagel, CH_2Cl_2:MeOH/10:1). Yield: 0.17 g (33%). Found C, 56.85; H, 5.26; N, 8.53%; $C_{60}H_{72}N_8O_{12}S_4Ni$ (1284. 18); requires C, 56.12; H, 5.65; N, 8.72 %; IR(Cell) ν_{max}: 2920–2840, 1600, 1530, 1450, 1400, 1350, 1200, 1160–1090 (CH_2OCH_2), 1040, 940, 750 cm^{-1}. MS (FAB), m/z (%): 1284 (98) $[M]^+$, 1136 (31) $[M\text{-}((CH_2CH_2O)_3CH_3)]^+$, 981 (12) $[M\text{-}2x((CH_2CH_2O)_3CH_3)]^+$, 843 (11) $[M\text{-}3x((CH_2CH_2O)_3CH_3)]^+$, 696 (26) $[M\text{-}4x((CH_2CH_2O)_3CH_3)]^+$.

2,3,9,10,16,17,23,24-Octakis(4,7,10-trioxaundecan-1-sulfanyl)-phthalocyanine (10)

Compound **7** (0.75 g, 1.55 mmol) was heated in dry 2-(dimethylamino)ethanol with stirring and refluxed for 24h under argon. After cooling, the mixture was added dropwise into petroleum ether with stirring to precipitate the solid, which was filtered and washed several times with petroleum ether. The green product was purified by column chromatography on silicagel using ethylacetate/MeOH (5/2) as eluent. Yield: 0.17 g (22%). Found C, 54.12; H, 6.48; N, 5.17%; $C_{88}H_{130}N_8O_{24}S_8$ (1940.48); requires C, 54.47; H, 6.75; N, 5.77 %; IR (Cell) ν_{max}: 3300(NH), 2920–2840, 1600, 1500, 1460, 1420, 1400, 1350, 1290, 1160–1100 (CH_2OCH_2), 1030, 940, 750 cm^{-1}; MS (FAB), m/z (%): 1939 (100) $[(M-1)]^+$, 1792 (36) $[(M-1)-(CH_2CH_2O)_3CH_3]^+$, 1645 (15) $[(M-1)-2x((CH_2CH_2O)_3CH_3)]^+$, 1512 (10), 1366 (7), 762 (8), 675 (36).

2,3,9,10,16,17,23,24-Octakis(4,7,10-trioxaundecan-1-sulfanyl)-phthalocyaninatonickel (11)

A mixture of **7** (0.75 g, 1.55 mmol), anhydrous $NiCl_2$ (0.067 g, 0.52 mmol) and anhydrous quinoline (1ml) was heated and stirred at 180°C for 8h under argon in a round-bottomed flask. The resulting green suspension was cooled and the product was precipitated by addition of petroleum ether. The crude dark green product was purified by column chromatography (Silicagel, CH_2Cl_2:MeOH/10:1). Yield:0.14 g (18%). Found C, 53.00; H, 6.43; N, 5.18%; $C_{88}H_{128}N_8O_{24}S_8Ni$ (1997.17); requires C, 52.92; H, 6.46; N, 5.61%; IR (Cell) ν_{max}: 2920–2840, 1600, 1530, 1450, 1410, 1380, 1350, 1290, 1250, 1200, 1140–1070 (CH_2OCH_2), 970, 860, 780, 750 cm^{-1}; MS (FAB), m/z (%): 1997 (37) $[M-1]^+$, 1982 (80) $[M-CH_3]^+$, 1850 (28) $[M-((CH_2CH_2O)_3CH_3)]^+$, 1834 (28), 1716 (26), 830 (21).

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