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Mesomorphic molecular materials

Influence of chain length on the structural properties of octa-alkyl substituted phthalocyanines

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Phthalocyanines R_8PcM (R=alkyl, M=H_2, Ni, Cu) substituted with alkyl chains have been synthesized and their liquid crystalline properties studied by differential scanning calorimetry and X-ray diffraction at small angles. The influence of the chain length on the mesomorphic properties has been determined. A model is proposed to rationalize the structural modifications induced by varying the nature of the connecting link between the macrocycle and the side chains (alkyl, alkoxymethyl, alkoxy).

1. Introduction

The introduction of substituents in peripheral positions of the phthalocyanine (Pc) macrocycle (for example, *t*-butyl [1], trimethylsilyl [2], *n*-alkyl [3, 4], branched alkyl [5], alkoxy and alkoxymethylene [6–8] groups) has been extensively used for increasing the solubility in organic media. Bridged oligomers and polymers of the type $[R_4\text{Pc}M(L)]_n$ or $[R_8\text{Pc}M(L)]_n$ (R = Et, *t*-Bu, SiMe_3, C_nH_{2n+1}, OC_nH_{2n+1}, $CH_2OC_nH_{2n+1}$; M = Fe, Ru, Os and L = 1,4-di-isocyanobenzene, pyrazine [9, 10] or M = Si, Ge, Sn and L = O [11–14] also demonstrate a higher solubility in most organic solvents.

Substitution of the phthalocyanine macrocycle (see figure 1) with six to eight paraffinic chains leads to liquid crystalline phases [15, 16]. In most cases, the aromatic

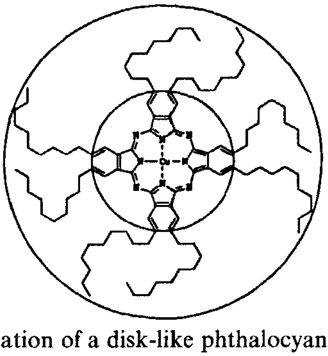

Figure 1. Schematic representation of a disk-like phthalocyanine substituted with long alkyl chains.

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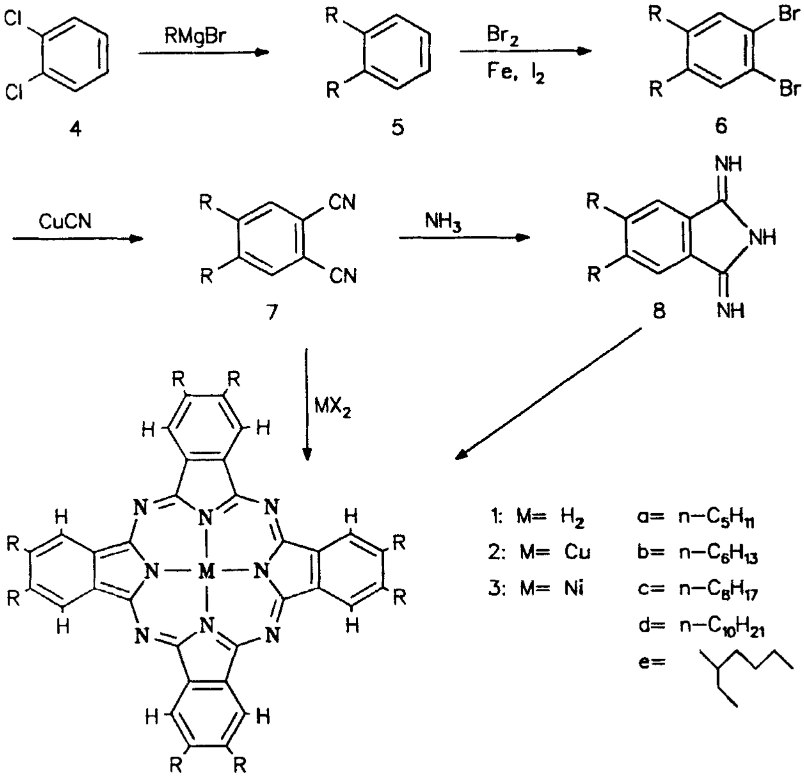

1a–e, 2a–d, 3b–e

Scheme 1. Chemical pathway used to synthesize the molecular units used in the present study.

cores stack in columns surrounded by the flexible alkyl side chains. These liquid crystalline phases are called discotic (from the disk-like shape of the molecules) or columnar mesophases [17, 18]. Columnar structures are particularly suitable for demonstrating one dimensional physical properties (electron-migration [19, 20] or energy transfer [21, 22]).

In this paper we describe the synthesis (scheme 1) of a series of octa-alkyl substituted phthalocyanines R_8PcM with $R = C_5H_{11}$, C_6H_{13}, C_8H_{17}, $C_{10}H_{21}$, 2-Et-C_6H_{13} and $M = H_2$, Ni and Cu. The influence of alkyl substitution of the phthalocyanine ring on the liquid crystalline properties and on the structures of the mesophases has been studied.

1.1. *Synthesis of the substituted phthalocyanine [23]*

The first octa-alkylphthalocyanine synthesized was $(H_3C)_8PcCu$ reported in 1934, starting from 1,2-dibromo-4,5-dimethylbenzene [24]. The octa-alkyl substituted phthalocyanines reported in this paper were synthesized according to scheme 1 [3, 4, 8]. 1,2-Dichlorobenzene (**4**) is reacted with the appropriate Grignard reagent in the presence of a nickel(II) diphosphine catalyst [25, 26] to give the corresponding 1,2-dialkylbenzene (**5**). This product is brominated to form the dibromobenzene (**6**). By a conventional Rosenmund–von Braun reaction, the dibromobenzenes (**6**) are converted with CuCN into the substituted phthalonitriles (**7**), which are then transformed into the corresponding di-iminoisoindoles (**8**). The phthalocyaninato copper and nickel complexes R_8PcM (M = Cu, Ni; $R = C_5H_{11}, C_6H_{13}, C_8H_{17}, C_{10}H_{21}$, 2-Et-$C_6H_{12}$; **2a–d, 3b–e**) are prepared in two ways. The substituted phthalonitrile (**7**) may be reacted, in the presence of DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) with $CuBr_2$ or $NiBr_2$ in pentan-l-ol. The di-iminoisoindoles (**8**) form the same complexes by reacting them with the nickel or copper salts in dimethylaminoethanol. The phthalocyaninato copper complexes (**2a–d**) are isolated as side products when the dibromobenzenes (**6**) are treated with CuCN. The metal-free phthalocyanines R_8PcH_2 (**1a–e**) are obtained from the substituted di-iminoisoindoles (**8**) by heating them in dimethylaminoethanol under reflux [27, 28].

The substituted phthalocyanines (**1a–e, 1a–d, 3b–e**) are all soluble in organic solvents such as $CHCl_3$, toluene or tetrahydrofuran; the phthalocyanines with decyl (**1d, 2d, 3d**) or 2-ethylhexyl (**1e, 3e**) side chains are easily purified by column chromatography; the other derivatives can be recrystallized from toluene.

2. Results

2.1. *Mesomorphic properties and structural parameters*

The mesomorphic properties of the octa-alkylphthalocyanines (**1a–e, 2a–d, 3b–e**) were determined by differential scanning calorimetry (see figures 2, 3, 4, and table 1). The octa-alkylphthalocyanines complexes are stable up to 410–420°C where they start to decompose. A similar degradation has already been reported for $(C_4H_9)_8$PcM at 425°C [3]. In the isotropic liquid phase, the octa-alkylphthalocyanines are unstable; $(C_5H_{11})_8PcH_2$, for example, starts to decompose at 380°C during melting. The clearing point of the copper complexes could not be observed up to 450°C.

For octa-alkylphthalocyanines (**1a–d**), liquid crystalline phases are found for side chains longer than C_4 (see figure 3). The domain of stability of the mesophases increases with chain length up to the octyl derivative, whereas both the C→M and M→I transition temperatures decrease (see figure 3). A very similar behaviour is obtained for the corresponding copper and nickel complexes (**2a–d, 3b–d**); the transition temperatures are however slightly higher and the M→I transition temperatures for the copper complexes (**2a–c**) could not be found (see figure 4 and table 1). In most cases, several different solid crystalline phases are observed, but their structural parameters could not be determined from the X-ray patterns. The structural parameters characterizing the mesophases were determined by X-ray diffraction at small angles. In all cases, with the exception of $(C_5H_{11})_8$PcCu (**2a**), all but one of the peaks observed may be assigned by assuming a hexagonal packing of the columns. The experimental intercolumnar distance is always smaller than the molecular dimensions of the octa substituted phthalocyanine (a_1, figure 5) calculated from the X-ray structures for the phthalocyanine ring [30] and from standard values for the molten aliphatic chains [31]. For the tilted arrangements, the macrocycles have been considered to form an angle of 46° with the columnar axis. Such a value is found for the β-form of crystalline unsubstituted phthalocyanines. Two arrangements have been taken into consideration, in which no interlacing or maximum interpenetration of the chains is considered. The experimental points (figure 5) are situated between these two extremes. A more detailed interpretation of this result is given later. An 'extra-peak' has been noticed in the X-ray diffraction pattern around 14–18 Å (see table 2). The extra peak was first assigned to a

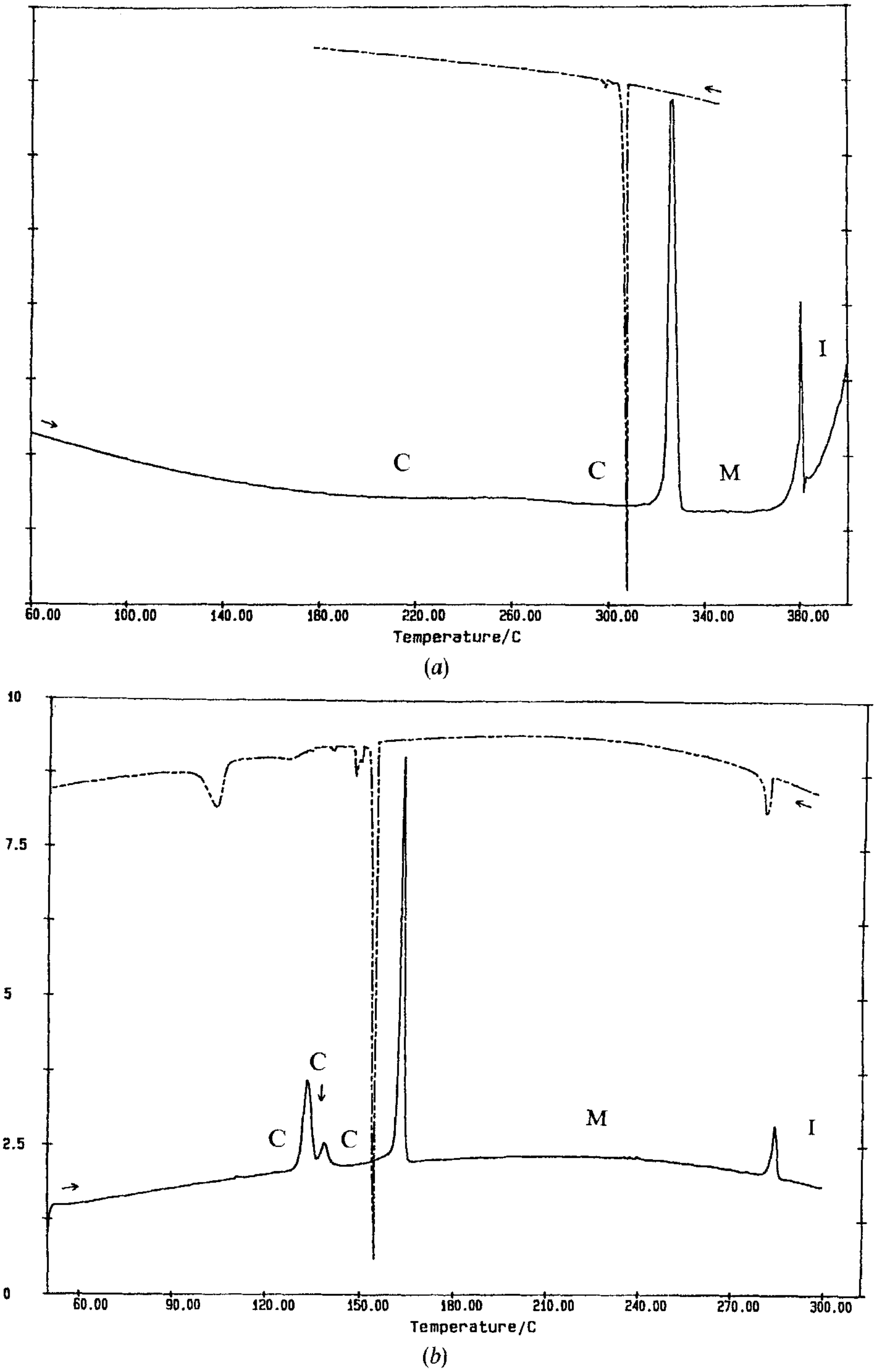

Figure 2. Differential scanning calorimetry data for (*a*) $(C_5H_{11})_8PcH_2$ **1a**, and (*b*) $(C_{10}H_{21})_8PcH_2$ **1d**; (rate of heating: 10°C min^{-1}).

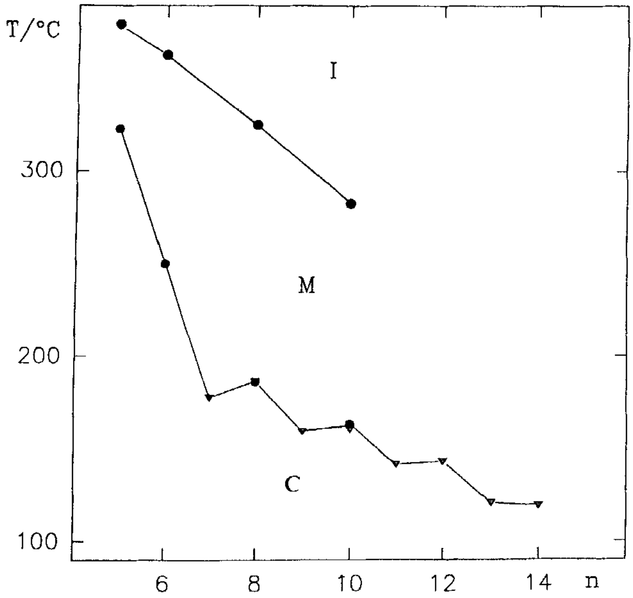

Figure 3. Stability domains for the octa-alkyl phthalocyanines R_8PcH_2 (**1a–d**) determined by DSC (●, present work; [▼], from [29]) as a function of the number of carbon atoms in the side chains (n); C crystalline phase; M, mesophase; I, isotropic liquid.

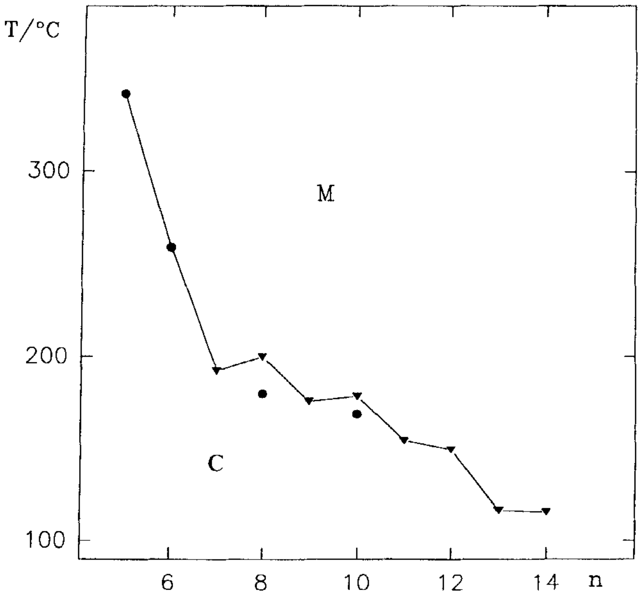

Figure 4. Stability domains for the octa-alkyl copper phthalocyanines R_8PcCu (**2a–d**) determined by DSC (●, present work; ▼, from [28]) as a function of the number of carbon atoms in the side chains (n).

Table 1. Transition temperatures [°C] of the octa-alkylphthalocyanines (**1a–e, 2a–d, 3b–e**) determined by DSC; C: crystal, M: mesophase, I: isotropic liquid; † product decomposes during transition; ‡ not found up to 450°C; § C→I; ¶ a value of ca. 200°C has been reported by other authors [29].

Compound	C→C [*T*/°C]	C→M [*T*/°C]	M→I [*T*/°C]
H_2, C_5 (**1a**))	250	323	379† (see figure 2(*a*))
H_2, C_6 (**1b**)	92, 135, 213	250	363†
H_2, C_8 (**1c**)	124	186	325
H_2, C_{10} (**1d**)	132, 138	163	282 (see figure 2 (*b*))
H_2, 2-Et-C_6 (**1e**)	78		267§
Cu, C_5 (**2a**)	260	342	‡
Cu, C_6 (**2b**)	55, 208	259	‡
Cu, C_8 (**2c**)	81	180¶	‡
Cu, C_{10} (**2d**)	112, 132	169	351
Ni, C_6 (**3b**)	82, 219	260	412†
Ni, C_8 (**3c**)	107, 187	190	373
Ni, C_{10} (**3d**)	125, 148	168	333
Ni, 2-Et-C_6 (**3e**)	84		293§

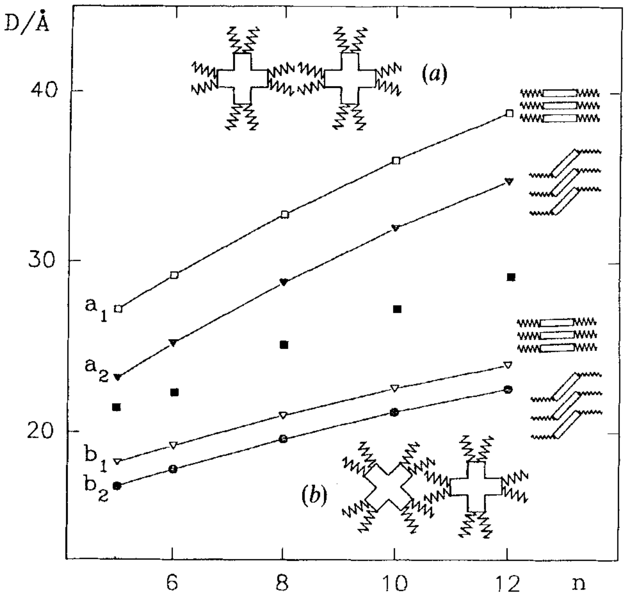

Figure 5. The intercolumnar distance *D* (hexagonal lattice) as a function of the chain length. (■), experimental points for **1a–d**; full lines, values obtained from the molecular dimensions with the arrangements shown in the figure (Pc-macrocycle, 13 Å [30]; molten aliphatic chains, see [3]; tilting angle 46°.

Table 2. The lattice parameters for the liquid crystalline phases of the octa-alkylphthalocyanines; T, temperature at which the X-ray pattern has been recorded; D_{exp}, intercolumnar distance; A, extra peak observed which cannot be interpreted in terms of a hexagonal lattice.

Compound	T/°C	D_{exp}/Å	A/Å	Halo 1/Å	Halo 2/Å
H_2,C_5 (**1a**)	340	21·4	13·9	—	3·9
H_2,C_6 (**1b**)	270	22·5	14·5	4·7	3·9
H_2,C_8 (**1c**)	210	25·1	16·3	4·9	3·9
H_2C_{10} (**1d**)	175	27·2	18·0	4·7	3·8
Cu,C_5 (**2a**)	360	19·6	—	5·1	3·8
Cu,C_8 (**2c**)	210	25·3	16·5	4·8	3·8
Cu,C_{10} (**2d**)	180	27·2	18·0	4·7	3·8
Ni,C_6 (**3b**)	280	22·6	15·0	4·9	3·9
Ni,C_{10} (**3d**)	180	27·2	18·0	4·7	3·8

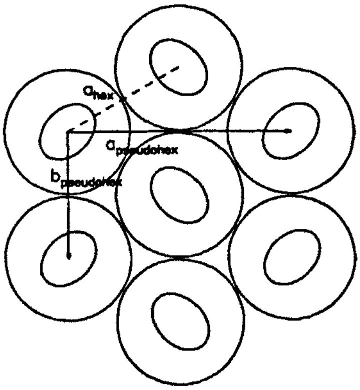

Figure 6. The rectangular lattice formed from the pseudohexagonal symmetry by tilting the aromatic cores within the columns (derived from [34]).

so called 'pincement de Skoulios–de Gennes' [32, 33]. This interpretation was dismissed and the peak was then attributed to a 210 reflection of a rectangular lattice [34] (see figure 6). Other reflections which should be associated with the rectangular lattice (for example $hkl = 120$) are not found, but these peaks are usually said to be very weak [34]. This extra peak is found with all our products except $(C_5H_{11})_8PcCu$ (**2a**). An alternative model may however be proposed. The volume of the molecular unit may be calculated from

$$V_{mol} = 8V_{CH3} + 8(n-1)V_{CH2} + V_{core},$$

where V_{CH3}, V_{CH2} and V_{core} are the molecular volumes of the methyl and methylene groups and of the central core respectively.

At room temperature, V_{CH3} and V_{CH2} may be obtained by plotting

$$\frac{M_W}{d} = 2V_{CH3} + (n-2)V_{CH2}$$

for various alkanes, where M_W and d are respectively the molecular weight and the density of the liquid considered [35]. A good correlation is obtained with n

Table 3. Volumes of the unit cell (V_{cell}) and of the molecule (V_{mol}).

	h	$V^{\dagger}_{cell}$	$V^{\ddagger}_{mol}$
$(C_{12}OCH_2)_8PcH_2$	3·56	2960	4060
$(C_{12}O)_8PcH_2$	3·4	3610	3830
$(C_{12})_8PcH_2$	3·7	2770	3600

† At $t = 200°C$: corrections made according to [34].
‡ Same temperature: corrections as indicated in the text.

varying form 3 to 17. In this way, it is found that $V_{CH2} = 25\,Å^3\,molecule^{-1}$ and $V_{CH3} = 54\,Å^3\,molecule^{-1}$ (RT). V_{CH2} in mesophases has been found to be slightly larger ($30\,Å^3\,molecule^{-1}$) [36]. Further calculations on molecular volumes must therefore be considered to underestimate the real value.

The variation of the molecular volumes with temperature may be taken into account. Straightforward derivations [35] show that the thermal expansion coefficient for benzene or alkanes is approximately the same ($10^{-3}\,°C^{-1}$) and that, in the latter case, it does not depend importantly on the chain length. The corresponding correction is made for the structures determined at different temperatures.

The volume of the phthalocyanine ring may be derived from CPK models ($V_{core} \sim 425\,Å^3$). The overall theoretical volume of the molecule may be compared with volume of the unit cell *considered in a hexagonal lattice*. The intracolumnar distance between the macrocycles must be known in this case. The value found at large angles in the X-ray diffraction patterns can be taken. The results are comparable for all chain lengths and calculations will be given only for the dodecyl derivatives (see table 3). For $(C_{12}O)_8PcH_2$, the volume of the cell is approximately equal to the volume of the molecule. This is not the case for the other two compounds: only approximately 0·75 of a molecule per unit volume can be accommodated. This clearly indicates that the unit volume cannot be associated with the crystallographic unit cell. In the case that the macrocycles are tilted relatively to the column axis, h cannot be taken to calculate the elementary volume. It is postulated in the previous model [34] that it corresponds to the interplanar distance, while this is not a periodicity parameter of the column.

The phthalocyanine derivative has a D_{4h} symmetry and it is therefore not possible to close pack this molecular unit in a hexagonal lattice (see figure 7). In order to preserve a hexagonal symmetry, rotation of the molecular units (or rotation averaged units in a column) must occur. Since the intercolumnar axis is smaller than the distance necessary for free rotation, irregular stacking of the macrocycles within one column must be postulated in which pinched areas alternate with domains having larger intermacrocyclic distances (see figure 8). A structurally related pincement de Skoulios has been found [32, 33], however, the interpenetration of the molecular units belonging to adjacent columns is the driving force of this effect. This was ignored in the previously described unidimensional model [32]. Here, only a fraction of a molecular unit occupies the 'apparent' unit cell (see figure 8), and the extra-peak (Λ) in this model arises from the periodicity between pinched and extended domains within one column. Studies of orientated mesophases should permit us to distinguish between the present model and the one previously proposed [34].

Calculations (MM2) were carried out on phthalocyanines with alkyl or alkoxymethylene side chains. In both cases, the paraffinic tails were found to be tilted

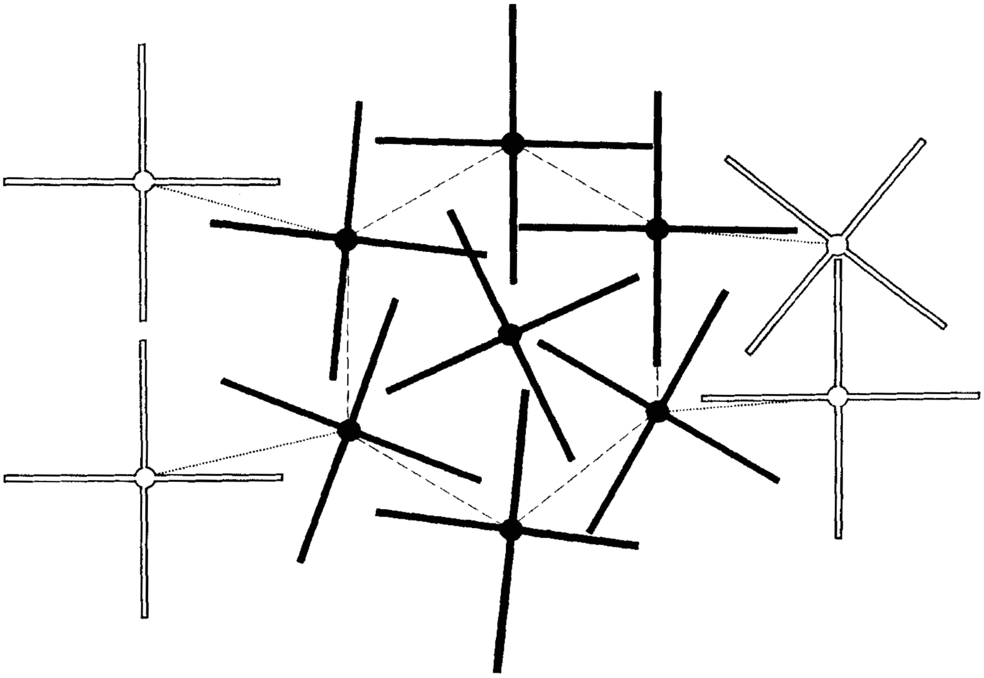

Figure 7. Closest-packing (right) and packing allowing free rotation (left) of molecular units of symmetry D_{4h}. In the experimentally found lattice, an intermediate situation is observed (middle).

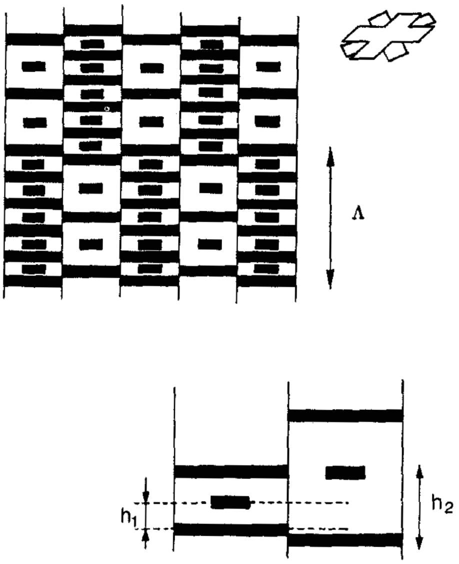

Figure 8. Schematic representation of the columnar organization arising in alkylphthalocyanine derivatives. h_1, intermacrocyclic distance in the pinched area; h_2, intermacrocyclic distance in the extended domain of the column.

relatively to the macrocycle by an angle of about 20°. For alkoxy side chains, force field methods show no inclination of the side chains relatively to the macrocycle.

The mesophase of $(C_5H_{11})_8PcCu$ (**2a**) has a rectangle lattice with symmetry D_{rd} (C2/m). For $(2\text{-Et-}C_6H_{13})_8PcH_2$ (**1e**) and $(2\text{-Et-}C_6H_{13})_8PcNi$ (**3e**) no mesophases were found. The branching of side chains near the core depresses the temperature at which unstacking of the columns occurs below the melting point of the side chains, and no mesophases are found [37, 38]. The high temperature crystalline phases in $(2\text{-Et-}C_6H_{13})_8PcM$ ($M = H_2$ (**1e**) and $M = Ni$ (**3e**)) can be attributed to a pseudohexagonal) rectangular lattice with $a = 38·1$, $b = 22·0$ Å (**1e**) and $a = 38·7$, $b = 22·3$ Å (**3e**).

3. Conclusion

A systematic study of the influence of the chain length on the mesomorphic properties of substituted phthalocyanines R_8PcM with $R = C_5H_{11}$, C_6H_{13}, C_8H_{17}, $C_{10}H_{21}$, $2\text{-Et-}C_6H_{13}$ and $M = H_2$, Ni and Cu is reported. Octa-alkyl substituted phthalocyanines (**1a–d, 2a–d, 3b–d**) show very high clearing points for molecular materials. When the chain length of the side chains is increased, the mesophase to isotropic liquid transition temperatures decrease approximately linearly. The crystalline to mesophase transition temperatures also decrease with increasing chain length. Further studies are in progress to distinguish between the two models which have been proposed to rationalize the X-ray diffraction data.

4. Experimental

4.1. *Analysis*

The spectroscopic, thermal and optical results were obtained with the following apparatus: NMR spectra: Bruker AC 250 (250 MHz), Bruker MSL 200 (50·325 MHz); IR spectra: Perkin–Elmer 398 IFS 48; UV–VIS spectra: Perkin–Elmer Lambda 5, Shimadzu UV-365; DSC: Perkin–Elmer Delta Series DSC 7 (under N_2, standard: In, Zn); polarized light microscopy: Pol Carl Zeiss.

4.2. *Synthesis of 1,2-dialkylbenzenes* (**5**)

In a typical procedure, 7·3 g (0·3 mol) of sublimated magnesium in suspension in 120 ml of diethylether are stirred under nitrogen. 1-Bromopentane, 45·3 g (0·3 mol) in 30 ml of Et_2O are added dropwise. The solution is heated under reflux for 1 h. The solution is cooled down and added in 20 min at 0°C to a mixture of 16·8 g (0·11 mol) of 1,2-dichlorobenzene (**4**) and 150 mg (0·28 mmol) of 1,3-bis(diphenylphosphine)propane nickel(II) chloride (Alfa) in 95 ml of Et_2O. The reaction mixture is heated under reflux for 12 h. At 0°C, the residual mixture is hydrolyzed with 2M HCl. The aqueous phase is shaken with Et_2O and the organic phase is washed with water. The combined organic phases are dried over $CaCl_2$ and evaporated to dryness. The product is purified by distillation under vacuum (yield: 60 per cent).

5a (b.p. 95°C, 3 mbar). Analysis: $C_{16}H_{22}$ (MW 218·4). Calculated (per cent): C 88·0, H 12·0; found (per cent): C 88·1, H 12·3. ^1H NMR (250 MHz, $CDCl_3$, σ [ppm], J [Hz]). 7·11 (m, 4 H, H_b, H_c); 2·59 (t, $J = 7·9$, 4 H, H_1); 1·58 (m, 4 H, H_2); 1·36 (m, 8 H, H_3, H_4); 0·9 (t, $J = 7·0$, 6 H, H_5). ^{13}H NMR (62·9 MHz, $CDCl_3$, σ [ppm]). 140·5 (C_a), 129·1 (C_b), 125·7 (C_c), 32·7 (C_1), 31·9 (C_3), 31·0 (C_2), 22·6 (C_4), 14·0 (C_5) MS (EI, 70 eV). 218 (M^+), 105 ($M^+ - 2\,C_4H_9{}^+ + H$). IR (Film, cm^{-1}). 3 062, 3 017 (arC–H, st); 2 957, 2 930, 2 870 (C–H, st); 1 490 (arC–C); 1 467 (CH_2 δ, CH_3 δ_{as}); 1 378 (CH_3, δ sy); 749 (δ_{oop}); 721 (CH_2, γ).

4.3. *Synthesis of 1,2-dibromo-4,5-dialkylbenzenes* (**6**)

A mixture of 21·9 g (0·1) mol) of **5a** and 20 ml of CH_2Cl_2 is mixed at 0°C under nitrogen with 100 mg of iron dust. Bromine, 33·6 g (0·27 mol, 10·7 ml) in 20 ml of CH_2Cl_2 is added dropwise in the absence of light (addition time: 4 h). The mixture is stirred for 3 days at 0°C and 1 day at room temperature. The reaction mixture is poured into a solution of 5 per cent $NaOH/NaHCO_3$ in water to remove Br_2. The organic layer is washed with water, dried over Na_2SO_4 and evaporated to dryness. The product is filtered through SiO_2 and recrystallized from *n*-hexane at −30°C (yield: 50 per cent).

6a, Analysis: $C_{16}H_{24}Br_2$ (MW 376·2). Calculated (per cent): C 51·1, H 6·4, Br 42·5; found (per cent): C 50·3, H 6·5, Br 41·9. ^1H NMR (250 MHz, $CDCl_3$, σ [ppm], J [Hz]). 7·36 (s, 2 H, H_b); 2·50 (t, $J = 7·9$, 4 H, H_l); 1·53 (m, 4 H, H_2); 1·35 (m, 8 H, H_3, H_4); 0·91 (t, $J = 6·8$, 6 H, H_5). ^{13}C NMR (62·9 MHz, $CDCl_3$, σ [ppm]). 141·7 (C_a), 133·8 (C_b), 121·3 (C_c), 32·0 (C_l), 31·8 (C_3), 30·6 (C_2), 22·6 (C_4), 14·0 (C_5). MS (EI, 70 eV). 374, 376, 378, (1 : 2 : 1, M^+), 261, 263, 265 (1 : 2 : 1, M^+–2 $C_4H_9^+$ + H^+). IR (Film, cm^{-1}). 2957, 2930, 2870, 2858 (C–H, st); 1467 (CH_2 δ, CH_3 δ_{as}); 1378 (CH_3, δ sy); 1360, 938, 884 (δ_{oop}); 721 (CH_2, γ); 655 (C–Br, st).

4.4. *Synthesis of 1,2-dicyano-4,5-dialkylbenzenes* (**7**)

11·3 g (0·03 mol) of **6a** and 8·1 g (0·09 mol) CuCN in 100 ml of freshly distilled DMF are heated under reflux and under N_2 for 3–5 h. The mixture is poured into 400 ml of a concentrated solution of NH_4OH at room temperature. Air is bubbled through the solution for 12 h. The mixture is filtered and shaken with Et_2O. The combined organic phases are washed with water, dried over $CaCl_2$ and evaporated to dryness. The crude product is purified by chromatography (SiO_2; eluent: *n*-hexane/toluene 2/3), R_f **7a**: 0·27 and monocyano 0·57 (yield: 70 per cent). **7a** Analysis: $C_{18}H_{24}N_2$ (MW 268·4). Calculated (per cent): C 80·5, H 9·0, N 10·5; found (per cent): C 80·2, H 9·8, N 9·8.

^1H NMR (250 MHz, $CDCl_3$, σ [ppm], J [Hz]). 7·56 (s, 2 H, H_b); 2·68 (t, $J = 7·9$, 4 H, H_1); 1·61 (m, 4 H, H_2); 1·34 (m, 8 H, (H_3, H_4); 0·90 (t, $J = 6·6$, 6 H, H_5). ^{13}H NMR (62·9 MHz, CDC13, σ [ppm]). 147·3 (C_a), 134·0 (C_b), 115·7 (C_d), 112·5 (C_c), 32·3 (C_l), 31·4 (C_3), 29·8 (C_2), 22·2 (C_4), 14·1 (C_5). MS (EI, 70 eV). 268 (M^+), 212 (M^+–$2C_2H_5^+$ + H^+), 197 (M^+–$C_3H_7^+$–$C_2H_5^+$), 183 (M^+–2 $C_3H_7^+$), 169 (M^+–$C_3H_7^+$–$C_4H_9^+$ + H^+), 156 (M^+–2 $C_4H_9^+$ + 2 H^+). IR (Film, cm^{-1}). 3036 (arC–H, st); 2959, 2931, 2872, 2860 (C–H, st); 2232, (CN, st); 1600, 1551, 1495 (arC–C); 1467 (CH_2 δ, CH_3 δ_{as}); 1379 (CH_3, δ sy); 1251; 1110; 901 (δ_{oop}); 772.

4.5. *Synthesis of 1,3-diimino-5,6-dialkylisoindoles* (**8**)

NH_3 is bubbled through a mixture of 3·2 g (0·012 mol) of **7a** and 140 mg (3·5 mmol) of NaOMe in 90 ml of MeOH while being heated under reflux. The final product crystallizes from the reaction medium (yield: 99 per cent).

8a Analysis: $C_{18}H_{27}N_3$ (MW 285·4). Calculated (per cent): C 75·8, H 9·5, N 14·7; found (per cent): C 74·1, H 10·6, N 13·9. The higher homologues of **8a** do not crystallize at room temperature. In this case, they are recrystallized from MeOH at −30°C. Compared **8e** does not crystallize, even at −80°C. ^1H NMR (250 MHz, $CDCl_3$, σ [ppm], J [Hz]). 8·25 (s, 3 H, N–H); 7·49 (s, 2 H, H_b); 2·65, (t, $J = 7·9$, 4 H, H_1); 1·53 (m, 4 H, H_2); 1·32 (m, 8 H, H_3, H_4); 0·88 (t, $J = 6·9$, 6 H, H_5). ^{13}H NMR (62·9 MHz, $CDCl_3$, σ [ppm]). 166·8 (C_d), 144·8 (C_a), 132·1 (C_c), 121·7 (C_b), 32·3 (C_l), 31·4 (C_3), 29·8 (C_2), 22·2 (C_4), 14·1 (C_5). MS (EI, 70 eV). 285 (M^+), 268 (M^+–NH_3). IR (Film, cm^{-1}). 3278 (N–H, st); 2956, 2925, 2857 (C–H, st); 1696; 1596; 1545; 1457; 1417; 1164; 1153; 1078; 875; 721 (CH_2, γ).

4.6. *Synthesis of 2,3,9,10,16,17,23,24-octa-alkyl-29H,31H-phthalocyanines* (1)

0·7 g (2·46 mmol) of **8a** in 1·7 ml of freshly distilled dimethylaminoethanol is heated under reflux for 24 h. At room temperature, ethanol (70 ml) is added and the mixture heated under reflux for 1 h. The product is filtered off, by purified by Soxhlet extraction with EtOH and recrystallized from toluene (yield 21 per cent).

1a Analysis: $C_{72}H_{98}N_8$ (MW 1075·6). Calculated (per cent): C 80·39, H 9·18, N 10·42; found (per cent): C 79·64, H 9·94, N 9·97. MS (EI, 70 eV): 1075. ^{1}H NMR (250 MHz, $CDCl_3$, 55°C, σ [ppm], J [Hz]). 8·9 (H_b, s), 3·2–3·05 (H_1, t, $J=8·0$), 2·15–1·95 (H_2, m), 1·85–1·45 ($H_{3-(n-1)}$, m), 1·18–0·98 (H_n, t, $J=6·8$), $-1·15$ (NH, s). UV–VIS ($CHCl_3$): 711, 675, 650, 613, 374sh, 344, 295. IR (KBr, cm^{-1}): 3298 (NH), 2955, 2929, 2870, 1626, 1467, 1454, 1322, 1104, 1015, 757, 708.

1b Analysis: $C_{80}H_{114}N_8$ (MW 1187·8). Calculated (per cent): C 80·89, H 9·50, N 9·43; found (per cent) C 80·91, H 9·96, N 8·97. MS (EI, 70 eV): 1187. ^{1}H NMR (250 MHz, $CDCl_3$, 55°C, σ [ppm], J [Hz]). 8·8 (H_b, s), 3·2–3·05 (H_1, t, $J=7·5$), 2·19–1·94 (H_2, m), 1·86–1·25 ($H_{3-(n-1)}$, m), 1·10–0·90 (H_n, t, $J=6·6$), $-1·45$ (NH, s). UV–VIS ($CHCl_3$): 710, 673, 648, 610, 375sh, 345, 295. IR (Nujol, cm^{-1}): 3289 (NH), 1105, 1015, 758.

1c Analysis: $C_{96}H_{146}N_8$ (MW 1412·3). Calculated (per cent): C 81·65, H 10·42, N 7·93; found (per cent): C 81·83, H 11·39, N 7·17. MS (EI): 1411. ^{1}H NMR (250 MHz, $CDCl_3$, 55°C, σ [ppm], J [Hz]). 9·0 (H_b, s), 3·24–3·08 (H_1, t, $J=7·3$), 2·19–1·98 (H_2, m), 1·89–1·10 ($H_{3-(n-1)}$, m), 0·99–0·87 (H_n, t, $J=5·7$), $-0·97$ (NH, s). UV–VIS ($CHCl_3$): 711, 675, 648, 611, 374sh, 346, 296. IR (KBr, cm^{-1}): 3292 (NH), 2953, 2923, 2854, 1617, 1506, 1465, 1377, 1105, 1016, 895, 758, 720, 707.

1d Analysis: $C_{112}H_{178}N_8$ (MW 1636·7). Calculated (per cent): C 82·19, H 10·96, N 6·85; found (per cent): C 82·04, H 11·10, N 6·54 MS (EI, 70 eV). ^{1}H NMR (90 MHz, toluene-d_8, 90°C, σ [ppm]). 9·1 (H_b, s), 3·19–3·02 (H_1, t), 1·89–1·33 ($H_{2-(n-1)}$, m), 0·92–0·78 (H_n, t), ** (NH) not detected. UV–VIS (toluene): 703, 667, 648, 641, 603, 346. IR (KBr, cm^{-1}): 3290, (NH), 2954, 2919, 2851, 1619, 1504, 1466, 1377, 1322, 1137, 1124, 1014, 895, 758, 719.

1e Analysis: $C_{96}H_{146}N_8$ (MW 1142·3). Calculated (per cent): C 81·65, H 10·42, N 7·93; found (per cent): C 80·73, H 10·71, N 8·28. MS (EI, 70 eV): 1411. ^{1}H NMR (250 MHz, $CDCl_3$, σ [ppm], J [Hz]). 9·15 (H_b, s), 3·3–3·0 (H_1, m), 2·1–1·9 (H_2, m), 1·8–1·2 ($H_{3,4,5,7}$, m), 1·1–1·0 (H_8, t, $J=7·3$), 1·0–0·8 (H_8, t, $J=7·0$), $-0·76$ (NH, s). UV–VIS ($CHCl_3$): 713, 678, 652, 615, 373, 346, 296. IR (KBr, cm^{-1}): 3293 (NH), 2959, 2928, 2873, 2858, 1626, 1503, 1461, 1379, 1106, 1014, 898, 759, 711.

4.7. *Synthesis of 2,3,9,10,16,17,23,24-octa-alkyl-metal-phthalocyanines* (2, 3)

Under nitrogen, 560 mg (1·79 mmol) of **8b** and 58·2 mg (0·447 mmol) of $NiCl_2$ in 2 ml of freshly distilled DMF is heated under reflux for 2 days. At room temperature, EtOH (80 ml) is added, and the mixture is heated under reflux for 1 h. The product is filtered off, purified by Soxhlet extraction with EtOH and recrystallized from toluene (yield 70 per cent). The same procedure is used for the copper complex.

2a Analysis: $C_{72}H_{96}CuN_8$ (MW 1137·2). Calculated (per cent): C 76·09, H 8·45, N 9·86; found (per cent): C 76·01, H 9·15, N 9·59. MS (EI, 70 eV): 1136. UV–VIS ($CHCl_3$): 688, 658sh, 618, 340. IR (KBr, cm^{-1}): 2954, 2926, 2856, 1621, 1509, 1453, 1412, 1377, 1329, 1102, 1076, 892, 748, 730.

2b Analysis: $C_{80}H_{112}CuN_8$ (MW 1249·4). Calculated (per cent): C 76·91, H 8·96, N 8·97; found (per cent): C 74·97, H 8·71, N 8·46. MS (EI, 70 eV): 1248. UV–VIS

($CHCl_3$): 689, 657sh, 620, 342, 292, 275. IR (KBr, cm^{-1}): 2956, 2924, 2855, 1620, 1559, 1466, 1455, 1412, 1376, 1366, 1343, 1107, 894, 871, 748, 729.

2c Analysis: $C_{96}H_{144}CuN_8$ (MW 1473·8). Calculated (per cent): C 78·24, H 9·85, N 7·60; found (per cent): C 77·97, H 10·15, N 7·79.

2d Analysis: $C_{112}H_{176}CuN_8$ (MW 1698·2). Calculated (per cent): C 79·21, H 10·45, N 6·60; found (per cent): C 78·99, H 10·56, N 6·38. MS (EI, 70 eV): 1698·9. UV–VIS (toluene): 681, 650, 613, 345, 298. IR (KBr, cm^{-1}): 2955, 2920, 2851, 1620, 1560, 1467, 1456, 1413, 1378, 1368, 1103, 890, 870, 748, 730.

3b Analysis: $C_{80}H_{112}N_8Ni$ (MW 1242·7). Calculated (per cent): C 77·20, H 9·07, N 9·00; found (per cent): C 76·64, H 9·62, N 8·43. MS (FD): 1242. ^1H NMR (250 MHz, $CDCl_3$, σ [ppm]). 8·8 (H_b, s), 3·1 (H_1, m), 2·0 (H_2, m), 1·8–1·3 ($H_{3-(n-1)}$, m), 1·14–0·80 (H_n, t). UV–VIS: 680, 650, 612, 370, 335, 300, 278. IR (KBr, cm^{-1}): 2955, 2920, 2853, 1622, 1538, 1457, 1418, 1340, 1110, 895, 752, 735.

3c Analysis: $C_{96}H_{144}N_8Ni$ (MW 1467·8). Calculated (per cent): C 78·56, H 9·81, N 7·63; found (per cent): C 77·66, H 10·43, N 7·02. MS (FD): 1467. ^1H NMR (250 MHz, $CDCl_3$, σ [ppm]). 8·75 (H_b, s), 3·1 (H_1, t), 2·0, H_2, m), 1·85–1·25 ($H_{3-(n-1)}$, m), 1·10–0·80 (H_n, t). UV–VIS ($CHCl_3$): 681, 652, 612, 370, 335, 300sh, 275. IR (KBr, cm^{-1}): 2954, 2920, 2852, 1535, 1467, 1455, 1420, 1334, 1108, 1082, 893, 753, 732.

3d Analysis: $C_{112}H_{176}N_8Ni$ (MW 1693·4). Calculated (per cent): C 79·44 H 10·48, N 6·62; found (per cent): C 79·20, H 10·58, N 6·35. MS (EI, 70 eV): 1693·0. ^1H NMR (90 MHz, $CDCl_3$, σ [ppm]). 9·03 (H_b, s), 3·07 (H_1, m), 1·32 (H_{2-9}, m), 0·86 (H_{10}, m). UV–VIS (toluene): 674, 645, 606, 365, 335, 297. IR (KBr, cm^{-1}): 2955, 2920, 2851, 1620, 1507, 1467, 1459, 1410, 1380, 880, 753, 732.

3e Analysis: $C_{96}H_{144}N_8Ni$ (MW 1467·8). Calculated (per cent): C 78·56, H 9·81, N 7·63; found (per cent): C 77·86, H 10·45, N 6·72. MS (EI, 70 eV): 1468. ^1H NMR (250 MHz, $CDCl_3$, σ [ppm], J [Hz]). 8·8 (H_b, s), 3·2, (H_1, m), 2·1 (H_2, m, 1·9–1·2 ($H_{3,4,5,7}$, m), 1·1–1·0 (H_8, t, $J=7{\cdot}3$), 0·96 (H_8, t, $J=7{\cdot}0$). UV–VIS: 685, 656, 616, 374, 336, 300sh, 279. IR (KBr, cm^{-1}): 2959, 2928, 2892, 2866, 1625, 1505, 1460, 1413, 1379, 1352, 1090, 884, 745, 736.

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