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Homologous series of liquid-crystalline metal free and copper octa-*n*-alkoxyphthalocyanines

by J. F. VAN DER POL, E. NEELEMAN, J. W. ZWIKKER, R. J. M. NOLTE†
and W. DRENTH

Department of Organic Chemistry, University at Utrecht, Padualaan 8,
3584 CH Utrecht, The Netherlands

J. AERTS, R. VISSER and S. J. PICKEN

Akzo Corporate Research Laboratories, Velperweg 76, 6800 SB Arnhem,
The Netherlands

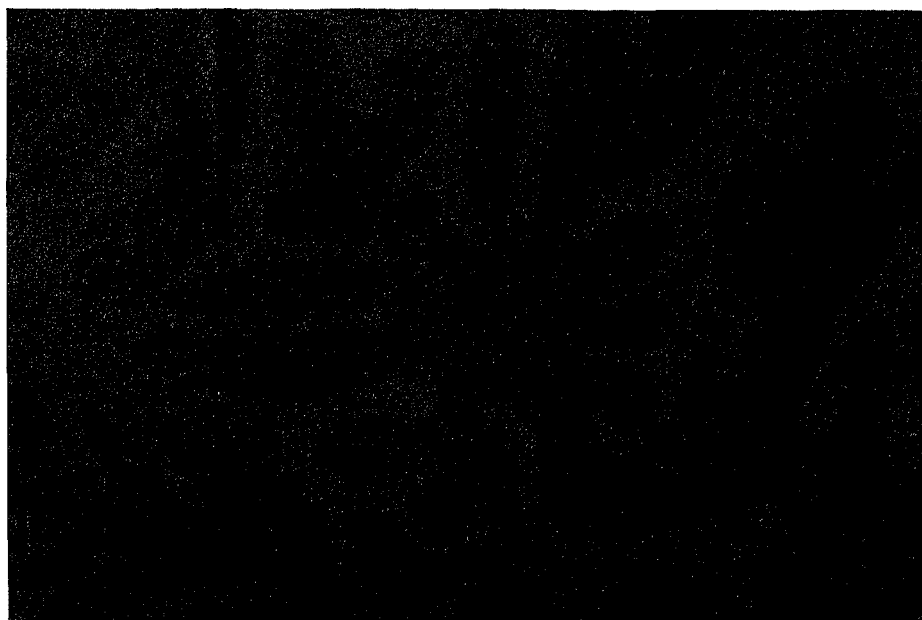
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Two series of discotic liquid crystals, one based on metal-free and the other on copper containing phthalocyanine (Pc) as the central core and eight peripherally *n*-alkoxy groups (C₆-C₁₂) as substituents have been synthesized and their mesomorphic properties and structural parameters have been determined. These compounds represent a series totally devoid of polymorphism, the mesophase in all cases being D_{h0}. In the solid state an orthorhombic two dimensional lattice with four molecules per unit cell and a presumably tilted stacking is present, while in the mesophase the planes of the molecules are on average perpendicular to the direction of the stacks. The aggregation behaviour of the C₈, C₁₀ and C₁₂ homologues was studied as a function of solvent polarity and of concentration. The electrical properties of the copper complexes of the *n*-dodecoxy and *n*-octoxy derivatives have been determined by means of complex impedance spectroscopy and compared with those of the non-mesogenic CuPc.

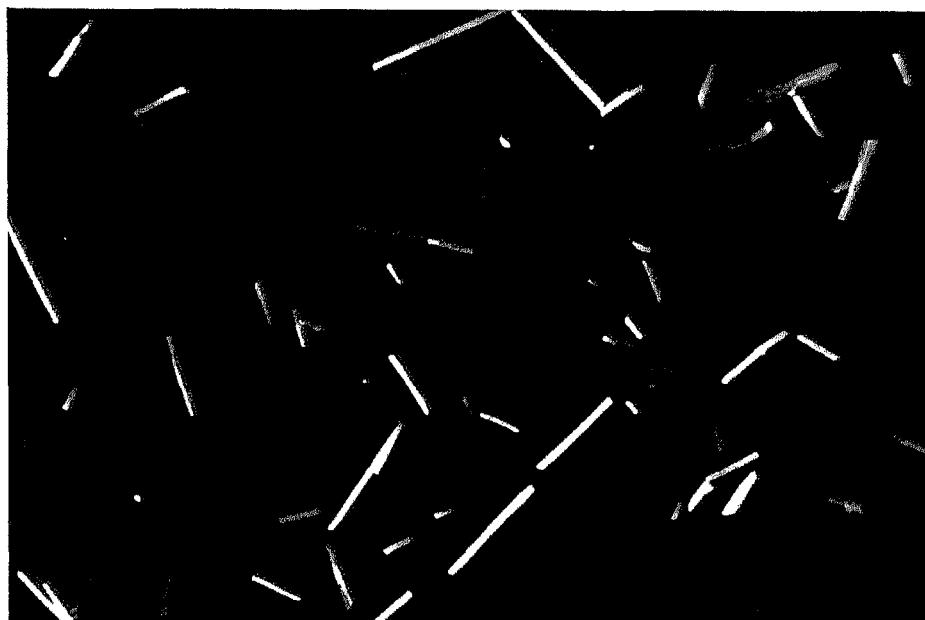
1. Introduction

The discovery of thermotropic liquid crystals in 1888 by Reinitzer [1] led to considerable interest in these materials [2, 3]. Much is known about the influence of chain length in the case of rod-like liquid crystals [4]. Generally, at a certain temperature, increase in the chain length leads to more organized mesophase structures [4, 5]. Thus, nematic phases are more stable with short chains, while smectic phases are thermodynamically favoured when longer chains are present. Compounds with intermediate chain length sometimes show polymorphism. In addition the influence of chain length on the structure and physical properties of some disc-like mesogens has been investigated. Examples include derivatives of benzene [6], truxene [7], triphenylene [8], penta-*O*-*n*-alkanoylglucopyranose [9] and metal complexes such as bis(3,4-*n*-alkoxybenzoyl)methanato-copper(II) [10], porphyrins [11], and phthalocyanines (Pc's) [12-17]. In all cases the length of the alkyl chain has a remarkable influence on the structure of the mesophase. Mesomorphic structures which have been identified are nematic [18] (N_D), lamellar (D_L) [19, 20] and columnar (ordered or disordered hexagonal, rectangular, oblique and cholesteric) [21-23]. Here we report the effect of alkyl chain length of two series of discotic liquid-crystalline octa-*n*-alkoxy-Pc's, **1** and **2**. The octoxy and dodecoxy derivatives have already been independently reported [12, 14-16].

† Department of Organic Chemistry, University at Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands



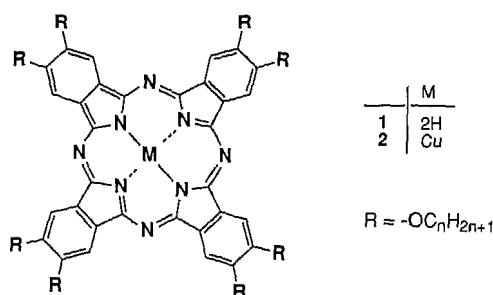
(a)



(b)

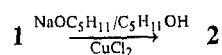
Figure 1. Micrographs of (a) digitate stars observed under a polarizing microscope upon slow cooling ($2^{\circ}\text{C}/\text{min}$) of compound **1** ($n = 11$) from the isotropic phase. Polarizer and analyser are parallel. (b) Linear birefringent defects; crossed polarizers.

Mesogenic phthalocyanines are of interest as potential one dimensional conductors [24]. However, thus far conductive properties have only been reported in the literature for bis(octa-*n*-octadodecoxymethylphthalocyaninato)lutetium [17]. Within the present series electrical conductivity measurements have been performed on the C₈ and C₁₂ homologues in their respective mesophases.



2. Synthesis

The metal-free phthalocyanines studied were synthesized and characterized as before [12]. Copper-Pcs were prepared from the free ligands by deprotonation with sodium pentanolate in pentanol and subsequent reaction with anhydrous copper(II) chloride.



After Soxhlet extraction with acetone pure **2** was isolated. Copper complexes **2** are less soluble in organic solvents than the free ligands **1**.

3. Mesomorphic properties

In order to establish the phase behaviour the compounds synthesized were investigated by polarizing microscopy and differential scanning calorimetry (D.S.C.). Upon heating above a certain temperature, the solid material melts into a highly viscous mass. In all cases polarization microscopy reveals the presence of a mosaic texture. The metal-free derivatives show a transition to the isotropic liquid for $n = 10, 11$ and 12 . Upon fast cooling ($20^\circ\text{C}/\text{min}$) the isotropic melt of these derivatives, linear birefringent defects appear, which are characteristic of (uniaxial) D_{ho}-phases [25]. Upon slow cooling ($2^\circ\text{C}/\text{min}$) digitate stars, as reported before for hexa-*n*-alkoxytriphenylenes [26] are observed when the analyser and the polarizer are parallel (see figure 1 (a)). These stars grow faster at the points where the positive curvature is large, which causes their particular shape. Eventually, the stars coalesce

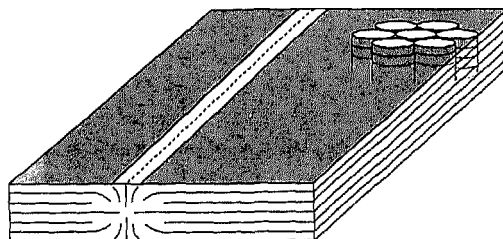


Figure 2. Schematic representation of the proposed molecular arrangement around a birefringent defect, the planes indicate the alignment of the Pc molecules and the stacks are perpendicular to these planes.

to a homeotropic aligned sample, in which linear defects are sometimes present (see figure 1 (*b*)). In figure 2 we propose a structure for these linear defects; in this the main deformation is a bend mode. We expect bend (elastic constant K_3) to be the easiest mode in analogy with rod-like molecules where splay (elastic constant K_1) is usually the easiest mode [26, 27]. This has in fact been observed in the N_D phase of discotic materials based on truxene derivatives by Warmerdam *et al.* [28, 29], and was predicted theoretically by Sokalski and Ruijgrok [30] in 1982. Moreover, Warmerdam *et al.* [28, 29] observed that at the $N_D \rightarrow D_{rd}$ transition the ratio K_1/K_3 approaches unity. Apparently, in our case of columnar D_{ho} mesophases the ratio K_1/K_3 does not approach unity, but K_1 is still larger than K_3 . In addition, no twist deformations are observed in the textures indicating that in our case the elastic constant for twist (K_2) is larger than K_3 .

Table 1. Mesomorphic properties of peripherally octa-*n*-alkoxy substituted phthalocyanines $MPc(OC_nH_{2n+1})_8$: transition temperatures and thermodynamic parameters†.

<i>M</i>	<i>n</i>	C	Transition temperature °C			$\Delta H/kJ mol^{-1}$	$\Delta S/JK^{-1} mol^{-1}$	$\Delta S/R$	
			D_{ho}	I					
2H	6	●	119[86]	●	‡	–	72	182	21.9
Cu	6	●	120[101]	●	‡	–	70	177	21.3
2H	7	●	104[75]	●	‡	–	86	228	27.4
Cu	7	●	110[78]	●	‡	–	73	190	22.9
2H	8	●	94[77]	●	‡	–	98	239	28.8
Cu	8	●	112[85]	●	‡	–	83	216	26.0
2H	9	●	101[71]	●	‡	–	94	251	30.2
Cu	9	●	106[71]	●	‡	–	93	245	29.5
2H	10	●	94[78]	●	345§	●	102	278	33.6
Cu	10	●	104[75]	●	‡	●	108	286	34.4
2H	11	●	83[66]	●	334§	●	108	303	36.5
Cu	11	●	92[70]	●	‡	–	101	277	33.3
2H	12	●	83[65]	●	309§	–	109	307	36.9
Cu	12	●	95[76]	●	‡	–	108	295	35.5

† Transition temperatures and enthalpies are observed during second and subsequent heating runs. Transition temperatures measured during a cooling run are given between square brackets. C is the crystalline phase, D_{ho} is the hexagonal ordered phase and I is the isotropic phase. Heating and cooling rate 10 K/min.

‡ No transition to the isotropic phase was visible under a polarizing microscope at temperatures below 345°C.

§ Only observed under the polarizing microscope with accompanying decomposition.

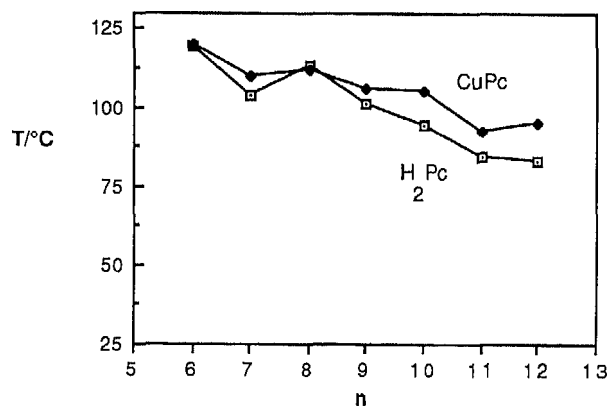


Figure 3. Transition temperature as a function of *n* for compounds 1 and 2.

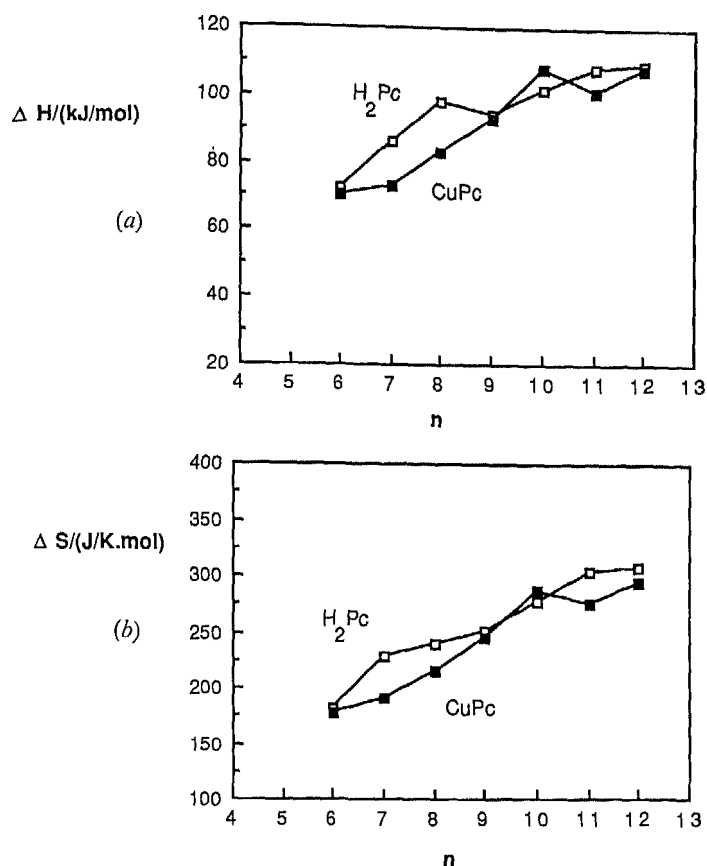


Figure 4. Enthalpy of transition ΔH (a) and entropy of transition ΔS (b) plotted as a function of n .

The transition temperatures and enthalpies were measured by D.S.C. Only one transition was detected for all compounds. The observed transition temperatures, enthalpies and calculated entropies for the solid \rightarrow mesophase transition are given in table 1. This table also gives the temperatures at which the mesophase \rightarrow isotropic liquid transition takes place for three of the free ligands. The latter temperatures were determined by hot stage (Mettler F52) polarization microscopy. These transitions could be detected by inserting a sample between two glass slides into the hot stage at 300°C and subsequently increasing the temperature at a rate of 10°C/min. Simultaneously, severe decomposition was observed at the edges of the sample. For all other compounds no transition to the isotropic liquid was detected. In figure 3 the measured crystalline to mesophase transition temperatures of **1** and **2** are plotted as a function of the number of carbon atoms n in the side chain. The transition temperature decreases with increasing n , except for some odd-even alterations. Qualitatively similar behaviour was observed for non-peripherally n -alkyl substituted Pc's [18]. In figure 4 the transition enthalpy and entropy are plotted as a function of n .

4. Structure

In the solid state, the synthesized compounds have a microcrystalline morphology, as was shown by electron microscopy (see figure 5) and electron diffraction. From the



Figure 5. Electron microscopy micrograph of the morphology of monocrystals of compound **2** ($n = 12$) at room temperature.

electron diffraction pattern it was deduced that the molecules stack in a direction parallel to the needle axis.

We have performed X-ray diffraction experiments on samples cooled from the mesophase to room temperature. An indexing scheme had to satisfy the following criteria: (i) Compounds **1** and **2** with equal side chains fitting the same scheme; (ii) all observed lines indexed; (iii) a reasonable number of molecules per unit cell; (iv) reasonable cell parameters; (v) reasonable calculated densities. In most cases approximately 20 lines varying in intensity from medium to weak were present, which could be indexed by an orthorhombic lattice with $Z = 2$. In addition approximately five very weak rings were present which could only be indexed by assuming an orthorhombic unit cell with $Z = 4$. The calculated densities vary between 1.1 for $n = 12$ and 1.4 for $n = 6$ for compounds **2**, which is in line with observed values of 1.6 for CuPc [32] and 1.1 for octa(dodecoxymethyl)phthalocyanine [33]. In all cases the 001 reflection corresponds to approximately 4.3 Å, which is the distance between two neighbouring Pc molecules within one stack. In figure 6 the calculated cell parameters a and b have been plotted against n . On average, both a and b increase with increasing n , although the variation in b is somewhat more pronounced than that in a . This might be explained by assuming that the molecules in the solid phase have a preferred tilt around the b axis, we will come back to this later. The difference between a and b becomes less with increasing n .

In the mesophase X-ray diffraction gives 4 to 5 reflections at small angles ($1/d = 1/\sqrt{3}: 1/\sqrt{4}: 1/\sqrt{7}: 1/\sqrt{9}$) corresponding to a hexagonal lattice, a broad and diffuse reflection around 4.6 Å as a consequence of the liquid-like order of the aliphatic chains and a strong and much sharper reflection at 3.4 Å which is ascribed, as before [13, 14, 15], to the ordering of discs within one column. In addition a broad and weak reflection with a spacing of 7.0 Å is present in all cases. With reference to work performed by

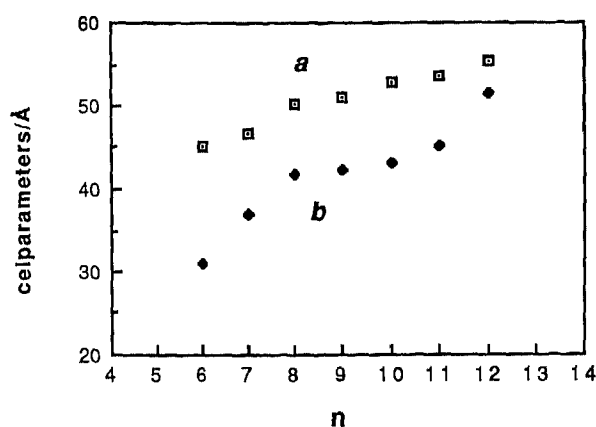


Figure 6. Cell parameters a and b of the orthorhombic lattice as a function of n .

De Jeu *et al.* [31] on monocrystals of hexa-*n*-hexylthiotriphenylene this reflection is ascribed to the presence of some kind of intracolumnar order. According to the nomenclature introduced by Destradé *et al.* [34] this structure is assigned the symbol D_{ho} , a picture of such a D_{ho} phase is presented in figure 7. Ordered columns are preferred for 2,3,9,10,16,17,23,24-octa-*n*-alkoxy-Pc-derivatives because of the low steric hindrance of the side chains, which allows a strong cohesion between the discs. Disordered columns are preferred for the corresponding *n*-alkoxymethyl substituted compounds, since their side chains point out of the plane of the aromatic Pc-nucleus [12, 15]. From the occurrence of only $hk0$ and $00l$ reflections it can be concluded that no correlations between molecules in different columns exist in contrast to what was observed for hexa-*n*-hexylthiotriphenylene, but here the driving mechanism for the existence of the correlations is probably the $D_{hd} \rightarrow D_{ho}$ transition, since general considerations predict that phase transitions are impossible in strictly one dimensional systems [35].

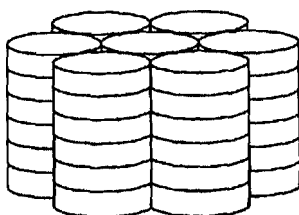


Figure 7. Schematic drawing of a D_{ho} phase.

The dependence of the intercolumnar distance on alkyl chain length was studied at 200°C (see figure 8). As expected this distance increases with chain length. An apparently linear relationship, similar to that reported before for other homologous series of columnar mesophases, is found [7, 35]. Such an empirical correlation has no physical basis, however [35] instead, D^2 should be studied as a function of n , as will be done from now on. For every additional methylene unit an average increase of 1.26 Å was found for both series 1 and 2.

When the intercolumnar distance D and intercore distance c are known, the molecular volume, V , and density, ρ , of the lattice can be calculated according

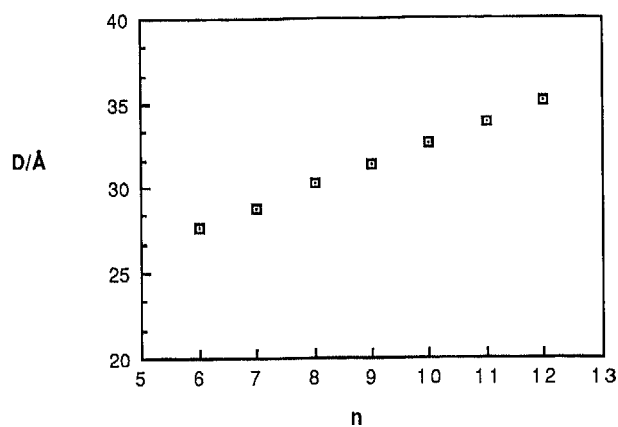


Figure 8. Intercolumnar distance as a function of n for compounds 1 and 2.

to

$$V = \frac{\sqrt{3}}{2} D^2 c$$

and

$$\rho = M/(N_A V),$$

where M is the molecular weight. The dependence of these parameters on n is shown in figures 9 and 10. The lattice volume increases linearly with n , implying a constant increment per added methylene group. The lattice density decreases as a consequence of the fact that the alkyl chains have a lower density than the Pc core. The volume of a molecule in the solid phase was calculated according to

$$V = abc/Z,$$

where Z is the number of molecules per unit cell, and this volume is also plotted in figure 9. The transition from solid to mesophase is thus accompanied by an increase in molecular volume.

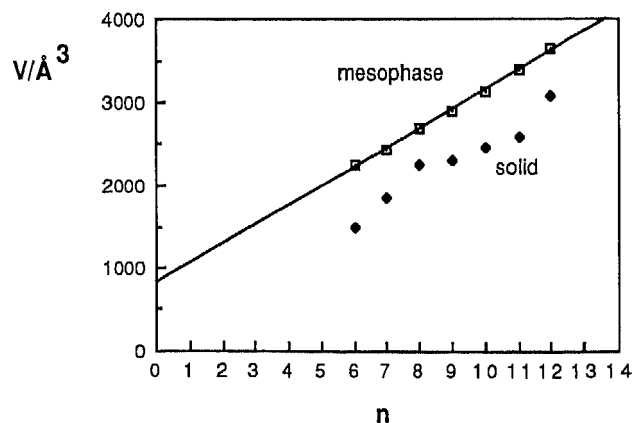


Figure 9. Molecular volume V in the solid and liquid-crystalline state as a function of n for compounds 2.

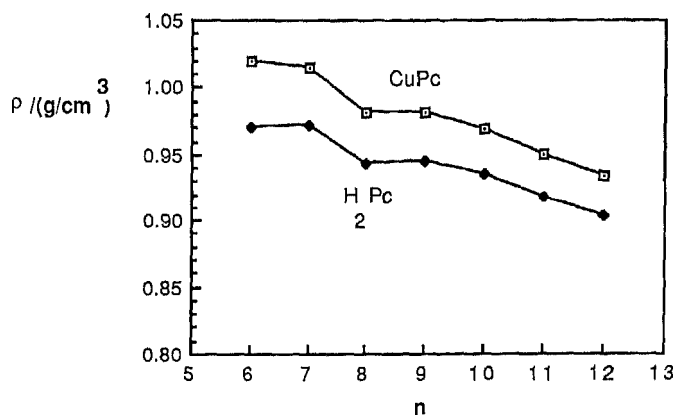


Figure 10. Lattice density (ρ) as a function of n for compounds **1** and **2**.

The apparent Pc core size can be estimated from

$$D_n^2 = D_0^2 + 32nV_m/\pi c, \tag{1}$$

where D_n is the diameter of a column for the n th homologue, D_0 is the core diameter, including the ether oxygen and the excess volume of the terminal methyl group, and V_m is the mean volume of a methylene group (see figure 11). A plot of D_n^2 as a function of n (see figure 12) gives a straight line from which values of 16.8 \AA for D_0 and 26.4 \AA^3 for V_m can be calculated. The value of D_0 found in this study is consistent with the diameter of 13.9 \AA calculated for unsubstituted Pc from X-ray studies [37] and the value of 17 \AA estimated for D_0 from CPK models. Although rotation of the whole molecule around the normal to the molecular plane and fluctuations of this axis around the core direction might be possible in the mesophase, this agreement implies

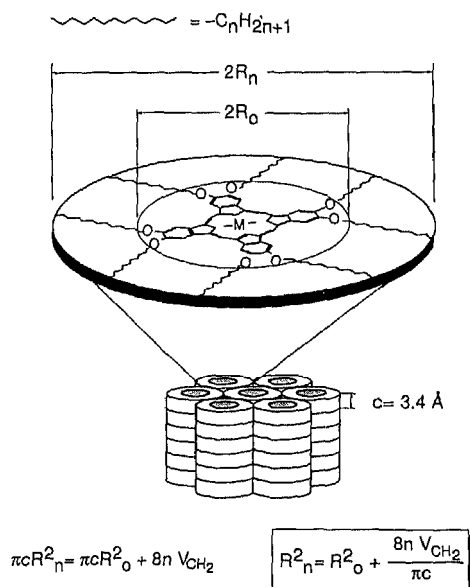


Figure 11. Model corresponding to equation (1).

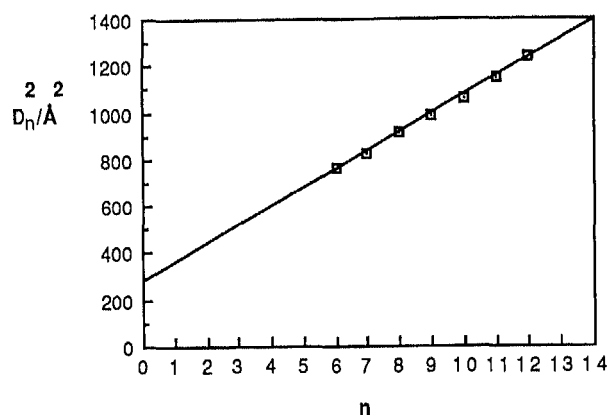


Figure 12. D_n^2 as a function of n for compounds 2.

that in the mesophase the plane of the Pc nucleus is on average perpendicular to the column axis. This untilted stacking gives rise to interesting physical phenomena, such as efficient exciton and electron migration through the columns [38–40]. The observed diffuse diffraction feature, shows that in the mesophase the aliphatic side chains are in a molten state. For disordered side chains in hexa- n -alkoxytruxenes a value of 27.4 Å^3 is found for V_m at 80°C , suggesting that in our case the side chains are somewhat less disordered than for truxenes [41]. Temperature dependent FTIR and CPMAS NMR studies will further clarify this point [42].

5. Aggregation behaviour in solution

In order to examine their aggregation behaviour in solution compounds 1 ($n = 8, 10, 12$) have been studied by absorption and fluorescence spectroscopy as a function of solvent polarity in mixtures of chloroform and methanol and as a function of concentration in chloroform solution.

5.1. Solvent polarity

Absorption spectra of metal-free mononuclear Pc in chloroform solution consist of two intense π - π^* transitions at 664 and 700 nm (Q bands) with associated higher energy vibrational components, and a second intense and broader π - π^* transition at 300–360 nm called the Soret band [43]. The intensity of the Q bands decreases if the solvent is changed from chloroform to more polar solvents such as methylene chloride, DMF, acetone and methanol. Similar spectroscopic changes are also observed in mixed solvents, e.g. by mixing methanol with chloroform. This effect is illustrated for compound 1 ($n = 10$) in figure 13; with increasing ratio of methanol to chloroform, the peak heights at 664 nm and 700 nm (mainly mononuclear species) decrease, but that at 625 nm (mainly aggregated species) [44, 45] increases. From the changes in absorption characteristics it can thus be concluded that aggregation becomes more important with increasing solvent polarity.

Mononuclear metal free Pc exhibits a fluorescent emission from the lowest π - π^* state (Q -band) near 707 nm (λ_1) [46]; this main band is accompanied by three other bands ($\lambda_2 = 666$, $\lambda_3 = 742$ and $\lambda_4 = 786$ nm). When these solutions are studied by fluorescence spectroscopy the main effect observed is a marked decrease in emission

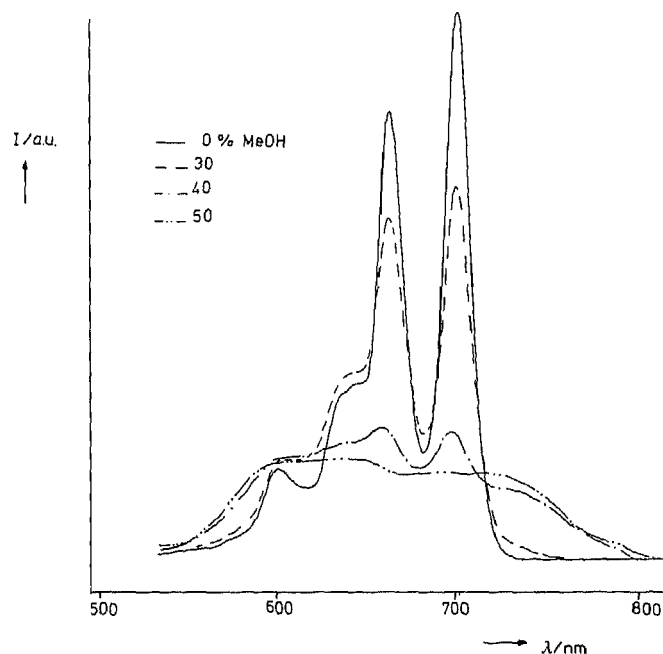


Figure 13. UV/Vis absorption spectra of **1** ($n = 10$) in chloroform and in mixtures with increasing amounts of methanol: 0 per cent, 30 per cent, 40 per cent and 50 per cent, concentration of **1** is $1 \times 10^{-6} \text{ mol/dm}^3$.

emission intensity, when methanol concentrations exceed 20 per cent v/v. This is illustrated in figure 14, where the intensity of the emission peak at 707 nm is plotted against the methanol content. The other characteristics of the emission spectra remain unchanged, i.e. the shape of the fluorescence spectra is independent of methanol content. The residual emission intensity present when the methanol concentration exceeds 30 per cent v/v, has an excitation spectrum identical to that of the monomer species, indicating that the aggregated species does not emit. This conclusion is in line

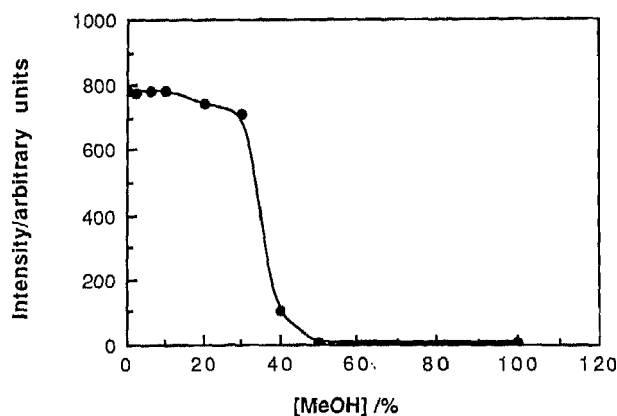


Figure 14. Decrease in emission intensity as a function of methanol content for compound **1** ($n = 10$).

with aggregation studies of dinuclear, tetranuclear, and polynuclear Pc's [47, 48], and studies of cation-induced dimerization [49]. The near absence of emission intensity of the aggregates might be caused by more efficient self-quenching through several possible mechanisms including relaxation to triplet states [49] and nonradiative vibrational relaxation.

5.2. Concentration study

The absorption properties of the metal free derivatives **1** ($n = 8, 10, 12$) have been studied in chloroform over the concentration range 6×10^{-4} to 10^{-6} mol/dm³. Within the concentration range studied, no significant changes in the absorption spectra occur and the species exhibit spectral typical of mononuclear Pc's. In contrast to this the luminescence spectra undergo a dramatic change upon increasing concentration. The emission maximum at λ_1 undergoes a red shift and the intensity of the emission spectra increases over the concentration range 10^{-6} and 10^{-5} mol/dm³. When the concentration is raised further the emission intensity decreases drastically, indicating that absorption processes become dominant. Simultaneously, the higher wavelength band becomes more dominant, the same behaviour is observed for the other homologues studied here. Similar effects have been observed by Knoesel *et al.* for $\text{H}_2\text{Pc}(\text{CH}_2\text{OC}_{12}\text{H}_{25})_8$ in benzene and 1-chloronaphthalene solution [51]. These authors interpret their observations in terms of aggregation of Pc-species. Aggregation is, however, not indicated by the absorption spectra. In line with the change in fluorescence characteristics upon aggregate formation when the solvent polarity is increased, a more feasible explanation might be based on reabsorption of emitted fluorescence intensity. Figure 15 shows that the absorption spectrum overlaps those luminescence bands which decrease in intensity upon increasing concentration.

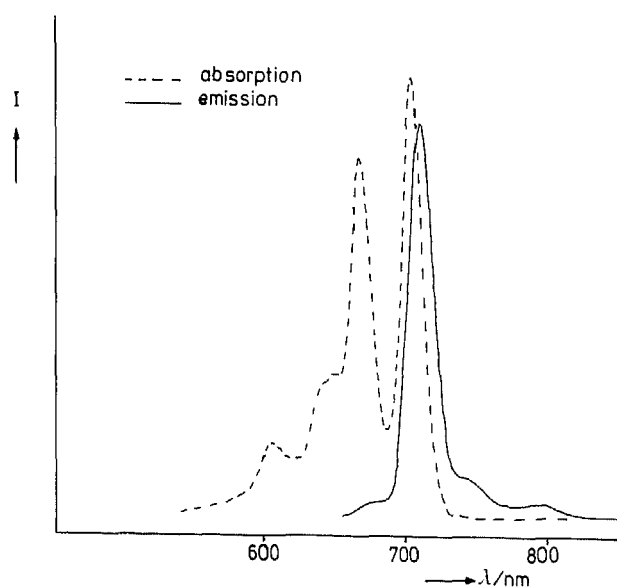


Figure 15. Fluorescence ($\lambda_{\text{exc}} = 300$ nm) and absorption spectra of compound **1** ($n = 10$) in chloroform solution, showing their overlap.

6. Electrical conductivity

The electrical properties of phthalocyanine **2** were studied for $n = 8$ and $n = 12$ on pressed pellets by complex impedance measurements as described previously [52]. Measurements on pressed pellets were possible because of the very high viscosity of the mesophase, although some difficulties were encountered in maintaining good contacts. Electronically conducting CuPc was used as a reference compound. Figure 16 shows some typical impedance spectra taken at various temperatures for the derivative with $n = 12$, similar spectra were obtained for the derivative with $n = 8$.

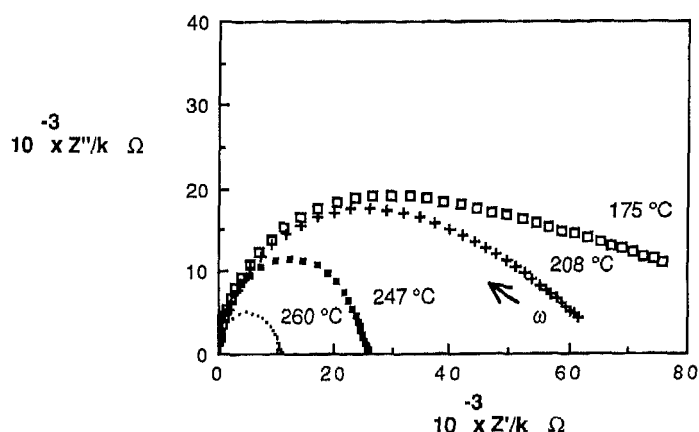


Figure 16. Impedance spectra as observed for compound **2** ($n = 12$) at 175, 208, 247 and 260°C.

The equivalent circuit to which the spectra could be fitted appear to be a RCQ -parallel. Here R is the resistance of the bulk material, C is the geometric capacitance and Q is a constant phase element $Q = Q_0 (i\omega)^{-\alpha}$ where ω stands for frequency. The capacitance was almost constant for these experiments. From the formula for a plane plate capacitor $C = \epsilon_0 \epsilon_r A/d$ the relative dielectric constant ϵ_r was calculated. In the columnar mesophase, the conductivity increases with increasing temperature, this behaviour is characteristic for semiconductive materials. The corresponding Arrhenius plots were constructed according to $\sigma = \sigma_0 \exp(-E_a/kT)$ and straight lines were obtained between 150 and 265°C for $n = 8$. For $n = 12$ a discontinuity in the Arrhenius plot (see figure 17) appears at approximately 250°C indicating a transition between an intrinsic transport regime at high temperatures (with a high activation energy) and an extrinsic one (with a lower activation energy) at low temperatures [53]. Extrinsic charge transport is found in most Pc's and is caused by the presence of trace impurities [53]. Upon going from the solid to the mesophase a slight decrease in conductivity was observed. The electrical conductivities at 175°C, activation energies for conduction and the preexponential factors σ_0 are presented in table 2. Conductivities found at 175°C are in the same range as for CuPc [54]. The activation energies are of the same order of magnitude as those found in columnar phases of hexa-*n*-alkoxytriphenylenes [55]. The activation energies given in table 2 are lower than those of the unsubstituted crystalline compounds. This difference might also be the result of a better orbital overlap between the Pc units in a stack, resulting in a substantial lowering of the gap between the valence and conduction bands of the material. This conclusion is in line with time resolved microwave conductivity

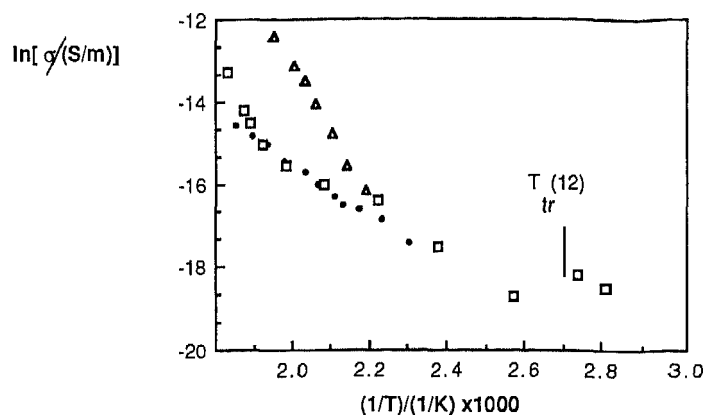


Figure 17. Arrhenius plots of the conductivity for CuPc, Δ , and compounds **2** for $n = 8$ denoted by \bullet and **12** represented by \square .

Table 2. Electrical conductivity σ and relative dielectric constants at 175°C, activation energy of conduction and preexponential factors for CuPcR_8 .

R	$\sigma_{175}/\text{S m}^{-1}$	$\epsilon_r(175^\circ\text{C})$	E_a/eV	$\ln[\sigma_0/\text{S m}^{-1}]$
H	6×10^{-8}	6.8 \ddagger	1.4	20.0
$-\text{OC}_8\text{H}_{17}$	5×10^{-8}	8.2	0.6	2.6
$-\text{OC}_8\text{H}_{17} + \text{I}_2^\dagger$	3×10^{-3}	—	—	—
$-\text{OC}_{12}\text{H}_{25}$	7×10^{-8}	8.8	$T < 250^\circ\text{C}: 0.5$ $T > 250^\circ\text{C}: 1.7$	4.7 21.6

\dagger Measured at 40°C.

\ddagger See [57].

measurements which have been performed on these compounds [56]. According to the work of Belarbi *et al.* [17] an activation energy of approximately 0.5 eV corresponds to intercolumnar electron hopping. Conductivities of both compounds studied are of the same order of magnitude within experimental error, indicating that bulk conductivity is not much dependent of side chain length.

Doping of molecular materials by strong electron donors or acceptors is expected to increase the conductivity, since free electrons or holes, respectively, are created in the conduction and valence bands. Doped samples were prepared by placing powdered **2** ($n = 8$) in an iodine atmosphere for two to three days. The molar ratio of **2** ($n = 8$) to I_2 was determined to be 1 to 1 by weight and by TGA. After this treatment the conductivity increases by at least four orders of magnitude (see table 2).

7. Conclusion

Two series of octa- n -alkoxyphthalocyanines have been synthesized. In the solid state these compounds are arranged in an orthorhombic lattice with four molecules per unit cell. At higher temperatures this lattice is converted to a hexagonal ordered columnar D_{10} mesophase for all the compounds studied. Comparison of absorption and fluorescence measurements in solution have shown that in the concentration range 6×10^{-4} to 10^{-6} mol/dm³, aggregation is not important. Conductivities of the derivatives with $n = 8$ and $n = 12$ have been determined and are of the order of

5×10^{-8} S/m. A slight decrease in conductivity is observed when going from crystal to mesophase. The activation energies for conduction are approximately 0.5 eV between 100 and 250°C. These low values might be related to an increased π - π overlap with respect to unsubstituted CuPc within a columnar stack.

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