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Liquid Crystals

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Discotic mesomorphism of 2,3,7,8,12,13,17,18-octakis (alkyl-thio) 5,10,15,20 tetraaza porphyrin and its complexes with some divalent transition metal ions Synthesis and characterization

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To cite this Article Lelj, Francesco , Morelli, Giancarlo , Ricciardi, Giampaolo , Roviello, Antonio and Sirigu, Augusto(1992) 'Discotic mesomorphism of 2,3,7,8,12,13,17,18-octakis (alkyl-thio) 5,10,15,20 tetraaza porphyrin and its complexes with some divalent transition metal ions Synthesis and characterization', *Liquid Crystals*, 12: 6, 941 – 960

To link to this Article: DOI: 10.1080/02678299208032810

URL: <http://dx.doi.org/10.1080/02678299208032810>

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**Discotic mesomorphism of 2,3,7,8,12,13,17,18-octakis (alkyl-thio)
5,10,15,20 tetraaza porphyrin and its complexes with some divalent
transition metal ions**

Synthesis and characterization

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(Received 13 March 1992; accepted 29 May 1992)

New discotic metallomesogens of 2,3,7,8,12,13,17,18-octakis (alkyl-thio) 5,10,15,20 tetraaza porphyrin (H2P_n) and some related complexes, obtained by reaction of first row transition metal ions Ni(II), Co(II), Cu(II), Zn(II) with the free porphyrin, have been prepared. All materials were characterized by DSC measurements and optical observations.

The microscopic structure of all mesophases was checked and characterized by X-ray diffraction. Except for H2P(7-12), all of the compounds are mesogenic; a few of them exhibit mesomorphic polymorphism. Melting (C→D) temperatures range from 40 to 85°C. Only NiP₄, CoP₄ and CuP₄ show higher values. Both temperature and ΔH of isotropization (D→I) show a regular trend with respect to the number of carbon atoms in the alkyl chains and of the nature of the metal. ΔH values for complexes with partially filled d-shell metals are very similar and show definite differences with respect to those of Zn(II).

Optical and X-ray data in the case of $n \geq 7$ indicate a columnar mesophase with hexagonal packing whereas in complexes with $n < 7$ the observed mesophase shows a non-hexagonal columnar packing.

CuP₆ and NiP₆ probably show both mesophases which are connected by a phase transition, presumably of second order or with exceedingly low enthalpy change but easily detected by polarizing microscopy because of sharp texture changes. As expected, no odd-even effect is detectable on the properties of the liquid-crystalline phases as a function of the number of carbon atoms in the aliphatic chains.

1. Introduction

Metallomesogens introduce into coordination chemistry the peculiar physical properties exhibited by liquid crystals. Among the reasons why this class of mesogens is attracting interest is the possibility to obtain new materials that can show properties not easily obtained by organic liquid crystals and that are useful in developing new optical devices, materials for molecular electronics, electrical and magnetic switches. The complexation of metals allows us to obtain highly absorbing substances in the UV and visible spectrum and introduces in an easy way magnetic properties by using

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metals with an odd number of electrons or metals in a high spin electronic configuration even preserving a low or moderate reactivity of the produced substances; in contrast such a task is not likely to be simple for organic substances.

Mesophase formation depends on the anisotropy of the spatial distribution (i.e. molecular shape) and the strength of intermolecular forces, therefore, in principle, both the molecular structure of the ligands and the coordination geometry to a specific metal atom can be relevant in defining the mesogenic nature of the complex. When the complex molecule is built with a single flat, disc-like, polydentate ligand the occurrence of discotic mesomorphism (D) is expected. Moreover the nature of the coordinated metal plays a more subtle role allowing fine tuning of the intramolecular interactions with further control of the macroscopic properties of the material obtained.

Among the different properties (for example optical and magnetic) that liquid crystals can have, electrical conductivity is particularly interesting. Several recent attempts have been reported [1–5] to produce conducting liquid crystals. Calamitic liquid crystals from rod-shaped molecules have been found to be insulators and any conductivity formed is ionic in nature [6–7]. In the case of the columnar liquid crystal phase of bis(octadecyl oxymethyl phthalocyaninato) lutetium [8] intracolumnar conduction is observed especially in partially oxidized materials as has been observed for other materials in the solid state [9–10].

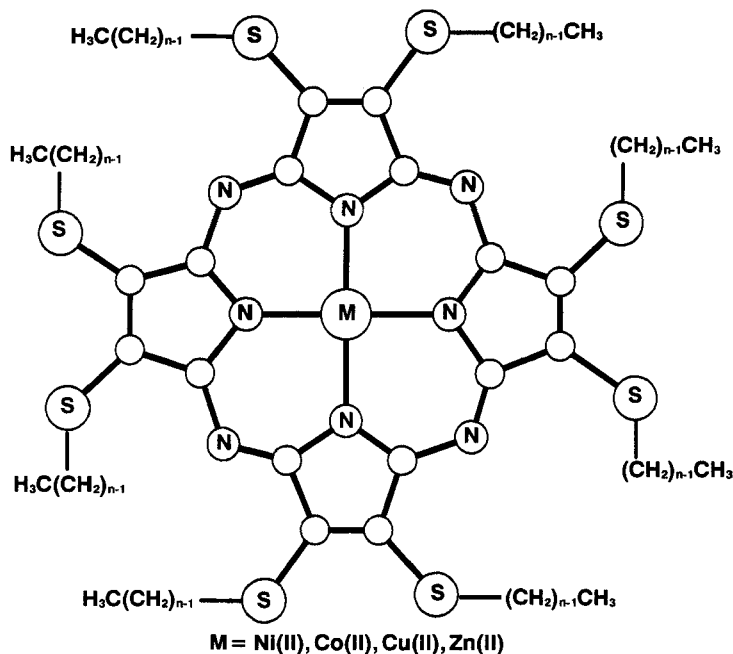
Among the single flat polydentate ligands phthalocyanine has been the most widely investigated [11] also in connection with different metals [12] though other disc-like polydentate ligands have been used: octa dodecyl tetrazapyrazino porphyrine [13], substituted dibenzo tetraazaannulenes [14] and substituted porphyrins [15]. Porphyrin complexes with Cu(II), Cd(II), Zn(II) and Pd(II) have been reported [15] and carefully characterized. The results indicate a clear influence of the metal and the length of the alkyl chains (i.e. the number of CH₂ units) on the mesomorphic behaviour although it cannot be related to simple models based on donor-acceptor interactions between stacked porphyrin molecules. Within this class of ligands the 2,3,7,8,12,13,17,18-octakis (alkyl-thio)-5,10,15,20 tetraaza porphyrin (hereafter S-Porphyrin) seem of particular interest because:

- (i) near the delocalized core, sulphur atoms are present which are more polarizable than oxygen and can increase the intrastack interactions and enhance possible intracolumnar and intercolumnar electron motions [18];
- (ii) efficient synthesis can be worked out that allows the easy introduction of alkyl chains with a variable number of carbon atoms and with very high yields.

The synthesis and mesomorphic behaviour of Co, Cu, Ni and Zn complexes of octakis(octylthio)tetraazaporphyrins has been reported recently by Doppelt and Huille [16] showing the hexagonal columnar nature of the mesophase. The results of an independent study by Morelli *et al.* [17] on the copper complex with the same ligand agree with those reported by Doppelt and Huille.

To characterize further the behaviour of this class of substances we have studied the role played by the nature of the alkyl chain length on the mesomorphic properties of four homologous series containing Ni(II), Co(II), Cu(II), Zn(II) ions (see structure) and different numbers of carbon atoms in the alkyl chains. The nature of the mesophase has been investigated and the mesogenic quantities related to the phase transitions measured. The study has been extended to the free S-Porphyrins (H₂Pm) related to the metal complexes. As far as the octylthio compounds are concerned, our results are in

substantial agreement with those previously obtained by Doppelt and Huille [16]. A few differences, mostly concern the solid phase and might be accounted for with the tendency to polymorphism shown by this class of compounds (*vide infra*).



2. Experimental

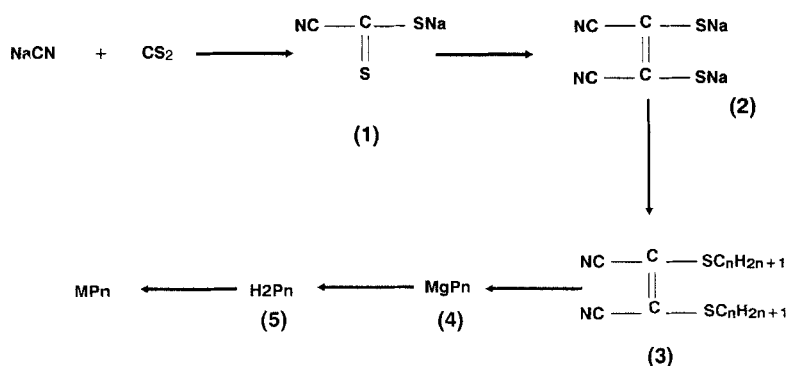
2.1. Characterization techniques

NMR. ^1H NMR spectra were recorded on a 300 MHz Bruker AM-300 spectrometer with $(\text{CH}_3)_4\text{Si}$ as the internal standard. UV-vis spectra were run using a Varian-Cary 2300 spectrometer at room temperature. IR spectra were recorded as nujol mulls with a Perkin-Elmer 830 spectrophotometer. Elemental analyses were performed by the Analytical Laboratory, Faculty of Engineering in Potenza, Italy and by the Analytical Laboratory, Drs H. and G. Reuter, Gunnersbach, Germany. FAB mass spectra were recorded on a VAG ZAB 2SE double focusing mass spectrometer equipped with a caesium gun operating at 25 kV (2 mA).

Optical observations of textures as a function of temperature were performed with a Leitz polarizing microscope equipped with a Linkam microfurnace. X-ray diffraction patterns were recorded by the photographic method (flat film camera) utilizing a temperature controlled microfurnace. Samples were kept under a dry nitrogen atmosphere in sealed Lindemann glass capillaries at the appropriate temperature (*vide infra*). Differential scanning calorimetry measurements were performed using a Perkin-Elmer DSC7. Electronic structure computations were performed in the neglect of differential overlap (NDO) approximation with the AM1 [19] parameterization using the version 6.0 of MOPAC [20] and by the EH model using the EHMACC program [21]. In the latter case a double zeta quality of Slater functions on the metal was used. Relative orientations of the molecules within an isolated column were modelled by a simple molecular mechanics [22] approach using Macromodel v 2.5 [23] and its MM2 force field implementation [24].

2.2. Synthesis

The ligands were synthesized according to the scheme by a modification of the method used by Schram and Hoffman [25] for the synthesis of the octakis-methylthio derivative. Standard chemicals (Aldrich Chemical, Fluka AG and Carlo Erba) were used as supplied without further purifications and sample handling was performed in the open air.



$\text{C}_4\text{N}_4\text{S}_2\text{Na}_2$ (1): Sodium *cis* 1,2-dicyano-1,2-ethylenedithiolate was prepared according to the procedure of Bahr *et al.* [26].

1,2-dicyano-1,2-bis(alkyl-thio)ethylene (2): Compounds with different alkyl moieties ($n=4,6,7,8,9,10,12$; where n is the number of carbon atoms in each alkyl chain) were obtained by the procedure of Bahr *et al.* [26] with some modifications. To a vigorously stirred suspension of 1 (8.0 g; 44.4 mmol) in methanol (20 ml) cooled by a water-ice bath (0°C) $\text{C}_n\text{H}_{2n+1}\text{Br}$ (in the case of $\text{C}_4\text{H}_9\text{Br}$: 6.27 g; 55.0 mmol) was added dropwise. The temperature was increased to 25°C and the solution was stirred continuously. After 24 h the resulting solution was kept overnight at -20°C . Compound 2 separated as a very malleable solid or very viscous oil. This compound, washed by water and dried over sodium sulphate, was further purified by silica gel chromatography using dichloromethane as eluent. The absence of alkyl halide was checked by NMR. The yield of the reaction was higher than 80 per cent.

MgPn (3): Magnesium 2,3,7,8,12,13,17,18-octakis (alkyl-thio) 5,10,15,20 tetraaza porphyrinato. 1.0 g (43.3 mmol) of Mg powder was refluxed overnight in 50 ml of *n*-propanol. 8.24 g (43.4 mmol) of 2 was added to the suspension under stirring and the solution was refluxed (24 h). The crude product was filtered when hot and the filter washed with boiling methanol and further with acetone. The solution obtained was dried under high vacuum. The highly viscous dark blue liquid was chromatographed in Florisil using chloroform as eluant and crystallized from acetone. (Yield: 70 per cent.)

H2Pn (4): 2,3,7,8,12,13,17,18-octakis (alkyl-thio) 5,10,15,20 tetraaza porphyrine. Pure solid 3 was dissolved in the minimum amount of CF_3COOH and carefully poured on to ice. The solution was then neutralized with concentrated ammonia. The dark product was then filtered. The solid obtained was washed in a separating funnel with water till full neutrality of the washing water. The solid was then dissolved in CHCl_3 and after removal of the solvent the crude product was chromatographed on Florisil using chloroform as the eluant. (Yield: 70 per cent.) Elemental analyses for all the alkyl derivatives are reported in table 1.

Table 1. Elemental analysis data for all the free H2Pn ($n=4, 6, 7, 8, 9, 10, 12$).

<i>n</i>		Per cent					
		C		H		N	
		Found	Calc.	Found	Calc.	Found	Calc.
4	C ₄₈ H ₇₄ N ₈ S ₈	56.54	56.48	7.31	7.28	10.99	10.85
6	C ₆₄ H ₁₀₆ N ₈ S ₈	61.78	61.70	8.59	8.60	9.10	9.10
7	C ₇₂ H ₁₂₂ N ₈ S ₈	63.76	63.70	9.07	9.10	8.26	8.20
8	C ₈₀ H ₁₃₈ N ₈ S ₈	65.48	65.80	9.50	9.53	7.61	7.72
9	C ₈₈ H ₁₅₄ N ₈ S ₈	66.86	66.78	9.82	9.85	7.09	7.00
10	C ₉₆ H ₁₇₀ N ₈ S ₈	68.11	68.15	10.12	10.18	6.62	6.60
12	C ₁₁₂ H ₂₀₂ N ₈ S ₈	70.16	70.20	10.62	10.59	5.85	5.90

MPn: Metal(II) 2,3,7,8,12,13,17,18-octakis (alkyl-thio) 5,10,15,20 tetraaza porphyrinato [M = Ni(II), Co(II), Cu(II), Zn(II)]. We report, for instance, the synthesis of CoP10. 0.100 g of H2P10 was dissolved in 15 cm³ of warm dioxane and a warm solution of CoCl₂·6H₂O (0.070 g) and anhydrous sodium acetate (0.020 g) in absolute ethanol was added under stirring. The solution was heated until boiling under stirring for 15 min. The crystallized compound was filtered and further dissolved in CHCl₃ and purified by column chromatography using silica gel. Further crystallization was performed using dioxane/ethanol 20/80 in volume. (Yield 0.08 g.)

Copper and Nickel derivatives were prepared with this procedure using chloroethanol as a solvent for the free porphyrin and absolute ethanol for the copper salt (CuCl₂·H₂O) and NiCl₂·6H₂O + sodium acetate, respectively. The products were purified by column chromatography using Florisil and chloroform as eluant.

All other compounds were prepared by dissolving the corresponding porphyrine in dioxane.

In the case of ZnP4 the solution containing the reaction product was dried under vacuum and the product purified by chromatography using basic alumina. The product was further crystallized from methanol.

FAB mass spectrometry was performed for NiP4 and NiP8. Molecular peaks were obtained at *M/Z* 1075–1077 and 1524–1526 respectively. For other compounds different techniques were used for probing the purity of the product (*vide infra*).

A few comments are in order about the synthetic procedure. The main point concerns the preparation of the free porphyrins and their metal derivatives. In particular we found along the whole series of alkyl derivatives ($n=4,6,7,8,9,10,12$) that, probably owing to the length of the alkyl chains, the reaction of stripping of magnesium gives better results if trifluoroacetic acid is used, as also recently found for the octyl derivatives [16, 17], instead of sulphuric acid as previously suggested [25]. Furthermore since this is a key step in the synthesis of the metal derivatives, we carefully purified the compounds and performed accurate analytical control of the compound purity (see tables 1 and 2 for the elemental analysis and NMR data, respectively).

As concerns the synthesis of the metal derivatives a new fast procedure was obtained that allows the reaction to be performed in solution instead of using heterogeneous phases [25]. In the new procedure the reaction takes virtually only the

Table 2. ^1H chemical shifts (ppm) for the alkylic hydrogens. Paramagnetic Co and Cu compounds are not reported due to broadening effects.

^1H NMR spectra of diamagnetic porphyrine derivatives MPn (σ ppm)						
<i>M</i>	<i>n</i>	S-CH ₂	CH ₂	CH ₂	(CH ₂) _{m-4}	CH ₃
H2	4	4.090 t	1.87 dt	1.64 dq	—	0.95 t
	6	4.088 t	1.87 dt	1.59 dt	1.28 m	0.82 t
	7	4.088 t	1.87 dt	1.58 dt	1.2 m	0.79 t
	8	4.087 t	1.87 dt	1.58 dt	1.2 m	0.78 t
	9	4.087 t	1.87 dt	1.58 dt	1.2 m	0.80 t
	10	4.088 t	1.87 dt	1.58 dt	1.2 m	0.80 t
Ni	4	4.01 t	1.81 dt	1.60 dq	—	0.92 t
	6	4.01 t	1.83 dt	1.57 dt	1.3 m	0.82 t
	8	4.01 t	1.83 dt	1.57 dt	1.2 m	0.79 t
	10	4.01 t	1.83 dt	1.57 dt	1.2 m	0.80 t
	12	4.01 t	1.84 dt	1.56 dt	1.2 m	0.84 t
		4.01 t	1.84 dt	1.56 dt	1.2 m	0.84 t
Zn	4	3.78 t	1.64 dt	1.50 dq	—	0.87 t
	6	3.79 t	1.65 dt	1.47 dt	1.2 m	0.82 t
	8	3.78 t	1.63 dt	1.46 dt	1.2 m	0.80 t
	10	3.77 t	1.66 dt	1.46 dt	1.2 m	0.80 t

t = triplet; dt = doublet-triplet; dq = doublet-quartet; m = multiplet.

time of mixing the two solutions. However, a few minutes (10–15 min) of reflux were allowed to complete the reaction.

The characterization of these compounds was partially obtained by elemental analysis of the metal percentage of some samples whereas careful characterization, in diamagnetic compounds, was obtained by NMR. In fact, the chemical shift of the hydrogen of the methylene group directly linked to the sulphur atoms shows a definite and regular trend as a function of the complexed metal (see table 2). Using the chemical shift it was easy to follow the metal insertion reaction further confirmed by the disappearance of the low field H_N resonance. A further check of the degree of contamination by the H2Pn in the samples of MPn was obtained by the thermodynamic data, i.e. the enthalpy and transition temperature for the discotic to isotropic transition. Here in fact, a few tenths of a per cent of impurities strongly modify the shape of the thermogram and transition temperatures, as well. Therefore we checked the thermogram and further purified the samples until the shape and the values of the thermodynamic data did not show any further significant change.

3. Results and discussion

3.1. Phase behaviour

Unsubstituted porphyrins (H2Pn). The relevant thermodynamic data concerning the phase behaviour of unsubstituted porphyrins are reported in table 3. Compounds H2P4 and H2P6, which are the only ones showing unambiguous evidence of mesomorphism, exhibit a strictly homologous phase behaviour also in the solid state.

Table 3. Temperature and enthalpy changes of melting (m) and isotropization (i) for MPn compounds.

M	H ₂			Co			Ni					
	T _m /°C	ΔH _m /kJmol ⁻¹	T _i /°C	ΔH _i /kJmol ⁻¹	T _m /°C	ΔH _m /kJmol ⁻¹	T _i /°C	ΔH _i /kJmol ⁻¹	T _m /°C	ΔH _m /kJmol ⁻¹	T _i /°C	ΔH _i /kJmol ⁻¹
4	113.1§	15.7	121.9	7.4	96.0	8.19†	271.0	>8.4	116.9	16.3	183.5	11.0
6	77.6§	56.2	92.2	4.6	45.2†	33.2	243.6	10.5	75.3	57.8	154.3†	8.74
7	75.0§	78.4		¶								
8	81.5	101		¶								
9	78.6	105		¶								
10	80.7	168		¶								
12	85.4	182		¶								

M	Cu			Zn				
	T _m /°C	ΔH _m /kJmol ⁻¹	T _i /°C	ΔH _i /kJmol ⁻¹	T _m /°C	ΔH _m /kJmol ⁻¹	T _i /°C	ΔH _i /kJmol ⁻¹
4	111.7§	15.5	222.8	11.7	53.6	22.9	208.0	5.4
6	80.3†	57.8†	189.7†	10.7	46§	76.0§	167.7	4.2
7	70.2	77.1	169.5†	8.9				
8	67.6§	99.6	151.7	8.6	40.8	39.4	119.6	3.5
9	61.8	114	132.9	7.9	48.8§	36.5		
10	68.7	147	121.7	7.4	53.7§	140	87.3	2.8
12	83.2	183	102.3	6.9				

† See text; ‡ further transition at 57.2°C with ΔH = 2.8 kJmol⁻¹; § polymorphism; || the sample decomposes; ¶ mesomorphism is not present.

Table 4. Observed d values measured by X-ray diffraction at different temperatures for MPn compounds. Diffuse halos are not reported.

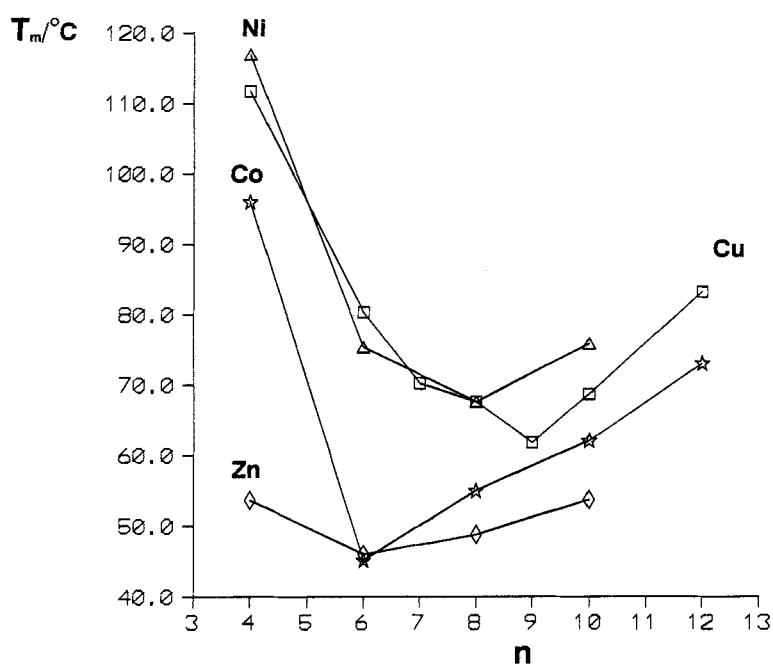
n		Co	Ni	Cu	Zn	H2
4	$d/\text{\AA}$	17.7	17.17	18.42	17.53	17.20
		14.8	16.43	15.99	15.07	15.07
	$T/^\circ\text{C}$	115	14.82	14.24	75	9.33
6	$d/\text{\AA}$	18.4	18.42	18.5	18.06	18.42
		17.2	10.2	10.4	10.2	10.2
	$T/^\circ\text{C}$	80	85	108	90	75
7	$d/\text{\AA}$			19.5	19.5	
				11.2	11.2	
	$T/^\circ\text{C}$			9.6	9.6	78
8	$d/\text{\AA}$	20.05	20.44	20.44	20.28	
		11.6	11.88	11.88	11.85	
	$T/^\circ\text{C}$	80	80	80	75	
9	$d/\text{\AA}$			21.88		
				12.5		
	$T/^\circ\text{C}$			10.8		92
10	$d/\text{\AA}$	22.6	22.47	22.6	22.6	
		12.8	12.89	12.92	12.92	
	$T/^\circ\text{C}$	80	85	80	75	
12	$d/\text{\AA}$	24.04		24.70		
		13.90		14.13		
	$T/^\circ\text{C}$	80		12.24		94

Both compounds undergo two solid phase transitions before melting to an anisotropic liquid. The optical textures observed are totally analogous to those shown in figures 4 and 5. For H2P4 both have been observed together.

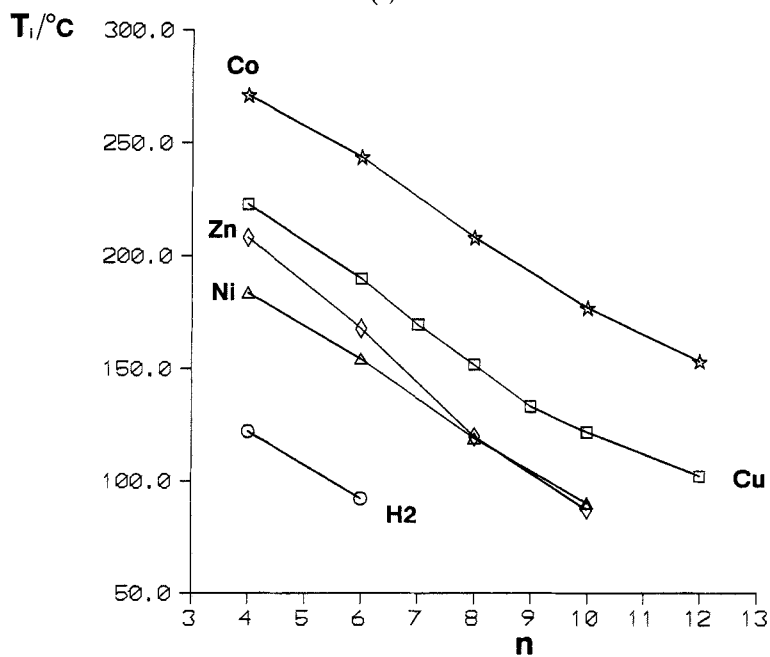
The X-ray diffraction pattern of the mesophase is characterized by a sharp, strong Bragg line at 17.20 Å and at 18.42 Å for H2P6. Two additional weak lines at smaller lattice distances are also observed for H2P4 (see table 4). For both compounds, a diffuse halo is observed at $0.12 \text{ \AA}^{-1} \sin \theta/\lambda$. A non-hexagonal columnar packing of the molecules is suggested. The absence of sharp Bragg lines at high angles is in favour of a disordered stacking of the molecules along the columnar axis.

No mesomorphic behaviour is shown by unsubstituted porphyrins for $n > 6$. A possible exception might be H2P7. The DSC curve for this compound, recorded on cooling the isotropic liquid, shows an exothermic peak, involving a very small molar enthalpy change, closely followed by the crystallization exotherm. No other evidence is available to support this monotropic mesomorphism.

Metal porphyrins (MPn). A comprehensive collection of the thermal data concerning metal porphyrins is shown in table 3. An easier view of the general trends is

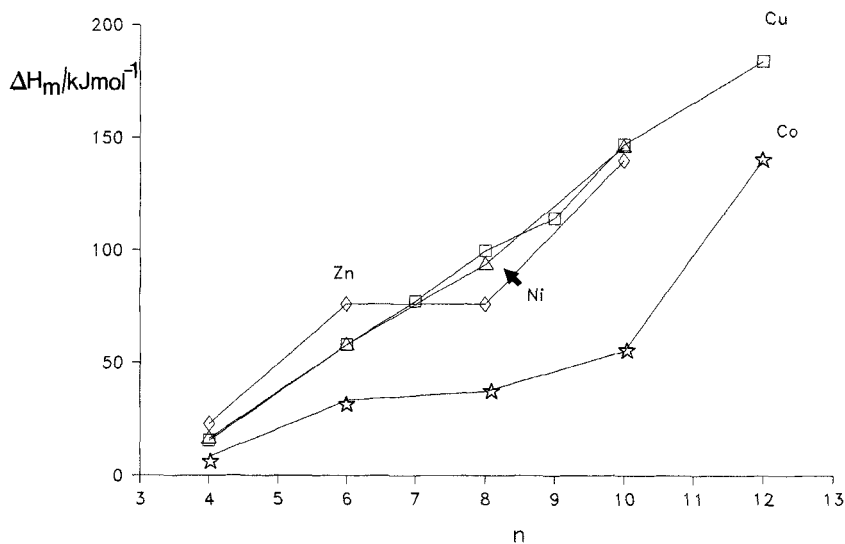


(a)

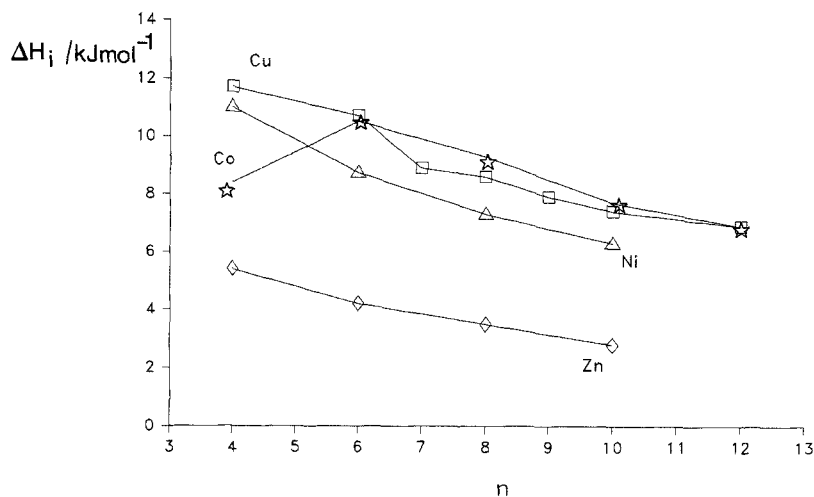


(b)

Figure 1. Melting (C→D) (a) and isotropization (D→I) (b) temperatures of MP n compounds as a function of the number (n) of carbon atoms in the alkyl chains.



(a)



(b)

Figure 2. Melting (C→D) (a) and isotropization (D→I) (b) enthalpy change as a function of the number (n) of carbon atoms in the alkyl chains.

available in figures 1 (a) and (b), for melting and isotropization temperatures and figure 2(b) for isotropization enthalpies. Two parameters having chemical and structural relevance distinguish the metal porphyrins reported here namely, the nature of the metal atom and the length of the flexible aliphatic chains. Although some subtle peculiarity may characterize each single compound, general features of the phase behaviour as a function of these parameters are quite apparent. All metal porphyrins are mesogenic. Mesomorphism is enantiotropic columnar in all cases, although some structural differences have been detected. Some evidence of polymorphic behaviour in the mesomorphic state has been found for CuP6 and NiP6. Within each homologous series of compounds containing the same metal species, isotropization temperature and

isotropization enthalpy decrease with increasing n . Within each homologous series of compounds characterized by the same value of n , cobalt porphyrins have the highest mesophase stability followed by copper porphyrins. Nickel and zinc containing homologues have lower mesophase stability but the differences between them are not as clearly defined. Without any reference to the nature of the metal atom, the discotic phase characterized by hexagonal columnar packing is stabilized by long chains.

As far as the solid state is concerned, most compounds are polymorphic. Polymorphism may occur in either or both of the following two forms:

- (i) multiple solid phases connected by sequential and reversible phase transitions;
- (ii) two solid phases formed either by solution crystallization or by melt crystallization that may be present together (one of them in a metastable condition) in the sample.

The liquid-crystalline behaviour of the metal porphyrins is the central point of this paper, therefore, although the solid state features of all compounds have been investigated thoroughly, we shall not discuss them in much detail but for a few rather peculiar cases. As to the melting temperatures shown in figure 1 (b), they relate to the most stable solid phase for each compound. We shall now discuss in detail the relevant features of the liquid-crystalline phase of the metal porphyrins.

3.2. Optical textures

The texture that almost invariably occurs on melting any metal porphyrin between two microscope glasses is the homeotropic one. Significant, non-pseudoisotropic textures were obtained by shearing the molten sample, in the liquid crystal phase and observing it without a cover glass. The pattern of the observed textures is rather uniform. The fan texture is exhibited by the liquid crystal phases whose X-ray diffraction spectrum indicates unambiguously a hexagonal packing. An example of such a texture, concerning CuP7 at 165°C, is shown in figure 3. In all other cases, either arced fan (see figure 4 for ZnP6 at 93°C) or pseudo spherulitic textures (see figure 5 for ZnP4 at 195°C) are observed. In some cases, for example for NiP4, both textures occur together.



Figure 3. Liquid-crystalline texture shown by CuP7 at 165°C; crossed polarizers.

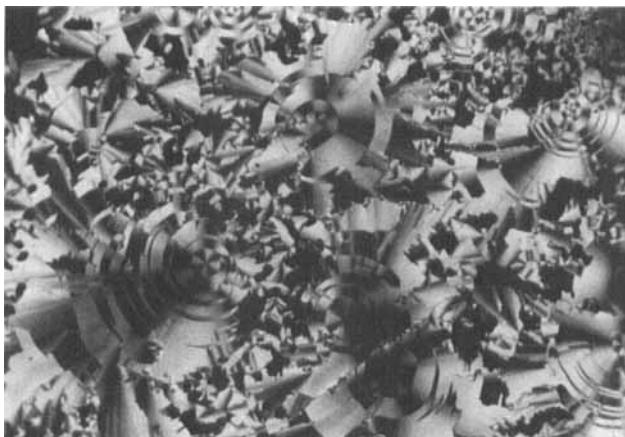


Figure 4. Liquid-crystalline texture shown by ZnP6 at 93°C; crossed polarizers.

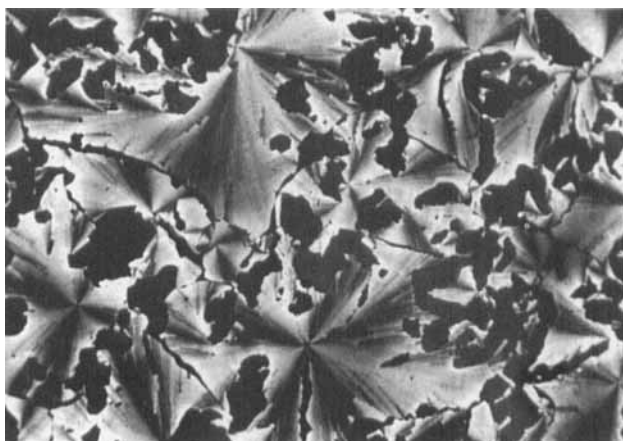


Figure 5. Liquid-crystalline texture shown by ZnP4 at 195°C; crossed polarizers. Blank areas are not significant; they indicate local absence of the substance.

3.3. X-ray diffraction patterns

The liquid-crystalline phase of metal porphyrins with $n \geq 7$ is characterized by a X-ray diffraction pattern containing three sharp Bragg equatorial lines (see table 4) that are related as the 10, 11 and 20 points of a two dimensional hexagonal lattice. The scarce dependence of the (homologous) lattice distances on the nature of the metal atom for compounds with equal n is consistent with a columnar packing in which the intercolumnar distance is only defined by the cross section of the ligand. For cobalt and copper containing porphyrins the square of the intercolumnar distance increases linearly with n . This feature is also consistent with a columnar packing of disc-shaped molecules whose basal area increases with increasing number of methylenic groups while keeping a constant thickness. In a previous paper reporting the mesomorphic behaviour of CuP8 a possible tilt of the disc-like molecules with respect to the columnar axis was discussed [17]. No clear cut evidence supporting this feature was collected for

other compounds. No short Bragg diffraction line was observed at high angles. For CuP8 and NiP8, in addition to the diffraction halo at $0.112 \text{ \AA}^{-1} \sin \theta/\lambda$ observed for most compounds, a second halo at $0.119 \text{ \AA}^{-1} \sin \theta/\lambda$ is present. For CoPn compounds a single diffraction halo at $0.119 \text{ \AA}^{-1} \sin \theta/\lambda$ was observed. These features indicate that the stacking of the molecules along the columns is substantially disordered in all cases. Any connection between the variance exhibited by cobalt porphyrins (as well as those concerning CuP8 and NiP8) and a possible shortening of the average distance between neighbouring molecules within a column, requires a more accurate measurement of the diffraction profiles.

The X-ray diffraction patterns characterizing the liquid-crystalline phase formed by compounds MPn with $n < 6$ on melting are complicated by an irregular morphology taken up by the molten samples that are almost invariably formed by a coarse assembly of macroscopic domains whose orientation is not entirely random. Nonetheless, some essential features are still detectable.

- (i) The intense inner diffraction ring, that is a single one in the hexagonally packed structures, is clearly split in two or three distinct diffractions of different intensity in the pattern of compounds with $n = 4$ (see table 4). No Bragg diffraction is detectable at wider angles, although the presence of some very feeble reflection cannot be excluded. These features are not compatible with a hexagonal columnar phase.
- (ii) No splitting is detectable in the intense inner ring characterizing the diffraction pattern of compounds with $n = 6$ recorded at temperatures not much higher than melting. A second, much less intense Bragg diffraction at $0.04902 \text{ \AA}^{-1} \sin \theta/\lambda$ is observed with copper, nickel and zinc containing compounds while no such reflection is detectable for the cobalt porphyrin at comparable exposure times. The lattice distances corresponding to the two Bragg lines are in the ratio 1:0.554 for copper and nickel porphyrins 1:0.565 for the zinc containing one. In the latter case only, the ratio is on the border of statistical significance for defining the two diffraction lines as the 10 and 11 of hexagonal packing.
- (iii) As for metal porphyrins with $n \geq 7$ no Bragg diffraction line was observed at high angles but only a diffuse halo at $0.112 \text{ \AA}^{-1} \sin \theta/\lambda$. For CuP4, a second diffuse halo at $0.128 \text{ \AA}^{-1} \sin \theta/\lambda$ is clearly observable. The only safe conclusion may be that for these compounds also the stacking of the discotic molecules along the column is disordered.

3.4. Calorimetric analysis

For all compounds but one, the calorimetric behaviour at isotropization is unequivocal. A single DSC peak characterizes the phase transition. The reverse phase transformation is equally well-resolved although some supercooling of the isotropic liquid does regularly occur. For CuP6 only, the DSC heating curve shows a discontinuous change of specific heat at a temperature (183°C) not far from isotropization. This thermal change is very subtle, yet it is accompanied by a remarkable change of the liquid texture. The fan type texture, that forms above 183°C (see figure 6), is similar to that observed for the hexagonal columnar phase of all compounds with $n \geq 7$. At lower temperatures the arced fan texture is found (see figure 7). In conclusion, calorimetric and textural analysis seemingly suggest that CuP6 is polymorphic in the liquid-crystalline state. The high value of the liquid crystal-liquid

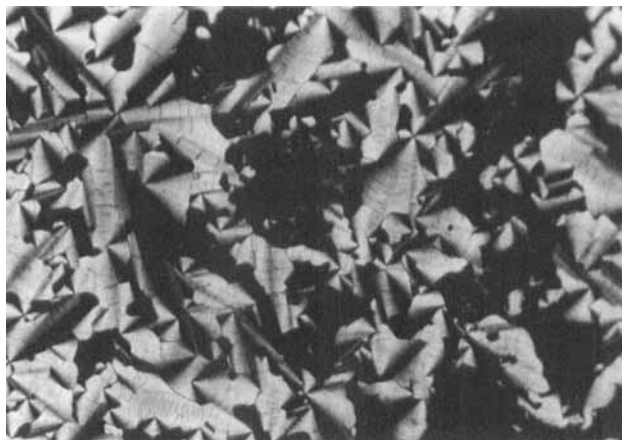


Figure 6. Liquid-crystalline texture shown by CuP6 at 183°C; crossed polarizers.

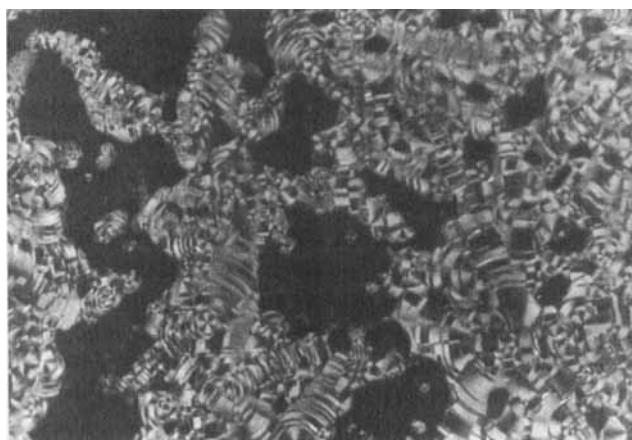


Figure 7. Liquid-crystalline texture shown by CuP6 at 178°C; crossed polarizers. Some sample and some area of figure 6.

crystal transition temperature and its proximity to isotropization prevented us from obtaining an X-ray diffraction pattern to confirm or to disprove the hexagonal columnar nature of the high temperature liquid crystal phase as suggested by the texture. A textural change (arced fan→fan) similar to that reported for CuP6 was observed at 136°C for NiP6 and at 83°C for CuP7 but a significant and reproducible, although very feeble, calorimetric feature is observed in correspondence only for NiP6 (see figure 8). In no case is any modification of the X-ray diffraction patterns (recorded at 145°C for NiP6 and at 93°C CuP7) detectable to support further a polymorphic liquid-crystalline behaviour of these compounds.

It has been mentioned previously that many MPn compounds exhibit solid polymorphism. Not all of them deserve a detailed description and so we shall limit the discussion to three cases. The solid state behaviour of CoP12 is particularly intricate. The DSC heating curve of a solution crystallized sample is shown in figure 9 (curve a).

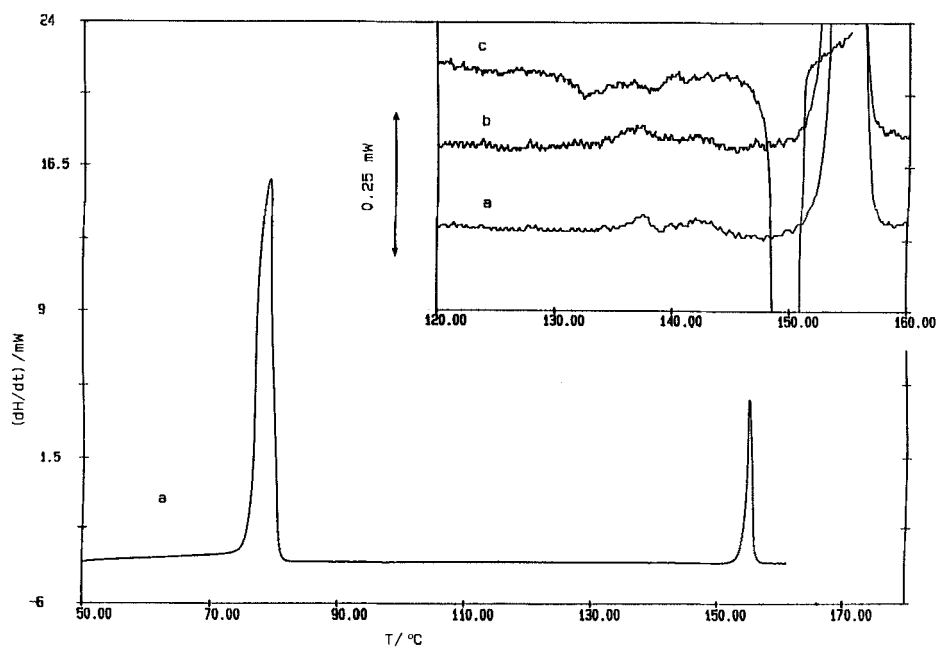


Figure 8. DSC curves of NiP6. Curves possibly indicative of mesomorphic polymorphism are reported in the upper right part with an enhanced heat flow scale. Scanning rate $10^{\circ}\text{C min}^{-1}$.

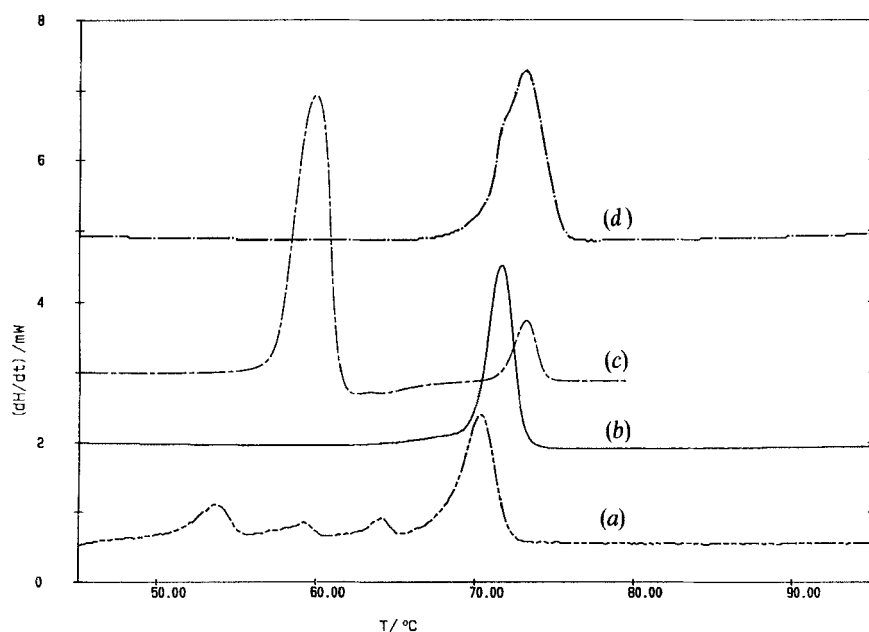


Figure 9. DSC curves of CoP12; (a) first heating curve of solution crystallized sample with no previous thermal treatment; (b) heating curve of annealed sample 66°C ; (c) heating curve of solid sample obtained by crystallization from the liquid phase; (d) heating curve of a melt crystallized sample previously annealed at 68°C for 10 min. Scanning rate $10^{\circ}\text{C min}^{-1}$.

The peak temperature corresponding to the melting endotherm is 70.4°C and the enthalpy change amounts to 52.3 kJ mol^{-1} . Melting is preceded by thermally detectable transformations of an unknown nature. If the sample is previously annealed at 66°C for 10 min, the successive heating DSC signal is smooth until melting occurs (curve b); the peak temperature moves to 71.7°C and the enthalpy change increases to 68.5 kJ mol^{-1} . The crystallization of the discotic phase is characterized by a single exothermic signal peaked at about 43°C with an enthalpy change of 146 kJ mol^{-1} . The thermal behaviour of a sample crystallized in this way is quite peculiar (curve c). A large endothermic signal peaked at 59.9°C is followed by a smaller endotherm at a higher temperature. The enthalpy change of the first phase transition is 140 kJ mol^{-1} (this is the integral value between 55.2 and 62.6°C and does not take into account a possible superimposed exothermic effect that might be responsible for the seemingly irregular baseline) while that corresponding to the second one depends on the thermal treatment, ranging between a few kJ mol^{-1} and 69.1 kJ mol^{-1} . The highest value was obtained when the sample was first heated to 63°C , then cooled to room temperature and finally heated again. However, if a melt crystallized sample is heated to 68°C (i.e. close to the onset of the second phase transition) and annealed for a few minutes or more at that temperature, the successive DSC curve does not show (curve d) a phase transition at 60°C . Melting occurs at 73°C with an enthalpy change of 69.1 kJ mol^{-1} , however, the DSC curve indicates that two unresolved phase transitions may be involved in the phenomenon. Seemingly, the annealing process produces some amount of a second crystal phase, namely that melting at 71.7°C , besides increasing the amount of the existing phase. In conclusion, CoP12 may form at least three distinct solid phases

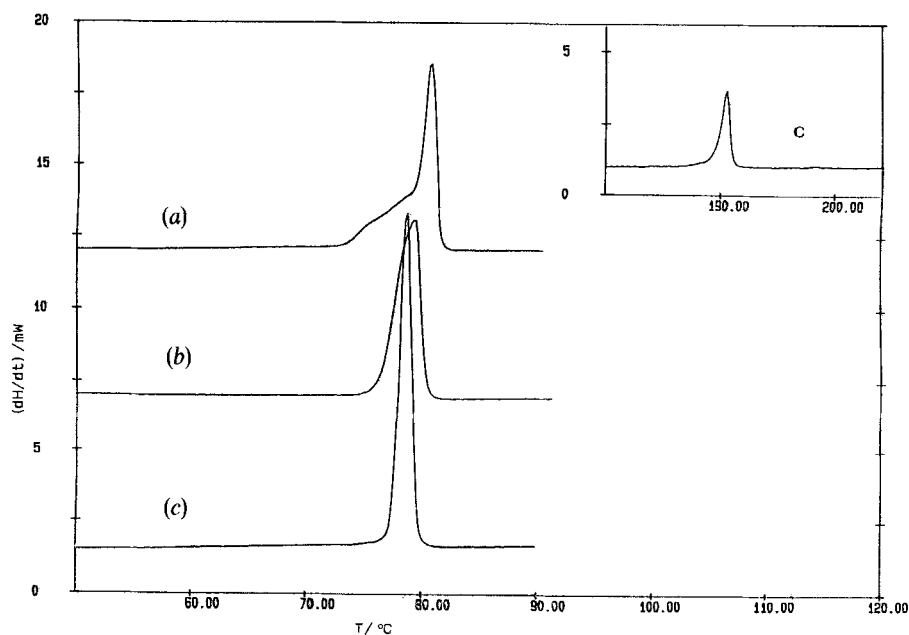


Figure 10. DSC curves of CuP6; (a) first heating curve of solution crystallized sample with no previous thermal treatment; (b) heating curve of sample of a melt crystallized sample, recorded soon after crystallization has taken place; (c) heating curve of a sample previously annealed at 78°C for 10 min; isotropization is shown in the upper right part of the figure. The thermal treatment does not significantly alter the sample. Scanning rate $10^{\circ}\text{C min}^{-1}$.

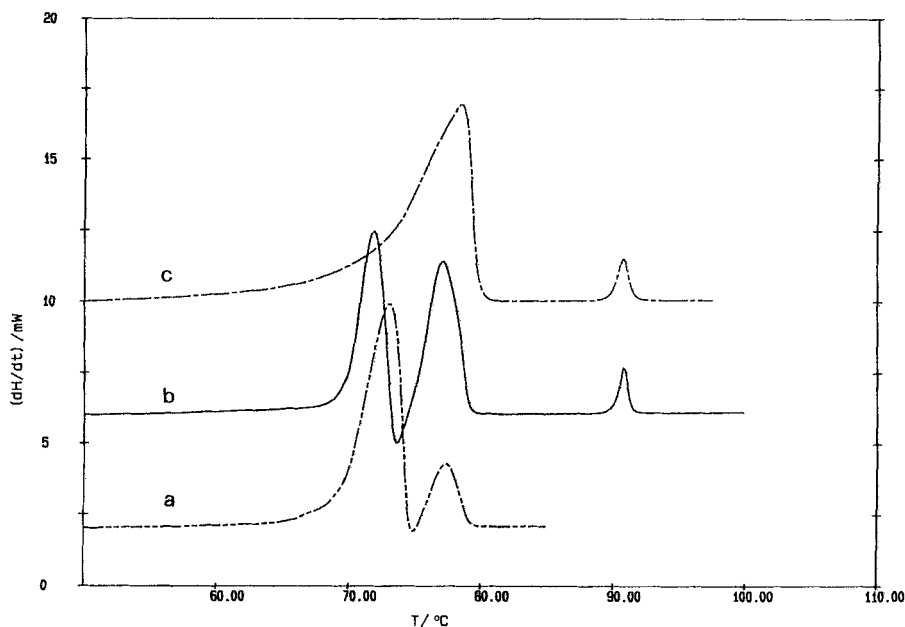


Figure 11. DSC curves of NiP10; (a) first heating curve of a solution crystallized sample with no previous thermal treatment; (b) same sample during the second DSC heating run; (c) heating curve after previous annealing at 74°C for 10 min. Scanning rate 10°C min⁻¹.

whose relative amounts depend on the thermal history. It is quite apparent that the behaviour outlined is to some extent a consequence of kinetic difficulties affecting the crystallization.

The solid state behaviour of CuP6 is similar in part to that of CoP12. The melting endotherm of a solution crystallized sample (see figure 10, curve a) is indicative of a multiphase system. The peak temperature is 80.3°C and the total enthalpic change amounts to 57.8 kJ mol⁻¹. If a second DSC heating scan is started soon after the sample has been cooled to room temperature at the rate of 10 K min⁻¹, the melting endotherm (curve b) is peaked at a lower temperature and, although still rather wide, it is seemingly a single one. However, if the melt crystallized sample is kept at room temperature for some time (few minutes) or the original sample is annealed at 78°C for 10 min, a single narrower endotherm peaked at 78.7–78.9°C corresponds to the successive melting of the sample (curve c). In both cases the same enthalpy change of 56.5 kJ mol⁻¹ is measured.

Compound NiP10 affords a fairly simple example of dimorphism with both solid phases present in the same sample. The DSC curve of a solution crystallized sample heated to melting shows two almost completely resolved peaks corresponding to the melting of two crystal phases that are present in different amounts (see figure 11, curve a). This is demonstrated by the behaviour of the same sample on the second DSC heating run (curve b): the amount of the crystal phase melting at a higher temperature is increased. The shape of the entire curve is also influenced by an exothermic effect due to a partial crystallization of the liquid that forms as the less stable crystal phase melts. Finally (curve c), by annealing at 74°C for 10 min the transformation to the high melting form is virtually complete (although the permanence of a small amount of the other phase cannot be ruled out).

3.5. Relative stability and electronic structure

Although Monte Carlo and molecule dynamics simulations [27] on a simple ensemble of disc-shaped molecules have shown [28] that the origin of the stability of a discotic mesophase is mainly due to entropic contributions, nevertheless it appears from the reported data that a clear influence of the nature of the metal is present.

Bulk properties such as the isotropization enthalpy and temperature are not simply related to bimolecular interactions. However it is useful from a heuristic point of view to try to look for relations between molecular parameters and modulation of the bulk properties. The data reported show that, irrespective of the number of carbon atoms in the aliphatic chains, isotropization temperatures are in the order $Zn \approx Ni < Cu < Co$. An attempt, without success, has been made to rationalize the relative stability of mesophases of octakis(octaalkyl ethyl ether) porphyrins complexes on the basis of their π donor-acceptor ability as modified by the complexed metal [15]. We have then performed a study of the electronic structure of both free molecules and complexes using an EH model so as to have a deeper insight into the behaviour of these compounds. Since no experimental study has been undertaken on the molecular structure we made a preliminary study of the electronic structure of the free octakis(methylthio) tetraaza porphyrin and octakis(thiohydro)tetraaza porphyrin and their Zn(II) complex with full geometry optimization using the AM1 model. We have then used the computed geometry in the EH calculations on the series of compounds using the octakis(thiohydro) porphyrin skeleton and choosing the SH conformation in a way that preserves the D_{4h} symmetry with minimum repulsive interaction between the hydrogen atoms. Concerning compounds of Co and Cu, EH calculations show that the Co derivative should have one electron in a π -type orbital with a large sulfur p_z contribution and a small metal p_z contribution while in the Cu derivative the unpaired electron is found in an orbital with a very large $d_{x^2-x^2}$ contribution. These results agree with those previously found [29] for copper tetraazaporphin whereas for cobalt tetraazaporphin and phthalocyanins previous [29] theoretical results predict that the unpaired electron is in the d_{xy} orbital. However, experimental EPR [30, 31] data and magnetic properties measurements [32, 33] indicate that this electron should be in a d_{z^2} orbital at least in the phthalocyanine complex. Since orbital interactions between stacked molecules are better for p_z or d_{z^2} (i.e. orbitals orthogonal to the molecular plane) than for $d_{x^2-x^2}$ orbitals, Co complexes should result in being more tightly bound within a stack than Cu ones. For Ni and Zn derivatives, where unpaired electrons are not present, less intense interactions exist between the stacked molecules. These interactions are, however, already not very strong for the copper octakis(methylthio) porphyrinato complex which forms dimers only at very low temperature in frozen organic solvent [25].

4. Orientation within columns

It has been suggested [34] that for the benzo-15-crown-5-substituted phthalocyanine complex of copper the phthalocyanine core is tilted by about 30° with respect to the mean planes of the crown ethers. Since X-ray data also suggest that at least in our case, CuP8, the molecules are tilted within the columnar packing, we have therefore performed some molecular mechanics calculations of supramolecular aggregates of four molecules of H2P8 starting from the geometry obtained by the AM1 computations for H2P1 to see if an arrangement of tilted cores can give a geometry that is compatible from the energetic point of view within a given column. This approach has been shown [35] to be useful in the description of local interactions for different

molecules forming liquid crystals. The results indicate that the macrocycle is tilted with respect to the mean plane of the aliphatic chains by an angle of 30° – 40° . This behaviour, as pointed out for crown-phthalocyanine [34], is due mainly to the fact that the equilibrium distance, between two contiguous aliphatic moieties and the two contiguous phthalocyanine groups are different. In fact these distances, evaluated by molecular mechanics computations, are within 0.42–0.44 nm and 0.33–0.35 nm, respectively. The computed values are in the range suggested by some experimental evaluation [36] so that their ratio is about 0.9 whose arcos [34] corresponds to an angle of about $37 \pm 7^{\circ}$.

5. Conclusions

Optical and X-ray data for $n \geq 7$ indicate a discotic mesophase with hexagonal columnar packing whereas in complexes with $n < 7$ the observed mesophase shows a non-hexagonal columnar packing. CuP6 and NiP6 seemingly show both mesophases; these are connected by a phase transition, presumably of second order (CuP6) or very weak first order (NiP6) but easily detected by polarizing microscopy because of sharp texture changes. Except for H2P(7–12), all of the compounds are mesogenic; a few of them exhibit mesomorphic polymorphism. Melting (C→D) temperatures range between 40 and 85°C . Only NiP4, CoP4 and CuP4 show higher values. Both temperature and ΔH of isotropization (D→I) show a regular trend with respect to the number of carbon atoms of the alkyl chain and of the nature of the metal. As expected, no odd–even effect is detectable on the properties of the liquid-crystalline phases as a function of the number of carbon atoms in the aliphatic chains. The stability order of the mesophase in the compounds studied seems mainly related to the presence and spatial distribution of unpaired electrons. In fact cobalt and copper compounds have the largest stability. Consistently nickel and zinc give less stable mesophases having a closed shell electronic structure.

This work has been partially supported by CNR grant and CNR grant 'Progetto Finalizzato Materiali Speciali per l'Elettronica'. The financial contribution of Ministero della Università e della Ricerca Scientifica is also acknowledged.

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