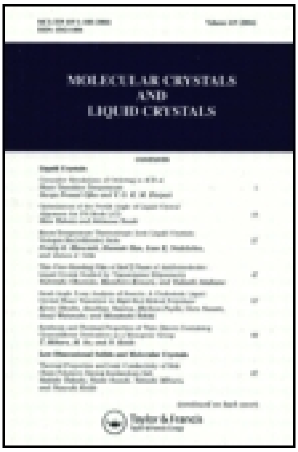

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Discotic Mesogens Possessing an Electrical Dipole Moment Perpendicular to the Molecular Plane: Synthesis and Mesomorphic Properties

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Discotic Mesogens Possessing an Electrical Dipole Moment Perpendicular to the Molecular Plane: Synthesis and Mesomorphic Properties†,‡

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Out-of-plane complexes (Pb^{II} and Sn^{II}) of octasubstituted phthalocyanine derivatives have been prepared. They are characterized by a large dipole moment perpendicular to the macrocycle plane. The lead derivatives are shown to form columnar liquid crystals as characterized by optical microscopy, differential scanning calorimetry and X-ray diffraction at small angle.

Keywords: phthalocyanines, antiferroelectric, liquid crystals, discotic

INTRODUCTION

Discotic mesogens are constituted of a central rigid core surrounded by flexible alkyl chains; such structurally constituted mesogens lead to columnar type mesophases where the rigid cores pile up to form columns which are usually arranged along a two-dimensional hexagonal array.[1–4] In most cases the high symmetry of the mesogens does not permit the presence of a permanent electrical dipole moment. Only one example of in-plane dipole moment in substituted phthalocyanine based mesogens has been described so far.[5,6] Discotic

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‡Part XXII of the series Annelides. For part XXI see D. Masurel, C. Sirlin and J. Simon, *Nouveau J. de Chimie*, in press.

mesogens with a dipole moment perpendicular to the molecular plane are also very rarely encountered.[7,8] However, such dipolar mesogens are of the utmost importance for making liquid crystals based devices where orientational properties are required.[9] This paper describes new types of discotic mesogens in which perpendicular dipole moment is ensured by an out-of-plane metallic complex of substituted phthalocyanine derivatives (Figure 1). The mesomorphic properties of these latter are now well established.[10,11] Large divalent metal ions such as Pb^{2+} (r = 1.2 Å) or Sn^{2+} (r = 0.93 Å) cannot be accommodated within the macrocyclic phthalocyanine cavity and form out-of-plane complexes.[12–14] This paper relates to the synthesis of the corresponding discotic mesogens, their physico-chemical properties, the O_2-complexing ability of the tin (II) derivative and the characterization of the associated liquid crystalline phases.

SYNTHESIS OF MESOGENS

The synthesis of the lead complexes is achieved starting from the corresponding unmetallated phthalocyanine derivatives $(Cn)_8PcH_2$ whose preparation has been previously described.[11] $(Cn)_8PcH_2$ (n = 8, 12, 18) is dissolved in a 1:1 mixture of n-pentanol and methanol under nitrogen at the temperature of reflux of methanol. A 10-fold excess of potassium pentanolate is then added leading to a colour change from blue-green to dark-green indicating the formation of the dianion $[(Cn)_8Pc]^{2-}$. Anhydrous lead nitrate dissolved in methanol is added (3-fold excess). The reaction between the dianion and Pb^{II} is followed by T.L.C. (SiO_2; 2.5% Et_2O in $CHCl_3$). After completion of the reaction, the mixture is evaporated to dryness; the residue is purified by chromatography over Al_2O_3 (eluent: $CHCl_3$) and the product is recrystallized from AcOEt (yield: 40–60%). It is worth pointing

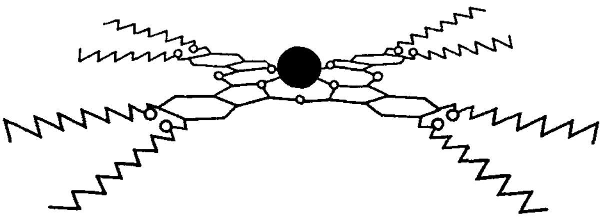

FIGURE 1 Representation of out-of-plane divalent complexes of octasubstituted phthalocyanine derivatives: $(Cn)_8PcM$ (M = Sn^{II}, Pb^{II}).

out that the lead complex is moderately stable and undergoes demetallation in weak acidic media or in CH_2Cl_2 in presence of light.

Microanalysis

—$(C_{12})_8PcPb$, $C_{136}H_{224}O_8N_8Pb$ ($M\omega$: 2306.5); $\lambda_{max} = 720$ nm
Calculated: C: 70.82; H: 9.79; N: 4.86; Pb: 8.98.
Found: 70.75; H: 10.44; N: 4.84; Pb: 8.92.
—$(C_{18})_8PcPb$ $C_{184}H_{320}O_8N_8Pb$ ($M\omega$: 2979.8)
Calculated: C: 74.17; H: 10.82; N: 3.76.
Found: C: 74.22; H: 11.22; N: 3.72.

The tin (II) derivatives are prepared following an identical chemical procedure using $SnCl_2$ as salt. However, the $(Cn)_8PcSn$ compounds are stable only in strict absence of air in which they are rapidly converted into the corresponding Sn (IV) derivatives. This transformation may be followed by absorption spectrometry as it is detailed in a following section. Only the dihydroxo tin (IV) derivatives have been characterized.[15]

—$(C_{12})_8PcSn(OH)_2{\cdot}2H_2O$: $C_{136}H_{226}O_{10}N_8Sn{\cdot}2H_2O$: ($M\omega = 2288$)
$\lambda_{max} = 704$ nm.
Calculated: C: 71.39; H: 10.13; N: 4.90.
Found: C: 71.19; H: 10.02; N: 4.62.

REACTION OF O_2 WITH $(Cn)_8PcSn$

The reaction of O_2 with $(Cn)_8PcSn$ may be readily followed in solution by absorption spectrometry (Figure 2). The unoxidized species absorbs at 720 nm (blue-violet colour) at the same wavelength as the lead derivatives. In presence of air, chloroformic solutions of $(Cn)_8PcSn$ are converted in a few minutes at room temperature to a new species absorbing around 700 nm. Such values are highly characteristic of the tetravalent form of the tin complex[16]:

$$(Cn)_8PcSn + O_2 \longrightarrow (Cn)_8PcSn,\ O_2 \xrightarrow{2H+} (Cn)_8PcSn(OH)_2$$

Surprisingly, the dihydroxoderivative may be reduced back to the tin (II) derivative by heating the solid $(Cn)_8PcSn(OH)_2$ around 130°C. This last process interferes in the polymerization process ultimately leading to $[(Cn)_8PcSnO]_n$.[15]

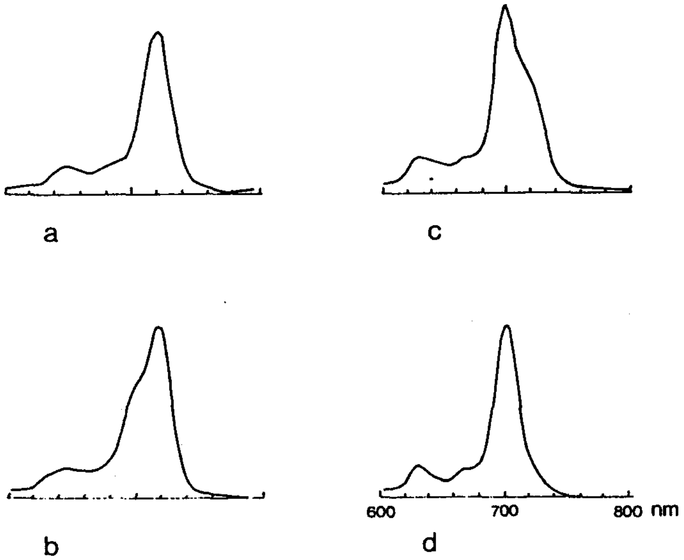

FIGURE 2 Absorption spectra of $(C_{12})_8PcSn$ as a function of the ambient:
a: $(C_{12})_8PcSn$ in absence of air
b–d: evolution with time in presence of air: oxidation process (see text).
The overall process takes a few mn.

CHARACTERIZATION OF THE MESOPHASES

The domain of stability of the mesophases has been determined for $(Cn)_8PcPb$ (n = 8, 12, 18) by polarizing optical microscopy and differential scanning calorimetry (Table I). By increasing the chain length, the temperatures of transition crystal–mesophase and mesophase–liquid tend to each other. It is noteworthy that the octyl-

TABLE I

Transition temperatures determined by D.S.C. for octasubstituted phthalocyaninato-lead (II) derivatives, $(Cn)_8PcPb$. In parentheses are indicated the corresponding enthalpies of transition (kcal/mole)

n	K	M	I
8	−45	(0.5)	155
12	−12	(6.5)	125
18	46[a]	(51)[b]	60[a]

[a] The two peaks may overlap depending on heating rate
[b] This value represents the sum of the K → M and M → I enthalpies of transition.
K: crystal; M: mesophase; I: isotropic liquid

and dodecyl-derivatives form stable liquid crystals even at room temperature. The case of the octadecyl derivative is more puzzling and well defined textures of the mesophase are only obtained from the isotropic liquid, and it seems that this phase is metastable with time even in the 46–60°C range.

X-ray diffraction patterns demonstrate the columnar structure of the mesophases.[17] In the case of $(C_8)_8$PcPb, X-ray diagram contains three narrow bands with reciprocal spacings in the ratio $1:\sqrt{3}:\sqrt{4}$ typical of a hexagonal array with intercolumnar spacing of 26.9 Å. Only one broad peak located at 7.4 Å may be observed in the wide-angle region. This distance may be interpreted as being due to the presence of pairs of molecules as it has been already encountered in the triclinic modification of unsubstituted PcPb.[12–14] The existence of such dimers suggest a strong antiferroelectric coupling of the electrical dipoles[17] (Figure 3).

X-ray studies on $(C_{12})_8$PcPb and $(C_{18})_8$PcPb show also a columnar structure with intercolumn spacings of 31 Å and 36 Å, respectively. A halo is observed at 4.5 Å for the octadecyl derivative while no peak at all is observed in this region for the dodecylderivative. In particular,

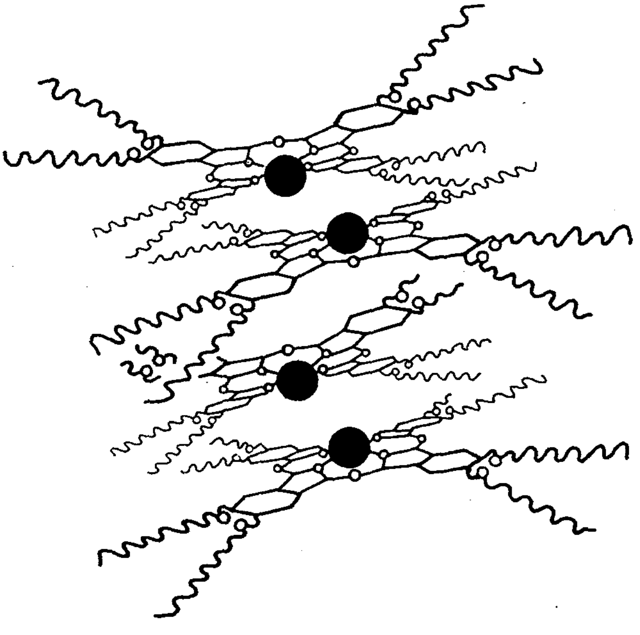

FIGURE 3 Schematic representation of the antiferroelectric coupling probably occurring in the mesophase of $(C_8)_8$PcPb.

the peak previously located at 7.4 Å cannot be observed in both cases. In consequence, no conclusions can be drawn as to the molecular organization occurring within the columns for these two compounds.

CONCLUSION

Octasubstituted lead phthalocyanine derivatives have been shown to form columnar liquid crystals where an electrical dipole moment is present perpendicular to the macrocyclic plane. In one case, a strong antiferroelectric coupling has been evidenced within the columns. Further studies are in progress to determine the possibility of obtaining intracolumnar ferroelectric order.

Acknowledgments

X-ray determinations have been carried out by P. Weber, D. Guillon and A. Skoulios in Strasbourg. These studies will be the object of a separate publication (see Ref. 17). Mr. Kaiser is gratefully acknowledged for microanalysis determinations.

This paper is dedicated to Mrs. G. Pouyet at the occasion of her retirement.

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