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Mesogenic Behaviour of 2,3,9,10,16,17,23,24- Octadodecyloxycarbonyl- phthalocyaninatogermanium- dihydroxide

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The synthesis of 2,3,9,10,16,17,23,24-octadodecyloxycarbonylphthalocyaninatogermaniumdihydroxide is described. The mesomorphic properties of this new material were studied by differential scanning calorimetry (DSC), optical microscopy and X-ray investigations. The described compound shows a discotic mesophase in an extremely large temperature interval including room temperature. The X-ray diffraction pattern of the mesophase of 2,3,9,10,16,17,23,24-octadodecyloxycarbonylphthalocyaninato-germaniumdihydroxide proves that it forms a hexagonal columnar mesophase of the type D_{hd} .

Keywords: *discotic liquid crystal, phthalocyanine, germanium complex*

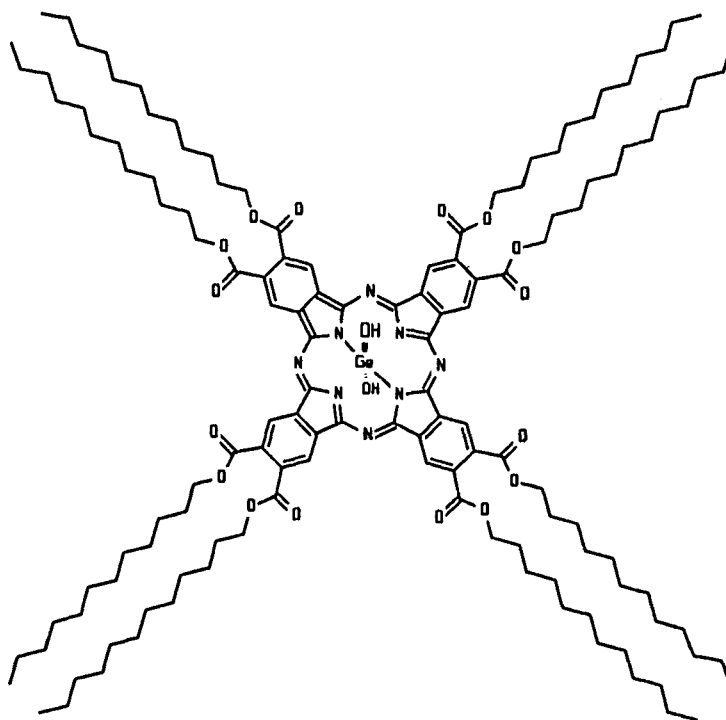
INTRODUCTION

Recently we described the synthesis and the mesomorphic properties of the metal-free 2,3,9,10,16,17,23,24-octaalkoxycarbonylphthalocyanines.¹ Starting from 2,3,9,10,16,17,23,24-octadodecyloxycarbonylphthalocyanine we synthesized 2,3,9,10,16,17,23,24-octadodecyloxycarbonylphthalocyaninatogermaniumdihydroxide. In this article we describe the synthesis of this new discogen and the characterization of its mesogenic behaviour. The formula of the title compound is shown in Scheme I.

This compound shows mesogenic properties as reported in the following section.

SYNTHESIS AND CHARACTERIZATION

The synthesis of 2,3,9,10,16,17,23,24-octadodecyloxycarbonylphthalocyaninato-germaniumdihydroxide was carried out under similar conditions as having been

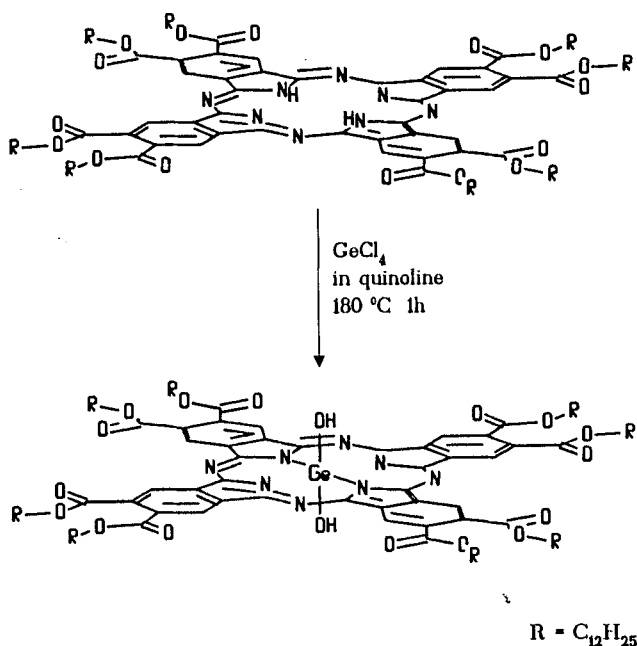
SCHEME I $\text{Ge(OH)}_2\text{Pc(COOC}_{12}\text{H}_{25})_8$

described for the synthesis of other germaniumphthalocyanines.^{2,3} The germanium ion was incorporated in the metal-free 2,3,9,10,16,17,23,24-octadodecyloxycarbonylphthalocyanine via germaniumtetrachloride in quinoline during one hour reaction time. The remaining two chloro ligands at the germanium atom were substituted by two hydroxo ligands during the aqueous work up. Scheme II outlines the synthetic route.

The purification of the desired product was carried out by column chromatography over silica gel with chloroform as eluent. The electronic spectrum of the product confirmed the completeness of the reaction. The singlet in the Q band region at 689 nm is typical for metal-containing phthalocyanines. Figure 1 shows the electronic spectra of the educt and of the product in comparison.

The fast atom bombardment mass spectrum (FABMS) of 2,3,9,10,16,17,23,24-octadodecyloxycarbonylphthalocyaninatogermaniumdihydroxide proved its structure. The peak of its adduct with chloroform, which had been used for the preparation of the sample, could be detected at 2431.

The IR spectrum as well as the ^1H -NMR spectrum and the ^{13}C -NMR spectrum of 2,3,9,10,16,17,23,24-octadodecyloxycarbonylphthalocyaninatogermaniumdihydroxide only show less significant differences compared to the spectra of the metal-free 2,3,9,10,16,17,23,24-octadodecyloxycarbonylphthalocyanine.¹ In the high field region of the proton NMR spectrum the signal of the N—H protons is replaced by the singlet resulting from the O—H protons.



SCHEME II

DSC MEASUREMENTS

The calorimetric investigation of 2,3,9,10,16,17,23,24-octadodecyloxycarbonyl-phthalocyaninatogermaniumdihydroxide by DSC resulted in a diagram showing an endothermic peak at -20.1°C . This peak correlates to the phase transition from the crystalline to the liquid crystalline phase as shown by the investigations by optical microscopy and X-ray diffraction. Another endothermic peak at 170.9°C was caused by the polycondensation of the investigated compound to the corresponding poly(germoxane).⁴ Because of that polycondensation in the mesophase no clearing point could be observed up to this temperature. As in the case of the metal-free 2,3,9,10,16,17,23,24-octaalkoxycarbonylphthalocyanines¹ the range of existence of the mesophase of the discotic liquid crystal presented in this study compared to other liquid crystalline phthalocyanines⁵⁻²⁶ is extraordinarily large. Again we ascribe this fact to the alkoxy-carbonyl side chains, which obviously have a stabilizing effect on the mesophase. The enthalpy of the phase transition at -20.1°C is $\Delta H = 20 \text{ kJ/mol}$, the corresponding entropy $\Delta S = 79 \text{ J/(K}\cdot\text{mol)}$. The values of the transition enthalpy and entropy are in the expected range compared with similar compounds.^{2,10,16,20}

OPTICAL MICROSCOPY

Optical microscopy proved the existence of the liquid crystalline phase. Already at room temperature the substance is a highly viscous mass, that shows birefringence

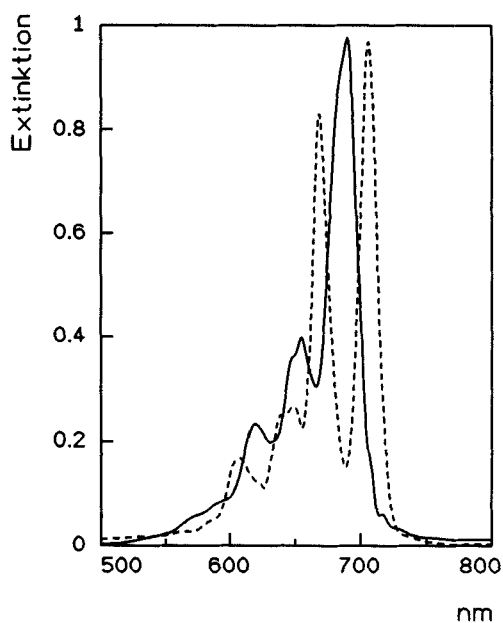


FIGURE 1 Part of the UV/VIS spectra of 2,3,9,10,16,17,23,24-octadodecyloxycarbonylphthalocyaninatogermaniumdihydroxide (—) and of the metal-free 2,3,9,10,16,17,23,24-octadodecyloxycarbonylphthalocyanine (---) (solvent: chloroform).

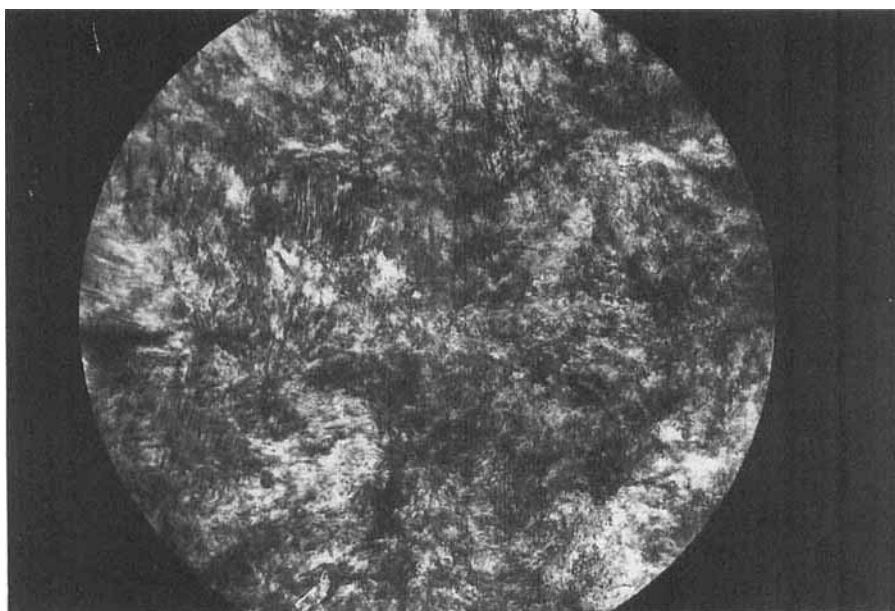


FIGURE 2 Optical textures of the liquid crystalline 2,3,9,10,16,17,23,24-octadodecyloxycarbonylphthalocyaninatogermaniumdihydroxide observed at 140°C (200×, crossed polarizers).

between crossed polarizers. Because of the polycondensation at temperatures above 150°C, the observation of optical textures is restricted to lower temperatures. As the substance is still rather viscous in that temperature range, the textures formed are not very clear. They resemble a mosaic-like type, which already has been reported in the case of columnar mesophases, see Figure 2.^{27–29}

X-RAY INVESTIGATIONS

Since the structure of the mesophase could not be determined solely on the basis of the optical textures, X-ray diffraction experiments were carried out. A powder diffractogram was sufficient to identify the mesophase as a D_{hd} -phase according to the nomenclature introduced by Destrade *et al.*³⁰ as will be shown in the following. The diffractogram showed three sharp reflections in the small angle region. Within the range of experimental accuracy the corresponding Bragg spacings of 27.8 Å, 16.3 Å and 14.2 Å are in the ratio $1:3^{-1/2}:4^{-1/2}$ which is typical for a two-dimensional hexagonal lattice.³¹ The distance between the adjacent columns is calculated from the (1,0)-reflection as $D = 32.1$ Å. In the wide angle region the disordered alkyl side chains gave rise to a broad amorphous halo located around 4.5 Å with a second broad weak maximum around 4.3 Å corresponding to the intermediate distance of the phthalocyanine rings. Additional sharp reflections in the wide angle region appeared at 3.8 Å, 3.9 Å and 4.4 Å which cannot be attributed to high order reflections of the two-dimensional hexagonal lattice because of their high intensity. Presumably they are due to intramolecular scattering within the aromatic phthalocyanine moiety.¹⁹ The structural unit of this liquid crystalline phase therefore is a two-dimensional hexagonal lattice which is formed by columns consisting of cofacially arrayed phthalocyanine molecules with the column axis normal to the aromatic ring plane. The intracolumnar distance of the phthalocyanine rings is irregular, consequently the mesophase is of the D_{hd} type. A disordered intracolumnar packing of the phthalocyanine rings had to be expected because of the hydroxyl groups perpendicular to the ring plane. A D_{hd} phase has also been reported for substituted phthalocyaninatosilicondihydroxides.¹⁹ The density derived from the X-ray data is $1.0 \text{ g} \cdot \text{cm}^{-3}$ (calculated from the (1,0)-reflection and the measured intercolumnar distance of the phthalocyanine molecules). Because of the lower intracolumnar order of the D_{hd} phase resulting in a less dense packing this value is a little bit smaller than in the case of the metal-free 2,3,9,10,16,17,23,24-octadecyloxycarbonylphthalocyanines.¹

CONCLUSION

As we could demonstrate in the present study, 2,3,9,10,16,17,23,24-octadecyloxycarbonylphthalocyaninatogermaniumdihydroxide forms a hexagonal columnar mesophase of the type D_{hd} . As in the case of the metal-free 2,3,9,10,16,17,23,24-octaalkoxycarbonylphthalocyanines the transition temperature of the transition from

the crystalline to the discotic liquid crystalline phase of 2,3,9,10,16,17,23,24-octadodecyloxycarbonylphthalocyaninatogermaniumdihydroxide is below 0°C. This reveals again the stabilizing effect of the alkoxycarbonyl substitution pattern on the mesophase. At temperatures above 150°C the described compound polymerizes in the mesophase. The characterization of the resulting poly(germoxane) is the subject of further studies.⁴

EXPERIMENTAL PART

IR spectra were recorded on a Philips Pye Unicam SP3-200 infrared spectrophotometer, UV/VIS spectra with a Perkin Elmer Lambda 15 spectrometer. NMR spectra were measured with a Bruker AC 250 spectrometer. Calorimetric studies were carried out using a DuPont DSC 2100. Optical textures were observed using a Zeiss Photomikroskop with a Leitz hotstage 350. X-ray diffraction experiments were performed with a Siemens diffractometer D 500 using Cu-K α radiation.

2,3,9,10,16,17,23,24-Octadodecyloxycarbonylphthalocyaninatogermaniumdihydroxide: In a 100 ml round bottomed flask equipped with a reflux condenser and a magnetic stirrer 580 mg (0.262 mmol) of 2,3,9,10,16,17,23,24-octadodecyloxycarbonylphthalocyanine together with 1 ml germaniumtetrachloride in 10 ml quinoline were heated for 1 h at 180°C. After cooling to room temperature the reaction mixture was diluted with 100 ml water and neutralized with sodiumhydrogencarbonate to remove the germanium as germaniumdioxide, which was filtered off. Afterwards the reaction mixture was extracted with chloroform. The organic phase was extracted ten times with half concentrated hydrochloric acid to remove the quinoline. The solvent was removed in vacuo and the product was purified by column chromatography (silica gel 60 μ m, chloroform).

Yield: 250 mg (41%)

elemental analysis (C₁₃₆H₂₁₀GeN₈O₁₈, 2317.8):

	C	H	N	Cl
calc.	70.48%	9.13%	4.83%	0.00%
found	70.07%	8.81%	5.31%	0.00%

FABMS: m/z =

2431.4	(M + CHCl ₃) ⁺ ·
2219.5	(M + CHCl ₃) ⁺ · —C ₁₂ H ₂₄ —CO ₂
2077.2	(M + CHCl ₃) ⁺ · —C ₁₂ H ₂₄ —C ₁₂ H ₂₅ OH
2007.2	(M + CHCl ₃) ⁺ · —C ₁₂ H ₂₄ —CO ₂
	—C ₁₂ H ₂₄ —CO ₂
1864.9	(M + CHCl ₃) ⁺ · —C ₁₂ H ₂₄ —CO ₂
	—C ₁₂ H ₂₄ —C ₁₂ H ₂₅ OH
1795.0	(M + CHCl ₃) ⁺ · —C ₁₂ H ₂₄ —CO ₂
	—C ₁₂ H ₂₄ —CO ₂
	—C ₁₂ H ₂₄ —CO ₂

$^1\text{H-NMR}$ (CDCl_3): δ =

- 4.4 ppm (s, OH)
- 0.8–2.0 ppm (m, alkyl-H)
- 4.7 ppm ($-\text{O}-\text{CH}_2-$)
- 9.4 ppm (arom. H)

$^{13}\text{C-NMR}$ (CDCl_3): δ =

- 14.1 ppm ($-\text{CH}_3$)
- 22.7 ppm ($-\text{CH}_2-\text{CH}_3$)
- 26.1 ppm ($-\text{O}-\text{CH}_2-\text{CH}_2-$)
- 28.8–29.7 ppm (7 inner alkyl-C)
- 31.9 ppm ($-\text{CH}_2-\text{CH}_2-\text{CH}_3$)
- 66.8 ppm ($-\text{O}-\text{CH}_2-$)
- 125.2 ppm (C–H arom.)
- 135.3 ppm, 137.0 ppm (arom. C)
- 149.4 ppm (N–C=N)
- 167.3 ppm ($-\text{COO}-$)

IR (KBr): σ =

- 2950 cm^{-1} , 2920 cm^{-1} , 2850 cm^{-1} (C–H)
- 1725 cm^{-1} (C=O)
- 1455 cm^{-1} ($-\text{CH}_2-$)
- 1280 cm^{-1} , 1180 cm^{-1} (C–C)
- 1080 cm^{-1} (C–H, pyrroloering)
- 1010 cm^{-1} (C–H)
- 740 cm^{-1} ($-\text{CH}_2-$)

UV/VIS (CHCl_3): λ =

- 689 nm (λ_{max} , $\epsilon = 20 \cdot 10^7 \text{ cm}^2/\text{mol}$)
- 652 nm, 355 nm

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