Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Description of a nematic liquid crystal based on the phthalocyanine subunit

D. Lelievre[a]; M. A. Petit[a]; J. Simon[a]
[a] E. S. P. C. I. (CNRS UA 429), Laboratoire de Chimie Inorganique et Electrochimie des Matériaux Moléculaires, Paris Cedex 05, France

To cite this Article Lelievre, D. , Petit, M. A. and Simon, J.(1989) 'Description of a nematic liquid crystal based on the phthalocyanine subunit', Liquid Crystals, 4: 6, 707 — 710
To link to this Article: DOI: 10.1080/02678298908033207
URL: http://dx.doi.org/10.1080/02678298908033207

LIQUID CRYSTALS, 1989, VOL. 4, NO. 6, 707–710

PRELIMINARY COMMUNICATION

Description of a nematic liquid crystal based on the phthalocyanine subunit

by D. LELIEVRE, M. A. PETIT and J. SIMON
E.S.P.C.I. (CNRS UA 429),
Laboratoire de Chimie Inorganique et Electrochimie des Matériaux Moléculaires,
10, rue Vauquelin, F-75231 Paris Cedex 05, France

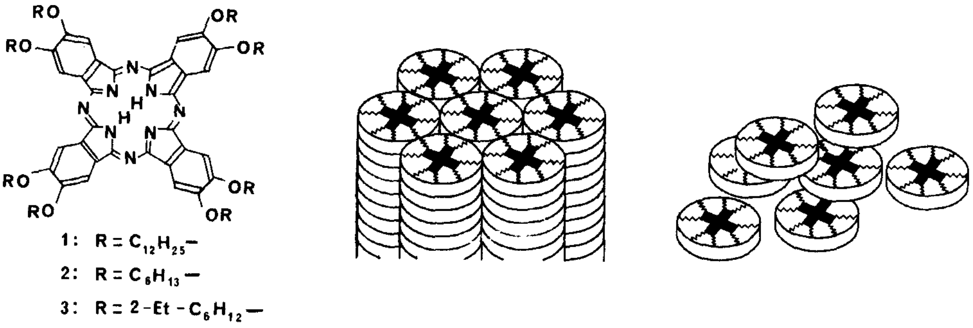
(*Received 23 January 1989; accepted 10 April 1989*)

Octasubstituted phthalocyanine derivatives have been synthesized and characterized. The mesophases were studied by optical microscopy, differential scanning calorimetry and small angle X-ray diffraction. For the 2-ethyl-hexyloxy-derivative, three transitions are observed at 170°C, 223°C and 270°C. In the latter temperature range, X-ray diffraction indicates the presence of a nematic phase which shows homeotropic orientation on untreated surfaces of a glass slide.

Octasubstituted phthalocyanine derivatives are well known to form columnar liquid crystals: in all cases, linear alkyl chains have been used and the macrocyclic phthalocyanines subunits stack to form columns [1, 2] (see figure 1). In the case of the triphenylene subunit, the use of bulky benzoate derivatives as side chains led to nematic mesophases in which the columnar arrangement is disrupted [3]. The same approach was unsuccessful with the phthalocyanine subunit [4]. However, in the truxene series, linear alkyl chains were found to lead to nematic phases [5]. It was decided therefore to use the 2-ethyl-hexyl side chains in order to promote the creation of nematic liquid-crystalline phases. At the same time, the synthesis of various substituted phthalocyanine derivatives was described [6] and, based only on optical microscopy observations, the presence of a cholesteric phase was reported.

The alkyl-substituted phthalonitriles were obtained in three steps starting from pyrocatechol, with an overall yield of approximately 43 per cent, following a previously reported chemical pathway [7, 8] ($R = C_6H_{13}$–, m.p. = 105°C; R = 2-Et-C_6H_{12}–, m.p. = 40°C). The phthalonitriles were converted into the corresponding phthalocyanines by an original electrochemical method [9] in 58 per cent yield for the 2-ethyl-hexyl derivative [10]. The optical absorption spectra of the final products (**3** in CH_2Cl_2: $\varepsilon_{699} = 2 \times 10^5$; $\varepsilon_{662} = 1{\cdot}7 \times 10^5$; $\varepsilon_{429} = 5{\cdot}6 \times 10^4$; $\varepsilon_{346} = 1{\cdot}14 \times 10^5$; $\varepsilon_{293} = 8{\cdot}5 \times 10^4$) are closely related to comparable compounds [7, 8]. The mesogens were synthesized to be used in devices in which only the orientational properties are required. In consequence no effort has been made to obtain the various pure racemates of compound **3**: we have only examined a diastereomeric mixture of this molecule with eight asymmetric carbons.

When heated between two glass slides, the 2-ethyl-hexyl derivative **3** shows, by optical microscopy, a transition at about 220°C to give a fairly fluid birefringent mass



1: $R = C_{12}H_{25}-$
2: $R = C_6H_{13}-$
3: $R = 2\text{-Et-}C_6H_{12}-$

Figure 1. Formula of the octasubstituted phthalocyanines synthesized and the two types of mesogens (columnar and nematic lenticular) which can be obtained.

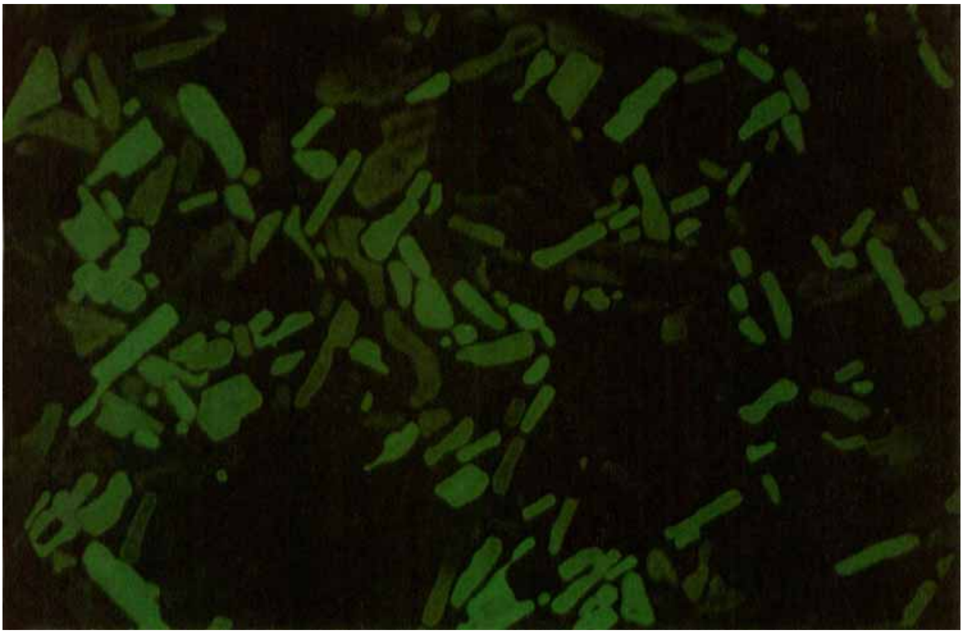


Figure 2. A photomicrograph between crossed polarizers of the compound **3** at 268°C under slight pressure (in the absence of pressure a homogeneously dark domain is observed).

which slowly leads to a homogeneous black domain. Birefringence reappears when defects are produced by a slight pressure on the glass cover (see figure 2). These defects relax spontaneously in a few minutes indicating the strong tendency to homeotropy of the preparation. At 270°C another transition is observed which leads to an isotropic liquid, insensitive to mechanical perturbations. By differential scanning calorimetry, another transition at about 170°C is found, with almost no change in the texture. The corresponding linear hexyl derivative has transitions at 102°C and at a temperature higher than 300°C. The enthalpies of transition are one order of magnitude smaller for the branched derivative than for the linear one (see the table). X-ray diffraction indicates that both solid phases are orthorhombic with similar parameter values. Compound **3** shows an unusual tetragonal mesophase in the temperature range 170–223°C. In this case, the normal to the macrocyclic central

Mesomorphic properties of the various discogens used in the present study. Temperatures in °C; enthalpies in kJ mol^{-1} in brackets; distances in Å.

		C	M_1	M_2	I
		91(130)			> 300
$(C_{12}O)_8PcH_2$ [7]	**1**	Orthorhombic		Hexagonal,	
		a, 27·8		D, 35	
		b, 25·8		h, 3·4	
		c, 4·3		L, 4·5	
		102(50)			> 300
$(C_6O)_8PcH_2$	**2**	Orthorhombic		Halos, 22·3;	
		a, 22·6		8·4; 4·8	
		b, 17·7		3·6	
		170(4·6)	223(7·61)		270(3·26)
$(2\text{-}Et\text{-}C_6O)_8PcH_2$	**3**	Orthorhombic	Tetragonal	Nematic	
		a, 23·4	a, 23·3	Halos, 21·4;	Halos, 22·4; 7·9
		b, 16·3		8·1; 4·3	4·3
				(245°C)	(285°C)

subunit is collinear with the axis of the column formed by superposition of the phthalocyanine rings whereas a tilt angle ($\theta = 50°$) occurs in the solid phase. The transition at 223°C drastically alters the X-ray pattern: only diffuse halos are observed at 21·4 Å, 8·1 Å and 4·3 Å (245°C). In the isotropic phase, these parameter values are conserved. CPK molecular models indicate that the overall size of the discogen is between 21 Å and 30 Å depending upon the conformation of the side chains. The distance of 21·4 Å is therefore probably related to the overall dimension of the mesogen. The value of 4·3 Å is conventionally found for disordered paraffinic chains. This has been confirmed by the X-ray diagram of 2-ethyl-hexyl bromide for which a correlation length of 4·3 Å was found. A faint halo at about 8 Å occurs in the X-ray diagram for the mesophase and the isotropic liquid phase of $(2\text{-}Et\text{-}C_6O)_8PcH_2$. The characteristic length of the molten hexyl side chains (7·91 Å) [11] is in accord with this value. Compound **2** gives a very similar X-ray pattern between 102°C and > 300°C. However, the nematic structure could not be assessed with certainty since homeotropic orientation could not be obtained.

In summary, $(2\text{-}Et\text{-}C_6O)_8PcH_2$ forms a mesophase, from 223°C to 270°C, which slowly reorients to form a homeotropic phase. X-ray diffraction at small angles shows only halos related to the molecular dimensions. The birefringence of the homeotropic phase reappears when pressure is applied to the cover slip. It can, therefore, be concluded that a nematic lenticular liquid crystal is formed. The phthalocyanine subunit is one of the most popular dyes [12]: it is used, for example, as blue and green filters in colour liquid crystal displays [13]. The use of liquid-crystalline orientable phthalocyanine derivatives in display devices can therefore be foreseen.

Mr. L. Bosio is thanked for the X-ray experiments and Mr. C. Sirlin is acknowledged for helpful discussions.

References

[1] Piechocki, C., Simon, J., Skoulios, A., Guillon, D., and Weber, P., 1982, *J. Am. chem. Soc.*, **104**, 5245; 1983, *Molec. Crystals liq. Crystals*, **100**, 275; 1985, *Ibid.*, **130**, 223.

[2] Piechocki, C., and Simon, J., 1985, *Nouv. J. Chim.*, **9**, 159.

[3] Destrade, C., Nguyen Huu Tinh, Gasparoux, H., Malthête, J., and Levelut, A. M., 1981, *Molec. Crystals liq. Crystals*, **71**, 111.

[4] KUCHARCZYK, N. (unpublished results).

[5] NGUYEN HUU TINH, MALTHÊTE, J., and DESTRADE, C., 1981, *Molec. Crystals liq. Crystals*, **64**, 251.

[6] IWHAN CHO, and YOUNGSOO LIM, 1987, *Chem. Lett.*, p. 2107; 1988, *Molec. Crystals liq. Crystals*, **154**, 9.

[7] OHTA, K., JACQUEMIN, L., SIRLIN, C., BOSIO, L., and SIMON, J., 1988, *Nouv. J. Chim.*, **12**, 751.

[8] MASUREL, D., SIRLIN, C., and SIMON, J., 1987, *Nouv. J. Chim.*, **11**, 455.

[9] PETIT, M., PLICHON, V., and BELKACEMI, H., *Nouv. J. Chim.* (in the press).

[10] N.M.R. data and elemental analysis are in agreement with the proposed structures. Microanalysis $(C_6O)_8PcH_2$: $C_{80}H_{114}N_8O_8$ (Mw, 1315·83). Calc. C, 73·02; H, 8·73; N, 8·52. Found: C, 71·97; H, 8·59; N, 8·20. $(2\text{-Et-}C_6O)_8PcH_2$: $C_{96}H_{146}O_8N_8$ (Mw, 1540·27). Calc.: C, 74·86; H, 9·56; N, 7·28. Found: C, 74·61; H, 9·48; N, 7·14.

[11] TANFORD, C., 1972, *J. phys. Chem.*, **76**, 3020.

[12] SIMON, J., and ANDRÉ, J. J., 1985, *Molecular Semiconductors* (Springer-Verlag).

[13] UCHIDA, T., YAMAMOTO, S., and SHIBATO, Y., 1983, *I.E.E.E. Trans. Electron. Devices*, **30**, 503.