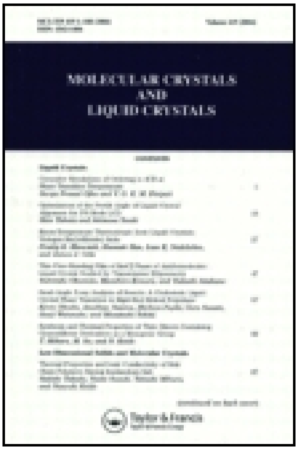


Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Dibenzophospholes: Phase Behavior of Novel Phosphorus-Based Chiral Liquid Crystals

Ernesto Durán [a] , Dolores Velasco [a] , Francisco López-Calahorra [a] & Heino Finkelmann [b]

[a] Departament de Química Orgànica, Facultat de Química, Universitat de Barcelona, Martí i Franquès 1-11, Barcelona, E-08028, Spain

[b] Institut für Makromolekulare Chemie, Albert-Ludwigs-Universität Freiburg, Hermann Staudinger Haus, Stefan-Meier-Straße 31, Freiburg, 79104, Germany

Version of record first published: 18 Oct 2010

To cite this article: Ernesto Durán, Dolores Velasco, Francisco López-Calahorra & Heino Finkelmann (2002): Dibenzophospholes: Phase Behavior of Novel Phosphorus-Based Chiral Liquid Crystals, Molecular Crystals and Liquid Crystals, 381:1, 43-57

To link to this article: http://dx.doi.org/10.1080/713738735

Mol. Cryst. Liq. Cryst., Vol. 381, pp. 43–57
Copyright © 2002 Taylor & Francis
1058-725X/02 \$12.00 + .00
DOI: 10.1080/10587250290102099

DIBENZOPHOSPHOLES: PHASE BEHAVIOR OF NOVEL PHOSPHORUS-BASED CHIRAL LIQUID CRYSTALS

Ernesto Durán, Dolores Velasco, and
*Francisco López-Calahorra**
Departament de Química Orgànica, Facultat de Química,
Universitat de Barcelona, Martí i Franquès 1-11, E-08028
Barcelona, Spain

Heino Finkelmann
Institut für Makromolekulare Chemie, Albert-Ludwigs-
Universität Freiburg, Hermann Staudinger Haus,
Stefan-Meier-Straße 31, 79104 Freiburg, Germany

A new family of phosphorus-based chiral liquid crystals is described. Dibenzophosphole oxides containing an asymmetric center at the phosphorus atom show cholesteric and smectic liquid crystalline behavior. The presence of the chiral center in the rigid heterocyclic core avoids the need for destabilizing chiral aliphatic branched substituents at the mesogenic unit. Racemic mixtures of the synthesized dibenzophospholes exhibit both nematic and smectic phases.

Keywords: phosphorus heterocycles; chiral phosphorus; chiral mesophases; cholesteric; smectic

INTRODUCTION

Over the last couple of decades several materials showing specific physical properties with respect to electronics and optics have been synthesized. A large number of liquid crystals have been produced in order to obtain a correlation between the chemical structure and the specific physical properties of the compounds. In this regard, the rigid carbazole unit has

---

Received 7 January 2002; accepted 7 February 2002.

This research was financially supported by the Spanish *Ministerio de Educación y Cultura*, grant PB96-1491, and a postgraduate fellowship to E. Durán from the *Generalitat de Catalunya*. We would also like to thank Dr. J. Carilla for carrying out and interpreting the DSC experiments.

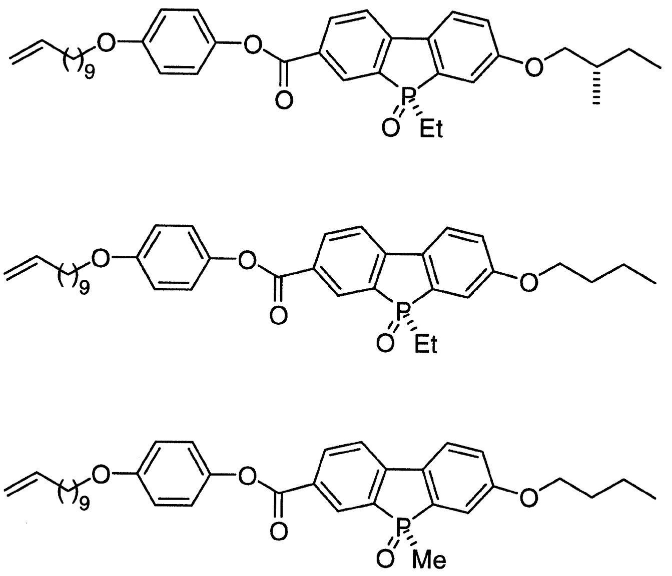
*Corresponding author. Fax 0034 93 3397878; E-mail: flopez@qo.ub.es interesting features and carbazole derivatives in the liquid crystalline state have been studied for several years [1–5]. We synthesized some liquid crystal side chain polysiloxanes based on the carbazolyl moiety containing chiral and achiral lateral chains [6,7], and analyzed their phase behavior. Unfortunately, they mainly exhibited monotropic smectic phases. Only one polymer showed a monotropic nematic phase, identified by the characteristic texture containing ± 1/2 singularities. Similarly, for the corresponding monomers only one derivative exhibited a nematic phase, while all others were crystalline.

Unlike in the case of carbazole derivatives substituted with laterally or ***end-on*** attached chiral substituents, a more effective chiral induction should be obtained if the stereocenter is placed directly within the rigid core of the mesogenic molecule [8]. Furthermore, polar groups attached directly to the stereocenter result in higher spontaneous polarization [9]. With this in mind, we decided to consider dibenzophosphole derivatives instead of carbazole systems in order to obtain new materials with phosphorus-based chiral liquid crystal phases. Dibenzophosphole oxides summarize both aspects: 1) the P=O double bond is highly polar and yields a dipolar system that is polarized perpendicularly to the long molecular axis; and 2) the phosphorus atom acts directly as a stereocenter. A pentavalent phosphorus atom does not contribute to the aromatic π system of dibenzophosphole as nitrogen does in carbazole systems. Therefore, the drawback present in carbazole and nonoxidized dibenzophosphole systems, namely the inversion process at phosphorus with an aromatic transition structure, is avoided. Consequently, the phosphorus atom maintains its absolute configuration even at high temperatures [10]. Moreover, the dibenzophosphole oxide groups can be more easily functionalized than carbazole systems in the 3 and 7 positions due to the *meta* activation of the benzene rings attached to the highly electron-withdrawing P=O function. These functions produce a donor-acceptor system that is polarized parallel to the long molecular axis. Higher yields are expected for the synthesis of the desired systems. In this paper we describe the phase behavior of some new phosphorus-based chiral liquid crystals.

SYNTHESIS

In light of the above-mentioned considerations we synthesized the three dibenzophosphole oxide derivatives summarized in Scheme 1, obtained after optical resolution of the corresponding racemic mixtures for compounds **2** and **3**, or the diastereomeric mixture for compound **1**.

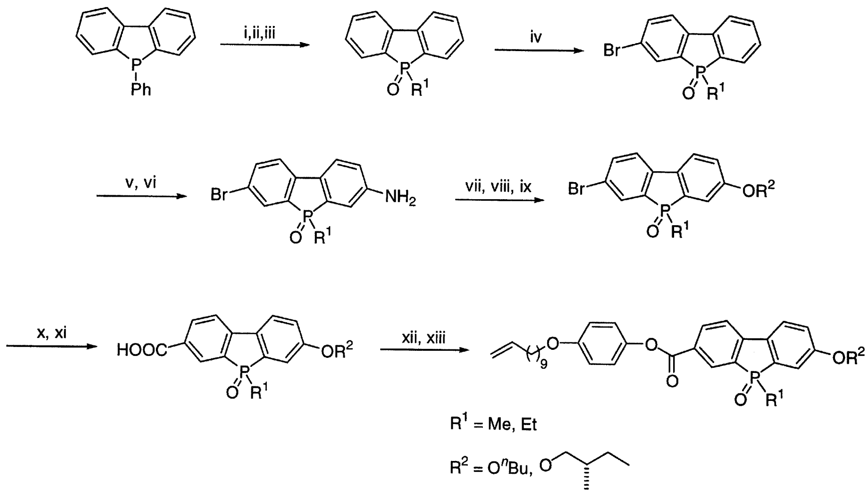
Compound **1** is structurally analogous to the previously synthesized carbazole derivatives and enables both rigid core heterocycles to be



SCHEME 1 Dibenzophosphole oxide mesogenes synthesized.

compared. The stereocenter in the lateral aliphatic chain is absent in compound **2**, as the phosphorus stereocenter will be sufficient to generate chiral mesophases. Furthermore, by avoiding branched alkyl chains substituted to the mesogenic unit, more stable mesophases are expected. In compound **3** the shorter lateral chain attached to the phosphorus atom will further help to optimize a calamitic molecular structure, and this will stabilize any mesophase that might be expected compared to the very similar compound **2**.

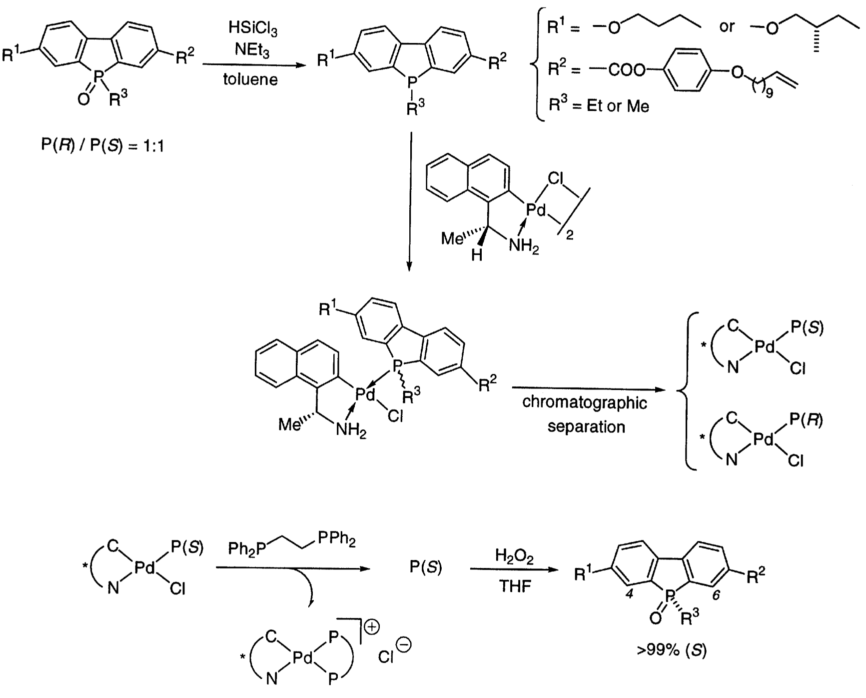
We recently described the synthesis and optical resolution of dibenzophosphole oxide **1** [11]. Compounds **2** and **3** were obtained in similar ways, according to the general procedure described in Scheme 2. We converted 5-phenyl-5*H*-dibenzophosphole into 5-ethyl-5*H*-dibenzophosphole 5-oxide by treatment with lithium in tetrahydrofurane followed by the addition of bromoethane or iodomethane and oxidation of the resulting 5-alkyl-5*H*-dibenzophosphole with hydrogen peroxide (steps i to iii). On studying some aromatic electrophilic substitution reactions within the dibenzophosphole system, we observed that bromination could be carried out under slow rate conditions that allowed the main formation of asymmetric 5-alkyl-3-bromo-5*H*-dibenzophosphole 5-oxide (step iv). Nitration of this dibenzophosphole in a fuming nitric/sulphuric acid mixture yielded 5-alkyl-3-bromo-7-nitro-5*H*-dibenzophosphole 5-oxide (step v). The nitro function was reduced to amino with iron in acidic conditions (step vi). The resulting



SCHEME 2 Reagents and conditions: i) Li, THF, r.t.; ii) EtBr or MeI, THF, r.t.; iii) H_2O_2, THF, r.t., 96% (steps (i) to (iii)); iv) Br_2, AcOH, MeOH, 45°C, 53%; v) HNO_3, H_2SO_4, 0°C, 100%; vi) Fe, HCl/H_2O, EtOH, reflux, 82%; vii) $NaNO_2$, H_2SO_4/H_2O, 0°C; viii) $Cu(NO_3)_2{\cdot}3H_2O$, Cu_2O, r.t., 87% (steps (vii) and (viii)); ix) *S*-2-methylbutyltosylate or 1-bromobutane, K_2CO_3, DMF, reflux, 95–100%; x) KCN, $Pd(OAc)_2$, PPh_3, $Ca(OH)_2$, DMF, 100°C, 92%; xi) HCl/H_2O, reflux, 80%; xii) DCC, DMAP, CH_2Cl_2, r.t.; xiii) 4-undec-10-enoxyphenol, r.t., 80% (steps (xii) and (xiii)).

amino group was converted into the diazonium salt with sodium nitrite in a cooled sulphuric acid/water mixture (step vii), followed by decomposition of the diazonium salt by adding copper (I) oxide in the presence of a large excess of copper (II) nitrate (step viii). Butyl and 2-methylbutyl lateral chains were incorporated by reaction of the phenol with the corresponding alkyl bromide or tosylate in the presence of potassium carbonate (step ix). The incorporation of the other lateral chain, in the position occupied by the bromine atom, was achieved in three steps. Cyano compound was obtained using potassium cyanide in mild conditions with palladium catalysis (step x). Hydrolysis of this compound in refluxing concentrated hydrochloric acid yielded the carboxylic acid (step xi), which was first activated by reaction with dicyclohexylcarbodiimide (step xii) and then converted into the final compounds by esterification with previously synthesized 4-undec-10-enoxyphenol (step xiii). Full details of the synthetic procedure have been recently reported [12].

Optical resolution of these compounds was successfully carried out following the general procedure described in Scheme 3. The first step was to reduce the dibenzophosphole 5-oxide by use of trichlorosilane; next, the reaction between the resulting reduced phosphine and an optically active



SCHEME 3 Optical resolution of dibenzophospholes.

dinuclear cyclopalladated compound derived from (*R*)-(+)-1-(1-naphthyl)-ethylamine gave a mixture of diastereomers that were separated by column chromatography, using a SiO_2 column with $CHCl_3$-acetone (100:3) as eluent. Up to 85% of each diastereomer was isolated, with d.e. > 95%. The third step of the resolution process was to decoordinate the dibenzophosphole through the reaction of the pure diastereomer with 1,2-bis(diphenylphosphino)ethane; the final step was to oxidate the optically pure ligand with hydrogen peroxide, yielding the corresponding dibenzophosphole 5-oxides with enantiomeric excess higher than 98% after chiral stationary phase HPLC analysis. Full details of the resolution procedure have been recently described [13].

PHASE BEHAVIOR OF THE DIBENZOPHOSPHOLES

All compounds were investigated with polarizing optical microscopy (POM), differential scanning calorimetry (DSC), and X-ray diffraction with regard to their liquid crystal behavior. Enantiopure compounds showed stable chiral cholesteric phases, and compound **3** showed stable smectic A and probably chiral smectic C phases as well. Racemic mixtures of compounds **2** and **3** showed nematic and smectic A phases, but complete crystallization of the mixture was observed some hours after preparation of the sample. All the compounds showed monotropic phases, which appeared only by cooling from the isotropic melt and not by heating the crystalline solid. Table 1 summarizes the thermal behavior of the synthesized dibenzophospholes.

Chiral Compound 1

The DSC study of this compound showed two phase transitions, the first from the isotropic liquid at 25°C with an associated enthalpy of 0.6 J/g, and the second at −4°C with an enthalpy of 0.8 J/g. Observation of the compound under the polarized light optical microscope showed a clear Grandjean-type cholesteric texture below 25°C with a high number of structural defects, but the typical reflection colors of a cholesteric sample were clearly observed. This cholesteric structure was further confirmed by the X-ray diffraction pattern at room temperature. The transition at −4°C could not be studied by X-ray diffraction for technical reasons.

Chiral Compound 2

Two phase transitions were observed by DSC experiments, the first from the isotropic melt at 40°C with an associated enthalpy of 0.6 J/g, and the second at −10°C with an enthalpy of 1.3 J/g. A cholesteric Grandjean texture was observed for a thin film of the sample under the polarizing microscope (Figure 1).

To confirm the cholesteric behavior of **2**, miscibility experiments were performed with the nematic solvent **4** (Scheme 4) (Merck, Darmstadt) between 40°C and −10°C. In order to determine whether the components were miscible over the whole concentration regime, a concentration gradient between both components was produced with a contact preparation, where the nematic solvent slowly diffuses into regions of the pure

TABLE 1 Phase Behavior of the Synthesized Dibenzophospholes

Compound	Phase behaviour temp. in °C
1(*S*)	Cryst 42 (S_X – 4) [0.8 J/g] (Ch 25) [0.6 J/g] I
2(*S*)	Cryst 60 (S_X – 10) [1.3 J/g] (Ch 40) [0.6 J/g] I
3(*S*)	Cryst 136 (S_X – 2) [0.5 J/g] (S_A 64) [1.6 J/g] (Ch 110) [0.2 J/g] I
2 (racemic)	Cryst 109 (S 1) [1.5 J/g] (N 81) [1.3 J/g] I
3 (racemic)	Cryst 121 (S_A 69) [0.3 J/g] (N 119) [2.6 J/g] I

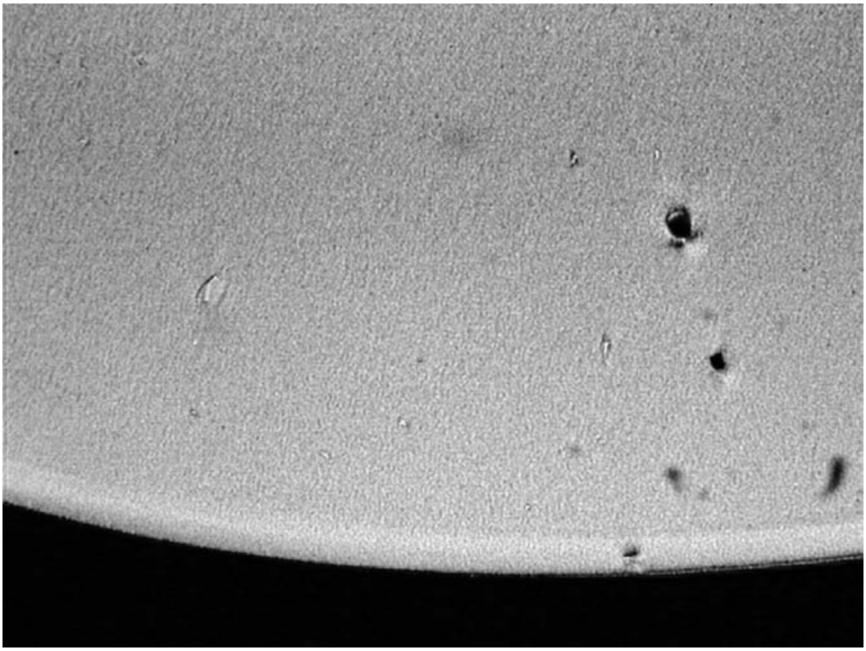
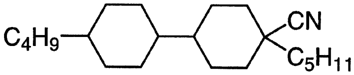


FIGURE 1 Grandjean texture of **2** at 25°C (See Color Plate I).

dibenzophosphole compound. After 90 h at 25°C a broad region with a proper concentration gradient could be observed between crossed polarizers, as shown in Figure 2. The regular appearance of Cano lines indicates the discontinuous jumps of the cholesteric pitch *p* by *p*/2 or *p* due to the concentration gradient of the chiral component. This experiment confirms that enantiopure dibenzophosphole **2** exhibits a cholesteric phase between 40 and −10°C.

Although the pure compound **2** only exhibits monotropic liquid crystalline phase behavior, the stability of the cholesteric texture at room temperature over a period of weeks enables the helical pitch *p* to be identified from measurements of the wavelength of reflection λ_R and the mean refractive index *n*. The reflection wavelength of the cholesteric



4

SCHEME 4 Nematic solvent.

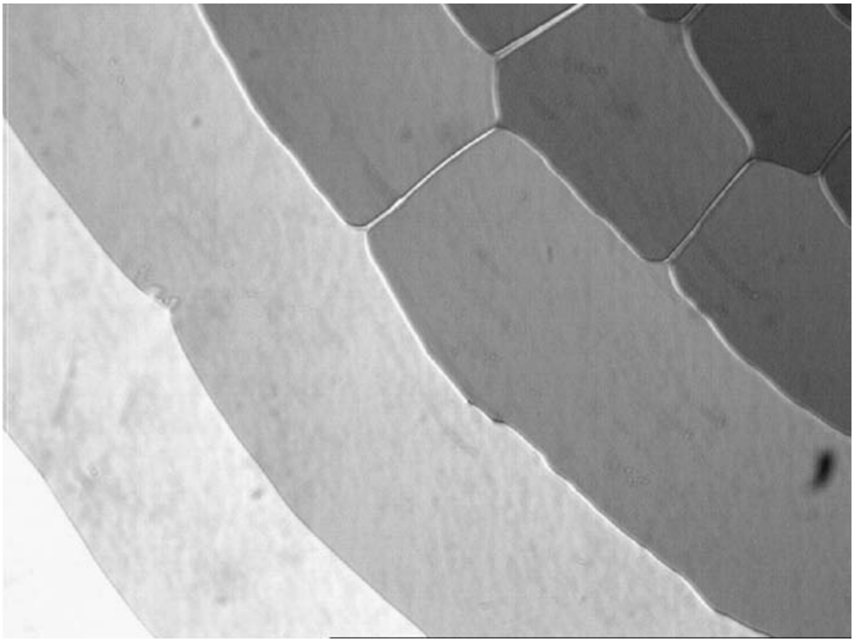


FIGURE 2 Concentration gradient between chiral compound **2** and nematic solvent **4** (after 90 h at 25°C) (See Color Plate II).

Grandjean textures was measured by absorption measurements giving $\lambda_R = 660\,\text{nm}$ at 25°C. With an Abbe refractometer the ordinary cholesteric refractive index of 1.597 and extraordinary index of 1.554 were measured at the same temperature. Converting the cholesteric refractive indexes into the refractive indexes of the basic nematic phase (i.e., the untwisted cholesteric phase) gave a value for the helical pitch of 414 nm.

Under X-ray diffraction, reflections were observed in the small angle region that corresponds to smectic fluctuations. The intensity of these reflections increased when cooling the sample from 40 to 25°C, indicating an expansion of the smectic fluctuations. This is a well-known phenomena in low molar mass cholesteric phases that exhibit a low temperature smectic phase. Unfortunately, the transition at −10°C could not be studied by X-ray diffraction for technical reasons.

For compounds **1** and **2**, the layer spacing distances obtained at 25°C for the smectic fluctuations inside the cholesteric phases were approximately the calculated mesogenic length of 33.6 Å in all *trans* conformation, indicating an orthogonal smectic A arrangement. This suggests that the low temperature smectic phase may be an S_A-phase.

Chiral Compound 3

For this compound three phase transitions were observed by DSC experiments: the first from the isotropic melt at 110°C with an enthalpy of 0.2 J/g; a second at 64°C with an associated enthalpy of 1.6 J/g; and the third at −2°C with an enthalpy of 0.5 J/g.

A typical Grandjean cholesteric texture was identified under the polarization microscope when a thin film of the sample was analyzed between crossed polarizers between 110 and 64°C (Figure 3). When the sample was cooled below 64°C into the regime between the second and the third DSC transition, the cholesteric Grandjean texture showed no visible changes, although the typical reflection color disappeared. This is obviously due to the high viscosity within this liquid crystalline phase, which does not allow the phase structure to be identified from the habits of the texture.

To identify the low temperature phase, X-ray diffraction experiments were performed, cooling the sample from the isotropic melt to room temperature. As described for the previous samples, even in the cholesteric state a small angle reflection was observed whose intensity increased when approaching the low temperature phase transition. Below the transition an

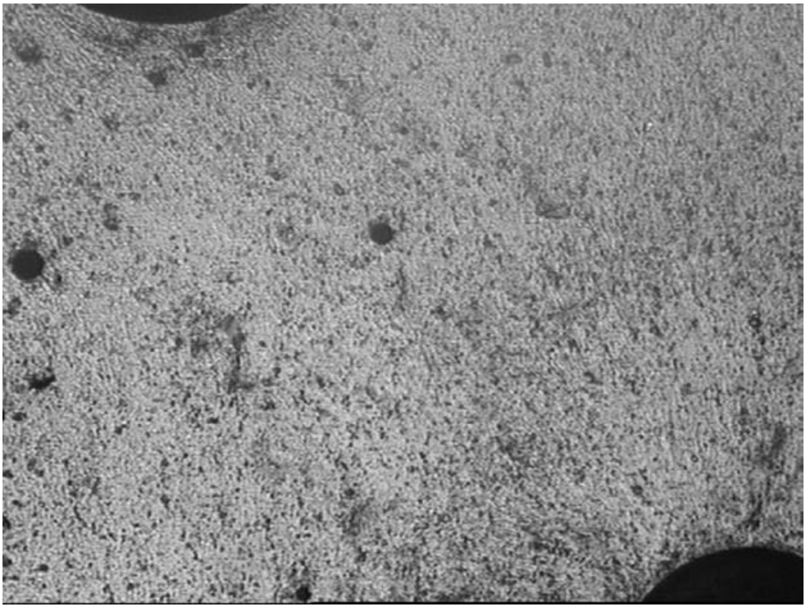
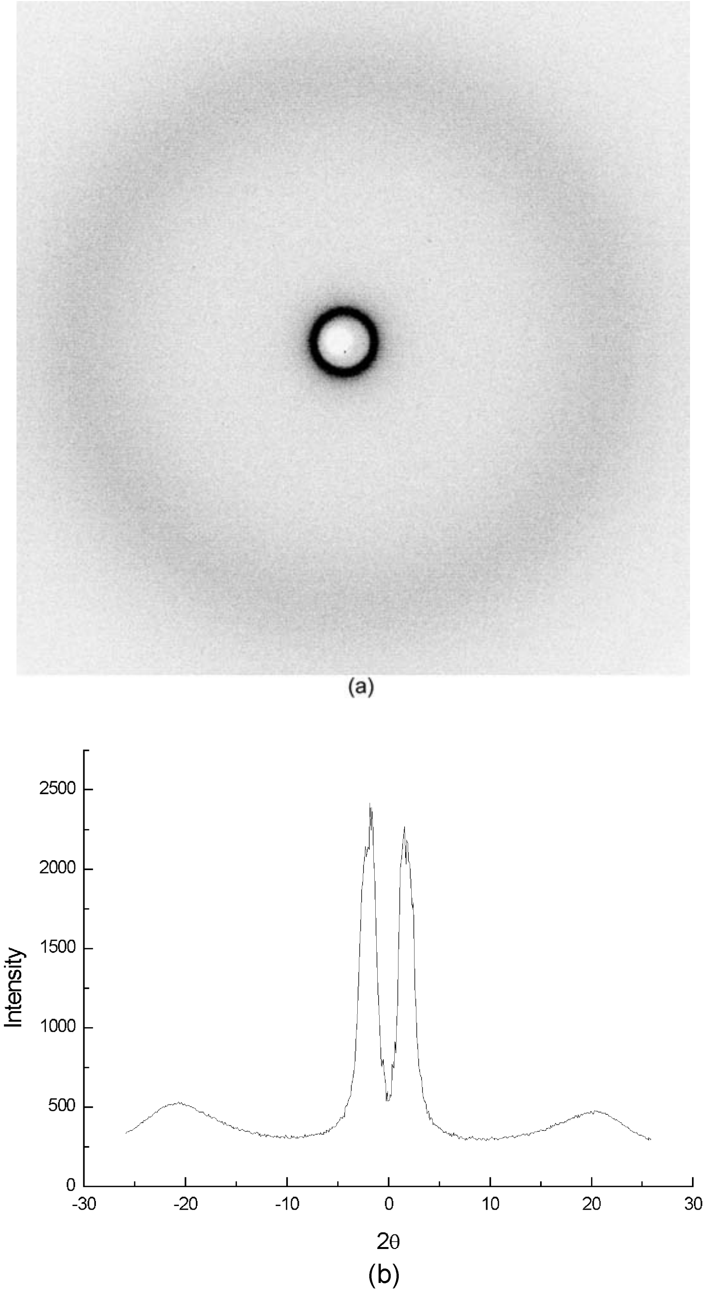


FIGURE 3 Cholesteric Grandjean texture of compound **3** at 90°C (See Color Plate III).


(a)

(b)

FIGURE 4 X-ray diffraction figure and profile for compound **3** in the smectic phase, at 28°C.

X-ray pattern as shown in Figure 4 could be observed, this being characteristic of smectic liquid crystalline phases.

Layer distances were calculated from X-ray diffraction profiles measured when cooling from the isotropic melt to room temperature. For chiral dibenzophosphole **3**, a layer spacing distance of 47.5 Å was measured at 25°C, a higher value than the calculated mesogenic length of 33.6 Å. The layer spacing distance decreased when cooling the cholesteric phase until transition to the smectic phase, it being more or less constant below this temperature (Figure 5).

The measured distance of 47.5 Å can be explained by a bimolecular association of the chiral dibenzophosphole **3** molecules, which stack their heterocyclic cores but place the long chains alternatively on both sides of the aromatic stack (Scheme 5). The calculated bimolecular length is 48 Å in all *trans* conformation for a total heterocyclic stacking.

In order to confirm the smectic A arrangement we oriented the sample in a 7.05 T magnetic field (300 MHz NMR magnet) while cooling slowly from the isotropic liquid (8°C/h), bringing the orientation through the Z-axis. After reaching room temperature the X-ray pattern was measured and two maxima were obtained in both small- and wide-angle azimuthal scattering distribution profiles (Figure 6), thus confirming the smectic A arrangement.

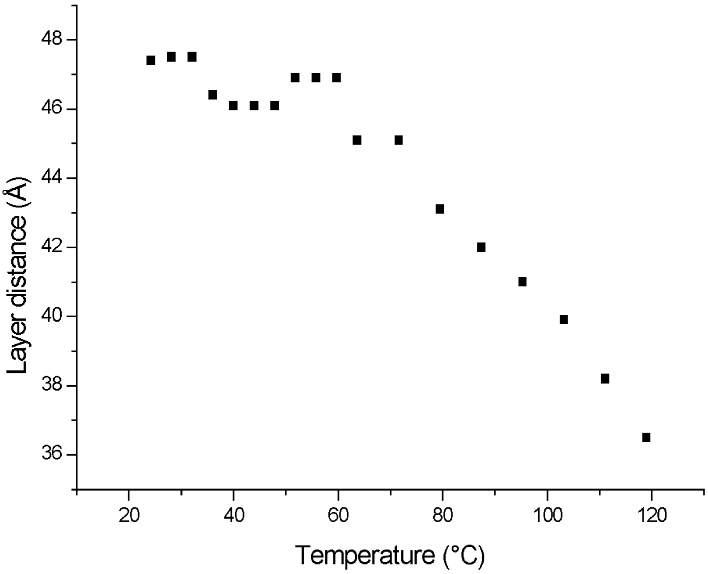
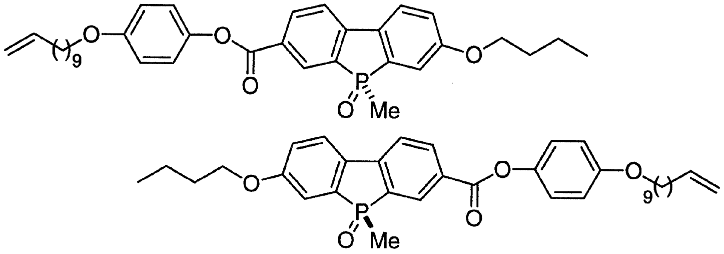


FIGURE 5 Layer distance dependence with temperature for chiral compound **3**.



SCHEME 5 Bimolecular association of chiral dibenzophosphole **3** with a total length of 48 Å.

Racemic Mixture of Compound 2

Two phase transitions were observed by DSC experiments, the first from the isotropic melt at 81°C with an associated enthalpy of 1.3 J/g, and the second at 1°C with an enthalpy of 1.5 J/g. A characteristic nematic *schlieren* texture with ± 1/2 singularities was observed under the polarization microscope when a thin film of the sample was analyzed between

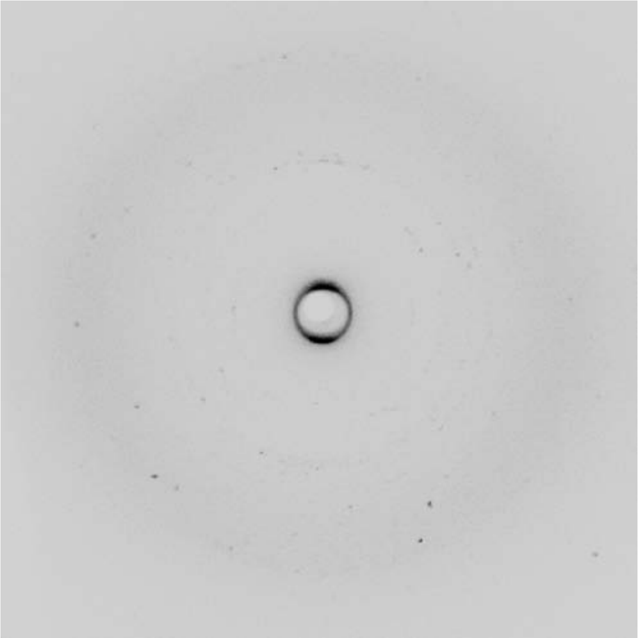


FIGURE 6 X-ray diffraction profile of the ordered smectic phase of compound **3** at 25°C.

crossed polarizers. The nematic behavior was confirmed by X-ray diffraction and reflections corresponding to smectic fluctuations were observed in the small angle regions. However, the rapid crystallization of the racemic mixture at room temperature prevented us from confirming the nematic behavior through miscibility experiments.

Racemic Mixture of Compound 3

Two phase transitions were observed by DSC experiments, the first from the isotropic melt at 120°C with an associated enthalpy of 2.6 J/g, and the second at 69°C with an enthalpy of 0.3 J/g. A ***schlieren*** nematic texture was observed under the polarization microscope between the two phase transition temperatures. The smectic behavior of the material below 69°C was determined by X-ray experiments. In contrast to the enantiopure compound, the measured layer spacing distance of the smectic phase, or the smectic fluctuations inside the nematic phase, the racemic mixture roughly corresponded to the molecular length of the mesogens in all ***trans*** conformation (Figure 7). The phase transition could be detected by an increase from 31.7 to 35.5 Å in the calculated layer distance between 63 and 72°C, which then decreased slowly to around 33.5 Å when cooling to room temperature.

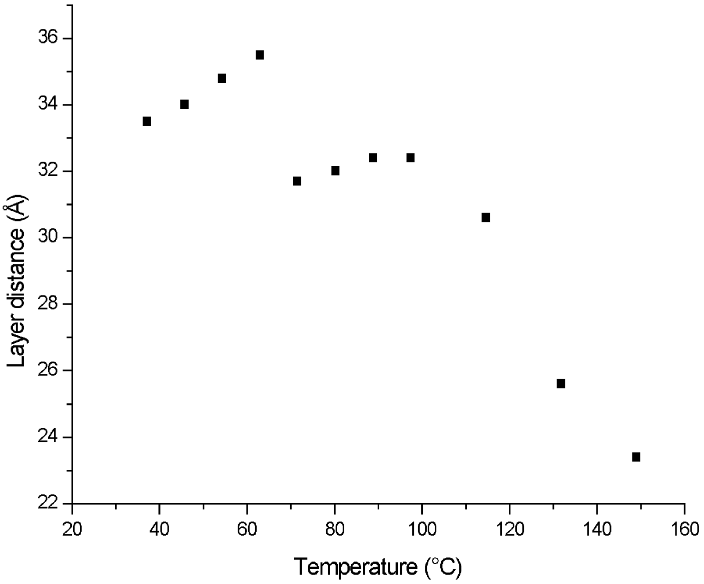


FIGURE 7 Layer distance dependence with temperature for racemic mixture of compound **3**.

The rapid crystallization of the smectic phase prevented us from confirming the smectic A behavior with a uniformly ordered sample, but the layer distance, being approximately equivalent to the calculated molecular length, indicates an orthogonal arrangement.

CONCLUSION

All the synthesized dibenzophosphole derivatives showed liquid crystalline behavior. They are the first liquid crystals to be derived from phosphorus heterocycles. Chiral compound **1**, the structural analogue to carbazole derivatives, showed a cholesteric phase even below room temperature. The voluminous phosphorus atom, and especially the pyramidal, pentavalent configuration with two out-of-plane groups, destabilize heterocyclic stacking of the mesogenic molecules. This fact explains the low melting points and transition temperatures observed for dibenzophosphole compounds compared with analogous carbazole derivatives.

When the chiral, branched aliphatic chain was substituted by a nonchiral linear *n*-butyl chain in compound **2**, the regime of existence of the cholesteric mesophase was stabilized. The most important aspect of this derivative is the stereocenter given by the phosphorus atom, which generates the chiral mesophase. No chiral substituents were necessary at the dibenzophosphole unit to induce chirality. The cholesteric phase of this compound was demonstrated by miscibility experiments and characterization of the helical pitch.

A broader cholesteric mesophase was observed for compound **3**. This is related to the substituents at the pyramidal, pentavalent phosphorus. This effect, which is well known for lateral substituents of conventional liquid crystals, is caused by the short methyl chain in **3**, rather than the ethyl chain in **2**, which is attached to the phosphorus atom.

As expected, racemic mixtures show monotropic, nematic, and smectic liquid crystalline phases in temperature intervals equivalent to that of the enantiopure dibenzophospholes. Unfortunately, these mixtures show a strong tendency towards crystallization, which prevents a detailed analysis of the phase structure.

It should be noted that the dibenzophosphole oxides are thermally stable and no decomposition or racemization occurs when these derivatives are heated at about 160°C for several days. However, further structural improvements have to be carried out in order to obtain enantiotropic, chiral mesophases. With respect to this problem, the reaction pathway described in this paper enables easy and numerous modifications of the dibenzophosphole oxide unit, and new syntheses are currently in progress.

ANALYTICAL TECHNIQUES

For polarizing microscopy a Mettler FP 82 hot stage controlled by a Mettler FP 80 central processor was used together with a Leitz Ortholux II Pol-BK microscope. Thermal analysis was performed using a Mettler-Toledo DSC821 differential scanning calorimeter at a heating rate of 10 K/min. X-ray diffractograms were monitored with an image plate system with Kiesig geometry.

REFERENCES

[1] Chapoy, L. L., Munck, D. K., Rasmussen, K. H., Diekmann, E. J., Sethi, R. K., & Biddle, D. (1984). *Mol. Cryst. Liq. Cryst.*, *105*, 353.
[2] Haarer, D., Meyer, H., & Strohriegl, P. (1991). *Makromol. Chem.*, *192*, 617.
[3] Kosaka, Y., Kato, T., & Uruyu, T. (1994). *Macromolecules*, *27*, 2658.
[4] Strohriegl, P., Lux, M., & Höcker, H. (1987). *Makromol. Chem.*, *188*, 811.
[5] Manickam, M., Kumar, S., Preece, J. A., & Spencer, N. (2000). *Liq. Cryst.*, *27*(5), 703.
[6] Arnim, V. V., Finkelmann, H., Dobarro, A., & Velasco, D. (1996). *Macromol. Chem. Phys.*, *197*, 2729.
[7] Dobarro, A., Velasco, D., Arnim, V. V., & Finkelmann, H. (1997). *Macromol. Chem. Phys.*, *198*, 2563.
[8] Bradshaw, M., Constant, J., & Raynes, E. (1986). *Ann. Conf. British Liquid Crystal Society*, Manchester, England.
[9] Otterholm, B., Nilsson, M., Lagerwall, S., & Skarp, K. (1987). *Liquid Crystals*, *2*(6), 757.
[10] Campbell, I. G. M., & Way, J. K. (1961). *J. Chem. Soc.*, 2133.
[11] Durán, E., Gordo, E., Granell, J., Velasco, D., & López-Calahorra, F. (2001). *Tetrahedron Lett.*, *42*, 7791.
[12] Durán, E., Velasco, D., & López-Calahorra, F. (2002). *Heterocycles* 57, 825.
[13] Durán, E., Gordo, E., Granell, J., Velasco, D., Solans, X., Font-Bardía, M., & López-Calahorra, F. (2001). *Tetrahedron: Asymmetry*, *12*, 1987.