Liquid Crystals
Publication details, including instructions for authors and subscription information:
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Laurent Douce[a]; Raymond Ziessel[a]; Rachid Seghrouchni[b]; Antoine Skoulios[b]; Eduardo Campillos[c]; Robert Deschenaux[c]
[a] Laboratoire de Chimie, d'Electronique et de Photonique Moléculaires, Ecole Européenne des Hautes Etudes des Industries Chimiques de Strasbourg, IPCMS, Strasbourg Cedex, France [b] Groupe des Matériaux Organiques, Institut de Physique et Chimie des Matériaux de Strasbourg, Strasbourg Cedex, France [c] Université de Neuchtel, Institut de Chimie, neuch, Switzerland

To cite this Article Douce, Laurent , Ziessel, Raymond , Seghrouchni, Rachid , Skoulios, Antoine , Campillos, Eduardo and Deschenaux, Robert(1996) '5,5'-Substituted-2,2'-bipyridines: A new series of liquid crystalline materials', Liquid Crystals, 20: 2, 235 — 242
To link to this Article: DOI: 10.1080/02678299608031130
URL: http://dx.doi.org/10.1080/02678299608031130

LIQUID CRYSTALS, 1996, VOL. 20, NO. 2, 235–242

5,5′-Substituted-2,2′-bipyridines: A new series of liquid crystalline materials

by LAURENT DOUCE and RAYMOND ZIESSEL*
Laboratoire de Chimie, d'Electronique et de Photonique Moléculaires,
Ecole Européenne des Hautes Etudes des Industries Chimiques de Strasbourg,
IPCMS, URM 46, 1 rue Blaise Pascal 67008 Strasbourg Cedex, France

RACHID SEGHROUCHNI and ANTOINE SKOULIOS*
Groupe des Matériaux Organiques, Institut de Physique et Chimie des Matériaux
de Strasbourg, URM 46, 23 rue du Loess, 67037 Strasbourg Cedex, France

EDUARDO CAMPILLOS and ROBERT DESCHENAUX
Université de Neuchâtel, Institut de Chimie, Av. de Bellevaux 51, 2000 Neuchâtel,
Switzerland

(*Received 7 August 1995; accepted 29 August 1995*)

Dissymmetric functionalization of 5,5′-dimethyl-2,2′-bipyridine with a 'stilbene type' chromophore bearing a terminal alkoxy group leads to a new family of mesomorphic compounds exhibiting a rich thermotropic polymorphism. A succession of smectic B, smectic A and nematic phases was observed. For the octyloxy compound, an additional phase was detected which was hexatic in symmetry.

1. Introduction

Significant advances have been made recently in the design, synthesis and characterization of thermotropic liquid crystal materials [1]. Such systems are formed by the spontaneous association of a large number of components into a specific phase with more or less well defined microscopic organization and macroscopic characteristics depending on its nature. These molecule based materials require the controlled assembly of specific building blocks that effectively transform discrete molecular properties into collective material properties. The tremendous development of liquid crystal based technologies require new types of mesomorphic materials that integrate novel structural elements and physical properties (optical, magnetic, resistivity or conductivity). Although transition metal complexes forming liquid crystals have been extensively studied, only a limited number of possible metal/ligand combinations have been investigated [1–3]. Among these, oligopyridines (for example, bipyridines, phenanthrolines, terpyridines) have been used for thermotropic liquid crystalline polymers based on homopolyesters of 5,5′-substituted 2,2′-bipyridine [4] and alkanoyl derivatives of 6,6′-diamino-2,2′-bipyridine and their metal complexes have also been previously studied [5]. Lyotropic mesomorphism has already been reported in a series of monosubstituted tris-(2,2′-bipyridine)ruthenium(II) complexes [6] and alkyl substituted terpyridine complexes of ruthenium(II) and rhodium(III) [7].

Recently, two simultaneous reports have described the mesomorphic behaviour of disubstituted 2,2′-bipyridine-esters (formula **A** below) [8] and stilbene-monosubstituted 2,2′-bipyridines (formula **B** below) [9].

The reasons which have led us and the others to adopt the 2,2′-bipyridine metal-binding domain are the following. The coordination chemistry of bipyridine has been intensively investigated during the past century [10]. This class of ligands is particularly attractive because of the easy formation of complexes with most elements in the periodic table, but those with transition metal ions have been most widely studied to date, giving rise to a wide variety of paramagnetic and luminescent complexes [11]. The introduction of conjugated linkages into these ligands is straightforward [12], allows control over the redox or photophysical properties of the metal centre and also permits further structural development of the system by specific covalent or non-covalent peripheral interactions of the substituents.

Here we wish to describe the synthesis and character-

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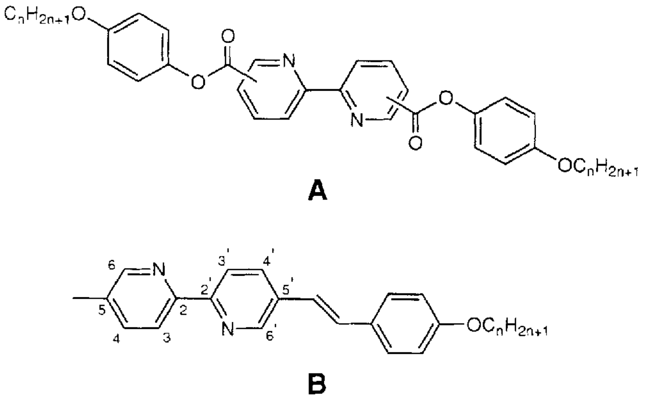
*Author for correspondence.



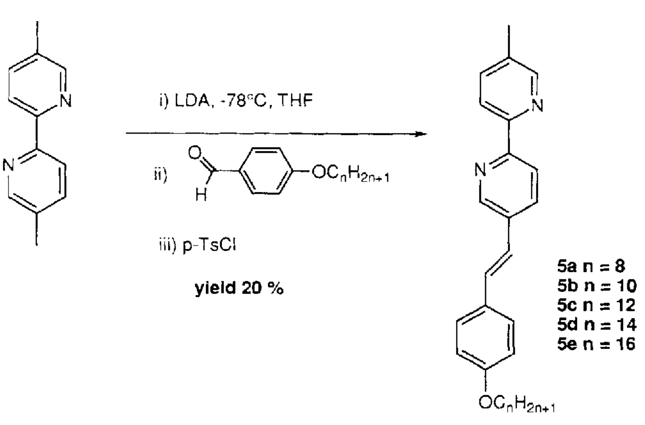
Molecular structures of the symmetric 2,2′-bipyridine-esters (**A**) [8] and asymmetric 2,2′-bipyridine stilbene compounds (**B**) [9].

ization of an asymmetric family of mesogenic compounds (formula **B** above) where $n = 8$, 10, 12, 14 and 16, based on a 2,2′-bipyridine core (potential complexation site) with an appended stilbene moiety in the 5-position (luminescent sensor), as well as the mesomorphic properties of the new liquid crystalline compounds. Some of these results have appeared in part as preliminary communication [9].

2. Synthesis

The preparation of the chelate based family of compounds is straightforward and involved the three step procedure depicted in the scheme.

The synthesis started from 5,5′-dimethyl-2,2′-bipyridine, obtained via Raney Nickel coupling of β-picoline [13]. Selective metallation at low temperature, followed by reaction with the appropriate aldehyde [14] afforded the vinyl compounds, after *in situ* dehydration in the presence of *p*-toluenesulphonyl chloride. The *trans*-stereoisomer was unambiguously assigned by a characteristic AB system with a coupling constant $J_{AB} =$ 16·4 Hz in the proton NMR spectrum (see the table for selected data). A *cis*-stereoisomer would exhibit a much lower coupling constant [15]. All new compounds were analysed by ^{1}H and $^{13}C\{^{1}H\}$ NMR, UV–vis and IR spectroscopy and elemental analysis. All data were consistent with the proposed molecular structures (see the table and experimental section for further details).



Scheme. Synthesis of the bipyridine stilbene compounds **5a**–**5e**.

3. Results and discussion

The liquid crystalline phases discussed in the present work were introduced in a recent preliminary communication [9] and are represented in the phase diagram shown in figure 1. The DSC thermograms registered upon heating and subsequent cooling between 0 and 230°C showed the presence of sharp peaks indicative of first order transitions. The peak occurring at the lowest temperature (see figure 1) corresponds to the melting of the crystal into a smectic $B_{(\mathrm{liq.\,cryst.})}$ phase. Related to the disordering of the paraffinic moiety, this peak involves an important enthalpy change increasing linearly with the number of carbon atoms of the alkyl chains (see figure 2). The corresponding slope ($3{\cdot}33 \pm 0{\cdot}15\,\mathrm{kJ\,mol^{-1}}$) gives a value of the melting enthalpy of the methylene groups of $238 \pm 11\,\mathrm{J\,g^{-1}}$ comparable to that found for the complete melting of linear paraffins ($289\,\mathrm{J\,g^{-1}}$ [16]) or for the transition of crystalline mesogens into a smectic phase ($272\,\mathrm{J\,g^{-1}}$ [17]). The peak corresponding to the transition from the smectic $B_{(\mathrm{liq.\,cryst.})}$ to the smectic A phase, related to the disordering of the aromatic cores of the molecules, involves an enthalpy change of about $3\,\mathrm{kJ\,mol^{-1}}$, independent of the length of the molecules as expected. Of relatively small enthalpy ($\Delta H < 3\,\mathrm{kJ\,mol^{-1}}$), the other transitions correspond to the change from one mesophase to another and ultimately to the full melting of the material into an isotropic liquid. It is of interest to note that the DSC thermograms of the $n = 8$ derivative contain an additional, hardly detectable peak ($\Delta H \sim 0{\cdot}01\,\mathrm{kJ\,mol^{-1}}$) at about 159°C (open circle in figure 1), suggesting a fifth, very weakly first order phase transition between the smectic A phase and a further mesomorphic phase, hexatic in nature as discussed below.

The optical textures observed upon slow cooling from the isotropic melt clearly show the existence of three distinct mesophases, namely a nematic (schlieren texture), a smectic A (focal-conic and homeotropic textures), and an ordered smectic mesophase (mosaic texture). The advent of a finely threaded texture on cooling the $n = 8$ derivative from the smectic A state fully confirmed the extra transition detected by DSC, corresponding to the occurrence of a hexatic phase between the S_A and S_B phases.

The nature of the liquid crystalline phases detected by DSC and identified by optical microscopy was con-

Table. Selected data for compounds **5a**–**5e**.

Compound	M_r	Calculated	Found	R_f[a]	λ/nm[b] (ε/M^{-1}cm^{-1})	$J(AB)$/Hz[c] ($\Delta\nu$/Hz)
5a	400·569	C 80·96	C 80·68	0·62	238	16·4
$n=8$		H 8·05	H 8·19		(24000)	(36·4)
		N 6·99	N 6·76			
5b	428·623	C 81·27	C 81·03	0·63	238	16·4
$n=10$		H 8·47	H 8·22		(25100)	(36·4)
		N 6·54	N 6·39			
5c	456·677	C 81·53	C 81·32	0·66	238	16·4
$n=12$		H 8·83	H 8·68		(25900)	(36·1)
		N 6·13	N 5·92			
5d	484·731	C 81·77	C 81·71	0·66	238	16·4
$n=14$		H 9·15	H 9·20		(25400)	(36·4)
		N 5·78	N 5·53			
5e	512·786	C 81·98	C 81·93	0·66	238	16·5
$n=16$		H 9·44	H 9·41		(27500)	(36·4)
		N 5·46	N 5·32			

[a] On alumina TLC in CH_2Cl_2 as eluent.
[b] In CH_2Cl_2 solvent.
[c] Determined by ^1H NMR in $CDCl_3$.

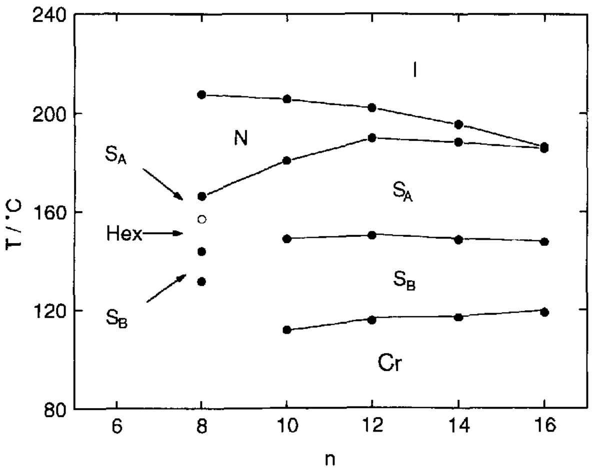


Figure 1. Phase diagram of compounds **5a–e** (I: isotropic liquid; N: nematic phase; S_A: smectic A phase; S_B: smectic B phase; Hex: hexatic phase: Cr: crystalline state.

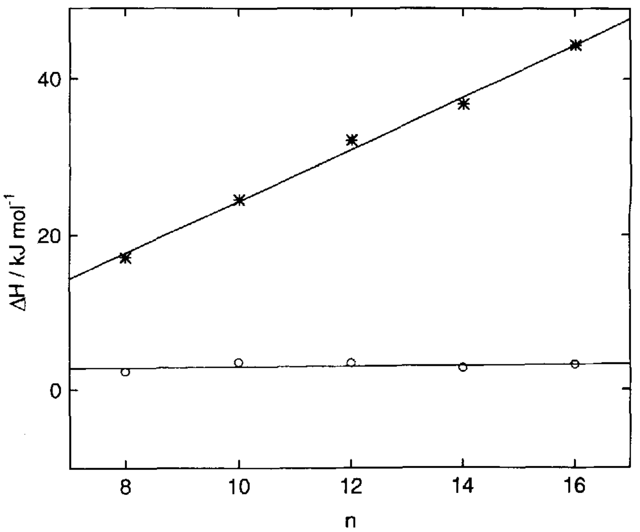


Figure 2. Phase transition enthalpies as a function of the number of carbon atoms in the alkyl chain; ✳, Cr–S; ○, S_B–S_A.

firmed by X-ray diffraction of magnetically oriented samples. The nature of the N phase was unambiguously established by the presence in the diffraction patterns of two equatorial diffuse spots at 4·5 Å, related to the lateral correlations of the elongated molecules oriented parallel to the magnetic field, and of two meridional diffuse spots at about $1/L$ (L being the molecular length), related to longitudinal correlations of the molecules within cybotactic groups (see figure 3 (*a*)). The nature of the smectic A phase was clearly confirmed by the persistence in the X-ray patterns of the two equatorial diffuse spots at 4·5 Å, related to the lateral packing correlations of the molecules, and by the sudden replacement (on cooling through the transition from the nematic) of the diffuse meridional spots by a series of equidistant sharp Bragg reflections aligned along the $0l$ axis normal to the equator, related to a smectic period of $d=L$ (see figure 3 (*b*)). The structure of the smectic B phase was proven by the replacement (upon cooling through the transition from S_A) of the diffuse equatorial spots of the smectic A phase by two fairly sharp reflections at 4·37 Å, related to the hexagonal lateral packing of the molecules within the smectic layers (see figure 3 (*c*)). The X-ray patterns of magnetically oriented samples of the extra

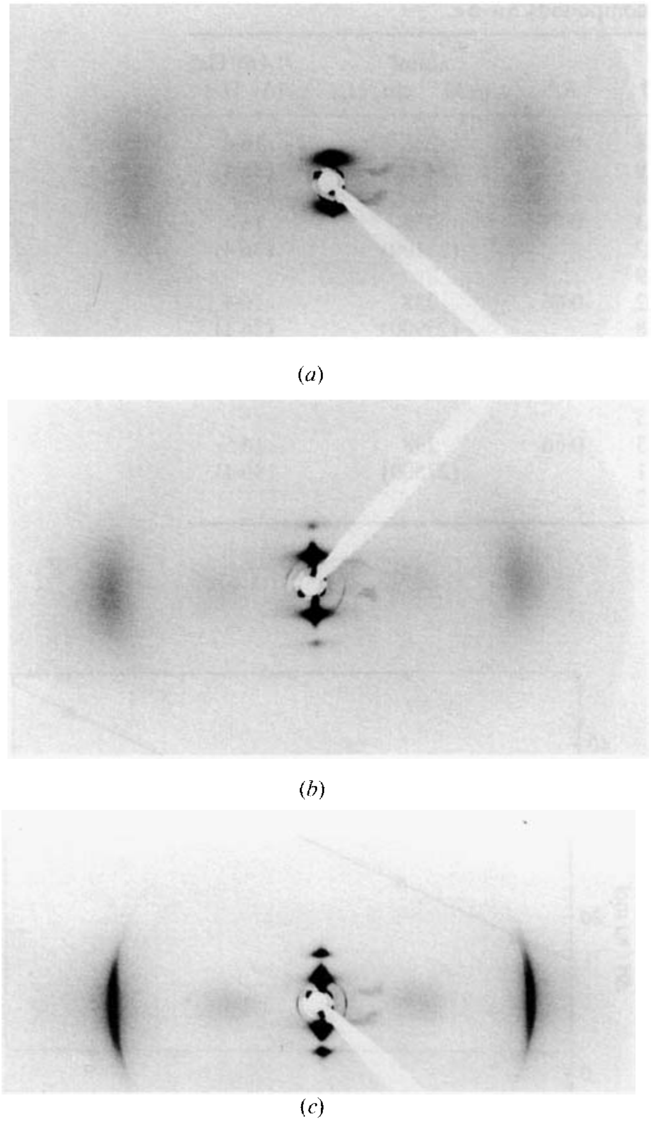


Figure 3. X-ray diffraction patterns of magnetically oriented samples slowly cooled from the nematic phase, recorded at high temperature with the magnetic field normal to the incident beam: (*a*) nematic phase of the $n = 12$ compound at 200°C; (*b*) smectic A phase of the $n = 8$ compound at 160°C; (*c*) smectic $B_{(\mathrm{liq.cryst.})}$ phase of the $n = 12$ compound at 140°C.

phase, observed with the $n = 8$ derivative between S_A and S_B, were very similar to those of S_B, the equatorial reflections being however slightly thicker. Its hexatic nature was definitely established by the X-ray patterns registered using samples oriented by following the 'freely suspended thin film' technique [18]. With the X-ray incident beam normal to the suspended film, the patterns contained six rather thick short arcs at 4·4 Å arranged hexagonally (see figure 4), related to the in-plane long range orientational order of the molecules. The thickness of all the (diffuse) equatorial reflections was grossly estimated from powder X-ray patterns (see figure 5) using a least-square Lorentzian fit; the in-plane positional correlation range of the molecules was thus found to be of the order 40 Å for smectic A at 162°C, 175 Å for the hexatic phase at 148°C, and 240 Å for the smectic B phase at 138°C.

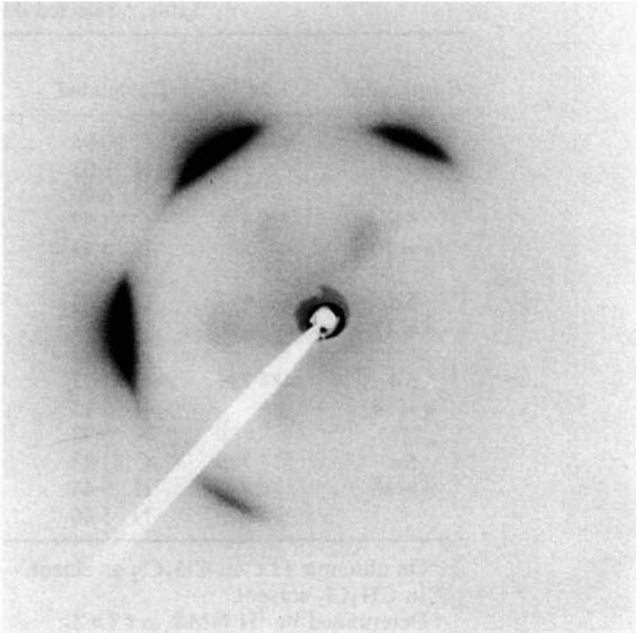


Figure 4. X-ray diffraction pattern of a freely suspended thin film of the hexatic mesophase of the $n = 8$ compound, recorded at 150°C with the incident beam normal to the smectic layers.

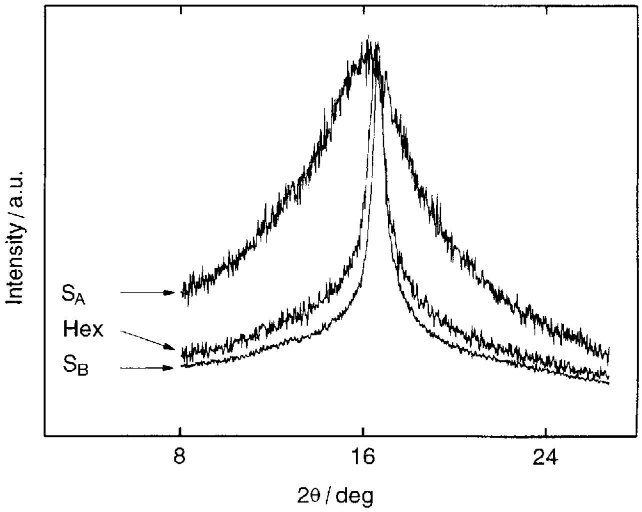


Figure 5. Profile of the wide-angle (diffuse) reflections of the smectic A, hexatic and smectic B phases of the $n = 8$ compound (X-ray powder patterns recorded with a curved position-sensitive INEL detector).

The structure of each smectic phase was then analysed quantitatively as a function of the molecular size. The smectic periods measured by X-ray diffraction with powder samples turned out to be very close to the molecular lengths estimated by molecular modelling (Sybyl software from Tripos). The smectic ordering corresponds therefore to a single-layered, head to tail arrangement of the aromatic cores oriented normal to the layers, with the alkyl chains in a disordered conformation standing between the smectic layers as already described for dissymmetric calamitic smectogens [19].

For the smectic B phase, the lateral packing of the upright aromatic cores is hexagonal with a unit cell parameter $D = 5{\cdot}05\,\text{Å}$, as deduced from the wide-angle reflection. The corresponding molecular area $s = (3)^{1/2}D^2/2 = 22{\cdot}1\,\text{Å}^2$ at 130°C is the same for all the compounds and equal to that (22–23 Å^2 [19]) usually found for calamitic smectogens in the smectic B state. As shown in figure 7, σ increases linearly with temperature. A least-squares linear fit of the data gives for the slope of the corresponding line a value of $\partial\sigma/\partial T = 11{\cdot}8 \times 10^{-3}\,\text{Å}^2\,\text{K}^{-1}$, and for the relative thermal expansion coefficient a value of $(1/\sigma)(\partial\sigma/\partial T) = 5{\cdot}3 \times 10^{-4}\,\text{K}^{-1}$, in agreement with values quoted in the literature [17]. As for the smectic period, it increases with the molecular size of the compounds in a linear manner (see figure 6). A least-squares linear fit of the data for $n \geqslant 10$ gives $d/\text{Å} = 20{\cdot}1 + 1{\cdot}28n$. The standard deviations are 0·5 Å for the Y intercept and 0·04 Å for the slope of the corresponding line. Quite interestingly, the Y intercept equals exactly the length of the aromatic core (~ 20 Å) estimated by molecular modelling, and the slope leads to a value of $\sigma(\partial d/\partial n) = 22{\cdot}1 \times 1{\cdot}28 = 28{\cdot}3\,\text{Å}^3$ at 130°C for the volume of one methylene group, equivalent to that ($28{\cdot}6\,\text{Å}^3$) quoted in the literature [20].

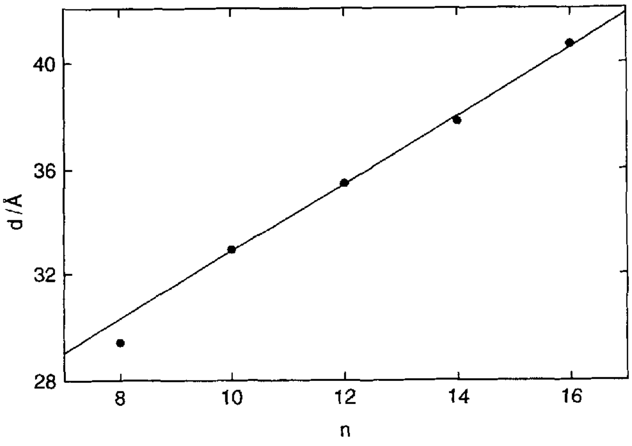


Figure 6. Variation of the layer thickness of the smectic B phases as a function of the number of carbon atoms in the alkyl chains of the molecules (130°C).

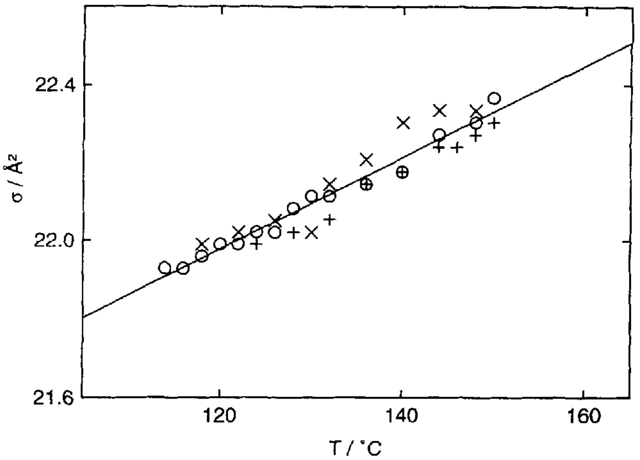


Figure 7. Temperature dependence of the lateral molecular area of the aromatic cores in the smectic B phase of compounds; (○) $n = 10$, (+) $n = 12$, and (×) $n = 16$.

It is fair to note that the period measured, experimentally for the smectic B phase of compound $n = 8$ (29·4 Å) is slightly lower (see figure 6) than the value (30·3 Å) expected from the least-squares fit line. This was confirmed otherwise by a systematic study of the temperature dependence of the smectic period of the $n = 8$ compared to the $n = 12$ derivative (see figure 8). Such a reduced smectic period suggests that the ordered smectic phase in question, which appears below the hexatic phase (see figure 1), is probably not a genuine smectic B, but an ordered crystal G phase with the molecules slightly tilted by a few degrees with respect to the layer normal, hardly visible in the X-ray patterns of magnetically oriented samples.

For the smectic A phase, the smectic period also increases in a linear manner with the molecular size (see figure 9), suggesting that the molecular area of the aromatic cores is practically independent of n. A least-square linear fit of the experimental data at 170°C gives: $d/\text{Å} = 19{\cdot}9 + 1{\cdot}29n$. The standard deviations are 0·3 Å for the Y intercept and 0·02 Å for the slope of the corresponding line. As for the smectic B phase, the Y intercept fits well with the calculated length of the aromatic core (~ 20 Å). From the slope of the line and the known value of the volume of one methylene group ($29{\cdot}5\,\text{Å}^3$ at 170°C [20]), one easily calculates for the average lateral packing area of the aromatic cores a value of $\sigma = 29{\cdot}5/(\partial d/\partial n) = 29{\cdot}5/1{\cdot}29 = 22{\cdot}9\,\text{Å}^2$, slightly larger than that found for the smectic B phase, in agreement with previous observations [19].

4. Conclusions

We have prepared and characterized a series of asymmetric substituted bipyridine ligands, containing a stilbene fragment covalently bond to the bipyridine

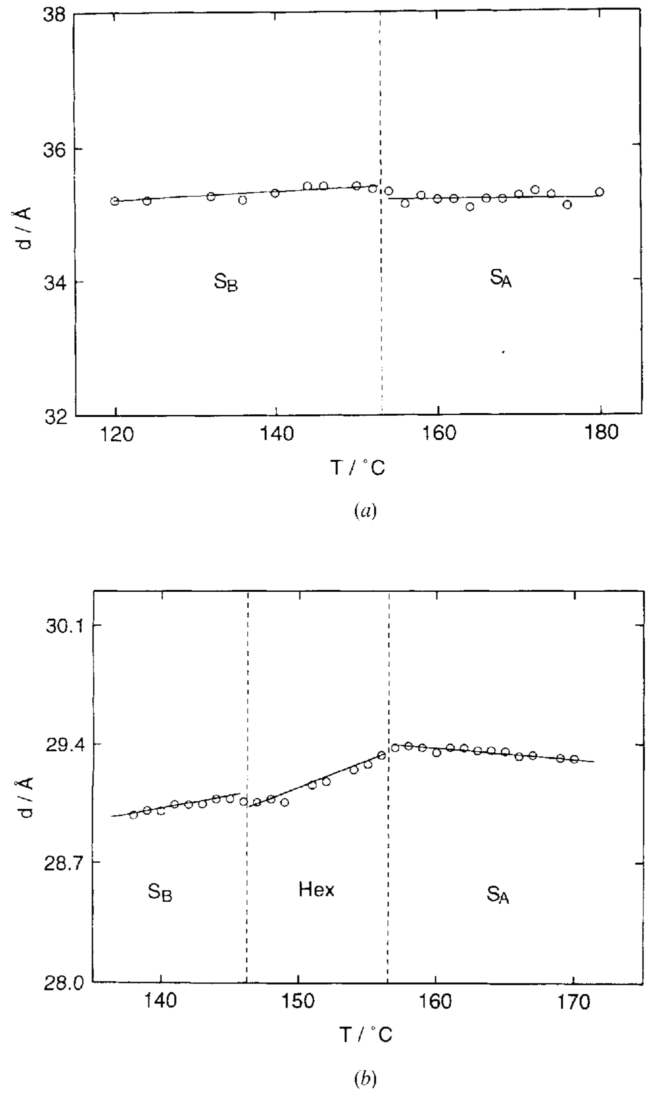


Figure 8. (*a*) Temperature dependence of the layer thickness of the smectic A and smectic B phases for **5c** $n = 12$. (*b*) Temperature dependence of the layer thickness of the smectic A, hexatic and smectic B phases for **5a** $n = 8$.

sub-unit and an alkoxy chain. We have found a succession of smectic $B_{(liq.cryst.)}$, smectic A and nematic phases on increasing temperature. For 5-methyl-5′-(4-*n*-octyloxyphenylvinyl)-2,2′-bipyridine, an additional hexatic phase was also characterized. We are continuing our studies on other substituted oligopyridines with the main objective of further establishing the potential to form novel metallomesogens with unexpected paramagnetic and/or luminescence properties.

5. Experimental section

All reactions were performed in Schlenk-type flasks under purified argon. The tetrahydrofuran was dried over sodium/benzophenone and distilled under argon.

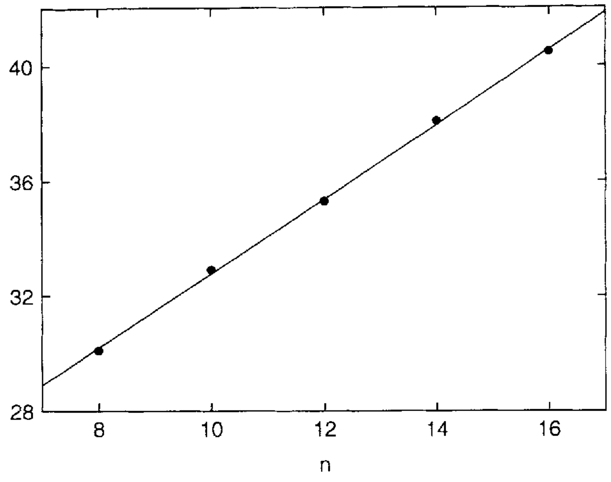


Figure 9. Variation of the layer thickness of the smectic A phases as a function of the number of carbon atoms in the alkyl chains (at 170°C).

Routine absorption spectra were measured using dichloromethane solutions at room temperature and a Uvikon 810 spectrophotometer. Infrared spectra were recorded in the region 4000–400 cm^{-1} on a FT-IR Bruker IFS-66 spectrophotometer. ^{1}H (200·1 MHz) and ^{13}C{^{1}H} (50·3 MHz) NMR spectra were recorded, at room temperature, on a FT Bruker WP-200 SY instrument. Deuteriated chloroform was used as a solvent and internal standard: δ(H) in ppm relative to residual protiated solvent (7·26) and δ(C) in ppm relative to $CDCl_3$ (77·03).

The liquid crystalline phases were investigated using (i) differential scanning calorimetry (Perkin–Elmer DSC7, heating and cooling rates of 5 K min^{-1}), (ii) polarizing optical microscopy (Leitz Orthoplan, Mettler FP82 hot stage), and (iii) X-ray diffraction. This last technique was used under various complementary conditions. Powder patterns were recorded either photographically or with a curved position-sensitive recorder (INEL-CPS120) using a Guinier focusing camera (bent-quartz monochromator, CuK$_{\alpha_1}$ radiation). Patterns of oriented specimens (either freely suspended thin films [18] or samples submitted to a 1·4 T magnetic field) were recorded photographically using a home-made pinhole camera (Ni-filtered copper radiation).

5.1. *5-Methyl-5′-[(4-octyloxyphenyl)vinyl]-2,2′-bipyridine* (**5a**)

A solution of *n*-butyl lithium in hexane (5·8 cm^3, 1·57 M, 8·14 mmol) was slowly added to a solution of di-isopropylamine (1·2 cm^3, 8·14 mmol) in THF (25 cm^3) at −78°C. After 0·5 h, solid 5,5′-dimethyl-2,2′-bipyridine (1·5 g, 8·14 mmol) was added to the stirred solution at −78°C. The solution turned immediately deep purple.

After 2 h, a solution of 4-octyloxybenzaldehyde (2·00 g, 1·05 eq, 8·55 mmol) in THF (5 cm^3) was added to the solution at −78°C via a cannula. After 0·25 h, the temperature was allowed to increase to room temperature; the homogeneous solution then became orange. The solution was stirred overnight and solid *p*-toluenesulphonyl chloride (1·55 g, 8·14 mmol) was then added. The solution became light yellow with formation of a precipitate. The solvent was distilled off under vacuum and the yellow-white solid was dissolved in CH_2Cl_2 and purified by column chromatography on alumina (CH_2Cl_2/hexane, 3/7, v/v as eluant). The second product was collected (R_f = 0·62, alumina, CH_2Cl_2), yield 0·67 g, 20 per cent. Analysis calculated for $C_{27}H_{32}N_2O$ (M_r = 400·569): C, 80·96; H, 8·05; N, 6·99. Found: C, 80·68; H, 8·19; N, 6·76. IR (KBr): 2923 (s), 2855 (m), 1602·5 (m), 1510·5 (m), 1467 (m), 1250 (m), 1024 (m), 1000 (m), 835 (m) cm^{-1}. UV(CH_2Cl_2) λ = 238 nm, ε = 24 000 M^{-1} cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 0·89 (t, 3 H, CH_3, ^3J(HH) = 6·5 Hz), 1·30 (m broad, 8 H, CH_2), 1·41 (m broad, 2 H, $OCH_2CH_2\mathit{CH}_2$), 1·79 (m broad, 2 H, $OCH_2\mathit{CH}_2$), 2·39 (s, 3 H, CH_3 bipy), 3·97 (t, 2 H, OCH_2, ^3J(HH) = 6·5 Hz), 7·07 (AB system, 2 H, *trans*-HC=CH, *J*(AB) = 16·4 Hz, Δν = 36·4 Hz), 7·19 (AB system, 4 H, H aromatic, *J*(AB) = 8·8 Hz, Δν = 113·1 Hz), 7·61 (dd, 1 H, $H_{4'or4}$ bipy, ^3J(HH) = 8·4 Hz, ^4J(HH) = 2·1 Hz), 7·92 (dd, 1 H, $H_{4'or4}$ bipy, ^3J(HH) = 7·6 Hz, ^4J(HH) = 2 Hz), 8·28 (d, 1 H, $H_{3'or3}$ bipy, ^3J(HH) = 8·4 Hz), 8·33 (d, 1 H, $H_{3or3'}$ bipy, ^3J(HH) = 7·6 Hz), 8·50 (d, 1 H, $H_{6or6'}$ bipy, ^4J(HH) = 2 Hz), 8·71 (d, 1 H, $H_{6or6'}$ bipy, ^4J(HH) = 2·1 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 14·05 (CH_3); 18·29 ($CH_{3\,bipy}$); 22·59, 26·0, 29·23, 29·32 and 31·78 (CH_2); 68·10 (OCH_2); 114·79, 120·45, 120·57, 122·44, 127·90, 129·35, 130·33, 133·00, 133·07, 133·13, 137·32, 147·74, 149·59, 151·73, 153·46, 154·64, 159·35 (C aromatic + bipy + C=C).

5.2. *5-Methyl-5′-[(4-decyloxyphenyl)vinyl]-2,2′-bipyridine* (**5 b**)

Same experimental procedure as for **5 a**. R_f = 0·63, yield 0·72 g, 21 per cent. Analysis calculated for $C_{29}H_{36}N_2O$ (M_r = 428·623): C, 81·27; H, 8·47; N, 6·54. Found: C, 81·03; H, 8·22; N, 6·39. IR (KBr): 2920 (s), 2851 (s), 1603 (m), 1511 (m), 1467 (m), 1250 (m), 1023 (m), 836 (m) cm^{-1}. UV(CH_2Cl_2) λ = 238 nm, ε = 25 100 M^{-1} cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 0·89 (t, 3 H, CH_3, ^3J(HH) = 6·4 Hz), 1·27 (m broad, 12 H, CH_2), 1·42 (m broad, 2 H, $OCH_2CH_2\mathit{CH}_2$), 1·80 (m broad, 2 H, $OCH_2\mathit{CH}_2$), 2·40 (s, 3 H, CH_3 bipy), 3·98 (t, 2 H, OCH_2, ^3J(HH) = 6·6 Hz), 7·08 (AB system, 2 H, *trans*-HC=CH, *J*(AB) = 16·4 Hz, Δν = 36·4 Hz), 7·19 (AB system, 4 H, H aromatic, *J*(AB) = 8·8 Hz, Δν = 113·6 Hz), 7·62 (dd, 1 H, $H_{4'or4}$ bipy, ^3J(HH) = 8·2 Hz, ^4J(HH) = 2·1 Hz), 7·93 (dd, 1 H, $H_{4or4'}$ bipy, ^3J(HH) = 8·4 Hz, ^4J(HH) = 2·2 Hz), 8·28 (d, 1 H, $H_{3'or3}$ bipy, ^3J(HH) = 8·2 Hz), 8·34 (d, 1 H, $H_{3or3'}$ bipy, ^3J(HH) = 8·4 Hz), 8·50 (d, 1 H, $H_{6'or6}$ bipy, ^4J(HH) = 2·1 Hz), 8·72 (d, 1 H, $H_{6or6'}$ bipy, ^4J(HH) = 2.2 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 14·08 (CH_3); 18·33 ($CH_{3\,bipy}$); 22·65, 26·0, 29·21, 29·27, 29·35, 29·53 and 31·86 (CH_2); 68·05 (OCH_2); 114·74, 120·45, 120·58, 122·37, 127·91, 129·27, 130·31, 132·98, 133·05, 133·20, 137·40, 147·77, 149·60, 153·41, 154·60, 159·31 (C aromatic + bipy + C=C).

5.3. *5-Methyl-5′-[(4-dodecyloxyphenyl)vinyl]-2,2′-bipyridine* (**5 c**)

Same experimental procedure as for **5 a**. R_f = 0·66, yield 0·73 g, 20 per cent. Analysis calculated for $C_{31}H_{40}N_2O$ (M_r = 456·677): C, 81·53; H, 8·83; N, 6·13. Found: C, 81·32; H, 8·68; N, 5·92. IR (KBr): 2955 (s), 2916 (s), 2850 (s), 1602 (m), 1510 (m), 1466 (m), 1422 (m), 1253 (m), 1023 (m), 835 (m) cm^{-1}. UV(CH_2Cl_2) λ = 238 nm, ε = 25 900 M^{-1} cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 0·90 (t, 3 H, CH_3, ^3J(HH) = 6·4 Hz), 1·28 (m broad, 16 H, CH_2), 1·43 (m broad, 2 H, $OCH_2CH_2\mathit{CH}_2$), 1·80 (m broad, 2 H, $OCH_2\mathit{CH}_2$), 2·40 (s, 3 H, CH_3 bipy), 3·99 (t, 2 H, OCH_2, ^3J(HH) = 6·5 Hz), 7·08 (AB system, 2 H, *trans*-HC=CH, *J*(AB) = 16·4 Hz, Δν = 36·1 Hz), 7·19 (AB system, 4 H, H aromatic, *J*(AB) = 8·7 Hz, Δν = 112·6 Hz), 7·62 (dd, 1 H, $H_{4'or4}$ bipy, ^3J(HH) = 8·1 Hz, ^4J(HH) = 1·8 Hz), 7·99 (dd, 1 H, $H_{4or4'}$ bipy, ^3J(HH) = 8·4 Hz, ^4J(HH) = 2·1 Hz), 8·30 (d, 1 H, $H_{3'or3}$ bipy, ^3J(HH) = 8·1 Hz), 8·35 (d, 1 H, $H_{3or3'}$ bipy, ^3J(HH) = 8·4 Hz), 8·51 (d, 1 H, $H_{6'or6}$ bipy, ^4J(HH) = 1·8 Hz), 8·72 (d, 1 H, $H_{6or6'}$ bipy, ^4J(HH) = 2·1 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 14·11 (CH_3); 18·35 ($CH_{3\,bipy}$); 22·68, 26·03, 29·24, 29·38, 29·59, 29·64 and 31·90 (CH_2); 68·11 (OCH_2); 114·77, 120·49, 120·60, 122·39, 127·94, 129·3, 130·33, 133·02, 133·22, 137·44, 147·77, 149·62, 159·32 (C aromatic + bipy + C=C).

5.4. *5-Methyl-5′-[(4-tetradecyloxyphenyl)vinyl]-2,2′-bipyridine* (**5 d**)

Same experimental procedure as for **5 a**. R_f = 0·66, yield 0·76 g, 19 per cent. Analysis calculated for $C_{33}H_{44}N_2O$ (M_r = 484·731): C, 81·77; H, 9·15; N, 5·78. Found: C, 81·71; H, 9·20; N, 5·53. IR (KBr): 2918 (s), 2850 (m), 1603 (m), 1512 (m), 1467 (m), 1252 (m), 1022 (m), 836 (m) cm^{-1}. UV(CH_2Cl_2) λ = 238 nm, ε = 25 400 M^{-1} cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 0·89 (t, 3 H, CH_3, ^3J(HH) = 6·4 Hz), 1·28 (m broad, 20 H, CH_2), 1·46 (m broad, 2 H, $OCH_2CH_2\mathit{CH}_2$), 1·81 (m broad, 2 H, $OCH_2\mathit{CH}_2$), 2·41 (s, 3 H, CH_3 bipy), 3·99 (t, 2 H, OCH_2, ^3J(HH) = 6·5 Hz), 7·09 (AB system, 2 H, *trans*-HC=CH, *J*(AB) = 16·4 Hz, Δν = 36·4 Hz), 7·20 (AB system, 4 H, H aromatic, *J*(AB) = 8·8 Hz, Δν = 113·2 Hz), 7·63 (dd, 1 H, $H_{4'or4}$ bipy, ^3J(HH) = 8·2 Hz, ^4J(HH) = 1·8 Hz), 7·94 (dd, 1 H, $H_{4or4'}$ bipy, ^3J(HH) = 8·4 Hz, ^4J(HH) = 2·2 Hz), 8·30 (d, 1 H, $H_{3'or3}$ bipy, $^3J(HH) = 8·2\,Hz$), 8·35 (d, 1 H, $H_{3or3'}$ bipy, $^3J(HH) = 8·4\,Hz$), 8·51 (d, 1 H, $H_{6'or6}$ bipy, $^4J(HH) = 1·8\,Hz$), 8·73 (d, 1 H, $H_{6or6'}$ bipy, $^4J(HH) = 2·2\,Hz$). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 14·11 (CH_3); 18·37 (CH_{3bipy}); 22·68, 26·04, 29·26, 29·38, 29·67 and 31·92 (CH_2); 68·13 (OCH_2); 114·81, 120·49, 120·63, 122·45, 127·95, 129·36, 130·37, 133·03, 137·42, 147·81, 149·65, 153·49, 156·47, 159·36 (C aromatic + bipy + C=C).

5.5. *5-Methyl-5′-[(4-hexadecyloxyphenyl)vinyl]-2,2′-bipyridine* (**5e**)

Same experimental procedure as for **5a**. $R_f = 0·66$, yield 0·79 g, 19 per cent. Analysis calculated for $C_{35}H_{48}N_2O$ ($M_r = 512·786$): C, 81·98; H, 9·44; N, 5·46. Found: C, 81·93; H, 9·41; N, 5·32. IR (KBr): 2916 (s), 2847 (m), 1603 (m), 1510 (m), 1466 (m), 1249 (m), 1022 (m), 835 (m) cm^{-1}. UV(CH_2Cl_2) $\lambda = 238\,nm$, $\varepsilon = 27\,500\,M^{-1}\,cm^{-1}$. ^1H NMR ($CDCl_3$) δ 0·90 (t, 3 H, CH_3, $^3J(HH) = 6·5\,Hz$), 1·27 (m broad, 24 H, CH_2), 1·43 (m broad, 2 H, $OCH_2CH_2\mathit{CH_2}$), 1·81 (m broad, 2 H, $OCH_2\mathit{CH_2}$), 2·41 (s, 3 H, CH_3 bipy), 3·99 (t, 2 H, OCH_2, $^3J(HH) = 6·5\,Hz$), 7·09 (AB system, 2 H, *trans*-HC=CH, $J(AB) = 16·5\,Hz$, $\Delta\nu = 36·4\,Hz$), 7·20 (AB system, 4 H, H aromatic, $J(AB) = 8·7\,Hz$, $\Delta\nu = 113·8\,Hz$), 7·63 (dd, 1 H, $H_{4'or4}$ bipy, $^3J(HH) = 8·2\,Hz$, $^4J(HH) = 2·0\,Hz$), 7·95 (dd, 1 H, $H_{4or4'}$ bipy, $^3J(HH) = 8·4\,Hz$, $^4J(HH) = 2·2\,Hz$), 8·29 (d, 1 H, $H_{3'or3}$ bipy, $^3J(HH) = 8·2\,Hz$), 8·35 (d, 1 H, $H_{3or3'}$ bipy, $^3J(HH) = 8·4\,Hz$), 8·51 (d, 1 H, $H_{6'or6}$ bipy, $^4J(HH) = 2·0\,Hz$), 8·73 (d, 1 H, $H_{6or6'}$ bipy, $^4J(HH) = 2·2\,Hz$). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 14·06 (CH_3); 18·29 (CH_{3bipy}); 22·62, 25·94, 29·18, 29·32, 29·49 and 31·83 (CH_2); 68·04 (OCH_2); 114·71, 120·54, 122·33, 127·87, 130·27, 132·97, 137·37, 147·74, 149·56, 153·37, 159·26 (C aromatic + bipy + C=C).

This work was partially supported by CNRS; R.Z. is most grateful to the EHICS for special financial support. R.D. acknowledges Ciba-Geigy–Jubiläums-Stiftung for a post-doctoral fellowship to E.C.

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