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Liquid Crystals

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Vinamidines and vinamidinium salts. New thermotropic liquid crystals

A. Zinsou^a; M. Veber^{ab}; H. Strzelecka^a; C. Jallabert^b; A. M. Leveluts^b

^a IESPCI, Laboratoire de Chimie et Electrochimie des matériaux moléculaires, Paris, Cedex 05, France ^b

Laboratoire de Physique des Solides, Bâtiment 5 10, Université Paris Sud, Orsay, France

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Vinamidines and vinamidinium salts New thermotropic liquid crystals

by A. ZINSOU†, M. VEBER*†‡, H. STRZELECKA†, C. JALLABERT‡,
and A. M. LEVELUT‡

†ESPCI, Laboratoire de Chimie et Electrochimie des matériaux moléculaires,
10 rue Vauquelin, 75231 Paris, Cedex 05, France

‡Laboratoire de Physique des Solides, Bâtiment 510, Université Paris Sud,
91405 Orsay, France

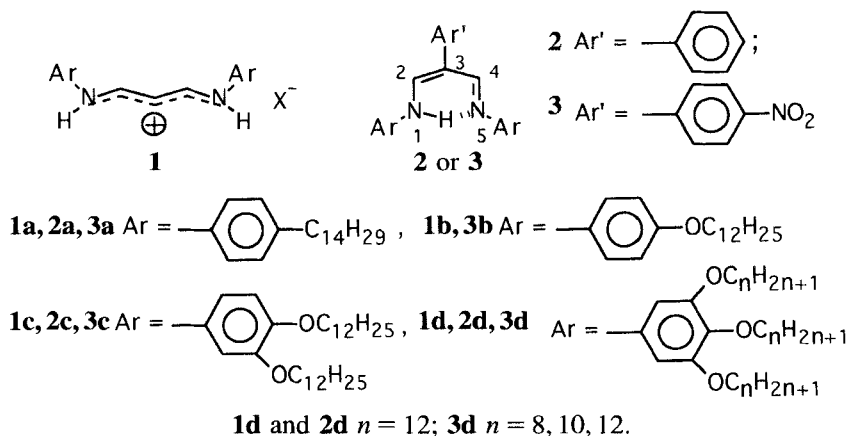
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Following studies concerning mesomorphic heteroaromatic salts (pyrylium, thiopyrylium, dithiolium), we present here new thermotropic liquid crystal materials based on 1,5-diazapentadienium (vinamidinium) salts and on the pseudocyclic vinamidine system (1,5-diazapentadiene). The mesomorphic properties of these systems have been studied by microscopic observations, DSC and X-ray diffraction.

1. Introduction

We have been interested for a long time in the synthesis and study of the mesomorphic properties of heteroaromatic ionic materials. 3,5-Diaryldithiolium salts and 2,6-diaryl- and 2,4,6-triaryl-pyrylium salts exhibit either S_A or columnar (D_h) phases, depending on the symmetry of the system and the number of paraffinic chains surrounding the heteroaromatic core [1, 2, 3]. In the case of pyrylium salts substituted by six paraffinic chains, we have shown that the anion determines the mesomorphic properties of the $n = 2$ and 3 homologues [2]. In all cases studied, the central rigid core was *ionic* and *cyclic*.

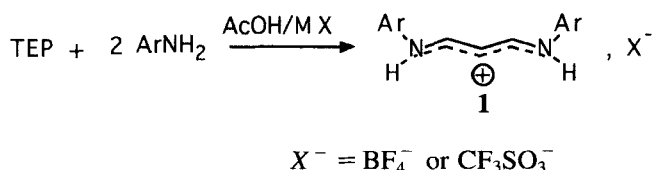
In order to find what the influence of an *open* ionic system or a *neutral* pseudoaromatic core would be upon the mesomorphism, we synthesized vinamidinium salts **1** and vinamidines **2** and **3** [4]



* Author for correspondence.

2. Synthesis

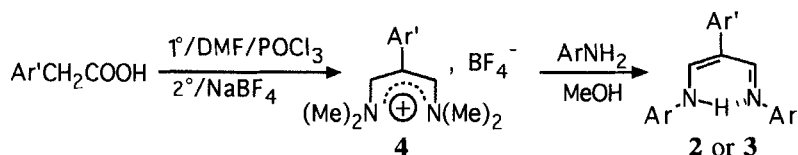
Vinamidinium salts **1** were obtained as described previously [5] by condensation of 1,1,3,3-tetraethoxypropane (TEP) with suitable anilines, according to the following scheme:



The synthesis and spectral characteristics of the precursor substituted anilines have been described elsewhere [5].

The yields of the vinamidinium salts **1** are given in table 1.

The vinamidines **2** and **3** were obtained starting from the arylacetic acid, by a modification of procedures described in the literature in the case of aniline itself and phenylacetic acids [6]



The Vilsmeier and Haack reaction on the arylacetic acid leads to the vinamidinium salts **4** which were converted into the desired vinamidines by aminolysis.

Yields of the vinamidines **2** and **3** are given in table 2. The experimental conditions are presented in §5.

3. Mesophase characterization

Mesophase types were identified by optical microscopic observations (Leitz Orthoplan polarizing microscope equipped with a Mettler FP80 variable temperature stage) and by X-ray diffraction studies. Transition temperatures were measured by microscopy and by DSC (DSC7 Perkin-Elmer).

Powder patterns for all the compounds studied were recorded with a Guinier camera: a monochromatic X-ray beam ($\lambda\text{CuK}_{\alpha_1} = 1.540 \text{ \AA}$) was obtained by reflection on a cylindrical, quartz, Johannson monochromator. The X-ray beam was in the shape of a small vertical linear segment ($10 \times 0.1 \text{ mm}^2$). The Guinier camera diameter was 114.7 mm. The sample in its Lindemann capillary tube ($\phi = 1.1 \text{ mm}$) was rotated about its vertical axis and heated by an air stream (temperature regulated to $\pm 2^\circ\text{C}$). Exposure times were typically $\approx 15 \text{ h}$.

3.1. Vinamidinium salts **1**

3.1.1. Microscopic observations and DSC

Transition temperatures for the vinamidinium salts **1** (determined either by microscopy or DSC) are given in table 3. Vinamidinium salts **1** with BF_4^- as anion are not stable enough to give reproducible microscopic data. Decomposition of the samples always occurs upon reaching the isotropic phase. The system can be stabilized by exchanging BF_4^- for CF_3SO_3^- .

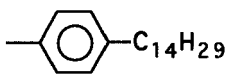
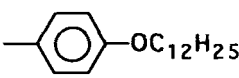
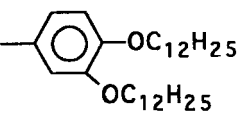
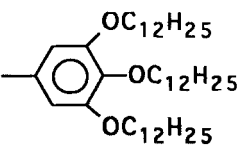
Table 1. Yields and recrystallization solvents for the synthesis of salts 1.

Compounds	Yields/per cent	Recrystallization solvent
1a	85	AcOEt
1b	77	AcOEt
1c	75	EtOH
1d	75	EtOH

Table 2. Yields and recrystallization solvents for the synthesis of vinamidines 2 and 3.

Compounds	Yields/per cent	Recrystallization solvent
2a	78	abs.EtOH
2b	35	AcOEt/MeOH
2d	30	AcOEt/MeOH
3a	90	Pentane
3b	66	abs.EtOH
3c	60	AcOEt/MeOH
3d, n = 8	55	Pentane
3d, n = 10	55	Pentane
3d, n = 12	60	Pentane

Table 3. Transition temperatures of vinamidinium salts 1.

Ar	X	Transition temperatures/°C (Transition enthalpies ΔH in J g ⁻¹)
1a 	BF ₄	C $\xrightarrow{184}$ I (dec.)
1b 	BF ₄	C $\xrightarrow{187}$ I (dec.)
1c 	CF ₃ SO ₃	$ \begin{array}{ccc} & \xrightarrow{95(42.3)} & \text{I} \\ \text{C}_X & & \swarrow \nwarrow \\ & \text{C} & \swarrow \nwarrow \\ & & \text{85} \end{array} $
1d 	CF ₃ SO ₃	$ \text{C}_1 \xrightleftharpoons[41]{50(8.3)} \text{C}_2 \xrightleftharpoons[57]{64} \text{C}_3 \xrightleftharpoons[62]{73(18.8)\dagger} \text{D}_h \xrightarrow{136(2)} \text{I} $

† ΔH given is for the combined C₂ → C₃ → D_h transitions.

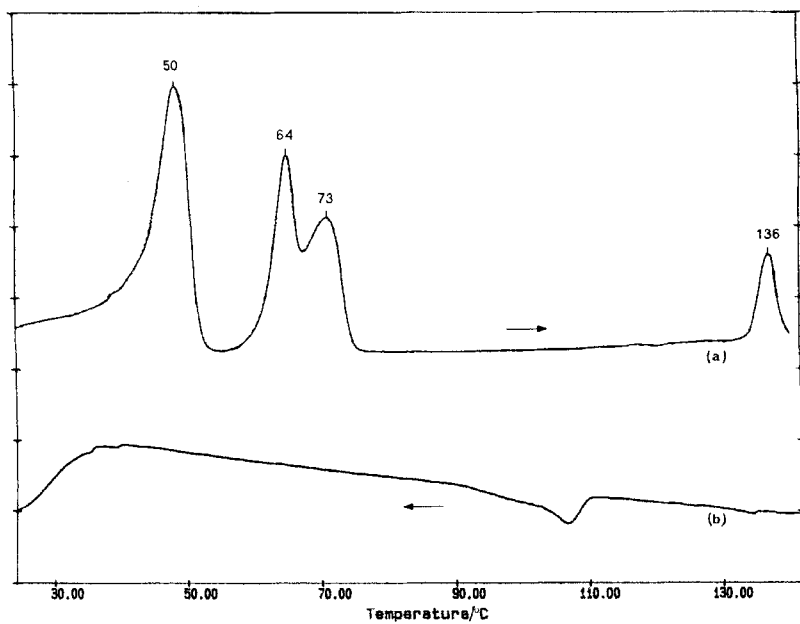


Figure 1. DSC diagram of salt **1d** obtained on heating into the isotropic phase and then cooling: (a) heating, (b) cooling.

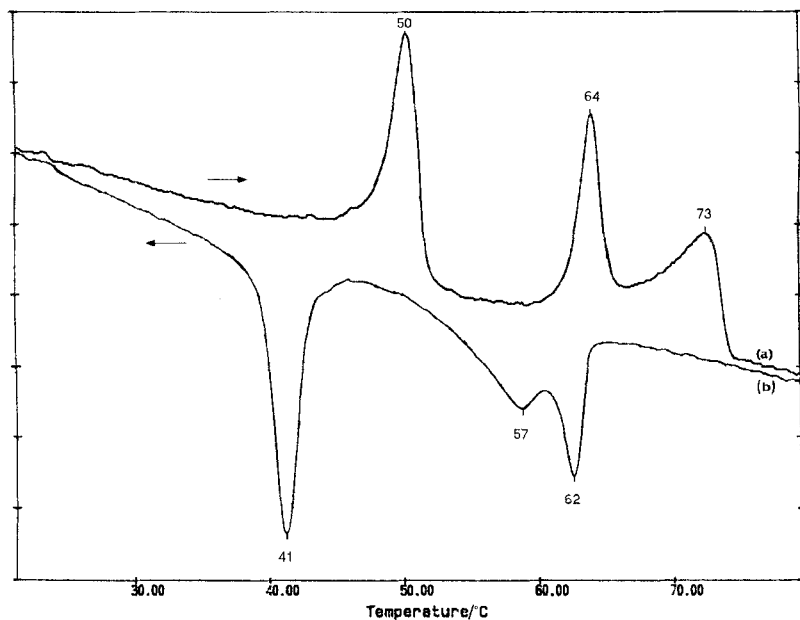
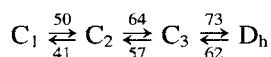


Figure 2. DSC diagram of salt **1d** obtained on heating only to 80°C and then cooling: (a) heating, (b) cooling.

Vinamidinium salts with two or four chains are crystalline materials. Only salt **1d** exhibits mesomorphic behaviour. Since some decomposition still occurs in the isotropic phase (even though it is less serious than in the case of tetrafluoroboric salt), characteristic textures were obtained as follows.

A small quantity of salt was placed on a glass slide and a drop of CH_2Cl_2 added. A cover slide was put on top of the preparation which was allowed to stand at room temperature for one hour. The sample was then slowly heated to 80°C (heating rate 1°min^{-1}). By slow evaporation of the solvent, textures for a columnar hexagonal phase were obtained. The phenomenon is reproducible, since by cooling the sample into its crystalline phase and then heating it to obtain the hexagonal phase, the same textures were obtained.

DSC curves of salt **1d** are given in figures 1 and 2. In the first case (see figure 1), the sample has been heated to the isotropic phase: the transitions are not now reversible. Thin layer chromatography (tlc, eluent: CH_2Cl_2) on the salt contained in the DSC cup showed some decomposition. In the second case (see figure 2), the compound has been heated to 80°C . Three reproducible transitions can be detected



The purity of the sample was checked by tlc: no decomposition had occurred during heating and cooling cycles giving rise to figure 2.

3.1.2. X-ray results

Figure 3 shows the X-ray powder pattern displayed by vinamidinium salt **1d**, at 97°C , in the mesomorphic range. A schematic representation of this pattern is also given.

At small angles, three reflections (*a*) can be detected. The corresponding lattice spacings are in the ratio: $1 : \sqrt{3} : 2$. This corresponds to a 2D hexagonal lattice, for which parameter $a = 31.80 \pm 0.1 \text{ \AA}$.

At wide angles, a weak diffuse ring (*b*) can be detected around $s = 1/4.4 \text{ \AA}^{-1}$ (s is the scattering vector $|s| = (2 \sin \theta)/\lambda$). This corresponds to the disordered parts of the molecules [2].

No extra reflection corresponding to some periodic stacking of the molecules along the column axes can be detected.

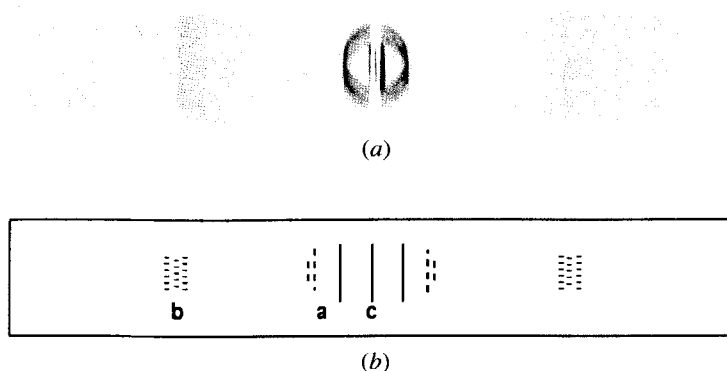


Figure 3. (a) Powder pattern of salt **1d** recorded at 97°C . (b) Schematic representation of the pattern: (a) Bragg reflections; (b) Diffuse ring; (c) Incident beam.

This diffraction pattern is characteristic of a columnar hexagonal phase, D_h , without any periodicity along the column axes [7], and confirms the microscopic observations.

3.1.3. Discussion

The X-ray patterns of the previously studied pyrylium salts show a diffuse ring at $s = 1/c$ ($c \approx 3.4 \text{ \AA}$) [2]. This ring was assigned to core–core interferences along the column axes. Therefore, it was possible to estimate the unit cell volume ($\sqrt{3}/2$) (a^2c) (where a is the hexagonal lattice constant), the number of molecules per unit cell, and the density ρ of the mesophase:

$$\rho = \frac{Z}{c} \times \frac{M_w}{N_A[(\sqrt{3}/2)a^2]}$$

where M_w is the molecular weight of salt **1d** (1476, $X^- = \text{CF}_3\text{SO}_3^-$, a the hexagonal lattice constant, and N_A the Avogadro number.

Hence:

$$\frac{Z}{c} = \frac{\rho N_A \sqrt{3}}{M_w} a^2.$$

Z/c measures the axial molecular density (along the column axis). In the case of vinamidinium salts, we cannot deduce c from the X-ray pattern, since there is no evidence for a ring related to core–core interferences only. However, it would be possible to estimate the axial molecular density.

$$\frac{1}{d_{\text{core}}} = \frac{\rho N_A \sqrt{3}}{M_w} a^2.$$

provided that the density (ρ) is known. This could not be measured directly due to the slow decomposition of the salt upon heating). If we assume $\rho \approx 0.9 \text{ g cm}^{-3}$ (for 2,4,6-triaryl pyrylium tetrafluoroborate substituted by 6 dodecyloxy chains, $\rho = 0.87 \text{ g cm}^{-3}$), $1/d_{\text{core}} = 1/3.1 \text{ \AA}$.

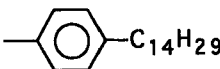
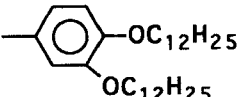
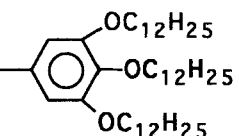
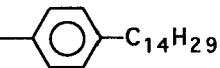
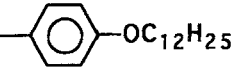
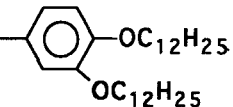
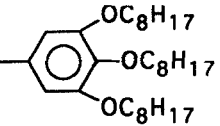
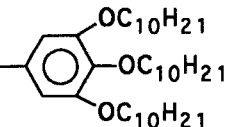
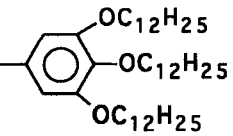
In order to compare the columnar phases formed by molecules which are substituted by a different number of chains, it is better to compare the linear chain density $n_{\text{ch}}/d_{\text{core}} = 1/d_{\text{ch}} = 1/0.52 \text{ \AA}$.

The mean inter-chain distance, for molten paraffinic chains, is of the order of 4.5–4.7 \AA and in a slice of column of 4.76 \AA one finds 9 chains, i.e. 1.5 molecules. This means that there are 3 molecules in a slice of column of thickness = 9.5 \AA . Since cores cannot approach at a distance of 3 \AA , we assume that the core stacking along the column axis is disordered and complex, which is consistent with the observed X-ray pattern.

If we assume that the core volume is $(\pi l_c^2/4)d_{\text{ch}} \times 6$ (with $Z = 1$ and $n_{\text{ch}} = 6$), where l_c is the diameter of the central part of the column occupied by the cores (l_c has been taken to be equal to the vinamidinium length, $l_c = 13.5 \text{ \AA}$, obtained from a crystallographic study of a vinamidinium–TCNQ salt [8]), the chain volume is

$$\frac{a^2\sqrt{3}}{2} d_{\text{ch}} - \frac{\pi l_c^2}{4} d_{\text{ch}}$$

Table 4. Transition temperatures of vinamidines 2 and 3.

Ar	Transition temperatures/°C (transition enthalpies ΔH in J g^{-1})
2a 	$C \xrightleftharpoons[28]{75} I$
2c 	$C \xrightleftharpoons[32]{72(91)} I$
2d 	$C_x \xrightleftharpoons[42]{60(70.1)} I$
3a 	$C \xrightleftharpoons[41]{79} I$
3b 	$C \xrightleftharpoons[35]{83(82.6)} I$
3c 	$C \xrightleftharpoons[53]{76(75.8)} I$
	$C_1 \xrightleftharpoons[95.5]{100(15.5)} C_2 \xrightleftharpoons[107]{110(22)} I$
3d 	$C \xrightleftharpoons[32]{35(6)} M_1 \xrightleftharpoons[37]{39.5(13.5)} M_2 \xrightleftharpoons[84]{85(1.2)} M_3 \xrightleftharpoons[97]{97(2.4)} M_4 \xrightleftharpoons[105]{107(23.1)} I$
	$C \xrightleftharpoons[54.5]{61(27.5)} D_{r1} \xrightleftharpoons[66.5]{70(0.5)} D_{r2} \xrightleftharpoons[85]{87(3)} D_{r3} \xrightleftharpoons[100]{103} D_{r4} \xrightleftharpoons[105]{110(19.3)} I$ D_{r5}



(a)



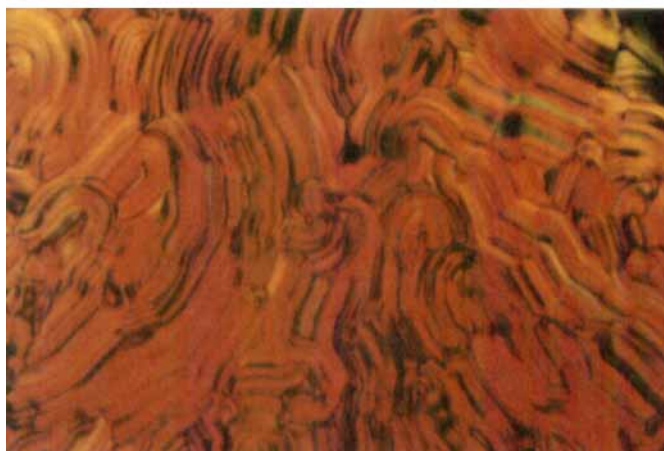
(b)



(c)



(d)



(e)

Figure 4. Compound **3d** textures obtained by (a) slow cooling of the isotropic phase at 106°C, (b) upon further cooling, $\theta = 100^\circ\text{C}$, (c) upon further cooling, $\theta = 92^\circ\text{C}$, (d) upon further cooling, $\theta = 63^\circ\text{C}$, and (e) upon cooling, without a cover slip, $\theta = 100^\circ\text{C}$.

and the volume per methylene group

$$\frac{d_{\text{ch}}}{12} \left(\frac{a^2\sqrt{3}}{2} - \frac{\pi l_c^2}{4} \right) \approx 31.7 \text{ \AA}^3,$$

which corresponds to a typical value for a columnar phase [9].

Therefore taking into account that (i) there is no sign of any interactions along the column axis from the X-ray pattern and (ii) four chains derivatives are crystalline materials, we can assume that the columns as constituted of an external crown of paraffinic chains surrounding an internal cylinder of paraffinic chains (somewhat as in phasmidic compounds [10]). So in this phase, the columns can be considered as series of slices of approximately 9.5 Å thickness containing 3 molecules of vinamidinium salt **1d** without positional order of the cores within the slices.

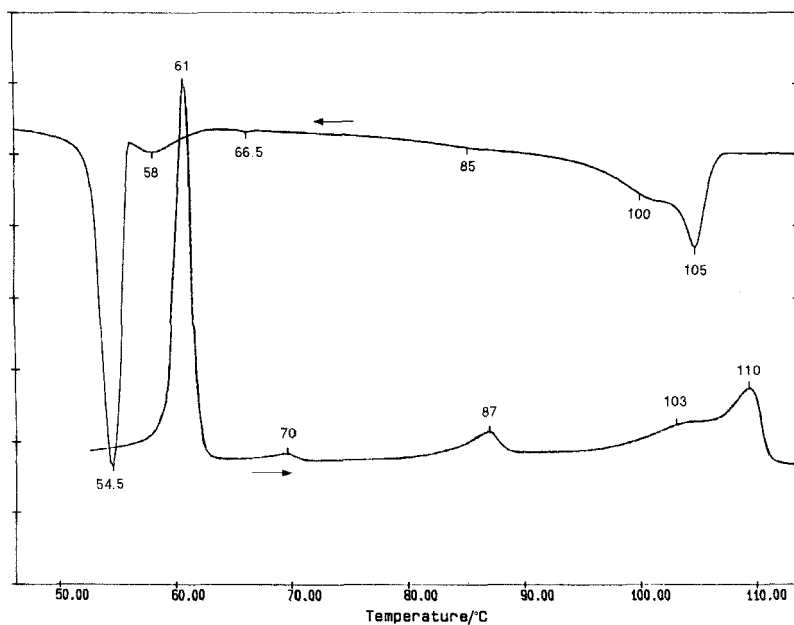


Figure 5. DSC diagram of compound **3d** ($n = 12$): (\rightarrow) heating, (\leftarrow) cooling.

3.2. Vinamidines **2** and **3**

3.2.1. Microscopic observations and DSC

Transition temperatures of the vinamidines (determined either by microscopic observations or by DSC) are given in table 4. Of all the compounds prepared, only the vinamidines **3d** ($n = 10$ and 12) with six alkoxy chains and a nitro group behave as liquid crystals. Miscibility experiments between the two homologues show that they are miscible in all proportions, and so the mesophases have the same symmetries.

Typical textures of compound **3d** ($n = 12$) are shown as a function of temperature in figures 4(a)–(d) (with a cover slide) and in figure 4(e) (without a cover slide). In (a) ($T = 106^\circ\text{C}$), just below the isotropic phase, fan-shaped textures can be seen. By slow cooling (cooling rate 2°min^{-1}), some zig-zag defects appear ((b), $T = 100^\circ\text{C}$). Finally, the defects invade all the fan-shaped domains with concentric rings (c) and (d), $T = 92$ and 63°C , respectively). In (e) the fingerprint textures can be seen in a sample observed without cover slide ($T = 100^\circ\text{C}$). All these textures are characteristic of either rectangular or oblique phases [11].

Reproducible DSC curves for **3d** ($n = 12$) are shown in figure 5. Five transitions are detected upon heating and six by cooling, some having very low transition enthalpies (0.5 and 0.15 J g^{-1} for example).

The thermal stability of the samples has been checked by tlc (eluent CH_2Cl_2).

3.2.2. X-ray results

Figure 6 shows a typical powder pattern taken by heating vinamidine **3d** ($n = 12$) just above the transition $\text{C} \rightarrow \text{M}$. Several sharp reflections can be seen at small angles; these have been indexed in a 2D rectangular centred lattice (See table 5). At wide angles, a

diffuse ring corresponding to the molten parts of the molecules [2] can be detected at around $S = 1/4.4 \text{ \AA}^{-1}$. Another diffuse ring corresponding to the stacking period of the molecules along the column axes is detected around $s = 1/3.5 \text{ \AA}^{-1}$.

This pattern is characteristic of the columnar rectangular centred phase D_r [7] for which the parameters are

$$a = 76.9 \pm 0.1 \text{ \AA}; \quad b = 35.1 \pm 0.1 \text{ \AA}; \quad c = 3.5 \pm 0.1 \text{ \AA}; \quad V \approx 9450 \text{ \AA}^3.$$

By further heating or cooling, the same kind of pattern is obtained, whatever the temperature in the mesophase; the only difference is the progressive disappearance of the wide angle rings at high temperature.

3.2.3. Discussion

Considering the volume of the unit cell and assuming that the density (ρ) of such a phase is close to one, the number of molecules per unit cell (n) has been calculated according to

$$n = \rho N_A V / M_w,$$

where V is the cell volume, N_A the Avogadro number, ρ the density, and M_w the molecular weight (1447).

In this way n has been found to equal 4 (3.9). To explain $N = 4$, the formation of 'pairs' of molecules, located at the corners and the centre of the unit cell, must be assumed.

In figure 7 (a) a section of the column is shown with the location of the molecules. The shape and the dimensions of the vinamidine core have been taken as equal to those of pyrylium [2]: 7 Å. Figure 7 (b) shows a postulated representation of the dimer, together with the dimensions of the rigid core so formed.

First of all, we can calculate the axial chain density from

$$d_{\text{ch}} = \frac{c}{n_{\text{ch}}},$$

(c is the mean core-to-core distance and n_{ch} chain number in c) which leads to $d_{\text{ch}} = 0.29 \text{ \AA}$.

Now we can calculate the mean volume per methylene group according to

$$V_{\text{CH}_2} = (V_{\text{column}} - V_{\text{core}}) / n_{\text{CH}_2}.$$

In this way, we find $V_{\text{CH}_2} = 27 \text{ \AA}^3$. Once more, this is a reasonable value in the case of columnar phases.

There remain to be explained the transitions observed in the DSC curves. Since no changes can be detected on the X-ray pattern concerning the symmetry or the dimensions of the cells, some suggestions may be made on the basis of the textures. Just below the isotropic phase, fan-shaped textures without defects are observed; this may be due to a rectangular columnar phase with molecules perpendicular to the columns. Then zig-zag defects appear, a sign of some tilt of the aromatic core with respect to the column axis. This must occur without any change in the dimensions of the unit cell, and can be achieved by the creation of 'steps' between two molecules in a column. This will result in an average tilt of the dimer with respect to the columnar axis.

Table 5. Proposed indexation for the powder pattern obtained upon heating compound **3d**.
 $a = 76.9 \pm 0.1 \text{ \AA}$, $b = 35.1 \pm 0.1 \text{ \AA}$, $c = 3.5 \pm 0.1 \text{ \AA}$; $V. \approx 9450 \text{ \AA}^3$, $n = 4$.

$h k$	Measured lattice spacings/ \AA	Calculated lattice spacings/ \AA
2 0	38.50	38.46
1 1	31.62	31.90
3 1	20.50	20.70
4 0	19.17	19.23
0 2	17.51	17.54
2 2	15.88	15.96
5 1	14.07	14.09
4 2	—	12.96
6 0	12.85	12.82
1 3	11.51	11.55
3 3	—	10.63
6 2	—	10.34
7 1	—	10.48
8 0	9.60	9.62
5 3	9.28	9.31
0 4	8.78	8.77
2 4	8.50	8.55
9 1	—	8.30
8 2	—	8.43
7 3	—	8.00
4 4	7.90	7.98
10 0	—	7.69
6 4	—	7.23
10 2	—	7.04
9 3	6.87	6.85
11 1	6.87	6.90
3 5	—	6.77
8 4	6.47	6.48
12 0	6.47	6.41
5 5	6.31	6.38
12 2	—	6.02
11 3	—	6.00
7 5	5.86	5.91
0 6	5.86	5.84
2 6	5.76	5.78
10 4	5.76	5.78
4 6	5.54	5.59
14 0	5.54	5.49
9 5	5.41	5.42
6 6	5.28	5.31



Figure 6. Powder pattern of compound **3d** ($n = 12$) recorded for the columnar, rectangular centred phase D_r upon heating just above the crystalline phase.

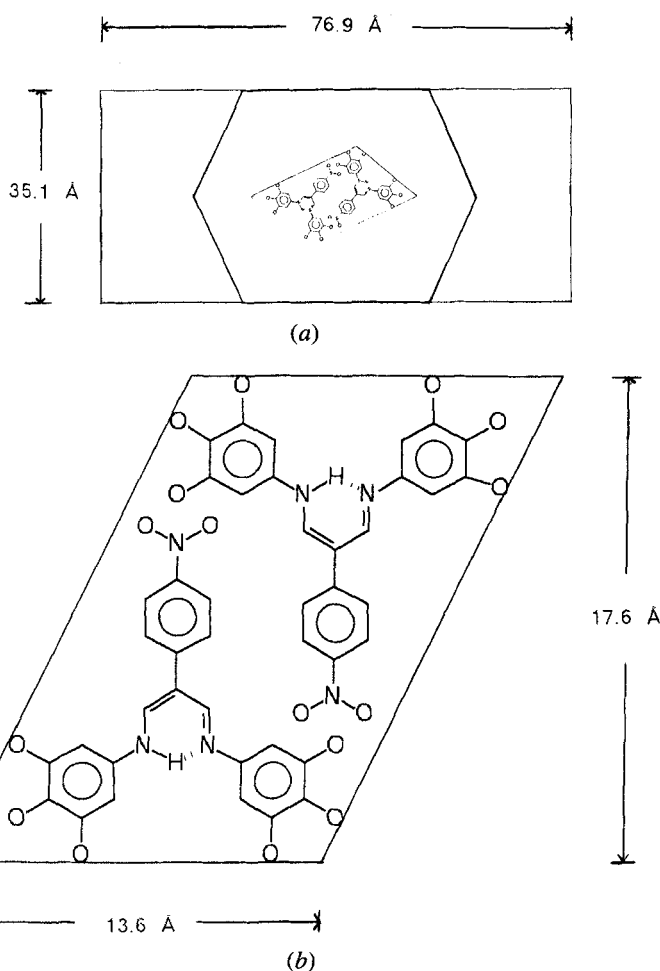


Figure 7. (a) Schematic representation of the section of a column; (b) Schematic representation of the dimers.

4. Conclusions

We have presented here the synthesis of long chain polysubstituted vinamidinium salts and vinamidines. The studies of their mesomorphic properties have shown that:

- (i) In all cases (vinamidinium salts and vinamidines), six paraffinic chains are required to obtain mesomorphic materials, in spite of the differences between the symmetries of the two systems.
- (ii) In the case of vinamidinium salts **1**, the choice of the anion is very important. As often as possible, triflate must be chosen instead of tetrafluoroborate. A hexagonal columnar phase with no regular stacking along the columns axis has been identified. Furthermore, it seems that the ionic character of vinamidinium salt contributes to the creation of some disorder, since the corresponding neutral vinamidines are crystalline materials.
- (iii) In the case of vinamidines **2** and **3**, rectangular centred phases have been identified for the compound with six dodecyloxy chains and a nitro group,

whatever the temperature in the mesomorphic range. The different mesophases have the same symmetry and the same parameters, and it seems that the transitions occur without altering the parameters of the unit cell. This may be possible if there are some changes in the tilt of the rigid core with respect to the column axis. The formation of 'pairs' of molecules must be postulated to account for the number of molecules per unit cell.

In this series, it seems that the presence of a nitro group (or at least a polar group) is essential to obtain mesomorphic compounds, since vinamidines with six dodecyloxy chains and no polar group are crystalline.

Until now, no lamella phase has been obtained with compounds containing two or four chains, and this differs strongly from the case of dithiolium and pyrylium salts.

5. Experimental

5.1. General

Vinamidinium salts **1** and 4-alkoxy-, 3,4-dialkoxy- and 3,4,5-trialkoxy-anilines were prepared according to published procedures [5]. 4-Tetradecylaniline, 4-nitrophenyl- and phenylacetic acid were purchased from Aldrich and used without purification.

^1H NMR spectra were recorded on a Bruker AC 300 spectrometer; CDCl_3 was the solvent, with TMS as reference. IR spectra (KBr pellets) were recorded on an FT-IR Perkin-Elmer spectrometer. Melting points were determined using a Leitz Orthoplan microscope equipped with a Mettler FP 80 hot stage.

Spectral characteristics are given for compounds with $n = 12$, unless stated otherwise.

5.2. Synthesis of vinamidinium salts **4**

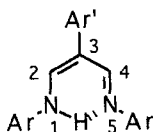
To 0.3 mol of POCl_3 was slowly added 0.5 mol of dimethylformamide. During the addition, the temperature was kept below 30°C . The mixture was allowed to stand at room temperature for 5 min. Then, the appropriate arylacetic acid, dissolved in the minimum volume of dimethylformamide, was added dropwise. After heating for 6 h at 90°C , the mixture was poured into ice water containing 0.6 mol of sodium tetrafluoroborate. The precipitate was filtered off, washed with water, recrystallized first from ethanol and then from methanol, and dried under vacuum over P_2O_5 .

5.2.1. 1,1,5,5-Tetramethyl-3-phenylvinamidinium tetrafluoroborate

Yield 52 per cent m.p. 185°C . ^1H NMR: $\delta = 2.5$ (s, 6H, $\text{N}(\text{CH}_3)_2$), 3.5 (s, 6H, $\text{N}(\text{CH}_3)_2$), 7.4 (m, 5H, aromatic H), 7.8 (s, 2H, diazapentadienium H). IR $\nu(\text{cm}^{-1})$: 1646 (vinamidinium skeleton), 1590 (phenyl nucleus), 1084 (BF_4^-). Microanalysis: found (calculated) per cent C 53.82 (53.80); H 6.58 (6.55); N 9.61 (9.65).

5.2.2. 1,1,5,5-Tetramethyl-3-(4'-nitrophenyl)vinamidinium tetrafluoroborate

Yield 78 per cent: m.p. 220°C . ^1H NMR: $\delta = 2.5$ (s, 6H, $\text{N}(\text{CH}_3)_2$), 3.5 (s, 6H, $\text{N}(\text{CH}_3)_2$), 6.9 (d, 2H, aromatic H), 7.4 (d, 2H, aromatic H), 7.8 (s, 2H, diazapentadienium H). IR $\nu(\text{cm}^{-1})$: 1646 (vinamidinium skeleton), 1590 (phenyl nucleus), 1330 (NO_2), 1084 (BF_4^-).

5.3. Synthesis of vinamidines **2** and **3**

10 mmol of the appropriate vinamidinium salt **4** and 28 mmol of the required aniline [5] were heated under reflux for 6 h in 25 ml of methanol. An oily phase was separated from the reaction mixture and a precipitate obtained by adding methanol. After 30 min stirring, the vinamidine was filtered off, washed with cold methanol and dried; yields and recrystallization solvents are given in table 2.

5.3.1. *Vinamidine 2a*

¹H NMR: δ = 0.8 (t, 6 H, CH₃), 1.2 (m, 48 H, (CH₂)₁₂), 2.5 (t, 4 H, Ar-CH₂), 7.1 (d, 4 H, 1,5 aromatic H), 7.3 (d, 4 H, 1,5 aromatic H), 7.5 (m, 5 H, 3 aromatic H), 8.1 (s, 2 H, H₂, H₄). IR ν (cm⁻¹): 3025 (C-N), 1641 (vinamidine skeleton), 1598 (phenyl nucleus). Microanalysis: found (calculated) per cent 85.20 (85.22); H 10.86 (10.72); N 3.87 (4.05).

5.3.2. *Vinamidine 2c*

¹H NMR: δ = 0.8 (t, 12 H, CH₃), 1.2 (m, 72 H, (CH₂)₉), 1.8 (q, 8 H, OCH₂CH₂), 4.0 (2t, 8 H, OCH₂), 6.6 (d, 2 H, 1,5 aromatic H), 6.7 (s, 2 H, 1,5 aromatic H), 6.9 (d, 2 H, 1,5 aromatic H), 7.4 (m, 5 H, 3 aromatic H), 8.0 (s, 2 H, H₂, H₄), 12.5 (broad s, 1 H, N...H-N). IR ν (cm⁻¹): 3234 (NH), 1639 (vinamidine skeleton), 1598 (phenyl nucleus), 1291 (=C-O-C). Microanalysis: found (calculated) per cent: C 79.56 (80.23); H 10.69 (10.85); N 2.65 (2.70).

5.3.3. *Vinamidine 2d*

¹H NMR: δ = 0.8 (t, 18 H, CH₃), 1.3 (m, 108 H, (CH₂)₉), 2.1 (q, 12 H, OCH₂CH₂), 4.0 (2t, 12 H, OCH₂), 6.4 (s, 4 H, 1,5 aromatic H), 7.4 (m, 5 H, 3 aromatic H), 8.0 (s, 2 H, H₂, H₄), 12.5 (broad s, 1 H, N...H-N). IR ν (cm⁻¹): 3234 (NH), 1639 (vinamidine skeleton), 1598 (phenyl nucleus), 1291 (=C-O-C).

5.3.4. *Vinamidine 3a*

¹H NMR: δ = 0.8 (t, 6 H, CH₃), 1.2 (m, 48 H, (CH₂)₁₂), 2.5 (t, 4 H, ArCH₂), 6.9 (d, 4 H, 1,5 aromatic H), 7.3 (d, 4 H, 1,5 aromatic H), 7.5 (d, 2 H, 3 aromatic H), 8.1 (s, 2 H, H₂, H₄), 8.2 (d, 2 H, 3 aromatic H), 12.9 (broad s, 1 H, N...H-N). IR ν (cm⁻¹): 3025 (C-N), 1641 (vinamidine skeleton), 1600 (phenyl nucleus), 1330 (NO₂).

5.3.5. *Vinamidine 3b*

¹H NMR: δ = 0.9 (t, 6 H, CH₃), 1.3 (m, 36 H, (CH₂)₉), 1.8 (q, 4 H, OCH₂CH₂), 3.9 (t, 4 H, OCH₂), 6.8 (d, 4 H, 1,5 aromatic H), 7.1 (d, 4 H, 1,5 aromatic H), 7.5 (d, 2 H, 3 aromatic H), 8.1 (s, 2 H, H₂, H₄), 8.2 (d, 2 H, 3 aromatic H), 13.2 (broad s, 1 H, N...H-N). IR ν (cm⁻¹): 3230 (NH), 1637 (vinamidine skeleton), 1586 (phenyl nucleus), 1329 (NO₂), 1291 (=C-O-C), 1242 (NO₂).

5.3.6. *Vinamidine 3c*

¹H NMR: δ = 0.8 (t, 12 H, CH₃), 1.4 (m, 72 H, (CH₂)₉), 1.9 (q, 4 H, OCH₂CH₂), 4.0 (2t, 8 H, OCH₂), 6.7 (d, 2 H, 1,5 aromatic H), 6.75 (s, 2 H, 1,5 aromatic H), 6.9

(d, 2 H, 1,5 aromatic H), 7.5 (d, 2 H, 3 aromatic H) 8.1 (s, 2 H, H₂, H₄), 8.2 (d, 2 H, 3 aromatic H), 13.2 (broad s, 1 H N...H-N). IR $\nu(\text{cm}^{-1})$: 3230 (NH) 1637 (vinamidine skeleton), 1586 (phenyl nucleus), 1329 (NO₂), 1291 (=C-O-C), 1242 (NO₂).

5.3.7. Vinamidine **3d** ($n = 12$)

¹H, NMR: $\delta = 0.8$ (t, 18 H, CH₃), 1.3 (m, 108 H, (CH₂)₉) 1.8 (q, 12 H, OCH₂CH₂), 3.9 (2t, 12 H, OCH₂), 6.3 (s, 4 H, 1,5 aromatic H), 7.4 (d, 2 H, 3 aromatic H), 8.0 (s, 2 H, H₂, H₄), 8.1 (d, 2 H, 3 aromatic H), 13.0 (broad s, 1 H, N...H-N). IR $\nu(\text{cm}^{-1})$: 3230 (NH), 1637 (vinamidine skeleton), 1586 (phenyl nucleus), 1329 (NO₂) 1291 (=C-O-C), 1242 (NO₂).

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