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Synthesis, Characterisation, and Phase Behaviour of Some Azines with Potential Optical Nonlinearities of Second Order

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Some azines with potential nonlinear optical properties of the second order have been synthesised by condensation of the appropriate hydrazones and aldehydes. The compounds have been chemically functionalised to allow their use in the synthesis of polymers containing the azine groups as side chain pendants. The characterisation of the phase behaviour, performed by DSC, X-ray diffraction and polarising microscopy methods, shows that most of the compounds exhibit enantiotropic liquid crystalline properties. Some peculiar features concerning solid state polymorphism have also been investigated.

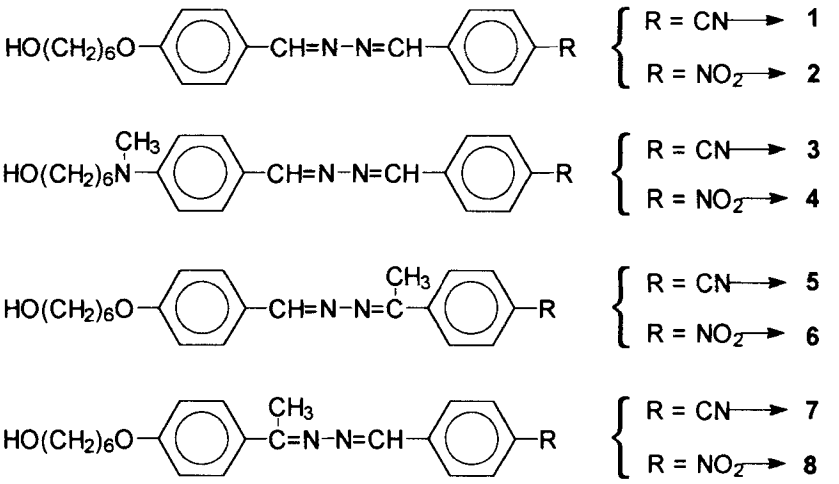
Keywords: Mesogenic azines, NLO materials

1. INTRODUCTION

In the quest for new materials possessing nonlinear optical (NLO) properties of the second order, chemical and structural variability and easy of processing appear to be qualities that suggest organic polymers are versatile candidates.[1,2] Among these, polymers bearing NLO-active segments as side chain pendants offer two valuable opportunities: a separate tailoring of the NLO-active segments and a relatively easy poling of these segments in the final material.[3–5]

An entire class of liquid crystalline (LC) polymers is characterised by having the mesogenic segments as side chain pendants. Therefore, appropriate tailoring of the chemical structure may produce a polymer that is both NLO-active LC.[3,4,6]

It is well known that because of the intrinsic microscopic order characterising a liquid crystal, its ordering on the macroscopic scale by the application of a force field of mechanical, electrical or magnetic nature is, greatly facilitated particularly for nematics. For side chain LC polymers, ordering is substantially limited to aligning the pendant segments. However, in order to have second order NLO activity as bulk property, alignment alone is not sufficient and poling has to be operated. The role that liquid crystallinity may play on the poling efficiency and on the stability in time of the poled materials has been investigated in some cases[3,4,7–11] with non-homogeneous results.



This article describes the synthesis and the characterisation of the phase behaviour of the following set of compounds which, for the sake of simplicity, we shall refer to as azines **1–8**:

These compounds are chemically characterised as containing an electron donor and an electron acceptor group linked in such a way to allow charge transfer from one to the other. These features conform to the requirements for significant first order molecular hyperpolarizability to show up.[1,3,6] The molecules have been designed and functionalized in such a way as to make them fit for inclusion as side chain segments in poly(acrylates) or poly(methacrylates), preventing a too close steric coupling of the rigid segments with the backbone chain. This is a desired feature for two reasons: to allow a successive poling of the material and to preserve as a polymer property the possible intrinsic mesogenic potential of the side chain segments. It will be shown that most of the synthesised azines exhibit LC properties.

2. EXPERIMENTAL

2.1 Materials

Hydrazine monohydrate (98%), 6-chloro-1-hexanol (96%), 4-cyanobenzaldehyde (98%), 4-nitrobenzaldehyde (99.5%), 4-cyanoacetophenone (99%) [Aldrich], and 4-nitroacetophenone (97%) and 4-hydroxyacetophenone (98%) [Janssen] were utilised as purchased.

2.2 Methods

The ^{1}H-NMR spectra were recorded on a Varian XL200 spectrometer. The differential scanning calorimetry measurements were performed by means of a Perkin Elmer DSC7 apparatus, under nitrogen atmosphere, using scanning rate of 10 K/min. As a standard for determining transition temperatures and enthalpies, an indium sample

of high purity was used. Optical observation was performed using a Leitz polarising microscope, combined with a Mettler FP5 microfurnace. X-ray diffraction patterns were recorded using a photographic flat-film camera with CuKα radiation. The samples were sealed into Lindemann capillaries, under nitrogen atmosphere. This apparatus was equipped with a microfurnace for temperature control.

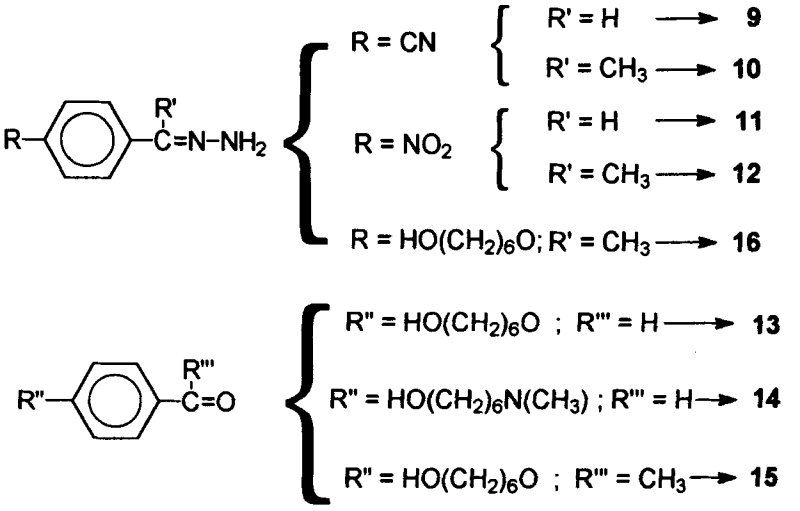
2.3 Synthesis of Azine Precursors 9–16

The chemical nature of the precursors synthesised as a preliminary step for the preparation of azines **1–8** is shown in scheme I:

In all cases ^{1}H NMR spectrometry data were consistent with the expected formulas and monitored the acceptable purity of the compounds obtained.

2.3.1 Synthesis of compounds **9–12.** As an example, a typical preparation of compound **9** is reported. In a 250 ml flask 10.0 g of 4-cyanobenzaldehyde (76.3 mmol) 11.1 ml of hydrazine monohydrate ($d = 1.032$; 228.8 mmol) and 80 ml of ethanol were introduced. The mixture was heated at reflux under mechanical stirring for about 10 min. After this, a further amount (22.2 ml, 457.6 mmol) of hydrazine monohydrate was added to the solution, and it was heated at reflux for 2 h. After cooling at room temperature, about 700 ml water was added slowly to the solution. The mixture was allowed to stand for 1 h at 5°C. The product, a crystalline light yellow solid, was recovered by filtration, washed thoroughly with water, and dried. Yield 85%; mp 70–73°C.

Compound **11** was obtained by an analogous procedure. The product was crystallised from chloroform/petroleum ether (bp 80–110°C) to produce a crystalline yellow solid. Yield 85%; mp 130–138°C.



SCHEME 1

Compounds **10** and **12** were prepared following the same type of procedure described above starting from 4-cyanoacetophenone and 4-nitroacetophenone respectively. Compound **10** was obtained as a crystalline light yellow solid. Yield 65%; mp 75–80°C; Compound **12** was purified by crystallisation from absolute ethanol to produce orange crystals. Yield 80%; mp 144–153°C.

2.3.2 Synthesis of compounds **13–16.** Compound **13** was obtained by reaction between 4-hydroxybenzaldehyde, 6-chloro-1-hexanol and potassium carbonate in dimethylformamide at reflux for 9 h, by adapting a previously reported procedure.[12] The crude product, which is liquid at room temperature, was sufficiently pure, according to the NMR spectrum, for use in the successive reaction step. A similar procedure, starting from 4-hydroxyacetophenone and 6-chloro-1-hexanol, was applied for obtaining compound **15**. In this case also the crude product (mp 56–64°C) was utilised in the successive reaction step with no further treatment. Compound **14** was prepared as reported to Robello.[2]

Finally, compound **16** was obtained by condenstion reaction between compound **15** and hydrazine monohydrate following the procedure described for the syntehsis of hydrazones **9–12**.

Compound **16** is a crystalline light yellow solid. Yield 80%; mp 100–110°C.

2.4 Synthesis of Azines 1–8

2.4.1 Synthesis of azines **1, 2, 5, 7, 8.** As an example, a typical preparation of azine **1** is reported. To 1.0 g (6.9 mmol) of azine **9**, dissolved in 10 ml of absolute ethanol was added under stirring 1.6 g azine **13** (7.2 mmol), dissolved in 10 ml of the same solvent. The solution was vigorously stirred at room temperature for about 30 min. During this time, a yellow solid precipitated. The compound was isolated by filtration and crystallised from dichloromethane/hexane (6:1). The same solvent mixture was used in the crystallisation of the crude azines **5** and **7**, while **2** and **8** were recrystallized from chlorofom/hexane (5:2). Yields for all the azines ranged between 70% and 85%.

2.4.2 Synthesis of azines **3** *and* **4.** Both compounds were obtained following the same procedure. In a typical preparation of azine **3**, 10 g of azine **9** (6.9 mmol) was added to 1.7 g of azine **14** (7.2 mmol) dissolved in 7 ml HPLC grade benzene and 2 ml of absolute ethanol. The solution was heated at reflux for about 30 min, under vigorous stirring. After this time, about 30 ml of petroleum ether (bp 80–110°C) were poured into the solution, thus affording precipitation of a red solid. The product was filtered and purified by recrystallization from chloroform/hexane (5:2). Azines **3** and **4** were both recrystllized from absolute ethanol.

2.4.3 Synthesis of azine **6.** In a typical preparation, 1.0 g (5.0 mmol) of azine **12** and 1.2 g (5.3 mmol) of azine **13** were dissolved in about 30 ml of *o*-dichlorobenzene. The solution was refluxed for 30 min, cooled at room temperature and poured into 400 ml of cold (– 20°C) hexane. The resulting orange solid precipitate was filtered, dried in air and recrystallized from absolute ethanol.

3. RESULTS AND DISCUSSION

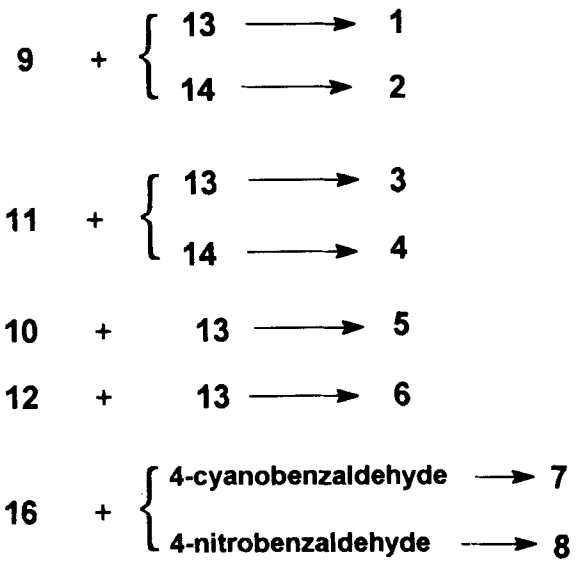
3.1 Synthetic Aspects

Since tha azines described here are disubstituted, a synthetic procedure involving two steps is required in this preparation. The priority order adopted in carrying out the two steps was dictated by the requirement of optimising the final yield and avoiding side products. Accordingly, on the ground of preliminary tests, compounds **1–6** have been prepared by condensation between hydrazones **9–12** and aldehydes **13**, **14**, according to the scheme II. Compounds **7** and **8** have been prepared by condensation between hydrazone **15** and 4-cyanobenzaldehyde or 4-nitrobenzaldehyde, according to the same scheme. The azines are red to yellow solids, soluble in chloroform, dichloromethane and acetone, poorly soluble in ethanol.

The ^{1}H-NMR spectra were in good agreement with the expected formula of the products, also giving evidence of the good purity of the isolated azines. Some relevant NMR data are reported in Table I.

3.2 Thermodynamic and Phase Behaviour

The relevant thermodynamic data concerning the phase transitions for azines **1–8** are reported in Table II. These compounds do not exhibit identical phase behaviour. Azines **1–2** and **5–8** exhibit enantiotropic LC behaviour, as detected both by DSC analysis (Figure 1 reports the DSC curves for azine **1** as an example) and polarising microscopy.



SCHEME 2

TABLE I

Selected ^{1}H NMR data (δ/ppm)

Azine				-O-CH$_2$-				
1	8.63[a]			4.04[b]	7.94[a]			6.49[a]
2	8.66[a]			4.04[b]		8.29[a]		6.98[a]
3	8.60[a]		3.03	3.39[b]	7.91[a]		6.70[a]	
4	8.64[a]		3.04	3.66[b]		8.27[a]	6.71[a]	
5	8.40	2.54		4.04[b]	8.02[a]			6.97[a]
6	8.42	2.56		4.03[b]		8.27[a]		6.97[a]
7	8.42	2.49		4.01[b]	7.92[a]			6.92[a]
8	8.43	2.50		4.01[b]		8.29[a]		6.93[a]

[a] doublet; [b] triplet

TABLE II

Phase transition temperatures (°C) and enthalpies (J/g)

Compound	T_m/°C[(a)]	ΔH_m/Jg^{-1}	T_i/°C[(a)]	ΔH_i/Jg^{-1}
1	130.8; 136.6[b]	83.6	190.2	3.4
2	146.9	105.4	172.6	1.6
3	103.9[c]	102.6	(f)	(f)
	(105.3; 118.5)			
4	118.9; 124.1[d]	10.3; 65.0		
5	125.9; 129.2[b]	122.8	154.6	2.8
6	133.8[e]			
	(118.9; 133.5)	97.6	137.5	1.3
7	103.9	91.1	162.3	3.6
8	111.3; 118.2[b]	90.8	144.3	1.7

[a] onset temperatures concerning the first heating run, unless oherwise specified; [b] more than one crystal form present; phase transition endotherms are not resolved; peak temperatures and total enthalpy change are given. [c]data concerning the first heating run of a sample crystallized from chloroform/*n*-hexane solution; peak temperatures for the two crystal forms obtained by melt-crystallization are given in parentheses; [d] two crystal forms; [e] data concerning the second heating run; peak temperatures for the two crystal forms obtained by solution-crystallization are given in parentheses; [f] monotropically mesogenic, isotropization temperature not measurable.

The nematic nature of the mesophase was detected from the observed optical pattern. A typical schlieren texture forms as the I-LC transition takes place, soon followed by a change in the homeotropic texture. Consistent support for this observation was obtained by means of X-ray diffraction. In particular, X-ray diffraction patterns were recorded for the azine with the lowest melting temperature, i.e. azine **7**, and for binary equimolar mixtures of azine **7** with all the other LC azines. The X-ray diffraction pattern of azine **7** is characterised by a diffuse halo peaked at $\sin(\theta)/\lambda = 0.111\,\text{Å}^{-1}$. No Bragg diffraction was detected for lattice distances shorter than 52 Å (upper limit of the apparatus).

The isotropization temperature (taken at the peak of the corresponding DSC endothermic signal) of each mixture is very close to the average of the isotropization

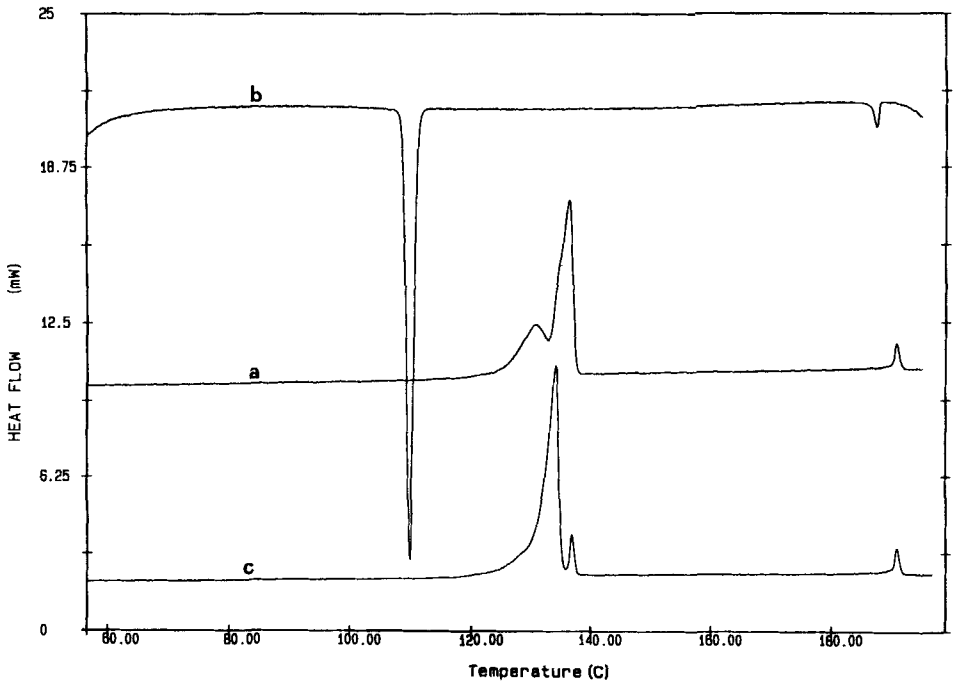


FIGURE 1 Azine 1-DSC thermal behaviour. First heating run (curve a); first cooling run (curve b); second heating run (curve c).

temperatures of the pure components, as expected for quasi-ideal mixtures of two nematogenic components of analogous structure:[13] ($T_{i(7/1)} = 177°C$; $T_{i(7/2)} = 167°C$; $T_{i(7/5)} = 158°C$; $T_{i(7/6)} = 150°C$; $T_{i(7/8)} = 154°C$). Consistently, for all mixtures, the X-ray diffraction pattern is typical of a nematic phase.

The structural affinity of the molecular skeleton of the nematogenic azines allows some correlation between thermodynamic data and the nature of the substituents to show up clearly.

The thermal stability of the nematic phase is lower for 4-nitrophenyl substituted azines than for the 4-cyanophenyl substituted homologues (isotropization temperatures and enthalpy changes reported in Table 1 follow a consistent trend). This feature is by no means peculiar to these compounds, a similar trend was reported long ago by Gray and Harrison for a homologous series of *n*-alkyl 4-*p*-substituted-benzylidene aminocinnamates.[14] In our case, the inverse trend followed by the melting temperature also produces a substantial reduction in the thermal stability interval of the mesophase for the nitro-substituted compounds.

Substitution of a hydrogen atom of the —HC=N—N=CH— group with a methyl group causes a decrease in the thermal stability of the mesophase. This feature is presumably related to an increase in the average cross section of the rigid molecular segment. However, the two sites of substitution are not equivalent: comparatively lower isotropization temperatures are observed when the substitution is at the carbon atom linked to the 4-cyanophenyl or 4-nitrophenyl group. A trend of the isotropization

temperature quite analogous to that followed by compounds **1**, **5**, and **7** has also been observed in model azines in which the 6-hydroxyhexyloxy tail has been substituted with a methoxy group. Furthermore, in this case, the results of a crystallographic investigation show that in the azine with lower isotropization temperature, i.e. the analogue of azine **5**, the molecule adopts a nonplanar conformation , due to a torsion around the N—N bond by ~ 150°C while for the analogues of azines **1** and **7** geometry is planar.[15]

Azines **3** and **4** exhibit drastically different properties: the former is monotropically smectogenic, the latter does not exhibit any LC property at all.

Figure 2 shows the DSC thermal behaviour of azine **3**. The isotropic-LC phase transition is indicated by the exothermic signal of curve b. The inverse transition is not DSC detectable because crystallisation takes place. However, it may be optically detected within a large temperature range up to ~ 91°C.

More particularly, the exothermic signal shown in the DSC cooling curve (Figure 2, b) can be attributed, on the ground of the microscopic observation of the typical fan texture (Figure 3), to an isotropic liquid-smectic A transition, whose inverse cannot be observed on heating owing to previous recrystallization.

In order to collect a preliminary indication about possible LC properties of binary copolymers derived from monomers stemming from azines **3** or **4**, equimolar binary mixtures of these with azine **7** were also examined. The optical observation shows that both mixtures melt to a homogeneous LC phase which isotropizes at a temperature

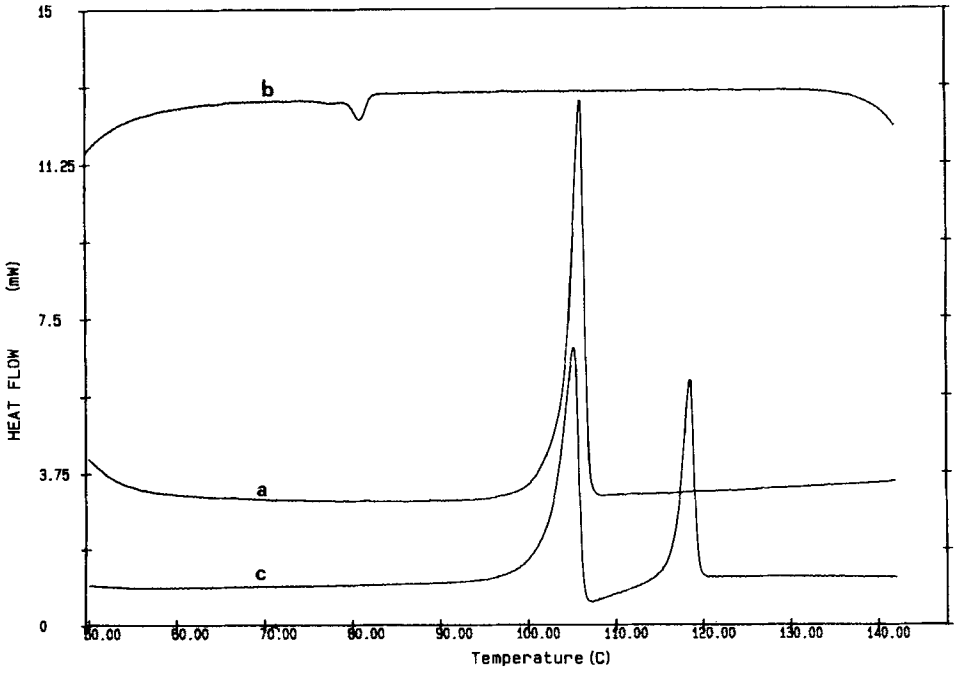


FIGURE 2 *Azine* **3**-DSC thermal behaviour. First heating run for a solvent-crystallised sample (curve a); cooling run (curve b); heating run for a melt-crystallised sample (curve c).

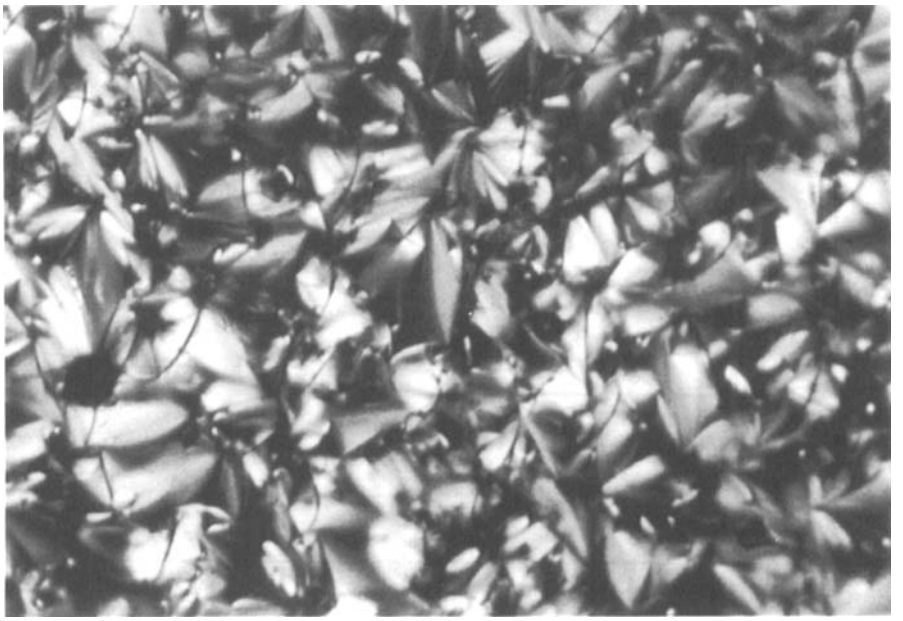


FIGURE 3 Azine **3**-LC texture at 71°C. Crossed polarizers.

considerably lower than found for pure azine **7** (129°C for **7/3**; 127°C for **7/4**). For both compositions, occurrence of LC polymorphism is clearly detectable: in addition to the nematic phase smectic mesomorphism is also exhibited.

The DSC thermal behaviour of **7/3** is reported in Figure 4. The N—S transition, which takes place below ~68°C and is clearly observed by microscopy is hardly detectable by DSC means (curve b). On the contrary, lack of crystallization makes the reverse transition quite evident (curve c). The optical texture observed (fan focal conics) recorded at 71°C (the sample was previously brought to the isotropic phase then cooled down) which is characterised by a diffuse halo peaked at $0.110\,\text{Å}^{-1}\sin(\theta)/\lambda$ and by a sharp Bragg diffraction corresponding to a lattice distance of 26.1 Å, in accordance with the expected molecular length. The mobile schlieren texture observed and the absence of the low angle Bragg line from the X-ray diffraction pattern recorded at 120°C support the nematic nature of the liquid crystalline phase stable above ~80°C. To be more specific, the persistence up to ~90°C of a weak diffraction at ~26 Å should be indicative of some cybotactic character of the nematic phase.

The DSC phase behaviour of mixture **7/4** is reported in Figure 5. The occurrence of LC polymorphism, which, once again, is clearly detectable by microscopy, may also be evidenced by DSC means if the crystallization of the molten mixture is prevented. Curves a (cooling from the isotropic state) and c (successive heating run) show the thermal effects associated to the liquid phase transitions. The schlieren optical texture observed at 116°C (Figure 6) is indicative of a nematic phase. This is confirmed by the X-ray diffraction pattern recorded at 118°C whose feature is a diffuse holo peaked at

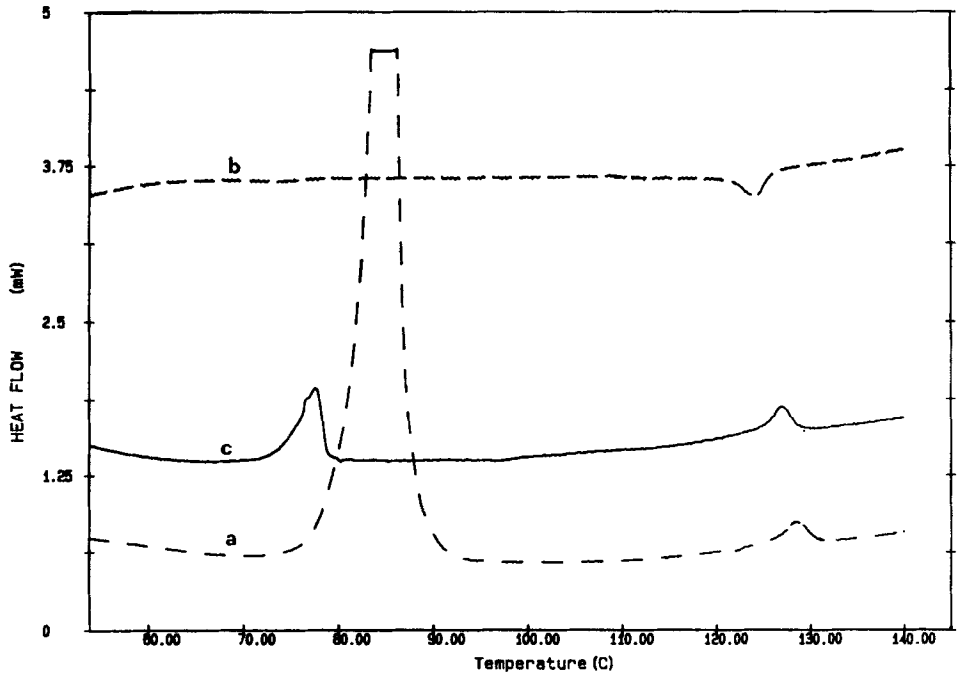


FIGURE 4 DSC thermal behaviour of the equilmolar mixture of azines **7** and **3**. First heating run (curve a); cooling run (curve b), second heating run (curve c).

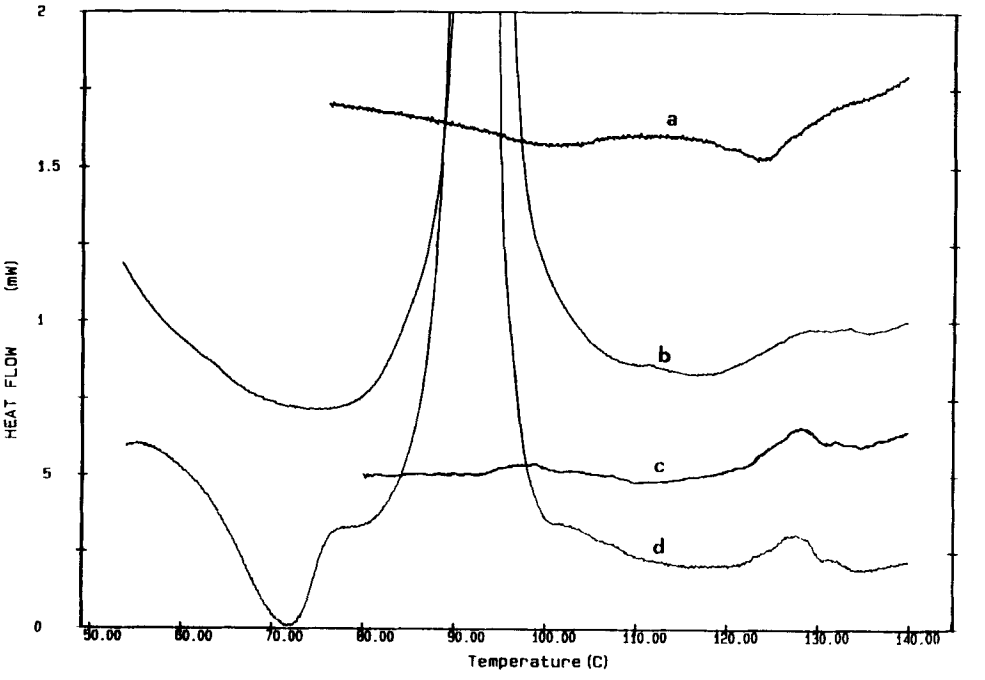


FIGURE 5 DSC thermal behaviour of the equimolar mixture of azines **7** and **4**. First heating run (curve b); cooling run (curve a); second heating run (curve c); third heating run (curve d).

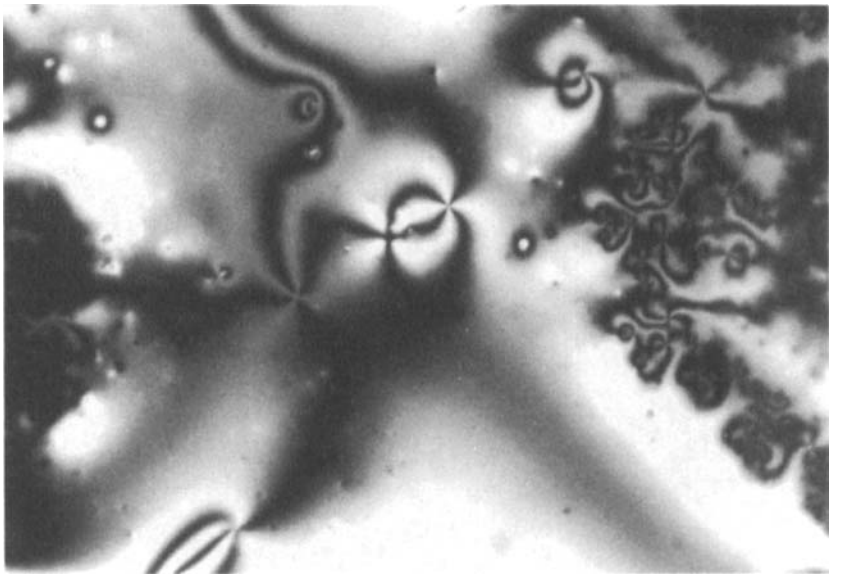


FIGURE 6 Equimolar mixture **7/4**. Nematic phase, schlieren texture at 116°C. Crossed polarizers.

$0.110\,\text{Å}^{-1}\sin(\theta)/\lambda$. The smectic nature of the low temperature LC phase is supported by the focal conics texture (Figure 7) observed at 93°C and by the X-ray diffraction pattern recorded at 91°C (Figure 8) which is characterized by a sharp Bragg diffraction corresponding to a lattice distance of 26.1 Å and by a diffuse halo peaked at $0.110\,\text{Å}^{-1}\sin(\theta)/\lambda$. The latter feature is consistent with a S_A smectic and rules out the possibility that the smectic phase might be of *B* type, as would be suggested by the presence, in the focal conics texture shown in Figure 7, of a morphological peculiarity analogous to the "transition bars" usually associated with the occurrence of an $S_B - S_A$ phase transformation.

Azines **1** and **3–8** show polymorphism in the solid state, as indicated by DSC measurements and confirmed by microscopy observations. At least two crystal forms could be observed in each case, their quantitative ratio dependng on the thermal history (the melting DSC curves shown in Figure 1 for azine **1**, show different behaviour of the same sample when solution-crystallised (curve a) and melt-crystallised (curve c)). Mixtures of different crystal forms are generally obtained when the azines are crystallized from common solvents. In the case of azine **3**, crystallised from absolute ethanol, the two solid phases observed present well separated melting ranges. By an appropriate choice of the crystallisation conditions (e.g. utilising a chloroform/*n*-hexane mixture as the solvent), it becomes possible to isolate only one form, namely the one melting at lower temperature (Figure 2, curve a). In both cases, a melt-crystallised substance contains the high melting phase in variable amounts (Figure 2, curve c). This becomes the only one present in case the crystallization of the liquid fraction is allowed to occur within the appropriate temperature interval, e.g., at 108°C, as shown in Figure 9 in the presence of the high-melting fraction.

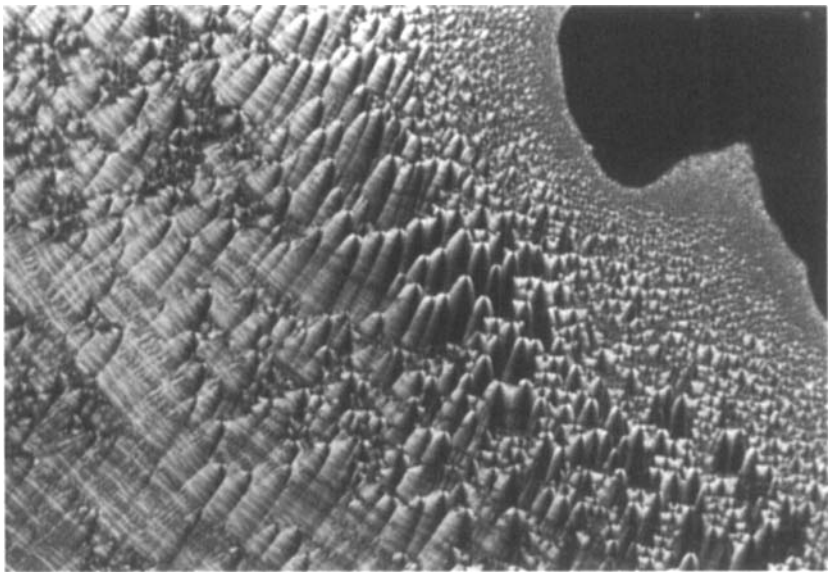


FIGURE 7 Equimolar mixture **7/4**. Smectic phase, focal conics texture at 93°C. Crossed polarizers.

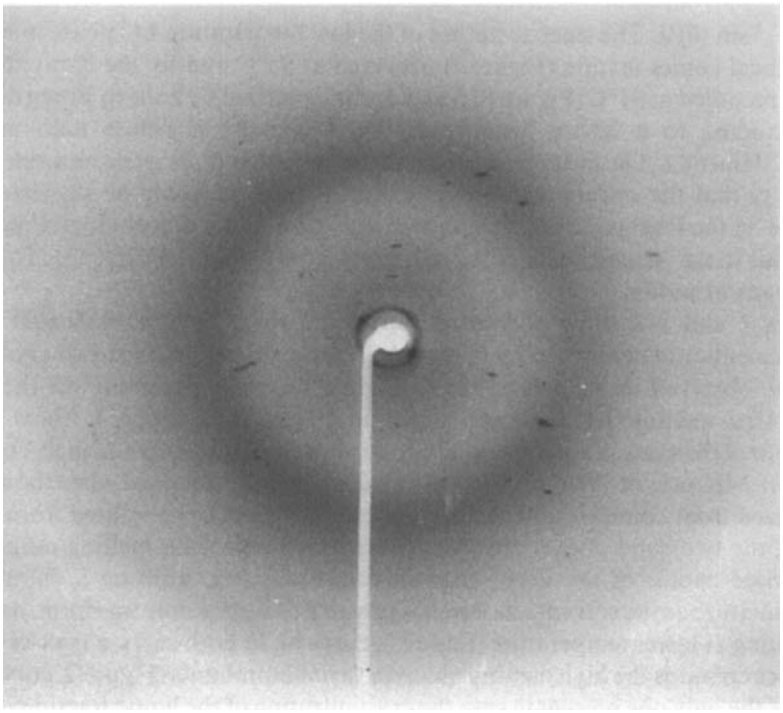


FIGURE 8 Equimolar mixture **7/4**. Smectic phase X-ray diffraction pattern recorded at 91°C. Sample containing a small crystallized fraction.

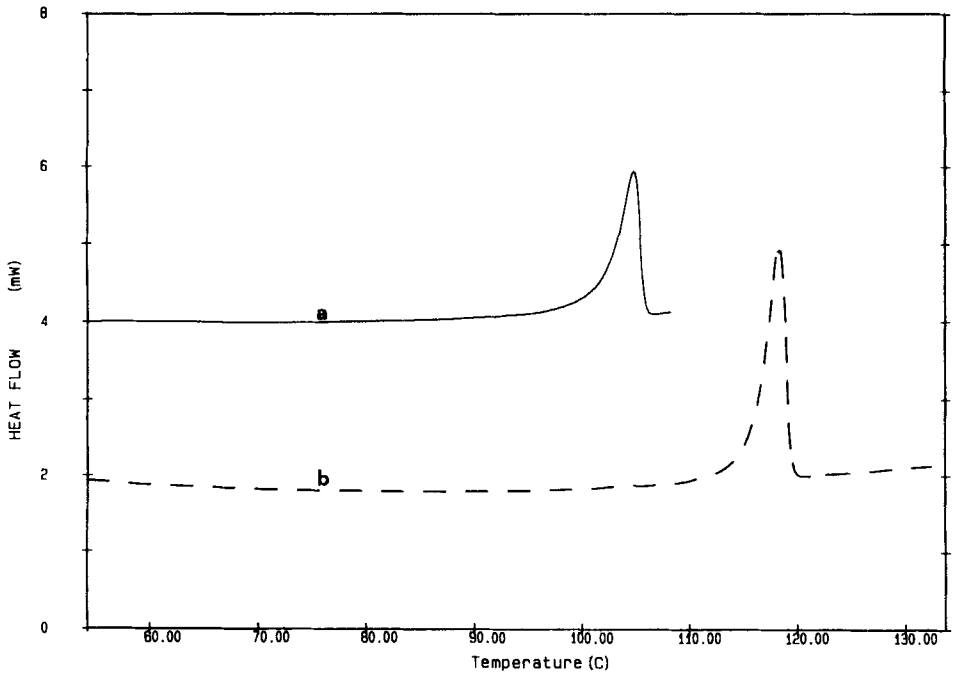


FIGURE 9 Azine **3**. DSC thermal behaviour. Curve a: melting of the low tempeature melting phase for a sample previously crystallised from the melt. Curve b: melting of the high temperature melting phase. The partially molten sample was previously crystallised at 108°C and then cooled at room temperature.

4. CONCLUSIONS

The nematogenic behaviour of azines **1**, **2** and **5–8**, affords a favourable starting point for their utilisation in the synthesis of LC side chain polymers. As for azines **3** and **4**, the lack of enantiotropic LC properties notwithstanding, an extensive ability to form LC mixtures with nematogenic azines is not unreasonably suggested by the behaviour found for equimolar mixtures **7/3** and **7/4**. This feature, together with the expected higher NLO efficiency stemming from the strong electron donor character of the amino group,[16] still makes them interesting starting materials for the synthesis of NLO active polymers.

Acknowledgements

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