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Synthesis and characterization of new liquid crystalline monomers for non-linear optics. X-ray study of re-entrant nematic behaviour with smectic-like fluctuations of C-type

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The syntheses and structural properties of four liquid crystalline monomers are presented. They were prepared by two different reaction pathways. Transition temperatures and phase characterization were done by DSC, polarization microscopy and X-ray diffractometry. The dependence of phase transition temperatures on the alkyl chain lengths and the lateral substitution of the aromatic core are discussed. Two of the compounds investigated show highly ordered smectic phases. The improvement of the conjugation by means of a lateral hydroxy group disturbs the occurrence of the E and B phases. The presence of a nematic re-entrant phase with smectic-like fluctuations of the C-type was observed in a compound with a lateral hydroxy group. The existence of this re-entrant nematic phase was confirmed by X-ray measurements both on cooling and heating of the sample.

1. Introduction

The possibility of using organic compounds for non-linear optical applications has been widely increased in the last few years. Nowadays different systems of NLO-active polymerizable molecules are available in the literature to make macromolecules such as epoxyresins [1], side [2] and main chain polymers [3], cross-linkable copolymers [4] and so on. The development of side chain polymers for optical second order non-linearity has been focused on systems involving just two rings attached to a methacrylate backbone [5], but only a few attempts have been made to synthesize monomers with three aromatic rings [6]. The most crucial point for all these investigations arises in the relaxation of the induced non-centrosymmetry after the orientation process or poling. This decreases the efficiency of the materials for practical uses [7].

The synthesis of five dyes started from a common precursor, 4-amino-4′-nitrostilbene, followed by condensation with aromatic aldehydes, and was developed previously in our group [8]. The SHG values in Guest–Host systems using PMMA as a host were controlled [9]. It is well known that the introduction of a hydroxy group in the *ortho*-position to the azomethine group improves the conjugation of the π system. The formation of a six-membered ring by hydrogen bonding between this hydroxy group and the free electron pair present on the nitrogen of the azomethine group increases the coplanarity of the central core. This effect usually results in a three-fold improvement of the non-linear optical phenomenon [10].

For liquid crystals, the usually observed sequence on heating is from ordered smectic phases to less ordered smectic or nematic phases. The re-entrant phenomenon consists in the reformation of the nematic phase at lower temperatures. This effect has usually been observed for liquid crystalline materials possessing strongly polar terminal groups like cyano or nitro. Since the discovery of the re-entrant nematic phase in liquid crystalline mixtures of terminal polar mesogens by Cladis [11], the re-entrant phenomenon has been extensively studied. Several models have been proposed to explain this behaviour [12, 13].

This paper describes the synthesis and structural properties of four new liquid crystalline compounds with three conjugated rings modelled on Schiff's bases as in our previous work [8, 9]. Here we introduce an aliphatic skeleton that has at the end a polymerizable methacrylate unit. The comparison with an improved conjugated system achieved using a hydroxy group is another point of discussion.

2. Experimental part

2.1. *General considerations*

The compounds investigated were characterized by ^{1}H NMR spectroscopy using a 300 MHz spectrometer

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(WM 300, Bruker), mass spectrometry (Varian MAT 311A) and elemental analysis (Perkin Elmer 240 B). The phase transition temperatures were determined using a differential scanning calorimeter (Dupont 990 Thermal Analyser) with an accuracy of ±0·1 K. A polarizing microscope (Leitz Orthoplan Pol) supported by a hot stage (Mettler Hotstation FP82) and a SVHS video system (Sony, Panasonic) allowed the observation of the phase transitions and the mesomorphic textures. The samples were supported on glass plates coated with ITO and a commercial polyimide (PI-KIT ZLI 2659, Merck). Normal glass plates were used as cover glasses.

X-ray measurements were made with CuK$_\alpha$ radiation using two techniques, namely a photographic method and X-ray diffractometry. The samples were contained in 1·0 mm glass capillaries (Lindemann) and held in a copper block. In the first method, the temperature was controlled within ±0·5 K and measured with a calibrated thermocouple. The samples were oriented using a permanent magnetic field of 0·8 T by cooling from the isotropic phase into the mesophase. In the second method, precise data for aligned samples in the small angle region were obtained using a horizontal two-circle X-ray diffractometer (STOE STADI 2) with a linear position-sensitive detector for data collection [14, 15]. By means of one differential temperature stabilizer near the location of the sample, it was possible to improve the temperature control to be better than ±0·1 K in the range of 30 to 250°C during the measurements. The samples were oriented using permanent magnets with a field strength of 0·3 T.

2.2. *Synthesis*

The commercial reactants were available from Aldrich and E. Merck. The amino-nitrostilbene (**6** in figures 1 and 2) was obtained in a modified way according to the procedure described by Hanemann *et al.* [8]. The numbers in brackets below refer to figures 1 and 2. The reaction pathway in figure 1 was used for the synthesis of compounds with $n=6$ as spacer. The synthetic pathway in figure 2 was used in the preparation of compounds with both $n=6$ and $n=11$ as spacer. In the following, the final products **7** and **12** are subdivided into **7a** and **12a** for $R=H$, and **7b** and **12b** for $R=OH$. Table 1 summarizes the elemental analytical results for the monomers.

2.2.1. *4-(6-Hydroxyhexyloxy)benzaldehyde* (**3**, $\boldsymbol{R}$=**H**)

A mixture of 0·05 mol of benzaldehyde **1**, $\boldsymbol{R}$=**H** and an equimolar amount of 50% aqueous KOH in 100 ml of ethanol were heated under reflux for one hour with stirring. After cooling, a catalytic amount of KI and 30 ml of triethylamine (TEA) together with 0·25 mol of

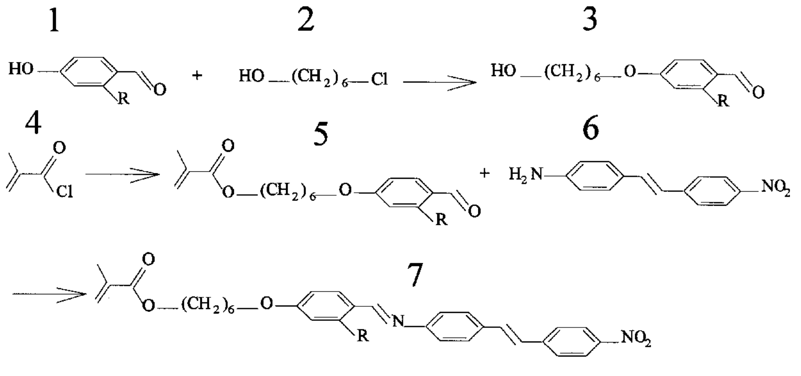


Figure 1. Reaction pathway for the synthesis of the monomers with a hexyl spacer (R=H, OH).

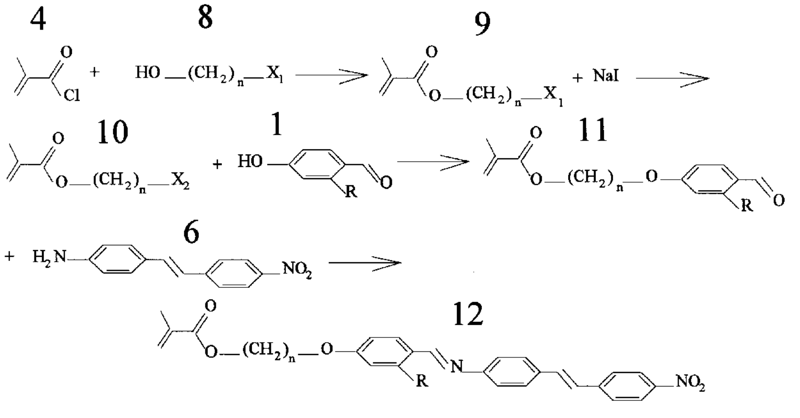


Figure 2. Reaction pathway for the synthesis of the monomers with X_1=Cl, Br; X_2=I, Br; n=6 and n=11 (R=H, OH).

Table 1. Yields and elemental analytical data.

Compound	Yield/%	Elemental analysis/%: found (calculated) C	H	N
7a	74·9	71·22 (72·66)	6·18 (6·25)	5·33 (5·47)
12a	[a]	72·22 (74·23)	7·19 (7·22)	4·66 (4·81)
7b	34·7	70·48 (70·45)	6·09 (6·06)	5·43 (5·30)
12b	37·1	71·97 (72·24)	7·10 (7·02)	4·80 (4·68)

[a] Total yield not determined.

6-chlorohexanol were added to the mixture which was boiled for two days with stirring. The triethylamine hydrochloride was filtered off, the solvent was removed under reduced pressure and the yellow oil washed with water. The product was extracted three times into diethylether and dried with Na_2SO_4 before removing the ether. The crude product was purified using column chromatography on silica gel with dichloromethane as eluent.

2.2.2. *Methacrylate of 4-(6-hydroxyhexyloxy)benzaldehyde* (5, *R*=H)

Methacrylic acid chloride **4** (0·05 mol) dissolved in 20 ml of dry toluene, and 10 ml of TEA was added dropwise to a stirred solution of 0·05 mol of **3, *R*=H** in 20 ml of dry toluene. The reaction temperature was controlled with an ice bath. After 48 hours of stirring, the TEA hydrochloride was filtered off and the solution washed with water. The organic layer was dried with Na_2SO_4 and the solvent evaporated under reduced pressure. The methacrylate of the hexyloxybenzaldehyde **5, *R*=H** was purified by column chromatography on silica gel using toluene–ethyl acetate 19:1 as eluent.

2.2.3. *Methacrylate of 4-[2-{4-[4-(6-hydroxyhexyloxy)benzylideneamino]phenyl}ethenyl]nitrobenzene* (7a)

To a suspension of aminonitrostilbene **6** in dry ethanol, an equimolar amount of **5, *R*=H** was added and the mixture reflux heated with stirring for 24 hours in the presence of a small amount of hydroquinone to stabilize the monomer. After this, the mixture was filtered and the methacrylate of azomethine **7a, *R*=H** was obtained as yellow needles which were recrystallized twice from ethanol.

2.2.4. *Methacrylate of 6-chloro-1-hexanol* (9, *n*=6, X_1=Cl)

The preparation of **9, *n*=6, X_1=Cl** was the same as described in §2.2.2 (compound **5, *R*=H**). The purification of the methacrylate **9, *n*=6, X_1=Cl** was achieved by column chromatography using toluene–ethyl acetate 9:1 as eluent.

2.2.5. *Methacrylate of 6-iodo-1-hexanol* (10, *n*=6, X_2=I)

A solution of sodium iodide (0·366 mol) in 250 ml of dry acetone and the methacrylate of 6-chloro-1-hexanol **9, *n*=6, X_1=Cl** was stirred at room temperature for 24 hours. Then the sodium chloride was filtered off and the organic mixture was washed with aqueous sodium thiosulphate and water and extracted three times into diethylether. The purification of compound **10, *n*=6, X_2=I** was the same as described in §2.2.4.

2.2.6. *Methacrylate of 11-bromo-1-undecanol* (10, *n*=11, X_2=Br)

Compound (**10, *n*=11, X_2=Br**) was prepared satisfactorily as described in 2.2.2.

2.2.7. *Methacrylate of 4-(11-hydroxyundecyloxy)benzaldehyde* (11, *n*=11, *R*=H)

To a mixture of 0·89 mol of aldehyde **1, *R*=H** in 90 ml of 2,5-dimethylbenzimidazolidone with an equimolar amount of compound **10, *n*=11, X_2=Br**, were added 0·9 mol of sodium hydrogen carbonate and a catalytic amount of hydroquinone as stabilizer. The mixture was kept at 100°C and the reaction was followed by thin layer chromatography. After one day, the same amount of sodium hydrogen carbonate was added to the reaction mixture. After another 24 hours, the reaction mixture was cooled and water was added. The product was extracted three times into diethylether. The organic layer was dried with Na_2SO_4 and the solvent distilled off under reduced pressure. Column chromatography on silica gel using the last mentioned eluent gave the methacrylate of the alkyloxy aldehyde **11, *n*=11, *R*=H** in a total yield of 60% starting from compound **8, *n*=11, X_1=Br**.

2.2.8. *Methacrylate of 4-[2-{4-[4-(11-hydroxyundecyloxy)benzylideneamino]phenyl}ethenyl]nitrobenzene* (12a, *n*=11)

Yellow needles of monomer **12a, *n*=11, *R*=H** were obtained starting from the methacrylate of 4-(11-hydroxyundecyloxy)benzaldehyde (**11, *n*=11, *R*=H**) in the same way as described for compound **7, *n*=6, *R*=H**.

2.3. *NMR data*

2.3.1. *4-(6-Hydroxyhexyloxy)benzaldehyde* **(3, *R*=H)**

^{1}H NMR ($CDCl_3$) δ: 9·86 (s, 1H, **CH=O**); 7·83 (d, 2H, **Arom.**); 6·99 (d, 2H, **Arom.**); 3·63 (m, 4H, HO–**CH_2**, **CH_2**–O); 2·53 (s, 1H, **OH**); 1·78 (m, 2H, CO_2–CH_2–**CH_2**); 1·3–1·62 (m, 6H, **CH_2**–CH_2–O, –**CH_2**–). J_{O}: 8·7 Hz.

2.3.2. *2-Hydroxy-4-(6-hydroxyhexyloxy)benzaldehyde* **(3, *R*=OH)**

^{1}H NMR ($CDCl_3$) δ: 11·47 (s, 1H, Arom.–**OH**); 9·69 (s, 1H, **CH=O**); 7·42 (d, 1H, **Arom.**); 6·52 (dd, 1H, **Arom.**); 6·40 (d, 1H, **Arom.**); 4·03 (t, 2H, **CH_2**–O); 3·66 (t, 2H, HO–**CH_2**); 1·80 (m, 2H, **CH_2**–CH_2–OH); 1·59 (m, 2H, HO–CH_2–**CH_2**); 1·38–1·52 (m, 4H, –**CH_2**–). J_{O}: 8·6 Hz; J_{m}: 2·3 Hz.

2.3.3. *Methacrylate of 4-(6-hydroxyhexyloxy)benzaldehyde* **(5, *R*=H)**

^{1}H NMR ($CDCl_3$) δ: 9·85 (s, 1H, **CH=O**); 7·81 (d, 2H, **Arom.**); 6·96 (d, 2H, **Arom.**); 6·09 (s, 1H, trans **H_2C**=C); 5·53 (s, 1H, *cis* **H_2C**=C); 4·15 (t, 2H, CO_2–**CH_2**); 4·01 (t, 2H, **CH_2**–O); 1·93 (s, 3H, H_2C=**CCH_3**); 1·81 (m, 2H, CO_2–CH_2–); 1·71 (m, 2H, **CH_2**–CH_2–O); 1·43–1·53 (m, 4H, –**CH_2**–). J_{O}: 8·7 Hz.

2.3.4. *Methacrylate of 2-hydroxy-4-(6-hydroxyhexyloxy)benzaldehyde* **(5, *R*=OH)**

^{1}H NMR ($CDCl_3$) δ: 11·48 (s, 1H, Arom.–**OH**); 9·70 (s, 1H, **CH=O**); 7·40 (d, 1H, **Arom.**); 6·51 (dd, 1H, **Arom.**); 6·40 (d, 1H, **Arom.**); 6·10 (s, 1H, *trans* **H_2C**=C); 5·55 (s, 1H, *cis* **H_2C**=C); 4·16 (t, 2H, CO_2–**CH_2**); 4·00 (t, 2H, **CH_2**–O); 1·94 (s, 3H, H–2C=**CCH_3**); 1·83 (m, 2H, CO_2–CH_2–**CH_2**), 1·72 (m, 2H, **CH_2**–CH_2–O); 1·43–1·55 (m, 4H, –**CH_2**–). J_{O}: 8·7 Hz; J_{m}: 2·3 Hz.

2.3.5. *Methacrylate of 4-[2-{4-[4-(6-hydroxyhexyloxy)benzylideneamino]phenyl}ethenyl]nitrobenzene* **(7a)**

^{1}H NMR ($CDCl_3$) δ: 8·41 (s, 1H, **CH=N**); 8·21 (d, 2H, **Arom.**–NO_2); 7·84 (d, 2H, **Arom.**–C_2H_2); 7·62 (d, 2H, **Arom.**–NO_2); 7·57 (d, 2H, **Arom.**–CH=N); 7·27 (d, 1H, **HC=CH**); 7·23 (d, 2H, **Arom.**–CH=N); 7·11 (d, 1H, **HC=CH**); 6·97 (d, 2H, **Arom.**–C_2H_2); 6·10 (s, 1H, *trans* **H_2C**=C); 5·55 (s, 1H, *cis* **H_2C**=C); 4·17 (t, 2H, CO_2–**CH_2**); 4·03 (t, 2H, **CH_2**–O); 1·92 (t, 3H, **CH_3**); 1·47–1·86 (m, 8H, –**CH_2**–). $J_{\mathrm{O}\ \phi\text{–CH=N}}$: 8·4 Hz; $J_{\mathrm{O}\ \phi\text{–}C_2H_2}$: 8·5 Hz; $J_{\mathrm{O}\ \phi\text{–}NO_2}$: 8·6 Hz; $J_{\mathrm{HC=CH}}$: 17·01 Hz. MS (70 eV) *m/z* 512 (M^{+}, 100 per cent).

2.3.6. *Methacrylate of 4-[2-{4-[2-hydroxy-4-(6-hydroxyhexyloxy)benzylideneamino]phenyl}ethenyl]nitrobenzene* **(7b)**

^{1}H NMR ($CDCl_3$) δ: 13·65 (s, 1H, Arom.–**OH**); 8·56 (s, 1H, **CH=N**); 8·22 (d, 2H, **Arom.**–NO_2); 7·63 (d, 2H, **Arom.**–NO_2); 7·59 (d, 2H, **Arom.**–C_2H_2); 7·29 (d, 2H, **Arom.**–C_2H_2); 7·28 (d, 1H, **Arom.**–CH=N); 7·28 (d, 1H, **HC=CH**); 7·13 (d, 1H, **HC=CH**); 6·49 (m, 2H, **Arom.**–CH=N); 6·10 (s, 1H, *trans* **H_2C**=C); 5·55 (s, 1H, *cis* **H_2C**=C); 4·17 (5, 2H, CO_2–**CH_2**); 4·00 (t, 2H, **CH_2**–O); 1·95 (t, 3H, **CH_3**); 1·82 (m, 2H, CO_2–CH_2–**CH_2**); 1·73 (m, 2H, **CH_2**–CH_2–O); 1·46–1·59 (m, 4H, **CH_2**). $J_{\mathrm{O}\ \phi\text{-CH=N}}$: 8·2 Hz; $J_{\mathrm{O}\ \phi\text{–}C_2H_2}$: 8·2 Hz; $J_{\mathrm{O}\ \phi\text{–}NO_2}$: 8·7 Hz; $J_{\mathrm{HC=CH}}$: 16·6 Hz. MS (70 eV) *m/z* 528 (M^{+}, 100 per cent).

2.3.7. *Methacrylate of 6-iodo-1-hexanol* **(10, *n*=6, X_2=I)**

^{1}H NMR ($CDCl_3$) δ: 6·10 (s, 1H, *trans* **H_2C**=C); 5·55 (s, 1H, *cis* **H_2C**=C); 4·15 (t, 2H, CO_2–**CH_2**); 3·54 (t, 2H, **CH_2**–I); 1·94 (s, 3H, H_2C=C–**CH_3**); 1·80 (m, 2H, CO_2–CH_2–**CH_2**); 1·71 (m, 2H, **CH_2**–CH_2–I); 1·35–1·60 (m, 4H, **CH_2**).

2.3.8. *Methacrylate of 11-bromo-1-undecanol* **(10, *n*=11, X_2=Br)**

^{1}H NMR ($CDCl_3$) δ: 6·09 (s, 1H, *trans* **H_2C**=C); 5·54 (s, 1H, *cis* **H_2C**=C); 4·13 (t, 2H, CO_2–**CH_2**); 3·18 (t, 2H, **CH_2**–Br); 1·94 (s, 3H, H_2C=C–**CH_3**); 1·80 (m, 2H, CO_2–CH_2–**CH_2**); 1·66 (m, 2H, **CH_2**–CH_2–Br); 1·20–1·38 (m, 14H, –**CH_2**–).

2.3.9. *Methacrylate of 4-(11-hydroxyundecyloxy)benzaldehyde* **(11, *n*=11, *R*=H)**

^{1}H NMR ($CDCl_3$) δ: 9·88 (s, 1H, **CH=O**); 7·83 (d, 2H, **Arom.**); 6·99 (d, 2H, **Arom.**); 6·10 (s, 1H, *trans* **H_2C**=C); 5·55 (s, 1H, *cis* **H_2C**=C); 4·14 (t, 2H, CO_2–**CH_2**); 4·04 (t, 2H, **CH_2**–O); 1·94 (s, 3H, H_2C=C–**CH_3**); 1·80 (m, 2H, CO_2–CH_2–**CH_2**); 1·66 (m, 2H, **CH_2**–CH_2–O); 1·30–1·48 (m, 14H, –**CH_2**–). J_{o}: 8·8 Hz.

2.3.10. *Methacrylate of 2-hydroxy-4-(11-hydroxyundecyloxy)benzaldehyde* **(11, *n*=11, *R*=OH)**

^{1}H NMR ($CDCl_3$) δ : 11·48 (s, 1H, Arom.–**OH**); 9·70 (s, 1H, **CH=O**); 7·42 (d, 1H, **Arom.**); 6·53 (dd, 1H, **Arom.**); 6·41 (d, 1H, **Arom.**); 6·10 (s, 1H, *trans* **H_2C**=C); 5·55 (s, 1H, *cis* **H_2C**=C); 4·14 (t, 2H, CO_2–**CH_2**); 4·00 (t, 2H, **CH_2**–O); 1·94 (s, 3H, H_2C=C–**CH_3**); 1·79 (m, 2H, CO_2–CH_2–**CH_2**); 1·67 (m, 2H, **CH_2**–CH_2–O); 1·30–1·45 (m, 14H, –**CH_2**–). J_{o} : 8·7 Hz; J_{m}: 2·2 Hz.

2.3.11. *Methacrylate of 4-[2-{4-[4-(11-hydroxyundecyloxy)benzylideneamino]phenyl}ethenyl]nitrobenzene* **(12a, *n*=11)**

^{1}H-NMR ($CDCl_3$) δ: 8·41 (s, 1H, **CH=N**); 8·21 (d, 2H, **Arom.**–NO_2); 7·85 (d, 2H, **Arom.**–C_2H_2); 7·63 (d, 2H, **Arom.**–NO_2); 7·57 (d, 2H, **Arom.**–CH=N); 7·28 (d, 1H, **HC=CH**); 7·23 (d, 2H, **Arom.**–CH=N); 7·12 (d, 1H, **HC=CH**); 6·98 (d, 2H, **Arom.**–C_2H_2); 6·10 (s, 1H, *trans* $\mathbf{H_2C}{=}C$); 5·55 (s, 1H, *cis* $\mathbf{H_2C}{=}C$); 4·14 (t, 2H, $CO_2{-}\mathbf{CH_2}$); 4·03 (t, 2H, $\mathbf{CH_2}{-}O$); 1·95 (t, 3H, $\mathbf{CH_3}$); 1·80 (m, 2H, $CO_2{-}CH_2{-}\mathbf{CH_2}$); 1·62 (m, 2H, $\mathbf{CH_2}{-}CH_2{-}O$); 1·30–1·47 (m, 14H, $\mathbf{CH_2}$). $J_{O\ \phi-N=CH}$: 8·4 Hz; $J_{O\ \phi-C_2H_2}$: 8·7 Hz; $J_{O\ \phi-NO_2}$: 8·9 Hz; $J_{HC=CH}$: 16·3 Hz. MS (70 eV) *m/z* 582 (M^{+}, 100 per cent).

2.3.12. *Methacrylate of 4-[2-{4-[2-hydroxy-4-(11-hydroxyundecyloxy) benzylideneamino]phenyl} ethenyl]nitrobenzene* (12b, *n* = 11)

^1H NMR ($CDCl_3$) δ: 13·65 (s, 1H, Arom.–**OH**); 8·56 (s, 1H, $\mathbf{CH}{=}N$); 8·23 (d, 2H, **Arom**.–NO_2); 7·64 (d, 2H, **Arom**.–NO_2); 7·59 (d, 2H, **Arom**.–C_2H_2); 7·29 (d, 2H, **Arom**.–C_2H_2); 7·28 (d, 1H, **Arom**.–CH=N); 7·28 (d, 1H, $\mathbf{HC{=}CH}$); 7·13 (d, 1H, $\mathbf{HC{=}CH}$); 6·50 (m, 2H, **Arom**.–CH=N); 6·10 (s, 1H, *trans* $\mathbf{H_2C}{=}$); 5·55 (s, 1H, *cis* $\mathbf{H_2C}{=}C$); 4·14 (t, 2H, $CO_2{-}\mathbf{CH_2}$); 4·00 (t, 2H, $\mathbf{CH_2}{-}O$); 1·95 (t, 3H, $\mathbf{CH_3}$); 1·79 (m, 2H, $CO_2{-}CH_2{-}\mathbf{CH_2}$); 1·65 (m, 2H, $\mathbf{CH_2}{-}CH_2{-}O$); 1·24–1·46 (m, 14H, $\mathbf{CH_2}$). $J_{O\ \phi-N=CH}$: 8·6 Hz; $J_{O\ \phi-C_2H_2}$: 8·5 Hz; $J_{O\ \phi-NO_2}$: 8·9 Hz; $J_{HC=CH}$: 16·3 Hz. MS (70 eV) *m/z* 598 (M^{+}, 100 per cent).

2.4. *Identification of the mesophases*

All the monomers synthesized (see figure 3) show liquid crystalline properties. Figure 4 presents the X-ray diffraction patterns in the high ordered phases for compounds **7a** and **12a**. Figures 5 and 6 show the layer periodicities of all compounds determined from the position of the small angle reflections. The transition temperatures determined by DSC, as well as the observed diffraction reflections, together with the unit cell parameters for the highly ordered E phases of compounds **7a** and **12a**, are summarized in tables 2 and 3, respectively. The parameters of the unit cell for the orthorhombic system were calculated using well known equations [16].

The characterization of mesophases above 200°C was done by polarizing microscopy and not by X-ray because of decomposition of the compounds at high temperature. To avoid preferential homeotropic orientation, the samples for texture investigation were prepared using glass slides covered by a thin layer of polyimide.

2.4.1. *Methacrylate of 4-[2-{4-[4-(6-hydroxyhexyloxy) benzylideneamino]phenyl}ethenyl]nitrobenzene* (7a)

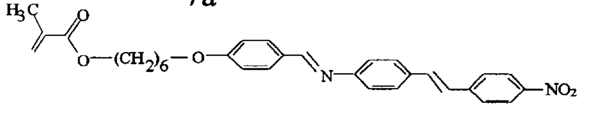
Compound **7a** developed a nematic phase (schlieren texture) at high temperature, before the transition to the isotropic phase. On cooling the N phase, a fan shaped texture typical of a smectic A phase was detected. Cooling from the homeotropic texture of the SmA phase, between normal glass supports, the platelet texture for the E phase was formed. In the observed texture it was possible to identify the ghost-like images characteristic of the birefringent platelet areas. They are quite representative of the E phase and very different from normal mosaic textures.

This behaviour correlates with the presence of sharp inner and diffuse outer reflections in the smectic A phase, as seen from the X-ray photographs. In the wide angle region, the E phase obtained on cooling shows two sharp peaks (figure 4(*a*)) at 20·40° and 22·04° in 2θ (115·7°C). This corresponds to the orthorhombic type of packing (see table 3). The layer periodicity is 40·4 ± 0·2 Å for the E phase and 40·0 ± 0·2 Å for the smectic A phase (see figure 5(*a*)). The layer thickness is almost 10 Å larger (see table 2) than the molecular length ($d/l \sim 1{\cdot}35$). This indicates the existence of a bilayered structure in the E phase as well as in the smectic A phase (SmAd).

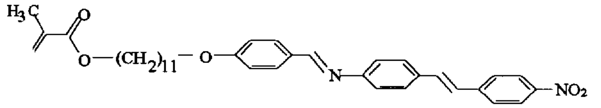
2.4.2. *Methacrylate of 4-[2-{4-[4-(11-hydroxyundecyloxy) benzylideneamino]phenyl}ethenyl] nitrobenzene* (12a)

By cooling from the isotropic phase compound **12a** developed a normal focal-conic fan shaped texture characteristic for smectic A phases. On cooling further, the same kind of texture for the E phase was observed under the same conditions as described for compound **7a**.

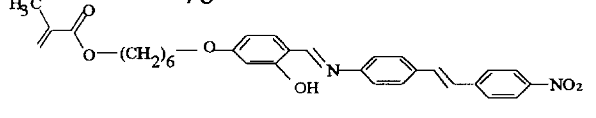
7a



12a



7b



12b

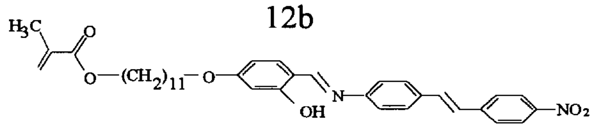


Figure 3. Chemical structures of the compounds investigated.

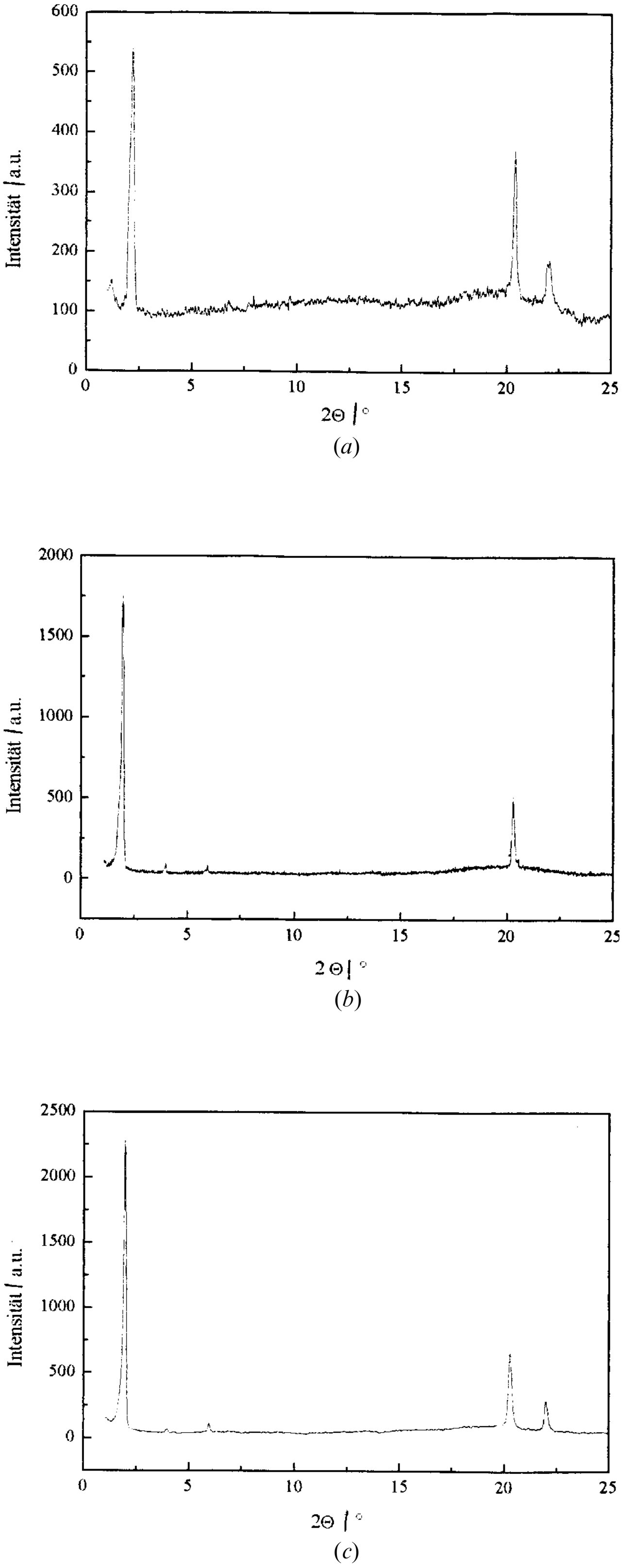


Figure 4. 2θ-scans for the compounds (*a*) **7a**, E phase at 115·7°C; (*b*) **12a**, SmB phase at 159·4°C and (*c*) **12a**, E phase at 132·0°C.

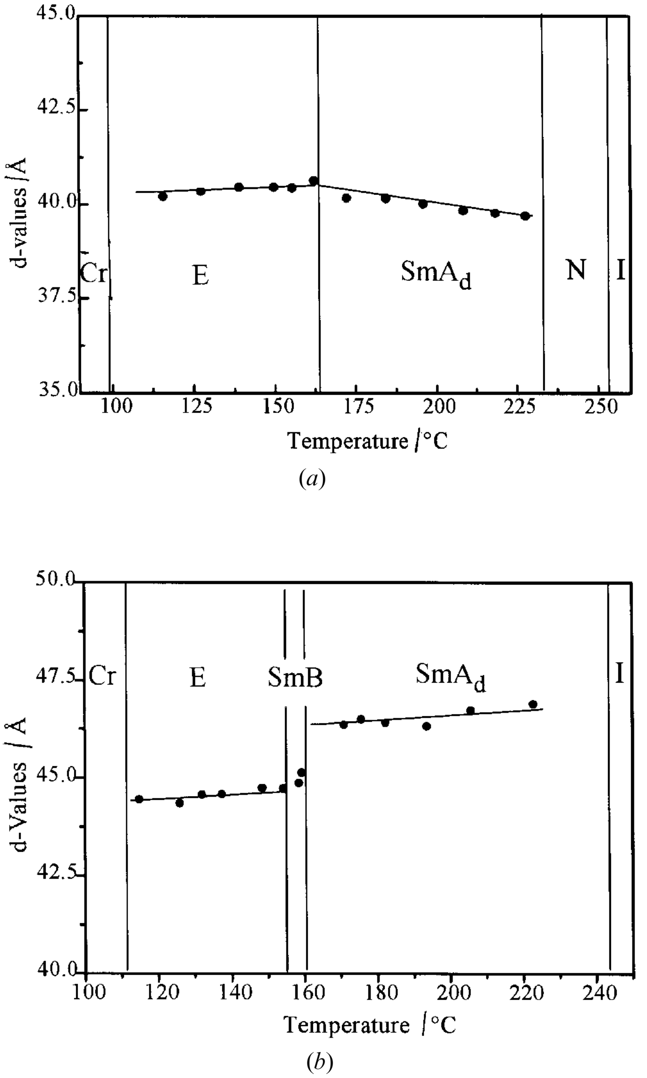
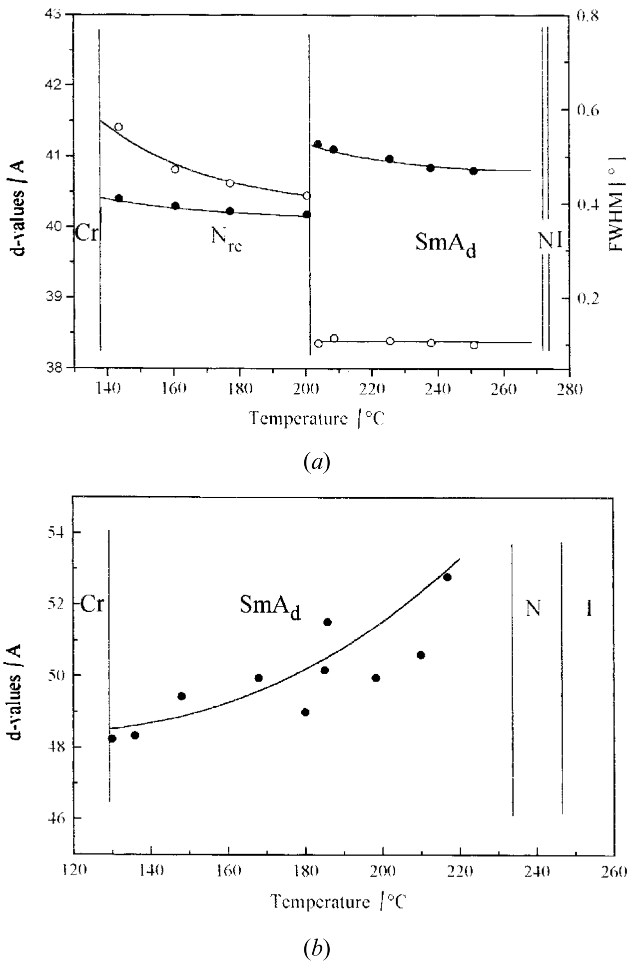


Figure 5. Temperature dependence of interlayer spacing for compounds (*a*) **7a** and (*b*) **12a**. The lines are guides for the eyes only.

The existence of a smectic B phase in a small temperature range between the E and SmA phases was confirmed by the presence of just one sharp reflection in the wide angle scattering region (figure 4 (*b*)). This corresponds to the in-plane hexagonal packing with a lattice parameter of $a=5{\cdot}06$ Å ($T=158{\cdot}6$°C).

The E phase has in the wide angle region two sharp reflections corresponding to the parameters of an orthorhombic lattice, $a=8{\cdot}06$ Å and $b=5{\cdot}20$ Å (table 3). Here, the layer spacing ($T=132$°C) amounts to $44{\cdot}6\pm0{\cdot}2$ Å ($d/l\sim1{\cdot}24$). In the smectic A_d phase the layer spacing is $46{\cdot}6\pm0{\cdot}3$ Å ($d/l\sim1{\cdot}29$) (see figure 5 (*b*)). In the narrow range smectic B phase the layer spacing is comparable to that in the E phase, but there is a jump from smectic B to smectic A_d.



(*a*)

(*b*)

Figure 6. Temperature dependence of interlayer spacing (●) for compounds (*a*) **7b** and (*b*) **12b** and FWHM (○) for compound (*a*) **7b**. The lines are guides for the eyes only.

2.4.3. *Methacrylate of 4-[2-{4-[2-hydroxy-4-(6-hydroxyhexyloxy)benzylideneamino]phenyl}ethenyl] nitrobenzene* (**7b**)

Compound **7b** shows, on cooling, a short temperature range nematic phase followed by a smectic $\mathrm{A_d}$ and a nematic re-entrant phase; *d*-values and full width at half maximum data (FWHM) are presented in figure 6(*a*). The FWHM data indicate a nematic re-entrant phase, which is also demonstrated in figure 7. This behaviour was proved to be enantiotropic. The X-ray photographs taken on cooling from the isotropic phase and on heating from the crystalline phase showed the typical diffraction patterns for an oriented nematic phase with smectic-like fluctuations of the C type (see figure 8). It consists of four intense spots distributed symmetrically around the edge of the sample.

The interlayer spacing in the smectic $\mathrm{A_d}$ is 41·0 ± 0·2 Å ($d/l \sim 1{\cdot}36$), but increases in the re-entrant nematic phase (see figure 6(*a*)) from 40·5 Å at 200°C to 41·4 Å at 145°C with decreasing temperature.

2.4.4. *Methacrylate of 4-[2-{4-[2-hydroxy-4-(11-hydroxyundecyloxy)benzylideneamino]phenyl} ethenyl]nitrobenzene* (**12b**)

For compound **12b**, optical microscopy studies showed the presence of a nematic phase at high temperature. On cooling, a smectic $\mathrm{A_d}$ phase was indicated from X-ray studies and texture observations. In the smectic $\mathrm{A_d}$ phase, the X-ray photographs for oriented samples showed two intense equatorial inner reflections and two outer diffuse reflections. The interlayer periodicity averaged to about 50·2 ± 2·0 Å, but increased from 48·2 to 52·7 Å on increasing the temperature (see figure 6(*b*)).

3. Results and discussion

3.1. *Synthesis*

Two different strategies of synthesis were developed to obtain monomers with elongated π-systems. The scheme shown in figure 1 was used to obtain the derivatives with 6 methylene groups as spacer.

The physical properties for the monomers with hexyl spacers were in accordance with those synthesized through the reactions shown in figure 2. The reaction to obtain the aldehyde **5**, ***R*** = **OH**, using 2,4-dihydroxybenzaldehyde, gives the possibility of substitution at both hydroxy groups, as was detected by ^{1}H NMR. After chromatographic purification, some disubstituted material always remains with the desired product. Nevertheless, the reaction to obtain the Schiff's base produces preferentially the mono-derivative **5**, ***R*** = **OH**. Therefore, no further purification in order to obtain the free mono-substituted aldehyde was necessary.

The reactions involved in figure 2 up to the iodo

Table 2. Transition temperatures in °C, and calculated molecular lengths (*l*) in Å.

Compound	Phase behaviour	*l*
7a	Cr–99·2–E–164·1–$\mathrm{SmA_d}$–233·0–N–253·0^a–I (decomp. 244·6)	30·1
12a	Cr–112·5–E–156·6–SmB–161·3—$\mathrm{SmA_d}$–244·1–I	36·1
7b	Cr–137·5–$\mathrm{N_{re}}$–200·0–$\mathrm{SmA_d}$–273·0–N–273·5^a–I (decomp. 262·2)	30·1
12b	Cr–129·7–$\mathrm{SmA_d}$–234·0–N–248·0^a–I	36·1

[a] Determined by polarizing microscopy.

Table 3. Reflection indices and cell parameters for the unit cells of the E phase of compounds **7a** and **12a**.

Compound **7a**: (T=115·7°C)				Compound **12a**: (*T*=132·0°C)			
	d/Å				*d*/Å		
2*θ*/°	exp	calc.	(*h k l*)	2*θ*/°	exp	calc.	(*h k l*)
2·19	40·21	40·21	(0 0 1)	1·98	44·57	44·57	(0 0 1)
20·40	4·35	4·35	(1 1 0)	3·98	22·19	22·48	(0 0 2)
22·04	4·03	4·03	(2 0 0)	5·96	14·81	14·99	(0 0 3)
				20·28	4·37	4·37	(1 1 0)
				22·02	4·03	4·03	(2 0 0)
a=8·06 Å, b=5·17 Å, c=40·21 Å, V=1675·6 Å				a=8·06 Å, b=5·20 Å, c=44·57 Å, V=1868·0 Å			

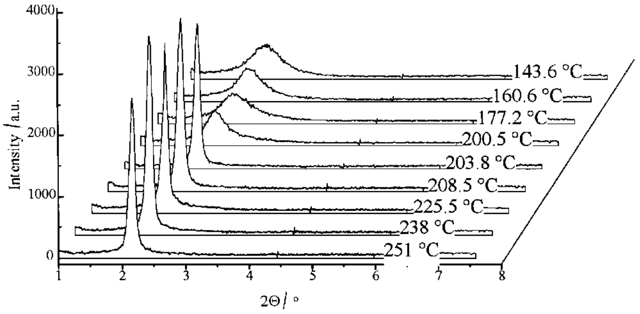


Figure 7. 2*θ*-scans at different temperatures for compound **7b**.

derivative **10, *n*=6, X_2=I** have been described by Brown *et al.* using 4-chlorobutanol as reactant [17]. The etherification to obtain **11, *n*=6/11, *R*=H/OH** was carried out in a slightly modified way according to the description of Pfeiffer and Haase [18]. The reaction pathway shown in figure 2 seems to be the most advantageous. It makes it possible to prepare new end products by choosing the proper aldehyde **1**.

3.2. *Structural discussion*

It is possible to subdivide the new compounds into two groups (see figure 3), without (**7a**, **12a**) and with (**7b**, **12b**) the lateral OH group. The former show highly ordered smectic phases. In this group, the increase in the aliphatic character of the molecule (5 methylene groups more than in compound **12a**) introduces a short temperature range smectic B phase, but diminishes the nematic phase (see table 2). The inclusion of a lateral hydroxy group in a rod-like molecule like the latter one suppresses the possibility of hexagonal packing necessary for some higher ordered phases. This behaviour is well known and has been reported before [19, 20].

Considering the *d*-values shown in figures 5 and 6 and the length of the molecules (see table 2), it is possible to assume the existence of partial double layering in all the liquid crystalline phases. The ratio of layer spacing to molecular length (*d*/*l*) is between 1·2 and 1·4. This phenomenon is typical for liquid crystals with strongly polar terminal moieties like cyano [21] and nitro [22] groups and has been extensively described by Haase *et al.* [23] for compounds with three aromatic rings within the molecules. The re-entrant phenomenon is also characteristic for molecules having strongly polar groups [24, 25]. Nevertheless, up to now, to the best of our knowledge, there have been no examples of the E phase in compounds having a terminal nitro group.

The strong increase of the interlayer distance on increasing the temperature for compound **12b** in the smectic A_d phase (figure 6 (*b*)) is in agreement with the behaviour for one other compound [23] containing a 4-NO_2 group, although Sigaud *et al.* [26] describe a similar behaviour for a mixture of two liquid crystals with three aromatic rings having a nitro group in the *para*-position. A small tendency for the *d*-values in the smectic A phase to increase is also seen for compound **12a** (figure 5 (*b*)), whereas for the compounds with a smaller spacer **7a** and **7b**, there is a small tendency for the *d*-values to decrease with increasing temperature (figures 5 (*a*) and 6 (*a*)). We interpret the special behaviour of compound **12b** as being due to the steric effect of the OH-group, as well as to the extended spacer length.

The length of the aliphatic spacer plays a very important role in relation to the appearance of the nematic phase with smectic C fluctuations. In the case of compound **12b**, no re-entrant behaviour was observed, but compound **7b** exhibits a broad range of re-entrant nematic phase with smectic-like fluctuation of the C type. The existence of the C-fluctuations may be understood by supposing the presence of a virtual triple nematic–smectic A–smectic C point (NAC) on the general phase diagram of the compounds under study. Such triple points are known to exist among frustrated smectics [26, 27]. In the case of **7b**, crystallization of course occurs before reaching the transition nematic re-entrant–smectic C. But due to the thermodynamic behaviour of our compound, the fluctuation effects influenced by the NAC point may be visible through the X-ray measurements.

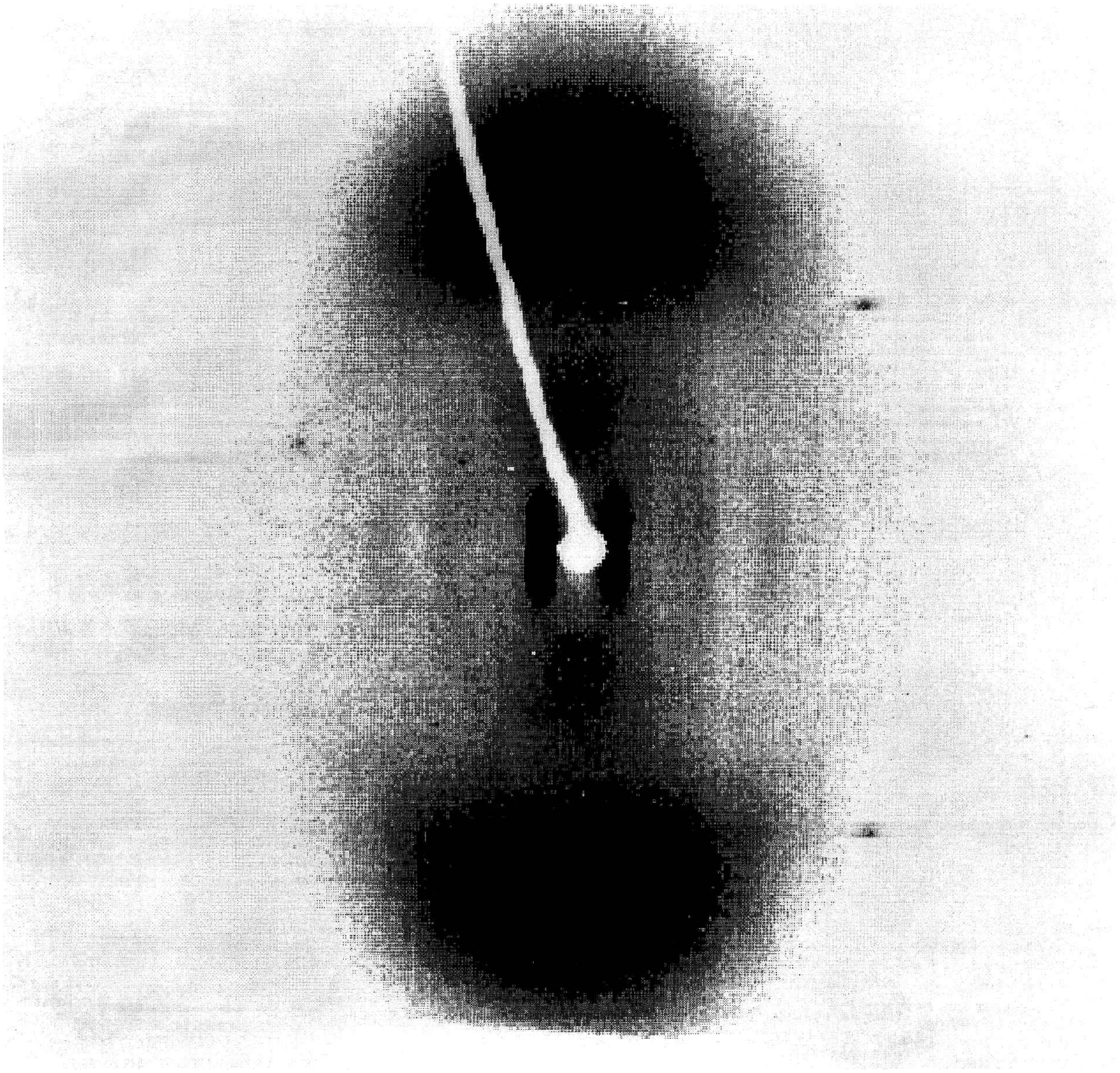


Figure 8. Diffraction pattern of an oriented sample of **7b** in the nematic re-entrant phase with smectic C-like fluctuations ($T = 175$°C).

Finally, the existence of the re-entrant nematic phase was proved to be enantiotropic. The same type of X-ray experiments were carried out on compound **7b** on cooling the sample from the isotropic phase and on heating it from room temperature. The results obtained were completely reproducible.

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