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S. Sudhakar[a]; T. Narasimhaswamy[a]; K. S. V. Srinivasan[a]
[a] Polymer Division, Central Leather Research Institute, Adyar, Chennai 600 020,

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Synthesis, characterization and thermal properties of 4,4′-bis(4-*n*-alkoxybenzoyloxy)benzylideneanilines and bis(4-benzylidene-4′-*n*-alkoxyaniline) terephthalates

S. SUDHAKAR, T. NARASIMHASWAMY and K. S. V. SRINIVASAN*

Polymer Division, Central Leather Research Institute, Adyar, Chennai 600 020, India

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Series of novel thermotropic liquid crystalline compounds which serve as models for mesogenic diols have been synthesized. The mesogen molecules are constructed from 1,4-disubstituted benzene rings linked through ester and azomethine units. Based on the number of phenyl rings, a *tetrad* or *pentad* classification has been assigned to the core molecule. The structures of these compounds were established by FTIR and NMR spectroscopy, while the mesomorphic behaviour has been confirmed using polarizing optical microscopy and DSC. All the compounds of the homologues series are mesomorphic in nature. The lower members of the series are nematogenic, while the higher members exhibit both nematic and smectic character, with high melting behaviour and wide mesophase ranges.

1. Introduction

Small molecules with geometrical anisotropy and high polarizability may exhibit one or more liquid crystalline phases besides the well known crystalline and isotropic phases [1]. Incorporation of such moieties into the main chain or side group of a polymer can result in the formation of liquid crystalline polymers that form mesophases at moderate temperatures. The formation of a liquid crystalline phase, as well as its type, is closely related to the molecular structure [2–4]. Polymers that exhibit liquid crystallinity, either in the melt or in solution, typically consist of comparatively rigid structures that confer a high degree of extension on the backbone of the macromolecule.

Typically, it has been found that liquid crystalline compounds have a rigid core which serves as the mesogenic unit and flexible alkyl chain(s) at the terminal end(s) [5]. This feature is of prime importance in the design and synthesis of new liquid crystalline compounds. The observation of thermotropic liquid crystalline behaviour in main chain polymers in which rigid core and flexible chain units alternate along the main chain of the polymer [6, 7] has prompted attention to the synthesis of new liquid crystalline materials of this type. The pioneering work of Lenz and others [7–9] in the field of thermotropic liquid crystalline polyesters established the concept of diad/triad mesogenic units as core molecules. These mesogens exhibit liquid crystalline behaviour as a result of their high aspect ratio (length to breadth ratio). The design of such mesogenic molecules is of significance for two reasons. Firstly the molecules should themselves support liquid crystallinity and secondly they should be easily translatable into polymerizable monomers by incorporating reactive functional groups enabling them to undergo radical or condensation polymerization to form liquid crystalline polymers.

Recently in our laboratory, we initiated a programme to prepare a series of liquid crystalline polyurethanes (LCPUs) from high aspect ratio mesogenic diols [10, 11]. The synthesis of LCPUs can be approached by two pathways: one involves the use of a mesogenic diisocyanate [12, 13], while the other is through a mesogenic diol [14–18]. This paper reports on the design and synthetic aspects of a series of novel high aspect ratio mesogenic compounds (classified as *tetrad* and *pentad*), which serve as models for the mesogenic diols.

2. Experimental

2.1. *Materials*

4-Hydroxybenzoic acid, 4-hydroxybenzaldehyde (Spectrochem, India), bromoethane, 1-bromobutane, 1-bromohexane, 1-bromo-octane, 1-bromodecane (E Merck, Germany), 4-aminophenol, 4-hydroxyacetanilide, *p*-phenetidine (Fluka, Switzerland), terephthalic acid (Lobachemie, India), 1-bromododecane, 1-bromotetradecane, 1-bromohexadecane (Siscochem, India), thionyl chloride, triethylamine (TEA) (S.D. Fine Chem, India), 1,3-dicyclohexylcarbodiimide (DCC), 4-dimethylaminopyridine

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*Author for correspondence; e-mail: polymer@vsnl.com

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(DMAP) (Aldrich, USA), were used without further purification. All other substances used were of commercial grade. Solvents were purified and dried according to standard procedures.

2.2. *Methods*

Spectral analysis of the compounds was carried out using a Nicolet Impact 400 FTIR spectrophotometer and a Brucker MSL 300P 300 MHz FTNMR spectrometer. For thermal analysis, a Seiko model SSC 5200H thermal analysis system was used attached to a TG/DTA 220 module and DSC 220C module. TG/DTA thermograms were recorded on samples in a nitrogen atmosphere and heated at a rate of 20°C min^{-1}. Similarly, DSC thermograms were recorded in nitrogen protected samples at a heating and cooling rate of 10°C min^{-1}. The mesophase textures were studied using a Reichert Jung Thermogallen hot stage polarizing optical microscope at a magnification of 100×.

2.3. *Synthesis of tetrad mesogens*

2.3.1. *N-4′-hydroxybenzylidene-4-hydroxyaniline (1)*

This compound was prepared by heating at reflux 0.1 mol (10.91 g) of 4-aminophenol and 0.1 mol (12.21 g) of 4-hydroxybenzaldehyde in 150 ml of ethanol for 2 h. The solid product obtained on cooling was filtered off and recrystallized from 1,4-dioxan (yield 88%). IR (KBr), 3262 cm^{-1} (OH), 1606 cm^{-1} (C=N). ^{1}H NMR (DMSO-d$_6$), 9.42 ppm (s, 2H, OH), 8.42 ppm (s, 1H, CH=N), 6.76, 6.86, 7.11 and 7.71 ppm (d, Ar). ^{13}C NMR (DMSO-d$_6$), 115.57, 115.63, 122.12, 127.88, 130.16, 143.19, 155.67, 156.86 ppm (Ar–C) and 160.11 ppm (C=N).

2.3.2. *4-n-Alkoxybenzoic acids (**2a–e**)*

These acids ($n = 2, 4, 6, 8, 10$) were prepared according to the procedure of Bennett and Jones [19]. All the compounds were characterized by FTIR, ^{1}H and ^{13}C NMR spectroscopy.

2.3.3. *4,4′-Bis(4-n-alkoxybenzoyloxy)benzylideneanilines (**3a–e**)*

These compounds were prepared by condensing *N*-4′-hydroxybenzylidene-4-hydroxyaniline (**1**) with the appropriate 4-*n*-alkoxybenzoic acids (**2a–e**) in the presence of DCC and DMAP. A typical procedure for the synthesis of the hexyloxy spacer *tetrad* model compound **3c** is the following. *N*-4′-Hydroxybenzylidene-4-hydroxyaniline (0.01 mol, 2.13 g), 4-*n*-hexyloxybenzoic acid (0.02 mol, 3.33 g) and DMAP (0.002 mol, 0.25 g) were dissolved in 25 ml of dry dimethylformamide/dichloromethane (DMF/DCM) mixture (50 : 50) and stirred at 0°C. To this solution, 0.02 mol (4.13 g) of DCC dissolved in 25 ml of DCM was added dropwise and stirred at 0°C during 1 h and then stirred at room temperature for 12 h. Finally, the reaction mixture was filtered and DCM removed from the filtrate by evaporation; the DMF solution was then precipitated in water. The precipitate was filtered off, washed with water and methanol, and then recrystallized from 1,4-dioxan. (yield 58%). IR (KBr), 1728 cm^{-1} (C=O of ester), 1606 cm^{-1} (C=N), 1255 cm^{-1} (C–O of ether). ^{1}H NMR (CDCl$_3$) 0.91 ppm (t, 6H, CH$_3$), 4.03 ppm (t, 4H, O–C$\underline{\mathrm{H}}_2$), 1.81 ppm (q$_n$, 4H, C$\underline{\mathrm{H}}_2$–Me), 1.2 to 1.6 ppm. (m, 12H, CH$_2$), 6.4 and 8.3 ppm (16H, Ar–H), 8.47 ppm (s, 1H, CH=N). ^{13}C NMR, (CDCl$_3$) 159.28 ppm (CH=N), 164.59, 165.05 ppm (C=O).

2.4. *Synthesis of pentad mesogens*

2.4.1. *Bis(4-formylphenyl) terephthalate (**4**)*

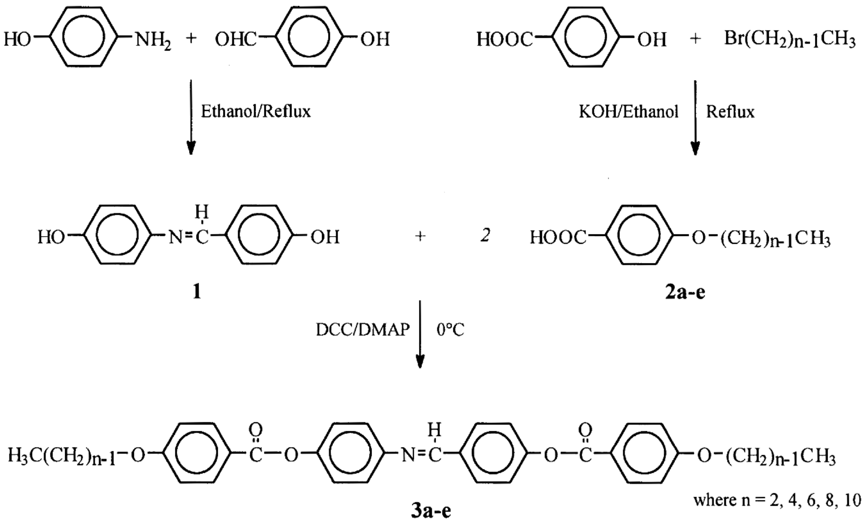
This compound was synthesized from terephthaloyl chloride and 4-hydroxybenzaldehyde by the procedure of Ahmed *et al.* [20] and recrystallized from 1,4-dioxan. IR (KBr), 2753, 2799 cm^{-1} (CH of aldehyde), 1691 cm^{-1} (C=O of aldehyde), 1740 cm^{-1} (C=O of ester). ^{1}H NMR (CF$_3$COOH + DMSO-d$_6$) 7.6, 8.2, 8.5 ppm (Ar–H), 10.05 ppm (CHO). ^{13}C NMR (CF$_3$COOH + DMSO-d$_6$), 166 ppm (C=O of ester), 196 (C=O of aldehyde).

2.4.2. *4-n-Alkoxyaniline (**6b–h**)*

4-Hydroxyacetanilide (0.05 mol, 7.55 g) and anhydrous K$_2$CO$_3$ (0.05 mol, 6.9 g) were taken in 30 ml of dry DMF and stirred at 90°C. To this stirred solution was added dropwise 0.05 mol (8.26 g) of 1-bromohexane and the reaction continued for 24 h. Finally the product was precipitated in dil. HCl solution, filtered off, washed with water, dried and then washed with petroleum ether. Hydrolysis of the 4-*n*-alkoxyacetanilide according to a literature procedure [21] yielded the title compounds (**6b–h**) (yield ~70%). IR (KBr), 3200 to 3500 cm^{-1} (NH stretching), ~1620 cm^{-1} (NH bending), ~1235 cm^{-1} (C–O of ether).

2.4.3. *Bis(4-benzylidene-4′-n-alkoxyaniline) terephthalates (**7a–h**)*

These were prepared by condensing bis(4-formylphenyl) terephthalate (**4**) with the corresponding 4-*n*-alkoxyaniline in 1,4-dioxan. Thus 0.01 mol (3.74 g) of **4** and 0.02 mol (3.87 g) of 4-*n*-hexyloxyaniline (**7c**) in 100 ml of 1,4-dioxan were heated at reflux for 1 h. The precipitate was filtered off, washed with 1,4-dioxan and then recrystallized from DMF (yield 70%). IR (KBr), 1742 cm^{-1} (C=O of ester), 1249 cm^{-1} (C–O of ether), 1622 cm^{-1} (C=N). ^{1}H NMR (CF$_3$COOH + CDCl$_3$), 0.89 ppm (6H, CH$_3$), 1.1 to 2.0 ppm (16H, CH$_2$), 4.17 ppm (4H, O–CH$_2$), 7.0 to 8.7 ppm (20H, Ar–H), 8.9 ppm (2H, CH=N). ^{13}C NMR (CF$_3$COOH + CDCl$_3$), 160.5 ppm (CH=N), 164.5 ppm (C=O of ester).



Scheme 1.

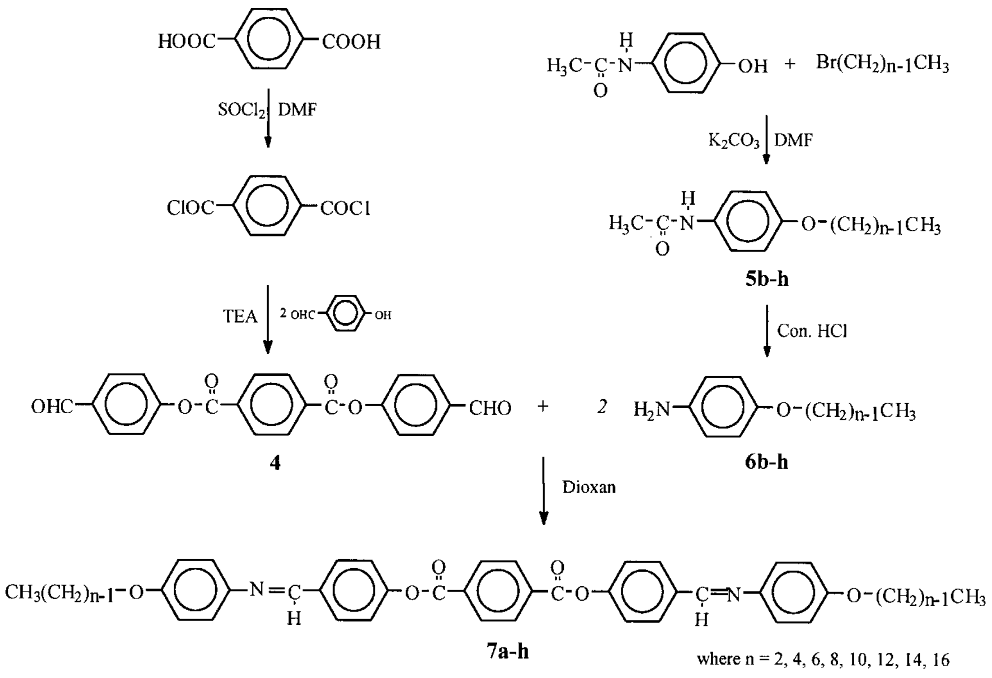
3. Results and discussion

3.1. *Synthesis and characterization*

The synthetic routes employed for the preparation of the homologous series 4,4′-bis(4-*n*-alkoxybenzoyloxy)-benzylideneanilines (**3a–e**) and bis(4-benzylidene-4′-*n*-alkoxyaniline) terephthalates (**7a–h**) are shown in schemes 1 and 2, respectively. Compounds **3a–e** were synthesized by coupling the corresponding 4-*n*-alkoxybenzoic acid with *N*-4′-hydroxybenzylidene-4-hydroxyaniline using DCC/DMAP in DCM/DMF solvent mixture (because of the insoluble nature of the reactants in DCM). Compounds **7a–h** were prepared by condensing the corresponding 4-*n*-alkoxyanilines with bis(4-formylphenyl) terephthalate in 1,4-dioxan. Variation of the alkoxy spacer length from ethoxy to decyloxy (even series) and from ethoxy to hexadecyloxy (even series), respectively, for compounds **3** and **7**, resulted in thirteen new compounds.

3.2. *IR spectroscopy*

The compounds obtained at each step were characterized using FTIR spectroscopy. The FTIR spectrum of the end products **3c** and **7e** are shown in figures 1 and 2, respectively. The characteristic absorption bands



Scheme 2.

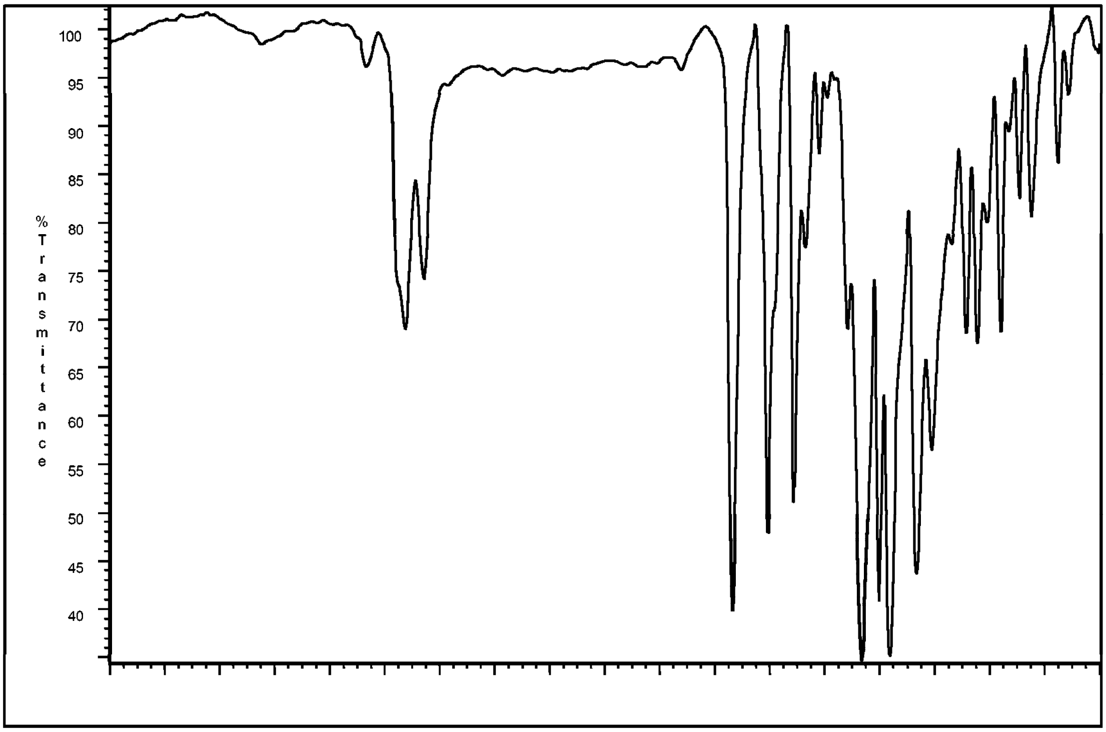


Figure 1. FTIR spectrum of compound **3c**.

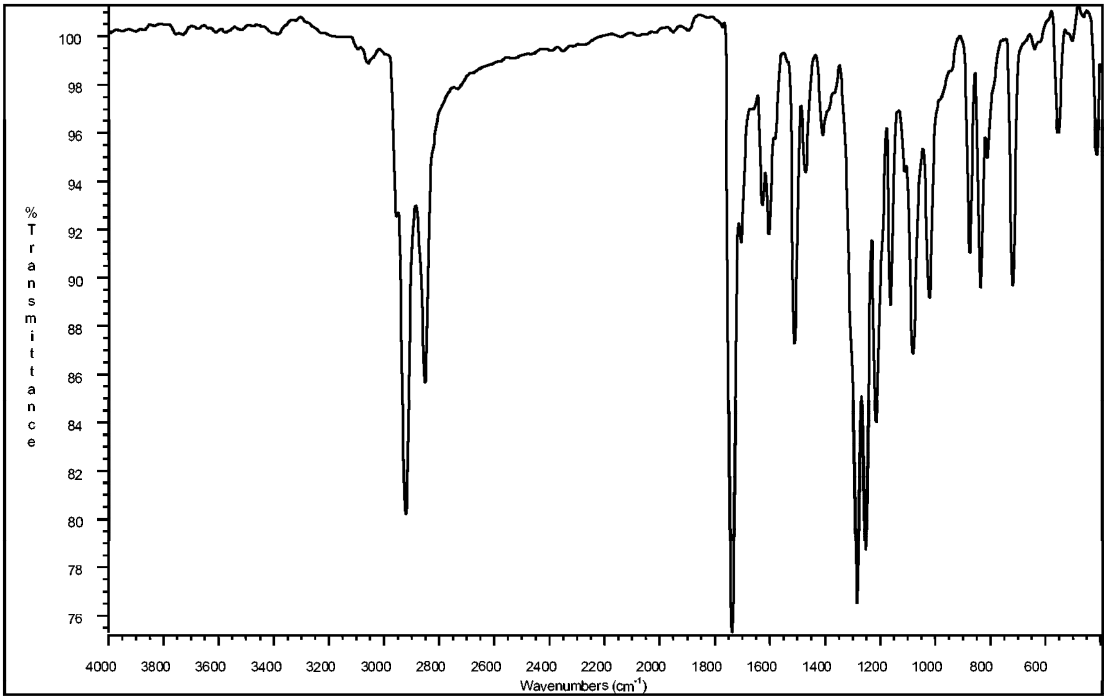


Figure 2. FTIR spectrum of compound **7e**.

of the ester carbonyl and the CH=N groups of compound **3c** appears at 1734 and 1605 cm^{-1}, respectively. The absorption peaks of the ester carbonyl and CH=N groups appear at 1742 and 1622 cm^{-1} respectively for compound 7e. Apart from the presence of these absorptions, the presence of the C–O stretching vibration of the ether linkage confirms the structure of the product. Within the homologous series, as the number of methylene groups in the alkoxy chain is increased, the intensity of the aliphatic C–H stretching vibration also increases.

3.3. *^{1}H and ^{13}C NMR spectroscopy*

Figures 3 and 4 show the ^{1}H and ^{13}C NMR spectra, respectively of compound **3c**. In the ^{1}H NMR spectrum, the methyl protons appear as a triplet at 0.91 ppm, the Ar–O–CH$_2$ protons as a triplet at 4.03 ppm, the methylene protons adjacent to the –OCH$_2$ group as a quintet at 1.81 ppm and the remaining protons as a broad multiplet between 1.2 and 1.6 ppm. The aromatic protons appear as a multiplet between 6.4 and 8.3 ppm, while the azomethine proton gives a singlet at 8.47 ppm. The ^{1}H NMR spectra of the other compounds of the homologous series were also in accordance with the structural assignment. Due to the unsymmetrical nature of the molecule, the ^{13}C NMR spectrum is complicated with a total of 25 peaks (figure 5). The remaining members of the homologous series also exhibited a similar pattern in the ^{13}C NMR spectrum except for the aliphatic region, which varied with the number of the methylene groups present in the spacer. The ^{1}H and ^{13}C NMR spectra of compound **7e** are shown in figures 6 and 7, respectively. Due to the insoluble nature of the compound in common deuteriated solvents like CDCl$_3$ and DMSO-d$_6$, the spectra were recorded by dissolving the compound in a CF$_3$COOH/CDCl$_3$ mixture. In the ^{1}H NMR spectrum, the protons of the methyl group appear at 0.89 ppm and the methylene protons of Ar–O–CH$_2$ appear as a triplet at 4.17 ppm; the remaining methylene protons appear between 1.1 and 2.0 ppm as a multiplet. The aromatic protons appear between 7.0 and 8.5 ppm, while the protons of the terephthaloyl unit give a singlet at 8.7 ppm. The azomethine protons appear at 8.85 ppm. The ^{13}C NMR spectrum was also consistent with the structural assignment. The aromatic carbons alone contribute to ten peaks. The ester carbonyl carbon appears at 164.5 ppm and the azomethine carbon at 160.5 ppm.

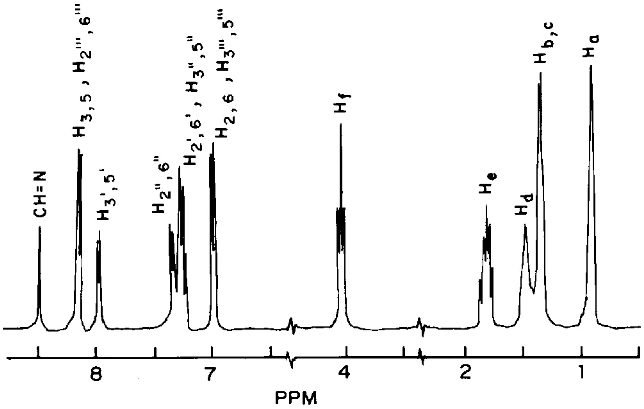


Figure 3. ^{1}H NMR spectrum of compound **3c**.

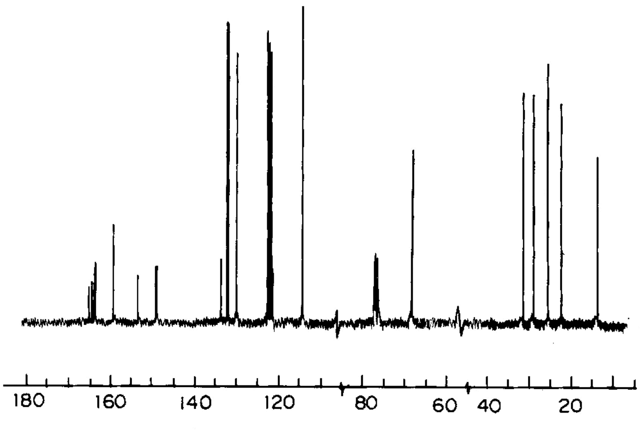


Figure 4. ^{13}C NMR spectrum of compound **7e**.

3.4. *Thermal and optical behaviour*

The phase transitions of the two homologous series of compounds were studied by DSC and optical microscopy. The thermal stability of the compounds was also studied using simultaneous thermogravimetric and differential thermal analysis. The phase transition temperatures and the initial decomposition temperatures for the two homologous series are presented in tables 1 and 2.

The tetrad series **3a–e** upon heating exhibited solid to liquid crystalline phase transitions at the temperatures given in table 1. On further heating, transitions from the liquid crystal to the isotropic liquid states were observed only for compounds **3d** and **3e**. Due to the rigid mesogenic core and short flexible spacer in compounds **3a–c**,

Table 1. Transition temperatures of tetrad series (**3a–e**).

Compound	*n*	Transition	Temperature/°C	ΔT/°C[b]
3a	2	Cr–N N–I	221.2 Dec.[a]	—
3b	4	Cr–N N–I	171.6 Dec.	—
3c	6	Cr–Cr$_1$ Cr$_1$–N N–I	92.3 153.9 Dec.	—
3d	8	Cr–SmA SmA–N N–I	113.1 199.1 310.0	196.9
3e	10	Cr–SmA SmA–N N–I	105.9 231.3 293.7	187.8

[a] Dec. = decomposes.
[b] $\Delta T = T_i - T_m$.

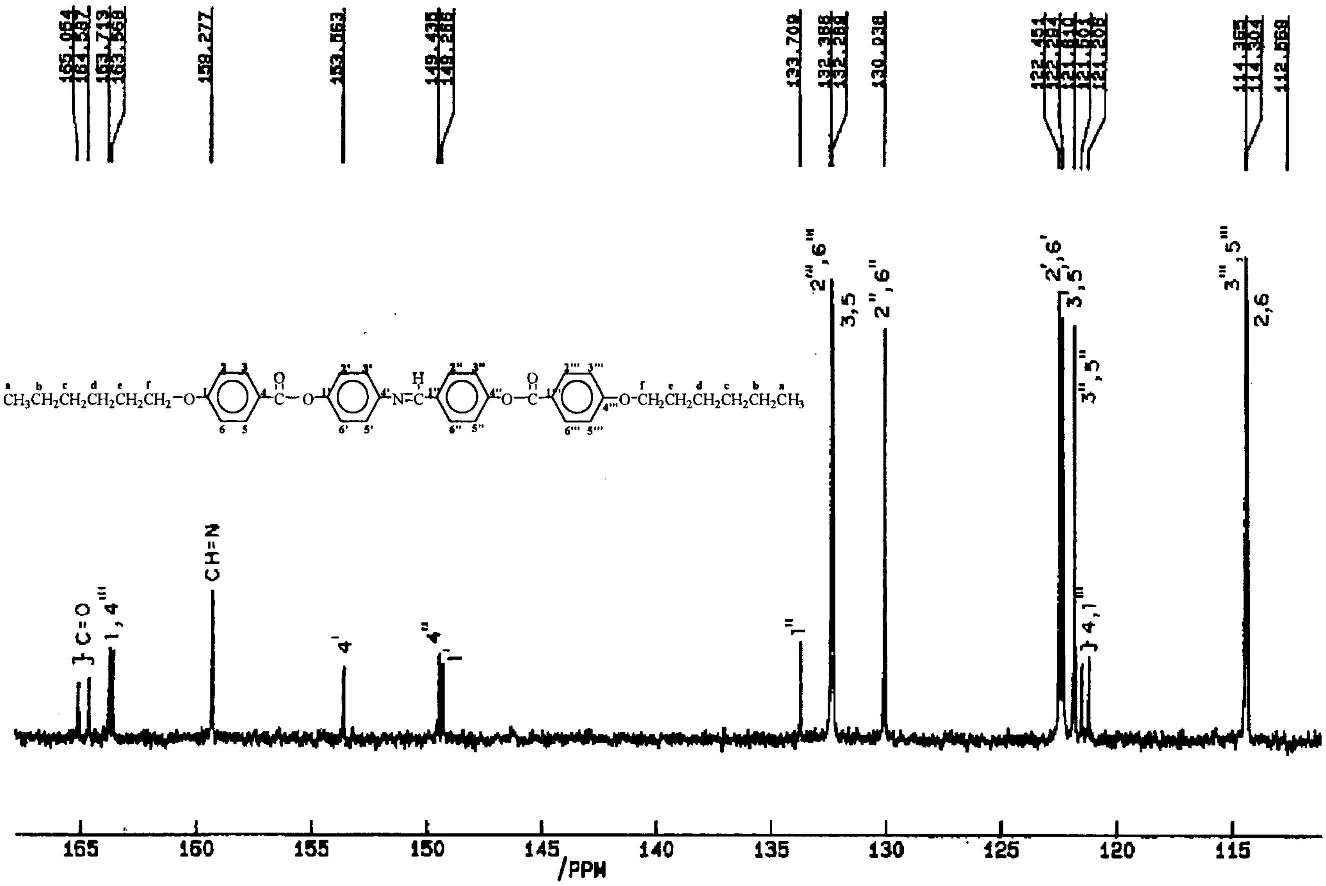


Figure 5. ^{13}C NMR spectrum of compound **7e** (expanded).

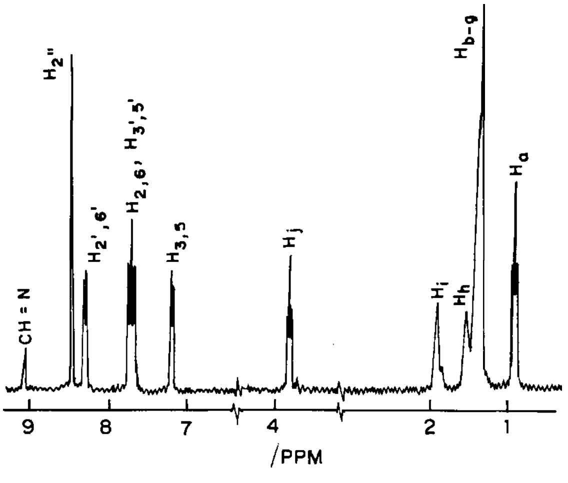


Figure 6. ^{1}H NMR spectrum of compound **7e**.

decomposition occurred before reaching the isotropic liquid state. When viewed between crossed polarizers, upon melting compounds **3a–c** showed a schlieren threaded texture typical of a nematic mesophase figure 8 (*a*). For compounds **3d** and **3e**, a focal-conic texture, figure 8 (*b*), characteristic of the smectic A mesophase was observed on melting and upon further heating this transformed to a nematic mesophase with a threaded schlieren texture before going to the isotropic liquid state. An increase in the alkyloxy spacer length brings the liquid crystal to isotropic liquid phase transition well below the decomposition temperature and hence for compounds **3d** and **3e**, the phase transitions were reproducible on repeated heating and cooling cycles.

In the case of the pentad series compounds, all eight compounds (**7a–h**) passed from the solid to the liquid crystalline state upon heating; transition temperatures are given in table 2. The presence of the additional phenyl ring in the mesogenic core results in higher melting temperatures than in the tetrad series. On further heating, the liquid crystalline melt of almost all the compounds started to decompose around 320°C. The decomposition was complete for the lower homologues, but partial for the higher homologues. Compounds **7a–c** upon heating form a nematic mesophase with a schlieren texture which decomposes due to the very high clearing temperature of about 400°C. The decomposition was partial in the case of compounds **7d–7h** and clearing transitions could be obtained for these compounds both by optical microscopy and DSC. Similar to the tetrad series, the pentad series exhibited polymesomorphism

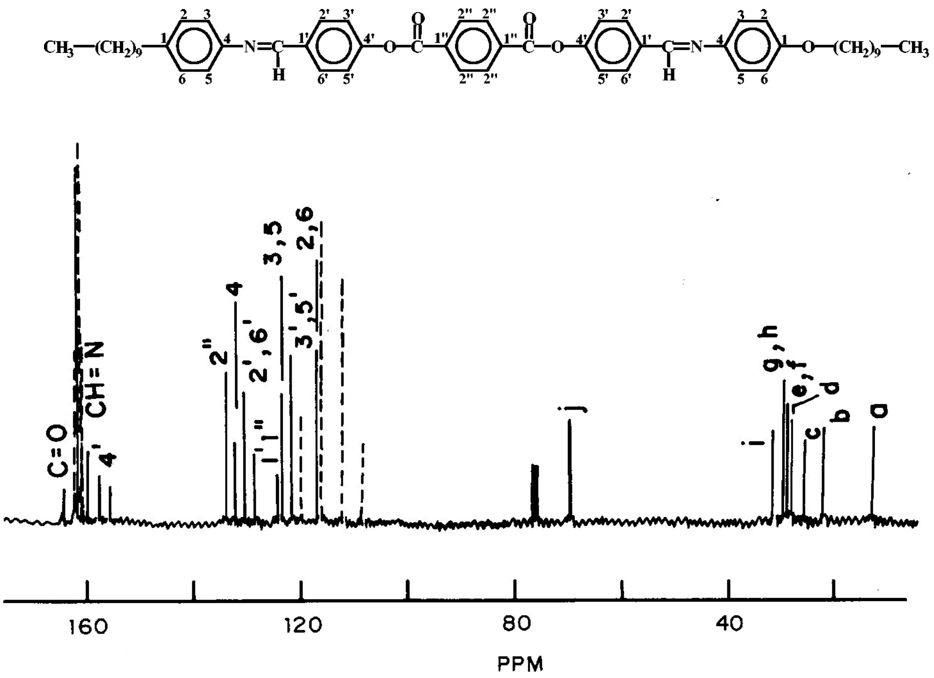
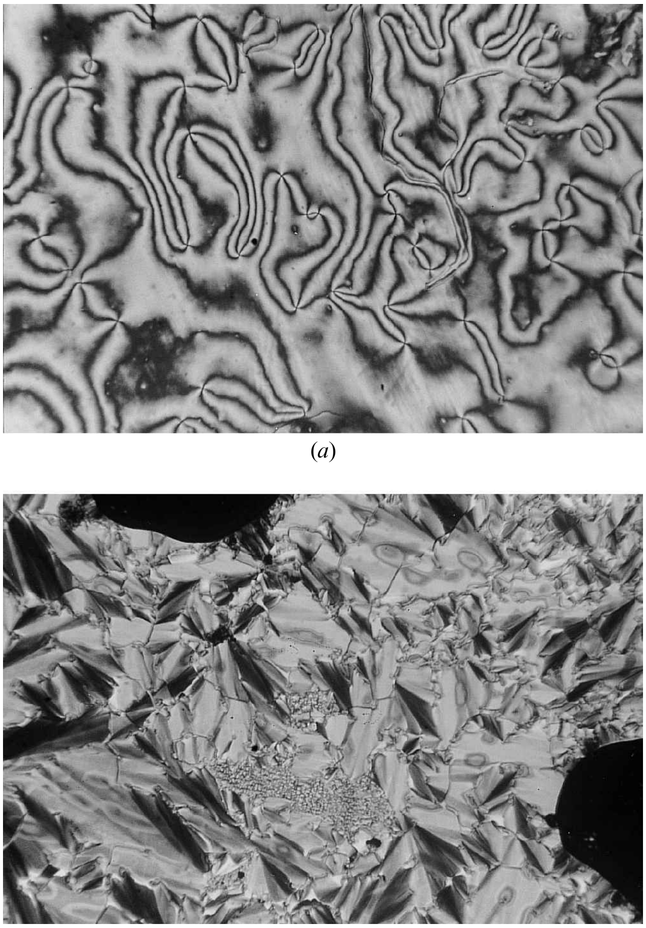


Figure 7. ^{13}C NMR spectrum of compound **7e**.

Table 2. Transition temperatures of pentad series (**7a–h**).

Compound	n	Transition	Temperature/°C	ΔT/°C[b]
7a	2	Cr–Cr$_1$	205.9	—
		Cr$_1$–N	267.6	
		N–I	Dec.[a]	
7b	4	Cr–Cr$_1$	77.9	—
		Cr$_1$–Cr$_2$	203.2	
		Cr$_2$–N	255.9	
		N–I	Dec.	
7c	6	Cr–Cr$_1$	111.6	—
		Cr$_1$–Cr$_2$	195.3	
		Cr$_2$–N	217.8	
		N–I	Dec.	
7d	8	Cr–Cr$_1$	139.7	165.9
		Cr$_1$–Cr$_2$	180.8	
		Cr$_2$–N	210.6	
		N–I	376.5	
7e	10	Cr–Cr$_1$	150.2	197.4
		Cr$_1$–SmA	158.2	
		SmA–N	174.4	
		N–I	355.6	
7f	12	Cr–Cr$_1$	155.0	178.8
		Cr$_1$–SmA	172.0	
		SmA–N	184.8	
		N–I	350.8	
7g	14	Cr–SmA	155.3	179.6
		SmA–N	170.6	
		N–I	334.9	
7h	16	Cr–SmA	154.5	176.2
		SmA–I	330.7	

[a] Dec. = decomposes.
[b] $\Delta T = T_i - T_m$.


(*a*)

(*b*)

Figure 8. Optical photomicrographs of (*a*) compound **3b** at 304°C, (*b*) compound **3d** at 166°C.

when the number of carbon atoms in the terminal alkyloxy chain was 10, 12 and 14. When $n = 16$, the compound exhibited only a smectic mesophase. Compounds **7e–g** showed the schlieren nematic texture and then the focal-conic texture characteristic of a smectic A mesophase, while compound **7h** showed only a smectic mesophase. Though an increase in the length of the terminal alkyloxy brings about a significant reduction in the melting and the isotropization temperatures, even the highest homologue of the series **7h** decomposed at its clearing temperature.

Mesogenic diols of the tetrad and pentad series were successfully prepared by replacing the methyl group of the terminal alkyloxy chain with a methylol group by suitable synthetic procedures and these diols will be employed to prepare thermotropic main chain liquid crystalline polyurethanes [22].

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