Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Synthesis and characterization of novel thermotropic liquid crystals containing a dimethylamino group

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

Online publication date: 11 November 2010

To cite this Article Narasimhaswamy, T. and Srinivasan, K. S. V.(2004) 'Synthesis and characterization of novel thermotropic liquid crystals containing a dimethylamino group', Liquid Crystals, 31: 11, 1457 — 1462
To link to this Article: DOI: 10.1080/02678290410001697530
URL: http://dx.doi.org/10.1080/02678290410001697530

LIQUID CRYSTALS, VOL. 31, NO. 11, NOVEMBER 2004, 1457–1462

Synthesis and characterization of novel thermotropic liquid crystals containing a dimethylamino group

T. NARASIMHASWAMY* and K. S. V. SRINIVASAN
Polymer Laboratory, Central Leather Research Institute, Adyar,
Chennai 600 020, India

(*Received 17 June 2003; in final form 26 January 2004; accepted 10 February 2004*)

Novel thermotropic liquid crystals containing a terminal dimethylamino group were synthesized via a multi-step route. Three phenyl ring units linked with ester and azomethine groups constituted the mesogenic core. All the compounds were characterized by spectroscopic techniques, polarizing microscopy and differential scanning calorimetry. An enantiotropic nematic phase was observed for all the systems studied.

1. Introduction

Much of the contemporary research on the assembly of thermotropic liquid crystals focuses primarily on non-covalent forces such as hydrogen bonding and charge-transfer interactions [1–9]. In both cases, the introduction of liquid crystallinity in the either donor or acceptor molecule is a prerequisite [7]. The majority of studies involving non-covalent interactions in thermotropic liquid crystals deal mainly with hydrogen bonding [1–4]. Recently, Li *et al*. [3] demonstrated the utility of hydrogen bonding and electron donor–acceptor interactions in stabilizing supramolecular side chain liquid crystalline polymers.

Our earlier studies on pentad- and tetrad-based thermotropic liquid crystals established ester and azomethine linking units as useful structural components for generating polymesomorphism [10, 11]. The present study deals with the synthesis and characterization of the novel thermotropic liquid crystals, the 4-alkoxybenzoic acid 4-[(4-dimethylaminobenzylidene)amino]phenyl esters and the isomeric 4-alkoxybenzoic acid 4-[(4-dimethylaminophenylimino)methyl]phenyl esters. Due to the presence of the dimethylamino group, these molecules may serve as mesogenic charge-transfer donors. FTIR, ^{1}H and ^{13}C NMR spectroscopic studies established the proposed structures, while polarizing optical microscopy (POM) and differential scanning calorimetry (DSC) confirmed the presence of an enantiotropic nematic mesophase for all the compounds.

*Author for correspondence;
e-mail: tnswamy99@hotmail.com

2. Experimental

2.1. *Reagents and characterization*

4-Hydroxybenzoic acid, 1-bromoethane, 1-bromobutane, 1-bromohexane, 1-bromooctane, 1-bromodecane, 1-bromododecane, thionyl chloride, 4-nitrophenol, triethylamine, methyl ethyl ketone (MEK), dimethylformamide, stannous chloride, 4-hydroxybenzaldehyde, 4-dimethylaminobenzaldehyde, potassium hydroxide, methanol, isopropanol, absolute ethanol (SD Fine and Merck, India) were used as received. 4-Dimethylaminoaniline was purchased from Aldrich, USA.

FTIR spectra of all the compounds were recorded using a Nicolet Impact 400 instrument, with samples in KBr pellet form. ^{1}H and ^{13}C NMR spectra of the compounds were recorded in deuterated chloroform solution at room temperature, using tetramethyl silane as internal standard, with a Bruker MSL 300 MHz instrument. The nature of the mesophase and the transition temperatures were determined with an Olympus BX50 polarizing optical microscope equipped with a Linkam THMS 600 hot stage and a TMS 94 temperature controller. Photomicrographs were taken using an Olympus SLR camera. DSC traces were recorded using a Perkin-Elmer DSC 7 instrument with a heating rate of $10\,min^{-1}$ in a nitrogen atmosphere. Each sample was subjected to two heating and two cooling cycles. The temperatures recorded on the second heating were considered for discussion.

2.2. *Synthesis of 4-hexyloxy benzoic acid 4-[(4-dimethylaminobenzylidene)amino]phenyl ester (HBDBAP)*

This synthesis is typical for the benzylidene-type esters.

Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online © 2004 Taylor & Francis Ltd
http://www.tandf.co.uk/journals
DOI: 10.1080/02678290410001697530

2.2.1. *4-Hexyloxybenzoic acid 4-nitrophenyl ester (HBNP)*

4-Hexyloxybenzoyl choride was prepared by reacting 4-hexyloxybenzoic acid with thionyl chloride in the presence of dimethylformamide using a standard procedure. Thus, 4-nitrophenol (100 mmol) and triethylamine (100 mmol) were dissolved in 300 ml MEK. 4-Hexyloxybenzoyl chloride (100 mmol) dissolved in 200 ml MEK was added dropwise at 0°C to the 4-nitrophenol solution, and the reaction mixture was stirred for 3 h at room temperature. The triethylamine salt was filtered off and the solvent was evaporated. The crystalline solid thus obtained was washed with 2×100 ml 5% aqueous sodium hydroxide and 2×100 ml water. The solid was recrystallized from methanol; yield 75%, m.p. 65.3°C. FTIR (KBr, cm^{-1}): 3081 (aromatic CH stretching); 2934, 2863 (CH stretching); 1740 (ester carbonyl stretching); 1516,1340 (NO_2 stretching). ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 0.89 (t, 3H), 1.34–1.44 (m, 6H), 1.85 (m, 2H), 4.00 (t, 2H), 6.90 (d, 2H), 7.39 (d, 2H), 8.12 (d, 2H), 8.30 (d, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 13.96, 22.52, 25.58, 28.96, 31.47, 68.38, 114.31, 120.33, 122.59, 125.00, 132.27, 145.16, 163.88, 164.00.

2.2.2. *4-Hexyloxybenzoic acid 4-aminophenyl ester (HBAP)*

HBNP (50 mmol), stannous chloride (250 mmol) and 150 ml absolute ethanol were heated gently at reflux for 1 h. The resulting solution was allowed to cool to room temperature and neutralized with 10% aqueous sodium hydroxide to pH 7. The fine precipitate formed was filtered and dried in a vaccum oven for 12 h. The dried solid was stirred with 500 ml acetone for 2 h and insoluble solid was filtered off. Evaporation of the acetone yielded the amine compound; yield 60%, m.p. 83°C. FTIR (KBr, cm^{-1}): 3406, 3312 (NH_2 stretching); 2933, 2860 (CH stretching); 1722 (ester carbonyl stretching). ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 0.91 (t, 3H), 1.33–1.46 (m, 6H), 1.80 (m, 2H), 3.63 (s, 2H), 4.01 (t, 2H), 6.65 (d, 2H), 6.92 (m, 4H), 8.09 (d, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 13.93, 22.48, 25.56, 28.97, 31.45, 68.19, 113.93, 115.46, 121.75, 122.24, 132.05, 143.06, 144.10, 163.28, 165.42.

2.2.3. *HBDBAP*

HBAP (10 mmol), 4-dimethylaminobenzaldehyde (10 mmol) and 100 ml absolute ethanol were heated under reflux for 1 h. The resulting solid was filtered and washed with methanol (2×100 ml); it was then dried in a vaccum oven and recrystallized from ethyl acetate; yield 70%, m.p. 153.70°C. FTIR (KBr, cm^{-1}): 2918, 2855 (CH stretching); 1729 (ester carbonyl stretching); 1601 (C=N stretching). ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 0.90 (t, 3H), 1.33–1.46 (m, 6H), 1.83 (m, 2H), 3.03 (s, 6H), 4.02 (t, 2H), 6.73 (d, 2H), 6.94 (d, 2H), 7.19 (m, 4H), 7.70 (d, 2H), 8.15 (d, 2H), 8.30 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm) 13.98, 22.54, 25.62, 29.03, 31.50, 40.10, 68.28, 111.40, 114.25, 121.69, 122.17, 122.52, 124.35, 130.33, 132.20, 148.44, 150.48, 152.51, 160.25, 163.46, 165.06.

2.3. *Synthesis of 4-octyloxybenzoic acid 4-[(4-dimethylaminophenylimino)methyl]phenyl ester (OBDPMP)*

4-Octyloxybenzoyl chloride was prepared from 4-octyloxybenzoic acid by reacting with thionyl chloride in the presence of dimethyl formamide. This synthesis is typical for the phenylimino-type esters.

2.3.1. *4-Octyloxybenzoic acid 4- formylphenyl ester (OBFP)*

4-Hydroxybenzaldehyde (100 mmol) and triethylamine (100 mmol) were dissolved in 300 ml MEK. 4-Octyloxybenzoyl chloride (100 mmol) dissolved in 200 ml MEK was added dropwise at 0°C to the 4-hydroxybenzaldehyde solution, and the reaction mixture was stirred for 3 h at room temperature. The triethylamine salt was filtered off and the solvent was evaporated. The solid thus obtained was washed with 5% aqueous sodium hydroxide (2×100 ml) followed by water (2×100 ml) and recrystallized from isopropyl alcohol; yield 75%, m.p. 53°C. FTIR (KBr, cm^{-1}): 2921, 2851 (CH stretching); 2751 (CH aldehyde stretching); 1729 (ester carbonyl stretching); 1694 (aldehyde carbonyl stretching). ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm); 0.87 (t, 3H), 1.30–1.45 (m, 10H), 1.82 (m, 2H), 4.02 (t, 2H), 6.94 (d, 2H), 7.32 (d, 2H), 8.00 (d, 2H), 8.13 (d, 2H), 9.99 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 14.06, 22.62, 25.94, 29.04, 29.18, 29.28, 31.76, 68.37, 114.41, 121.94, 122.57, 131.19, 131.79, 133.87, 155.90, 163.86, 164.20, 190.96.

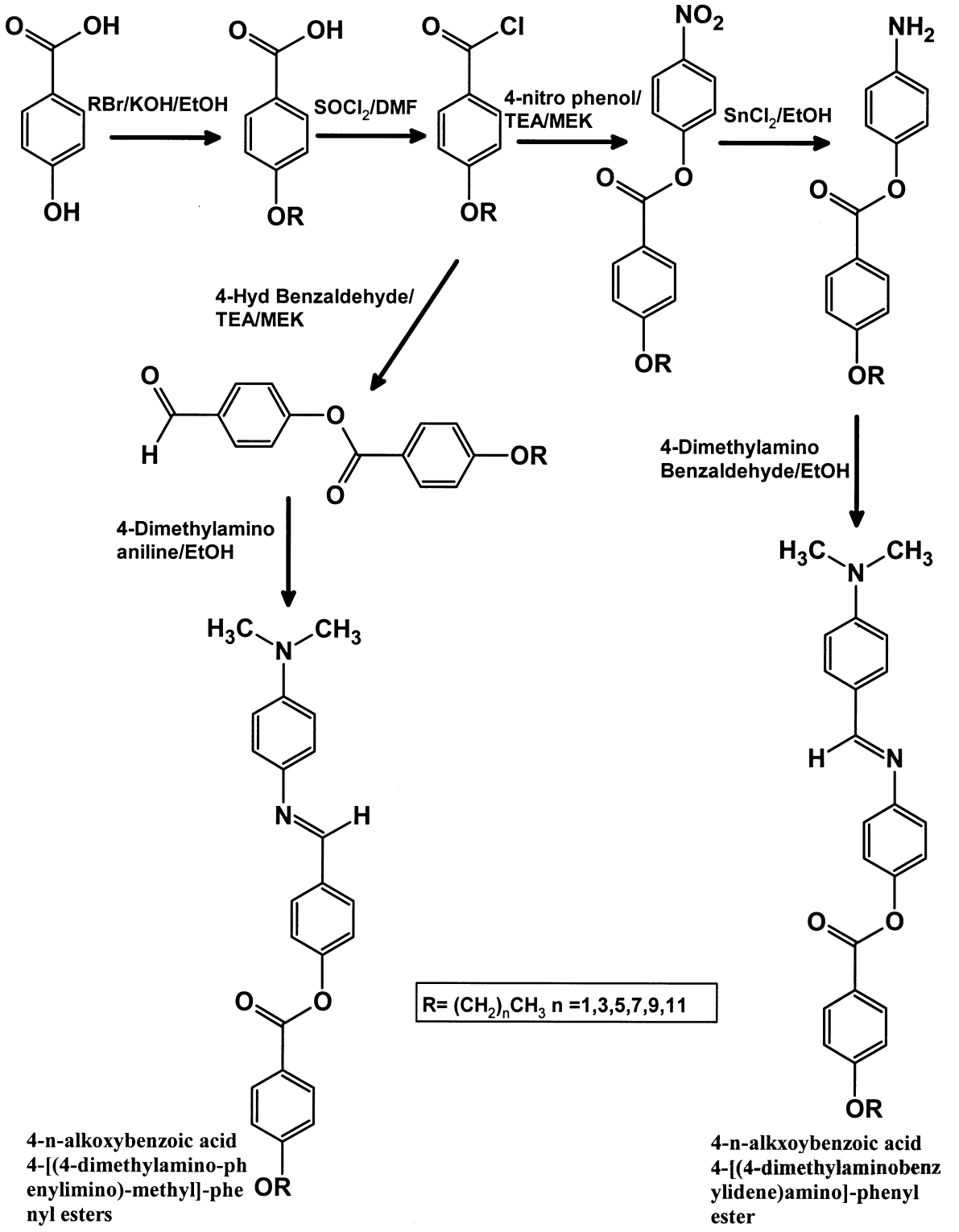
2.3.2. *OBDPMP*

OBFP (10 mmol), 4-dimethylaminoaniline (10 mmol) and 100 ml absolute ethanol were heated under reflux for 1 h. The solid obtained was filtered off and washed with 2×100 ml methanol; it was than dried under vaccum and recrystallized from ethyl acetate; yield 65%, m.p. 140.03°C. FTIR (KBr, cm^{-1}): 2919, 2850 (CH stretching); 1730 (ester carbonyl stretching); 1601.9 (C=N stretching). ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 0.89 (t, 3H), 1.27–1.47 (m, 10H), 1.83 (m, 2H), 2.98 (s, 6H), 4.03 (t, 2H), 6.96 (d, 2H), 7.26 (d, 2H), 7.31 (m, 4H), 7.94 (d, 2H), 8.15 (d, 2H), 8.51 (s, 1H).

^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 14.25, 22.81, 26.09, 29.20, 29.68, 29.75, 32.00, 40.84, 68.44, 112.97, 114.44, 121.40, 122.22, 122.40, 129.54, 132.43, 134.57, 140.81, 149.67, 152.91, 154.86, 163.74, 164.77.

3. Results and discussion

The scheme shows the strategy adopted for the synthesis of the novel thermotropic liquid crystals containing a dimethylamino group. The



Scheme. Synthetic strategy for the compounds studied.

4-*n*-alkoxybenzoic acid 4-[(4-dimethylaminobenzylidene)amino]phenyl ester series and and the 4-*n*-alkoxybenzoic acid 4-[(4-dimethylaminophenylimino)methyl]phenyl esters were synthesized from 4-*n*-alkoxybenzoic acids ($n=2$, 4, 6, 8, 10, 12 where n denotes the number of carbons in the alkoxy chain). Some of the intermediates, such as the 4-*n*-alkoxybenzoic acid 4-nitrophenyl esters and the 4-*n*-alkoxybenzoic acid 4-formylphenyl esters are known [12, 13]. Griffin *et al*. [12] reported the mesogenic nature of the 4-alkoxybenzoic acid 4-nitrophenyl esters; Dave and Patel [13] studied the mesomorphism of 4-*n*-alkoxybenzoic acid 4-formylphenyl esters. Reduction of the nitro compounds to the corresponding amines by the stannous chloride method [14] resulted in the loss of liquid crystallinity. Recently, Lee *et al*. [15] reported the synthesis of ($n=4$, 10) 4-alkoxybenzoic acid 4-aminophenyl esters.

3.1. *Spectral studies*

FTIR, ^{1}H and ^{13}C NMR spectroscopic techniques were used for confirming the structure of all the compounds in both series. The FTIR spectrum of HBDBAP shows an ester carbonyl stretch at 1729 cm^{-1} and a C=N stretching vibration at 1601 cm^{-1}. The absence of 3406 and 3312 cm^{-1} bands due to amine stretching vibrations confirms the formation of the compound. In the case of HBDPMP, the appearance of bands at 1731 and 1602 cm^{-1} which are due to ester carbonyl, and azomethine, respectively, and the absence of an aldehyde carbonyl stretching vibration at 1680 cm^{-1} supports the proposed structure. The ^{1}H NMR spectrum of HBDBAP shows the characteristic methyl protons of the dimethylamino group at 3.03 ppm as a singlet and the azomethine proton at 8.32 ppm also as singlet. The other signals and their splitting pattern is consistent with the proposed structure of the compound. In the case of HBDPMP, singlets at 2.98 and 8.51 ppm which are due to dimethylamino and azomethine protons, respectively, confirm the formation of the compound.

The proton-decoupled ^{13}C NMR spectrum of HBDBAP shows 21 lines. The methyl carbons of the dimethylamino group are observed at 40.10 ppm. The characteristic azomethine carbon is seen at 160.25 ppm. The assignment of all other carbons with the observed spectral lines is achieved by iterating the spectrum using a commercial software package. The HBDPMP spectrum also shows 21 lines. The appearance of peaks at 40.84, 154.86 and 164.77 ppm which are attributed to the methyl carbon of the dimethylamino group, azomethine carbon and ester carbonyl carbon, respectively, further confirm the structure of the compound.

3.2. *Microscopy and phase transition studies*

All the compounds synthesized in the present study have been characterized using POM and DSC. POM studies of all the compounds clearly show the appearance of an enantiotropic nematic phase. Figure 1 shows the characteristic nematic schlieren texture for OBDPMP. In the case of the dodecyl homologue of both the series, a monotropic smectic A (focal-conic fan texture) phase is also observed.

DSC studies further supported the appearance of an enantiotropic nematic phase in all the compounds studied. Figure 2 shows the second heating and cooling DSC curves of DoBDBAP. The table shows the melting temperature (T_m), clearing temperature (T_i), and associated enthalpy (ΔH) and molar entropy (ΔS) values of all the compounds. The enthalpy values clearly support the assignment of crystal–nematic and nematic–isotropic transitions in all the compounds. The influence of the terminal alkyl chain length on the melting and clearing temperatures for both series in general follows that characteristically seen for calamitic systems. A decrease in T_m and T_i values is noticed on increasing the terminal alkyl chain length in both series. The compounds synthesized in the present study are structurally similar except for the reversal of the imine linkage. The effect of the imine linking pattern on the T_m and T_i values, however, is rather irregular (see the table). In the case of the dodecyl member in both series, the formation of a monotropic smectic A phase just before crystallization with an associated low transitional enthalpy is observed in DSC, thereby supporting the POM observations. The dimethylamino group, although supporting conjugative interactions in the molecule, is low in the terminal group efficiency order for promoting the N–I temperature, because it lies out of the molecular plane [16]. In the present study, despite

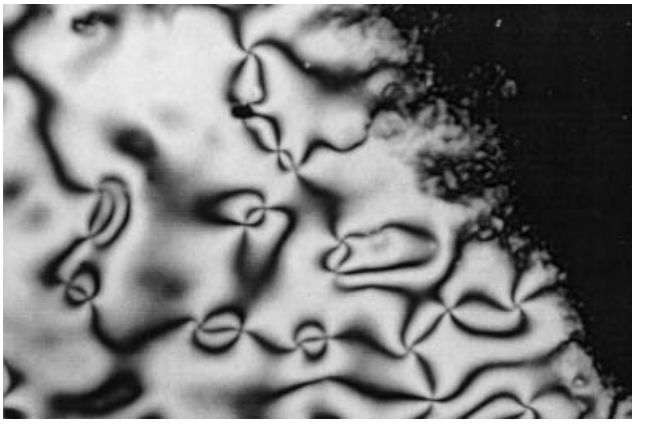


Figure 1. Polarizing optical micrograph of OBDPMP showing the nematic schlieren texture just before clearing.

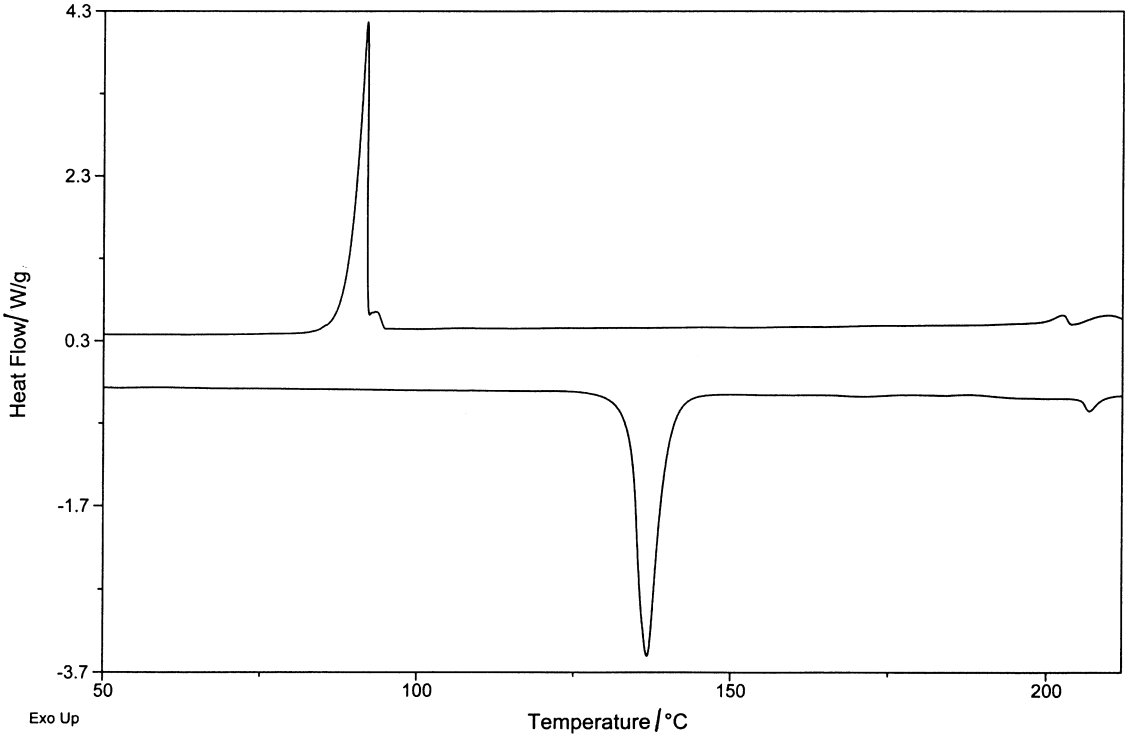


Figure 2. DSC heating and cooling curves of DoBDBAP.

Table. Transition temperatures, and associated enthalpy and entropy changes of the compounds studied.

n	Compound	Melting temperature °C (T_m) Cr–N	Clearing temperature °C (T_i) N–I	Enthalpy Change ΔH/kJ mol^{-1}		Entropy change (ΔS) (10^{-3}) kJ mol^{-1} K^{-1}	
				Cr–N	N–I	Cr–N	N–I
4-n-Alkyloxybenzoic acid 4-[(4-dimethylaminobenzylidene)amino]phenyl esters							
2	EBDBAP	193.0	296.0	33.9	2.2	72	3.8
4	BBDBAP	189.3	270.3	31.7	2.1	68	3.9
6	HBDBAP	153.7	250.0	32.5	1.6	76	3.0
8	OBDBAP	150.7	223.0	32.6	1.2	77	2.4
10	DBDBAP	145.7	210.7	33.6	1.3	80	2.6
12	DoBDBAP	135.9 (93.7 SmA)[a]	205.9	41.7	1.3	101	2.8
4-n-Alkyloxybenzoic acid 4-[(4-dimethylaminophenylimino)methyl]phenyl esters							
2	EBDPMP	197.0	283.3	31.8	1.1	67	2.1
4	BBDPMP	167.7	275.7	29.9	2.4	67	4.1
6	HBDPMP	138.0	252.7	30.8	2.3	74	4.5
8	OBDPMP	140.0	235.3	34.6	2.0	83	4.0
10	DBDPMP	133.3	221.7	28.3	1.9	69	3.8
12	DoBDPMP	146.0 (107.1 SmA)[a]	209.3	40.6	2.1	96	4.0

[a]( ) indicates monotropic phase

the presence of the dimethylamino group in the terminal position in all the compounds, the appearance of an enantiotropic nematic phase with a reasonable phase stability indicates the high anisotropic polarizability of these molecules.

4. Conclusion

All the compounds synthesized in the present investigation exhibit an enantiotropic nematic phase with excellent phase stability. In the case of the dodecyl members, a monotropic smectic A phase is also

observed. The presence of the dimethylamino group renders these systems suitable components for building charge-transfer-based liquid crystals with an appropriate choice of acceptor molecule.

One of the authors (T.N.S.) thank Dr T. Ramasami, Director, CLRI for his keen interest, constant support and encouragement.

References

[1] PALEOS, M. C., and TSIOURVAS, D., 2001, *Liq. Cryst.*, **28,** 1127.
[2] LI, M., and WU, Y., 2002, *Liq. Cryst.*, **29,** 1031.
[3] LI, X., GOH, H. S., and LAI, H. Y., 2002, *Liq. Cryst.*, **29,** 675.
[4] SONG, X., LI, J., and ZHANG, S., 2003, *Liq. Cryst.*, **30,** 331.
[5] IMRIE, C. T., and CRAIG, A. A., 1997, *Polymer*, **38,** 4951.
[6] IMRIE, C. T., KARASZ, F. E., and ATTARD, G. S., 1991, *Liq. Cryst.*, **9,** 47.
[7] IMRIE, C. T., SCHLEEH, T., KARASZ, F. E., and ATTARD, G. S., 1993, *Macromolecules*, **26,** 539.
[8] PRAEFCKE, K., and SINGER, D., 1998, in *Hand Book of Liquid Crystals*, Vol. 2B, edited by D. Demus, J. Goodby, G. W. Gray, H. W. Spiess, and V. Vill, (Weinheim: Wiley-VCH), pp. 945–967.
[9] KANG, S. Y., and ZIN, W. C., 2002, *Liq. Cryst.*, **29,** 369.
[10] SUDHAKAR, S., NARASIMHASWAMY, T., and SRINIVASAN, K. S. V., 1998, *Macromolecules-New Frontiers*, Vol. 1 (New Delhi: Allied Publishers), pp. 228–231.
[11] SUDHAKAR, S., NARASIMHASWAMY, T., and SRINIVASAN, K. S. V., 2000, *Liq. Cryst.*, **27,** 1525.
[12] GRIFFIN, O. A., FISHER, F. R., and HAVENS, J. S., 1978, *J. Am. chem. Soc.*, **100,** 6329.
[13] DAVE, J. S., and PATEL, R. N., 1978, *Ind. J. Chem.*, **16A,** 893.
[14] BELLAMY, F. D., and OU, K., 1984, *Tetrahedron Lett.*, **25,** 839.
[15] LEE, J. W., JIN, J. I., ACHARD, M. F., and HARDOUIN, F., 2001, *Liq. Cryst.*, **28,** 663.
[16] LUCKHURST, G. R., and GRAY, G. W., 1979, *The Molecular Physics of Liquid Crystals* (New York: Academic Press).