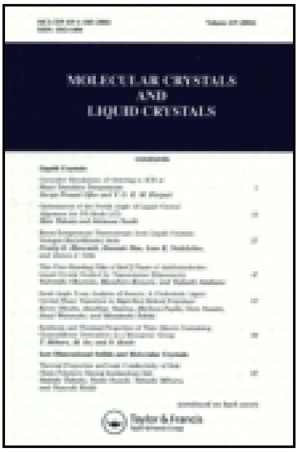


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Synthesis and Mesomorphic Characteristics of Fluoroaniline Derivatives with Different Lateral Groups

Jayrang S. Dave [a], Purvang D. Patel [a] & Himanshu Bhatt [a]
[a] Department of Applied Chemistry, Faculty of Technology and Engineering, The M.S. University of Baroda, Vadodara, India

To cite this article: Jayrang S. Dave , Purvang D. Patel & Himanshu Bhatt (2012): Synthesis and Mesomorphic Characteristics of Fluoroaniline Derivatives with Different Lateral Groups, Molecular Crystals and Liquid Crystals, 562:1, 76-84

To link to this article: http://dx.doi.org/10.1080/10426507.2012.669678

Mol. Cryst. Liq. Cryst., Vol. 562: pp. 76–84, 2012
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/10426507.2012.669678

Synthesis and Mesomorphic Characteristics of Fluoroaniline Derivatives with Different Lateral Groups

JAYRANG S. DAVE, PURVANG D. PATEL,*
AND HIMANSHU BHATT

Department of Applied Chemistry, Faculty of Technology and Engineering,
The M.S. University of Baroda, Vadodara, India

Two new homologous series of liquid crystals viz. 4-(4'-n-alkoxybenzoyloxy)-2-chlorophenylazo-4"-fluorobenzenes(I) and 4-(4'-n-alkoxybenzoyloxy)-2-methylphenyl azo-4"-fluorobenzenes(II) with terminal fluoro, lateral chloro(I) and methyl(II) group and central ester and azo linkages are synthesized and their mesomorphic properties are studied. Both the series are similar in molecular structure with the difference in their lateral substitutions; series I has chloro group and series II has methyl group as laterally substituted groups. All the twelve homologues of each of the series are mesogenic in nature. Series I shows nematic mesophase from the first C_1 to the last C_{16} derivative synthesized; smectic mesophase is exhibited by last two viz. C_{14} and C_{16} derivative, where as all the members from C_1 to C_{16} of series II only show nematic mesophase. The nematic mesophase shows marble texture and the smectic mesophase shows Schlirene texture of the Smectic C variety. Both the series are compared with structurally related series.

Keywords Azo and ester central linkage; chloro and methyl lateral groups; homologues series; mesophase thermal stability; smectic C and nematic mesophase

Introduction

A number of homologous series with ester and azo central linkages have been synthesized having different terminal and lateral groups [1–8]. Lateral substituent in central ring system effects mesomorphic properties and play a vital role in imparting liquid crystallinity to a potentially mesogenic compound. Central phenyl ring having lateral substitution makes molecules broad; which play an effective role in mesogenic property of a mesogenic compound. Studies on the effect of lateral substitution have been comparatively less explored than terminal substitution. A survey of the literature indicates that generally the mesophase range of the mesogens having lateral substituent is less than laterally unsubstituted mesogens [9–15]. In order to establish the co-relation between chemical constitution and mesomorphism, two new homologous series with ester and azo central linkages, fluoro

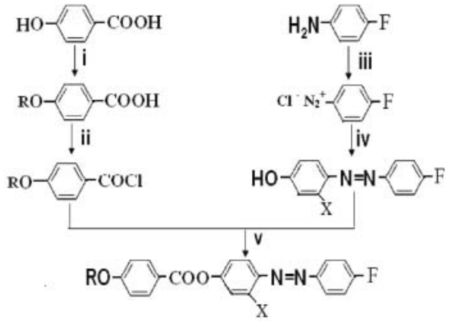
---

*Address correspondence to Purvang D. Patel, Department of Applied Chemistry, Faculty of Technology and Engineering, The M.S. University of Baroda, Vadodara, India. Tel.: +919825355636. E-mail: pdzpatel1983@yahoo.com terminal group and lateral chloro (Series I) and lateral methyl (Series II) groups on central ring are synthesized and their mesomorphic properties are studied.

Experimental

4-Hydroxy benzoic acid, the appropriate n-alkyl halides, p-fluoro aniline, m-chloro phenol, and m-cresol are of Merck grade and used as received. Solvents are dried and distilled prior to use. Microanalyses of some of the representative compounds are performed on Perkin Elmer Series II 2400-CHN analyzer; IR spectra are recorded on a Perkin Elmer GX-FTIR, NMR spectra are measured on a Bruker Avance II-500 spectrometer. Liquid crystalline properties are investigated on Leitz Laborlux 12 POL polarizing microscope provided with a Kofler heating stage. DSC are performed on a Mettler Toledo Star SW 7.01.

1. 4-n-Alkoxy benzoic acids and 4-n-alkoxy benzoyl chlorides are synthesized by known methods [16].
2. 2-Chloro-4-hydroxyphenylazo-4′-fluorobenzene, 2-methyl-4-hydroxyphenylazo-4′-fluoro benzene are prepared by known method [17].
3. The series, namely 4-(4′-n-alkoxybenzoyloxy)-2-chlorophenylazo-4″-fluorobenzenes, and 4-(4′-n-alkoxybenzoyloxy)-2-methylphenylazo-4″-fluoro benzenes are synthesized by adding dropwise a cold solution of 2-chloro-4-hydroxyphenylazo-4′-fluoro benzene (for series I), 2-methyl-4-hydroxyphenylazo-4′-fluoro benzene (for series II), respectively, in dry pyridine to a cold solution of 4-n-alkoxy benzoyl chloride. The mixture is allowed to stand overnight at room temperature. It is acidified with 1:1 cold HCl and the separated solid is filtered and recrystallized from ethanol until constant transition temperatures are obtained. The elemental analysis of some of the representative compounds are found to be satisfactory. The synthetic route of the series is shown in Scheme 1.



Where X = - Cl, - CH$_3$

R= C_nH_{2n+1} n=1to8,10,12,14,16

(i) Alcohol, KOH, R-Br (ii) SOCl$_2$ (iii) HCl ,NaNO$_2$,0^0-5^{0}C

(iv) m-chloro phenol or m-cresol, aq.NaOH,0^0-10^{0}C

(v) Dry pyridine, 1:1 HCl

Scheme 1. Synthetic route for series I and II.

FTIR (Nujol, KBr pellets, cm^{-1}) :
Series I: 4-(4′-n-pentyloxybenzoyloxy)2-chlorophenylazo-4″-fluorobenzenes:
2930, 1740 (–COO–), 1610(–N=N–), 1516, 1360, 1250, 890, 755, 692.

Series I: 4-(4′-n-decyloxybenzoyloxy)2-chlorophenylazo-4″-fluorobenzenes:
2944, 1731 (–COO–), 1606(–N=N–), 1504, 1319, 1264, 1041, 850, 755, 689.

^{1}H NMR : ($CDCl_3$, 500 MHz, δ, ppm, standard TMS)

Series I: 4-(4′-n-pentyloxybenzoyloxy)2-chlorophenylazo-4″-fluorobenzenes :
δ 0.98 (3H, t, $-CH_3$), 1.45–1.82 (m, alkyl chain),
4.06 (2H, t, $-OCH_2-CH_2$), 6.95 (1H, S, H^4), 7.0 (2H, d, H^5),
7.38 (2H, d, H^2), 7.9 (2H, d, H^1), 7.95 (2H, d, H^6), 8.15 (2H, d, H^3)

Series I: 4-(4′-n-decyloxybenzoyloxy)2-chlorophenylazo-4″-fluorobenzenes:
δ 0.9 (3H, t, $-CH_3$), 1.4–1.79 (m, alkyl chain),
4.05 (2H, t, $-OCH_2-CH_2$), 6.98 (1H, S, H^4), 7.0 (2H, d, H^5),
7.48 (2H, d, H^2), 7.9 (2H, d, H^1), 8.0 (2H, d, H^6), 8.1 (2H, d, H^3)

FTIR (Nujol, KBr pellets, cm^{-1}):

Series II: 4-(4′-n-butyloxybenzoyloxy)2-methylphenylazo-4″-fluorobenzenes:
2946, 1735 (–COO–), 1603(–N=N–), 1490, 1317, 1260, 842, 724, 689.

Series II: 4-(4′-n-heptyloxybenzoyloxy)2-methylphenylazo-4″-fluorobenzenes:
2946, 1731 (–COO–), 1606(–N=N–), 1530, 1353, 1264, 890, 728, 681.

^{1}H NMR: ($CDCl_3$, 500 MHz, δ, ppm, standard TMS)

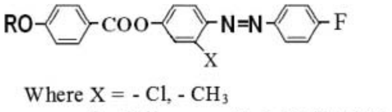
Series II: 4-(4′-n-butyloxybenzoyloxy)2-methylphenylazo-4″-fluorobenzenes:
δ 0.9 (3H, t, $-CH_3$), 1.5–1.8 (m, alkyl chain), 2.33 (3H, S, Ar-CH_3)
4.0 (2H, t, $-OCH_2-CH_2$), 6.98 (2H, d, H^4), 7.0 (2H, d, H^5),
7.30 (2H, d, H^2), 7.9 (2H, d, H^6), 8.1 (2H, d, H^1), 8.2 (2H, d, H^3)

Series II: 4-(4′-n-heptyloxybenzoyloxy)2-methylphenylazo-4″-fluorobenzenes:
δ 0.96 (3H, t, $-CH_3$), 1.40–1.85 (m, alkyl chain), 2.30 (3H, S, Ar–CH_3)
4.0 (2H, t, $-OCH_2-CH_2$), 6.98 (1H, S, H^4), 7.1 (2H, d, H^5),
7.26 (2H, d, H^2), 7.93 (2H, d, H^1), 7.95 (2H, d, H^6), 8.1 (2H, d, H^3)

Results and Discussion

In the present study, 12 homologues from each of the two homologues series viz. 4-(4′-n-alkoxy benzoyloxy)-2-chlorophenylazo-4″-fluorobenzenes (series I) and 4-(4′-n-alkoxy benzoyloxy)-2-methy lphenylazo-4″-fluorobenzenes (series II) are synthesized and their mesomorphic properties are studied.

The general molecular structure of the series is;



All the twelve homologues of the series I are mesogens (Table 1); the nematic phase commences from the very first derivative and remains up to the last hexadecyl derivative synthesized while Smectic C phase commences from the tetradecyl derivative and remains to be exhibited upto the last hexadecyl derivative synthesized. Figure 1, i.e., the plot of transition temperatures against number of carbon atoms in alkoxy chain indicates that N–I curve shows overall falling tendency and merges as the series is ascended; no odd–even effect is observed in N–I curves. The Cr–M transitions show overall falling tendency with a rising jump at decyl derivative. The nematic phase of the series shows marble texture and the smectic phase shows schlieren texture of smectic C variety.

Table 1. Transition temperature °C of the series I. Series I: 4-(4′-n-alkoxybenzoyloxy)-2-chlorophenylazo-4″-fluorobenzenes

	Transition temperatures (°C)		
R = n-alkyl group	Smectic C	Nematic	Isotropic
Methyl	—	114	182
Ethyl	—	104	170
Propyl	—	102	163
Butyl	—	90	158
Pentyl	—	78	160
Hexyl	—	71	157
Heptyl	—	65	149
Octyl	—	62	144
Decyl	—	85	138
Dodecyl	—	79	129
Tetradecyl	70	86	114
Hexadecyl	68	92	111

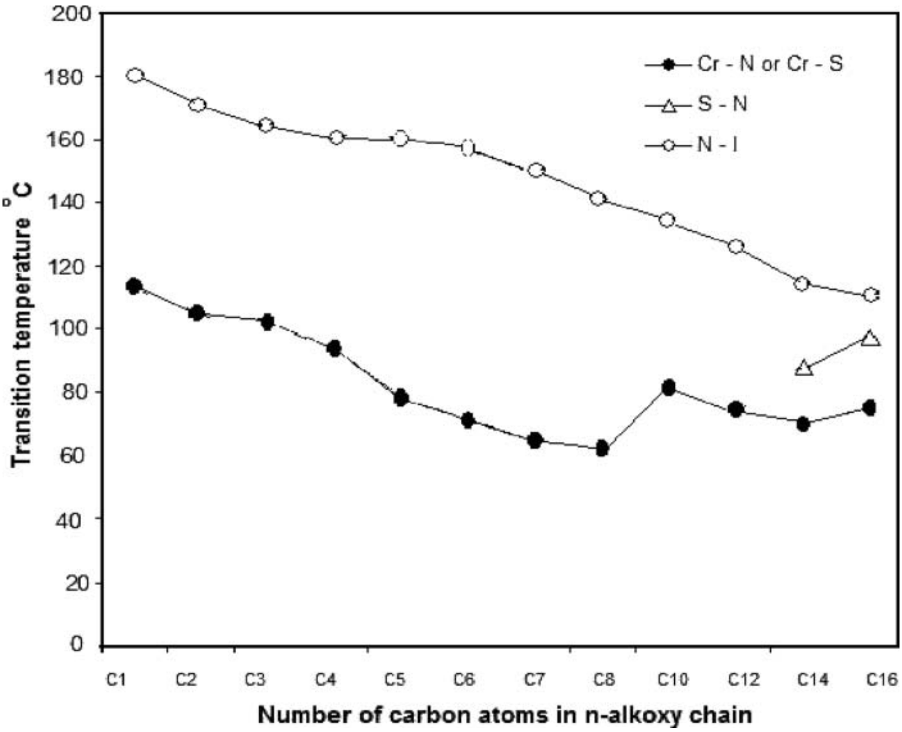


Figure 1. 4-(4′-n-alkoxybenzoyloxy)-2-chloro phenylazo-4″-fluorobenzenes (series I).

Table 2. Transition temperature °C of the series II. Series II: 4-(4′-n-alkoxybenzoyloxy)-2-methylphenylazo-4″-fluorobenzenes

	Transition temperatures °C		
R = n-alkyl group	Smectic	Nematic	Isotropic
Methyl	—	120	165
Ethyl	—	122	158
Propyl	—	110	138
Butyl	—	92	140
Pentyl	—	84	135
Hexyl	—	78	131
Heptyl	—	63	129
Octyl	—	67	128
Decyl	—	61	122
Dodecyl	—	72	117
Tetradecyl	—	76	112
Hexadecyl	—	68	98

All the 12 homologues of the series II are mesogens (Table 2); the nematic phase commences from the very first derivative and remains upto the last hexadecyl derivative synthesised. Figure 2, i.e., the plot of transition temperatures against number of carbon atoms in alkoxy chain indicates that N–I curve shows overall falling tendency as the series is ascended. Here also no odd–even effect is observed in N–I curve. The Cr–M transitions

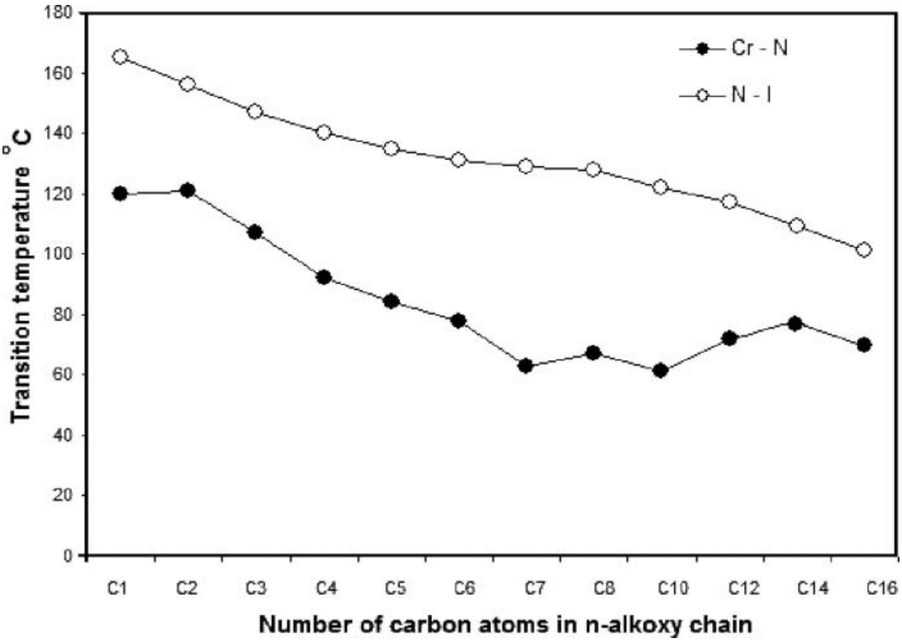


Figure 2. 4-(4′-n-alkoxybenzoyloxy)-2-methyl phenylazo-4″-fluorobenzenes (Series II).

Table 3. Average thermal stability °C

Series	Nematic	Smectic	Commencement of smectic mesophase
I	147.19 (C_1 to C_{16})	89.00 (C_{12} to C_{16})	C_{14}
II	131.08 (C_1 to C_{16})	–	–
A	189.70 (C_1 to C_{10})	116.80 (C_8 to C_{16})	C_8
B	143.80 (C_1 to C_{12})	103.66 (C_{12} to C_{16})	C_{12}
C	117.09 (C_1 to C_{14})	88.00 (C_{14} to C_{10})	C_{14}

show overall falling tendency from methyl to hexadecyl derivative with slight rise at ethyl, octyl, and tetradecyl derivative. Here also nematic phase of the series shows marble texture and the smectic phase shows schlieren texture of smectic C variety.

The average thermal stabilities of series I and II are compared with structurally related other homologous series; table 3 gives the average thermal stabilities and figure 3 gives the molecular structures of the series in comparison. The average nematic mesophase thermal stability of series I is 147.91°C and series (II) is 131.08°C similarly the average smectic mesophase thermal stability of the series (I) is 89.0°C; where as Series II shows only nematic mesophase. Comparison of average mesophase thermal stability of both the series (Table 3) shows that the nematic mesophase thermal stability of series II is lower than that of series I. Here, the nature of lateral substituents has important implications on phase transition temperatures and average mesophase thermal stability; series I has lateral chloro group where as series II has lateral methyl group. Gray has also reported a system where in lateral methyl substituent has lower thermal stability than lateral chloro substituent [18].

Comparison of series I and II with structurally related homologous series shows that all the series in comparison are structurally more or less similar, consisting of three aromatic cores, azo and ester central linkages. The difference between molecules of series I, II, and A [19] is only the lateral substitution; series I has chloro group, series II has methyl group as lateral substituent, while series A is laterally unsubstituted. The effect of the lateral group in the central benzene ring causes disruption in the molecular packing, which reduces the transition temperatures and melting points as well as the mesophase thermal

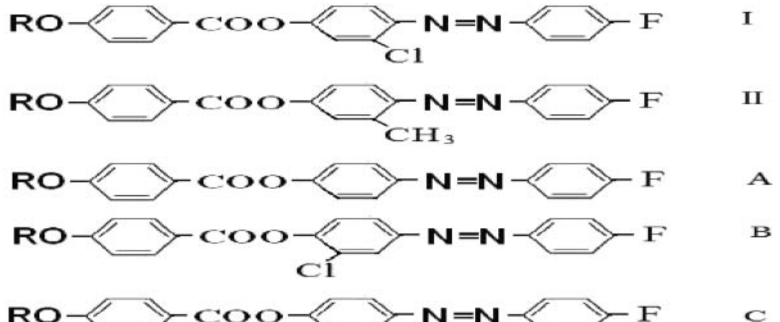
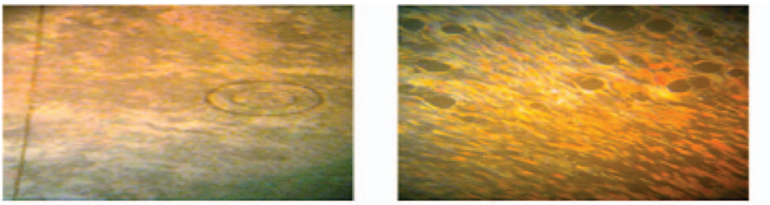


Figure 3. Selected homologous series for comparison.

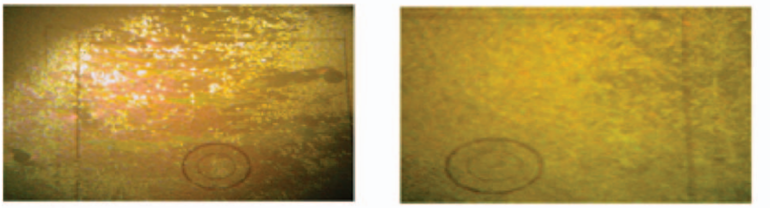
Table 4. Elemental analysis

		Calculated			Found		
Series	Homologue	C%	H%	N%	C%	H%	N%
I	C_5	69.81	5.33	6.78	70.53	5.86	6.11
I	C_{10}	72.12	6.63	5.80	73.88	6.70	5.27
II	C_4	70.93	5.66	6.89	71.57	5.91	7.05
II	C_7	72.32	6.47	6.25	73.00	6.81	6.56



(a) Marble texture of nematic mesophase
Series I C16 member

(b) Schlirene texture of smectic mesophase
Series I C16 member



(c) Marble texture of nematic mesophase
Series II C2 member

(d) Marble texture of nematic mesophase
Series II C6 member

Figure 4. Photomicrographs of the texures of representative derivatives.

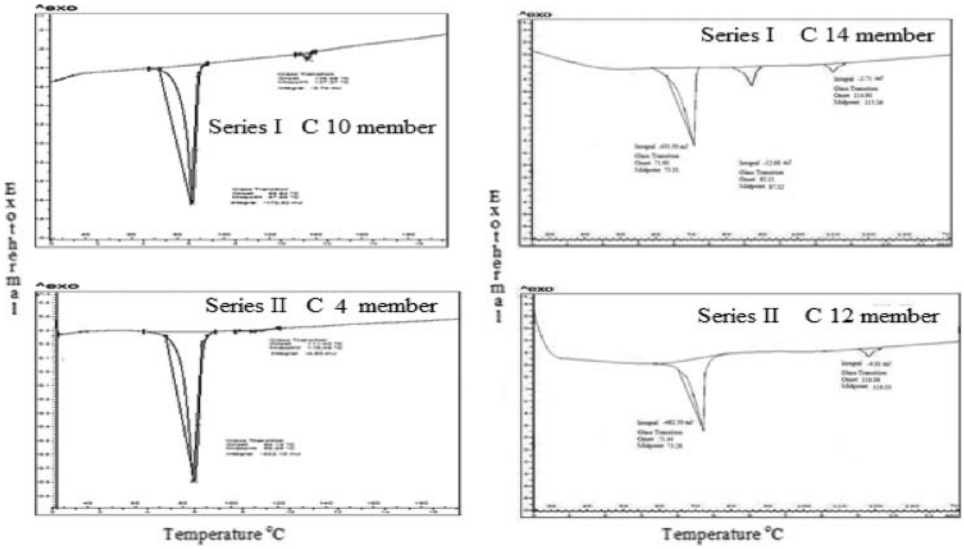


Figure 5. DSC curves.

Table 5. DSC data

Series	Member	Heating rate/°C min^{-1}	Transition temperature°C	Δ H/ Jg^{-1}	Δ S/ J g^{-1} K^{-1}
I	Decyl	5	Cr–N 87	48.00	0.1330
			N–I 138	1.038	0.0025
I	Tetradecyl	5	Cr–Sm 70	80.85	0.2343
			Sm–N 86	2.26	0.0063
			N–I 114	0.483	0.0012
II	Butyl	5	Cr–N 92	41.29	0.1133
			N–I 140	0.62	0.0015
II	Dodecyl	5	Cr–N 72	80.08	0.2323
			N–I 117	0.79	0.0020

stability compared to the laterally unsubstituted analogues. Thus, introduction of chloro group (Series I) and methyl group (Series II) in the ortho position of the azo linkage effectively reduce both the clearing and melting points compared to those of the parent compound (Series A). It is seen that the breadth of the molecules of the series I and II are increased due to the presence of lateral group on the central benzene ring which decreases both smectic and nematic thermal stabilities [20].

Series I and series B [19] has lateral chloro group on ortho position and meta position to the azo central linkage respectively. The average nematic mesophase thermal stability of series I is 147.91°C and that of series B is 143.8°C which is not marked different in series I. However, the average smectic mesophase thermal stability of series I is 89.0°C while that of series B is 103.66°C. Thus, the average smectic mesophase thermal stability of series I is less than series B, which can be due to the difference in position of lateral chloro group. Series I is having chloro group in the ortho position to the azo linkage whereas series B is having chloro group in the ortho position to the ester linkage.

Similarly, Series II and series C [19] has lateral methyl group on ortho position and meta position to the azo central linkage respectively. The average nematic mesophase thermal stability of series II is 131.08°C and that of series C is 117.09°C. Thus, the average nematic mesophase thermal stability of series II is higher than series C, which can be due to the difference in position of lateral methyl group. Series II is having methyl group in the ortho position to the azo linkage whereas series C is having methyl group in the ortho position to the ester linkage.

Figure 4 shows the photomicrographs of some of the representative compounds. The enthalpies of decyl and tetradecyl derivative of series I and butyl and dodecyl derivative of series II are measured by DSC. The DSC data are recorded in Table 5. Figure 5 shows the DSC curves.

Conclusion

Two new homologous series with lateral chloro(I) and lateral methyl(II) groups are synthesized. The positional effect of –Cl and $–CH_3$ lateral substituent on phase behaviour, phase transition temperatures with respect to azo central linkage are studied. These lateral substituents depress both melting point and clearing points of the liquid crystals. Mesogens with lateral substitution have reduced smectic and nematic mesophase thermal stability than the corresponding unsubstituted homologues.

Acknowledgment

The authors thank the Head of Applied Chemistry Department, Faculty of Technology and Engineering, The M.S. University of Baroda, Vadodara for providing research facilities.

References

[1] Demus, D., & Zaschke, H. (1984). *Flussige Kristalle in Tabllen II*, VEB Deutscher Verlag fur Grundstoffindustrie: Leipzig.
[2] Dave, J. S., & Menon, M. R. (1998). *Mol.Cryst. Liq. Cryst.*, *319*, 51.
[3] Dave, J. S., & Menon, M. R. (2000). *Bulletin of Material Science*, *23*(3), 237.
[4] Patel, P. R., & Dave, J. S. (2006). *Liq. Cryst.*, *33*(9), 1065.
[5] Dave, J. S., Menon, M. R., & Patel, P. R. (2002). *Mol. Cryst. Liq. Cryst.*, *378*, 1.
[6] Dave, J. S., Menon, M. R., & Patel, P. R. (2001). *Mol.Cryst. Liq. Cryst.*, *364*, 575.
[7] Dave, J. S., & Dhake, K. P. (1992). *Bull. Chem. Soc. Jpn.*, *65*, 559.
[8] Shah, N. H., Vora, R. A., & Jadav, N. D. (1991). *Mol. Cryst. Liq. Cryst.*, *209*, 291.
[9] Prajapati, A. K., & Pandya, H. M. (2003). *Mol. Cryst. Liq. Cryst.*, *393*, 31.
[10] Hasegawa, H., Masuda, T., Matsunaga, Y., Seo S., & Yasuhara, K. (1989). *Bull. Chem. Soc. Jpn.*, *62*, 2875.
[11] Gisse, P., Cluzeau, P., Ravaine, V., & Nguyen, H. T. (2002). *Liquid Crystals*, *29*(1), 91.
[12] Kasipar, M., Hamplova, V., Pakhomov, S. A., Stibor, I., Sverenyaak, H., Bubnov, A. M., Glogarovaa, M., &Vaneik, P. (1997). *Liquid Crystals*, *22*(5), 557.
[13] Bezborodov, V. S., & Perrov, V. F. (1997). *Liquid Crystals*, *23*(6), 771.
[14] Bristol, D. W., & Schroeder, J. P. (1974). *J. Org. Chem.*, *39*(21), 3138.
[15] Sun, H., Cheung, W. S., & Fung, B. M. (2000). *Liquid Crystals*, *27*(11), 1473.
[16] Dave, J. S., & Vora, R. A. (1970). In: J. F. Johnson & R. S. Porter, (Eds.), (*Liquid Crystals and Ordered Fluids*, Plenum Press: New York, p. 477.
[17] Furniss, B. S., Hannford, A. J., Smith, P. W. G., & Tatchell, A. R. (Revisors). (1989). *Vogel's Textbook of Practical Organic Chemistry* (4th Edn.), Longman Singapore Publishers Pvt. Ltd.: Singapore, pp. 563–649.
[18] G. W. Gray. (1974). In: G. W. Gray & P. A. Winsor (Eds.), *Liquid Crystals and Plastic Crystals*, Chapter 4. Ellis Horwood: Chichester, pp. 125–129.
[19] Dave, J. S., Upasani, C. B., & Patel, P. D. (2010). *Mol. Cryst. Liq. Cryst.*, *533*, 73.
[20] Gray, G. W. (1974). In G. W. Gray & P. A. Winsor (Eds). *Liquid Crystals and Plastic Crystals*, Ellis Horwood Limited: Chichester, England, 1, pp. 130–131.