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

New mesogens with a fluoro-substituted bent core

Renu Mahajan[a]; Himani Nandedkar[a]; Alpesh Vora Corresponding author[a]; K. K. Raina[b]
[a] Applied Chemistry Department, Faculty of Technology and Engineering, M.S.University of Baroda, Kalabhavan, Vadodara 390 001, India [b] School of Basic and Applied Sciences, Thapar Institute of Engineering and Technology, Patiala 147 001, India

To cite this Article Mahajan, Renu , Nandedkar, Himani , Vora Corresponding author, Alpesh and Raina, K. K.(2004) 'New mesogens with a fluoro-substituted bent core', Liquid Crystals, 31: 2, 161 — 167

To link to this Article: DOI: 10.1080/02678290310001599215

URL: http://dx.doi.org/10.1080/02678290310001599215

Liquid Crystals, Vol. 31, No. 2, February 2004, 161–167

New mesogens with a fluoro-substituted bent core

RENU MAHAJAN, HIMANI NANDEDKAR, ALPESH VORA*
Applied Chemistry Department, Faculty of Technology and Engineering,
M.S.University of Baroda, P.B.No.-51, Kalabhavan, Vadodara 390 001, India

and K. K. RAINA
School of Basic and Applied Sciences, Thapar Institute of Engineering and
Technology, P.O. Box No. 32, Patiala 147 001, India

(*Received 23 January 2003; in final form 10 May 2003; accepted 14 May 2003*)

Ferroelectric properties in liquid crystals are no longer restricted to materials with a chiral molecular structure; ferroelectricity has been observed in a smectic phase formed by bent achiral molecules. Accordingly, two homologous series possessing a central biphenyl methane core have been synthesized, the central core having two lateral fluoro substituents. Both the series have six-ring structures and exhibit smectic mesophases of high thermal stability. The flexible biphenyl methane core imparts a slight curve to the molecules, giving them a bent shape.

1. Introduction

Non-conventional liquid crystals with molecules deviating from the classical rigid rod shape are a recent field of interest [1–6]. Banana-shaped molecules are being synthesized because of their associated ferroelectric properties [7, 8]. Biphenylmethane derivatives have not been studied extensively, as normally such central cores are not very conducive to mesomorphic properties. In the present work, however, two series of biphenylmethane derivatives with lateral fluoro substituents and having six benzene rings have been synthesized and their mesomorphic properties evaluated.

2. Experimental

2.1. *Synthesis*

The syntheses of series I and II compounds are outlined in schemes 1 and 2, respectively.

2.1.1. *4-n-Alkoxybenzoic acids and 4-n-alkoxybenzoyl chlorides*

These were synthesized by the method of Dave and Vora [9]. The transition temperatures were in good agreement with reported values.

2.1.2. *4-(4-n-Alkoxybenzoyloxy)benzaldehydes*

These were synthesized by the method of Dave and Kurian [10]. Again, transition temperatures were in good agreement with reported values.

2.1.3. *4,4-diamino-3,3-difluorobiphenylmethane*

A mixture of 20 ml hydrochloric acid and 40 ml water was added to 10 ml (0.09 mol) of 2-fluoroaniline in a beaker heated on a water-bath with constant stirring. After the reaction mixture had reached 60°C, 45 ml of 3% formaldehyde solution was added drop-wise and with constant stirring. The reaction mixture was heated at 65°C for 2 h with constant stirring and was then allowed to cool to room temperature. Ice-cold water was added to the reaction mixture to lower its temperature; it was then neutralized with 10% sodium hydroxide solution. The precipitate obtained was filtered, washed with water and dried; crude 4,4′-diamino-3,3′-difluorobiphenylmethane was purified by crystallization from methanol; m.p. = 70°C.

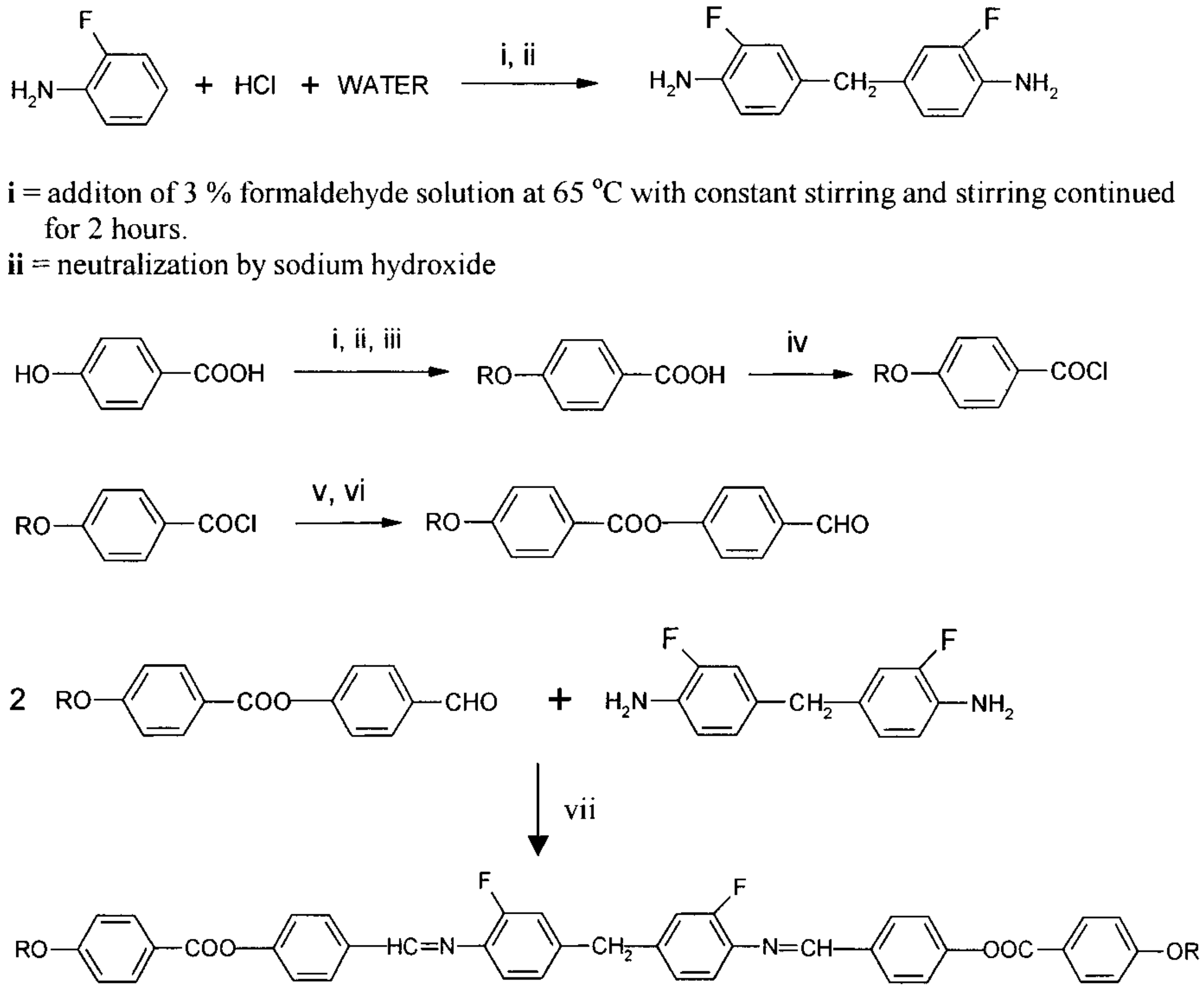
2.1.4. *Synthesis of Schiff's bases containing two lateral fluoro substituents (series I)*

Twelve homologues (methoxy – *n*-hexadecyloxy) were synthesized by condensation of 4,4′-diamino-3,3′-difluorobiphenylmethane (0.01 mol) with the required 4-(4′-*n*-alkoxybenzoyloxy)benzaldehyde (0.02 mol) in ethanol. The reaction mixture was heated at reflux for 3 h on a sand bath. The reaction mass was cooled and the solid obtained was filtered to obtain the crude Schiff's base. Crude Schiff's bases were purified by recrystallization

---

*Author for correspondence; e-mail: Alpesh_vora@rediffmail.com

Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online © 2004 Taylor & Francis Ltd
http://www.tandf.co.uk/journals
DOI: 10.1080/02678290310001599215



i = additon of 3 % formaldehyde solution at 65 °C with constant stirring and stirring continued for 2 hours.

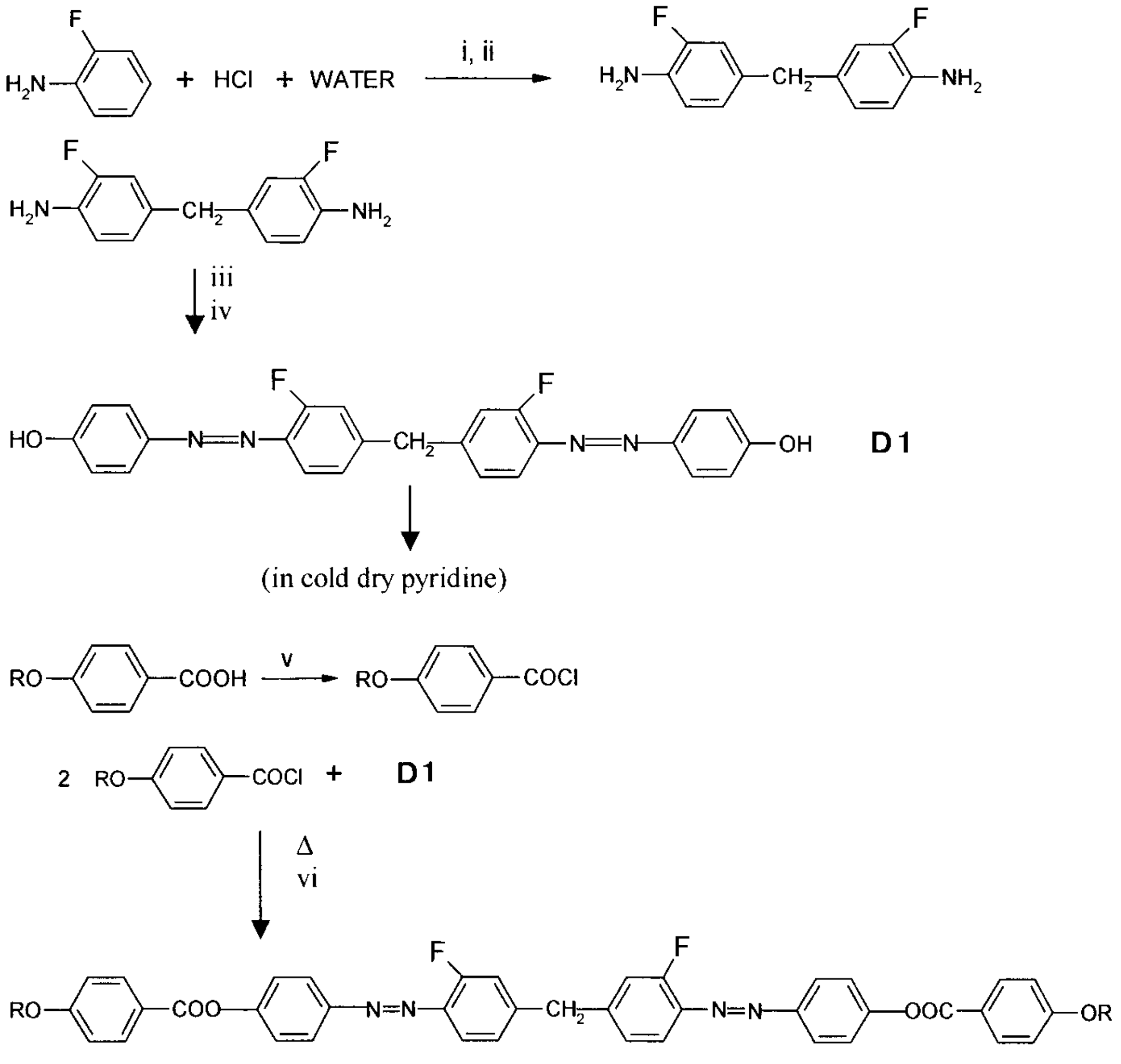
ii = neutralization by sodium hydroxide

i = RBr, KOH, ethanol, reflux for 4 – 6 hours.
ii = 10 % aqueous KOH, reflux for 2 hours.
iii = 1:1 cold HCl
iv = $SOCl_2$, Δ
v = 4-hydroxy benzaldehyde in dry pyridine, Δ.
vi = cold 1:1 HCl
vii = ethanol, reflux for 3 hours.

R = n-alkyl group, n = 1 to 8, 10, 12, 14 and 16.

Scheme 1. Synthetic route for series I compounds.

from ethanol/ethyl acetate until constant transition temperatures were obtained. The methoxy derivative is non-mesogenic; the ethoxy – *n*-hexadecyloxy derivatives all exhibit smectic mesophases. The compounds were characterized by elemental analysis, IR and NMR spectroscopy. The transition temperatures were determined by using a Leitz Labourlux 12 POL polarizing microscope with a heating stage, and are reported in table 1. Elemental analysis, IR and NMR spectroscopy data are given in tables 2 and 3. The purity of the mesogens was confirmed by TLC (Merck). From their texture the smectic mesophases appears to be smectic A. This was confirmed by the contact method and miscibility studies.



i = additon of 3 % formaldehyde solution at 65 °C with constant stirring and stirring continued for 2 hours.
ii = neutralization by sodium hydroxide
iii = Diazotization, 0 – 5 °C, 1:1 HCl, $NaNO_2$
iv = Coupling with phenol in NaOH, 0 – 10 °C.
v = $SOCl_2$, Δ
vi = 1:1 cold HCl

R = n-alkyl group, n = 1 to 8, 10, 12, 14 and 16.

Scheme 2. Synthetic route for series II compounds.

2.1.5. *Synthesis of azo-esters (series II)*

Azo dye D1, methylene bis-(3-fluoro-4-hydroxyazobenzene), was synthesized by diazotisation of 4,4′-diamino-3,3′-difluorobiphenylmethane followed by coupling with phenol [11]. Crude dye D1 was purified by crystallization from ethanol; m.p. = 113°C.

Table 1. Transition temperatures of series I compounds.

		Transition temperatures /°C	
Compound	$R=n$-alkyl group	Smectic	Isotropic
I/1	Methyl	—	212.0
I/2	Ethyl	(192.0)[a]	205.0
I/3	Propyl	(194.0)	200.0
I/4	Butyl	161.0	204.0
I/5	Pentyl	144.0	203.0
I/6	Hexyl	145.0	196.0
I/7	Heptyl	141.0	183.0
I/8	Octyl	115.0	185.0
I/9	Decyl	125.0	182.0
I/10	Dodecyl	145.0	176.0
I/11	Tetradecyl	113.0	173.0
I/12	Hexadecyl	111.0	173.0

[a] Values in parenthesis indicate monotropy.

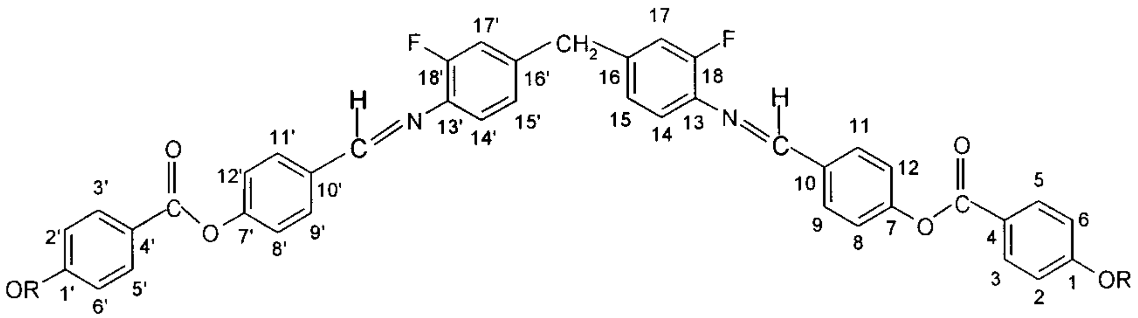
Table 2. Elemental analysis of some series I compounds.

		Required %			Found %		
Compound	Homologue	C	H	N	C	H	N
I/1	*n*-Pentyl	74.45	5.84	3.41	74.13	5.74	3.09
I/2	*n*-Octyl	75.5	6.62	3.10	75.10	7.0	2.94
I/3	*n*-Decyl	76.1	7.1	2.91	76.31	7.09	3.22

A homologous series of azo-esters (methoxy–*n*-hexadecyloxy) was synthesized from the azo dye D1 and the required 4-*n*-alkoxybenzoyl chlorides.

Dye D1 (0.01 mol) was dissolved in 10 ml of dry pyridine and added to the cold 4-*n*-alkoxybenzoyl chloride (0.02 mol) slowly and with stirring. The reaction mixture was heated gently on a water bath for half an hour and left overnight. The contents were poured into cold 1:1 hydrochloric acid to obtain the crude azo-ester. The azo-esters were filtered, washed with water, 10% sodium hydroxide and again with water. They were recrystallized from DMF until constant transition temperatures were obtained. The methoxy and *n*-propyloxy derivatives are non-mesogenic; the ethoxy – *n*-hexadecyloxy derivatives all exhibit enantiotropic smectic mesophase. The compounds were characterized as described in §2.1.4. Transition temperatures are reported in table 4; elemental analysis, IR and NMR spectroscopy data are given in tables 5 and 6. From their texture, the smectic mesophases appear to be smectic A. This was confirmed by the contact method and miscibility studies.

Table 3. Spectral data for the *n*-pentyl homologue of series I.



R = n-Pentyl group

Proton NMR Spectra (CDCl$_3$, 200 MHz, δ ppm, standard TMS).

0.9 δ (t, 6H, $2\times CH_3$ of alkoxy chain at C_1 & C_1);
1.2–1.9 δ (m, 12H, $6\times CH_2$ of alkoxy chain at C_1 and C_1);
3.66–4.15 δ (m, 6H, $2\times OCH_2$ of alkoxy chain at C_1 and $C_{1'}$ overlapped with two central methylene protons);
7.0 δ (d, $J=8.9$ Hz, 4H of C_2, C_6, $C_{2'}$ and $C_{6'}$);
7.08–7.16 δ (m, 4H of C_{14}, C_{15}, $C_{14'}$ and $C_{15'}$);
7.35 δ (d, $J=8.5$ Hz, 4H of C_8, C_{12}, $C_{8'}$ and $C_{12'}$);
8.0 δ (d, $J=8.6$ Hz, 4H of C_9, C_{11}, $C_{9'}$ and $C_{11'}$);
8.15 δ (d, $J=8.8$ Hz, 4H of C_3, C_5, $C_{3'}$ and $C_{5'}$);
8.54 δ (s, 2H of two azomethine protons).

FTIR (KBr) Spectra: bending and stretching vibrations cm^{-1}.

3414.35, 2933.20, 1732.73, 1630.52, 1605.45(–CH–N–), 1509.99, 1318.11, 1258.32, 1203.36, 1170.58, 1115.62, 1071.26, 1014.37, 882.27, 845.63, 762.71, 587.61, 516.83.

Table 4. Transition temperatures of series II compounds.

		Transition Temperatures °C	
Compound	$R = n$-alkyl group	Smectic	Isotropic
II/1	Methyl	—	190.0
II/2	Ethyl	(178.0)[a]	202.0
II/3	Propyl	—	185.0
II/4	Butyl	(159.0)	200.0
II/5	Pentyl	(147.0)	167.0
II/6	Hexyl	156.0	174.0
II/7	Heptyl	139.0	144.0
II/8	Octyl	124.0	176.0
II/9	Decyl	119.0	154.0
II/10	Dodecyl	105.0	134.0
II/11	Tetradecyl	116.0	141.0
II/12	Hexadecyl	81.0	110.0

[a] Values in parentheses indicate monotropy.

Table 5. Elemental analysis of some series II compounds.

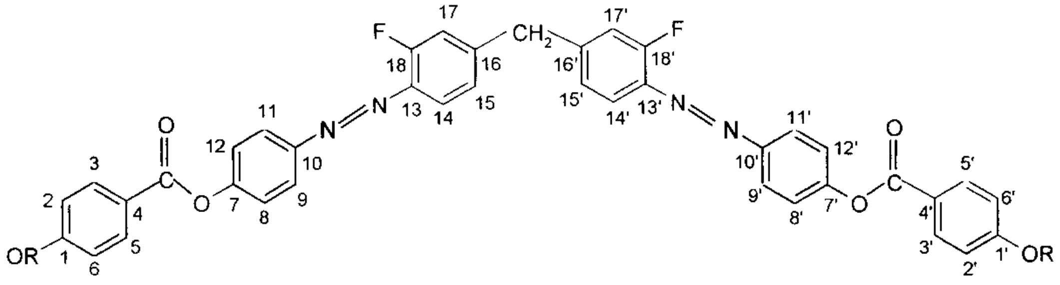
		Required %			Found %		
Compound	Homologue	C	H	N	C	H	N
II/1	*n*-Pentyl	71.36	5.60	6.80	70.91	5.24	7.21
II/2	*n*-Octyl	72.68	6.39	6.17	72.21	6.17	5.87
II/3	*n*-Decyl	73.6	6.65	5.82	73.58	6.39	6.29

2.2. *Electro-optic investigation*

Cells were constructed with conducting plates and having a uniform thickness. They were pretreated with polymide and unidirectionally rubbed to obtain homogeneous alignment. A sample of the compound was introduced by capillary action at about 100°C. The temperature was controlled to an accuracy of 0.1°C using a Linkam temperature controller model TP94 and THMS 600. Observations were made via an Olympus polarizing microscope model BX5IP at 10X. The whole set-up was interfaced with a computer, and textures were recorded using LINsys software. The sample was cooled at a rate of $0.1°\mathrm{C\,min}^{-1}$ from the isotropic liquid and heated at a rate of $3–5°\mathrm{C\,min}^{-1}$. On applying a triangular voltage, at a relatively high threshold the electric field showed some switching by the material. The spontaneous polarization was very small and could not be measured.

The sample of compound showed an SmA phase at 135°C and then a chiral smectic (ferroelectric) phase was obtained. In an applied electric field it showed a switching effect and ferroelectric behaviour. However, spontaneous polarization was very small.

Table 6. Spectral date for the *n*-octyl homologue of series II.



R = n-Octyl group

Proton NMR spectra ($CDCl_3$, 200 MHz, δ ppm, standard TMS).

0.9 δ (t, 6H, $2 \times CH_3$ of alkoxy chain at C1 and $C_{1'}$);
1.2–1.9 δ (m, 24H, $12 \times CH_2$ of alkoxy chain at C_1 and $C_{1'}$);
4.05 δ (t, 4H, $2 \times OCH_2$ of alkoxy chain at C_1 and $C_{1'}$);
4.1 δ (s, 2H of central methylene protons);
7.0 δ (d, $J = 8.9$ Hz, 4H, of C_2, C_6, $C_{2'}$ and $C_{6'}$);
7.05–7.15 δ (m, 4H at C_{14}, C_{15}, $C_{14'}$ and $C_{15'}$);
7.35 δ (d, $J = 8.8$ Hz of 4H at C_8, C_{12}, $C_{8'}$ and $C_{12'}$);
8.05 δ (d, $J = 8.8$ Hz of 4H at C_9, C_{11}, $C_{9'}$ and $C_{11'}$);
8.15 δ (d, $J = 8.8$ Hz of 4H at C_3, C_5, $C_{3'}$ and $C_{5'}$).

FTIR (KBr) Spectra: bending and stretching vibrations cm^{-1}.

3414.35, 2924.52, 1729.83, 1607.38(–N–N–), 1509.99, 1421.28, 1318.11, 1259.29, 1198.54, 1165.76, 1058.73, 880.35, 778.14, 515.86,

3. Reaults and discussion

Two homologous series of compounds containing a biphenylmethane central core with lateral fluoro substituents were synthesized to evaluate the effect of such a semi-flexible linkage on mesomorphism. Series I compounds, possessing azomethine and ester linkages, exhibit smectic phases from the ethoxy derivative onwards. All the homologues are thermally stable and, even though the system has six benzene rings with lateral fluoro substituents, no decomposition is observed. Series II compounds, having azo and ester linkages, exhibit smectic mesophases from the second member onwards. The homologues are thermally very stable.

The presence of the flexible methylene group may impart a slight curvature or bend [6] to the molecules. The bent structure, if present, may impart ferroelectricity and antiferroelectricity which should not be restricted to chiral tilted phases [8–11]. These molecules represent a new sub-group of thermotropic liquid crystals different from classical types such as calamitic and discotics. Both series exhibit smectic mesophases, even though lateral substituents are present. Banana-shaped molecules are known to exhibit smectic mesophases because of the close packing of one molecule into the curvature of another; the two fluoro substituents, because of their small size, may not disrupt the molecular packing and hence series I and II exhibit smectic mesophases. The mesophase thermal stabilities of the present series I and II are compared with those of the unfluorinated series A. The average thermal stability of the series is recorded in table 7. The geometry of all the series is given in the figure.

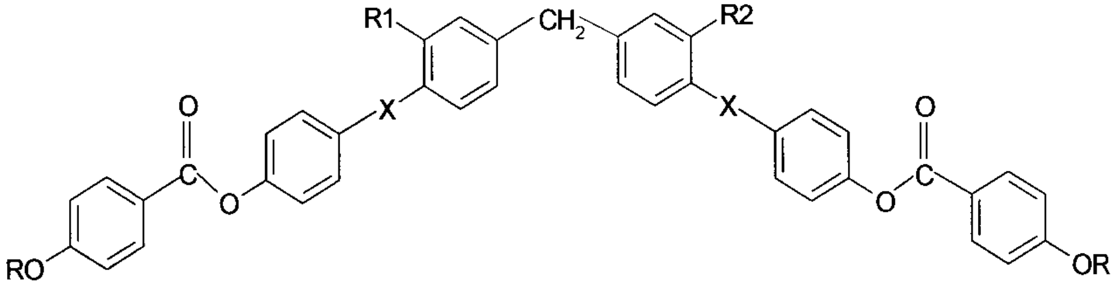
Table 7. Average thermal stabilities of C_2 and C_4–C_{16} compounds.

Series	Sm—I/°C	Commencement of smectic phase
I	187.0	Ethyl
II	152.0	Ethyl
A	202.0	Methyl

The average smectic thermal stabilities of series I compounds is slightly higher than those of series II compounds. This can be attributed to the more polarizable nature of the azomethine linkage as compared with the azo linkage. The average smectic thermal stabilities of series I and II are lower than those of series A. This is due to the presence of the two lateral fluoros substituents of series I and II.

Reference to table 3 indicates that there is a small difference of 15°C in the average smectic thermal stability of series I and A [6]. This is quite surprising, since in bent molecules the two lateral fluoro substituents should have an adverse effect on smectic mesophases. The comparison indicates that the molecules of series I probably arrange in smectic layers in which the lateral fluoro substituents are accomodated.

The authors are grateful to the Dean, Faculty of Technology and Engineering, and Head of Applied



R = n-alkyl group

Series	X	R1	R2
I.	—N=CH—	F	F
II.	—N=N—	F	F
A.	—N=CH—	H	H

Figure 1. Structure of series I, II and reference series A compounds.

Chemistry Department, M.S.University of Baroda, for providing the research facility. A. V. is grateful to CSIR for financial assistance.

References

[1] Jakli, A., Lischka, Ch., Weissflog, W., Pelzl, G., and Saupe, A., 2000, *Liq. Cryst.*, **27,** 1405.

[2] Bedel, J. P., Rouillion, J. C., Marcerou, J. P., Lafuerre, M., Nguyen, H. T., and Achard, M. F., 2000, *Liq. Cryst.*, **27,** 1411.

[3] Sudhakar, S., Narsimhaswamy, T., and Srinivasan, K. S. V., 2000, *Liq. Cryst.*, **27,** 1525.

[4] Artal, M. C., Toyne, K. J., Goodby, J. W., Barbera, J., and Photinos, D. J., 2001, *J. mater. Chem.*, **11,** 2801.

[5] Niori, T., Sekine, T., Watanabe, J., Furukawa, T., and Takezoe, H., 1996, *J. mater. Chem.*, **6,** 1231.

[6] Kuboshita, M., Matsunaga, Y., and Miyauchi, T., 1995, *Mol. Cryst. Liq. Cryst.*, **264,** 145.

[7] Niori, T., Sekine, T., Watanabe, J., Furukawa, T., and Takezoe, H., 1996, *J. mater. Chem.*, **6,** 1231; Niori, T., Sekine, T., Watanabe, J., Furukawa, T., and Takezoe, H., 1997, *Mol. Cryst. Liq. Cryst.*, **337,** 301; Sekine, T., Takanashi, Y., Niori, T., Watanabe, J., and Takezoe, H., 1997, *Jpn. J. appl. Phys.*, **1(36),** 1201.

[8] Shen, D., Diele, S., Pelzl, G., Wirth, I., and Tschierske, C., 1999, *J. mater. Chem.*, **9,** 661.

[9] Dave, J. S., and Vora, R. A., 1970, *Liquid Crystals and Ordered Fluids*, edited by J. F. Johnson, and R. S. Porter (New York: Plenum Press), p. 477.

[10] Dave, J. S., and Kurian, G., 1975, *J. Phys. (Paris), Colloq.*, **C1,** 403.

[11] Vogel, A. I., 1994, *A Text Book of Practical Organic Chemistry*, 5th edn (E.L.B.S and Longman Group), p. 948.