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Fluorine-substituted unsymmetrical bent-core mesogens derived from resorcinol

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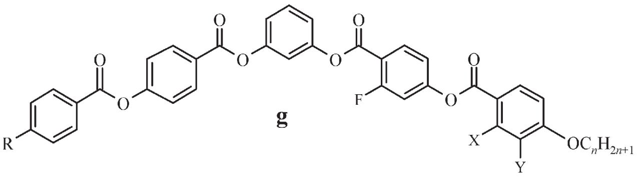
Forty new bent-core compounds, unsymmetrically substituted about a central phenyl ring, were investigated for their mesomorphic properties. The effect of fluorine substituents in different positions of the phenyl rings of one of the arms of the bent-core compounds on the mesophases were examined in detail. Most of the compounds exhibit the lamellar antiferroelectric B_2 mesophase. The mesophases were investigated by textural observation by polarizing microscopy, differential scanning calorimetry, X-ray diffraction and electro-optical studies.

1. Introduction

The study of the mesomorphic properties of compounds composed of bent-core molecules has gained considerable importance since the discovery of polar switching in such achiral compounds [1], followed by a detailed analysis of the switching process [2]. Although seven different phases were identified initially and assigned the symbols B_1, B_2...B_7 which is rather arbitrary [3], there have been a several reports on the occurrence of new mesophases [4]. The relationship between chemical structure and mesomorphic properties is still not clearly understood. However, systematic investigations carried out on a relatively large number of homologous series of compounds have shown that the intercalated smectic (B_6) phase, the rectangular columnar (B_1) phase and the lamellar antiferroelectric (B_2) phase occur in that sequence as a function of the length of the terminal chain [5–7]. In general, bent-core compounds with longer terminal chains exhibit polar mesophases. Amongst all the B phases, the lamellar antiferroelectric B_2 phase, which occurs in a large number of systems, has been extensively studied and in detail. Depending on the tilt sense of the molecules in adjacent layers there can be two types of arrangement in the B_2 phase. If the tilt sense is synclinic the resulting B_2 phase is racemic (SmC_SP_A); if it is anticlinic then the chiral B_2 phase (SmC_AP_A) is obtained.

Over the past few years several hundred bent-core compounds have been synthesized and their mesomorphic properties evaluated [3–8]. Most of these are five-ring symmetrical compounds derived from resorcinol or substituted resorcinol [3, 5, 6, 8]. In general, most of the compounds contain *n*-alkoxy terminal groups which are varied in a symmetrical fashion. As is well known, fluorine has been used as a lateral substituent for modifying mesomorphic properties. In fact fluorine is used as a lateral substituent on the central as well as outer phenyl rings, which has resulted in new mesophases and mesophase sequences [9–13]. In all these systems, fluorine was substituted symmetrically on both arms of the bent-core compounds.

In this paper, we report the mesomorphic behaviour of several unsymmetrical bent-core compounds belonging to four different homologous series. All the compounds are derived from resorcinol and contain fluorine substituents on only one of the arms. In addition, one of the terminal positions has been kept constant with an *n*-dodecyloxy or *n*-dodecyl chain while varying the length of the other terminal chain. The effect of replacing the *n*-alkoxy chain by an *n*-alkyl chain in these systems has also been examined. The general structure of the compounds investigated, **g**, is:



g

$R = n\text{-}C_{12}H_{25}O$ $X = F$, $Y = H$ series I
$X = H$, $Y = F$ series II
$R = n\text{-}C_{12}H_{25}$ $X = F$, $Y = H$ series III
$X = H$, $Y = F$ series IV

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2. Experimental

2.1. *General methods*

All the compounds were purified by column chromatography on silica gel (60–120 mesh) and repeated crystallization using suitable solvents. The chemical structure of all the compounds was confirmed by spectroscopic techniques. ^{1}H NMR spectra were recorded using a Bruker AMX 400 MHz or 500 MHz spectrometer. Tetramethylsilane in deuteriochloroform was used as an internal standard. Infrared spectra were recorded from KBr pellets/nujol mull on a Shimadzu FTIR-8400 spectrophotometer. Elemental analysis was carried out using a Carlo-Erba 1106 analyser. The thermal behaviour of the compounds was investigated using a Perkin-Elmer, Model Pyris 1D, differential scanning calorimeter (DSC). The calorimeter was calibrated using pure indium as a standard; heating and cooling rates were $5°\mathrm{C\,min^{-1}}$. The transition temperatures reported in tables 1–4 were determined from DSC thermograms. The clearing temperatures and the associated enthalpy values for the monotropic phases were obtained after cooling the respective isotropic phases to the mesophase and reheating. Optical textures were observed under a Leitz Laborlux 12 POL/Olympus BX50 polarizing microscope equipped with a Mettler FP 82 HT heating stage and a Metttler FP 5 controller. X-ray diffraction (XRD) studies were carried out on non-oriented samples using Cu Kα radiation ($\lambda = 1.54$ Å) from a Rigaku Ultrax 18 rotating anode generator. The X-ray patterns were recorded on a Marresearch 2D-image plate detector. The electro-optical measurements were carried out using homemade cells; the antiferroelectric switching behaviour was examined using the triangular-wave method.

2.2. *Synthesis*

The synthetic pathway used to prepare the unsymmetrical bent-core compounds having the general structure **g** is shown in the scheme. Benzyl-4-hydoxybenzoate and resorcinol were commercial compounds and used without further purification. 3-Benzyloxyphenol was prepared by monobenzylation of resorcinol in the presence of anhydrous potassium carbonate. 2-Fluoro-4-benzyloxybenzoic acid, 2-fluoro-4-*n*-alkoxybenzoic acids and 3-fluoro-4-*n*-alkoxybenzoic acids were prepared according to procedures reported in the literature [14, 15]. The detailed synthetic procedure for one of the representative compounds and the associated physical data are given below.

2.2.1. *Benzyl 4-(n-dodecyloxybenzoyloxy)benzoate,* **a** *($R = n\text{-}C_{12}H_{25}O$)*

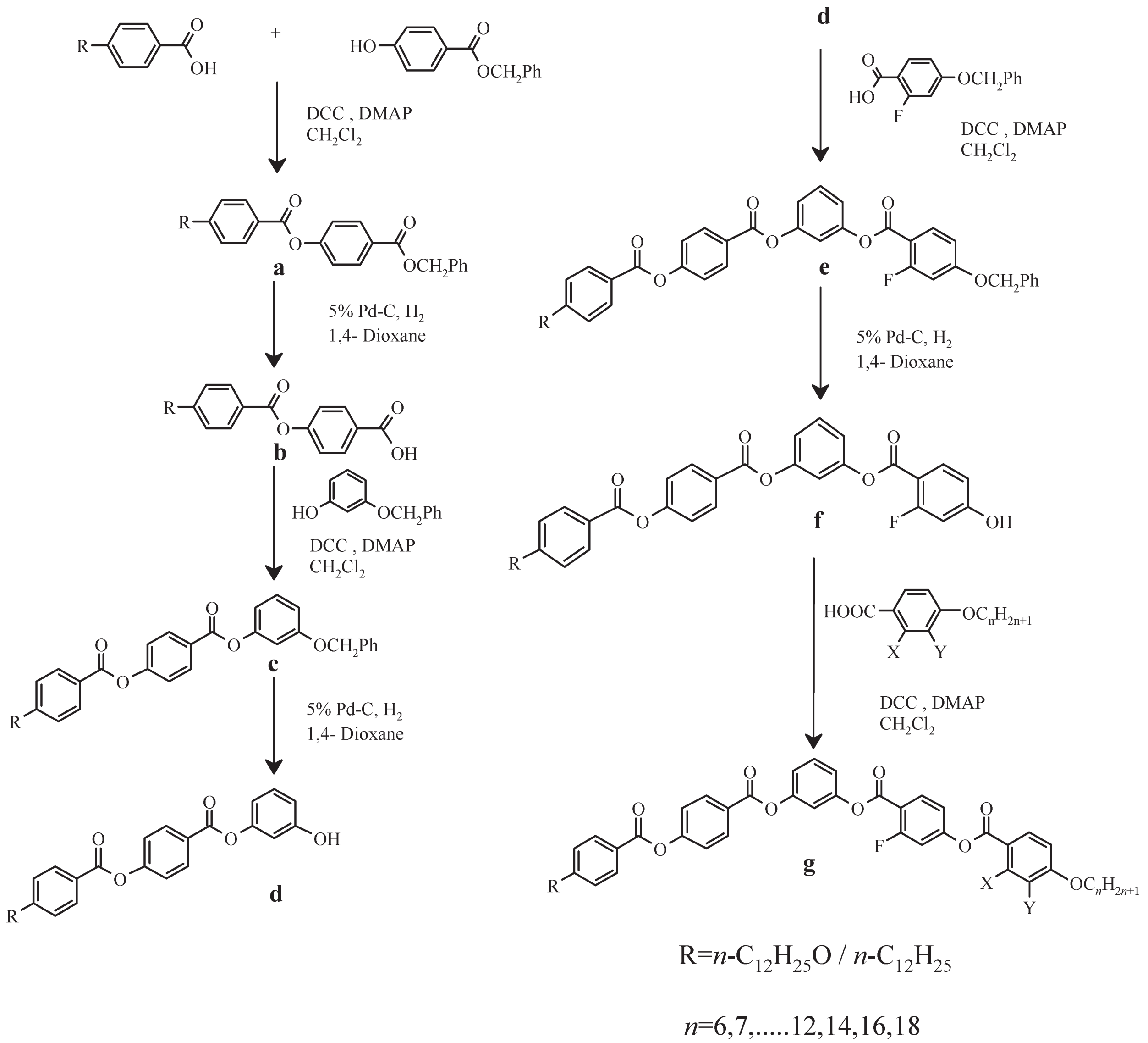
A mixture of 4-*n*-dodecyloxybenzoic acid (9.0 g, 29.4 mmol), benzyl-4-hydroxybenzoate (6.7 g, 29.4 mmol), a catalytic amount of 4-(*N*,*N*-dimethylamino)pyridine (DMAP), and dry dichloromethane (100 ml) was stirred for 10 min. To this mixture *N*,*N*′-dicyclohexylcarbodiimide (DCC), (6.66 g, 32.3 mmol) was added and stirring continued overnight. The reaction mixture was diluted with dichloromethane and the precipitated *N*,*N*′-dicyclohexylurea filtered off. The filtrate was washed successively with 5% aqueous acetic acid (25 ml × 2), 5% ice-cold sodium hydroxide solution, (25 ml × 2) and water (25 ml × 3); it was then dried over anhydrous sodium sulphate. The solvent was removed to yield a residue that was purified by column chromatography on silica gel using chloroform as eluant. Removal of solvent from the eluate gave a white material, which was crystallized from a mixture of chloroform and acetonitrile; yield 13.1 g (86%), m.p. 62–63°C. IR (nujol) $\nu_{\max}$: 2918, 2851, 1732, 1714,1608, 1470, 1292 $\mathrm{cm^{-1}}$. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.16–8.12 (m, 4H, Ar–H), 7.46–7.35 (m, 5H, Ar–H), 7.30–7.28 (d, 2H, ^3J8.72 Hz, Ar–H), 6.98–6.96 (d, 2H, ^3J8.92 Hz, Ar–H), 5.38 (s, 2H, $-O-CH_2-Ar$), 4.06–4.02 (t, 2H, ^3J6.52 Hz, $Ar-O-CH_2-$), 1.85–1.78 (quin, 2H, ^3J7.0 Hz, $Ar-O-CH_2-C\underline{H_2}-$), 1.50–1.43 (quin, 2H, ^3J7.0 Hz, $Ar-O-CH_2-CH_2-C\underline{H_2}-$), 1.32–1.27 (m, 16H, $8 \times -CH_2-$), 0.90–0.86 (t, 3H ^3J6.6Hz, $-CH_3$). Anal: $C_{33}H_{40}O_5$ requires C 76.71, H 7.80; found C 76.65, H 7.94%.

2.2.2. *4-n-Dodecyloxybenzoyloxy-4-benzoic acid,* **b**

Compound **a** (13.0 g, 25.1 mmol), was dissolved in 1, 4-dioxane (100 ml). To this solution 5% Pd-C catalyst (2.7 g) was added and the mixture was stirred at 40°C under hydrogen until the required quantity of hydrogen was absorbed. The reaction mixture was filtered and the solvent removed from the filtrate under reduced pressure. The product thus obtained was crystallized from a mixture of 1,4-dioxane and petroleum ether (b.p. 60–80°C); yield 9.9 g (92%), m.p.119–120°C. IR (nujol) $\nu_{\max}$: 3070, 2972, 2851, 2548, 1732, 1688, 1603, 1261, 1161 $\mathrm{cm^{-1}}$. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.21–8.18 (d, 2H, ^3J8.68 Hz, Ar–H), 8.15–8.13 (d, 2H, ^3J8.88 Hz, Ar–H), 7.35–7.32 (d, 2H, ^3J8.68 Hz, Ar–H), 6.99–6.97 (d, 2H, ^3J8.88 Hz, Ar–H), 4.06–4.03 (t, 2H, ^3J6.52 Hz, $Ar-O-CH_2-$), 1.86–1.79 (quin, 2H, ^3J7.0 Hz, $Ar-O-CH_2-C\underline{H_2}-$), 1.51–1.44 (quin, 2H, ^3J7.0 Hz, $Ar-O-CH_2-CH_2-C\underline{H_2}-$), 1.36–1.26 (m, 16H, $8 \times -CH_2-$), 0.90–0.86 (t, 3H, ^3J6.48 Hz, $-CH_3$). Anal: $C_{26}H_{34}O_5$ requires C 73.21, H 8.03; found C 73.61, H 8.3%.

2.2.3. *1-Benzyloxy-3-[4-(4-n-dodecyloxybenzoyloxy)-benzoyloxy]benzene,* **c**

This compound was prepared using the procedure described for compound **a**. Quantities: compound **b**



Scheme. Synthetic pathway used to prepare the unsymmetrical bent-core compounds.

(9.8 g, 23 mmol), 3-benzyloxyphenol (4.6 g, 23 mmol), catalytic amount of DMAP, DCC (5.2 g, 25.3 mmol) and dry dichloromethane (50 ml); yield 12.0 g (86%), m.p. 97–98°C. IR (nujol) ν_{max}: 2924, 2856, 1736, 1605, 1256, 1061 cm^{-1}. ^{1}H NMR (500 MHz, CDCl$_3$) δ: 8.28–8.26 (d, 2H, ^3J8.65 Hz, Ar–H), 8.16–8.14 (d, 2H, ^3J8.8 Hz, Ar–H), 7.45–7.32 (m, 8H, Ar–H,), 7.00–6.98 (d, 2H, ^3J8.8 Hz, Ar–H), 6.92–6.84 (m, 3H, Ar–H), 5.08 (s, 2H, O–CH$_2$–Ar), 4.07–4.04 (t, 2H, ^3J6.55 Hz, Ar–O–CH$_2$–), 1.86–1.80 (quin, 2H, ^3J7.1 Hz, Ar–O–CH$_2$–C$\underline{H}_2$–), 1.51–1.45 (quin, 2H, ^3J7.1 Hz, Ar–O–CH$_2$–CH$_2$–C$\underline{H}_2$–), 1.28–1.37 (m, 16H, 8 × –CH$_2$–), 0.90–0.87 (t, 3H, ^3J6.7 Hz, –CH$_3$). Anal: C$_{39}$H$_{44}$O$_6$ requires C 76.95, H 7.29; found C 76.50, H 7.43%.

2.2.4. *3-Hydroxyphenyl 4-(4-n-dodecyloxybenzoyloxy)-benzoate,* ***d***

This compound was prepared using the procedure described for compound **b**. Quantities: compound **c** (11.8 g, 19.4 mmol), 1, 4-dioxane (75 ml), 5% Pd-C (1.8 g); yield 9.1 g (90%), m.p. 124.5–125.5°C. IR (nujol) ν_{max}: 3377, 3315, 2922, 2853, 1734, 1713, 1605, 1252, 1067 cm^{-1}. ^{1}H NMR (500 MHz, CD$_3$COCD$_3$) δ: 8.66 (s, 1H, Ar–OH, exchangeable with D$_2$O), 8.27–8.25 (d, 2H, ^3J8.7 Hz, Ar–H), 8.16–8.14 (d, 2H, ^3J8.9 Hz, Ar–H), 7.51–7.49 (d, 2H, ^3J8.7 Hz, Ar–H), 7.29–7.26 (t, 1H, ^3J7.45 Hz, Ar–H), 7.14–7.12 (d, 2H, ^3J8.9 Hz, Ar–H), 6.81–6.77 (m, 3H, Ar–H), 4.17–4.14 (t, 2H, ^3J6.5 Hz, Ar–O–CH$_2$–), 1.86–1.81 (quin, ^3J7.1 Hz, 2H, Ar–O–CH$_2$–C$\underline{H}_2$–), 1.54–1.48 (quin, 2H, ^{3}J7.1 Hz, Ar–O–CH$_2$–CH$_2$–C$\underline{H}_2$–), 1.40–1.30 (m, 16H, 8 × –CH$_2$–), 0.90–0.87 (t, 3H, ^{3}J6.7 Hz, –CH$_3$). Anal: $C_{32}H_{38}O_6$ requires C 74.11, H 7.39; found C 74.52, H 7.35%.

2.2.5. *1-(2-Fluoro-4-benzyloxybenzoyloxy)-3-[4-(4-n-dodecyloxybenzoyloxy)benzoyloxy]benzene,* ***e***

This compound was prepared using the same procedure as described for compound **a**. Quantities: compound **d** (3.5 g, 6.8 mmol), 2-fluoro-4-benzyloxybenzoic acid (1.66 g, 6.8 mmol), catalytic amount of DMAP, DCC (1.53 g, 7.4 mmol) and dry dichloromethane (20 ml); yield, 3.8 g (75%), m.p.103–104°C. IR (nujol) $\nu_{\max}$: 2923, 2853, 1737, 1723, 1604, 1256, 1163, 1063 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$) δ: 8.28–8.26 (d, 2H, ^{3}J8.68 Hz, Ar–H), 8.16–8.14 (d, 2H, ^{3}J8.88 Hz, Ar–H), 8.08–8.04 (t, 1H, ^{3}J8.6 Hz, Ar–H), 7.49–7.36 (m, 7H, Ar–H), 7.18–7.16 (m, 4H, Ar–H), 7.0–6.98 (d, 2H, ^{3}J8.88 Hz, Ar–H), 6.88–6.85 (dd, 1H, ^{3}J8.84 Hz, ^{4}J2.36 Hz, Ar–H), 6.80–6.76 (dd, 1H, ^{3}J12.48 Hz, ^{4}J2.28 Hz, Ar–H), 5.14 (s, 2H, O–CH$_2$–Ar), 4.07–4.04 (t, 2H, ^{3}J6.52 Hz, Ar–O–CH$_2$–), 1.86–1.80 (quin, 2H, ^{3}J6.92 Hz, Ar–O–CH$_2$–C$\underline{H}_2$–), 1.50–1.27 (m, 18H, 9 × –CH$_2$–), 0.90–0.87 (t, 3H, ^{3}J6.52 Hz, –CH$_3$).

2.2.6. *1-(2-Fluoro-4-hydroxybenzoyloxy)-3-[4-(4-n-dodecyloxybenzoyloxy)benzoyloxy]benzene,* ***f***

This was synthesized following the procedure described for the preparation of compound **b**. Quantities: compound **e** (3.5 g, 7.97 mmol), 1, 4-dioxane (50 ml), 5% Pd-C (0.8 g); yield 2.7 g (88%), m.p.181–182°C. IR (nujol) $\nu_{\max}$: 3346, 3072, 2922, 2853, 1742, 1726, 1715, 1697, 1601, 1248, 1136, 1055 cm^{-1}. ^{1}H NMR (400 MHz, CD$_3$COCD$_3$) δ: 10.1 (s, 1H, Ar–OH, exchangeable with D$_2$O), 8.44–8.42 (dd, 2H, ^{3}J8.76 Hz, ^{4}J2.0 Hz, Ar–H), 8.30–8.28 (dd, 2H, ^{3}J8.92 Hz, ^{4}J2.0 Hz, Ar–H), 8.19–8.14 (t, 1H, ^{3}J8.68 Hz, Ar–H), 7.73–7.64 (m, 3H, Ar–H), 7.46–7.38 (m, 3H, Ar–H), 7.27–7.25 (dd, 2H, ^{3}J8.92 Hz, ^{4}J2.0 Hz, Ar–H), 7.0–6.97 (dd, 1H, ^{3}J8.76 Hz, ^{4}J2.0 Hz, Ar–H), 6.90–6.86 (dd, 1H, ^{3}J12.8 Hz, ^{4}J2.8 Hz, Ar–H), 4.30–4.27 (t, 2H, ^{3}J6.5 Hz, Ar–O–CH$_2$–), 1.99–1.93 (quin, 2H, ^{3}J6.92 Hz, Ar–O–CH$_2$–C$\underline{H}_2$–), 1.53–1.30 (m, 18H, 9 × –CH$_2$–,), 1.03–1.0 (t, 3H, ^{3}J6.5 Hz, –CH$_3$)

2.2.7. *1-[4-(2-Fluoro-4-n-decyloxybenzoyloxy)-2-fluorobenzoyloxy]-3-[4-(4-n-dodecyloxybenzoyloxy)-benzoyloxy]benzene,* **5**

This compound was prepared using the same procedure as described for compound **a**. Quantities: compound **f** (0.150 g, 0.23 mmol), 2-fluoro-4-*n*-decyloxybenzoic acid (0.069 g, 0.23 mmol), catalytic amount of DMAP, DCC (0.053 g, 0.026 mmol) and dry dichloromethane (10 ml); yield 69%, m.p. 87.0°C. IR (KBr) $\nu_{\max}$: 3071, 2922, 2851, 1744, 1734, 1616, 1603, 1252, 1128, 1059 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$) δ: 8.29–8.27 (d, 2H, ^{3}J8.76 Hz, Ar–H), 8.20–8.14 (m, 3H, Ar–H), 8.06–8.01 (t, 1H, ^{3}J8.68 Hz, Ar–H), 7.52–7.48 (t, 1H, ^{3}J8.16 Hz, Ar–H), 7.39–7.36 (d, 2H, ^{3}J8.76 Hz, Ar–H), 7.21–7.17 (m, 5H, Ar–H), 7.0–6.98 (d, 2H, ^{3}J8.92 Hz, Ar–H), 6.80–6.78 (dd, 1H, ^{3}J8.92 Hz, ^{4}J2.28 Hz, Ar–H), 6.72–6.68 (dd, 1H, ^{3}J12.76 Hz, ^{4}J2.32 Hz, Ar–H), 4.07–4.02 (2t, 4H, ^{3}J6.6 Hz, 2 × Ar–O–CH$_2$–), 1.84–1.79 (m, 4H, 2 × Ar–O–CH$_2$–C$\underline{H}_2$–), 1.48–1.27 (m, 32H, 16 × –CH$_2$–), 0.90–0.87 (m, 6H, 2 × –CH$_3$).

3. Results and discussion

3.1. *Optical and thermal behaviour*

Transition temperatures and enthalpy data, as determined from DSC thermograms, for compounds of series I are collected in table 1. Two types of mesophase were observed in this homologous series of compounds. Compounds **1** and **2** are monotropic and when observed through a polarizing microscope exhibit similar optical textures on cooling from the isotropic liquid. The growth of a mosaic or spherulitic texture clearly indicated that the mesophase is a rectangular columnar B$_1$ phase. A typical texture developing from the isotropic liquid of compound **1** is shown in figure 1.

When the length of one of the arms was increased by a methylene unit, compound **3** was obtained; this was also monotropic but exhibited a fringe pattern or a schlieren texture on cooling the isotropic liquid. Compounds **4–10** showed similar optical textures. Typical textures obtained for the mesophase of compound **5** are shown in figures 2(*a*) and 2(*b*).

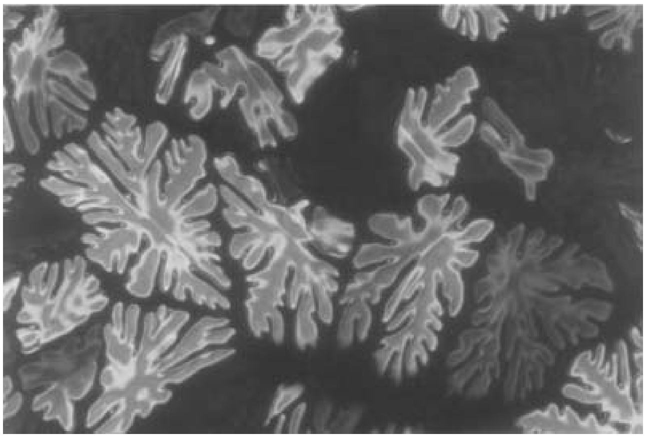


Figure 1. An optical photomicrograph obtained for the B$_1$ mesophase of compound **1**.

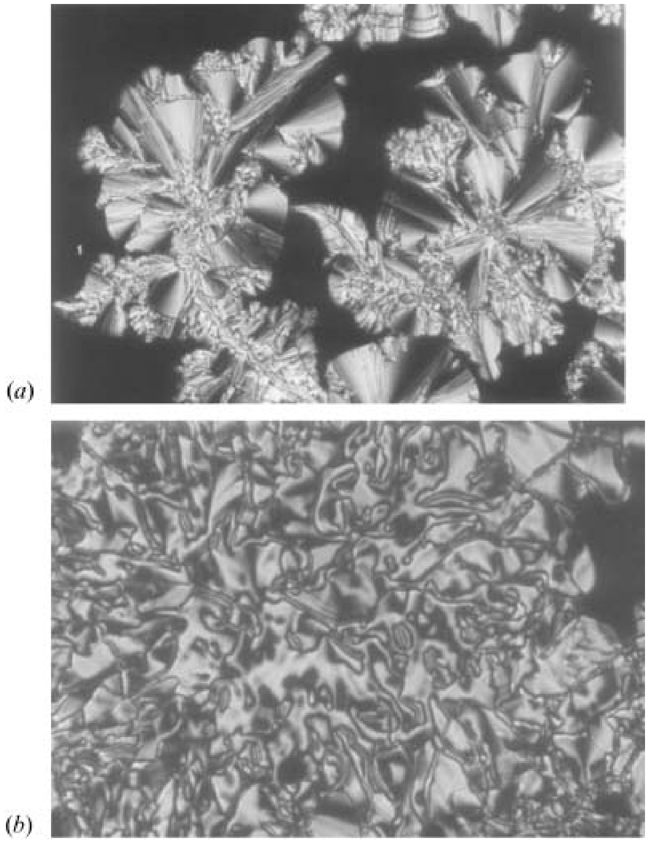
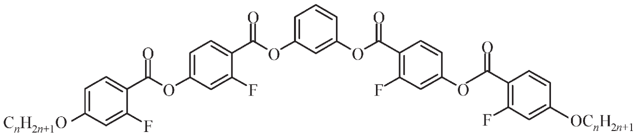


Figure 2. (*a*) and (*b*). Optical photomicrographs obtained for the B_2 mesophase of compound **5**.

These suggest that the mesophase could be a lamellar B_2 phase, which was confirmed through XRD and electro-optical studies.

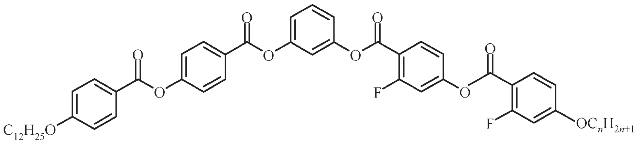
We reported earlier a systematic study of the influence of a lateral fluorine substituent on the mesomorphic properties of symmetrical five-ring esters derived from resorcinol [11]. A comparison of the properties exhibited by the unsymmetrical compounds of series I (see table 1) with those of the symmetrical compounds (Structure **A**) indicates that in both the symmetrical and unsymmetrical compounds, B_1 and B_2 phases are observed. However, the unsymmetrical compounds have lower melting points as a result of which the thermal ranges of the mesophases are greater.

Interestingly, a fluorine substituent which is *ortho* to the terminal *n*-alkoxy chain in symmetrical compounds induces ferroelectric mesophases [9–13], especially for longer terminal chain lengths. It is of interest, therefore, to explore other structural requirements for obtaining the rarely observed ferroelectric mesophases in achiral bent-core compounds. With this in view, several compounds were synthesized in which fluorine substitution was effected in only one of the arms of the bent-core compounds.



Structure **A** [11]

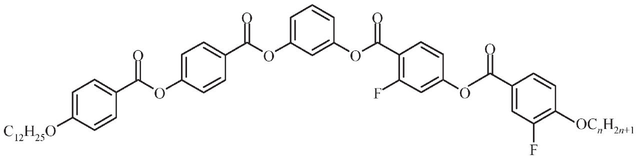
Table 1. Transition temperatures (°C) and associated enthalpies (kJ mol^{-1}) for the unsymmetrical compounds **1**–**10** of series I. Cr = crystalline phase; B_2 = smectic antiferroelectric phase; B_1 = rectangular columnar phase; I = isotropic phase; *compounds have crystal–crystal transition, enthalpy denoted in italics is the sum of all such transitions.



Compound	*n*	Cr		B_2		B_1		I
1	6	•	97.5 *53.6*	—		(•	87.0) *13.5*	•
2	7	•	97.0 *60.6*	—		(•	86.0) *14.6*	•
3	8	•	97.0* *61.2*	(•	90.5) *18.5*	—		•
4	9	•	98.0* *73.9*	(•	94.0) *19.2*	—		•
5	10	•	87.0* *29.5*	•	97.0 *20.2*	—		•
6	11	•	90.0* *33.2*	•	99.5 *21.2*	—		•
7	12	•	91.0 *38.6*	•	101.5 *20.9*	—		•
8	14	•	86.0 *56.5*	•	104.0 *22.5*	—		•
9	16	•	86.0* *53.4*	•	105.0 *23.0*	—		•
10	18	•	93.0 *56.4*	•	106.0 *23.6*	—		•

The transition temperatures and associated enthalpies for the homologues of series II are summarized in table 2. These contain a fluorine *ortho* to the terminal *n*-alkoxy chain and another fluorine *ortho* to the carboxylate group of the middle phenyl ring. Compound **11** is non-mesomorphic while compounds **12**–**20** showed enantiotropic B_2 phase. It can be seen from tables 1 and 2 that the clearing temperatures of the compounds of series II are enhanced by 13–20°C, with a marginal increase in the melting points. Thus, shifting the fluorine substituent from *meta* to the *ortho*-position with respect to the terminal *n*-alkoxy chain has resulted

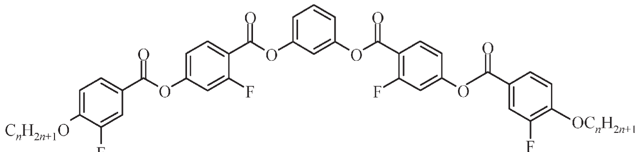
Table 2. Transition temperatures (°C) and associated enthalpies (kJ mol^{-1}) for the unsymmetrical compounds **11**–**20** of series II. For key see table 1.



Compound	n	Cr		B$_2$		I
11	6	●	101.0 *40.5*	—		●
12	7	●	101.0 *30.4*	●	106.0 *19.7*	●
13	8	●	100.5* *34.0*	●	110.0 *20.9*	●
14	9	●	101.0* *28.9*	●	112.5 *21.0*	●
15	10	●	100.0* *28.9*	●	114.5 *22.2*	●
16	11	●	99.5* *20.1*	●	116.0 *22.6*	●
17	12	●	97.0* *62.3*	●	117.5 *22.8*	●
18	14	●	95.0* *43.2*	●	119.0 *24.1*	●
19	16	●	94.0* *47.0*	●	119.5 *24.0*	●
20	18	●	93.0* *52.1*	●	119.5 *23.8*	●

in a reasonably large thermal range for the B$_2$ mesophase.

Again, comparing the mesomorphic properties of the compounds of series II with those of the symmetrical compounds (Structure **B**) already reported [11], it can be inferred that the higher homologues of the latter exhibit ferroelectric properties while the corresponding unsymmetrical compounds are antiferroelectric in nature. Thus, the position and the number of fluorine substituent(s) play an important role in inducing ferro-/antiferro-electric properties in these five-ring bent-core ester compounds.



Structure **B** [11]

In addition, a comparison can be made of the melting and clearing temperatures for the compounds of series I and II which exhibit the B$_2$ phase, and a plot of these is shown in figure 3. It can be seen that the thermal range of the B$_2$ phase is wider for compounds of series II and all these compounds exhibit an enantiotropic B$_2$ phase.

It is now relatively well established that compounds containing an *n*-alkyl chain have lower transition temperatures than their *n*-alkoxy analogues. Bent-core compounds containing an *n*-alkyl chain are few in number. In order to see the effect of replacing the *n*-alkoxy chain present in compounds of series I and II by an *n*-alkyl chain, two more homologous series of compounds (series III and IV) were prepared. The transition temperatures and the associated enthalpy values for the compounds of series III are summarized in table 3. It can be seen that the phase behaviour is similar to those compounds of series I. As expected the *n*-alkyl analogues have lower melting points and hence a large thermal range for the B$_2$ mesophase.

It is appropriate to point out here the observations made in other systems. There has been a systematic study of the influence of fluorine substitution on a central 3, 4′-disubstituted biphenyl unit and some of these bent-core compounds exhibit SmCP$_A$ phases with extremely large values of spontaneous polarization [16]. Similarly, detailed investigations on the effect of replacing the terminal *n*-alkoxy chains by *n*-alkyl chains on the mesophases formed using this central unit have also been carried out [17].

In the fourth series of compounds, which are the *n*-alkyl analogues of compounds of series II, the phase behaviour is similar. The transition temperatures and the associated enthalpies for compounds of series IV are summarized in table 4. Except for compound **31**, which is non-mesomorphic, the remaining homologues exhibit an enantiotropic B$_2$ phase. In this series also,

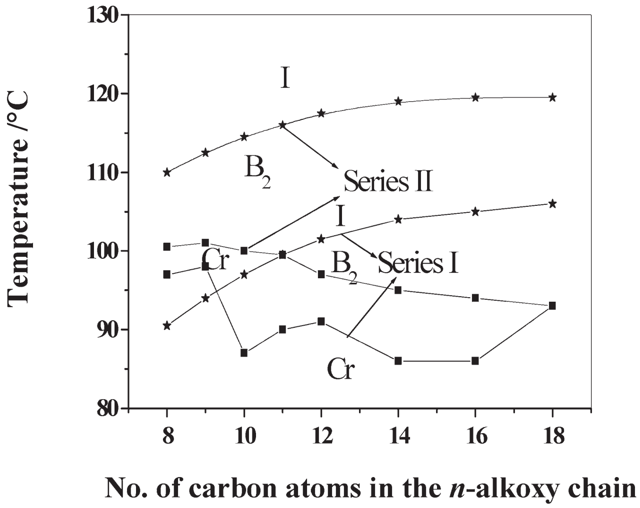
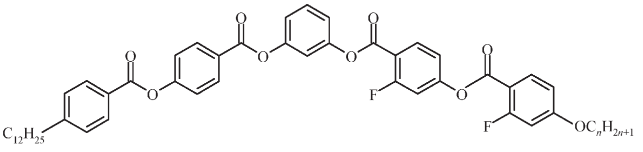


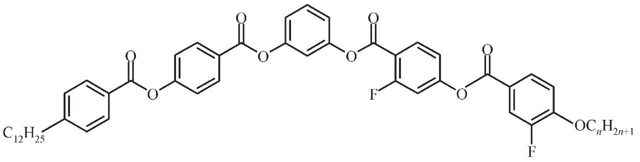
Figure 3. A comparison of transition temperature as a function of the number of carbon atoms in the *n*-alkoxy chain for compounds of series I and II.

Table 3. Transition temperatures (°C) and associated enthalpies (kJ mol^{-1}) for the unsymmetrical compounds **21**–**30** of series III. For key see table 1.



Compound	*n*	Cr		B_2		B_1		I
21	6	•	90.0 *47.1*	—		(•	82.0) *13.7*	•
22	7	•	88.0 *47.7*	(•	85.0) *17.3*	—		•
23	8	•	77.0 *15.3*	•	90.0 *18.6*	—		•
24	9	•	84.0 *36.3*	•	93.5 *19.5*	—		•
25	10	•	89.5 *41.6*	•	97.0 *20.1*	—		•
26	11	•	73.5 *25.7*	•	99.0 *20.8*	—		•
27	12	•	72.0 *24.3*	•	100.0 *21.3*	—		•
28	14	•	73.5 *43.5*	•	102.0 *22.0*	—		•
29	16	•	69.0 *35.3*	•	103.0 *23.2*	—		•
30	18	•	72.5 *45.6*	•	103.5 *23.9*	—		•

Table 4. Transition temperatures (°C) and associated enthalpies (kJ mol^{-1}) for the unsymmetrical compounds **31**–**40** of series IV. For key see table 1.



Compound	*n*	Cr		B_2		I
31	6	•	103.0 *41.0*	—		•
32	7	•	98.5 *21.5*	•	104.0 *19.6*	•
33	8	•	97.5 *21.3*	•	108.0 *20.7*	•
34	9	•	96.0* *40.1*	•	110.5 *20.8*	•
35	10	•	95.0* *43.9*	•	112.5 *22.1*	•
36	11	•	94.0* *63.4*	•	113.5 *22.9*	•
37	12	•	94.0* *50.5*	•	114.5 *22.9*	•
38	14	•	90.0* *55.1*	•	115.0 *23.5*	•
39	16	•	87.0 *14.8*	•	115.5 *23.6*	•
40	18	•	82.0 *71.5*	•	115.5 *24.0*	•

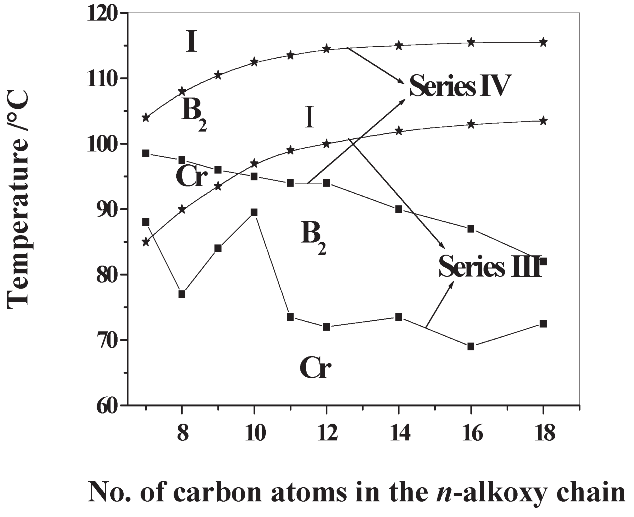


Figure 4. A comparison of transition temperature as a function of the number of carbon atoms in the *n*-alkoxy chain for compounds of series III and IV.

there is a reduction of temperature in both the melting and clearing points, as compared with those of series II. A comparison of the transition temperatures of compounds exhibiting the B_2 phase for these two series III and IV is shown in figure 4. It is clear from this figure that the *meta*-fluoro-substituted (with respect to the *n*-alkoxy chain) compounds of series III have lower transition temperatures.

3.2. *X-ray diffraction studies*

To confirm the mesophase structures, we carried out XRD studies on different compounds representing the four homologous series. The samples were taken in Lindemann capillaries (0.7 mm) the ends of which were sealed. The XRD patterns were collected on an image plate. The *d*-spacings obtained for all the compounds investigated are given in table 5.

Compound **1** gave two reflections in the small angle region at $d_1 = 25.5$ Å and $d_2 = 20.8$ Å. This can be indexed as the (1 1) and (0 2) reflections of a rectangular lattice.

The *d*-values obtained in the small angle region for compounds **5** and **10** indicate that the mesophases are smectic. The *d*-values obtained for compounds **15** and **20**, which are isomeric with compounds of **5** and **10** (series II), are somewhat interesting. The *d*-sapcings of compounds **15** and **20** are larger by 3–5 Å as compared with the isomeric compounds. This is due to the presence of fluorine, which is *ortho* to the *n*-alkoxy chain, and has an influence on its conformation. Similarly, the *d*-values obtained for compounds **22** and **30** can be compared with those of the isomeric compounds **32** and **40**. Here also one sees a larger *d*-spacing for the compounds that have fluorine in the *ortho*-position with respect to the *n*-alkoxy chain.

Thus, from XRD studies we can clearly conclude that the compounds of series I and III, exhibiting a smectic phase, have a different *n*-alkoxy chain conformation than their isomeric analogues in series II and IV. The *d*-spacings obtained for the different compounds examined are given in table 5. However, it is also possible that in the case of compounds of series I and series III which exhibit the B_2 phase, the shortened layer spacings observed could be due to steric reasons caused by the lateral fluorine substituent. This factor would enhance the separation of the aromatic cores thereby allowing the *gauche* conformations of the chain, which results in the observed shorter layer spacings.

3.3. *Electro-optical studies*

To confirm the antiferroelectric nature of the B_2 phase of compounds of series I to IV, triangular–wave electric field experiments were carried out on representative compounds belonging to the four homologous series. The general behaviour in all the compounds, studied was the same. For these experiments, home-made cells treated for homogeneous alignment of the sample were used. The cells were constructed by coating polyimide onto ITO coated glass plates, which were rubbed unidirectionally. The thickness of the cells was adjusted with Mylar spacers. The sample of compound **5**, which was filled into the cell in the isotropic phase, was cooled slowly from the isotropic phase under a triangular-wave electric field. When the voltage was above the threshold, two polarization current peaks per half cycle were observed. Figure 5 shows the switching current response obtained for the mesophase of compound **5** at a voltage of 184 V_{pp} at 40 Hz. By these triangular-wave experiments, we infer that the mesophase has an antiferroelectric ground state which is a typical feature of the B_2 phase.

Table 5. The *d*-values obtained from XRD studies of different compounds belonging to series I to series IV, and their Miller indices.

Compound	*d*-values/Å d_1	d_2	d_3	Phase type
1	25.5 (11)	20.8 (02)	—	B_1
5	33.1 (01)	16.5 (02)	11.0 (03)	B_2
10	38.2 (01)	—	12.7 (03)	B_2
15	37.8 (01)	18.9 (02)	9.5 (04)	B_2
20	41.3 (01)	—	13.8 (03)	B_2
22	31.6 (01)	15.8 (02)	—	B_2
30	37.5 (01)	—	12.5 (03)	B_2
32	36.2 (01)	18.1 (02)	—	B_2
40	41.3 (01)	—	13.8 (03)	B_2

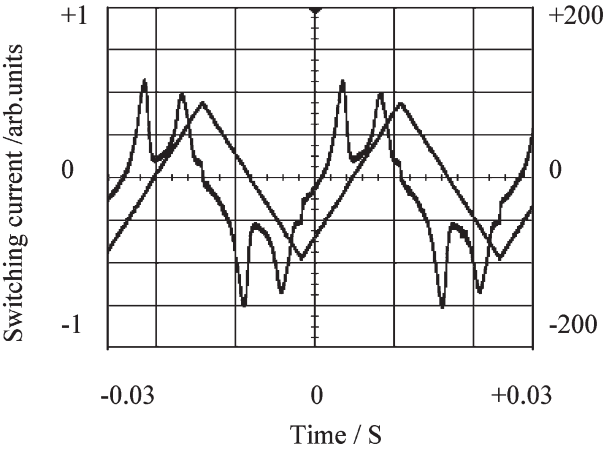


Figure 5. Switching current response obtained for compound **5** on applying a triangular-wave electric field (±92 V, 40 Hz,); the saturated polarization value is ≈585 nC cm^{-2}, cell thickness 10.8 μm.

Since a fluorine substituent *ortho* to the *n*-alkoxy chain resulted in symmetrical compounds showing ferroelectric mesophases, we carried out electro-optical experiments on compounds of series II. A sample of compound **20** was taken in a cell treated for homogeneous alignment of the sample of thickness 12.8 μm. On applying a voltage of 292 V_{pp} at 8 Hz, two polarization current peaks were observed, indicating

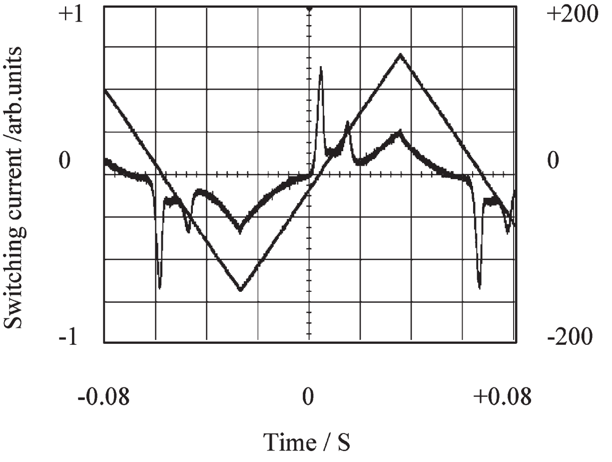


Figure 6. Switching current response obtained for compound **20** on applying a triangular-wave electric field (±146 V, 8 Hz,); the saturated polarization value is ≈605 nC cm^{-2}, cell thickness 12.8 μm.

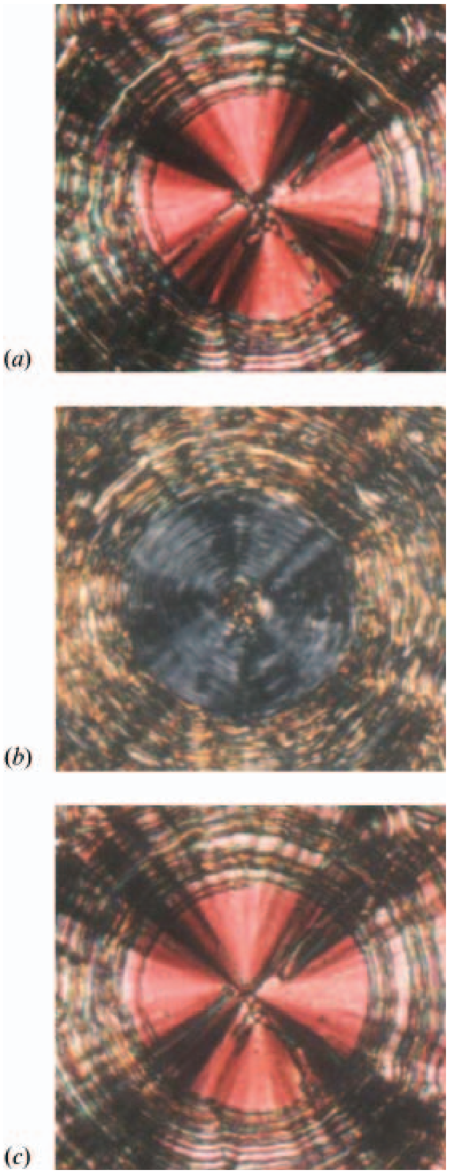


Figure 7. Optical photomicrographs of compound **5** showing the effect of a d.c. field: (*a*) $-5\,\mathrm{V\,\mu m^{-1}}$, (*b*) 0 V, (*c*) $+5\,\mathrm{V\,\mu m^{-1}}$; the rotation of brushes indicates the anticlinic tilt of the molecules in the B_2 (SmC_AP_A) phase.

the antiferroelectric ground state. Thus, unlike symmetrical *ortho*-substituted compounds, the unsymmetrical compounds showed antiferroelectric behaviour. A typical switching current response obtained for compound **20** is shown in figure 6.

To study the tilt sense in the antiferroelectric B_2 phase we carried out d.c. field experiments. A sample of compound **5** was taken in a cell treated for homogeneous alignment of the sample of thickness 10 μm and cooled slowly from the isotropic phase under a d.c. voltage of $5\,\mathrm{V\,\mu m^{-1}}$. Circular domains with dark brushes making an angle with respect to the analyser were obtained, which indicates a synclinic tilt of the molecules in a field-induced state. When the polarity of the applied field was reversed the orientation of the brushes rotated in an anticlockwise direction and the mesophase shifted to another ferroelectric state. However, when the field was switched off, the brushes rotated along the analyser direction. Optical photomicrographs obtained with and without the field are shown in figures 7 (*a–c*). This tristable switching indicates that the compound has a SmC_AP_A ground state structure, and on applying a d.c. field shifts to a SmC_SP_F structure.

4. Conclusions

The mesomorphic properties of 40 unsymmetrical achiral BC compounds belonging to four different homologous series were investigated. These are esters and are thermally stable. A majority of the compounds investigated show an antiferroelectric B_2 phase. XRD studies of compounds with fluorine substitution at the *ortho*-position with respect to the *n*-alkoxy chain (series II and IV) show a B_2 phase with larger *d*-spacings than those of compounds with fluorine at the *meta*-position (series I and III). This indicates that the conformation of the *n*-alkoxy chain is affected by the presence of the highly electronegative fluorine substituent in the *ortho*-position. The position and number of fluorine substituents play a role in inducing the ferro-/antiferroelectric mesophases in these five-ring bent-core achiral compounds.

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