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Novel bent-shaped liquid crystalline compounds II. Synthesis and properties of the 1,3-bis{4-[4-(4-alkyloxybenzoyloxy)benzylidene]aminophenoxy}propan-2-ols

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Novel bent-shaped liquid crystalline compounds
II. Synthesis and properties of the 1,3-bis{4-[4-(4-alkyloxybenzoyloxy)benzylidene]aminophenoxy}propan-2-ols†

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A series of new symmetric dimer compounds was synthesized, constaining 2-hydroxy-1,3-dioxypropylene as the central linkage and terminal alkyl chains with different lengths. The chemical structures of the liquid crystal dimers (2ES-*n*) were examined by FTIR and ^{1}H NMR spectroscopy. Their mesomorphism, thermodynamic properties and optical textures were investigated by differential scanning calorimetry, polarizing optical microscope and X-ray diffraction. For homologues with terminal propyloxy and butyloxy chains, no liquid crystalline phase was observed. Homologues with pentyloxy and hexyloxy terminal chains showed nematic phases, while those with heptyloxy, octyloxy, nonyloxy and decyloxy terminal chains displayed nematic phases and smectic phases. The results confirmed that the liquid crystalline phase changes from nematic to smectic as the terminal chain length increases.

1. Introduction

Liquid crystalline dimers (dimesogens, twins, bimesogens, etc.) have attracted much attention in recent years because they exhibit a variety of phases and serve as useful models for semi-flexible, main chain liquid crystal polymers [2–4]. In typical dimers, symmetric [5, 6] or non-symmetric [7, 8], two individual mesogenic entities are linked via flexible spacer units. Dimers with an even-numbered spacer form SmA phases and/or nematic phases while homologous compounds with an odd-numbered spacer exhibit SmC phases [9, 10]. The structure of the smectic phases can also be modified through change in spacer length and terminal chain length. If the length of the terminal chains is smaller than or comparable to the length of the spacer, an intercalated SmC structure of the bent molecules, characterized by a random mixing of the terminal chains and the spacer [9, 10], is formed. On the other hand, when the terminal chains are significantly longer than the spacer, the tails and the spacer can segregate from each other, giving rise to a biaxial structure where the bent molecules are packed in smectic layers with a uniform bent direction [11]. The compounds also form two-dimensional frustrated smectic phases when the lengths of the spacer and the terminal chains are between the ranges described above [11].

The molecular structures of the dimeric compounds synthesized in the present study are shown in figure 1. Two identical three-ring mesogenic units are linked through a 2-hydroxy-1,3-dioxypropylene spacer, thus introducing a polar hydroxy group in the centre of the polymethylene spacer moiety of the molecules. The mesomorphic properties of the compounds were studied by differential scanning calorimetry (DSC), polarizing optical microscopy (POM) and X-ray diffraction (XRD).

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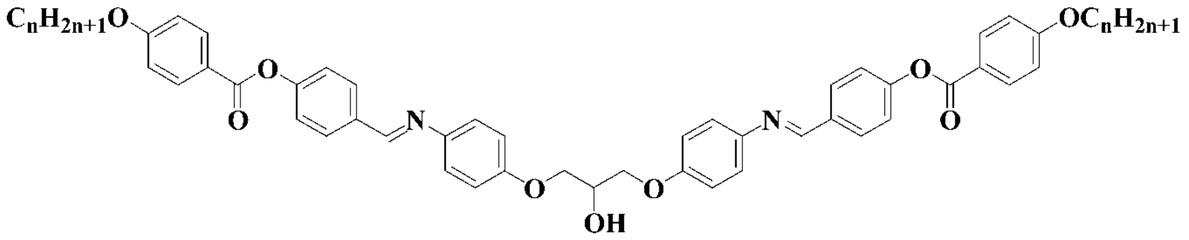


2ES-*n* (*n* = 3 - 10)

Figure 1. Chemical structure of the 2ES-*n* series.

2. Experimental

2.1. *Materials*

n-Alkyl bromides, *p*-hydoxybenzoic acid, *p*-hydroxybenzaldehyde (HBA), anhydrous EtOH, MeOH, 1,3-dichloro-2-propanol, *p*-hydroxynitrobenzene, 1,3-dicyclohexylcarbodiimide (DCC), *p*-dimethylaminopyridine (DMAP), *p*-toluenesulphonic acid monohydrate (PTSA), and palladium on activated carbon (10% Pd/C) were purchased as GR grade reagents from Aldrich Chemical Co. and used as received. Tetrahydrofuran (THF) was dried from sodium benzophenone ketyl and stored under nitrogen; other solvents were dried by standard procedures. All column chromatography was performed with the use of silica gel (230–400 mesh, Merck Co.) as the stationary phase in a column.

2.2. *Characterization*

IR spectra were recorded with a Perkin-Elmer 1000 FTIR spectrophotometer using KBr pellets. ^{1}H NMR spectra were recorded with a Varian Mercury 300 (300 MHz) NMR spectrometer. DSC analysis was performed using a TA instruments 910S DSC under dry nitrogen at a scanning rate of 10°C min^{-1}. Transition temperatures were taken at the peak maximum for each sample. Transition enthalpies were evaluated from the integrated area of endothermic peaks using a reference indium sample as standard. Elemental analyses were performed using an Eager 200 elemental analyser. Optical microscopy observation was carried out using a polarizing microscope (Nikon Labophot-2) fitted with a hot stage (Mettler FP-82HT) operated by a RTC-1 temperature controller (Instec Inc., Broomfield, Co.). XRD was performed at the 3C2 and 4C1 beamline in Pohang Accelerator Laboratory (PAL).

2.3. *Synthesis*

1,3-Bis(*p*-aminophenoxy)propan-2-ol (APP) [12] and 4-(4-alkyloxybenzoyloxy)benzaldehydes (FPE-*n*) [13, 14] were synthesized according to literature methods.

2.3.1. *1,3-Bis{4-[4-(4-alkoxybenzoyloxy)benzylidene]-aminophenoxy}propan-2-ol, 2ES-*n

The target compounds were synthesized by the following procedure. The required 4-(4-alkoxybenzoyloxy)-benzaldehyde (2 eq, 22 mmol) was dissolved in anhydrous EtOH (150 ml), and 1,3-bis(*p*-aminophenoxy)-2-propanol (2 eq, 11 mmol) and a catalytic quantity of PTSA were added to the flask. The resulting solution was stirred for 24 h at room temperature under nitrogen. The resulting precipitate was filtered and washed with anhydrous MeOH, and then recrystallized from chloroform to give pure product as white crystals (61–81%).

2ES-3: 83%. FTIR (KBr, cm^{-1}): 3462 (O–H), 1732 (C–O), 1624 (C–N). ^{1}H NMR (CDCl$_3$, δ, ppm): 0.96 (t, 6H, –CH$_3$), 1.75 (m, 4H, –$\underline{\mathrm{CH_2}}CH_2$O–), 2.50 (broad, 1H, –OH), 3.94 (t, 4H, –OCH$_2$–), 4.09 (m, 4H, –OCH$_2$–), 4.23 (m, 1H, –CH–), 6.92 (m, 8H, Ar–H), 7.18–7.21 (m, 8H, Ar–H), 7.69–8.20 (m, 8H, Ar–H), 8.39 (s, 2H, CH–N). Elemental analysis: calcd for $C_{49}H_{46}N_2O_9$, C 72.94, H 5.75, N 3.47; found. C 72.81, H 5.80, N 3.50%.

2ES-4: 61%. FTIR (KBr, cm^{-1}): 3430 (O–H), 1729 (C–O), 1622 (C–N). ^{1}H NMR (CDCl$_3$, δ, ppm): 0.95 (t, 6H, –CH$_3$), 1.33 (m, 4H, –CH$_2$–), 1.77 (m, 4H, –$\underline{\mathrm{CH_2}}CH_2$O–), 2.50 (broad, 1H, –OH), 3.95 (t, 4H, –OCH$_2$–), 4.07 (m, 4H, –OCH$_2$–), 4.23 (m, 1H, –CH–), 6.92 (m, 8H, Ar–H), 7.18–7.21 (m, 8H, Ar–H), 7.69–8.20 (m, 8H, Ar–H), 8.32 (s, 2H, CH–N). Elemental analysis: calcd for $C_{51}H_{50}N_2O_9$, C 73.36, H 6.04, N 3.36; found, C 73.40, H 5.98, N 3.43%.

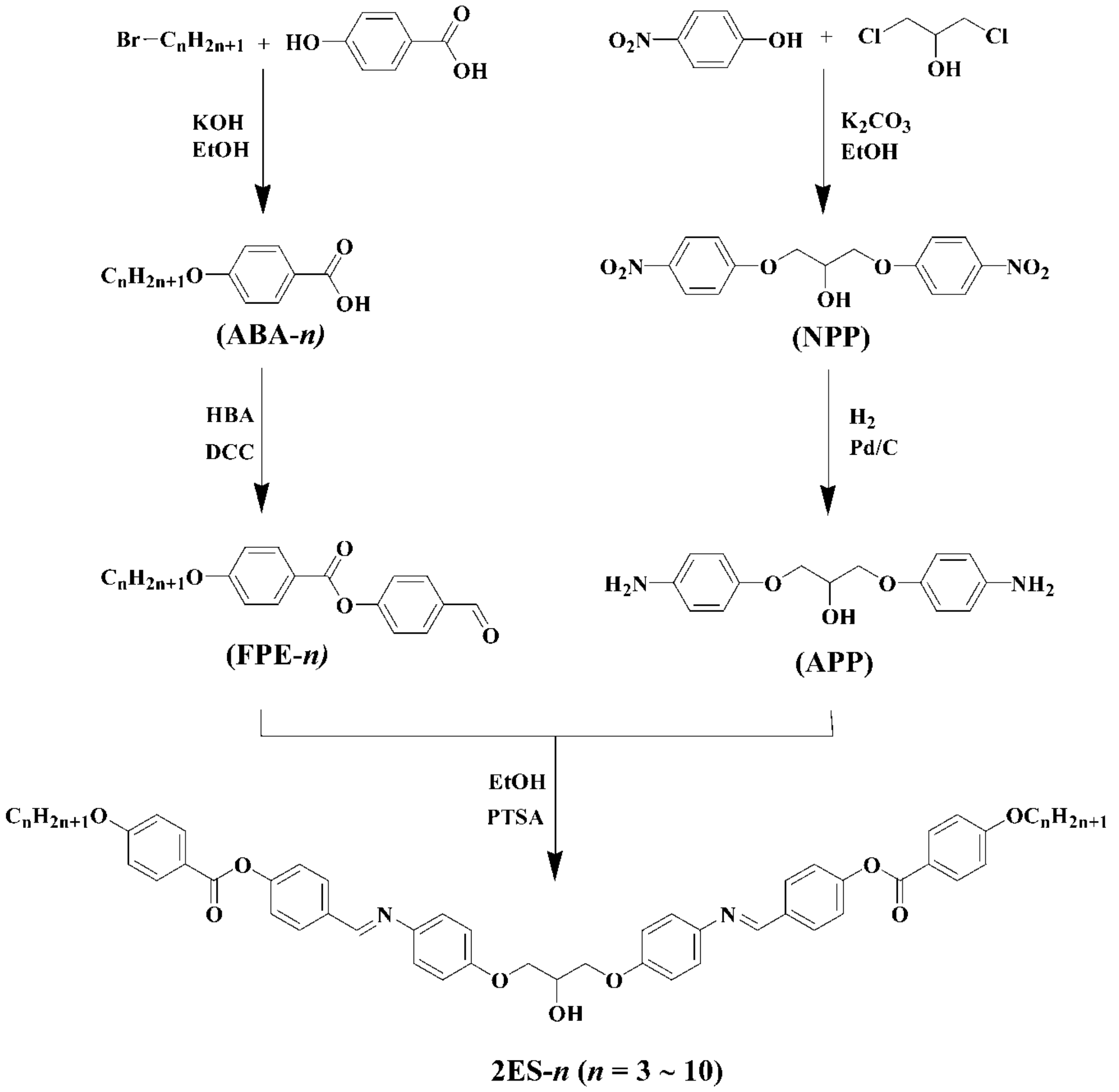
2ES-5: 75%. FTIR (KBr, cm^{-1}): 3488 (O–H), 1733 (C–O), 1620 (C–N). ^{1}H NMR (CDCl$_3$, δ, ppm): 0.97 (t, 6H, –CH$_3$), 1.35 (m, 8H, –(CH$_2$)$_2$–), 1.75 (m, 4H, –$\underline{\mathrm{CH_2}}CH_2$O–), 2.50 (broad, 1H, –OH), 3.89 (t, 4H, –OCH$_2$–), 4.10 (m, 4H, –OCH$_2$–), 4.23 (m, 1H, –CH–), 6.92 (m, 8H, Ar–H), 7.18–7.21 (m, 8H, Ar–H), 7.69–8.20 (m, 8H, Ar–H), 8.42 (s, 2H, CH–N). Elemental analysis: calcd for $C_{53}H_{54}N_2O_9$, C 73.76, H 6.31, N 3.25; found, C 73.83, H 6.29, N 3.30%.

2ES-6: 78%. FTIR (KBr, cm^{-1}): 3487 (O–H), 1734 (C–O), 1623 (C–N). ^{1}H NMR (CDCl$_3$, δ, ppm): 0.96 (t, 6H, –CH_3), 1.39 (m, 12H, –$(CH_2)_3$–), 1.75 (m, 4H, –$\underline{CH_2}CH_2O$–), 2.50 (broad, 1H, –OH), 3.95 (t, 4H, –OCH_2–), 4.10 (m, 4H, –OCH_2–), 4.23 (m, 1H, –CH–), 6.92 (m, 8H, Ar–H), 7.18–7.21 (m, 8H, Ar–H), 7.69–8.20 (m, 8H, Ar–H), 8.29 (s, 2H, CH–N). Elemental analysis: calcd for $C_{55}H_{58}N_2O_9$, C 74.14, H 6.56, N 3.14; found, C 74.19, H 6.70, N 3.08%.

2ES-7: 70%. FTIR (KBr, cm^{-1}): 3407 (O–H), 1725 (C–O), 1625 (C–N). ^1H NMR ($CDCl_3$, δ, ppm): 0.95 (t, 6H, –CH_3), 1.41 (m, 16H, –$(CH_2)_4$–), 1.82 (m, 4H, –$\underline{CH_2}CH_2O$–), 2.50 (broad, 1H, –OH), 4.01 (t, 4H, –OCH_2–), 4.09 (m, 4H, –OCH_2–), 4.23 (m, 1H, –CH–), 6.92 (m, 8H, Ar–H), 7.18–7.21 (m, 8H, Ar–H), 7.69–8.20 (m, 8H, Ar–H), 8.32 (s, 1H, CH–N). Elemental analysis: calcd for $C_{57}H_{62}N_2O_9$, C 74.49, H 6.80, N 3.05; found, C 74.55, H 6.89, N 2.93%.

2ES-8: 81%. FTIR (KBr, cm^{-1}): 3489 (O–H), 1734 (C–O), 1622 (C–N). ^1H NMR ($CDCl_3$, δ, ppm): 0.98 (t, 6H, –CH_3), 1.31 (m, 20H, –$(CH_2)_5$–), 1.78 (m, 4H, –$\underline{CH_2}CH_2O$–), 2.50 (broad, 1H, –OH), 3.91 (t, 4H, –OCH_2–), 4.07 (m, 4H, –OCH_2–), 4.23 (m, 1H, –CH–), 6.92 (m, 8H, Ar–H), 7.18–7.21 (m, 8H, Ar–H), 7.69–8.20 (m, 8H, Ar–H), 8.39 (s, 2H, CH–N). Elemental analysis: calcd for $C_{59}H_{66}N_2O_9$, C 74.82, H 7.02, N 2.96; found, C 74.81, H 6.98, N 3.10%.

2ES-9: 68%. FTIR (KBr, cm^{-1}): 3488 (O–H), 1723 (C–O), 1624 (C–N). ^1H NMR ($CDCl_3$, δ, ppm): 0.97 (t, 6H, –CH_3), 1.36 (m, 24H, –$(CH_2)_6$–), 1.77 (m, 4H,



Scheme. Synthetic routes for 2ES-*n* series.

–CH_2CH_2O–), 2.50 (broad, 1H, –OH), 3.91 (t, 4H, –OCH_2–), 4.07 (m, 4H, –OCH_2–), 4.23 (m, 1H, –CH–), 6.92 (m, 8H, Ar–H), 7.18–7.21 (m, 8H, Ar–H), 7.69–8.20 (m, 8H, Ar–H), 8.29 (s, 2H, CH–N). Elemental analysis: calcd for $C_{61}H_{70}N_2O_9$, C 75.13, H 7.23, N 2.87; found. C 75.10, H 7.18, N 2.90%.

2ES-10: 73%. FTIR (KBr, cm^{-1}): 3462 (O–H), 1736 (C–O), 1623 (C–N). ^{1}H NMR ($CDCl_3$, δ, ppm): 0.94 (t, 6H, –CH_3), 1.35 (m, 28H, –$(CH_2)_7$–), 1.83 (m, 4H, –CH_2CH_2O–), 2.50 (broad, 1H, –OH), 3.99 (t, 4H, –OCH_2–), 4.09 (m, 4H, –OCH_2–), 4.23 (m, 1H, –CH–), 6.92 (m, 8H, Ar–H), 7.18–7.21 (m, 8H, Ar–H), 7.69–8.20 (m, 8H, Ar–H), 8.31 (s, 2H, CH–N). Elemental analysis: calcd for $C_{63}H_{74}N_2O_9$, C 75.42, H 7.43, N 2.79; found, C 75.53, H 7.40, N 2.81%.

3. Results and discussion

The synthetic routes for the preparation of dimesogenic liquid crystals 2ES-*n* containing –COO– and –CH=N– units are outlined in the scheme. The preparation of 2ES-*n* compounds involved three steps: (i) the conventional etherification of *p*-hydroxybenzoic acid with alkyl halides, and *p*-nitrophenol with 1,3-dichloropropan-2-ol; (ii) hydrogenation of the nitro group of 1,3-bis(*p*-nitrophenoxy)propan-2-ol (NPP) to produce the 1,3-bis(*p*-aminophenoxy)propan-2-ol (APP) [12], and DCC coupling of *p*-alkyloxybenzoic acid (ABA-*n*) with 4-hydroxybenzaldehyde to afford the 4-(4-alkyloxybenzoyloxy)benzaldehyde (FPE-*n*) [12, 13]; (iii) the reaction of these products (FPE-*n*, 2 eq.) with the diamine (APP, 1 eq.) to yield the dimesogens 2ES-*n*.

The structures of all intermediates and final products

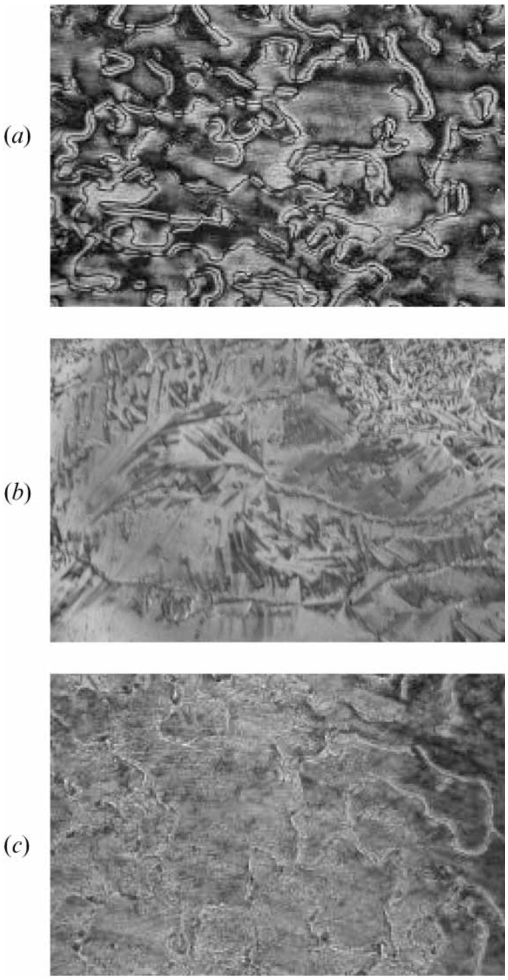


Figure 3. Optical micrographs of (*a*) FPE-8 at 60°C, (*b*) 2ES-8 at 200°C, and (*c*) 2ES-8 at 240°C.

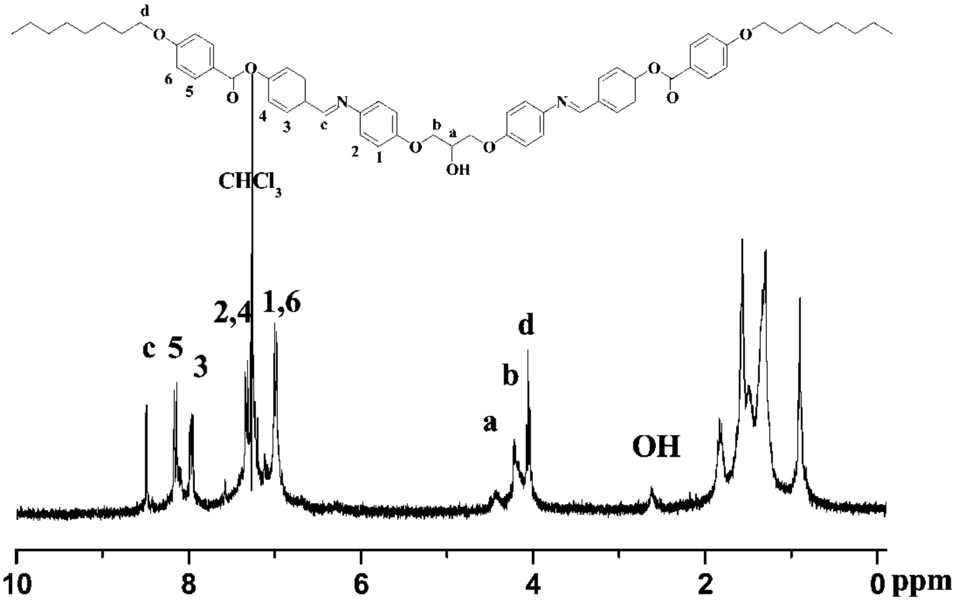


Figure 2. ^{1}H NMR spectrum of 2ES-8 ($CDCl_3$).

Table 1. Phase transition temperatures (°C) and textures of 4-(4-alkyloxybenzoyloxy)benzaldehydes (FPE-*n*).

	Cr		N		I	Textures
FPE-3	●	74.3		—	●	—
FPE-4	●	90.9		—	●	—
FPE-5	●	49.4		—	●	—
FPE-6	●	46.5	●	99.3	●	threaded
FPE-7	●	44.1		—	●	—
FPE-8	●	57.4	●	64.6	●	threaded
FPE-9	●	53.2	●	68.1	●	threaded
FPE-10	●	62.7	●	67.4	●	threaded

Table 2. Phase transition temperatures (°C) and transition enthalpies [kJ mol^{-1}] of the 2ES-*n* homologous series.

	Cr		Sm		N		I
2ES-3	●	198.1 [85.40]		—		—	●
2ES-4	●	197.2 [32.81]		—		—	●
2ES-5	●	184.1 [33.50]		—	●	297.0 [2.20]	●
2ES-6	●	184.0 [38.42]		—	●	297.9 [3.08]	●
2ES-7	●	179.8 [19.37]	●	196.6 [0.27]	●	279.8 [1.68]	●
2ES-8	●	176.5 [45.20]	●	224.4 [0.92]	●	276.3 [4.24]	●
2ES-9	●	168.8 [41.76]	●	235.7 [1.18]	●	267.4 [3.98]	●
2ES-10	●	169.5 [48.43]	●	244.8 [1.90]	●	259.5 [5.06]	●

were confirmed by the ^{1}H NMR (figure 2) and IR spectroscopy. The IR spectral frequencies of the synthesized 2ES-*n* compounds were obtained using KBr pellets, as described in § 2. The absorption peak of the ester group was observed at 1720–1735 cm^{-1}, C=N stretching frequencies of the target compounds occurred at 1620–1625 cm^{-1}, and a broad absorption band of the OH group showed at 3410–3452 cm^{-1}. In the precursor FPE-*n*, aryl C=O stretching vibration absorptions of the aldehyde and ester groups were seen at 1697–1719 and 1719–1736 cm^{-1}, respectively. In proton NMR, the spectral data displayed similar patterns: the synthesized 2ES-*n* showed CH=N peaks at 8.29–8.42 ppm, and the central CH and OH peaks were located at 4.23 and 2.50 ppm, respectively. In the precursor FPE-*n*, the aryl CH=O peak singlets occurred at 9.85–9.95 ppm.

The properties of the liquid crystal phases were studied using POM with a hot stage, DSC and XRD. Nematic phases (N) were assigned based on their marbled and schlieren optical textures which flashed under mechanical stress, combined with the high mobility of the phase.

The precursor 4-(4-alkyloxybenzoyloxy)benzaldehyde (FPE-*n*) showed nematic phases having a threaded texture, figure 3 (*a*), when $n \geqslant 6$ except for $n = 7$ (table 1). The plots in figure 4 represent all DSC heating traces of the dimer series 2ES-*n*. The heating scans of $n = 3,4$, show only a single melting transition temperature, indicating that these compounds are not liquid crystalline. But those of $n = 7$–10 showed smectic (Sm) phases, figure 3 (*b*), and nematic phases figure 3 (*c*), for $n = 5$, 6 only nematic behaviour is seen. Table 2 lists the phase transition properties for the eight homologous symmetric dimers 2ES-*n*, for $n = 3$–10.

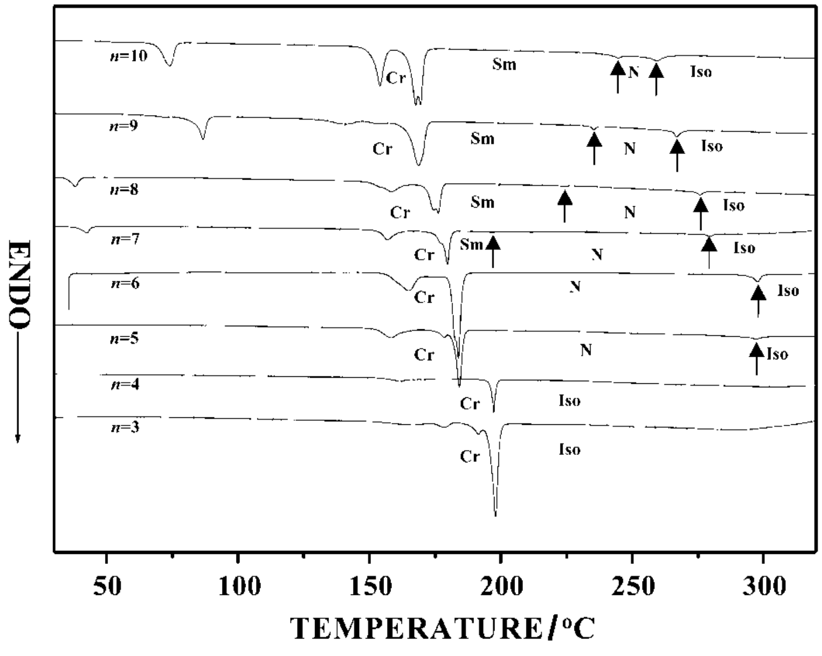


Figure 4. DSC thermograms for the 2ES-*n* series.

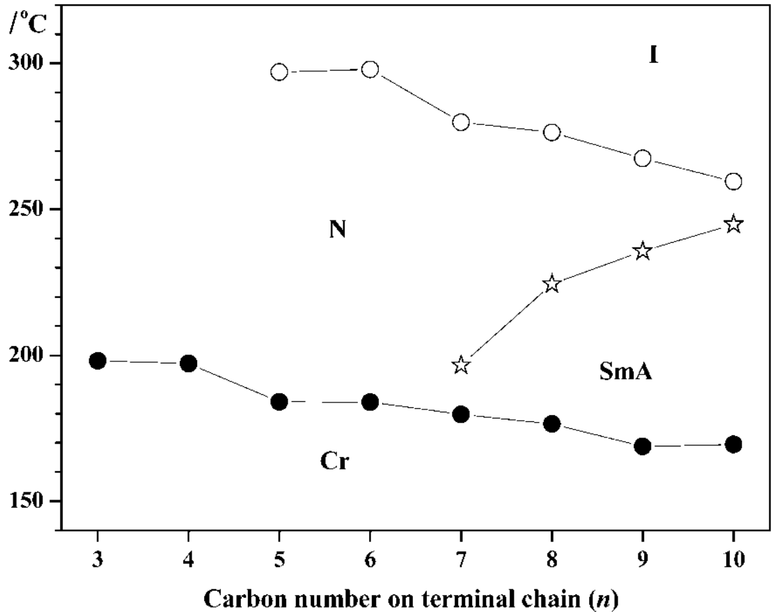


Figure 5. Dependence of transition temperatures on the length of the terminal alkyloxy chains for the 2ES-*n* series. Melting points are denoted by ●; ○ indicates nematic–isotropic transitions, ☆ indicates smectic–nematic transition.

Figure 5 shows the dependence of the transition temperatures on terminal chain length *n*. 2ES-3 and 2ES-4 show no nematic to isotropic transition, but increasing the length of the terminal chain causes the clearing temperature to fall. This behaviour is typical of a series of conventional mesogens having high clearing points. Figure 5 also illustrates the smectic phases shown when $n \geqslant 7$. The temperature range of the smectic phases widens with the increase in *n*, demonstrating the increase of smectic phase stability with alkyloxy chain length. On the other hand, the nematic phase range narrows quickly with increasing alkyloxy chain length. Thus, the effects on transition temperatures and phases behaviour of increasing length of terminal chains in this series are in accord with those observed for conventional low molar mass mesogens.

4. Conclusion

We have synthesized a new series of homologous symmetric dimers (2ES-*n*) where two three-ring mesogenic units are connected by a 2-hydroxy-1,3-dioxypropylene spacer. For homologues with short terminal chains ($n = 3,4$), no liquid crystalline phases were observed. Homologues with intermediate length of terminal chains ($n = 5,6$) exhibited nematic phases, while homologues with long terminal chains ($n = 7$–10) displayed nematic and smectic phases. The effect of terminal alkyloxy chain length on the liquid crystalline behaviour of this series was similar to that seen in conventional low mass mesogens.

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