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Liquid Crystals

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Phase transfer Pd(0)/Cu(I) catalysed polymerization reactions 7. Synthesis and thermotropic behaviour of 1,4-bis[2-(3',3''-difluoro-4',4''-di-*n*-alkyloxyphenyl)-ethynyl]benzene dimers

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LIQUID CRYSTALS, 1991, VOL. 10, NO. 2, 229–242

Phase transfer Pd(0)/Cu(I) catalysed polymerization reactions
7. Synthesis and thermotropic behaviour of 1,4-bis[2-(3′,3″-difluoro-4′,4″-di-*n*-alkyloxyphenyl)-ethynyl]benzene dimers†

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The symmetrically difluorinated aryl-acetylene dimers, 1,4-bis[2-(3′,3″-difluoro-4′,4″-di-*n*-alkyloxyphenyl)ethynyl]benzenes ($n = 7$–12), were prepared by a one pot phase transfer. Pd(0)/Cu(I) catalysed, three step coupling of 1,4-diiodobenzene with 2-methyl-3-butyn-2-ol and the appropriate 1-bromo-3-fluoro-(4-*n*-alkyloxy)benzene. All members of the series display enantiotropic nematic and smectic C phases as well as an additional smectic mesophase in the sequence C–S–S_C–N–I. The textures observed by polarized optical microscopy strongly support identification of the second smectic phase as a S_E mesophase. The S_C temperature window increases as the length of the *n*-alkyloxy substituent increases, whereas the stability of the nematic and S_E temperature windows decrease. In these fluorinated dimers, destabilization of mesomorphic behaviour by lateral fluorine substitution is compensated by stabilization due to the large length to breadth ratio of the mesogen, such that melting and crystallization are depressed more than isotropization when compared to the non-fluorinated dimers.

1. Introduction

Fluorinated liquid crystals are of tremendous interest because of the tendency of the fluorine substituent(s) to transform smectic A (S_A) into smectic C (S_C) mesophases [1, 2] to suppress and eliminate more ordered smectic mesophases [1–5] and to decrease the positive dielectric anisotropy ($\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp}$) [1–3]. The dielectric anisotropy becomes more negative as the number of fluorine substituents increases, with 2,3-difluorination being especially effective [1–3]. We recently described the synthesis and thermotropic behaviour of a series of mono- and difluorinated 1,2-(4,4′-di-*n*-alkyloxyaryl)acetylene monomers [6]. All odd members of the symmetrically difluorinated 1,2-[3,3′-difluoro-(4,4′-di-*n*-alkyloxy)phenyl]acetylene series ($n = 4$–12) are crystalline with a virtual nematic mesophase. All even members of this series present monotropic nematic mesophases. The thermotropic behaviour of the asymmetric, monofluorinated 1-[3-fluoro-(4-*n*-alkyloxy)phenyl]-2-(4′-*n*-alkyloxyphenyl)acetylene series ($n = 5$–12) changes continuously as the length of the *n*-alkyloxy substituent increases. The $n = 5$ derivative is crystalline. The $n = 6$–10 derivatives each have an enantiotropic nematic mesophase. In addition, the $n = 7$ and 8 derivatives each exhibit an enantiotropic

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smectic mesophase, and the $n=9$ and 10 derivatives exhibit monotropic S_C mesophases. Both the nematic and S_C mesophases of the $n=11$ and 12 derivatives are monotropic.

Although none of the mono- or difluorinated 1,2-(4,4′-di-*n*-alkyloxyaryl(acetylenes exhibit enantiotropic S_C mesophases, we have found that the liquid-crystalline mesophases of 1,2-(4,4′-dialkyloxyaryl)acetylenes are stabilized by extending the mesogen by one phenylethynyl unit [7]. For example, while 1,2[3,3′-dimethyl-(4,4′-di-*n*-heptyloxy)phenyl]acetylene is crystalline [8], 1,4-bis[2-(3′,3″-dimethyl-4′,4″-di-*n*-heptyloxyphenyl)ethynyl]benzene displays an enantiotropic nematic mesophase. We have therefore prepared the corresponding 1,4-bis[2-(3′,3″-difluoro-4′,4″-di-*n*-alkyloxyphenyl)ethynyl]benzene series with $n=7$–12 in order to enhance the S_C thermal stability of fluorinated diarylacetylene liquid crystals. While the 1,2-(4,4′-dialkyloxyaryl)acetylenes are monomers, these bis- derivatives can be considered arylacetylene dimers with one *n*-alkyloxy end group and one *n*-alkyloxyaryl end group. The synthesis and thermotropic behaviour of the difluorinated dimers are reported here.

2. Experimental

2.1. *Materials*

Bis(triphenylphosphine)palladium (II) chloride (Aldrich, 99 per cent), cuprous iodide (Alfa, 98 per cent), 2-methyl-3-butyn-2-ol (Fluka, 99 per cent), tetrabutylammonium hydrogen sulphate (TBAH) (Aldrich, 97 per cent), and triphenylphosphine (Aldrich, 99 per cent) were used as received. 1,4-Diiodobenzene (Aldrich, 99 per cent) was recrystallized from methanol. Triethylamine (Fisher Scientific, reagent) was distilled under argon from KOH. Tetrahydrofuran (THF) (distilled from $LiAlH_4$) was deaerated before each use by bubbling argon through the solvent for at least 30 min. The 1-bromo-3-fluoro-(4-*n*-alkyloxy)benzenes ($\geqslant$98·6 per cent) were prepared as described previously [1].

2.2. *Techniques*

200 MHz ^1H NMR spectra (δ, ppm) were recorded on a Varian XL-200 spectrometer. All spectra were recorded in $CDCl_3$ with TMS as the internal standard. Purity was determined by high pressure liquid chromatography/gel permeation chromatography (HPLC/GPC) with a Perkin–Elmer Series 10 LC instrument equipped with an LC-100 column oven (40°C), an LC 600 autosampler, and a Nelson Analytical 900 Series data station. Measurements were made using a UV detector after ^1H NMR demonstrated that non-UV-absorbing impurities were absent, with $CHCl_3$ as solvent and a 100 A PL gel column (0·90 ml min^{-1}).

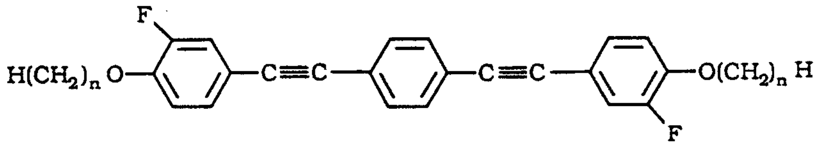
A Perkin–Elmer DSC-4 differential scanning calorimeter equipped with a TADS 3600 data station was used to determine the thermal transitions which were read as the maximum or minimum of the endothermic or exothermic peaks. All heating and cooling rates were 10°C min^{-1}. Tabulated thermal transitions were read from reproducible second or later heating scans and first or later cooling scans. Both enthalpy changes and transition temperatures were determined using indium as a calibration standard.

A Carl–Zeiss polarized optical microscope (magnification × 100) equipped with a Mettler FP 82 hot stage and a Mettler FP 800 central processor was used to observe the thermal transitions and to analyse the anisotropic textures [9, 10]. Thin samples were prepared in two ways. In the usual method, the sample was prepared by melting a minimum amount of compound between a clean glass slide and a coverslip, and rubbing the coverslip with a spatula. Thinner samples were prepared by melting the compound on a glass slide next to a coverslip and allowing the isotropic liquid to run under the coverslip by capillary flow.

2.3. *Synthesis of 1,4-bis[2-(3′,3″-difluoro-4′,4″-di-*n*-alkyloxyphenyl)ethynyl]benzenes*

The 1,4-bis[2-(3′,3″-difluoro-4′,4″-di-*n*-alkyloxyphenyl)ethynyl]benzenes with *n* = 7–12 were prepared by a one pot phase transfer, Pd(0)/Cu(I) catalysed aryl-acetylene coupling reaction as in the following example. A solution of 2-methyl-3-butyn-2-ol (0·92 g, 11 mmol) and triethylamine (2·2 g, 22 mmol) in deaerated THF (15 ml) was added via an addition funnel to a mixture of cuprous iodide (0·31 g, 1·6 mmol), triphenylphosphine (0·62 g, 2·4 mmol), $PdCl_2(PPh_3)_2$ (0·31 g, 0·45 mmol), and 1,4-diiodobenzene (1·6 g, 9·8 mmol I) in a round bottom flask equipped with a reflux condenser connected to an argon inlet/outlet. The reaction mixture was heated to reflux for 4 h, during which time a lot of $NEt_3H^+I^-$ had accumulated on the sides of the flask. 1-Bromo-3-fluoro-(4-*n*-nonyloxy)benzene (3·3 g, 10 mmol) in deaerated THF (8 ml), and an intimately ground mixture of TBAH (0·74 g, 2·2 mmol) and KOH (1·8 g, 32 mmol) were then added successively. After refluxing for 23·5 h, the reaction was allowed to cool to room temperature and a saturated aqueous solution of ammonium chloride (150 ml) was added. This was stirred for 1 h and then extracted six times with toluene, leaving a very blue aqueous phase. The toluene extracts were dried over $MgSO_4$, filtered, and the solvent was removed by rotary evaporation. The residue was purified by column chromatography on silica gel using hexane toluene (2 : 1) as eluant. The colour was removed from the resulting orange solid by precipitating a $CHCl_3$

Table 1. Synthesis of 1,4-bis[2-(3′,3″-difluoro-4′,4″-di-*n*-alkyloxyphenyl)-ethynyl]benzene dimers.†



n	mmol -I	mol Ar^2X / mol–I	Reaction time (h) after KOH addition	Yield (%)	$Yield^{1/3}$
7	6·1	0·95	22·5	60	84
8‡	6·1	1·09	24·0	52	82
9	9·8	1·05	23·5	55	79
10	4·2	1·07	24·0	12	49
11	6·1	0·95	23·5	50	79
12	9·8	1·05	17·0	66	87

† -I from 1,4-diiodobenzene (1st addition). Ar^2X (2nd addition) = 1-bromo-3-fluoro-(4-*n*-alkyloxy)benzene. Reaction conditions of 1st addition: 1·5–1·7 ml THF, 1·01–1·11 mmol 2-methyl-3-butyn-2-ol, and 4·3–4·7 mol per cent $PdCl_2(PPh_3)_2$ per mmol -I; 2 mol NEt_3 per mol 2-methyl-3-butyn-2-ol; CuI : Pd : PPh_3 = 3·7–3·8 : 1 : 5·2–5·3; reflux 4 h. Reaction conditions of 2nd addition: 0·8–1·0 ml THF per mmol Ar^2X; 2·8–3·1 mol KOH and 20 mol per cent TBAH per mol 2-methyl-3-butyn-2-ol of 1st addition.

‡ 3·6 mol KOH per mol 2-methyl-3-butyn-2-ol.

solution (approx. 10 ml) with ethanol (100 ml). The precipitate was collected and dried *in vacuo* to obtain 1·6 g (55 per cent) of tan coloured solid. This was then recrystallized from hexane (100 ml) to yield 0·84 g (29 per cent) of 1,4-bis[2-(3′,3″-difluoro-4′,4″-di-*n*-nonyloxyphenyl)ethynyl]benzene as light tan coloured crystals; purity 99·8 per cent.

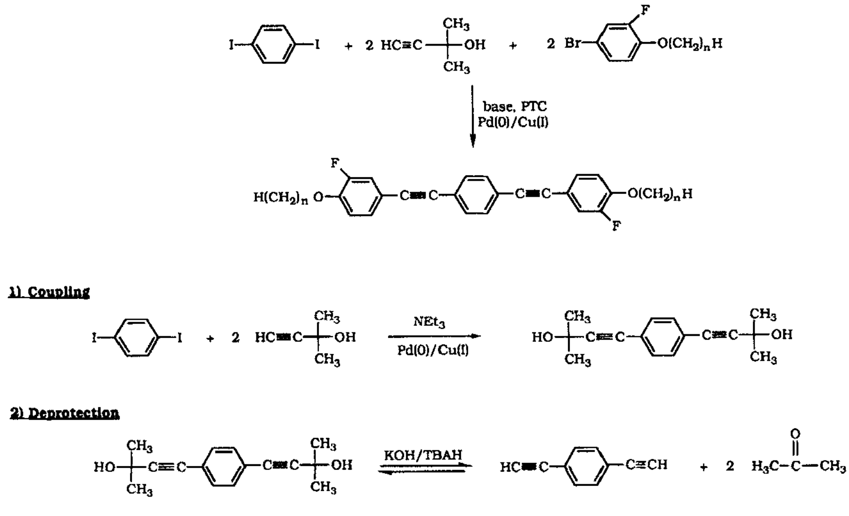
The results of the acetylene coupling reactions are presented in table 1. The purity of all resulting compounds is ⩾99·8 per cent. The ^{1}H NMR chemical shifts of the 1,4-bis[2-(3′,3″-difluoro-4′,4″-di-*n*-alkyloxyphenyl)ethynyl]benzenes are identical: 0·89 (t,-C$\underline{H}_3$, 6 protons), 1·30 (m, -[C$\underline{H}_2$]-$_{n-3}$, 4[*n*-3] protons), 1·83 (m, -OCH$_2$C$\underline{H}_2$-, 4 protons), 4·06 (t, -OC$\underline{H}_2$-, 4 protons), 6·92 (t, 2 aromatic protons ortho to -OR), 7·26 (d, 4 aromatic protons ortho to -C≡C-Ph-C≡C-), 7·48 (s, 4 aromatic protons of central ring).

3. Results

3.1. *Synthesis of 1,4-bis[2-(3′,3″-difluoro-4′,4″-di-*n*-alkyloxyphenyl)ethynyl]benzenes*

The 1,4-bis[2-(3′,3″-difluoro-4′,4″-di-*n*-alkyloxyphenyl(ethynyl]benzene dimers were prepared by a one pot, solid–liquid phase transfer Pd(0)/Cu(I) catalysed aryl-acetylene coupling procedure as described previously [11]. The three step, one pot synthesis outlined in the scheme was adapted from Carpita *et al.* [12] liquid–liquid phase transfer catalysed synthesis of diheteroarylacetylenes. In the first step, 1,4-diiodobenzene is coupled with 2-methyl-3-butyn-2-ol by a traditional (non-phase transfer catalysed) Pd(0)/Cu(I) coupling procedure using triethylamine as base in refluxing THF. As described in another publication [7], this coupling step is complete within two hours. The resulting dicarbinol is then deprotected and coupled with a 1-bromo-3-fluoro-(4-*n*-alkyloxy)benzene using a solid-liquid phase transfer catalysed system. Only the final product is isolated and purified.

The results of the phase transfer Pd(0)/Cu(I) catalysed coupling reactions using 1,4-diiodobenzene and 1-bromo-3-fluoro-(4-*n*-alkyloxy)benzenes are presented in table 1. The difluorinated dimers are much less soluble than the corresponding monomers, and



Scheme. One pot, three step, phase transfer Pd(0)/Cu(I) catalysed synthesis of 1,4-bis[2-(3′,3″-difluoro-4′,4″-di-*n*-alkyloxyphenyl)ethynyl]benzene dimers.

are not readily recrystallized. That is, once enough solvent is used to dissolve them, they do not readily crystallize back out. The chromatographed compounds were therefore precipitated from a chloroform solution with ethanol in order to accurately determine the yield, and then recrystallized from hexane or hexane and a minimum amount of toluene, with some loss, for thermal characterization. The final products were generally obtained in 50–66 per cent overall yield, or 79–87 per cent average yield from each of the three steps. This is slightly higher than the yields achieved using 1-iodo-3-methyl-(4-*n*-heptyloxy)benzene and 1-bromo-(4-*n*-heptyloxy)benzene [12].

3.2. *Thermal characterization*

The extension of the fluorinated mesogen of the 1,2-diarylacetylene by one phenylethynyl unit continues our investigations of the effect of structural variations on the thermotropic behaviour of 1,2-(4,4′-dialkyloxyaryl)acetylenes. We first presented the effect of the *n*-alkyloxy chain length of linear 1,2-(4,4′-di-*n*-alkyloxyphenyl) acetylenes ($n=1$–12) [8]. All compounds with $n \geqslant 4$ exhibit enantiotropic nematic mesophases. The lower homologues with $n=4$–8 also show crystalline and crystalline/smectic polymorphism, while the higher homologues with $n=10$–12 display an enantiotropic S_C mesophase in the sequence C–S_C–N–I. Upon cooling, those compounds with $n=9$–12 also exhibit an additional monotropic smectic mesophase before crystallizing.

As mentioned in the Introduction, we have also examined both symmetric and asymmetric methyl branching in either the alkyloxy substituents or in the aromatic ring(s) of the mesogen [7, 8, 11] as well as extension of the mesogens by one phenylethynyl unit [7, 11]. In general, both symmetry and methyl branching destabilize the liquid-crystalline phases more than the crystalline, while extension of the mesogenic length has a stabilizing effect. The chiral methyl branched 1-(4-*n*-alkyloxyphenyl)-2-[4′-[*S*(-)-2-methylbutyloxy]phenyl]acetylenes were also prepared [13]. Those compounds with $n=8$–10 present enantiotropic cholesteric mesophases, and those with $n=11$ or 12 present monotropic cholesteric mesophases. The $n=6$ derivative is crystalline with either a second crystalline phase or a highly ordered monotropic smectic mesophase.

We have now prepared the $n=7$–12 derivatives of the 1,4-bis[2-(3′,3″-difluoro-4′,4″-di-*n*-alkyloxyphenyl)ethynyl]benzene series because only the $n=10$–12 and the $n=9$–12 derivatives of the linear and the symmetrically difluorinated 1,2-(4,4′-dialkyloxyaryl)acetylenes, respectively, display S_C mesophases. In addition, the dimer with $n=7$ can be compared with the corresponding linear and methyl substituted 1,4-bis[2-(4′,4″-di-*n*-heptyloxyaryl)ethynyl]benzene dimers.

The DSC traces observed on heating and cooling the 1,4-bis[2-(3′,3″-difluoro-4′,4″-di-*n*-alkyloxyphenyl)ethynyl]benzene dimers are presented in figure 1. Their complete thermal transitions are summarized in table 2. Table 2 also lists the thermal transitions of the first heating scan of those compounds which are substantially different from subsequent heating scans ($n=8, 11, 12$). Although these three dimers crystallize better from solution than from the melt, the liquid crystalline transitions are reproduced in second and later heating scans. As shown in figure 1 and table 2, the length of the *n*-alkyloxy substituents has no effect on the mesophases exhibited by these difluorinated dimers. Surprisingly, all compounds not only exhibit a nematic mesophase, but also the S_C mesophase is observed in the monomers with longer *n*-alkyloxy substituents; the smectic mesophase is observed in the monofluorinated monomers with $n=7$ or 8. All liquid-crystalline phases are enantiotropic. However, as the length of the *n*-alkyloxy

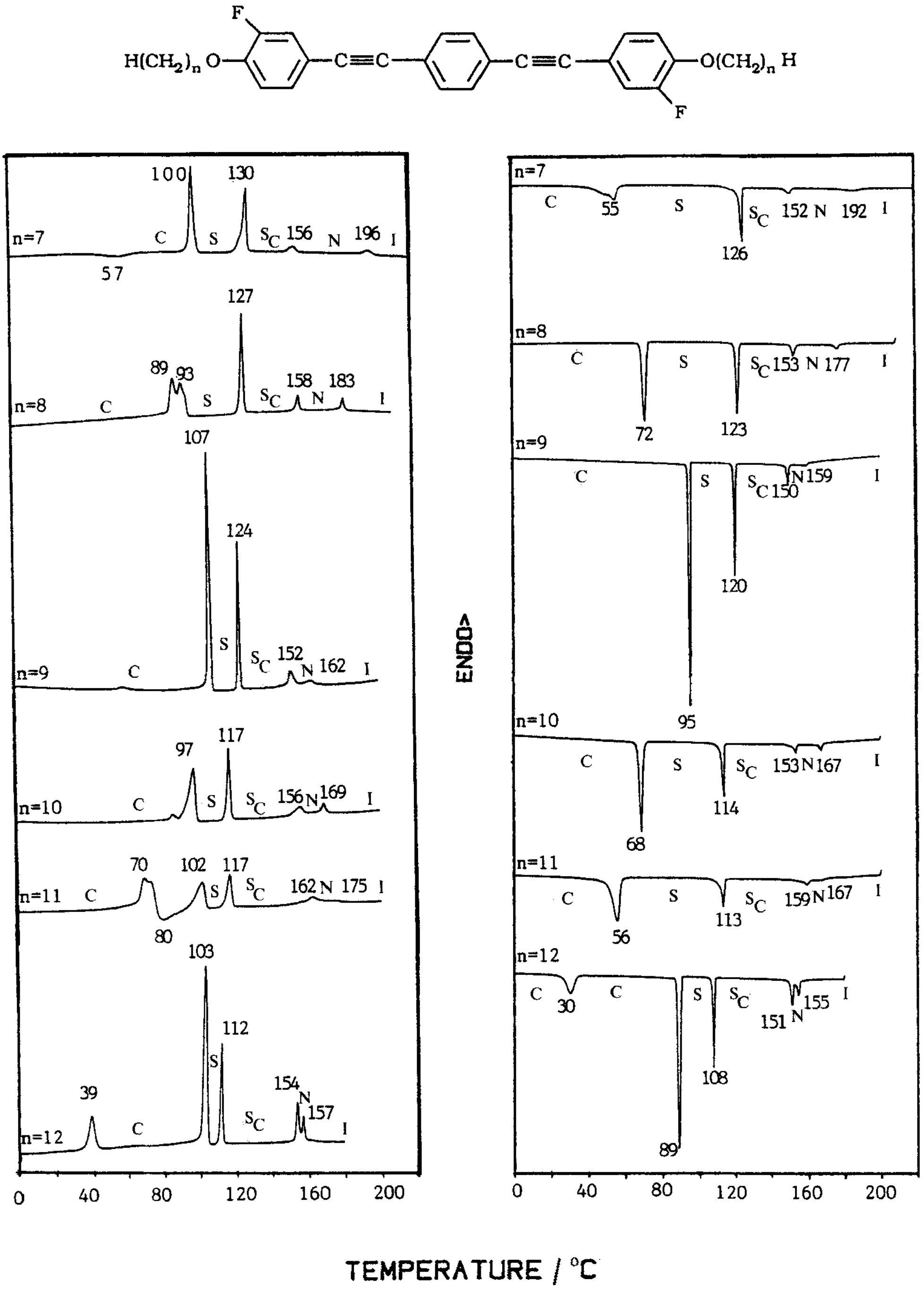


Figure 1. DSC heating and cooling scans of 1,4-bis[2-(3′,3″-difluoro-4′,4″-di-*n* alkyloxyphenyl) ethynyl]benzene dimers.

Table 2. Thermal transitions and thermodynamic parameters of 1,4-bis[2-(3′,3″-difluoro-4′,4″-di-*n*-alkyloxyphenyl)ethynyl]benzene dimers†.

n	Phase transitions (°C) and the corresponding enthalpy changes (kJ mol^{-1}) in parentheses
7	rC 57·1 (4·27) C 100·2 (13·8) S 130·0 (12·1) S_C 155·9 (1·93) *n*196·3 (1·80) I I 192·3 (2·35) N 152·2 (2·00) S_C 126·0 (11·7) S 55·1 (12·8) C
8	‡C 99·4 (21·6) S 128·0 (12·9) S_C 158·9 (2·60) N 182·8 (2·39) I C 89·2 C 92·8 (19·2)§ S 127·5 (13·0) S_C 158·0 (2·59) N 182·3 (2·11) I I 177·3 (1·80) N 153·4 (2·94) S_C 123·1 (12·7) S 72·0 (20·6) C
9	C 107·3 (29·9) S 123·6 (11·7) S_C 151·7 (4·52) N 162·4 (2·31) I I 158·9 (2·86) N 150·0 (4·79) S_C 120·2 (11·5) S 95·2 (33·2) C
10	C 85·9 C 97·4 (20·7)§ S 117·2 (10·6) S_C 155·8 (3·70) N 169·1 (2·82) I I 166·8 (2·87) N 153·0 (3·45) S_C 113·6 (10·8) S 68·4 (22·4) C
11	‡C 81·7 (22·9) C 104·3 (23·1) S 115·8 (8·33) S_C 161·1 N 172·6 (6·60)§ I C 69·5 (23·3) rC 79·7 (6·88) C 101·6 (12·0 (S 117·0 (8·51) S_C 162·0 N 174·9 (7·06)§ I I 166·5 N 158·9 (6·85)§ S_C 113·0 (8·95) S 55·5 (29·2) C
12	‡C 68·8 (29·9) C 103·9 (35·8) S 112·0 (11·9) S_C 153·9 N 157·5 (9·94)§ I C 39·0 (11·1) C 102·9 (39·0) S 111·6 (12·1) S_C 153·5 N 156·9 (10·3)§ I I 154·6 N 150·9 (10·4)§ S_C 107·9 (12·2) S 89·1 (38·6) C 30·2 (12·0) C

† C = crystalline, RC = recrystallization, S = smectic, N = nematic, I = isotropic; unless otherwise stated first line of data obtained from second and later heating scans, last line data obtained on cooling.

‡ From first heating scan.

§ Overlapped with previous transition.

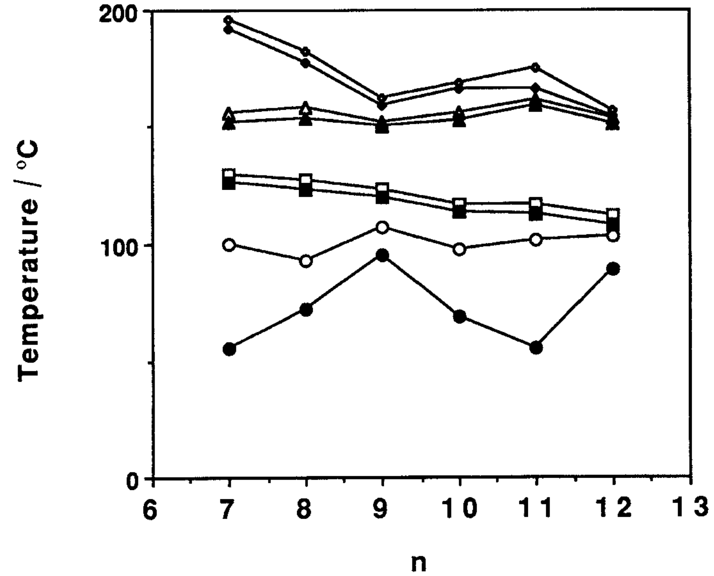
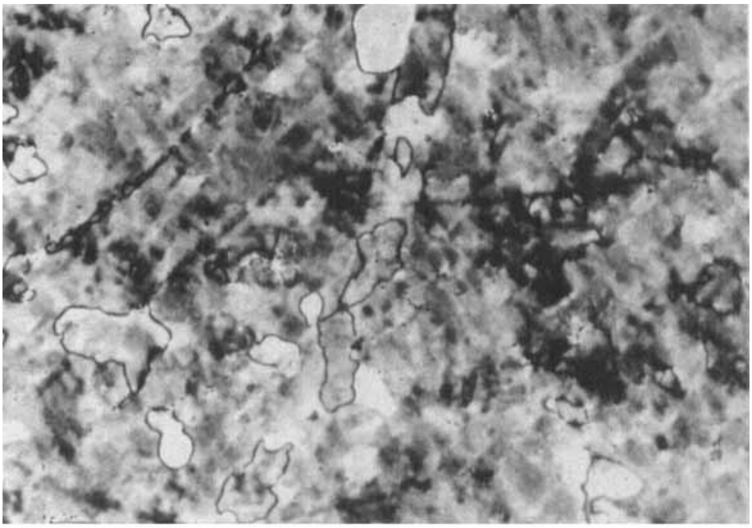
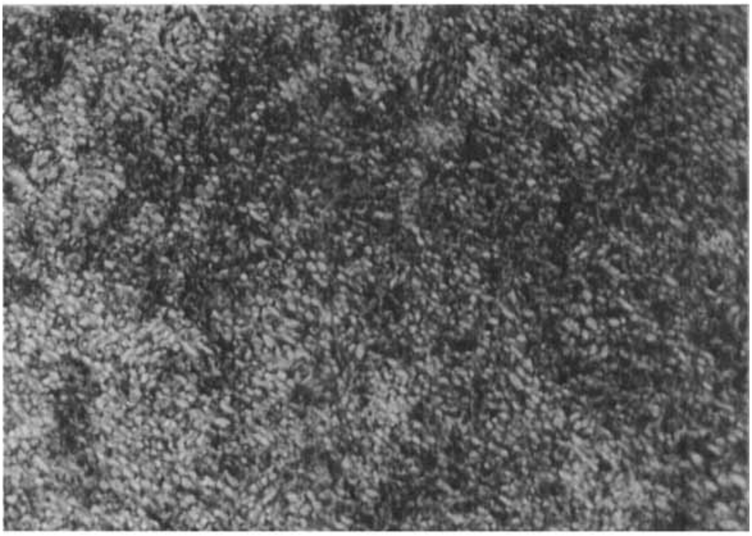


Figure 2. Phase transition temperatures of 1,4-bis[2-(3′,3″-difluoro-4′,4″-di-*n*-alkyloxyphenyl)ethynyl]benzene dimers as a function of *n*. The filled symbols represent data obtained from second heating scan, whereas for *n* = 8 and 11 the open symbols represent data obtained from cooling scans. ○, C–S, □, S–S_C; △, Sc–N; ◇, N–I; ●, S–C; ■, S_C – S; ▲, N–S_C; ◆, I–N.


(a)


(b)


(c)

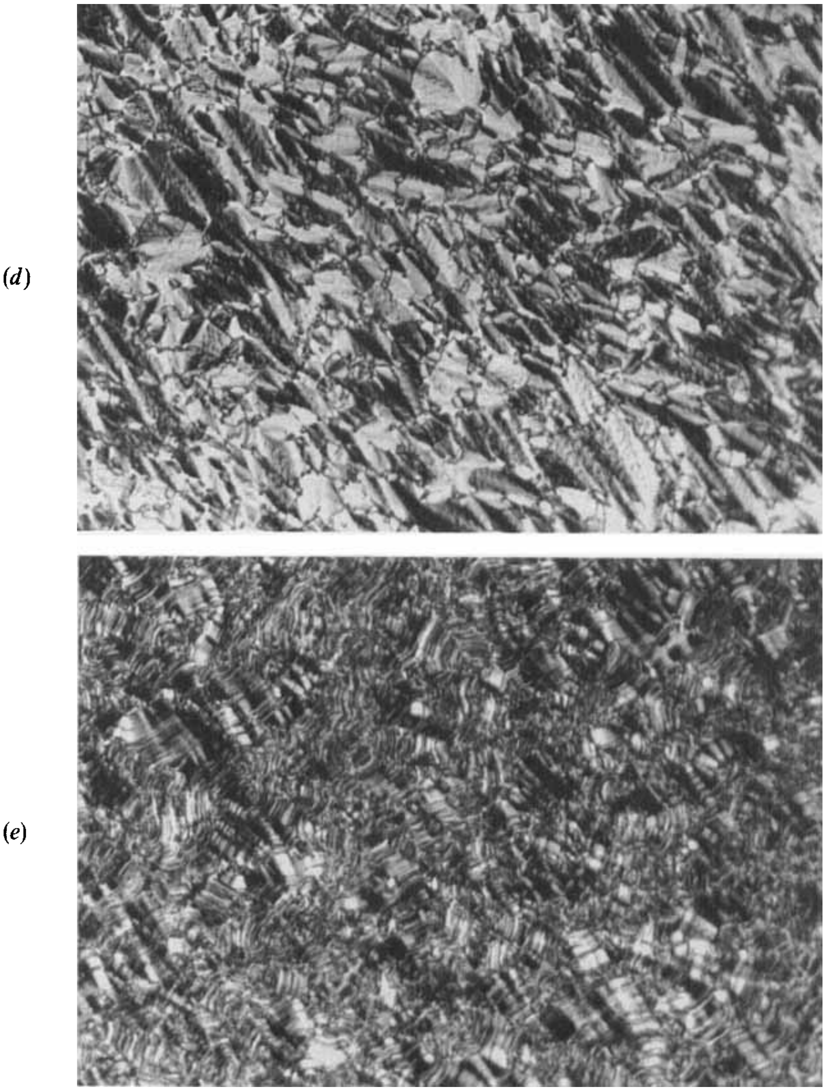
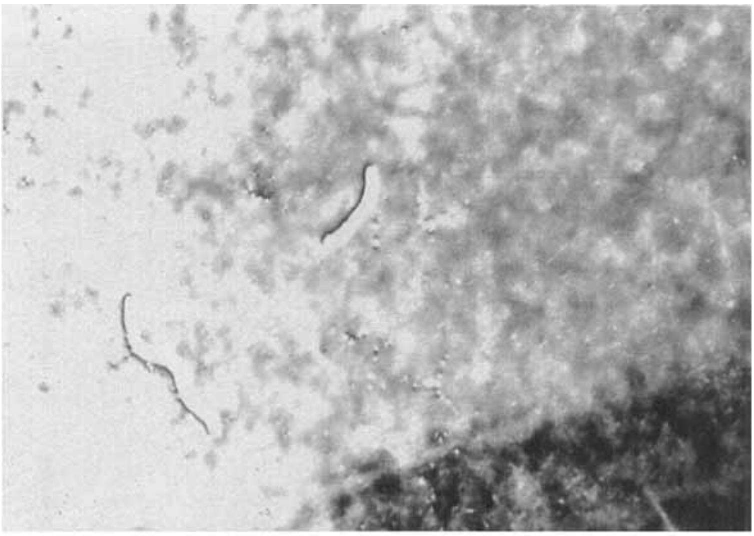


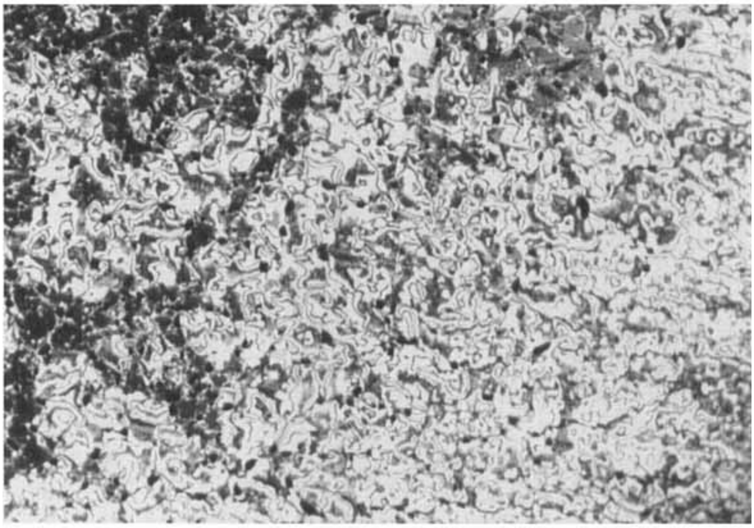
Figure 3. Sequence 1. Microscopic textures (magnification ×100) observed on cooling 1,4-bis[2-(3′,3″-difluoro-4′,4″-di-*n*-dodecyloxyphenyl)ethynyl]-benzene from the isotropic state; normal sample preparation. (*a*) 154·5°C, marbled nematic texture; (*b*) 152·2°C, nematic to S_C transition; (*c*) 149·7°C S_C broken focal conic fan texture; (*d*) 114·3°C S_C broken focal conic fan texture with colour change and grainy appearance; (*e*) 109·4°C, paramorphotic banded focal conic fan texture typical of S_E mesophases.

substituents increases, on the heating scan there is both a decrease in the temperature windows of the nematic and second smectic mesophases, and an increase in the thermal stability window of the S_C mesophase (see figure 2). This increase in S_C stability with increasing *n* corresponds to the fact that S_C mesophases are usually observed in dialkyloxy compounds with long chains [14].

The mesophases of all compounds in this series exhibit the same textures. Figures 3 and 4 present several optical micrographs from two compounds typical of the nematic, S_C, and the second smectic mesophase as exhibited by two types of thin film



(a)



(b)

(c)

(*d*)

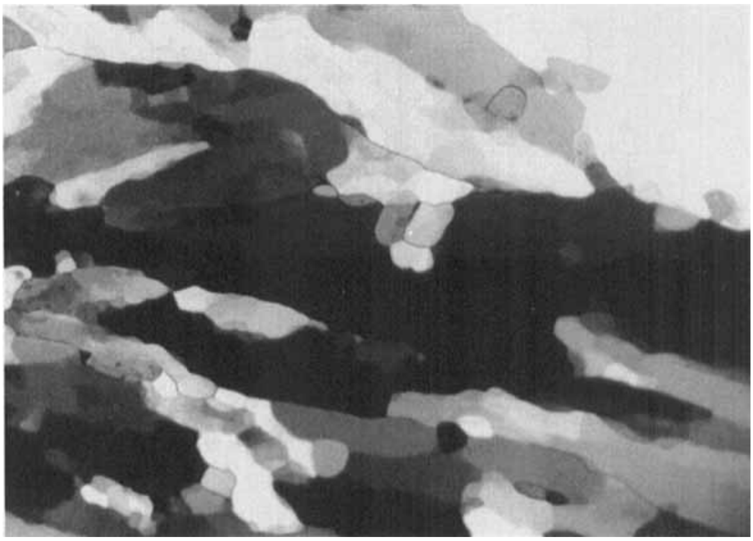


Figure 4. Sequence 2. Microscopic textures (magnification × 100) observed on cooling 1,4-bis[2-(3′,3″-difluoro-4′,4″-di-*n*-nonyloxyphenyl)ethynyl]-benzene from the isotropic state; sample prepared by capillary flow. (*a*) 159·0°C, homogeneous nematic texture; (*b*) 145·6°C, S_C schlieren and focal conic fan textures; (*c*) 120·9°C, banded focal conic fan and platelet textures typical of S_E mesophases; (*d*) 121·1°C, platelet or mosaic texture typical of S_E mesophases; another region.

preparations. Figure 3 (*a*) presents the marbled nematic texture exhibited by normal sample preparations, and figure 4 (*a*) presents a more homogeneous nematic texture exhibited by samples prepared by capillary flow.

Figure 3 (*b*) shows the typical blurring of the entire field of view at a nematic to S_C transition [8, 9, 15]. However, although the focal conic S_A texture separates from nematic mesophases in the form of bâtonnets [10], the broken focal conic fan texture shown in figure 3 (*c*) could be confused with a S_A mesophase. The two natural textures of the S_A mesophase are the homeotropic and focal conic fan textures; the homeotropic S_A texture can often be induced by capillary flow preparations [10]. However, as shown in figure 4 (*b*) the two natural textures exhibited by this type of mesophase when induced by capillary flow preparations are the schlieren and focal conic fan textures. Both textures form simultaneously as is not uncommon for S_C mesophases [10]. Figures 3 (*c*) and (*d*) also demonstrate that the birefringent colour of the S_C texture changes by cooling the sample by 36°C as the tilt angle changes, with concurrent sanding of the fan domains.

We believe that the second smectic mesophase formed by these fluorinated dimers is S_E because all three textures typical of, and unique to, S_E mesophases are exhibited. Upon cooling the S_C broken focal conic fan texture of figures 3 (*c*) and (*d*), continuous lines appear across the backs of the fans, and remain throughout the temperature range of this mesophase (see figure 3 (*e*)). This non-transitory banded texture is unique to the S_E mesophase; only the S_G mesophase also exhibits a banded fan texture, but in this case the lines are broken [10]. The banded fans are also observed by cooling the samples prepared by capillary flow (see figure 4 (*c*)). However, in this case a platelet texture is also formed from the schlieren S_C texture. This texture is again unique to the S_E

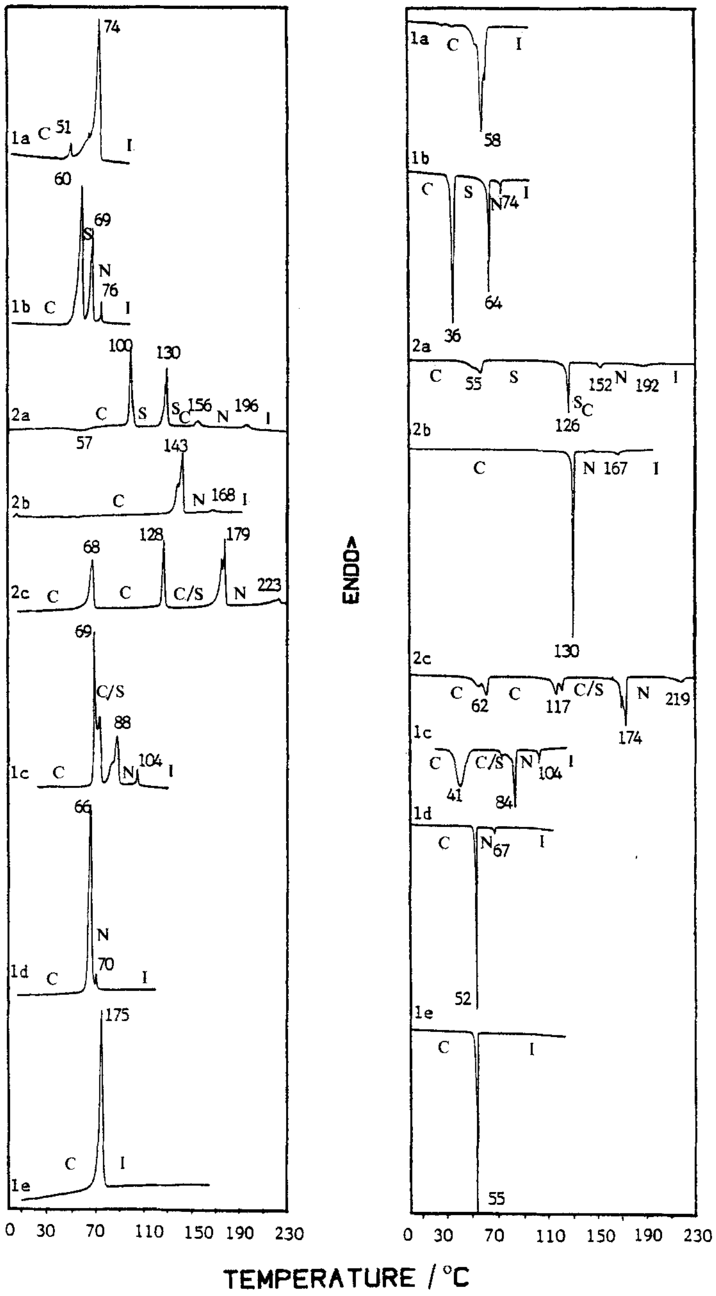
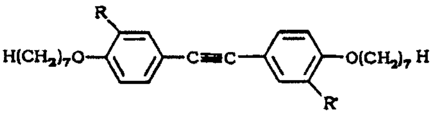
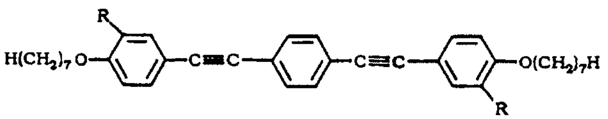


Figure 5. DSC heating and cooling scans of 1,2-(4,4′-di-*n*-heptyloxyaryl)acetylene monomers and 1,4-bis[2-(4′,4″-di-*n*-heptyloxyaryl)-ethynyl]benzene dimers with either fluorine or methyl branches in the mesogen, and their hydrogen analogues.



1a $R=R'=F$
b $R=F, R'=H$
c $R=R'=H$
d $R=CH_3, R'=H$
e $R=R'=CH_3$



2a $R=F$
b $R=CH_3$
c $R=H$

mesophase in that ghost-like images appear where transparent platelets overlap [10]. As shown in figure 4 (*d*), the platelet domains can be quite large, resembling the natural S_E texture.

The S_E phase is highly ordered with an almost infinite interlayer correlation [10]. The S_E mesophase of these fluorinated dimers is therefore quite viscous although they do shear. The C–S_E–S_C–N–I sequence is unusual if it is correct. That is, S_E mesophases are usually obtained by cooling either S_A or S_B phases, although they do form in a few compounds directly from the isotropic melt [10]. The natural S_E texture is the same texture observed when cooling the 1,2-(4,4′-di-*n*-alkyloxyphenyl)acetylenes with $n=4$–8 from the nematic mesophase [8], except that the latter textures appear to be immiscible polymorphs with an overlapping crystallization transition. This smectic mesophase is apparently the same smectic mesophase formed by cooling the nematic mesophases of 1,2-(4,4′-di-*n*-nonyloxyphenyl)acetylene, the 1,2-(4,4′-di-*n*-alkyloxyphenyl)acetylenes with $n=4$–8, and the monofluorinated 1-[3-fluoro-(4-*n*-alkyloxy) phenyl]-2-(4′-*n*-alkyloxyphenyl)acetylenes with $n=7$ or 8.

4. Discussion

The DSC traces of 1,4-bis[2-(3′,3″-difluoro-4′,4″-di-heptyloxy-phenyl)ethynyl] benzene, 1,4-bis[2-(3′,3″-dimethyl-4′,4″-diheptyloxyphenyl)-ethynyl] benzene, 1,4-bis[2-(4′,4″-diheptyloxyphenyl)ethynyl]benzene, and the analogous diarylacetylene monomers are plotted in figure 5. As with the hydrogen and methyl substituted dimers, increasing the length of the fluorinated diarylacetylenes by one phenylethynyl unit increases both the temperature of all phase transitions, and the temperature window of each phase. It also increases the extent of supercooling of all phase transitions. For example, while the isotropic–nematic and nematic–smectic C transitions of the monomers are supercooled by approximately 2°C, that of the dimers is typically supercooled by 3–8°C.

Figure 5 demonstrates that methyl substitution, especially symmetrical substitution, depresses isotropization more than melting [7, 8], while extension of the mesogenic length has a stabilizing effect on the liquid-crystalline phases [7]. This is also true of fluorine substitution in the monomer although the smaller fluorine substituent has less of a destabilizing effect than does methyl. In contrast, symmetrical fluorine substitution in the dimeric mesogen depresses crystallization/melting much more than isotropization. The crystallization/melting depression is great enough that a second smectic mesophase is also realized. Therefore, in the fluorinated dimers, the mesomorphic destabilization by lateral substitution is compensated by extension of the mesogenic length.

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