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Smectic C phenylpyridines with an alkenyloxy chain

by S. M. KELLY*, J. FÜNFSCHILLING and A. VILLIGER

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The known 5-*n*-alkyl-2-[4-(*n*-alkoxy)phenyl]pyridines exhibit high smectic C transition temperatures as well as various highly ordered smectic mesophases. An unsaturated carbon-carbon double bond has now been introduced into the terminal alkoxy chain of these heterocyclic materials to produce the corresponding alkenyloxy substituted derivatives. The position and nature (*E/Z*) of the double bond has been varied systematically and the effect on the liquid crystal transition temperatures determined. A number of homologous series of the most promising alkenyloxy substituted materials has been prepared and evaluated. The position and nature (*E/Z*) of the double bond changes the conformation of the alkenyloxy chain to a significant degree. This can lead to slightly higher smectic C transition temperatures for compounds with a *trans*-double bond (*E*) at an even number of carbon atoms from the molecular core. However, the highly ordered mesophase transition temperatures are increased to a greater degree leading to a reduction in the smectic C temperature range. Significantly lower transition temperatures (including the melting point) are observed for materials with a *cis*-double bond (*Z*) at an odd number of carbon atoms from the molecular core. Comparisons with the corresponding alkoxy substituted materials (i.e. without a double bond) are made. These new alkenyloxy materials can be used to increase the smectic C and nematic transition temperatures of chiral mixtures for electrooptical display devices based on ferroelectric effects.

1. Introduction

The known 5-*n*-alkyl-2-[4-(*n*-alkoxy)phenyl]pyridines [1–4] exhibit high smectic C transition temperatures as well as a range of highly ordered smectic mesophases. Such compounds are sometimes [4] used to increase the chiral smectic C transition temperature of optically active mixtures for electro-optical display devices based on ferroelectric effects, namely surface-stabilized, deformed helix and short pitch bistable ferroelectric liquid crystal displays (SSFLCDs, DHFLCDs and SBFLCDs) [5–13]. However, at the concentrations required, highly ordered phases are often induced at low temperatures as well as broad smectic A mesophases at high temperatures. At the same time the nematic phase required for a good orientation can be suppressed. It has recently been shown [14, 15] that the introduction of a carbon-carbon double bond of a defined configuration (*E/Z*) at certain positions in the terminal alkoxy chain of the known 5-*n*-alkyl-2-[4-(*n*-alkoxy)phenyl]pyrimidines [16] to produce the corresponding alkenyloxy materials can not only lead to substantial modifications in the temperature range of the observed smectic mesophases, but also change the number and type of mesophases shown [14]. This can be of advantage [15] in the preparation of optimized chiral smectic C mixtures for electro-optic display devices based on ferroelectric effects. Therefore, it was decided to conduct a similar investigation of the effect of the introduction of a carbon-carbon double bond at various positions in

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the terminal chain of the analogous 5-*n*-alkyl-2-[4-(alkoxy)phenyl]pyridines [1–4] on their liquid crystal transition temperatures. In order to investigate the suitability of these new alkenyloxy substituted materials as non-optically active components of chiral smectic C mixtures for electro-optic display devices based on the above mentioned ferroelectric effects a parallel study of their physical properties in admixture with each other and in a standard chiral S_C* mixture was also conducted [15].

The substances to be investigated (**1–72**) could be synthesized easily according to a standard method [14] in one step from the known 4-(5-*n*-alkyl-2-pyridinyl)phenols [1–4, 17] and the same alcohols and bromides incorporating a carbon–carbon double bond of a defined configuration (*E/Z*) at various positions in the chain that were prepared for the analogous 5-*n*-alkyl-2-[4-(*n*-[alkenyl]oxy)phenyl]pyrimidines [14].

2. Mesomorphic properties






















The liquid crystal transition temperatures of the 5-heptyl-, octyl-, and nonyl-2-([4-(octyl)oxy]phenyl)pyridines (**1**, **8**, and **15**) and those of the corresponding 5-heptyl-, octyl-, and nonyl-2-([4-(alkenyl)oxy]phenyl)pyridines (**2–7**, **9–14**, and **16–21**) are collated in table 1. The position of the unsaturated carbon–carbon double bond is moved systematically from the beginning to the end of the terminal alkenyloxy chain in each series. The configuration at the alkenic double bond is alternately *trans* and *cis* (*E* and *Z*). The 7-octenyloxy chain incorporating a double bond in a terminal position is neither *trans* nor *cis* due to the equivalence of the two hydrogen atoms on the end carbon atom. The width of the smectic C mesophase, i.e. the mesophase type of most direct interest for electro-optic displays utilizing ferroelectric effects) is recorded in the last column.

The liquid crystal transition temperatures of the 5-heptyl-, octyl-, and nonyl-2-([4-(octyl)oxy]phenyl)pyridines (**1**, **8**, and **15**) [1–3] reveal a relatively broad smectic C mesophase (20°C, on average) up to relatively elevated temperatures (83°C, on average) above an ordered smectic mesophase (either designated as S_I [3] or S_F [4]) at a relatively high temperature (62°C, on average). Without X-ray analysis it is not possible to say with any real degree of certainty whether the highly smectic mesophases observed for these esters are smectic F or the closely related I mesophase. Optical microscopy studies strongly indicate the smectic I mesophase. The same is true of the second highly ordered smectic mesophase observed below the smectic I mesophase which has been designated as a smectic G mesophase based on optical microscopy.

The introduction of a *trans*-unsaturated carbon–carbon double bond into either the 2-, 4- or 6-position of the terminal alkoxy chain to yield the compounds **2**, **4**, **6**, **9**, **11**, **13**, **16**, **18** and **20** results in a minimal increase (1°C, on average) in the smectic C transition temperature and a substantial increase (13°C, on average) in the ordered smectic mesophase (here designated as S_I) which results in a significant narrowing (–11°C, on average) of the smectic C mesophase range (now 9°C, on average). The double bond in the 4-position leads to a very narrow smectic C mesophase range (1°C, on average). A second ordered smectic mesophase (here designated as S_G) is also observed (at 58°C, on average).

The influence of the introduction of a *cis*-unsaturated carbon–carbon double bond into either the 3- or 5-position of the terminal alkoxy chain to yield the compounds **3**, **5**, **10**, **12**, **17** and **19** is to displace the smectic C and the ordered smectic mesophase transition temperature (S_I) to lower values (65°C and 55°C, respectively, on average).

Table 1. The liquid crystal transition temperatures for the 5-heptyl-, octyl-, and nonyl-2-([4-*n*-(octenyloxy)phenyl]pyridines 1-21).

| <i>n</i> | <i>R</i> | C-S/°C | S _G -S _I /°C | S _I -S _B /S _C /I/°C | S _B -S _C /°C | S _C -S _A /I/°C | S _A -I/°C | ΔT _{S_C} /°C |
|----------|---|--------|------------------------------------|--|------------------------------------|--------------------------------------|----------------------|---------------------------------|
| 1 |  | 47 | - | 58 | - | 81 | - | 23 |
| 2 |  | 53 | 68 | 76 | - | 84 | - | 8 |
| 3 |  | 32 | - | 51 | - | 58 | - | 7 |
| 4 |  | 81 | - | 82 | - | 84 | - | 2 |
| 5 |  | 38 | 49 | 60 | - | 66 | - | 6 |
| 6 |  | 48 | 51 | 58 | - | 80 | - | 22 |
| 7 |  | 30 | (29) | 48 | - | 73 | - | 25 |
| 8 |  | 38 | - | 62 | - | 82 | - | 20 |
| 9 |  | 43 | 57 | 75 | - | 85 | - | 10 |
| 10 |  | 11 | - | 40 | - | 61 | - | 21 |
| 11 |  | 61 | 72 | 84 | - | 85 | - | 1 |
| 12 |  | 16 | - | 60 | - | 67 | - | 7 |
| 13 |  | 36 | - | 66 | - | 80 | - | 14 |
| 14 |  | 23 | - | 53 | - | 75 | - | 22 |
| 15 |  | 37 | - | 66 | 69 | 85 | - | 16 |
| 16 |  | 36 | 53 | 77 | - | 88 | - | 11 |
| 17 |  | 27 | - | 65 | - | - | - | 0 |
| 18 |  | 37 | 49 | 85 | - | 86 | - | 1 |
| 19 |  | 37 | - | - | 61 | 71 | - | 10 |
| 20 |  | 35 | - | - | 74 | 84 | - | 10 |
| 21 |  | 33 | - | 62 | - | 77 | 78 | 15 |

() represents a monotropic transition temperature.

The temperature range of the smectic C phase decreases (-11.5°C , on average) although large deviations from this average value are observed for individual homologues (for example **10** and **17**). A second ordered smectic mesophase (here designated as S_G) is also induced for one homologue (**5**) below the smectic C phase (49°C).

The double bond in a terminal position of the alkenyloxy chain in compounds **7**, **14** and **21** also leads to a displacement of the smectic C and the ordered smectic mesophase transition temperature (S_I) to lower values (75°C and 54°C , respectively, on average), while the temperature range of the smectic C phase remains constant (20°C , on average). The observed decreases (-8°C , on average for both mesophases) are about half that for the smectic C phase (-19.5°C , on average) and about the same for the ordered phase (-6°C , on average), determined for the corresponding *cis*-substituted materials **3**, **5**, **10**, **12**, **17** and **19**. However, the S_I mesophase is found at a significantly lower temperature (54°C , on average) than that for either the *trans*-compounds **2**, **4**, **6**, **9**, **11**, **13**, **16**, **18** and **20** (75°C , on average) or that (65°C , on average) of the corresponding *cis*-substituted materials **3**, **5**, **10**, **12**, **17** and **19**.

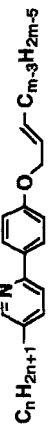
In order to determine the usefulness of the 5-heptyl-, octyl-, and nonyl-2-[(4-(alkenyl)oxy)phenyl]pyridines (**2–7**, **9–14**, and **16–21**) as non-optically active components of chiral smectic C mixtures for electro-optic display device applications based on ferroelectric effects (SSFLCDs, DHFLCDs and SBFLCDs) a fixed amount (15 wt%) was dissolved in a standard chiral smectic C mixture (see the Experimental section). The liquid crystal transition temperatures ($C-S_C^*$, $S_X-S_C^*$, $S_C^*-S_A$, S_A-N^* and N^*-I) the spontaneous polarizations (P_s) and the observed switching times (τ) of the resulting mixtures were then measured. These investigations indicated that the substances with a *trans*-double bond in the 2-position (**2**, **9** and **16**) and the terminally substituted materials (**7**, **14** and **21**) were the most interesting from a technological point of view and fulfilled the expectations referred to in the Introduction [15]. Therefore, it was decided to prepare three homologous series of each type.

The liquid crystal transition temperatures of the heptyl-, octyl- and nonyl-2-[(*E*)-2-alkenyl]oxy)phenyl]pyridines (**2** and **22–29**, **9** and **30–37** and **16** and **38–45**, respectively) are recorded in table 2 and plotted against the total number of carbon atoms (m) in the terminal alkenyloxy chain in figures 1–3, respectively.

The plots of the smectic C–nematic/isotropic transition temperatures against the number of carbon atoms (m) in the terminal alkenyloxy chain of the heptyl-2-[(4-(*E*)-2-alkenyl]oxy)phenyl]pyridines (**2** and **22–29**) depicted in figure 1 rise sharply for the shortest chain lengths possible ($m = 4$ and 5), and then rise gently for the remaining homologues to reach a maximum for the longest chain lengths studied ($m = 12$). The plots of the smectic I–smectic C and smectic G–smectic I transition temperatures start at a slightly longer alkenyloxy chain ($m = 5$) and then rise more gently. All the plots show a certain degree of alternation. The melting point plot starts at a high value and then falls irregularly to a minimum ($m = 11$) before rising steeply. A nematic phase is only observed for short chains ($m = 4$ and 5). The consequence of these trends is narrow-range smectic C and smectic I phases and a wide-range smectic G phase especially for long chains.

The plots of the liquid crystal transition temperatures of the octyl-2-[(4-(*E*)-2-alkenyl]oxy)phenyl]pyridines (**9** and **30–37**) against the total number of carbon atoms (m) in the terminal alkenyloxy chain shown in figure 2 are very similar to those of the corresponding heptyl homologues (**2** and **22–29**) depicted in figure 1. However, the smectic G phase appears at lower temperatures (58°C instead of 66°C , on average, respectively) and the melting points are on the whole, higher (45°C instead of 39°C ,

Table 2. The liquid crystal transition temperatures and enthalpies of fusion for the 5-heptyl-, octyl-, and nonyl-2-[4-n-[(E)-2-alkenyloxy]phenyl]-pyridines 2, 9, 16, 22-45.

| |  | | $S_G-S_I/^\circ\text{C}$ | $S_I-S_B/S_C/^\circ\text{C}$ | $S_B-S_C/^\circ\text{C}$ | $S_C-S_A/N/I/^\circ\text{C}$ | $S_A-N/I/^\circ\text{C}$ | $N-I/^\circ\text{C}$ |
|----|--|----------|--------------------------|------------------------------|--------------------------|------------------------------|--------------------------|----------------------|
| | <i>n</i> | <i>m</i> | $C-S/N/^\circ\text{C}$ | | | | | |
| 22 | 7 | 4 | 71 | - | - | (61) | - | 84 |
| 23 | 7 | 5 | 47 | 63 | - | 75 | - | 76 |
| 24 | 7 | 6 | 43 | 73 | - | 82 | - | - |
| 25 | 7 | 7 | 36 | 66 | - | 81 | - | - |
| 2 | 7 | 8 | 53 | 72 | - | 84 | - | - |
| 26 | 7 | 9 | 40 | 76 | - | 84 | - | - |
| 27 | 7 | 10 | 14 | 75 | - | 85 | - | - |
| 28 | 7 | 11 | 9 | 77 | - | 84 | - | - |
| 29 | 7 | 12 | 38 | 75 | - | 84 | - | - |
| | | | | 68 | - | 85 | - | - |
| 30 | 8 | 4 | 53 | - | 57 | 70 | - | 82 |
| 31 | 8 | 5 | 48 | 63 | - | 79 | - | - |
| 32 | 8 | 6 | 55 | 58 | - | 83 | - | - |
| 33 | 8 | 7 | 48 | 52 | - | 82 | - | - |
| 9 | 8 | 8 | 43 | 57 | - | 85 | - | - |
| 34 | 8 | 9 | 39 | 54 | - | 84 | - | - |
| 35 | 8 | 10 | 43 | 59 | - | 86 | - | - |
| 36 | 8 | 11 | 41 | 58 | - | 86 | - | - |
| 37 | 8 | 12 | 35 | 62 | - | 86 | - | - |
| 38 | 9 | 4 | 53 | - | 69 | 76 | 79 | 86 |
| 39 | 9 | 5 | 60 | - | 78 | 81 | - | - |
| 40 | 9 | 6 | 47 | - | 76 | 87 | - | - |
| 41 | 9 | 7 | 39 | - | 76 | 85 | - | - |
| 16 | 9 | 8 | 36 | - | - | 88 | - | - |
| 42 | 9 | 9 | 27 | - | - | 87 | - | - |
| 43 | 9 | 10 | 36 | - | - | 89 | - | - |
| 44 | 9 | 11 | 32 | - | - | 89 | - | - |
| 45 | 9 | 12 | 44 | - | - | 90 | - | - |

() represents a monotropic transition temperature.

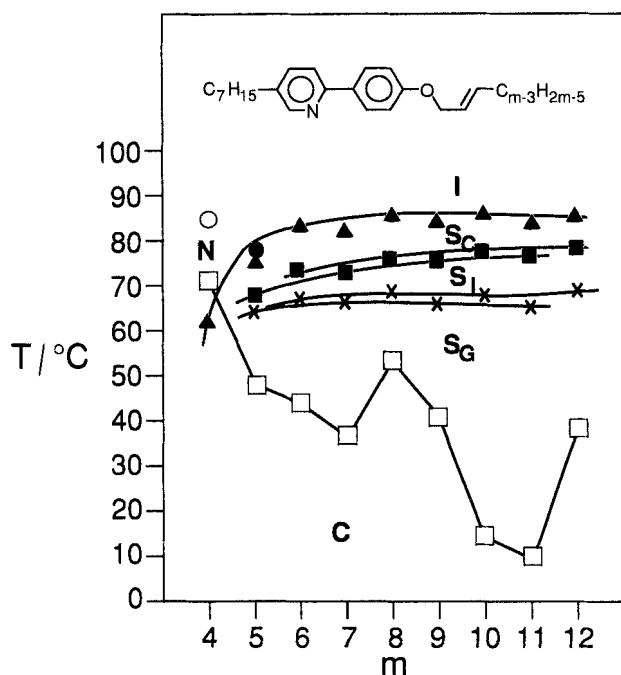


Figure 1. Plots of the transition temperatures against the number of carbon atoms (m) in the alkenyloxy chain of the 5-heptyl-2-[4-((*E*)-2-alkenyl)oxy]phenyl]pyridines **2** and **22–29**.

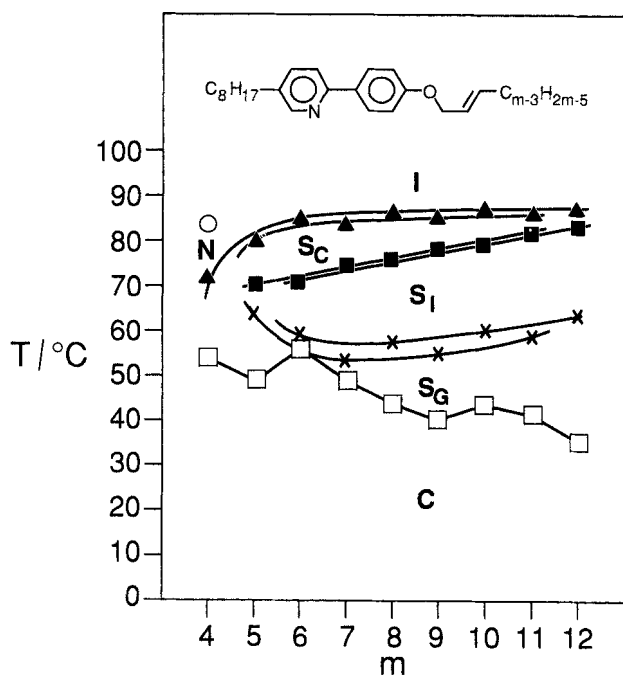


Figure 2. Plots of the transition temperatures against the number of carbon atoms (m) in the alkenyloxy chain of the 5-octyl-2-[4-((*E*)-2-alkenyl)oxy]phenyl]pyridines **9** and **30–37**.

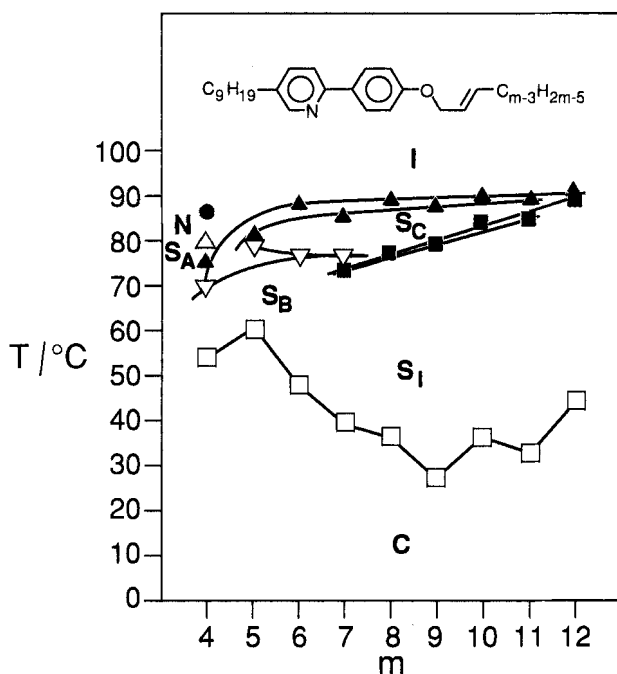


Figure 3. Plots of the transition temperatures against the number of carbon atoms (m) in the alkenyloxy chain of the 5-nonyl-2-[4-[(*E*)-2-alkenyl]oxy]phenyl]pyridines **16** and **38–45**.

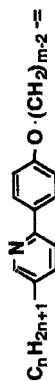
on average, respectively) than those of the analogous heptyl homologues. This results in a much narrower smectic G phase (see figure 2).

The nonyl-2-[4-[(*E*)-2-alkenyl]oxy]phenyl]pyridines (**16** and **38–45**) exhibit a higher degree of smectic polymorphism (S_A and S_B mesophases) than either the corresponding heptyl and octyl homologues (**2** and **22–29** and **9** and **30–37**). However, whereas the shapes of the plots of the smectic I–smectic C and smectic C–isotropic transition temperatures are almost identical to those of the corresponding heptyl and octyl homologues, the nonyl homologues do not exhibit a smectic G mesophase. This results in an enantiotropic smectic I phase for most of the members of the series studied (see figure 3).

The liquid crystal transition temperatures of the heptyl-, octyl- and nonyl-2-[4-[alkenyl]oxy]phenyl]pyridines (**7** and **46–54**, **14** and **55–63** and **21** and **64–72**, respectively) are recorded in table 3 and plotted against the total number of carbon atoms (m) in the terminal alkenyloxy chain in the figures 4–6, respectively.

The plots of the smectic A–isotropic transition temperatures against the number of carbon atoms (m) in the terminal alkenyloxy chain of the heptyl-2-[4-[alkenyl]oxy]phenyl]pyridines (**7** and **46–54**) delineated in figure 4 rise sharply for the shortest chain lengths possible ($m = 3$ and 4) and then rise gently for the remaining homologues to reach a maximum for the longest chain lengths studied ($m = 11, 12$). The plots of the smectic C–smectic A transition temperatures are almost parallel to those of the smectic A–isotropic transition temperatures. For the shortest chain lengths ($m = 3$ and 4), a smectic B mesophase is also observed. The plots for the smectic I and G mesophases are also more or less parallel, falling from initial high values ($m = 5$) to a minimum for intermediate chain lengths ($m = 8$). The plots for the smectic I phase continues to rise to reach a maximum for the longest chain length synthesized ($m = 12$), whereas the plots for the smectic G mesophase stop at

Table 3. The liquid crystal transition temperatures and enthalpies of fusion for the 5-heptyl-, octyl-, and nonyl-2-(4-*n*-(alkenyl)oxyphenyl)pyridines 7, 14, 21, 46-72.



| | <i>n</i> | <i>m</i> | C-S/ $^{\circ}C$ | S_G-S_I / $^{\circ}C$ | S_I-S_C / $^{\circ}C$ | S_B-S_A / $^{\circ}C$ | S_C-S_A / $^{\circ}C$ | S_A-I / $^{\circ}C$ | N-I/ $^{\circ}C$ |
|----|----------|----------|------------------|-------------------------|-------------------------|-------------------------|-------------------------|-----------------------|------------------|
| 46 | 7 | 3 | 48 | - | - | 58 | - | 62 | 64 |
| 47 | 7 | 4 | 41 | - | - | 50 | - | 55 | - |
| 48 | 7 | 5 | 54 | 45 | 59 | - | 72 | 73 | - |
| 49 | 7 | 6 | 23 | 32 | 49 | - | 66 | - | - |
| 50 | 7 | 7 | 21 | 34 | 52 | - | 75 | 77 | - |
| 7 | 7 | 8 | 30 | (29) | 48 | - | 73 | - | - |
| 51 | 7 | 9 | 36 | (31) | 52 | - | 75 | 78 | - |
| 52 | 7 | 10 | 37 | - | 55 | - | 74 | 76 | - |
| 53 | 7 | 11 | 31 | - | 62 | - | 75 | 78 | - |
| 54 | 7 | 12 | 42 | - | 63 | - | 73 | 76 | 82 |
| 55 | 8 | 3 | 59 | - | - | 65 | - | 66 | - |
| 56 | 8 | 4 | 37 | - | - | 56 | - | 58 | - |
| 57 | 8 | 5 | 43 | - | 65 | - | 70 | 75 | - |
| 58 | 8 | 6 | 31 | - | 54 | - | 68 | - | - |
| 59 | 8 | 7 | 26 | - | 59 | - | 76 | - | - |
| 14 | 8 | 8 | 23 | - | 53 | - | 75 | - | - |
| 60 | 8 | 9 | 33 | - | 61 | - | 78 | - | - |
| 61 | 8 | 10 | 32 | - | 60 | - | 77 | - | - |
| 62 | 8 | 11 | 31 | - | 65 | - | 79 | - | - |
| 63 | 8 | 12 | 38 | - | 66 | - | 77 | - | - |
| 64 | 9 | 3 | 58 | - | - | 70 | - | 72 | - |
| 65 | 9 | 4 | 46 | - | - | 63 | - | 64 | - |
| 66 | 9 | 5 | 46 | - | 72 | - | - | 78 | - |
| 67 | 9 | 6 | 41 | - | 64 | - | 70 | 73 | - |
| 68 | 9 | 7 | 34 | - | 68 | - | 75 | 82 | - |
| 21 | 9 | 8 | 33 | - | 62 | - | 77 | 78 | - |
| 69 | 9 | 9 | 32 | - | 69 | - | 80 | 82 | - |
| 70 | 9 | 10 | 37 | - | 67 | - | 80 | - | - |
| 71 | 9 | 11 | 36 | - | 73 | - | 82 | - | - |
| 72 | 9 | 12 | 37 | - | 72 | - | 80 | - | - |

() represents a monotropic transition temperature.

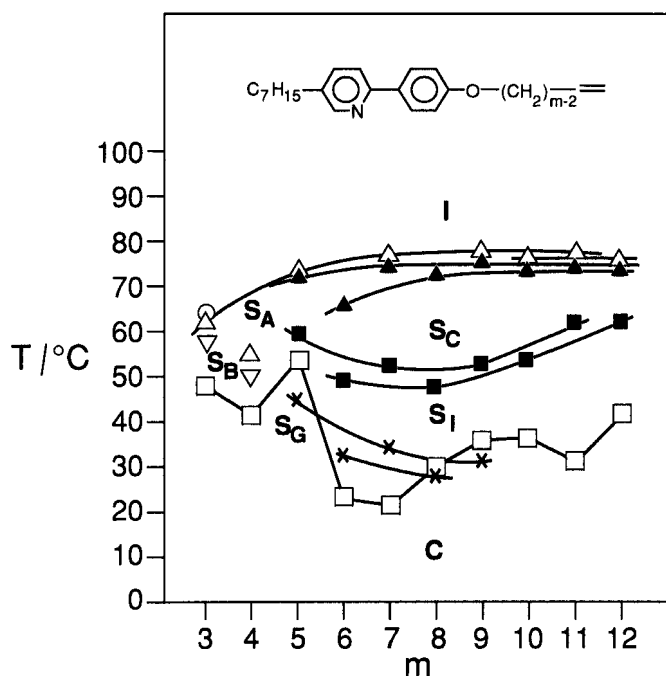


Figure 4. Plots of the transition temperatures against the number of carbon atoms (m) in the alkenyloxy chain of the 5-heptyl-2-[(4-[alkenyl]oxy)phenyl]pyridines **7** and **46–54**.

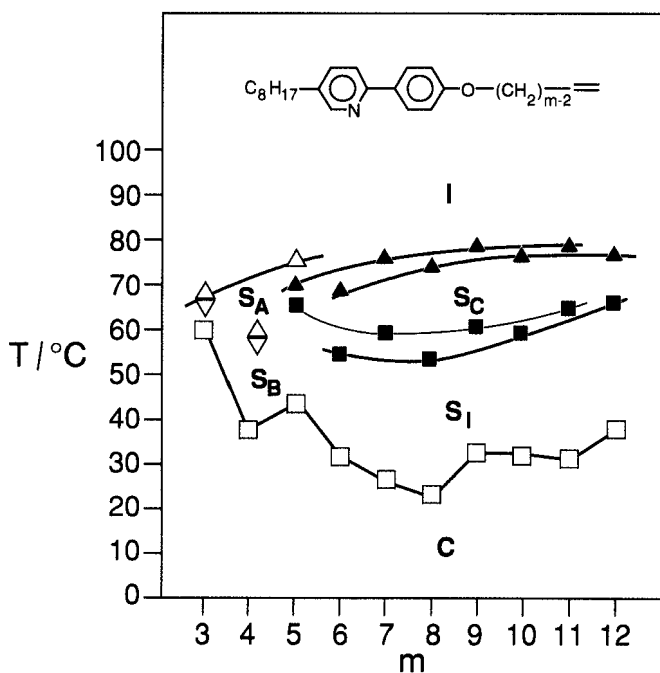


Figure 5. Plots of the transition temperatures against the number of carbon atoms (m) in the alkenyloxy chain of the 5-octyl-2-[(4-[alkenyl]oxy)phenyl]pyridines **14** and **55–63**.

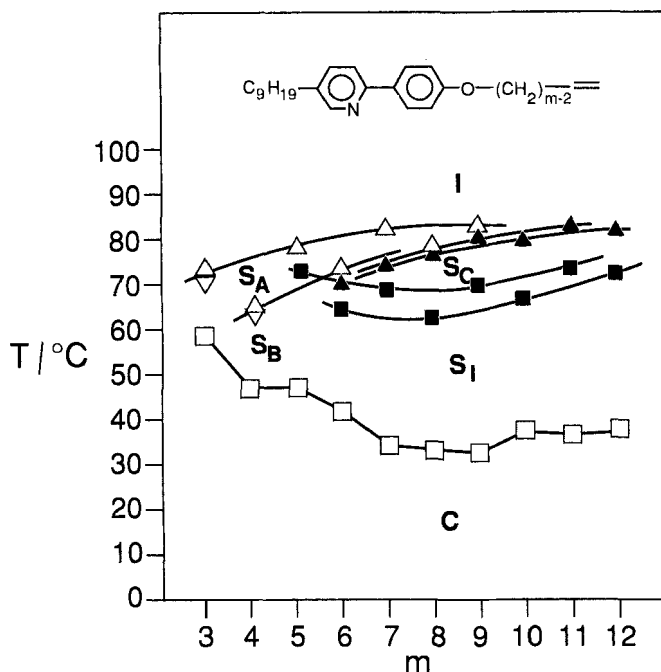


Figure 6. Plots of the transition temperatures against the number of carbon atoms (m) in the alkenyloxy chain of the 5-nonyl-2-[(4-[alkenyl]oxy)phenyl]pyridines **21** and **64–72**.

intermediate chain lengths ($m = 9$). The plot of the melting point is irregular as is often the case.

The plots of the liquid crystal transition temperatures of the octyl-2-[(4-[alkenyl]oxy)phenyl]pyridines (**14** and **55–63**) against the total number of carbon atoms (m) in the terminal alkenyloxy chain shown in figure 5 are very similar to those of the corresponding heptyl homologues (**7** and **46–54**) depicted in figure 4. However, the smectic G phase observed for the heptyl substituted materials has disappeared in the corresponding octyl materials. The smectic I–smectic C transition temperature is also higher (60°C instead of 55°C, on average respectively). This results in a wider-range smectic I mesophase (see figure 5).

The plots of the liquid crystal transition temperatures of the nonyl-2-[(4-[alkenyl]oxy)phenyl]pyridines (**21** and **64–72**) against the total number of carbon atoms (m) in the terminal alkenyloxy chain shown in figure 6 are almost identical to those of the corresponding octyl homologues (**14** and **55–63**) depicted in figure 5. However, the smectic A phase is observed for more homologues ($m = 3–9$ instead of $m = 3–5$) and the smectic I–smectic C transition temperatures are higher (68°C instead of 60°C, on average, respectively). The plots of the melting points are similar, although the values for the octyl homologues are, in general, somewhat lower (35°C instead of 40°C, on average, respectively). Thus the smectic I mesophase range is somewhat greater (28°C instead of 25°C, on average, respectively) for the nonyl homologues.

3. Physical properties

In order to investigate the suitability of the 5-*n*-alkyl-2-[4-(alkenyloxy)phenyl]pyridines (**1–72**) as non-optically active components of chiral smectic C mixtures for electro-optic display device applications based on ferroelectric effects (SSFLCDs,

Table 4. A comparison of the liquid crystal transition temperatures, the spontaneous polarizations and the switching times for mixtures 1 and 2 consisting of the base mixture (SCO 1014) doped with 15 wt% of the reference compound (1) and the test substance (18) respectively

| Mixture | $C/S_X-S_C^*/^{\circ}C$ | $S_C^*-S_A/^{\circ}C$ | $S_A-N^*/^{\circ}C$ | $N^*-I/^{\circ}C$ | $P_s/nC\text{ cm}^{-2}$ | $\tau/\mu\text{s}$ |
|---------|-------------------------|-----------------------|---------------------|-------------------|-------------------------|--------------------|
| 1 | -8.8 | 62.2 | 68.1 | 73.4 | 16.9 | 120 |
| 2 | -11.4 | 63.8 | 67.3 | 73.7 | 17.8 | 126 |

DHFLCDs and SBFLCDs), a fixed amount (15 wt%) of selected homologues of the ethers was dissolved in a standard chiral smectic C mixture (SCO 1014, see the Experimental section) and the liquid crystal transition temperatures ($C-S_C^*$, $S_X-S_C^*$, $S_C^*-S_A$, S_A-N^* and N^*-I) the spontaneous polarizations (P_s) and the observed switching times (τ) of the resulting mixtures were determined under standard conditions (τ : 10 Vpp/ μ square wave, time to maximum current, at 25°C; P_s : 10 Hz, 10 Vpp/ μ , triangle). The results of a systematic study of the physical properties of the 5-*n*-alkyl-2-[4-(*n*-[alkenyl]oxy)phenyl]pyridines (1–72) as non-optically active components of chiral smectic C mixtures for electro-optic display device applications based on ferroelectric effects (SSFLCDs, DHFLCDs and SBFLCDs) will be described in detail elsewhere [15]. As a typical example of these results the liquid crystal transition temperatures ($C-S_C^*$, $S_X-S_C^*$, $S_C^*-S_A$, S_A-N^* and N^*-I) and the observed switching times (τ) for the mixtures 1 and 2 consisting of the base mixture (SCO 1014) doped with 15 wt% of either the saturated compound 5-octyl-2-[4-([octyl]oxy)phenyl]pyridine (1) or the 5-octyl-2-[4-([(E)-4-octenyl]oxy)phenyl]pyridine (18) are collated in table 4. It is clear from the table that the addition of the alkenyloxy-substituted substance (18) to the base mixture results in a higher chiral smectic C-smectic A transition temperature (+1.6°C) and a lower crystallisation temperature [18–20] (-2.6°C) than for the corresponding mixture containing the alkoxy-substituted reference compound (1). This leads to a not insubstantial increase in the temperature range of the chiral smectic C mesophase (+4.2°C). The addition of the alkenyloxy-substituted substance (18) to the base mixture also results in an increase in the temperature range of the nematic mesophase (+1.1°C). The slight increase in the spontaneous polarization indicates a corresponding increase in the tilt angle.

4. Experimental

The liquid crystal transition temperatures of the compounds prepared recorded in tables 1–3 were determined by optical microscopy using a Leitz Ortholux II POL BK microscope in conjunction with a Mettler FP 82 heating stage and FP 80 control unit. All the monotropic liquid crystal phases could be observed using a microscope and no virtual values (extrapolated) had to be determined. When necessary, the Mettler stage could be cooled (-50°C) by allowing N₂ gas, cooled by liquid N₂, to pass through the stage at a controlled rate. The liquid crystal transition temperatures were also determined using a Mettler DTA TA 2000.

The purity and structure of the compounds were determined as described in detail in preceding publications [14, 17].

The chiral smectic C mixture SCO 1014 consists of 4-[*trans*-4-([(R)-2-fluorohexanoyl]oxy)cyclohexyl]phenyl-2,3-difluoro-4-(octyloxy)benzoate ester (16 wt%),

2-(4-(hexyloxy)phenyl)-5-nonylpyrimidine (24 wt%), 2-[4-(nonyloxy)phenyl]-5-nonylpyrimidine (24 wt%), 2-[4-(nonyloxy)phenyl]-5-heptylpyrimidine (12 wt%), 2-[4-decyloxy)phenyl]-5-octylpyrimidine (12 wt%). The determination of the physical properties of the chiral mixtures containing the new esters was carried out as previously described [18–20].

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