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# The influence of double bonds in the terminal chain of 2-ring compounds on the physical properties of $S_C^*$ mixtures

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We present the properties of $S_C^*$ mixtures containing new 2-ring 5-*n*-alkyl-2-(4-*n*-alkenyloxyphenyl)pyridines and pyrimidines with systematically varying positions and configurations of the double bond *Trans* configurations at odd positions (counting the number of atoms from the core including the oxygen and the first carbon atom of the double bond) suppress the $S_A$ phase, increase the $S_C^*$ tilt angle, $\theta$, and the spontaneous polarization, $P_S$, and lead to long switching times $\tau$. *Cis* configurations at even positions suppress the nematic phase in favour of smectic phases, decrease $\theta$ and $P_S$, and shorten $\tau$. Other positional configurational combinations strongly reduce the clearing point. Furthermore, our results indicate that the preferred conformation of the alkenyloxy chain consists of alternating *cis* and *trans* units.

## 1. Introduction

From investigations of nematic liquid crystals, it is well known that double bonds in the terminal chain of liquid crystal molecules have a strong influence on their physical properties. Of great practical importance are, for example, the effects on the phase transition temperatures and on the elastic constants. It was also found that the position of the double bond as well as its configuration (*cis* or *trans*) are important for the observed changes [1, 2]: for double bonds within the chain only *trans* configurations at odd positions induced a large nematic phase. Double bonds at the 2-position drastically reduced the clearing point, the *trans* configuration more so than the *cis* configuration [3]. Terminal double bonds generated a strong odd–even effect in most liquid crystal parameters [4].

Since the end chains in nematics are usually quite short, double bonds are close to the core and steric interactions between the core and the double bond are certainly important. Smectic materials, on the other hand, have much longer end chains, and we can explore the effect of a double bond further away from the core. Furthermore, there are parameters typical for smectics (for example the tilt angle in the $S_C$ phase) which have no counterpart in the nematic phase, and it is not immediately clear how these parameters are affected by the double bonds in the chain. These questions are of considerable importance, for example, for the development of new ferroelectric mixtures, since double bonds can be introduced in virtually every molecule of a smectic mixture, so that fine tuning of the relevant parameters becomes feasible.

The synthesis and characterization of the 2-ring pyridine- and pyrimidine-alkenyloxy [5] compounds studied in this work are described elsewhere in detail. In

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this paper we describe the properties of these compounds in two standard mixtures: one exhibits the phase sequence I–N*–$S_A$–$S_C^*$ required for surface stabilized ferroelectric [6] applications and the other the sequence I–$S_A$–$S_C^*$ used in electrically oriented devices like short pitch bistable ferroelectric [7] or deformed helix ferroelectric [8] liquid crystal displays. For two selected compounds where the difference in the influence of their double bond is most striking, two binary mixtures between a chiral dopant and each of the $S_C$ components are investigated in more detail.

## 2. Experimental

### 2.1. *The materials*

The two series of compounds presented in this work incorporate either a terminal octyloxy chain (as reference compounds) or an octenyloxy chain with the double bond in various positions and with differing configurations (*cis* and *trans*) as shown in figure 1. The positions and configurations of the double bonds are chosen according to the half-ring notation shown in this figure. The configuration of the unsaturated carbon–carbon double bond was confirmed by H NMR spectroscopy—the *trans*–olefinic coupling constants ($\approx$12–18 Hz) are larger than those of the corresponding *cis*-olefinic coupling constants ($\approx$7–11 Hz)—and by infrared spectroscopy, monitoring the *trans* absorption at 970–960 $cm^{-1}$ and the *cis* absorption at 730–675 $cm^{-1}$ [5].

Our choice of configurations is strongly supported by the data presented in table 1 and later in table 2 for the related hexyloxy and hexenyloxy substituted phenylpyrimidines **1**–**8** chosen as a model system for a study of the effect of both *cis* and *trans* configurations of the double bond in all possible positions of the hexenyloxy side chain: the compounds **3**, **4** and **7**, which have different double bond configurations from those suggested by the scheme of figure 1, have strongly reduced clearing points and no $S_C^*$ phase.

The long pitch surface stabilized ferroelectric standard mixture I is composed of achiral 2-ring 5-*n*-alkyl-2-(4-*n*-alkoxyphenyl)pyrimidines [9] and 17 per cent of a chiral α-fluoro-ester [10] dopant; it has the phase sequence I 74·1°C N* 67·3°C $S_A$ 60·5°C $S_C^*$ and a $P_S$ of 20·6 nC $cm^{-2}$. The short pitch surface stabilized ferroelectric mixture II contains 30 wt% of a chiral *p*-terphenyl diester [11] dopant and exhibits the phase sequence I 63·4°C $S_A$ 60·5°C $S_C^*$ and a $P_S$ of 88 nC $cm^{-2}$. With these two standard

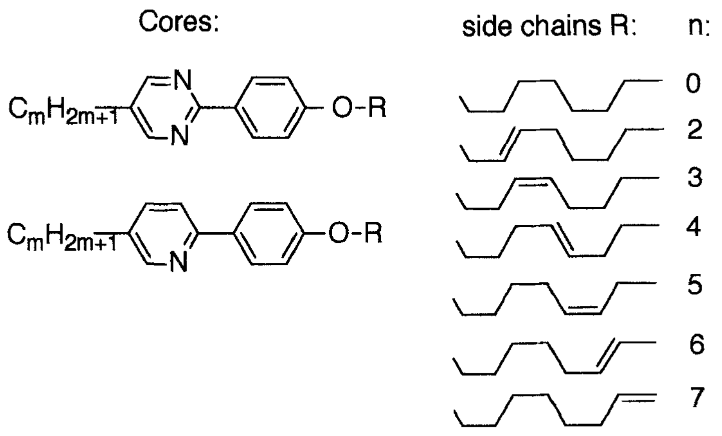
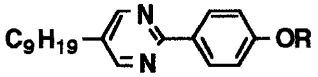


Figure 1. The two series studied. *m* is 7, 8 or 9. Each of the 6 cores is combined with each of the 7 side chains. The number *n* labels the position of the double bond.

Table 1. Comparison of phases and transition temperatures of compounds with configurations that correspond to the scheme of figure 1 (**2**, **5**, **6**, **7**) with those that do not fit this scheme (**3**, **4**).



| | *R* | C | | $S_C$ | | $S_A$ | | N | | I |
|---|---|---|---|---|---|---|---|---|---|---|
| **1** | Hexyl | ● | 33°C | ● | 48°C | ● | 71°C | ● | 72°C | ● |
| **2** | *trans*-2-Hexenyl | ● | 49°C | ● | 63°C | ● | 70°C | ● | 72°C | ● |
| **3** | *cis*-2-Hexenyl | ● | 32°C | | — | (● | 17°C) | | — | ● |
| **4** | *trans*-3-Hexenyl | ● | 26°C | | — | ● | 42°C | | — | ● |
| **5** | *cis*-3-Hexenyl | ● | 58°C | (● | 41°C | ● | 56°C) | | — | ● |
| **6** | *trans*-4-Hexenyl | ● | 48°C | (● | 35°C) | ● | 70°C | | 72°C | ● |
| **7** | *cis*-4-Hexenyl | ● | 22°C | | — | ● | 46°C | | — | ● |
| **8** | 5-Hexenyl | ● | 48°C | | — | ● | 62°C | | — | ● |

mixtures corresponding sample mixtures I and II respectively, were prepared by doping them with 15 wt % of the compounds shown in figure 1. These sample mixtures were investigated in 8 $\mu$m cell gap displays. The following parameters were measured: (i) the liquid crystal transition temperatures, (ii) the spontaneous polarization $P_S$ and (iii) the switching time $\tau$, using a $10\,V_{p-p}\,\mu m^{-1}$ square wave field and measuring the time required to reach the current maximum (both at 25°C).

The *trans*-2- and the *cis*-3- compounds of the $m = 9$ series of phenylpyrimidines were studied in more detail as binary mixtures with a chiral dopant. They were chosen because they exhibit a very pronounced difference in their physical parameters: all the properties typical for *cis* and *trans* are strongly pronounced. Each of the compounds was mixed with 15 wt % of an $\alpha$-fluoro-ester dopant. The *cis* binary mixture has the phase sequence I 54·2°C $S_A$ 41·0°C $S_C^*$ and the *trans* binary mixture I 69·0°C $S_C^*$.

For these two mixtures the spontaneous polarization $P_S$, the switching time $\tau$ and the tilt angle $\theta$ were measured as a function of temperature. To avoid damage to the texture, the driving field was kept low ($1{\cdot}4\,V\,\mu m^{-1}$, 50 Hz, triangular waveform). Current and light transmission were monitored simultaneously. To determine the switching angle, we first inspected the current peak and then took as reference fields those just before and just after the peak to determine the switching angle. This procedure minimized the contribution of the electroclinic effect to the switching angle. This is especially important close to the upper limit of the $S_C^*$ phase. In the following we assume, that the tilt angle is half of this experimental switching angle.

## 3. Results

### 3.1. *The liquid crystal phase ranges*

The liquid crystal phases and transition temperatures for the sample mixtures I are presented in figures 2 and 3. The transition temperatures exhibit a pronounced odd–even effect—or a *cis–trans* effect. Due to our choice of configurations there is a 1 : 1 correspondence between {odd, *trans*} and {even, *cis*}, respectively. Note that odd or even refers to the number of atoms—the oxygen included—between the phenyl ring and the double bond, whereas the label *n* indicates the number of carbon atoms between the oxygen atom and the first atom of the double bond. It is evident from these figures, that *trans* configurations yield much wider $S_C^*$ phases than *cis* configurations;

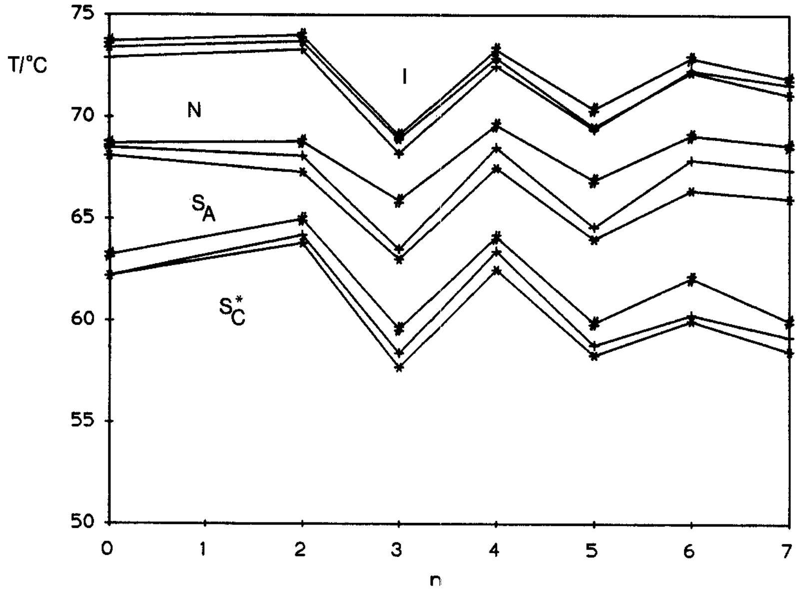


Figure 2. Phase transition temperatures of the pyridine sample mixtures I; *n* is defined in figure 1. The labels *, + and # denote $m=7$, 8 and 9, respectively.

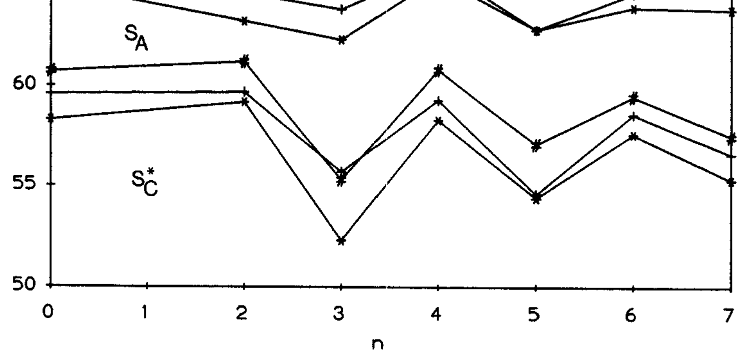


Figure 3. Phase transition temperatures of the pyrimidine sample mixtures I; *n* and the labels are defined in figure 2.

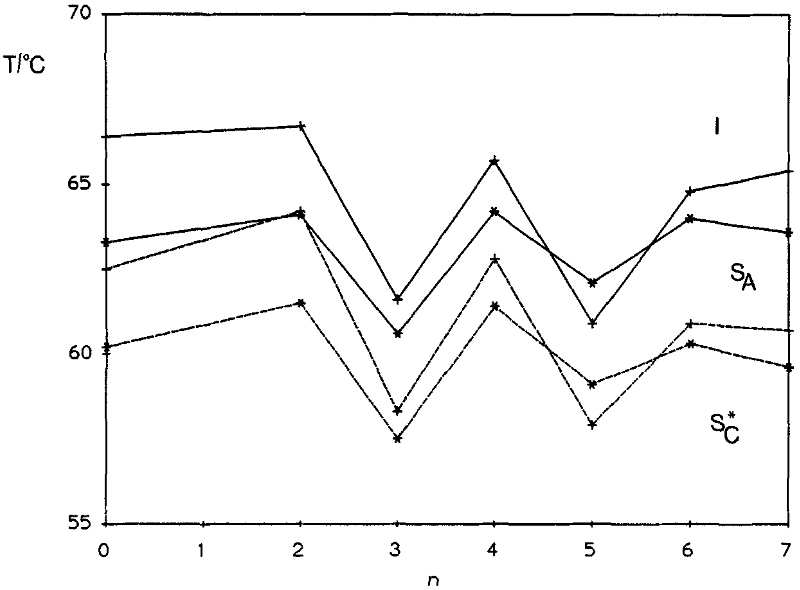


Figure 4. Phase transition temperatures of the $m=7$ pyridine (label: +) and the $m=9$ pyrimidine (label: *) sample mixtures II; $n$ is defined in figure 2.

some are even larger than those of the saturated compounds (denoted by $n=0$). Equally important, the nematic mesophases of the *trans* compounds are significantly increased at the cost of the $S_A$ phase. This is an important feature for designing surface stabilized ferroelectric mixtures.

Figure 4 shows corresponding results for sample mixtures II. The phases follow the same trend. However, presumably because the nematic phase is absent, the width of the $S_A$ phase is not as strongly modulated.

### 3.2. *Other $S_C^*$ parameters*

Figure 5 shows the switching times and figure 6 the spontaneous polarizations of sample mixtures I. Despite some scatter in the data it is evident that *trans* configurations have larger spontaneous polarizations and longer switching times than *cis* configurations. Both these effects are probably due to the larger $S_C^*$ tilt angle of the *trans* configuration (see the Discussion). To summarize, *trans* configurations in the terminal chains of the compounds under investigation in mixture I lead to:

a wider nematic phase at the expense of the $S_A$ phase,
a larger spontaneous polarization,
a longer switching time,
a larger tilt angle.

The results for the two binary mixtures are shown in the next few figures: the temperature dependence of spontaneous polarization and tilt angle is shown in figures 7 and 8, respectively. In the *trans* mixture, both, the tilt angle and the spontaneous polarization increase much more steeply at the phase transition than in the *cis* mixture. This is expected and follows from the different nature of the phase transition (first order for *trans*, second order for *cis*). If the quantity $(P_S/\theta)$ is plotted versus $\theta^2$, the data can be fitted by a straight line (see figure 9), in accordance with the theories discussed below.

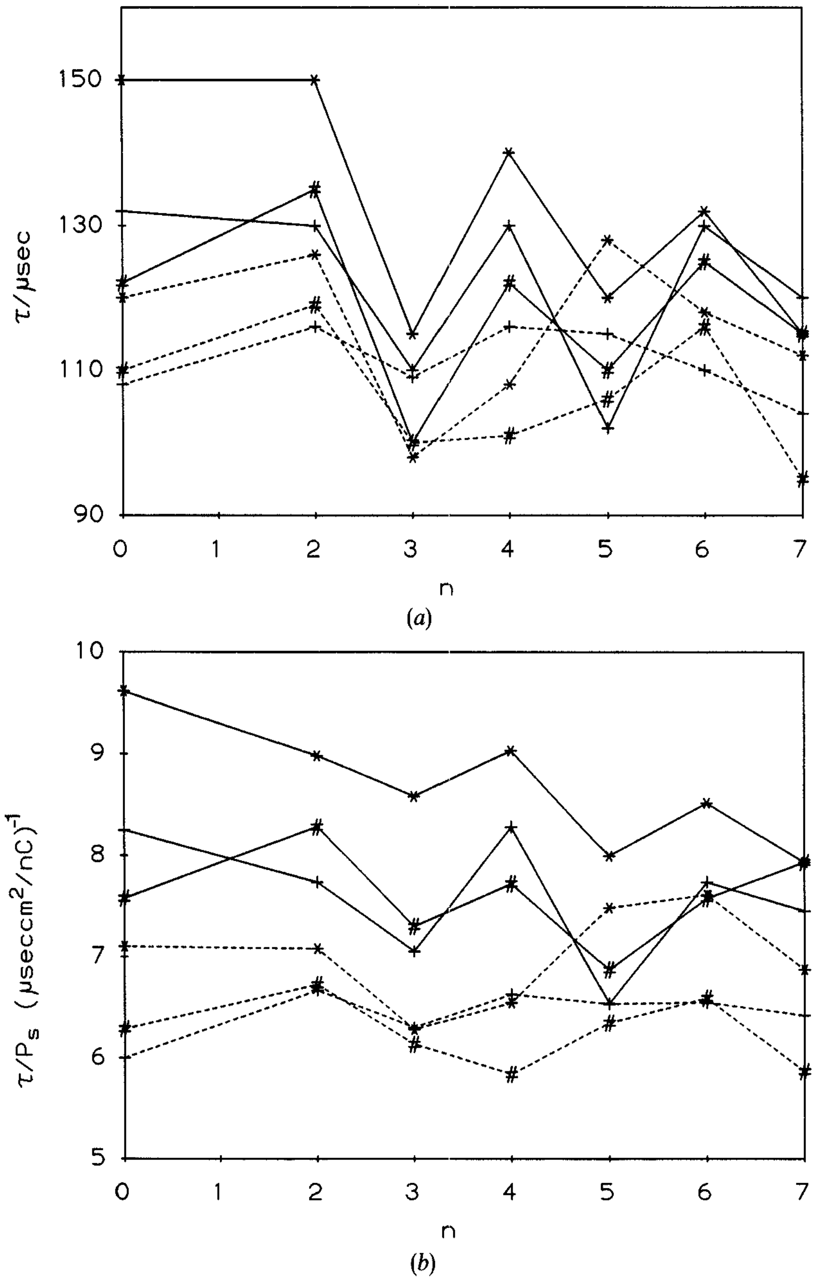


Figure 5. (*a*) Switching time $\tau$ and (*b*) ($\tau/P_S$) of the pyridine (dotted line) and the pyrimidine (solid line) for sample mixtures I; $\tau$ is the time to reach the current maximum if a $10\,V_{pp}\,\mu m^{-1}$ square wave electric field is applied. The temperature is 25°C; *n* and the labels are defined in figure 2.

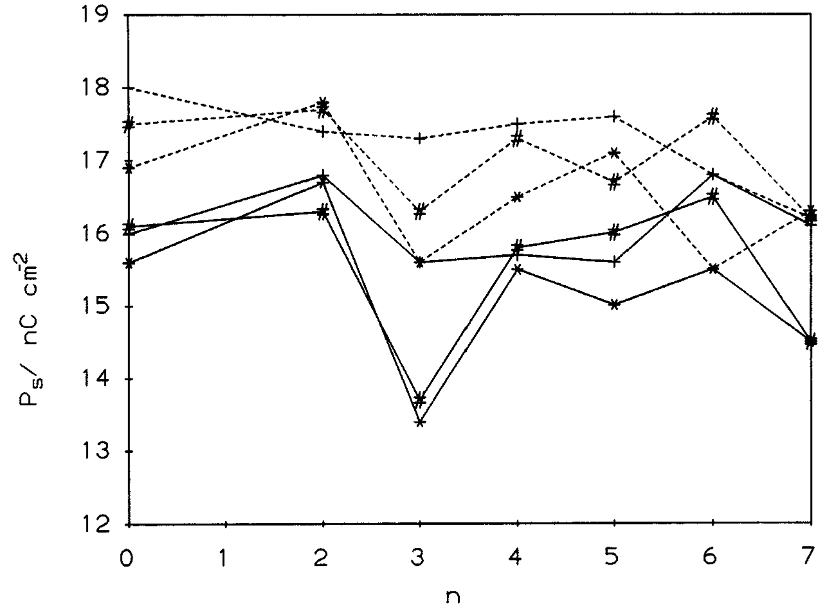


Figure 6. Spontaneous polarizations $P_S$ of the sample mixtures I; $n$, the labels and line styles are defined in figure 5.

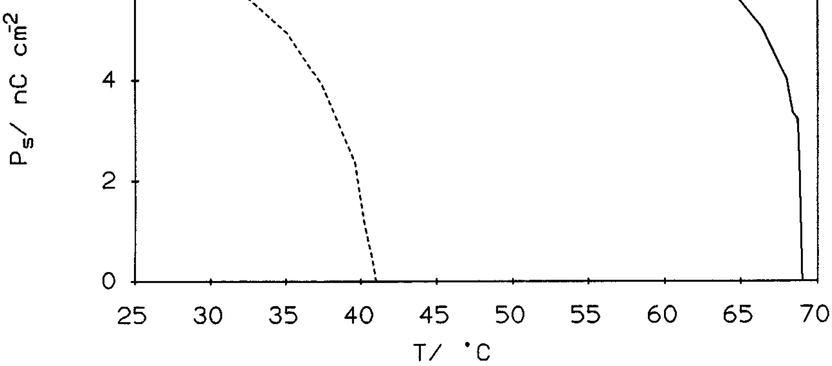


Figure 7. The spontaneous polarization $P_S$ of binary mixtures of a *trans*-2- and a *cis*-3-phenylpyrimidine ($m=9$) with a chiral dopant as a function of temperature $T$.

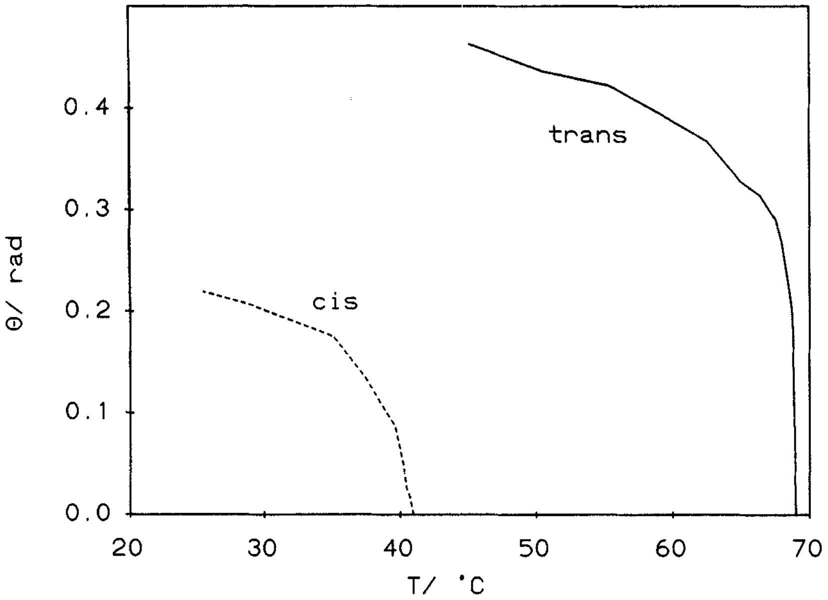


Figure 8. Tilt angle $\theta$ of the two binary mixtures of figure 7 as a function of temperature $T$.

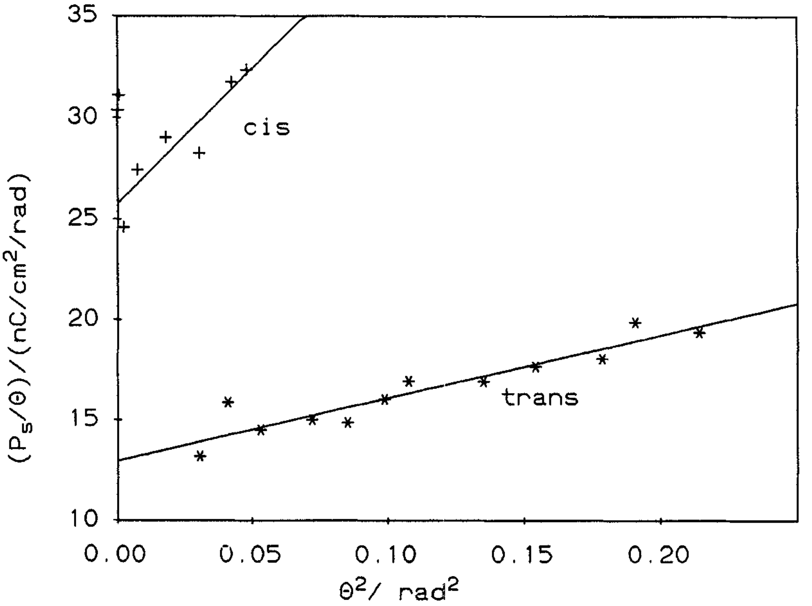


Figure 9. $(P_S/\theta)$ versus $\theta^2$ for the data of figures 7 and 8.

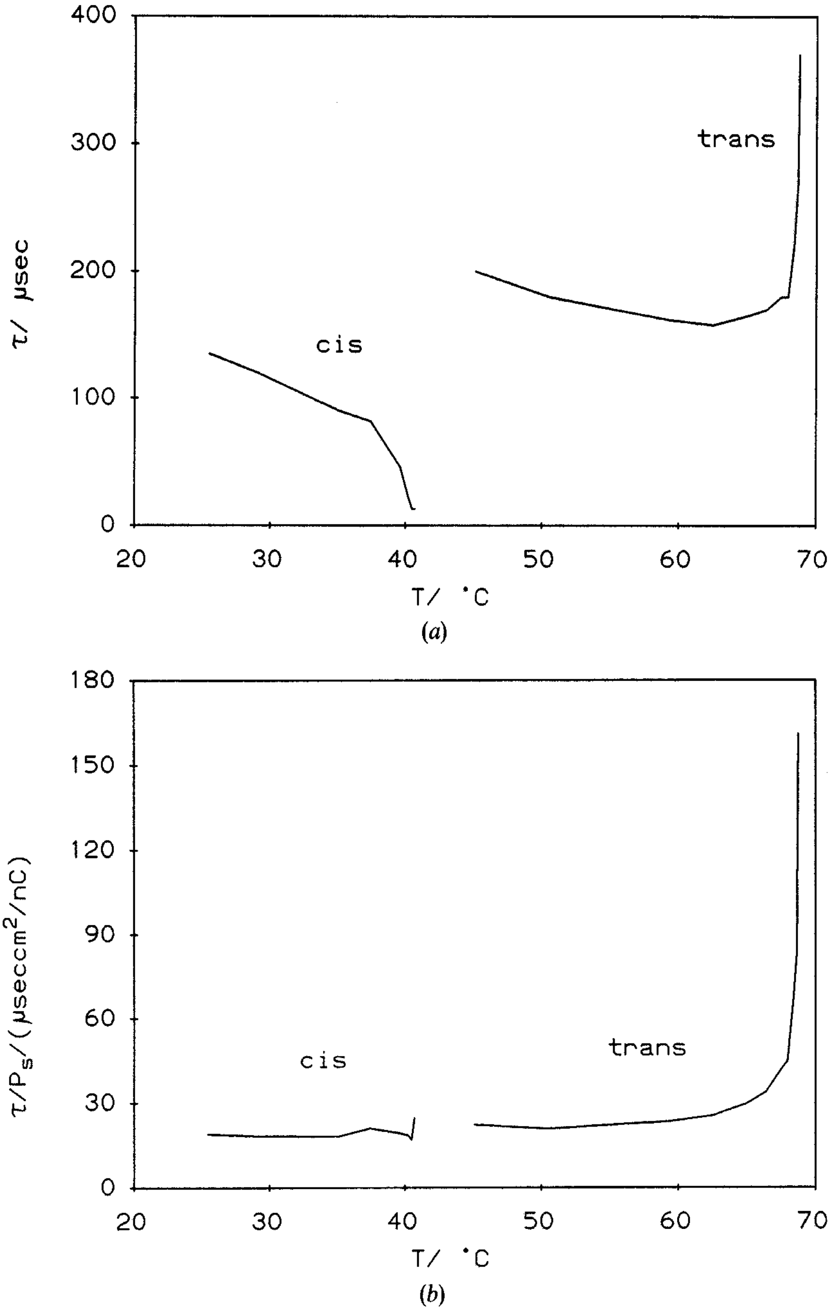


Figure 10. Temperature dependence of (*a*) the switching time $\tau$ and (*b*) the ratio ($\tau/P_S$) of the two mixtures of figure 7.

Finally in figure 10 the switching time $\tau$ is plotted as a function of temperature. The drastic increase of $\tau$ close to the nematic phase is not yet understood, but it cannot be attributed to the tilt angle (see equation (5)): if $\tau/P_S$ is plotted (see figure 10), an analogous increase is observed.

## 4. Discussion

### 4.1. *The conformation of the end chain*

Since it has long been postulated that in the saturated alkyl chain of nematic compounds the all-*trans*-conformation is preferred, it may not come as a surprise that *cis* configurations of double bonds lead to lower clearing points. However, according to this argument, illustrated in the column labelled 'all-*trans* conformation model' in table 2, the *trans*-3-hexenyl compound should have a similar clearing point to that of the *trans*-2 or the *trans*-4, whereas $T_c$ of the *cis*-3-hexenyl compound should be much lower. However, the clearing point of *trans*-3 is 30°C lower than that of *trans*-2 or *trans*-4, and still 15°C lower than that of *cis*-3. This odd–even effect for the *trans* form is complemented by a corresponding even–odd effect for the *cis* configurations. This follows also from table 2. Both findings are conveniently expressed by the notations shown in the column labelled 'alternating *cis*–*trans* conformation model' in table 2: it correctly predicts that the clearing point of the *trans*-3-hexenyl compounds is lower than that of the *cis*-3-hexenyl compounds.

The fact that most *cis*–*trans* effects presented here hold for all positions except for the terminal ones strongly suggests that this conformational model is applicable to all but the last position of the double bond.

### 4.2. *The difference between cis and trans compounds*

We have shown above, that *trans* compounds:

exhibit high clearing points,
suppress the $S_A$ phase
lead to high spontaneous polarizations, long switching times and large tilt angles.

Correspondingly, *cis* compounds:

exhibit low clearing points,
induce smectic phases,
lead to low spontaneous polarizations, short switching times and small tilt angles.

In the following, we discuss to what extent these properties are correlated and manifestations of one or two basic differences between the two types of compounds.

#### 4.2.1. *The role of the tilt angle*

Let us first discuss the relation of the spontaneous polarization, switching time and viscosity to the tilt angle $\theta$, using the simplest model approaches found in the literature. For the spontaneous polarization we write [12]

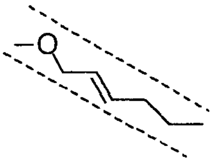
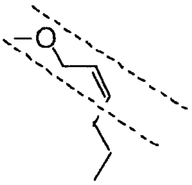
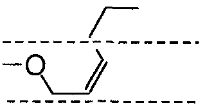
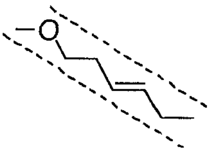
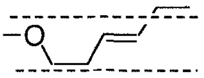
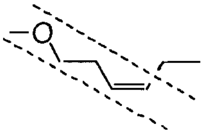
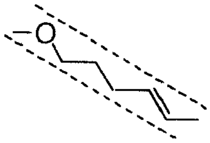
$$P_S = P_0 \sin\theta, \tag{1}$$

where $P_0$ is a constant.

An effective viscosity $\gamma_{\mathrm{eff}}$ is defined by [13]

$$\gamma_{\mathrm{eff}}\dot{\phi} + P_S E \sin\phi = 0, \tag{2}$$

Table 2. Two possible notations that model the conformations of the hexenyloxy chain: on the left the all-*trans* conformation leads, for every position of the double bond, to the straightest chain and the highest clearing point (c.p.). The alternating *cis–trans* notation predicts a higher clearing point for the *cis*-3- than for the *trans*-3-hexenyl compounds, as is observed experimentally (see right hand column and Table 1).

| All-*trans* conformation model | Configuration of double bond | Alternating *cis-trans* conformation model | c.p. predicted | | c.p. exp. °C |
|---|---|---|---|---|---|
| | | | all-*tr.* | *cis*/*tr.* | |
|  | *trans*-2 |  | High | High | 72 |
|  | *cis*-2 |  | Low | Low | (17) |
|  | *trans*-3 |  | High | Low | 42 |
|  | *cis*-3 |  | Low | High | (56) |
|  | *trans*-4 |  | High | High | 72 |

where $\phi$ is the angle of rotation on the $S_C^*$ cone and $E$ the applied electric field. This leads to a switching time $\tau$ of

$$\tau = \frac{\gamma_{\mathrm{eff}}}{P_S E}. \tag{3}$$

The relation between $\gamma_{\mathrm{eff}}$ and $\theta$ is given by

$$\gamma_{\mathrm{eff}} = \gamma_0 \sin^2 \theta, \tag{4}$$

where $\gamma_0$ is a constant. Since the tilt angle is difficult to measure, it is useful to eliminate it from the above formulae

$$\frac{\tau}{P_S} = \frac{\gamma_0}{P_0^2 E}. \tag{5}$$

The ratio ($\tau/P_S$) thus measures the variations of $\gamma_0$ or $P_0$. In figure 5(*b*) ($\tau/P_S$) is plotted and can be compared with the values of $\tau$ in figure 5(*a*). As can be seen, in this representation the odd–even effect is strongly reduced. We thus conclude that it is primarily the tilt angle $\theta$ that is affected by the position of the double bond. Similar conclusions can be drawn from figure 10(*b*), if the temperature region close to the clearing point of the *trans* mixture is excluded. In both cases, however, the *cis* mixtures seem slightly faster than the *trans* mixtures. This holds even if the influence of the tilt angle is eliminated.

### 4.2.2. *Thermodynamic models*

The temperature dependence of the $S_C^*$ parameters has been described by many authors. To describe the relation between tilt angle and spontaneous polarization upon changing the temperature, equation (1) is replaced by an expansion of $P_S$ in terms of powers of $\theta$ [14, 15]

$$P_S = a_1\theta + a_2\theta^3, \tag{6}$$

where $a_1$ is related to the bilinear coupling of tilt and spontaneous polarization, whereas $a_2$ is a measure for various higher order interactions. Note $a_1$ is equal to $P_0$ of equation (1).

If ($P_S/\theta$) is plotted versus $\theta^2$, equation (6) predicts a straight line with the slope $a_2$ and the intercept $a_1$. Figure 9 shows, that the experimental points can indeed be fitted with a straight line. From the values of $a_1$ and $a_2$ for the *cis* and the *trans* mixture, we conclude that both the bilinear coupling as well as the higher order interactions are stronger in *cis* than in *trans* compounds. The data are also in accordance with the higher speed of the *cis* compounds: $a_1$ is larger and therefore $\tau$ should be shorter (cf. equation (5) for the *cis* mixture.

The bilinear tilt–spontaneous polarization coupling as well as the more complicated interactions are typical for the $S_C^*$ phase. We believe, that there is a connection between the tendency of the *cis* compounds to suppress nematic phases and their stronger $S_C^*$ interactions, but so far neither experiments nor theory are far enough advanced to establish this relationship.

## 5. Conclusion

We have presented material data for mixtures of 2-ring 5-*n*-alkyl-2-(4-*n*-alkenyloxyphenyl)-pyridines and -pyrimidines with double bonds in the alkenyloxy side chain. The results allow the preferred conformation of the side chains to be deduced. We confirm the relationships between $S_C^*$ parameters such as spontaneous polarization $P_S$, switching time $\tau$ and tilt angle $\theta$ predicted by simple models. The differences between these parameters in *cis* and *trans* configurations are traced to differences in the polarization–tilt couplings, which are larger in the *cis* compounds.

For display applications, the large $S_C^*$ phases of the new *trans* compounds are attractive, especially for surface stabilized ferroelectric applications, where a nematic phase is needed to achieve good alignment. The *cis* compounds with their faster speed and lower tilt angles are useful for short pitch bistable ferroelectric devices. There, their destructive influence on the nematic phase is not important for alignment and the decrease of the $S_C^*$ phase due to the *cis* compounds is less pronounced in the short pitch bistable ferroelectric sample mixtures II. Furthermore, both *cis* and *trans* configurations lower the crystallization temperatures of the mixtures studied.

All the data presented for the sample mixtures reflect the effect of adding only 15 wt% of a 2-ring alkenyloxy compound to a mixture with saturated side chains. To achieve larger effects, larger concentrations can be used, or the correct alkenyloxy chain can be introduced for example in the dopant molecules as well. The selective introduction of double bonds then allows the liquid crystal parameters to be tuned over a wide range.

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