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Competition between dipolar and steric interactions in swallow-tailed compounds

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A new class of swallow-tailed mesogen with the longitudinal dipole moment in the direction of the non-branched 'head' is presented. Mixtures of these compounds with 'conventional' swallow-tailed substances were investigated by polarization microscopy and dielectric measurements. In the mixtures, dipolar and steric interactions favour opposite arrangements of the molecules in the short range order.

1. Introduction

Swallow-tailed molecules with **Y**-shaped geometry possess a strong tendency to adopt an antiparallel orientation in the short range order as has already been detected by dielectric investigations [1]. Driving forces for this effect are dipole–dipole and steric interactions. In order to decide which kind of interaction is dominant, two classes of substances were synthesized:

(i) swallow-tailed compounds with the longitudinal dipole moment μ_l in the direction of the swallow-tail (S4, S10) and
(ii) swallow-tailed substances with the longitudinal dipole moment μ_l in the direction of the head (SN, SC1, SC2).

Mixtures of swallow-tailed substances different in the direction of μ_l were investigated by polarization microscopy and dielectric measurements in order to study the molecular arrangement in the short range order. Figure 1 shows two 'mixed' pairs of molecules in a simple way. The arrows mark the direction of the longitudinal dipole moments μ_l. An antiparallel arrangement of μ_l (*a*) is favoured by the dipole–dipole-interactions, but is unfavourable for geometrical reasons, because of the large excluded volume. The arrangement given in (*b*) possesses a small excluded volume, but the

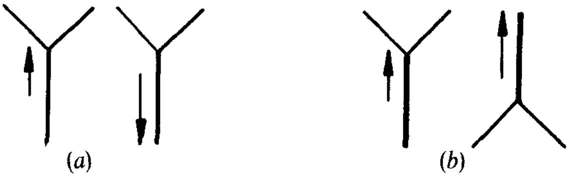

Figure 1. Simplified representation of the parallel (*a*) and antiparallel (*b*) arrangements of a 'mixed' pair of molecules.

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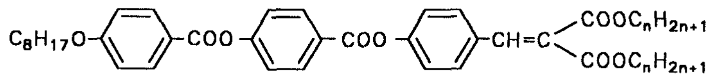
longitudinal dipole moments point in the same direction. This arrangement can give ferroelectric domains which it should be possible to confirm by measurement of the spontaneous polarization provided that they reach a critical size. Summarizing, we can say that dipolar and steric interactions favour opposite arrangements in these mixtures.

2. Materials

As components with μ_1 in the direction of the swallow-tail we used two homologous di-*n*-alkyl 4-[4-(4-octyloxybenzoyloxy)benzoyloxy]benzylidenemalonates

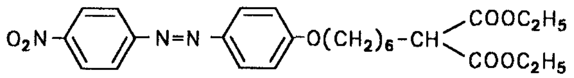


S4 $n=4$ C 343·5 K S_A 365 K N 387·5 K I

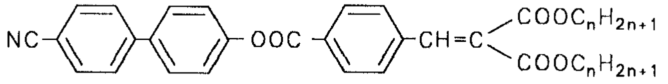
S10 $n=10$ C 336 K S_A 358·5 K N 365·5 K I

The synthesis has already been described [2].

The following three compounds possess a longitudinal dipole moment in the direction of the head:



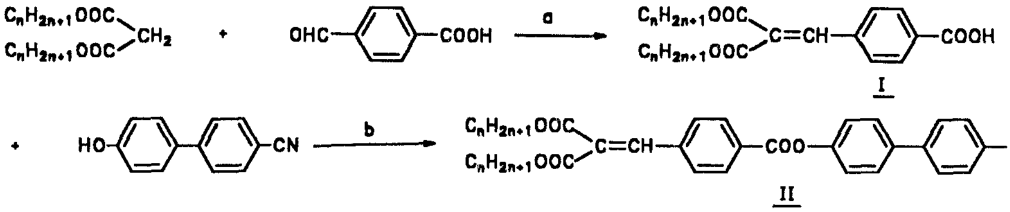
SN C 390 K I



SC1 $n=10$ C (S_A 353 K) 362 K N 364 K I

SC2 $n=12$ C (S_C 348 K S_A 361 K N 363 K) 368 K I

SN is an intermediate product in the synthesis of liquid crystalline polymers [3] and does not itself possess liquid crystalline properties. The synthesis of SC1 and SC2 was carried out according to the scheme:



a = piperidine/CH_3COOH; b = *N*-cyclohexyl, *N'*-(2-morpholinoethyl)carbodiimide methyl-*p*-toluenesulphonate.

While the usual methods were appled to obtain acid I, the esterification (step b) was a problem which was solved by using water-soluble carbodiimides [4, 5] in the presence of 4-dimethylaminopyridine (DMAP).

3. Results and discussion

Phase diagrams of the investigated systems S10/SC1, S10/SC2, S4/SN and S4/S10 are given in figure 2. The systems S10/SC1 and S10/SC2 show the highest temperatures S_A–N transition curves indicating special interactions which stabilize the layer structure. Because of the strong tendency of the molecules to give rise to a homeotropic arrangement, the microscopic investigation of S4/SN mixtures was complicated. This is

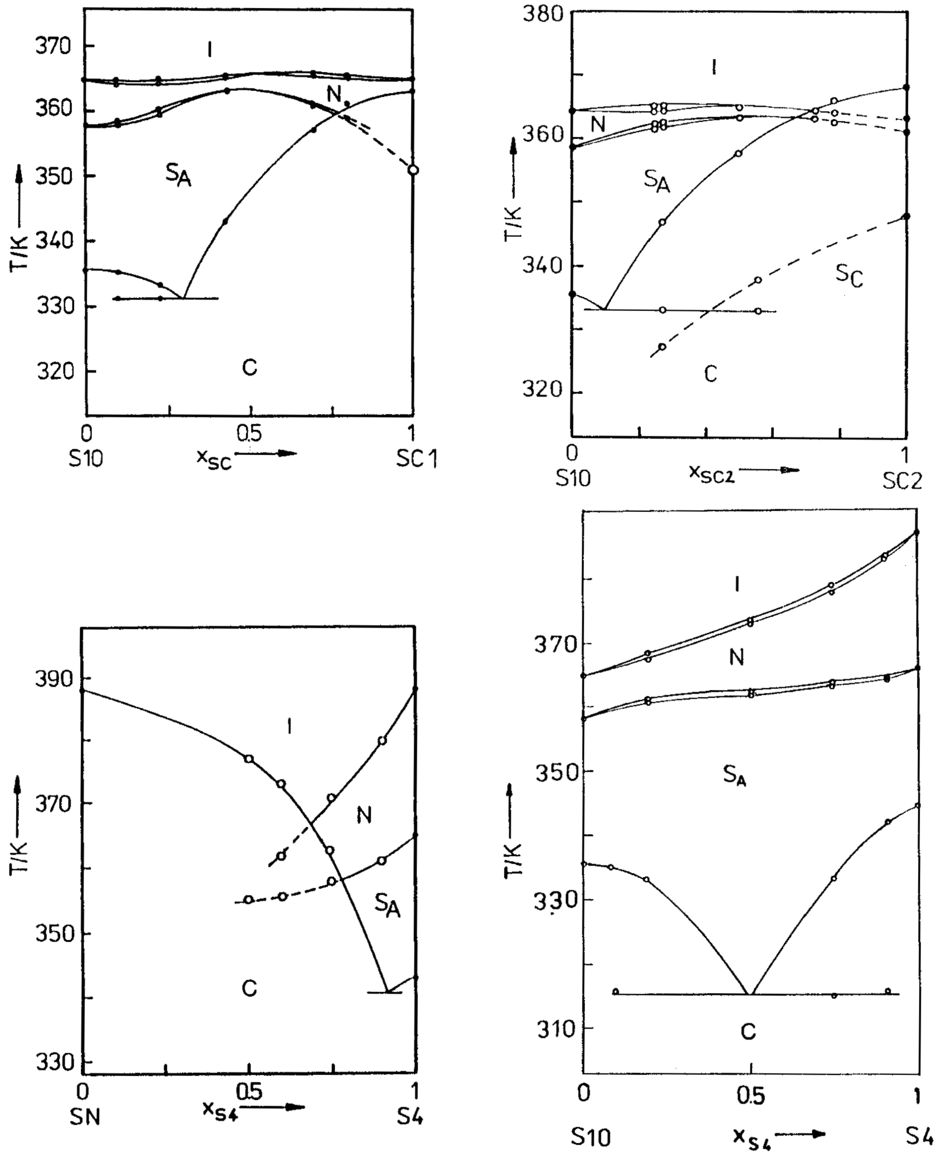


Figure 2. Isobaric phase diagrams of binary systems S10/SC1, S10/SC2, S4/SN and S4/S10.

why we present average transition temperatures instead of two phase regions. The diagram is characterized by the destabilization of the nematic phase with increasing content of the non-liquid crystalline compound. It should be noted that the decrease in T_{NS_A} is much smaller than the decrease in T_{IN}. A monotropic smectic phase for SN could not be detected.

Dielectric measurements were carried out on SC2 and three mixtures of S10/SC2 and S4/SN. The concentrations are given in table 1. The results obtained were compared with those of the pure components S4 [6], S10 [1] and the equimolar mixture S4/S10. Figure 3 shows the temperature dependence of $\varepsilon_\parallel$, $\varepsilon_\perp$ (regarded as static

Table 1. Concentration in mol% of the dielectrically investigated mixtures.

S10/SC2	x_{S10}	0·50	0·75	0·88
S4/SN	x_{S4}	0·60	0·75	0·90

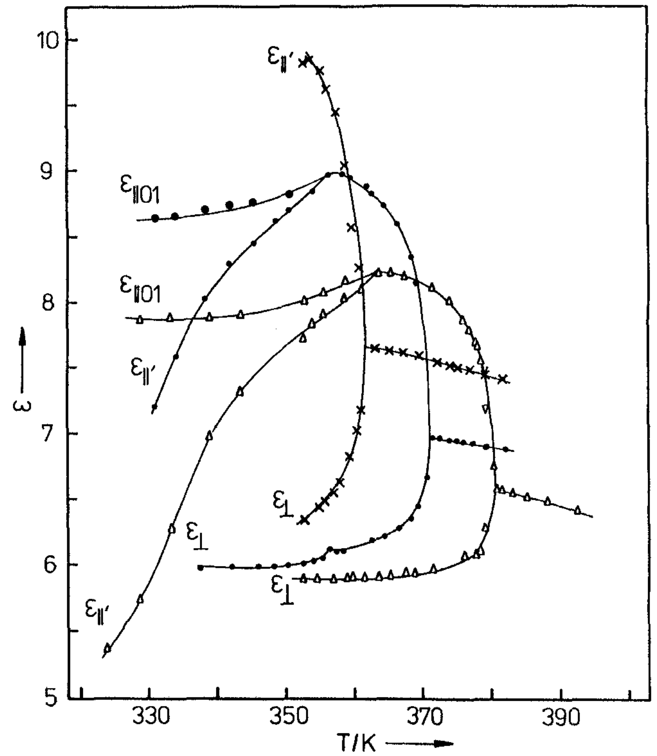


Figure 3. Dielectric constants of the 60 mol% (×), 75 mol% (●) and 90 mol% (△) S4 containing mixture versus temperature.

values) and $\varepsilon_{\parallel 01}$ for three S4/SN mixtures. $\varepsilon_{\parallel}'$ was measured at $f = 10$ kHz. In the case of the 60 mol% S4-containing mixture (×), no values could be obtained in the S_A phase because of crystallization. For comparison, in figure 4 the dielectric constants of S4, S10 and of the equimolar mixture S4/S10 are plotted versus temperature. Common features of the mixtures in figures 3 and 4 are a positive dielectric anisotropy in the nematic state and the decrease of $\varepsilon_{\parallel 01}$ at the N–S transition. This decrease, due to the partial compensation of μ_l is less pronounced in figure 3 than in figure 4. In the S4/SN mixtures, ε_I, $\varepsilon_{\parallel}$ and $\Delta\varepsilon$ increase with growing content of SN. This suggests a preference for the arrangement shown in figure 1 (*b*). In table 2 the dielectric anisotropies and the differences between theoretical $\varepsilon_{\parallel}$ values and measured values are listed. Under the assumption of the Maier–Meier theory [7], $\varepsilon_{\parallel}$(theor) can be calculated from extrapolated ε_I values and $\varepsilon_{\perp}$ using the following formula:

$$\varepsilon_I(\text{extrapol}) = \bar{\varepsilon} = \frac{1}{3}(\varepsilon_{\parallel} + 2\varepsilon_{\perp}).$$

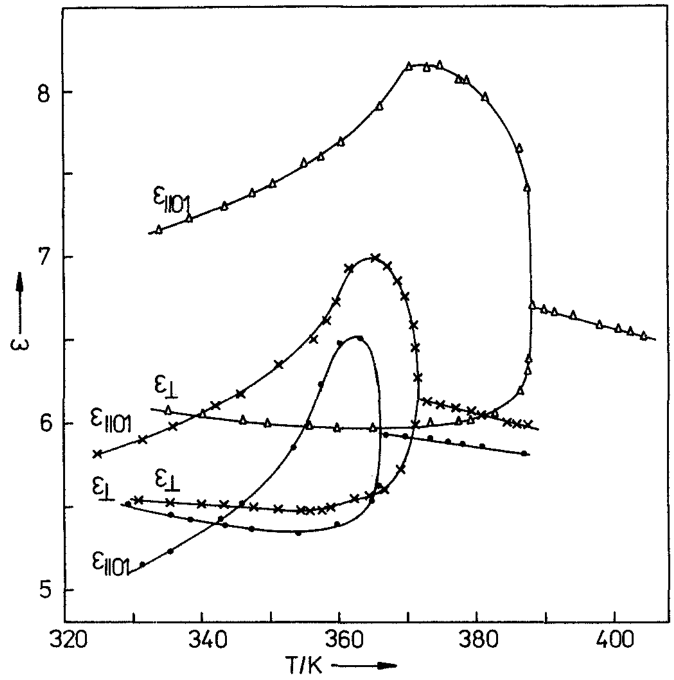


Figure 4. Dielectric constants of S10 (●), S4 (△) and of the equimolar mixture S4/S10 (×) versus temperature.

Table 2. Dielectric anisotropy and difference between theoretical and measured value of $\varepsilon_{\parallel}$ for S4 and the mixtures S4/S10 and S4/SN.

		$T_{NI}-T=20\,K$ $\Delta\varepsilon$	$T_{NI}-T=10\,K$ $\varepsilon_{\parallel}(\text{theor})-\varepsilon_{\parallel}$
S4		2·00	0·5
S4/S10	50 mol% S4	0·92	0·5
S4/SN	75 mol% S4	2·86	−0·1
S4/SN	90 mol% S4	2·23	0

For S4 and the mixture S4/S10 10 K below the clearing point, the measured $\varepsilon_{\parallel}$ is smaller than the theoretically expected value. In the S4/SN mixture with $x_{S4}=0{\cdot}90$, the values agree and in the mixture containing 75 mol% S4, the measured value is somewhat higher than the calculated value. These results indicate an enlarged effective dipole moment μ_1 for the S4/SN mixtures compared with S4 and the preference for the arrangement in figure 1 (*b*) as already mentioned.

The temperature dependence of the dielectric constants for SC2 and the S10/SC2 mixtures is shown in figure 5. Vector analyses [8] showed that SC2 exhibits a higher dipole moment μ_1 (14×10^{-30} C m) than S10 (8×10^{-30} C m). That is why a higher $\varepsilon_{\parallel}$ for SC2 is to be expected. Experimentally, the opposite was found. The maximum of $\varepsilon_{\parallel}$ in the nematic state is 6·5 for S10 and 6·3 for SC2. The compound S10 also exhibits higher values of ε in the isotropic state than SC2 (see figure 6). At the N–S_A transition the typical decrease of $\varepsilon_{\parallel 01}$ could be observed in SC2, also. Unfortunately, no more

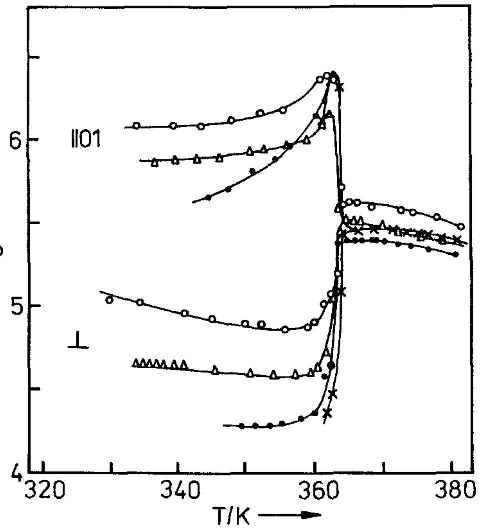


Figure 5. Dielectric constants of SC2 (×) and the S10/SC2 mixtures. The symbols correspond to the mole fraction of S10: ×, 0; ○, 0·75; △, 0·50; ●, 0·22.

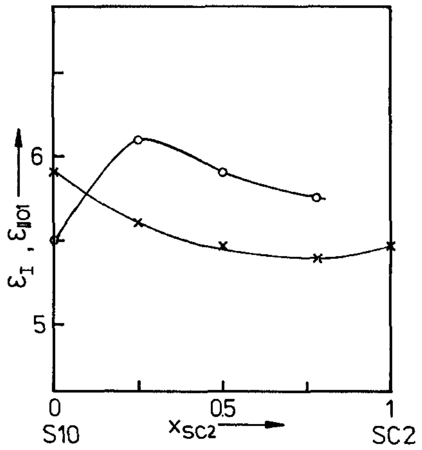


Figure 6. Concentration dependence of $\varepsilon_\perp$ (×, $T-T_{NI}=5$ K) and $\varepsilon_{\parallel 01}$ (○, $T-T_{NI}=-20$ K) for the binary system S10/SC2.

values could be measured for the smectic phase because of crystallization. The relatively small dielectric constants of SC2 in the nematic and isotropic phase, and the decrease of $\varepsilon_{\parallel 01}$ at the N–S_A transition are due to the antiparallel arrangement of the molecules. The tendency to adopt this arrangement is caused by strong dipolar interactions as well as the anisotropy of the repulsive forces. In figure 6, $\varepsilon_{\parallel 01}$ and $\varepsilon_\perp$ are plotted versus concentration. At about 75 mol% S10, $\varepsilon_{\parallel 01}$ reaches a maximum, indicating an increase of the effective dipole moment μ_l by the addition of SC2 to S10. But, if the arrangement in figure 1 (*b*) is favoured, the equimolar mixture should have the highest value of $\varepsilon_{\parallel 01}$. The observed smaller $\varepsilon_{\parallel 01}$ for the equimolar mixture compared with that for the mixture containing 75 mol% of S10 is possibly caused by

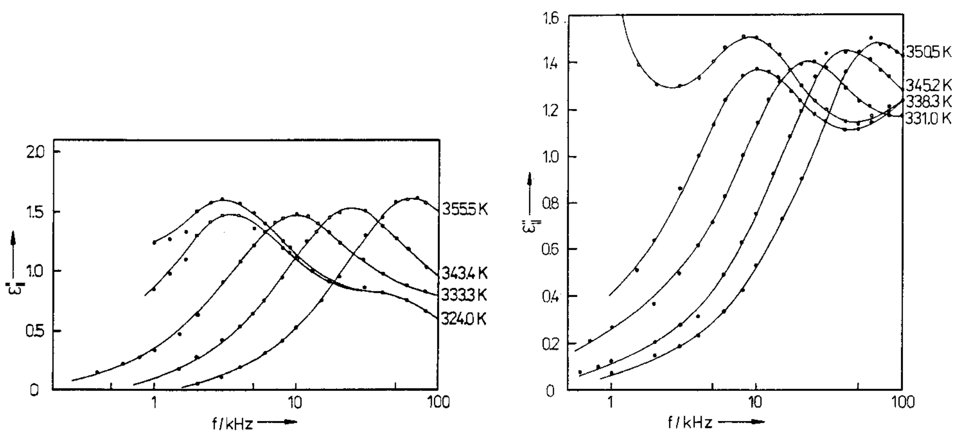


Figure 7. Relaxation curves of S4/SN mixtures, $x_{S4}=0{\cdot}90$ (left), $x_{S4}=0{\cdot}75$ (right). At 324·0 K and 331·0 K, respectively, are plotted the measured loss (upper curve) as well as the dielectric loss (lower curve) separated from the conductivity part of the loss.

strong interactions between the SC2 molecules. A spontaneous polarization could not be registered for these mixtures ($f = 200$ Hz, $U_{pp} = 280$ V). This means that large regions of uniformly oriented dipoles do not occur.

The S4/SN as well as the S10/SC2 mixtures show a broad dielectric absorption region in parallel direction. The relaxation curves for two S4/SN mixtures are shown in figure 7. By means of a computer, the measured curves were separated into two Debye processes. The process at higher frequencies is related to the reorientation of SN molecules around their short axes and that at lower frequencies to the reorientation of S4 molecules around their short axes.

4. Experimental

4.1. *Synthesis of SC1 and SC2*

To a solution of 2·17 g (3·8 mmol) of the carboxylic acid I in 20 cm^3 of CH_2Cl_2 were added 30 mg of DMAP, 1·74 g (3·8 mmol) of 4-cyano-4'-hydroxybiphenyl and 1·93 g (4·56 mmol) of a water-soluble carbodiimide. The mixture was stirred for 24 h at room temperature. The organic layer was washed 5 times with 20 cm^3 of water, and once with 20 cm^3 of saturated aqueous $NaHCO_3$ and 20 cm^3 of saturated aqueous NaCl. After drying over Na_2SO_4 the solvent was evaporated and the product was recrystallized from *n*-hexane/ethyl acetate. Yield: 64 per cent.

^{1}H NMR ($CDCl_3$)δ: 0·8 (m, 6H), 1·2 (m, 36 H), 1·6 (m, 4 H), 4·24 (t, 4 H), 7·29–8·21 (q, 4 H) 7·55 (s, 1 H), 7·59–7·76 ppm (m, 8 H).

4.2. *Optical microscopy*

Phase diagrams were obtained by polarization microscopy using a hot stage polarizing microscope from Carl Zeiss.

4.3. *Dielectric measurements*

Dielectric measurements were carried out using a modified Sawyer–Tower bridge [9]. The measuring cell was a double plate silver capacitor ($A = 2$ cm^2, $d = 0{\cdot}2$ mm). In order to investigate the temperature dependence of the dielectric constants ε_{I}, $\varepsilon_{\perp}$, and $\varepsilon'_{\parallel}$

were measured at 10 kHz during cooling. By means of a magnetic field ($H = 0{\cdot}8$ T), the samples could be oriented. In the parallel direction, relaxation measurements in the frequency range from 10 Hz to 100 kHz were carried out at different temperatures. The $\varepsilon_{\parallel 01}$ values were estimated from Cole–Cole plots [10]. The error in ε' is smaller than 5% and in ε'' up to 10 per cent. Because of the small frequency range of the applied bridge, the characterization of the former process is not so exact.

5. Conclusions

Dielectric investigations on mixtures of swallow-tailed substances with an opposite direction of the longitudinal mipole moment prove that the antiparallel arrangement of molecules is favoured, although this arrangement is not advantageous for the dipolar interactions. Steric effects and repulsive forces have a decisive influence on the molecular arrangement. Large 'ferroelectric' regions with uniform orientation of the molecular dipoles are not observed. In this case, the $\varepsilon_{\parallel 01}$ values should have been significantly higher than those obtained and the relaxation frequencies should have been lower.

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