Anomalous Behaviour in Helical Pitch of Ferroelectric Liquid Crystal Mixtures

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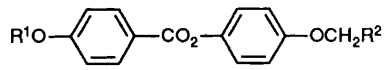
Anomalous behaviour in SC* helical pitch of ferroelectric liquid crystal mixtures has been found: phenyl benzoate derivatives **1** and **2** (Sol-RH) unwind the SC* helical pitch of either (*R*)- or (*S*)-enantiomer of **4** (Rel-RH or Sed-LH).

Ferroelectric liquid crystals have attracted a great deal of interest because of their quick response and bistability. In order to obtain bistability in devices of the Clark–Lagerwall type,[1] it is required to unwind the helical pitch by mixing ferroelectric liquid crystal components of opposite helical sense.[2] Goodby has determined the SC* helical sense by the contract method[3–5] which is based on theory as follows. The helical pitch is unwound when two components of opposite helical sense are mixed, whereas it is not if they have the same helical sense.

We report anomalous cases where the helical pitch is unwound by mixing two components of the same helical sense. Goodby has determined the helical sense of 4-[(*S*)-2-methylbutoxy]phenyl 4-octyloxybenzoate **1** to be Sol-RH on the basis of the contact method.[5] However, we have found that **1** unwinds the helical pitch of either the (*R*)- or the (*S*)-biphenyl diester **4** (Fig. 1). At each point in the miscibility diagram, each mixture exhibited the SC* phase and disclination lines indicating the helical pitch were not observed. This anomalous phenomenon was also obtained in the binary mixture of the benzoate **2** which has the same central core as **1** and either enantiomer of **4**. Even in the 1 : 1 mixture of **3** (an achiral version of **1**) and **4** (either enantiomer), the helical pitch disappeared in the SC* phase. From these observations, it could be said that the series of phenyl benzoates **1–3** are likely to unwind the helix of **4**, irrespective of the helical sense.

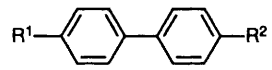
We obtained this anomalous phenomenon not only with **4** but also in **5–7**. When **1** is mixed with **5–7**, the helical pitch was



1; $R^1 = C_8H_{17}$, $R^2 = CH(Me)Et$

2; $R^1 = C_{10}H_{21}$, $R^2 = CH(OMe)Pr^i$

3; $R^1 = C_8H_{17}$, $R^2 = Pr^n$



4; $R^1 = C_8H_{17}CO_2$, $R^2 = CO_2CH_2CH(Cl)Pr^i$

5; $R^1 = C_8H_{17}OCO_2$, $R^2 = OCOCH(Cl)CH(Me)Et$

6; $R^1 = C_8H_{17}O$, $R^2 = OCOCH(Me)CH(Me)Et$

7; $R^1 = C_8H_{17}O$, $R^2 = OCOCH(Cl)Pr^i$

8; $R^1 = C_8H_{17}O$, $R^2 = CO_2CH_2CH(Me)Et$

Table 1 Structures of ferroelectric crystals 1–8[a]

Compound	Helical sense
1	Sol-RH[d]
2	Sol-RH[b]
3	Achiral
4	Sed-LH, Rel-RH[d]
5	Sol-RH[c,d]
6	Sol-RH[c,d]
7	Sol-RH[d]
8	Sed-LH[d]

[a] The optical rotation [dextro-(+) or laevo-(−)] of SC* phase was directly observed in the homotropic orientation. See ref. 6. [b] The optical rotation of **2** was observed in 75 wt. % concentration in 4-hexyloxyphenyl 4-octyloxybenzoate. [c] The helical sense of **5** and **6** is dependent only on the absolute configuration of the chlorinated carbon. [d] Direct method.

Table 2 Transition temperatures (°C) of compounds[a]

		M.p./°C
1	C ←(20)— SC* ←(44)→ SA ←(58)→ I	42
2	C ←(30)— SA ←(33)→ I	35
3	C ←(41)— SC ←(55)→ SA ←(65)→ N ←(89)→ I	54
4	C ←(0)— SI* ←(10)— SC* ←(40)→ SA ←(54)→ I	37
5	C ←(25)— SC* ←(29)→ SA ←(41)→ I	29
6	C ←(33)— SI* ←(36)— SC* ←(53)→ SA ←(64)→ I	48
7	C ←(63)— SC* ←(69)→ SA ←(80)→ I	76
8	C ←(36)— SC* ←(43)— SA ←(64)→ I	46

[a] The transition temperatures of the compounds and mixtures were determined by microscopic observation, temperature dependence of the relative permittivity, and differential scanning calorimetry.

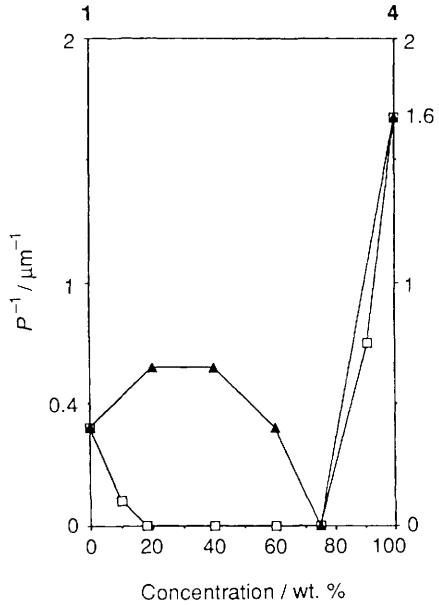


Fig. 1 The pitch length of the mixture of **1** and **4**. The pitch length was observed in a 100 μm cell at *ca.* 10 °C at the SC*–SA transition temperature: □, (*S*)-enantiomer; ▲, (*R*)-enantiomer.

unwound even though they all have the same helical sense. However, this anomaly was not observed in the combination of **4** (either enantiomer) and **8** (which have the same structure as **1** except for the position of the ester group).

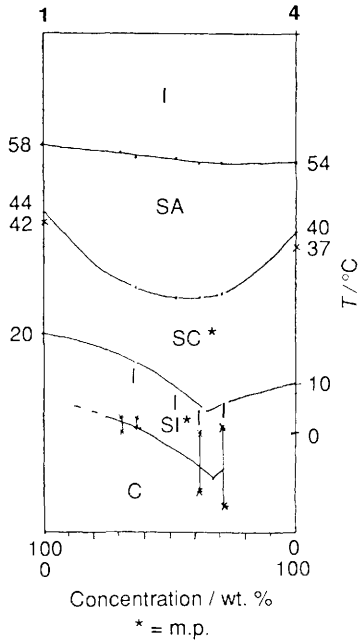


Fig. 2 Phase diagram of **1** and **4**

In our experiments, we obtained the anomalous mixtures by the combination of the phenyl benzoate series **1–3** and biphenyl ester series **4–8**. The origin of this anomalous phenomenon does not lie in the absolute spatial configuration of the components. It is possible that the difference of the position of the large dipoles within the molecular structure of these two components had a great influence on the helical structures of the mixtures. A detailed discussion awaits further investigations.

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