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Liquid Crystals

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**Novel liquid crystals and dopants
(for induced ferroelectricity)
possessing a chiral 2-oxetanone unit**

A comparison with corresponding dioxolanones

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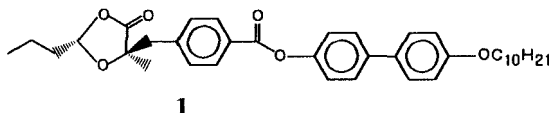
(Received 2 January 1992; accepted 13 March 1992)

The mesomorphic properties, induced spontaneous polarizations, and response times of a new type of liquid crystal and ferroelectric liquid crystal mixtures containing di- or trisubstituted 2-oxetanones as a chiral unit are described. By heating above 140°C oxetanones, bearing a three core mesogenic part, suffer cycloelimination of carbon dioxide yielding liquid-crystalline olefines with nematic, smectic C and higher ordered smectic phases, which are best suited as host materials for induced S_C^* phases using the corresponding oxetanones as dopants. Compared with 1,3-dioxolan-4-ones recently synthesized and investigated, the oxetanones show minor mesomorphism.

1. Introduction

Chiral heterocycles combining a laterally acting dipole and one or two centres of chirality in a rigid core proved to be advantageous building blocks in designing new and promising ferroelectric liquid crystals. Starting with oxirane ethers [1] and oxiranecarboxylic esters [2], thiiranes [3], thiiran-S-oxides [4], γ -lactones [5], δ -lactones [6], dioxolanones [7] oxazolidinones [8] and recently β -lactames [9] have been exploited. Recently, we have synthesized the 1,3-dioxolan-4-one derivative **1** exhibiting a S_C^* phase and a P_S value of about 66 nC cm^{-2} [7]. There are two structural features of **1**, which could be improved with respect to its ferroelectric properties.

- (i) The oxygen in the 1 position weakens the lateral dipole moment generated by the lacton-carbonyl group. Removal of this oxygen could enhance the spontaneous polarization of the ferroelectric liquid crystal or mixture.
- (ii) The methyl group in the 5 position presumably prevents a broader S_C^* phase in the system.

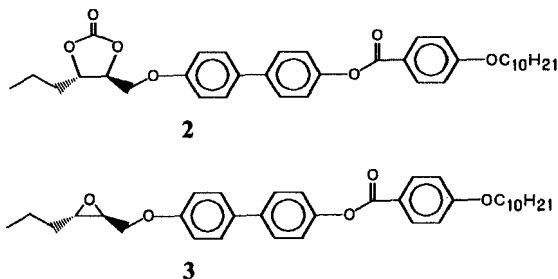


Two other possibilities with which to increase the lateral dipole moment are: (a) shifting the oxygen to be adjacent to the carbonyl group, i.e. taking 1,3-dioxolan-2-ones as the

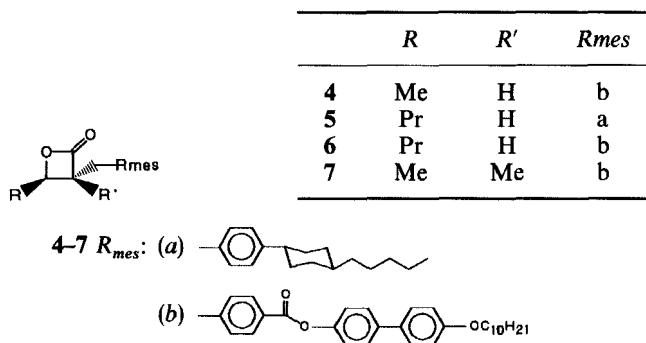
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chiral heterocycle, (b) reducing the ring size. Both possibilities have been checked in our Group, for example, the 1,3-dioxolan-2-one **2** [10] and the three membered oxirane **3** [3],



These compounds have no additional methyl group close to the mesogenic part. Compound **3** has a broad S_C^* phase (more than 50 K), whereas compound **2** only exhibits a 20 K wide S_A phase. To continue our investigations referring to the influence of either the ring size or the kind of heterocycle we have synthesized mesogenic substituted, chiral, non-racemic 2-oxetanones which can be considered as a compromise between oxirane **3** and 1,3-dioxolan-2-one **2**. 2-oxetanones combine a strong lateral dipole moment with a strained four membered ring system, which leads to a good restriction in free rotation without disturbing significantly the parallel longitudinal orientation in the mesophases. A further goal of our investigations on oxetanones was to investigate the influence of the methyl group adjacent to the mesogenic part as seen in the 5 position of dioxolanone **1**. Finally, we have synthesized an oxetanone with a two core mesogenic part without an ester linkage (**5**), to reduce the viscosity in ferroelectric liquid crystal mixtures. It has been established, that three core mesogenic esters, in general, have a higher viscosity than mesogenic hydrocarbons or pyrimidines [11]. The oxetanones synthesized and investigated are summarized in the scheme.



2. Results and discussion

2.1. Mesogenic properties

Phase types and transition temperatures of 2-oxetanones **4-7** and the corresponding 1,3-dioxolan-4-one **1** are summarized in table 1. All of the oxetanones synthesized do not exhibit a S_C^* phase, whereas the similar dioxolanone **1** does. Oxetanone **6** exhibits monotropic blue phases BP I and BP II (see figure 1) and a cholesteric phase. Oxetanone **4** also forms a S_A phase. To find out, what might be responsible for this

Table 1. Phase types and transition temperatures of oxetanones 4–7 and dioxolanone 1.

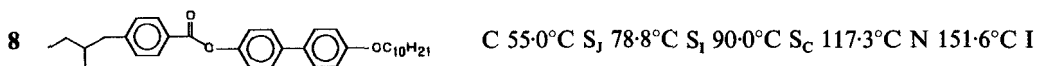
4		C $\xrightarrow{159^\circ\text{C}}$ I \curvearrowright 143°C S _A 148°C N* 152°C BP 153°C ✓
5		C 62°C I
6		C $\xrightarrow{135.9^\circ\text{C}}$ I \curvearrowright 115°C N* 120.9°C BPI 121.9°C BPII 122.1°C ✓
7		C 163°C I
1		C 71°C S _C * 75°C N* 85°C I \curvearrowright 56°C S _C * ✓

different influence of the five membered heterocycle in **1** compared with the four membered one in **4** and **6**—either the larger ring system having 2,5-disubstitution or the additional methyl group in **1**—we have synthesized oxetanone **7** having a similar substitution pattern as **1**. **7** can be compared with the dioxolanone **1**, though it has a shorter alkyl chain at the heterocycle, because **4** and **6**, having the same difference show similar phase behaviour. By introducing the methyl group in **4** yielding **7**, all mesomorphic properties are lost. **7** has a sharp melting point at 163°C, in a temperature range, where elimination of carbon dioxide begins. This result demonstrates, that the more favourable 2,5-disubstitution in the five membered heterocycle is mainly responsible for the formation of the S_C* phase. Probably, a dioxolanone without ramification in the 5 position might have a broader S_C* phase than **1**.

2.2. Spontaneous polarization and response time

To measure the spontaneous polarization of the oxetanones synthesized as dopants we sought suitable hosts. First, we tried the M 89/85 mixture from Hoechst (C 9°C S_C 84°C S_A 93°C N 105°C I) as host but the oxetanones **4**, **6** and **7** with a three core mesogenic part are not sufficiently soluble in that matrix, and oxetanone **5** suppresses the S_C phase.

With the knowledge that compound **8** [12] exhibits a S_C phase, we decomposed the oxetanones **4–7** to the corresponding olefines **9–12** to obtain solvents with identical structures in the mesogenic part compared with the respective oxetanones. The elimination of carbon dioxide in compounds **4–7** begins at 140°C and is complete within 1 h at 200°C. The three core olefines **9**, **11** and **12** have phase transitions similar to compound **8** while the two core olefine **10** is an isotropic liquid at room temperature. The phase types and transition temperatures are summarized in table 2.



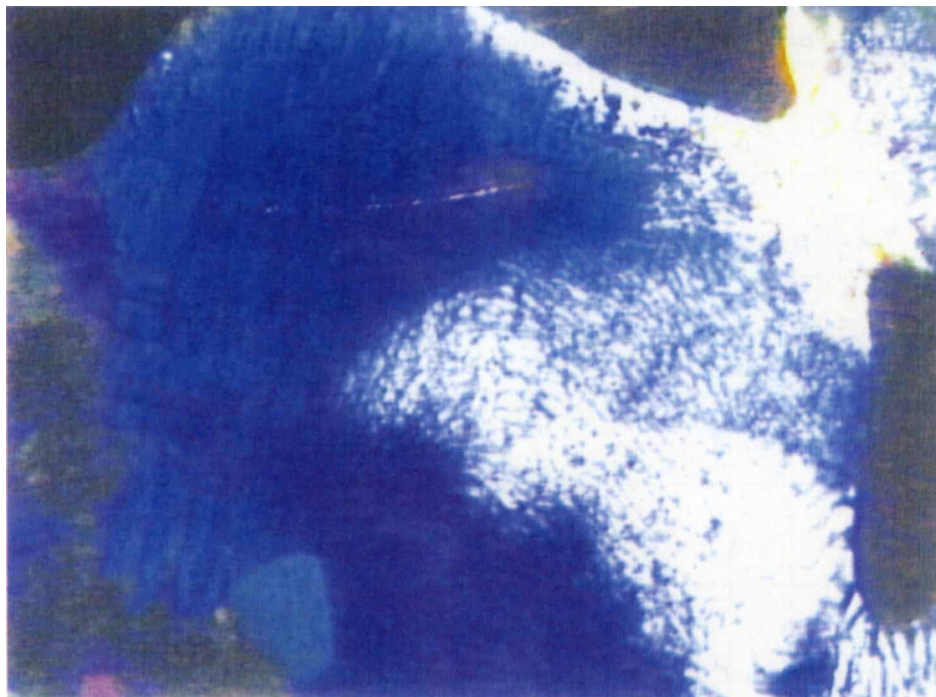
**BP I.****BP II.****Figure 1. Blue phase I and II of oxetanone 4.**

Table 2. Phase types and transition temperatures of olefines 9-12.



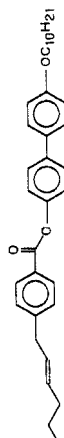

9		$C \xrightarrow{116.8^\circ C} S_c \xrightarrow{122.5^\circ C} N \xrightarrow{141.8^\circ C} I$ $\swarrow \quad \searrow$ $90.8^\circ C \quad S_x \quad 105.9^\circ C$
10		Liquid at room temperature
11		$C \xrightarrow{108^\circ C} S_c \xrightarrow{124^\circ C} N \xrightarrow{137^\circ C} I$ $\swarrow \quad \searrow$ $88^\circ C \quad S_x \quad 103^\circ C$
12		$C \xrightarrow{99^\circ C} S_c \xrightarrow{106^\circ C} N \xrightarrow{114^\circ C} I$ $\swarrow \quad \searrow$ $65^\circ C \quad S_x \quad 99^\circ C$

Table 3. Transition temperatures, concentration, P_s values and response times of the mixtures investigated; temperatures in parentheses.

Mixture		$c/\text{mol}\%$	$P_s/\text{nC cm}^{-2}$	t/ms
4 in 9	C $\xrightarrow{112.8^\circ\text{C}}$ $\rightarrow S_2^* \xrightarrow{121.4^\circ\text{C}}$ N* $\xrightarrow{145^\circ\text{C}}$ I $\searrow 81.5^\circ\text{C}$ $S_x \xrightarrow{101.7^\circ\text{C}}$ \swarrow	9.24	10.5 (105°C)	1.1 (120°C)
6 in 11	C $\xrightarrow{113.4^\circ\text{C}}$ $\rightarrow S_2^* \xrightarrow{123.5^\circ\text{C}}$ N* $\xrightarrow{134.8^\circ\text{C}}$ I $\searrow 88.8^\circ\text{C}$ $S_x \xrightarrow{95.7^\circ\text{C}}$ \swarrow	9.29	8.3 (105°C)	1.3 (120°C)
6 in M 89/85	C $\xrightarrow{76.5^\circ\text{C}}$ $\rightarrow S_A \xrightarrow{89^\circ\text{C}}$ N* $\xrightarrow{103.5^\circ\text{C}}$ I $\searrow 61^\circ\text{C}$ $S_x^* \xrightarrow{68.8^\circ\text{C}}$ \swarrow	8.75	2.5 (63°C)	—
7 in 12	C $\xrightarrow{95.8^\circ\text{C}}$ $\rightarrow S_2^* \xrightarrow{105.7^\circ\text{C}}$ N* $\xrightarrow{114.9^\circ\text{C}}$ I $\searrow 48.0^\circ\text{C}$ $S_x^* \xrightarrow{88.3^\circ\text{C}}$ \swarrow	9.26	<1 (100°C)	—

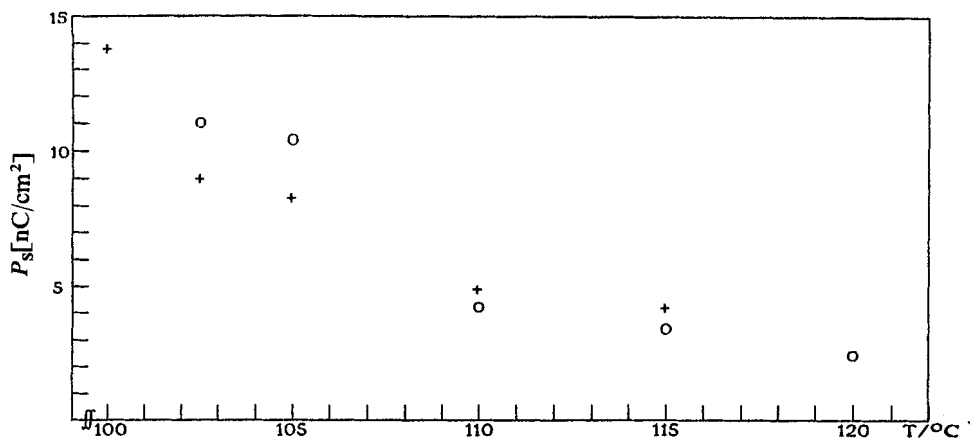


Figure 2. Spontaneous polarization versus temperature for **6** in **11** (+) and **4** in **9** (o).

For measurement of the induced spontaneous polarization about 9 wt% of **4**, **6** and **7** were dissolved in their corresponding olefines. For these mixtures the mesomorphic and ferroelectric properties were investigated by using 4 μm rubbed test cells on a heating stage under a polarizing microscope. All of the mixtures show the same, yet chiral, phase types and little change in the transition temperatures as compared with the pure olefines (see table 3).

These mixtures and the comparative mixture of oxetanone **6** in M89/85 exhibit ferroelectric switching in the temperature range of the induced S_C^* phase. (The switching behaviour and P_S values were measured before the oxetanone crystallizes in the S_C phase of M 89/85.) The response times of **4** in **9** and **6** in **11** are approximately 1 ms. This relative slowness is probably due to a relatively high rotational viscosity caused by the ester functions in the ferroelectric mixtures. The P_S values of oxetanones **4** and **6** in the olefines **9** and **11**, respectively (see figure 2) decrease with temperature which is in agreement with the behaviour of mixtures reported in the literature [13]. Thus the highest P_S values are measured near to the transition to the S_X phase. In M 89/85 compound **6** induces a P_S of only 2.5 nC cm^{-2} at 63°C . For the mixture of **7** in **12** the spontaneous polarization is below the recording limit of the apparatus used.

In summary we have shown, that 3,4-*trans*-disubstituted 2-oxetanones having a three core mesogenic substituent in the 3 position exhibit different monotropic liquid crystal phases including two blue phases, but no S_C^* phases. The mesomorphic olefines, obtained by cycloelimination of carbon dioxide from the oxetanones do show S_C phases and are excellent hosts for their corresponding oxetanones with respect to solubility and spontaneous polarization. An indication might be the P_S value for **6** in **11**, which is almost two to five times higher than for the mixture of **6** in M 89/85, presumably because of better geometrical ordering between the molecules. Oxetanone **6** with a longer alkyl chain in the 4 position seems to have higher P_S values than **4** with the shorter chain; especially when we take into account the fact that **6** has only about 75 per cent enantiomeric purity, whereas oxetanone **4** was enantiomerically pure [14].

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