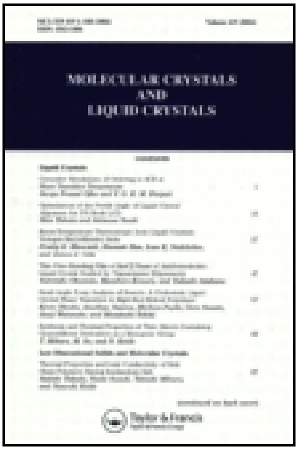

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# Tricyclic Smectic C Compounds Incorporating a 1,3-Dioxan Ring

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# Tricyclic Smectic C Compounds Incorporating a 1,3-Dioxan Ring†

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About 80 mesogenic achiral 1,3-dioxans substituted in the 2 position by a p-(benzoyloxy)phenyl, 4-biphenylyl, 2-phenyl-5-pyridyl, or a 2-phenyl-5-pyrimidyl core have been synthesized. Most of them exhibit broad smectic C temperature ranges at elevated temperatures. The influence of the aromatic moiety, of a lateral fluorine atom and of an alkyl vs. an alkoxy side chain on the smectic C temperature range and, in some cases, on the viscosity behaviour and the thermal stability of the smectic C* phase in a ferroelectric liquid crystal mixture is studied. Many of the tricyclic 1,3-dioxans are well suited for the use in low viscosity wide-range ferroelectric smectic C* materials.

*Keywords: smectic C, 1,3-dioxan*

## INTRODUCTION

A useful concept to formulate ferroelectric $S_C^*$ mixtures suited for display applications is to dope an achiral $S_C$ host with optical active compounds imparting ferroelectric properties.[1] Frequently, the achiral host material is a mixture of 5-alkyl-2-(p-alkoxyphenyl)pyrimidines[2] (and/or other bicyclic $S_C$ compounds) and tricyclic compounds enhancing the higher end of the $S_C$ phase. The majority of such tricyclic compounds incorporates a fully aromatic rigid core. Replacement of an aromatic by a saturated ring would lead to a lower birefringence, which allows the use of thicker cells. For viscosity reasons, among saturated rings the trans-1,4-disubstituted cyclohexane ring is favored. Smectic C compounds containing such a ring are possible,[3–5] if they incorporate an ester linking group or a nitrogen-containing heterocyclic ring. Another saturated ring, i.e., the trans-2,5-disubstituted 1,3-dioxan ring, which, however, leads to higher rotational viscosity,[6] has been successfully used to prepare $S_C$ compounds with a chiral-branched chain.[7–9] Here, we present a variety of achiral tricyclic 1,3-dioxan compounds, exhibiting

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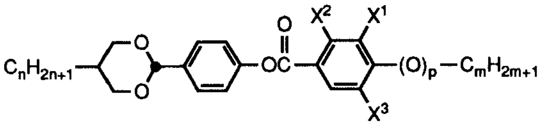
## TABLE I

Transition temperatures (°C) for compounds I



IA: p = 0
IB - E: p = 1

IC: $X^1$ = F
ID: $X^1$ = $X^2$ = F

IE: $X^1$ = $X^3$ = F
($X^n$ not specified = H)

| p | $X^1$ | $X^2$ | $X^3$ | n | m | C | $S_B$? | $S_C$ | N | I |
|---|---|---|---|---|---|---|---|---|---|---|
| 0 | H | H | H | 7 | 8 | • 80. 3 | (• 67.6 | • 76.7) | • 141 | • |
|  |  |  |  | 8 | 8 | • 65.5 | • 66.6 | • 87.7 | • 137.5 | • |
|  |  |  |  | 10 | 8 | • 66.7 | • 81.2 | • 102.5 | • 132.5 | • |
| 1 | H | H | H | 10 | 6 | • 77.7 | (• 44.2) | • 89.7 | • 158 | • |
|  |  |  |  | 7 | 8 | • 89.5 | (• 64) | • 90.5 | • 154.5 | • |
|  |  |  |  | 10 | 8 | • 65.0 | (• 51.6) | • 111.1 | • 163 | • |
|  |  |  |  | 9 | 12 | • 82.5 | (• 56.3) | • 122.6 | • 148.5 | • |
|  |  |  |  | 10 | 12 | • 82.3 | (• 53) | • 127.2 | • 146.7 | • |
| 1 | F | H | H | 7 | 6 | • 96.5 |  | (• 93.6) | • 153 | • |
|  |  |  |  | 9 | 6 | • 81.0 |  | • 105.5 | • 147 | • |
|  |  |  |  | 10 | 6 | • 75.7 |  | • 109.5 | • 144 | • |
|  |  |  |  | 7 | 8 | • 78.3 |  | • 104.5 | • 146 | • |
|  |  |  |  | 9 | 8 | • 70.4 |  | • 116.5 | • 142.5 | • |
|  |  |  |  | 10 | 8 | • 65.2 |  | • 119.5 | • 139 | • |
| 1 | F | F | H | 7 | 8 | • 74.0 |  | • 114.8 | • 149.5 | • |
|  |  |  |  | 9 | 8 | • 69.8 |  | • 123 | • 145.5 | • |
|  |  |  |  | 10 | 8 | • 77.3 |  | • 123.5 | • 141.5 | • |
| 1 | F | H | F | 7 | 8 | • 35.0 | $S_F$? 68 | • 110.8 | • 122.5 | • |
|  |  |  |  | 9 | 8 | • 32.5 | • 68.5 | • 118.0 | • 121 | • |
|  |  |  |  | 10 | 8 | • 47.3 | • 64 | • 117.8 | • 118.6 | • |

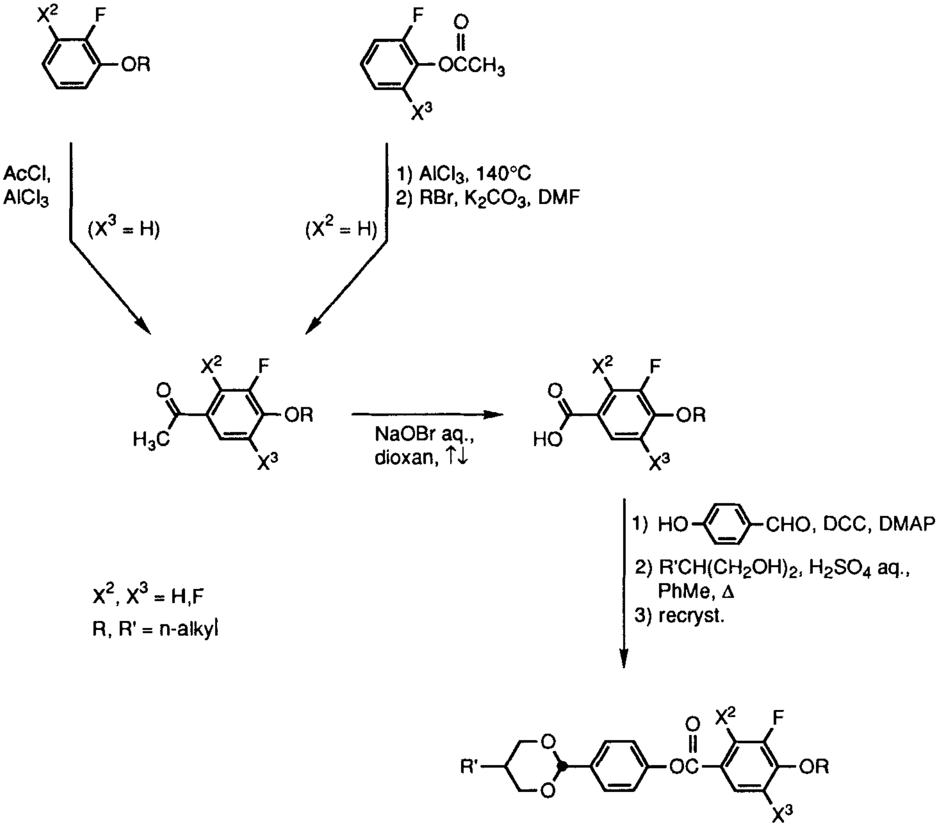
broad-range smectic C phases. According to the aromatic moiety, they are divided into four classes.

## RESULTS

### a) p-(1,3-Dioxan-2-yl)phenyl benzoates I

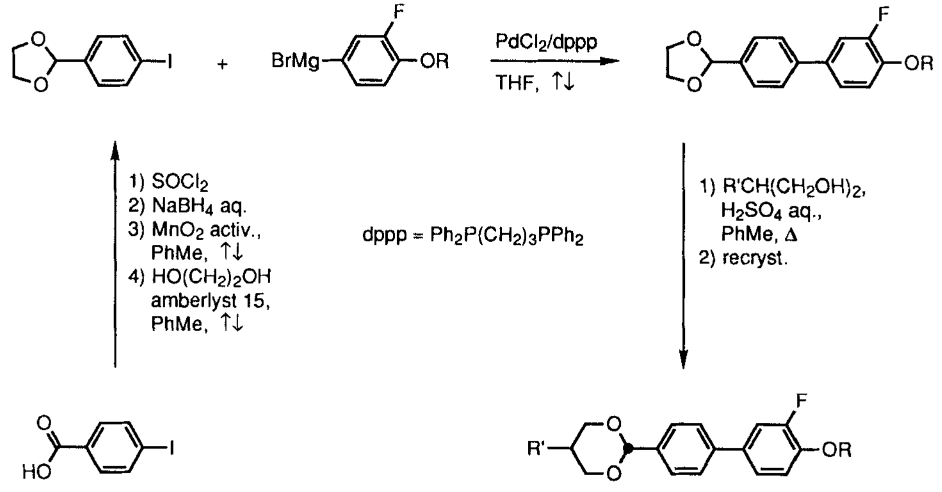
According to the substitution pattern of the benzoate moiety, the class I is divided into the series IA–E (Table I). Short-chain members of the laterally unsubstituted p-alkyl- and p-alkoxy-benzoates (IA, B) are known.[10] The synthesis of the laterally fluorinated compounds (IC–E) is outlined in Scheme I.

The mesogenic transition temperatures are listed in Table I. Below a nematic phase, all the series, even the p-alkylbenzoates IA, exhibit an $S_C$ phase. The additional orthogonal smectic (probably $S_B$) phase occurring in IA, B is removed by lateral fluorination (IC–E). The low-melting 4-alkoxy-3,5-difluorobenzoates IE possess a further tilted smectic (possibly $S_F$) phase.



IC, D, E

SCHEME I



IIC

SCHEME II

Within a series, the transition temperature from the $S_C$ to the nematic phase ($T_{CN}$) generally increases with increasing chain lengths. Lateral fluorination still leads to higher $T_{CN}$ values. The decrease of $T_{CN}$ upon replacement of an alkoxy by an alkyl chain (IB → IA) is surprisingly small.

A compound containing two ester groups, i.e. 9DPePe9 (for the formula-code see footnote to Table VIII) has the phase sequence C 76.3 S 86.5 $S_C$ 124.5 N 152 I.

### b) 4-(1,3-Dioxan-2-yl)biphenyls II

The synthesis of the 4′-alkoxy-3′-fluoro-4-(trans-5-alkyl-1,3-dioxan-2-yl)biphenyls IIC is outlined in Scheme II. The preparation of the 2-(1E-alkenyl)-1,3-propanediols required for the series IIE has been described.[11] Short-chain representatives of the laterally unsubstituted series IIA, B are known.[12]

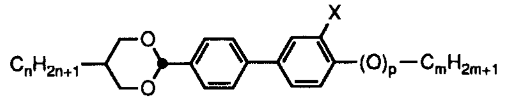
The mesogenic transition temperatures of the series IIA–C are recorded in Table II. Melting points are generally low (46–69°C), clearing points somewhat higher than in the corresponding ester series I.

The 4′-alkylbiphenyl series (IIA) exhibits a wide-range highly ordered orthogonal smectic (probably $S_B$) phase until about 10°C below the clearing point, followed by an $S_A$ and, in the short-chain members, by a nematic phase. Only for the compound with the longest chain ($C_{12}$) at the dioxan ring a very narrow $S_C$ phase is detected.

The laterally unsubstituted 4′-alkoxybiphenyl series (IIB) shows above a wide-range highly ordered smectic phase rather broad $S_C$ phase ranges, followed only by the nematic mesophase. Introduction of a lateral fluorine substituent in an ortho position to the alkoxy group (IC) decreases the transition temperature from the highly ordered smectic to the $S_C$ phase by about 40°C. On the other hand, the nematic phase is replaced by the $S_A$ phase and the upper limit of the $S_C$ phase is

TABLE II

Transition temperatures (°C) for compounds IIA, B, C



IIA p = 0, X = H
IIB p = 1, X = H
IIC p = 1, X = F

| p | X | n | m | C | $S_B$? | $S_C$ | $S_A$ | N | I |
|---|---|---|---|---|---|---|---|---|---|
| 0 | H | 7 | 6 | • 46.0 | • 137.3 | | • 149 | • 153.5 | • |
| | | 7 | 8 | • 46 | • 139 | | • 150 | • 150.5 | • |
| | | 8 | 8 | • 50.5 | • 140.5 | | • 148.8 | | • |
| | | 10 | 8 | • 57.5 | • 143.5 | | • 149 | | • |
| | | 12 | 8 | • 65.2 | • 142.2 | • 143 | •146.3 | | • |
| 1 | H | 7 | 7 | • 66.6$^{1)}$ | • 122 | • 153 | | • 173 | • |
| | | 7 | 8 | • 65.2$^{2)}$ | • 123 | • 155 | | • 170 | • |
| | | 9 | 8 | • 65.8 | • 142 | • 163 | | • 168.5 | • |
| 1 | F | 8 | 6 | • 48.4 | • 91.5 | • 126.5 | • 155.5 | | • |
| | | 8 | 7 | • 52.9 | • 88.4 | • 126.5 | • 152.5 | | • |
| | | 8 | 8 | • 52.6 | • 81.3 | • 127.2 | • 149 | | • |
| | | 8 | 10 | • 55.0 | • 82.0 | • 123.5 | • 147.5 | | • |
| | | 10 | 6 | • 56.4 | • 98.9 | • 133.5 | • 153.8 | | • |
| | | 10 | 7 | • 57.5 | • 95.6 | • 138.2 | • 151 | | • |
| | | 10 | 10 | • 63.3 | • 89.5 | • 138.5 | • 146 | | • |
| | | 12 | 6 | • 62.0 | • 98.8 | • 134.8 | • 150.5 | | • |
| | | 12 | 7 | • 66.5 | • 93.4 | • 141 | • 148.5 | | • |
| | | 12 | 10 | • 68.9 | • 88.5 | • 142.5 | • 143.5 | | • |

further S - S transition: 1) 92.9°C, 2) 96.7°C

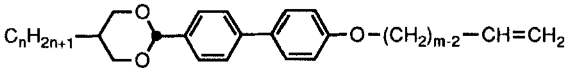
lowered. The temperature range of the $S_C$ phase increases with increasing chain length of the end groups, especially of the alkyl chain at the dioxan ring.

Table III shows the transition temperatures of the 4′-(ω-alkenyloxy)biphenyls IID. The presence of the double bond has nearly no influence on the melting point, but leads to a small decrease of the $S_C$ temperature range and to the appearance of a narrow $S_A$ phase.

The replacement of the alkyl group at the dioxan ring by a 1E-alkenyl group in IIE (Table IV) causes a small increase of $T_{CN}$ (about 5°C). On the other hand, the occurrence of an additional tilted S (possibly $S_F$) phase narrows the $S_C$ temperature range, and the melting point is clearly increased.

TABLE III

Transition temperatures (°C) for compounds IID

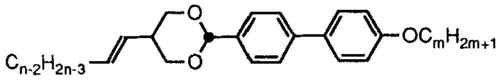


IID

| n | m | C | $S_B$? | $S_C$ | $S_A$ | N | I |
|---|---|---|---|---|---|---|---|
| 8 | 7 | • 53.4 | • 135 | • 155 | • 157 | • 169.5 | • |
| 8 | 9 | • 61.1 | • 135 | • 154.5 | • 156.5 | • 163 | • |
| 8 | 11 | • 68.4 | • 133.7 | • 152.7 | • 155 | • 158.5 | • |
| 10 | 7 | • 62.9 | • 141.4 | • 157 | • 162.7 | • 165 | • |
| 10 | 9 | • 64.6 | • 140.5 | • 156.5 | • 158.5 | • 160 | • |
| 10 | 11 | • 71.2 | • 138.9 | • 155 | • 156 | | • |

TABLE IV

Transition temperatures (°C) for compounds IIE



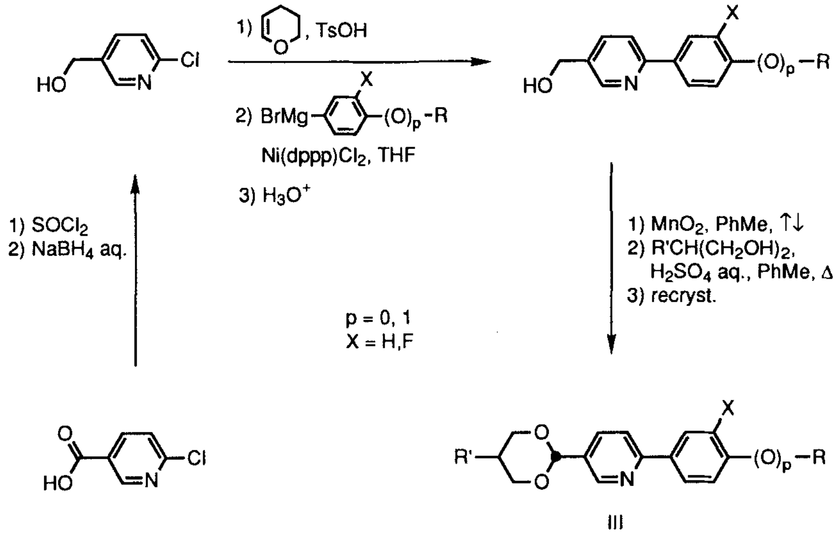
IIE

| n | m | C | $S_B$? | $S_F$? | $S_C$ | N | I |
|---|---|---|---|---|---|---|---|
| 6 | 6 | • 87.7 | • 133 | • 137.4 | • 149.5 | • 189 | • |
| 6 | 7 | • 91.3 | • 132 | • 138.5 | • 152.5 | • 185.5 | • |
| 6 | 8 | • 100.9 | • 130.7 | • 138.2 | • 154 | • 181 | • |
| 7 | 6 | • 81.5 | • 115.3 | • 133 | • 154 | • 191.5 | • |
| 7 | 7 | • 71.0 | • 115.5 | • 135.5 | • 158 | • 182 | • |
| 7 | 8 | • 82.0 | • 117.5 | • 136.5 | • 160 | • 182.5 | • |

### c) 5-(1,3-Dioxan-2-yl)-2-phenylpyridines III

The synthesis of the compounds III comprising this novel mesogenic rigid core is given in Scheme III. A key step is the nickel-catalyzed heterocoupling of the tetrahydropyranyl ether of 6-chloro-3-pyridinecarbinol with the appropriate Grignard reagent. All synthetic steps proceeded in high yields.

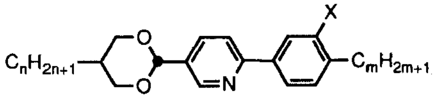
The liquid crystal temperature ranges of the dialkyl compounds (series IIIA, B) are listed in Table V, those of the alkoxy compounds (IIIC, D) in Table VI. Compared to the biphenyl class II, in the laterally unsubstituted series IIIA, C the



SCHEME III

TABLE V

Transition temperatures (°C) for compounds IIIA, B



IIIA: X = H
IIIB: X = F

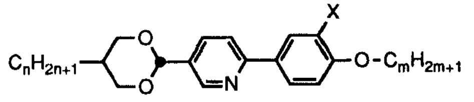
| X | n | m | C | S | S$_C$ | S$_A$ | I |
|---|---|---|---|---|---|---|---|
| H | 7 | 8 | • 55.5 | • 145.5 |  | • 173.7 | • |
|  | 8 | 8 | • 58.5 | • 145 |  | • 171 | • |
|  | 10 | 8 | • 64.0 | • 144.5 | • 156 | • 167 | • |
|  | 12 | 8 | • 71 | • 143.5 | • 165 |  | • |
| F | 10 | 9 | • 54.9 | • 99.7 | • 136.5 | • 153.5 | • |
|  | 12 | 9 | • 65.1 | • 101.5 | • 142.5 | • 150 | • |

thermal stability of the S$_C$ phase and the clearing point are elevated by about 20°C, whereas the upper limit of the highly ordered smectic phase and the melting point are almost unchanged. A fluorine substituent in an ortho position to the alkoxy group destabilizes the highly ordered smectic phase much more than in the biphenyl class, so that in the dialkyl series (IIIB) smectic C temperature ranges increase up to 40°C and in the alkoxy series (IIID) even to 80°C and more.

The solubility of compounds of the classes II and III decreases with increasing

TABLE VI

Transition temperatures (°C) for compounds IIIC, D



IIIC: X = H
IIID: X = F

| X | n | m | C | S | $S_C$ | $S_A$ | N | I |
|---|---|---|---|---|---|---|---|---|
| H | 7 | 6 | • 60.4 | • 141.0 | • 169.5 | • 181 | • 190 | • |
| | 7 | 7 | • 69.9 | • 141.5 | • 169 | • 181 | • 188 | • |
| | 7 | 8 | • 76.1 | • 137.5 | • 169.5 | • 181.7 | • 187 | • |
| | 8 | 6 | • 62.4 | • 141.2 | • 176 | • 181 | • 186 | • |
| | 8 | 7 | • 71.5 | • 140.5 | • 176.5 | • 179.5 | • 183 | • |
| | 8 | 8 | • 67.3 | • 139.5 | • 177 | • 182 | • 185 | • |
| | 10 | 6 | • 75.5 | • 141.5 | • 180 | • 182.8 | • 183 | • |
| | 10 | 7 | • 79.5 | • 139.5 | • 180.5 | • 181.5 | | • |
| | 10 | 8 | • 69.7 | • 137.5 | • 179 | | | • |
| F | 7 | 8 | • 80.6 | | • 111 | • 174.5 | | • |
| | 8 | 6 | • 72.7 | | • 146 | • 174.5 | | • |
| | 8 | 7 | • 79.5 | | • 145 | • 171 | | • |
| | 8 | 10 | • 81.4 | | • 136 | • 167.3 | | • |
| | 10 | 6 | • 76.5 | | • 159 | • 172.3 | | • |
| | 10 | 7 | • 81.8 | | • 160 | • 167.5 | | • |
| | 10 | 8 | • 77.8 | | • 160.5 | • 167.5 | | • |
| | 10 | 10 | • 81.1 | | • 158 | • 163.5 | | • |
| | 12 | 6 | • 79.1 | | • 160 | • 168.3 | | • |
| | 12 | 7 | • 85.9 | | • 161.5 | • 165 | | • |
| | 12 | 10 | • 84.8 | | • 159.5 | • 159.7 | | • |

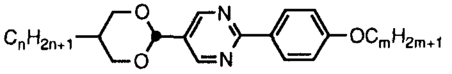
chain length at the dioxan ring. Compared to the biphenyls II, the solubility of phenylpyridines is somewhat inferior, but still satisfactory.

### d) 2-(p-Alkoxyphenyl)-5-(trans-5-alkyl-1,3-dioxan-2-yl)pyrimidines IV

Applying a known synthetic pathway,[13] some pyrimidine derivatives IV have been prepared. The transition temperatures are listed in Table VII. The melting points are relatively high and the solubilities very poor. Furthermore, the chain length of the alkyl group at the 1,3-dioxan ring is crucial for the occurrence of the $S_C$ phase. The decyl and dodecyl compounds exhibit broad $S_C$ phases situated at high temperatures, whereas the lower-melting octyl compound does not show an $S_C$ phase.

TABLE VII

Transition temperatures (°C) for compounds IV



IV

| n | m | C | S | $S_C$ | $S_A$ | I |
|---|---|---|---|---|---|---|
| 8 | 10 | • 87.3 | (• 78.5) | | • 179 | • |
| 10 | 6 | • 112 | • 124 | • 164.5 | • 183 | • |
| 10 | 10 | • 101.9 | • 124 | • 164.5 | • 177 | • |
| 12 | 6 | • 107.7 | • 126 | • 172.5 | • 180.5 | • |

TABLE VIII

Influence of I, II or III (13 mole %) in a ferroelectric base mixture (M) to the viscosity parameter $\gamma\sin^2\theta$, the spontaneous polarization ($P_S$), the parameter $\gamma\sin^2\theta/P_S$ (measured at 25°C) and the transition temperature from the smectic C to the smectic A or chiral nematic phase ($T_{CA}$ or $T_{CN}$)

| X | | $\gamma\sin^2\theta$ (mPa·s) | $P_s$ ($nC\cdot cm^{-2}$) | $\gamma\sin^2\theta/P_s$ ($mPa\cdot s\cdot nC^{-1}\cdot cm^2$) | $T_{CA}$ (°C) |
|---|---|---|---|---|---|
| M | | 20 | 6.5 | 3.1 | 53 |
| 7DPP8 | (IIA) | 19.1 | 4.34 | 4.4 | 51.1 |
| 8DPdP8 | (IIIA) | 19.9 | 4.15 | 4.8 | 52.3 |
| 7DPPO8 | (IIB) | 43.3 | 6.60 | 6.6 | 63.0 |
| 9DPPO8 | (IIB) | 33.6 | 5.80 | 5.8 | 65.4 |
| 8DPdPO8 | (IIIC) | 35.9 | 5.90 | 6.1 | 67.0 |
| $7DPdP_FO8$ | (IIID) | 39.1 | 5.68 | 6.9 | 58.0 |
| $10DPdP_FO8$ | (IIID) | 42.4 | 4.77 | 8.9 | 61.4 |
| 7DPeP8 | (IA) | 58.5 | 6.37 | 9.2 | 62.0 |
| | | | | | $T_{CN}$ |
| 7DPePO8 | (IB) | 111.7 | 8.29 | 13.5 | 64.0 |
| $7DPeP_FO8$ | (IC) | 129.8 | 9.29 | 14.0 | 65.8 |

Meaning of the code for the formulae: D trans-1,3-dioxan-5,2-ylene, P p-$C_6H_4$, $P_F$ 3-F-1,4-$C_6H_3$, Pd 5,2-pyridylene, e OOC, cipher x $C_xH_{2x+1}$.

### e) Properties in a Ferroelectric Liquid Crystal Mixture

Some 1,3-dioxans of the classes I, II, III have been added (13 mole %) to a ferroelectric mixture M having the phase sequence I 87 N* 78 $S_A$ 53 $S_C^*$. M is composed of phenylpyrimidines,[2] (cyclohexylethyl)phenyl benzoates[3] and chiral tricyclic cyclohexyl 2-fluoroalkanoates.[14] The influence of the tricyclic dioxans on the viscosity parameter $\gamma \sin^2\theta$ ($\gamma$ rotational viscosity, $\theta$ tilt angle), the spontaneous polarization ($P_S$) and $T_{CA}$ or $T_{CN}$ is given in Table VIII (partly published in Reference 15). The quotient $\gamma \sin^2\theta/P_S$ is approximately proportional to the response times.[16]

Table VIII reveals some interesting trends. The response time decreases drastically, if a central ester linking group is removed (I → II) or an alkoxy chain is replaced by an alkyl chain. Introduction of a lateral fluorine substituent does not much increase the viscosity, and the viscosities of the biphenyls II and the phenylpyridines III are comparable.

Laterally unsubstituted esters I enhance the thermal stability of the $S_C^*$ phase more than expected and about as much as analogous biphenyl compounds do. Phenylpyridines III lead to a slightly stronger increase of $T_{CA}$ than biphenyls II. Introduction of a lateral fluorine substituent stabilizes in the ester class (IC) the $S_C^*$ phase further, whereas in the phenylpyridine series IIID it favors the $S_A$ phase strongly, leading to disappointingly low $T_{CA}$ values. The directly linked dialkyl compounds IIA, IIIA do not increase $T_{CA}$, whereas the corresponding ester compounds (IA) again cause an overproportional thermal stabilization of the $S_C^*$ phase.

For the use in fast-responding broad-range ferroelectric mixtures, among the series studied in Table VIII, IIIC, IIB and, to a lesser extent, IA are the most promising ones, provided that highly ordered smectic phases are easily suppressable. If this is not the case, they should be partly replaced by laterally fluorinated representatives. (Characteristic data of three ferroelectric mixtures containing compounds of the series IIC, IID and IIIC are given in Reference 15.)

### Acknowledgment

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