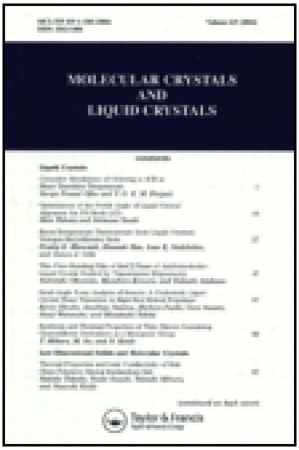

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New Optically Active Dopants Based on Chiral Dioxanes

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New Optically Active Dopants Based on Chiral Dioxanes†

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With the exception of natural products and their derivatives, chiral dopants for ferroelectric and nematic applications with chiral rings were scarcely reported in the literature. Especially six membered rings were not investigated so far. We now report on the synthesis and physical properties of chiral dioxanes. They exhibit a medium spontaneous polarization in ferroelectric and a small helical pitch in nematic mixtures. A possibility to invert the sign of the spontaneous polarization without change of the helix sense is demonstrated. Some representatives exhibit an almost temperature independent helical pitch.

Keywords: nematic dopants, ferroelectric dopants, chiral dioxanes

1. INTRODUCTION

Enantiomerically pure chiral dopants are important constituents of almost all liquid crystal mixtures used in LCD applications. In all different types of TN devices they are necessary for the induction of a helical twist and for temperature compensation. Ferroelectric mixtures require chiral dopants for induction of a large spontaneous polarization, pitch compensation e.g. in SSFLC-devices[1] or induction of a short helical pitch in the newer DHF-[2] and SBF-devices.[3] Very recently a new projection principle based on cholesteric polarization filters was presented.[4] For this application a combination of chiral dopants, able to induce a well defined and temperature independent helical pitch is of crucial importance.

The large majority of known chiral dopants are either steroid or terpenoid derivatives mainly used in TN applications or derivatives of established liquid crystal structures modified by the introduction of chiral side chains. This latter type of dopants, mainly used in ferroelectric applications, was directly designed in order to achieve a high spontaneous polarization. It is generally agreed that the spontaneous polarization is increased by a) increasing proximity of the chiral center and the core, b) a restricted conformational mobility of the chiral part, c) a strongly electronegative atom linked to the chiral center creating a permanent dipole and d) polarizable groups close to the chiral center. As a consequence of requirement

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†Presented at the 13th International Liquid Crystal Conference, Vancouver, B.C., Canada, 22–27 July 1990.

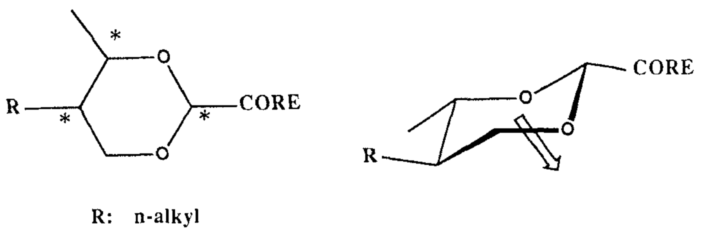


FIGURE 1 Basic structure of chiral dioxanes with three centers of chirality.

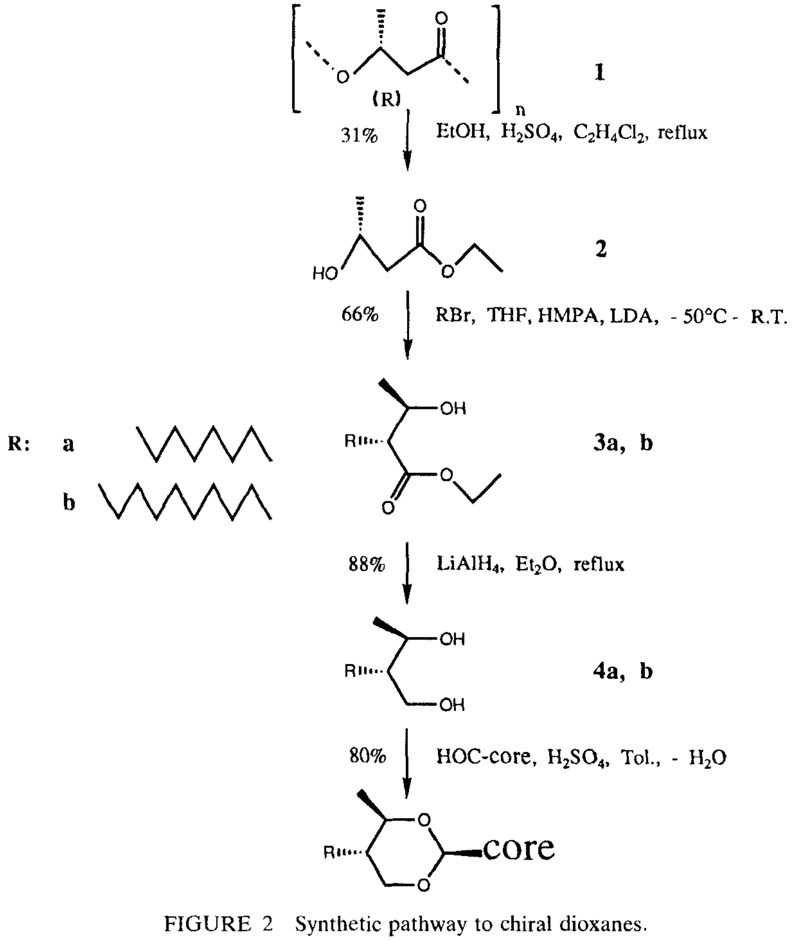
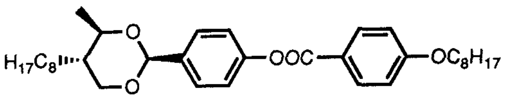
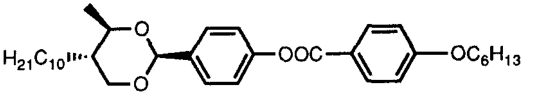
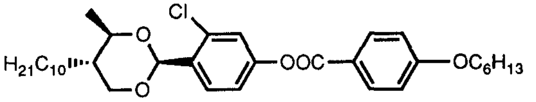
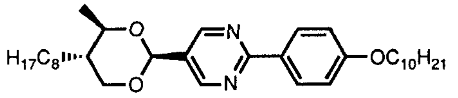
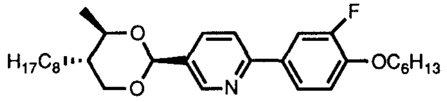


FIGURE 2 Synthetic pathway to chiral dioxanes.

b) it seems of advantage to introduce the chirality directly into a ring system instead of a flexible side chain. Sporadic examples have recently appeared in the literature where five membered acetals, lactones and carbonates were presented.[5,6] We decided to synthesize chiral six membered 1,3-dioxanes, which are expected to represent a more suitable substructure for liquid crystal molecules. The originally symmetric 1,3-dioxane ring loses its symmetry by the formal introduction of an additional substituent (e.g. CH_3) at 4-position (Figure 1). Thus three chiral centers

TABLE I

Chiral dioxanes for ferroelectric mixtures without additional chiral element: transition temperatures t (°C), ethalpy of fusion ΔH_m [kJ/mol], spontaneous polarization P_s [nC/cm^2], twisting power 1/pc [μ^{-1}] and tilt angle ϑ [deg]. P_s, 1/pc and ϑ were measured in mixture S_c7 1007 (7 wt%) 15°C below $S_C^* - S_A$ transition. P_s is extrapolated to 100%.

Compound / $t_{transition}$	**ΔH_m**	**P_S**	**1/pc**	**ϑ**
 **5** C 52 S_A 57.4 N* 100.5 I	35.1	- 29	11	35
 **6** C 77 N* 100.5 I	42.7	- 22	--	32
 **7** C 47.5 I	18.8	+ 9	8.3	30
 **8** C 67.5 N* 100.6 I	25.3	26	--	--
 **9** C 77.7 I	31.8	12	--	--

are created. The relative configuration of all centers was designed in a way that allows all substituents to have an equatorial position. This forces the ring to a thermodynamically stable chair conformation with a resulting dipole moment almost perpendicular to the ring plane and to the molecular axis. The core was selected to minimize the phase depression in the host mixture.

2. SYNTHESIS

The synthetic pathway (Figure 2) starts with the easily available natural Poly-(R)-3-hydroxy-butyric acid **1**, which was depolymerized to the monomeric ester **2**.[7]

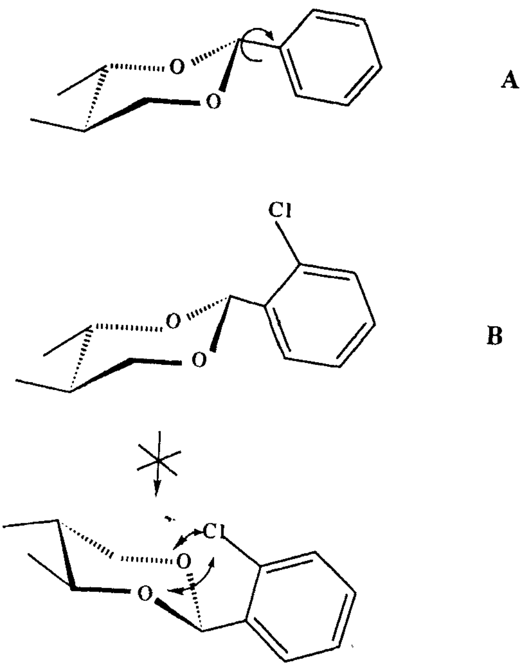


FIGURE 3 Conformations of unsubstituted and chloro-substituted phenyldioxanes.

Diastereoselective alkylation according to a procedure published by G. Fràter *et al.*[8] gave both hydroxy esters **3a** and **3b** which were subsequently reduced with LAH to the corresponding diols **4a** and **4b**. Comparison of the optical rotation of **2** with literature values[7] and NMR studies of acetals formed from **4a** and **4b** revealed enantiomeric and diasteromeric purities of >95%. Formation of the 1,3-dioxanes with different core aldehydes were performed as usual. Thermodynamic control during acetal formation strongly favoured the chirality of the third chiral center formed during the reaction as shown in Figure 1.

3. PHYSICAL PROPERTIES

a) Properties Related to Ferroelectric Applications

Phase transitions, spontaneous polarization (P_s), twisting power (1/pc) and tilt angle (ϑ) of three similar phenylbenzoates are collated in Table I. The unsubstituted benzoates **5** and **6** exhibit mainly a cholesteric mesophase, while the large chloro substituent in **7** prevents the formation of a mesophase. The P_s values (measured in a chiral host of pyrimidines and esters, S_c7 1007, 15°C below S_c^* transition) are in the medium range compared to other known dopants. In comparison to fluoroesters recently measured in the same mixture[9] about half of this value is reached, whereas a considerably higher twisting power is observed.

If the aromatic ring in **6** is substituted by a chloro atom at ortho position relative to the dioxane ring, compound **7** is obtained. Whereas the sense of the helical twist

TABLE II

Chiral dioxanes for ferroelectric mixtures with an additional chiral element. For conditions see caption Table I.

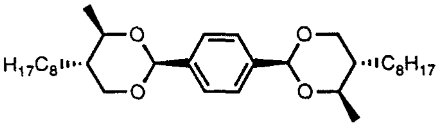
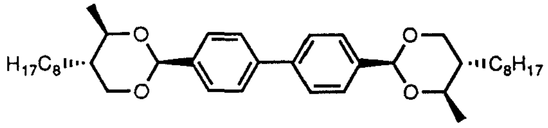
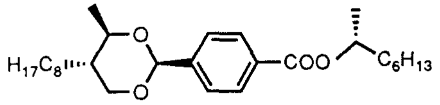
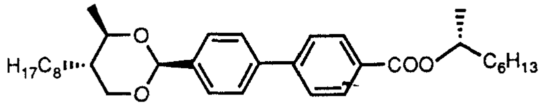
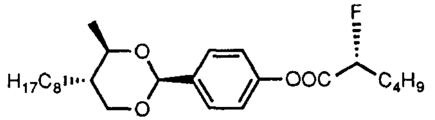
Compound / $t_{transition}$	ΔH_m	P_S	1/pc	ϑ
 **10** C 80.4 I	30.8	27	9.1	29
 **11** C 95.3 N* 120.5 I	22.8	59	--	30
 **12** C <0 I	--	6.8	--	--
 **13** C 21.6 I	13.7	34	1.6	--
 **14** C 59.1 I	38.2	58	--	14.5

TABLE III

Chiral dioxanes for nematic mixtures without additional chiral element: transition temperatures t (°C), enthalpy of fusion ΔH_m [kJ/mol], pitch [μm] and coefficients *A*, *B* and *C*. Pitch and *A* – *C* were measured at a concentration of 1% wt in broad temperature mixture Ro 3010 from F. Hoffmann-La Roche at 22°C. All components measured induced a positive (right-handed) pitch.

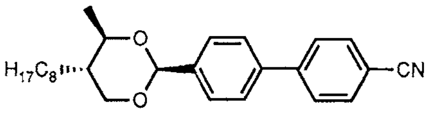
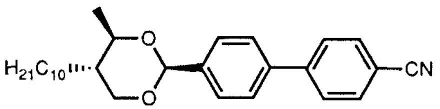
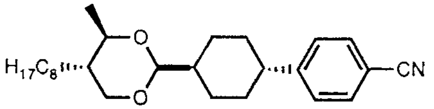
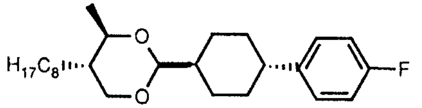
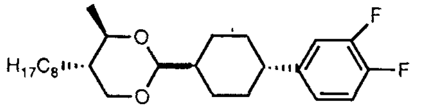
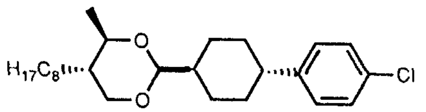
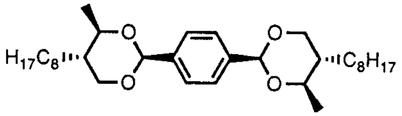
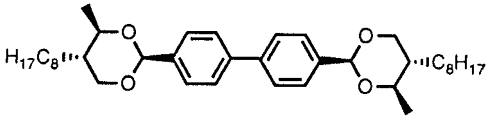
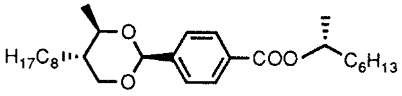
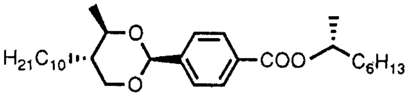
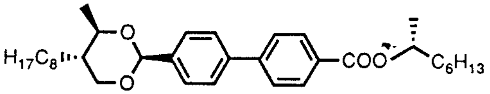
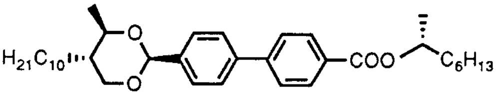
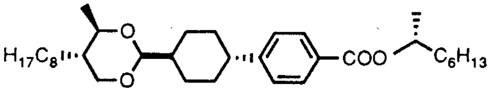
Compound / $t_{transition}$	ΔH_m	pitch	A	B	C
			$(x10^{-2})$	$(x10^{-4})$	$(x10^{-6})$
 **15** C 114.5 S_A 128.4 I	27.9	---	---	---	---
 **16** C 115.2 S_A 130.6 I	32.6	14.9	6.699	0.832	0.444
 **17** C 65.3 N* 91.2 I	22.2	15.8	6.308	- 0.328	0.690
 **18** C 63.5 I	23.7	17.3	5.7964	- 0.0023	- 0.0653
 **19** C 32.9 I	27.8	17.0	5.8956	- 0.0824	- 0.5718
 **20** C 66.7 I	24.7	17.2	5.8035	0.1030	- 0.1569

TABLE IV

Chiral dioxanes for nematic mixtures with an additional chiral element.
For conditions see caption Table III.

Compound / $t_{transition}$	ΔH_m	**pitch**	**A**	**B**	**C**
			($\times 10^{-2}$)	($\times 10^{-4}$)	($\times 10^{-6}$)
 **10** C 80.4 I	30.8	7.4	16.26	2.729	- 2.461
 **11** C 95.3 N* 120.5 I	22.8	12.2	8.476	2.806	1.028
 **23** C <0 I	---	6.3	15.864	0.703	0.789
 **12** C <0 I	---	6.5	15.42	- 2.946	- 4.192
 **21** S -25 I	---	6.79	14.72	1.757	- 1.138
 **13** C 21.6 I	13.7	7.5	13.52	1.315	- 1.480
 **22** C 24.8 I	14.7	---	---	---	---

remains unchanged, a remarkable sign change of the spontaneous polarization of **7** is observed. Conformational studies based on reported X-ray data of more than 40 similar model compounds clearly demonstrate the preferred conformation of **7** as shown in Figure 3(*B*). The chloro substituent prefers the longest possible distance from the oxygens and obviously overcompensates their dipole moments. For **6** the conformation depicted in Figure 2(*A*) is only one possibility of many different conformations for phenyldioxanes found in the literature. The rotational energy between the dioxane and aromatic ring is here less than 1 kcal/Mol. One of both directly linked N-heterocycles (Table I, pyrimidine **8**) exhibits a cholesteric mesophase and roughly the same P_s value as the esters **8** and **9**. The lower P_s of **9** is not easy to understand since the tilt angles are identical.

In Table II the data of a number of chiral dioxanes possessing a second element of chirality are listed. The absolute configuration of this new chiral part was adapted in order to reinforce the P_s value. The tetracyclic dimeric dioxane **11** still exhibits a cholesteric mesophase. As expected its P_s is roughly doubled. All other dopants possess no longer an enantiotropic mesophase. The P_s values are only additive if two rings are situated between the chiral elements (cf. **11**, **13**). Otherwise a much lower spontaneous polarization than expected is observed (cf. **10**, **12**, **14**).‡ Obviously the chiral parts are not completely decoupled here.

B) Properties Related to Nematic Applications

The relatively large helical twisting power of the chiral dioxanes suggested to investigate them also as chiral dopants for nematic applications. In addition modified dioxanes with cores better adapted for nematics (cyclohexane rings, terminal cyano and halogen substituents) were synthesized. Their structures and relevant data are compiled in Table III. All measurements were performed at 22°C and with a concentration of 1 percent in Ro 3010, a nematic broad temperature mixture of F. Hoffmann-La Roche. The temperature dependence of the helical twisting power 1/pc of a nematic mixture doped with a chiral additive of concentration *c* is represented by the formula[10]:

$$1/\mathrm{pc}(T) = A + B(T - 22°\mathrm{C}) + C(T - 22°\mathrm{C})^2 + \ldots .$$

A represents the reciprocal helical pitch at 22°C ($c = 1\%$). Its sign determines the helix sense ($-$ = left). Coefficient *B* essentially determines the temperature dependence of the helical twisting power. The values of Table III show the following facts: The nitriles exhibit an S_A or cholesteric mesophase. The chirality sense chosen for the dioxanes induces a right-handed helix with a pitch in the range of 15–17 μm.

The aromaticity or saturation of the ring adjacent to the chiral dioxane (cf. **16** and **17**) as well as the polarity of the terminal substituent (cf. **17**–**21**) has no significant influence to the pitch. Comparing the constants B, however, large differences in the temperature dependence are observed. The almost complete independence of the fluorinated compound **18** is striking and for **19** and **20** B is still

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‡A corresponding biphenyl-α-fluoroester without dioxane ring exhibits a P_s of 56 in the same mixture.[9]

surprisingly small. In Table IV the corresponding data for the dioxanes with a second chiral element are collated. Unlike the P_s values in Table II the pitches are strictly additive. Small differences may be attributed to different molecular weights. Comparison of the pitches of **10** and **12** lead to the conclusion that the contributions of the chiral dioxane and the chiral octanolate are comparable. Of great interest here are the almost identical but opposite values of term B, which allows an excellent temperature compensation.

4. CONCLUSIONS

A large number of different compounds with chiral 1,3-dioxane rings were investigated under ferroelectric and nematic aspects. While only moderate spontaneous polarizations were found, the inversion of sign on lateral substitution of the neighbouring ring is noteworthy. The new compounds represent some valuable chiral dopants for different nematic applications including the newly developed polarized colour projection filters.[4] They improve the possibility of temperature compensation or, in some cases, even make it unnecessary.

Acknowledgment

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References

1. N. A. Clark and S. T. Lagerwall, *Appl. Phys. Lett.*, **36**, 899 (1980).
2. J. Fünfschilling and M. Schadt, *J. Appl. Phys.*, **66**, 3877 (1989).
3. J. Fünfschilling and M. Schadt, Digest SID 90, (Society for Information Display), 106 (1990).
4. M. Schadt and J. Fünfschilling, *Jap. J. Appl. Phys.*, **29**, 1974 (1990).
5. a) H. R. Dübal, C. Escher, D. Günther, W. Hemmerling, I. Müller, D. Ohlendorf and R. Wingen, 14th Jpn. Intern. LC Conf., Sendai, 1988. b)K. Sakaguchi and T. Kitamura, 2nd Int. Conference on Ferroelectric Liquid Crystals, Göteborg, 1989.
6. J. Gay and G. Scherowsky, 12th Int. Liquid Crystal Conference, Freiburg, 1988.
7. D. Seebach and M. F. Züger, *Helv. Chim. Acta*, **65**, 492 (1982).
8. G. Fràter, U. Müller and W. Günther, *Tetrahedron*, **40**, 1269 (1984).
9. R. Buchecker, S. M. Kelly and J. Fünfschilling, *Liquid Crystals*, **8**, 217 (1990).
10. A. Göbl-Wunsch and G. Heppke, *Zeitschr. Naturforsch.*, **34a**, 594 (1979).