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NOVEL DOPANTS FOR FERROELECTRIC MIXTURES INCORPORATING CHIRAL DIOXANE OR TETRAHYDROPYRANE RINGS

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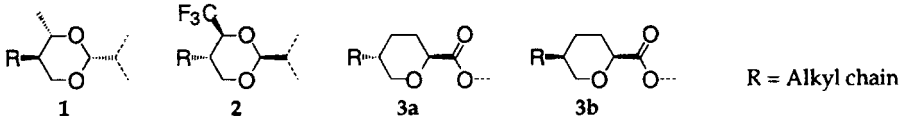
Abstract The synthesis, mesomorphic properties and use as chiral dopants in ferroelectric mixtures of chiral dioxane and tetrahydropyrane derivatives are presented. The dioxanes induce a sufficiently high spontaneous polarisation and a very small pitch if added to achiral Sc-mixtures.

INTRODUCTION

In a previous paper we have introduced novel chiral dopants which are characterised by the presence of a chiral 4-methyl-1,3-dioxane ring (**1**) as structural subunit[1]. Due to their strong helical twisting power (HTP) such compounds turned out to be valuable dopants for cholesteric mixtures. Furthermore a few of them also showed a promising potential for ferroelectric DHF-applications. We have now synthesised a number of new dopants specifically designed and tested for DHF-mixtures. In addition we have synthesised and studied dopants incorporating a 4-trifluoromethyl-1,3-dioxane ring (**2**) with enhanced polarity in comparison to the methyldioxane **1**.



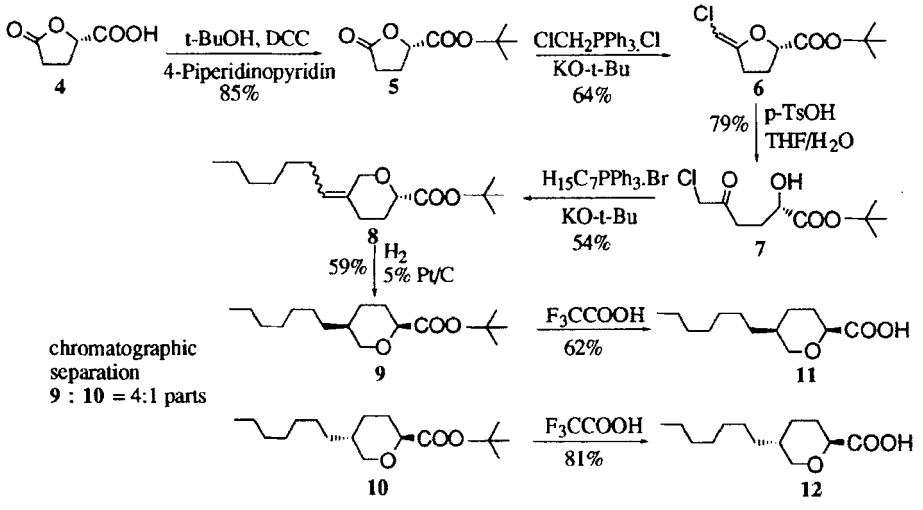
1 **2** **3a** **3b**

FIGURE 1 Chiral subunits incorporated in novel dopants

Only a few chiral dopants incorporating a 2,5-disubstituted tetrahydropyrane ring have been reported in the literature and all of them have at least one further oxygen atom directly attached to the ring e.g. [2-4]. This might cause at least partial compensation of the dipole moment of the ring oxygen atom. To avoid this potential disadvantage we decided to synthesise enantiomerically pure tetrahydropyrane derivatives bearing only carbon atoms directly linked to the ring (subunits **3a, 3b**).

SYNTHESIS

The Synthesis of analogous 2,5-methyldioxanes (subunit 1) starting with optically active 3-hydroxybutyric acid has been described previously[1]. The trifluoromethyl derivatives (subunit **2**) have been synthesised analogously starting from optically active 3-hydroxy-4,4,4-trifluorobutyric acid. The synthesis of the tetrahydropyranes **3a** and **3b** was not known from the chemical literature. Several attempts starting from sugar derivatives failed. It was finally accomplished as depicted in Scheme 1.



SCHEME 1 Synthesis of (2S, 5S) and (2S, 5R) 5-heptyltetrahydropyrane-2-carboxylic acid

The synthesis starts from the commercially available optically active lactone **4** and includes essentially two interesting key steps. First the unusual Wittig reaction at the carboxylic group of lactone **5** to the enolether **6**. Then the second

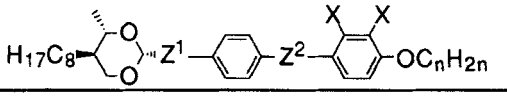
Wittig reaction with the α-chloroketone **7** which proceeds directly to the cyclic ether **8.** The expected α-chloroalkenyl derivative formed by the vinylation step obviously is cyclised spontaneously ofter being by attack of the hydroxyl group at the allylic chloro substituted centre.

The subsequent hydrogenation of **8** (cis/trans ratio 4:1) and the ester hydrolysis to **11** and **12** were performed according to standard procedures. To our knowledge this is the first report of the successful synthesis of optically active 5-alkyltetrahydropyrane-2-carboxylic acids.

RESULTS AND DISCUSSION

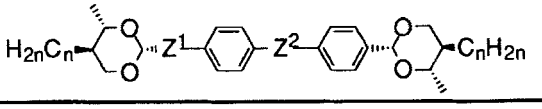
In Tabs. 1 and 2 the thermodynamic properties of dopants incorporating one or two chiral 4-methyldioxane subunits respectively are collated. All of them exhibit enantiotropic chiral nematic mesophases. In comparison to Tab. 1 the introduction of a second 4-methyldioxane ring (Tab. 2) does not depress the clearing temperature but surprisingly increases it. The presence of a forth ring obviously overcompensates the presence of an additional bulky subunit.

TABLE 1 Transition temperatures [C], enthalpy of fusion Δ H [kJ/Mol] and specific optical rotation $[\alpha]_D$ [ ] 1% in $CHCl_3$, of compounds incorporating one chiral 4-methyldioxane unit.



	n	Z^1	Z^2	X	K	S_X	N*	I	ΔH	$[\alpha]_D$
13	6	---	---	H	77.8	(71.1)	102		32.6	-16.2
14	6	$(CH_2)_2$	---	H	50.5		76.7		---	-16.0
15	6	CH_2O	---	H	71.0		83.1		---	-18.7
16	8	---	---	F	42.7		57.1		35.4	-14.3
17	8	---	OOC	H	57.5		99.8		50.6	-14.2
18	8	---	OOC	F	45.1		84.5		35.2	-13.4

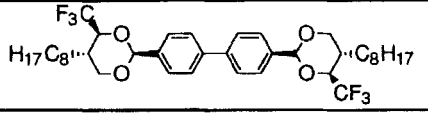
TABLE 2 Transition temperatures [C], enthalpy of fusion Δ H [kJ/Mol] and specific optical rotation $[\alpha]_D$ [ ] 1% in $CHCl_3$ of compounds incorporating two chiral 4-methyldioxane units.



	n	Z^1	Z^2	K	S_X	N*	I	ΔH	$[\alpha]_D$
19	6	---	---	103.8		134.2	21.6	-28	
20	7	---	---	90.0	93.5	135.2	21.1	-26.9	
21	8	---	---	96.5		123.4	24.3	-25.9	
22	9	---	---	88.5		108.8	23.4	-24.6	
23	8	---	COO	90.8		123.5	47.5	-25.6	
24	9	---	≡	99.8		148.8	36.1	-23.3	
25	8	$(CH_2)_2$	---	70.2	(47)	95.1	---	-26.6	

The replacement of both methyl groups by the slightly larger trifluoromethyl groups designed to increase the lateral dipole moment resulted in compound **26** (Tab. 3). The compound exhibits the complete disappearance of the enantiotropic mesophase.

TABLE 3 Transition temperatures [C] and enthalpy of fusion Δ H [kJ/Mol] of a compound incorporating two chiral 4-trifluoromethyl dioxane units.

	Structure	K	S_X	N*	I
26		142			

Simple ester formation of the optically active 5-heptyltetrahydropyranyl carboxylic acids **11** and **12** with a suitable pyrimidinyl phenol gave the chiral dopants **27** and **28**. (Tab. 4). Due to the presence of only one oxygen atom, the 2,5 *disubstituted six membered ring* is chiral and therefore needs no longer a lateral methyl group for the induction of chirality. The trans isomer **28** exhibits a

microfurnace and FP5 temperature controller. Transitions were confirmed calorimetrically using a Perkin Elmer DSC7-PC with indium metal as the reference standard. The complexes prepared may be divided in to two sub-groups: those in where R^1 possesses a single aromatic ring, and those where R^1 contains two rings.

TABLE 1 Analytical data for the oxovanadium(IV) complexes

Complex	Yield / %	$\nu_{V=O}$ / cm^{-1}	μ / μ_B	% C Calc (Found)	% H Calc (Found)
10OP7	69	955	1.45	71.4 (71.7)	9.6 (9.5)
10OP9	43	955	1.52	72.3 (72.6)	9.8 (9.8)
10OP11	61	965	1.55	73.5 (73.4)	9.8 (10.1)
10OP13	39	960	1.63	74.1 (74.0)	10.2 (10.3)
10OP7CH	49	980	1.65	74.6 (74.3)	10.1 (9.9)
8OFP8	68	965	1.60	68.1 (68.4)	9.1 (8.8)
7BCH8	81	980	1.49	75.2 (75.2)	11.6 (11.3)
7PCH8	60	995	1.83	76.7 (76.6)	8.6 (8.5)
8BP8	67	995	1.71	77.2 (77.1)	9.0 (9.1)
FBP9	75	995	1.52	76.7 (76.8)	7.7 (7.5)
FBP7BCH	59	970	1.46	76.3 (76.0)	8.2 (8.3)

For the single ring systems, monotropic smectic phases were observed in all cases where R^2 was a simple n-alkyl chain, smectic A for short chain lengths and smectic A and C for longer chain lengths. If R^2 was a 4-n-heptylcyclohexyl unit (10OP7CH), an enantiotropic smectic A phase resulted with an additional monotropic smectic C phase. The overall length of this complex is comparable with 10OP11 and the molecular weight is the same as in 10OP13, yet the melting point is stabilised by 43 and 40 °C respectively. We have attributed the increased mesophase stability of 10OP7CH to rotational damping of the alkyl chain by the inclusion of the more rigid cyclohexane ring close to the co-ordinating core which allows for better molecular packing in the smectic layers. Additionally, the frequency of the V=O stretch in the IR spectrum of 10OP7CH indicates very little intermolecular O...V association while the lower values obtained

TABLE 5 Isotropic/nematic, smectic A/smectic C transition temperatures [C], spontaneous polarisation P_S [nC | cm ^{2}], switching time τ [μs] of 7% wt of **13 - 23** and **25 - 28** in mixture SC9-1219 and helical twisting power A determined from the change of the selective reflection when 3% wt of dopant were added to a left handed and a right handed mixture of 500 nm pitch size and specific optical rotation $[\alpha]_D$ of 1% in chloroforme [ ]. All measurements in mixtures were performed at 25 C

Dopant	—	**13**	**14**	**15**	**16**	**17**	**18**	**19**
I/N	103	103	101	102	101	102	102	104
S_A/S_C	76.5	69.6	69.7	70.8	64	64	64	65.5
P_S	—	6	6.9	4	1.4	4.2	3.8	11.7
τ	—	800	670	960	1650	1100	1500	540
A		-6	-13			-12	-9	
Dopant	**20**	**21**	**22**	**23**	**25**	**26**	**27**	**28**
I/N	103	104	104	103	103	102	93.4	107
S_A/S_C	65.2	67.4	66.9	62.3	67.8	—	65.3	73
P_S	10.6	10.1	10.7	8.7	10.4	—	3.5	0.7
τ	510	490	540	640	500	—	500	2500
A		-17			-21			

CONCLUSIONS

Optically active 4-methyldioxane derivatives generally do not exhibit Sc* phases. However they are able to induce an exceptionally small helical pitch when added to undoped mixtures. Furthermore they possess a sufficiently high spontaneous polarisation. 4-methyldioxane derivatives therefore are valuable candidates as dopants for DHF mixtures.

The 4-trifluoromethyldioxane derivative presented here was not liquid crystalline and deteriorated the smectic C phase completley when added to the basic mixture.

The first synthesis of optically active cis- and trans-5-alkyltetrahydropyrane-2-carboxylic acids lead to representative chiral dopants. The trans isomer exhibits a chiral smectic C phase but a rather small spontaneous polarisation while the cis isomer shows no mesophase but induces a spontaneous polarsation enhanced by the factor of five compared to the trans isomer.

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