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New Chiral Ether Derivatives of 2-Arylidene-*p*-Menthane-3-Ones as Components of Induced Ferroelectric Systems

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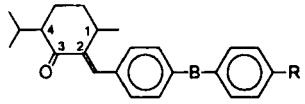
New 2-arylidene-*p*-menthane-3-ones containing the ether bridging group in the arylidene fragment have been synthesized and studied as chiral dopants in ferroelectric liquid crystal mixtures. The ferroelectric properties of these compositions were compared with those for compositions including chiral dopants that do not contain any bridging group. The influence of bridging group and terminal alkyl substituent length in the dopant molecule on the ferroelectric parameters of systems studied is discussed.

Keywords: induced ferroelectricity; chiral dopants

INTRODUCTION

1*R*,4*R*-2-Benzylidene-*p*-menthane-3-one ethers derivatives (1) are of interest as potential chiral components for the induction of ferroelectricity in smectic-C liquid crystals (LC). The compounds of this series have been shown to induce strong helicity in achiral nematic systems [1] and high spontaneous polarization in doped smectic C phases [2]. The pre-

sence of the OCH_2 group between benzene rings can improve the compatibility of the compounds **1**, with respect to **2**, when mixed with LC.



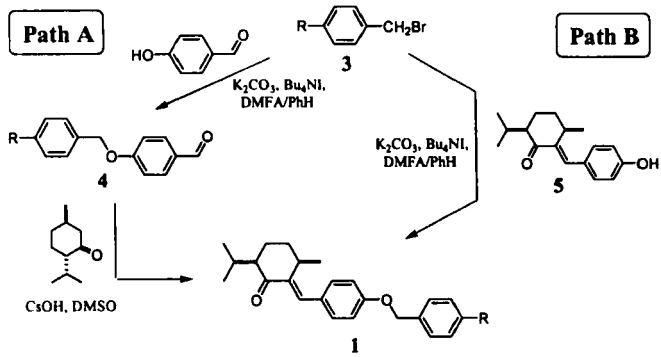
1, B = OCH_2, R = H, CH_3(**a**), OC_nH_{2n+1}, n = 1(**b**), 4(**c**), 5(**d**), 6(**e**), 7(**f**).
2, B = single bond, R = H(**a**), OC_nH_{2n+1}, n = 5(**b**), 6(**c**), 7(**d**).

For the compounds of the homologous series **1**, their influences as chiral dopants (CDs) on the phase transition temperatures and the ferroelectric properties of LC compositions, based on eutectic mixtures with 4-hexyloxyphenyl-4'-octyloxybenzoate (49 mol. %) and 4-hexyloxyphenyl-4'-decyloxybenzoate (51 mol. %), have been investigated. For comparison, some compounds of series **2** have been studied.

RESULTS AND DISCUSSION

Synthesis

Two possible paths leading to desired compounds **1** have been used (Scheme 1).



Scheme 1

The first one (**Path A**) is crotonic condensation of (–)-menthone with substituted benzaldehydes **4**. The compounds **1a** and **1b** have been obtained by this way using CsOH as a base similarly to described in [3].

However, our attempts to prepare any higher homologues of **1** by this way ended in failure. The most probable reason of this is an increase of solubility of these compounds in the reaction mixtures with lengthening of terminal alkyl- or alkoxysubstituent.

Alternative way to **1** is alkylation of 1*R*,4*R*-2-(4-hydroxybenzylidene)-*p*-menthan-3-one **5** by corresponding *p*-alkoxybenzylbromides **3** (**Path B**). By this path, the mixtures of two substances in 75:25 ratio (obviously, 1*R*,4*R*- and 1*R*,4*S*-2-(4-arylmethyleneoxybenzyliden)-*p*-menthane-3-ones) have been obtained. Predominant 1*R*,4*R*-diastereomers (**1c–f**) have been isolated by crystallization (**1c-e**) or flash chromatography (**1f**). Presumably, the formation of both diastereomeric 2-arylidenmenthanones is the result of equilibrium epimerisation of as starting *p*-hydroxybenzylidenmenthanone **5** as target compounds **1** under the reaction conditions via the corresponding dienol derivatives.

The structures of compounds obtained have been proved by ^{1}H NMR, MS and IR spectra (Tables 1, 2). Their 1*R*,4*R*-configuration follows from the same multiplets character and chemical shifts values in the NMR ^{1}H spectra (Table 2) with those for other 1*R*,4*R*-2-arylidenmenthanones studied before [4]. Significant distinction in spectra of compounds **1** and some known 1*R*,4*S*-diastereomers[5] supported also this stereochemical assignment.

TABLE 1 Characteristics of 2-aryliden-*p*-menthan-3-ones **1**.

	R	Yield, % [1]	m.p., C	$[\alpha]_D^{25}$, ($CHCl_3$)	IR, cm^{-1} (KBr)	
					$\nu_{C=O}$	$\nu_{C=C}$, ν_{Ar}
1a	CH_3	52	109–110	–213.7	1672	1604
1b	OCH_3	12.5	113–114	–185.7	1678	1602
1c	OC_4H_9	15	89–90	–171.0	1678	1602
1d	OC_5H_{11}	18	84-86	–169.7	1678	1602
1e	OC_6H_{13}	45	92-93	–163.8	1677	1602
1f	OC_7H_{15}	33	98-99	—	1678	1602

[1] yield of purified substances is given

ABLE 2 The main ^{1}H NMR and mass spectral characteristics of 2-arylidenmenthanones **1**.

R	MS[1)]	Chemical shifts in NMR ^{1}H spectra (ppm.)									
		1-CH_3[d)]	1-H[m)]	4-H[m)]	H_i[sd)]	$(CH_3)_i$[d)]	5,6-CH_2[m)]	=CH[s)]	OCH_2[s)]	$Ar_1.Ar_2$[m)]	Alk, C
CH_3	362, 257, 105	1.21	3.43	2.21	2.56	0.89, 0.96	1.84	7.12	5.04	6.96, 7.33	2.36
OCH_3	—	1.21	3.43	2.22	2.58	0.89, 0.96	1.825	7.12	5.01	6.95, 7.35	3.82
OC_4H_9	420, 163, 107	1.21	3.43	2.22	2.57	0.89, 0.96	1.83	7.12	5.00	6.96, 7.34	0.98[t] 1.49[t] 3.97[t]
OC_5H_{11}	434, 177, 107	1.21	3.44	2.22	2.57	0.89, 0.96	1.83	7.12	5.00	6.96, 7.34	0.92[t] 1.42[t] 3.96[t]
OC_6H_{13}	448, 191, 107	1.21	3.43	2.22	2.57	0.89, 0.96	1.83	7.12	5.00	6.96, 7.34	0.91[t] 1.40[m] 3.96[t]
OC_7H_{15}	462, 252, 220	1.21	3.44	2.22	2.57	0.89, 0.96	1.83	7.12	5.00	6.96, 7.34	0.89[t] 1.39[m] 3.96[t]

he first given signal is the molecular ion peak and others are the most intensive peaks; [d)] doublet; [m)] complic
ltiplet; [sd)] septete of doublets; [s)] singlet; [t)] triplet.

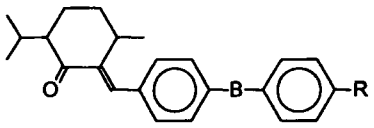
The behaviour of the chiral dopants in the induced ferroelectric LC systems.

The results obtained earlier [2] for the compounds **2a, 2d** which exhibits a relatively high spontaneous polarization (see Table 3), indicates that the molecular skeleton of 2-aryliden-*p*-menthan-3-ones favors the induction of ferroelectric properties. This effect is intensified by the introduction of an elongated terminal alkoxy substituent into the 4 position of the terminal phenyl ring. However, these compounds essentially decrease phase transition temperatures of host phases [2].

As follows from the Table 3, all chiral compounds **1, 2** effect a decrease of phase transition temperatures for studied SmC compositions. The most sensitivity to chiral compound added is observed for phase transition SmA→SmC*. In all cases, effects mentioned are weakened as terminal substituent R is lengthened. The compounds **1** with OCH_2 bridging group exhibit a weaker influence on the SmA→SmC* phase transition temperature but a stronger one in the case of the I→N* transition in comparison with analogous CD of the **2** series containing the same extended terminal substituent. This effect can be caused by conformational flexibility of the exocyclic fragment of CD molecules **1**. One can suppose that the CD **1** molecule being conformationally flexible builds itself in a more favorable packing constraint into the SmC* phase in comparison to mixtures containing CD **2**. Moreover, the solubility of the new materials in the LC host is enhanced in relation to those without the OCH_2 bridging group in the biphenyl fragment [2].

The temperature dependence of the smectic tilt angle θ was found to be typical for second order phase transition systems and can be described as follows: $\theta(\Delta T) = \theta_0 \Delta T^{\alpha}$, $\alpha = 0.52 \pm 0.05$. The θ_0 value decreases linearly in depending on the CD concentration. This seems to be related to the fact that the CD molecules are shorter in comparison with the LC matrix ones. The introduction of the OCH_2 group into the CD molecular core does not cause any marked differences in this dependence. Conversely, the introduction of a rather long alkoxy substituent (OC_7H_{15}) into the terminal phenyl ring of compounds **1, 2** results in a damping of the influence of the CD on the LC smectic tilt angle.

BLE 3 The behaviour of the chiral dopants in the induced ferroelectric LC systems.



B	R	Stability of the mesophases, dT/dC, °C/mol%			$\frac{d\theta}{dC}$, °/mol%	P_s, nC/cm²/m
		I—Ch	Ch—SmA	SmA—SmC*		
OCH_2	H	–0.88 ± 0.01	–1.87 ± 0.05	–2.7 ± 0.1	–0.74 ± 0.02	0.67 ± 0.
OCH_2	CH_3	–0.69 ± 0.05	–1.43 ± 0.05	–2.3 ± 0.1	–0.8 ± 0.1	0.80 ± 0.
OCH_2	OCH_3	–0.44 ± 0.01	–0.70 ± 0.05	–2.4 ± 0.3	–0.60 ± 0.05	0.81 ± 0.
OCH_2	OC_4H_9	–0.37 ± 0.01	–0.65 ± 0.04	–1.34 ± 0.05	–0.35 ± 0.01	0.90 ± 0.
OCH_2	OC_5H_{11}	–0.44 ± 0.01	–0.52 ± 0.03	–1.16 ± 0.05	–0.40 ± 0.04	0.91 ± 0.
OCH_2	OC_6H_{13}	–0.38 ± 0.01	–0.43 ± 0.03	–1.06 ± 0.05	–0.32 ± 0.02	1.03 ± 0.
OCH_2	OC_7H_{15}	–0.49 ± 0.03	–0.36 ± 0.03	–0.91 ± 0.05	–0.22 ± 0.02	1.10 ± 0.
—	H	–0.77 ± 0.04	–2.19 ± 0.06	–2.9 ± 0.2	–0.93 ± 0.2	0.53 ± 0.
—	OC_5H_{11}	–0.25 ± 0.05	–1.13 ± 0.1	–1.69 ± 0.07	—	—
—	OC_6H_{13}	–0.14 ± 0.01	–0.65 ± 0.03	–1.44 ± 0.08	—	—
—	OC_7H_{15}	–0.14 ± 0.01	–0.63 ± 0.04	–1.25 ± 0.04	–0.19 ± 0.03	1.00 ± 0.

The high values of the spontaneous polarization P_S are associated with the large dipole moment of the carbonyl group, which is rigidly attached to the chiral fragment of the molecule and is orthogonal to the long molecular axis. Incorporation of the OCH_2 bridging group or terminal alkyl substitutent does not change significantly the molecular dipole, nevertheless, the spontaneous polarization increases 1.5 to 2 times accordingly. We suppose it is a result of interaction of CD studied molecules with LC host environment, as was predicted for the CDs of type II according [6]. Thereby, supramolecular helical ordering with a high resulting spontaneous polarization is created.

For CD concentration of less than 8 mol. %, the rotational viscosity γ_φ of the LC compositions is essentially defined by the rotational viscosity of the LC matrix and is equal to 0.185 ± 0.005 Poise at $\Delta T = 20°$. For higher concentrations, the γ_φ value increases linearly depending on the CD concentration.

EXPERIMENTAL

IR spectra was recorded on Specord M80 spectrometer. NMR ^1H spectra was recorded on Jeol JNM-LA 400 FT NMR spectrometer. Mass spectra was recorded on a Finnigan-MAT 1020 automated GC/MS. Optical rotations of chiral materials were determined using a AA10 Automatic polarimeter. The analysis of reaction mixtures and purity determination of target compounds were carried out by high performance liquid chromatography (HPLC) using a Milichrom-5 liquid chromatograph equipped with a 2×6 mm Silasorb 600 normal phase column and 34–50 vol. % dichloroethane in heptane as eluent.

The intermediate 4-(4-alkylbenzyl)- and 4-(4-alkoxybenzyl)oxybenzaldehydes **4** (Scheme 1) have been synthesized similarly to described in [7]. The preparation procedure for 1*R*,4*R*-2-(4-methylbenzyl)- (**1a**) and 1*R*,4*R*-2-(4-methoxybenzyl)-oxybenzyliden-*p*-menthane-3-ones (**1b**) is analogous to described in [3].1*R*,4*R*-2-(4-Hydroxybenzyliden-)-*p*-

menthane-3-one **4** have been synthesized by modified in [3] protocol under way described in [8].

The 1*R*,4*R*-2-(4-arylmethyleneoxybenzyliden)-*p*-menthan-3-ones 1c–d (Path B, Scheme 1, typical procedure)

The mixture of 1.9 g 4-hydroxybenzylidenmenthan-3-one **5** (7.3 mmol), 2.5 g of K_2CO_3 (18.2 mmol) and catalytic amount of Bu_4NI in 10 ml of dimethylformamide and 30 ml of benzene was refluxed under azeotropic water remove until major part of water separated. Then 9.5 mmol of corresponding benzylbromide **3** was added. After refluxing during 2.5–3 h, the mixture was diluted by 200 mL 2.5% aqueous solution of acetic acid and then extracted into benzene. The combined organic extracts were washed with water, dried over $CaCl_2$, filtered off and benzene was evaporated. Residue were crystallized from 0.1 % KOH in methanol. Desired compounds were isolated by 3–4 times recrystallization from acetonitrile (**1c-e**) or flash-chromatography (**1f**) (eluent – benzene, silica gel Woelem 5-40 μm).

The yield, melting point and specific optical rotation are listed in Table 1.

Measurement of LC mixtures properties

The polarization measurements were carried out with a polar aligned cell having a thickness 10 μm an active area 24 mm^2. Spontaneous polarization and switching time have been determined by the polarization reversal method. Rotational viscosity was found from the measured value of polarization and switching time. The tilt angle was determined from the rotation of the optical axis of sample under the switching electric field.

CONCLUSION

The results obtained for ferroelectric LC mixtures containing compounds of the new homologous series 2-arylidene-*p*-menthane-3-ones

confirm that their molecular skeleton is of advantage in the design of chiral polar dopants. Incorporation of the OCH_2 bridging group between benzene rings increases the conformational flexibility of the exocyclic fragment of CD molecule and results in the decrease of CD effect on smectic phase transition temperatures and enhances solubility of the CDs.

Acknowledgment

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