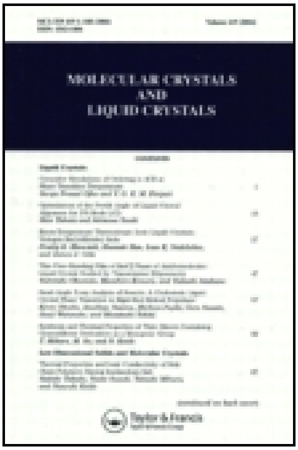

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Liquid Crystalline Thiadiazole Derivatives V: New Ferroelectric Thiaoiazole Derivatives

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LIQUID CRYSTALLINE THIADIAZOLE DERIVATIVES V: NEW FERROELECTRIC THIADIAZOLE DERIVATIVES

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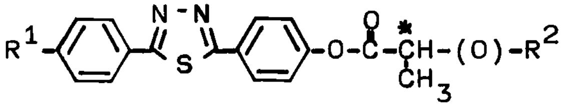
Abstract Some chiral 2,5-disubstituted 1,3,4-thiadiazole derivatives, (S)-2-methylcarboxylates and (S)-2-alkoxypropionates were prepared. The liquid crystalline and ferroelectric properties of these materials were investigated.

INTRODUCTION

The interest in ferroelectric liquid crystalline materials has been recently increased because of their potential applicability for fast switching devices [1,2]. Smectic liquid crystals posessing chiral smectic C* phases, high spontaneous polarization and broad mesogenic phases are required. Hence the synthesis of new substances and the investigation of the physical properties are important for the development of new materials. In previous studies the 2,5-disubstituted 1,3,4-thiadiazole derivatives have been found to exhibit broad smectic C mesomorphic ranges [3-5]. Chiral 2-chlorocarboxylates incorporating a 1,3,4-thiadiazole structural unit and with large values of the spontaneous polarization have been described in a recent paper [6]. But there are some problems with the chemical stability of these chlorocompounds in strong electric fields, due to the highly reactive 2-chlorocarboxylate structural unit [7].
Therefore we have synthesized some novel chiral thiadiazole derivatives, 2-methylcarboxylates and 2-alkoxypropionates of the general formula 1:

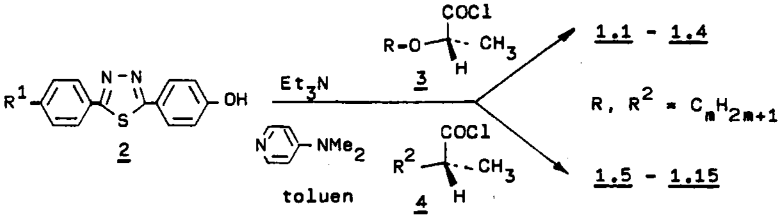
1



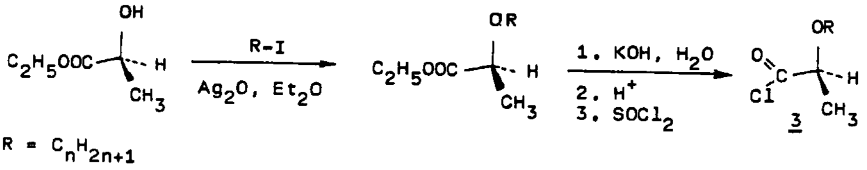
$R^1 = -(O)C_nH_{2n+1}$
$R^2 = -C_mH_{2m+1}$

SYNTHESIS

The compounds have been synthesized by esterification of 5-substituted 2-(4-hydroxyphenyl)-1,3,4-thiadiazoles 2 [5] with chiral 2-alkoxypropionylchlorides 3 or 2-methyl carboxylic acid chlorides according to standard procedures using triethylamine and catalytic amounts of 4-dimethylaminopyridine (DMAP) [8]:



(S)-2-Methylbutyric acid has been obtained by oxidation of (S)-2-methylbutanol with $KMnO_4$, while (S)-2-methyldecanoic acid was obtained by enantioselective alkylation using EVANS's procedure [10].
2-Alkoxypropionic acids were prepared by alkylation of (S)-ethyl lactate with an excess of the appropriate n-alkyliodide in the presence of Ag_2O [11, 12]. The resulting esters were saponified and afterwards treated with thionyl chloride:

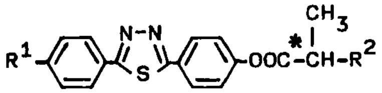


The enantiomeric excess of the compounds has been checked at the stage of the carboxylic acids using NMR-techniques (chiral lanthanide shift reagents [13], diastereomeric derivatives with homochiral amines [14]) and has been found to exceed 95% ee in the cases of (S)-2-alkoxypropionic acids and to be in the range between 75 and 85% for the compounds 4.

RESULTS and DISCUSSION

The transition temperatures of the new materials are collected in table I:

TABLE I Transition temperatures of the chiral 2,5-disubstituted 1,3,4-thiadiazole derivatives.



comp.	R^1	R^2	cr	S_1	S_C^*	Ch	is
1.1	$C_5H_{11}O-$	$-C_2H_5$	• 155	- -	• 161	• 163	•
1.2	$C_8H_{17}O-$	$-C_2H_5$	• 89	- -	• 165	- -	•
1.3	$C_8H_{17}O-$	$-C_8H_{17}$	• 79	(• 74)	• 141	- -	•
1.4	$C_{10}H_{21}-$	$-C_2H_5$	• 126	- -	• 140	- -	•
1.5	$C_5H_{11}O-$	$-OCH_3$	• 97	- -	• 155	• 165	•
1.6	$C_5H_{11}O-$	$-OC_6H_{13}$	• 96	- -	• 140	- -	•
1.7	$C_5H_{11}O-$	$-OC_{10}H_{21}$	• 92	- -	• 133	- -	•
1.8	$C_8H_{17}O-$	$-OCH_3$	• 95	- -	• 160	• 166	•
1.9	$C_8H_{17}O-$	$-OC_6H_{13}$	• 86	- -	• 144	- -	•
1.10	$C_8H_{17}O-$	$-OC_7H_{15}$	• 83	- -	• 141	- -	•
1.11	$C_8H_{17}O-$	$-OC_{10}H_{21}$	• 81	- -	• 136	- -	•
1.12	$C_9H_{19}O-$	$-OCH_3$	• 101	- -	• 163	• 166	•
1.13	$C_9H_{19}O-$	$-OC_6H_{13}$	• 78	- -	• 145	- -	•
1.14	$C_{10}H_{21}-$	$-OCH_3$	• 108	- -	• 139	• 140	•
1.15	$C_{10}H_{21}-$	$-OC_6H_{13}$	• 110	- -	• 121	- -	•

All compounds exhibit broad smectic C* ranges, which may be accompanied by a cholesteric mesophase in the cases of short chain derivatives (R^2 = $-OCH_3$, $-C_2H_5$). The clearing temperatures of the corresponding 2-alkoxypropionates and 2-alkylpropionates are surprisingly similar. This is in contrast to the observation, that non conjugated oxygen atoms in the aliphatic chain generally decrease the mesophase stability of calamitic liquid crystals [14, 15]. Since the melting temperatures of the 2-alkoxypropionates are often significantly lower, these compounds exhibit more extended S_C^* ranges. The clearing points decrease with increasing length of the terminal alkyl chain attached to the chiral centre (R^2). Therefore, the stability of the smectic C*phase decreases with in-

creasing length of this chain but it slightly increases by elongation of the other alkyl chain (R^1).
The spontaneous polarization was measured at $T_{cl} - T = 30$ K:

TABLE II Spontaneous polarization

compound	P_S ($nC \cdot cm^{-2}$; $\Delta T = 30K$)	n	m
1.6	188	5	6
1.7	172	5	10
1.9	221	8	6
1.10	152	8	7
1.11	168	8	10

If we take into account an error of 10% due to the incomplete orientation and errors in the measurement of P_S only the P_S-value of compound 1.9 is relatively high. Therefore, further investigations of homologous substances are necessary.

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