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Ferroelectric liquid crystals and dopants containing the chiral thiirane unit. A comparison with analogous oxiranes

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Ferroelectric liquid crystals and dopants containing the chiral thiirane unit

A comparison with analogous oxiranes

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The synthesis and mesomorphic properties of a new type of ferroelectric liquid crystals and dopants (for induced ferroelectric phases) containing cis or trans disubstituted thiiranes as the chiral unit are described. A comparison of the thiiranes with the corresponding oxiranes is given. In the thiirane series the tendency to exhibit mesophases is less pronounced. S_C^* phases occur for three aromatic cores in the mesogenic part of the molecule. The temperature ranges of the liquid crystal phases are broader and the transition temperatures are higher in the trans compared with cis configured thiiranes and oxiranes. Cis configured thiiranes exhibit a higher spontaneous polarization than the corresponding trans compounds.

1. Introduction

To succeed in obtaining high spontaneous polarization in ferroelectric liquid crystals a rigid steric coupling between asymmetric centres and polar groups is generally assumed to be advantageous [1]. Incorporation of the chiral 2,3-epoxy alcohol unit into the tail of a smectogenic liquid crystal was shown to result in ferroelectric properties [2]. We have recently found a favourable combination of the chiral oxirane ring with an adjacent dipole of a carbonyl group [3]. The aim of this work was to investigate the influence of sulphur instead of oxygen in the three membered ring on liquid crystal properties and spontaneous polarization. Thiiranes exhibit a smaller dipole moment (1·84 D) than oxiranes (2·30 D). On the other hand sulphur has a higher polarizability and is larger than oxygen. The elucidation of the effect of the cis versus the trans arrangement of the substituents at the three membered ring was another goal of this investigation.

2. Synthesis

The reaction sequence leading to the mesogenic chiral thiiranes is shown in scheme 1. The chiral oxiranes **2** were obtained by asymmetric epoxidation of cis and trans configured allylic alcohols **1** via the Sharpless procedure [4]. The enantiomeric excess was determined by the Mosher method [5]. The mesogenic oxiranes **3** were synthesized by the Mitsunobu reaction [6], using diethyl azodicarboxylate (DEAD) and triphenylphosphine (TPP) as coupling reagents to combine the oxirane alcohol with the mesogenic phenols. Treatment of the resulting oxirane ether with trifluoroacetic acid and triphenylphosphine sulphide [7] yielded the corresponding thiirane ether **4**. The proposed mechanism of this reaction involves a Walden inversion at both asymmetric C-atoms and thus leads to thiiranes of inverse absolute configuration.

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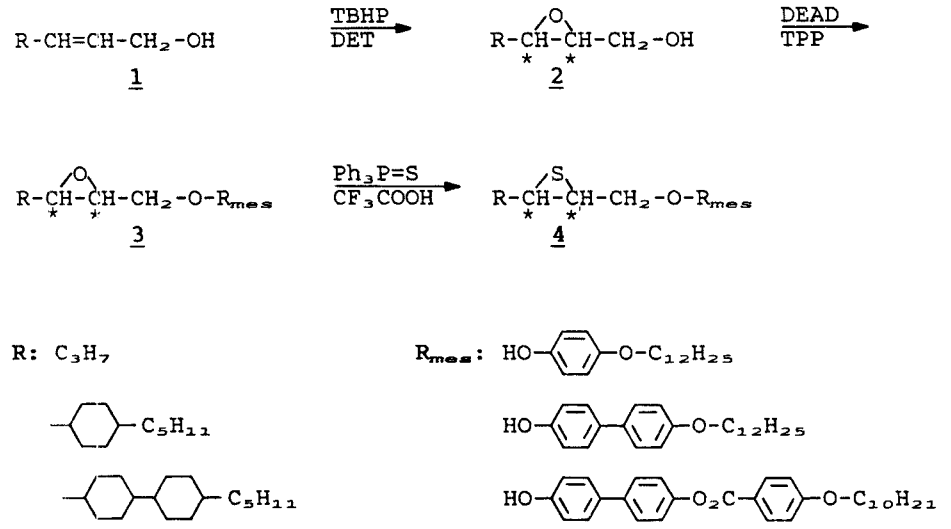
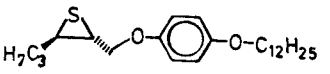
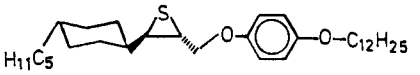
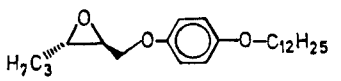
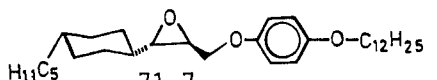


Scheme 1. Reaction pathway to chiral thiiranes.

Table 1. Trans configured thiiranes and oxiranes with one aromatic core; their phase sequence and spontaneous polarization in M89.

		P_S/nC cm^{-2}
4a	 C 49°C I	
4b	 C 69°C I	−8 (20°C)
4c	 C 92°C I	
3a	 C 65°C I	
3b	 71.7 $C_1 \leftarrow C_2$ (S_B 53·6°C) S_A 74·1°C I	0·7 (20°C)†
3c	 C 76·2°C S_B 130·8°C S_A 140·4°C I	

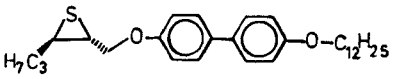
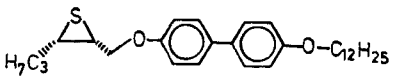
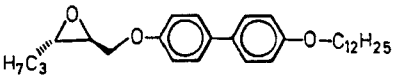
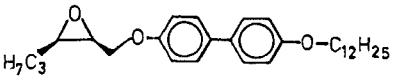
† P_S value of 20 mol % mixture.

3. Results and discussion

3.1. *Liquid crystal properties of thiiranes in comparison with oxiranes*

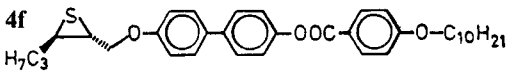
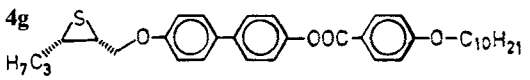
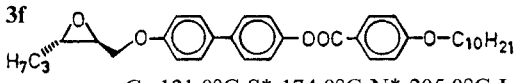
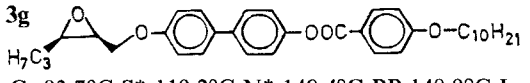
Oxiranes in general exhibit better mesomorphic properties than thiiranes. Connected to mesogens comprising one or two aromatic rings only oxiranes have liquid crystal-phases (see table 1: **3b**, **3c**; table 2: **3d**, whereas the corresponding thiiranes do not have liquid crystal phases. Chiral smectic C phases are observed in thiiranes where three aromatic cores in the mesogenic part (see table 3: **4f**, **4g** are present. The same phase sequence occurs in the corresponding thiiranes and oxiranes (see table 3: **3f**, **4f**, **3g**, **4g**. A blue phase is also observed in compound **3g**. Thiiranes have lower clearing points than the corresponding oxiranes.

Table 2. Cis and trans configured thiiranes and oxiranes with two aromatic cores; their phase sequence and spotaneous polarization in M89.

		P_S/nC cm^{-2}
4d		< 0·3 (20°C)†
	C 112°C I	
4e		15 (20°C)
	C 84°C I	
3d		13 (30°C)
	C 118·0°C S_B 124·7°C S_A 128·5°C I	
3e		35 (30°C)
	C 86°C I	

† P_S value of 10 mol % mixture.

Table 3. Cis and trans configured thiiranes and oxiranes with three aromatic cores; their phase sequence.

4f	
	C 103·0°C S_C^* 148·5°C N* 169·5°C I
4g	
	C 82·5°C S_C^* 114·0°C N* 126·0°C I
3f	
	Cr 121·0°C S_C^* 174·0°C N* 205·0°C I
3g	
	Cr 83·7°C S_C^* 119·2°C N* 148·4°C BP 148·9°C I

3.2. *Cis versus trans configuration*

The liquid crystal phases are broader in trans configured thiiranes and oxiranes compared with their cis-isomers (table 3: **4f**, **4g** and **3f**, **3g**). The cis-isomers have lower melting points (tables 2 and 3).

3.3. *Ferroelectric properties*

The spontaneous polarization of the new thiiranes was measured for some typical examples (see tables 1 and 2: **4b**, **4d**, **4e**). The values given are extrapolated from those obtained in a mixture of 10 per cent dopant in the non-chiral matrix M 89 (Hoechst AG, phase sequence: C 10°C S_C 84·5°C S_A 93·5°C N 105°C I). The spontaneous polarization of thiiranes having the chiral unit localized between two mesogens seems to be higher compared with the corresponding oxiranes (see table 1: **3b**, **4b**). If the chiral unit is positioned terminally, oxiranes exhibit higher spontaneous polarization than the thiiranes (see table 2: **3d**, **3e** vs **4d**, **4e**). In thiiranes **4f** and **4g** having S_C^* phases, the spontaneous polarization could not be measured because decomposition of these compounds occurs during heating above the clearing point. If we compare the cis versus trans arrangement of the substituents at the thiirane ring (see table 2: **4d**, **4e**), the higher value of the spontaneous polarization for the cis-compound is obvious. The larger steric hindrance to rotation around the molecular long axis in the cis-compound is probably responsible for this effect.

4. Experimental part

^{1}H N.M.R.: Bruker WM 400. M.S.: Varian MAT 711 (70·0 eV). I.R.: Perkin Elmer PE 225 or PE 257. Specific rotation: Perkin Elmer PE 241 polarimeter. Texture observations: Jenapol polarizing microscope in conjunction with a Linkam heating stage and a TMS 90 control unit. Measurements of spontaneous polarization: in test cells with a spacing of 2 μm. The glass substrates of the cells were coated with polyimide and both substrates were rubbed. The cells were filled by capillary action and were thermostated during the measurements in a Mettler heating stage FP 82. Spontaneous polarization was obtained with a Diamant bridge [8, 9]: applied voltage: 5–20·0 V, frequency: 50–100 Hz. Chromatographic purifications were performed by flash chromatography (FC) on ICN Biomedicals silica (32–63 μm). Elemental analysis: Microanalytical department of the Institut of Organic Chemistry. Petroleum ether (PE): b.p. 40–60°C.

(2S,3S)-(−)-3-(trans-4-pentylcyclohexyl)-2,3-epoxy-propanol **2b**. A 50 ml round-bottom flask was oven dried, then fitted with a serum cap, and flushed with nitrogen. The flask was charged with dry dichloromethane (20 ml) and cooled by stirring in a −23°C bath. Then the following liquids were added sequentially while stirring in the cold bath: 0·70 ml of titanium tetraisopropoxide (0·68 g, 2·38 mmol), 0·41 ml of L-(+)-diethyl tartrate (L-(+)-DET; 0·49 g, 2·38 mmol), the mixture was stirred for 5 min before the next addition of 0·54 g (2·38 mmol) of 3-(trans-4-pentylcyclohexyl)-E-2-propenol (synthesized from trans-4-pentylcyclohexyl aldehyde by the Horner-Wittig reaction and reduction with diisobutylaluminum hydride) and, finally of 1·59 ml (4·76 mmol) of a *t*-butyl hydroperoxide solution (3·0 molar in toluene). The resulting homogeneous solution was then stored overnight at −23°C. The flask was placed in a −23°C bath, a 10 per cent aqueous tartaric acid solution (5·9 ml) was added, on stirring the aqueous layer solidified. After 30 min the cold bath was removed and stirring was continued at room temperature until the aqueous layer became clear.

After separation, the organic layer was washed once with water and concentrated *in vacuo*. The residue was diluted with ether (40·0 ml), the resulting solution was cooled in an ice bath, and then 1 N NaOH (7·1 ml) was added. This two-phase mixture was stirred at 0°C for 30 min. The ether phase was washed with brine, dried with $MgSO_4$ and concentrated to give a clear oil.

FC with ether/PE yielded 0·37 g (63 per cent) of **2b**, which was shown to be > 90 per cent enantiomerically enriched by ^{1}H N.M.R. analysis of the derived α-methoxy-α-(trifluoromethyl)-phenyl acetic acid (MTPA) ester.

$[\alpha]_D^{20} = -23{\cdot}6°$ (c 1·0 in $CHCl_3$).

I.R. (CCl_4): 3450 br(OH) cm^{-1}.

^{1}H N.M.R. ($CDCl_3$): δ = 0·79–0·92 (m; 2 H), 0·88 (t, J = 7 Hz; 3 H), 1·07–1·33 (m; 12 H), 1·65 (dd, J = 7 and 5·5 Hz; OH), 1·70 (dbr, J = 12 Hz; 1 H), 1·78 (dbr, J = 12 Hz; 2 H), 1·89 (dbr, J = 12 Hz; 1 H), 2·75 (dd, J = 6·5 and 2·5 Hz; C*H), 2·98 (ddd, J = 4·5, 3 and 2·5 Hz; C*H), 3·61; 3·91 (AB_{dd}, J = 13 Hz; part A: dd, J = 7·5 and 4·5 Hz; part B: dd, J = 5·5 and 3·5 Hz; 2 H). M.S. (RT): m/e = 226 (0·5 per cent, M^+), 208 (6, $M-H_2O$), 195 (7·5, $M-CH_2OH$), 165 (18), 137 (10), 109 (30), 95 (80), 81 (77), 67 (68), 55 (100).

$C_{14}H_{26}O_2$: calculated C 74·28; H 11·58, found C 73·97; H 11·27.

(2S,3S)-(−)-3-(4-trans-pentylcyclohexyl)-2-(4-dodecyloxyphenyloxy)-methyl-oxirane **3b**. To a stirred solution of 452 mg (2 mmol) **2b**, 556 mg (2 mmol) p-dodecyloxyphenol and 524 mg (2 mmol) triphenylphosphine (TPP) in 4 ml dry THF were added at room temperature 348 mg (2 mmol) diethyl azodicarboxylate (DEAD). After 4 d the solution was concentrated under reduced pressure and then diluted with a small quantity of ether. Any precipitated solid was rejected. The filtrate was evaporated *in vacuo* and the residue purified by F.C. with PE as eluent.

Yield: 574 mg (58 per cent), m.p.: 71·7°C.

$[\alpha]_D^{20} = -14{\cdot}0°$ (c 1·1 in $CHCl_3$).

^{1}H N.M.R. ($CDCl_3$): δ = 0·89 (t, J = 7 Hz; 6 H), 0·90–0·95 (m; 2 H), 1·08–1·20 (m; 4 H), 1·20–1·39 (m; 24 H), 1·44 (quint, J = 7 Hz; 2 H), 1·75 (quint, J = 7 Hz; 2 H), 1·72 (dbr, J = 12 Hz; 1 H), 1·79 (dbr, J = 12 Hz; 2 H), 1·90 (dbr, J = 12 Hz; 1 H), 2·73 (dd, J = 6·5 and 2 Hz; C*H), 3·13 (ddd, J = 5, 3·5 and 2 Hz; C*H), 3·89 (t, J = 6·5 Hz; 2 H), 3·93; 4·11 (AB_d, J = 11 Hz; part A: d, J = 5 Hz; part B: d, J = 3·5 Hz; 2 H), 6·81; 6·84 (AA′BB′, J = 9 Hz; 4 H).

MS (90°C): m/e = 486 (20 per cent, M^+), 278 (28, $C_{18}H_{30}O_2$), 208 (8), 152 (34), 135 (18), 110 (100, $C_6H_6O_2$).

$C_{32}H_{54}O_3$: calculated. C 78·96; H 11·18, found C 78·50; H 11·02.

(2R,3R)-(+)-3-(4-trans-pentylcyclohexyl)-2-(4-dodecyloxyphenyloxy)-methyl-thiirane **4b**. A solution of 0·2 mmol each of the oxirane **3b** (97 mg) and triphenylphosphine sulphide (59 mg) was prepared in 2 ml dry benzene. To this solution, an equivalent amount of trifluoroacetic acid was added with stirring. The reaction was carried out at 38°C overnight. Then 0·22 mmol (18 mg) solid sodium bicarbonate was added and the mixture stirred for 15 min at room temperature. Then 10 ml ether were added, the organic phase washed once with water, dried with $MgSO_4$ and concentrated *in vacuo*. The residue was purified by F.C. with PE/CH_2CL_2 as eluent.

Yield: 75 mg (75 per cent), m.p.: 69°C.

$[\alpha]_D^{20} = +52{\cdot}0°$ (c 1·1 in $CHCl_3$).

^{1}H N.M.R. ($CDCl_3$): δ = 0·88 (t, J = 7 Hz; 6 H), 0·79–0·92 (m; 2 H), 1·10–1·20 (m; 4 H), 1·20–1·39 (m; 24 H), 1·43 (quint, J = 7 Hz; 2 H), 1·75 (quint, J = 7 Hz; 2 H), 1·77 (dbr, J = 12 Hz; 2 H), 1·86 (dbr, J = 12 Hz; 2 H), 2·56 (dd, J = 8 and

5·5 Hz; C*H), 2·99 (ddd, J = 7·5, 5·5 and 5 Hz; C*H), 3·75; 4·17 (AB_d, J = 10·5 Hz; part A: d, J = 7·5 Hz; part B: d, J = 5·5 Hz; 2 H) 3·88 (t, J = 6·5 Hz; 2 H), 6·81 (s, 4 H).

MS (70°C): m/e = 502 (8 per cent, M^+), 470 (14, M–S), 278 (100, $C_{18}H_{30}O_2$), 225 (8), 110 (98, $C_6H_6O_2$), 95 (38), 67 (46).

$C_{32}H_{54}O_2S$: calculated C 76·44; H 10·82, found C 76·65; H 10·95.

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