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New dopants for induced ferroelectric S_C^* phases containing 1,3-dioxolan-2-one as a chiral heterocycle†

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The synthesis, phase behaviour and spontaneous polarization of a new class of chiral dopants for induced ferroelectric phases of general structure **6** and **9**, possessing a 1,3-dioxolan-2-one ring, are described. One of the new compounds exhibits a S_A phase. When the chiral ring system is positioned terminally to the mesogen (**6**) the *cis* disubstituted compounds show higher induced spontaneous polarization than those with an analogous *trans* configuration.

1. Introduction

Ferroelectricity in liquid crystals first postulated and soon afterwards demonstrated experimentally by Meyer *et al.* [1], now attracts great interest in both fundamental research and technological application. In its early stage the investigation of ferroelectric liquid crystals has been concentrated mainly upon compounds with chiral smectic C phases. However, for the practical use in ferroelectric mixtures, chiral compounds do not have to possess a S_C^* phase, because they are prone to induce a spontaneous polarization in host mixtures exhibiting a non-chiral S_C phase. So there is a need for chiral dopants inducing high spontaneous polarization. Polar groups directly attached to the sterogenic centre have been shown to increase the spontaneous polarization [2]. A steric hindrance to free rotation of the lateral dipole around the molecular long axis is another factor leading to an increase of the spontaneous polarization [3]. Therefore incorporating the chiral centre to which the lateral dipole is attached into a ring system proved to be advantageous [4].

Chiral three membered heterocyclic rings (oxiranes [4], *trans* and *cis* oxirane carboxylates [5] and thiiranes [6]) as well as five membered rings (pyrrolidines [7], dioxolane-carboxylates [7]), γ-lactones [8], δ-lactones [9], 1,3-dioxolan-4-ones [10] and 1,3-oxazolidin-2-ones [11] have been investigated in this respect. Dopants inducing a spontaneous polarization up to 78 nC cm^{-2} in a 10 per cent solution have been found [7]. In this context the five membered 1,3-dioxolan-2-one ring system containing two chiral centres to which one (**6**) or two mesogens (**9**) are attached seemed to us to be of interest due to the strong lateral dipole moment and the restriction of rotational freedom. The elucidation of the effect of *cis* versus *trans* arrangement of the substituent at the ring system was a further goal of this work.

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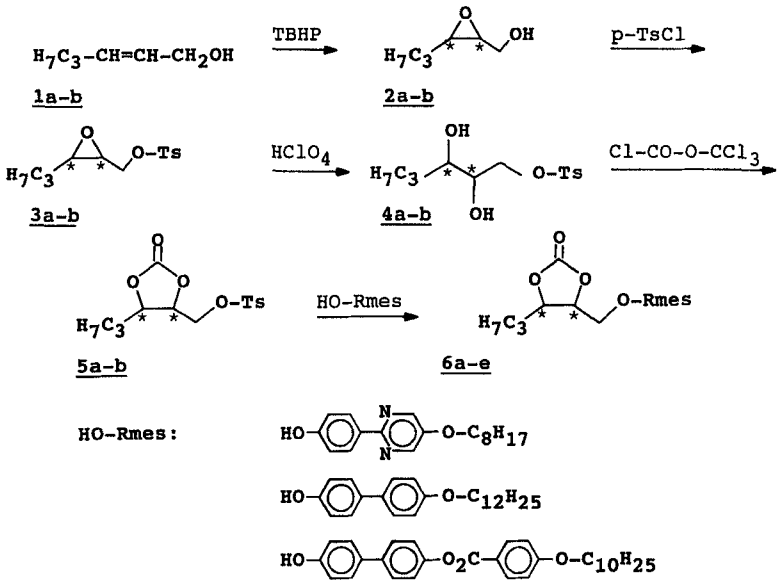
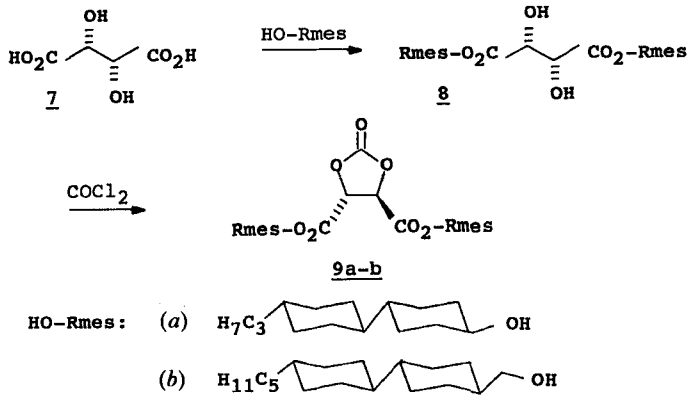
2. Synthesis

The synthetic pathways leading to the new chiral dopants are shown in schemes 1 and 2. For the dioxolanones positioned terminally to one mesogenic unit (compounds **6**) the Sharpless epoxidation of *cis* or *trans* allylic alcohol **1** was the starting reaction [12]. The enantiomeric excess of compounds **2** was established by the Mosher method [13]. After tosylation of the epoxy alcohol **2** the oxirane ring was opened by 70 per cent aqueous $HClO_4$ yielding the chiral diols **4** which showed a slight loss of enantiomeric purity as already described by Behrens *et al.* [14]. The recyclization of the diols **4** to give the dioxolanones **5** was performed by diphosgene. Coupling of the tosylates **5** with mesogenic phenols resulted in the target compounds **6**.

The dioxolanones **9** containing the chiral unit between two mesogenic moieties were synthesized starting from *L*-(+)-tartaric acid **7**. Esterification with mesogenic alcohols afforded the esters **8**. Treatment with phosgene solution [15] yielded compounds **9**.



Scheme 1. Reaction pathway to *cis* (a) and *trans* (b) disubstituted chiral dioxolanones containing one mesogenic substituent.



Scheme 2. Reaction pathway to chiral dioxolanones with two mesogenic substituents.

3. Discussion and results

3.1. *Liquid-crystalline-properties of dioxolanones localized*

3.1.1. *Terminally (table 1)*

A smectic A phase only occurs in connection with a mesogen consisting of three aromatic cores (**6c**). The corresponding *cis* configured compound **6d** does not have a liquid crystal phase. The deviation from the rod-like shape might be the reason for this.

3.1.2. *Centrally (table 2)*

For both compounds **9a** and **9b** no liquid crystal phase was observed.

Table 1. *trans* and *cis* configured dioxolanones connected terminally with two or three aromatic cores; phase transitions and spontaneous polarization.

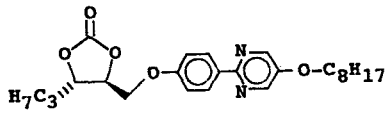
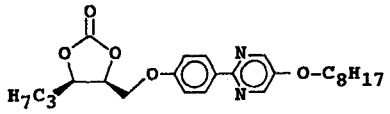
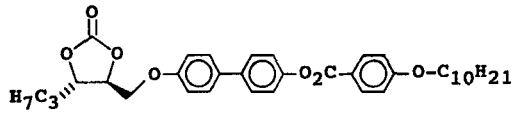
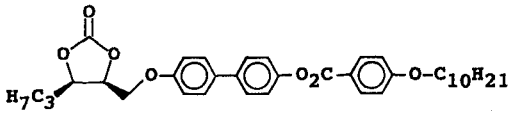
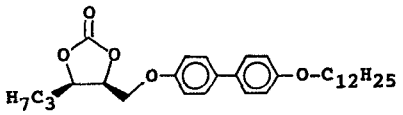
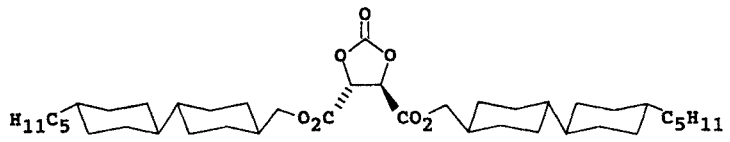
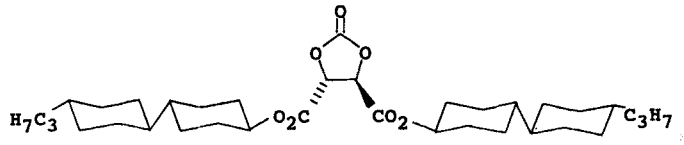
Compound and phase transitions	P_S nC cm^{-2}
6a 	11·7 30°C 10 mol%
C 83°C I	
6b 	18·4 30°C 10 mol%
C 100°C I	
6c 	2·0 50°C 7·2 mol%
C 133·5°C S_A 146·5°C I	
6d 	4·9 50°C 7·2 mol%
C 122·5°C I	
6e 	6·8 40°C 8·5 mol%
C 94°C I	

Table 2. *trans* configured dioxolanones localized between two mesogens; phase transition and spontaneous polarization.

Compound and phase transition	P_S nC cm^{-2}
9a  C 179°C I	<0·3 20°C 5 mol%
9b  C 238°C I	<0·3 20°C 5 mol%

3.2. *Ferroelectric properties*

The spontaneous polarization induced by the new dioxolanones was measured 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). For solubility reasons the concentrations of the dopants are partly different (the values are given in tables 1 and 2). Comparing the *cis* versus the *trans* arrangement of the substituents at the dioxolanone ring (see table 1: **6a/6b**, **6c/6d**) the higher value of the spontaneous polarization for the *cis* compounds is obvious. Probably the larger steric hindrance to rotation around the molecular long axis in the *cis* compounds is responsible for this effect. Further investigations are under way and the results will be discussed in comparison with the effect of other chiral heterocyclic moieties in a separate paper.

4. Experimental

^{1}H NMR: Bruker WM 400. MS: Varian MAT 711 (70 eV). IR: 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 the spontaneous polarization were performed 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 thermostatted during the measurements in a Mettler heating stage FP 82. Spontaneous polarization was obtained by the Diamant bridge [16]; applied voltage: 5–20 V, frequency: 50–100 Hz. Chromatographic purifications were performed using flash chromatography on ICN Biomedicals silica (32–63 μm). Elemental analysis: Microanalytical department of the Institute of Organic Chemistry. Petroleum ether (PE): bp 40–60°C.

4.1. (2S,3R)-(−)-*1-tosyloxy-2,3-epoxy hexane* (**3a**)

To a solution of *p*-toluene sulphonyl chloride (906 mg; 4·75 mmol) and triethylamine (480 mg; 4·75 mmol) in 10 ml of dry dichloromethane at 0°C (2*S*,3*R*)-2,3-epoxy hexanol **2a** (500 mg; 4·3 mmol) dissolved in 2 ml of dry dichloromethane were added.

The reaction mixture was stirred at 0°C for 10 min and at room temperature overnight. The organic phase was washed with water (3 × 5 ml), dried ($MgSO_4$) and evaporated in vacuum. Purification by flash chromatography with PE/ether gave 0·90 g (77 per cent) of **3a** as an oil.

$[\alpha]_{D^{20}} = -10{\cdot}0°$ (*c.* 1·5 in $CHCl_3$). IR($CHCl_3$): 1600, 1370, 1180 cm^{-1}. ^1H NMR($CDCl_3$): $\delta = 0{\cdot}93$ (t, $J = 7$ Hz; 3 H), 1·36–1·51 (m; 4 H), 2·45 (s; 3 H), 2·98 (ddd, $J = 6{\cdot}5$, 5·5 and 4 Hz; C*H), 3·15 (ddd, $J = 6{\cdot}5$, 5 and 4 Hz; C*H), 4·09; 4·17 (AB_d, $J = 11$ Hz, part A: d, $J = 6{\cdot}5$ Hz; part B: d, $J = 5$ Hz; 2 H), 7·36; 7·81 (AA'BB', $J = 9$ Hz; 4 H). MS (85°C): $m/e = 270$ (0·3 per cent, M^+), 227 (4·5, M-C_3H_7), 190 (10), 155 (84), 91 (100, C_7H_7). $C_{13}H_{18}O_4S$.

4.2. (2S,3S)-(−)-*1-tosyloxy-2,3-hexanediole* (***4a***)

A solution of **3a** (1·03 g; 3·8 mmol) in 40 ml of 60 per cent aqueous Me_2SO was treated with 0·08 ml of 70 per cent aqueous $HClO_4$ and heated while stirring at 80°C for $2\frac{1}{2}$ h. The reaction mixture was diluted with 150 ml of ether and washed with water (2 × 20 ml). The organic phase was dried ($MgSO_4$), concentrated in vacuum to afford 0·78 g of an oil. Flash chromatography with PE/ether gave 0·54 g (49 per cent) of **4a** as colourless crystals. mp: 60°C.

$[\alpha]_{D^{20}} = -7{\cdot}5°$ (*c.* 1·4 in $CHCl_3$). IR($CHCl_3$): 3580; 3400 (OH), 1600, 1370, 1180 cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 0{\cdot}91$ (t, $J = 7$ Hz; 3 H), 1·31–1·54 (m; 4 H), 2·15 (sbr; 2 OH), 2·45 (s; 3 H), 3·60 (ddd, $J = 8{\cdot}5$, 4 and 3 Hz; C*H), 3·71 (ddd, $J = 7$, 4·5 and 3 Hz; C*H), 4·05; 4·11 (AB_d, $J = 10$ Hz, part A: d, $J = 7$ Hz, part B: d, $J = 4{\cdot}5$ Hz; 2 H), 7·36; 7·80 (AA'BB', $J = 9$ Hz; 4 H). MS/CI (90°C): $m/e = 289$ (66 per cent, M + 1), 271 (50, M-H_2O + 1), 197 (28), 159 (14), 117 (71), 99 (100), 81 (68). $C_{13}H_{20}O_5S$.

4.3. (4S,5S)-(−)-*5-propyl-4-tosyloxymethyl-1,3-dioxolan-2-one* (***5a***)

A solution of **4a** (404 mg; 1·4 mmol) in 20 ml dry THF at 0°C was treated with diphosgene (177 mg; 1·4 mmol) and triethylamine (90 mg; 0·8 mmol). The reaction mixture was stirred for 10 min at 0°C and overnight at room temperature. Any precipitated solid was separated and washed with ether. To the combined filtrates 5 ml of water were added and the stirring continued for 1 h. The organic phase was separated, washed with brine, dried ($MgSO_4$) and evaporated in vacuum. Purification by flash chromatography with PE/ether afforded 426 mg (97 per cent) of **5a** as an oil.

$[\alpha]_{D^{20}} = -35{\cdot}0°$ (*c.* 0·8 in $CHCl_3$). IR($CHCl_3$): 1810 (CO), 1600, 1380, 1190 cm^{-1}. ^1H NMR (C_6D_6): $\delta = 1{\cdot}21$ (t, $J = 7$ Hz; 3 H), 1·31–1·60 (m; 4 H), 2·45 (s; 3 H), 3·45 (ddd, $J = 6$, 4·5 and 4 Hz; C*H), 3·54; 3·67 (AB_d, $J = 11{\cdot}5$ Hz, part A: d, $J = 4{\cdot}5$ Hz, part B: d, $J = 4$ Hz; 2 H), 3·75 (ddd, $J = 7{\cdot}5$, 6 and 5 Hz; C*H), 6·73; 7·74 (AA'BB', $J = 9$ Hz; 4 H). MS (140°C): $m/e = 314$ (5 per cent, M^+), 172 (8, TsOH), 155 (50, $C_7H_7SO_2$), 91 (100, C_7H_7), 81 (58). $C_{14}H_{18}O_6S$.

4.4. (4S,5S)-(−)-*4-[4-(5-octyloxypyrimidine-2-yl)-phenyloxymethyl]-5-propyl-1,3-dioxolan-2-one* (***6a***)

A solution of **5a** (204 mg; 0·65 mmol), 2-(4-hydroxyphenyl)-5-octyloxypyrimidine (195 mg; 0·65 mmol) and K_2CO_3 (90 mg; 0·65 mmol) in 10 ml of acetone was heated under reflux overnight. The reaction mixture was diluted with 50 ml of ether and washed with water (2 × 20 ml). The organic phase was dried ($MgSO_4$) and evaporated in vacuum. Purification by flash chromatography with PE/dichloromethane afforded 220 mg (76 per cent) of **6a**. mp: 83°C.

$[\alpha]_{D^{20}} = -19{\cdot}5°$ (*c*. 1·3 in $CHCl_3$). IR ($CHCl_3$): 1800 (CO), 1610, 1590 cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 0{\cdot}89$ (t, $J = 7$ Hz; 3 H), 1·01 (t, $J = 7$ Hz; 3 H), 1·21–1·40 (m; 8 H), 1·47 (quint, $J = 7$ Hz; 2 H), 1·50–1·61 (m; 2 H), 1·70–1·90 (m; 2 H), 1·82 (quint, $J = 7$ Hz; 2 H), 4·08 (t, $J = 6{\cdot}5$ Hz; 2 H), 4·19; 4·25 (AB_d, $J = 10$ Hz, part A: d, $J = 4{\cdot}5$ Hz, part B: d, $J = 4$ Hz; 2 H), 4·59 (ddd, $J = 5{\cdot}5$, 4·5 and 4 Hz; C_4*H), 4·70 (ddd, $J = 8$, 5·5 and 5 Hz; C_5*H), 6·98; 8·30 (AA'BB', $J = 9$ Hz; 4 H), 8·42 (s; 2 H). MS (150°C): $m/e = 442$ (26 per cent, M^+), 330 (14), 125 (10), 111 (19), 97 (30), 85 (37), 71 (59), 57 (100). $C_{25}H_{34}N_2O_5$: calc. C 67·85 per cent; H 7·74 per cent; N 6·33 per cent, found C 67·61 per cent; H 7·57 per cent; N 6·20 per cent.

4.5. (4S,5R)-(−)-4-[4-(5-octyloxypyrimidine-2-yl)-phenyloxymethyl]-5-propyl-1,3-dioxolan-2-one (**6b**)

mp: 100°C. $[\alpha]_{D^{20}} = -3{\cdot}0°$ (*c*. 1·0 in $CHCl_3$). IR($CHCl_3$): 1810 (CO), 1610, 1590 cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 0{\cdot}89$ (t, $J = 7$ Hz; 3 H), 0·98 (t, $J = 7$ Hz; 3 H), 1·24–1·40 (m; 8 H), 1·43–1·52 (m; 2 H), 1·57–1·74 (m; 3 H), 1·83 (quint, $J = 7$ Hz; 2 H), 1·84–1·94 (m; 1 H), 4·08 (t, $J = 6{\cdot}5$ Hz; 2 H), 4·24; 4·28 (AB_d, $J = 10{\cdot}5$ Hz, part A: d, $J = 5$ Hz, part B: d, $J = 4$ Hz; 2 H), 4·85 (ddd, $J = 10$, 8 and 3 Hz, C_5*H), 4·96 (ddd, $J = 8$, 5 and 4 Hz; C_4*H), 6·98; 8·30 (AA'BB', $J = 9$ Hz; 4 H), 8·42 (s; 2 H). MS (150°C): $m/e = 442$ (18 per cent, M^+), 330 (12), 250 (14), 217 (22), 188 (19), 84 (50), 71 (62), 57 (100). $C_{25}H_{34}N_2O_5$: calc. C 67·85 per cent; H 7·74 per cent; N 6·33 per cent, found C 67·70 per cent; H 7·69 per cent; N 6·22 per cent.

4.6. (4S,5S)-(−)-4-[4-(4-decyloxybenzoyloxy)-biphenyl-4'-yloxymethyl]-5-propyl-1,3-dioxolan-2-one (**6c**)

mp: 133·5°C. $[\alpha]_{D^{20}} = -17{\cdot}4°$ (*c*. 0·2 in $CHCl_3$). IR($CHCl_3$): 1800; 1730 (CO), 1600 cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 0{\cdot}89$ (t, $J = 7$ Hz; 3 H), 1·02 (t, $J = 7$ Hz; 3 H), 1·23–1·41 (m; 12 H), 1·48 (quint, $J = 7$ Hz; 2 H), 1·43–1·62 (m; 2 H), 1·71–1·90 (m; 2 H), 1·82 (quint, $J = 7$ Hz; 2 H), 4·05 (t, $J = 6{\cdot}5$ Hz; 2 H), 4·18; 4·24 (AB_d, $J = 10$ Hz, part A: d, $J = 4{\cdot}5$ Hz, part B: d, $J = 4$ Hz; 2 H), 4·60 (ddd, $J = 5{\cdot}5$, 4·5 and 4 Hz; C_4*H), 4·71 (ddd, $J = 8$, 5·5 and 5 Hz; C_5*H), 6·98; 8·16 (AA'BB', $J = 9$ Hz; 4 H), 6·98; 7·54 (AA'BB', $J = 9$ Hz; 4 H), 7·25; 7·58 (AA'BB', $J = 9$ Hz; 4 H). MS (180°C): $m/e = 588$ (2·5 per cent, M^+), 328 (7, $C_{19}H_{20}O_5$), 277 (9), 261 (100, $C_{17}H_{25}O_2$), 185 (10), 121 (77). $C_{36}H_{44}O_7$: calc. C 73·44 per cent; H 7·53 per cent, found C 72·68 per cent; H 7·38 per cent.

4.7. (4S,5R)-(−)-4-[4-(4-decyloxybenzoyloxy)-biphenyl-4'-yloxymethyl]-5-propyl-1,3-dioxolan-2-one (**6d**)

mp: 122·5°C. $[\alpha]_{D^{20}} = -3{\cdot}5°$ (*c*. 0·9 in $CHCl_3$). IR(KBr): 1790; 1725 (CO), 1605 cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 0{\cdot}89$ (t, $J = 7$ Hz; 3 H), 0·99 (t, $J = 7$ Hz; 3 H), 1·22–1·41 (m; 12 H), 1·48 (quint, $J = 7$ Hz; 2 H), 1·43–1·53 (m; 1 H), 1·64–1·75 (m; 2 H), 1·82 (quint, $J = 7$ Hz; 2 H), 1·85–1·95 (m; 1 H), 4·05 (t, $J = 6{\cdot}5$ Hz; 2 H), 4·22; 4·26 (AB_d, $J = 10$ Hz, part A: d, $J = 5$ Hz, part B: d, $J = 4$ Hz; 2 H), 4·86 (ddd, $J = 10$, 7·5 and 3 Hz; C_5*H), 4·97 (ddd, $J = 7{\cdot}5$, 5 and 4 Hz; C_4*H), 6·97; 8·16 (AA'BB', $J = 9$ Hz; 4 H), 6·98; 7·54 (AA'BB', $J = 9$ Hz; 4 H), 7·25; 7·58 (AA'BB', $J = 9$ Hz; 4 H). MS (290°C): $m/e = 588$ (10 per cent, M^+), 261 (100, $C_{17}H_{25}O_2$), 121 (21). $C_{36}H_{44}O_7$: calc. C 73·44 per cent; H 7·53 per cent, found C 73·07 per cent; H 7·43 per cent.

4.8. (2R,3R)-(+)-*di*-[trans-4-(trans-4-*pentylcyclohexyl*)-*cyclohexylmethyl*] *tartrate* (***8a***)

A mixture of *R,R*-(+)-tartaric acid (0·75 g; mmol), *trans*-4-(*trans*-4-pentylcyclohexyl)-cyclohexylmethyl alcohol (3·20 g; 12 mmol) and *p*-toluene sulphonic acid (0·05 g; 0·3 mmol) was refluxed azeotropically in toluene for 18 h. The solvent was removed in vacuum and the residue crystallized from dichloromethane/ether to give 2·7 g (84 per cent) of **8a**.

mp: 202°C. $[\alpha]_{D20} = +4{\cdot}7°$ (*c.* 0·2 in $CHCl_3$). IR(KBr): 3520 (OH), 1740 (CO) cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 0{\cdot}78$–$0{\cdot}92$ (m; 6 H), 0·88 (t, $J = 7$ Hz; 6 H), 0·93–1·05 (m; 18 H), 1·11–1·18 (m; 4 H), 1·20–1·34 (m; 12 H), 1·60–1·82 (m; 16 H), 3·13 (d, $J = 7$ Hz; 2OH), 4·04; 4·10 (AB_d, $J = 10$ Hz and 6·5 Hz; 4 H), 4·53 (d, $J = 7$ Hz; 2 C*H). MS (250°C): $m/e = 646$ (< 1 per cent, M^+), 248 (84, $C_{18}H_{32}O$), 95 (100). $C_{40}H_{70}O_6$: calc. C 74·30 per cent; H 10·83 per cent, found C 74·07 per cent; H 11·00 per cent.

4.9. (4R,5R)-(−)-*1,3-dioxolan-2-one-di*-[trans-4-(trans-4-*pentylcyclohexyl*) *cyclohexylmethyl*]-*4,5-dicarboxylate* (***9a***)

To a solution of **8a** (1·0 g; 1·5 mmol) and pyridine (0·2 g; 3·0 mmol) in 10 ml of dry $CHCl_3$ 5 ml of a phosgene solution (20 per cent in toluene) were added while stirring at 0°C. The mixture was stirred at 0°C for 1 h and at room temperature for 3 h. Then 5 ml of water were added and stirring continued for $\frac{1}{2}$ h. The organic phase was separated, dried ($MgSO_4$) and the solvent was evaporated in vacuum. Flash chromatography with dichloromethane gave 0·77 g (74 per cent) of **9a**.

mp: 179°C. $[\alpha]_{D20} = -18°$ (*c.* 0·5 in $CHCl_3$). IR($CHCl_3$): 1850; 1765 (CO) cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 0{\cdot}80$–$0{\cdot}90$ (m; 4 H), 0·88 (t, $J = 7$ Hz; 6 H), 0·92–1·05 (m; 16 H), 1·11–1·18 (m; 4 H), 1·20–1·34 (m; 16 H), 1·60–1·82 (m; 16 H), 4·09 (d, $J = 6{\cdot}5$ Hz; 4 H), 5·08 (s; 2C*H). MS (175°C): $m/e = 672$ (7·5 per cent, M^+), 293 (5, M-$C_{18}H_{33}COO$), 248 (100, $C_{18}H_{32}$). $C_{41}H_{68}O_7$: calc. C 73·21 per cent; H 9·67 per cent, found C 73·30 per cent; H 9·93 per cent.

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