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Chiral spiro-connected 2,3,3-trisubstituted oxiranes New dopants for induced ferroelectric phases

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Chiral spiro-connected 2,3,3-trisubstituted oxiranes
New dopants for induced ferroelectric phases

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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 A and B, possessing a 2,3,3-trisubstituted oxirane ring spiro-connected with four-, five- or six-membered carbocycles are described. In a series of these compounds with the same mesogenic building blocks the one with the five-membered carbocycle exhibits the highest induced spontaneous polarization. Introduction of a carbonyl group adjacent to the oxirane ring leads to an increased induced spontaneous polarization. The sign of the helical twisting power is positive for compounds with a cyclobutane ring and negative for those with a cyclopentane or a cyclohexane ring, although the absolute configuration at the chiral carbon is the same for all compounds.

1. Introduction

Ferroelectricity in liquid crystals (FLCs) attracts great interest in both fundamental research and technological applications. In addition to their use in FLC displays, now developed to commercial applicability, ferroelectric materials are suitable for non-linear optics as well as for piezoelectric sensors. To fulfil the necessity of short response times in electrooptical devices, two main features are required for new FLC materials: (i) high spontaneous polarization (P_S) and (ii) low rotational viscosity. Because of the difficulty of obtaining substances which have both favourable properties, FLC materials are often prepared by doping non-chiral liquid crystalline mixtures exhibiting low viscosity and a broad S_C phase range with chiral compounds having large spontaneous polarizations.

Chirality—necessary to obtain spontaneous polarization in a S_C phase—has often been introduced in the molecule by using nature's chiral pool. Thus FLCs containing 2-methylbutyl, 3-methylpentyl, 4-methylhexyl, 2-octyl or terpenoid ether or ester functions as naturally available chiral end groups, or lactates, or mandelates as chiral core units have been developed. Ready chemical transformations of such materials have made further compounds accessible like 2-chloropropyl esters, cyanohydrin esters, cyano- and chloro-alkanoates. Recently fluoroalkyl compounds, compounds with substituted 2-hydroxypropyl groups, fluoroalkyl esters [1], and 2-fluoroalkanoates [2] have been used.

Though a variety of substances has been developed in this way, not all of them fulfil the guidelines which have been laid down for the design of suitable ferroelectric materials [3–5]. The separation of optical enantiomers and stereospecific synthesis are other tools used to obtain a large number of potentially interesting compounds which are not available from natural resources.

It is considered that the magnitude of the spontaneous polarization is related to the lateral dipole moment neighbouring the chiral centre of the LC molecule. Furthermore

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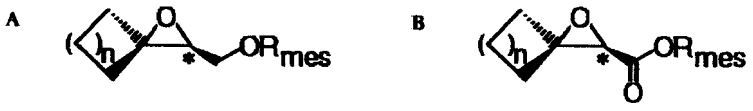
rigid steric coupling between asymmetric centres and polar groups is generally supposed to be advantageous to obtain high P_S values. Chiral ring systems can fulfil these demands. Therefore several different types of liquid crystal materials containing units such as oxiranes [5], oxirane carboxylic esters [6], thiiranes [7], oxetanes [8], 2-oxetanones [9], 1,3-dioxolan-4-ones [10], 1,3-dioxolan-2-ones [11], γ-lactones [12], δ-lactones [13] and others have been synthesized and investigated.

The favourable ferroelectric properties of 2,3-disubstituted oxiranes inspired us to synthesize 2,3,3-trisubstituted oxiranes (A, B; $n = 1$–3) which have a rigid spiro-connection of the oxirane unit with four-, five- or six-membered carbocycles.



It has been observed that restriction of the rotation around the long axis of the molecule near the lateral dipole has a favourable impact on the spontaneous polarization. For example, *cis*-2,3-substituted oxiranes show significantly higher P_S values than the corresponding *trans*-2,3-substituted oxiranes [14]. For both new types of oxirane, A and B, we expected an analogous effect due to the steric hindrance to free rotation caused by the spiro-connected carbocycle and therefore that they would have valuable properties as dopants for FLC mixtures. In this context the influence of the ring size on the properties of the compounds was of interest.

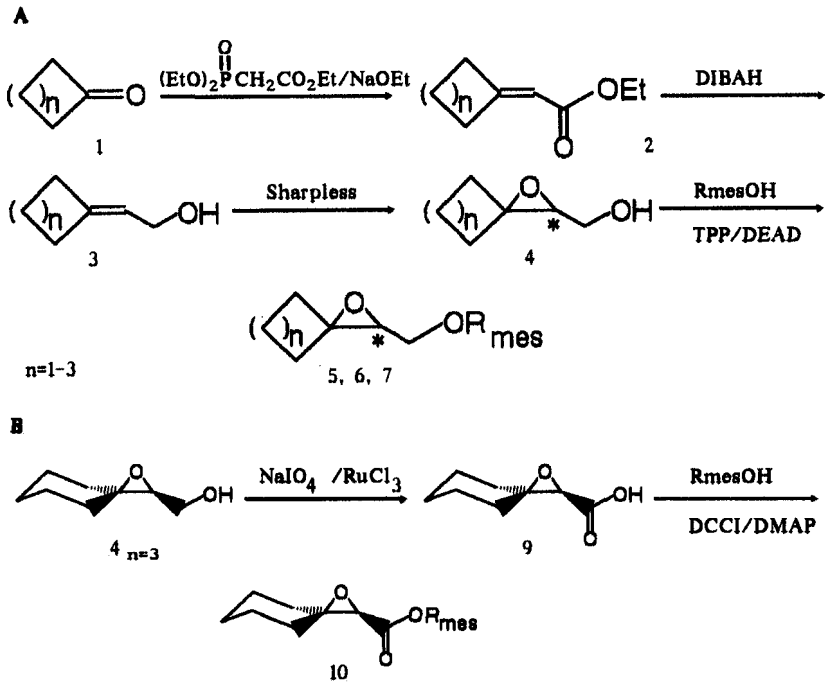
Furthermore, a comparison of the oxirane ethers A and the oxirane carboxylic esters B was a goal of this work. For 2,3-disubstituted 2-oxirane carboxylic esters we have found generally higher P_S values compared with the analogous ethers [6] due to the enhancement of the oxirane dipole by the adjacent carbonyl group. Will this effect also be valid for A and B?

2. Synthesis

LCs containing the chiral 2,3,3-trisubstituted oxirane unit were synthesized starting from the cyclic ketones **1** with $n = 1$–3 (see the scheme). For comparison, the open-ring compound **8** (see the table) was prepared in an analogous manner. Horner–Emmons reaction with diethyl(ethoxycarbonylmethyl)phosphonate transformed **1** into the α,β-unsaturated carboxylic esters **2**. Reduction of the esters with di-isobutylaluminium hydride gave the allylic alcohols **3**. Catalytic Sharpless epoxidation [15] afforded the (*S*)-epoxy alcohols **4**. Etherification of the alcohols **4** with mesogenic phenols was accomplished by the Mitsunobu method [16] yielding the ethers **5**–**7**. To obtain the spiro-connected carboxylic esters of type B, the epoxy alcohols **4** were oxidized to the oxirane carboxylic acids **9** using $RuCl_3$ (catalytic amounts)/$NaIO_4$ in a two-phase system [17]. This oxidation worked only for the cyclohexyl-connected epoxy alcohol and failed for the compounds with smaller carbocycles ($n = 1$ and 2) which suffered from oxidative decomposition. Steglich esterification gave the carboxylic ester **10** [18].

3. Spontaneous polarization

The induced spontaneous polarization was measured using 10 mol% solutions in the non-chiral host M89/85 (C 9°C S_C 84°C S_A 93°C N 105°C I) from Hoechst AG. The P_S values presented were obtained from the 10 mol% solutions and are not extrapolated. The helical twisting power (HTP) was determined for the cholesteric phase of the mixtures, using the Cano wedge method.



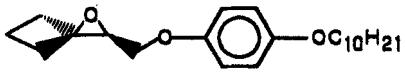
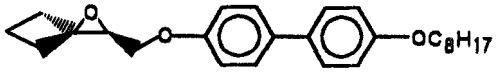
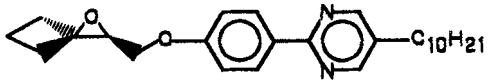
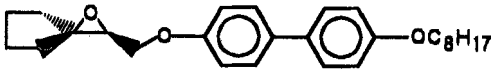
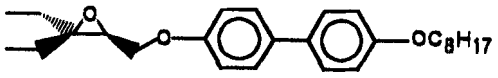
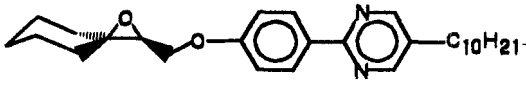
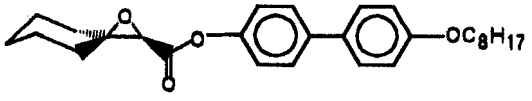
Scheme.

4. Phase behaviour

As far as has been investigated by textural observations, compounds of type A and B tend to form only crystal modifications. Using mesogenic groups with one or two aromatic cores, no liquid crystalline phases are obtained. The spiro-connected carbocycles do not act as an additional mesogenic moiety. Mesophases might be obtained by lengthening the molecules with an additional core in the mesogenic part or with an alkyl chain at the carbocycle.

5. Discussion

In the group of spiro-connected oxirane ethers (type A), ring enlargement from cyclobutane **5a–c** to cyclopentane **6** causes a strong increase in the spontaneous polarization (see the table). It is remarkable that the more flexible open-ring compound **8** shows a four-times smaller P_S value than **6**. Further ring expansion leads to a dramatic decrease in the P_S value: **7** with a cyclohexane ring exhibits nearly the same P_S value as the open-ring compound **8**. With the same chiral group and a constant dipole moment, we would expect rather a continuous decrease with increasing ring size due to the increase in the molecular weight. This behaviour is well known for substances with one alkyl chain at the chiral moiety (although an odd–even effect might occur). A possible explanation might be found in the following reflections: (i) The cyclopentane ring is nearly as rigid as the cyclobutane ring. Rotation is more restricted due to the larger ring size leading to a larger P_S for the cyclopentane compound. (ii) The cyclohexane ring is rather flexible, and therefore comparable with the open-ring compound **8**. This results in a strong decrease in the P_S for this compound. Nevertheless the reason for the observed P_S maximum for the cyclopentane derivative is not yet clear. Further investigations are required.

		$HTP/\mu m^{-1}$	$P_s/nC\,cm^{-2}$
5a	 C_1 43·8°C C_2 48·0°C I	+1·54 (74°C)	+7·8 (25°C)
5b	 C 82·6°C I		+7·8 (25°C)
5c	 C_1 84·6°C C_2 87·3°C I	+1·46 (81°C)	+8·5 (27·0°C)
6	 C 92·8°C I	−1·42 (83°C)	+16·4 (25·0°C)
8	 C 77·0°C I		+3·9 (27·7°C)
7	 C_1 43·0°C C_2 64·0°C C_3 83·5°C I	−1·82 (81°C)	+4·4 (25·3°C)
10	 C 79·0°C I		+19·7 (33·0°C)

The highest spontaneous polarization of the synthesized compounds in our series of spiro-connected oxiranes is observed for the carboxylic ester compound **10** (type B). This is compatible with the expected enhancement of the dipole moment by the carbonyl group, as mentioned previously.

The sign of the helical twisting power (*HTP*) shows an interesting behaviour: surprisingly it changes from positive to negative when the ring is enlarged from cyclobutane ($n=1$) to cyclopentane ($n=2$). Going to cyclohexane ($n=3$), no further change in sign occurs. It is remarkable that the sign of the spontaneous polarization does not correspond with the sign reversal of the *HTP* and is positive for all investigated compounds.

6. Experimental

^{1}H NMR: Bruker WM 400. Specific optical rotation: Perkin–Elmer PE 141 polarimeter. Texture observations: JENAPOL polarizing microscope and Linkam THMSE 600 heating/freezing stage. Measurements of spontaneous polarization: in test cells with a spacing between 2 and 3 μm. The glass substrates of the cells were coated with polyimide and both substrates were rubbed. The cells were filled by capillary interaction and were thermostatted during the measurements by a Linkam TMS 90 precision temperature control system. Spontaneous polarization was obtained by the triangular wave method [19]; applied voltage: *c.* 20 V, frequency: 80 Hz. The sign of the spontaneous polarization was determined by investigation of the switching behaviour, considering the temperature dependence of the switching angle. Chromatographic purifications were performed using flash chromatography (FC) on ICN Biomedicals silica (32–63 μm).

6.1. *Synthetic procedures for representative compounds*

6.1.1. *Ethyl 3,3-(cyclohexylidene)acrylate* ($\mathbf{2}_{n=3}$)

A mixture of cyclohexanone (5·992 g, 61·14 mmol) and diethyl-(ethoxycarbonylmethyl)phosphonate (15·140 g, 67·59 mmol) in 25 ml of dry toluene under nitrogen was treated with 25 ml of a solution of sodium ethoxide prepared from sodium (1·557 g, 67·70 mmol) and 25 ml of dry ethanol, and stirred for 24 h. Thereafter, the reaction solution was poured on to a mixture of 150 g ice and 100 ml of water. After stirring for 10 min, the phases were separated, followed by extraction of the aqueous phase with MTBE, washing of the combined organic phases with water and drying over magnesium sulphate. Concentration and purification by distillation yielded 10·06 g (98 per cent) of ethyl 3,3-(cyclohexylidene)acrylate $\mathbf{2}_{n=3}$ as an intense smelling, colourless oil. ^{1}H NMR ($CDCl_3$): δ, 1·27 (t, $J=7$ Hz, 3 H), 1·55–1·69 (m, 6 H), 2·19 (t(br), $J=6$ Hz, 2 H), 2·82 (t(br), $J=6$ Hz, 2 H), 4·13 (q, $J=7$ Hz, 2 H), 5·60 p.p.m. (s, 1 H). MS (80°C): *m/e* 168 (75 per cent, M^+), 140 (74), 123 (93), 95 (63), 80 (100), 67 (68), 55 (95).

6.1.2. *3,3-(cyclohexylidene)-2-propene-1-ol* ($\mathbf{3}_{n=3}$)

A solution of ethyl 3,3-(cyclohexylidene)acrylate $\mathbf{2}_{n=3}$ (10·06 g, 59·9 mmol) in 25 ml of dry toluene was treated with 116 ml of a 1·2 M solution of DIBAH in toluene at 0°C, under nitrogen, over a period of 4 h 25 min, and stirred for 3 days, while allowing the mixture to warm to room temperature. The reaction was quenched by adding 4 ml of methanol and stirring for 10 min. Thereafter, the reaction mixture was diluted with 30 ml of MTBE, treated with 11 ml of saturated, aqueous ammonium chloride and stirred for 1·25 h. The precipitate was filtered off, the phases were separated and the organic phase was dried over magnesium sulphate. After concentration the crude product was purified by chromatography. A colourless liquid, 5·63 g (75 per cent), which proved to be 3,3-(cyclohexylidene)-2-propene-1-ol $\mathbf{3}_{n=3}$, was obtained. ^{1}H NMR

($CDCl_3$): δ, 1·32 (s(br), 1 H), 1·48–1·60 (m, 6 H), 2·10 (t(br), $J = 5·5$ Hz, 2 H), 2·17 (t(br), $J = 5·5$ Hz, 2 H), 4·12 (d, $J = 7$ Hz, 2 H), 5·25 p.p.m. (t(br), $J = 7$ Hz, 1 H). MS (220°C): *m/e* 126 (22 per cent, M^+), 108 (84, $M-H_2O$), 93 (88), 83 (89), 79 (100), 67 (88), 55 (74).

6.1.3. (*2S*)-*3,3-(cyclohexylidene)-2-hydroxymethyloxirane* ($\mathbf{4}_{n=3}$)

A mixture of powdered, commercially activated 4 Å molecular sieves (2·5 g) and 60 ml of anhydrous dichloromethane under nitrogen was cooled to 0°C. L-(+)-diethyl tartrate (472 mg, 2·29 mmol) and titanium tetra-isopropoxide (437 mg, 1·54 mmol) were added sequentially. After cooling to −25°C, *tert*-butylhydroperoxide (19 ml, 57mmol, 3 M in toluene) was added and the resulting mixture was stirred for 1 h 15 min, whereupon a solution of 3,3-(cyclohexylidene)-2-propene-1-ol $\mathbf{3}_{n=3}$ (3·373 g, 26·77 mmol) in 9 ml of dry dichloromethane (dried over powdered 4 Å molecular sieves prior to addition to the reaction) was added. Stirring was maintained for 4 h 25 min at *c.* −25°C. Thereafter the reaction mixture was refrigerated at −31°C for 14·5 h. After warming to 0°C, the catalyst was quenched by adding 9 ml of water and stirring for 1 h 25 min, while allowing to warm to room temperature. Hydrolysis of the tartrate was effected by adding 2·6 ml of a 30 per cent aqueous solution of NaOH saturated with sodium chloride and stirring for 55 min. After phase separation, extraction of the aqueous phase with dichloromethane, drying over magnesium sulphate, concentration and chromatography yielded 2·50 g (68 per cent) of (2*S*)-3,3-(cyclohexylidene)-2-hydroxymethyloxirane $\mathbf{4}_{n=3}$ as a colourless oil. $[\alpha]_D^{29} = -12·4°$ (*c* 11·4 mg in $CHCl_3$). ^1H NMR ($CDCl_3$): δ, 1·46–1·63 (m, 6 H), 1·65–1·80 (m, 4 H), 2·97 (dd, $J = 7$ and 4 Hz, 1 H), 3·69 (dd, $J = 12$ and 7 Hz, 1 H), 3·85 p.p.m. (dd, $J = 12$ and 4 Hz, 1 H). MS (220°C): *m/e* 142 (2 per cent, M^+), 124 (16, $M-H_2O$), 111 (60, $M-CH_2OH$), 106 (33, $M-H_2O-H_2O$), 99 (52, $M-CH_2OH-C$), 95 (52, $M-CH_2OH-O$), 67 (71), 55 (100).

6.1.4. (*2S*)-*2-[4-(5-Decylpyrimidin-2-yl)phenyloxymethyl]-3,3-cyclohexylideneoxirane* (**7**)

A solution of 2-(4-hydroxyphenyl)-5-decylpyrimidine (155 mg, 0·50 mmol) in 20 ml of dry THF was cooled to 0°C. Triphenylphosphine (127 mg, 0·48 mmol) and (2*S*)-3,3-(cyclohexylidene)-2-hydroxymethyloxirane $\mathbf{4}_{n=3}$ (78 mg, 0·55 mmol)—each of them dissolved in 2 ml of dry THF—and diethyl diazodicarboxylate (84 mg, 0·48 mmol) were added by syringe. The resulting mixture was stirred for 0·5 h at 0°C and 16 h at room temperature. Thereafter, the solution was concentrated and the crude product was purified by chromatography yielding 45 mg of **7** (21 per cent). $[\alpha]_D^{29} = -8·3°$ (*c* 4·6 mg in $CHCl_3$). ^1H NMR ($CDCl_3$): δ, 0·88 (t, $J = 7$ Hz, 3 H), 1·20–1·40 (m, 14 H), 1·64 (quint., $J = 7$ Hz, 2 H), 1·50–1·83 (m, 10 H), 2·60 (t, $J = 7$ Hz, 2 H), 3·16 (t(br), $J = 5$ Hz, 1 H), 4·16 (dd, $J = 11$ and 5·5 Hz, 1 H), 4·21 (dd, $J = 11$ and 4·5 Hz, 1 H), 7·02, 8·36 (AA'BB', $J = 9$ Hz, 4 H), 8·57 p.p.m. (s, 2 H). MS (160°C): *m/e* 436 (100 per cent, M^+), 325 (74, $RmesOCH_2$), 312 (59, M–RmesO–H), 297 (64), 199 (40), 185 (51), 125 (90).

6.1.5. (*2R*)-*3,3-Cyclohexylideneoxirane-2-carboxylic acid* (**9**)

A flask was charged with carbon tetrachloride (4·8 ml), acetonitrile (4·8 ml), water (7·2 ml), (2*S*)-3,3-(cyclohexylidene)-2-hydroxymethyloxirane $\mathbf{4}_{n=3}$ (502 mg, 3·54 mmol) and sodium metaperiodate (2·061 g, 9·64 mmol). To this biphasic solution, ruthenium trichloride hydrate (40 mg, 0·19 mmol, 5·4 mol%) was added, and the mixture was stirred vigorously overnight at room temperature. Then 50 ml of dichloromethane were added, and the phase separated. The aqueous phase was extracted three times with dichloromethane, and the combined organic extracts were dried over magnesium

sulphate and concentrated. The catalyst was partially removed by filtration of an ethereal solution through a celite pad. The (2*R*)-3,3-cyclohexylideneoxirane-2-carboxylic acid **9** (367 mg, 67 per cent) was used for the next step without further purification. ^{1}H NMR ($CDCl_3$): δ, 1·42–1·83 (m, 8 H), 3·40 p.p.m. (s, 1 H).

6.1.6. *(2R)-4'-Octyloxybiphenyl-4-yl 3,3-cyclohexylideneoxirane-2-carboxylate* (**10**)

A solution of (2*R*)-3,3-cyclohexylideneoxirane-2-carboxylic acid **9** (85 mg, 0·54 mmol), *N*,*N*-dicyclohexyl-carbodiimide (115 mg, 0·56 mmol), 4-hydroxy-4'-octyloxybiphenyl (163 mg, 0·55 mmol) and 4,4-dimethylaminopyridine (7 mg, 0·06 mmol) in 25 ml of dry dichloromethane was stirred at room temperature overnight. Thereafter, the *N*,*N*-dicyclohexylurea was filtered off and the solution was concentrated. The residue was purified by FC, yielding 38 mg (16 per cent) **10**. $[\alpha]_D^{28} = -36·3°$ (*c* 2·9 mg in $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ, 0·89 (t, $J = 7$ Hz, 3 H), 1·22–1·89 (m, 22 H), 3·59 (s, 1 H), 3·99 (t, $J = 7$ Hz, 2 H), 6·96, 7·47 (AA'BB', $J = 9$ Hz, 4 H), 7·15, 7·55 p.p.m. (AA'BB', $J = 9$ Hz, 4 H). MS (120°C): *m/e* 436 (28 per cent, M^+), 298 (45, RmesOH), 186 (100, HO–C_6H_4–C_6H_4–OH).

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References

[1] NOHIRA, H., NAKAMURA, S., and KAMEI, M., 1990, *Molec. Crystals liq. Crystals*, **180B**, 379.
[2] WATANABE, S., ENDO, H., FUJITA, T., and SAKAMOTO, M., 1990, *J. fluorine Chem.*, **47**, 187. For recent developments in the synthesis of LC materials see also GRAY, G. W., HIRD, M., and TOYNE, K. J., 1991, *Molec. Crystals liq, Crystals*, **204**, 91.
[3] GOODBY, J. W., CHIN, E., LESLIE, T. M., GEARY, J. M., and PATEL, J. S., 1986, *J. Am. chem. Soc.*, **108**, 4729.
[4] GOODBY, J. W., and CHIN, E., 1986, *J. Am. chem. Soc.*, **108**, 4736.
[5] WALBA, D. M., SLATER, S. C., THURMES, W. M., CLARK, N. A., HANDSCHY, M. A., and SUPON, F., 1986, *J. Am. chem. Soc.*, **108**, 5210.
[6] SCHEROWSKY, G., GAY, J., and SHARMA, N. K., 1990, *Molec. Crystals liq. Crystals*, **178**, 179.
[7] SCHEROWSKY, G., and GAY, J., 1989, *Liq. Crystals*, **5**, 1253.
[8] SCHEROWSKY, G., LOTZ, A., and SEFKOW, M., 1990, *13th International Liquid Crystal Conference*, Vancouver FER-55-P.
[9] SCHEROWSKY, G., and SEFKOW, M., 1992, *Liq. Crystals*, **12**, 355.
[10] SCHEROWSKY, G., and SEFKOW, M., 1991, *Molec. Crystals liq. Crystals*, **202**, 207.
[11] SCHEROWSKY, G., GAY, J., and GUNARATNE, M., 1992, *Liq. Crystals*, **11**, 745.
[12] SAKAGUCHI, K., and KITMURA, T., 1991, *Ferroelectrics*, **114**, 265.
[13] SAKASHITA, K., SHINDO, M., NAKAUCHI, J., UEMATSU, M., KAGEYAMA, Y., HAYASHI, S., IKEMOTO, T., and MORI, K., 1991, *Molec. Crystals liq. Crystals*, **199**, 119.
[14] DÜBAL, H. R., ESCHER, C., GÜNTHER, D., HEMMERLING, W., INOGUCHI, Y., MÜLLER, I., MURAKAMI, M., OHLENDORF, D., and WINGEN, R., 1988, *Jap. J. appl. Phys.*, **27**, L2241.
[15] GAO, Y., HANSON, R. M., KLUNDER, J. M., KO, S. Y., MASAMUNE, H., and SHARPLESS, K. B., 1987, *J. Am. Chem. Soc.*, **109**, 5765. See also SHARPLESS, K. B., and KATSUKI, T., 1980, *J. Am. chem. Soc.*, **102**, 5974.
[16] CARLSON, P. H. J., KATSUKI, T., MARTIN, V. S., and SHARPLESS, K. B., 1981, *J. org. Chem.*, **46**, 3937.
[17] BITTNER, S., and ASSAF, Y., 1975, *Chemy Ind.*, p. 281; MANHAS, M. S., HOFFMAN, W. H., LAL, B., and BOSE, A. K., 1975, *J. chem. Soc. Perkin Trans.* **1**, 461. See also MITSUNOBU, O., 1981, *Synthesis*, 1.
[18] NEISES, B., and STEGLICH, W., 1978, *Angew. Chem.*, **90**, 556.
[19] MIYASATO, K., ABE, S., TAKAZOE, H., FUKUDA, A., and KUZE, E., 1983, *Jap. J. appl. Phys.*, **22**, L661.