New mesogenic compounds with *trans*-stilbene oxide as the central chiral core

Bianca F. Bonini[a]; Giovanni Gottarelli[a]; Stefano Masiero[a]; Gian Piero Spada[a]; Paolo Mariani[b]; Bin Yang[b]

[a] Dipartimento di Chimica Organica 'A. Mangini', Università di Bologna, Bologna, Italy [b] Istituto di Scienze Fisiche, Facoltà di Medicina, Università di Ancona, Ancona, Italy

PLEASE SCROLL DOWN FOR ARTICLE

New mesogenic compounds with *trans*-stilbene oxide as the central chiral core

by BIANCA F. BONINI, GIOVANNI GOTTARELLI*, STEFANO MASIERO,
and GIAN PIERO SPADA

Dipartimento di Chimica Organica 'A. Mangini', Università di Bologna,
via S. Donato, 15, I-40127 Bologna, Italy

PAOLO MARIANI and BIN YANG

Istituto di Scienze Fisiche, Facoltà di Medicina, Università di Ancona,
via Ranieri, 65, I-60131 Ancona, Italy

Several derivatives with the *trans*-stilbene oxide moiety as the central chiral core were synthesized. With the appropriate substituents, nematic and smectic C phases were observed. One derivative was obtained with an *ee* of 47 per cent by asymmetric synthesis. The chemical stability of these epoxides is low and they rearrange to give substituted phenyl benzylketones which are also liquid-crystalline. The structure of the two solid phases present in all the derivatives and of the smectic C phases was investigated by X-ray diffraction.

1. Introduction

With the exception of cholesterol derivatives, almost all chiral mesogens described in the literature have one or more chiral centres in the terminal groups, but very recently a few reports have appeared in which the chiral elements are in the central part of the molecule [1–4]. The presence of an oxirane ring in the centre of the molecule is interesting not only as a source of chirality, but also because it gives a lateral dipole which could be useful for obtaining smectic C mesophases [4].

From previous experience in this field [1], we chose the *trans*-stilbene oxide as our central core, as this chiral unit is conformationally related to MBBA and similar systems [5]; compared to the chiral oxirane carboxylic ester unit, reported recently by Scherowsky *et al.* [4], this system should be more rigid and the averaging of the lateral dipole should be reduced. Finally, our data on the helical twisting powers of aryl epoxides [6] indicate that a possible cholesteric mesophase obtained from a mesogen of this type should have an extremely short pitch.

2. Results and discussion

2.1. *Synthesis and mesomorphic properties*

The oxiranes were obtained by oxidation of the corresponding alkenes **1a–l** with perbenzoic acid as reported in [7] (see scheme 1). Several ether and ester derivatives were also synthesized with only alkyl chains, i.e. without the two benzoic acid units esterifying the phenolic hydroxy groups of the diaryloxirane, but none showed even monotropic mesophases. In table 1 are reported the phases and the transition

*Author for correspondence.
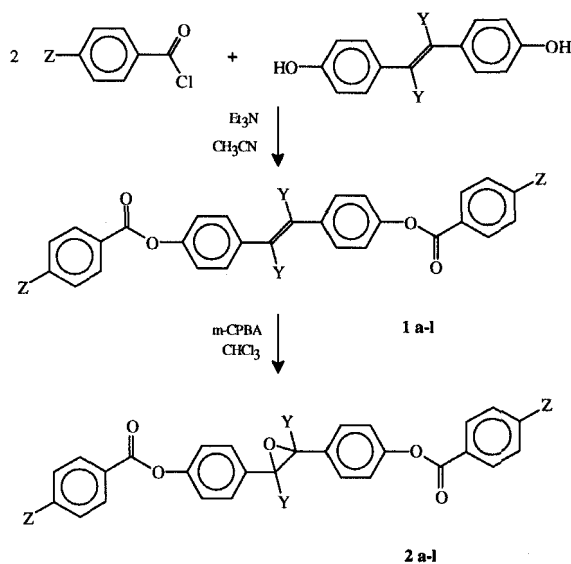
	Y	Z
a	H	OC_4H_9
b	H	OC_6H_{13}
c	H	OC_7H_{15}
d	H	OC_8H_{17}
e	H	OC_9H_{19}
f	H	$OC_{10}H_{21}$
g	H	$OC_{12}H_{25}$
h	H	C_5H_{11}
i	H	C_7H_{15}
j	C_2H_5	C_5H_{11}
k	C_2H_5	OC_4H_9
l	C_2H_5	OC_7H_{15}

Table 1.   Phases sequence and transition temperatures for compounds **2a–l** (dec. indicates that decomposition occurs).

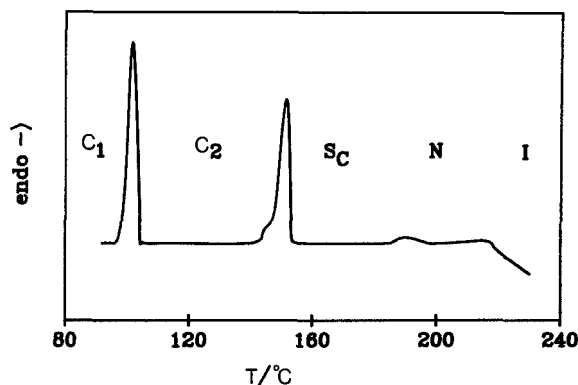| Compound	Phase behaviour						
2a	C		202°C		N	290°C dec.	I
2b	C		149°C		N	270°C dec.	I
2c	C		150°C		N	250°C dec.	I
2d	C	155°C	S_C	163°C	N	280°C dec.	I
2e	C	153°C	S_C	187°C	N	220°C dec.	I
2f	C	143°C	S_C	170°C	N	220°C dec.	I
2g	C	138°C	S_C		187°C		I
2h	C		145°C		N + I	222°C dec.	I
2i	C		160°C		N + I	224°C dec.	I
2j	C		140°C		N + I	148°C	I
2k	C		200°C		N + I	213°C	I
2l	C		143°C		N	154°C	I

Figure 1. Differential scanning calorimetry of **2e** (heating rate $5°C$ min^{-1}).

temperatures for derivatives **2a–l** as deduced from DSC and optical microscopy. Assignment of the phases was made from microscopic observations and confirmed by X-ray diffraction that also showed the existence of two crystalline phases (see below); in particular, the smectic phases all showed typical schlieren textures with four brushes or sanded textures [8]. Transition bars were also frequently observed [9] at the nematic–smectic C transitions. A typical DSC trace (relative to **2e**) is shown in figure 1, where decomposition of the compound is evident above 200°C. From an inspection of table 1, the following conclusions can be drawn: (i) to observe liquid-crystalline phases, it is necessary to have two p-substituted benzoic acid moieties esterifying the phenolic groups of the diaryloxirane; (ii) p-alkyl substituents give biphasic systems and longer homologues give only crystal to isotropic transitions (see **2h–i**); (iii) ethyl substituents on the oxirane ring reduce the mesophase stability (but increase the chemical stability) and inhibit the formation of smectic phases (see **2j–l**); (iv) p-alkoxy substituents give the widest mesophase ranges. As is often observed with other core structures, short alkoxy groups give nematic phases (see **2a–c**); by progressively increasing the number of carbon atoms, the smectic phase begins to appear (see **2d–f**) and becomes exclusive for longer chains (see **2g**).

2.2. *Chemical stability*

As shown by the DSC of figure 1, the epoxides begin to decompose around 200°C. But even at room temperature, chemical transformation occurs and the data reported in table 1 are true only for freshly purified samples. In particular we studied the decomposition of derivative **2c**. An optically active sample of the epoxide (see below) was left at 160°C for 1 h under an argon atmosphere. After cooling, a second spot appeared on TLC. Separation afforded unreacted epoxide (74 per cent), showing the same specific rotation as the original sample, and an optically inactive compound, **3c**, (26 per cent), whose spectral data are in agreement with the rearrangement product suggested in scheme 2. The same compound was observed in the epoxidation reaction mixture, as well as in purified samples of epoxide left for a few weeks at room temperature. It is worth noting that derivative **3c** shows two crystalline phases, a smectic C and a nematic phase (C_1 80–120°C C_2 170°C S_C 215°C N 230°C I). It is well-known that stilbene oxides can undergo thermal and acid catalysed rearrangement [10], but the product is generally a diphenylacetaldehyde [11]. Studies devoted to elucidating this discrepancy are in progress.
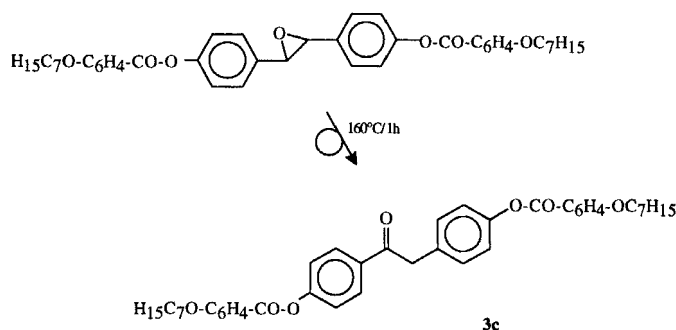
2.3. *Asymmetric synthesis*

In order to check the hypothesis regarding the short cholesteric pitch reported in the Introduction, we obtained derivative **2c** in an optically active form by asymmetric epoxidation with (R,R)-(+)-(2)-(d-α-bromo-π-camphorsulphonyl)-3-(2-chloro-5-nitrophenyl)oxaziridine [12, 13]. The enantiomeric excess was $c.47$ per cent from ^{1}HNMR with (R)-(−)-2,2,2-trifluoro-1-(9-anthryl)ethanol. The dextrorotatory enantiomer obtained should have the R-absolute configuration according to the model reported by [12]. This assignment was confirmed by the sign of the helical twisting power measured using a solution in MBBA [6]; the sign for (+)-**2c** is negative and the signs are negative for a series of analogous aryloxiranes with R-configurations [6]. We tried to measure the cholesteric pitch by the Grandjean–Cano–Heppke technique [14] with a series of samples of different optical purity, but in no case could we obtain the desired disclinations. This was probably due to thermal decomposition of the compound at 150°C, the temperature necessary to obtain the cholesteric phase. However, we could obtain an indirect indication of the pitch from the pitch values of the cholesteric phase induced in MBBA, and measured at room temperature. The pitch for derivative **2c** at a 1 per cent concentration (mol/mol) is $c.1\cdot5\,\mu\text{m}$, whereas the value for cholesteryl nonanoate is $10\,\mu\text{m}$ [15] and that for the 'short pitch' chiral dopant CB15 [(+)-4-cyano-4'-(2-methylbutyl)biphenyl from B.D.H.] is $15\,\mu\text{m}$ [16] (both at the same concentration in a 4-cyanobiphenyl type liquid crystal host). Pure cholesteryl nonanoate gives a cholesteric phase with a pitch in the visible region [17]. This indicates that for pure oxirane **2c**, the cholesteric pitch must be very short indeed.

2.4. *X-ray diffraction*

The measurements were carried out on different derivatives as a function of the temperature. The results confirm the proposed phase sequences and also a crystal to crystal phase transition, detected in all samples. In figure 2 we report some diffraction patterns relating to the freshly purified **2f** derivative. The two different crystalline phases (frames *a* and *b*) are characterized by the presence of a large number of strong and narrow diffraction peaks: from the position of these peaks, an orthorhombic and a monoclinic unit cell were derived, respectively. The corresponding lattice parameters were calculated and refined by using a computer program that minimizes the difference between the experimental and the calculated data. For both structures, the sharp low angle reflection was indexed as (001), while the stronger angle peak was indexed as the overlap of the (100) and (200) peaks. This indicates that in both cases the molecules are arranged in layers and have hexagonal close packing; however, at low temperature, the molecules appear untilted with respect to the layer planes (the lattice constants at 20°C
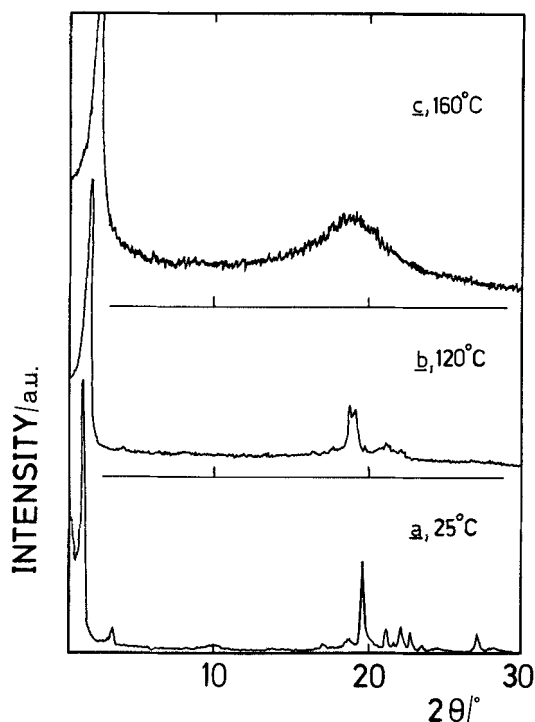
Figure 2. X-ray diffraction pattern of **2f** at different temperatures.

are: $a = 9\cdot08$ Å, $b = 5\cdot24$ Å, $c = 48\cdot20$ Å and $\beta = 90°$), while a tilt occurs at higher temperature (the lattice constants at 100°C are: $a = 11\cdot70$ Å, $b = 5\cdot42$ Å, $c = 48\cdot01$ Å and $\beta = 53\cdot3°$).

As usual, in the smectic phase, the diffraction profile shows a very strong low angle peak and only a broad band in the high angle region (see figure 2, frame c). This diffraction profile confirms the smectic C structure. In fact, the high angle diffuse band corresponds to the liquid-like ordering of the molecules within the smectic layers, while the layer spacing ($33\cdot7$ Å at 160°C) is smaller than the length of **2f** ($49\cdot9$ Å, as estimated by minimum energy conformation calculations) and indicates that the molecular long axes are tilted with respect to the layer plane by $c.$ $42\cdot5°$. The other derivatives show very similar structural properties. Differences were observed in the layer thickness (i.e. lattice parameters) of the two crystalline phases; furthermore, the smectic phase is absent in derivatives with a chain length lower than 8 carbon atoms. Also the low temperature crystalline phase observed for **2b** seems to present a different structure; however a detailed study was precluded by the low chemical stability of this compound. Some structural data are reported in table 2 together with the molecular lengths as determined by minimum energy calculations.

It seems interesting to analyse the variations of the layer thickness as a function of the length of the terminal alkyl chains. As shown in figure 3, a linear behaviour is detected for both the crystalline phases as well as for the smectic C mesophase. The regression parameters relative to the first crystalline phase indicate that the diaryloxirane central core has a length of $c.$ 26 Å, which corresponds exactly to the core dimensions estimated from molecular models. Moreover, the increment for any added CH_2 give a value equal to $1\cdot12$ Å, which is lower than the value usually assumed

Table 2. Some structural data for the crystalline and liquid-crystalline phases exhibited by compounds **2b–d** and **2f–g** (m.l.: molecular length; l.t.: layer thickness; Θ: angle between the molecular long axis and the layer plane).

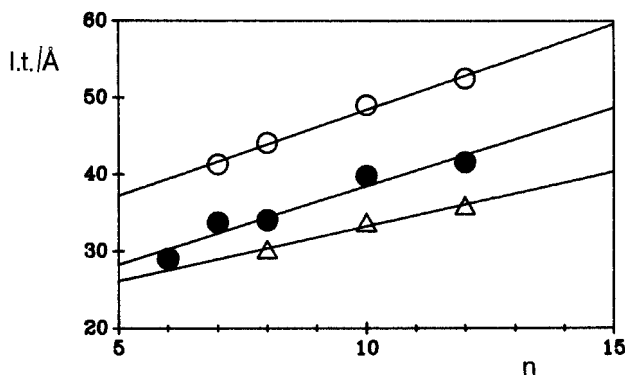|	2b		2c		2d			2f			2g		
m.l./Å	39·8		42·4		44·8			49·9			55·0		
T/°C	25	130	25	100	25	100	160	25	120	160	25	120	180
Phase	C_1	C_2	C_1	C_2	C_1	C_2	S_C	C_1	C_2	S_C	C_1	C_2	S_C
l.t./Å		29·0	41·3	33·7	44·1	34·0	30·2	49·0	39·8	33·7	52·5	41·6	35·9
Θ/°		46·8	90·0	52·6	90·0	49·4	42·4	90·0	52·9	42·5	90·0	49·1	40·8

Figure 3. Dependence of the layer thickness on the number of carbon atoms in the alkoxy group. $\bigcirc$, C_1; $\bullet$, C_2; $\triangle$, S_C.

(1·25 Å). This seems to indicate that, as for many systems, including polymers, the alkyl terminal groups are not in the fully extended conformation [18]. Also the parameters relative to the high temperature crystalline phase give some interesting information. As estimated from the intercept value, the central core appears tilted with respect to the layer plane by $c. 45°$. If this angle is constant when the length of the alkyl substituents increases, the hydrocarbon chains must be less tilted than the central core (about 63° as estimated from the straight line slope). This could be related to the different steric interactions and the flexibility of the alkyl and aromatic parts of the molecules. In the smectic C phase, from the intercept value we determine a tilt angle of $c. 46°$ for the molecular central core. As expected, considering the liquid-like conformation of the alkyl chains, the slope appears quite different, and in particular the addition of a CH_2 unit to the terminal groups increases the layer thickness by only 0·71 Å. It must be finally emphasised that, during the X-ray diffraction measurements, chemical transformations do seem to occur. These transformations induce the appearance of very large biphasic regions corresponding to the phase transitions.

3. Experimental
3.1. *Optical, calorimetric and X-ray diffraction measurements*
Microscopic measurements were carried out with a Zeiss microscope equipped with a Linkham TH/CO600 hot stage, and DSC measurements with a Perkin–Elmer DSC7 instrument. X-ray scattering measurements were performed with a Rigaku Denki RU300 rotating anode generator equipped with a conventional vertical powder diffractometer and a small angle medium resolution pin-hole Hentschel camera. The

resolution and contrast in the photographs were improved by filling the camera with helium to reduce air scattering. Ni-filtered Cu–K$_\alpha$ radiation ($\lambda = 1.54$ Å) was used. The sample heating was carried out by a hot-stage equipped with electrical resistors; the temperature was controlled by an RT 300/301 control system supplied by SMC (Grenoble, France). Before each experiment, the sample was equilibrated for at least 10 min at the new temperature.

3.2. *Synthesis*

4,4′-Dihydroxy-*trans*-stilbene was prepared according to Sieber [19]. 4,4′-Dihydroxy-α,β-diethyl-*trans*-stilbene, *m*-chloroperbenzoic acid (*m*-CPBA), *p*-alkylbenzoyl chlorides and (+)-2-bromocamphor-8-sulphonic acid ammonium salt were purchased from the Aldrich Chemical Company and used without additional purification. The *p*-alkoxybenzoyl chlorides were either obtained commercially or prepared from *p*-bromophenol by standard methods. (*R,R*)-(+)-(2)-(*d*-α-Bromo-π-camphorsulphonyl)-3-(2-chloro-5-nitrophenyl) oxaziridine was prepared as described by Davis [12].

General procedure for the synthesis of diesters **1a–l**. 4,4′-Dihydroxy-*trans*-stilbene or 4,4′-dihydroxy-α, β-diethyl-*trans*-stilbene (1·9 mmol) was suspended in dry acetonitrile (10 ml) under an inert atmosphere. Redistilled triethylamine (4·8 mmol) was added and the mixture was gently boiled for 10 min. The appropriate *p*-alkoxybenzoyl chloride (4·8 mmol) was then added. The mixture was heated under reflux overnight and filtered. The precipitate was washed with acetonitrile (4 × 3 ml), water (2 × 3 ml), acetonitrile (2 × 3 ml) and dried under vacuum. The crude product was then crystallized from toluene.

4,4′-Di(*p*-butoxybenzoyloxy)-*trans*-stilbene, **1a**: 80 per cent; δ_H(CDCl$_3$), 0·98 (t, 6 H, CH$_3$), 1·40–1·88 (m, 8 H, CH$_2$), 4·03 (t, 4 H, OCH$_2$), 6·90–8·20 ppm (m, 18 H, vinylic and aromatic); ν_{MAX}(CHCl$_3$), 1725 cm^{-1} (C=O).

4,4′-Di(*p*-hexyloxybenzoyloxy)-*trans*-stilbene, **1b**: 87 per cent; δ_H(CDCl$_3$), 0·90 (t, 6 H, CH$_3$), 1·30–1·90 (m, 16 H, CH$_2$), 4·03 (t, 4 H, OCH$_2$), 6·90–8·20 ppm (m, 18 H, vinylic and aromatic); ν_{MAX}(KBr), 1715 cm^{-1} (C=O); MS 621 (M$^+$), 205 (M$^+$-2C$_6$H$_{13}$OC$_6$H$_4$CO), 121, 93.

4,4′-Di(*p*-heptyloxybenzoyloxy)-*trans*-stilbene, **1c**: 82 per cent; δ_H(CDCl$_3$), 0·91 (t, 6 H, CH$_3$), 1·20–1·91 (m, 20 H, CH$_2$), 4·05 (t, 4 H, OCH$_2$), 6·90–8·20 ppm (m, 18 H, vinylic and aromatic); ν_{MAX}(CHCl$_3$), 1720 cm^{-1} (C=O).

4,4′-Di(*p*-octyloxybenzoyloxy)-*trans*-stilbene, **1d**: 87 per cent; δ_H(CDCl$_3$), 0·88 (t, 6 H, CH$_3$), 1·20–1·90 (m, 24 H, CH$_2$), 4·03 (t, 4 H, OCH$_2$), 6·90–8·20 ppm (m, 18 H, vinylic and aromatic); ν_{MAX}(KBr), 1720 cm^{-1} C=O).

4,4′-Di(*p*-nonyloxybenzoyloxy)-*trans*-stilbene, **1e**: 84 per cent; δ_H(CDCl$_3$), 0·87 (t, 6 H, CH$_3$), 1·20–1·90 (m, 28 H, CH$_2$), 4·03 (t, 4 H, OCH$_2$), 6·90–8·20 ppm (m, 18 H, vinylic and aromatic); ν_{MAX}(KBr), 1720 m^{-1} (C=O).

4,4′-Di(*p*-decyloxybenzoyloxy)-*trans*-stilbene, **1f**: 78 per cent; δ_H(CDCl$_3$), 0·87 (t, 6 H, CH$_3$), 1·10–1·90 (m, 32 H, CH$_2$), 4·02 (t, 4 H, OCH$_2$), 6·90–8·20 ppm (m, 18 H, vinylic and aromatic); ν_{MAX}(CHCl$_3$), 1720 cm^{-1} C=O).

4,4′-Di(*p*-dodecyloxybenzoyloxy)-*trans*-stilbene, **1g**: 76 per cent; δ_H(CDCl$_3$), 0·84 (t, 6 H, CH$_3$), 1·20–1·90 (m, 40 H, CH$_2$), 4·03 (t, 4 H, OCH$_2$), 6·90–8·20 ppm (m, 18 H, vinylic and aromatic); ν_{MAX}(CHCl$_3$), 1720 cm^{-1} C=O).

4,4′-Di(*p*-pentylbenzoyloxy)-*trans*-stilbene, **1h**: 66 per cent; δ_H(CDCl$_3$), 0·91 (t, 6 H, CH$_3$), 1·22–1·78 (m, 12 H, CH$_2$), 2·68 (t, 4 H, benzylic CH$_2$), 7·05–8·20 ppm (m, 18 H, vinylic and aromatic); ν_{MAX}(CHCl$_3$), 1730 cm^{-1} (C=O).

4,4'-Di(*p*-heptylbenzoyloxy)-*trans*-stilbene, **1i**: 67 per cent; δ_H(CDCl$_3$), 0·7–2·0 (m, 26 H, aliphatic), 2·7 (t, 4 H, benzylic CH$_2$), 7·0–8·3 (m, 18 H, vinylic and aromatic); ν_{MAX}(CHCl$_3$), 1730 cm^{-1} (C=O).

4,4'-Di(*p*-pentylbenzoyloxy)-α,β-diethyl-*trans*-stilbene, **1j**: 72 per cent; δ_H(CDCl$_3$), 0·75–2·76 (m, 32H, aliphatic), 6·90–8·20 (m, 16 H, aromatic); ν_{MAX}(CHCl$_3$), 1730 cm^{-1} (C=O).

4,4'-Di(*p*-butoxybenzoyloxy)-α,β-diethyl-*trans*-stilbene, **1k**: 50 per cent; δ_H(CDCl$_3$), 0·80 (t, 6 H, CH$_3$), 1·00 (t, 6 H, CH$_3$), 1·40–1·91 (m, 8 H, CH$_2$), 2·20 (q, 4 H, allylic CH$_2$), 4·05 (t, 4 H, OCH$_2$), 6·91–8·25 ppm (m, 16 H, aromatic); ν_{MAX}(CHCl$_3$), 1720 cm^{-1} (C=O).

4,4'-Di(*p*-heptoxybenzoyloxy)-α,β-diethyl-*trans*-stilbene, **1l**: 78 per cent; δ_H(CDCl$_3$), 0·72–0·92 (t, 12 H, CH$_3$), 1·20–1·90 (m, 20 H, CH$_2$), 2·20 (q, 4 H, allylic CH$_2$), 4·05 (t, 4 H, OCH$_2$), 6·90–8·20 ppm (m, 16 H, aromatic); δ_C(CDCl$_3$), 13·39, 14·14, 22·71, 26·09, 28·70, 29·16, 29·27, 31·91, 68·61, 114·74, 121·74, 122·18, 130·08, 132·69, 139·47, 140·35, 150·12, 164·10, 165·48 ppm; ν_{MAX}(CHCl$_3$), 1720 cm^{-1} (C=O).

General procedure for the synthesis of racemic epoxides **2a–l**. The alkene **1** (0·15 mmol) and *m*-CPBA (0·22 mmol) were suspended in dry chloroform (6 ml) under an inert atmosphere. The mixture was sonicated for 15–30 min then allowed to stir for 30–60 h at room temperature. Additional solvent was added and the solution was washed several times, first with 5 per cent Na$_2$CO$_3$ and then with water. The organic layer was dried over Na$_2$SO$_4$ and the solvent removed under reduced pressure. The residual white solid was chromatographed on silica gel plates (20 × 20 cm, 1 mm thickness, about 10 mg of mixture per plate), eluting with CH$_2$Cl$_2$/petroleum ether 5:1. The product was extracted with chloroform and finally crystallized from toluene.

($\pm$)-4,4'-Di(*p*-butoxybenzoyloxy)-*trans*-stilbene oxide, **2a**: 58 per cent; δ_H(CDCl$_3$), 0·98 (t, 6 H, CH$_3$), 1·40–1·88 (m, 8 H, CH$_2$), 3·88 (s, 2 H, oxiranic), 4·00 (t, 4 H, OCH$_2$), 6·90–8·20 ppm (m, 16 H, aromatic); ν_{MAX}(CHCl$_3$), 1725 cm^{-1} (C=O).

($\pm$)-4,4'-Di(*p*-hexyloxybenzoyloxy)-*trans*-stilbene oxide, **2b**: 62 per cent; δ_H(CDCl$_3$), 0·93 (t, 6 H, CH$_3$), 1·40–1·88 (m, 16 H, CH$_2$), 3·90 (s, 2 H, oxiranic), 4·05 (t, 4 H, OCH$_2$), 6·90–8·20 ppm (m, 16 H, aromatic); ν_{MAX}(CHCl$_3$), 1725 cm^{-1} (C=O).

($\pm$)-4,4'-Di(*p*-heptyloxybenzolyloxy)-*trans*-stilbene oxide **2c**: 76 per cent; δ_H(CDCl$_3$), 0·90 (t, 6 H, CH$_3$), 1·30–1·88 (m, 20 H, CH$_2$), 3·89 (s, 2 H, oxiranic), 4·05 (t, 4 H, OCH$_2$), 6·95–8·20 ppm (m, 16 H, atomatic); ν_{MAX}(CHCl$_3$), 1720 cm^{-1} (C=O); λ_{MAX} 265 nm ($\varepsilon = 6·0 \times 10^4$, $c = 2·0 \times 10^{-5}$ M in CH$_2$Cl$_2$).

($\pm$)-4,4'-Di(*p*-octyloxybenzoyloxy)-*trans*-stilbene oxide, **2d**: 55 per cent; δ_H(CDCl$_3$) 0·87 (t, 6 H, CH$_3$), 1·20–1·90 (m, 24 H, CH$_2$), 3·87 (s, 2 H, oxiranic), 4·05 (t, 4 H, OCH$_2$), 6·90–8·20 ppm (m, 16 H, aromatic); ν_{MAX}(CHCl$_3$), 1720 cm^{-1} (C=O).

($\pm$)-4,4'-Di(*p*-nonyloxybenzoyloxy)-*trans*-stilbene oxide, **2e**: 30 per cent; δ_H(CDCl$_3$), 0·89 (t, 6 H, CH$_3$), 1·20–1·90 (m, 28 H, CH$_2$), 3·90 (s, 2 H, oxiranic), 4·05 (t, 4 H, OCH$_2$), 6·95–8·17 ppm (m, 16 H, aromatic); ν_{MAX}(CHCl$_3$), 1720 cm^{-1} (C=O).

($\pm$)-4,4'-Di(*p*-decyloxybenzoyloxy)-*trans*-stilbene oxide, **2f**: 81 per cent; δ_H(CDCl$_3$), 0·87 (t, 6 H, CH$_3$), 1·20–1·88 (m, 32 H, CH$_2$), 3·88 (s, 2 H, oxiranic), 4·03 (t, 4 H, OCH$_2$), 6·90–8·20 ppm (m, 16 H, aromatic); ν_{MAX}(CHCl$_3$), 1720 cm^{-1} (C=O).

($\pm$)-4,4'-Di(*p*-dodecyloxybenzoyloxy)-*trans*-stilbene oxide, **2g**: 38 per cent; δ_H(CDCl$_3$), 0·89 (t, 6 H, CH$_3$), 1·20-1·90 (m, 40 H, CH$_2$), 3·90 (s, 2 H, oxiranic), 4·05 (t, 4 H, OCH$_2$), 6·95–8·20 ppm (m, 16 H, aromatic); ν_{MAX}(CHCl$_3$), 1720 cm^{-1} (C=O).

($\pm$)-4,4'-Di(*p*-pentylbenzoyloxy)-*trans*-stilbene oxide, **2h**: 62 per cent; δ_H(CDCl$_3$), 0·7–2·0 (m, 18 H, aliphatic), 2·7 (t, 4 H, benzylic), 3·9 (s, 2 H, oxiranic), 7·1–8·4 ppm (m, 16 H, aromatic); ν_{MAX}(CHCl$_3$), 1720 cm^{-1} (C=O).

($\pm$)-4,4'-Di(*p*-heptylbenzoyloxy)-*trans*-stilbene oxide, **2i:** 57 per cent; δ_H(CDCl$_3$), 0·7–2·0 (m, 26 H, aliphatic), 2·8 (t, 4 H, benzylic), 3·9 (s, 2 H, oxiranic), 7·3–8·4 ppm (m, 16 H, aromatic); ν_{MAX}(CHCl$_3$), 1725 cm^{-1} (C=O).

($\pm$)-4,4'-Di(*p*-pentylbenzoyloxy)-α,β-diethyl-*trans*-stilbene oxide **2j:** 28 per cent; δ_H(CDCl$_3$), 0·75 (t, 6 H, CH$_3$), 0·91 (t, 6 H, CH$_3$), 1·15–1·90 (m, 16 H, CH$_2$), 2·71 (t, 4 H, benzylic CH$_2$), 7·20–8·20 ppm (m, 16 H, aromatic); δ_C(CDCl$_3$), 8·75 (CH$_3$), 13·79 (CH$_3$), 22·33 (CH$_2$) 27·63 (CH$_2$), 30·66 (CH$_2$), 31·29 (CH$_2$), 35·94 (CH$_2$), 72·45 (oxiranic C), 121·50 (CH), 127·16 (C), 128·22 (CH), 128·84 (CH), 130·40 (CH), 136·95 (C), 149·64 (C), 150·28 (C), 165·44 ppm (C), ν_{MAX}(CHCl$_3$), 1720 cm^{-1} (C=O).

($\pm$)-4,4'-Di(*p*-butoxybenzoyloxy)-α,β-diethyl-*trans*-stilbene oxide, **2k:** 73 per cent; δ_H(CDCl$_3$), 0·73 (t, 6 H, CH$_3$), 0·97 (t, 6 H, CH$_3$), 1·10–1·90 (m, 12 H, CH$_2$), 4·04 (t, 4 H, OCH$_2$), 6·9–8·2 ppm (m, 16 H, aromatic); δ_C(CDCl$_3$), 8·71, 13·55, 19·01, 27·63, 31·02, 68·03, 72·44, 114·49, 121·51, 121·80, 128·18, 132·41, 136·89, 150·39, 163·88, 165·05 ppm; ν_{MAX} (CHCl$_3$), 1720 cm^{-1} (C=O).

($\pm$)-4,4'-Di(*p*-heptoxybenzoyloxy)-α, β-diethyl-*trans*-stilbene oxide, **2l:** 77 per cent; δ_H(CDCl$_3$), 0·77 (t, 6 H, CH$_3$), 0·91 (t, 6 H, CH$_3$), 1·10–1·90 (m, 24 H, CH$_2$), 4·05 (t, 4 H, OCH$_2$), 6·90–8·20 ppm (m, 16 H, aromatic); δ_C(CDCl$_3$), 9·05, 14·16, 22·72, 26·10, 27·94, 29·17, 29·28, 31·92, 68·64, 72·74, 114·78, 121·83, 122·05, 128·49, 132·72, 137·17, 150·67, 164·17, 165·40 ppm; ν_{MAX}(CHCl$_3$), 1720 cm^{-1} (C=O).

Asymmetric epoxidation. 4,4'-Di(*p*-heptyloxybenzoyloxy)-*trans*-stilbene **1c** (0·320 g, 0·49 mmol) and (*R,R*)-(+)-(2)-(*d*-α-bromo-π-camphorsulphonyl)-3-(2-chloro-5-nitrophenyl) oxaziridine (0·187 g, 0·38 mmol) were dissolved in 4 ml of chloroform and the mixture heated under reflux for 4 h. The solvent was then removed under reduced pressure and the crude reaction mixture was chromatographed on silica gel plates (see above), with eluant benzene and double elution. After extraction with chloroform, the product was further chromatographed on silica gel plates, with eluant benzene. 0·101 g (40 per cent yield) of (+)-4,4'-di (*p*-heptyloxybenzoyloxy)-*trans*-stilbene oxide **2c** were obtained. The compound showed IR, NMR and DSC spectra identical to those reported above for the racemic derivative; $[\alpha]_D = +91°$ ($c = 0·27$ in benzene); $\Delta\varepsilon = 5·25$ at 273 nm ($c = 2·0 \times 10^{-5}$ M in CH$_2$Cl$_2$); enantiomeric excess = 47 per cent (determined by ^{1}H NMR with (*R*)-(−)-2,2,2-trifluoro-1-(9-anthryl)ethanol).

NMR spectra were recorded with a Varian Gemini 200 spectrometer. NMR data are reported with tetramethylsilane as reference. IR spectra were obtained either with a Perkin-Elmer 177 or with a Perkin–Elmer 1600 series FTIR spectrometer. Optical rotations were measured with a JASCO DIP-360 polarimeter. Mass spectra were obtained with a VG 7070 spectrometer. UV spectra were recorded with a JASCO UVIDEC-650 spectrophotometer. Circular dichroism spectra were recorded with a JASCO J-500A spectropolarimeter.

References

[1] SOLLADIÉ, G., BARTSCH, R., ZIMMERMAN, R., and GOTTARELLI, G., 1985, *Israel J. Chem.*, **25**, 51.

[2] YAMAMURA, K., OKADA, Y., ONO, S., WATANABE, M., and TABUSHI, I., 1988, *J. chem. Soc. Chem. Commun.*, p. 443.

[3] BARBERA, J., OMENAT, A., and SERRANO, J. L., 1989, *Molec. Crystals liq. Crystals*, **166**, 167.
[4] SCHEROWSKY, G., GAY, J., and SHARMA, N. K., 1990, *Molec. Crystals liq. Crystals*, **202**, 207.
[5] GOTTARELLI, G., and SPADA, G. P., 1985, *Molec. Crystals liq. Crystals*, **123**, 377.
[6] GOTTARELLI, G., MARIANI, P., SPADA, G. P., SAMORÌ, B., FORNI, A., SOLLADIÉ, G., and HIBERT, M., 1983, *Tetrahedron*, **39**, 1377.
[7] REIF, D. J., and HOUSE, H. O., 19XX, *Org. Synthesis*, Coll. IV, 860.
[8] GRAY, G. W., and GOODBY, J. W., 1984, *Smectic Liquid Crystals* (Leonard Hill).
[9] DEMUS, D., and RICHTER, L., 1978, *The Textures of Liquid Crystals* (Verlag Chemie), p. 136.
[10] PARKER, R. E., and ISAACS, N. S., 1959, *Chem. Rev.*, **59**, 737.
[11] HOUSE, H. O., 1955, *J. Am. chem. Soc.*, **77**, 3070.
[12] DAVIS, F. A., HARAKAL, M. E., AWAD, S. B., 1983, *J. Am. chem. Soc.*, **105**, 3123.
[13] DAVIS, F. A., JENKINS, R. H., Jr., AWAD, S. B., STRINGER, O. D., WATSON, W. H., and GALLOY, J., 1982, *J. Am. chem. Soc.*, **104**, 5412.
[14] HEPPKE, G., and OESTREICHER, F., 1977, *Z. Naturf. (a)*, **32**, 899.
[15] HIBERT, M., and SOLLADIÉ, G., 1981, *Molec. Crystals liq. Crystals Lett.*, **64**, 211.
[16] Information available from BDH catalogues.
[17] KELKER, H., and HATZ, R., 1980, *Handbook of Liquid Crystals* (Verlag Chemie), p. 300.
[18] CARFAGNA, C., AMENDOLA, E., NICOLAIS, L., ACIERNO, D., FRANCESCANGELI, O., YANG, B., and RUSTICHELLI, F., 1991, *J. appl. Polym. Sci.*, **43**, 839.
[19] SIEBER, R. H., 1969, *Justus Liebigs Annln Chem.*, **730**, 31.