Recl. Trav. Chim. Pays-Bas 114, 470–475 (1995)
SSDI 0165-0513(95)00080-1

0165-0513/95/11/12470-06$9.50

The influence of the chiral environment in the photosynthesis of enantiomerically enriched hexahelicene.

A sudden change in the chirality of hexahelicene by a change in the temperature of a chiral crystalline medium

W.J.C. Prinsen and W.H. Laarhoven

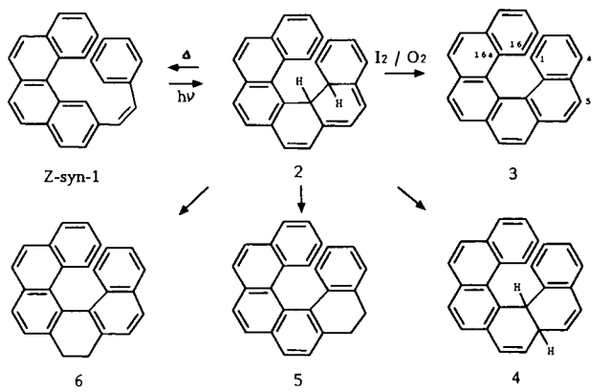
Department of Organic Chemistry, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands
(Received March 2, 1995)

Abstract. The enrichment of one of the enantiomers (*P* or *M*) of hexahelicene (**3**) synthesized by the photochemical cyclodehydrogenation of 2-styryl-benzo[*c*]phenanthrene (**1**) in chiral media has been (re)investigated. Four different chiral solvents, two cholesteric liquid crystals, two chiral crystals, all at several temperatures, and two chiral polymers were used as media. To avoid erroneous values from circular-dichroism (CD) measurements due to contributions of chiral side-products, the enantiomeric excess (*ee*) was determined by HPLC analysis.
In general the observed *ee* is small (< 7%). In chiral solvents the *ee* increases with decreasing temperatures. In the liquid crystals the macroscopic helix of the cholesteric phase has a small but distinct effect on the *ee*, probably due to the preferred fitting of one enantiomer of *Z*-**1** to the helix of the 'solvent'. In chiral crystals the *ee* is relatively larger. A peculiar effect is observed when **1** is irradiated in ethyl (*S*)-(+)-O-(4-phenylbenzoyl)lactate. Below −19°C the *M* enantiomer and above −14°C the *P* enantiomer of **3** is the preferred photoproduct. In the polymer triacetylcellulose, *M*-hexahelicene is formed in 4.5% excess; in β-cyclodextrine only a very small amount of **3** is formed, due to the preferred photo-isomerization into *E*-**1**.

Introduction

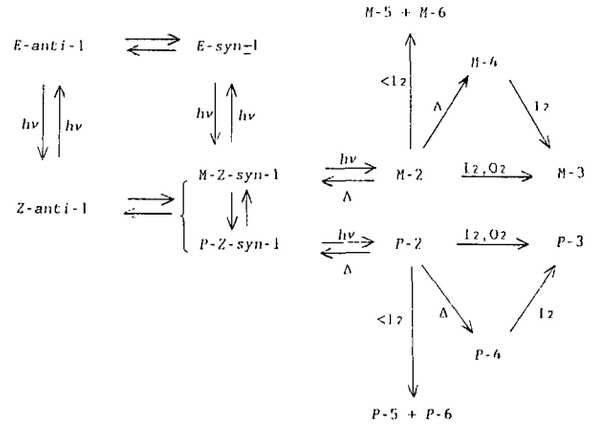
The *ortho*-annellated polycyclic aromatic compound hexahelicene [a] (**3**) has a non-planar structure due to overcrowding of the terminal rings[1]. As a consequence it occurs in two enantiomeric forms: *P*- and *M*-hexahelicene [b]. It can be obtained in high yield (80–90%) by irradiation of 2-styrylbenzo[*c*]phenanthrene (**1**) in the presence of a dehydrogenating agent. The primary photocyclization product, *trans*-16d,16e-dihydrohexahelicene (**2**) is then converted into hexahelicene[1–4] (Scheme 1). At room temperature and in the absence of any oxygen or other dehydrogenating agent, the primary photocyclization product **2** is not very stable and most of it will return to the starting material **1**. Only a minor part will rearrange by a [1,5] H shift into 6a,16d-dihydrohexahelicene (**4**)[5]. Depending on the amount and type of dehydrogenating agent other stable helicene-like compounds may be formed from **2**. Thus in the absence of oxygen, but in the presence of a very small amount of iodine (< 0.5% of **1**) 4,5-dihydrohexahelicene (**5**) and 7,8-dihydrohexahelicene (**6**) (Scheme 1) are formed[6].

The chiral configuration of the helicene skeleton is introduced and fixed by the photochemical ring closure. The *Z* isomer of **1** equilibrates between two antipodal conformers: *P*-*Z*-*syn*-**1** and *M*-*Z*-*syn*-**1** (Scheme 2). The photocyclodehydrogenation of the *P* conformer yields *P*-hexahelicene; the ring closure of the *M* conformer leads to the *M* enantiomer of **3**. In fact there is yet another *Z* isomer, the *Z*-*anti*-**1**. However, this isomer does not give rise to a photocyclization product[7]. Next to the photocyclization



Scheme 1.

[a] IUPAC name: phenanthro[3,4-*c*]phenanthrene.
[b] P (plus) denotes the enantiomer with the right-handed helix, which is dextrorotatory.



<I2 means a very small amount of iodine, see text.
Scheme 2.

reaction, there is a second photoreaction, the photoisomerization to the *E* isomer, which is the most efficient one. The complete reaction scheme is given in Scheme 2. Since in an isotropic solvent there is no preference for one of the conformers of *Z-syn*-**1** after photocyclodehydrogenation, the resulting hexahelicene is racemic.

Several attempts have been made to create conditions under which the synthetic route is changed in such a way that one of the enantiomers of **3** is formed in excess. Because of the large specific optical rotation of *P*-**3**, $[\alpha]_{25}^{D}$ 3640°, even very small values of optical yield [([α] of product/[α] of pure enantiomer) * 100%] can be determined with accuracy, provided that no interfering side-products are formed. (Optical yield corresponds with the per cent excess of one enantiomer over the other, *ee*)

Right-handed (or left-handed) circularly polarized light was used for irradiation of **1** to excite preferentially one of the conformers of *Z-syn*-**1**. By assuming that the excited conformers of *Z*-**1** are not in equilibrium, because of the increased double bond character of the single bonds in that state, an excess of one of the enantiomers of **3** was expected[8]. However, though this excess was observed, the optical yield was very small, about 0.05%. Only on using an *o*-Chloro-substituted phenyl group in **1** did the optical yield increase[8] to 0.33.

It might be expected that in a chiral solvent the equilibrium of the conformers of *Z-syn*-**1** is shifted in the direction of the conformer which fits best in that solvent. Irradiation of **1** in a chiral solvent resulted indeed in an enrichment of one enantiomer of **3**. The observed optical yields varied over a wide range (0.04–3.1), depending on the solvent and the temperature[9]. Using special chiral compounds, which contains an aromatic group in their molecular structure, as solvents leads to higher optical yields. On using ethyl (*S*)-(−)-lactate as solvent the optical yield was 0.42%; using ethyl (*S*)-(+)-O-benzoyllactate 0.84% and with ethyl (*S*)-(+)-O-(1-naphthoyl)lactate 1.6% was found[9]. Next to the effect of the chiral solvent on the equilibrium of *Z*-**1**, there might also be a difference in the rate of ring opening of *P*-**2** and *M*-**2** by the chiral solvent, which will also influence the enantiomeric excess of **3**.

A special category of chiral solvents is formed by cholesteric liquid crystals[10]. They possess a macroscopic helical structure and seem to be ideal chiral matrices for the asymmetric synthesis of **3**. There is, however, much controversy in the literature about the effect of the cholesteric phase on asymmetric synthesis. *Kagan* et al.[11] concluded, after reinvestigating several cases of asymmetric induction, that in general the effect of the cholesteric mesophase on the induction is negligible, and argued that the solute molecules are very small with respect to the pitch of the macroscopic helix, which is usually > 400nm. The solute molecules experience in their neighbourhood only a nematic chiral microstructure. Nevertheless, the results of two groups[12,13] who used cholesterol derivatives as cholesteric liquid crystals, show an increase in the optical yields of **3** when **1** was irradiated in the cholesteric phase, compared with the result in the isotropic phase of the same liquid crystals. However, the results of the two investigations are contradictory, right-handed *P*-hexahelicene is formed in a right-handed helix of the cholesteric phase in one case[12] and in the left-handed helix in the other case[13]. Because of these results and the fact that the presence of the dihydrohelicenes, mentioned above, and their contribution to the optical activity are ignored, we decided to reinvestigate the influence of liquid crystals on the optical yield of hexahelicene. To obtain optimal results, use was made of cholesteric liquid crystals, TM74 and TM75, which contain an aromatic group in their molecular structure and possess a small helical pitch. To get a better insight, some temperature-dependent irradiations of **1** in isotropic chiral solvents and crystals were also performed. Moreover two other chiral media *viz.* β-cyclodextrin and triacetylcellulose in ethanol as solvent were used as media to study the chiral induction. As in the past the presence of dihydrohexahelicenes was ignored, analysis of the product by determination of only the rotation by polarimetry or circular-dichroism (CD) measurements might lead to erroneous results. Therefore, for the analysis of the irradiation products and the enantiomeric excess (*ee*) we used the HPLC method for the separations of helicenic enantiomers[14]. By this method, using columns with silica gel coated with (*R*)-(−)-TAPA, the accuracy is not affected by contaminations in the sample. Independent CD measurements were made to observe the differences in the methods.

Materials and experimental

Materials

The synthesis of 2-styrylbenzo[*c*]phenanthrene **1** and its photocyclodehydration product hexahelicene **3** have been published previously [see references in Ref.1]. The synthesis of the chiral isotropic solvents: diethyl (*R,R*)-(+)-tartrate, diethyl (*R,R*)-(+)-O,O′-dibenzoyltartrate, ethyl (*S*)-(+)-O-(1-naphthoyl)lactate and ethyl (*S*)-(+)-O-(2-phenylbenzoyl)lactate, as well as the chiral crystalline phases ethyl (*S*)-(+)-O-(2-naphthoyl)lactate and ethyl (*S*)-(+)-O-(4-phenylbenzoyl)lactate, have also been described previously[9].

As cholesteric phases, the chiral nematic mixtures TM74 and TM75 of BDH Chemicals Ltd. were used. They consist of derivatives of biphenyl substituted with a chiral alkyl group[15,16]. The cholesteric phase of these mixtures possess a very short pitch of 230 nm. Moreover these mixtures possess a smectic phase.

Properties of the liquid crystals

The temperatures of transition from the cholesteric phase to the isotropic phase, $T_{Ch\text{-}I}$, were determined by observation of the melting process under a polarizing microscope[17]. The data on the pure mixtures TM74 and TM75 were obtained from BDH. The presence of foreign molecules and prolonged irradiation influenced the physical properties of the cholesteric mixtures as is illustrated by the data in Table 1.

The temperature dependence of the pitch (p) of TM75 containing **1** and iodine was determined before and after the photochemical conversion by calculating the wavelength (λ_{refl}) of the reflected, circularly polarized light as a function of temperature, using the relation[18–20] $\lambda_{refl} = n_m \cdot p$, in which n_m, the mean refractive index, was estimated[18] to be 1.5. The wavelength of the reflected light was determined by measurement of the transmitted light[21] outside the absorption bands of the sample (λ_{refl} > 380 nm). For the determina-

Table I Transition temperatures of the smectic to cholesteric phase ($T_{S\text{-}Ch}$) and cholesteric to isotropic phase ($T_{Ch\text{-}I}$) of the liquid crystals TM74 and TM75.

Liquid crystal mixture	$T_{S\text{-}Ch}$ (°C)	$T_{Ch\text{-}I}$ (°C)
TM74	-32.6	15.9
TM74 + 2 wt% **1** + 0.3 wt% iodine		13.5
TM74 + 2 wt% **1** + 0.3 wt% iodine after 60 h irradiation with 360 nm light		11
TM75	41.3	53.2
TM75 + 2 wt% **1** + 0.3 wt% iodine	36	49
TM75 + 2 wt% **1** + 0.3 wt% iodine after 60 h irradiation with 360 nm light	28	42

tion of the pitch of a cholesteric mixture with $\lambda_{refl} < 380$ nm, the optical-rotary-dispersion (ORD) method of *Stegemeyer* et al.[22-24] was used. The handedness of the pitch of the cholesteric mixture TM75 was deduced from the ORD measurements according to the method of *de Vries*[20]. TM75 has a right-handed helix. TM74 also has a right-handed helix, as could be deduced from the properties of the cholesteric phase[25] of a mixture of TM74 and TM75.

General experimental procedure

A 2% (by weight) solution of **1** in the chiral medium to which 15–20 mol% (relative to **1**) of iodine had been added, was prepared. In the case of a liquid-crystalline or crystalline medium, the mixture was heated slightly above the melting point. About 150 mg of the solution was sandwiched in a cell, consisting of two pyrex plates separated by a 0.1-mm teflon spacer. To ensure a planar alignment of the preparation of the liquid-crystalline sample, (helical axis perpendicular to the plates), the upper plate was carefully polished by rubbing it several times in a single direction with a lens tissue[26]. The desired temperature was obtained by placing the cell in an alumina holder on a thermostatted copper block. A stream of dry air was applied above the cell to avoid any overheating during irradiation or the formation of ice on the cell at low temperatures. The sample was exposed to 360-nm UV light from a fluorescent tube (Sylvania F15T6-BL) at a distance of 5 cm for 60 h. After irradiation the chiral solvent was removed by flash chromatography on silica gel with n-hexane as eluent. HPLC analysis on a reversed phase column demonstrated that, apart from hexahelicene, the purified sample contained the *Z* and *E* isomer of the precursor **1** and the two dihydrohexahelicenes **5** and 6[c]. To remove **1**, the sample, after removal of the chiral solvent, was dissolved in 2 ml of a mixture of water and methanol (1/9) and injected on a Lobar column (Merck, size A: 20×240 mm) packed with LiChroprep RPS (size 40–63 μm; mobile phase: water/methanol (1/9); flow rate 2 ml/min). The fraction containing hexahelicene was analysed by HPLC on a LiChrospher RP18 column to ensure that the sample was completely free from the precursor **1**, because the peaks of *cis*- and *trans*-**1** overlapped the peaks of the enantiomers of **3**. No effort was made to separate **3** completely from the two dihydrohexahelicenes **5** and **6**, since these compounds did not interfere with the determination of the enantiomeric excess (*ee*) of **3**. The value of the *ee* (% of **3**) in a sample could be determined with an accuracy of 0.3%. (The procedure for the determination of the accuracy is given in Ref. 14.) The complete experimental procedure was tested with racemic hexahelicene as substrate in all the chiral solvents used. Enantiomeric enrichment of **3** due to this procedure was never observed.

Apparatus

UV spectra were measured with a Perkin-Elmer 555 spectrophotometer. CD spectra were measured with a Jouan Dichrograph Model Mark III and the ORD spectra with a Jasco spectrometer. A Perkin-Elmer 241 polarimeter was used for the measurements of optical rotations. A Leitz melting point microscope was used for the determination of the transition temperatures of the phases of the liquid crystals.

Differential-scanning-calorimetry (DSC) measurements were performed on a Setaram III instrument at the department of Thermodynamics of the University of Utrecht.

HPLC analysis was performed on a Spectra-Physics HPLC system, made up of a solvent delivery system (SP8700) equipped with a 254 nm detector (SP8300) and a computing integrator (SP4100). The modification of the HPLC columns with TAPA and details of the separation have been described previously[14].

Results and discussion

Chiral isotropic solvents

Although in our former experiments the influence of the chiral solvent was clearly demonstrated[9], it could not be predicted beforehand whether or not the differences in experimental procedure [irradiations in tubes instead of between pyrex plates and only polarimetric determination of the enantiomeric excess (*ee*) instead of the HPLC method] were of decisive influence on the observed *ee* values. Therefore the measurements were repeated under the new conditions and at several temperatures.

In isotropic solvents the solutes: **1**, iodine and oxygen, are more homogeneously distributed than in liquid crystals or in crystalline phases. Nevertheless, the dihydrohexahelicenes **5** and **6** are formed under the experimental condition used. This may be due to the relatively thin layer between the pyrex plates, from which oxygen can easily escape. The results of the irradiations at different temperatures are collated in Table II.

The observed *ee* of the formed hexahelicene at room temperature is in all but one case [ethyl (*S*)-(+)-O-(1-naphthoyl)lactate] the same as found previously[9]. The difference can be explained by the isolation technique of the helicene by TLC, used previously[9]. When the separation of the bands in the chromatogram is good the purity of the isolated **3** is also good. When there is some overlap with small bands of side-products or chiral solvent, the purity of **3** is less good. Although the effect of temperature is not very large, an increase of the *ee* at lower temperature is evident.

Cholesteric liquid crystals

In Tables III and IV the results of irradiation of **1** in the liquid crystals TM74 and TM75 are given.

The results show that *P*-hexahelicene is the preferential enantiomer in all samples. Because the values for the *ee* of **3** were less than 1% in all samples, we used the extended HPLC analysis[14], combining the peak area and the peak height, to minimize the experimental error. In addition we attempted to determine the *ee* of **3** by means of the measurement of the CD of the sample, neglecting the influences of the two dihydrohexahelicenes, **5** and **6**, on the CD spectrum. By relating the CD of the sample to the molar ellipticity of **3**[27] the *ee* of **3** could be calculated. The discrepancies between the values derived from CD and those obtained from HPLC (see Tables) prove that the CD method is unreliable.

Comparison of the *ee* values obtained in the isotropic phases of TM74 and TM75 with those in the chiral liquids in Table II, reveals a smaller effect in the former cases. From the data in Tables III and IV it follows that the smectic phases, which are more ordered than the cholesteric phases, induce higher *ee* values than the isotropic phases, but lower ones than observed in the cholesteric phases. The *ee* obtained in the cholesteric

[c] *Hibert*[12] noticed, that some of the samples of hexahelicene obtained from the cholesteric phases were contaminated with a dihydrohexahelicene. He suggested that it was the intermediate **2**, but taking into account that it is not possible to isolate this highly unstable compound, it is very likely that the sample contained the dihydrohexahelicenes **5** and/or 6.

Table II Enantiomeric excess (ee) obtained in the asymmetric synthesis of hexahelicene in four chiral isotropic solvents at various temperatures.

Chiral Solvent	temp. [a] (°C)	*ee* [b] HPLC	*P*/*M* [c]
diethyl (*RR*)-(+)-tartrate	−33	2.7	M
	−25	1.9	M
	+16	1.0	M
	+51	0.3	M
diethyl (*RR*)-(+)-*O*,*O*′-dibenzoyltartrate	−25	1.1	P
	− 6	1.0	P
	+16	1.1	P
	+51	0.4	P
ethyl (*S*)-(+)-*O*-(1-naphthoyl)lactate	−60	1.0	M
	−33	1.3	M
	− 6	0.8	M
	+ 5	0.8	M
	+51	0.4	M
ethyl (*S*)-(+)-*O*-(2-phenylbenzoyl)lactate	−33	1.6	M
	− 6	1.0	M
	+16	0.3	M
	+51	0.5	M

[a] ±1°C. [b] ±0.3%. [c] Enantiomer of **3** preferentially formed.

phases reveals a small but significant increase of 0.5-0.8%. In accordance with the results of *Hibert*[12] the right-handed cholesteric phases promote the formation of right-handed *P*-hexahelicene. The effect of the macroscopic helix of the cholesteric phases becomes more important as the pitch is shorter, which follows from a comparison of the results in cholesterol esters, with pitches of 1600–4900 nm and an *ee* of about 0.4%[12], with the present results.

The observed influence of the cholesteric phase is not readily explained, when taking into account the arguments of molecular dimensions and the heat of phase transitions of the cholesteric phase. The two-dimensionally ordered smectic phase, which is closer to a crystalline phase, should induce a higher *ee* than the cholesteric phase, in which the solute molecules of the precursor 'see' a nematic phase with a one-dimensional arrangement at the molecular level. The higher *ee* values found in the cholesteric phases must be caused by its macroscopic, helical arrangement. This leads to the question as to how the solute molecules 'experience' the helical structure of the cholesteric phase. Some possibilities may be considered.

(*a*) Circularly polarized light (CPL) might be generated by the cholesteric phase. Although this might be responsible for some chiral induction in our experiments, the effect will only be very small, because CPL induces only a slight *ee* in isotropic solvents (see introduction). Moreover, the results of *Hibert*[12] cannot be explained in this way, because a cholesteric phase with a pitch of > 1600 nm cannot generate a wavelength in the range 300–400 nm.

(*b*) The cholesteric phase could influence the absorption of light by the conformers of **1** by the liquid crystal induced circular dichroism (LCICD) effect. This LCICD effect has been demonstrated by achiral molecules, such as anthracene, dissolved in cholesteric liquid crystals, which display induced CD corresponding to their own absorption bands[28–30]. This effect suggests that the absorption of light can be influenced by the macroscopic helix of the cholesteric phase, although the solute molecules experience in their neighbourhood a nematic microstructure. Such a difference in absorption should account for the effect of the cholesteric phase on the asymmetric induction.

(*c*) The third possibility for asymmetric induction by a cholesteric phase is at the molecular level. The cholesteric phase provides a helical matrix, into which one of the conformers of **1** has a better fit. It is known that chiral compounds induce a cholesteric phase in a nematic liquid crystal. Solladie studied the conversion of nematic phases into cholesteric phases by optically active compounds[31,32], and found that biaryl derivatives with a *P* helicity induce a cholesteric phase of the same *P* helicity in a nematic phase of 4′-pentylbiphenyl-4-carbonitrile (an achiral isomer of a component of TM74 and TM75). He argued that the *P* helicity of the chiral inducer is transferred to a nearby molecule of the liquid crystal and from this to the next one and so on, via chiral conformations. Therefore, the *P* helicity of the induced cholesteric phase is the result of a chiral distortion at the molecular level. The mechanism of the induction of a cholesteric phase by chiral compounds implies a connection between a chiral distortion at the molecular level and the chiral macroscopic arrangement of the cholesteric phase. In the case of the precursor **1** in a cholesteric phase with *P* helicity, such a chiral distortion will favour the *P* conformer of **1** and induce the formation of hexahelicene enriched in the *P* enantiomer. The present observations are consistent with this explanation for the chiral induction in a cholesteric phase.

Chiral Crystals

Because of the scattering of light by crystals, the photochemical conversion of **1** into **3** is much slower than in other phases. The procedure described above was slightly adapted by increasing the amount of iodine to 100% relative to **1**, to overcome the lower accessibility for oxy-

Table III The enantiomeric excess (ee) of P-hexahelicene (P-3) obtained by irradiation of 2-styrylbenzo[c]phenanthrene 1 in the liquid crystal TM74.

	Phase		*ee* of **3** (%)		Composition of product mixture (%)		
Temp. [a] (°C)	Type [b]	Pitch [c] (nm)	HPLC [d]	CD [e]	**3**	**5**	**6**
−33	smectic	–	0.4	0.1	83	7	10
−25	chol.	260	0.8	0.3	47	41	12
−19	chol.	240	0.6	0.1	33	44	23
−14	chol.	230	1.0	0.9	58	25	17
−10	chol.	230	0.8	0.2	71	15	14
− 6	chol.	230	0.7	0.4	25	44	31
− 1	chol.	230	0.8	0.3	54	31	15
− 5	chol.	230	0.9	0.5	43	31	26
+10	chol	230	0.9	0.3	30	35	35
+24	isotr.	–	0.1	0.1	80	11	9
+51	isotr.	–	0.2	0.2	75	10	15

[a] ±1°C. [b] chol. = cholesteric; isotr. = isotropic. [c] ±10 nm. [d] ±0.2%. [e] ±0.1%.

Table IV The enantiomeric excess (ee) of P-hexahelicene (P-3) obtained by irradiation of 2-styrylbenzo[c]phenanthrene 1 in the liquid crystal TM75.

	Phase			*ee* of **3** (%)		Composition of product mixture (%)		
Temp. [a] (°C)	Type [b]	Pitch [c] (nm) 1	2	HPLC [d]	CD [e]	**3**	**5**	**6**
+15	smectic	–	–	0.4	0.4	90	8	2
+24	smectic	–	–	0.4	0.3	85	10	5
+35	smectic/chol.	–	240	0.6	0.2	37	27	36
+36	smectic/chol.	–	230	0.6	0.4	66	16	18
+38	chol.	330	230	0.5	0.2	49	27	24
+39	chol.	270	230	0.5	0.4	51	15	34
+45	chol./isotr.	230	–	0.8	0.5	58	17	25
+62	isotr.	–	–	0.1	0.0	98	1	1

For notes see Table III.
1: pitch before irradiation; 2: pitch after irradiation of the mixture.

gen. The molten mixture, about 150 mg, was placed between the pyrex plates of the cell and allowed to crystallize. After irradiating for 150 h at 360 nm, 20–30% of the precursor had been converted into hexahelicene **3**. This amount was sufficient for chromatographic isolation and determination of the *ee* by HPLC. However, the accuracy was only 0.5% due to the small amount of **3** that could be isolated. The *ee* was determined independently by CD measurements. Two chiral crystalline phases, ethyl (*S*)-(+)-O-(2-naphthoyl)lactate (mp 64–65°C) and ethyl (*S*)-(+)-O-(4-phenylbenzoyl)lactate (mp 88–89°C), were studied at several temperatures. The results are presented in Table V.

As expected for these highly ordered chiral environments, the *ee* is relatively high (up to 7%). The CD and HPLC determinations are consistent when the contamination of the sample with dihydrohexahelicenes is small. A temperature dependence of the *ee* is observed in both crystalline phases. In ethyl (*S*)-(+)-O-(2-naphthoyl)lactate the *ee* decreases with increasing temperature while in ethyl (*S*)-(+)-O-(4-phenylbenzoyl)lactate a decrease of the excess of the preferential *M* enantiomer with increasing temperature is only observed up to −19°C; above −14°C the *P* enantiomer is the preferred product. The sudden change of the preferred product is fully reproducible. A similar temperature effect has previously been reported for the chemically induced asymmetric photosynthesis of a hexahelicene derivative[33]. It suggests a change in the crystal structure of the medium. In order to check this, crystal structure analyses of the solid solvent were performed at two temperatures, −25°C and +20°C respectively[34]. A comparison of the two structure determinations shows that neither the crystal structure nor the molecular configuration is affected by the change in temperature. This conclusion is corroborated by differential scanning calorimetry (DSC). A DSC measurement of 60 mg of the solid solvent did not detect any phase transition in the range −70 to +80°C. A change in the crystal structure involving an enthalpy of transition of more than 0.1 kJ/mol would have been detected by the DSC measurement. However, these results do not exclude the possibility that a guest molecule **1**, which replaces a molecule in the crystal structure, does change its preferential conformation at the given temperature. Assuming that the difference in *ee* depends only on the preferred conformation of the crystalline solvent, this suggestion is corroborated by the difference in entropies of activation below and above −14°C calculated from the observed enantiomeric excess. In Figure 1 this is illustrated by a plot of the temperature (*T*) *versus* $-RT \ln (K^*)$, where K^* = equilibrium constant, $k(P)/k(M) = 0.5\ (100 + ee)/0.5\ (100 - ee)$, according to the equation $-RT \ln (K^*) = \Delta G^* = \Delta H - T\Delta S^*$.

It had to be expected that without a change in conformation no sudden change in entropy of activation will occur. The change of the entropy as shown in Fig. 1 is an indication that a change in the system of crystalline solvent and **1** takes place around −14°C.

Triacetylcellulose and β-cyclodextrin

These two compounds were used in preliminary experiments to observe the photochemical behaviour of **1** adsorbed on a powder of chiral polymers. To this aim a solution of 5 mg of **1** in 250 ml of ethanol to which 5 g of the polymer was added was refluxed for 3 h after which the ethanol was evaporated *in vacuo*. The resulting dry powder was irradiated for 60 h with 300 nm light at room temperature in a rotating pyrex vessel. After irradiation the powder was extracted three times with ethanol. The

Table V The enantiomeric excess (ee) of hexahelicene (3) obtained by irradiation of 2-styrylbenzo[c]phenanthrene (1) in two chiral crystalline media.

	ee of **3** (%)			Composition of product mixture (%)		
Temp [a] (°C)	*P*/*M* [b]	HPLC [c]	CD [d]	**3**	**5**	**6**
	ethyl (S)-(+)-O-(2-naphthoyl)lactate					
−26	*M*	5.9	5.2	64	14	22
−19	*M*	5.3	5.4	84	11	5
+16	*M*	1.7	1.6	92	1	7
+51	*M*	3.0	3.1	99	–	1
	ethyl (S)-(+)-O-(4-phenylbenzoyl)lactate					
−26	*M*	6.8	5.3	78	5	17
−24	*M*	5.0	4.4	94	2	4
−19	*M*	4.1	3.5	89	5	6
−14	*P*	2.6	2.3	78	9	13
+16	*P*	2.8	2.2	90	4	6
+51	*P*	3.0	2.2	91	2	7

[a] ±1°C. [b] Enantiomer of **3** preferentially formed. [c] ±0.5%. [d] ±0.2%.

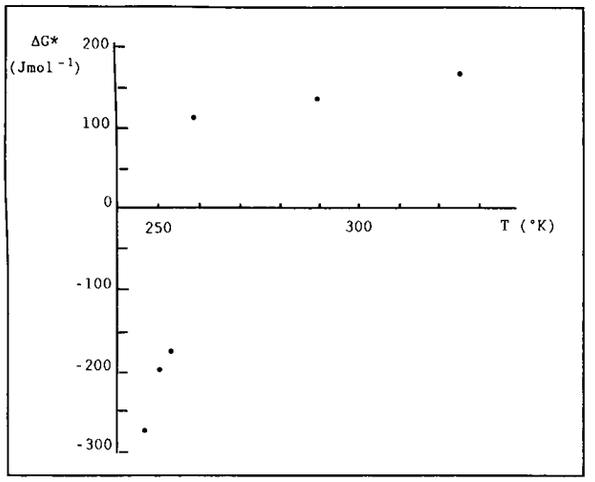


Figure 1. Plot of temperature vs. ΔG, derived from the enantiomeric excess (ee) of hexahelicene (3) in ethyl(s)-(+)-O-(4-phenylbenzoyl)lactate.*

ethanol of the combined fractions was evaporated *in vacuo* and the residue analyzed by HPLC on a reversed phase column.

The analysis of the sample obtained from triacetylcellulose demonstrated that 20% of **1** had been converted into hexahelicene, which had an *ee* value of 4.5% in favour of the *M* enantiomer.

The sample obtained from β-cyclodextrin contained less than 1% hexahelicene. The *trans / cis* ratio of **1** had increased from about 3 to 20. As only the *cis* isomer of **1** can be converted photochemically into **2** (the precursor of **3**), the large excess of the *trans* isomer will delay the conversion of **1** into hexahelicene.

Conclusion

Notwithstanding the generally low optical yield of the photoproduct hexahelicene, the influence of the medium is undeniable. The increase of the *ee* with decreasing temperature can be explained by the increase of the lifetime of the primary photoproduct **2** and a change in the equilibrium between *M-Z-syn*-**1** and *P-Z-syn*-**1**. The overall low yield might be a result of the combination of a small difference between the association constants of *P*- and *M-Z-syn*-**1** and a high rate of interconversion between these enantiomers. The high mobillity of molecules adsorbed to a solid is well known from other experiments[35]. The peculiar results of the change in the preference for a certain enantiomer caused by a change in the temperature of the solid medium ethyl (*S*)-(+)-O-(4-phenylbenzoyl)lactate may be explained by a change in the preferred conformation of the 'solvent' induced by the presence of a guest molecule.

Acknowledgement

We thank Prof. Dr. *H. Stegemeyer*, Institute of Physical Chemistry, University Paderborn, for his help with the experiments on liquid crystals and for his hospitality; Dr. *J.C. Miltenburg*, Department of Thermodynamics, Utrecht, for performing the DSC measurements; Dr. *H.P.J.M. Dekkers*, Gorlaeus Laboratory, Leiden for his help and for the use of the apparatus for the CD spectra and Prof. Dr. *P.T. Beurskens*, Crystallography Laboratory, Nijmegen for the crystallographic measurements.

References

[1a] *R.H. Martin*, Angew. Chem. Int. Ed. Engl. **13**, 649 (1974);
[b] *W.H. Laarhoven* and *W.J.C. Prinsen*, Top. Curr. Chem. **125**, 63 (1984).
[2] *K.A. Muszkat*, Top. Curr. Chem. **88**, 89 (1980).
[3] *W.H. Laarhoven*, Recl. Trav. Chim. Pays-Bas **102**, 185; 241 (1983).
[4] *W.H. Laarhoven*, Organic Photochemistry, Vol. 10, *A. Padwa*, Ed. Marcel Dekker, New York, 1989, p.163.
[5] *W.H. Laarhoven, Th.J.H.M. Cuppen* and *H.H.K. Brinkhof*, Tetrahedron **38**, 3179 (1982).
[6] *W.J.C. Prinsen* and *W.H. Laarhoven*, J. Org. Chem. **54**, 3689 (1989).
[7] *W.H. Laarhoven, Th.J.H.M. Cuppen* and *R.J.F. Nivard*, Tetrahedron **26**, 4865 (1970).
[8] *W.J. Bernstein, M. Calvin* and *O. Buchardt*, J. Am. Chem. Soc. **95**, 527 (1973).
[9] *W.H. Laarhoven* and *Th.J.H.M. Cuppen*, J. Chem. Soc., Perkin **II**, 315 (1978).
[10] *G.W. Gray* and *P.A. Wilson*, in 'Liquid Crystals and Plastic Crystals' Vol.1, Ellis Horwood Ltd., Chichester (1974).
[11] *C. Eskenazi, J.F. Nicoud* and *H.B. Kagan*, J. Org. Chem. **44**, 995 (1979).
[12] *M. Hibert* and *G. Solladie*, J. Org. Chem. **45**, 5393 (1980).
[13a] *M. Nakazaki, K. Yamamoto* and *K. Fujiwara*, Chem. Lett. 863 (1978);
[b] *M. Nakazaki, K. Yamamoto, K. Fujiwara* and *M. Maeda*, J. Chem. Soc. Chem. Comm. 1086 (1979).
[14] *W.J.C. Prinsen* and *W.H. Laarhoven*, J. Chromatography **393**, 377 (1987).
[15] *G.W. Gray* and *D.G. McDonnell*, Mol. Cryst. Liq. Cryst. **37**, 189 (1976).
[16] *G.W. Gray* and *D.G. McDonnell*, Mol. Cryst. Liq. Cryst. **48**, 37 (1978).
[17] *D. Demus* and *L. Richter*, 'Textures of Liquid Crystals' Verlag Chemie, Weinheim, (1978).
[18] *J.L. Fergason*, Mol. Cryst. Liq. Cryst. **1**, 293 (1966).
[19] *C. Oseen*, Trans. Faraday Soc. **29**, 883 (1966).
[20] *H. de Vries*, Acta Crystallogr. **4**, 219 (1951).
[21] *H. Baesler* and *M.M. Labes*, Mol. Cryst. Liq. Cryst. **6**, 419 (1970).
[22] *H. Stegemeyer* and *K.J. Mainusch*, Chem. Phys. Lett. **6**, 5 (1970).
[23] *H. Stegemeyer* and *K.J. Mainusch*, Chem. Phys. Lett. **16**, 38 (1972).
[24] *H. Stegemeyer* and *H. Finkelmann*, Chem. Phys. Lett. **23**, 227 (1973).
[25] *G.W. Gray* and *D.G. McDonnell*, Mol. Cryst. Liq. Cryst. **44**, 211 (1977).
[26] *F.D. Saeva* and *G.R. Olin*, J. Am. Chem. Soc. **98**, 2709 (1976).
[27] *M.S. Newman, R.S. Darlak* and *L.L. Tsai*, J. Am. Chem. Soc. **89**, 6191 (1967).
[28] *F.D. Saeva* and *J.J. Wysocki*, J. Am. Chem. Soc. **93**, 5928 (1971).
[29] *F.D. Saeva*, Mol. Cryst. Liq. Cryst. **18**, 375 (1972).
[30] *F.D. Saeva, P.E. Sharpe* and *G.R. Olin*, J. Am. Chem. Soc. **95**, 7656 (1973).
[31] *G. Solladie* and *R. Zimmermann*, Angew. Chem. **96**, 335 (1984).
[32] *G. Solladie* and *G. Gottarelli*, Tetrahedron **43**, 1425 (1987).
[33] *J.-M, Vanest* and *R.H. Martin*, Recl. Trav. Chim. Pays-Bas **98**, 113 (1979).
[34] *W.H. Laarhoven, W.J.C. Prinsen, H. Behm, W.P. Bosman* and *P.T. Beurskens*, J. Cryst. Spectr. Res. **19**, 215 (1989).
[35] *A. Tol* and *W.H. Laarhoven*, J. Org. Chem. **51**, 1663 (1986).