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The effect of substituents on the helical twisting power of aldol condensation products of menthone

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The helical twisting powers of the *E*-isomers of aldol condensation products of menthone and aromatic aldehydes are higher than those of the *Z*-isomers. In order to find out which chiral centre of these menthone derivatives is responsible for the value of the helical twisting in both isomers, the *E*-isomers of aldol condensation products of 3-methylcyclohexanone and 2-isopropylcyclohexanone were prepared and photoisomerized to form *Z*-isomers. The physical properties of these species were determined. It was concluded that the strong helical twisting power of the *E*-isomers of the derivatives of menthone is caused by the chiral carbon atom containing the methyl group in the ring. The relatively low helical twisting power of the *Z*-isomers and the composition of the *E*–*Z* isomers in the photostationary state are determined mainly by the other chiral centre containing the isopropyl group.

1. Introduction

Cholesteric liquid crystalline materials have received much attention due to their capability of reflecting circularly polarized light. On the basis of this property several applications have been explored, ranging from paints to organic broadband mirrors [1, 2]. The reflection colour can be chosen via the ratio of nematic and chiral material. The colour can subsequently be changed after applying such a mixture by making use of the thermochromic effect [3] or diffusion techniques [4]. In the latter case it is possible to make materials which reflect different colours in different areas after polymerization of the mixture. Another way of making patterned colour reflectors is by using photochromic systems in which the helical twisting power of the chiral component can be tuned by means of ultraviolet irradiation. On the basis of this process, Shibaev *et al.* [5] and Van de Witte *et al.* [6, 7] prepared polymers of which the reflection wavelength could be changed from the UV to the infrared by simply changing the UV dose. The chiral component of these polymers was derived from menthone, which undergoes an *E* to *Z* isomerization under irradiation. This isomerization is accompanied by a large drop in helical twisting power (HTP). Meanwhile several applications of these polymers have been explored [7, 8].

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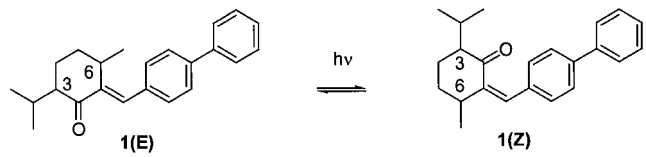
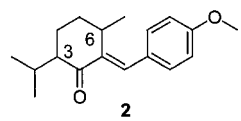
The HTP change that occurs upon irradiation of menthone derivatives in liquid crystalline mixtures was first reported by Yarmolenko *et al*: [9]





The HTP of **1**(***E***) in 5CB is $-37\,\mu m^{-1}$ while that of **1**(***Z***) is only $-1\,\mu m^{-1}$. **1**(***E***) contains two chiral centres. With the aid of X-ray analysis of compound **2**, it was shown that 3R, 6R epimers are obtained in simple aldol condensation reactions of menthone with aromatic aldehyde [10]. Carbon 3 is epimerized with respect to its original configuration in menthone, a process which proceeds very quickly under the reaction conditions, resulting in derivatives like **1** and **2**. The 3S, 6R epimer of **1** was obtained via a more complex synthetic route [11]. This compound exhibits the same HTP as the 3R, 6R epimer. A compound similar to **1** and **2**, but whose biphenylyl group has been replaced by a 4-bromophenyl group, exhibits a HTP of $-28\,\mu m^{-1}$. When the hydrogen

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atom at position 3 was substituted by a methyl group or by bromine, only minor changes in the HTP were observed [12]. Isomerization experiments have not been performed with the latter compounds. From these results it can be concluded that chiral centre 6 in **1*E*** is mainly responsible for the high HTP of this compound.

Another way to investigate the contribution of each chiral centre to the HTP of this class of compounds is by studying compounds which contain only one of the chiral centres. Furthermore, with respect to the application of photochromism, it is also interesting to study the effect of these substituents on the HTP change upon irradiation. For these reasons we decided to prepare model compounds **3–6** (see scheme 1) and perform HTP measurements before and after irradiation.

2. Experimental

2.1. *Materials and methods*

E7 (a mixture of nematic liquid crystal materials derived from cyanobiphenyl) and S811, (*S*)-1-methylheptyl 4-(4-hexyloxybenzoyloxy)benzoate, were obtained from Merck. 2-Isopropylcyclohexanone was prepared according to Stork *et al.* [13] 4-(1-Ethoxyethoxy)-benzaldehyde (**9**) was prepared in a similar manner to that described for 4-(tetrahydropyran-2-yloxy)benzaldehyde [8]. All the other chemicals were obtained from Aldrich.

UV spectra were recorded with the aid of a Unicam UV2-100 spectrometer using acetonitrile solutions. NMR spectra were recorded with the aid of a Bruker DP300 spectrometer using deuteriated dichloromethane solutions. The ^{1}H spectra were interpreted with the aid of ^{1}H-^{13}C-correlation spectra. The ^{1}H and ^{13}C NMR data were fully consistent with the required structures and purity of all final products.

The enantiomeric excesses of compounds **5** and **6** were determined with the aid of chiral HPLC—Chiralcel OD ($250 \times 4.6\,mm^2$, Daicel) column using a 95/5 heptane/ethanol mixture as the eluant.

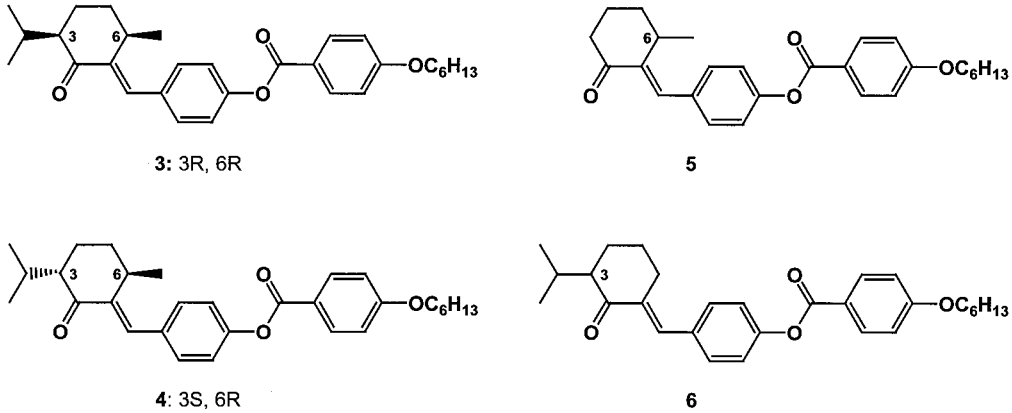
The helical twisting power was determined using the Grandjean–Cano method [14]. Wedge cells (EHC Japan, tan $\alpha = 0.0083$) were filled with solutions of compounds **3–6** in E7 and solutions of compounds **3–6** with S811 in E7 (in order to determine the sign of the HTP). The distance between disclination lines was measured before and after irradiation with 365 nm light.

2.2. *Synthesis*

2.2.1. *Synthesis of 4-([S]-3-isopropyl-[R]-6-methyl-2-oxo-cyclohexylidenemethyl)phenyl 4-hexyloxybenzoate (**4**)*

A solution of 5.2 g of 4-([*R*]-3-isopropyl-[*R*]-6-methyl-2-oxo-cyclohexylidenemethyl)phenol (**7**) and 0.2 g of perchloric acid in 80 ml of dioxane was stirred at 40°C for 2 h. After cooling it was added dropwise to 200 ml of water. The solid formed was collected on a filter and dried over silica in vacuum. ^{1}H NMR analysis revealed that it was a 2:1 mixture of the starting compound and its epimer: 4-([*S*]-3-isopropyl-[*R*]-6-methyl-2-oxo-cyclohexylidenemethyl)phenol (**8**).

3.2 g of the mixture of **7** and **8**, 2.7 g of 4-hexyloxybenzoic acid, 0.15 g of 4-*N*,*N*-dimethylaminopyridine and 35 ml of dichloromethane were cooled together in an ice bath. 2.8 g of *N*,*N*′-dicyclohexylcarbodiimide was added and the mixture was stirred for one more hour in the ice bath. After removal of the ice bath, stirring was continued for one day at room temperature. The crude product, obtained after removing *N*,*N*′-dicyclohexylurea by filtration and evaporation of the dichloromethane, was eluted with dichloromethane through silica. Compound **3** was obtained from the first fractions and compound **4** from the following fractions. 0.3 g of pure **4** was obtained after crystallization from methanol.



Scheme 1. Structures of compounds **3–6**.

2.2.2. *Synthesis of 4-(6-methyl-2-oxo-cyclohexylidene-methyl)phenyl 4-hexyloxybenzoate (**5**)*

A mixture of 67 mg of cupric triflate, (3,5-dioxa-4-phospha-cyclohepta[2,1-*a*;3,4-*a*′]dinaphthalen-4-yl)-bis(1-phenylethyl)amine [15] and 95 ml of toluene was cooled to −40°C. Subsequently were added: 3.0 g. of 4-(1-ethoxyethoxy)benzaldehyde (**9**) and 1.5 ml of cyclohexenone, followed slowly by 8.5 ml of a 2M solution of dimethylzinc in toluene. The mixture was stirred for 2 days at −40°C and then poured into 100 ml of saturated aqueous sodium chloride. 4.3 g of 2-{[4-(1-ethoxyethoxy)-phenyl]hydroxymethyl}3-methylcyclohexanone (**10**) (81%) was obtained after extraction of the mixture with 100 ml of ether, drying over magnesium sulphate and evaporation.

A solution of 3.5 g of compound **10** and 7.6 g of triethylamine in 50 ml of dichloromethane was cooled to 0°C. 4.15 g of methanesulphonyl chloride was added dropwise. After stirring for 4 h at room temperature, the mixture was poured into a mixture of 50 ml of toluene and 50 ml of water. The organic layer was washed with water, dried over magnesium sulphate and the low boiling dichloromethane evaporated. To the remaining toluene solution containing **11**, was added 7.5 g of diazabicycloundecene. This solution was heated at 75°C for 2 h. After cooling it was successively washed with 50 ml of 2.5M hydrochloric acid and 50 ml of water, dried over magnesium sulphate and evaporated. The crude product **12** obtained in this way was dissolved in 100 ml of methanol. After addition of 400 mg of pyridinium 4-toluenesulphonate, it was heated at 50°C for 1 h. After addition of 100 ml of water, the mixture was shaken with 100 ml of toluene; the toluene solution was washed with 100 ml of water, dried over magnesium sulphate and evaporated. 4-(6-Methyl-2-oxo-cyclohexylidene-methyl)phenol (**13**) (1.6 g, 73%) was obtained after elution through silica with dichloromethane containing 2% of methanol.

0.75 g of compound **13**, 0.80 g of 4-hexyloxybenzoic acid, 60 mg of 4-*N*,*N*-dimethylaminopyridine and 25 ml of dichloromethane were cooled in an ice bath. 0.72 g of *N*,*N*′-dicyclohexylcarbodiimide was added and the mixture was stirred for another hour in the ice bath. After removal of the ice bath, stirring was continued for one day at room temperature. The crude product, obtained after filtration through a thin silica layer followed by evaporation of the dichloromethane, was recrystallized from methanol. Compound **5** (0.5 g, 36%) was obtained as white crystals.

2.2.3. *Synthesis of 4-(3-isopropyl-2-oxo-cyclohexylidene-methyl)phenyl 4-hexyloxy-benzoate (**6**)*

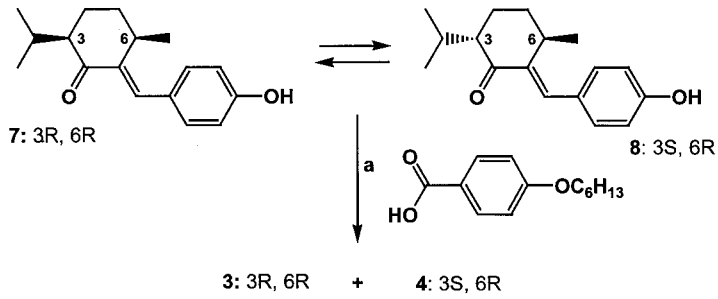
To a solution of 64 g of 4-(1-ethoxyethoxy)-benzaldehyde (**9**) and 40 g of 2-isopropylcyclohexanone in 200 ml of tetrahydrofuran was added 10 g of potassium *t*-butoxide. After stirring for 2 days, the mixture was poured into 400 ml of water and shaken with 400 ml of toluene. The toluene extract was washed twice with 200 ml of water, dried over magnesium sulphate and evaporated. The crude intermediate 2-[4-(1-ethoxyethoxy)-benzylidene]-6-isopropylcyclohexanone (**14**) was obtained after elution through a short aluminium oxide column with hexane. It was then mixed with 120 ml of tetrahydrofuran, 10 ml of water and 500 mg of 4-toluenesulphonic acid. After stirring this mixture for 2 h, 400 ml of water and 200 ml of ethyl acetate were added. After separation, the ethyl acetate layer was washed with 200 ml of water, dried over magnesium sulphate and evaporated. The crude product was eluted through silica with toluene, giving 23.8 g of 4-(3-isopropyl-2-oxo-cyclohexylidenemethyl)phenol (**15**) (36%) as a white solid.

3.0 g of compound **15**, 2.7 g of 4-hexyloxybenzoic acid, 0.15 g of 4-*N*,*N*-dimethylaminopyridine and 35 ml of dichloromethane were cooled in an ice bath. 2.8 g of *N*,*N*′-dicyclohexylcarbodiimide was added and the mixture was stirred for another hour in the ice bath. After removal of the ice bath, stirring was continued for one day at room temperature. The crude product obtained after filtration through a thin layer of silica and evaporation of the dichloromethane was recrystallized from ethanol. 4.1 g of the racemic mixture of **6** (76%) was obtained as white crystals. Both enantiomers (100 mg) were obtained from 240 mg after separation by means of chiral HPLC, using a Chiralcel OD ($250 \times 20\,mm^2$, Daicel) column and a 95/5 heptane/ethanol mixture as the eluant.

3. Results and discussion

3.1. *Synthesis*

Compound **3** was prepared by esterification of **7** with 4-hexyloxybenzoic acid as described in [8]. Both **7** and **3** have the 3R, 6R configuration typical of the condensation products of menthone with aromatic aldehydes. They exhibit typical ^{1}H NMR signals at 2.5 and 2.2 ppm corresponding to the methine proton of the isopropyl group and the methine proton at the α position of this isopropyl group, respectively (see table 1). These signals were observed in the same region as those of the condensation product of anisaldehyde and menthone **2**, for which the absolute configuration has been determined by X-ray measurements [10]. In order to obtain **8**, compound **7** whose carbon-3 has the R configuration, was epimerized with the aid of acid (see scheme 2). An equilibrium mixture was obtained containing **7** and **8** in a 2:1 ratio. In the ^{1}H NMR spectra, the olefinic proton of **7** was observed at 7.1 ppm and that of **8** at 7.0 ppm.



Scheme 2. Epimerization of **7** and **8** and formation of **3** and **4** from **7** and **8**, respectively. *a*: $HClO_4$ in dioxane.

Table 1. ^{1}H NMR (δ in ppm) data for the *E*- and *Z*-isomers of compounds **3–6** obtained in deuterated dichloromethane.

	E-isomer			*Z*-isomer		
Compound	Ha	Hb	Hc	Ha	Hb	Hc
3	2.5	2.2	7.0	2.1	2.3	6.2
4	2.1	2.1	6.9	2.1	2.3	6.2
5	—	—	7.1	—	—	6.3
6	2.4	2.2	7.3	2.1	2.3	6.3

Separation of **7** and **8** proved to be rather difficult. For this reason the mixture was esterified with 4-hexyloxybenzoic acid to obtain a mixture of **3** and **4** which could be easily separated by means of chromatography. The ^{1}H NMR spectrum of **4** differs considerably from that of **3**, see table 1. The signals of the methine proton of the isopropyl group and the methine proton at the α position to this isopropyl group were now both observed at 2.1 ppm in the ^{1}H NMR spectra (table 1). Table 2 shows that compound **4** has a much lower melting point than **3**. This difference was also observed on comparing the 3R, 6R and 3S, 6R epimers of compound **1**.

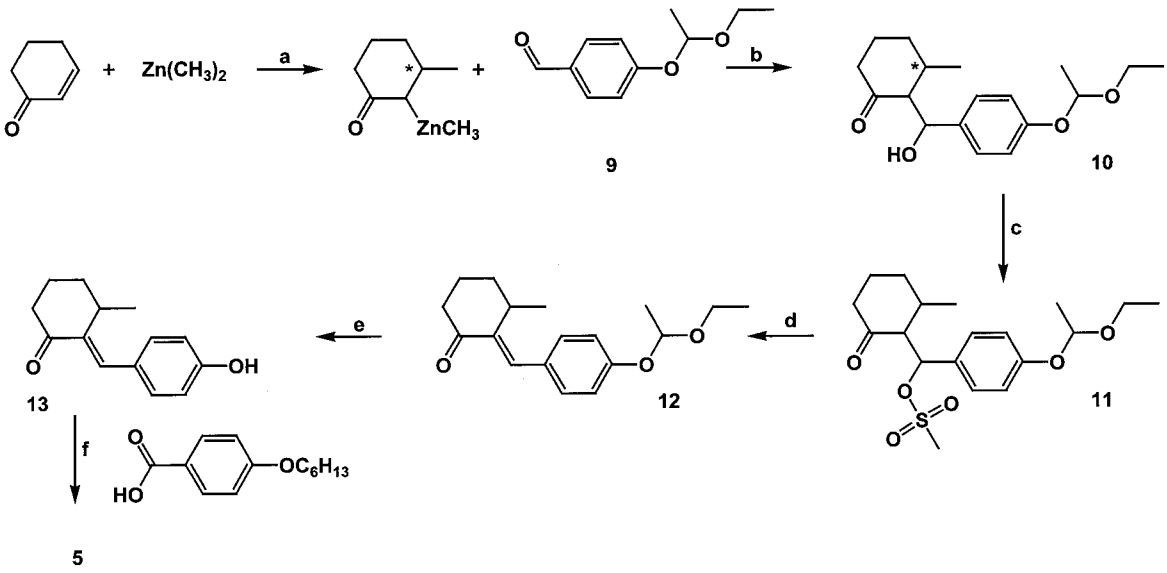
In order to make compound **5**, condensation of commercially available 3-methylcyclohexanone with aromatic aldehydes was attempted. Only the less hindered aldol condensation product could be obtained, so an alternative route had to be used. In this route (see scheme 3), described by Feringa *et al.* [15], 2-cyclohexenone is methylated by dimethylzinc using a chiral catalyst. The zinc-containing intermediate obtained with high enantiomeric excess reacted with aldehyde **9** to obtain the β-hydroxycarbonyl compound **10**. Dehydration of **10** under basic or acidic conditions failed. In most cases decomposition occurred. Mesylation to form **11**, followed by elimination of methanesulphonic acid, resulted in the unsaturated ketone **12** which, after deprotection, yielded phenolic compound **13**. Product **5** was obtained after esterification by 4-hexyloxybenzoic acid as described above. Chiral HPLC revealed an enantiomeric excess of 97%. Unfortunately it was not possible to determine the absolute configuration at carbon-6.

A racemic mixture of **6** was prepared in the same way as for menthone derivative **3**, replacing menthone by 2-isopropylcyclohexanone (see scheme 4). The enantiomers of **6** were separated by means of preparative chiral HPLC. Both enantiomers were obtained in an enantiomeric excess of more than 98%. The absolute configuration was again not determined.

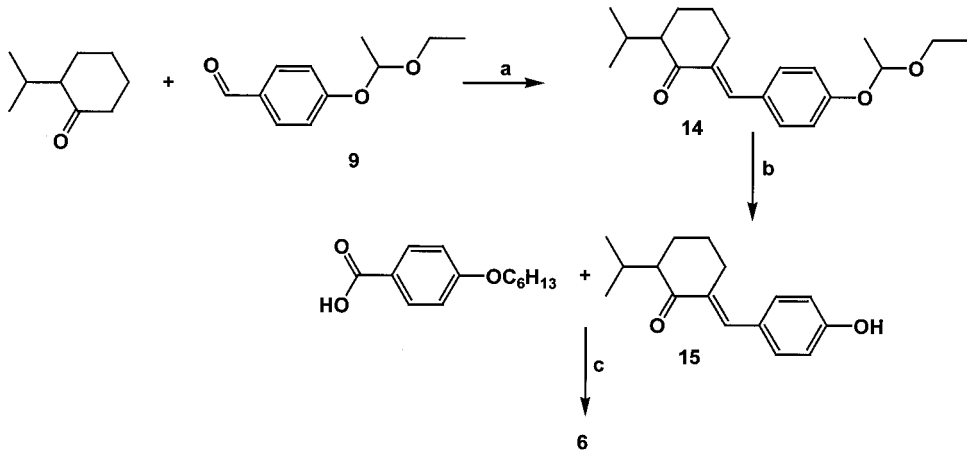
X-ray analysis of compound **2**, which has the same configuration as **3**, revealed that the cyclohexanone moiety has a chair-like conformation with the methyl

Table 2. Physical data for compounds **3–6** before and after irradiation.

	E-isomer, before irradiation					Photostationary state		*Z*-isomer, calculated		
			UV data in CH_3CN		HTP	% *E* from	HTP		UV data in CH_3CN	
Compound	Phase transitions /°C	Configuration	λ (max)/nm	ε (max)	in E7 /μm^{-1}	HPLC and NMR data	in E7 /μm^{-1}	HTP /μm^{-1}	λ (max)/nm	ε (max)
3	$T_{Cr\text{-}I} = 101$	3S, 6R	277	35×10^3	−19	3	−3.0	−3.0	268	32×10^3
4	$T_{Cr\text{-}I} = 53$	3R, 6R	276	31×10^3	−19	3	−5.0	−5.0	267	30×10^3
5	$T_{Cr\text{-}I} = 66$		277	32×10^3	−16	22	−4.0	−0.6	268	30×10^3
6	$T_{Cr\text{-}N} = 95$ ($T_{Sm\,A\text{-}N} = 66$) $T_{N\text{-}I} = 101$		282	32×10^3	−7.0	3	+2.0	+2.0	268	30×10^3



Scheme 3. Synthetic route to **5**. *a*, *b*: catalyst see text, in toluene at −40°C; *c*: CH_3SO_2Cl, Et_3N in CH_2Cl_2; *d*: DBU in toluene at 75°C; *e*: PPTS in CH_3OH at 50°C; *f*: DCC, DMAP in CH_2Cl_2.



Scheme 4. Synthetic route to **6**. *a*: t-C_4H_9OK in THF; *b*: PTSA in THF; *c*: DCC, DMAP in CH_2Cl_2.

group at carbon 6 in the axial position and the isopropyl group at carbon 3 in the equatorial position [10]. In this configuration the methyl group is less hindered by the aromatic ring, and the relatively large isopropyl group is in its favourable equatorial position. Comparison of the ^{1}H NMR spectra of **3** and **4** (table 1) reveals that the methine proton of the isopropyl group is shifted 0.4 ppm to higher field in the case of epimer **4**. This means that its environment has a higher electron density than that of **3**, probably due to an axial, and thus less favourable, position of this isopropyl group. In compound **6**, which lacks the methyl group determining the conformation of the cyclohexanone moiety, the isopropyl group has more freedom to find an energetically favourable position. In this case only a shift to higher field of 0.1 ppm of the methine proton relative to **3** was observed. This implies that the isopropyl group in compound **3** indeed has a more favourable position than that in compound **4**. For this reason compounds having a stereochemical structure similar to **3** are formed preferentially to those with a structure similar to that of **4** in condensation reactions between menthone and aromatic aldehydes.

3.2. *Properties of the compounds*

Table 2 shows the physical properties of the compounds. As mentioned above, the 3S, 6R epimer **4** has a lower melting point than **3**. The packing of the isopropyl group probably fits better in the crystal structure of the latter compound. This might be explained by the fact that the conformation of the cyclohexane ring is determined mainly by the interaction of the aromatic

ring and the methyl group at position 6. The melting point of compound **6** is closer to that of **3** than to that of **4**. This is again an indication that in the packing of the isopropyl groups, **3** is similar to **6**. Of the four compounds, only **6** exhibits liquid crystalline phases: an enantiotropic cholesteric phase and a monotropic smectic A phase. It is the only compound which lacks a methyl group at position 6 and therefore this methyl group seems to have a suppressing effect on the formation of liquid crystalline phases.

X-ray investigations of derivatives of menthone similar to **3** showed that this methyl group has an axial position in the cyclohexane ring and therefore a perpendicular position relative to the ring systems [10]. It lowers the aspect ratio of the molecules and hence the temperature of the liquid crystalline phase transitions.

The UV spectra of compounds **3**, **4** and **5** are very similar. Compound **6** exhibits a red shift of 5 nm relative to the other compounds (see table 2). The chromophore of these compounds consists of the cinnamoyl system whose maximum absorption is determined by the torsion angle of the carbonyl and the double bond and by the torsion angle of the double bond and the aromatic ring. The repulsion between the methyl group and the aromatic ring will increase both angles and therefore decrease the maximum absorption wavelength of compounds **3**, **4** and **5** relative to that of **6**.

Within experimental errors, the HTPs of **3** and **4** in E7 are the same. Thus, the configuration of carbon 3 in these epimers plays a minor role in determining the HTP. The same observation was made on comparing both epimers of compound **1** [12]. Compound **5**, which lacks the isopropyl group, exhibits a slightly lower HTP. In contrast, compound **6**, which lacks the methyl group, exhibits a much smaller HTP. This shows that the contribution of the methyl group to the HTP is more important than that of the isopropyl group. It may hence be concluded that the chiral centre of carbon 6 is mainly responsible for the relatively high HTP values of compounds **3** and **4**.

In a theoretical approach, a more or less linear relation between the HTPs of several menthone-based derivatives and a calculated dissymmetry function was found by Kutulya *et al.* [16]. When these functions were calculated for the aldol condensation products of 3-methylcyclohexanone and 2-isopropylcyclohexanone with benzaldehyde, HTP values almost identical to that of the condensation product of menthone and benzaldehyde were obtained. The present measurements show that these dissymmetry functions are not however reliable, as indicated by the difference in the HTP values of compound **5** derived from 3-methylcyclohexanone and compound **6** derived from 2-isopropylcyclohexanone. Products similar to **3**, but prepared from the chiral ketones camphor and nopinone instead of menthone, showed HTP values much lower than that of **3** [17]. It is possible that the lack of a methyl group at the α-position of the double bond is responsible for the low HTP in these cases too.

3.3. *E–Z isomerization of the compounds*

All four compounds **3**, **4**, **5** and **6** showed *E–Z* isomerisation upon irradiation with light of 365 nm. Apart from other spectral changes, the most striking change measured with the aid of ^{1}H NMR spectroscopy was the shift of the olefinic proton to higher field shown in table 1. Spectral observations were used to monitor the degree of conversion in the photoisomerization. The composition of the photostationary state was calculated from the spectra when spectral changes had ceased upon prolonged irradiation. The degree of conversion of the *E*-isomer after reaching the photostationary state is presented in table 2. The isopropyl-containing compounds **3**, **4** and **6** showed almost complete conversion, while compound **5** showed a 78% degree of conversion. It is possible that the spectral difference between the *Z*- and *E*-isomers is responsible for this relatively incomplete conversion of the latter compound, as proved in the case of similar compounds derived from other chiral ketones [17]. It is also possible that the presence of the isopropyl group in the other three compounds is responsible for the high degree of conversion.

The UV spectrum of the *Z*-isomer of **5** was calculated from the spectrum in the photostationary state (78% conversion) with the use of the spectrum before irradiation. The UV spectra of the *E*- and *Z*-isomers of **5** were similar to those of **3** and **4**. This makes it unlikely that the composition of the photostationary state is determined by the spectral properties of both isomers of **5**. Therefore the high degree of conversion of the isopropyl-containing monomers is probably attributable to this isopropyl group in the excited state, this group determining which isomer is formed after excitation. A more thorough study of similar compounds with substituents at different positions in the cyclohexane ring will be performed to investigate this effect.

As mentioned above, the UV spectra of the *Z*-isomers of all four compounds are similar. This means that the effect of the interaction between the methyl group at position 6 and the phenyl group on the torsion angles in the cinnamoyl moiety is decreased as a result of the *E–Z* isomerization.

The HTP values obtained after irradiation of both menthone derivatives **3** and **4** are presented in table 2. A difference is observable, which is probably due to the difference in the chirality of carbon 3 of the cyclohexane moiety. The HTP of the pure *Z*-isomer of compound **5** was calculated using the value of 78% conversion. The

calculated HTP change of 15 is similar to the changes of 16 and 14 calculated for the menthone derivatives **3** and **4**, respectively. The isopropyl compound **6** showed a lower HTP change of 9 and a pitch inversion. This implies that the methyl group at position 6 is not only of importance for obtaining a high HTP in the case of *E*-isomers, but also causes a relatively high pitch change in the *Z*-isomers upon isomerization.

Unfortunately, it was not possible to determine the exact configuration of the carbon atoms 3 and 6 in compounds **6** and **5**, respectively. This makes it difficult to determine the contribution of these chiral centres to the HTP of menthone derivatives **3** and **4**. Compound **5** has an HTP of almost zero after complete isomerization and compound **6** has a somewhat higher HTP after complete isomerization. This implies that chiral centre 6 plays a minor role in the HTP of the *Z*-isomers, probably because it is not close to the aromatic ring. Therefore it is probable that the chiral centre of carbon 3 is responsible for the HTP of the *Z*-isomers of menthone derivatives **3** and **4**.

The ^{1}H NMR spectra of the isopropyl-containing compounds **3**, **4** and **6** obtained after irradiation show the methine protons of these isopropyl groups at 2.1 ppm. The fact that these chemical shifts are smaller than in the case of the starting *E*-compound is due to the different chemical environment resulting from the displacement of the aromatic moiety. The fact that they all exhibit the same chemical shift shows that they are all in the same chemical environment which is no longer influenced by the ring conformation, which in turn was determined by the interaction of the methyl group with the aromatic ring.

4. Conclusions

The chiral centre in position 6 of the cyclohexanone ring largely determines the helical twisting power of the *E*-isomer of condensation products of menthone with aromatic aldehydes. The helical twisting power of the *Z*-isomer of these compounds is much lower than that of the *E*-isomer and is no longer determined by this chiral centre. The isopropyl group at position 3 plays an important role in the conversion of the *E*-isomer to the *Z*-isomer during irradiation.

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