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Camphor and nopinone derivatives as new photosensitive chiral dopants

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E–Z photoisomerizable chiral dopants are a class of materials that can be used to prepare birefringent optical components with patterned optical properties. Two new photoisomerizable chiral dopants have been synthesized and analysed. The materials were derived from nopinone and camphor. The properties of these compounds were compared with the properties of the methone derivative described in earlier publications. The *E*-isomers of the nopinone and camphor derivatives had helical twisting powers of 2.7 and 1.7 μm^{-1}, respectively. This is a factor of about 10 lower than the value obtained for the menthone derivative ($-19\,\mu m^{-1}$). Due to the high absorption of the *Z*-isomers relative to the *E*-isomers of the nopinone and camphor derivatives, isomerization during 365 nm UV exposure proceeded to a much lesser extent than the isomerization of the menthone derivative. At shorter wavelengths, the absorption of the *Z*-isomer is much lower than that of the *E*-isomer and much higher degrees of conversion could be achieved.

1. Introduction

Recently, the development of photoisomerizable chiral molecules has received much interest. Such materials can be used in for instance: optical components in LCDs [1], data storage [2], photosensitive ferroelectric devices [3] and molecular motors [4]. For each of these applications, the physical properties of the chiral compounds have to be carefully optimized. Important requirements for application of the materials in optical components in LCDs are: (1) the materials should be transparent to visible light, (2) the materials should have a high helical twisting power (β), (3) the differences in β between the two photoisomers should be large, and (4) the materials should show no tendency for thermal back reactions. Most of the photoisomerizable chiral liquid crystals reported in the literature are not transparent to visible light and have relatively low β values (see refs. in [1]). In this respect, menthone derivatives prove to be a particularly interesting class of compounds [5–8]. The materials are transparent to visible light, β values can be very high and depend strongly on the *E*/*Z* ratio. We thought it would be interesting to investigate the effects of chemical structure on the properties of compounds of this type. To this end we have carried out some photochemical research on two new compounds that are related to the menthone derivatives. The new photoisomerizable chiral dopants are camphor and nopinone derivatives. The structural formulae of the compounds are shown in figure 1. The changes in β observed during photoisomerization will be related to the spectroscopic properties of the compounds and compared with the menthone derivative [6].

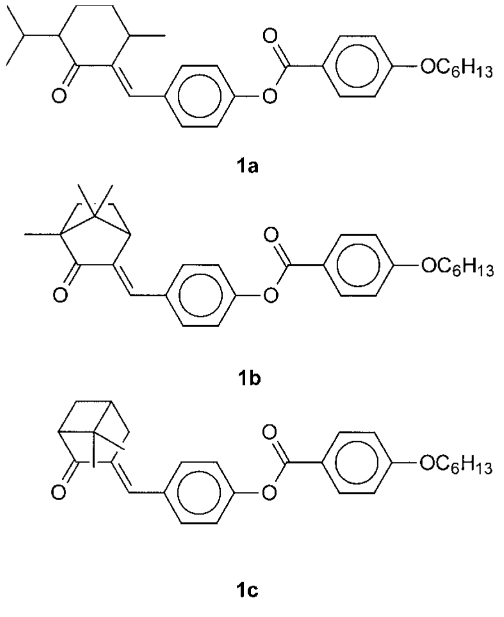

Figure 1. Chemical structures of the menthone (**1a**), camphor (**1b**) and nopinone (**1c**) derivatives.

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2. Experimental

2.1. *Materials*

The solvents, the nematic mixture E7 and the chiral dopant S811 were obtained from E. Merck Ltd; (−)-camphor was obtained from Fluka and the other chemicals from Aldrich. 4-(Tetrahydropyran-2-yloxy)-benzaldehyde **2** and (*E*)-(1*R*,4*R*)-2-[4-(hexyloxy-benzoyloxy)benzylidene]menth-3-one **1a** were prepared according to procedures described in the literature [6].

2.2. *Synthesis of camphor derivative 1b* (see the scheme)

2.2.1. *(R,E)-3-(4-Hydroxybenzylidene)-bornan-2-one 4b*

3.3 g of powdered potassium hydroxide was stirred for 15 min with 10 ml of dimethylsulphoxide in a nitrogen atmosphere. Then 7.61 g of (−)-camphor and 10.31 g of 4-(tetrahydropyran-2-yloxy)benzaldehyde **2** were added. After stirring for one day at room temperature, 65 ml of diethyl ether and 40 ml of water were added. After separation, the diethyl ether solution was washed twice with 30 ml of water and once with 30 ml of saturated brine. After drying over magnesium sulphate, the solvent was evaporated. The crude intermediate **3b** was obtained as a red oil. It was dissolved in 50 ml of ethanol together with 1 g of pyridinium 4-toluenesulphonate. The mixture was stirred and heated at 50°C for 5 h in a nitrogen atmosphere. The pink paste obtained after evaporation of the ethanol was crystallized from 20 ml of isopropanol; 2.6 g of **4b** (20%) was obtained as a white powder.

2.2.2. *Synthesis of (R,E)-3-[4-(4-hexyloxybenzoyloxy)-benzylidene]-bornan-2-one 1b*

2.8 g of *N,N'*-dicyclohexylcarbodiimide was added to a mixture of 1.30 g of **4b**, 1.20 g of 4-hexyloxybenzoic acid, 0.06 g of 4-*N,N*-dimethylaminopyridine and 25 ml of dichloromethane, cooled in an ice bath. The mixture was stirred for one day at room temperature. After filtration through a thin layer of silica and evaporation of the dichloromethane, the product was recrystallized from ethanol; 1.45 g of **1b** (59%) was obtained as white crystals.

2.3. *Synthesis of R-3-[4-(4-hexyloxybenzoyloxy)-benzylidene]-nopinone 1c*

2.3.1. *(R,E)-3-(4-Hydroxybenzylidene)-nopinone 4c*

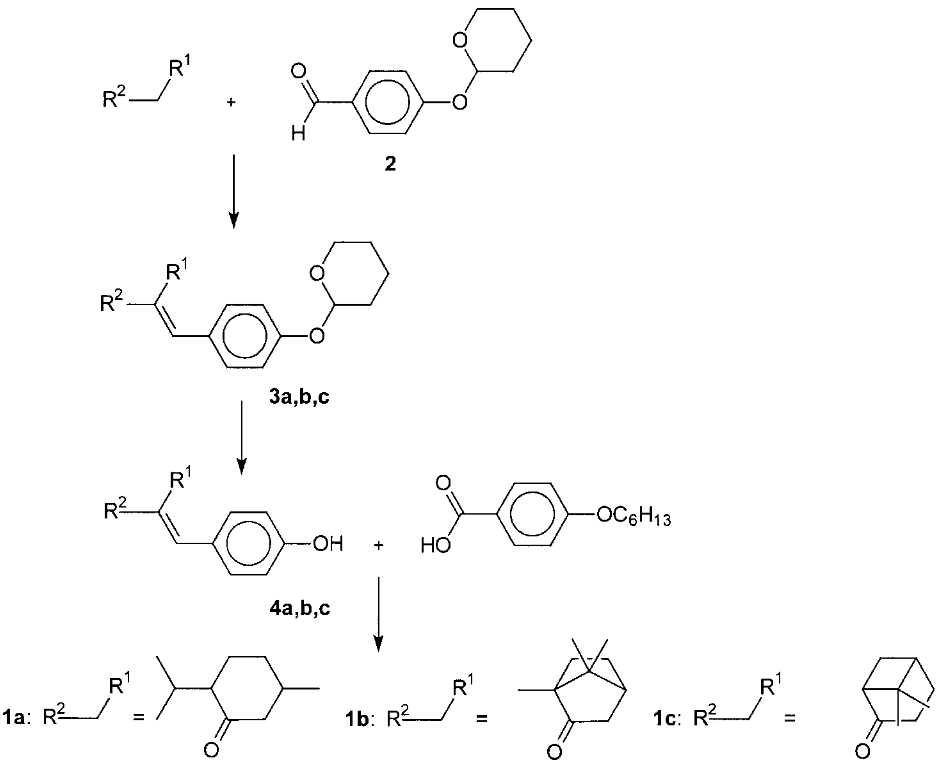
This compound was obtained in a 19% yield in the same way as described for the formation of **4b**.

2.3.2. *(R,E)-3-[4-(4-Hexyloxybenzoyloxy)benzylidene]-nopinone 1c*

This compound was obtained in a 70% yield in the same way as described for the formation of **1b**.

2.3. *Methods*

The irradiation in the near UV region was done using a Philips PL-10 source with an intensity of 2.05 mW cm^{-2} at $\lambda = 365$ nm. A HgXe lamp fitted with an interference filter was used for irradiation at 303 nm



Scheme. Synthesis of the menthone (**1a**), camphor (**1b**) and nopinone (**1c**) derivatives.

(intensity ~3.3 mW cm^{-2}). During most of the experiments the solutions were kept in a 1 cm thick quartz cell. The helical twisting power was determined using the Grandjean–Cano method. A solution of the compounds in the commercial active matrix liquid crystal E7 was filled into wedge cells (EHC, Japan, tan $\alpha = 0.0083$) [9]. UV spectra were recorded using a Unicam UV 2 Series spectrometer. Dichloromethane and acetonitrile were used as solvents in the studies of the photochemistry in solutions. Compositional analysis was performed using HPLC equipped with a photodiode array for the detection. The sample was injected onto a RP18 column (Intertsil 5 ODS-3, 250 × 4.6, gradient of acetonitrile/water and flow 1 ml min^{-1}). The chromatogram was recorded at the isobestic point: 313 nm in the case of **1b** and 325 nm in the case of **1c**. ^{1}H NMR and ^{13}C NMR spectra were measured using a Bruker DPX 300 spectrometer; samples were dissolved in $CDCl_3$ with TMS as internal standard. Chemical shifts are given in ppm. 2D NOESY spectra were recorded using the experimental settings described in [10].

3. Results and discussion

3.1. *Synthesis and characterization*

The synthesis of menthone derivative **1a** has been described in previous publications [6]. The syntheses of **1b** and **1c** were performed in an analogous way to that of **1a**. Using X-ray analysis of analogous compounds, it was shown by Yarmolenko *et al.* that the benzylidene-menthone moiety in derivative **1a** has the *E*-conformation [5]. ^{1}H NMR spectra of **1a** show the signal of the benzylidene proton at 6.97 ppm in the case of the *E*-isomer and at 6.24 ppm in the case of the *Z*-isomer obtained by means of irradiation. In the case of **1b** and **1c** these signals were observed at 7.15 and 7.57 ppm, respectively. On the basis of the spectral behaviour of **1a**, **1b** and **1c**, it may be assumed that all compounds are *E*-isomers. NOE-NMR spectroscopy was used to confirm the isomeric structure of both compounds. In the case of compound **1b** an interaction was observed between the bridgehead proton H^a at 3.12 ppm and the aromatic protons H^b at 7.51 ppm (figure 2). This interaction can take place only if the distance between protons H^a and H^b is less than approximately 0.3 nm. Model studies show that the interaction can occur only in the case of the *E*-isomer of **1b**. Similar results were obtained with compound **1c**. In this compound interactions were observed between protons H^c and $H^{c'}$, both found at approximately 3.1 ppm, and aromatic protons H^d at 7.60 ppm. Thus, both compounds **1b** and **1c** were obtained as the pure *E*-isomers.

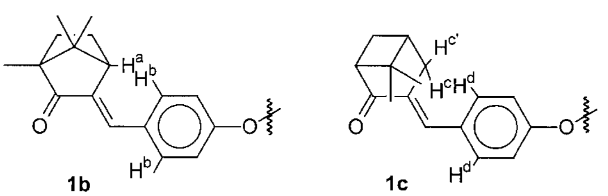


Figure 2. Assignment of protons for NOE-NMR spectroscopy.

3.2. *Properties*

Table 1 shows some physical properties of **1a**, **1b** and **1c**. The melting points of the two new compounds are somewhat lower than that of **1a**. None of the three compounds exhibits liquid crystalline properties. The UV spectra of the compounds are presented in figure 3. The highest λ_{max} was observed for the camphor derivative **1b** (see also table 1). This might be due to the rigid structure of the norbornane skeleton whose carbonyl functionality lies more in the plane of the benzylidene moiety.

3.3 *Helical twisting power*

The helical twisting power β was calculated using the pitch p induced in the commercial liquid crystal mixture E7 and the weight fraction χ of the chiral molecule: $\beta = (p\chi)^{-1}$. In order to determine the twisting sense of the helical twisting power, small amounts of the commercial chiral dopant S811 were added. This commercial material induces a left-handed twist and thus increases

Table 1. Properties of compounds **1a**, **1b** and **1c**.

Compound	m.p./°C	λ_{max}/nm	$\varepsilon_{max} \times 10^{-3}$	β_E/μm^{-1}
1a	96	278	480	− 19
1b	86	292	580	+ 1.7
1c	88	283	710	+ 2.7

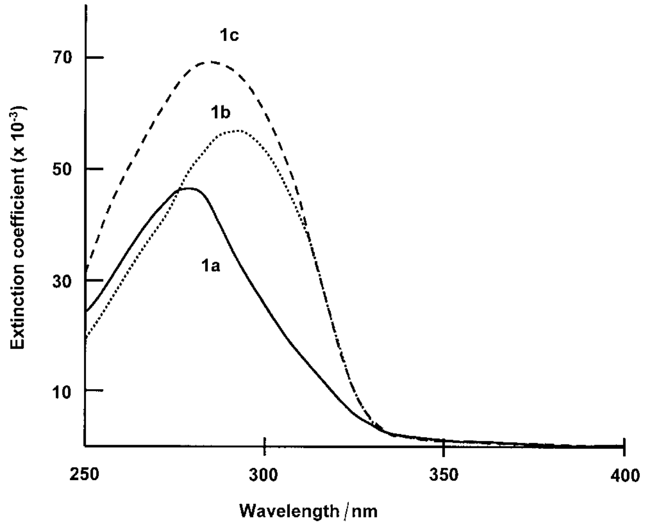


Figure 3. UV spectra of compounds **1a**, **1b**, **1c** in acetonitrile.

the pitch if the other chiral molecule induces a right-handed twist, and reduces the pitch if it induces a left-handed twist. The results are shown in table 1. The absolute values of β_E obtained for the camphor derivative **1b** and nopinone derivative **1c** are much lower than the value obtained for the menthone derivative **1a** [6]. Thus it is clear that the structure of the chiral moiety of the molecules has a strong effect on β. It is possible that the chiral groups of the cage-like structures of the two new derivatives **1b** and **1c** show less interaction with the liquid crystalline hosts and therefore have a smaller β than **1a** with its more open chiral structure. The twisting senses of **1b** and **1c** are opposite to that of **1a**.

3.4. *E–Z isomerization of the compounds*

The *E–Z* isomerization was studied using spectroscopic techniques and HPLC analysis. Compound **1a** shows an efficient *E–Z* isomerization by using UV light of 365 nm [6]. Table 2 shows that this compound forms a photostationary state in which 97% of the compound is isomerized to the *Z*-isomer.

The *E–Z* isomerization of **1b** and **1c** was followed by means of ^{1}H NMR spectroscopy using irradiation at 365 nm. In both cases spectral changes were observed which could be attributed to these isomerizations. Thus, the protons attached to the vinylic part of the benzylidene groups in **1b** and **1c** shifted from 7.15 to 6.49 ppm and from 7.57 to 6.66 ppm, respectively. No spectral changes occurred after prolonged irradiation and a photostationary state was assumed. With the aid of the integral values of these NMR spectra, the conversions at the photostationary states were calculated (see table 2). They were much lower than that of **1a**. No changes were observed in the NMR spectra of the irradiated samples upon storage in the dark at room temperature. It is therefore assumed that the isomerization is not thermally reversible under these conditions.

Figure 4 shows the UV absorbance difference spectra of the three compounds in acetonitrile (changes relative to the spectrum of the non-irradiated sample) after 10 min of irradiation at 365 nm. Longer irradiation times did not alter these spectra. The difference spectra obtained before reaching the photostationary state gave rise to the formation of isosbestic points at 313 and 327 nm in the case of **1b** and **1c**, respectively. At shorter wavelength, isosbestic points were observed at 272, 262 and 269 nm for compounds **1a**, **1b** and **1c**, respectively. Assuming that the kinetics of the *E–Z* and *Z–E* conversions of the three compounds are similar, these spectra can explain some of the differences in conversion during irradiation. In the case of **1a** the extinction of the *Z*-isomer is lower than that of the *E*-isomer at 365 nm. For this reason isomerization back to the *E*-isomer is less likely to take place and the photostationary state will contain mainly the *Z*-isomer. In the case of **1b** and **1c**, the extinction of the *E*-isomer is lower than that of the *Z*-isomer, so the latter is more likely to be isomerized to the *E*-isomer, leading to an excess of the starting *E*-isomer in the photostationary state. HPLC analysis of the isomerized solutions of **1b** and **1c** showed the presence of only the two isomers and no side-products. This is in accordance with the isosbestic points found in the UV spectra and means that a clean isomerization reaction indeed took place. The amount of *E*-isomer present in the photostationary state was 80% in the case of **1b** and 75% in the case of **1c**. These results are similar to those obtained in the NMR experiments. These values will be used in further experiments.

In order to check whether the isomerization of **1b** is more efficient in the spectral range in which the *Z*-isomer has a lower extinction than the *E*-isomer, an experiment was performed to the left of the isosbestic point at 313 nm, namely at 303 nm. HPLC analysis indeed revealed a conversion of more than 50% to the *Z*-isomer. Unfortunately, several side-products were observed in the HPLC traces. It was not clear whether these side products were the result of destruction of one of the

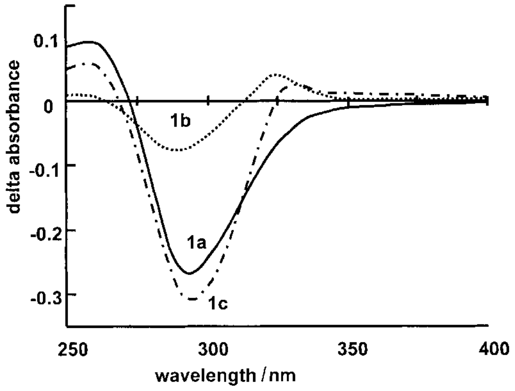


Figure 4. Absorbance difference UV spectra of the irradiated samples with the original samples for compounds **1a**, **1b** and **1c** in acetonitrile after the photostationary state has been reached at 365 nm.

Table 2. Properties of compounds **1a**, **1b** and **1c** after exposure to 365 nm.

Compound	χ_E/wt %[a]	β'/µm^{-1} [b]	β_Z/µm^{-1} [c]
1a	3	− 1.2	− 0.7
1b	83	+ 1.0	− 2.3
1c	76	+ 1.2	− 3.4

[a] Percentage of the *E*-isomer observed in the photostationary state after irradiation with 365 nm.

[b] Helical twisting power in the photostationary state after irradiation with 365 nm.

[c] Calculated from percentage of the *E*-isomer and β' in the photostationary state.

isomers or both. It is possible that a rupture of the ester bond in the molecule is responsible for the formation of these products, as was shown for similar structures containing ester bonds [11]. Due to the high extinction coefficient at 303 nm (see figure 3) analysis of the irradiation products at the high concentrations necessary for NMR was not possible. After the mixture had subsequently been irradiated at 365 nm, the same ratio of *Z*- and *E*-isomers was obtained as was obtained by irradiating the *E*-compound with 365 nm UV light. This is in accordance with the expectations for the photostationary state. During this irradiation with 365 nm UV light no changes were observed in the peaks of the side-products.

The effect of prolonged irradiation at 365 nm on the β-values of **1a**, **1b** and **1c** in the commercially available liquid crystal mixture E7 are outlined in table 2. If we assume that the photostationary states in these mixtures are the same as those found in the NMR experiments, the helical twisting power of the pure *Z*-isomer (β_Z) can be calculated according to a linear mixing rule: $\beta'(\chi_E + \chi_Z) = \beta_E \chi_Z + \beta_Z \chi_Z$, β' being the helical twisting power after prolonged irradiation at 365 nm. It is interesting to note that the *Z*-isomers of **1b** and **1c** have an opposite handedness of the pitch to the *E*-isomers. This was not observed for menthone derivative **1a**. This again shows the powerful effect of the structure of the chiral moiety of the molecules on the helical twisting power.

4. Conclusions

Despite similarities in chemical structure, the properties of the camphor and nopinone derivatives differ from the corresponding properties of the menthone derivatives. The helical twisting power of the new materials is a factor of 10 lower. Due to differences in the spectral behaviour of the *E*- and *Z*-isomers of the compounds, the *E*–*Z* photoisomerization at 365 nm proceeds to a much lesser extent than in the case of menthone derivatives. Apparently, the interaction of the chiral groups and also the photoisomerization properties are very susceptible to modifications in the chiral ring structure. These materials may be suitable for recording polarization-sensitive images in liquid crystalline media [12].

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