

# Synthesis, characterization and photoreactivity of liquid crystalline cinnamates

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## Abstract

A series of liquid crystalline cinnamate derivatives has been synthesized and characterized. The reactivity of photoreactive samples containing these compounds and a low percentage of a triplet sensitizer has been investigated at different temperatures and phases. No topochemical reaction occurs by irradiation on the solid phase. However, by irradiation at mesophase the presence of photoproducts have been detected by FTIR and UV-Vis. However, when temperature increases above 200 °C, thermal reactivity predominates. The photoproducts were studied by NMR. A relatively low percentage of *E-Z* isomerization was measured together with [2 + 2] photocycloaddition. The resulting isomeric cyclobutane rings depend on the molecular ordering of the fluid phase. Thus smectic mesomorphic ordering mainly favors a  $\beta$ -truxinic acid derivative but isotropic phase mainly favors a  $\delta$ -truxinic acid derivative.

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*Keywords:* Liquid crystals; Cinnamates; Photoreactivity

## 1. Introduction

The photoreactivity of liquid crystal systems has been widely investigated in the last years as a consequence of different technological applications such as photo-alignment of liquid crystals [1], optical storage [2,3], nonlinear optics [4], etc. Different groups such as azobenzenes [5], stilbenes [6], cinnamates [7] or coumarines [8,9], are compatible with mesomorphic ordering and also exhibit photoreactivity. Qualitatively, the more important photochemical reactions studied on liquid crystals involve *trans-cis* isomerization (e.g. azobenzenes) and [2 + 2] cycloaddition, which is exhibited by the cinnamates. Probably the most investigated application of this photoreactivity is the photoinduced liquid crystal alignment produced by exposing a polymer film to polarized UV and the development of structural anisotropy on its surface. Thin films of poly(vinyl cinnamate) have attracted special attention owing to its high photoreactivity [10]. However, due to the significant thermal relaxation of the poly(vinyl cinnamate), which causes randomization, new cinnamic liquid crystalline polymers have been developed [11].

The synthesis of low molecular weight liquid crystalline cinnamates and the study of their photoreactivity provide a suitable background towards the design and optimization of liquid crystalline cinnamate polymers. The topochemical reactions described for cinnamic acid derivatives on photoirradiation at >300 nm has been extended to bifunctional molecules [12] and liquid crystals [13]. In fact, the mesomorphic ordering must influence on the photoreactivity as occurs in the topochemical reactions of the  $\alpha$  and  $\beta$  forms of the *trans*-cinnamic acid. In the present work we describe the synthesis and characterization of new liquid crystals derived from 4-hydroxycinnamic acid (series p) in order to evaluate the influence of the central core in the mesomorphic properties. Furthermore, we have also prepared a series (series m) of materials derived from 3-hydroxycinnamic acid. Both series are shown in Fig. 1. The photoreactivity of some of the prepared mesomorphic and nonmesomorphic cinnamates has been studied by FTIR, UV-Vis and NMR.

## 2. Experimental

### 2.1. Synthesis

Compounds of series p and m were synthesized according to synthetic methods as previously described [14] (see

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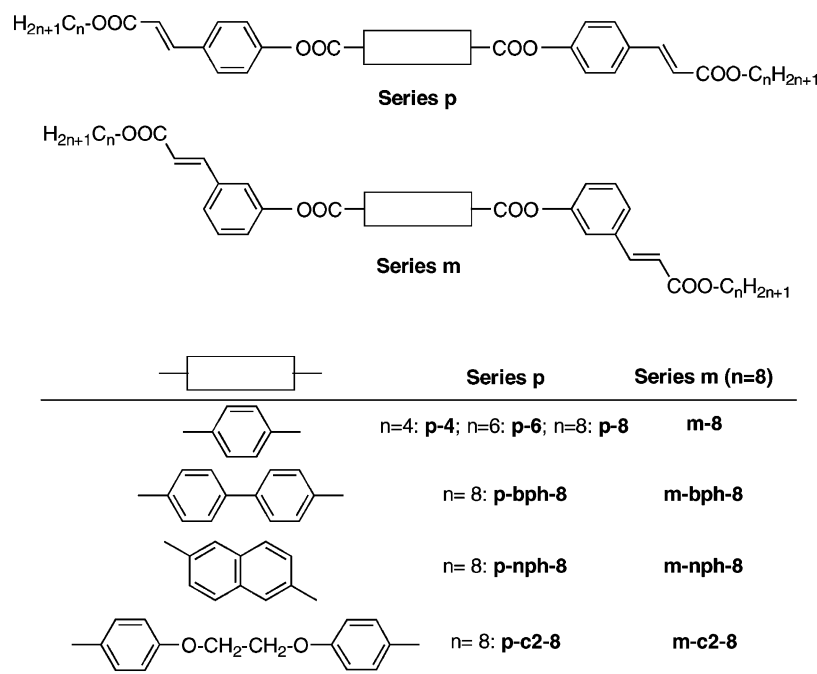


Fig. 1. Structure and nomenclature of the synthesized photoreactive materials.

Fig. 2) using acid dichlorides (represented as a rectangle in Fig. 2) obtained from commercial carboxylic acids except 1,2-bis(4-carboxyphenoxy)ethane which was synthesized according to the literature [15]. All the compounds were characterized by elemental analysis, FTIR, UV-Vis and NMR. Table 1 collects the yield, elemental analysis, FTIR and UV-Vis data.

### 2.1.1. $^1\text{H}$ NMR ( $\text{CDCl}_3$ , $\delta$ : ppm, $J$ : Hz)

*p-8* (this compound is included as reference; *p-4* and *p-6* exhibited very similar spectra which only differ in the in-

tegration of the aliphatic region): 0.87 (t,  $J = 6.6$ , 6H), 1.20–1.50 (m, 20H), 1.60–1.80 (m, 4H), 4.19 (t,  $J = 6.6$ , 4H), 6.43 (d,  $J = 15.9$ , 2H), 7.27 (d,  $J = 8.6$ , 4H), 7.61 (d,  $J = 8.6$ , 4H), 7.68 (d,  $J = 15.9$ , 2H), 8.32 (4H, s).

*p-bph-8*: 0.87 (t,  $J = 6.5$ , 6H), 1.27–1.39 (m, 20H), 1.67–1.69 (m, 4H), 4.19 (t,  $J = 6.7$ , 4H), 6.42 (d,  $J = 16$ , 2H), 7.27 (d,  $J = 8.7$ , 4H), 7.60 (d,  $J = 8.7$ , 4H), 7.68 (d,  $J = 16$ , 2H), 7.79 (d,  $J = 8.5$ , 4H), 8.30 (d,  $J = 8.5$ , 4H).

*p-nph-8*: 0.87 (t,  $J = 6.9$ , 6H), 1.27–1.36 (m, 20H), 1.58–1.69 (m, 4H), 4.19 (t,  $J = 6.6$ , 4H), 6.43 (d,  $J = 15.9$ , 2H), 7.30 (d,  $J = 8.5$ , 4H), 7.62 (d,  $J = 8.5$ , 4H), 7.69 (d,  $J = 15.9$ , 2H), 8.12 (d,  $J = 8.7$ , 2H), 8.28 (dd,  $J = 8.7$ , 2H), 8.84 (s, 2H).

*p-c2-8*: 0.87 (t,  $J = 6.9$ , 6H), 1.27–1.38 (m, 20H), 1.66–1.71 (m, 4H), 4.18 (t,  $J = 6.6$ , 4H), 4.45 (s, 4H), 6.40 (d,  $J = 15.9$ , 2H), 7.04 (d,  $J = 8.8$ , 4H), 7.22 (d,  $J = 8.8$ , 4H), 7.57 (d,  $J = 8.8$ , 4H), 7.69 (d,  $J = 15.9$ , 2H), 8.16 (d,  $J = 8.8$ , 4H).

*m-8*: 0.87 (t,  $J = 6.7$ , 6H), 1.17–1.24 (m, 20H), 1.56–1.59 (m, 4H), 4.09 (t,  $J = 6.7$ , 4H), 6.37 (d,  $J = 16.1$ , 2H), 7.17 (m, 2H), 7.32–7.37 (m, 6H), 7.58 (d,  $J = 16.1$ , 2H), 8.224 (s, 4H).

*m-bph-8*: 0.86 (t,  $J = 6.9$ , 6H), 1.26–1.37 (m, 20H), 1.66–1.68 (m, 4H), 4.18 (t,  $J = 6.9$ , 4H), 6.46 (d,  $J = 16$ , 2H), 7.20 (m, 2H), 7.41–7.44 (m, 6H), 7.67 (d,  $J = 16$ , 2H), 7.79 (d,  $J = 8.7$ , 4H), 8.30 (d,  $J = 8.7$ , 4H).

*m-nph-8*: 0.87 (t,  $J = 6.9$ , 6H), 1.26–1.40 (m, 20H), 1.66–1.71 (m, 4H), 4.19 (t,  $J = 6.8$ , 4H), 6.47 (d,  $J = 16$ , 2H), 7.29 (m, 2H), 7.44–7.48 (m, 6H), 7.68 (d,  $J = 16$ , 2H), 8.13 (d,  $J = 8.2$ , 2H), 8.28 (dd,  $J = 8.2$ , 2H), 8.84 (s, 2H).

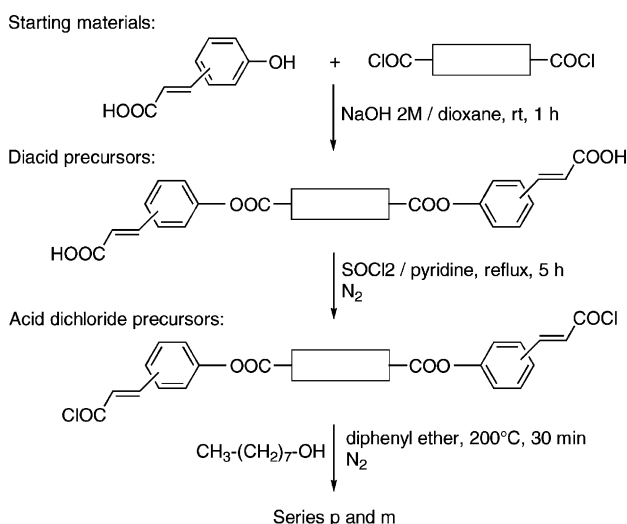
Fig. 2. Synthetic pathway of the photoreactive materials  $n = 8$ .

Table 1  
Elemental analysis, FTIR and UV-Vis spectroscopic data of the synthesized cinnamate compounds

| Compound | Elemental analysis (experimental) |             | FTIR, $\nu$ ( $\text{cm}^{-1}$ ) |      |      | $\lambda$ (nm)              |
|----------|-----------------------------------|-------------|----------------------------------|------|------|-----------------------------|
|          | C (%)                             | H (%)       | C=O                              | C=C  | =C-H |                             |
| p-4      | 71.58 (71.27)                     | 5.96 (6.18) | 1741, 1708, 1698                 | 1639 | 987  | 226, 282, 301 <sup>sh</sup> |
| p-6      | 72.84 (72.64)                     | 6.71 (7.02) | 1729, 1714                       | 1641 | 982  | 226, 283, 303 <sup>sh</sup> |
| p-8      | 73.90 (74.20)                     | 7.33 (7.71) | 1728, 1708                       | 1641 | 982  | 226, 283, 302 <sup>sh</sup> |
| p-bph-8  | 71.91 (72.00)                     | 4.12 (4.15) | 1738, 1721, 1704                 | 1638 | 983  | 227, 298                    |
| p-nph-8  | 70.87 (70.60)                     | 3.94 (3.88) | 1745, 1719                       | 1642 | 983  | 226, 246, 289, 300, 357     |
| p-c2-8   | 66.45 (66.70)                     | 4.23 (4.20) | 1726, 1704                       | 1630 | 982  | 227, 283                    |
| m-8      | 73.90 (73.83)                     | 7.33 (7.78) | 1738, 1732, 1715, 1702           | 1645 | 983  | 224, 272                    |
| m-bph-8  | 71.91 (71.80)                     | 4.12 (4.19) | 1729, 1718                       | 1641 | 978  | 227, 284                    |
| m-nph-8  | 70.87 (70.90)                     | 3.94 (3.98) | 1737, 1721, 1703                 | 1644 | 983  | 226, 247, 277, 343, 347     |
| m-c2-8   | 66.45 (66.66)                     | 4.23 (4.18) | 1727, 1712                       | 1637 | 986  | 226, 274                    |

*m-c2-8*: 0.87 (t,  $J = 6.9$ , 6H), 1.27–1.36 (m, 20H), 1.58–1.69 (m, 4H), 4.19 (t,  $J = 6.6$ , 4H), 4.45 (s, 4H), 6.43 (d,  $J = 16.1$ , 2H), 7.04 (d,  $J = 8.9$ , 4H), 7.20 (m, 2H), 7.37–7.43 (m, 6H), 7.69 (d,  $J = 16.1$ , 2H), 8.16 (d,  $J = 8.9$ , 4H).

## 2.2. Techniques

Elemental analysis was performed with a Perkin Elmer 240C microanalyzer. IR spectra were measured on a Perkin Elmer 1725X from KBr pellets.  $^1\text{H}$  NMR spectra were recorded on a Varian Unity 300 spectrometer operating at 300 MHz using deuterated chloroform solutions.

Mesomorphic behavior and transition temperatures were determined on an Olympus BH-2 polarizing microscope equipped with a Linkam THMS600 hot-stage central processor. Differential scanning calorimetry (DSC) was carried out on a Perkin Elmer DSC 7 using aluminum pans. Scans were runned under nitrogen atmosphere at  $10^\circ\text{C}/\text{min}$ . Temperatures were read at the onset of the transition peaks. Thermogravimetric (TGA) analysis was performed on a Perkin Elmer TGA 7 by using finely powdered polymeric samples at a rate of  $10^\circ\text{C}/\text{min}$  from 40 to  $600^\circ\text{C}$  under nitrogen.

Photoreactive samples were prepared by solving the selected cinnamate and Michler's ketone as sensitizer (2%, w/w) in freshly distilled dichloromethane. The solvent was evaporated at room temperature and then under vacuum at  $30^\circ\text{C}$  for 24 h. For the FTIR study of the photoreactivity KBr pellets were prepared with a 1% (w/w) content of the photoreactive sample. The KBr pellets were heated in a thermostatic stage at a controlled temperature and irradiated with a Hg lamp Ultracure 100 from Efos Inc. (intensity  $4\text{ mW}/\text{cm}^2$  at 365 nm). For the UV-Vis measurements thin films were prepared onto quartz plates from dichloromethane solutions of the photoreactive samples (0.6–0.8%, w/w) by spin-coating (300 rpm for 5 s and 750 rpm for 55 s). These films were irradiated as described above. Finally, the samples for NMR studies were heated and irradiated as described in aluminum pans.

## 3. Results and discussion

### 3.1. Synthesis and characterization

The synthetic pathway of compounds of series p and m is briefly shown in Fig. 2. These compounds were synthesized according to methods previously described and were adequately characterized. The synthesis and thermal characterization of compounds p-4, p-6 and p-8 was reported elsewhere [14]. The *E*-configuration of the double bond of the cinnamic group was confirmed by FTIR (out of plane = C-H band at  $970\text{--}990\text{ cm}^{-1}$ ) and  $^1\text{H}$  NMR (two signals at approximately 6.45 and 7.65). An in-depth study of the thermal and mesomorphic properties was carried out using DSC and polarized optical microscopy. The transition temperatures and the enthalpy values of the final compounds are gathered in Table 2. The thermal stability was additionally studied by thermogravimetry under nitrogen atmosphere. All the materials exhibit good thermal stability and weight loss decomposition is only detected at temperatures above  $325^\circ\text{C}$ . However, no thermal reactions without weight loss can be ruled out at lower temperatures.

The highly linear shape of these materials, in particular the compounds derived from 4-hydroxycinnamic acid is in principle suitable for the formation of mesomorphic melts. In the case of series m the bent structure introduced by the 3-hydroxycinnamic acid is disadvantageous for the development of mesomorphic ordering. In spite of this fact, these materials were synthesized as models for the comparison of the photoreactivity in the mesomorphic or in the isotropic state at relatively low temperatures. Compounds of series p exhibit crystalline polymorphism, detected by DSC, and are highly mesogenic as consequence of their electronic conjugation and polarizability, high *L/D* ratio and linearity. As it was mentioned in a previous work [14] for compounds having a 1,4-phenylene central unit, a nematic phase is observed at high temperature only for short aliphatic terminal chains (p-4) while long terminal aliphatic chains favor smectic C phase. The central unit has also a high influence on the melting temperature and the mesophase temperature

Table 2  
Transition temperatures (°C) and enthalpies (kJ/mol) of the synthesized cinnamate compounds

| Compound | Thermal transitions <sup>a</sup>  |
|----------|---|
| p-4      | C 110 (33.3) [S <sub>C</sub> 96] <sup>b</sup> S <sub>A</sub> 253 (1.6) N 269 (0.8) I              |
| p-6      | C 46 (3.8) C' 109 (35.9) S <sub>C</sub> 170 <sup>c</sup> S <sub>A</sub> 245 (5.2) I               |
| p-8      | C 46 (10.2) C' 97 (1.1) C'' 108 (35.6) S <sub>C</sub> 201 <sup>c</sup> S <sub>A</sub> 231 (6.0) I |
| p-bph-8  | C 94 (37.7) S <sub>C</sub> 305 (0.2) S <sub>A</sub> 323 <sup>dec</sup> (5.8) I                    |
| p-nph-8  | C 139 (36.9) S <sub>C</sub> 267 (0.1) S <sub>A</sub> 274 (6.7) I                                  |
| p-c-2-8  | C 161 (50.3) I  |
| m-8      | C 106 (50.5) I  |
| m-bph-8  | C 101 (34.4) I  |
| m-nph-8  | C 133 (61.0) I  |
| m-c-2-8  | C 99 (49.4) I   |

<sup>a</sup> Enthalpies given in brackets.

<sup>b</sup> Monotropic transition detected by optical microscopy.

<sup>c</sup> Detected by optical microscopy.

range. Thus, the biphenyl derivative (p-bph-8) exhibits the lowest melting temperature as well as a wide smectic C temperature range. Furthermore, evidence of thermal reactivity (decomposition) is observed under the microscope at temperature close to isotropization. Naphtylene unit (p-nph-8) has been widely used in the preparation of smectogenic materials. However, p-nph-8 has a relatively high melting temperature. The high rigidity and *L/D* ratio of p-c-2-8, which has a dimeric structure is the reason of the high melting temperature exhibited by this compound.

### 3.2. Photoreactivity

The photoreactivity of some selected materials was studied by different techniques in order to investigate the influence of the temperature, the state of matter (solid or fluid phase) and the mesomorphic ordering on the reactivity. We first selected p-4, which exhibit S<sub>A</sub> and N phases, and p-6 which exhibit a S<sub>C</sub> and S<sub>A</sub> phase, in attempt to compare the photoreactivity at a similar temperature but in a different smectic (S<sub>A</sub> or S<sub>C</sub>) or nematic phase vs. isotropic phase. The photoreactivity of cinnamic derivatives can be increased by using sensitizers which absorbs, in the main, quite narrow wavebands in the region which a mercury lamp emits (in particular 365 nm). For this reason we use Michler's ketone (in 2%, w/w proportion) as triplet sensitizer which has proved to have a high relative sensitization on cinnamate derivatives [16]. Furthermore, triplet sensitization for cyclodimerization of cinnamates can avoid side reactions such as photo-Fries rearrangements [17].

FTIR was used as a technique for evaluating the modification of the cinnamic double bonds by irradiation. KBr discs containing 1% (w/w) of the photoreactive mixture were prepared for this purpose and heated to the selected temperature before irradiating [18]. The photoreactivity was checked by monitoring the evolution of C=C stretching band at 1640 cm<sup>-1</sup>, and taking as reference band the skeletal vibration band at 715 cm<sup>-1</sup> corresponding to aliphatic chains which are not involved in photochemical or thermal reactions. This band was selected because it is more easily mea-

sured than other reference bands such as the C–H 2963 cm<sup>-1</sup> band. In order to evaluate the reactivity, we defined the following function:

$$F_{1640} = 1 - \frac{(A_{1640}/A_{715})_i}{(A_{1640}/A_{715})_0}$$

where  $(A_{1640}/A_{715})_i$  is the relative reactivity of the double bonds of a sample which has been irradiated at a selected temperature and during a selected time of irradiation;  $(A_{1640}/A_{715})_0$  represents the reactivity of a reference sample which has been heated at the same temperature during the same time but without irradiation. In that way, the thermal reactivity is corrected and  $F_{1640}$  only represents the disappearance of double bonds due to photoreactions. If  $F_{1640} > 0$  the reactivity of the double bonds of the irradiated sample is higher than the corresponding to reference sample as a consequence of photoinduced reactions.

Fig. 3 shows the values of  $F_{1640}$  of samples of p-4 or p-6 irradiated at different temperatures for 1 h. As can be observed from this figure no topochemical reactivity is detected in the solid state (at temperatures  $\leq 90$  °C) [19] that may

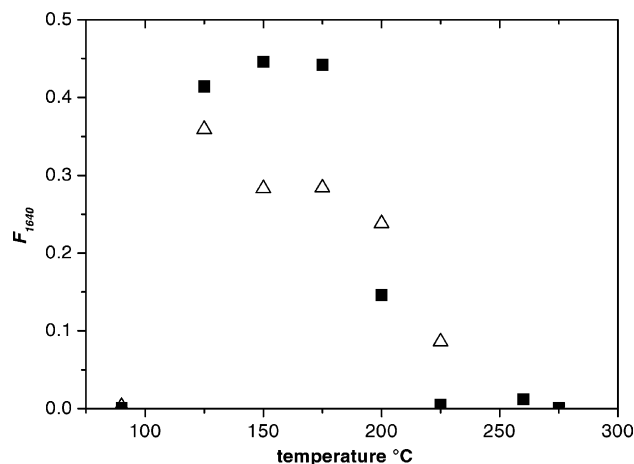


Fig. 3. Dependence of  $F_{1640}$  on the irradiation temperature (irradiation time = 1 h): (■) p-4; (△) p-6.

be consequence of the orientation and the distance between adjacent double bonds is not suitable for the cyclodimerization. However, when sample is irradiated at the mesophase temperature up to 200 °C, photoreactivity is clearly detected which seems to confirm that the molecular mobility, distance and orientation in the smectic mesophase is adequate for giving [2 + 2] cycloaddition. According to the value of  $F_{1640}$ , this reactivity seems to be higher in p-4 than in p-6, and point to a slightly higher reactivity in the mesophase  $S_A$  than in the  $S_C$  mesophase. This [2 + 2] cycloaddition is also confirmed by the displacement of the C=O double band due to the loss of conjugation. It is worth mentioning that the decrease in the C=C band reflects the overall reactivity of cinnamate groups although side reactions, such as photo-Fries, occurs to a minor extent. However, when the temperature increases the photoreactivity is negligible ( $F_{1640} \approx 0$ ), thermal reactivity predominates and a yellowing of the samples is clearly detected as a consequence of thermal decomposition and reactions such as Fries rearrangement which is confirmed by a band at 1650  $\text{cm}^{-1}$ .

In order to confirm these results, thin films of the photoreactive samples, prepared by spin-coating, were studied by UV-Vis spectroscopy at different temperatures and irradiation times. The results obtained were similar in both compounds p4 and p-6. Fig. 4a represents the spectra measured at 90 °C (solid phase). In accordance with the FTIR measurements there is no modification of the electronic spectrum on irradiation. However, in the fluid phase a modification of the UV-Vis spectrum is detected. Thus in the smectic phase at  $t \leq 200$  °C there is a decrease of the absorbance of the band at 284 nm which can be mainly assigned to the reaction of double bonds (Fig. 4b and c). The spectrum at 150 °C without irradiating was also measured at different annealing times for reference but no significant modifications were detected. The loss of electronic conjugation gives rise to a blue shift and a new band appears at 248 nm. This photoreactivity of the cinnamate chromophores is in accordance with the cyclodimerization of mesogenic units. An attempt to measure the UV-Vis spectrum at 260 °C was also carried out, but the thermal reactivity is very high and even before irradiating there is a modification of the electronic spectrum as consequence of the thermal reactivity of double bonds (Fig. 4d). Furthermore, there is a yellowing of the sample and an increase of the absorbance at  $\lambda > 350$  nm, which may assigned to Fries rearrangements.

In order to characterize the photoproducts, irradiated samples of p-4 and p-6 at 150 °C in the mesomorphic state for 1 h have been studied by NMR. Besides an irradiated sample of m-8 at 150 °C has also been also studied. At this temperature this sample is isotropic and can be useful as reference to investigate the influence of the mesomorphic order on the photoreactivity. Additionally, a sample of p-4 was irradiated for 7 min in order to compare the photoproducts contents at different irradiation times. Figs. 5–7 show the NMR spectra corresponding to photoirradiated samples at 150 °C. At a first sight, signals corresponding to initial double bonds of

the cinnamic group are observed in all cases, which proves that it is not a complete reaction of these bonds. To explain this, it must be taken into account that a large amount of sample is necessary for these measurements and the irradiated samples are thicker than in other techniques which require a less amount of sample. As a consequence, photoreactions mainly take place in the surface. In addition, signals at 3.03 and 6.67 correspond to Michler's ketone used as sensitizer.

The study of the spectrum corresponding to p-4 irradiated for 7 min (Fig. 5) reveals the presence of the Z-isomer characterized by two signals at 6.92 and 5.97 ppm with a  $J = 12.7$  Hz. Additionally, two signals at 4.44 and 3.82 are detected and correspond to a cyclobutane ring, which were assigned to a derivative of a  $\beta$ -truxinic acid according to the reported values for different photoproducts of cinnamates [20,21]. The spectrum of the sample irradiated during 1 h (Fig. 6) also exhibited the signals corresponding to the Z-isomer and the signals previously assigned to the  $\beta$ -truxinic acid derivative. Furthermore, there is a new signal at 3.45 together with a broadening of the signal at ca. 3.8, which evidences the existence of protons corresponding to a new cyclobutane ring. The coupling of these signals (3.45 and 3.78) were confirmed by decoupling experiments. By comparison with the literature the new cyclobutane ring that appears on increasing the irradiation time was identified as a  $\delta$ -truxinic derivative [20].

Similar products are detected in p-6 (irradiated at 150 °C in the  $S_C$  phase) and, surprisingly in m-8 irradiated at the same temperature in a isotropic liquid phase (see Fig. 7). Apparently, these results seem to prove a low influence of the mesomorphic order in the photoreactivity. However, the integration of the signals corresponding to the cyclobutane rings do reveal that influence. Table 3 collects the percentage of double bonds which have reacted by irradiation at 150 °C. As can be observed that there is about 20% of unreacted double bonds after 1 h of irradiation which is a consequence of the thickness of the sample. On the other hand, the percentage of Z-isomers is quite similar in the three samples, which proves that there is a E-Z steady state isomerization depending on the molecular mobility and consequently on the temperature. The percentage of double bonds which

Table 3  
Percentage of cinnamate double bonds (calculated from the  $^1\text{H}$  NMR spectra) which have been transformed by irradiation of photoreactive samples at 150 °C

| Photoreactive compound and irradiation time (t) | Phase <sup>a</sup> | Percentage (%) <sup>b</sup> |    |         |          |
|---|--------------------|-----------------------------|----|---------|----------|
|   |                    | E                           | Z  | $\beta$ | $\delta$ |
| p-4; t = 420 s                                  | $S_A$              | 84                          | 4  | 12      | –        |
| p-4; t = 3600 s                                 | $S_A$              | 28                          | 10 | 45      | 17       |
| p-6; t = 3600 s                                 | $S_C$              | 21                          | 9  | 47      | 23       |
| m-8; t = 3600 s                                 | I                  | 27                          | 10 | 17      | 46       |

<sup>a</sup> Temperature = 150 °C.

<sup>b</sup> E: unreacted E-double bonds; Z: double bonds transformed into the Z-isomer;  $\beta$ : transformed into the  $\beta$ -truxinic derivative cyclobutane ring;  $\delta$ : transformed into the  $\delta$ -truxinic derivative cyclobutane ring.

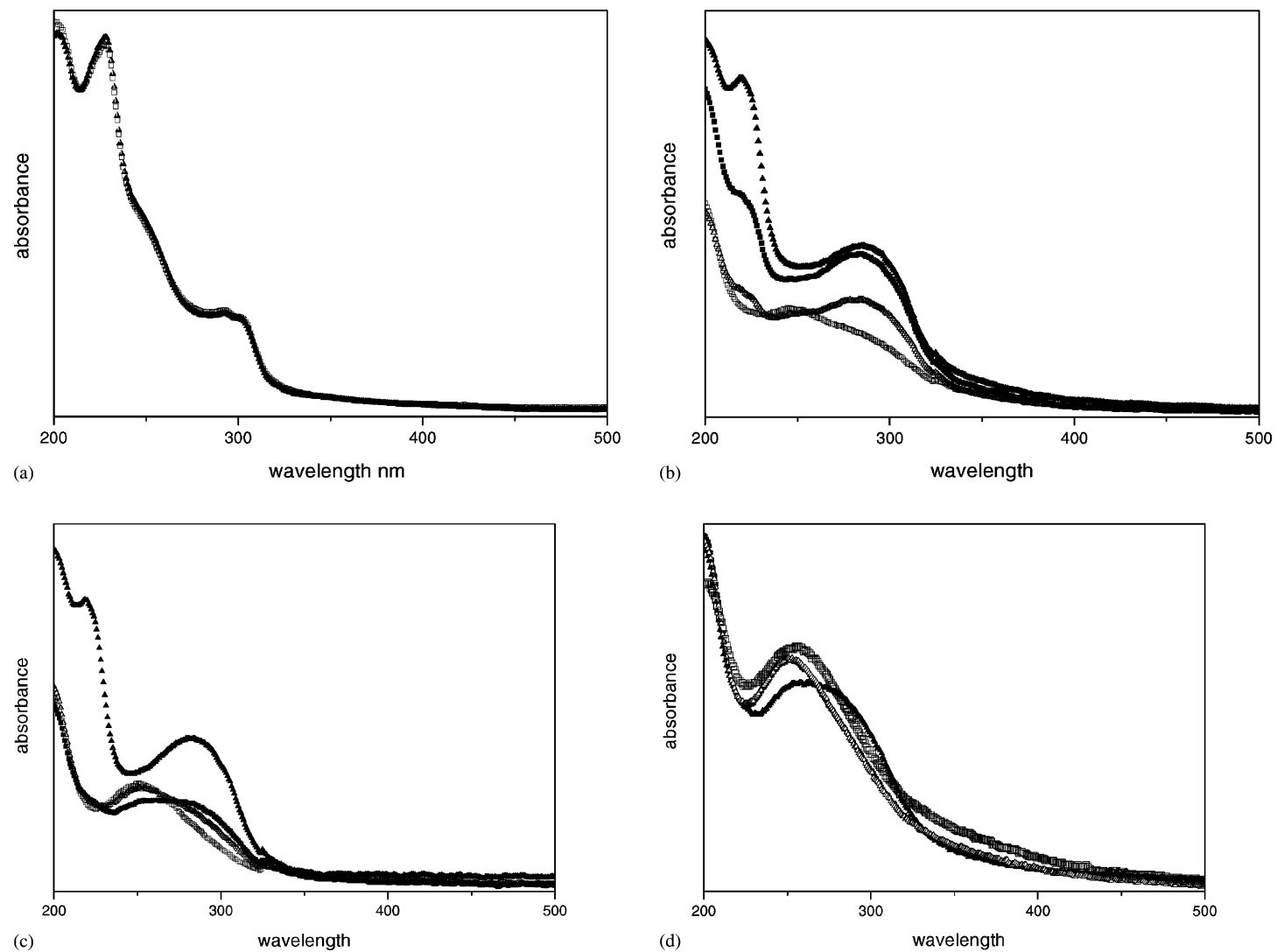


Fig. 4. Dependence of the UV-Vis spectrum of the photoreactive sample p-6 irradiated at different temperatures: (a) irradiation temperature: 90 °C, solid phase; (b) 150 °C, smectic C phase; (c) 200 °C, smectic A phase; (d) 260 °C isotropic liquid phase. Times of irradiation: (▲) 0 s; (■) 180 s; (△) 420 s; (□) 3600 s.

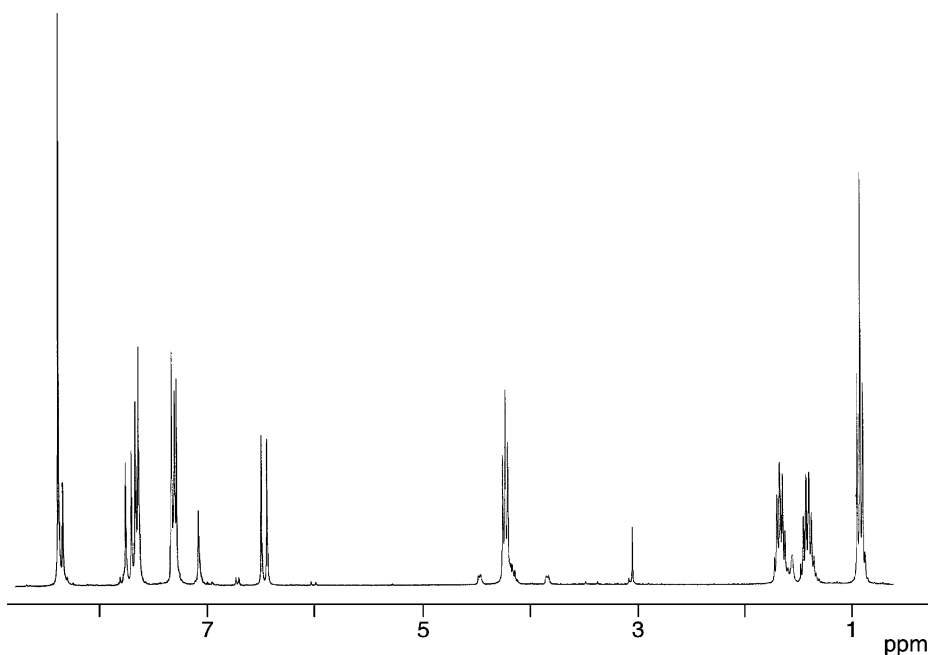


Fig. 5.  $^1\text{H}$  NMR spectrum corresponding to a sample of p-4 containing 2% (w/w) of Michler's ketone and irradiated for 420 s at  $150^\circ\text{C}$  in the smectic A phase (deuterated chloroform as solvent). Signals at 3.03 and 6.67 ppm correspond to Michler's ketone.

gives rise to [2 + 2] cyclodimerization is also similar in the three samples but the difference between samples irradiated at smectic or isotropic phase is the predominant cyclobutane derivative. In fact, the  $\beta$ -truxinic derivative is mainly obtained by irradiation at the mesophase and the  $\delta$ -truxinic

derivative is mainly obtained at the isotropic state. As it can be seen in Fig. 8, both types of cyclobutane rings derive from a head-to-head approach. The parallel orientation of the mesogens within the smectic layers mainly favors approach (a) which can justify the appearance of a  $\beta$ -truxinic deriva-

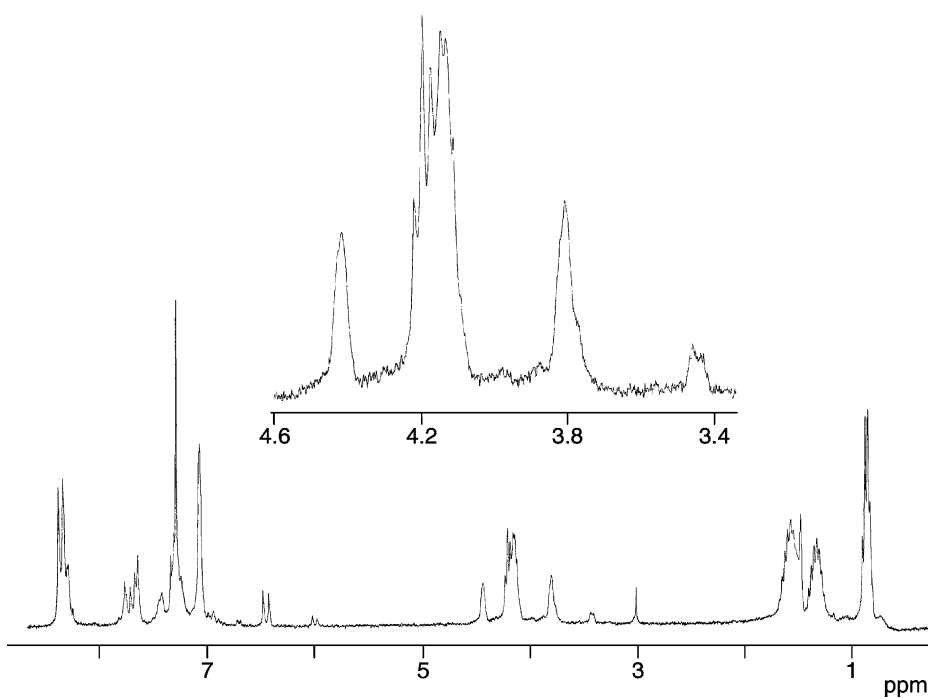


Fig. 6.  $^1\text{H}$  NMR spectrum corresponding to a sample of p-4 containing 2% (w/w) of Michler's ketone and irradiated for 3600 s at  $150^\circ\text{C}$  in the smectic A phase (deuterated chloroform as solvent). Signals at 3.03 and 6.67 ppm correspond to Michler's ketone.



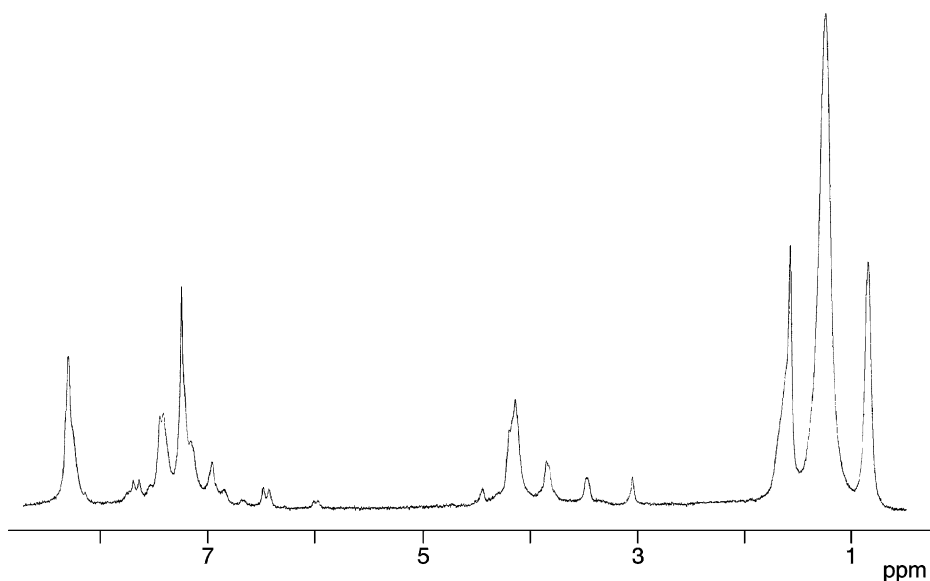


Fig. 7.  $^1\text{H}$  NMR spectrum corresponding to a sample of m-8 containing 2% (w/w) of Michler's ketone and irradiated for 3600 s at  $150^\circ\text{C}$  in the isotropic liquid phase (deuterated chloroform as solvent). Signals at 3.03 and 6.67 ppm correspond to Michler's ketone.

tive. In the case of an isotropic state the intermolecular interactions between the rigid cores also favor a head-to-head approach, but in this case the molecular disorder might justify the  $\delta$ -truxinic derivative as the main photoproduct. Finally, the appearance of the  $\delta$ -truxinic derivative when a meso-

morphic sample is irradiated for a long time can be justified because as a consequence of the [2 + 2] cyclodimerization and the *E-Z* isomerization there is greater molecular disorder and a mesophase-isotropic phase transition takes place during irradiation [22]. It must be taken into account

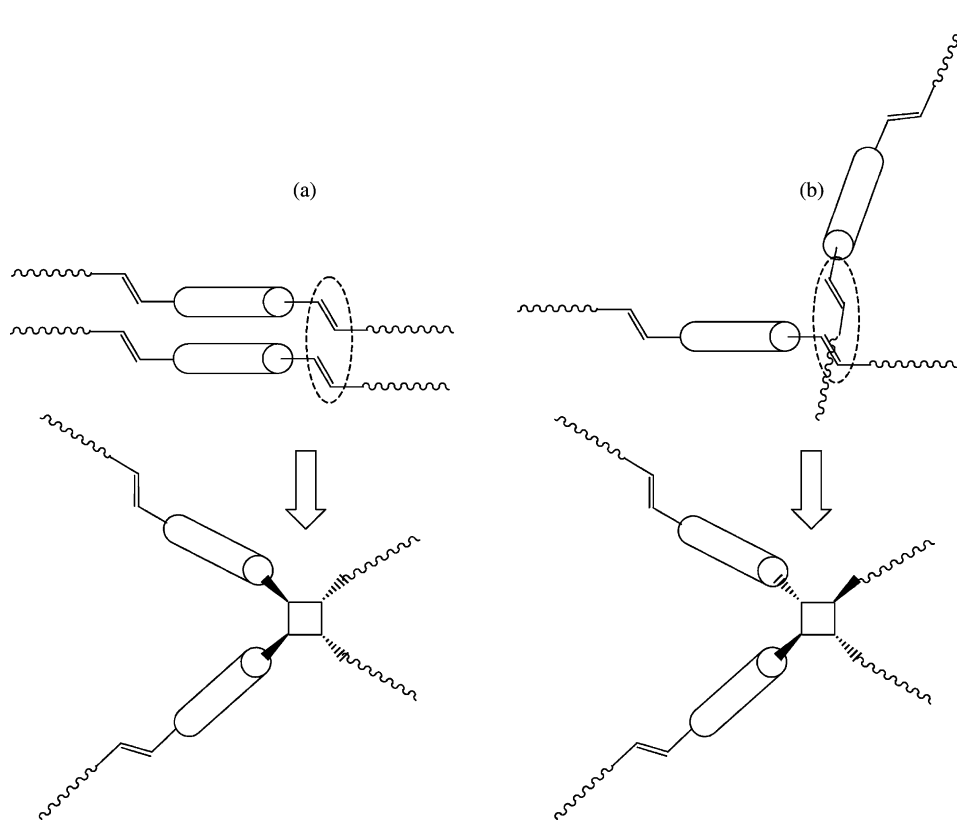


Fig. 8. Schematic representation of head-to-head approaches of cinnamate double bonds.



that the *Z*-isomer and the cyclobutane derivatives formed by irradiation are not mesogenic. In triplet sensitization it has been reported that the cyclodimerization proceeds by a two-step mechanism where a biradical is formed in the first step and the cyclobutane ring can close in the second step after one of the spins of the biradical is inverted [23]. According to this mechanism, the steric hindrance to the rotation about single bonds on the intermediates, that is imposed by the long alkyl chains and the central core, could explain the stereoselective formation of the two cyclobutane rings obtained.

In order to confirm the photoinduced phase transition, a very thin sample of p-4 and p-6 (with a 2% of Michler's ketone) was studied by optical microscopy. These samples were heated at 150 °C and a smectic texture was developed. When the sample is irradiated during a short period of time (e.g. 7 min) a biphasic system is observed (mesophase and isotropic phase). Samples irradiated for 1 h were isotropic amorphous materials confirming the photoinduced phase transition.

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