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Photoreactive furan derivatives

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Abstract

Several furan compounds bearing conjugated *trans* C=C plus carbonyl moieties appended at the C2 position of the heterocycle were synthesized and characterized. Near-UV irradiation in bulk and in concentrated solutions induced their dimerization through a $[\pi 2 + \pi 2]$ cycloaddition reaction between an excited and a ground state molecule. In dilute solutions, the excited species underwent predominantly *trans–cis* isomerization to give the equilibrium mixture of the isomers.
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1. Introduction

Within the last decade growing interest has been attached to the synthesis of polymers derived from renewable resources (cellulose, lignin, starch, chitin, etc.). The interest in this strategy is double: on the one hand, a large variety of products is available either directly or after chemical modification and, on the other hand, these sources are continuously renewed and ubiquitous.

Our laboratory has been involved for a long time in the valorization of some of these renewable resources [1,2] and among the numerous studies carried out in different domains, attention has also been focused on materials for printing processes, viz. inks [3] and photopolymers for offset plates[4,5]. In the latter context, the specific properties of the furan heterocycle were exploited, furfural being one of the most significant industrial chemicals obtained from the vegetable biomass [6].

Williams and Borden [7] were the first to exploit the photoreactivity of a polymeric structure bearing pendant furan-vinylene groups to obtain a cross-linked material. Several years later, Lahav and Schmidt [8] investigated the photodimerization of 2-furanacrylic acid and its esters in the solid-state and Karminsky-Zamola and Jakopêié [9] irradiated them in a dilute medium. These studies showed that the photochemistry of these compounds was strikingly similar to that of their cinnamic homologues, and led to the characterization of both forms of the ensuing cyclodimers, namely the truxillic and truxinic isomers.

In our laboratory, several investigations were devoted to the photochemistry of furan derivatives, including 2,5-furandiacrylic acid [10] and furan-vinylene derivatives [11]. More recently [4], the latter chromophores were grafted onto polyvinyl alcohol and the resulting polymers exposed to near-UV radiation. Their notable aptitude to cross-link made them good candidates as negative resins for offset plates [12].

In the present study we report the photochemical behavior of a series of furan compounds characterized by a common structural feature, namely the −C=C−(C=O)− moiety appended at the C2 position of the heterocycle, as shown below:
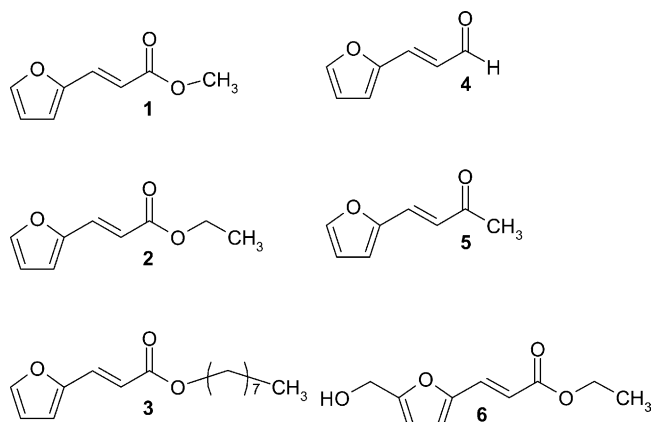
The implication of this investigation was its subsequent extension to the synthesis of photoactive polymers bearing these chromophores either in the macromolecular backbone, or as pendant groups.

2. Experimental

2.1. Materials

Commercial furfural was distilled before used, and hydroxymethyl furfural (HMF) was synthesized in our laboratory. The other reagents, catalysts and solvents were high-purity commercial products used as received.

2.2. Synthesis of 2-furanacrylic acid esters

Synthesis of methyl ester **1**: 10 g (7×10^{-2} mol) of furanacrylic acid and 19 mL (9×10^{-2} mol) of $SOCl_2$ were mixed, together with a few drops of DMF as catalyst and stirred for 4 h at 80 °C in a nitrogen atmosphere. Five grams (3×10^{-2} mol) of the ensuing product (after distillation) was made to react in a nitrogen atmosphere with 6 mL (15×10^{-2} mol) of methanol in methylene chloride, in the presence of triethylamine as HCl scavenger. After 10 h at room temperature, the mixture was washed three times with distilled water and the organic phase recuperated, dried over Na_2SO_4 and filtered. The solvents were then removed under reduced pressure. The ethyl (**2**) and octyl (**3**) esters were synthesized following the same procedure, using the corresponding alcohols, with yields of 78% and 70%, respectively. Table 1 shows that the characterization of these compounds confirmed their expected structure and purity.

2.3. Synthesis of furfurylidene derivatives 4 and 5 [13]

A solution of 2 g of NaOH in 50 mL of water was added dropwise to a stirred mixture of 5 g (5×10^{-2} mol) of furfural and 11.5 g (13×10^{-2} mol) of acetaldehyde, keeping the temperature below 20 °C. The reaction mixture was left un-

der stirring for 2 h and then neutralized with acetic acid and washed three times with distilled water. The organic phase was recovered, dried over Na_2SO_4 and filtered. The solvents were then removed under reduced pressure and compound **4** was characterized. The homologous compound **5** was synthesized in the same way using furfural and acetone. Table 1 gives the results of their characterization, which indicate the success of these syntheses.

2.4. Synthesis of 2-hydroxymethyl-5-furanacrylic acid ethyl ester 6 [14]

10.3 g (8×10^{-2} mol) of HMF, 10.2 g (4.5×10^{-2} mol) of triethylphosphoacetate, 3 g of water and 15 g (2.3×10^{-2} mol) of K_2CO_3 were added to 200 mL of dioxane in a flask equipped with a magnetic stirrer and a reflux condenser. The mixture was heated at 70 °C for 4 h under stirring and then filtered before removing the solvent under reduced pressure. The excess HMF was eliminated by a dichloromethane/water separation. The organic phase was recovered, dried over Na_2SO_4 and filtered. The solvents were then removed under reduced pressure. Table 1 shows the data proving that compound **6** was indeed obtained.

2.5. Analytical techniques

^1H NMR spectra were taken with a Brüker AC200 in deuterated dichloromethane solutions. FTIR spectra were recorded with a Perkin-Elmer Paragon 1000 using KBr pellets or NaCl plates. UV–vis spectra were taken with a ThermoSpectronic UNICAMUV 500 using spectrophotometric grade solvents. Differential scanning calorimetry (DSC) was carried out with a Setaram DSC92 using aluminum pans. Scans were run under a nitrogen atmosphere, scanning at 10 °C min^{-1} from −140 °C to 150 °C.

2.6. Irradiation procedures

The irradiations were carried out in a nitrogen atmosphere using a 500 W medium-pressure mercury arc provided with a Pyrex filter to limit the excitation to wavelengths higher than 270 nm. Samples were placed alternatively between two NaCl plates, in KBr pellets or in dichloromethane or toluene solutions.

3. Results and discussion

3.1. Syntheses and characterizations

The synthetic pathways leading to the furan compounds **1**–**6** is briefly sketched below and Table 1 provides the data relevant to their structure.
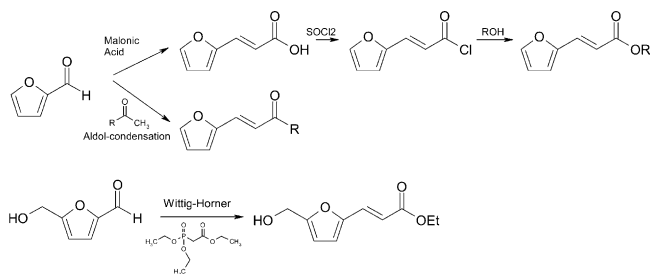
The *trans*-configuration of the double bond of all these compounds was confirmed by FTIR with the presence of the characteristic peak at 970 cm^{-1}, and by ^{1}H NMR with a coupling constant of the double bond protons of 16 Hz. All the compounds exhibited a glass transition, except **5**, which only exhibited a melting peak. Compound **3** had a lower T_g, because of the longer aliphatic moiety, which provided a higher molecular flexibility. The UV data (λ, ε) were in tune with published results related to similar structures [14,15].

3.2. Photochemistry

All the compounds showed a good absorption coincidence with the 313 nm emission line of the mercury lamp. In concentrated media (i.e. in bulk, or in 2–4 M solutions), the irradiation induced a [$\pi2 + \pi2$] cycloaddition reaction between an excited and a ground state molecule, viz.:
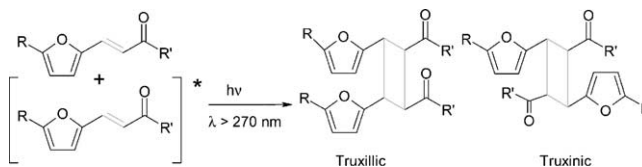
Indeed, when we followed this reaction by FTIR spectroscopy (Fig. 1), we noticed the progressive disappearance of the peaks characterizing the alkenyl double bond (1610–1620 cm^{-1} for C=C and ca. 970 cm^{-1} for CH= trans)

Table 1
Characterization of the furan photoactive compounds

| Compound	FTIR (cm^{-1})	^{1}H NMR (CD$_2$Cl$_2$) (ppm)	UV (CH$_2$Cl$_2$) λ_{max} (nm) ε (l mol^{-1} cm^{-1})	DSC transitions (°C)
1	Furan: 3130; 1017 COO: 1715 CH=CH*trans*: 1640; 972 CH$_3$: 2951	H$_1$: 7.51 (s, 1). H$_2$: 6.49 (d, 1). H$_3$: 6.64 (d, 1). H$_4$: 7.45 (d, 1, 16 Hz). H$_5$: 6.33 (d, 1, 16 Hz). H$_6$: 3.75 (t, 3).	302 21,800	$T_g = -55$
2	Furan: 3130; 1017 COO: 1708 CH=CH*trans*: 1640; 972 CH$_2$CH$_3$: 2982–2954	H$_1$: 7.51 (s, 1). H$_2$: 6.49 (d, 1) H$_3$: 6.64 (d, 1). H$_4$: 7.44 (d, 1, 16 Hz). H$_5$: 6.32 (d, 1, 16 Hz). H$_6$: 4.25 (q, 2). H$_7$: 1.32 (t, 3).	300 23,500	$T_g = -57$
3	Furan: 3125; 1017 COO: 1711 CH=CH*trans*: 1640; 972 CH$_2$CH$_3$: 2857–2954	H$_1$: 7.59 (s, 1). H$_{2-5}$: 6.49–6.47 (d, 2). H$_3$: 6.81 (d, 1). H$_4$: 7.28 (d, 1, 16 Hz). H$_5$: 6.32 (d, 1, 16 Hz). H$_6$: 4.17 (m, 2). H$_7$: 1, 3 (m, 10). H$_8$: 1.68 (q, 2). H$_9$: 0.89 (t, 3).	300 23,500	$T_g = -70$ $T_{cryst} = -27$ $T_m = 11$
4	Furan: 3128; 1019 CO: 1676 CH=CH*trans*: 1627; 962	H$_1$: 7.51 (s, 1). H$_2$: 6.49 (d, 1). H$_3$: 6.64 (d, 1). H$_4$: 7.44 (d, 1, 16 Hz). H$_5$: 6.59 (d, 1, 16 Hz). H$_6$: 9.62(d, 1).	316 25,700	
5	Furan: 3130; 1031 CO: 1661 CH=CH*trans*: 1624; 962 CH$_3$: 2856–2960	H$_1$: 7.52 (s, 1). H$_2$: 6.52 (d, 1). H$_3$: 6.7 (d, 1). H$_4$: 7.29 (d, 1, 16 Hz). H$_5$: 6.61 (d, 1, 16 Hz). H$_6$: 2.29 (s, 3).	316 23,600	$T_m = 48$
6	Furan: 3122; 1020 OH: 3455 COO: 1707 CH=CH*trans*: 1637; 969 CH$_2$CH$_3$: 2857–2981	H$_1$: 3.57 (s, 1). H$_2$: 4.57 (s, 2) H$_3$: 6.36 (d, 1). H$_4$: 6.57 (d, 1) H$_5$: 7.38 (d, 1, 16 Hz) H$_6$: 6.27 (d, 1, 16 Hz) H$_7$: 4.23 (q, 2), H$_8$: 1.31 (t, 3)	308 24,650	$T_g = -53$ $T_{cryst} = -8$ $T_m = 34$
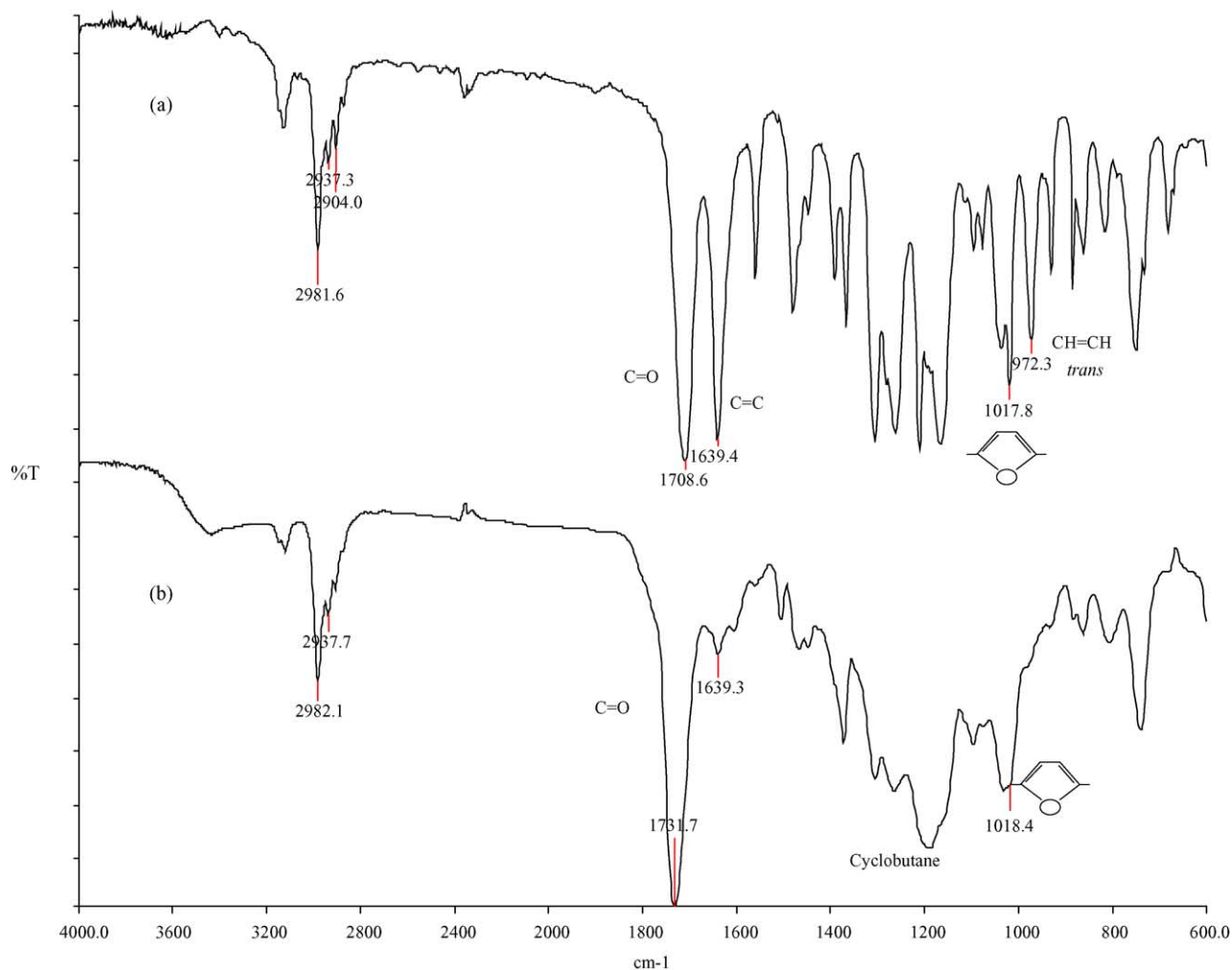
Fig. 1. FTIR spectra (NaCl disks) of **2** before (a) and after (b) 6 h irradiation.

the appearance of peaks corresponding to the cyclo-butane ring, near 1200 cm^{-1} for the CH bending mode and near 735 cm^{-1} for the ring deformation, and the displacement of other peaks due to the new non-conjugated electronic environment. In particular, the carbonyl band shifted from around 1710 cm^{-1} to about 1730 cm^{-1} as a result of this loss of conjugation.

This displacement of the peak characterizing the carbonyl moiety passed through an isobestic point, as shown in Fig. 2. This behavior suggested that the photoreaction of the conjugated chromophores followed the *single* reaction pathway [16] sketched above.

The presence of this isobestic point was verified using Mauser's diagram [17], by plotting the decrease of the absorbance at several frequencies $\Delta A_i(t)$ against the decrease of the absorbance $\Delta A_{max}(t)$ related to the peak of the C=C double bond, where t is the irradiation time (Fig. 3). The linear dependence with a zero intercept indicated a uniform A→B reaction, which confirmed our proposed single-step pathway.

The conversion of these reactions was calculated using the following equation:

$$\alpha(t) = \frac{D_0 - D}{D_0}(\upsilon_{C=C})$$

where D_0 and D are the absorbance of the irradiated compound at $t = 0$ and at time t, respectively.
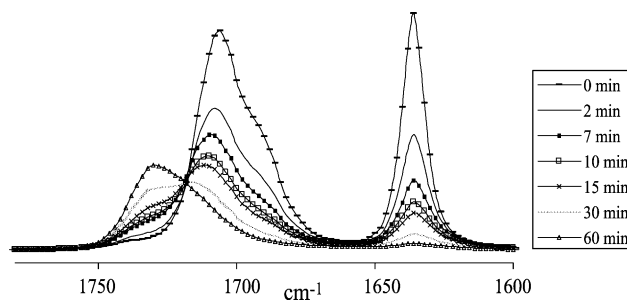

Fig. 2. Evolution of the FTIR (NaCl disks) spectrum of **6** with irradiation time in the region of both carbonyl and alkenyl absorption.
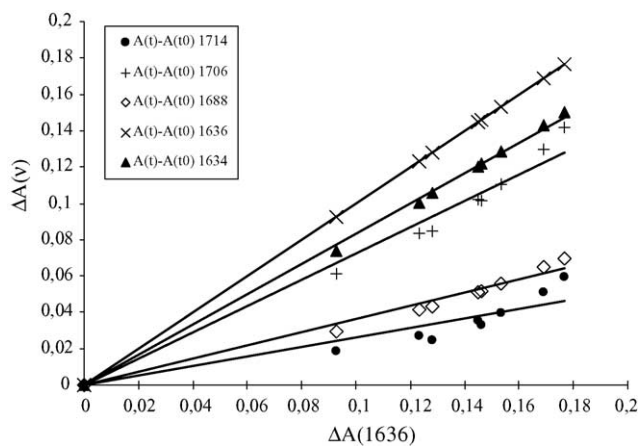
Fig. 3. Mauser diagrams of the photocycloaddition of **6**.

Fig. 5. Typical first-order plot for the cyclodimerization of **2**.

The photoreaction rates depended on the actual structure submitted to irradiation (Fig. 4) and the esters were found to be less reactive because of the steric crowding of the alkyl moiety [18]. Compound **6** was the most reactive ester, probably because the hydroxy group facilitated the cycloaddition through intermolecular hydrogen bonding. The fact that **5** displayed the highest reactivity was attributed to (i) the good match between the wavelengths of its absorption maximum and of the 313 nm line of the Hg lamp and (ii) its high crystallinity, which favored the photodimerization between preoriented molecules.

The kinetics of cyclodimerization were also examined and Fig. 5 shows the typical first-order plot relative to one of these experiments.

The UV analyses (Fig. 6) clearly confirmed the proposed mechanism by the progressive decrease in the intensity of the peak around 300 nm (disappearance of the C=C double bond and hence of the conjugation it assured between the furan ring and the carbonyl group) and the concomitant appearance of a peak at 230 nm due to the $\pi\pi^*$ transition of the unconjugated furan moieties in the dimers.
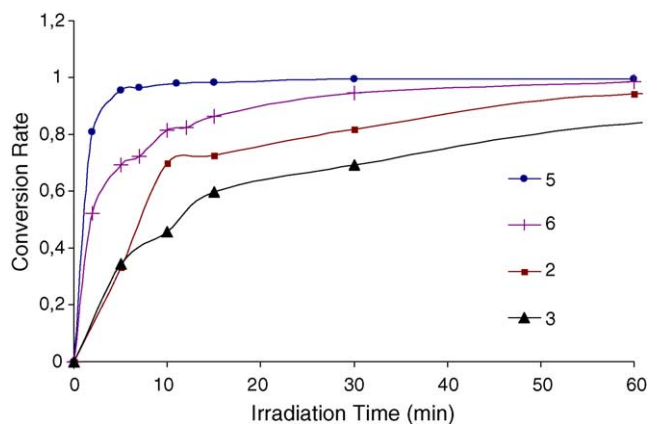
The molecular character of these photodimerizations was confirmed by the fact that the presence of an added radical inhibitor, TEMPO or hydroquinone, did not alter the course of the reactions.

The NMR spectrum of the product isolated after the irradiation of **5** in a 2 M CD_2Cl_2 solution (Fig. 7) shows the presence of two distinct cyclodimers, corresponding to the truxinic and the truxillic isomers in a 50–50 proportion. The photochemical behavior of **4** was entirely similar to that of **5**.

The irradiation of the esters **1**, **2**, **3** and **6** in the same conditions also induced some *trans–cis* isomerization (Table 2), as suggested by the appearance of additional peaks at 5.7 and 6.7 ppm (Fig. 8) characterizing the *cis* isomer, with its typical coupling constants of 11 Hz.

When all these compounds, which were in their *trans* conformation, were irradiated in dilute media (ca. 0.1 M), they underwent a progressive unimolecular *trans–cis* isomerization to reach the equilibrium concentration of conformers. When these reactions were followed by FTIR spectroscopy (Fig. 9), a peak characterizing the *cis* isomer appeared at $820\,cm^{-1}$ and its intensity increased with time to reach a constant value, reflecting the onset of the *cis–trans* equilibrium.

In comparison, the solid-state irradiation of *trans*-benzalacetone leads to dimerization [19]. In the same way, the irradiation of liquid *trans*-ethyl cinnamate leads to cycload-

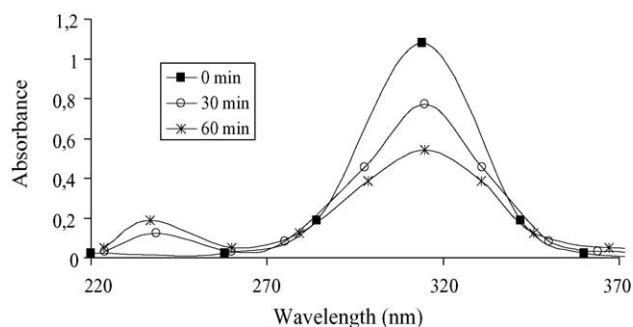Fig. 4. Photodimerization rate of selected compounds.

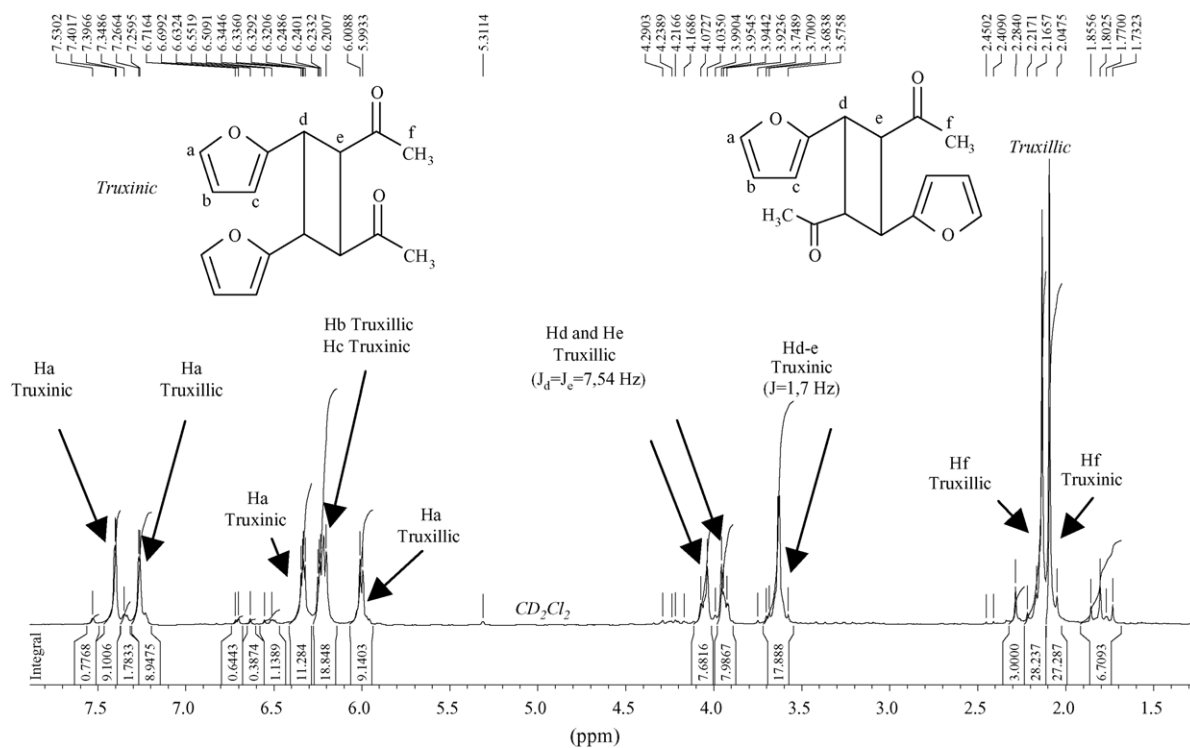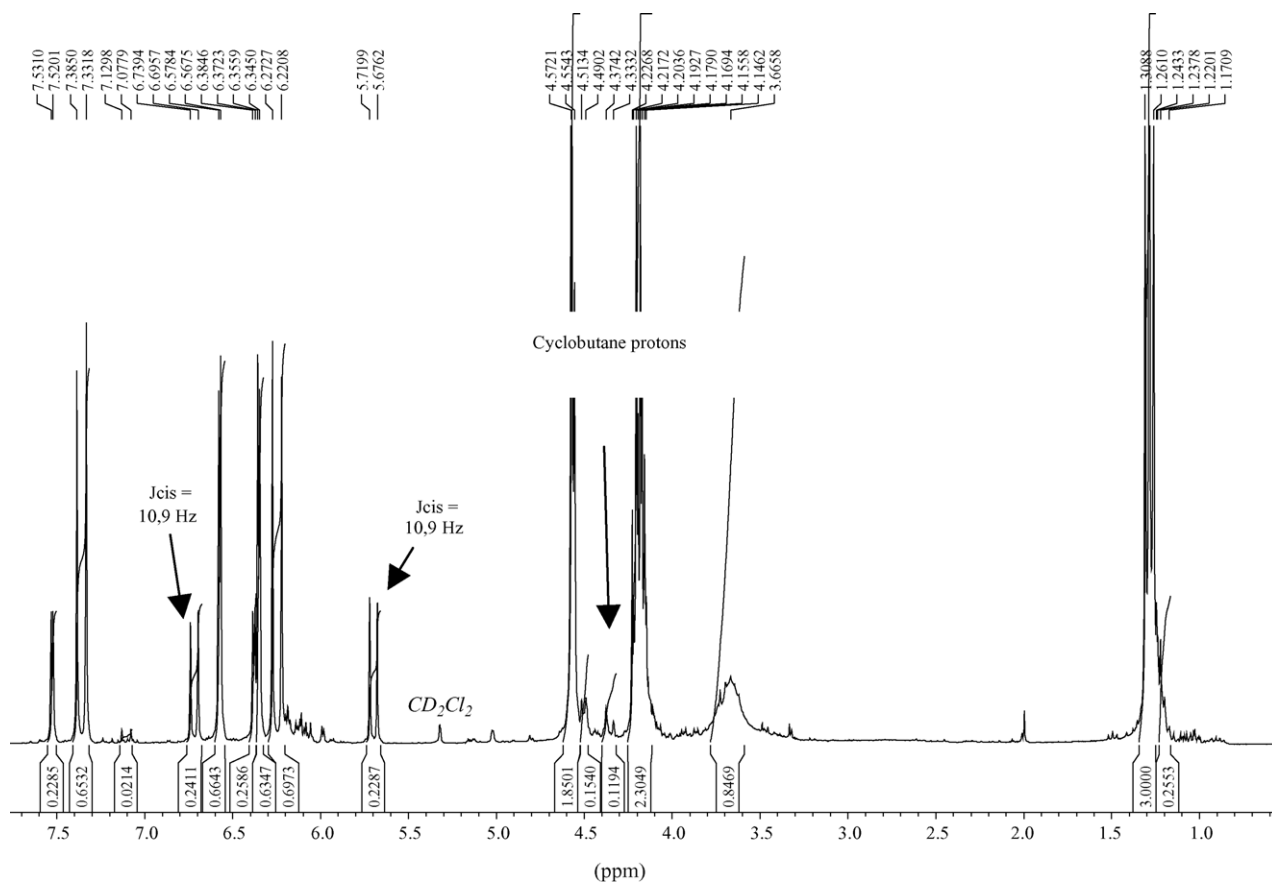Fig. 6. Evolution of the UV spectrum of **5** with irradiation time.

Fig. 7. ^{1}H NMR spectrum of **5** after 12 h of irradiation in CD_2Cl_2.

Fig. 8. ^{1}H NMR spectrum of **6** irradiated for 5 h in CD_2Cl_2.

Table 2
Ratio of isomerization and dimerization during irradiation in a 2 M CD_2Cl_2 solution

Irradiation time	1 h		2 h		3 h		6 h	
Ratio	$\alpha(I)$ %	$\alpha(D)$ %	$\alpha(I)$ %	$\alpha(D)$ %	$\alpha(I)$ %	$\alpha(D)$ %	$\alpha(I)$ %	$\alpha(D)$ %
1	4.9	0	7.6	0	10.5	0	15.1	0
2	6.5	0	8.3	0	11.1	0	15.1	0
5	0	34.2	0	54.6	0	66.6	0	88.9
6 ($C = 1.6$ M)	11	2.6	15.7	3.6	5.6	20.3	8.7	26.1

$\alpha(I)$%: ratio of isomerization, $\alpha(D)$%: ratio of dimerization.
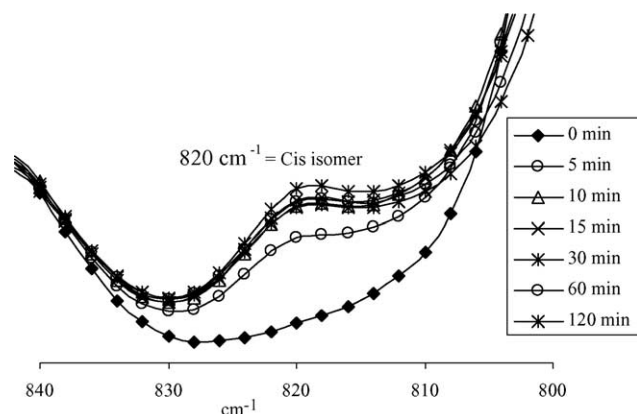

Fig. 9. Evolution of the FTIR spectrum of a dilute CH_2Cl_2 solution of **6** with irradiation time.

dition products in high yield (55% of truxillate and 25% of truxinate) [20]. However, the irradiation of methyl cinnamate in the solid-state ($T_m = 33\,°C$) results in a complex mixture of dimeric species and *cis*-methyl cinnamate [21]. But, in dilute solution, the photochemical cyclodimerization of cinnamic acid derivatives is highly inefficient due to the very rapid competing photoisomerization [21].

4. Conclusion

The exploitation of chemicals derived from renewable resources produced furan photosensitive structures, which, when irradiated with near-UV light, followed the classical photocycloaddition mechanism of cinnamic derivatives.

The inclusion of these chromophores into macromolecular structures is being studied in order to obtain novel photocross-linkable materials.

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