

Photodimerization of heteroarylene-vinylenes

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Abstract

Various furanic and thiophenic compounds bearing conjugated structures, based on the bridging of heterocycles with alkenyl moieties, were excited in the near-UV in the solid state and in solution. *E-Z* isomerization, leading to thermodynamic composition, was the dominant photochemical pathway in dilute solution, whereas $[\pi 2 + \pi 2]$ cyclodimerization through external unsaturation occurred in concentrated media and, more efficiently, with crystalline morphologies. Compounds containing two independent chromophores dimerized giving the corresponding cyclophane-type macrocycles. © 1997 Elsevier Science S.A. All rights reserved.

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1. Introduction

Although the photochemistry of six-membered-ring aryleno-vinylene compounds has been widely studied both in terms of the cyclodimerization of monofunctional species and of the polymerization of difunctional homologues [1], much less work has been performed on similar structures bearing five-membered heteroaromatic moieties, such as furan and thiophene rings. Williams and Borden [2] were the first to exploit the photoreactivity of a polymeric structure with pendant furan-vinylene groups to obtain a crosslinked material. Several years later, a more scientific approach was applied by Lahav and Schmidt [3] to the photodimerization of 2-furanacrylic acid and its esters in the solid state. This study showed the similar reactivity of these compounds compared with that of the cinnamic homologues, and led to the characterization of both forms of the cyclodimer, namely the truxinic and truxillic isomers.

Tsuda [4] attached furanacrylic moieties to polyvinyl alcohol and photocrosslinked the resulting polymers. Very little has been reported on the photochemistry of compounds containing two alkenyl groups attached to a five-membered heteroaromatic ring. Hasegawa et al. [5] reported the photopolymerization of 1,4-difurylvinylbenzene, and concluded that oligomeric non-linear products were formed, but their detailed structural features were not explored. More recently,

an investigation was carried out in our laboratory on the photodimerization of 2,5-furandiacyric acid (FDA), in which it was shown that the irradiation of this crystalline compound in the near-UV led to the "classical" cyclobutane dimer in which the substituents were placed in a symmetric fashion [6]. This dimer decomposed at 220 °C to give its precursor. Further unpublished work was carried out on the possibility of photopolymerizing the solid dimer using shorter wavelengths, but the ensuing products did not show the expected regular structure, suggesting the occurrence of side reactions induced by the higher excitation energy.

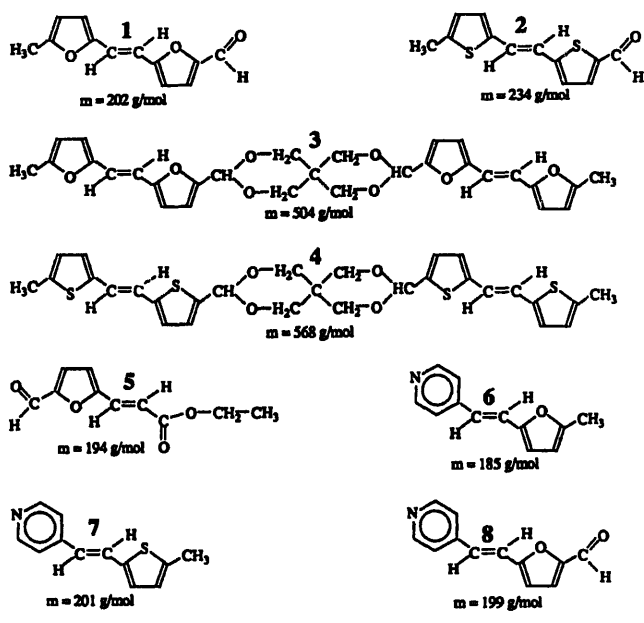
Our laboratory has been engaged for the last decade in a thorough study of the synthesis and properties of furanic polymers [7,8] and, of the various structures explored, we recently envisaged the possibility of preparing photosensitive macromolecules bearing furan-alkenyl groups in order to develop novel photocrosslinkable materials. This investigation is in full progress and this report deals with its first phase, namely the synthesis of model compounds containing characteristic chromophores, including both furanic and thiophenic derivatives, and the study of their photochemistry in the near-UV. It was deemed advisable to acquire this knowledge before applying it to more complex polymeric systems.

2. Synthesis and characterization of the photosensitive compounds

The syntheses and structural characterizations described below involved standard equipment and procedures as well

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Table 1
Structures of the photosensitive compounds



as commercial reagents and solvents of high purity, except when stated otherwise.

Table 1 gives the structures of the different compounds synthesized in this investigation. Compound 1 was prepared by base-catalysed self-condensation of 5-methylfurfural (MF) in a water–methanol mixture. A systematic study of the influence of the relevant parameters led to the following optimized conditions. MF (4 ml) was dissolved in a mixture of 20 ml of water and 10 ml of methanol containing 0.6 g of NaOH. The solution was brought to boiling point and refluxed for 1 h. The reddish product was vacuum distilled and gave 40% of pure 1. The synthesis of the thiophene homologue 2 was carried out in the same conditions, using 5-methylthiophene carboxaldehyde, and gave directly 45% of the crystalline dimeric condensation product. Both 1 and 2 were obtained as pure *E* isomers. Their acetalization reactions with pentaerythritol were conducted in dimethylsulphoxide (DMSO) at room temperature for 24 h using *p*-toluenesulphonic acid as catalyst. The resulting mixture was poured into an excess of water in order to precipitate the corresponding disubstituted derivatives 3 and 4, which were thus separated in 50% yield from the remaining unreacted materials and monosubstituted intermediates. The furanic aldehyde acrylate 5 was prepared in 50% yield by the oxidation of the corresponding alcohol [9], kindly provided by Professor Gaset of Toulouse National Polytechnic Institute, using an excess of activated MnO_2 .

Structures 6 and 7 containing pyridinic moieties were synthesized by condensing 4-methylpyridine with MF and 5-methylthiophene carboxaldehyde respectively. These reactions were conducted in a mixture of acetic acid and acetic anhydride under reflux for 4 h. After neutralization with

sodium carbonate, the products were isolated in approximately 20% yield by extraction with methylene chloride. Compound 8 was prepared from carefully purified 2,5-furandicarboxaldehyde (which was in turn obtained by the oxidation of hydroxymethylfurfural with V_2O_5 and purified by several recrystallizations) and a large excess of 4-methylpyridine, which was used as the reaction medium, in the presence of catalytic amounts of HCl. After a 1 h reflux, the yield of the condensation product 8 was about 50%.

Table 2 reports the major features related to the characterization of these products. All spectroscopic data showed unambiguously that the structures were correct and that no detectable impurities were present in the samples, which were therefore used as prepared for the irradiation experiments.

3. Photochemical behaviour

The light sources used in this work comprised two high-pressure mercury lamps yielding 125 and 500 W and a medium-pressure 400 W Fe/Co iodide lamp. In all instances, a Pyrex filter was used to cut out any wavelength lower than about 300 nm. Thus, for the Hg lamps, the 313 and 366 nm lines were mostly responsible for the excitation, whereas with the metal iodide lamp the irradiation occurred essentially through several lines between 320 and 400 nm. No qualitative difference was encountered when one lamp was replaced by another for a given system, showing that the main photochemical features of the various structures investigated do not depend on the specific spectral distribution within the wavelength range 300–400 nm. It was therefore decided that a more detailed study on the influence of the excitation wavelength was not a priority with respect to the understanding of the photochemical mechanisms proposed below.

The major part of the study was conducted by irradiating solid samples of compounds 1–8 either in the form of crystals dispersed in a solid KBr matrix or as a fine crystalline powder suspended in a non-solvent, namely distilled water for structures 1–5 and *n*-dodecane for structures 6–8 which were partly soluble in water. Solution photolyses were also carried out with compound 1 which was irradiated at room temperature in methylene chloride, chloroform and CCl_4 under a nitrogen atmosphere. The course of the photolyses was followed by Fourier transform IR (FTIR) and proton nuclear magnetic resonance ($^1\text{H-NMR}$) spectroscopy, and the final products were submitted to the same thorough characterization as their precursors.

The furanic unsaturated aldehyde 1 was the object of a systematic investigation with respect to its photosensitivity. Its irradiation in relatively dilute solutions (around 0.1 M) resulted in a monomolecular *E-Z* isomerization, which reached an equilibrium distribution within less than 1 h with the more powerful lamp. Fig. 1 shows the $^1\text{H-NMR}$ spectrum of the mixture of the two isomers in thermodynamic equilibrium. Further irradiation of this mixture did not produce any detectable additional change. These features were also

Table 2
Characterization of the photosensitive compounds

Structure	T_m (°C)	UV-visible, λ_{max} (nm), ϵ ($1 \text{ mol}^{-1} \text{ cm}^{-1}$)	Mass M^{+} (m/z)	FTIR (KBr pellet) (cm^{-1})	$^1\text{H-NMR}$ (300 MHz, TMS, solvent CD_2Cl_2) (ppm)
1	86	CH_2Cl_2 , 393, 4.9×10^4	202 (187, 159, 131, 173)	Furans: 3021; 1591; 1472; 1271; 1020; 982; 973. $-\text{CH}=\text{CH}-$ trans: 1626; 957. $-\text{CH}_3$: 2810	H_a : 2.32 (3H, s); H_b : 6.08 (1H, d); H_c : 6.40 (1H, d); H_d, H_e : 6.73 and 6.78 (2H, q); H_f : 6.48 (1H, d); H_g : 7.21 (1H, d); H_h : 9.54 (1H, s)
2	108	CH_2Cl_2 , 392, 19400	234 (219, 205, 190, 111)	Thiophenes: 1456; 1433; 1047; 812; 791. $-\text{CH}=\text{CH}-$ trans: 1605; 947. $-\text{CH}_3$: 2924; 2854	H_a : 2.48 (3H, s); H_b : 6.95 (1H, d); H_c : 7.09 (1H, d); H_d, H_e : 6.70 and 6.87 (2H, q); H_f : 7.24 (1H, d); H_g : 7.85 (1H, d); H_h : 9.80 (1H, s)
3		CH_2Cl_2 , 354	504 (272, 202, 187, 173, 131, 77)	Furans: 3136; 1540; 1402; 1173; 1018; 968; 941. $-\text{CH}=\text{CH}-$ trans: 1587; 987. $-\text{C}-\text{O}-\text{C}-$ acetal: 1173. $-\text{CH}_3$ and $-\text{CH}_2$: 2930; 2854	H_a : 2.31 (6H, s); H_b : 6.01 (2H, d); H_c : 6.26 (2H, d); H_d, H_e : 6.70 and 6.73 (4H, q); H_f : 6.23 (2H, d); H_g : 6.44 (2H, d); H_h : 5.51 (2H, s); H_i : 3.41–4.72 (8H, m) ^a
4		CH_2Cl_2 , 354.3	568 (304, 234, 219, 205, 111)	Thiophenes: 3136; 1433; 1036; 804. $-\text{CH}=\text{CH}-$ trans: 1607; 949. $-\text{C}-\text{O}-\text{C}-$ acetal: 1144. $-\text{CH}_3$ and $-\text{CH}_2$: 2930; 2854	H_a : 2.40 (6H, s); H_b : 6.73 (2H, d); H_c : 6.97 (2H, d); H_d, H_e : 6.94 and 7.01 (4H, q); H_f : 6.79 (2H, d); H_g : 7.03 (2H, d); H_h : 5.63 (2H, s); H_i : 3.64 (2H, d) and 3.77–3.91 (4H, d) and 4.54 (2H, s) ^a
5		CH_2Cl_2 , 332	194 (165, 137, 149, 121)	Furans: 1591; 1472; 1271; 1020; 982; 973. $-\text{CH}=\text{CH}-$ trans: 1625; 980. $-\text{CHO}$: 2720; 1705	H_a : 9.65 (1H, s); H_b : 7.41 (1H, d); H_c : 6.54 (1H, d); H_d, H_e : 6.77 and 7.26 (2H, q); H_f : 4.23–4.25 (2H, m); H_g : 1.28–1.33 (3H, m)
6		CH_2Cl_2 , 393	185 (156, 170, 142, 115, 93, 77, 39)	Furans: 3125; 1574; 1196; 1019; 980; 953. Pyridines: 3100; 3000; 1615; 873; 935. $-\text{CH}=\text{CH}-$ trans: 983; 953	H_a : 2.35 (3H, s); H_b : 6.37 (1H, d); H_c : 6.07 (1H, d); H_d, H_e : 6.81 and 7.06 (2H, q); $\text{H}_f, \text{H}_g, \text{H}_h, \text{H}_i$: 7.27–8.49 (4H, q)
7		CH_2Cl_2 , 392	201 (186, 174, 167, 89, 77, 51)	Thiophenes: 3018; 1595; 1414; 1034; 810; 790. Pyridines: 3133; 1539; 873. $-\text{CH}=\text{CH}-$ trans: 983; 951	H_a : 2.48 (3H, s); H_b : 6.80 (1H, d); H_c : 7.11 (1H, d); H_d, H_e : 6.73 and 7.67 (2H, q); $\text{H}_f, \text{H}_g, \text{H}_h, \text{H}_i$: 7.48–8.51 (4H, q)
8	104	Methanol, 342, 39300	199 (170, 142, 115, 63, 51, 39)	Furans: 3125; 1500; 1030; 797. Pyridines: 3100; 1668; 810. $-\text{CH}=\text{CH}-$ trans: 984. $-\text{CHO}$: 2730	H_a : 9.65 (3H, s); H_b : 7.62 (1H, d); H_c : 7.00 (1H, d); H_d, H_e : 7.28 and 7.52 (2H, q); $\text{H}_f, \text{H}_g, \text{H}_h, \text{H}_i$: 7.27–8.49 (4H, m)

^aSolvent DMSO.

observed with higher dilutions and were independent of the solvent polarity for dielectric constants in the range 2–10. There seems to be no ambiguity in the mechanism of this photolysis, which obviously involves the triplet state obtained on excitation of the π electron of the alkenyl function, giving a freely rotating $\pi\pi^*$ state, which yields a thermodynamic mixture of the two conformations of about 80% *E* and 20% *Z* when deactivation occurs with the re-establishment of the C–C π bond.

When more concentrated solutions were irradiated, the isomerization was accompanied by intermolecular events which became detectable when 2–4 M solutions in CD_2Cl_2 were irradiated directly in the NMR tube. In order to assess the mechanism of these photoaggregation reactions, we switched to the irradiation of solid samples of **1**. The FTIR, $^1\text{H-NMR}$ and electronic spectra of the irradiated samples as a function of the reaction time were the same when the solid was dispersed in a KBr pellet or in water, and showed a

progressive transformation of **1** into its cyclodimer **9**. Evidence for this mechanism is shown in Figs. 2–4 which give the spectra of the product. The structural features associated with the consumption of the alkenyl function and the corresponding formation of the cyclobutane moiety appear clearly in the FTIR spectrum (Fig. 2), compared with that of **1**, from the absence of the bands at 1628 and 982 cm^{-1} and the presence of a new band at 1516 cm^{-1} . Moreover, the carbonyl band is now at 1670 cm^{-1} , i.e. some 40 cm^{-1} higher than in **1** because of the decrease in the extent of conjugation. The $^1\text{H-NMR}$ spectrum of the product of the solid state irradiation of **1** is also in agreement with structure **9** as shown in Fig. 3. In particular, the alkenyl protons of **1** at 6.7 and 7.1 ppm have disappeared, being replaced by the cyclobutane counterparts at 4.41 ppm. The fact that the latter resonance appears as a singlet is strong evidence in favour of a symmetrical structure around the cyclobutane ring, as indicated in formula **9**. Fig. 4 shows the UV spectrum of **9** which differs substantially from

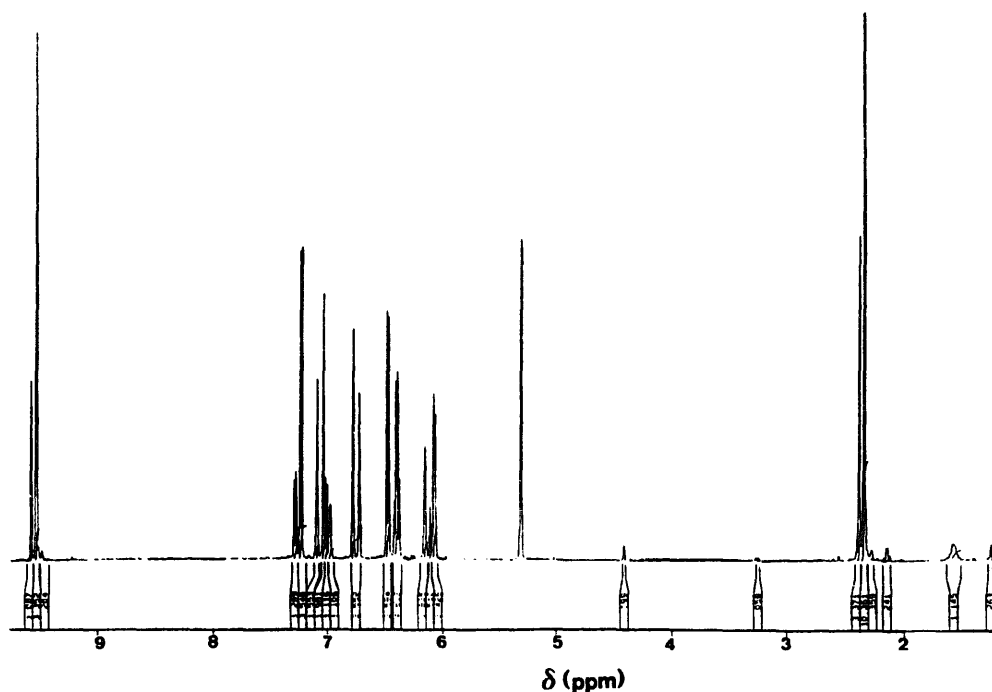


Fig. 1. $^1\text{H-NMR}$ (300 MHz) spectrum of a solution of **1** in CD_2Cl_2 after 1 h of irradiation.

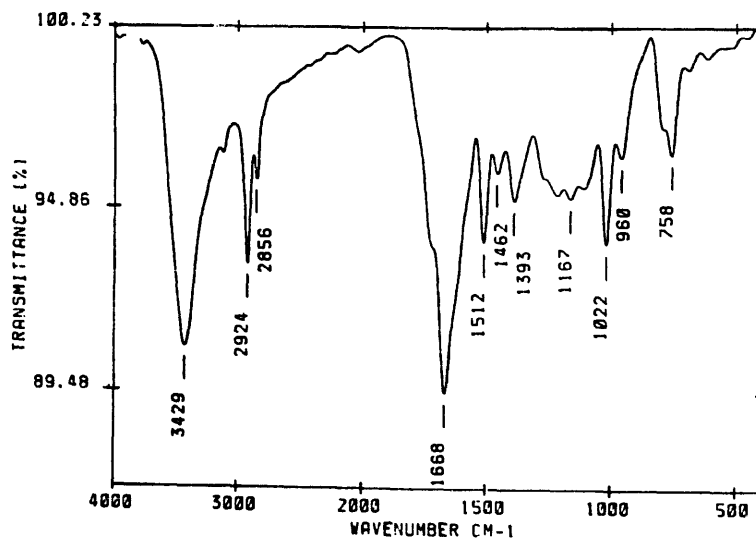


Fig. 2. FTIR spectrum of **9** (KBr pellet).

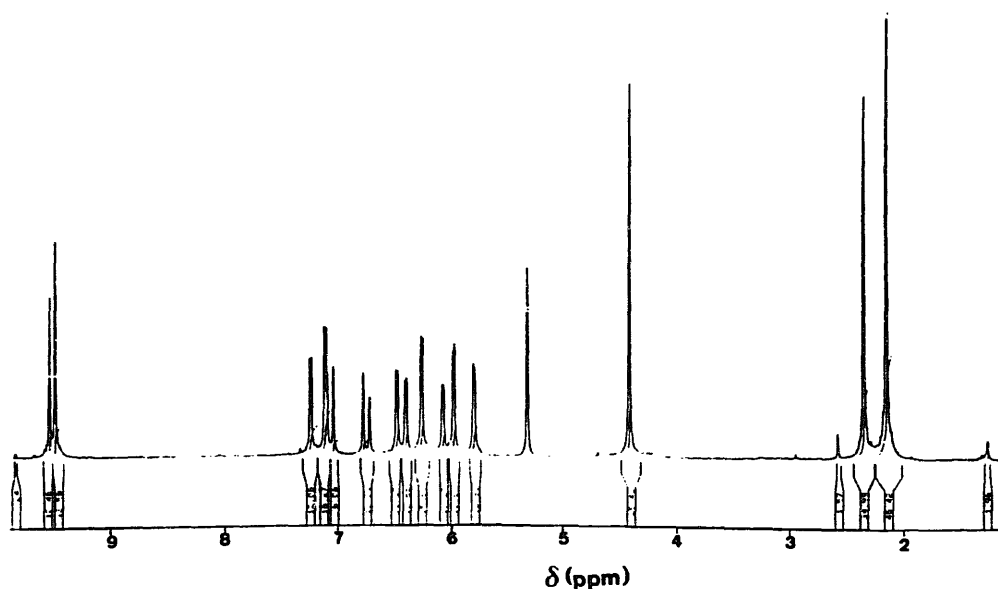
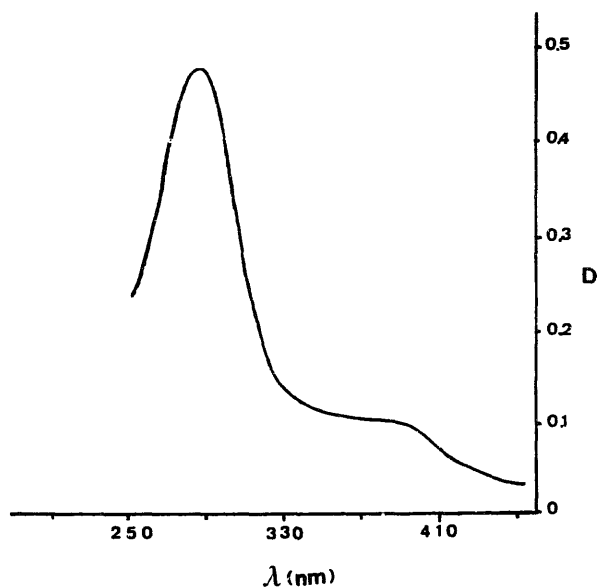
that of **1** by the loss of conjugation, which produces a hypsochromic shift of more than 100 nm and a strong decrease in the extinction coefficient.

The extent of photodimerization was found to depend on the purity of **1**, particularly in terms of the crystallinity. Fig. 5 shows this trend expressed as the yield vs. irradiation time for two samples treated in the same conditions, but possessing different degrees of crystallinity, namely close to 100% and between 50% and 70%, as estimated by X-ray diffraction patterns. Clearly, the photodimerization requires a regular intermolecular spacing in order to occur, and therefore the amorphous microphases do not contribute substantially to this

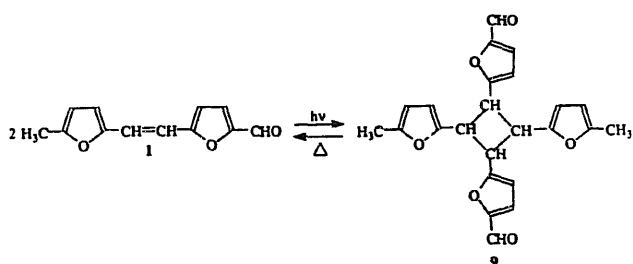
reaction, as shown by the limiting yield attained with the incompletely crystallized sample.

In conclusion, the furanic unsaturated aldehyde **1**, irradiated in the solid state, gives a clean $[\pi 2 + \pi 2]$ photodimerization leading to a single symmetric product through the reaction of the excited triplet state with a ground state molecule. On the other hand, irradiation of dilute solutions of **1** promotes monomolecular isomerization to give a thermodynamic mixture of *Z* and *E* conformers.

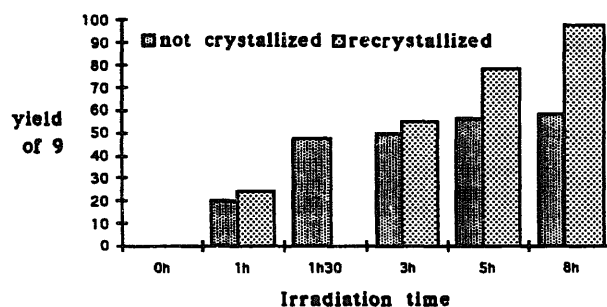
The cyclobutane dimer of **1** was found to be thermally unstable when analysed by differential scanning calorimetry (DSC). Indeed, its melting features could not be observed

Fig. 3. $^1\text{H-NMR}$ (300 MHz) spectrum of **9** in CDCl_3 .Fig. 4. UV spectrum of **9** in CH_2Cl_2 .

clearly because of the onset of decomposition from about 170 °C. The photochemical and thermochemical behaviour of this system can therefore be described as



Compound **2**, the thiophene analogue of **1**, was submitted to the same photolytic study and gave a similar set of features, albeit with much lower photochemical yields, probably caused by the lower extinction coefficient of **2** compared with

Fig. 5. The role of crystallinity in the photodimerization yield of **1**.

that of **1** (see Table 2) in the relevant absorption region, namely between 330 and 430 nm. Table 3 gives the spectroscopic data relevant to the symmetrical cyclobutane photodimer of **2** which was also thermally unstable and decomposed to its monomer.

The mixed heterocyclic structures **6**, **7** and **8** were irradiated in the solid state as KBr pellets and as fine crystalline powder suspended in *n*-dodecane. For compound **8**, which is the pyridinic counterpart of **1** and **2**, dimerization was the only photochemical transformation detected and a single symmetrical dimeric structure was obtained, as shown by the spectroscopic features given in Table 3. Here, the NMR resonance of the cyclobutane protons consists of a doublet, instead of a singlet for the symmetrical dimers of **1** and **2**, because of the presence of two different heterocycles in **8**, but it is still the reflection of a single symmetrical structure. The formation mechanism of this dimer is therefore likely to involve the same pathway as for the photodimerization of **1** and **2**. Compounds **6** and **7**, on the other hand, gave a mixture of two isomeric photodimers, as indicated by the presence of multiple resonances in the $^1\text{H-NMR}$ spectra of these products, as shown in Fig. 6 for the dimer of **7**. It seems that the replacement of the polar aldehyde function in **1** and **2** with a methyl group in these two compounds, apart from decreasing the

Table 3
Spectroscopic characterization of various photodimers

Product from	UV-visible λ_{\max} (nm)	FTIR (KBr pellet) (cm^{-1})	$^1\text{H-NMR}$ (300 MHz, TMS, solvent CD_2Cl_2) (ppm)
1	CH_2Cl_2 , 284.3	Furans: 3115; 1468; 1398; 1244; 1022; 982; 973. Cyclobutane: 1516. $-\text{CH}_3$: 2853. $-\text{CHO}$: 1668	$-\text{CH}_3$: 2.15 (3H, s); $-\text{CH}-$: 4.41 (4H, s); Fu: 5.80 (1H, d), 5.98 (1H, d), 6.07 (1H, d), 7.08 (1H, d); $-\text{CHO}$: 9.52 (1H, s)
6		Furans: 3125; 1193; 1028. Pyridines: 3100	$-\text{CH}_3$: 1.87 (s), 2.07 (s); $-\text{CH}-$: 3.9–4.6 (m); Fu: 5.74 (s), 5.91 (d); $-\text{C}_5\text{H}_4\text{N}$: 7.14–8.34 (m)
7		Pyridines: 3433; 808. Thiophenes: 3018; 1034; 949. $-\text{CH}_3$: 2856	$-\text{CH}_3$: 2.30 (3H, s); $-\text{CH}-$: 4.21 and 4.63 (4H, m); Tp: 6.45 (1H, d), 6.53 (1H, d); $-\text{C}_5\text{H}_4\text{N}$: 7.08 and 8.38 (4H, q)
8		Furans: 3125; 1252; 1030; 797. Pyridines: 3100; 1668; 810. Cyclobutanes: 1515.	$-\text{CH}-$: 4.64–4.76 (4H, q); Fu: 6.66 (1H, d), 7.40 (1H, d); $-\text{C}_5\text{H}_4\text{N}$: 8.34 (4H, d); $-\text{CHO}$: 9.44 (1H, s)

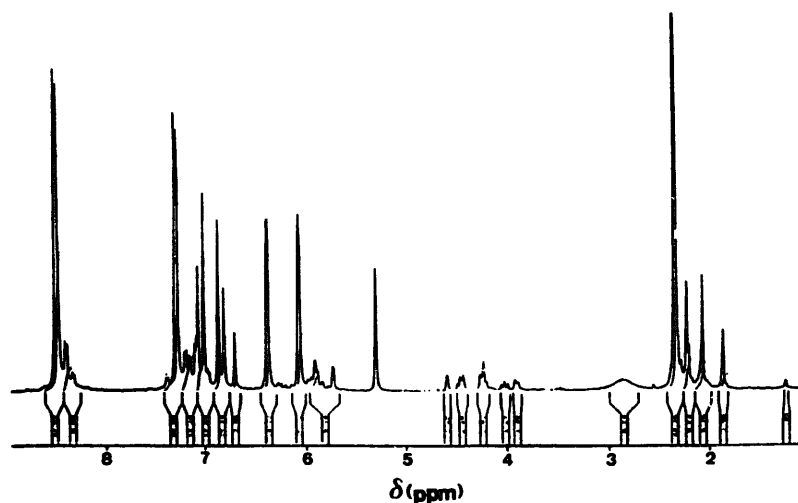


Fig. 6. $^1\text{H-NMR}$ (300 MHz) spectrum (CD_2Cl_2) of the products of the solid state irradiation of 7.

rates of photodimerization because of the lower absorption domain, allows different pathways for the dimerization process leading to at least two different products. Table 3 contains the spectroscopic data for these dimers.

The furanacrylate 5 was irradiated in the solid state and yielded two distinct dimers corresponding to the truxinic (10) and truxillic (11) isomers

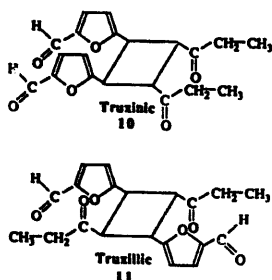


Fig. 7 shows the $^1\text{H-NMR}$ spectrum of the mixture of these two products and Table 4 gives a detailed analysis of this spectrum as well as the FTIR features related to the dimers. Once again, the photochemical behaviour of 5 was limited to the $[\pi 2 + \pi 2]$ cycloaddition reaction without evidence of other free radical or molecular mechanisms.

The bis-heterocyclic acetals 3 and 4 were finally investigated in terms of their solid state photoreactivity. The furanic

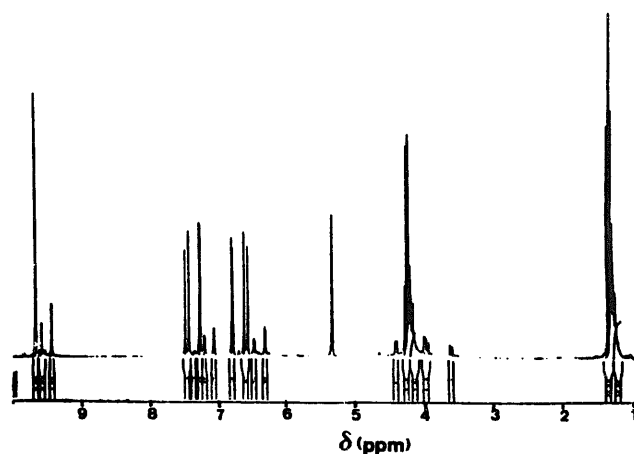


Fig. 7. $^1\text{H-NMR}$ (300 MHz) spectrum (CD_2Cl_2) of the products formed in the solid state irradiation of 5.

homologue 3 was submitted to a thorough screening and the fundamental result was that macrocyclization through telechelic coupling occurred, giving the cyclophane structure 12

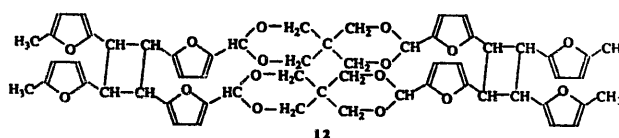


Table 4
Spectroscopic characterization of the photodimers **10** and **11**

FTIR (KBr pellet) (cm ⁻¹)	¹ H-NMR (300 MHz, TMS, solvent CD ₂ Cl ₂) (ppm)
Furans: 3115; 1020; 982; 973. Cyclobutane: 1556. –CO: 1705. –CHO: 2720	Truxillic isomer: –CH ₃ : 1.24–1.33 (6H, m); –CH ₂ –: 4.16–4.27 (4H, m); –CH–: 3.58 and 4.96 (4H, q); Fu: 6.35 (2H, d), 6.49 (2H, d); –CHO: 9.43 (2H, s) Truxinic isomer: –CH ₃ : 1.24–1.33 (6H, m); –CH ₂ –: 4.16–4.61 (4H, m); –CH–: 3.96 and 4.96 (4H, q); Fu: 6.50 (2H, d), 7.20 (2H, d); –CHO: 9.57 (2H, s)

Table 5
Spectroscopic characterization of **12**

FTIR (KBr pellet) (cm ⁻¹)	¹ H-NMR (300 MHz, TMS, solvent DMSO) (ppm)
Furans: 3136; 1540; 1402; 1173; 1018; 968. Cyclobutane: 1516. –CH ₃ , CH ₂ , CH: 2930; 2854. Acetal: 1086	–CH ₃ : 2.12 (s); –CH ₂ –: 3.21 (s), 3.60 (s), 4.12 (s); –CH< (acetal): 5.33 (s); Fu: 5.86 (m), 5.99 (d), 6.10 (d), 6.23 (d); –CH–: 3.69 and 3.82 (q)

The irradiation of **3** as a fine powder suspended in water gave a single crystalline product, which was soluble in numerous common solvents and gave non-viscous solutions. The evidence for the formation of the macrocyclic structure postulated above stems essentially from the fact that the ¹H-NMR spectrum exhibits a single resonance for the cyclobutane protons, appearing as a quadruplet as shown in Table 5, which also contains the other spectroscopic features related to this cyclodimer. Supporting evidence for structure **12** comes from:

1. the very sharp melting endotherm in the DSC thermogram (m.p., 144 °C), excluding the possibility of an oligomeric or polymeric structure;
2. the absence of absorptions related to unsaturations external to the furanic rings;
3. the lack of peaks above 220 nm in the UV spectrum, indicating the total loss of conjugation outside the furan moiety which, in the present context, absorbs around 200 nm.

The crystalline structure of **3** must therefore imply an intermolecular organization which permits the simultaneous coupling of its two ends between an excited and a ground state molecule to give the macrocycle **12**. No other photoreaction was detected, indicating the very specific nature of this bis-cyclodimerization. The thiophenic analogue **4** gave the same behaviour. The solution irradiation of **3** and **4** will be studied,

particularly with concentrated systems, to see whether any photopolymerization occurs.

4. Conclusions

The photochemical behaviour of alkenylfuran and alkenylthiophene derivatives in the crystalline state is similar to that of their aromatic homologues in that the photodimerization reaction giving the corresponding cyclobutane dimer is the dominant mechanism. The extension of this clean mode of coupling to the elaboration of photosensitive polymeric materials bearing these chromophores will be reported elsewhere.

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