Photochemistry of substituted methyl-α-aryl-cinnamates: 
ortho- and para-substitution

Christopher H. Evans a,*, Jóhannes Reynisson a,b, Jón K.F. Geirsson a, Ágúst Kvaran a, W.G. McGimpsey b

a Science Institute, University of Iceland, Dunhaga 3, IS-107 Reykjavik, Iceland
b Department of Chemistry and Biochemistry, Worcester Polytechnic Institute, 100 Institute Rd., Worcester, MA 01609-2280, USA

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Abstract

The 308 nm laser photochemistry of a series of substituted methyl-α-aryl-cinnamates has been studied in deoxygenated hexane and acetonitrile. Methyl-α-phenyl-cinnamate (1a) and derivatives that are p-substituted with electron withdrawing (chloro, 1b) or electron donating (methoxy, 1c) groups exhibited very similar photochemistry and spectroscopic properties, with the photostationary state (pss) composition ([E]/[Z]) being, on the average, 2.8 for these substances. By contrast the pss value for the α,α-dichloro substituted aryl-cinnamate (1d) was found to be only 0.5. This difference is discussed in terms of possible influences of the α,α-dichloro substituents on the excited state potential energy surface for aryl-cinnamate photoisomerization. © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

Photoisomerization of ethylenic molecules has been the subject of intense study for decades. This interest arises from the potential to obtain detailed understanding of the events resulting in relaxation in chemical systems after electronic excitation by light [1–3]. Olefinic photoisomerizations also play a central role in biological phototropic systems such as vision and photomorphism in plants [4,5]. Photoisomerizations are relatively easy to study and are chemically simple.

The prototype olefin photoisomerization is the trans- to cis-stilbene phototransformation. A great deal of effort has been placed on studying all aspects of this reaction and a fairly detailed picture has developed [1,2,6–12]. One of the major achievements has been the detailed elucidation of the potential energy surfaces involved in the isomerization.

Methyl-α-phenyl-cinnamate, 1a, is a stilbene derivative which undergoes E/Z photoisomerization from the excited singlet state as well as a ring closure reaction to form the 4a,4b-dihydrophenanthrene derivative (2) [13,14]. In the presence of oxidizing agents, this species converts to methyl-9-phenanthroate (3) [13,14]. These processes are summarized in Scheme 1. Cinnamates are of current research interest because of their use for the design of photoactive polymers, molecular assemblies, supramolecular devices and UV filters [15].

We report here our most recent study of substituted methyl-α-aryl-cinnamate photochemistry. The series investigated includes compounds para-substituted with an electron withdrawing, electron donating or electroneutral group on the β-phenyl ring as well as a compound that is α,α-dichloro substituted on the β-phenyl ring. The cinnamate derivatives used in this work are depicted in Scheme 2. While ring substitution in stilbene derivatives is not normally recognized as

* Corresponding author.
leading to major changes in photochemistry [1,16,17], we have observed a significant effect of o,o-dichloro substitution on the \( \beta \)-phenyl ring.

2. Experimental

Methyl-\( \alpha \)-phenylecinnamate isomers (\( E \)-1a and \( Z \)-1a) and their derivatives were prepared via the Horner–Wadsworth–Emmons modification of the Wittig reaction [13,18]. Individual isomers were found to be pure (\( > 99\% \)) by HPLC and GC.

Methyl-9-phenanthroate (3) was prepared by literature procedures [19]. Solvents were of the highest quality commercially available (spectral or HPLC grade) and were used as received. Inorganic salts (Janssen, BDH, Merck) were used as received. Nitrogen was of ultra-high purity grade.

Photostationary states were prepared by photolyzing \( 1 \times 10^{-4} \) M samples of the cinnamates in degassed hexane with pulses (308 nm, ca. 10 ns, \( \leq 40 \) mJ/pulse) from a Lumonics 510 excimer laser operating with a XeCl mixture. The photostationary state compositions were obtained via analytical HPLC using an LDC Analytical Consta Metric 3200 HPLC system operating with a 10-cm column. The mobile phase was 1% ethylacetate in \( n \)-hexane. Detection was based on absorbance at 280 nm. HPLC response was calibrated against authentic samples.

Quantum yields for isomerization and phenanthrene formation were determined by ferrioxalate actinometry using the arrangement recommended by Muto, et al. [20] and Bunce [21] for laser excitation.

Fluorescence spectra of \( 1 \times 10^{-4} \) M esters in hexane or methylcyclohexane were recorded at room temperature with a Spex Fluoromax Spectrofluorometer (Instruments SA). Excitation was at 270 nm and the band width was typically 2 nm. The emission spectra were uncorrected. Absorption spectra were recorded with a Shimadzu UV–Visible Absorption Spectrometer.

The laser flash photolysis apparatus used for one- and two-laser experiments has been described in detail elsewhere [22,23]. In the one-laser experiment, samples were irradiated by the UV pulses of a Lumonics EX 510 excimer laser (308 nm, 10 ns, \( \leq 40 \) mJ/pulse). In the two-laser experiment, the UV laser was followed after a short delay by the pulse from a Candela SLL 250 flashlamp-pumped dye laser using a Coumarin 480 dye (468 nm, 350 ns, \( \leq 150 \) mJ). Ester samples, ca. \( 1 \times 10^{-4} \) M in acetonitrile, were allowed to flow continuously through a specially constructed \( 7 \times 7 \) mm\(^2\) quartz cell, ensuring that a fresh volume of sample was irradiated by each laser pulse (or pair of pulses in the two-laser experiments). Unless otherwise indicated all samples were deoxygenated before irradiation by bubbling a stream of nitrogen through the sample for 20 min. For flowing samples, nitrogen was continuously bubbled through the sample reservoir.

Molecular mechanics calculations for the ground states of the cinnamates were performed in a Macintosh environment using the MM2(91) software package in conjunction with MacMimic from Instar Software.

3. Results

Table 1 summarizes photostationary state compositions and isomerization quantum yields for 1a and three substituted derivatives. The same pss composition was obtained starting from the \( E \)- or the \( Z \)-isomer. For 1a and its \( p \)-substituted derivatives (1b, 1c) the photostationary state (pss) composition was found to be rich in the \( E \)-isomer as has been reported previously for related compounds [13,14]. The behavior of the o,o-dichlorocinnamate, 1d, was in marked contrast to 1a and its \( para \) derivatives in that the pss contained much more \( Z \)-than \( E \)-isomer.

Table 2 summarizes ground state absorption data for the cinnamates. In each case, the bands were broad and featureless and there is little difference between the \( E \) and \( Z \) isomers. In terms of transition energies, 1a and its \( para \) derivatives were similar to each other and to other arylecinnamates that have been examined [13]. That the absorption of both \( E \)- and \( Z \)-arylccinnamates generally resembles that of \( cis \)-stilbene [3,13] has been attributed to larger angles of
twist between the aryl groups and the plane of the double bond in the arylcinnamates as compared to stilbene, even when the aryl rings are in a trans conformation [13]. The degree of non-planarity will be large in both the E- and Z-aryl cinnamates as large groups are present on both sides of the double bond in these systems. In this sense, both E- and Z-cinnamates resemble cis-stilbene (relatively large phenyl ring twist angle) rather than trans-stilbene (smaller phenyl ring twist angle). These trends were confirmed by the molecular modelling estimates of the aryl group twist angles presented in Table 3.

The band maximum of 1d was significantly blue shifted relative to the three other compounds examined here and in fact lay in a range similar to that observed for alkylcinnamates [24]. The results presented in Table 3 suggest that this may be due to the extreme non-planarity of 1d in the ground state resulting in minimal resonance interaction of the 2,6-disubstituted ring with the rest of the molecule's π-system.

Fig. 1 shows a series of fluorescence spectra measured for $1 \times 10^{-4} \text{M E-1a}$ in air saturated hexane at room temperature. The spectra were measured without sample flow. They represent different periods of time that the sample was in the cell holder of the fluorometer and subject to excitation at 270 nm. The first spectrum (‘zero’ time) represents, at most, 1 min of 270 nm exposure. As the exposure time increased, the intensities of the bands at 360, 378 and 400 nm also increased. We assign the fluorescence observed between 350 and 450 nm to emission from the ring closure oxidation product, methyl-9-phenanthroate (3a, Scheme 1). This assignment is based on measurement of the fluorescence spectrum of a genuine sample of 3a which proved to have features identical to those shown in Fig. 1. Similar phenanthrene-like fluorescence spectra were obtained for all four E-cinnamates upon photolysis in the cell holder of the fluorometer. In each case, we attribute the observed fluorescence to formation of the corresponding fully oxidized phenanthroate derivative.

Room temperature fluorescence was also recorded under non-flow conditions for the Z-isomers. Essentially, the same behavior was observed for the Z-isomers as for the E-isomers. That is, formation of progressively increasing amounts of the corresponding phenanthroate 3 were observed. Presumably, this occurs via Z to E photoisomerization within the fluorometer. The very weak fluorescence observed at short times (zero time) after the samples are exposed to the light from the fluorometer, and the fact that it is in the same spectral region as the fluorescence of the corresponding phenanthroates indicates that the cinnamates have a very small fluorescence quantum yield, i.e., below the sensitivity threshold of our fluorometer. This is in accord with the fluorescence quantum yield for cis-stilbene of ca. 0.0001 reported by Saltiel et al. [25]. The fact that the Z-cinnamate also has a negligible fluorescence yield contrasts with trans-stilbene for which $\phi_F$ is ca. 0.04 [11]. Again this can be explained by the fact that steric interaction between the large groups on the double bond reduces resonance within the molecule with the probable result that the small (ca. 4 kcal/mol [1–3]) stabilization of trans-stilbene on the excited state surface is lost in the Z-cinnamate.

Fig. 2 shows the transient absorption spectrum obtained when $1 \times 10^{-4} \text{M E-1a}$ was irradiated with 308 nm excimer laser photolysis of a flowing, deoxygenated $1 \times 10^{-4} \text{M}$ solution of 1a in acetonitrile.

![Graph](image-url)

**Table 3**

Out-of-plane aryl ring twisting angles for various stilbene derivatives. α' and β' refer to the angles of the ring on the ester-bearing carbon and the hydrogen-bearing carbon, respectively.

<table>
<thead>
<tr>
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<th>E-Isomer</th>
<th>E-Isomer</th>
<th>Z-Isomer</th>
<th>Z-Isomer</th>
</tr>
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<tbody>
<tr>
<td>α'</td>
<td>Z6–50°</td>
<td>0°</td>
<td>nearly planar*</td>
<td>-</td>
</tr>
<tr>
<td>β'</td>
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<td>39°</td>
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<tr>
<td>β''</td>
<td>62°</td>
<td>62°</td>
<td>37°</td>
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*Results of molecular mechanics calculations, except where noted.


laser pulses in flowing, deoxygenated acetonitrile. The UV absorption which appears as a sharply rising shoulder and the weaker visible absorption centered near 460 nm are characteristic of the absorption of the 4a,4b-dihydrophenanthrene (DHP, 2) intermediates formed upon initial ring closure of stilbene derivatives [26]. For example, the DHP of stilbene itself exhibited bands at 450 (band I), 310 and 297 (band II), and 237 nm (band III) [26,27]. We were only able to observe band I and the shoulder of band II in our system because of increasing absorption by the 1a ground state below 300 nm. The transient absorption was thus distorted by depletion of the ground state at these wavelengths.

The transient shown in Fig. 2 was found to be very long lived, showing no decay over a period of 2 ms, the longest measurable time scale of our instrument. This is also consistent with the lifetime reported for 2a which was several minutes in deoxygenated hexane [14]. It is safe to conclude, then, that the transient absorption in Fig. 2 is that of dihydrophenanthrene 2a.

Additional evidence for this assignment was provided by the results of two-laser experiments. In these experiments, 308 nm irradiation of 1 \times 10^{-4} \text{M} \text{E-la} in flowing hexane resulted in formation of 2a. Subsequent irradiation of the DHP with a pulse at 488 nm from the dye laser firing a few \mu s after the 308 nm pulse, resulted in complete bleaching of the transient absorption. As there was virtually no conversion of the ground state (< 10%) as judged by ground state absorption measurements, we can conclude that the second pulse is causing a photochemical reversion of 2a to \text{E-la}, which is itself a known process, Scheme I [26].

Similar spectra and lifetimes were observed for 1b and 1c in flowing, deoxygenated acetonitrile. The only difference between these two transients and 1a was that band I of 1c was relatively weak compared to that of 1a and 1b. The transients observed for 1b and 1c may thus also be attributed to their corresponding DHPs.

The transient spectrum (Fig. 3) obtained when 1d was photolyzed with 308 nm laser pulses in flowing, deoxygenated acetonitrile was different than those observed for the other three cinnamates. Bands I and II were now both clearly visible and the transient absorption was thus distorted by depletion of the ground state at these wavelengths.

The observation of \text{E}-rich pss compositions for cinnamates 1a-c makes them typical of arylcinnamates (Table 1) [13]. This is in contrast to pss values observed for alkylcinnamates which are smaller by about a factor of 3 when irradiation takes place at similar wavelengths [24]. It has been proposed [13] that this difference is due to the fact that the arylcinnamates have an additional reaction channel open to them, namely ring closure to form dihydrophenanthrenes (DHPs), which reduces the amount of excited \text{E}-isomer available to undergo isomerization. In turn this reduces the amount of \text{Z} remaining in the pss. While our transient results indicate that ring closure to the DHP form occurs for all the cinnamates studied, there is a significant reduction in the amount of \text{E}-isomer relative to \text{Z}-isomer in the pss of 1d, i.e., the compound with the o,c-dichloro substitution of the \beta-ring. In fact nearly all the properties of 1d examined in this study differ markedly from those of the \text{p}-substituted analogs, 1a-c.

The source of the low \varepsilon_{1a} value is apparently not electronic in nature as electron donating or withdrawing substitution at other locations (1a-1c) has no influence on the arylcinnamate photochemistry. Recent work [6,12] on potential
energy surfaces for stilbene photoisomerization has shown that the details of the decay processes for the Franck–Condon excited cis- and trans-stilbene depend strongly on the extent of interaction between the two phenyl rings as well as on the twist angle about the (former) double bond following excitation. These two properties are in fact reaction coordinates for relaxation from the excited surface to the ground state surface. The decay routes open to excited cis-stilbene are found to be combinations of twist angle and ring separation. Any given relaxation path may be dominated by one or the other factor or an admixture of both. By contrast, the behavior of excited trans-stilbene is dominated by movement along the ‘bond twist’ coordinate as the ring separation is fairly large and the interaction between rings fairly weak in this case. In the context of the arylcinnamates one might expect group–group interactions to play a role even for the Z-isomers (which correspond to trans-stilbene) because of the presence of the ester group. This will be even more relevant in the case of 1d where the stericly large o,o-dichloro substitution will strengthen ring–ring (for E-1d) and ring–ester (for Z-1d) interactions. One may thus conclude that the decay paths open to the Franck–Condon excited states of E-1d and Z-1d can be very different from those proposed for the corresponding excited stilbenes and also from those available to the less sterically constrained 1a–1c. It seems likely, then, that the difference in pss value for 1d vs. 1a–c can be traced to differences in the nature of the group–group reaction coordinate on the corresponding excited state surfaces.

5. Conclusion

In summary, we have observed that o,o-dichloro substitution of methyl α-phenylcinnamate causes a dramatic change in the composition of the pss from E-isomer-rich to Z-isomer-rich. This can be traced to variations in the value of the Z to E photoisomerization quantum yield which probably arise due to differences in the degree of interaction between large groups attached to the α- and β-carbons of the double bond on the excited state reaction surface. In order to gain more insight into this issue we are currently undertaking a study involving a series of o,o-disubstituted arylcinnamates in which the steric size and electronic character of the substituents is varied.

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