



# The effect of molecular environment on the photochemistry of *p*-methoxycinnamic acid and its esters

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## Abstract

In addition to rapid, reversible *trans-cis* photoisomerisation, air-saturated solutions of *p*-methoxycinnamic acid and 2-ethylhexyl-*p*-methoxycinnamate in polar solvents undergo a slower, irreversible photoreaction when exposed to ultraviolet radiation. However, no such reaction is evident in polar solvents that are deoxygenated or in air-saturated, non-polar solvents. The fluorescence spectra were also dependent on the solvent polarity with a shift to longer wavelengths in polar solvents. This behaviour suggests a degree of charge transfer character in the lowest excited singlet state responsible for fluorescence in a polar molecular environment. The fluorescence yields of solutions of these cinnamoyl molecules were low,  $\leq 1.6 \times 10^{-3}$ , indicating that there are very efficient non-radiative pathway/s for non-radiative relaxation of the excited singlet states of these molecules. © 1998 Elsevier Science S.A. All rights reserved.

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## 1. Introduction

There has been considerable interest in the photophysics and subsequent photochemistry of *p*-methoxycinnamic acids and their esters because of the esters' widespread use as UVB blocking compounds in cosmetic sunscreens [1–3]. This use in sunscreens exploits the high extinction coefficient of these compounds in the UVB spectral region. However, to be effective as a UV protective agent, not only must the compound have a high UV absorbance, it must also be able to harmlessly dissipate the absorbed energy. Cinnamates accomplish this by *trans-cis* isomerisation about the propenyl double bond in the first excited singlet state. This process has been extensively studied and the involvement of charge transfer, CT, states resulting from rotation about the double bond is well established [1,4–10]. As such, solvent polarity plays a role in this process by decreasing the energy gap between the CT and  $\text{III}^*$  excited states, thereby enhancing mixing of these excited states in a polar medium [5–10]. Indeed, the charge transfer character of the lowest excited singlet state of related arylpropenes is apparent from the sensitivity of the spectral position of fluorescence originating from this state on solvent polarity [8].

Solvent participation in hydrogen bonding with cinnamic acids is another important molecular environmental factor which affects photoisomerisation. Diethyl ether has been shown to enhance photoisomerisation by competing with and thereby disrupting, the hydrogen bonding between cinnamic acid and other polyene carboxylic acid molecules which impedes rotation about their double bonds [8–11]. Photoisomerisation is reversible and, after a period of exposure to UV radiation, a photostationary, *trans-cis* equilibrium is attained [1–10]. As the UVB absorbance of the *cis* isomer is less than that of the *trans* isomer, the absorbance of the photostationary *cis-trans* mixture is only 60–70% that of the initial *trans* isomer.

In addition to the reversible photoisomerisation which causes a reduction in UV absorption of cinnamates, irreversible reactions of *p*-methoxycinnamates occur in some solvents at the high concentrations used in skin-care sunscreens and these are accompanied by a further reduction of UVB absorbance on UV photolysis [12,13]. Photodimerization to give truxillic acid-type products i.e. a 2 + 2 cycloaddition across the propenylic double bonds, has been implicated in this process [12,13]. Again the solvating properties of the surrounding medium, particularly polarity and solute-solvent hydrogen bonding, are expected to be the important factors in determining the extent of this reaction.

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Although, twisting about the propenyl double bond of cinnamoyl compounds in their excited states is an extremely efficient pathway for internal conversion to the similarly configured intermediate in the ground electronic state, there appear to be conditions under which some intersystem crossing to the triplet state occurs. This is inferred from the formation of singlet oxygen by UV photolysis of some *p*-methoxycinnamates [14]. Thus, while Morliere et al., [11] observed no singlet oxygen production from irradiation of dilute aqueous solutions of *trans p*-methoxycinnamic acid diethanolamine salt at pH 8.8 or from 2-ethoxyethyl-*p*-methoxycinnamate in 5% w/w ethanol-water solution, Allen and Gossett [14] have reported this excited state of oxygen as a result of photolysis of 2-ethylhexyl-*p*-methoxycinnamate, pMCE, in aqueous solution. Since singlet oxygen is such a highly reactive oxidant, it is likely that in the molecular environments which favour its formation, the cinnamoyl compounds would be subject to photooxidation/degradation with a consequent diminution of UVB absorbance.

The research reported herein was specifically designed to establish the extent to which photooxidation contributes to the irreversible reduction in the absorbance of *p*-methoxycinnamic acid and its ethylhexyl ester and how solvent polarity affects this reaction. To avoid equivocal results, the cinnamoyl concentrations used were low, i.e.  $\sim 20 \mu\text{M}$ , thereby, eliminating the effect of the competing photodimerization reactions.

## 2. Experimental details

The all *trans* isomers of 4-methoxycinnamic acid, pMCA, Aldrich puriss grade, and the 2-ethylhexyl-4-methoxycinnamate, pMCE, from Givaudan-Roure, Geneva were used without further purification. The solvents used covered a wide range of polarities. The cyclohexane was purified by passage through an activated silica gel column and BDH, Analar grade methanol was purified by distillation. The acetonitrile and diethyl ether were BDH, HPLC grade.

Dilute solutions ( $\approx 2 \times 10^{-5} \text{ mol dm}^{-3}$ ) of the pMCA and pMCE were prepared in the solvents with optical densities of  $1.0 \pm 0.15$  at the maximum absorbance  $\approx 315 \text{ nm}$ . Deoxygenation of solutions, where required, was achieved by gentle bubbling with oxygen-free nitrogen. The solutions were contained in 10 mm square, fused silica cuvettes and were exposed to UV radiation from a Wotan 200 W superhigh pressure mercury arc lamp filtered by a water heat filter and WG305 and KG3 Schott glass optical filters. The intensity and spectral distribution of the radiation were measured using a double monochromator spectroradiometer and were a good match to unobstructed, midsummer solar UV radiation at  $40^\circ\text{S}$ . The actinic intensity of the radiation, i.e. that calculated by integrating the UV intensity spectral distribution of the radiation weighted by the absorption spectra of the compounds, was  $2 \text{ mW cm}^{-2}$ .

The absorption spectra of the solutions before irradiation and the absorbance at 315 nm over the duration of the UV photolysis were determined with a Hewlett Packard 8451A spectrophotometer. The fluorescence emission spectra, excited at 315 nm, were recorded with a Hitachi 3010 spectrofluorimeter. Absolute fluorescence yields were determined by comparison of the spectrally integrated emission of the cinnamoyl solutions with that from a solution of quinine bi-sulphate in 1N sulphuric acid of the same optical density at the excitation wavelength of 315 nm ( $\phi_F = 0.55$ ) [15].

## 3. Results

### 3.1. Effect of photolysis on absorbance

In all the solvents, a rapid decrease in the absorbance of the solutions was observed on their exposure to simulated solar UV radiation. Within 5–10 min of irradiation, the absorbance of pMCA and pMCE in cyclohexane attained a photostationary state at  $\sim 70\%$  of the initial optical density. Similar results were obtained with the deoxygenated solutions with the polar solvents. This temporal behaviour of absorbance as a result of exposure to simulated solar UV radiation is depicted in Fig. 1(a) and (b).

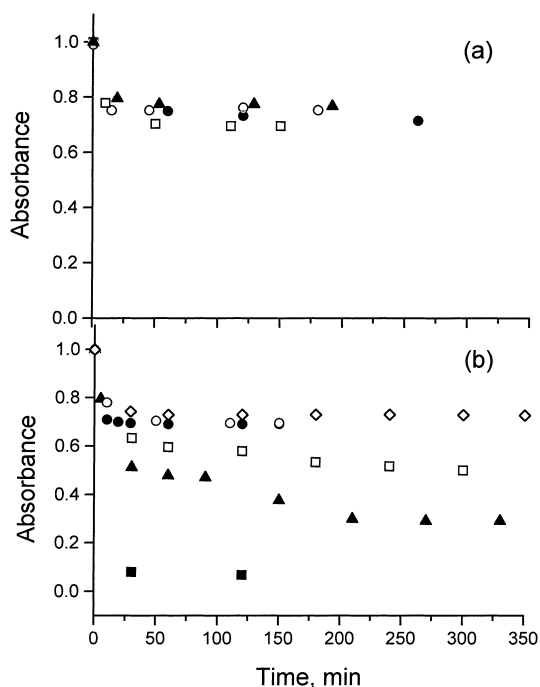


Fig. 1. The decrease in absorbance at 315 nm with irradiation time in (a) cyclohexane;  $\bullet\bullet\bullet$  pMCA;  $\square\square\square$  pMCA with oxygen;  $\blacktriangle\blacktriangle\blacktriangle$  pMCE with oxygen;  $\circ\circ\circ$  pMCE without oxygen. (b) polar solvents;  $\blacksquare\blacksquare\blacksquare$  pMCA in methanol + oxygen;  $\blacktriangle\blacktriangle\blacktriangle$  pMCE in methanol + oxygen;  $\square\square\square$  pMCE in acetonitrile + O<sub>2</sub>;  $\bullet\bullet\bullet$  pMCA in methanol without oxygen;  $\circ\circ\circ$  pMCE in methanol without oxygen;  $\diamond\diamond\diamond$  pMCE in acetonitrile without oxygen.

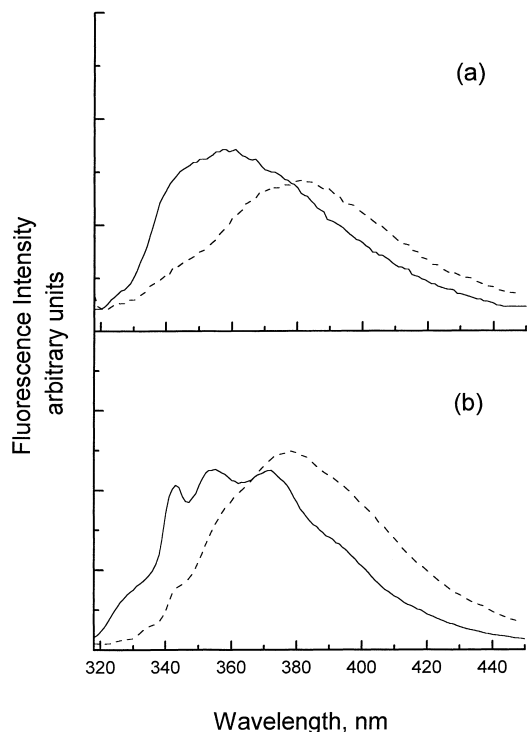


Fig. 2. (a) Fluorescence emission spectra, excited 315 nm of pMCA in cyclohexane —, and acetonitrile ----- (b) Fluorescence emission spectra, excited at 315 nm of pMCE in cyclohexane —, and acetonitrile -----.

In polar solvents (viz. methanol and acetonitrile), in the presence of oxygen, after the initial rapid decrease, the absorbance continued to decrease, though at a significantly slower rate.

### 3.2. Fluorescence spectra and yields

The fluorescence emission spectra of pMCA and pMCE in acetonitrile and cyclohexane are shown in Fig. 2(a) and (b). (The spectra observed in methanol were virtually identical to those in acetonitrile). The maxima in the fluorescence spectra of pMCA and pMCE in cyclohexane are at 358 and 350 nm, respectively. The emission maxima for both these compounds are at substantially longer wavelengths in methanol and acetonitrile. Another solvent dependent feature of the pMCE fluorescence is the spectral shape. In cyclohexane, the emission spectrum exhibits vibrational structure, whereas, in acetonitrile and methanol the fluorescence is redistributed and broadened to an extent that individual vibrational maxima cannot be resolved. The absolute fluorescence yields in methanol, cyclohexane and acetonitrile are given in Table 1. The fluorescence yield of pMCE is approximately five times greater than that of pMCA in all the solvents studied.

Addition of small quantities, (~1%), of the hydrogen-bond disrupting solvent, ether, to cyclohexane solutions of pMCA and pMCE had no observable effects on either the fluorescence spectra or the fluorescence yields.

Table 1

Absolute fluorescence yields,  $\Phi_F$ , of pMCA and pMCE in cyclohexane, acetonitrile and methanol

Compound	Solvent	$\Phi_F$
pMCA	Cyclohexane	$4.0 \times 10^{-4}$
	Acetonitrile	$3.6 \times 10^{-4}$
	Methanol	$4.3 \times 10^{-4}$
pMCE	Cyclohexane	$1.5 \times 10^{-3}$
	Acetonitrile	$1.6 \times 10^{-3}$
	Methanol	$1.3 \times 10^{-3}$

## 4. Discussion

The photophysics/chemistry of pMCA and pMCE can be conveniently discussed by reference to Fig. 3 which depicts the way solute-solvent interactions and rotation about the propenyl double bond perturbs the electronic state energy levels.

### 4.1. Isomerism

A feature of the photochemistry of arylalkenes, including the cinnamoyl molecules, is their propensity to undergo rotation about the propenyl double bond in the excited singlet state. The rapid decrease in absorbance of both compounds at low concentrations in all the solvents agreed with the previously published reports and has been attributed to *trans*  $\rightarrow$  *cis* isomerisation [1–10].

### 4.2. Fluorescence

#### 4.2.1. Spectra

The solvent dependence of the fluorescence spectra of arylalkenes is represented by the energy-level/rotation configuration diagrams for polar and non-polar media shown in Fig. 3. The fluorescence originates from excited singlet states of either the *trans* or *cis* isomers but not from the  $90^\circ$  twisted configuration [4,10,16]. Although the positions

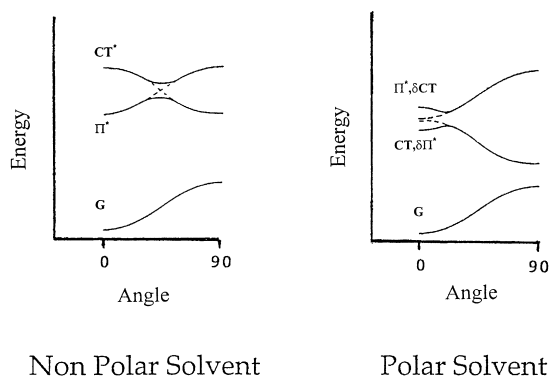


Fig. 3. Schematic diagrams of the double bond rotation angular dependence of the energies of the lowest excited singlet and ground states of cinnamoyl compounds in polar and non-polar solvents.

of the fluorescence emission spectra, i.e. the energies of the lowest excited singlet states, are at longer wavelengths in polar solvents, the positions of the absorption spectra are the same in both polar and non-polar solvents.

The stabilisation of the emitting singlet state, therefore, apparent as a spectral red-shift, is the result of solute-solvent interactions that develop and are realised by solvent reorientation within the lifetime of the excited singlet state. In the *trans* configuration (angle of  $0^\circ$ ), cinnamoyl-type molecules in a non-polar environment are postulated to have a  $\text{III}^*$  lowest excited singlet state with a CT excited state at a higher energy. In polar solvents, the CT state is stabilised relative to the  $\text{III}^*$  state, thereby, reducing the energy gap between the states and promoting mixing of the states. The effect of this mixing is to produce a  $\text{III}^*/\text{CT}$  state at a lower energy than that of the zeroth order,  $\text{III}^*$  state.

Another distinctive feature of the emission spectra from pMCE in polar solvents compared with that observed in non-polar media is the loss of vibrational structure. Two mechanisms can account for this phenomenon, operating separately, or in concert. Firstly, it could be a consequence of the minimum in the potential energy surface, i.e. the lowest vibrational level, associated with the *trans* excited singlet state being displaced a small angle of rotation with respect to the *trans* minimum on the ground-state potential energy surface. In this situation a vertical, Frank-Condon transition from the lowest vibrational level of the *trans*, excited singlet state produces a highly vibrationally excited ground state at an energy above those of the discrete vibrational levels. Secondly, the loss of vibrational structure could arise from a broadening of the vibrational lines that will occur when the excited state experiences interactions of different magnitudes with the surrounding polar solvent molecules.

#### 4.2.2. Yields

Rotation about the propenyl double bond has the effect of lowering the energy of the zeroth order CT state while raising that of the  $\text{III}^*$  state so that at a twist angle of  $90^\circ$ , the order of the energy levels is reversed. Twisting about the double bond also raises the energy of the ground state and at  $90^\circ$  the CT excited state and ground state approach each other energetically. Since the rate of internal conversion is inversely related to the energy gap between the ground and lowest excited singlet states, the  $90^\circ$  twist configuration provides a facile conduit for non-radiative relaxation of the excited state and the very low fluorescence quantum yields observed in this work attest to the efficiency of this process in both pMCA and pMCE.

In some circumstances hydrogen bond interactions between the solute and solvent can also affect the photo-physics of this type of molecule. Previous research on the fluorescence of the closely related *m*-methoxycinnamic acid found that the addition of diethyl ether to non-polar, non-hydrogen-bonding solvents, in small amounts (1–2% v/v) that are insufficient to significantly alter the polarity of the

medium, have a profound impact on the fluorescence yield [9,17]. This phenomenon was shown to be a result of the ether molecules disrupting the association between arylalkene molecules arising from intermolecular hydrogen bonding. This allows rotation about the double bond with consequent promotion of non-radiative relaxation of the fluorescent state. However, in this work, the addition of small quantities of ether to solutions of pMCA and pMCE in cyclohexane had no observable effect on the fluorescence yields and it is therefore concluded that rotation about the propenyl bond is not impeded in these compounds by intermolecular hydrogen bonding.

#### 4.3. Intersystem crossing and photooxidation

The triplet state energies of arylalkenes are less sensitive to rotation about the double bond than those of the excited singlet and ground states [17,18] and they are lower than the energies of the excited singlets in their *trans* and *cis* configurations. However, in polar solvents, as the molecules rotate about their double bonds the potential energy surface of the lowest excited singlet state approaches, and may even cross, the energy surface of the triplet state (see Fig. 3). Thus, in the  $90^\circ$  twisted configuration in polar environments, some intersystem crossing to the triplet state may be possible even though it is spin-forbidden. Although Morliere et al. [1], were unable to detect any transient triplet state formation by direct photolysis of a 5% ethanol-water solution of ethoxyethyl-*p*-methoxycinnamate or in an ethanolic solution of pMCE, Allen and Gossett [14] have detected singlet oxygen by UV photolysis of pMCE in an aqueous solution which indicates some triplet state formation in this system. Excited singlet states can undergo spin allowed reactions with oxygen, but they are diffusion controlled and, therefore, probably not within the brief lifetime of excited singlet state. Reactions with oxygen are far more probable via the longer-lived triplet state. Despite the same concentrations of oxygen being present in air saturated solutions of pMCA and pMCE in all the solvents used in this work, the slow irreversible decrease in absorbance of those compounds associated with photooxidation was only observed in polar solvents. This can be explained in terms of the solvent stabilising the lowest excited singlet state in such a way as to enable some, albeit minor, intersystem crossing to produce triplet states. The subsequent reaction of oxygen with triplet states is assisted in polar solvents by coulombic stabilisation of the charge-transfer encounter complex between these reactants [19] in this type of molecular environment. The resultant oxidative degradations of pMCA and pMCE are apparent as reductions in their absorbances at 315 nm.

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