

Proton, electron and energy transfer processes in excited phenol–olefin dyads

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Received (in Cambridge, UK) 31st May 2005

First published as an Advance Article on the web 19th July 2005

DOI: 10.1039/b416410p

Dyads containing phenol and olefin subunits are versatile models for the investigation of proton, electron and energy transfer processes. As they are readily accessible, a number of analogues (allylphenols, cinnamylphenols and derivatives) have been prepared with a wide range of photophysical and photochemical properties. By means of appropriate structural modification of a very simple initial structure, it is possible to reproduce, at will, different types of behaviour. In addition to providing valuable fluorescence emission data, these systems are chemically productive, giving rise to irreversible photoreactions that constitute a fingerprint for the mechanism involved. They include photocyclisation to 5- and 6-membered ring cyclic ethers, *Z/E* isomerisation, di- π -methane rearrangement, formation of *ortho*-quinone methides, photohydration and photodehalogenation. This rich photochemistry is highly sensitive to the microenvironment experienced, as indicated by the dramatic modifications observed within cyclodextrin cavities. Intramolecular OH $\cdots\pi$ interactions, both in their ground and excited states, play a key role in the interesting properties of 2-allylphenol derivatives. This is supported by experimental data and also by theoretical calculations.

1 Introduction

The IUPAC Compendium of Chemical Terminology defines a chromophore as “the part (atom or group of atoms) of a

molecular entity in which the electronic transition responsible for a given spectral band is approximately localized”.¹ A bichromophoric system contains two chromophoric units, represented in Scheme 1 as A (acceptor) and D (donor). The subunits are connected through a molecular bridge that does not participate in electronic coupling.^{2,3} The absorption spectrum of the bichromophore and the added spectra of the two separate chromophores are superimposable.

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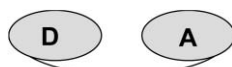
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Scheme 1

Upon light absorption, intramolecular electron, energy or proton transfer processes, as well as exciplex formation, can occur between D and A (Fig. 1). In some cases, irreversible formation of stable photoproducts is also possible.

An appropriate molecular design for the bichromophoric system will allow the control of which of the above processes predominate.

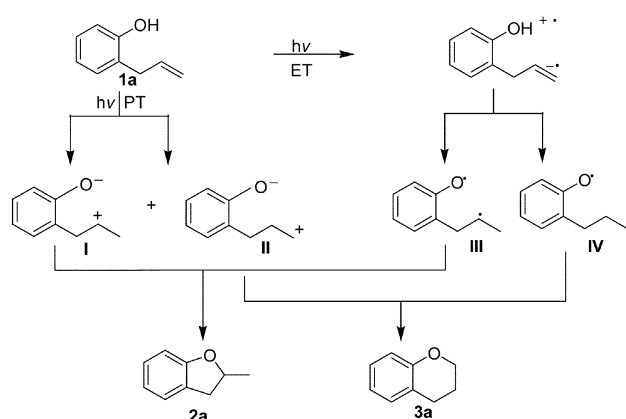
In the last 20 years, bichromophoric compounds have found wide application for a number of purposes in different fields.^{4–9} For example, modelling photosynthetic reaction centres, the design of organic photoconducting polymers for light harvesting applications, mimicking of drug–biomolecule systems, the development of energy conversion devices, optical sensing, photoaffinity labelling, the design of molecular switches, *etc.* In addition, bichromophoric systems have been employed to achieve a better understanding of basic photochemical mechanisms, as well as finding applications in selected organic syntheses.

Bichromophores containing phenol and olefin subunits are readily accessible, versatile models in which convenient structural modifications on a very simple initial structure allow the reproduction, at will, of proton, electron or energy transfer processes. The photophysical⁴ and photochemical⁵ properties of the isolated chromophores are well known. Thus, the changes observed in the bichromophoric systems are easily rationalised and highly relevant to the disclosure of the nature of the intramolecular processes taking place.

2 Allylphenols

2.1 Photocyclisation

2-Allylphenol, **1a**, can be considered as the simplest dyad containing both phenol and non-conjugated olefin moieties. The UV–vis absorption spectrum of **1a** is superimposable on that of its hydrogenation product (2-propenylphenol), and thus the allyl unit does not act as a real chromophore under normal irradiation conditions. However, this section is devoted to its photochemical behaviour as it is the starting



Scheme 2 Photocyclisation of 2-allylphenol.

point for the construction of more complex bichromophoric systems, such as the cinnamylphenols.

Photocyclisation of **1a** and its derivatives to give dihydrobenzofurans and/or dihydrobenzopyrans has been known since two independent reports by Schmid and Horspool in 1967.^{10,11} The initially proposed mechanism (which remains essentially valid) involves excited state intramolecular proton transfer (ESIPT) from the phenolic sub-unit to the double bond. Cyclisation of the resulting zwitterions leads to 5- (or 6-) membered ring ethers.^{10–18} Alternatively, excited state intramolecular electron transfer (ESIET) from the phenolic moiety to the olefin has been proposed as a key step in this process (Scheme 2).¹⁹ The ESIPT route would be in agreement with the sharp pK_a decrease of phenols in their excited singlet states (down to *ca.* 3–4 units). In contrast, the ESIET route would be thermodynamically disfavoured, based on the known redox potentials and excited state energies.

Both mechanisms would explain the preferential formation of the 5-membered ring product **2a**, due to the higher stability of the secondary carbenium ion, **I**, or radical, **III**, intermediates.

In principle it is not possible to generate olefin excited states by direct irradiation at $\lambda > 200$ nm. Therefore in the ESIPT model, the process should take place by intramolecular protonation of the ground state olefin by the first excited singlet state of phenol, which is the absorbing chromophore. Intersystem crossing does not compete efficiently with ESIPT

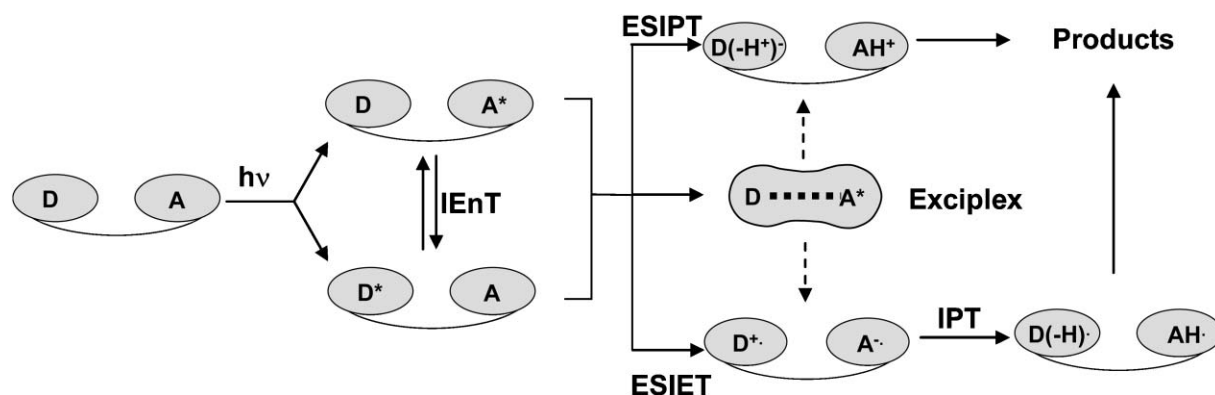


Fig. 1 The main photochemical and photophysical pathways that take place in bichromophoric systems.

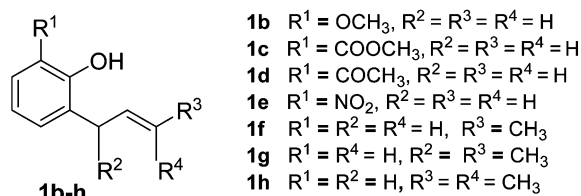


Chart 1

from the phenolic singlet, thus preventing photocyclisation from the triplet manifold.¹²

It has been suggested that intramolecular hydrogen bond formation between the hydroxylic group and the double bond plays a key role in the photocyclisation process,^{10,12–18} with experimental results appearing to support the above hypothesis. Thus, irradiation of **1a** in presence of dioxane or alcohols (which have lone pairs capable of competing for the proton) proceeds with very low efficiency, compared to solvents unable to participate in hydrogen bonding; disruption of the intramolecular $\text{OH}\cdots\pi$ interaction being the origin of this effect.

In this context, Shani *et al.* have investigated a series of 2-allylphenol derivatives containing different substituents in the phenolic ring (Chart 1, compounds **1b–e**).^{14,15} The results provide evidence for the role of intramolecular hydrogen bond formation in the photocyclisation reaction.

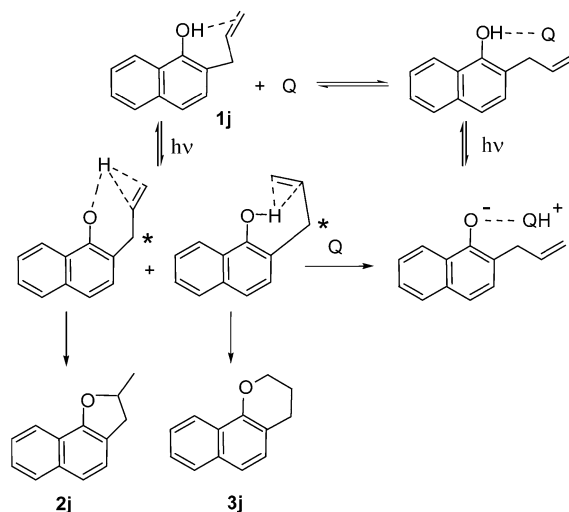
Thus, polar groups *ortho* to the phenolic OH favour formation of a strong intramolecular hydrogen bond between the substituent and the hydroxylic group, thereby preventing photocyclisation.

On the other hand, substitution at the end of the olefinic chain (Chart 1, compounds **1f–h**) modifies the regioselectivity, giving rise to dihydrobenzopyrans as the major products.¹⁰

2.2 Theoretical calculations

Malrieu has performed a semi-empirical quantum mechanical (PCILO) study on 2-allylphenol in the ground state. Calculations show that the most stable conformation is folded, and that its lowest energy minimum corresponds to a structure with $\text{OH}\cdots\pi$ bonding. The hydrogen bond stabilisation energy is estimated at *ca.* 4 kcal mol^{−1}. The results indicate that charge transfer is the origin of this $\text{OH}\cdots\pi$ delocalisation.²⁰

More recently, a systematic study has been undertaken on **1a** and its higher homologue 2-(3-butenyl)phenol, **1i**, combining experimental measurements of the ground and the excited state intramolecular interactions with *ab initio* calculations. Thus, the gas phase FTIR spectrum of **1a** shows two bands in the OH stretching zone assignable to free (3650 cm^{−1}) and intermolecularly associated (3590 cm^{−1}) OH. By way of contrast, in **1i**, the only observable signal is attributed to a free OH group. The interchromophoric interaction in the excited state is evident from the low values of the fluorescence quantum yield for **1a**, compared with those reported for phenol. This value is intermediate for **1i**, suggesting that the interaction decreases with phenol–olefin distance. *Ab initio* calculations show that the $\text{OH}\cdots\pi$ interaction is an electrostatic stabilisation rather than a true chemical bond. This is consistent with the fact that the variations in bond order are very small (lower than 2%).²¹



Scheme 3 Static and dynamic quenching in the photocyclisation of 2-allyl-1-naphthol.

2.3 Allylnaphthols

Mechanistic studies on the photocyclisation of 2-allyl-1-naphthol, **1j**, and 1-allyl-2-naphthol, **1k**, have been performed by Chow.¹⁸ Irradiation of **1j** and **1k** leads to the dihydrofuran and pyran ethers **2j,k** and **3j,k**. On the basis of quenching experiments of the products formation, fluorescence and determination of the excited state pK_a , the authors propose that cyclisation occurs from the phenolic singlet excited state, *via* intramolecular proton transfer.

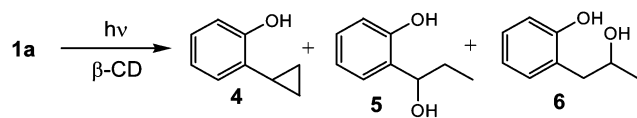
Kinetic analyses reveal the formation of two intramolecular proton transfer complexes (shown for **1j** in Scheme 3, a similar mechanism would operate in the case of **1k**); one is the precursor of the furanyl ethers and the other the precursor of the pyran ethers. Photocyclisation is mainly subjected to static quenching, arising from the ground state hydrogen bonding intermolecular interaction, and to a minor extent by a dynamic intramolecular quenching.

2.4 Alternative photoreaction pathways

In addition to photocyclisation, other photoreaction pathways have been reported for 2-allylphenols. Kitamura *et al.* have studied the comparative photobehaviour of **1a** and its phenoxide anion, with methanol as solvent. Under these conditions di- π -methane rearrangement and formation of 2-cyclopropylphenol, **4**, as major product after long irradiation times is observed.¹⁷

More recently, in a reinvestigation of the photochemistry of **1a** in concentrated cyclohexane solution, besides the cyclic ethers **2a** and **3a**, seven additional minor photoproducts were detected in trace amounts. Their formation has been rationalised through intermolecular processes involving two molecules of 2-allylphenol.²²

Furthermore, the photochemistry of **1a**–cyclodextrin complexes in aqueous solution has been investigated. In this medium, the photoreactivity is dramatically modified and photohydration of the acyclic olefin moiety is by far the predominant process. This is accompanied by di- π -methane



Scheme 4 Irradiation of 2-allylphenol in β -cyclodextrin.

rearrangement, eventually followed by photohydration with concomitant ring opening.²³

Hence, cyclisation to **2a** is totally suppressed, to the benefit of alcohols **5** and **6**, the hydration products of **4** and **1a**, respectively (Scheme 4).

Photohydration of the allylic double bond is a remarkable result. Monosubstituted, non-conjugated, acyclic olefins are unable to absorb light of wavelengths longer than 200 nm, which are employed under normal irradiation conditions. Neither direct nor sensitised irradiation of acyclic or large ring cyclic alkenes results in the addition of protic solvents; the only reported process being *E/Z* isomerisation, which is a hidden, non-observable process in the case of monosubstituted olefins such as **1a**. Only tri- or tetra-alkyl substituted olefins (through their Rydberg excited states), medium ring cycloalkenes and conjugated aryl olefins undergo addition of nucleophilic solvents *via* photoprotonation.

Although the excited state proton transfer pathway may provide an important contribution to olefin photohydration, it is not the only mechanism operating. As this process also occurs in the case of the methyl ether derivative of **1a**, there must be at least one other pathway leading to **6**. In this context, photohydration might involve nucleophilic attack by water at an intramolecular charge transfer exciplex. Although such species are not detected by fluorescence spectroscopy of the ether, intramolecular exciplex emission has been observed in closely related systems.

The olefin moiety has also been included in a cyclic system, as in **1l-r** (Chart 2). In the case of **1l-n**, photocyclisation takes place in non-polar solvents in a non-regioselective manner.¹⁰

More recently it has been reported that 6-alkylidenecyclohexa-2,4-dienones (*ortho*-quinone methides, **V**) are generated by photolysis of 2-(2'-cycloalkenyl)phenols, **1l-r**; trapping by methanol giving the ring-opened products **7l-r**^{24,25} (Scheme 5). The best results have been obtained with the cyclohexenyl derivatives **1m**, **1p** and **1q**.

The reaction mechanism for the photoisomerisation of 2-(2'-cyclohexenylphenol) **1m** to the *ortho*-quinone methide, **Vm**, has been theoretically studied using density functional theory (DFT) methods. Thermal isomerisation of **1m** (S_0) to the *ortho*-quinone methide **Vm** (S_0) presents a barrier of 50.4 kcal mol⁻¹. This very large value clearly prevents the isomerisation process. In addition, the reaction is very

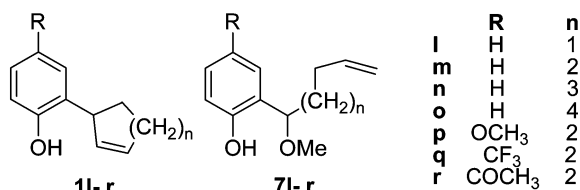
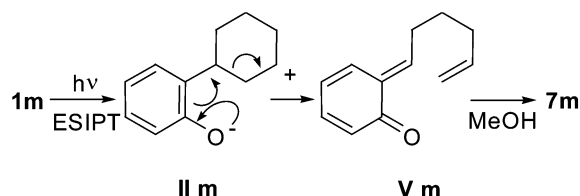


Chart 2



Scheme 5 Mechanism for the formation of **7m** by irradiation of **1m** in methanol.

endothermic (25.5 kcal mol⁻¹). Therefore under thermal equilibration conditions, formation of **Vm** is kinetically and thermodynamically very unfavourable. The calculated energy for the vertical excitation (CIS) of **1m** (S_0) to **1m** (S_1) is 112.8 kcal mol⁻¹. This species could be converted into the more stable **II m** (S_1), that lies 23.3 kcal mol⁻¹ below **1m** (S_1). The barrier for the transformation of **II m** (S_1) into **Vm** (S_1), *via* **TSm** (S_1), is 11.5 kcal mol⁻¹. In addition, transformation of **II m** (S_1) into **Vm** (S_1) is slightly exothermic, by 1.4 kcal mol⁻¹. These values allow us to understand the conversion of intermediate **II m** (S_1) into **Vm** (S_1). A schematic representation is given in Fig. 2.

In the case of the cyclopentenyl derivative **1l**, photoproduct **7l** is not observed, while only small amounts of **7n** and **7o** are formed from the 7- and 8-membered ring analogues **1n** and **1o**. Therefore ring size appears to be a key factor in the formation of *ortho*-quinone methides. On the other hand, phenol substitution also appears to play a role in the process. Thus electron withdrawing groups, such as CF₃ (compound **1q**), accelerate the reaction, while the opposite is true for electron donating groups, such as OCH₃ (compound **1p**). This is explained by the ESIPT mechanism, as the above results are consistent with the excited state acidities of the different phenols. The lack of reactivity in the case of ketone **1r**, where the intersystem crossing quantum yield is close to unity, allows a mechanism involving the triplet state to be ruled-out.

2-Allyl-3-aminophenol, **1s**, constitutes a separate case, because it is a simple model that combines the known photochemistry of 2-allylphenols and 2-allylanilines in the same molecule. As stated above, the former react *via* ESIPT, while the latter are known to undergo ESIET to give indolines as the final photoproducts (Scheme 6).

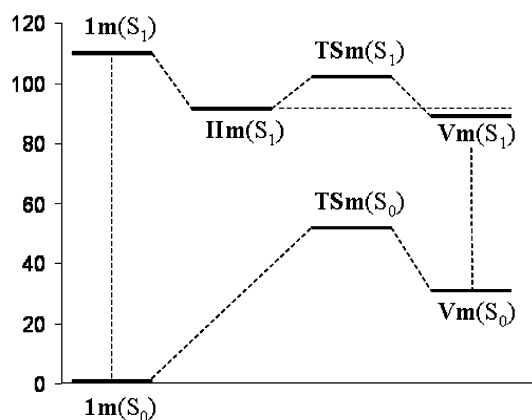
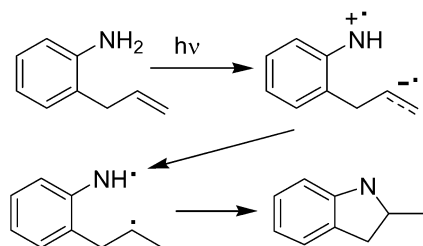


Fig. 2 Energy profile (in kcal mol⁻¹) for the isomerisation of **1m** into **Vm** in the S_0 and S_1 states.



Scheme 6 Photocyclisation of 2-allylaniline via ESIET.

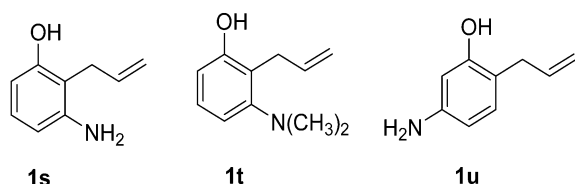


Chart 3

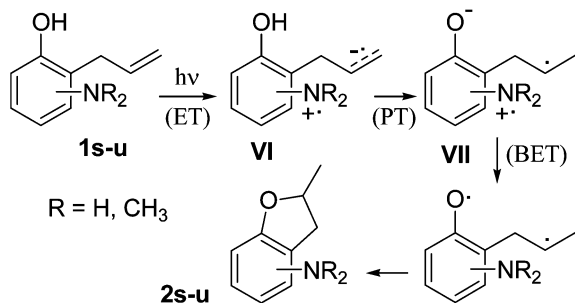
The photochemistry of **1s** (Chart 3) has been compared with that of mono-functional reference compounds under the same conditions.²⁶

Cyclisation to dihydrobenzofuran, **2s**, (phenol-like behaviour) is the overwhelming process, although minor amounts of indoline (the aniline-derived product) are also formed. Moreover, in the case of **1s**, the conversion is much higher and the reaction kinetics are *ca.* 10 times faster than for **1a** or 2-allylaniline. Clearly the combination of the hydroxy and amino substituents on the same ring produces a dramatic synergic effect.

A coupled electron transfer/proton transfer (ET/PT) mechanism that reasonably explains the enhanced photocyclisation to **2s** is outlined in Scheme 7. It is initiated by ESIET from the aniline to the olefin moiety, to give a diradical ion. Protonation of the anionic site by the phenolic group and subsequent back electron transfer (BET) from the phenoxide to the aniline radical cation leads to the final product, after the collapsing of the 1,5-diradical intermediate.

Unambiguous evidence for this mechanism is provided by the behaviour of the dimethylamino derivative, **1t**, as it also undergoes a very fast photoreaction to give **2t**. In contrast, methylation of the phenol group results in a much slower photocyclisation.

Furthermore, ET also occurs with an amino group located at the *para*-position—as in compound **1u**, ET proceeds very



Scheme 7 Coupled ET/PT mechanism explaining the photocyclisation of **1s-1u**.

rapidly to give **2u**. By way of contrast, moving the hydroxy substituent away from the allyl group results in a sharp decrease in the photoreactivity.

Thus a dramatic enhancement of the photocyclisation rate is observed in cases **1s**, **1t** and **1u**, as a consequence of a coupled ET/PT process. This increases the potential interest in polyfunctional systems containing proton donating, electron donating and electron accepting moieties, and allows one to obtain photochemical (in addition to photophysical) information through irreversible reactions that constitute a fingerprint for the mechanism involved.

3 Conjugation of the allyl chromophore: *trans*-2-cinnamylphenol

In *trans*-2-cinnamylphenol, **8a** (Chart 4), the allylic double bond is part of a styrene chromophore. The extended conjugation of the olefin allows easy access to its excited states upon direct irradiation, in competition with the usual excitation of the phenolic portion. As expected for a bichromophoric system, the absorption spectrum of **8a** and the added spectra of 2-methylphenol and β -methylstyrene are superimposable.

In general, irradiation of *trans*-2-cinnamylphenol leads to *cis*-2-cinnamylphenol, **8b**, 2-benzyl-2,3-dihydrobenzofuran, **8c**, and 2-phenyl-3,4-dihydro-2*H*-benzopyran, **8d** (Fig. 3).²⁷

3.1 The nature of the reactive excited states

3.1.1 Photochemical evidence. Irradiation of **8a** has been carried out under a variety of conditions. Direct irradiation under an inert atmosphere, using hexane as solvent, leads to the *cis* isomer, **8b**, as the major photoproduct, although cyclisation to **8c** and **8d** also takes place. The presence of oxygen produces a marked decrease of the yield of **8b**,

λ (nm)	$\log \epsilon$		λ (nm)	$\log \epsilon$
271	3.9		250	4.2
			284	3.0
			293	2.9

Chart 4

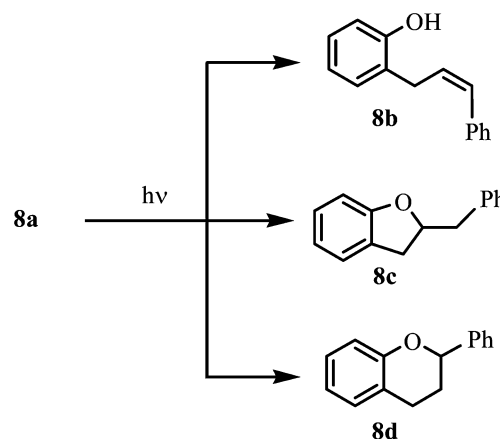
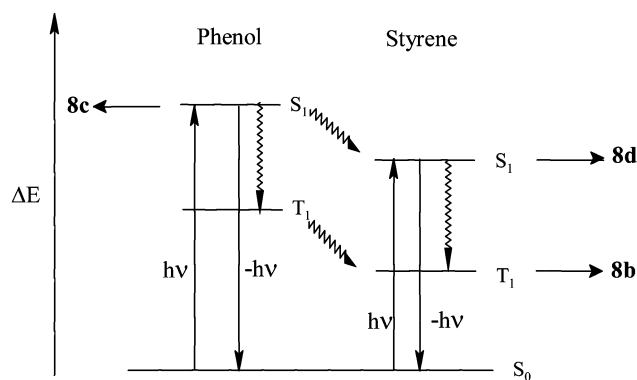


Fig. 3 The photochemistry of **8a**.



Scheme 8 Excited states involved in the photochemistry of **8a**.

concomitant with enhancements in the yields of **8c** and **8d**. This points to the possible involvement of excited states of different multiplicity: the styrenic triplet (partially quenched by oxygen) in the double bond isomerisation and the phenolic or the styrenic singlets in the cyclisation.

In order to gain a further insight into the mechanisms of the photochemical processes, a series of photosensitisation experiments have been performed. The use of benzene as solvent ($E_S = 110 \text{ kcal mol}^{-1}$) to attempt an enhanced generation of the phenolic singlet ($E_S = 103 \text{ kcal mol}^{-1}$ for phenol) results in higher conversions, a marked predominance of cyclisation and an enhanced **8c** : **8d** ratio (45 : 30). The use of photosensitisers with lower singlet energies, such as toluene ($E_S = 106 \text{ kcal mol}^{-1}$), methyl benzoate ($E_S = 102 \text{ kcal mol}^{-1}$) or *para*-dichlorobenzene ($E_S = 101 \text{ kcal mol}^{-1}$), favours the formation of **8d**. This suggests that a styrenic singlet ($E_S = 98 \text{ kcal mol}^{-1}$ for styrene) is actually involved in the photocyclisation to form the 6-membered ring product, **8d**.

On the other hand, when the photolysis is carried out in acetone ($E_T = 80 \text{ kcal mol}^{-1}$) to provide easy access to the styrenic triplet ($E_T = 62 \text{ kcal mol}^{-1}$) and a pyrex filter is used to prevent direct absorption by this chromophore, the photocyclisation is completely suppressed, and instead, a clean and efficient *trans*-*cis* isomerisation to **8b** takes place. The conversion is slightly higher under an inert atmosphere, as expected for a triplet excited state.

The above results indicate that **8b** is formed from a styrenic triplet, while photocyclisation to ethers **8c** and **8d** takes place from the phenolic and styrenic singlets respectively (Scheme 8).

3.1.2 Photophysical evidence. The emission spectrum of **8a** in hexane (Fig. 4) supports the above rationalisation. It consists of one fluorescence band, having a maximum at 309 nm and a shoulder at 300 nm. The excitation spectra corresponding to both emissions are identical to each other, and also similar to the absorption spectrum, which suggests a common ground state precursor.

Nevertheless, the decrease in fluorescence quantum yield of **8a** with increasing amounts of triethylamine (long wavelength region), and also with higher temperatures, suggests that each fluorescence maximum can be associated with a different chromophore in the molecule.

On the other hand, the low value of the fluorescence quantum yield of **8a** (0.014), compared with those of phenol

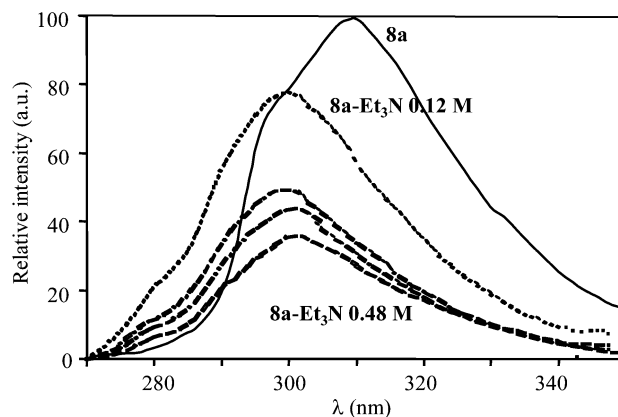


Fig. 4 Fluorescence spectra of **8a** at room temperature and in the presence of increasing amounts of Et_3N .

and β -methylstyrene measured under the same conditions, is evidence of a significant interchromophoric interaction in the excited state.

3.1.3 Theoretical calculations. The $\text{OH}\cdots\pi$ interaction has been evaluated for **8a** by means of an *ab initio* conformational analysis, using restricted Hartree–Fock calculations and the 3-21G and 6-31G** basis sets.²¹ Fig. 5 shows the two optimised conformations obtained by the 6-31G** method.

The C=C–O–H dihedral angle in **8aA** is *ca.* 331° . Such a geometrical arrangement results from a favourable interaction between the hydroxylic hydrogen and the π system of the 2-propenyl substituent. The energetics of the optimised geometries show that **8aA** is the most favourable conformation (by 0.3 – $0.7 \text{ kcal mol}^{-1}$). This is the result of two opposed contributions: (i) a favourable $\text{OH}\cdots\pi$ interaction and (ii) conformational strain due to the spatial arrangement. Related calculations using suitable models indicate that the $\text{OH}\cdots\pi$ interaction produces a stabilisation of between 3.2 and $4.9 \text{ kcal mol}^{-1}$. The nature of the $\text{OH}\cdots\pi$ interaction has been studied by means of a frequency analysis. The results (3-21G) corresponding to the stretching vibration of the H–O bond show that this parameter decreases in **8aA** relative to **8aF**. A detailed analysis of the data points to a parallel variation in the force constants. These results can be understood as a favourable electrostatic interaction between the positive region of the H–O bond and the π system of the carbon–carbon double bond, which increases the polarisation of the former.

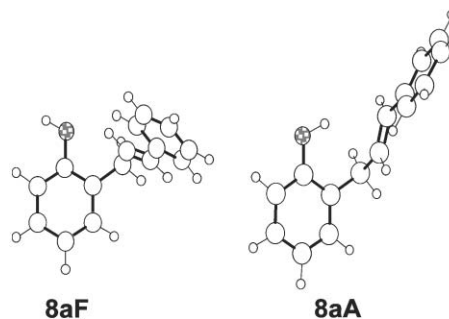
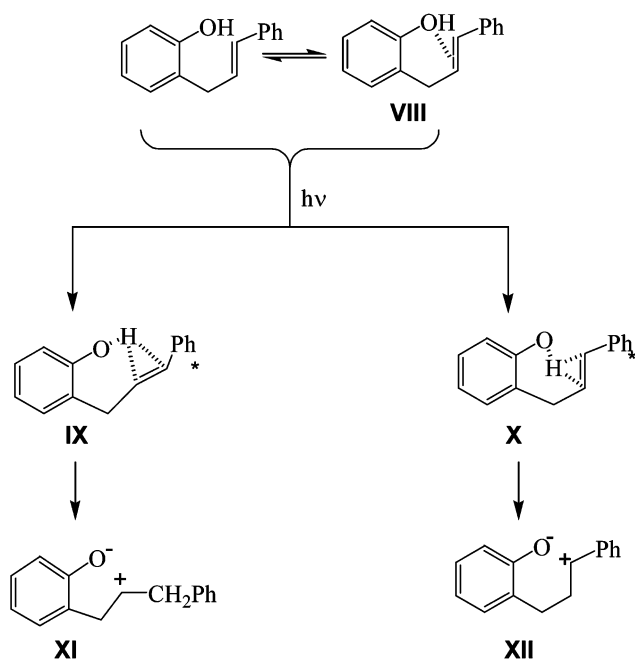


Fig. 5 HF/6-31G** geometries of the structures **8aF** and **8aA**.



Scheme 9 Photocyclisation mechanism for *trans*-2-cinnamylphenol.

3.2 Photocyclisation via proton transfer

In order to check whether a proton transfer mechanism is involved in the photocyclisation of **8a**, bases capable of establishing hydrogen bonds with the ground state of *trans*-2-cinnamylphenol have been used. Such irradiations result in a clear quenching of the photocyclisation process. This quenching can be, in principle, static or dynamic, depending on whether it occurs, in the ground, VIII, or excited state π -complexes, IX–X (Scheme 9). To investigate this, **8a** has been irradiated in benzene solutions containing variable amounts of methanol or dioxane. As expected, the percentages of cyclisation products decreased with increasing concentrations of methanol and dioxane, while the opposite was true for the amount of remaining **8a**. This effect (shown for MeOH in Fig. 6) is more pronounced in the case of the 6-membered ring product **8d**, probably due to the higher contribution of dynamic quenching.

On the other hand, the FTIR spectrum of **8a** in the gas phase shows two different absorptions in the region of the O–H stretching at 3651 and 3581 cm^{-1} (Fig. 7). This is in good agreement with a ground state association. The former peak can be assigned to the free hydroxyl band, while the latter corresponds to the intramolecularly hydrogen bonded group.

The photochemistry of *trans*-2-cinnamylphenol can therefore be justified as follows: Photocyclisation to **8c** and **8d** is initiated by promotion of the ground state π -complex, VIII, to the excited singlet states of the phenolic or styrenic chromophores respectively. The corresponding conformations of the excited state complexes (which justify the observed regioselectivities) are IX and X. These species would decay rapidly to the zwitterions XI and XII respectively, to afford the corresponding cyclisation products, after intramolecular nucleophilic attack. These processes are summarised in Scheme 9.

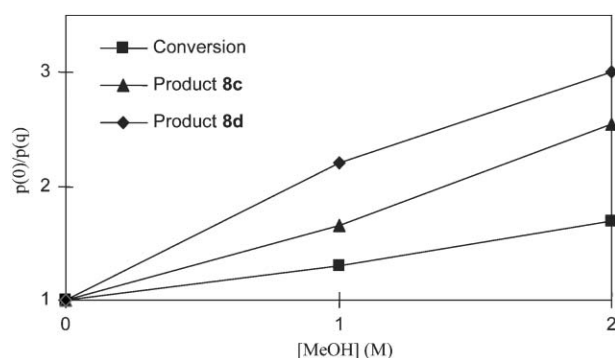


Fig. 6 Quenching of the photocyclisation of **8a** by methanol. $p(0)/p(q)$ is the ratio between the percentage yields of **8c** and **8d** in the absence and presence of methanol.

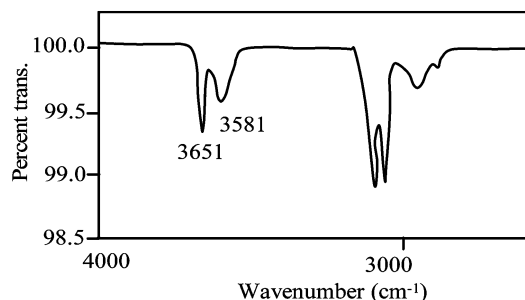


Fig. 7 Detail of the FTIR spectrum of **8a** in the gas phase.

3.3 Contribution of the electron transfer mechanism

In apparent contradiction to the efficient quenching of the formation of **8c** by trimethylamine or triethylamine, the photocyclisation to **8d** is markedly enhanced in the presence of these additives (Fig. 8).

These results suggest that the use of tertiary amines makes available a new route to product **8d**, involving an electron transfer (ET) mechanism. This is in agreement with the reported formation of radical ion pairs upon photochemical excitation of styrene–amine mixtures. The resulting radical anion would undergo intramolecular proton transfer to afford intermediate XIII. Subsequent BET to the amine radical cation, followed by collapse of the diradical XIV, would lead to the 6-membered ring product **8d**. (Fig. 9).

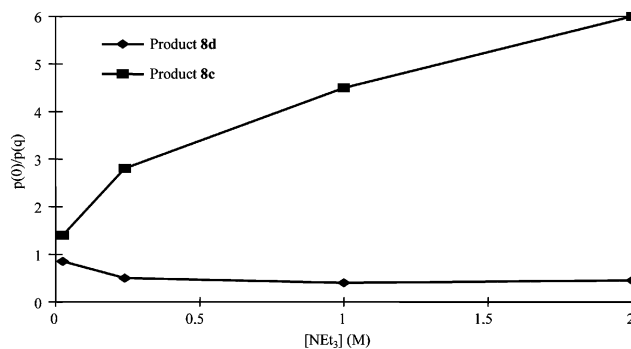


Fig. 8 Influence of triethylamine on the photocyclisation of **8a**. The parameter $p(0)/p(q)$ is the ratio between the percentage yields of **8c** and **8d** in the absence and presence of triethylamine.

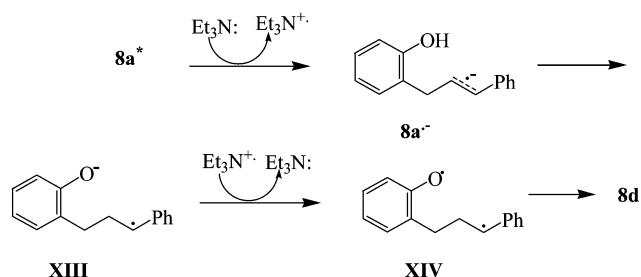


Fig. 9 ET mechanism for the photocyclisation of **8a** in the presence of amines.

This hypothesis is also supported by thermodynamic evidence resulting from the application of the Rehm–Weller equation for the ET process from the ground state of the amine to the styrenic S_1 :

$$\Delta G_F \text{ (kcal mol}^{-1}\text{)} = 23.06 (E_{D/D^+} - E_{A/A^-}) - E^*$$

where E_{D/D^+} and E_{A/A^-} are the redox potentials of the donor (amine) and acceptor, and E^* is the singlet energy of the styrenic chromophore. This allows the estimation of a ΔG_F (the free energy change associated with the formation of free radical ions) of ca. $-20 \text{ kcal mol}^{-1}$. In contrast, the analogous process involving the styrene triplet does not fulfil the thermodynamic requirements (ΔG_F value ca. $+15 \text{ kcal mol}^{-1}$).

4 Substituent effects

Other *trans*-2-cinnamylphenols where the singlets of both chromophores are involved and proton transfer is the main photocyclisation mechanism are *trans*-2-cinnamyl-4-methylphenol, **9a**, *trans*-2-cinnamyl-4-phenylphenol, **10a**,²⁸ *trans*-2-cinnamyl-1-naphthol, **23a**, and *trans*-1-cinnamyl-2-naphthol, **24a**.²⁹

Appropriate structural modifications of the parent *trans*-2-cinnamylphenol (such as substitution at the phenolic or styrenic ring or the use of a molecular bridge, different from the methylene group) can be helpful for obtaining a deeper understanding of the photoreaction mechanism. On the other hand, the structural changes can also favour some of the possible photophysical deactivation routes, or even provide alternative reaction pathways. For this reason, a number of **8a** derivatives have been prepared (Chart 5) and their photophysical and photochemical behaviour studied. The obtained results allow the classification of the substituted cinnamylphenols, **9a–22a**, and cinnamyl-naphthols, **23a–25a**, into several groups, according to the main effect observed upon substitution.

In general, upon irradiation of compounds **9a–25a**, the *cis* isomers, **9b–25b**, the dihydrobenzofurans, **9c–25c**, and the dihydrobenzopyrans, **9d–25d**, are obtained.

4.1 Modification of the relative excited state energies

Usually, substitution at a phenolic or styrenic ring results in a decrease in the energy of the excited states of the chromophore bearing the substituent(s). After irradiation of the bichromophore, energy transfer leads to the lowest energy singlet and

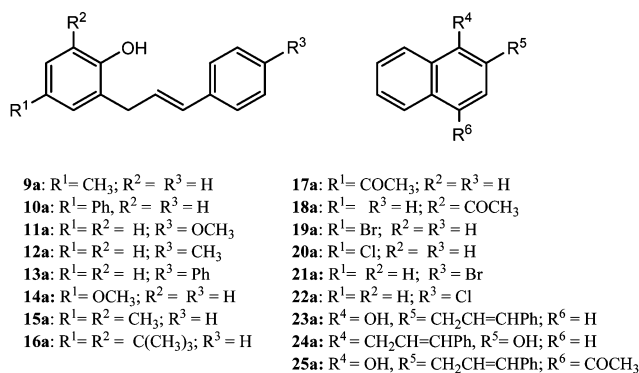


Chart 5 Structures of the substituted *trans*-2-cinnamylphenols, **9a–22a**, and cinnamyl-naphthols, **23a–25a**.

triplet excited states responsible for the photochemical and photophysical behaviour. This pattern can be illustrated with *trans*-2-[3-(4-methoxy)-2-propenyl]phenol, **11a**.^{30,31}

The photochemistry of **11a** can be summarised as follows: Direct irradiation of the substrate yields dihydrobenzopyran, **11d**, as the major product, accompanied by smaller amounts of the *cis* isomer, **11b**, and the 5-membered ring compound, **11c**. Irradiation using acetone as solvent gives rise to **11b** as a single product, confirming the nature of the styrenic triplet as the precursor of the *trans*–*cis* isomerisation.

The photocyclisation results can best be explained by intramolecular proton transfer in the excited singlet state. The ground state interaction between the phenolic OH and the styrenic double bond is evident from the presence of two bands in the OH stretching zone of the GC–FTIR spectra of **11a**: the free OH appears at a higher wavenumber (3651 cm^{-1}) relative to the intramolecularly associated OH (3572 cm^{-1}). On the other hand, irradiation of **11a** in the presence of dioxane produces a dramatic decrease in the yield of the cyclic ethers **11c** and **11d**, with a parallel increase in the yield of **11b**.

The fluorescence spectrum of **11a** at room temperature in a non-polar solvent has a maximum at ca. 325 nm. This value indicates that the major contribution to the fluorescence spectrum of this compound is due to the styrenic chromophore, since the reported data on the emission maxima of 4-methoxystyrene and phenol are 320 and 300 nm respectively.

The fact that the only significant emission observed at room temperature is that of the styrenic chromophore, independent of the excitation wavelengths, indicates that intramolecular energy transfer deactivates most of the phenolic singlets. Further proof favouring the styrenic nature of S_1 in this compound, is provided by the fluorescence spectrum of its hydrogenated derivative, whose maximum appears close to 300 nm (similar to the value obtained for phenol).

The fluorescence quantum yield of **11a** is 0.064, much lower than that of styrene or its substituted derivatives (typically 0.4). This can be explained in terms of intramolecular quenching of the styrenic singlet by proton transfer, which ultimately leads to photocyclisation.

On the other hand, when the fluorescence spectrum of **11a** is measured in a solid matrix of methylcyclohexane (77 K), a dramatic change in the shape and position of the bands is observed upon excitation at different wavelengths. This is

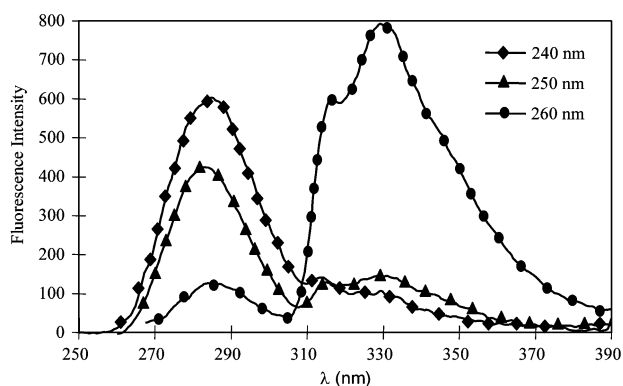


Fig. 10 Fluorescence emission of **11a** at 77 K.

illustrated in Fig. 10. Thus, while excitation at 260 nm results in emission from the styrenic singlet, the use of shorter excitation wavelengths (240–250 nm) produces emission spectra similar to those obtained for the parent phenol in a low temperature methylcyclohexane matrix. The fact that energy transfer is blocked under these conditions suggests that intramolecular singlet–singlet energy transfer takes place through a Dexter mechanism. At 77 K, the conformational dynamics are nearly frozen, so it may be difficult for the two chromophores to interact in the relatively spatial arrangement when energy transfer is possible.

Attachment of other substituents to the styrenic ring of *trans*-2-cinnamylphenol also produces a decrease in the singlet energy of the styrenic moiety. As a consequence, the resulting styrenic chromophore (lower in energy) becomes responsible for the photophysical and photochemical properties. As a result, a marked regioselectivity towards 6-membered ring products is observed, *via* an excited state proton transfer. Other **8a** derivatives in which the styrenic chromophore predominates are *trans*-2-[3-(4-methylphenyl)-2-propenyl]phenol, **12a**, and *trans*-2-[3-(4-biphenyl)-2-propenyl]phenol, **13a**.³⁰

4.2 Modulation of the redox properties

Introduction of appropriate substituent(s) at the phenolic ring can decrease the oxidation potential of the phenolic nucleus, resulting in a more effective involvement of the ET mechanism. The behaviour of **14a**, possessing an electron donating methoxy substituent, is illustrative of this situation.^{32,33}

4.2.1 Photocyclisation *via* electron transfer. Irradiation of **14a** in benzene leads to the 6-membered ring product, **14d**, as the major product. Only minor amounts of **14b** and **14c** are obtained. In view of the low oxidation potential of the phenolic nucleus of **14a**, the preferred cyclisation to **14d** does not appear to involve the usual excited state proton transfer process, and must be associated with the operation of an excited state ET mechanism. Unambiguous confirmation of this suggestion has been obtained by performing the irradiation of **14a** in the presence of dioxane. Under these conditions, no quenching associated with intermolecular proton transfer is observed for **14c** formation. Taking into account the oxidation potentials and the excitation energies of *para*-methoxyphenol and styrene, the Rehm–Weller equation predicts that ET

would be thermodynamically allowed, either upon excitation of the donor or the acceptor substructures of **14a** (see below). This would explain the parallel decrease observed for both the yields of **14b** and **14c**, compared with the unsubstituted compound, **8a**. The possible participation of the styrene triplet in this process has been ruled out in view of the lack of **14d** formation upon acetone-sensitised photolysis of **14a**, and the exclusive formation of the *cis* isomer, **14b**, instead. Thus, the phenolic and styrenic singlets must be the excited states involved in intramolecular ET.

4.2.2 Exciplex formation. The fluorescence spectra of **14a** in hexane (Fig. 11) displays a single band of $\lambda_{\text{max}} = 320$ nm, clearly attributable to emission from the lowest lying phenolic singlet (compare trace B, Fig. 11a with trace A, Fig. 11b). The same result is obtained by exciting either at 250 nm (styrene) or at 290 nm (phenol), clearly due to efficient energy transfer between the excited singlets of both chromophores. In contrast, a completely different behaviour is observed in the more polar solvent acetonitrile. The most remarkable result is the presence of a much longer wavelength band centred at 420 nm and the concomitant disappearance of the phenolic emission at 320 nm (see Fig. 11b). This new band is clearly attributable to a charge transfer exciplex, whose formation would be exergonic according to the Rehm–Weller equation. Using the excitation energy determined from the intersection between the normalized excitation and emission spectra, together with the reported literature values for the redox

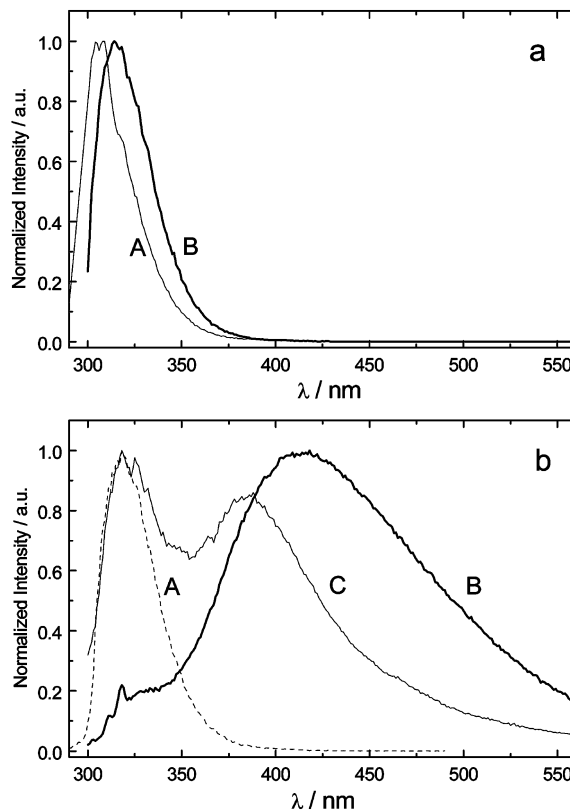


Fig. 11 Fluorescence spectra of: (a) β -methylstyrene (trace A) and 4-methoxyphenol (trace B); (b) **14a** in hexane (trace A), acetonitrile (trace B) and 9 : 1, CH_2Cl_2 – CH_3CN (trace C).

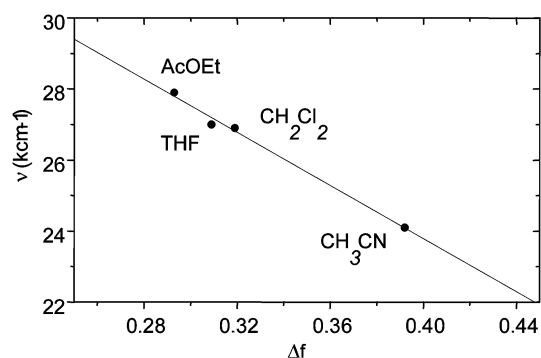


Fig. 12 Solvent polarity dependence of the exciplex emission maxima for **14a**. The solvent parameter Δf has been calculated as follows: $\Delta f = [(\epsilon - 1)/(2\epsilon + 1)] - [(n^2 - 1)/(4n^2 + 2)]$ where ϵ is the dielectric constant and n is the refraction index of the solvent.

potentials, the resulting Gibbs free energy associated with exciplex formation is *ca.* $-25 \text{ kcal mol}^{-1}$. Emission spectra have also been obtained for solutions of **14a** in solvents of intermediate polarity and for a variety of solvent mixtures. For instance, using CH_2Cl_2 – CH_3CN (9 : 1, v/v), both the monomer and the exciplex bands are observed (see trace C, Fig. 11b). As expected for a charge transfer exciplex, the position of the longer wavelength band shows a clear dependence on the solvent polarity (see Fig. 12 for the Lippert–Mataga plot with the data obtained in pure solvents).

The quantum yield of emission at 415 nm is 0.05, and the lifetime is relatively long (5.1 ns), compared with the monomer under the same conditions (1.0 ns). The exciplex is quenched by oxygen ($k_q = 4.2 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$) and by tetrabutylammonium hydrogensulfate ($k_q = 3.3 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$). The Stern–Volmer plot for quenching by the ammonium salt is shown in Fig. 13. Similar salt effects have been observed for other exciplexes and have been attributed to their dissociation into radical ions, with a concomitant decrease in fluorescence.

To check whether the corresponding intermolecular exciplex is also observable, equimolar mixtures of 4-methoxyphenol

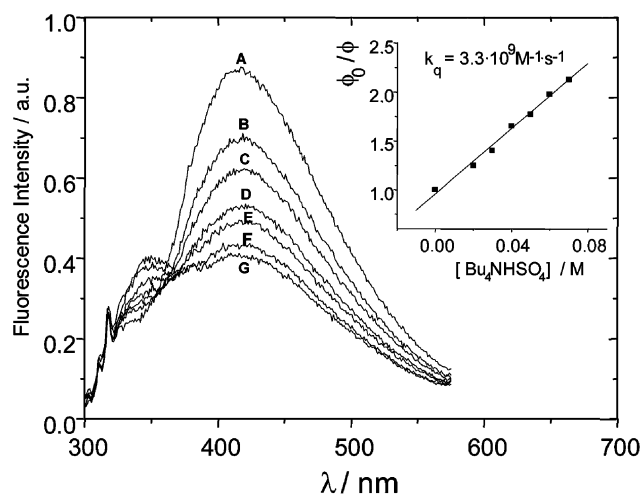


Fig. 13 Quenching of the exciplex fluorescence of **14a** by $[\text{Bu}_4\text{NHSO}_4]$ at different molar concentrations. Curve (A) 0.0 M, (B) 0.02 M, (C) 0.03 M, (D) 0.04 M, (E) 0.05 M, (F) 0.06 M, (G) 0.07 M.

and β -methylstyrene in acetonitrile have been studied. The emission spectra consist of the bands assignable to the isolated chromophores (either phenolic maximum at 320 nm—upon excitation at 290 nm, or styrenic maximum at 310 nm—when exciting at 250 nm). However, when using much higher concentrations of the partners (0.1 M), the exciplex emission at *ca.* 440 nm is also clearly observable.

4.2.4 Related cases. The intramolecular excited state interaction between phenol and styrene, directly observed as an exciplex emission in the case of **14a**, supports the mechanistic proposals to explain the photochemistry of some related bichromophoric cinnamylphenols with electron donating substituents at the phenolic ring. For example, 2-cinnamyl-4,6-dimethylphenol, **15a**, and 2-cinnamyl-4,6-di-*tert*-butylphenol, **16a**,³³ exhibit photophysical and photochemical properties similar to those of **14a**.

4.3 Enhancement of intersystem crossing

As stated above, photocyclisation takes place *via* the phenolic and styrenic singlets. This means that an efficient deactivation of these states to their corresponding triplets would result in a substantial decrease in the photocyclisation yield. The acetyl derivative **17a** has been chosen as a model to show the consequences of favouring intersystem crossing in phenolic chromophores.²⁸ As usual, the UV-vis absorption spectrum of **17a** and the added spectra of β -methylstyrene and *para*-acetylphenol are superimposable. The latter is characterised by one band of $\lambda_{\text{max}} = 265 \text{ nm}$ ($\log \epsilon = 4.17$).

In the parent cinnamylphenol, **8a**, photocyclisation occurs, in competition with intersystem crossing to the styrenic triplet that is responsible for *trans*–*cis* isomerisation. However, direct irradiation of **17a** leads exclusively to the *cis* isomer, **17b**. This result is compatible with the reported excited state energies of *para*-acetylphenol ($E_S = 83 \text{ kcal mol}^{-1}$ and $E_T = 72 \text{ kcal mol}^{-1}$). The efficiency of *trans*–*cis* isomerisation is markedly higher in acetone, confirming that the styrenic triplet is involved in this transformation.

These results can be summarised as follows: After irradiation of **17a**, a cascade of photophysical processes (mainly energy transfer and intersystem crossing) lead to the lowest energy state, the styrenic triplet, which is the precursor of the *cis* isomer (Fig. 14).

Accordingly, when photophysical measurements are performed on **17a**, no fluorescence emission is observed. This

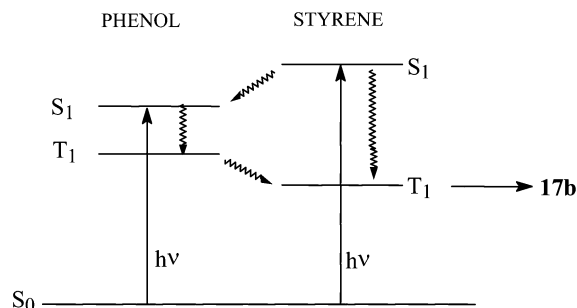


Fig. 14 Excited states involved in the photochemistry of **17a**.

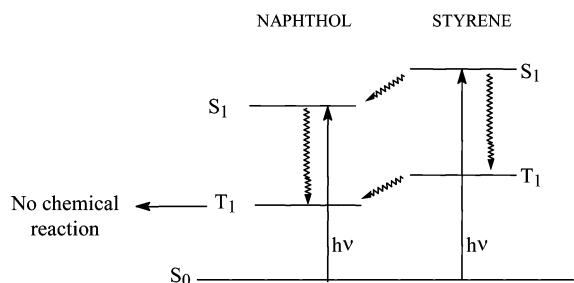


Fig. 15 Excited states involved in the photochemistry of **25a**.

agrees well with a rapid deactivation of the lowest singlet excited state by intersystem crossing.

A similar trend is observed for the *ortho*-acetyl derivative, **18a**.²⁷ In this case, the phenolic hydroxyl is expected to be strongly chelated with the adjacent carbonyl group. This structural feature prevents the formation of a π -complex of type **IX**, but, on the other hand, facilitates an efficient, energy wasting deactivation of the phenolic singlet *via* proton exchange between the two oxygen atoms, followed by thermal tautomerisation. As expected, the only process observed upon irradiation of **18a** in either benzene or acetone is *trans-cis* isomerisation, a markedly higher efficiency in the latter solvent being found.

The acetylnaphthol derivative, **25a**, exhibits a similar behaviour; however, due to the different relative energies of the chromophores, no photochemical reaction is observed. The lowest triplet is phenolic in nature and therefore unreactive (Fig. 15).²⁹

4.4 Alternative reaction pathways

Incorporation of halogen substituents into the aromatic rings of the parent cinnamylphenol, **8a**, provides an alternative pathway for the deactivation of excited states, by means of carbon–halogen bond cleavage. A representative example of such an effect is provided by *trans*-4-bromo-2-cinammylphenol, **19a**.³⁴

When **19a** is irradiated in benzene, a mixture of the dihydrobenzopyran, **19d**, and the solvent-derived cyclic ethers **10c** and **10d** are obtained. When these results are compared with those obtained for the parent compound **8a**, two differences are particularly remarkable: (1) the absence of the 5-membered ring product **19c** and (2) the formation of cyclic derivatives related to *trans*-2-cinnamyl-4-phenylphenol, **10c** and **10d**. If photocyclisation to **19c** is assumed to occur from the excited phenolic singlet, the existence of a new competing reaction pathway (by cleavage of the carbon–halogen bond) would result in a less efficient formation of this product.

Thermodynamic considerations show that complete C–Br bond homolysis is possible upon excitation. Thus, the singlet energy of compound **19a**, obtained from its fluorescence spectra, is found to be 97 kcal mol^{−1}, while the corresponding C–Br bond energy in the model compound bromobenzene is only 75 kcal mol^{−1}. To rule out the possibility that the benzene-derived products could be formed by secondary photolysis of the halogen-containing cyclic ethers, compounds **19c** and **19d** have been subjected to irradiation under the same

conditions. No significant reaction is observed in these control experiments, indicating that *trans*-2-cinnamyl-4-phenylphenol is formed first, *via* addition of the corresponding aryl radical to the solvent. The subsequent photochemical transformation of **10a** into **10c** and **10d** is a known process.

In principle, dehalogenation can also occur from an excited triplet state. This appears to be less likely as the value of triplet energy (*ca.* 60–70 kcal mol^{−1}) is too low to fulfil the thermodynamic requirements, unless some degree of C–C bond making occurs concomitantly with C–Br bond breaking. To investigate this possibility, photolysis of **19a** has also been carried out using acetone as the photosensitiser. Under these conditions, compounds **10c** and **10d** are not formed, and the only process observed is *trans-cis* isomerisation. Hence, dehalogenation does not take place from an excited triplet state.

A similar pattern is followed by other halogen-substituted cinnamylphenols, such as *trans*-4-chloro-2-cinammylphenol, **20a**, *trans*-2-[3-(4-bromophenyl)-2-propenyl]phenol, **21a**, and *trans*-2-[3-(4-chlorophenyl)-2-propenyl]phenol, **22a**.³⁴ Introduction of chlorine or bromine into either the phenolic or the styrenic rings of a bichromophoric cinnamylphenol produces a decrease in the corresponding singlet excited state energies. When such energies lie above those required to cleave the carbon–halogen bond, photodehalogenation (eventually followed by solvent addition) efficiently competes with photocyclisation. This is especially remarkable in the case of compounds substituted at the phenolic chromophore, where formation of dihydrobenzofurans is completely prevented. The processes occurring are summarised in Fig. 16.

4.5 Substitution at the spacer

An ethyl substituent has been attached at the methylene spacer, both to enhance the prospects of di- π -methane rearrangement providing an alternative reaction pathway, and to provide a marker for analysis of the stereoselectivity of photocyclisation.³⁵

In this context, if fully zwitterionic intermediates were actually intervening in the photochemical behaviour of *E*- and *Z*-2-(1-ethyl-3-phenylpropenyl)phenol (**26a** and **26b** respectively), the same stereoisomeric ratio should be observed for the cyclised products, irrespective of the *Z/E* stereochemistry of the starting cinnamylphenol. However, a certain degree of stereochemical memory would indicate that the proton is not completely transferred in the excited state, thus supporting the involvement of bridged species, such as **I** (Scheme 1), as the direct precursors of the final products.

4.5.1 Photochemical results. The photochemistry of **26a** has been investigated in cyclohexane at 254 nm. The structures of the products are shown in Chart 6. Photocyclisation is again the major process, giving *E*-**26c**, *E*-**26d** and *Z*-**26d**.

It is remarkable that the two possible dihydrobenzopyrans, *E/Z*-**26d**, are obtained in significant amounts, although *Z*-**26d** is the major product. By contrast, only one of the two possible dihydrobenzofurans (the *E*-isomer) is obtained, since formation of the *Z*-isomer is disfavoured by steric hindrance.

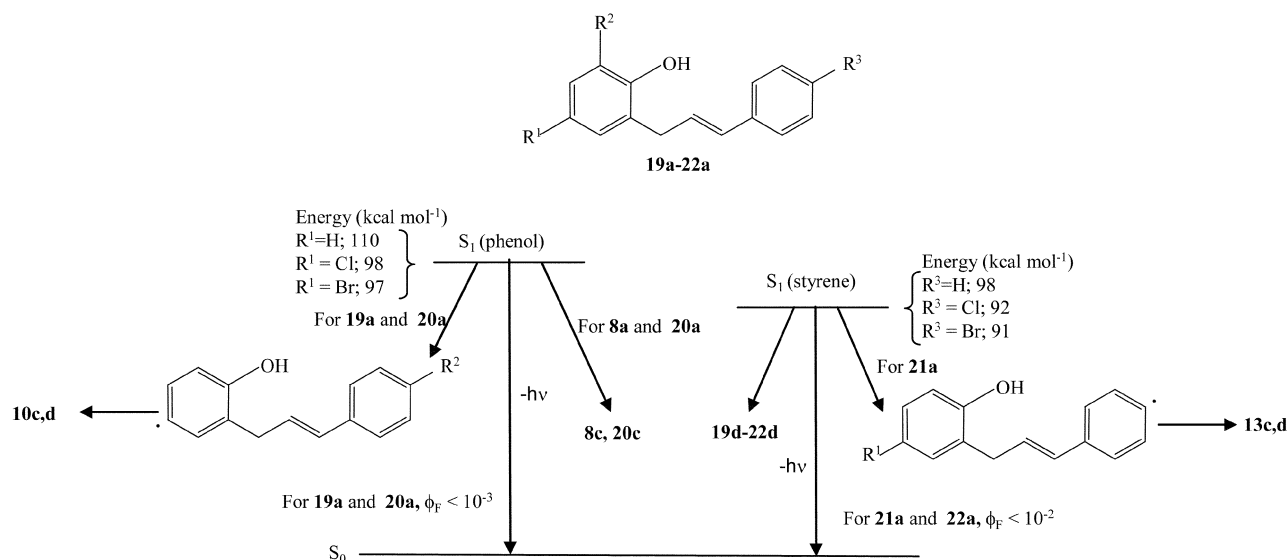


Fig. 16 Photochemical and photophysical deactivation pathways for **19a-22a**.

Small amounts of the olefins **26b** and **29**, resulting from double bond isomerisation, are also formed. The *E* to *Z* phototransformation is common in cinnamylphenols; however migration of the double bond in these compounds has been much less well documented. Besides, cyclopropanes **27** and **28**, arising from di- π -methane rearrangement, have been detected as minor products. As in the case of related 1,3-diphenylpropenes, their formation must involve the styrenic chromophore.³⁶

On the other hand, irradiation of **26b** in cyclohexane at 254 nm gives rise to **26a** and **27-29**, with the cyclic ethers again being the major products. The most interesting data is the ratio *E*-**26d** : *Z*-**26d**, that in this case is found to be 1.23 : 1. Thus, starting from **26b**, benzopyran, *E*-**26d**, predominates over its *Z*-isomer. This result is exactly the opposite to that mentioned above for **26a**, where formation of *Z*-**26d** is favoured and the ratio *E*-**26d** : *Z*-**26d** is 0.68 : 1.

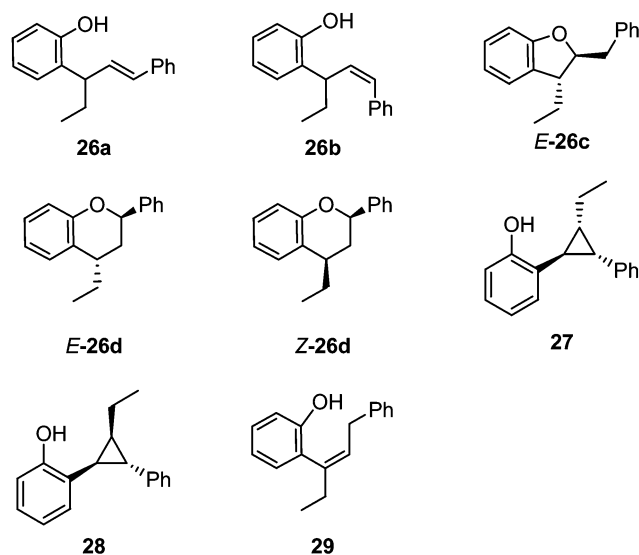


Chart 6

4.5.2 Chemical cyclisation. Chemical cyclisation of **26a** and **26b** has also been achieved by treatment with HBr. Under these conditions, the only products are *E*-**26d** and *Z*-**26d**, with an *E* : *Z* ratio of 1.38, either starting from the propene *E* or *Z* isomer. The absence of *E*-**26c** in the reaction mixture is consistent with preferential formation of the benzylic cation upon protonation of the double bond. On the other hand, the lack of dependence of the *E*-**26d** : *Z*-**26d** ratio on the *Z*/*E*-stereochemistry of the starting olefin agrees well with the planar arrangement expected for carbocations.

4.5.3 Involvement of H-bridged species. The diverging behaviour observed in the photochemical vs. chemical process points to the involvement of different intermediates. As a consequence, the results cannot simply be explained by the generation of long-lived zwitterions such as **XVI** and **XVII** (Fig. 17).

If such species (with full charge separation) were the key intermediates, the photolysis results would be very similar to

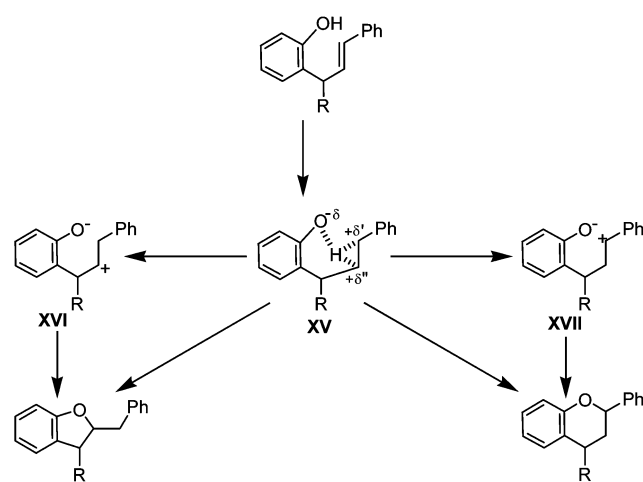


Fig. 17 H-bridged intermediates in the photocyclisation of **26a**.

those obtained in the acid catalysed cyclisation, which is clearly not the case. So although the involvement of shorter-lived zwitterions cannot be completely ruled out, direct cyclisation of a bridged entity such as **XV**, with a certain degree of charge development at the oxygen ($-\delta$) and the formerly olefinic carbons atoms ($+\delta'$ and $+\delta''$), appears to be more consistent with the experimental observations. The residual π -bonding of **XV** would justify the different stereoselectivities (*E/Z*-**26d** ratio) observed in the 6-*endo-trig* photocyclisation of the two *E/Z* isomers **26a** and **26b**.

4.5.4 Elongation of the spacer. The phenol and cinnamyl chromophores can be further separated by the use of an ethylene instead of a methylene bridge, as is the case for *trans*-2-(4-phenylbut-3-enyl)phenol, **30a**.²¹ Photolysis of **30a** in benzene leads to the *cis* isomer **30b**, in addition to the cyclic ethers 2-benzyl-2,3-dihydrobenzofuran, **30d**, and 2-phenyl-2,3,4,5-tetrahydro-1-benzoxepin, **30e**. The **30e/30d** ratio is *ca.* 10 times higher than the **8d/8c** ratio observed for **8a**. Excited state proton transfer appears to play an important role in the photocyclisation mechanism, as suggested by the enhanced formation of the cyclic ethers and by the partial reaction quenching that follows the addition of dioxane, a solvent able to disrupt the intramolecular OH $\cdots\pi$ association. However, it has to be stressed that intramolecular association in the ground state is not observable by studying the OH stretching zone of **30a**'s IR spectrum.

Concerning the fluorescence properties of **30a**, the spectrum shows two maxima, at 295 and 302 nm, indicating that emission from both the phenolic and the styrenic moieties takes place. The fluorescence quantum number ϕ_F value for **30a** is 0.031, suggesting some intramolecular interaction in the excited state. This fact can, in principle, be attributed to the deactivation of the excited singlet state by intramolecular proton, electron and/or energy transfer, and to the occurrence of the photochemical reaction, which is also an efficient energy-wasting channel that deactivates excited states.

5 Summary and outlook

Phenol–olefin bichromophoric systems are versatile models for investigating the fundamental aspects of proton, electron and energy transfer processes. Due to their structural simplicity, they are readily accessible and a number of analogues (allylphenols, allylnaphthols, cycloalkenylphenols, cinnamylphenols, butenylphenols, *etc.*) have been prepared that exhibit a wide range of photophysical and photochemical properties. By means of an appropriate molecular design, it is possible to reproduce, at will, a desired pattern of behaviour that involves diverse photochemical mechanisms.

The intramolecular interactions in the excited state can be studied by examining the emission data, particularly the position of the fluorescence bands and the quantum yields. More interestingly, unlike most bichromophores, phenol–olefin systems are chemically productive, giving rise to irreversible photoreactions that constitute a fingerprint of the mechanism involved. The most common process observed is photocyclisation to 5- and 6-membered ring cyclic ethers. However, depending on the particular structure and the

experimental conditions, additional photoreactions such as *Z/E* isomerisation, di- π -methane rearrangement, formation of *ortho*-quinone methides, photohydration and photodehalogenation are also observed.

Intramolecular OH $\cdots\pi$ interactions, both in ground and excited states, play a key role in the interesting photophysical and photochemical properties of 2-allylphenol derivatives. This is supported by experimental data (detection of associated OH bands in gas phase FTIR spectra, quenching of photocyclisation by hydrogen bonding solvents, *etc.*) and also by theoretical calculations.

This rich photochemistry and photophysics is highly sensitive to the microenvironment experienced, as indicated by the dramatic modifications observed within cyclodextrin cavities. Therefore, studies within other confined spaces (zeolites, micelles, *etc.*) may deserve further investigation in the near future.

Most of the observed photoreactions result in the formation of products containing asymmetric carbon atoms. Hence, it would be interesting to explore the possible stereoselectivity induced by the attachment of chiral substituents to different positions relative to the prochiral centre, or by the use of chiral media or chiral complexing agents.

Finally, photocyclisation of 2-allylphenol and its derivatives occurs from excited singlet states and is thought to proceed through zwitterionic or diradical intermediates. However, direct detection of such transient species has proven unsuccessful thus far, due to their expectedly short lifetimes (subnanosecond timescales). As fast reaction kinetics facilities are becoming increasingly available (down to the femtosecond range), it would be interesting to attempt the detection of the proposed intermediates using them.

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