Enhanced reactivity in OH/NH/π polyfunctional systems through coupled proton/electron transfer in the excited state: the photocyclisation of 2-allyl-3-aminophenol

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The photocyclisation rate of 2-allyl-3-(or 5-)aminophenols (1, 4 and 8) is dramatically enhanced, when compared with reference compounds, as a consequence of a coupled proton/electron transfer process.

Excited state proton transfer (PT) and electron transfer (ET) are two of the most important photochemical processes. Competition between PT and ET (as well as coupled PT/ET) has recently attracted considerable attention, both from the fundamental and practical points of view. In this context, polyfunctional systems that contain a proton donor, an electron donor and an accepting moiety have been studied. For instance, 4-dialkylaminosalicylaldehyde and 4′-dialkylamino-3-hydroxyflavone exhibit dual fluorescence associated with intramolecular proton transfer and charge transfer in the excited singlet state.[1–4]

By contrast with the available photophysical and theoretical studies on polyfunctional systems, the chemical reactions arising from coupled PT/ET processes remain practically unexplored. In the present work, a simple model (compound **1**, Chart 1) has been designed to address this issue by combining the known photochemistry of 2-allylphenols (AP)[5–10] and 2-allylanilines (AA)[11,12] in the same molecule. The former react *via* intramolecular PT, while the latter undergo intramolecular ET; dihydrobenzofurans and indolines are the respective final photoproducts (Scheme 1). Thus, irreversible processes provide a photochemical (rather than photophysical) fingerprint for the involved mechanism.

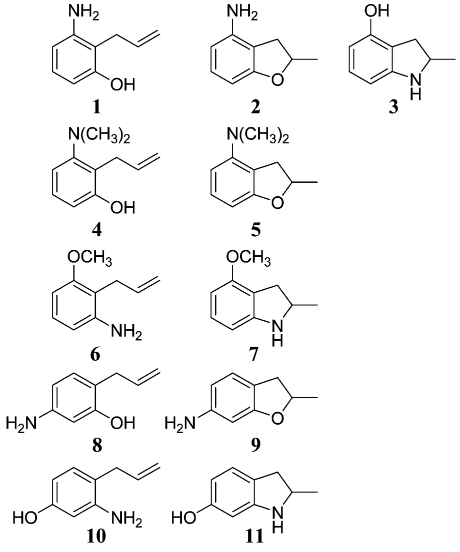
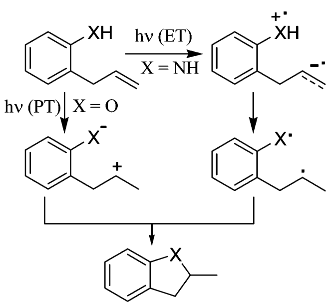


Chart 1

Fig. 1 shows the fluorescence spectra of **1** and its reference compounds phenol, aniline, 2-allylphenol and 2-allylaniline. They were measured in acetonitrile, using isoabsorptive solutions ($A = 0.1$) at the excitation wavelength (280 nm). The emission maximum of **1** was close to that of aniline, and its intensity was extremely weak. It is known that *ortho*-allyl substitution of phenol and aniline decreases the emission intensity, due to the occurrence of photocyclisation.[10,11] Thus, in the case of **1** a high photoreactivity was anticipated.



Scheme 1 Photocyclisation of 2-allylphenol and 2-allylaniline *via* PT or ET, respectively.

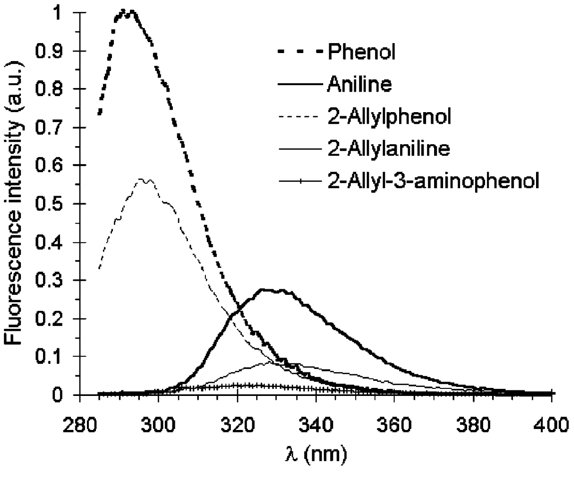


Fig. 1 Emission spectra of **1** and some of its reference compounds.

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Table 1 Photoproducts distribution found for compounds **1**, **4**, **6**, **8**, **10**, 2-allylaniline and 2-allylphenol after 30 minutes irradiation

Entry	Compd	Conversion (%)	**2**	**3**	**5**	**7**	**9**	**11**	Indoline[a]	Dihydrobenzofuran[a]
1	2-allylaniline	6	—	—	—	—	—	—	100	—
2	2-allylphenol	7	—	—	—	—	—	—	—	100
3	**1**	56	85	15	—	—	—	—	—	—
4	**4**	37	—	—	100	—	—	—	—	—
5	**6**	11	—	—	—	100	—	—	—	—
6	**8**	41	—	—	—	—	100	—	—	—
7	**10**	4	—	—	—	—	—	100	—	—

[a] The photoproducts were 2-methylindoline for 2-allylaniline and 2,3-dihydro-2-methylbenzofuran for 2-allylphenol.

The photochemistry of **1** was compared with that of monofunctional reference compounds under the same conditions.† The results are shown in Table 1. Cyclisation to dihydrobenzofuran **2** (phenol-like behaviour) was the overwhelmingly major process, although minor amounts of indoline **3** (aniline-derived product) were also formed. This cannot be accounted for on the basis of the relative reactivities of AP and AA (see Table 1, entries 1 and 2, and Fig. 2). Moreover, in the case of **1** the conversion was much higher (Table 1, entry 3) and the reaction kinetics much faster (Fig. 2) than in either of the reference compounds. Clearly, combination of the hydroxy and amino substituents on the same ring produces a dramatic synergetic effect.

A coupled PT/ET mechanism that reasonably explains the enhanced photocyclisation to **2** is outlined in Scheme 2. It would be initiated by excited state intramolecular ET from the aniline to the olefin moiety, to give a biradical ion. Protonation of the anionic site by the phenolic group and subsequent back electron transfer (BET) from the phenoxide to the aniline radical cation would lead to the final product after the collapse of the 1,5-biradical intermediate. The first and last steps of this mechanism are identical to those that have been widely accepted for AA derivatives, as shown in Scheme 1.‡ The key step would be the intramolecular PT at the biradical anion stage, where both phenol and aniline radical cation may act as donors. Unambiguous evidence for the predominance of the former was supported by the behaviour of the dimethylamino derivative **4**, that also underwent a very fast photoreaction, to give **5** (see Table 1, entry 4, and Fig. 2). By contrast, methylation of the phenol group as in **6** resulted in a much slower photocyclisation, to afford indoline **7** (Table 1, entry 5 and Fig. 2). The proposed BET from the phenoxide to the aniline radical cation is thermodynamically favourable in view of the redox potentials found in the literature.[13]

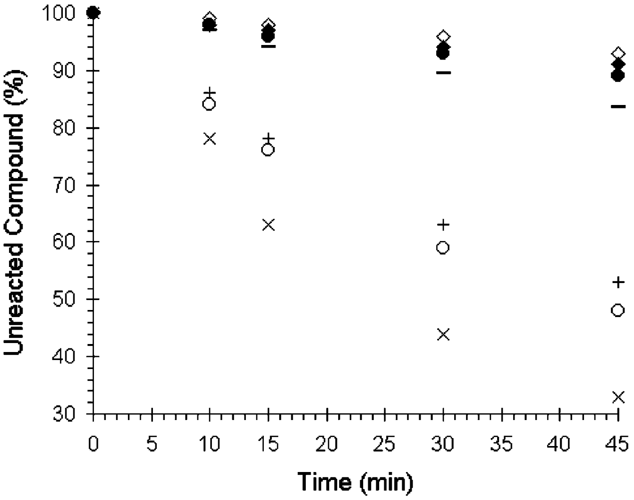
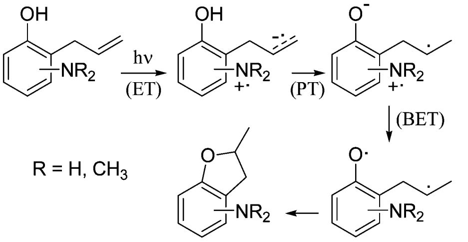


Fig. 2 Photoreaction kinetics of **1** (×), **4** (+), **6** (−), **8** (○), **10** (◇), 2-allylphenol (●) and 2-allylaniline (◆).



Scheme 2 Coupled PT/ET mechanism explaining the photocyclisation of **1**.

According to this mechanism, electron transfer should also occur with an amino group located at the *para*-position. This was confirmed by photolysis of compound **8**, that proceeded very fast to give **9** (Table 1, entry 6, and Fig. 2). By contrast, moving the hydroxy substituent away from the allyl group as in **10** resulted in a sharp decrease of the photoreactivity to give **11**, that became comparable to that of AA (Table 1, entry 7, and Fig. 2). Although all irradiations reported in Table 1 were carried out under the same conditions, the photocyclisation quantum yields were determined for two selected compounds (**1** and 2-allylphenol), in order to obtain more quantitative data for comparison. The values (obtained using the *E*/*Z*-isomerization of β-methylstyrene as chemical actinometer)[14] were 0.25 (for **1**) and 0.02 (for 2-allylphenol). This is in good agreement with the preparative data shown in entries 3 and 2 of Table 1 and confirms that the reaction efficiency increases by one order of magnitude as a consequence of coupled proton/electron transfer.

In summary, a dramatic enhancement of the photocyclisation rate (when compared with the reference compounds AP and AA) is observed in the case of **1**, **4** and **8** as a consequence of a coupled PT/ET process. This increases the potential interest of polyfunctional systems containing proton donor, electron donor and accepting moieties and allows one to obtain photochemical (in addition to photophysical) information, through irreversible reactions that constitute a fingerprint for the involved mechanism.

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Notes and references

† Irradiations were performed through quartz in a multilamp photoreactor, equipped with four 4 W low pressure Hg lamps with a maximum emission at 254 nm, employing acetonitrile as solvent. The reaction course was followed by GC/MS and ^{1}H NMR. The photoproducts were isolated by column chromatography (silica gel and hexane/ethyl acetate as eluent) and identified by ^{1}H, ^{13}C NMR and MS.

‡ Electron transfer from the excited singlet state of anilines to alkenes would be thermodynamically favoured, according to the Weller equation: $\Delta G = 23.06\,[E_{D/D+\cdot} - E_{A/A\cdot-}] - E_S^{*}$.[15] The estimated free energy change (ΔG) is *ca.* -10 kcal mol^{-1}, based on the relevant redox potentials ($E_{D/D+\cdot} = 0.8$–0.9 V;[16] $E_{A/A\cdot-} = -2.6$ V *vs.* SCE)[17] and on the excited singlet state energies of anilines ($E_S^{*} = 88$–94 kcal mol^{-1}).[18]

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