Ground and excited-state intramolecular interactions in phenol–olefin bichromophoric compounds

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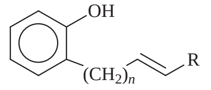
The intramolecular $OH\cdots\pi$ interactions of the phenolic and olefinic chromophores in *o*-propenyl and *o*-butenyl phenols 1a–d in the ground and excited states have been studied by (a) *ab initio* Hartree–Fock calculations using the 3-21G and 6-31G basis sets, (b) FTIR spectral measurements in the gas phase, (c) fluorescence emission studies and (d) product studies. Such interactions appear to play a key role in the photochemical behaviour of the four compounds.**

Introduction

Compounds containing two different chromophores covalently linked through a rigid or flexible spacer have been the subject of intensive studies, owing to interest in their use as suitable models to reproduce key photochemical processes (energy or electron transfer) and to their potential application in a number of fields (mimicking of photosynthesis or other biological phenomena, design of photoconducting polymers or other new materials, *etc.*).[1,2] The photochemistry of phenol–olefin bichromophores has attracted some attention from the mechanistic point of view.[3–6] Thus, *o*-propenylphenols (for instance **1a** and **1b**) undergo photocyclization to dihydrobenzofurans and dihydrobenzopyrans, which has been explained as the result of intramolecular excited state proton transfer (ESPT). The analogous *o*-butenylphenol **1c** has been studied in less detail, but it appears to undergo photocyclization less readily; in this case only the six-membered ring product has been identified.[7]



1a: $n = 1$, R = H
1b: $n = 1$, R = Ph
1c: $n = 2$, R = H
1d: $n = 2$, R = Ph

Structures of compounds **1a**–**d**

Previous semiempirical PCILO-calculations[8] (PCILO = perturbative configuration interaction using localized orbitals) on **1a**,**c** have led to the conclusions that: (a) a $OH\cdots\pi$ hydrogen bond exists in both cases, which is significantly weaker in the compound with the longer phenol–olefin distance (**1c**) and (b) the intramolecular interaction in the ground state can be correlated with the photochemical behaviour; this would justify the higher photoreactivity of the propenyl derivative **1a**.

In the present work we have undertaken a systematic study on the ground and excited state intramolecular interactions existing in four phenol–olefin bichromophoric compounds (**1a**–**d**), with different size of the spacer (methylene *versus* dimethylene) and different conjugation of the olefinic moiety (ethylenic *versus* styrenic). *Ab initio* calculations at 3-21G and 6-31G** levels have been performed in order to assess the nature of the $OH\cdots\pi$ interaction. The experimental observations on this phenomenon (IR spectra in the gas phase) have been compared with the *ab initio* results.

The interchromophoric interaction in the excited state is evidenced by the intramolecular fluorescence quenching. The product studies indicate that such quenching is, at least partially, due to ESPT processes, since the regioselectivity can be correlated with the relative stability of the intermediate carbocations.

Results

Theoretical studies

The interaction between the hydroxy group and the double bond has been evaluated for *o*-propenyl and *o*-butenyl phenols (**1a**–**d**), by means of an *ab initio* conformational analysis, using restricted Hartree–Fock calculations and the 3-21G and 6-31G** basis sets.[9] Fig. 1 shows the two optimised conformational structures for each compound obtained with the 6-31G** method.

From the data shown in Table 1, it is clear that the **A** structures present a C=C–O–H dihedral angle of *ca.* 331° for **1aA**, **1bA** and *ca.* 306° for **1cA**, **1dA**, thus showing a larger deviation from planarity for the latter. The dihedral angles with the alkenyl substituents also show a larger twist for **1cA**, **1dA** than for **1aA**, **1bA**. This geometrical arrangement results from a favourable interaction between the hydroxylic hydrogen and the π system of the prop-2-enyl and the but-3-enyl substituent.

Table 2 shows the energetics of the optimised geometries. The two levels of calculation show that the most favourable structures are **1aA**, **1bA** for the propenylphenols and **1cF**, **1dF** for the butenyl substituted analogues. The absolute values of ΔE range from 0.3 to 1.4 kcal mol^{-1}. This is the result of two opposed contributions: (i) a favourable $OH\cdots\pi$ interaction and (ii) a conformational strain due to the twist of both hydroxylic and alkenyl substituents. Related calculations with suitable models (see Experimental section) indicate that the $OH\cdots\pi$ interaction produces a stabilisation between 3.2 and 4.9 kcal mol^{-1}. This appears to be enough to counterbalance the unfavourable contribution in the case of **1a**,**b**, but not in the case of **1c**,**d**.

The nature of the $OH\cdots\pi$ interaction has been studied by means of a frequency analysis. Table 3 shows the results (3-21G) corresponding to the stretching vibration of the H–O bond. This parameter decreases in the **A** structures relative to the **F** structures. A detailed analysis of the data shows that these variations are related to a decrease of the force constants. These results can be understood as a favourable electrostatic

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Table 1 Selected HF/6-31G** geometrical parameters for the structures **1aF–1dF** and **1aA–1dA**

	1aF	**1bF**	**1cF**	**1dF**	**1aA**	**1bA**	**1cA**	**1dA**
Interatomic distances/Å								
C(β) · · · H(O)					2.442	2.457	2.450	2.480
C(α) · · · H(O)					2.598	2.621	2.718	2.786
Dihedral angles/°								
C=C–O–H	181.4	181.3	181.2	181.3	331.4	331.2	305.9	304.8
C=C–CH_2–CH	79.6	79.4			67.0	67.7		
C=C–CH_2–CH_2			79.9	79.8			90.6	91.7
C–CH_2–CH=CH	121.6	120.7			233.6	232.9		
C–CH_2–CH_2–CH			181.7	181.9			181.9	284.4
CH_2–CH_2–CH=CH_2			241.3	241.0			109.6	109.1

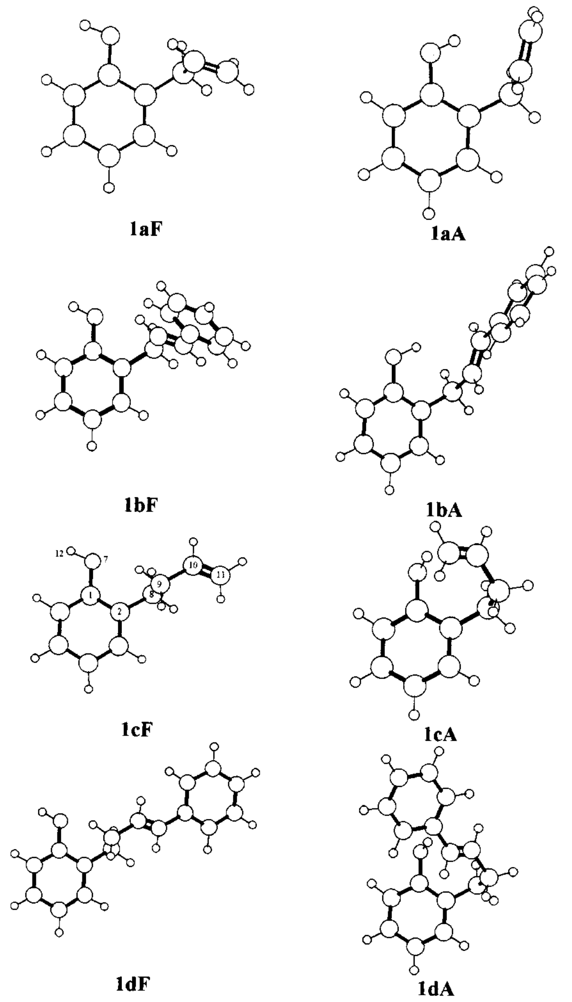


Fig. 1 HF/6-31G** geometries of the structures **1aF–1dF** and **1aA–1dA**

interaction between the positive region of the H–O bond and the π system of the C–C double bond, which increases the polarisation of the former.

Finally, a Wiberg bond index analysis[10] of the structures **1aA**, **1cA** at 6-31G** level points out that the bond order between the hydroxylic H and the C(α) or the C(β) olefinic carbons is very small, lower than 1%. This result is in agreement with a similar decrease of the C(α)–C(β) bond order. Again, this suggests that the OH · · · π interaction is an electrostatic stabilisation rather than a true chemical bond.

Intramolecular OH · · · π association in the ground state

This point was addressed by examining the IR spectra of compounds **1a–d** in the gas phase (GC–FTIR), in order to prevent the possibility of intermolecular interactions.[11] For the compounds with a single methylene group between the phenolic and olefinic substructures (**1a**,**b**), the spectra showed two bands in the OH stretching zone. The free OH appeared at *ca.* 3650 cm^{-1}, while the intramolecularly associated OH gave rise to a well-defined band at lower wavenumber values. By contrast, in the analogues with a longer spacer (**1c**,**d**), the only signal clearly observable was that attributed to the free OH group (Fig. 2).

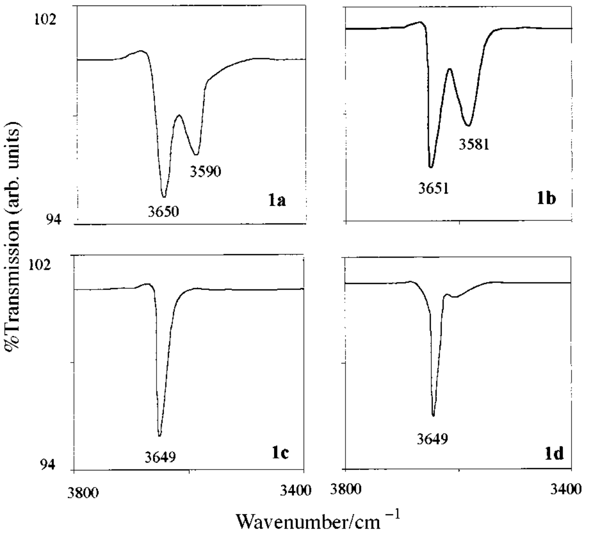


Fig. 2 GC–FTIR spectra (3400–3800 cm^{-1} zone) of compounds **1a–d**

Interchromophoric interaction in the excited state

In order to obtain information about the nature of the involved excited states of compounds **1a–d**, their fluorescence spectra were recorded. The results obtained, at room temperature in a non-polar solvent (cyclohexane), are summarised in Table 4.

The reported data of the singlet energies of phenol and styrene are 103 and 98 kcal mol^{-1}, respectively.[12] Thus, the values of E_s obtained for **1a**,**c** indicate that, as expected, the only contribution in the fluorescence spectra of these compounds is due to the phenolic chromophore. By contrast, the spectra of **1b**,**d** can be explained in terms of emission from both the phenolic and the styrenic moieties.

The interchromophoric interaction in the excited state is evidenced by the low values of the fluorescence quantum yields (φ_F) compared with those reported for phenol (0.08)[12] and styrene (0.24).[13] These values are even lower for compounds **1a**,**b** than for **1c**,**d**, suggesting that such interaction decreases with the phenol–olefin distance.

Product studies

As the photochemistry of the propenyl phenols **1a**,**b** has been previously studied in detail,[5,6] only the butenyl analogues **1c**,**d** have been investigated in this work. The absorption spectra of **1c**,**d** showed their maxima below 300 nm; hence irradiations were carried out through quartz. The samples were purged with argon before irradiation and the solvent employed was benzene.

Table 2 3-21G and 6-31G** Total and relative energies of the structures **1aF**–**1dF** and **1aA**–**1dA**

Method	Compound	E_F/a.u.	E_A/a.u.	$E_{A'}$[a]/a.u.	ΔE[b]/kcal mol^{-1}	ΔE_{OH}[c]/kcal mol^{-1}
HF/3-21G	**1a**	−419.133 007	−419.133 751	−419.125 868	−0.47	−4.93
	1b	−647.404 405	−647.404 887	−647.397 405	−0.30	−4.68
	1c	−457.953 153	−457.951 476	−457.944 596	1.05	−4.30
	1d	−686.224 632	−686.223 29	−686.216 199	0.84	−4.43
HF/6-31G**	**1a**	−421.493 970	−421.495 397	−421.489 178	−0.89	−3.89
	1b	−651.054 446	−651.055 590	−651.049 895	−0.72	−3.56
	1c	−460.532 548	−460.530 435	−460.524 970	1.32	−3.42
	1d	−690.093 051	−690.090 810	−690.085 655	1.40	−3.22

[a] Single point calculations for the **A** structures with the H–O bond in opposite orientation to the OH···π interaction. [b] $E_A - E_F$. [c] OH···π interaction computed from $E_A - E_{A'}$.

Table 3 HF/3-21G Vibrational frequency analysis and relative frequencies of the OH stretching band for the structures **1aF**–**1dF** and **1aA**–**1dA**

	1a	1b	1c	1d
Structures **F**				
Frequencies	3919.22	3918.76	3918.15	3918.05
Reduced masses	1.0669	1.0669	1.0669	1.0669
Force constants	9.655	9.653	9.650	9.669
Structures **A**				
Frequencies	3864.09	3860.97	3844.79	3839.88
Reduced masses	1.0658	1.0658	1.0649	1.0650
Force constants	9.376	9.361	9.275	9.252
$\Delta_{\text{Frequencies}}$/cm^{-1}	55.13	57.80	73.36	78.17

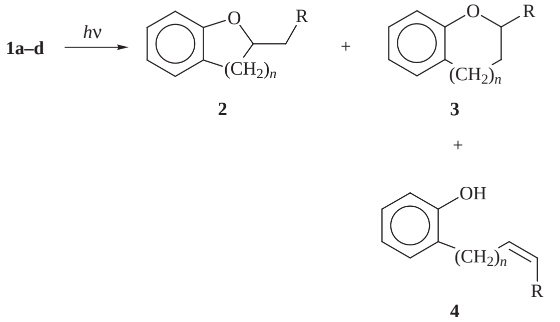
Table 4 Photophysical data of compounds **1a**–**d** at room temperature in cyclohexane

Compound	λ_{exc}/nm	λ_{em}/nm	E_S/kcal mol^{-1}	φ_F
1a	260	293	101	0.012
1b	250	300, 309	99	0.014
1c	270	293	101	0.041
1d	270	295, 302	100	0.031

Table 5 Irradiation of compounds **1a**–**d**

Entry	Compound	Conversion (%)	Yield (%) 2	3	4
1	**1a**[a]	34	91	9	—
2	**1b**[b]	80	45	30	25
3	**1c**	20	75	25	—
4	**1d**	91	20	74	6
5	**1b**[c]	47	25	14	61
6	**1d**[c]	61	19	54	27

[a] Ref. 5. [b] Ref. 6. [c] In the presence of 2 M dioxane.



Scheme 1 Photochemical reaction scheme for compounds **1a**–**d**

The results are summarised in Table 5, together with those previously reported for **1a**,**b**, to facilitate discussion.

Irradiation of **1c**[4] in benzene yielded the dihydrobenzopyran **2c**[4] as the major product, accompanied by the seven membered ring compound **3c**[14] (Table 5, entry 3). These results are similar to those obtained for *o*-allylphenol (**1a**) under the same conditions (Table 5, entry 1). In the case of **1d**, photolysis in benzene led to the *cis* isomer **4d**, in addition to the cyclic ethers **2d**[15] and **3d** (Table 5, entry 4). The **3**/**2** ratio was *ca.* 10 times higher than that observed for **1c** (**3d**/**2d** = 3.5, as compared with **3c**/**2c** = 0.3).

Discussion

The theoretical studies correlate fairly well with the experimental observations on OH···π intramolecular association in the ground state. Thus, they predict that the energy of structures **A** is lower than that of structures **F** for the propenylphenols **1a**,**b**, while the reverse is true for the butenylphenols **1c**,**d**. Accordingly, the stretching bands attributed to associated OH groups can only be observed in the IR spectra of compounds **1a**,**b** in the gas phase.

By means of vibrational frequency analysis, it has been possible to calculate the Δν of the associated OH bond vibrations. The estimated values range between 55 and 78 cm^{-1}, which are in excellent agreement with the experimental observations for **1a**,**b**. This parameter was overestimated by semiempirical calculations (PCILO methods), which led to values three times too large (*ca.* 290 cm^{-1}).[8]

Concerning the nature of the OH···π interaction, it was previously considered as a weak hydrogen bond, whose origin was thought to be charge transfer due to a $\pi \longrightarrow$ OH* ($\pi \longrightarrow \sigma^*$) delocalization.[8] However, the *ab initio* calculations performed in this work show that the OH···π interaction is an electrostatic stabilisation rather than a true chemical bond; in fact, the variations in the bond order are very small (lower than 2%).

As regards the intramolecular interaction in the excited state, clear evidence about this has been obtained by measuring the fluorescence quantum yields and by comparing them with those previously reported for the isolated chromophores phenol and styrene. The φ_F values are even lower in the case of the *o*-propenylphenols **1a**,**b**, with a single methylene bridge, than for their butenyl analogues **1c**,**d** with a longer spacer. This fact can be in principle attributed to deactivation of the excited singlet state by intramolecular proton, electron and/or energy transfer processes. Of course, the occurrence of photochemical reactions is also an efficient energy-wasting channel, which deactivates the excited states. In this context, excited state proton transfer appears to play an important role in the mechanism of photocyclisation, as suggested by the variation in the product selectivity, which can be roughly attributed to the relative stability of the carbocations (primary, secondary or benzylic) generated upon intramolecular protonation of the double bond. However, formation of **2b** would involve a secondary carbocation, less stable than the benzylic carbocation leading to **3b**. This might originate from kinetic effects related to the ground-state geometry of the cinnamylphenol **1b**. The role of excited state proton transfer was confirmed by the lower conversions and the decrease in the yield of products **2** and **3** when the irradiations were carried out in the presence of dioxane as quencher of proton transfer (see Table 5, entries 5 and 6).

Finally, it has to be stressed that photocyclisation occurs even when intramolecular association in the ground state is not observable from the study of the OH stretching zone in the IR spectra (compounds **1c**,**d**). As pointed out by the *ab initio* calculations, the strength of the OH $\cdots\pi$ interaction in structures **1aA**–**1dA** does not depend significantly on the length of the spacer; this is shown in Table 2, last column.[16] In fact, although the population of conformers **1cA**, **1dA** is very minor, due to their higher total energy (see Table 2, column 6), photocyclisation might still occur through their intermediacy. The partial reaction quenching by addition of dioxane, a solvent able to disrupt the intramolecular OH $\cdots\pi$ association, appears to support this view.

Experimental

Calculations

The *ab initio* study on the (OH $\cdots\pi$) interaction was carried out with the Gaussian 94 suite of programs.[17] The geometries of the different compounds have been fully optimised at the restricted Hartree–Fock (RHF) level with the 3-21G and 6-31G** basis sets.[9] Their optimisations were achieved using the Berny analytical gradient method.[18,19] The search for minima was done in a preliminary way by means of an AM1 semiempirical[20] study of the stationary points on the potential energy surface. The AM1 geometries were then used as starting points in the *ab initio* study. The AM1 results (not included) were found to be very similar to those resulting from the *ab initio* study. To evaluate the OH $\cdots\pi$ interaction single point calculations for new auxiliary structures **A′**, with the alkenyl side chain as in the **A** structures but with the O–H as in the **F** structures, have been carried out.

Analysis of the stretching vibration of the O–H bond has been carried out by means of frequency analyses for the optimised geometries using the FREQ option of Gaussian 94. Finally, the bond order has been determined by means of the Wiberg bond indexes[10] computed by using the Natural Bond Orbital analysis[21,22] as implemented in Gaussian 94.

Experimental procedures

UV spectra were recorded in cyclohexane in a Shimadzu UV-160A; λ_{max} (nm) and log ε values (in brackets) are given for each absorption band (ε in dm^3 mol^{-1} cm^{-1}). IR spectra were obtained with a GC–FTIR Hewlett-Packard 5965; ν_{max} (cm^{-1}) is given for all the absorption bands. ^{1}H NMR spectra were measured in CDCl$_3$ with a 300-MHz Varian Gemini-300; chemical shifts are reported in δ (ppm) values and *J* values are in Hz, using TMS as internal standard. Mass spectra were obtained under electron impact using a Hewlett-Packard 5988 A spectrometer; the ratios *m*/*z* and the relative intensities (%) are indicated for the significant peaks. Emission spectra were recorded in cyclohexane, at 25 °C, with a Perkin-Elmer LS50 instrument. The samples (absorbance between 0.1 and 0.3) were thoroughly purged with nitrogen prior to fluorescence measurements. Phenol was used as a standard for determining the fluorescence quantum yields. High-resolution mass spectra were conducted on a VG Autospec instrument.

Irradiations

Solutions 10^{-2} M of the corresponding substrate in benzene were placed into quartz tubes surrounding a centrally positioned quartz cooling jacket containing a 125 W medium-pressure Hg lamp and irradiated under argon for 1 h. In the case of **1b** and **1d**, parallel irradiations were carried out adding dioxane to the benzene solutions of the substrates (final dioxane concentration: 2 M). The reaction mixtures were analyzed by GC–MS and ^{1}H NMR. Isolation and purification were done by conventional column chromatography on silica gel Merck 60 (0.063–0.200 mm) using dichloromethane as eluent, or by means of isocratic HPLC equipment provided with a semipreparative Microporasil column, using hexane–ethyl acetate as eluent.

Synthesis of the substrates 1a–d

Compound **1a** was purchased from Merck. The substrate **1b** was prepared as previously described in the literature.[6] In the case of **1c**,**d**, their synthesis was carried out as reported by Yates *et al.* for **1c**:[23] Dihydrocoumarin (14.6 g, 0.10 mol) in dry toluene (250 ml) was cooled to −78 °C and treated over a period of 2 h with diisobutylaluminum hydride (25% in toluene, 74.6 ml, 0.11 mol). The reaction mixture was stirred for a further 2 h at −78 °C. After dropwise addition of water (50 ml), the mixture was warmed to room temperature, treated with Celite and suction filtered. The filtrate was extracted with diethyl ether and dried over MgSO$_4$. Evaporation of the solvent gave 12.5 g of chroman-2-ol. Under a nitrogen atmosphere, 1.05 g (0.05 mol) of NaH was added to DMSO (20 ml). The mixture was heated at 80 °C until gas evolution ceased. To this solution, methyltriphenylphosphonium bromide or benzyltriphenylphosphonium bromide (0.04 mol) in DMSO (75 ml) were added at room temperature. After 15 min a solution of chroman-2-ol (3.23 g, 0.02 mol) in DMSO (5 ml) was added. After a further 30 min, the reaction mixture was quenched with water and the solution was neutralized with aqueous HCl, extracted with diethyl ether and dried over MgSO$_4$. The solution was evaporated and the residual oil was purified by column chromatography.

Spectral data of the new compounds

***trans*-2-(4-Phenylbut-3-enyl)phenol (1d).** Yield 15%. Viscous oil. λ_{max}/nm 252 (log ε 4.2), 216 (4.0); ν_{max}/cm^{-1} 3649 (OH), 3032, 2938, 2863, 1589, 1492, 1454, 1217, 746; δ_H 2.55 (dt, J_1 7, J_2 6, 2H, C*H*$_2$CH=CH), 2.80 (t, *J* 7, 2H, C*H*$_2$CH$_2$CH=CH), 4.77 (s, 1H, OH), 6.28 (dt, J_1 16, J_2 6, 1H, CH$_2$C*H*=CH), 6.43 (d, *J* 16, 1H, CH$_2$CH=C*H*), 6.75 (dd, J_1 8, J_2 1, 6-ArH), 6.87 (dt, J_1 8, J_2 1, 4-ArH), 7.05–7.37 (m, 7H, ArH); *m*/*z* 224 (M$^+$, 19), 118 (11), 117 (100), 115 (39), 107 (72), 91 (16), 77 (20); Calcd. for $C_{16}H_{16}O$: 224.1201. Found: 224.1208.

2-Phenyl-2,3,4,5-tetrahydro-1-benzoxepin (3d). ν_{max}/cm^{-1} 3073, 2939, 1580, 1488, 1234, 1040, 955, 754; δ_H 1.60-2.21 (m, 4H, CHC*H*$_2$C*H*$_2$), 2.73–3.10 (m, 2H, ArC*H*$_2$), 4.60 (m, 1H, C*H*), 7.00-7.48 (m, 9H, ArH); *m*/*z* 224 (M$^+$, 30), 117 (100), 115 (27), 107 (73), 91 (26), 77 (16); Calcd. for $C_{16}H_{16}O$: 224.1201. Found: 224.1202.

***cis*-2-(4-Phenylbut-3-enyl)phenol (4d).** ν_{max}/cm^{-1} 3648 (OH), 3069, 3023, 2935, 2867, 1591, 1493, 1455, 1203, 745; δ_H 2.65 (dt, J_1 7, J_2 7, 2H, C*H*$_2$CH=CH), 2.76 (t, *J* 7, 2H, C*H*$_2$CH$_2$CH=CH), 4.90 (s, 1H, OH), 5.74 (dt, J_1 11, J_2 7, 1H, CH$_2$C*H*=CH), 6.45 (d, *J* 11, 1H, CH$_2$CH=C*H*), 6.73 (dd, J_1 8, J_2 1, 7-ArH), 6.85 (dt, J_1 8, J_2 1, 4-ArH), 7.02–7.45 (m, 7H, ArH); *m*/*z* 224, (M$^+$, 30), 117 (100), 115 (45), 107 (90), 91 (22), 77 (26); Calcd. for $C_{16}H_{16}O$: 224.1201. Found: 224.1195.

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