Photohydration Reaction of 1-(1-Naphthyl)buta-1,3-diynes

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Irradiation of 1-(1-naphthyl)buta-1,3-diynes (**1**)–(**3**) in aqueous sulphuric acid yields both type-A (**4**), (**6**), (**8**) and type-B (**5**), (**7**), (**9**) hydration products. The type A/B product ratio was 0.8–1 : 1 in neutral conditions, while the ratio increases as the acidity of the medium increases. The fluorescence of compounds (**1**) and (**3**) decreased but that of compound (**2**) was invariant with increasing acidity. The medium-acidity effect on the quantum yields of hydration, and azulene-quenching studies suggest that the singlet excited state yields both type-A and type-B photoadducts, while the triplet excited state yields only type-B photoadducts when R is an alkyl group.

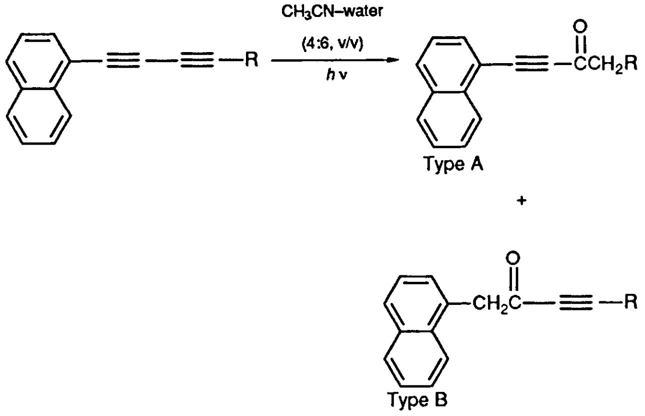
It is well known that 1-arylacetylenes are generally not hydrated in neutral solution and very slowly hydrated in 25% (w/w) aq. sulphuric acid at room temperature.[1] The compounds can, however, easily be hydrated photochemically under mild conditions due to their marked increase in basicity on excitation.[1–3] The reaction seems to proceed *via* a vinyl cation produced by an initial rate-determining protonation step. Photolysis of aryl olefins without a nitro-substituent in aq. solution yields anti-Markovnikov hydration (type-A) products only *via* a zwitterionic singlet excited state, while nitro-substituted analogues give Markovnikov hydration (type-B) products *via* a triplet excited state.[1] Similar products were obtained from arylacetylenes.

The plot of photohydration quantum yield in phenylacetylenes (except for nitro-substituted analogues) shows a strong sigmoidal curve dependence on pH (or acidity function H_0), with an inflection point near pH 0, suggesting strongly that the protonation of the excited substrate is the rate-determining step. The fluorescence quenching also showed a sigmoidal dependence on acidity. The results have been attributed to external acid catalysis by H_3O^+. The estimated $pK_a(BH^+)^*$-values for singlet excited states (S_1) of phenylacetylenes are typically in the range of 0 to -2.[1]

There are just a few reports on the photochemical properties of conjugated diynes and polyynes even though conjugated polyyne photochemistry is attracting a lot of interest because a number of conjugated polyynes are known to be phototoxic to a variety of micro-organisms.[4–9] Studies on these compounds have been centred around the biochemical aspects only, and the photochemical behaviour of conjugated di- and poly-ynes is not understood at all even though such knowledge is essential in order to understand the molecular mechanism of the phototoxicity. We therefore investigated the photohydration mechanism of 1-(1-naphthyl)buta-1,3-diynes, a conjugated diacetylene system.

Results and Discussion

Photoreaction.—Irradiation of compounds (**1**)–(**3**)† in aq. acetonitrile (0–5% sulphuric acid) at 350 nm gave the type-A (**4**), (**6**), (**8**) and type-B (**5**), (**7**), (**9**) hydration products in moderate yields, and polymers as by-products.‡ Since photoreduction and other side-reactions have been reported along with photoprotonation of alkynes in hydroxylic solvents (alcohols and carboxylic acids), aq. sulphuric acid medium was used to avoid these side-reactions. This also allowed us to control the medium's acidity (at least for low acidities).



	Type-A products	Type-B products
R = Ph (1)	(4)	(5)
Me (2)	(6)	(7)
Bu^t (3)	(8)	(9)

The structure of these photoproducts was determined by elemental, ^{1}H NMR, UV, IR, and mass spectral analyses. In the ^{1}H NMR spectrum of type-B products (**5**), (**7**), and (**9**) the resonance peaks of the methylene protons appeared at δ 4.2–4.3, and those of the type-A products (**4**), (**6**), and (**8**) were upfield shifted to δ 4.02, 2.82, and 2.79, respectively. The peaks of the methylene and methyl protons, for compound (**6**) in particular, appear as a quartet at δ 2.82 and a triplet at δ 1.30, indicating the presence of an ethyl group. UV absorption maximum near 325 nm, strong $\nu_{C=O}$ and $\nu_{C\equiv C}$ bands in the IR spectra, and strong *m/z* 179 peaks (base peak) support the existence of the 1-naph-C≡C–C=O moiety in the type-A hydration products. A UV absorption maximum near 285 nm, strong $\nu_{C=O}$ and $\nu_{C\equiv C}$ bands in the IR spectra, and *m/z* 141 and (M^+ − 141) peaks which are the first and second most abundant peaks also support the existence of 1-naph-CH_2- and O=C–C≡C–R moieties in the

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† We chose diynes containing the naphthyl group because those containing a phenyl group do not fluoresce, and so emission spectrophotometry cannot be used to study the singlet excited state.

‡ Total yield in one particular condition is not important because the yield varies according to the reaction conditions (pH, irradiation time, concentration, *etc.*).

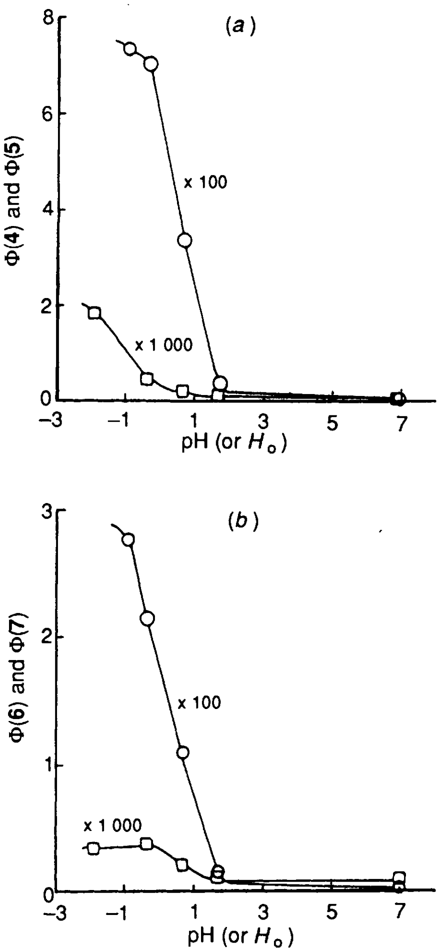

Figure 1. Photohydration quantum yield (Φ_{pdt}) as a function of acidity of medium for substrates (**1**) and (**2**). (*a*) Φ_{pdt} of (**4**)(○) and (**5**)(□). (*b*) Φ_{pdt} of (**6**)(○) and (**7**)(□).

type-B hydration products. The type-A photoadducts can undergo Norrish type-I reaction (α-cleavage) on further irradiation due to their strong absorption of light in the wavelength range used, but the type-B photoadducts do not absorb light of the wavelength used and no secondary photoproduct was observed for these products.*

Photohydration Quantum Yields and Fluorescence Quenching.—The photohydration quantum yields were measured as a function of medium acidity for compounds (**1**) and (**2**) at substrate concentrations of 10^{-4}–10^{-3} mol dm^{-3}. They are very sensitive to substrate concentrations because of photopolymerization to give by-products at high concentration. The quantum yields exhibit sigmoidal curves when the medium acidity (pH or H_0) is varied, the type-A products being more sensitive to medium acidity than the type-B products, as shown in Figure 1, suggesting that protonation of excited substrate is the rate-determining step as observed previously in phenylacetylenes.[1]

The first singlet excited state of arylacetylenes (phenyl- or naphthyl-acetylenes) has zwitterionic character (positively charged C-1 and negatively charged C-2).[10] In 1-arylbuta-1,3-diynes, however, charge separation seems to be dichotomic (C-1 or C-4 is positively charged in the singlet excited state), the structure with a positively charged C-1 being dominant.

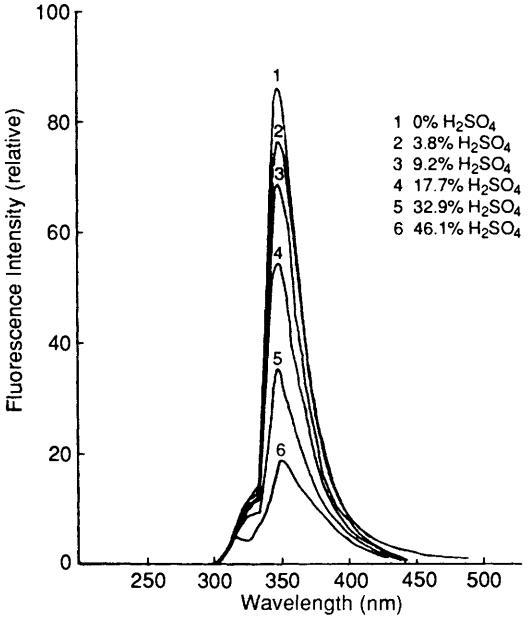

Figure 2. Quenching of fluorescence in aq. H_2SO_4 for 5,5-dimethyl-1-naphthylhexa-1,3-diyne (**3**) (exciting wavelength 310 nm).

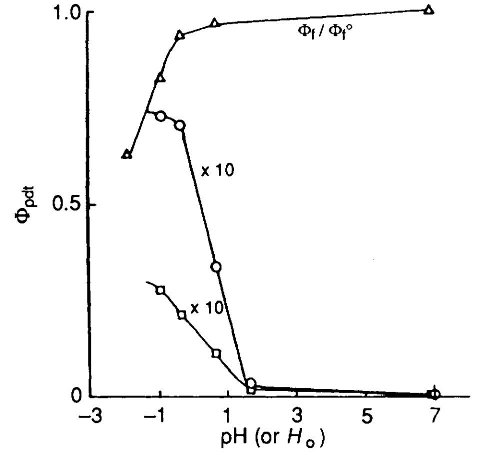

Figure 3. Complementary product quantum yield (Φ_{pdt}) and fluorescence quenching (Φ_f/Φ_f^0) curves for photoadducts (**4**)(○) and (**5**)(□).

Azulene-quenching experiments showed that the singlet excited state yielded type-B photoadducts, supporting the dual charge separation of the singlet excited state. The type-B photoadduct cannot be formed through the singlet excited state having the formal positive charge at C-1.

Fluorescence of compounds (**1**) and (**3**) is quenched by sulphuric acid [see Figure 2 for 5,5-dimethyl-1-(1-naphthyl)-hexa-1,3-diyne (**3**)], while no significant fluorescence quenching was observed for compound (**2**). The results may be related to the relatively low photohydration quantum yield of compound (**2**) compared with those of compounds (**1**) and (**3**). The effect of the medium's acidity on the relative fluorescence quantum yield (Φ_f/Φ_f^0) [where Φ_f^0 is the fluorescence quantum yield in acetonitrile–water (4:6, v/v) at pH 7] is shown in Figure 3 for compound (**1**). It shows that the quenching of singlet excited state (S_1) enhances photohydration efficiency. The Stern–Volmer constants ($k_q \cdot \tau$) were calculated and k_q is assumed to be equal to the protonation rate constant k_{H^+} for the singlet excited state[1] because proton acts as a fluorescence quencher (Figure 4).

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* Light absorption by azulene at 313 nm was corrected for.

Photohydration Mechanism.—An efficient triplet quencher, azulene, quenches the photohydration compound (**2**). Stern–Volmer plots, Φ^0_{pdt}/Φ_{pdt} *vs.* [Az], show that the triplet excited states give the type-B photohydration products only, as shown in Figure 5.

Figure 5(*a*) shows almost constant quantum yields for product (**6**) (Φ_{pdt} 4.2×10^{-3}) with increasing azulene concentration, suggesting that the photoadduct (**6**) is formed only from the singlet excited state. However, the plot for compound (**7**) [in Figure 5(*b*)] is curved, reaching a plateau at about Φ^0_{pdt}/Φ_{pdt} *ca.* 1.46, indicating the contribution of both singlet and triplet excited states.[11] The values of the singlet, Φ^0_S, and triplet excited state, Φ^0_T, contribution to total quantum yields for compound (**7**) were Φ^0_S 3.5×10^{-3} and Φ^0_T 1.6×10^{-3}. After subtraction of the singlet excited state contribution, values of $\Phi^{0'}_{pdt}/\Phi'_{pdt}$ *vs.* [Az] were plotted to obtain a linear Stern–Volmer plot [as shown in Figure 5(*c*)], yielding a pure triplet state Stern–Volmer constant ($k_q \cdot \tau_T$) of 56 600 dm^3 mol^{-1}, and the triplet lifetime was calculated to be 56.6 μs (a k_q-value of 10^9 dm^3 mol^{-1} s^{-1} was employed)[12] in 30%-MeCN–water. The long triplet lifetime indicates the triplet state to be relatively unreactive to water and suggests that the triplet excited state has a weak polar character compared with the singlet excited state.

The S_1 state of compound (**2**) is probably highly charge separated, while the T_1 state is weakly charged even though T_1 state of acetylenes is normally considered to be similar to that of diradicals and the T_1 state yields the type-B hydration products in low yield due to its very low reactivity to water.

The charge in the singlet excited state seems to be delocalized throughout the conjugated system. This is supported by the structure of type-A and type-B photoadducts which were formed by protonation of C-1 or C-4 followed by attack of water on C-2 or C-3.

A possible charge distribution of excited states is shown in Scheme 1. The direct protonation of the S_1 state increases with increasing acidity of the medium whilst intersystem crossing decreases, leading to marked increase of the type-A photoadduct and slight increase of the type-B photoadduct. The rapid increase of the type-A photoadduct quantum yield with increasing acidity of the medium supports the proposed mechanism. A plausible photohydration mechanism involving both singlet and triplet excited states of 1-(1-naphthyl)buta-1,3-diynes is shown in Scheme 2.

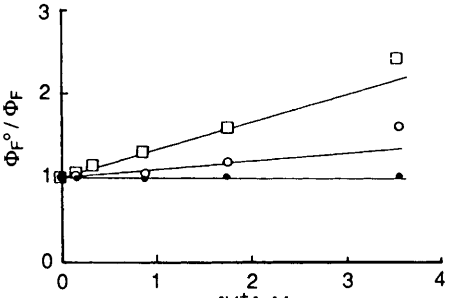
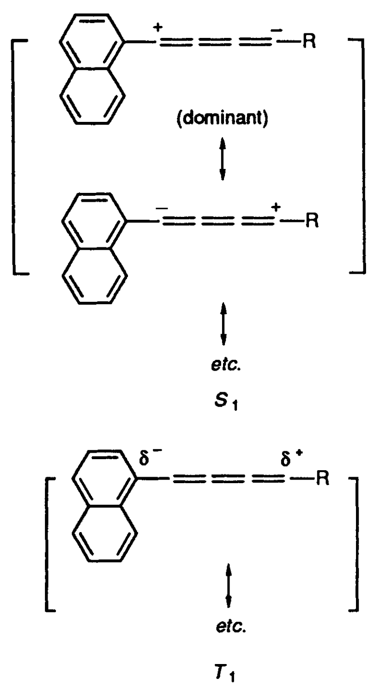


Figure 4. Plots of Φ^0_F/Φ_F *vs.* [H$^+$] for (**1**)(○), (**2**)(●), and (**3**)(□). ($k^1_{H^+} \cdot \tau_0 = 0.13, k^2_{H^+} \cdot \tau_0 = 0, k^3_{H^+} \cdot \tau_0 = 0.33$).



Scheme 1.

When aqueous solutions of compounds (**1**)–(**3**) are irradiated, highly polarized singlet excited states are formed. Radiationless decay processes seem to be the major deactivation pathway from this singlet excited state because fluorescence quantum yields are very small (*ca.* 10^{-3}) and decrease as the solvent polarity increases. In highly polar solvents such as water, the singlet excited state seems to have a zwitterionic character with charge delocalized all over the conjugated system. When no acid is added, the protonation of the S_1 state is relatively slow. With a medium acidity increase, protonation of the S_1 state becomes fast, leading to the increase of both type-A and type-B photohydration quantum yields. However, only the type-A hydration quantum yields *markedly* increased because the type-B hydration product originating from the triplet excited state decreases due to the decrease in intersystem crossing.

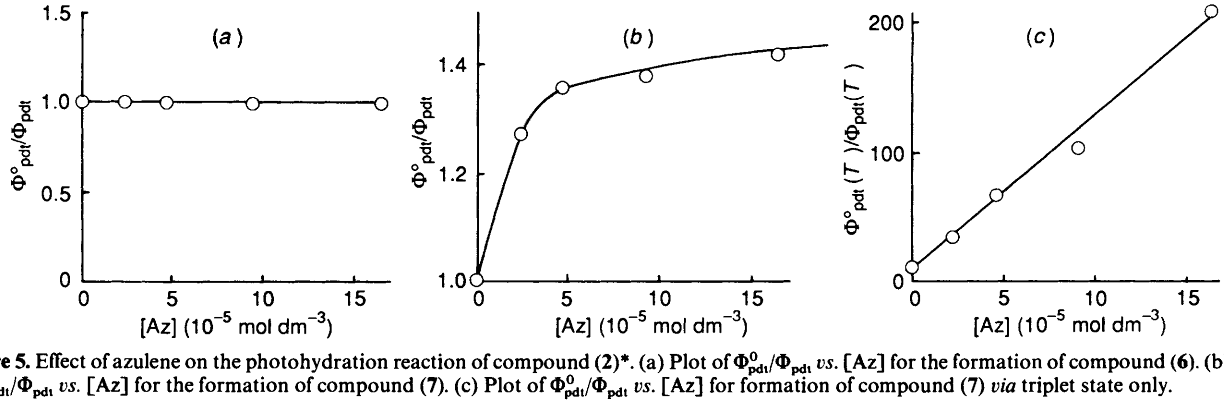
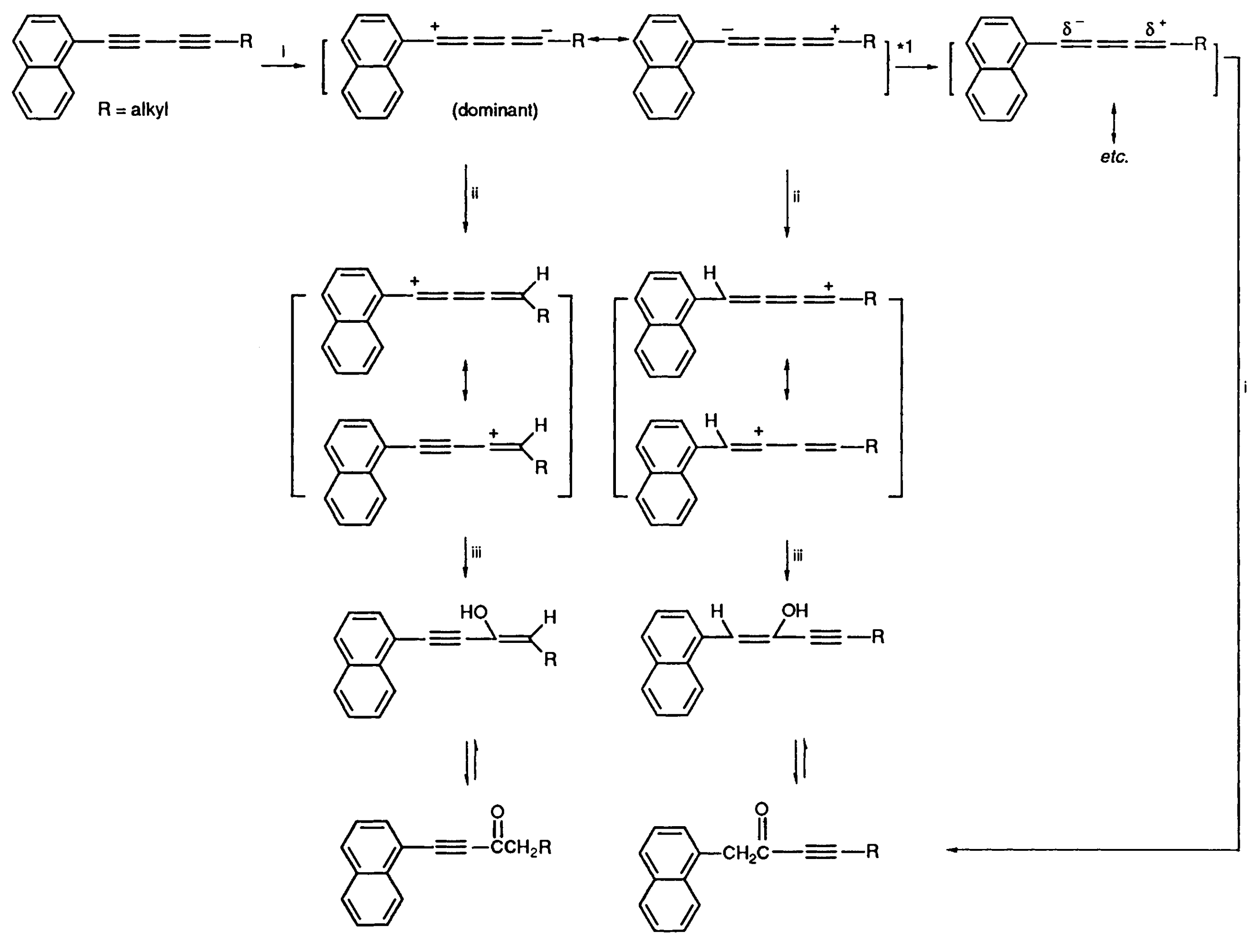


Figure 5. Effect of azulene on the photohydration reaction of compound (**2**)*. (a) Plot of Φ^0_{pdt}/Φ_{pdt} *vs.* [Az] for the formation of compound (**6**). (b) Plot of Φ^0_{pdt}/Φ_{pdt} *vs.* [Az] for the formation of compound (**7**). (c) Plot of Φ^0_{pdt}/Φ_{pdt} *vs.* [Az] for formation of compound (**7**) *via* triplet state only.



Scheme 2. *Reagents and conditions:* i, MeCN–water, *h* ν; ii, H^+; iii, water.

The photohydration reaction appears to be a general reaction for non-halogeno-substituted aromatic alkenes and alkynes, and two photohydration mechanisms (involving singlet excited state only or triplet excited state only) in which the substituent on the aromatic ring leads to only one mechanism being operative are proposed.

On the other hand, in 1-(1-naphthyl)buta-1,3-diynes, a mixed mechanism involving both singlet and triplet excited state is operative. The substituents on C-4 of the diynes affect the photohydration quantum yield only, and not the product structure (reaction mechanism); in addition it is clear that the electron distribution of excited states of conjugated aryl polyacetylenes is significantly influenced by the number of conjugated triple bonds.

Experimental

Instruments.—^1H NMR spectra were run in $CDCl_3$ on Varian FT-80A and Bruker AM-200-SY spectrometers. IR spectra were obtained on a Perkin-Elmer 283B spectrophotometer for KBr pellets or a NaCl cell. UV–Visible spectra were recorded on a Cary-17 spectrophotometer. Mass spectra were determined at 70 eV with a Hewlett Packard 5985A GC/MS system by electron impact. Elemental analyses were carried out on an F & M Scientific Corporation C,H,N analyser Model 180. High-performance liquid chromatography (HPLC) was performed on a Waters Associates Model 244 liquid chromatograph equipped with a Model 6000A solvent delivery system, Model 440 UV absorbance detector fixed at 254 nm and 280 nm, and Model U6K universal injector.

Materials.—Compounds (**1**)–(**3**) were prepared by the literature method.[13] Azulene was purchased from Aldrich Chemical Co. and was used after vacuum sublimation. Extra-pure solvents were used after purification by distillation or by standard methods.[14] Chromatographic and spectroscopic grade solvents (Merck) were used for HPLC, absorption, and emission spectroscopy. Column chromatography was performed by using Kieselgel 60 (Merck, 70–230 mesh and 230–400 mesh).

Photohydration Reaction of Compounds (**1**)–(**3**).—Deaerated 10^{-3} mol dm^{-3} solutions (water–MeCN [6:4, v/v; H_2SO_5 5% (v/v)] of compound (**1**), (**2**), and (**3**) were separately irradiated with 350 nm UV light in a Rayonet Photochemical Reactor Model RPR 208 equipped with RUL-3500Å lamps. After irradiation for 12 h,* the reaction mixture was extracted with hexane–diethyl ether (5:1, v/v). The organic phase was dried over $MgSO_4$ and was evaporated under reduced pressure. The reaction mixture was separated by column chromatography with hexane–diethyl ether (20:1, v/v as eluent. Pure samples of photohydration products were isolated by preparative HPLC using a preparative μ-Bondapak C_{18} column and methanol–water (5:1 or 10:1, v/v) as solvent. Compound (**4**) showed $\delta(CDCl_3)$ 8.00–7.25 (12 H, m) and 4.05 (2 H, s); ν_{max}(NaCl) 3 080, 2 980, 2 205, 1 680, 1 610, 1 600, 1 520, 1 510, 1 465, 1 455, 1 410, 1 340, 1 300, 1 120, 1 040, 810, 780, 760, 750, 710, and 690 cm^{-1}; λ_{max}(MeOH) 330, 295, and 232 nm; *m/z* 270 (M^+, 5.6%), 179 ($C_{13}H_7O^+$, 100), and 91 ($C_7H_7^+$, 40.7) (Found: C, 88.9; H, 5.2. Calc. for $C_{20}H_{14}O$: C, 88.86; H, 5.22%); Compound (**5**) showed δ($CDCl_3$) 8.10–7.25 (12 H, m) and 44.0 (2 H, s); ν_{max}(NaCl) 3 080, 2 980, 2 950, 2 880, 2 220, 1 680, 1 610, 1 585, 1 520, 1 500, 1 455, 1 405, 1 365, 1 290, 1 250, 805, 795, 780, 760, and 690 cm^{-1}; λ_{max}(MeOH) 280 and 220 nm; *m/z* 270 (M^+, 4.6%), 141 ($C_{11}H_9^+$, 26.8), and 129 ($C_9H_5O^+$, 100) (Found: C, 88.9; H, 5.2%); Compound (**6**) showed δ($CDCl_3$) 8.50–7.20 (7 H, m), 2.82 (2 H, q), and 1.30 (3 H, t); ν_{max}(NaCl) 3 080, 3 000, 2 960, 2 200, 1 680, 1 520, 1 470, 1 408, 1 386, 1 350, 805, and 777 cm^{-1}; λ_{max}(MeOH) 328, 318, and 220 nm; *m/z* 208 (M^+, 21.9%) and 179 ($C_{13}H_7O^+$, 100) (Found: C, 86.5; H, 5.85. Calc. for $C_{15}H_{12}O$: C, 86.43; H, 5.81%); Compound (**7**) showed δ($CDCl_3$) 8.20–7.35 (7 H, m), 4.29 (2 H, s), and 1.95 (3 H, s); ν_{max}(NaCl) 3 080, 2 980, 2 940, 2 220, 1 680, 1 610, 1 520, 1 405, 1 360, 1 330, 1 255, 1 170, 785, and 740 cm^{-1}; λ_{max}(MeOH) 282 and 221 nm; *m/z* 208 (M^+, 12.0%), 141 ($C_{11}H_9O^+$, 100), and 67 ($C_4H_3^+$, 87.8) (Found: C, 86.5; H, 5.8%); Compound (**8**) showed δ($CDCl_3$) 8.50–7.42 (7 H, m), 2.79 (2 H, s), 1.25 (9 H, s); ν_{max}(NaCl) 3 080, 2 980, 2 900, 2 200, 1 670, 1 600, 1 560, 1 520, 1 480, 1 410, 1 377, 1 320, 1 210, 1 115, 1 070, 1 030, 800, 775, and 710 cm^{-1}; λ_{max}(MeOH) 330, 320, and 218 nm; *m/z* 250 (M^+, 14.0%) and 179 ($C_{13}H_7O^+$, 100) (Found: C, 86.4; H, 7.3. Calc. for $C_{18}H_{18}O$: C, 86.36; H, 7.25%); Compound (**9**) showed δ($CDCl_3$) 8.10–7.40 (7 H, m), 4.29 (2 H, s), and 1.09 (9 H, s); ν_{max}(NaCl) 3 080, 2 980, 2 900, 2 200, 1 680, 1 620, 1 520, 1 490, 1 470, 1 410, 1 377, 1 280, 1 200, 1 125, 1 070, 1 030, 792, 780, 740, and 710 nm; λ_{max}(MeOH) 282 and 220 nm; *m/z* 250 (M^+, 16.2%), 141 ($C_{11}H_9^+$, 96.5), and 109 ($C_7H_9O^+$, 100) (Found: C, 86.4; H, 7.3%).

Fluorescence Quenching of Compounds (**1**)–(**3**).—Fluorescence intensity of 10^{-4} mol dm^{-3} acetonitrile–water (4:6, v/v) solutions of the conjugated diynes was monitored whilst the acidity of the medium was varied. The Stern–Volmer constants ($k_q \cdot \tau$) were obtained from the slope of Stern–Volmer plots [equation (1)].

$$\Phi_F^0/\Phi_F = 1 + k_q \cdot \tau[H^+] \qquad (1)$$

Quantum Yield Measurements for Compound (**1**).—Samples (3 cm^3) of acetonitrile–water (4:6, v/v) solutions of compound (**1**) in the presence of various concentrations of sulphuric acid (0–32%) were degassed by three freeze-pump-thaw cycles with cooling in liquid nitrogen and were then sealed. These samples were irradiated with 366 nm monochromatic light in a merry-go-round apparatus with a Hanovia 450 W medium-pressure mercury lamp (Type 679A36). The mercury emission line of 366 nm was isolated by Corning glass filters #0-52 and #7-37. Ferrioxalate actinometry was used to monitor the intensity of the light absorbed. Quantitative analyses were carried out by HPLC after saturation with NaCl, using compound (**2**) as internal standard, Radialpak C_{18} column, and methanol–water (5:1, v/v) solvent.

Quantum Yield Measurement for Compound (**2**).—Exactly the same procedure used for compound (**1**) was followed for compound (**2**), but with irradiation of the sample with 313 nm light which was isolated by Corning glass filter #7-54 and aq. 0.0025 mol dm^{-3} $K_2Cr_2O_7$ in 1% Na_2CO_3 (0.7 cm path length). Quantitative analysis was carried out by HPLC after saturation with NaCl, using compound (**1**) as internal standard, and Radialpak C_{18} column and methanol–water (5:1 v/v) solvent.

Effect of Azulene on the Photohydration Reaction of Compound (**2**).—A sample solution [MeCN–water (4:6, v/v); 3 ml] in Pyrex ampoules containing various concentrations of azulene (0–1.6 × 10^{-4} mol dm^{-3}) were degassed with three freeze-pump-thaw cycles with cooling in liquid nitrogen and were then sealed. These samples were irradiated in a merry-go-round apparatus with 313 nm monochromatic UV light. Quantitative analysis was carried out by HPLC using μ-Bondapak C_{18} column and methanol–water–tetrahydrofuran (10:5:1, v/v) solvent; a connection was applied for the absorption of azulene.

Acknowledgements

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