1,1-Dicyano-2,2-diphenyl-1,2-dihydronaphthalene: Photochromism and Evidence for Photochemically Induced C–CN Bond Cleavage

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Abstract: The photoreactions of the 1,1-dicyano-2,2-diphenyl-1,2-dihydronaphthalene (**DHN-1**) have been studied by photochemical techniques under various conditions at room temperature. A transient species, $\mathbf{T_C}$, with a major maximum at 545 nm in the UV-visible spectrum, detected in small yield in polar aprotic solvents and in large yield in trifluoroethanol (TFE) and hexafluoropropan-2-ol (HFP), is assigned as a carbocation (1-cyano-2,2-diphenylnaphthalenium), which is generated photochemically by elimination of CN^-. The decay of $\mathbf{T_C}$ was found to be a first-order process in HFP, in which the longest lifetime of 0.4 s was observed; in TFE, the carbocation decays on the ms timescale, while the shortest lifetime of 1 μs was found in ethanol. The yield of $\mathbf{T_C}$ increases strongly upon addition of water to alcohols or acetonitrile, and remains substantial in the presence of large amounts of water (1–20 M). On addition of water to TFE or HFP, the lifetime of the carbocation becomes much shorter. This is supported by pulse-induced charge formation due to the carbocation and release of CN^-; the conductivity decay is related to the lifetime of the carbocation under selected conditions. In addition, a major irreversible and a minor thermally reversible photoprocess were spectroscopically observed in solvents of low as well as high polarity. The former photoproduct, absorbing below 300 nm, is tentatively ascribed to benzobicyclohexenes **A** produced by phenyl-vinylmethane rearrangement. In the latter process, a longer-lived benzoquinodimethane derivative **B**, having a maximum at 400–430 nm, is formed; this is related to ring opening and closure and represents a new example of photochromic ten-electron electrocyclisation. The distinct differences between the photochromism of DHN and that of dihydroazulene (DHA) stem mainly from stereoelectronic effects. This study, however, has also revealed that photochemically induced bond heterolysis and photochemical/thermal electrocyclisation, representing two basic processes of photochromism, may occur in one molecular unit.

Keywords: charge separation · electrocyclization · naphthalene derivatives · photochromism · stereoelectronic effects

Introduction

Photochromic systems are subjects of intense investigations.[1–5] Ten-electron photochromism has in recent years been shown to be a viable concept for molecular switching.[5] In particular, the 1,8a-dihydroazulene-1,1-azulenedicarbonitriles (DHAs) have proved to be most versatile compounds.[6] Typically, these DHAs are photoconverted into deeply coloured, photochemically unreactive 10,10-dicyanovinylheptafulvenes (VHFs), which reconvert thermally. The properties of the DHA/VHF couple have been analyzed in great detail.[5–11] In particular, we have reported on the photochemical behaviour of 1,8-dihydro-2-aryl-1,1-azulenedicarbonitriles.[8] Their DHA forms are efficiently photoconverted into the VHF forms on a subnanosecond timescale. Using femtosecond-resolved transient absorption spectroscopy, the lifetime of the excited state of cyclopentane-condensed dihydroazulene **DHA-1**, corresponding to the ring-opening reaction, was measured as about 600 fs.[10] Theory predicts a conical intersection in the excited-state regime.[11] Recent measurements with even shorter pulses revealed an ultrafast two-way photochemical interconversion between DHA-2 and s-*cis*-VHF-2 (Scheme 1).[12]

Another dicarbonitrile-containing biphotochromic system is based on the photoconversion of a dithienylene, 1,8a-dihydro-2,3-bis-3-(2,5-dimethylthienyl)azulene-1,1-dicarbonitrile, into both the VHF and thienobenzothiophene forms, the thermal and photochemical properties of which have recently been studied.[9] For comparison, a diphenylethene, 1,8a-dihydro-2,3-diphenylazulene-1,1-dicarbonitrile, was also ex-

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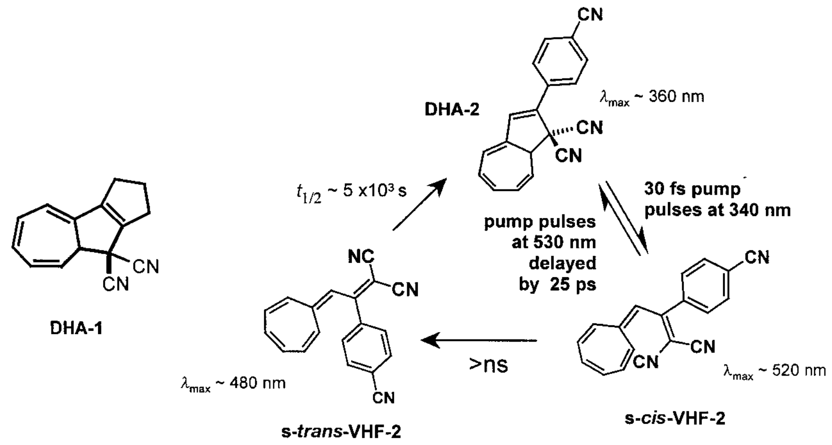
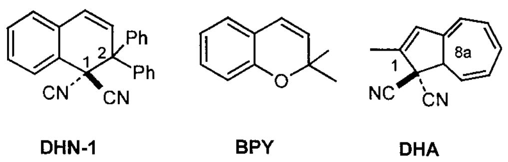
amined; this compound can be photoconverted to the VHF form, but not to dihydrophenanthrene.[9b]

It seemed interesting to study 1,1-dicyano-2,2-diphenyl-1,2-dihydronaphthalene (**DHN-1**), representing a potential photochrome of the 1,2-dihydronaphthalene (DHN) type in which 1,2-elimination of HCN is precluded by the presence of two phenyl groups at C-2. From a structural point of view, DHN represents the dicyanomethine analogue of chromene-type photochromes.[13] Photochromism of a 2*H*-1-benzopyran (BPY) derivative was reported in 1966.[14] A recent review surveys benzo- and naphthopyrans and their potential applications.[15] DHN is related to BPYs, in which two merocyanine isomers (*tt*: *trans-trans* and *tc*: *trans-cis*) are involved,[16–18] and to flindersine,[19] a photochrome found in nature belonging to this category of compounds.

It seemed of interest to extend the study to potential photochromes, the structures of which would allow a 1,1-dicyanomethine-assisted ten-electron reorganisation as in DHA/VHF, while being embedded in a divergent molecular and electronic structure. The azulene/naphthalene dichotomy, as represented by compounds DHA and DHN (Scheme 2), would comply with these requirements. With regard to the electronic configuration, ring-opening of the dihydronaphthalene DHN yields an "alternating" *ortho*-quinoid species, whereas ring-opening of the DHA results in a "non-alternating" VHF. The stereoelectronic situations in the two compounds are also different. Dissociation of the C8a–C1 bond in DHA leads to substantial overlap with the cycloheptatriene π orbitals, whereas in the case of DHN the π orbitals are orthogonal to the σ orbitals of the elongating C1–C2 bond. However, elongation of the C1–CN bond would be expected to generate an overlapping orbital situation in the latter case.[20]



Scheme 1. Photochemical and thermal interconversions of the DHA/VHF system.



Scheme 2. Structurally related photochromes.

In this work, photochemical results concerning **DHN-1** are presented for the first time. One photoreaction is photoisomerisation. In the course of this study, we unexpectedly also observed the formation of a carbocation. It appears in wet polar solvents at room temperature, especially in the presence of 2,2,2-trifluoroethanol (TFE) or 1,1,1,3,3,3-hexafluoropropan-2-ol (HFP). These fluoroalcohols are solvents that are known to stabilise ions.[21–25] They are also able to stabilise the zwitterionic merocyanine form of spiropyrans and spirooxazines.[26] On addition of water to **DHN-1** in TFE or HFP, the yield of the observed carbocation remains substantial, but its decay is strongly accelerated.

Results and Discussion

Time-resolved absorption properties: The steady-state absorption spectrum of **DHN-1** in any of the solvents used has its main band at around 200 nm and a shoulder at 250 nm. Generally, the transient spectra ($\lambda_{exc} = 248$ nm) show an absorption increase at 300–600 nm; this occurs within the laser pulse width or after the disappearance of a scattering signal. In a polar solvent such as acetonitrile, excitation of **DHN-1** leads to transient absorption spectra attributable to two species (Figure 1b). One (denoted as **B**) gives rise to a quasi-permanent absorption increase with a maximum centered at $\lambda_B = 430$ nm (Figure 1c). The second species is a shorter-lived transient with a maximum at $\lambda_C = 540-550$ nm, denoted as $\mathbf{T_C}$. Transient $\mathbf{T_C}$, which is formed within the pulse width, is not sensitive to oxygen and its spectrum overlaps with that of species **B** in the range from about 350 to 500 nm.

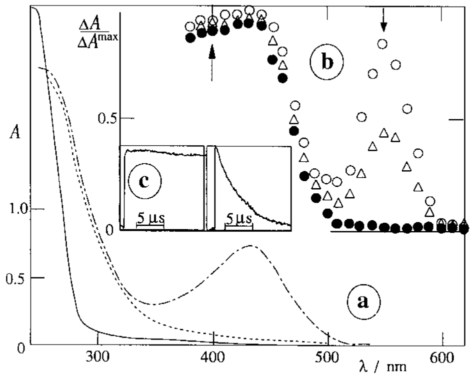


Figure 1. a) Absorption spectrum of **DHN-1** in acetonitrile prior to (——) and after (•–•–) excitation at 248 nm, and after relaxation (…); b) transient absorption spectra at 20 ns (○), 4 µs (△) and 20 µs (●) after the pulse (abscissa as in a); c) kinetics at 400 nm (left) and 545 nm (right).

The decay of $\mathbf{T_C}$ is a first-order process in most solvents (Table 1), with the shortest lifetime ($\tau_C = 1/k_{obs}$) of 1 µs being observed in ethanol. The presence of water in acetonitrile (up to 30 M) does not have a strong influence on τ_C, but the peak at 545 nm is enhanced (Figure 2). In fact, the ΔA_{545} value strongly increases with increasing water concentration (Figure 3a). The spectral changes in methanol or ethanol are similar, whereas those in dichloromethane, *tert*-butanol, or propan-2-ol reveal only (or predominantly) the formation of the quasi-permanent component **B** (Table 1 and Table 2). Again, the ΔA_{545} value in these solvents strongly increases with $[H_2O]$ (Figure 3a). It is interesting to note that in each of the four alcohols and in their mixtures with water (1–20 M), no solvated electrons could be detected just after the pulse, thus ruling out photoionisation as the origin of $\mathbf{T_C}$ (see below).

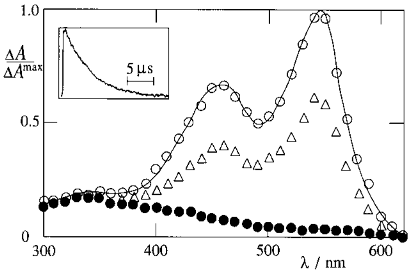


Figure 2. Transient absorption spectra for **DHN-1** in MeCN/H_2O (1:1) at <0.1 (○), 3 (△) and 10 µs (●) after the 248 nm pulse; inset: kinetics at 545 nm.

Table 1. Lifetime and relative yield of the carbocation.[a]

Solvent	E_T[b]	Additive	τ_C [ms]	ΔA_C[c]
MCH	0		–	< 0.02
dichloromethane	0.31		–	< 0.02
tert-butanol	0.39		–	< 0.05
acetonitrile	0.46		≤ 0.006	0.1
		H_2O (15 M)	≤ 0.006	0.6
propan-2-ol	0.55		–	< 0.05
ethanol	0.65		0.001	0.08
		H_2O (5 M)	0.001	0.3
methanol	0.76		0.001	0.05
TFE	0.90		1/10[d]	1
		H_2O (5 M)	2	1
		EtOH (2 M)	0.2	1
		MeCN (2 M)	0.2	1
HFP	1.07		450	1
		H_2O (5 M)	50	0.9
		EtOH (10 M)	0.1	0.9

[a] $\lambda_{exc} = 248$ nm. [b] Polarity parameter (normalised) from ref. [32]. [c] Relative values, measured at $\lambda_C = 545$ nm (note: $\Delta A_B^{max} = 0.1 \times \Delta A_C^{max}$). [d] Two components.

Table 2. Maxima and relative yields of **A** and **B**.[a]

Solvent	λ_B/nm	Φ_A^{rel}[b]	Φ_B^{rel}[c]	ΔA_B[d]
MCH	400	0.5	0.5	0.5
dichloromethane	410	0.5	0.5	0.5
acetonitrile	430	1	1	1
tert-butanol	410			0.6
propan-2-ol	400			0.6
ethanol	410	0.6	0.6	0.5
TFE	< 400	0.8	0.4	< 0.5
HFP	< 400	0.8	< 0.2	

[a] From light-induced changes of the absorption spectrum; $\lambda_{exc} = 248$ nm. [b] Relative values, measured at 290 nm. [c] Relative values, measured at λ_B. [d] From transient measurements at 1 µs.

A much longer half-life of $\mathbf{T_C}$ and a higher ΔA_{545} value was observed for **DHN-1** in HFP (Figure 4a) and in TFE; both are polar, protic solvents in which ions or radical ions are known to be stabilised.[21–25] The time-resolved spectra in TFE (Figure 5a) can be fitted by two first-order decay components with $t_{1/2} = 1$ ms and 10 ms. On addition of water (0.5–5 M) to TFE, the decay of $\mathbf{T_C}$ becomes faster and monoexponential, indicating a single component. An example with $\mathbf{T_C}$ as the major species and $\tau_C = 0.1$ ms is seen in TFE/H_2O (1:1) (Figure 5b). The plot of $\log k_{obs}$ shows an almost linear dependence on $[H_2O]$ (Figure 3b). A first-order decay of $\mathbf{T_C}$ and the longest lifetime of $\tau_C = 0.4$ s were observed for **DHN-1** in HFP (Figure 4a). The yield of $\mathbf{T_C}$ (ΔA_{545} value) does not depend markedly on $[H_2O]$ (Figure 3a). The plot of $\log k_{obs}$ versus $[H_2O]$ is similar to that in the case of TFE, but is shifted by about two orders of magnitude to smaller values (Figure 3b). In the presence of water (Figure 4b) or ethanol

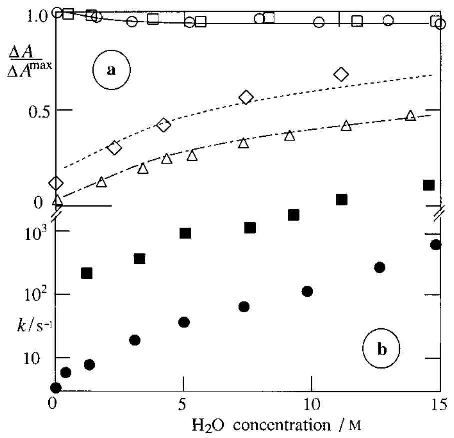


Figure 3. Plots versus $[H_2O]$ of a) the relative ΔA_{545} value (open symbols) and b) $\log k_{obs}$ (filled symbols) for **DHN-1** in HFP (circles), TFE (squares), ethanol (△) and acetonitrile (◇).

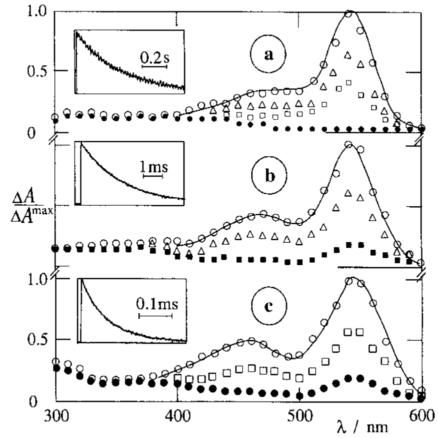


Figure 4. Transient absorption spectra for **DHN-1** in a) neat HFP at <1 µs (○), 0.1 s (△), 0.2 s (□) and 1 s (●) after the 248 nm pulse; b) HFP/H_2O (1:1, v/v) at <1 µs (○), 1 ms (△) and 10 ms (■) and c) HFP/EtOH (1:1) at <1 µs (○), 0.1 ms (□) and 10 ms (●); insets: kinetics at 545 nm.

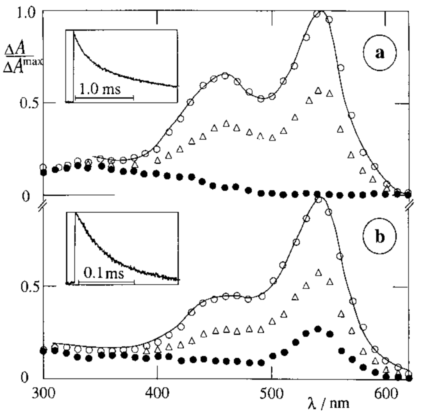


Figure 5. Transient absorption spectra for **DHN-1** in a) neat TFE at <1 µs (○), 1 ms (△) and 0.1 s (●) after the 248 nm pulse and b) TFE/H_2O (1:1) at <1 µs (○), 3 ms (△) and 10 ms (●); insets: kinetics at 545 nm.

(Figure 4c), T_C is the major species. The yields in neat polar media are much lower than those in HFP or TFE (Table 1).

Time-resolved conductivity: The pulse-induced conductivity signals of **DHN-1** in acetonitrile/water (pH 7) (1:1, v/v) and water/TFE mixtures (1:1; 1:9), as well as in HFP in the presence of 5 and 0.5 M water, are shown in Figure 6a–e, respectively. The amplitude increases within 0.1 µs and decays according to first-order kinetics, almost reverting to the value prior to the pulse. The lifetimes in the cases illustrated are $\tau'_C = 6$ µs, 50 µs, 170 µs, 50 ms and 0.25 s, respectively.

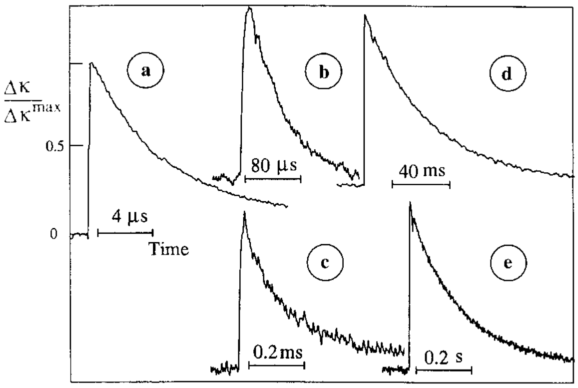
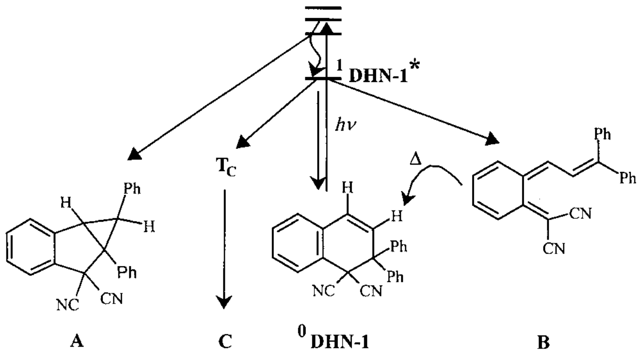


Figure 6. Traces of conductivity signals of **DHN-1** in a) water (pH 7)/acetonitrile (1:1, v/v), b) water/TFE (1:1), c) water/TFE (1:9), and in HFP in the presence of d) 5 M and e) 0.5 M water after the 248 nm pulse.

Photoconversion and thermal relaxation: Only weak fluorescence below 400 nm was observed for **DHN-1** in methylcyclohexane (MCH) or ethanol at 25 and –196 °C, and virtually no phosphorescence could be detected in glassy media. This indicates rapid deactivation processes from the excited singlet state (^{1}**DHN-1***). One reaction is the irreversible formation of product **A** (Scheme 3), which can best be detected at around 290 nm. The relevant spectra are shown for the cases of acetonitrile (Figure 1a) and MCH (Figure 7a) at room temperature.



Scheme 3. Schematics representing ground state and excited state transformations.

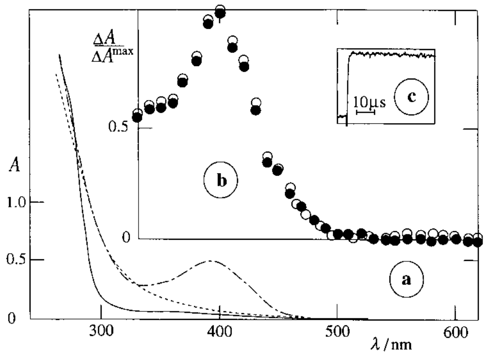


Figure 7. a) Absorption spectrum of **DHN-1** in MCH prior to (——) and after (•–•–) excitation at 248 nm and after relaxation (...); b) transient absorption spectra at <100 ns (○) and 0.1 ms (●) after the pulse; c) kinetics at 400 nm.

The spectral changes that follow 248 nm excitation of **DHN-1** in dichloromethane, *tert*-butanol and propan-2-ol reveal species **A** and the quasi-permanent component **B** (Table 2), but not T_C. This is also the case in the nonpolar MCH, in which the transient absorbs from <270 nm to about 500 nm with a maximum centered at $\lambda_B = 400$ nm (Figure 7a) and exhibits no further changes for a duration of up to a few seconds (Figure 7b,c). In fact, the absorption increase is practically the same as that recorded within 0.1–1 min following removal of the light source. A similar increase in absorption above 265 nm and a pronounced band with $\lambda_B =$ 430 nm was recorded in acetonitrile (Figure 1a). The presence or absence of oxygen has no discernible effect.

The band at λ_B in the steady-state absorption spectrum of **DHN-1** in several solvents after pre-irradiation (for example, at 248 nm) is related to a ring-opened form of **DHN-1**, namely the benzoquinodimethane (**B**) form (see below). The thermal relaxation time (τ_B) was fitted by a first-order decay. Note that a smaller portion remains or disappears over a much longer timescale; in addition, the maximum is slightly red-shifted with time. These phenomena might be due to (*E*)/(*Z*)-stereoisomerism of **B**.[18] The values for the major initial part of τ_B in several solvents at room-temperature range from 10^2 to 10^3 s. On increasing the temperature, τ_B becomes shorter, but analysis failed due to the small magnitude of the effect (at the required low conversion).

The increase at 290 nm (product **A**) with increasing dose of incident radiation is initially linear and then approaches a constant value (Figure 8b), whereas the signal at λ_B reaches a maximum value and decreases upon further pulsing (Figure 8a). When the light is removed, the two parts of the spectrum that are separated by a minimum at about 360 nm behave differently. The changes to the UV absorption are essentially retained, whereas the band at $\lambda_B = 400-430$ nm reverts thermally to a value close to zero (see below). Two quantum yields were therefore measured for low conversion, that is, from the linear parts in Figure 8: one relates to product formation at 290 nm (Φ_A^{rel}) and the other to reversible photocolouration (Φ_B^{rel}). These effects were observed in virtually all organic solvents. In the presence of water, the product formation at 290 nm is similar, but the reversible photocolouration is small, especially when compared with the contrasting findings regarding the ΔA_{545} value under the same conditions. The λ_B values and the Φ_A and Φ_B values are listed in Table 2. The yields are substantial in most organic solvents and are largest in acetonitrile.

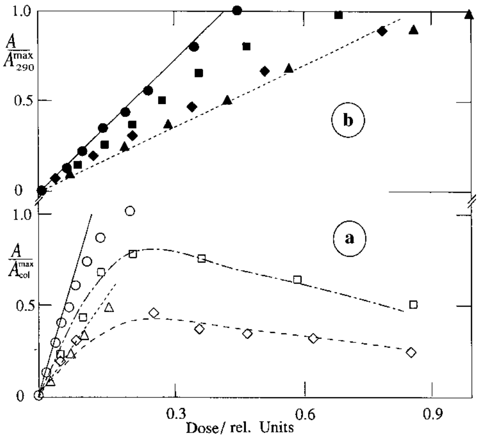


Figure 8. Increase of absorption a) at λ_B (400–430 nm) and b) at 290 nm versus the 248 nm dose for **DHN-1** in MCH (triangles), acetonitrile (circles), TFE (squares), and ethanol (diamonds).

Comparable results, that is reversible colour (**B**) and irreversible product formation (**A**), provided that the irradiation time was markedly shorter than the thermal relaxation time, were found using continuous irradiation ($\lambda_{\mathrm{irr}} = 254$ nm). Species **B** could not be enhanced by prolonged irradiation at 254 nm. The absolute quantum yield of conversion upon pulsed excitation is relatively large and does not show a marked dependence on the solvent or the amount of added water (Table 3). Photodecomposition of **DHN-1** in various solvents was also monitored by HPLC (reversed-phase column) at 215–290 nm. Under conditions for which transient $\mathbf{T_C}$ was the major intermediate (see above), the major product was found to elute after a retention time of 3.8 min, indicating that the subsequent product (**C**) is more polar than **DHN-1**, which has a retention time of 4.2 min. In other media, such as MCH, several minor peaks with longer retention times appeared, indicating less polar products.

Table 3. Absolute quantum yield of photoconversion.[a]

Solvent	$[H_2O]$/M	Φ[b]
acetonitrile	none	0.5 (0.4)[c]
	28	0.4 (0.3)
ethanol	none	0.4
	5	0.3
TFE	5	0.2
HFP	5	0.2

[a] From light-induced changes of the absorption spectrum, $\lambda_{\mathrm{exc}} = 248$ nm. [b] Absolute values, measured by HPLC. [c] Values in parentheses refer to $\lambda_{\mathrm{irr}} = 254$ nm.

^{1}H NMR spectroscopy and FD mass spectrometry: To gain a deeper insight into the photochemistry of **DHN-1**, ^{1}H NMR spectroscopy was used in combination with mass spectrometry (FD-MS). In one experiment (a), a wet soltuion of **DHN-1** in acetonitrile (< 12 mg **DHN-1** in CD_3CN containing 20% D_2O; ca. 0.8 mL) was placed in a quartz NMR tube and irradiated with light of $\lambda_{\mathrm{irr}} = 254$ nm. New minor signals appeared in the ^{1}H NMR spectrum at around $\delta = 7.0-7.8$ ppm following irradiation for 78 min. However, the photoproduct could not be positively identified (such as by ^{1}H NMR difference spectra), since most of the product signals were coincident with the intense **DHN-1** signals. Attempts to accumulate the photoproduct by irradiation for an additional 360 min were unsuccessful because of decomposition. An attempt to induce changes by thermal relaxation at room temperature in the dark (24 h) also failed.

A mass spectrometric investigation of the photoproduct mixture revealed compounds with $m/z = 305.1$ (3%), 333.1 (29%) and 334.1 (6%), besides the **DHN-1** signal at $m/z = 332.1$ (100%).[27] The compound with $m/z = 305.1$ is tentatively assigned as the naphthalene derivative **C-1** (Scheme 4), which was presumably formed via the cationic intermediate $\mathbf{T_C}$. Upon addition of aqueous $AgNO_3$ solution to a photoproduct mixture, a colourless precipitate was formed, which we attribute to AgCN. This precipitate arising from **DHN-1**, which was not observed in the absence of light, supports the proposed initial photochemical step in Scheme 4. In a second experiment (b), **DHN-1** (< 7 mg) was dissolved in about 0.8 mL of a CF_3CH_2OD/CD_3CN mixture (1:1) due to its limited solubility in neat CF_3CH_2OD. Irradiation (for 15–355 min) under otherwise identical conditions as in experiment (a) caused very similar effects as those discerned from the aforementioned ^{1}H NMR spectra.

Salient molecular signals can be discerned in the FD mass spectrum of the photoproduct mixture at $m/z = 324.2$ (100%) and $m/z = 332.2$ (68%), along with some weak ones, for example, at $m/z = 305.1$ (5%) and 405.2 (1%). Peaks at $m/z = 324.2$ and $m/z = 405.2$ may be assigned to compounds **C-2** and **C-3**, formed by trapping of the carbocation $\mathbf{T_C}$ with residual OD^- and $CF_3CH_2O^-$, respectively (Scheme 4).

The identity of transient $\mathbf{T_C}$: At least three photoproducts, all of which are formed via the excited singlet state of the **DHN-1** form within 20 ns (Scheme 3), have to be considered: species **A** and **B**, absorbing at 250–300 nm and at $\lambda_B = 370-440$ nm, respectively, as well as transient $\mathbf{T_C}$. For $\mathbf{T_C}$, several alter-

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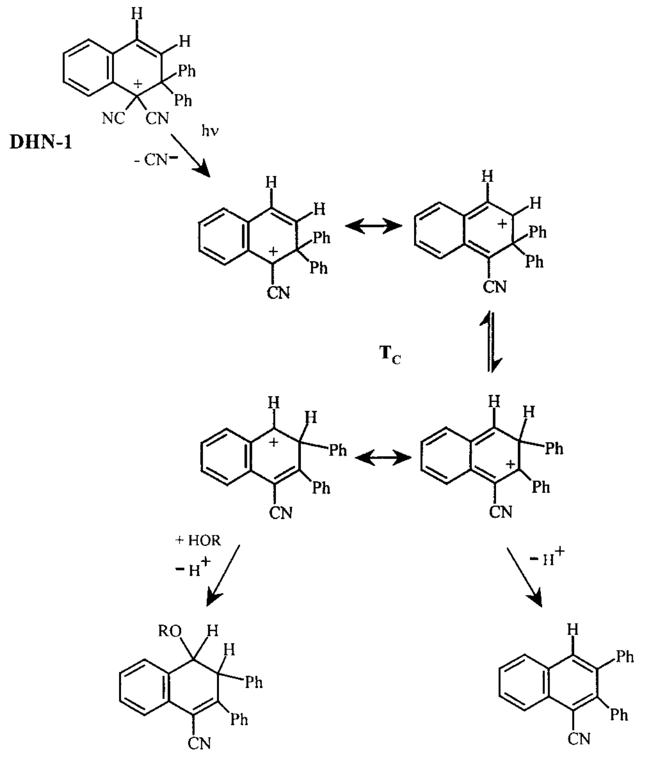

C-2: R=D (324.40)
C-3: R=CH_2CF_3 (405.42)
C-1 (305.38)

Scheme 4. Assumed carbocation route of the **DHN-1** photochemistry.

natives to a carbocation may be considered: a triplet state, a radical, a biradical, a zwitterion, a radical cation and a radical anion. The triplet state can be excluded as oxygen does not reduce the lifetime τ_C. Moreover, attempts to generate a **DHN-1** triplet state under sensitised excitation, by using acetone, acetophenone or naphthalene in argon-saturated acetonitrile at room temperature, failed. The lack of any reaction with oxygen is also strong evidence against the hypotheses of $\mathbf{T_C}$ being a radical or biradical.

Fluoroalcohols are able to stabilise the zwitterionic merocyanine form of spiropyrans and spirooxazines by hydrogen bonding.[26] The appearance of $\mathbf{T_C}$ in polar media, with a maximum in the visible region at $\lambda_C = 545$ nm, might be suggestive of it being a zwitterion. However, the independence of the spectral bands of the polarity of the medium and the effects of water concentration on the yield and lifetime (Table 1) are not consistent with this hypothesis.

Excitation of aromatic molecules with 5.0 eV pulses may well lead to photoionisation products arising from the solvated electron and the radical cation as primary species.[28, 29] However, $\mathbf{T_C}$ cannot be assigned to a radical cation, since its counterpart, the solvated electron, was not detected under conditions (e.g., in ethanol and in mixtures with water) under which it is normally readily detectable.[29–31] Note that in acetonitrile the solvated electron is scavenged within 1 ns. One could, however, argue that the solvated electron rapidly reacts with **DHN-1**. If this occurs intermolecularly, the solvated electron should be detectable within about 1 μs, given a diffusion-controlled rate constant and a **DHN-1** concentration of 0.1 mM. If electron transfer occurs intramolecularly, however, then a radical anion moiety should be observable, which will subsequently react with oxygen. The rate constant for this reaction is typically $2 \times 10^{10}\,\mathrm{M^{-1}\,s^{-1}}$ in ethanol or acetonitrile.[30, 31] Thus, a radical anion with a half-life of > 1 μs is excluded, since $\mathbf{T_C}$ does not react with oxygen.

Features of the carbocation: The most plausible possibility is that $\mathbf{T_C}$ is a carbocation (Scheme 4), this being in agreement with all the results. For example, $\mathbf{T_C}$ was not detected in neat dichloromethane, *tert*-butanol or propan-2-ol, and its yield was rather low in methanol, ethanol and acetonitrile, these being media with polarity parameters[32] below 0.8 (Table 1). On addition of water to these solutions, the yield increases substantially (Figure 3a). In HFP, in which the longest lifetime was observed (Figure 4a), $\mathbf{T_C}$ decays according to first-order kinetics. In TFE, $\mathbf{T_C}$ also has a rather long half-life and two first-order decay components in the ms range (Figure 5a). On addition of water to TFE or HFP, the yield remains substantial or decreases only slightly (Figure 3a), but the decay becomes much faster (Figure 3b).

The presence of water in acetonitrile or alcohols is necessary for efficient formation of the observed carbocation. The proposed reasons are better solvation of $\mathbf{T_C}$ and of the released CN^- (Scheme 4), as well as the possible formation of hydrogen cyanide. It is interesting to note that for the photoheterolysis of 9-fluorenol, a related case, it has been suggested that protonation of the molecule occurs even in the ground state and that the driving force is separation of the two ions by one water molecule.[26] Analogously, we propose that the photoheterolysis of **DHN-1** involves an assistance of ion separation by a water molecule. The first-order decay kinetics of the carbocation and the shorter lifetime in mixtures of HFP with alcohols (ROH) or water (Figure 4a–c) exclude the back reaction with CN^-. Instead, the decay kinetics of the carbocation can be attributed to the addition of ROH and deprotonation. In the presence of Br^- in aqueous TFE, the lifetime τ_C is strongly reduced, and this is ascribed to a corresponding addition reaction (RO^- is replaced by Br^-).

To account for the final re-aromatisation of the naphthalenium ion, a rearrangement has to occur (Scheme 4). The major product with a retention time of 3.8 min upon HPLC, formed under conditions under which transient $\mathbf{T_C}$ is the major intermediate, especially in the presence of water, is compatible with the above assignment to 1-cyano-2,3-diphenylnaphthalene (**C-1**) or to the dihydronaphthalene derivatives **C-2** and **C-3**. Fluorescence and a structured absorbance would be expected for naphthalene **C-1**. However, no fluorescence could be observed under conditions under which $\mathbf{T_C}$ is the major intermediate, indicating that re-aromatisation to the naphthalene structure does not occur, at least not to any spectroscopically detectable extent, under the applied conditions. It is more probable that the presence of the naphthalene derivative **C-1** in the FD-MS spectrum (see above) is merely due to its formation from **C-2** or **C-3** through extrusion of ROH in the course of the FD-MS experiment.

The proposed mechanism is supported by pulse-induced ion formation (Figure 6). The initial conductivity increase in the presence of neutral water is due to the formation of the carbocation and CN^-, the latter, in terms of charges, being rapidly replaced by OH^-. The ensuing decrease in conductivity results from neutralisation in the course of the decay of the carbocation. The increase in its lifetime from $\tau'_C = 6\,\mu s$ in water/acetonitrile (1:1) to 0.2 s in water/HFP mixtures (1:100) is in reasonable agreement with the findings of absorption spectroscopy. In particular, in HFP in the presence of 0.5 and 5 M water, the lifetimes from the two methods are consistent.

Other photoreactions: The photoreaction of **DHN-1** relating to species **B** (benzoquinodimethane isomers) is suggested to be ring-opening and to involve a thermal relaxation process, in agreement with the synthesis of **DHN-1**. This photochromism of **DHN-1** is a minor process and may be interpreted in terms of the following reaction mechanism. Irradiation populates the ^{1}**DHN-1*** state, and the ring-opening takes place on the appropriate reaction coordinate in the excited singlet moiety, since intersystem crossing does not occur at all. The thermal relaxation process (Scheme 3) differs from that of chromene or other spiro compounds in that the kinetics deviate from a monoexponential decay. Interestingly, two ring-opening reactions have also been considered for chromene and both photoprocesses involve thermal relaxation.[17]

Species **A**, being only weakly characterised by an absorption increase of the irreversible part below 400 nm, is tentatively ascribed to a 1,1a,6,6a-tetrahydrocycloprop[*a*]indene derivative resulting from a phenylvinylmethane rearrangement of **DHN-1** (Scheme 3).[33, 34] Photoinduced formation of **A**, **B** and **C** are competing processes, but the vibrationally relaxed ^{1}**DHN-1*** state must be questioned as a common precursor for species **A** as well, since the formation of **A** is not sufficiently suppressed when the yield of **C** reaches a maximum (Tables 1–3). We therefore propose that the pathways to **B** and **C** are competing deactivation processes of the vibrationally relaxed ^{1}**DHN-1*** state and that the formation of **A** takes place from the Franck–Condon state or via relaxation to the ^{1}**DHN-1*** state.

Figure 9 shows DHA and DHN in their ground states. This clearly demonstrates that the C1–C2 σ bond in **DHN-1** is essentially orthogonal to both the π system of the benzene unit and the C3–C4 π bond. In contrast, for DHA an overlapping orbital situation between the lengthening C8a–C1 σ bond and the cycloheptatriene π system may contribute to the efficient C8a–C1 bond cleavage in this photochrome. From Figure 9, it also follows that one of the C–CN bonds in DHN is aligned almost parallel to the benzene π system, whereas in DHA the corresponding interaction is less.

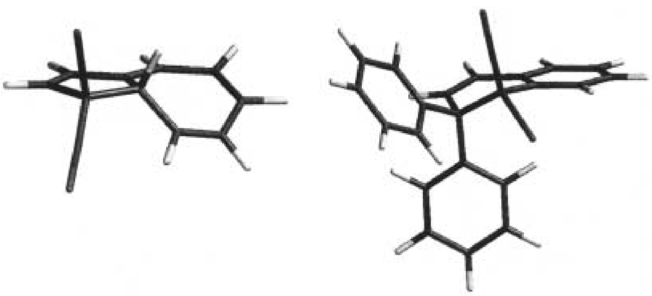

Figure 9. Structures of DHA (left) and **DHN-1** (right). After geometry optimisation using force field methods, the calculations were carried out with Spartan[35] on a semiempirical level using AM1.

Conclusion

Photoinduced charge separation and bond cleavage, as fundamental steps in energy conversion, underpin a wide range of processes, extending from molecular dimensions (light-induced solvolysis, photoinduced heterolytic bond cleavage)[36] up to photosynthetically active membrane-integrated protein-pigment complexes,[37] photovoltaic devices[38] and materials for photolithographic applications.[39] A heterolytic bond cleavage involving the cyano groups is suggested as the driving force for carbocation ($\mathbf{T_C}$) formation from electronically excited 1,1-dicyano-2,2-diphenyl-1,2-dihydronaphthalene. The three suggested photoprocesses all occur on a timescale of less than 10 ns. Photochromic ring opening and closure via the benzoquinodimethane analogue **B** is a side reaction under these conditions, which becomes even less efficient in the presence of water. Water in organic solvents is necessary for the efficient formation of the observed carbocation, but the quantum yield of photoconversion (leading also to species **A**, presumably through a phenyl-vinylmethane rearrangement) is rather independent of the solvent polarity and the amount of added water. This suggests competing photoprocesses, decomposition of **DHN-1** via **A**, photochromic ring-opening via **B**, and formation of carbocation $\mathbf{T_C}$, which eventually yields stable compounds. These presumably have dihydronaphthalenoid and naphthalenoid structures (**C-1** to **C-3**). As already addressed in the introduction, structural and stereoelectronic reasons may be the decisive factors responsible for the competition of electrocyclisation and heterolytic bond cleavage. Further investigations of 2,2-diphenyl-1,2-dihydronaphthalene and 1,1-diphenyl-1,2-naphthalene derivatives with better leaving group(s) and more efficient stabilisation of the cationic intermediate should be helpful to shift the photoprocesses more efficiently towards the two photochromic pathways, electrocyclisation and photoinduced bond dissociation.

Experimental Section

Synthesis: The photochromic chromene-like 6π-electron system **DHN-1** was synthesised according to Scheme 5.[27] *o*-Iodobenzyl alcohol (**1**) was first converted to *o*-iodobenzyl bromide (**2**) with HBr according to ref. [40]; this was then converted to the corresponding phosphonium salt (2-iodobenzyl)triphenylphosphonium bromide (**3**) with triphenylphosphine according to ref. [41]. Both reactions proceeded in near quantitative yield. Wittig reaction[42] of **3** with diphenylacetic aldehyde gave *cis/trans*-3,3-diphenyl-1-(2-iodophenyl)propene and 1,1-diphenyl-3-(2-iodophenyl)propene (**4**), the latter being a tautomeric product formed by base-induced rearrangement. Palladium-catalysed coupling of **4** and malonodinitrile with *t*BuOK as base in dimethoxyethane[43] yielded a mixture of isomeric dicyano compounds (**5**), with one isomer predominating, namely the tautomeric form 1,1-diphenyl-3-(2-dicyanomethylphenyl)propene. In a final one-pot dehydrogenation reaction, the benzoquinodimethane deriv-

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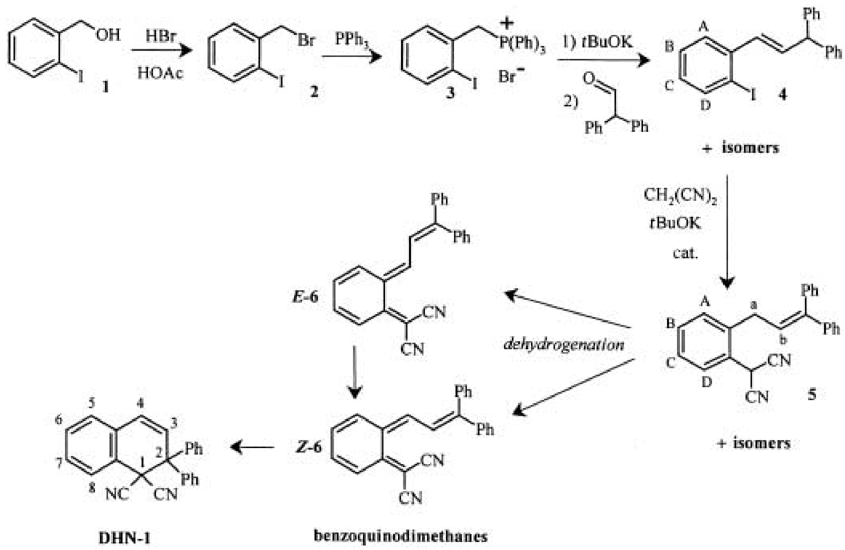

Scheme 5. Synthesis of **DHN-1**.

atives **6** were produced by allylic and benzylic mono- or dibromination of **5** with NBS/AIBN in a first step, followed by thermolytic dehydrobromination and debromination, respectively.[44] Under the applied reaction conditions, the (*E*)/(*Z*)-benzoquinodimethane isomers **6** immediately rearranged to **DHN-1**.

(*E*/*Z*)-**4** (and tautomeric form): Under N_2, **3** (2.0 g, 3.6 mmol) was suspended in THF (25 mL). *t*BuOK (0.40 g, 3.6 mmol) was then added portionwise under ice-cooling, whereupon the reaction mixture immediately became orange. Stirring was continued for a further 20 min, and then diphenylacetic aldehyde (0.64 mL, 3.5 mmol) was slowly added. The mixture was stirred for 5 h at room temperature, while the colour faded to a yellowish hue. The reaction mixture was then diluted with diethyl ether and 0.1 M aqueous HCl. After separation of the layers, the aqueous phase was extracted a further four times with Et_2O. The combined organic layers were washed with water, dried over anhydrous Na_2SO_4 and filtered. After evaporation of the solvent in a rotary evaporator, column chromatography of the residue on silica gel eluting with CH_2Cl_2/PE (1:5) afforded 0.87 g (2.2 mmol, 63 %) of a yellowish resin. IR (KBr): $\tilde{\nu} = 3078, 3059, 3028, 2926, 2860, 1643, 1598, 1560, 1012, 968, 747, 700\ cm^{-1}$; ^1H NMR (250 MHz, $CDCl_3$, mixture of three isomers): $\delta = 3.55$ (d, 2H, $J = 7.53$ Hz; -$\mathbf{CH_2}$ of tautomeric form), 4.98–4.88 (m, 2H; -$CPh_2\mathbf{H}$ of *cis* and *trans* forms), 7.40–6.15 (m, 43H; aromatic and olefinic **H**), 7.48 (dd, 1H, $J_1 = 7.93$ Hz, $J_2 = 1.59$ Hz; $\mathbf{H}^A$ or $\mathbf{H}^D$), 7.87, 7.81, 7.79 ppm (3 dd, 1H per isomer, $J_1 = 7.93$ Hz, $J_2 = 1.19$ Hz for all isomers; $\mathbf{H}^A$ or $\mathbf{H}^D$); ^{13}C NMR (62.9 MHz, $CDCl_3$):[45] $\delta = 41.24$ ($\mathbf{C}H_2$ of tautomeric form), 54.20, 49.09 (-$\mathbf{C}Ph_2H$ of *cis* and *trans* forms), 100.72, 100.01, 99.73 ppm (-**C**I of all three isomers); MS (70 eV, EI): *m*/*z* (%): 396 (70) [M^+], 318 (23) [$M^+ - Ph$], 269 (27) [$M^+ - I$]; elemental analysis calcd (%) for $C_{21}H_{17}I$ (396.27): C 63.65, H 4.32; found C 63.71, H 4.42.

5 (stereoisomeric and tautomeric forms): Under N_2, $[Pd(PPh_3)_4]$ (23 mg, 20 µmol), $CH_2(CN)_2$ (66 mg, 1.0 mmol) and *t*BuOK (130 mg, 1.2 mmol) were suspended in DME (10 mL), and the mixture was stirred for 10 min at room temperature. Then, compound **4** (200 mg, 0.50 mmol, isomeric mixture) was added, and the reaction mixture was refluxed for 24 h. At least three new spots were detected by TLC (CH_2Cl_2/PE, 1:1, $R_f = 0.30$–0.52), indicative of product formation. After the addition of further portions of $[Pd(PPh_3)_4]$ (23 mg, 20 µmol) and *t*BuOK (130 mg, 1.2 mmol), refluxing was continued for another two days. The mixture was then cooled to room temperature, diluted with 0.1 M HCl and stirred for 10 min. The layers were allowed to separate, and the aqueous phase was extracted another four times with Et_2O. The combined organic layers were dried over anhydrous Na_2SO_4 and filtered. After evaporation of the solvent in a rotary evaporator, column chromatography of the residue on silica gel eluting with CH_2Cl_2/PE (1:1) ($R_f = 0.30$–0.52) afforded 66 mg (0.20 mmol, 39 %) of a brown resin. IR (KBr): $\tilde{\nu} = 3061, 3030, 2924, 2257, 2226, 1600, 761, 701\ cm^{-1}$; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 3.56$ (d, 2H, -$\mathbf{CH_2}^a$ of tautomeric form, $J = 7.43$ Hz), 4.76 (s, 1H, -$C(CN)_2\mathbf{H}$ of tautomeric form), 6.11 (t, 1H, $\mathbf{H}^b$ of tautomeric form, $J = 7.43$ Hz), 7.82–7.00 ppm (m, aromatic **H** of all three isomers); MS (70 eV, EI): *m*/*z* (%): 334 (55) [M^+].

1,1-Dicyano-2,2-diphenyl-1,2-dihydronaphthalene (DHN-1): Under N_2, compound **5** (mixture of isomers; 0.39 g, 1.2 mmol), NBS (0.21 g, 1.2 mmol), and AIBN (catalytic amount) were heated in CCl_4 at 120 °C for 24 h. The progress of the reaction was monitored by TLC (CH_2Cl_2/PE, 1:1), irradiating the TLC plate with 254 nm light (UV lamp), while cooling it in liquid N_2. The product could be identified from a red spot, which immediately faded when the plate was warmed to room temperature. After cooling to room temperature, the reaction mixture was filtered, and the residue was washed twice with CCl_4. Evaporation of the solvent in a rotary evaporator, followed by column chromatography of the residue on silica gel eluting with CH_2Cl_2/PE (1:1) ($R_f = 0.50$) afforded a still impure product. Further purification by washing several times with *n*-pentane/diethyl ether yielded 54 mg (0.16 mmol, 13 %) of a colourless solid. M.p. 188 °C; IR (KBr): $\tilde{\nu} = 3079, 3034, 2243, 1791, 1600, 1487, 754, 701\ cm^{-1}$; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 3.95$ (m, 2H, 3- and 4-**H**), 7.54–7.26 (m, 13H, phenyl- and benzo-**H**), 7.61–7.57 ppm (m, 1H, benzo-**H**); MS (70 eV, EI): *m*/*z* (%): 332 (100) [M^+]; HRMS calcd for $C_{24}H_{16}N_2$: 332.1313; found: 332.1310.

Methods: Melting points: uncorrected, Büchi SMP 20 and Reichert Thermovar. IR: Bio-Rad FTS 155. EI-MS: Varian CH-5. FD-MS: MAT 95. NMR: Bruker AC 250 (24 °C) and ARX 400 (21 °C) spectrometers at 250/400 MHz for ^1H and 101 MHz for ^{13}C (ARX 400). Chemical shifts δ are reported with respect to TMS as an internal standard. Solvents and reagents for synthesis were used as purchased without further purification unless stated otherwise (CCl_4 was dried over P_2O_5; THF and DME were dried over Na/K). The progress of reactions was monitored by TLC. In all cases, solvent impurities were removed in vacuo by using oil-diffusion pumps. Further methods were as described elsewhere.[9, 27]

The molar absorption coefficient of **DHN-1** in methylcyclohexane was $\varepsilon_{248} = 1.0 \times 10^4\ M^{-1}\ cm^{-1}$. The solvents used for spectroscopic investigations (Merck) were of analytical (TFE, *tert*-butanol, propan-2-ol, methanol) or Uvasol grade (acetonitrile). MCH was purified by passage through a basic alumina column (Woelm); HFP (Aldrich) and ethanol were distilled; water was from a milli-Q system. Steady-state measurements were performed by using a diode-array spectrophotometer (Hewlett Packard 8453) and a spectrofluorimeter (Perkin Elmer LS-5). Continuous irradiation at $\lambda_{irr} = 254$ nm was achieved by using a low-pressure Hg lamp. The relative quantum yields were based on absorption increases as a function of the irradiation time or laser dose. Uridine in aqueous solution at pH 7 was used as an actinometry standard.[46] To determine the absolute quantum yield, the decomposition of **DHN-1** was monitored by HPLC using a reversed-phase Nucleosil 3-C-18 column (125 × 4.6 mm, 0.8 mL min^{-1}), detection at 215–290 nm and with methanol/water (5:1) as eluent. Laser flash photolysis with a time resolution of 20 ns was carried out using radiation of $\lambda_{exc} = 248$ nm from an excimer laser.[8, 9] The relative yields were obtained from the linear part of the absorption increase at 290 nm and the long wavelength maximum (λ_B) versus the laser intensity using optically matched solutions. Time-resolved conductometry was carried out as described elsewhere.[31] Unless otherwise indicated, measurements refer to 25 °C.

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