ELSEVIER

Journal of Photochemistry and Photobiology
A: Chemistry 85 (1995) 217–224

Journal of PHOTOCHEMISTRY AND PHOTOBIOLOGY A:CHEMISTRY

Photoreaction of dihydroazulenes into vinylheptafulvenes: photochromism of nitrophenyl-substituted derivatives[☆]

Helmut Görner[a], Christian Fischer[b], Jörg Daub[b]
[a]*Max-Planck-Institut für Strahlenchemie, D-45413 Mülheim an der Ruhr, Germany*
[b]*Institut für Organische Chemie der Universität Regensburg, D-93040 Regensburg, Germany*

Received 23 May 1994; accepted 28 June 1994

Abstract

The photophysical and photochemical properties of five nitro-substituted dihydroazulene (DHA) derivatives, 1,8a-dihydro-2-(R-phenyl)-1,1-azulenedicarbonitrile, where R is 2-NO_2, 3-NO_2, 4-NO_2, 2,4-$(NO_2)_2$ and 3,5-$(NO_2)_2$ (2-, 3-, 4-, 2,4- and 3,5-D respectively) were studied in solvents of different polarity at various temperatures. Irradiation of the DHAs in fluid solution leads to the corresponding vinylheptafulvenes (VHFs) which show neither emission nor photoreactivity. At room temperature, the quantum yield of the DHA → VHF photoreaction depends on the substitution and solvent; $\Phi_{D\rightarrow V}$ is substantial for 4-D (approximately 0.5) and very small (0.02–0.005) for 2- and 2,4-D, while for 3- and 3,5-D $\Phi_{D\rightarrow V}$ decreases with increasing solvent polarity. Fluorescence from the excited singlet state of 4-, 3- and 3,5-D is observed at low temperatures; the quantum yield is largest for 4-D ($\Phi_f \geq 0.5$ at -196 °C) and much smaller (0.002 or less) for 2- and 2,4-D. At room temperature, Φ_f is very low throughout. The absorption spectrum of the triplet state is observed at room temperature for those cases, e.g. 2- and 2,4-D, for which $\Phi_{D\rightarrow V}$ is small, and enhanced triplet–triplet absorption is found in all cases using sensitizers, e.g. xanthone in acetonitrile. The DHA triplet energy was estimated from energy transfer measurements to be about 220 kJ mol^{-1}. The triplet state is not involved in the photochromism of the nitro-substituted DHAs. The effects of nitro groups at different positions in the phenyl ring on the photophysical and photochemical behaviour are discussed.

Keywords: Dihydroazulenes; Vinylheptafulvenes; Photochromism

1. Introduction

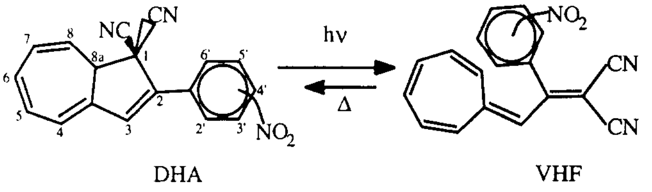
Applications, such as the rapid processing of information, have stimulated the search for suitable photochromic materials [1–3]. Dihydroazulene (DHA) and its derivatives constitute a new class of photochromic compounds [4–14]. DHAs exhibit an efficient photoreaction to the vinylheptafulvenes (VHFs) which convert thermally back to the corresponding valence isomers [10–14]. The DHA–VHF system, in particular the nitroaryl derivatives, can be used to generate light-triggered pulse sequences of an electric current [5] and contains enormous potential as a molecular switching unit [4–10]. These compounds show pronounced substituent effects of covalently bound groups because the alternant π system of DHA is converted into a non-alternant π system of VHF.

It has recently been demonstrated that the incorporation of different substituents in the DHAs is a flexible tool for examining the properties of the DHA–VHF system [4–10]. In a preceding study, we have shown that the DHA → VHF photoreaction occurs via singlet states and that substituents such as CN, Cl, Br, OCH_3 or NH_2 at the para position in the phenyl ring do not change the mechanism fundamentally [14]. Incorporation of a nitro group, however, may have a significant impact on the DHA → VHF pathway. The nitro group is well known to change the electronic properties of aromatics significantly and thus, e.g. by enhancing the quantum yield of intersystem crossing (Φ_{isc}), the photochemistry of the nitro-substituted compound may be remarkably different from that of the parent compound [15–20]. For example, the properties of the DHA triplet state can be examined at ambient temperatures, since in the nitro-substituted DHAs there are cases in which the VHF photoconversion does not hinder a spectral analysis of the triplet state, as occurs in the parent compound.

[☆] Dedicated to Professor Wolfgang Lüttke on the occasion of his 75th birthday.

SSDI 1010-6030(94)03913-F

This paper deals with the photophysics and photochemistry of five nitro-substituted DHA derivatives, which are substituted on the phenyl ring ($R \equiv 2\text{-}NO_2$, $3\text{-}NO_2$, $4\text{-}NO_2$, $2,4\text{-}(NO_2)_2$ and $3,5\text{-}(NO_2)_2$; 2-, 3-, 4-, 2,4- and 3,5-D respectively).



(1)

	C-2'	C-3'	C-4'	C-5'
D	H	H	H	H
2-D	NO_2	H	H	H
3-D	H	NO_2	H	H
4-D	H	H	NO_2	H
2,4-D	NO_2	H	NO_2	H
3,5-D	H	NO_2	H	NO_2

Time-resolved and steady state photochemical techniques were employed to examine the reaction pathways. A few results of the photoreaction and the thermal back reaction (Eq. (1)) have already been reported for 4-D [14]. These studies are now extended in order to characterize the effects quantitatively and to gain a better understanding of the photophysical parameters and the reaction mechanism.

2. Experimental details

The synthesis of the five nitro-substituted DHA molecules and some of their properties have been described elsewhere [9–12]. The solvents (Merck, Fluka) were Uvasol (acetonitrile) or analytical quality (glycerol triacetate (GT) and cyclohexane); methylcyclohexane (MCH) was purified by passing through a basic alumina column (Woelm); toluene, 2-methyltetrahydrofuran (MTHF), butyronitrile and ethanol were distilled. The sensitizers (E_T in kilojoules per mole [19]) were essentially the same as used previously: xanthone (310), benzophenone (287), 2-nitronaphthalene (238), 1-nitronaphthalene (229), pyrene (204), benzanthrone (197), 9,10-dibromoanthracene (172) and rose bengal (165).

Steady state measurements were performed using an absorption spectrophotometer (Perkin-Elmer, 554) and two spectrofluorometers (Perkin–Elmer, LS-5 and a Spex-Fluorolog); the latter was used for corrected spectra, whereas the former could also be used for time-resolved spectra [14,20]. The quantum yield of fluorescence was obtained using 9,10-diphenylanthracene in ethanol as reference ($\Phi_f = 1.0$ at −196 °C). A 1000 W Hg–Xe lamp combined with a monochromator was used for continuous irradiation and the quantum yield ($\Phi_{D\rightarrow V}$) was obtained using ferrioxalate as actinometer [21]. Laser flash photolysis was carried out as described previously [14,18]; the wavelengths of excitation (353 and 248 nm) were provided by a neodymium laser (pulse width, 15 ns) and an excimer laser (20 ns) respectively.

3. Results

3.1. DHA → VHF photoreaction

The absorption spectra of 3- and 4-D are similar to those of the parent compound. They have a maximum (λ_D) at approximately 350 nm (Fig. 1a) in virtually all the solvents used (Table 1). The spectrum of 3,5-D exhibits $\lambda_D \approx 365$ nm (Fig. 2), while that of 2-D is blue shifted, $\lambda_D \approx 320$ nm. This blue shift is also seen for 2,4-D, where in addition the main absorption band is broader (Fig. 3). The displacement of λ_D to shorter wavelengths for the two ortho-substituted DHAs indicates steric hindrance, e.g. a stronger twisting of the phenyl group with respect to the five-membered ring.

Continuous irradiation at 366 nm of 2- and 3-D (Fig. 1) or 4-D in solution at ambient temperatures causes a clean photoreaction with a red-shifted maximum of the product (λ_V) and (up to four) isosbestic points; the two longest (λ_i) are listed in Table 1 (e.g. $\lambda_i = 303$ and 385 nm for 4-D in MCH). From previous results with 4-D and a comparison with parent D [14], it is clear that the photoproduct is the corresponding VHF.

To examine the influence of the solvent polarity, MCH (or cyclohexane), toluene and acetonitrile (or ethanol) were used as examples of non-polar, moderately and strongly polar media respectively. For measurements at low temperatures, MTHF and butyronitrile were taken as moderately and strongly polar solvents respectively. The spectral properties of the VHF form of the three mononitro compounds depend only slightly on the polarity of the solvent; the most pronounced

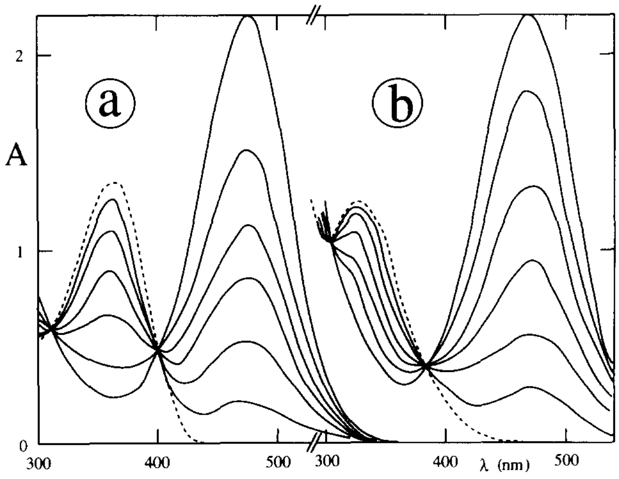


Fig. 1. Absorption spectra in toluene at 24 °C prior to (broken line) and during (full lines) irradiation at 366 nm: (a) 3-D; (b) 2-D.

Table 1
Isosbestic points, absorption maxima of DHA and VHF and quantum yield of the DHA → VHF photoreaction[a]

Compound	Solvent	λ_i (nm)	λ_i (nm)	λ_D (nm)	λ_V (nm)	$\Phi_{D\rightarrow V}$
D[b]	MCH	304	382	349	440	0.35
	Toluene	308	387	354	459	0.6
	Ethanol	308	390	348	468	0.5
	Acetonitrile	302	390	350	468	0.55
4-D	MCH	303	385	340	446	0.50
	Toluene	305	396	355	466	0.42[c]
	Ethanol	302	392	350	474	0.53[c]
	Acetonitrile	303	394	352	472	0.59[c]
3-D	MCH	300	390	352	454	0.58
	Toluene	310	402	360	472	0.60[c]
	Ethanol	310	400	352	478	0.41
	Acetonitrile	303	398	352	476	0.12
3,5-D	MCH	298	400	362	464	0.55
	Toluene	308	412	368	482	0.45[c]
	Ethanol	328	420	364	492	0.09
	Acetonitrile	310	410	364	490	0.002[c]
2-D	MCH					0.012
	Toluene	300	382	325	468	0.016
	Ethanol	295	375	320	475	0.022
	Acetonitrile		380	320	474	0.028
2,4-D	Toluene	300	434	310	480	0.005
	Ethanol	–	–	315	470	$\leqslant 0.008$[d]
	Acetonitrile	–	–	320	488	$\leqslant 0.0004$[d]

[a] In non-degassed solutions at 24 °C, $\lambda_{irr} = 366$ nm.
[b] $\Phi_{D\rightarrow V}$, λ_D and λ_V values were taken from Ref. [14].
[c] Same value in argon-saturated solution.
[d] Limiting value due to thermal back conversion.

effect is a red shift on going from the non-polar to a more polar solvent (Table 1). The molar extinction coefficient of the VHF form (ϵ_V) is generally larger than that of the respective DHA.

The characteristic spectral data (e.g. ϵ_V, λ_i) of 3,5-D are similar to those of 2-, 3- or 4-D, apart from minor red shifts of λ_D and λ_V, which result in analogous shifts of the two λ_i values (Table 1). The maximum λ_V of 2,4-D is essentially independent of the solvent polarity, but the quantum yield of conversion ($\Phi_{D\rightarrow V}$) is much smaller than for the other compounds.

$\Phi_{D\rightarrow V}$ of 4-D, in contrast with the other four compounds, is substantial at room temperature and does not depend greatly on the solvent properties (Table 1). $\Phi_{D\rightarrow V}$ of 3- and 3,5-D is large only in MCH and toluene and markedly smaller in more polar solvents, the reduction being much stronger for 3,5-D. The solvent also has a pronounced effect for 2- and 2,4-D. The smallest value ($\Phi_{D\rightarrow V} \leqslant 0.0004$) was found for 2,4-D in acetonitrile, where decomposition was observed on prolonged irradiation. In total, $\Phi_{D\rightarrow V}$ covers a range of three orders of magnitude for the five nitro compounds in solution at room temperature.

On going to lower temperatures $\Phi_{D\rightarrow V}$ of 4-D shows a trend to smaller values (Fig. 4). $\Phi_{D\rightarrow V}$ decreases moderately in the fluid range and strongly when the viscosity increases by many orders of magnitude [22]. Above the glass transition temperature, around −60 °C for GT and between −130 and −150 °C for MTHF, butyronitrile and ethanol, $\Phi_{D\rightarrow V}$ becomes almost independent of the temperature. The influence of viscosity as an additional parameter for $\Phi_{D\rightarrow V}$ of 4-D can be

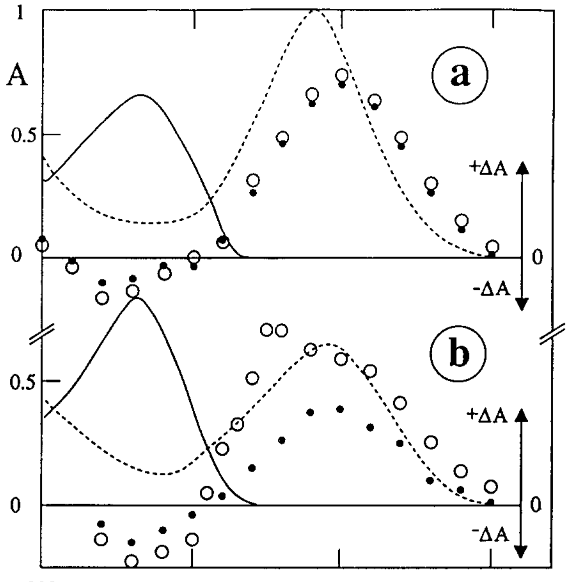


Fig. 2. Absorption spectra of 3,5-D in toluene (a) and acetonitrile (b) at 24 °C; steady state spectra (left side) prior to (——) and after (– – –) 366 nm irradiation and transient difference spectra under argon (right side) at 0.1 μs (○) and 10 μs (●) after the pulse ($\lambda_{exc} = 353$ nm).

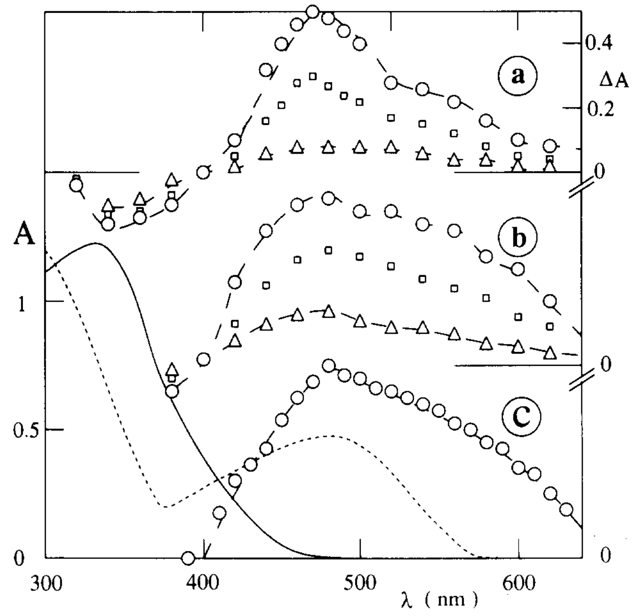


Fig. 3. Transient absorption (difference) spectra (right side) at 24 °C of 2,4-D in MCH (a), toluene (b) and acetonitrile (c) under argon at 0.1 μs (○), 2 μs (□) and 10 μs (△) after the pulse ($\lambda_{exc} = 353$ nm); absorption spectrum in acetonitrile (left side) prior to (——) and after (– – –) 366 nm irradiation.

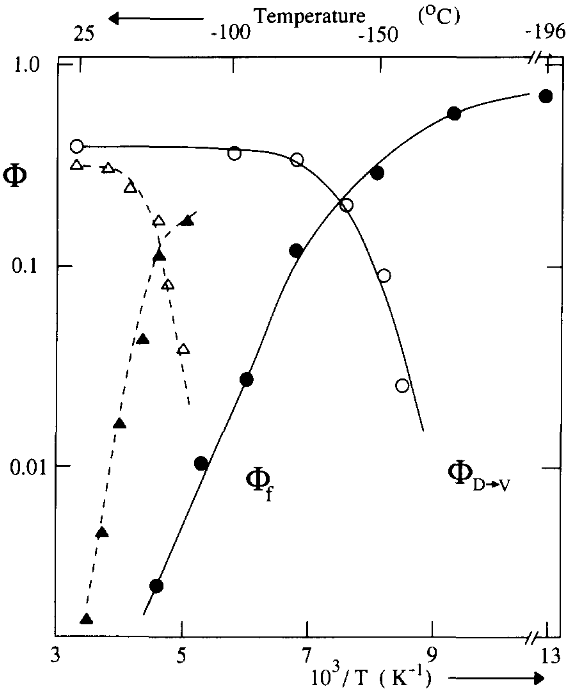


Fig. 4. Temperature dependence of $Φ_f$ (filled symbols) and $Φ_{D→V}$ (open symbols) for 4-D in GT (triangles) and ethanol (circles); $λ_{exc}$ = 366 nm.

Table 2
Excitation and fluorescence emission maxima of DHAs and quantum yield of fluorescence[a]

Compound	Solvent	$λ_f^{ex}$ (nm)	$λ_f$ (nm)	$Φ_f$
D[b]	MCH	360	476	0.9
	MTHF	365	478	0.7 ($<3×10^{-4}$)[c]
	Ethanol	362	480	0.9 ($3×10^{-4}$)
4-D	MCH	360	480	0.5
	MTHF		474	0.5
	Butyronitrile		471 (460)[c]	0.7 ($<3×10^{-3}$)
	Ethanol	363	474	0.8 ($<1×10^{-3}$)
3-D	MCH	372	482	0.2 ($<3×10^{-3}$)
	Ethanol		480	0.1
3,5-D	MCH	377	480	0.05
	MTHF	377	485	0.2
	Butyronitrile	379	490	0.3
	Ethanol	376	482	0.4 ($<1×10^{-3}$)
2-D	MCH		<500	
	Ethanol		480	$<2×10^{-3}$
2,4-D	MCH		<500	$<2×10^{-3}$
	Ethanol		<500	$<2×10^{-3}$

[a] At −196 °C, unless indicated otherwise, $λ_{exc}$ = 366 nm; non-degassed solutions.

[b] Taken from Ref. [14].

[c] Values in parentheses refer to 24 °C.

seen from a comparison of GT with ethanol (Fig. 4). In GT the change occurs in a much smaller temperature range than in ethanol or in the cases of the other more fluid media.

3.2. Fluorescence properties

Only weak emission was detected for 4-D in solution at room temperature. For example, a maximum ($λ_f$) around 460 nm was recorded for 4-D in butyronitrile using $λ_{exc}$ = 366 nm. In other cases, e.g. 2-D in MCH or ethanol, no emission was detected at all. On going to lower temperatures the emission of 4-D becomes stronger, showing $λ_f ≈ 475$ nm and a quantum yield of $Φ_f$ = 0.5–0.8 in glasses at −196 °C (Table 2). The emission and excitation spectra of 3-D in MCH and of 4-D in ethanol are shown in Figs. 5(a) and 5(b) respectively. The emission is attributed to fluorescence on the basis of a comparison with the spectral and kinetic properties of D [14].

For 3- and 3,5-D at −196 °C the spectra are similar and the fluorescence is also strong, but $Φ_f$ is smaller than for 4-D. $Φ_f$ of 3,5-D increases markedly with increasing solvent polarity (Table 2). The matching of the excitation spectrum (maximum $λ_f^{ex}$) with the absorption spectrum demonstrates that the fluorescence arises from the ^{1}DHA* state and excludes trace impurities. For 2- and 2,4-D virtually no emission was recorded in either non-polar or polar media; the limit is $Φ_f < 2×10^{-3}$. The temperature dependence of $Φ_f$ for 4-D in GT and ethanol (Fig. 4) resembles that of D and other derivatives [14]. From the almost linear part of log $Φ_f$ vs. T^{-1}, activation energies of 19 and 37 kJ mol^{-1} were obtained for 4-D in ethanol and GT respectively.

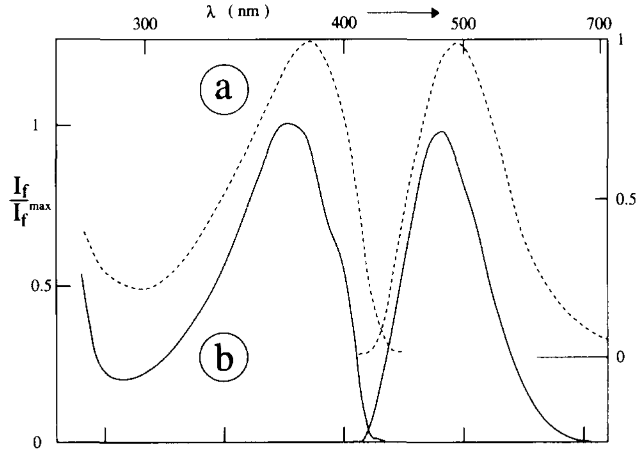


Fig. 5. Fluorescence excitation (left) and emission (right) spectra at −196 °C of 3-D in MCH (a) and 4-D in ethanol (b) 0; $λ_{exc}$ = 366 nm, $λ_f$ = 500 nm.

For D and several derivatives in glassy media, where $Φ_f$ is in the range 0.2–0.8, typically two fluorescence decay components were recorded by single-photon counting, a minor component with a lifetime of $τ_f ≈ 0.6$ ns and a major component with $τ_f ≈ 3$–4 ns [14]. This pattern was also obtained for 4-D at −196 °C. For 3-

and 3,5-D in MCH or ethanol, where Φ_f is comparable or slightly smaller, the main component corresponds to $\tau_f=2.5$–2.9 ns. From the changes in Φ_f with temperature (Table 2), fluorescence lifetimes of a few picoseconds can be expected for all five nitro-substituted DHA derivatives at room temperature.

3.3. Direct triplet formation

A transient, showing a broad spectrum with $\lambda_{max} \approx 480$ nm and a shoulder around 550 nm, was detected for 2,4-D in several solvents at room temperature using laser flash photolysis with either $\lambda_{exc}=353$ or 248 nm. The spectrum depends slightly on the solvent properties, as shown in Figs. 3(a)–3(c) for MCH, toluene and acetonitrile. In addition, there is a bleaching area between 310 and 400 nm. The transient absorbance (ΔA) appears within the pulse width and decays by first-order kinetics (here, a small remaining ΔA was first subtracted). The lifetime ($\tau_T=1/k_{obs}$) in argon-saturated solutions is $\tau_T \approx 4$ μs (Table 3) and decreases slightly when either the laser intensity or the DHA concentration is increased markedly with respect to the lowest possible values under our conditions. In the presence of oxygen the decay rate constant is substantially larger in all solvents. From the values in argon-, air- and oxygen-saturated acetonitrile, a rate constant for quenching by oxygen of 4×10^9 M^{-1} s^{-1} was obtained. The results are characteristic for triplet states and in agreement with those from sensitized generation (see Section 3.4). Thus the transient is assigned to the triplet state (^{3}DHA*) of 2,4-D.

Close inspection of the difference spectra (Figs. 3(a) and 3(b)) reveals that the kinetics are the same when ΔA is positive, i.e. above about 400 nm, or negative, but in the bleaching area a long-lived negative ΔA component (which is actually permanent) can also be seen. This is compatible with the DHA→VHF conversion in low yield. A comparison with the benzophenone triplet in acetonitrile using the same absorbance ($A_{353}=1$) and laser intensity shows an approximately tenfold smaller ΔA^{max} value for 2,4-D.

The transient difference spectrum of 3,5-D in acetonitrile at the end of the pulse indicates the formation of both VHF and ^{3}DHA* (Fig. 2(b)). The increase in ΔA above 410 nm and the decrease in ΔA between 310 and 400 nm are in full agreement with the photochemical DHA→VHF changes in the steady state spectrum; the absorption around 500 nm is much larger than that for 2,4-D. The difference in ΔA between 20 ns and about 10 μs is ascribed to triplet–triplet (T–T) absorption with $\lambda_{max}=440$ nm. This is further supported by a triplet lifetime of 3–4 μs in deoxygenated solution (Table 3). However, for 3,5-D in solvents of lower polarity, where $\Phi_{D\rightarrow V}$ is much larger (see Table 1), the possible contribution of the triplet to the total ΔA value at the end of the pulse could not be observed due to a small Φ_{isc} value. This rapid VHF formation is illustrated in Fig. 2(a) for 3,5-D in toluene.

For 3-D in ethanol at 24 °C it was possible to record the T–T absorption even though $\Phi_{D\rightarrow V}$ is large, whereas similar attempts for 4-D failed. In glassy media, where $\Phi_{D\rightarrow V}$ is virtually zero (Fig. 4), the problem of a hidden T–T absorption does not arise. In fact, the triplet could be recorded for 3- and 4-D (Table 3). A time-resolved absorption difference spectrum is shown in Fig. 6(a) for 4-D in GT at −70 °C. For 4-D and the other cases, τ_T at −196 °C is only a factor of four longer than at

Table 3
Triplet–triplet (T–T) absorption maximum and triplet lifetime of DHAs on direct excitation[a]

Compound	Solvent	Temperature (°C)	λ_{max} (nm)	τ_T (μs)
D[b]	Ethanol	−196	440	7
4-D	MTHF	−180	430	10
	GT	−70	430	8
	Ethanol	−196	430	10
3-D	Ethanol	24	440	2
	Ethanol	−196	430	12
3,5-D	Ethanol	24	450, 500sh	4
	Acetonitrile	24	440	4
2-D	Ethanol	24	430	4
2,4-D	MCH	24	470, 550sh	4
	Toluene	24	500, 540sh	3
	Ethanol	24	480, 540sh	4
	Acetonitrile	24	480, 560sh	4

[a] Under argon, $\lambda_{exc}=248$ nm, except for toluene where $\lambda_{exc}=353$ nm.
[b] Taken from Ref. [14].

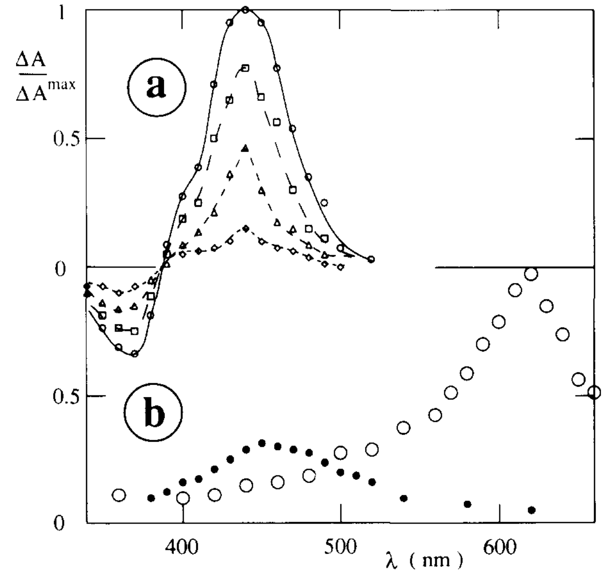


Fig. 6. Transient absorption spectra of 4-D in GT (a) at −70 °C at 0.2 μs (○), 2 μs (□), 5 μs (△) and 15 μs (◇) after the pulse and in argon-saturated acetonitrile (b) at 24 °C in the presence of xanthone at 0.5 μs (○) and 3 μs (●) after the pulse; $\lambda_{exc}=248$ nm.

room temperature, a result which is remarkable and only seldom found for a triplet state under these conditions [23].

3.4. Triplet energy transfer to DHA

Further information about the DHA triplet was gained by energy transfer measurements at room temperature using high-energy triplet donors (S), such as xanthone, having a triplet energy of $E_T = 310$ kJ mol^{-1}. The first-order decay rate constant of triplet xanthone in acetonitrile, measured at the T–T absorption maximum of 620 nm, increases on addition of 2,4-D. The rate constant (k_q), obtained from the linear dependence of k_{obs} vs. the concentration of the energy acceptor, is about 1.5×10^{10} M^{-1} s^{-1}, i.e. close to the diffusion-controlled limit. A longer lived transient, remaining after the decay of triplet xanthone, is assigned to ^{3}DHA* (Eq. (2))

$$^3\text{S}^* + \text{DHA} \xrightarrow{k_q} \text{S} + {}^3\text{DHA}^* \qquad (2)$$

Virtually the same spectra were recorded with several other sensitizers (Table 4). The triplet state of all five nitro compounds can be detected by this method. An example is shown in Fig. 6(b) for 4-D using conditions of approximately 70% quenching of the xanthone triplet. The maximum of the T–T absorption spectrum is placed at about 440 nm and the triplet lifetime lies in the 2–5 μs time range (Table 4).

The energy transfer, due to the small $\Phi_{D\rightarrow V}$ values, can be observed much better for 2,4-D than for 4-D, where $\Phi_{D\rightarrow V}$ is substantial and the triplet is spectroscopically hidden by the efficient formation of the corresponding VHF. To estimate the energy of ^{3}DHA*, the rate constant k_q was measured for 2,4-D in argon-saturated acetonitrile, using a variety of sensitizers with different triplet energies. A plot of the logarithm of k_q vs. E_T (Fig. 7) shows essentially a linear increase and a plateau. The intercept at about 220 kJ mol^{-1} represents the triplet energy of 2,4-D. It should be mentioned that the slope is much smaller than expected for energy transfer to a rigid acceptor molecule, as expressed by the broken line for Δ log k_q vs. $\Delta E_T/2.3RT$ [24,25].

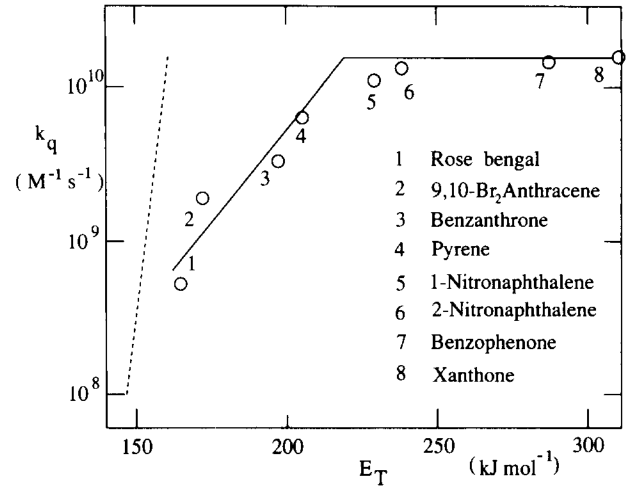


Fig. 7. Rate constants for quenching of sensitizer triplets by 2,4-D (log scale) vs. E_T in argon-saturated acetonitrile at 24 °C; $\lambda_{exc} = 248$ nm; the broken line represents Δ log k_q vs. $\Delta E_T/2.3RT$.

Table 4
Maximum and lifetime of the DHA triplet, obtained by sensitized excitation[a]

Compound	Sensitizer	λ_{max} (nm)	τ_T (μs)
D[b]	Xanthone	440	≈5
4-D	Xanthone	≈430	≤5
3-D	Xanthone	≈440	
3,5-D	Xanthone	450	3
2-D	Xanthone	430	4
2,4-D	Acetophenone	480, 570sh	3
	Xanthone	490	2
	Thioxanthone	490	2.5
	Biacetyl	470, 570sh	2
	9,10-Dibromoanthracene	480	3

[a] In argon-saturated acetonitrile solution at room temperature, $\lambda_{exc} = 248$ nm; typical concentrations, 0.2 mM.
[b] Taken from Ref. [14].

4. Discussion

4.1. Photochromism of the parent DHA–VHF couple

The photophysical deactivation processes of D are fluorescence and intersystem crossing at the DHA geometry, but their contribution is small compared with the photochemical DHA → VHF conversion [14]. Fluorescence plays a significant role only when $\Phi_{D\rightarrow V}$ is small, e.g. in rigid glasses. The existence of the DHA triplet state of D is based on results from laser flash photolysis at room temperature in the presence of a sensitizer and at low temperatures in the absence of additives [14]. Internal conversion, due to small Φ_f and Φ_{isc}, should account for the major part of the difference $1 - \Phi_{D\rightarrow V}$; this can occur not only for the DHA form but for any other geometry along the excited singlet surface.

The energy surface of the excited singlet state of parent D has qualitatively been described by a small energy barrier close to the DHA geometry and a steady decrease with increasing the mean distance between the C-1 and C-8a positions as a measure of the reaction coordinate, until a minimum is reached. This may be at a larger reaction coordinate than the location of the maximum (perpendicular VHF) between the s-trans and s-cis VHF ground states [14]. A rather small gap at this conformation gives rise to rapid internal conversion of the excited s-trans isomer and explains the absence of any other measurable photoreaction from the ^{1}VHF* state. The absence of any detectable fluorescence from the s-trans VHF form indicates that rotation around the exocyclic double bond is responsible for fast radiationless deactivation [26].

In order to account for a driving force for the route from ^{1}DHA* to the s-cis geometry of ^{1}VHF*, charge transfer on excitation into the singlet state has been proposed [14]. Twisting, together with intramolecular charge transfer, is a well-known phenomenon [27]. The initial ring opening of DHAs is proposed to be assisted by a charge separation, where the positive charge is at the seven-membered ring and the negative charge delocalization at the cyano groups.

4.2. Photochromism of nitro-substituted DHAs–VHFs

The nitro derivatives differ from the parent compound by the fact that one (2-, 3- and 4-D) or two (2,4- and 3,5-D) nitro group(s) are introduced at the phenyl ring. Compounds 4- and 3-D, and to a certain extent 3,5-D, are characterized by an absorption maximum $\lambda_D \approx 350$ nm in solution at ambient temperature, as observed for parent D (Table 1). Fluorescence is virtually absent in fluid media and plays a significant role only for 4-, 3- and 3,5-D in glasses (Table 2).

A pathway via the triplet manifold in the DHA → VHF reaction is ruled out for 4-, 3- and 3,5-D since the conversion to VHF is completed within 20 ns while the decay of the triplet is much longer, $\tau_T \approx 4$ μs (Tables 3 and 4). The conversion to VHF should therefore occur in the excited singlet manifold; a DHA → VHF reaction in the ground state is not possible. The temperature dependences of $\Phi_{D\rightarrow V}$ and Φ_f for 4-D indicate a small activation barrier for the ^{1}DHA* → VHF pathway which causes the observed effects of temperature and viscosity (see Fig. 4). The main reason for the contribution of viscosity is that the molecule requires a larger volume on the ^{1}DHA* → VHF pathway [14]. No indication was found either for a photochemical back reaction or fluorescence from ^{1}VHF*.

The dominant photochemical process for 4-, 3- and 3,5-D is the formation of s-trans VHF with $\lambda_V = 450$–480 nm in a clean reaction, documented by isosbestic points, two of which (λ_i in Table 1) mark the bleaching area. When the photoconversion is strongly retarded, e.g. in a rigid glass at −196 °C, the dominant deactivation step is fluorescence (Fig. 5), e.g. for 4-D in all solvents. From the absorption and fluorescence spectra (Tables 1 and 2), it follows that the energy of the ^{1}DHA* state is about 290 kJ mol^{-1}. An estimation of the energy of ^{1}VHF* is about 220 kJ mol^{-1}, as observed for D [14]. Since the properties of fluorescence and photoconversion are similar for D, 3- and 4-D, it is suggested that nitro substitution in the para or meta position does not change significantly the electronic structure of the excited singlet state.

4.3. Mechanistic implications

Obviously, the electronic structure of the excited singlet state is strongly distorted when the nitro group is substituted in the ortho position. Φ_f of 2- and 2,4-D is very small even at −196 °C, indicating a rapid deactivation channel which successfully competes with fluorescence. This cannot be conversion into the VHF derivative since this is completely inhibited in rigid media. One possibility could be that the ortho nitro group causes a steric hindrance for ring opening. The phenyl ring is probably twisted relative to the five-membered ring since λ_D is blue shifted (Table 1). The steric hindrance could lead to a minimum in the excited singlet state at a geometry close to s-cis VHF. This, however, cannot be the only reason for a small $\Phi_{D\rightarrow V}$ value since this argument would not hold for 3,5-D in polar solvents where $\Phi_{D\rightarrow V}$ (at 24 °C) is also small but $\Phi_f \approx 0.3$ (at −196 °C).

Another reason for a small $\Phi_{D\rightarrow V}$ value could be efficient intersystem crossing to ^{3}DHA* and further deactivation to the ground state, i.e. no triplet pathway to VHF. This raises the question of the Φ_{isc} value. A comparison of direct triplet formation for 2,4-D with that of benzophenone in acetonitrile shows a ΔA^{max} value of about 10% relative to the reference (see Section 3.3). Φ_{isc} is calculated by using $\Phi_{isc} = 1$ for benzophenone and the ratio of the absorbances and the molar extinction coefficients for T–T absorption. The value for benzophenone in acetonitrile is $\epsilon_{520} = 6.5 \times 10^3$ M^{-1} cm^{-1} [28] and that of 2,4-D is obtained from energy transfer experiments using xanthone as sensitizer. From the two ΔA values for maximum T–T absorption, a molar extinction coefficient of $\epsilon_{490} \approx 3 \times 10^3$ M^{-1} cm^{-1} would result for 2,4-D using $\epsilon_{620} = 8 \times 10^3$ M^{-1} cm^{-1} [28] for triplet xanthone (70% energy transfer). A similar ϵ value can be obtained for 4-D (Fig. 6(b)). This would indicate that the triplet yield of 2,4-D is quite substantial, $\Phi_{isc} = 0.2$, but not large enough to account for the very small $\Phi_{D\rightarrow V}$ value. The proposed reason for the low Φ_f and $\Phi_{D\rightarrow V}$ values is a rapid reversal interaction of the ortho nitro group with the proximate double bond of the DHA conformation.

A much smaller Φ_{isc} value results for 3,5-D in acetonitrile. Here the photoconversion directly after the pulse can be used for calibration. The product $\epsilon_V \times \Phi_{D\rightarrow V}$ (filled circles in Fig. 2(b)) is virtually the same as the product $\epsilon_{TT} \times \Phi_{isc}$ (difference at 450 nm). Since $\epsilon_V \times \Phi_{D\rightarrow V}$ is 100 M^{-1} cm^{-1} or less, a Φ_{isc} value of less than 0.01 is estimated. Thus a singlet route for the DHA → VHF pathway is concluded for the nitro compounds.

With regard to $\Phi_{D\rightarrow V}$, the five nitro compounds in different solutions at ambient temperature can be classified as follows: (a) for 4-D in all solvents and 3- and

3,5-D in solvents of low polarity, the photophysical and photochemical properties resemble those of the parent compound; (b) 2,4-D and, to a certain extent, 2-D are photochemically more or less unreactive; (c) 3- and 3,5-D in polar solvents (Table 1) are intermediate between cases (a) and (b).

The proposed charge transfer effect is operative for 4-D in all solvents and 3- and 3,5-D in solvents of low polarity. The question arises as to the origin of the retarded photoconversion of compounds 3- and 3,5-D in polar solvents (Table 1). Steric hindrance and intersystem crossing may have a minor effect, but cannot account for the decreasing $\Phi_{D \to V}$ values with increasing polarity. Here, a qualitative description of the potential energies of the excited singlet state is not sufficient. The decrease in the energy of the $S_0 \to S_1$ transition in the order $D \approx$ 4-D1,3-D1,3,5-D is noteworthy and in accord with an enhancing contribution of charge transfer for 3,5-D. We propose that the presence of the nitro group(s) in the meta position at the phenyl ring introduces an electronic distortion effect, hindering charge separation between one of the two cyano groups and the seven-membered ring. This process, introduced by the meta nitro group, becomes significantly stronger with increasing polarity of the solvent.

A parallel may be found in the effect of polarity on the processes of fluorescence and trans → cis photoisomerization for certain *trans*-stilbenes containing push and pull groups, e.g. 4-dimethylamino-4′-nitrostilbene; here, a strongly polar excited singlet state with a trans configuration has been postulated for the decrease in Φ_f with increasing polarity [20,24]. Why para nitro substitution in the case of DHA does not have a comparable reducing effect is not yet known. Nevertheless, the effect of polarity on $\Phi_{D \to V}$ (Table 1) is explained by electron delocalization in the ^{1}DHA* state, and excludes an alternative mechanism where a biradical is the intermediate in ring opening.

Acknowledgments

We thank Professor D. Schulte-Frohlinde and the Fonds der Chemischen Industrie for support and Mrs. S. Roos, E. Hüttel, A. Keil and Mr. L.J. Currell for technical assistance.

References

[1] H. Dürr and H. Bouas-Laurent (eds.), *Photochromism – Molecules and Systems,* Studies in Organic Chemistry, 40, Elsevier, Amsterdam, 1990.

[2] A.V. El'tsov (ed.), *Organic Photochromes,* Consultants Bureau, New York, 1990.

[3] G.H. Brown (ed.), *Photochromism,* Techniques of Chemistry, Wiley Interscience, New York, 1971.
D.A. Parthenopoulos and P.M. Rentzepis, *Science, 245* (1989) 843.
H. Dürr, *Angew. Chem., Int. Ed. Engl., 28* (1989) 413.
H. Dürr, *Pure Appl. Chem., 62* (1990) 1477.

[4] J. Daub, T. Knöchel and A. Mannschreck, *Angew. Chem., Int. Ed. Engl., 23* (1984) 960.

[5] J. Daub, S. Gierisch, U. Klement, T. Knöchel, G. Maas and U. Seitz, *Chem. Ber., 119* (1986) 2631.

[6] S. Gierisch and J. Daub, *Chem. Ber., 122* (1989) 69.

[7] J. Daub, C. Fischer, T. Knöchel, H. Kunkely and K.M. Rapp, *Angew. Chem., Int. Ed. Engl., 28* (1989) 1494.

[8] S. Gierisch, W. Bauer, T. Burgemeister and J. Daub, *Chem. Ber., 122* (1989) 2341.
H. Dürr, in H. Dürr and H. Bouas-Laurent (eds.), *Photochromism – Molecules and Systems,* Studies in Organic Chemistry, 40, Elsevier, Amsterdam, 1990, p. 510.

[9] S. Gierisch, *Ph.D. Thesis,* Universität Regensburg, 1989.

[10] J. Daub, C. Fischer, J. Salbeck and K. Ulrich, *Adv. Mater., 2* (1990) 366.

[11] C. Fischer, *Diplomarbeit,* Universität Regensburg, 1989.

[12] C. Fischer, *Ph.D. Thesis,* Universität Regensburg, 1991.

[13] J. Achatz, C. Fischer, J. Salbeck and J. Daub, *J. Chem. Soc., Chem. Commun.,* (1991) 504.

[14] H. Görner, C. Fischer, S. Gierisch and J. Daub, *J. Phys. Chem., 97* (1993) 4110.

[15] Y.L. Chow, in S. Patei (ed.), *The Chemistry of Amino, Nitroso and Nitro Compounds and Their Derivatives,* Suppl. F, Wiley, New York, 1982, p. 181.

[16] A.V. El'tsov, A.I. Ponyaev, E.R. Zahks, D. Klemm and E. Klemm, in A.V. El'tsov (ed.), *Organic Photochromes,* Consultants Bureau, New York, 1990, p. 177.

[17] R. Guglielmetti, in H. Dürr and H. Bouas-Laurent (eds.), *Photochromism – Molecules and Systems,* Studies in Organic Chemistry, 40, Elsevier, Amsterdam, 1990, p. 314.

[18] H. Görner, F. Elisei, U. Mazzucato and G. Galiazzo, *J. Photochem. Photobiol. A: Chem., 43* (1988) 139.
H. Görner and E. Fischer, *J. Photochem. Photobiol. A: Chem., 57* (1991) 235.

[19] H. Görner, E. Fischer and N. Castel, *J. Photochem. Photobiol. A: Chem., 52* (1990) 123.

[20] H. Gruen and H. Görner, *J. Phys. Chem., 93* (1989) 7144.

[21] C.G. Hatchard and C.A. Parker, *Proc. R. Soc. (London), Ser. A, 255* (1956) 518.
H.J. Kuhn, S.E. Braslavsky and R. Schmidt, *Pure Appl. Chem., 61* (1989) 187.

[22] G. Fischer and E. Fischer, *Mol. Photochem., 8* (1977) 279.

[23] J.C. Scaiano (ed.), *Handbook of Organic Photochemistry,* CRC Press, Boca Raton, 1989.

[24] H. Görner and H.J. Kuhn, *Adv. Photochem.,* in press.

[25] W.G. Herkstroeter, *J. Am. Chem. Soc., 97* (1975) 4161.

[26] Y. Sugihara, S. Wakabayashi, I. Murata, M. Jinguli, T. Nakazawa, G. Persy and J. Wirz, *J. Am. Chem. Soc., 107* (1985) 5894.

[27] Z.R. Grabowski, K. Rotkiewicz, A. Siemarczuk, D.L. Cowley and W. Baumann, *Nouv. J. Chim., 3* (1979) 443.
W. Rettig, *Angew. Chem., Int. Ed. Engl., 25* (1986) 971.
W. Rettig, *Top. Curr. Chem., 169* (1994) 253.

[28] I. Carmichael and G.L. Hug, *J. Phys. Chem. Ref. Data, 15* (1986) 1.