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Photoproducts and triplet reactivity of 4′-nitro- and 2′,4′-dinitro-substituted 4-hydroxystilbenes

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ABSTRACT

The properties of triplet-excited *trans*-4-hydroxy-4′-nitrostilbene were studied by photochemical means. This species produces singlet molecular oxygen with a quantum yield of $\Phi_\Delta = 0.4$ in benzene and 0.05 in acetonitrile. Population of the triplet state was also detected by flash photolysis. The triplet yield is substantial in benzene or toluene and small in polar solvents. The major photoprocess is *trans* → *cis* isomerization, whose quantum yield is $\Phi_{\text{t-c}} = 0.45$ in benzene and smaller in more polar media. The effects of solvent polarity on the triplet reactivity were revealed. For *trans*-4-hydroxy-2′,4′-dinitrostilbene, Φ_Δ and $\Phi_{\text{t-c}}$ are much smaller. The photoreaction to the corresponding hydroxyphenylisatogen was examined and mechanistic aspects were discussed.

1. Introduction

The *trans* → *cis* photoisomerization of stilbene and several derivatives is the subject of many fundamental investigations [1–18]. The quantum yield of *trans* → *cis* isomerization ($\Phi_{\text{t-c}}$) of parent stilbene is large [13–17] with a fraction of $\alpha = 0.5$ for branching from the excited singlet state to *cis*-stilbene as upper limit. The quantum yield of intersystem crossing (Φ_{isc}) for *trans*-stilbenes is generally small. This is supported by a low quantum yield of singlet molecular oxygen formation (Φ_Δ) [19]. Therefore, only singlet states are involved in photoisomerization of various stilbenes [13–17]. However, for *trans*-4-benzoylstilbene, intersystem crossing and twisting in the triplet manifold has been reported [20].

trans-Nitrostilbenes constitute another group with efficient intersystem crossing. Substitution of stilbene by a nitro group strongly enhances Φ_{isc}, thereby inducing photoisomerization via a triplet-excited state [1–12]. This mechanism is operating for 4-nitrostilbene and several 4-nitrostilbenes substituted in the 4′-position by an electron donor moiety. The photophysics and photochemistry of *trans*-2,4-dinitrostilbene and the effect of intramolecular charge transfer have been studied [8]. The Φ_Δ value of *trans*-4-nitrostilbene was found to be much lower than Φ_{isc} [7]. The effect of solvent polarity on the deactivation of excited *trans*-nitrostilbenes has been extensively investigated [1–12]. The lifetime (τ_f) and the quantum yield of fluorescence (Φ_f) are very small for *trans*-4-nitrostilbene.

Trans → *cis* photoisomerization via the singlet-excited state can be assumed for resveratrol (3,5,4′-trihydroxystilbene). The radiolysis of this compound was examined [21] and its specific role as antioxidant was attributed to the hydroxystilbene moiety [22]. Elementary reactions of such an antioxidant action of *trans* isomers of resveratrol and 4-hydroxystilbene have been reported [21–28]. The fluorescence and *trans* → *cis* photoisomerization of hydroxystilbene are subjects of several studies [29–34]. Substitution of *trans*-stilbene by a hydroxy group leads to substantial changes in the properties of the *trans* singlet-excited state, prolongs τ_f and enhances Φ_f [32].

Only a few photochemical features of hydroxy(di)nitrostilbenes are known [35–39]. The fluorescence properties of *trans*-4-hydroxy-4′-nitrostilbene (*trans*-HN) and the 2′,4′-dinitro analogue (*trans*-HDN) have been recently studied [35]. The ortho-nitro group gives rise to a specific photoreaction with at least two intermediates (I-1 and I-2, Scheme 1); the corresponding hydroxyphenylisatogen and 2-amino-4-nitrobenzaldehyde were identified as products of HDN in benzene upon irradiation at 365 nm or with sunlight [36]. Some photophysical features of a rigid analogue of HN have been reported [28].

In this work, *trans* → *cis* isomerization and intersystem crossing of HN and HDN were examined by time-resolved and steady-state methods in various solvents at room temperature to reveal the role of these processes in the deactivation from the excited states. Gen-

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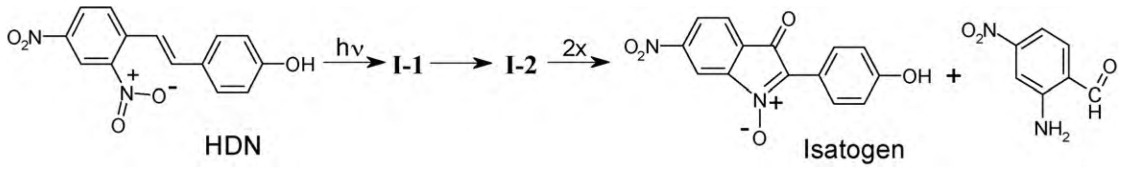


Scheme 1.

erally, both hydroxy and nitro groups changes the photoprocesses of stilbene drastically.

2. Materials and methods

HN, HDN, 4-nitrostilbene and 2,4-dinitrostilbene were the same as used previously [3,8,35]. All stilbenes hereafter mentioned refer to the *trans* isomers unless otherwise noted. The solvents (Aldrich, Merck) were of the purest spectroscopic quality (Uvasol) and used as received. The solubility of HN and HDN in cyclohexane or carbon tetrachloride was found to be too low. The absorption spectra were monitored on a HP 8453 spectrophotometer. HPLC analysis was performed on a reverse phase ODS-3HD (PerfectSilTarget, 3 μm) column (0.8 ml min^{-1}) with mobile phase gradient, composed of 0.5% trifluoroacetic acid and either a 1:5 mixture of acetonitrile:water or neat acetonitrile as eluent. The retention time of HDN was 17.2 min. $\Phi_{\text{t-c}}$ of HN and HDN were determined employing 4-nitrostilbene in benzene as reference for which $\Phi_{\text{t-c}} = 0.5$ was reported [3,4]. The scale in Fig. 1 refers to $A' = (A_0 - A_t)/(A_0 - A_e)$, where A_t, A_0 and A_e are the absorbances at a given irradiation time, before irradiation and in the photostationary equilibrium, respectively. An excimer laser (Lambda Physik, EMG 200, pulse width of 20 ns and energy <100 mJ) served as source of excitation pulses at 308 nm. For the measurement of relative yields optically matched solutions, typically with absorbances of 0.2–2 (per 1 cm) at the excitation wavelength, were used. The absorption signals were measured with two digitizers (Tektronix 7912AD and 390AD). Phosphorescence of singlet molecular oxygen at 1269 nm was detected after the pulse using a cooled Ge detector (North Coast, EO 817FP), a silicon filter and interference filter and an amplifier (Comlinear, CLC-103) as described elsewhere [8]. The signal, which can be overlapped by fluorescence and/or scattered light, was extrapolated to the end of the 20-ns pulse (I_Δ). At a fixed laser intensity, I_Δ was found to show a linear dependence on the absorbed energy, being proportional to $(1–10^{-A})$, and deviation from the linearity was observed only at high intensities. The quantum yield of singlet molecular oxygen formation (Φ_Δ) was determined from the I_Δ values in optically matched solutions ($A_{308} = 0.8$) using 2-acetonaphthone in benzene as reference, which has a well-established $\Phi_\Delta = 0.81$ value [8,40]. The solvent dependence of the radiative rate constant of singlet molecular oxygen was taken into account [40]. The experimental error in Φ_Δ and $\Phi_{\text{t-c}}$ is ±20%. The measurements refer to 24 ± 2 °C.

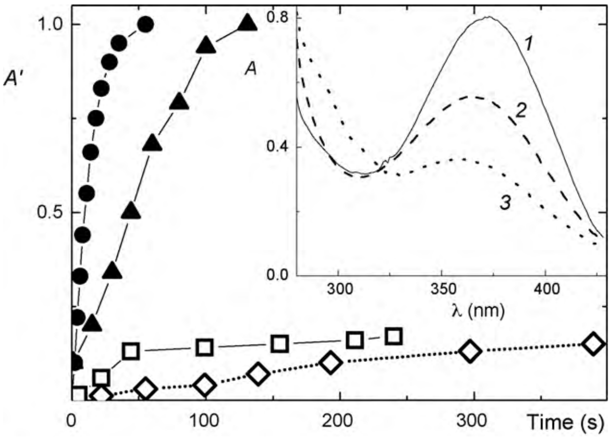


Fig. 1. Time-dependence of the absorbance decrease at 390 nm due to *trans* → *cis* isomerization of HN in argon-saturated benzene (circles) *vs.* the time of irradiation at 366 nm; relative changes in dichloromethane (triangles), acetonitrile (squares) and ethanol (diamonds); insets: absorption spectra in benzene at 0, 2 and 10 s irradiation time, 1–3, respectively.

3. Results

3.1. *Trans* → *cis* isomerization

UV irradiation of HN in argon-saturated acetonitrile decreases the absorbance of the band centered at $\lambda_t = 376$ nm, and a concomitant increase at the maximum of the *cis* isomer ($\lambda_c = 270$ nm) was observed. For irradiation at 366 nm in benzene, the absorbance decrease is stronger, and the photostationary equilibrium contains more *cis* isomer (Fig. 1, inset). The photoprocess is attributed to *trans* → *cis* isomerization. Irradiations with a continuous light of 406 nm wavelength or with the pulses of a XeCl excimer laser ($\lambda_{exc} = 308$ nm) bring about similar spectral changes (not shown). The photostationary state in the latter case contains more *trans* isomer. The alteration of the HN absorbance at 375 nm (A_{375}) in benzene, dichloromethane, acetonitrile and ethanol as a function of irradiation time is plotted in Fig. 1. The $\Phi_{\text{t-c}}$ values, derived from the slopes of the initial linear parts are compiled in Table 1. Efficient photoisomerization was found in benzene ($\Phi_{\text{t-c}} = 0.42$), but $\Phi_{\text{t-c}}$ significantly diminishes with increasing solvent polarity, reaching 0.02 in acetonitrile and an even smaller value in ethanol. The absence or presence of oxygen had no discernible effect.

The absorption maximum of HDN is red-shifted by ca. 25 nm with respect to that of HN. Examples for the change of the absorption spectra upon irradiation at 366 nm are shown in curves 1–3 of Fig. 2 and in the inset of Fig. 3. The time-dependence of the absorbance at 400 nm (Fig. 3) could be attributed to *trans* → *cis* isomerization. $\Phi_{\text{t-c}}$ is 0.08 for HDN in benzene and even smaller in solvents of larger polarity. Inspired by the pioneering work of Splitter and Calvin [36], we also studied the phototransformation of HDN. In sufficiently concentrated solutions, HPLC analyses showed two major product peaks with retention times 16.4 and 9.3 min, which are attributed to the corresponding hydroxyphenylisato-

Table 1
Absorption maximum of *trans*-hydroxynitrostilbenes and quantum yield of *trans* → *cis* isomerization[a].

Solvent	E_T^N	λ_t (nm)		$\Phi_{\text{t-c}}$	
		HN	HDN	HN	HDN
Toluene	0.10	372	398	0.42	
Benzene	0.11	372	395	0.40	0.08
Trichloroethene	0.16	375	398	0.32	
Tetrahydrofuran	0.21	378	403	0.24	
Chloroform	0.26	380	406	0.14	
Dichloromethane	0.31	372	400	0.12	0.04
Acetonitrile	0.46	376	399	0.02	0.03
Ethanol	0.65	382	406	0.01	0.01

[a] In argon-saturated solution, $\lambda_{irr} = 366$ nm.

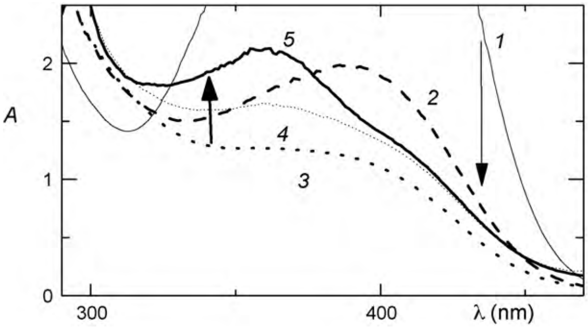


Fig. 2. Absorption spectra of HDN in argon-saturated benzene at 0, 240 and 300 s irradiation at 366 nm, 1–3, respectively; and at 1 (4) and 4 h (5) thermal relaxation.

gen and 2-amino-4-nitrobenzaldehyde, respectively. The molar absorption coefficient of 2-(4-hydroxyphenyl)-6-nitroisatogen in benzene is $\varepsilon_{320} = 1.6 \times 10^4\ \mathrm{M^{-1}\,cm^{-1}}$ [36]. The photoconversion is essentially the same in benzene and toluene and not affected by the absence or presence of air. Moreover, the same two product peaks were also found when the reaction was performed in dichloromethane or acetonitrile. Careful inspection revealed a significant variation of the absorption spectra when monitored after ceasing photoirradiation (see curves 3–5 in Fig. 2) indicating the transformation of the photoproducts via thermal reaction(s).

3.2. Phosphorescence of singlet molecular oxygen

Singlet molecular oxygen was detected upon pulsed excitation of (di)nitrostilbenes in air-saturated solution. The quantum yield (Φ_Δ) of $O_2(^1\Delta_g)$ formation, measured in various solvents (Table 2), can be considered as minimum measure of Φ_{isc}. For HN, Φ_Δ is between 0.45 in benzene and 0.03 in acetonitrile. The introduction of a second nitro substituent markedly decreases Φ_Δ and the largest $\Phi_\Delta = 0.2$ value was obtained in benzene.

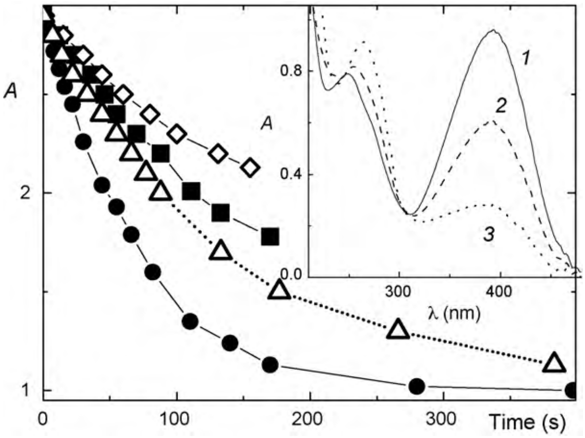


Fig. 3. Plots of the absorbance at 410 nm as a function of the time of irradiation at 366 nm for HDN in argon-saturated benzene (circles), dichloromethane (triangles), acetonitrile (squares) and ethanol (diamonds); insets: absorption spectra of in acetonitrile at 0, 1 and 5 min photolysis time, 1–3, respectively.

Table 2
Quantum yield of singlet molecular oxygen formation Φ_Δ of *trans*-hydroxynitrostilbenes[a].

Solvent	4-Nitrostilbene[b]	2,4-Dinitrostilbene[b]	HN	HDN
Toluene	0.16 (0.19)[c]	0.10	0.43	
Benzene	0.14	0.22	0.45	0.2
Dichloromethane	0.12	0.04	0.12	0.05
Acetonitrile			0.03	<0.02

[a] In oxygen-saturated solution, $\lambda_{exc} = 308$ nm.
[b] Taken from Ref. [8].
[c] In cyclohexane.

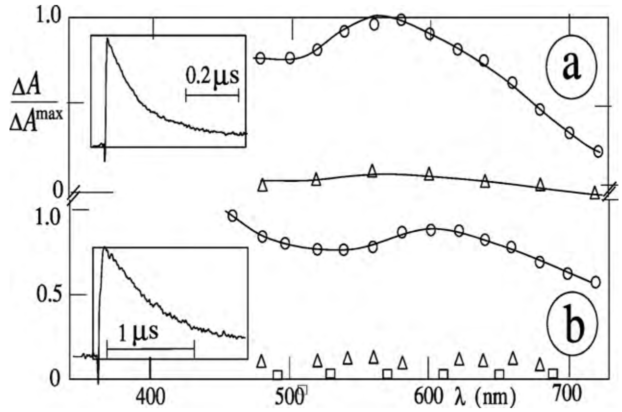


Fig. 4. Transient absorption spectra of *trans*-HN in argon-saturated (a) benzene and (b) acetonitrile at 20 ns (○), 1 µs (△) and 10 µs (□) after the 308 nm pulse; inset: kinetics at 560 nm.

3.3. Triplet absorption properties

Pulsed excitation of HN or HDN at 308 nm in solvents of different polarity leads to fluorescence followed by the appearance of a T-T absorption signal when the fluorescence is weak. The T-T absorption spectra are generally broad with one or two maxima (λ_T), e.g. $\lambda_T = 560$ nm for HN in benzene, whereas $\lambda_T = 450$ and 600 nm in acetonitrile. Examples of the T-T absorption spectra and the signals corresponding to the formation and decay of triplet-excited species are shown in Figs. 4 and 5 for HN and HDN, respectively. The triplet lifetime (τ_T) of HN under argon is $\tau_T = 0.2$–$1\ \mu$s. T-T annihilation has virtually no significance since it contributes to the decay only at high laser intensities. Oxygen quenches the triplet with a rate constant of typically $k_{ox} = (2–4) \times 10^9\ \mathrm{M^{-1}\,s^{-1}}$. The triplet yield relative to that in benzene or toluene (Φ_{isc}^{rel}) varies between 1 and 0.04 reaching the latter value in ethanol. The attachment of the second nitro group barely affects τ_T, but significantly decreases Φ_{isc}^{rel} (Table 3).

4. Discussion

4.1. Deactivation pathways of excited HN

The *trans* → *cis* isomerization of 4-nitrostilbene occurs via the Franck-Condon state ($^1trans_{FC}^*$), the excited *trans* singlet state ($^1trans^*$) and the lowest *trans* triplet state ($^3trans^*$) [7]. The triplet

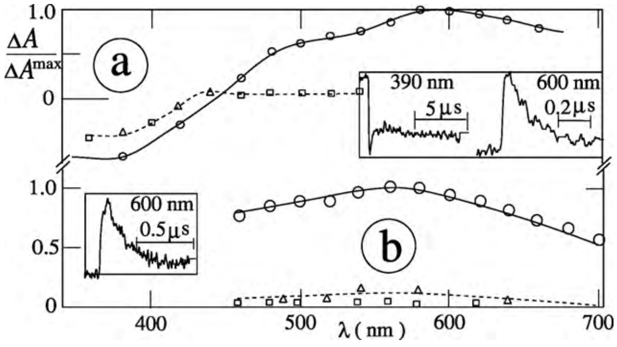


Fig. 5. Transient absorption spectra of *trans*-HDN in argon-saturated (a) benzene and (b) acetonitrile at 20 ns (○), 1 µs (△) and 10 µs (□) after the 308 nm pulse; inset: kinetics as indicated.

Table 3
Triplet properties of *trans*-hydroxynitrostilbenes[a].

Solvent	τ_T (μs)		k_{ox} (10^9 M^{-1} s^{-1})		$\Phi_{isc}{}^{rel\ b}$	
Benzene	0.23	0.27	4	4	0.98	0.18
Dichloromethane	0.8	0.4		2	0.3	0.12
Acetonitrile	0.9	0.3	4	3	0.1	0.08
Ethanol	0.4				0.08	0.08

[a] In argon-saturated solution, λ_{exc} = 308 nm.

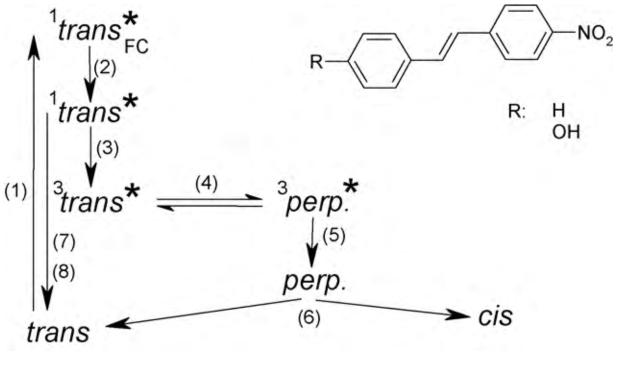
[b] Taking ΔA_{580} and using $\Phi_{isc}{}^{rel}$ = 1 for HN in toluene.

mechanism also involves an equilibrium between triplet-excited species of *trans* and perpendicular ($^3perp^*$) conformations. This is well established for *trans*-4-nitrostilbenes [3–11] and is now also proposed for HN (Scheme 2). After excitation into the $^1trans_{FC}{}^*$ state (1), the $^1trans^*$ state is populated (2), which decays mainly by intersystem crossing to the *trans* triplet state (3). Twisting around the C═C double bond then populates the $^3perp^*$ state (4). After the second intersystem crossing, further twisting leads to the perpendicular ground state (5), through which the *cis* form is produced (6).

The results for HN (Tables 1–3) are in accordance with *trans* → *cis* photoisomerization via the triplet mechanism. There are, however, significant differences caused by the presence of the hydroxy group. One is the decrease of Φ_{isc} with increasing solvent polarity. This is in contrast to the behaviour of *trans*-4-nitrostilbene, which has larger Φ_{isc} in polar media [3,6,7]. E_T^N parameters were used for the characterization of solvents [41]. Another difference is photoionization. Upon pulsed excitation of hydroxystilbenes in aqueous solution biphotonic ionization is possible, this has been reported for phenols [42]. The (monophotonic) quantum yield of ionization, i.e. formation of the phenoxyl radical from phenol, has been found to be 0.05 in several non-aqueous solvents [42]. In analogy to phenol, photoelectron detachment could occur for hydroxystilbenes.

4.2. Fluorescence vs. intersystem crossing

For 4-methoxy- or 4-alkylamino-substituted 4′-nitrostilbenes, fluorescence (7) and internal conversion at the *trans* side (8), which compete with intersystem crossing (3), are sensitive to the solvent properties [4,7]. Owing to the much larger dipole moment of the $^1trans^*$ state compared to that of the ground state, the excited state properties (energy, lifetime, rate constants) depend on the polarity and polarizability of the medium. The fluorescence properties of HN, i.e. the changes in excitation and emission spectra, Φ_f and τ_f, have recently been investigated [35]. The results can be rationalized by the competing deactivation pathways of the $^1trans^*$ state. In solvents of low polarity, the largest Φ_{isc} is observed, which is accompanied by small Φ_f and short τ_f values. These indicate that the main deactivation of HN in solvents of low polarity is step (3). With increasing E_T^N, the energy of $^1trans^*$ is lowered, Φ_f grows and Φ_{isc} is reduced. Both Φ_f and τ_f have a maximum in butyronitrile or dichloromethane, i.e. in solvents with E_T^N = 0.3–0.4. The opposite change of Φ_{isc} and Φ_f evidences that the rate constant of step (3) strongly diminishes when the solvent polarity is raised from benzene to butyronitrile. This effect may indicate intersystem crossing via a higher triplet-excited state (T_n). In an apolar medium, such as benzene, the energy of the T_n state is close to that of $^1trans^*$ facilitating rapid intersystem crossing. However, the interaction with more polar solvents enhances the energy gap between $^1trans^*$ and T_n states thereby decelerating triplet formation. In strongly polar solvents, the enhanced charge transfer character of the $^1trans^*$ state leads to accelerated internal conversion, step (8). Thus, the significant increase of Φ_f and τ_f from apolar to medium polar solvents is attributed to the deceleration of intersystem crossing, whereas the decrease of $\Phi_{isc,}$ Φ_f and τ_f from medium polar to polar solvents originates from the growing rate of internal conversion.



Scheme 2.

4.3. Effects of the 4-hydroxy substituent

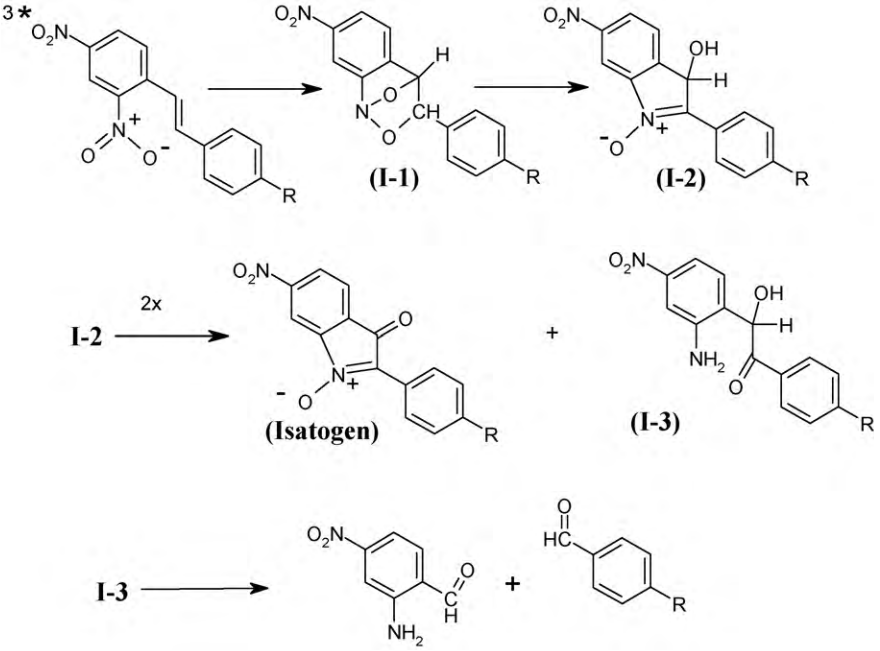
The most important effect of the introduction of a hydroxy group is that it brings about solvent dependent fluorescence behaviour [35]. This is in contrast to the properties of 4-nitrostilbene, which has small Φ_f irrespective of the solvent [7]. Another feature of the hydroxy derivatives is the large effect of solvent polarity on *trans* → *cis* photoisomerization, see Table 1. $\Phi_{t\text{-}c}$ of HN in toluene or benzene are only slightly smaller than that of nitrostilbene (Fig. 1 and Table 1) since intersystem crossing is the dominant process in both singlet-excited compounds. However, the $\Phi_{t\text{-}c}$ values of 4-nitrostilbene are not sensitive to solvent polarity [7] because transition to the triplet state is very efficient irrespective of the medium. On the other hand, the triplet lifetime of nitrostilbene is generally short [27]. Similar τ_T values are found for hydroxynitrostilbenes, but they are somewhat longer for HN in dichloromethane and acetonitrile (Table 3).

4.4. Effects of the o-nitro group

Φ_f of 2,4-dinitrostilbene is relatively small, e.g. Φ_f = 0.004 in methyltetrahydrofuran [8], but enhanced with respect to 4-nitrostilbene. For the corresponding hydroxy-substituted derivatives, an opposite trend was observed; the fluorescence of HDN is always weaker [35]. The second nitro group in HDN reduces Φ_{isc} in polar solvents resulting in smaller $\Phi_{t\text{-}c}$ values. These changes probably arise from the significant acceleration of the internal conversion from the $^1trans^*$ state. The combined electron withdrawing effects of the two nitro groups enhance the charge transfer character of the lowest singlet-excited state of HDN leading to a substantial increase in the rate of energy dissipation via radiationless transitions to the ground state. This is the reason for the significantly smaller $\Phi_{t\text{-}c}$ values of HDN (Table 1), compared to $\Phi_{t\text{-}c}$ = 0.48 in cyclohexane and 0.3 in acetonitrile for 2,4-dinitrostilbene [8]. The τ_T values listed in Table 3 are longer than those of 2,4-dinitrostilbene, which range from 45 ns in cyclohexane to 65 ns in ethanol [8]. The difference may originate from the slower isomerization in the case of the former compound.

Indol-3-one-1-oxides (isotagens) and 2-amino-4-nitrobenzaldehyde have been identified as photoproducts of several *trans*-4-R-2′,4′-dinitrostilbenes (R: dimethylamino or hydroxy [36]). Phototransformations to isotagens have been also reported by other groups [37–39]. In all cases in the literature (as far as we know) benzene was employed as solvent without exclusion of oxygen [36–39]. Splitter and Calvin proposed a reaction sequence including the photoinduced formation into two intermediates (I-1 and I-2).

The mechanism is shown in Scheme 3. As modification, we suggest intermediate (I-3) as reduced equivalent to the hydrox-



Scheme 3.

yphenylisatogen of HDN (R: OH). Splitting of I-3 is proposed to account for formation of 2-amino-4-nitrobenzaldehyde. We further suggest that the main photoreaction is a *trans* → *cis* isomerization. This would provide the necessary flexibility as premise for the two cyclization steps prior to formation of I-1, which could be short-lived. Once I-2 is formed, the redox reaction to the hydroxyphenylisatogen and I-3 is slow, see curves 3–5 in Fig. 2. HDN and I-1/I-2 are spectroscopically indistinguishable with our method. Apparently, the solvent has no specific role for the product pattern, but can influence the efficiency of the phototransformation of HDN. The photochemical reaction is much more important for 4-dimethylamino-2′,4′-dinitrostilbene, where even in slightly polar solvents ($E_T^N > 0.1$) virtually no cis isomer is formed [8]. The estimate of $\Phi_{\text{t-c}} = 0.08$ for HDN in benzene probably corresponds to the quantum yield of the total photoconversion.

5. Conclusion

Laser flash photolysis studies with transient absorption and singlet molecular oxygen phosphorescence detection demonstrated that the quantum yield of triplet HN and HDN formation is strongly solvent dependent. The *trans* → *cis* photoisomerization of the two hydroxynitrostilbenes takes place via the triplet-excited state. The dominant relaxation process of the singlet-excited HN is intersystem crossing in apolar media, but its rate significantly decreases when the solvent polarity is enhanced. Internal conversion exhibits an opposite solvent polarity dependence, therefore, it becomes the fastest deactivation pathway in polar medium. Introduction of a second nitro substituent enhances the charge transfer character of the lowest singlet-excited state bringing about efficient internal conversion in all solvents. The small values of Φ_{isc}, Φ_{f}, $\Phi_{\text{t-c}}$ and τ_{f} for singlet-excited HDN under all conditions are due to the rapid transition to the ground state. The two observed products of prolonged irradiation of HDN are 2-(4-hydroxyphenyl)-6-nitroisatogen and 2-amino-4-nitrobenzaldehyde.

Acknowledgements

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