

# Intense Long-Lived Fluorescence of 1,6-Diphenyl-1,3,5-Hexatriene: Emission from the S<sub>1</sub>-State Competes with Formation of O<sub>2</sub> Contact Charge Transfer Complex

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## ABSTRACT

The fluorescence kinetics of 1,6-diphenyl-1,3,5-hexatriene (DPH) dissolved in cyclohexane was investigated as a function of temperature, concentration and 355 nm excitation pulse energy. At concentrations above 2.5 μM and excitation energies above 1 mJ a long-lived, very intense emission, which appears within less than 5 ns and lasts up to 70 ns, is observed. During the first 50 ns the decay does not follow an exponential but rather a linear behaviour. In oxygen saturated solutions the long-lived emission is suppressed and solely short-lived fluorescence with  $\tau < 5$  ns can be detected. A kinetic simulation was performed, based on a model whereupon the long-lived emission originates from the S<sub>1</sub>-state and competes with the formation of DPH-O<sub>2</sub> contact charge-transfer complexes and intersystem crossing which both quench the fluorescence. Our investigations show that even the small amount of oxygen dissolved in nitrogen saturated solutions has a distinct influence on the fluorescence kinetics of DPH.

**Keywords:** DPH; Time-Resolved; Fluorescence; Simulations; Kinetics; Diphenylpolyenes

## 1. Introduction

Carotenes constitute an important molecular class for photosynthesis. They are part of the light-harvesting complex, where they absorb visible light and transfer the energy to the reaction center of the photosystem. All-*trans*- $\alpha,\omega$ -diphenylpolyenes (also referred to as minicarotenes) are well established as model compounds for the bigger carotenoids such as  $\beta$ -carotene or lutein [1-6]. The latter absorb light and transfer the energy to the chlorophyll unit of the pigment [7]. Another function is protection of the photosynthetic apparatus against damage by highly reactive singlet oxygen [8]. The photophysical properties of these molecules are complex and not fully understood.

Because of its strong emission 1,6-diphenyl-1,3,5-hexatriene (DPH) is used as a fluorescence probe in biological membrane systems [9]. It is known, that the measured fluorescence lifetime is longer than that calculated using the Stickler-Berg [10] relationship and that the lifetime varies with the solvent [11,12]. Hudson and Kohler found evidence that the lowest excited singlet state in diphenyloctatetraene is the <sup>1</sup>A<sub>g</sub>-state with the

<sup>1</sup>B<sub>u</sub>-state lying slightly above and applied this ordering of states to other polyenes as well [12-14]. Alford and Palmer stated that DPH emission occurs from both states [15]. In the gas phase fluorescence lifetimes up to 90 ns are reported and assigned to S<sub>1</sub>-(<sup>1</sup>A<sub>g</sub>) state emission with intensity borrowing from the S<sub>2</sub>-(<sup>1</sup>B<sub>u</sub>) state [16].

Combined density functional theory/multi reference configuration interaction (DFT/MRCI) calculations of the low-lying singlet and triplet states of mini- $\beta$ -carotenes showed that the sequence of states depends on conjugation length and nuclear geometry [17]. According to the DFT/MRCI calculations for DPH the lowest excited singlet state upon vertical excitation is the <sup>1</sup>B<sub>u</sub>-state, while it switches order with the <sup>1</sup>A<sub>g</sub>-state during geometry relaxation [18]. Equilibration of the states takes place within less than a picosecond [19,20], due to the conical intersection between the S<sub>1</sub> and S<sub>2</sub> potential energy hypersurfaces [18].

Emission from the S<sub>1</sub>-state is symmetry forbidden, but it can occur via mixing with the S<sub>2</sub>-state, due to the small S<sub>1</sub>-S<sub>2</sub> energy gap [21,22]. Unlike the S<sub>1</sub>-state, the energy of the S<sub>2</sub>-state is influenced by the solvent, which leads to a solvent dependent S<sub>1</sub>-S<sub>2</sub> energy gap and because of the state mixing to a solvent dependent S<sub>1</sub> radiative rate

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[14].

Saltiel *et al.* presented evidence showing that the fluorescence spectrum of DPH not only consists of the combined  $S_1/S_2$ -emission, but also of emission from the *s-cis* conformers of DPH [23-27]. Catalán confirmed the influence of *s-cis* conformers on the emission spectra also for other minicarotenes by calculations [28,29]. A detailed resolution of the emission spectra was accomplished by Turek *et al.* [30].

We observe DPH emission with an exceptionally long lifetime which decays non-exponentially under special experimental conditions. The long lifetime may be due to the emission originating from a forbidden transition. But to understand the unusual temporal behaviour, additional influences have to be considered. In this work we studied the temporal fluorescence behavior under different conditions like various DPH and  $O_2$  concentrations and different temperatures and excitation laser pulse energies to identify the various competing processes like formation of DPH- $O_2$  contact charge-transfer (CCT) complexes, whose interplay leads to the linear decay of the long-lived emission.

## 2. Materials and Methods

1,6-Diphenyl-1,3,5-hexatriene (98%, Aldrich) and cyclohexane (99+%, Acros Organics) were used without further purification. The nanosecond transient fluorescence setup (Applied Photophysics) utilizes the output from a frequency tripled (355 nm) pulsed Nd:YAG laser (Inolas) for photoexcitation. DPH samples were excited with 0.01 - 5 mJ pump energy at 5 ns laser pulse width and 1 or 10 Hz repetition rate. The short laser pulse is created by cutting out the maximum of the 12 ns pulse with a pockels cell. The pump beam of 1 cm diameter is directed into the sample (a flow-through 3.5 mL cuvette) perpendicular to the fluorescence sampling direction. If not stated otherwise, the solution reservoir was purged with nitrogen during the experiment to remove dissolved oxygen from the solutions. The same setup was used to saturate the solutions with oxygen. The samples were purged at least for 20 minutes before the start of the first measurement. The fluorescence light is dispersed behind the sample with a grating monochromator (Applied Photophysics) for wavelength selection. The output signal is detected by a photomultiplier (R928, Hamamatsu) and digitized by an oscilloscope (Agilent Infinium). Typically 16 laser pulses are averaged to record a kinetic trace at a selected wavelength. Stationary absorption spectra were recorded with a Cary 50 (Varian) spectrometer.

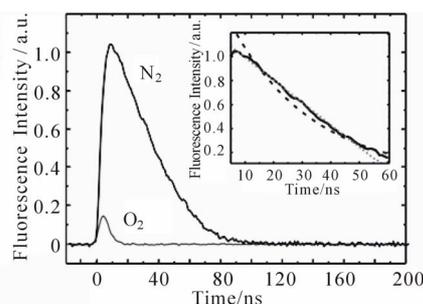
The simulations of the kinetic curves were performed with Mathcad 2001 (MathSoft, Inc.) by solving the coupled nonlinear partial differential equations by numerical integration.

## 3. Results and Discussion

1,6-Diphenyl-1,3,5-hexatriene in cyclohexane shows strong absorption in the region of 300 - 380 nm [11, 21,31]. The excitation wavelength used for our transient fluorescence measurements (355 nm) is near to the absorption maximum of DPH at 353 nm. The emission is very intense and can be detected in solutions with DPH concentrations below  $10^{-10}$  mol/L (spectra not shown here). After excitation, the fluorescence kinetics can be investigated in our setup. **Figure 1** shows the fluorescence decay of an  $8.0 \times 10^{-6}$  M DPH solution flushed with nitrogen. The fluorescence intensity reaches its maximum within the 5 ns laser pulse and subsequently decreases linearly until 50 ns after the laser pulse, where the decay becomes monoexponential. As can be seen in the inset, a monoexponential fit does not describe the observed fluorescence decay as well as a linear fit. Linear decay kinetics are characteristic for zero order reactions which are typical for systems saturated by the reactants (no concentration change) or for processes where the minority partner is regenerated, like a catalyst. The rate constant  $k$  obtained according to the rate law  $[DPH]_t = -kt + [DPH]_0$  is  $1.85 \times 10^7 \text{ M}\cdot\text{s}^{-1}$ .

If the same sample is flushed with oxygen, fluorescence intensity and lifetime decrease dramatically (**Figure 1**).

Under these conditions the fluorescence decay is best described monoexponentially, with a decay time of  $\tau = 4.59 \text{ ns} \pm 0.11 \text{ ns}$ , which corresponds to the laser pulse width. Thus, the observed decay time does represent an upper limit for the emission lifetime. The dispersed emission spectra after laser excitation of both the nitrogen and oxygen flushed samples agree with the stationary emission spectrum, except for the distortion in the region around 470 nm, where  $S_1 \rightarrow S_n$  absorption takes place [32,33]. If the oxygen flushed sample is flushed

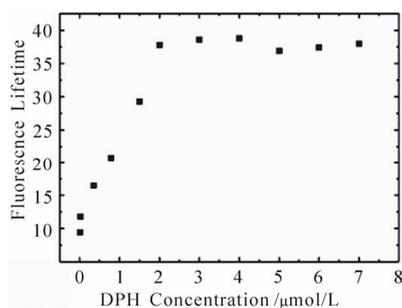


**Figure 1.** Kinetic curves of DPH ( $8.0 \times 10^{-6}$  M) at 427 nm upon excitation at 355 nm with 1 mJ pulse energy. The sample flushed with nitrogen shows long-lived fluorescence. In the presence of oxygen intensity and lifetime of the fluorescence are decreased significantly. The decay of the nitrogen flushed sample can be seen on a larger scale in the inset with monoexponential (dashed line) and linear (dotted line) fits.

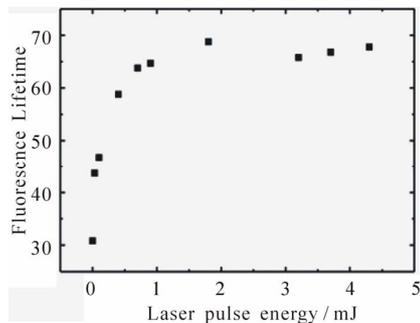
again with nitrogen, the long-lived fluorescence reappears. The decrease of fluorescence lifetime and intensity is thus not caused by oxygen induced chemical degradation of DPH but by a reversible physical process.

Both intensity and lifetime of the long-lived fluorescence increase with increasing concentration, see **Figure 2**. At concentrations below 1  $\mu\text{M}$  the fluorescence decays exponentially. Above 1  $\mu\text{M}$  the decay shows the aforementioned linear behaviour. Therefore the fluorescence lifetimes shown in **Figure 2** were obtained by monoexponential ( $[\text{DPH}] < 1 \mu\text{M}$ ) and linear ( $[\text{DPH}] > 1 \mu\text{M}$ ) fits of the kinetic traces. Upon excitation with 0.3 mJ pulse energy the lifetime reaches a plateau at 37 ns and does not increase further with increasing concentration. At concentrations below 1  $\mu\text{M}$  the number of DPH molecules within the excitation volume is smaller than the number of photons irradiating the sample ( $N_{\text{photon}} \approx 5.4 \times 10^{14}$ ). The saturation plateau at  $\approx 1.8 \mu\text{M}$  DPH at 0.3 mJ pulse energy can thus be explained by nearly complete photon absorption if the number of molecules exceeds the number of photons sufficiently.

A further increase of fluorescence lifetime can be



**Figure 2.** Fluorescence lifetime of DPH in cyclohexane at 427 nm upon excitation at 355 nm with 0.3 mJ pulse energy as a function of DPH concentration. The kinetic curves were fitted monoexponentially at concentrations below 1 mM ( $\tau$  given in ns) and linear above 1 mM ( $\tau$  given in  $\text{ns}\cdot\text{M}^{-1}$ ).

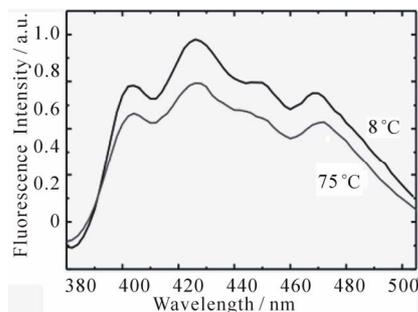


**Figure 3.** Dependence of fluorescence lifetime of DPH in cyclohexane ( $8.0 \times 10^{-6} \text{ M}$ ) at 427 nm upon pumping at 355 nm on excitation laser pulse energy. For calculation of the lifetime the kinetic curves were fitted linear ( $\tau$  given in  $\text{ns}\cdot\text{M}^{-1}$ ).

reached by an increase of laser pulse energy. The effect of pulse energy on the fluorescence lifetime of an  $8.0 \times 10^{-6} \text{ M}$  DPH solution is shown in **Figure 3** between 0.01 mJ and 4 mJ. In the region of laser pulse energies below 1 mJ ( $N_{\text{photon}} < 1.8 \times 10^{15}$ ) the lifetime increases with increasing laser pulse energy, since the number of photons is smaller than the number of molecules ( $N_{\text{molecule}} \approx 2.4 \times 10^{15}$ ). Above 1 mJ once again a plateau is reached (at 68 ns for the  $8.0 \times 10^{-6} \text{ M}$  DPH solution). Our results thus show that fluorescence intensity and lifetime depend on the concentration of excited molecules.

The observed concentration dependence points to aggregate formation as possible cause of the long-lived fluorescence. It is well known that larger carotenoids are capable of forming aggregates easily. The emission of the aggregates is generally blue-shifted with respect to the emission of the monomer [34]. Increase of temperature leads to aggregate dissociation and a corresponding red-shift of the emission [35]. To check if the long-lived emission originates from DPH aggregates, the emission spectra of DPH were measured at different solution temperatures, spanning the complete range between melting point and boiling point of cyclohexane. The spectra at 8°C and 75°C are shown in **Figure 4**. While the shape of the kinetic traces stays unchanged (see **Supplementary Material S1**), it is evident that an increase of temperature leads to a decrease of fluorescence intensity. This behaviour is reversible, *i.e.* decreasing the temperature leads to recovery of the intensity. However, no spectral changes could be observed. Therefore, we assume that DPH does not form aggregates in cyclohexane to an appreciable extent in the concentration range of our studies. We attribute the change of intensity to an increased molecular diffusion rate at higher temperatures and therefore increased collisional quenching of the fluorescence.

The correct mechanism for generation of the long-lived fluorescence has to take the following experimental findings into account: 1) fluorescence lifetimes up to  $\sim 70$  ns, see **Figure 1**; 2) zero order decay of fluorescence intensity at short times followed by exponential decay,



**Figure 4.** Emission spectra of DPH in cyclohexane ( $8.0 \times 10^{-6} \text{ M}$ ) upon excitation at 355 nm with 1 mJ pulse energy at 8°C and 75°C. The spectra were obtained by integrating the emission during the first 30 ns after the laser pulse.

see **Figure 2**; 3) significant population of the DPH triplet state, because we observed intense triplet-triplet absorption (spectra not shown here, since they are well known [19,20,24,36,37]; 4) fluorescence lifetime depends on the concentration of electronically excited DPH, see **Figures 2 and 3**; 5) fluorescence intensity decreases with increasing temperature, see **Figure 4**; 6) fluorescence is quenched by higher oxygen concentrations, see **Figure 1**.

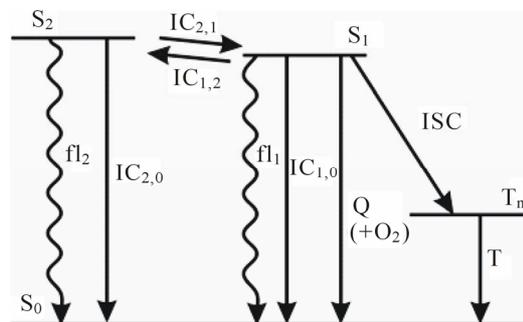
Different mechanisms can be discussed to explain these effects. It is known, that triplet-triplet annihilation (TTA) generates excited singlet state population with an increased fluorescence lifetime. But TTA is diffusion controlled and therefore, at the concentrations studied in this work, too slow to explain the <5 ns fluorescence risetime observed in our experiments [38]. Furthermore, the triplet ground state of DPH is very low in energy, so that the energy available by triplet-triplet annihilation is insufficient to populate the lowest excited singlet state [24,39]. Additionally, the quantum yield for intersystem crossing (ISC) of DPH is very small (*i.e.* 0.02 in benzene and ethanol) [40]. Nevertheless the triplet state has to be included in any model explaining the long-lived fluorescence since ISC is a competing pathway for depopulation of excited singlet states.

Ionisation, followed by electron-cation recombination to electronically excited singlet states, could also cause long fluorescence lifetimes in principle. By the recombination process, the emitting singlet state becomes populated during a certain time period, which extends the emission time. To ionize DPH (ionisation potential: 7.27 eV [41]) upon excitation with 355 nm (3.49 eV) a multiphoton process is required. The lifetime should be longer in polar solvents but very short in nonpolar solvents, since electrons are not stabilized in nonpolar solvents and recombine immediately. All experiments presented here were performed in cyclohexane, a nonpolar solvent. We did observe long-lived fluorescence in other solvents as well, but no correlation between polarity of the solvent and fluorescence lifetime was discernible from our experiments. Therefore, ionisation and recombination is not considered to be important for the emergence of long-lived DPH fluorescence.

We instead propose the mechanism displayed in **Figure 5** to explain the intense long-lived DPH fluorescence. The corresponding kinetic equations, which are used to simulate the observed kinetic traces, are as follows:

$$\frac{d[S_0]}{dt} = k_{\beta_1}[S_1] + k_{\beta_2}[S_2] + k_Q[S_1][O_2] + k_{IC_{2,0}}[S_2] + k_{IC_{1,0}}[S_1] + k_T[T_n] \quad (1.1)$$

$$\frac{d[S_1]}{dt} = -k_{\beta_1}[S_1] - k_Q[S_1][O_2] + k_{IC_{2,1}}[S_2] - k_{IC_{1,2}}[S_1] - k_{IC_{1,0}}[S_1] - k_{ISC}[S_1] \quad (1.2)$$



**Figure 5. Proposed mechanism for emergence of long-lived fluorescence. Photoisomerization processes are not shown for clarity reasons.**

$$\frac{d[S_2]}{dt} = -k_{\beta_2}[S_2] - k_{IC_{2,1}}[S_2] - k_{IC_{2,0}}[S_2] + k_{IC_{1,2}}[S_1] \quad (1.3)$$

$$\frac{d[T]}{dt} = k_{ISC}[S_1] - k_T[T_n] \quad (1.4)$$

After excitation of DPH into the  $S_2$ -state a cascade of processes follows. Internal conversion into the  $S_1$ -state ( $IC_{2,1}$ ) as well as the  $S_0$ -state ( $IC_{2,0}$ ) occurs fast and competes with (short-lived) fluorescence ( $fl_2$ ) from the  $S_2$ -state. The lifetime of the  $S_1$ -state is affected by internal conversion into the ground state ( $IC_{1,0}$ ), reverse internal conversion into the  $S_2$ -state ( $IC_{1,2}$ ) and intersystem crossing into the triplet state (ISC). Additionally, CCT complex formation with oxygen takes place. Other  $O_2$ -induced processes may occur as competing processes, e.g. singlet oxygen formation or photoisomerization [42]. These processes, with the CCT complex formation as main reaction are described as oxygen quenching, (Q). In the simulation non-radiative, non-oxygen induced processes which depopulate the  $S_1$ -state are indistinguishable from each other, as long as the emerging state or species has no influence on the  $S_1$ -state. This includes  $IC_{1,0}$  and ISC as well as other possible processes, like isomerization (iso, not shown in **Figure 5**). Therefore it is appropriate to use a combined rate constant  $k_{dep}$  for  $S_1$ -state depopulation.

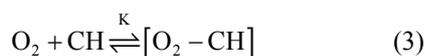
$$k_{dep} = k_{IC_{1,0}} + k_{ISC} + k_{iso} + \dots \quad (2)$$

$IC_{1,2}$  is not included, since here the  $S_2$ -state is repopulated and subsequently  $IC_{2,1}$  takes place, which means that the  $S_1$ -state population is influenced by the state emerging from this process. Emission from the  $S_1$ -state to the electronic ground state ( $fl_1$ ) is symmetry forbidden and should be weak, but can be promoted by intensity borrowing via  $S_1$ - $S_2$ -state mixing. The triplet state is depopulated within several microseconds (T) [24].

In the following we substantiate our model. Kohler and Spiglanin observed a DPH fluorescence lifetime of 90.7 ns in the gas phase and assigned this to emission

from the  $S_1$ -state which borrows intensity from the nearby  $S_2$ -state [16]. We follow this assignment and ascribe the long-lived fluorescence observed in our experiments to emission from the  $S_1$ -state. The zero order fluorescence decay of deoxygenated DPH solutions necessitates a quencher of constant concentration. The most obvious candidate is oxygen which at high concentrations quenches the long-lived fluorescence of DPH completely. Although the solutions were purged with nitrogen continuously during the experiments to avoid quenching, a small amount of oxygen remains in the solution [43]. It is well known, that molecular oxygen forms contact complexes with hydrocarbons [43-46], whether they are unsaturated, like DPH, or saturated, like cyclohexane (CH), from which absorption to the contact charge-transfer complex ( $M^+O_2^-$ ) can take place. Strong  $O_2/CH$  CCT complex absorption occurs in the region around 210 nm [43]. A deconvolution of the broad absorption band was carried out for unpurged cyclohexane as well as for nitrogen and oxygen saturated cyclohexane, and the  $O_2$ -CH contact complex concentrations were determined (see **Table 1**) using the extinction coefficients published by Brownrigg and Kenny [43] (for a detailed description see **Supplementary Material S2**). The same analysis was carried out for a solution of DPH in cyclohexane. By saturating the unpurged solutions with nitrogen, the contact complex concentration is reduced by at least an order of magnitude, but the amount of remaining oxygen is still considerable ( $[O_2 - CH] = 0.2$  mM).

We assume that oxygen bound in the  $O_2$ -CH complex does not contribute to quenching of the DPH fluorescence in contrast to free oxygen which is in equilibrium with the  $O_2$ -CH contact complex:



To include the oxygen quenching into the simulation it

**Table 1. Concentration of the contact complex  $[O_2-M]$  in cyclohexane and in a DPH/cyclohexane solution ( $8.0 \cdot 10^{-6}$  M), calculated from deconvoluted UV/Vis absorption and the extinction coefficients published by Brownrigg and Kenny [43].**

sample	purging gas	$[O_2-M]$
		mol·L <sup>-1</sup>
cyclohexane	O <sub>2</sub>	- <sup>a)</sup>
cyclohexane	unpurged	$2.1 \times 10^{-3}$
cyclohexane	N <sub>2</sub>	$2.4 \times 10^{-4}$
DPH + cyclohexane	O <sub>2</sub>	- <sup>a)</sup>
DPH + cyclohexane	unpurged	- <sup>a)</sup>
DPH + cyclohexane	N <sub>2</sub>	$2.5 \times 10^{-4}$

<sup>a)</sup>Complex absorption too large to determine complex concentration.

is thus necessary to estimate the amount of free oxygen contained in the solution. It is safe to assume that the equilibrium is strongly located on the side of the contact complex [46-48]. For some hydrocarbons the value of the equilibrium constant  $K$  is known to be larger than 1000 M<sup>-1</sup>. In our case this would imply a free oxygen concentration on the order of  $3 \times 10^{-8}$  M. This is not sufficient to effectively quench the triplet state, but formation of contact complexes between oxygen and excited DPH molecules can occur and thereby depopulate the  $S_1$ -state. Ultimately, the complexes will break apart under formation of ground or triplet state DPH and free O<sub>2</sub> [44,45]. The  $O_2$ -CH complex serves as oxygen reservoir, the concentration of free oxygen  $[O_2]$  therefore can be regarded as constant. Directly after the laser pulse the O<sub>2</sub> concentration is distinctly smaller than the concentration of  $S_1$ -state DPH so that the reaction rate depends on constant  $[O_2]$  and nearly constant  $[S_1]$  which serves as excess reservoir. This results in zero order reaction kinetics. Later on, when  $[S_1]$  and  $[O_2]$  are in the same order of magnitude, the reaction rate depends on the declining  $S_1$  concentration and the constant  $[O_2]$  and the quenching of  $S_1$ -DPH becomes a first order reaction. With these assumptions made, the kinetic trace of the DPH fluorescence was simulated by fitting the rate constants to the experimental kinetic trace of the  $8.0 \times 10^{-6}$  M DPH solution, excited with 1 mJ pulse energy. The value for  $k_T$  was set to  $5.0 \times 10^4$  s<sup>-1</sup>, according to the triplet state lifetimes known from literature [24,36,49,50] and  $[O_2]$  to 0.03 μM according to the estimations described in Supplementary Materials S2.

The fluorescence signal detected in the experiments is composed of contributions from the  $S_1$ -state and the  $S_2$ -state. For comparison to the emission intensity detected during the first 100 ns after the laser pulse, the time-dependent evolution of the combined  $S_1 + S_2$  population derived from the simulation is depicted in **Figure 6(a)** (signal intensity simulation: grey curves). The resulting set of rate constants is displayed in **Table 2** together with the time constants derived thereof.

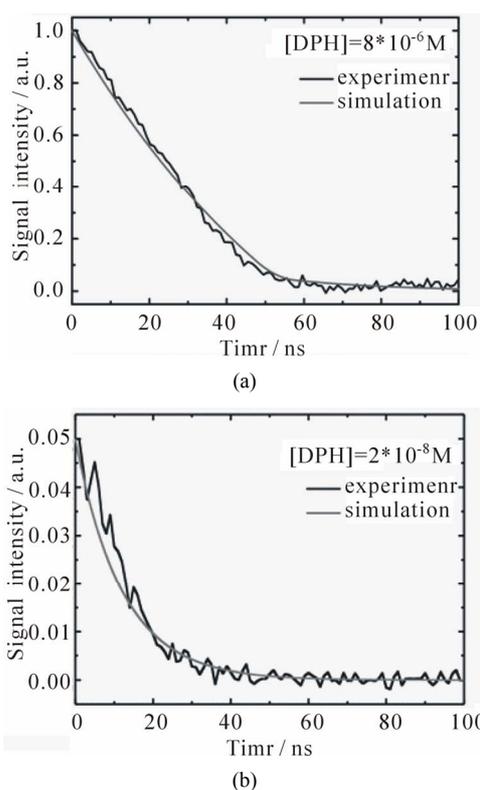
The slope of the experimental data is emulated considerably better than by a simple monoexponential fit (see inset of **Figure 1**). Since the concentration of free oxygen could only be estimated, it is advisable to discuss the value of  $[O_2] \cdot k_Q$  rather than  $k_Q$  alone.

Apparently, the long emission lifetime detected in our experiments derives from the  $S_1$  fluorescence, while fluorescence from the  $S_2$ -state with its lifetime of 1.3 ns (**Table 2**) cannot be held responsible. The value for  $k_{f_2}$  obtained in our simulation corresponds well with the Einstein probability of spontaneous emission ( $A_{21} = 7.98 \times 10^8 \cdot s^{-1}$ ), which can be calculated via equation 4 with the oscillator strength  $f_{21} = 2.16$ , determined by Ye *et al.*: [51,52].

**Table 2. Rate constants derived from the simulation of the time dependent fluorescence of DPH in cyclohexane ( $8.0 \times 10^{-6}$  M), flushed with N<sub>2</sub>, upon excitation with 1 mJ pulse energy.**

	process	rate constant/s <sup>-1</sup>	time constant/s
fl <sub>2</sub>	S <sub>2</sub> -state fluorescence	$<8.0 \times 10^8$	$>1.3 \times 10^{-9}$
fl <sub>1</sub>	S <sub>1</sub> -state fluorescence	$1.1 \times 10^5$	$9.4 \times 10^{-6}$
Q	oxygen quenching <sup>a)</sup>	$1.7 \times 10^9$	$5.9 \times 10^{-10}$
IC <sub>2,1</sub>	internal conversion (S <sub>2</sub> →S <sub>1</sub> )	$7.3 \times 10^{11}$	$1.4 \times 10^{-12}$
IC <sub>1,2</sub>	reverse internal conversion (S <sub>2</sub> →S <sub>1</sub> )	$4.1 \times 10^8$	$2.4 \times 10^{-9}$
IC <sub>2,0</sub>	internal conversion (S <sub>2</sub> →S <sub>0</sub> )	$<1.0 \times 10^{10}$	$>1.0 \times 10^{-10}$
dep	radiationless depopulation processes (IC <sub>1,0</sub> , ISC, iso, ...)	$<2.8 \times 10^5$	$>3.6 \times 10^{-6}$

<sup>a)</sup>with free oxygen concentration [O<sub>2</sub>] = 0.03 μM.



**Figure 6. Time dependent fluorescence of DPH in cyclohexane at 427 nm upon excitation with 1 mJ pulse energy, flushed with N<sub>2</sub>. The grey curves show the sum of concentrations of S<sub>1</sub> and S<sub>2</sub>-state DPH obtained from the simulations. (a) [DPH] =  $8.0 \cdot 10^{-6}$  M (b) [DPH] =  $2.0 \cdot 10^{-8}$  M.**

$$A_{21} = \frac{8\omega^2 \pi^2 e^2}{m_e c} \frac{g_1}{g_2} f_{21} \quad (4)$$

Increasing the value for  $k_{\beta_2}$  to the theoretical rate constant determined by Turek *et al.* [30] ( $k_{\beta_2} = 2.2 \times 10^9 \cdot s^{-1}$ ) also leads to satisfying results with the root-

mean-square deviation of the simulation slightly increasing from 0.005 to 0.006.

Simulations with  $k_{\beta_2} < 7.98 \times 10^8 s^{-1}$  (even with  $k_{\beta_2} = 0$ ) describe our experimental data equally well. However, exclusion of S<sub>2</sub>-state emission influences the simulation during the first picoseconds. Without S<sub>2</sub>-state emission, an increase of emission intensity should be observed within the first 5 ps. This rise should not be observable if emission from the S<sub>2</sub>-state occurs, since S<sub>2</sub>-state emission would superimpose the S<sub>1</sub>-state emission. Since this is far beyond our experimental time resolution, we can make no substantiated statement whether S<sub>2</sub>-state emission occurs in DPH or not.

In simulations with larger  $k_{\beta_2}$  or smaller  $k_{IC_{2,1}}$  combined with smaller  $k_{\beta_2}$  emission occurs from the S<sub>2</sub>-state with a long lifetime but the decay is strictly exponential rather than showing the described linear behaviour during the first 50 ns. The linearity can only be obtained by including the O<sub>2</sub> quenching as competing process to S<sub>1</sub> fluorescence.

The simulation starting value for  $k_{IC_{2,1}}$  was set to  $1.6 \times 10^{12} s^{-1}$ , which is the value corresponding to the S<sub>2</sub>-state lifetimes obtained by Hirata *et al.* [20], but a better agreement with our experimental data was obtained with  $k_{IC_{2,1}} = 7.3 \times 10^{11} s^{-1}$ . Decreasing  $k_{IC_{2,0}}$  to values below  $1.0 \times 10^{10} s^{-1}$  has no effect on the simulation at all, while higher values for this rate lead to insufficient simulations. Therefore  $1.0 \times 10^{10} s^{-1}$  is only an upper bound for  $k_{IC_{2,0}}$ .

It was found that the fluorescence intensity decreases with increasing temperature, while the shape of the kinetic trace stayed unchanged. The emission intensity strongly depends on the S<sub>2</sub>-state concentration. At higher temperatures, depopulation of the S<sub>2</sub>-state by collisional quenching increases. Since this process competes with IC<sub>2,1</sub>, the S<sub>1</sub>-state is populated less at higher than at lower temperatures. This results in a decrease of emission intensity. Apparently, collisional quenching plays a minor role in S<sub>1</sub>-state depopulation.

With an adjusted initial [S<sub>2</sub>] the same rate constants can also be used to describe the fluorescence of DPH solutions at much lower concentrations, as is shown in **Figure 6(b)** for [DPH] =  $2.0 \times 10^{-8}$  M. In this case [S<sub>1</sub>] is already smaller than [O<sub>2</sub>] directly after the laser pulse. The fluorescence decay is therefore exponential, in the experiment as well as in the simulation. The emission in oxygen saturated solutions resembles the shape of the laser pulse with its lifetime of 5 ns, see **Figure 1**. In oxygen saturated solutions [O<sub>2</sub>] is much higher than the initial concentration of excited state DPH. This leads to a very fast O<sub>2</sub>-quenching of the S<sub>1</sub>-state in our simulations, which results in a fluorescence decay within 1 ns. Due to our 5 ns laser pulse it is not possible in our setup to measure the correct fluorescence lifetime of the oxygen

saturated sample.

#### 4. Conclusion

At high pulse energies of the excitation laser the singlet emission of 1,6-diphenyl-1,3,5-hexatriene can occur via two different pathways. On the one hand, after excitation to the  $S_2$ -state, emission occurs directly from the pumped state. On the other hand, IC into the  $S_1$ -state takes place. The fluorescence from the  $S_1$ -state features long lifetimes since it is symmetry forbidden and can only occur by intensity borrowing via state mixing with the  $S_2$ -state. The  $S_1$ -state is depopulated by several processes like reverse IC, ISC and fluorescence. Most important competing process is the formation of DPH- $O_2$  contact complexes, which at low oxygen concentrations considerably influences the kinetic trace of the long-lived fluorescence and quenches the long-lived fluorescence considerably at high oxygen concentrations.

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### Supplementary Material 1

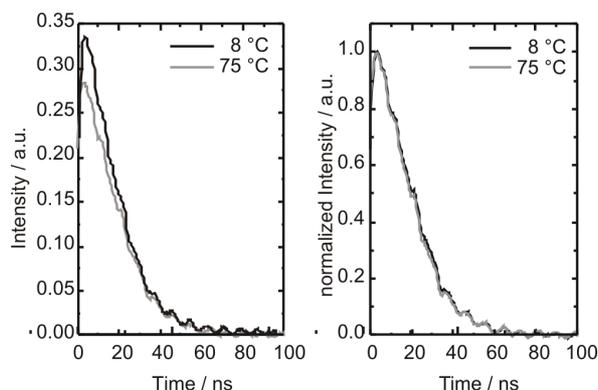
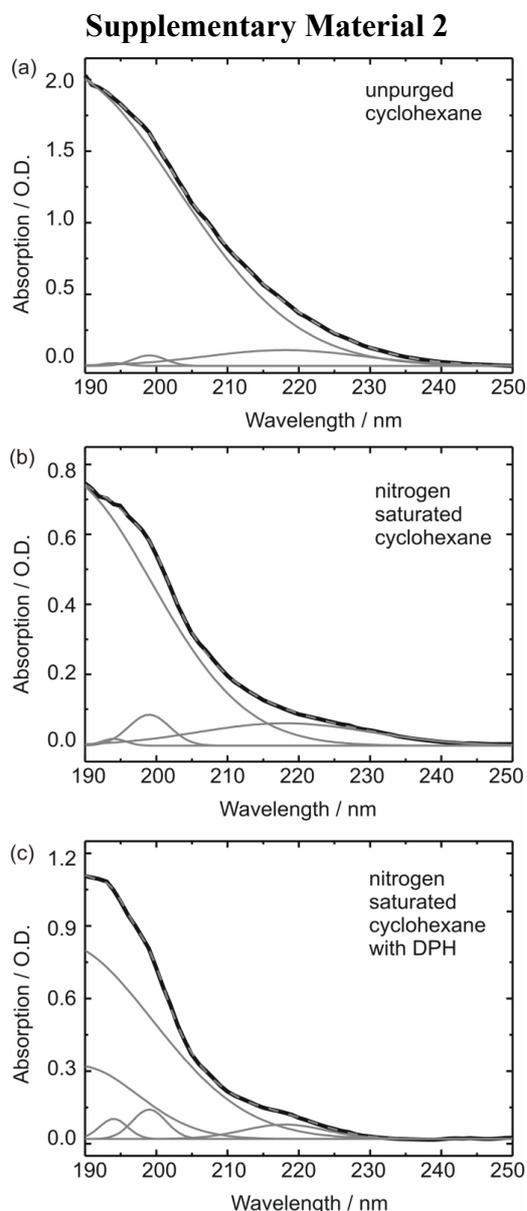


Figure S1: Kinetic curves of DPH ( $8.0 \times 10^{-6}$  M in cyclohexane flushed with nitrogen) at 25 °C and 75 °C upon excitation at 355 nm with 1 mJ pulse energy. The emission intensity decreases with increasing temperature, while the shape of the kinetic curves does not depend on the temperature.



**Figure S2. Absorption spectra and Gauss deconvolutions of the O<sub>2</sub>-CCT complex absorption in (a) unpurged cyclohexane; (b) cyclohexane saturated with nitrogen; (c) DPH in cyclohexane ( $8.0 \times 10^{-6}$  M) purged with nitrogen. The experimental absorbance spectrum is depicted in black, the sum of the Gaussian curves in dashed grey (nearly perfect overlap with the black curve) and the individual Gaussian contributions in grey.**

The intense curves with maxima <190 nm depend on O<sub>2</sub> concentration and can thus be described to absorption of O<sub>2</sub>-M CCT complexes. In pure cyclohexane, neither

purged with nitrogen or oxygen, the CCT absorption band can be emulated by one Gaussian curve with  $\lambda_{\max} = 186$  nm and three distinctly smaller Gaussian curves with maxima at 199 nm, 194 nm and 218 nm. Unfortunately, it is not possible to investigate absorption bands below 190 nm with our UV/Vis spectrometer; hence  $\lambda_{\max} \approx 186$  nm is merely a guess. The sample was purged with nitrogen for 15 minutes and an absorption spectrum was measured every minute. Only the intensity of the Gaussian curve with  $\lambda_{\max} \approx 186$  nm had to be adjusted to emulate the spectra, while all other contributing curves remained unchanged. Therefore we assign this band to the O<sub>2</sub>-cyclohexane CCT complex absorption. The other bands are due to cyclohexane absorption and will be disregarded when calculating the contact complex concentration. Obviously the oscillator strengths of the CCT complex bands are much higher than those of uncomplexed cyclohexane in the displayed spectral range.

After seven minutes the sample was saturated with nitrogen and no changes could be observed in the absorption spectra any more. The measured CCT-absorption of the sample purged with oxygen for 15 minutes at 210 nm lies well beyond 1 O.D. where the Lambert-Beer law is not valid any more. For this sample no concentration could be determined. The concentration was calculated using the CCT extinction coefficients determined by Brownrigg and Kenny in the region of the red flank of the 186 nm band:  $\epsilon_{210\text{nm}} = 250 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-2}$ ,  $\epsilon_{220\text{nm}} = 120 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-2}$  and  $\epsilon_{230\text{nm}} = 40 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-2}$  and the corresponding intensities obtained by our deconvolution. The concentrations given in **Table 1** in the article are obtained by averaging over the values for the different wavelengths.

The same analysis was performed for an  $8.0 \times 10^{-6}$  M DPH solution in cyclohexane. In this case not only the oxygen saturated but also the unpurged solution features an absorption band with intensities above 1 O.D. For the nitrogen saturated solution an additional Gaussian band with  $\lambda_{\max} = 189$  nm was needed to emulate the CCT complex absorption, which may be due to formation of the O<sub>2</sub>-DPH CCT complex. Therefore, the summarized intensities of the Gaussian curves with  $\lambda_{\max} = 186$  nm and  $\lambda_{\max} = 189$  nm were used to calculate the combined contact complex concentration. It was assumed that the different CCT complexes exhibit comparable extinction coefficients.