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Mechanistic Insights into the Photochromism of *trans*-10b,10c-Dimethyl-10b,10c-dihydropyrene Derivatives

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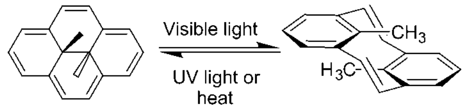
Abstract: A series of dimethyldihydropyrene derivatives was studied to elucidate the photochemical mechanism associated with the switching between the dimethyldihydropyrene (DHP, closed) and metacyclophanediene (CPD, open) forms of the molecule. Quantum yields of ring opening and closure, fluorescence quantum yields and lifetimes, as well as laser flash photolysis studies were performed to establish the effect of substituents on the switching efficiency. Ring opening of the DHPs occurs from the first singlet excited state. The low quantum yields for the ring opening reaction observed ($\leq$0.042) are a consequence of the low rate constant ($\leq 1.7 \times 10^7$ s^{-1}) for this process. The quantum yields for ring closure of the CPD were determined for select compounds and were of the order of 0.1−0.4. These results show that the efficiency for ring opening of this class of compounds is intrinsically low, but can be modulated to some extent by the introduction of substituents. These properties should be taken into account when considering what type of photoswitching devices DHPs might be useful for.

Introduction

Photochromic compounds are molecules that can be reversibly switched between different states by the use of light. The two states should have distinct spectroscopic properties, such as absorption and fluorescence spectra, to monitor the concentration changes of the two states. To be useful, the conversion between states has to be efficient, and the thermal back reaction should be absent or slow. Finally, the compound should be stable and undergo many photoswitching cycles (>10 000) before decomposition is detected. Such photochromic molecules then have potential uses in materials such as nonlinear optics[1] and optical switches.[1−8]

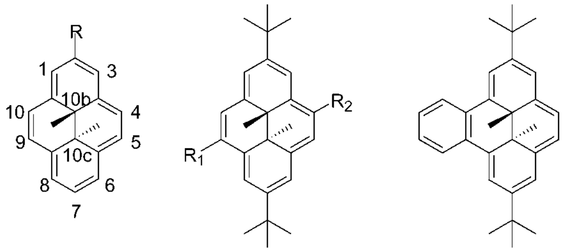
Dimethyldihydropyrene (DHP) and its derivatives are photochromic, and advances in their synthesis[9,10] have led to the design of sophisticated systems, including multichromophoric architectures.[10,11] One of the advantages of DHPs is that these compounds are relatively stable. DHP is converted photochemically to its isomeric "open" metacyclophanediene (CPD) by visible light. In the case of the parent compound **1**, the CPD form (Scheme 1) can be both photochemically (UV light, fast) and thermally (slow) converted back to the more stable DHP isomer.[12,13] The relative energies between the DHP and CPD forms can be modulated by substituents.[10,14] Although there are examples where the CPD form is the more stable of the two isomers,[10,14,15] the present work concentrated on derivatives (Chart 1) where the DHP is the isomer of lowest energy.

Scheme 1



DHP-**1** CPD-**1**

Chart 1



1: R=H
3: R=COCH$_3$
2: R$_1$=R$_2$=H
4: R$_1$=COCH$_3$, R$_2$=H
5: R$_1$= —C≡C—C(CH$_3$)$_2$OH, R$_2$=H
6: R$_1$=R$_2$= —C≡C—C(CH$_3$)$_2$OH
7

Despite achievements in the synthesis of DHP derivatives, the photochemical characterization has not been explored in

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depth. Early reports suggested[12,13,16,17] that the quantum yield for the photochemical formation of CPD is low. More extensive work has been done on the thermal reversion reaction of CPD back to DHP,[10,12,13,18,19] and it was shown that the nature of the substituent affects the rate constant for this process. However, the effect of substituents has not been studied in detail for the photochemical reactions.

Our preliminary work [20] on the photophysics of **1** showed the presence of several transients on different time scales. We expand on this preliminary report by combining spectroscopic techniques with quantum yield measurements to understand how substituents can be used to design more efficient photoswitches. The parent compound **1** was used as the base system to which all compounds were compared. Compounds **2** and **3** were studied to illustrate the effect of substitution at the 2- and 2,7-positions, where the majority of the electron density has been calculated to occur for the ground state.[19,21] Compounds **4**−**6** were synthesized to study the effect of 4- and 4,9-substitution. The acetylenes were chosen as substituents because these conjugating units are models for molecular wire type structures.[22,23] Finally, compound **7** was studied, because qualitative evaluations showed that benzene fusion at the [e]-position led to more efficient ring opening of the DHP.[18,19] The detailed photophysical characterization presented here shows that the ring opening of DHPs is intrinsically a low-efficiency process, but that it can be modulated to some extent with the use of suitable substituents. Knowledge of the photophysics of the compounds studied will aid in the design of compounds containing multiple switches.

Results

Syntheses. The preparation of compounds **1**, **2**, **3**, **4**, and **7** has been previously reported.[9,17,24−27] Synthesis of the acetylene derivatives **5** and **6** was respectively accomplished via a Sonogashira coupling of 2-methylbut-3-yn-2-ol with iodide **8** and dibromide **9**,[28] both of which were prepared from **2** (Scheme 2).

Absorption Spectra. The DHP isomer of all compounds shows absorption bands that cover most of the visible region of the spectrum (Figure 1).[29] The lowest energy band for all compounds with the exception of **7** was observed between 640 and 680 nm and was the band with lowest molar absorptivity (inset, Figure 1). Substitution with conjugated systems, such as acetyl (**3**, **4**) and acetylene (**5**, **6**), led to a red shift of all absorption bands (Figure 1). Benzo[e]-fusion (**7**) broadened the band in the 500 nm region, and the absorption above 600 nm appeared as a shoulder (Figures 1 and 2). The open CPD isomer was formed for all compounds when the DHP isomers were irradiated with visible light. The absorption spectra for the CPDs were shifted to the UV region (Figure 1B), because in the CPD isomer the conjugation of the annulene ring is lost, and the

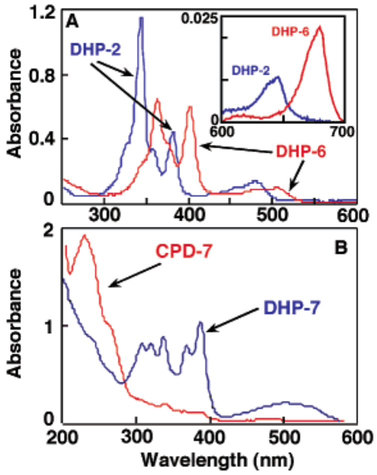


Figure 1. (A) Absorption spectra of **2** and **6** in cyclohexane. The inset shows the expanded spectra above 600 nm. (B) Absorption spectra of DHP-**7** and CPD-**7** in cyclohexane at room temperature. A small residual DHP absorption is apparent on the tail absorption for CPD-**7** because the conversion to CPD was not complete.

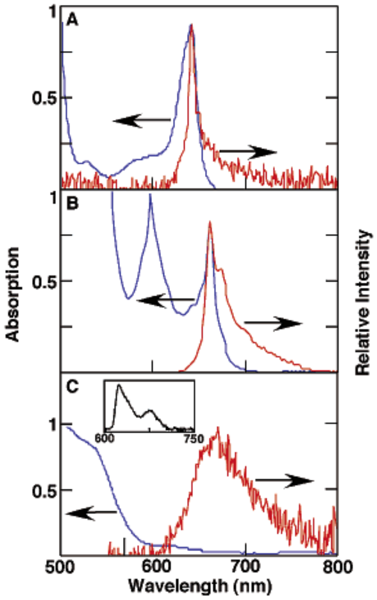
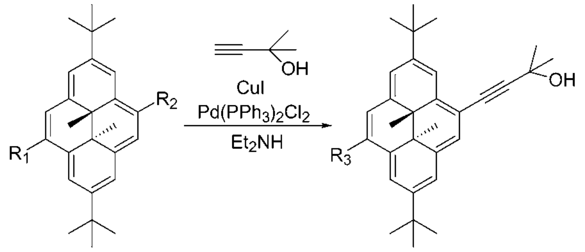


Figure 2. Normalized absorption spectra above 500 nm and fluorescence spectra in cyclohexane for compounds **2** (A), **3** (B), and **7** (C). The inset shows the fluorescence spectrum of **7** at 77 K.

Scheme 2



8: $R_1 = H, R_2 = I$
9: $R_1 = R_2 = Br$

5: $R_3 = H$
6: $R_3 = —C{\equiv}C—C(CH_3)_2OH$

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(29) Molar absorptivity values at several maxima are presented in Table S1 in the Supporting Information.

Table 1. Fluorescence Emission Maxima (λ_{em}), Energy of the First Singlet Excited State (E_{S1}), Calculated HOMO−LUMO Energy Difference ($E_{HOMO-LUMO}$), Fluorescence Quantum Yields (ϕ_f), Lifetimes (τ_f), and Rate Constants (k_f) for the DHP Form of Compounds **1**−**7** in Aerated Cyclohexane[a]

compound	λ_{em}/nm	E_{S1}/kcal/mol^{-1}	$E_{HOMO-LUMO}$/kcal/mol[b]	ϕ_f /10^{-3}	τ_f /10^{-9} s	k_f /10^5 s^{-1}
1	641	44.6 ± 0.1	45.6	0.61 ± 0.03	5.4 ± 0.1	1.13 ± 0.06
2	641	44.6 ± 0.1	44.3	2.03 ± 0.07	5.6 ± 0.1	3.6 ± 0.1
3	660	43.3 ± 0.1	39.6	0.64 ± 0.07	4.4 ± 0.2	1.5 ± 0.2
4	666	42.94 ± 0.05	38.5	4.61 ± 0.05	4.2 ± 0.1	11.0 ± 0.3
5	663	43.1 ± 0.1	41.7	2.29 ± 0.03	4.6 ± 0.1	5.1 ± 0.1
6	679	42.12 ± 0.05	39.9	2.2 ± 0.2	3.8 ± 0.1	5.8 ± 0.5
7	620[c]	46.1 ± 0.2	34.1[d]	0.9 ± 0.1	2.4 ± 0.1	3.8 ± 0.5

[a] The values for ϕ_f and τ_f correspond to the average of two independent experiments; the errors correspond to average deviations. [b] Spartan DFT (pBP(DN**)), PC Spartan Pro V1.0, Wave function Inc. Irvine, CA. [c] From the fluorescence spectrum at 77 K. [d] The energy difference between HOMO and LUMO + 1 is 43.4 kcal/mol.

steplike nature of the cyclophane prevents extended conjugation. The absorption maxima for the CPDs of compounds **1**−**7** were between 230 and 320 nm.

Fluorescence Measurements. Fluorescence was observed for all DHPs, indicating that the first excited singlet state of these compounds is emissive to some extent. The emission spectra were found to be independent of the excitation wavelengths. The fluorescence spectra (Figure 2) for compounds **1**, **2**, **4**, **5**, and **6** were very narrow. No Stokes shift was observed for these compounds as the emission peaks were found to overlap with the 0,0 band of the ground-state absorption spectra. The energy for the first singlet excited state was calculated from the 0,0 band (Table 1). The emission spectra for compounds **5** and **6** were found to be increasingly red shifted. The emission spectrum of **7** displayed a different behavior since its fluorescence spectrum was broad and a noticeable Stokes shift was observed (Figure 2C). The DFT calculations for the HOMO → LUMO energy differences for all DHPs are included in Table 1. Qualitatively the calculated values are consistent with the experimental ones with the exception for the benzo[e]-fused system **7**, where the calculated energy difference was much smaller. In this case, the HOMO → LUMO + 1 energy difference (43.4 kcal/mol) is closer to the experimental value.

Low-temperature (77 K) fluorescence spectra were acquired in an attempt to further resolve the emission spectra. The spectra for **1**, **2**, **5**, and **6** at low temperature exhibited the same band shape as that displayed at room temperature. The low-temperature emission spectrum for the fused system, **7**, was observed to resolve into two bands (inset, Figure 2C). It is worth noting that the energy for the singlet excited state of **7**, calculated by using the highest energy maximum for the spectrum at low temperature, was higher than that for the other DHPs.

The CPD isomers for **3** and **7** were obtained by extensive irradiation of their respective DHPs. The CPD forms of these compounds are relatively stable. A weak fluorescence between 320 and 360 nm was observed when the CPDs of **3** and **7** were excited at 280 nm.

Fluorescence quantum yields of the DHPs in aerated solutions were measured for all compounds at 20 °C (Table 1). $Ru(bipy)_3Cl_2$ was used as the primary standard[30] for compounds **2**, **3**, **5**, and **7**. Compound **2** was then used as a secondary standard for compounds **1** and **3**−**7**. The emission quantum yields were found to be below 0.005, indicating that less than 0.5% of all singlet excited states led to fluorescence. The substitution of an alkyl group in the 2-position increased the fluorescence quantum yield, whereas addition of a conjugating acetyl group (**3**) did not alter this parameter. Further, the addition of conjugating acetylene groups (**5**, **6**) did not affect the emission quantum yield, but the substitution with an acetyl group in the 4-position (**4**) led to an enhancement by a factor of ca. 2. Benzo[e]-fusion (**7**) led to a decrease of the emission efficiency.

The decays for the fluorescence emission were monoexponential, and the lifetimes in aerated cyclohexane solutions varied between 2.4 and 5.6 ns (Table 1). The lifetime of **2** in solutions purged with nitrogen was 6.5 ns as compared to that of the aerated solution where it was 5.6 ns. The shortening of the lifetime in aerated solutions indicates that oxygen quenches the singlet excited state of the DHP of **2** in a diffusional process.[31,32] A similar quenching efficiency was obtained from steady-state measurements. For all compounds, the emission spectra recorded for the lifetime measurements were consistent with the steady-state emission spectra. The fluorescence rate constants were calculated as the ratio of the fluorescence quantum yield and the lifetimes (ϕ_f/τ_f, Table 1).

Quantum Yields for Ring Opening/Closing. The efficiency of ring opening for all compounds was examined using potassium ferrioxalate as a primary standard and by irradiating the samples at 380 nm.[33,34] Absorbance measurements were used to follow the disappearance of the DHPs. In some cases, **1** was used as a secondary standard because the samples could be irradiated at longer wavelengths (480 nm) where the CPD isomers do not absorb. This was particularly important for compounds **5** and **6**, where a smaller quantum yield was observed when the DHPs were irradiated at shorter wavelengths (<400 nm), due to the absorption of their CPD isomers in this spectral region. Within experimental errors, the same quantum yields were observed when the solutions were purged with nitrogen and oxygen. This result indicates that the ring opening occurs from the singlet excited state.[35]

The ring opening quantum yields for **2** and **4** (Table 2) were found to agree with the literature values of 0.002 and 0.005, respectively.[17] However, the ring opening quantum yield for **1** was found to be lower (0.006) than that previously reported

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(32) The quenching rate constant was estimated to be 10^{10} M^{-1} s^{-1} based on an oxygen concentration in aerated cyclohexane of 2.4 mM.[31] This quenching rate constant is of the same order of magnitude as the diffusional rate constant in cyclohexane (7×10^9 M^{-1} s^{-1}).[31]

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(35) Although the singlet excited state is quenched by oxygen at a diffusional rate constant, the fact that the same ring opening quantum yields were obtained is a reflection of the large errors for this parameter and the modest quenching by oxygen calculated from the change in lifetimes when the cyclohexane sample was saturated with oxygen (15%).

Table 2. Quantum Yield for the Ring Opening ($\phi_{\mathrm{DHP}\rightarrow\mathrm{CPD}}$), Ring Closing ($\phi_{\mathrm{CPD}\rightarrow\mathrm{DHP}}$), and the Rate Constants for the Ring Opening Reactions ($k_{\mathrm{DHP}\rightarrow\mathrm{CPD}}$) of DHP Derivatives in Aerated Cyclohexane[a]

compound	$\phi_{\mathrm{DHP}\rightarrow\mathrm{CPD}}/10^{-3}$	$\phi_{\mathrm{CPD}\rightarrow\mathrm{DHP}}$ [b]	$k_{\mathrm{DHP}\rightarrow\mathrm{CPD}}/10^5\ \mathrm{s}^{-1}$
1	6 ± 2 (7)		11 ± 4
2	1.5 ± 0.1 (2)		2.7 ± 0.2
3	12 ± 2 (2)	0.1−0.4[c]	27 ± 5
4	3.8 ± 0.5 (2)		9 ± 1
5	0.56 ± 0.09 (3)		1.2 ± 0.2
6	0.52 ± 0.08 (1)		1.4 ± 0.2
7	42 ± 2 (4)	0.37 ± 0.07 (2)[d]	180 ± 10

[a] For experiments performed more than twice, the errors correspond to standard deviations; for experiments performed twice, the errors correspond to average deviations. [b] Only for compounds **3** and **7** is a conversion from DHP to CPD greater than 90% achieved. [c] Only a range is indicated (see text). [d] Average of one actinometry and one laser flash photolysis experiment.

(0.02).[13,17] Acetylene substitution (**5**,**6**) lowered the ring opening quantum yield of **2**, whereas the substitution of acetyl at the 2-position (**3**) or benzo[e]-fusion (**7**) substantially increased this yield. The rate constants for the ring opening reaction ($k_{\mathrm{DHP}\rightarrow\mathrm{CPD}}$) were calculated from the ratio of the quantum yields and the fluorescence lifetimes.

The CPD isomers of **3** and **7** were formed by irradiating a DHP sample of **3** or **7** until conversion to their CPDs was 90% or greater. The quantum yield of the ring closing reaction, that is, photochemical conversion of the CPD isomer into the DHP isomer, was determined by irradiation into the CPD absorption band where the DHP absorption is minimal (ca. 254 nm). The appearance of DHP was measured at several DHP absorption maxima. The quantum yield for the ring opening measured for **7** using actinometry was the same within experimental error as was measured from laser flash photolysis studies (see below). However, in the case of the CPD of **3**, a higher quantum yield (0.4) was measured by actinometry (see below). In any event, the ring opening quantum yields for the CPDs are significantly lower when compared to the estimates of a unity quantum yield previously reported.[13]

Laser Flash Photolysis Experiments. Preliminary work on compound **1**[20] showed that two transients were formed, one of which has a lifetime shorter than the time resolution of the laser flash photolysis system (10 ns) and a second transient with a lifetime in the microsecond time domain. This long-lived transient was assigned to the triplet excited state of the CPD form of **1** as it was quenched by oxygen and β-carotene.

Transient studies were performed by exciting the DHPs either at 355 nm (YAG) or above 470 nm (YAG/OPO). With the exception of **2**, the CPDs of all compounds absorbed at 355 nm leading to complex transient kinetics. For this reason, excitation in the visible region was employed. The transient spectra for **2**,[36] **5**, and **6** are similar to those observed for **1**.[20] The bleaching of the DHPs was observed in the 350−600 nm region. In the UV region, two different transient species were detected. At short delays after the laser excitation (<30 ns), a spectrum was observed that is red shifted (315, 330, and 345 nm for **2**, **5**, and **6**, respectively) when compared to the spectra at longer delays (290, 300, and 310 nm for **2**, **5**, and **6**, respectively). In the spectra for **3** and **4**, the transient with short lifetime appeared as a shoulder between 300 and 350 nm. The transient spectrum of **7** at short delays showed some positive absorption in the same spectral region, where at long delays the bleaching of the DHP was observed (Figure 3). In addition, below 300 nm a growth of the transient absorption was observed after the laser pulse. These results suggest that the absorption for the transient with the short lifetime for **7** had an absorption that overlapped with the bleaching region of the DHP form. The spectra at short and long delays were normalized at 490 nm, and the spectrum at long delays was subtracted from the spectrum at short delays. This procedure led to the spectrum of the transient with the short lifetime (inset, Figure 3A), which has a maximum at 330 nm, whereas the CPD in the laser flash photolysis studies showed a maximum at 280 nm.[37] The maximum for the short-lived component is in the same spectral region as observed for **2**, **5**, and **6** (see above).

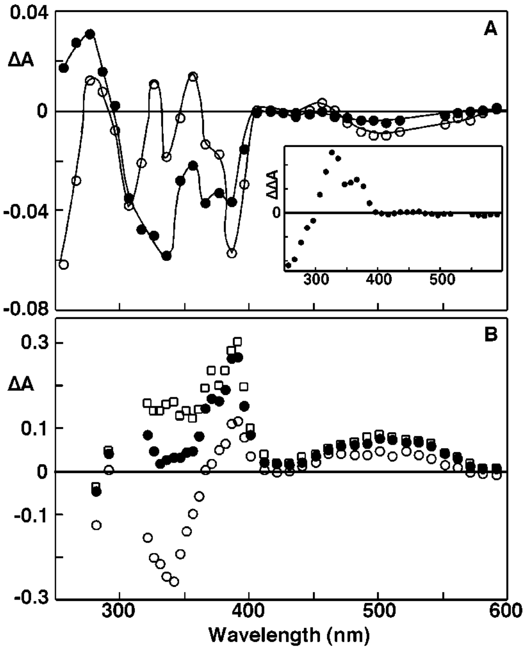

Figure 3. (A) Transient absorption spectra for the DHP of **7** at delays of 2.5 ns (○) and 100 ns (●), when excited at 532 nm in cyclohexane (the lines were included to guide the eye). The inset shows the difference spectrum for the spectra at 2.5 ns and 100 ns when normalized at 490 nm. (B) Transient absorption spectra for the CPD of **7** at delays of 5.2 ns (○), 53 ns (●), and 111 ns (□), when excited at 308 nm.

Irradiation of the CPDs of compounds **3** and **7** led to the formation of their DHPs, with absorption features characteristic for the absorption of the ground states (Figure 3B). At short delays a strong negative signal was observed, which was assigned to the fluorescence of the CPD of **7**.[38]

For all compounds the same transient kinetics were observed for the photolysis of the DHPs. A short-lived transient with a lifetime shorter than the time-resolution of the system (<10 ns) was observed (inset Figure 4). This initial transient was followed by a second transient with a microsecond lifetime (Figure 4), which had been previously assigned to a triplet excited state.[20] This assignment was confirmed in quenching experiments by oxygen ($(1.9 \pm 0.2) \times 10^9\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$) and β-carotene ((1.4 ±

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(36) Transient absorption spectra for **2** and **3** are shown in the Supporting Information.

(37) Note that the absorption maximum for CPD-**7** in the laser flash photolysis experiment is shifted to the red when compared to the maximum in the ground-state absorption spectrum (Figure 1B). This is due to the fact that in the laser flash photolysis experiment a difference spectrum is measured.

(38) Fluorescence appears as a negative signal in the absorption spectra because it increases the light intensity detected by the system after the laser pulse when compared to the light intensity before the laser pulse.

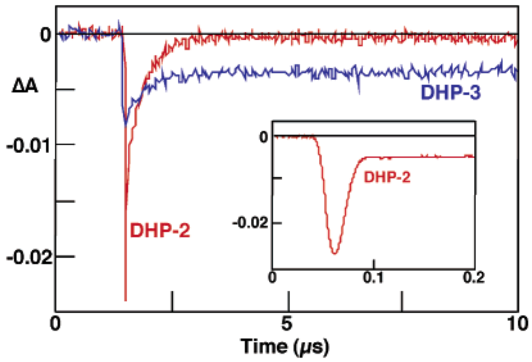

Figure 4. Kinetics at 465 nm for the recovery of the bleaching of **2** and **3** after irradiation at 480 nm for samples with matched ground-state absorbance at 480 nm. The inset shows the kinetics for **2** at a shorter time domain.

0.1) × 10^{10} M^{-1} s^{-1}),[39] which have excited-state energies of 22[40] and 21 kcal/mol, respectively.[31] In the case of β-carotene, the growth of the triplet state of this quencher was observed at 520 nm, and the lifetimes were similar to those for the decay of the transient for DHP. The DHP transient was not quenched by ferrocene, a compound that has a triplet energy of 38 kcal/mol.[41] Benzophenone has a triplet energy of 69 kcal/mol,[31] and this compound was used as a sensitizer. This ketone was excited at 266 nm where the DHP absorption is low. The triplet of benzophenone was quenched by DHP-**2** with a rate constant of (1.3 ± 0.1) × 10^{10} M^{-1} s^{-1}, and after complete quenching of the triplet ketone, the same transient spectrum was observed as for direct excitation of DHP-**2**. These results confirm that the transient with microsecond lifetime for the DHPs of **1** to **7** has triplet character and has an energy between 21 and 38 kcal/mol.

The decay of the transients for the DHPs led to a residual bleaching in the visible region, as well as a residual positive absorption in the UV region of the spectrum, which corresponds to the amount of DHP that was converted to CPD. The thermal reaction for all compounds is much slower ($t_{1/2} > 96$ min, 20 °C) than the time scales used for the laser flash photolysis experiments. Therefore, the residual absorption can be related to the quantum yield of ring opening ($\Phi_{DHP\to CPD}$) when samples (**1**−**5** and **7**) were irradiated that had the same absorption at the excitation wavelength. This procedure was necessary to ensure that in each case the same concentration of excited states for each DHP was formed. The final concentration of CPDs was calculated by using the molar absorptivity for each DHP at 465 nm.[42] Relative quantum yields for the ring opening reactions (Table 3) were obtained by normalizing the concentrations of DHP bleached to the concentration measured for compound **1**. Within experimental errors, the relative quantum yields recovered from the laser flash photolysis experiments were the same as those obtained from the actinometry measurements.

The quantum yield for the formation of the long-lived transient of the DHP can be estimated from the absorption decrease at 465 nm when triplet excited benzophenone[31] is used as standard (eq 1; $\phi_{ISC}(BP) = 1$; $\epsilon_{520} = 6500$ M^{-1} cm^{-1}). Solutions of DHP-**2** and benzophenone with matched absorptions at the laser wavelength of 355 nm were employed, and the absorption changes at 465 and 340 nm for DHP and 520 nm for benzophenone were measured at several laser pulse energies. A linear relationship between the changes in absorption for the DHP bleaching and the triplet benzophenone was observed, and the intersystem crossing quantum yield for DHP-**2** was determined to be 0.005 ± 0.001 (Table 3). The quantum yields for the other DHPs were calculated using DHP-**2** as a secondary standard (eq 1). Samples with matched ground-state absorbances were excited at 480 nm, and the bleaching was measured at 465 nm. This procedure was necessary because compounds **3**−**7** could not be excited at 355 nm (see above), and benzophenone does not absorb at 480 nm.

Table 3. Relative CPD Concentrations As Determined from Laser Flash Photolysis Experiments, Relative Quantum Yields of Ring Opening Calculated from the Data in Table 2, and Intersystem Crossing Quantum Yields for the DHP Derivatives in Aerated Cyclohexane

compound	relative [CPD][a]	relative $\phi_{DHP\to CPD}$	$\phi_{isc}/10^{-3}$ [b]
1	1	1	6 ± 1
2	0.26 ± 0.05	0.25 ± 0.08	5 ± 1[c]
3	2.8 ± 0.6	2.0 ± 0.8	2.9 ± 0.6
4	0.8 ± 0.2	0.6 ± 0.2	18 ± 4
5	0.19 ± 0.04	0.09 ± 0.03	4 ± 1
7	3.7 ± 0.7	7 ± 2	

[a] Assuming an error of 20% in the measurement of the ΔA values. [b] Measured using DHP-**2** as a secondary standard. [c] Measured using triplet benzophenone as a primary standard.

$$\Delta A_{BP} = \frac{\phi_{isc}(BP)\epsilon_{BP}}{\phi_{isc}(DHP)\epsilon_{DHP}} |\Delta A_{DHP}| \qquad (1)$$

Excitation of the CPDs of **3** and **7** led to the observation of a fast bleaching, where the recovery had a lifetime that was shorter than 10 ns. This bleaching was assigned to the fluorescence of the CPD isomers of both compounds. In the case of **7**, there was no change in the magnitude of the transient absorption after the recovery from the fluorescence. In the case of **3**, a slow increase in the absorption was observed, which is due to excitation of residual DHP present in solution, because of the incomplete conversion of DHP into CPD.

The quantum yields for the ring closing reactions for compounds **3** and **7** were measured against the triplet formation of benzophenone using eq 1, where $\phi_{isc}(DHP)$ is substituted by $\phi_{CPD\to DHP}$. A linear relationship was observed for the dependence of the residual absorption for the DHPs of **3** and **7** with the triplet benzophenone absorption, and the quantum yield for ring opening (Table 2) was obtained from the slope of eq 1.

In the case of CPD-**7**, the same ring closing quantum yield was obtained by laser flash photolysis (0.31 ± 0.03) and actinometry measurements (0.42 ± 0.07). For CPD-**3**, a lower value (0.1) was obtained from laser flash photolysis experiments when compared to the value measured by actinometry (0.4). Possible reasons for this discrepancy are the fact the thermal back reaction would lead to the formation of DHP during the actinometry experiments, since these experiments take a much longer time to complete than the laser flash photolysis measurement. For this reason, the value determined by actinometry represents an upper limit for this quantum yield. In this respect,

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(39) The quenching rate constants (k_q) were obtained from the dependence of the decay rate constant (k_{obs}) with the quencher concentration ($k_{obs} = k_0 + k_q$ [quencher]).

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(42) The molar absorptivity values at 465 nm for **1**−**7** are shown in Table S2 in the Supporting Information.

it is worth noting that the rate constant for the thermal reaction of CPD to DHP is ca. 100 times larger for **3** (unpublished) than for **7**.[18,19] In contrast, the quantum yield obtained from the laser flash photolysis measurement constitutes a minimum value, because at the excitation wavelengths some photons were absorbed by the residual DHP isomer. This inner filter effect would lead to a decrease in the measured quantum yield value. A range has been included in Table 3, because at this point it is not clear which measurement is the more reliable one.

Discussion

The photophysical processes of the closed (DHP) and open (CPD) isomers of the DHPs have to be understood to explain the observed quantum yields for this class of molecules, and to devise strategies to use these molecules as functional switching units. Excitation of the DHPs leads to the formation of their singlet excited states. The lifetimes of these excited states were remarkably long (2−6 ns) as compared to those of other photochromic switching molecules. In comparison, the lifetime of the excited state of *cis*-stilbene is less than 300 fs, leading to the formation of dihydrophenanthrene, and the photochemical ring opening of the latter back to *cis*-stilbene occurs in less than 500 fs.[43] In the case of spirooxazines, the singlet excited-state lifetime is shorter than a picosecond,[44,45] and the ring opening rate constant for this photoswitch is of the order of 10^{12} s^{-1}. Picosecond processes were also observed in the case of fulgides[46,47] and diarylethenes.[48,49] In this respect, the long lifetime for the singlet excited states of the DHPs suggests that the primary photocleavage reaction is a slow process.

The transient absorption spectra showed that two transients with different lifetimes were formed when the DHPs were excited. The species with a lifetime shorter than 10 ns is likely to correspond to the absorption of the singlet excited state, since fluorescence experiments showed that the lifetimes for these excited states were similar to the duration of the laser pulse. The transient absorption could also be due to a product from the reaction of the singlet excited state. A likely product would be the singlet biradical formed after the cleavage of the transannular bond. However, this biradical would be short-lived, because re-formation of the transannular bond or the rearrangement of the molecular framework to form the CPD are expected to be faster than the singlet lifetime of several nanoseconds. For this reason, a significant concentration of the biradical, if formed, would not accumulate during the laser pulse.

The singlet excited states of the DHPs decay by fluorescence, formation of the CPD, and intersystem crossing to the triplet state. The sum of the quantum yields for these three processes is between 0.007 (**5**) and 0.046 (**7**), suggesting that most singlet excited states (>95%) decay back to the ground state of the DHPs. The quantum yield for CPD formation from the DHPs led to rate constants for this process between 1.2×10^5 and 1.8×10^7 s^{-1}. These rate constants are low if one considers that the photochemical ring opening in a concerted reaction from the singlet excited state is symmetry allowed by the Woodward−Hoffmann rules.[13] One reason for this low reactivity could be that the bond cleavage reaction is an activated process from the singlet excited state of the DHPs. Indeed, a temperature dependence was observed for the ring opening quantum yield of 1,3,6,8-hexamethyl-DHP, when the photoreaction was measured between 23 and −175 °C.[12] However, an activated process does not explain the results for compounds **1**−**7**, because no correlation was observed between the rate constant for CPD formation and the energy of the singlet excited state. If an activated process was occurring, it would be expected that the rate constant for the CPD formation would increase for higher excited-state energies. For example, the value of $k_{\mathrm{DHP}\rightarrow\mathrm{CPD}}$ is the same for compounds **5** and **6**, while the E_{S1} values are different by ca. 1 kcal/mol, which would lead to a difference in rate constants of ca. 5 if cleavage of the transannular bond proceeded over an activation barrier.

The low cleavage rate constant for the singlet excited state of the DHPs could be related to the fact that the reaction is not concerted but involves the intermediate formation of a biradical from the singlet excited state. The low quantum yield for CPD formation could be explained if most of the biradicals decayed back to ground-state DHP. This partition between CPD formation and decay to the ground state is feasible, because the biradical has singlet multiplicity, and, therefore, the re-formation of the transannular bond is an allowed process. The biradical will not intersystem cross to the triplet biradical, because the radical centers are held in close proximity by the molecular framework leading to a large splitting between the energies for the singlet and triplet biradicals.[50] The upper limit for the rate constant leading to the biradical formation can be estimated by assuming that the internal conversion quantum yield between S_1 and S_0 is zero. Because more than 95% of the singlet excited states of DHP decay back to ground-state DHP, the upper limit for the formation rate constant ($0.95/\tau_f$) of the biradical is between 1.7×10^8 and 4.0×10^8 s^{-1}. It is worth noting that this rate constant is also much lower than the cleavage rate constants for other photochromic compounds.

From the current experiments, it is not possible to differentiate between a concerted mechanism with a low reaction probability and the mechanism involving the formation of a biradical. The difference between the DHPs and other photochromic molecules, such as spirooxazines and fulgides, is that the reaction pathway that leads from the “closed” isomer to the “open” isomer in the case of the DHPs requires a much smaller motion of the molecular framework. The ring in the DHPs holds the system in a relatively restricted environment, and the reactive species, that is, singlet excited state or biradical, cannot explore a variety of nuclear motions on the reaction surface. This restriction could affect both the concerted and the biradical reactions in a similar manner, that is, by not making the reaction modes available that lead to the formation of the CPD.

The rigidity of the singlet excited state is responsible for the absence of a Stokes shift between the absorption and emission spectra of **1** to **6**, and the relatively low values for the

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fluorescence rate constant (k_f). The absence of a Stokes shift indicates that the geometry of the first singlet excited state of the DHPs of **1** to **6** is very similar to the ground-state geometry of these molecules. The values for k_f for these compounds were between 1×10^5 and 1×10^6 s^{-1}. In comparison, the fluorescence rate constants for benzene, naphthalene, and pyrene (nonpolar solvent) are 1.6×10^6, 2.0×10^6, and 1.0×10^6 s^{-1}, respectively.[31] These hydrocarbons have low fluorescence rate constants because of their rigidity and high symmetry. It is interesting to note that even in the case of **7** the fluorescence rate constant is as low as for the other DHPs, although the absorption and emission spectra do not show the same resolution as observed for the other DHPs. This result suggests that the benzo[e]-fusion leads to a lower symmetry, but does not affect the rigidity of the molecule.

The second transient detected for the excitation of the DHPs in the laser flash photolysis experiments is a triplet excited state. This species is not a transient involved in the formation of the CPD, because oxygen did not lead to a significant decrease of the CPD formation quantum yield. The quenching of the triplet excited state by oxygen is very efficient, and if this excited state was involved in the formation of the CPD, a decrease by a factor of at least 10 would have been expected for the quantum yield of CPD formation.[51] The spins for the electrons in the HOMO and LUMO of the triplet state are parallel and therefore correlated, and this excited state has biradical character. For this reason, the triplet state of DHP can be viewed as a biradical in which the transannular bond is cleaved. In the triplet biradical the molecular framework would rearrange to that observed for the ground-state CPD, where the carbons 10b and 10c rehybridize, and the unpaired electrons of the biradical are delocalized over the rings. In this respect, the structures of the triplet excited DHP and triplet excited CPD are the same. This structure explains the larger absorption for the transient in the UV-region of the spectrum at the expense of the absorption in the visible region. The biradical nature of the triplet state of DHP/CPD is similar to the structure of triplet states for photoenols and xylylenes, where the triplet excited states are the biradicals of the corresponding ground-state molecules.[52−54]

Excitation of the CPD isomers of **3** and **7** led to the detection of a weak fluorescence. No appreciable formation of triplet CPD was observed, suggesting that intersystem crossing cannot compete with other deactivation processes. The lower intersystem crossing quantum yield can be explained by the larger energy gap between the S_1 and T_1 states for CPD than for DHP, since rate constants for nonradiative transitions are known to decrease when the energy gap increases.[55] This energy can be estimated from the difference in the S_1 energies of CPD and DHP, since the triplet excited states of DHP and CPD are likely to be the same from the structural point of view and, therefore, have the same energy. The S_1-T_1 energy gap is ca. 40 to 50 kcal/mol higher for CPD than for DHP. The singlet excited CPD decays either to DHP or back to its ground state. The quantum yield for the ring closing reactions is smaller than 0.5, which is much lower than previously estimated,[13] but it is not out of line when compared to other photochromic systems.[56−59] The reaction from the singlet excited state of CPD does not follow adiabatically through the singlet excited state of DHP, as was observed for other photochemical rearrangement reactions.[60] If this were the case, the DHP emission and the absorption for the triplet excited state should have been observed. The formation of DHP from the singlet excited state of CPD could either occur in a concerted reaction or through the same singlet biradical discussed above for the reaction of the singlet excited DHP. Irrespective of the mechanism, some singlet excited CPD decays through internal conversion to ground-state CPD, because the quantum yield for ring closing is significantly lower than unity.

The rate constant for CPD formation is much more sensitive to the nature and the position of the substituents than the fluorescence rate constant. For example, for **7** and **3**, when compared to **2**, the bond cleavage rate constants increased by factors of 67 and 10 leading to an increase in the bond cleavage quantum yield of 30 and 8, respectively (Table 2). However, the addition of other conjugating systems, such as acetylenes, led to a marked decrease of the bond cleavage quantum yield. Conversely, the addition of an acetyl group to the 4-position led to an increase of this parameter. These results show that subtle structural changes have a significant effect on the rate constants for the cleavage of the transannular bond; however, no trends could be identified for the compounds studied besides the much larger rate constant observed for **7**.

The photophysical characterization of compounds **1**−**7** showed that the ring opening rate constant is low, leading to a small photoswitching quantum yield. This property will have to be taken into account when using DHPs for photoswitching devices. These molecules will only be useful for such applications where the number of photons is not an issue; that is, the devices should not be designed with a one photon−one molecule conversion in mind. For example, DHPs have been employed in molecules where the intended switching function is conductance[8] and high-intensity irradiation is not an issue. In addition, some structural aspects can be explored to enhance the photoswitching ability of DHPs. Introduction of alkyl groups in the 2- and 7-positions increases the ease of synthesis,[10] but leads to a decrease of the ring opening quantum yield by a factor of 4 when compared to compound **1**. In this respect, substitution of acetyl groups at position 2 and/or 7 is more desirable, since the 2-acetyl-DHP (**3**) showed an increased opening quantum yield. It is also worth noting that if acetylenes are going to be used to build molecular wires by substituting compound **2**, a price of another factor of 3 when compared to DHP-**2** will have to be paid in the ring opening quantum yield. The end result would be that the opening quantum yield as compared to the unsubstituted DHP-**1** was decreased by over 1 order of magnitude. An alternate approach to build multichromophoric compounds containing DHP units would be to use rigid saturated hydrocarbon bridges, such as

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(51) On the basis of the quenching rate constant of the triplet state by oxygen, a triplet lifetime of 3 μs, and an oxygen concentration in cyclohexane of 2.4 mM, the ratio of the quantum yields in the absence and presence of oxygen was calculated to be 14.7.

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norbornylene bridges. The most successful change to the DHP structure with respect to the ring opening quantum yield was benzo[e]-fusion. An increase in the ring opening rate constant was observed, which was somewhat offset by a shorter fluorescence lifetime. However, the net effect was a substantial increase of the ring opening quantum yield. We are currently exploring if the combination of acetyl substitution in the 2-position and benzo[e]-fusion leads to a higher ring opening quantum yield, as well as the effect of further conjugation of the fused ring.

In summary, the characterization of the photochromism of DHPs has shown that these molecules have an intrinsically low quantum yield for switching, which can be moderately affected by the use of substituents. The choice of substituents for the design and synthesis of more sophisticated photoswitches, such as compounds containing several chromophores that can be switched in discrete steps, will have to rely on studies on how these substituents affect the photophysics of the DHP units. As shown in the examples for the acetylene substituted DHPs, strategies used for other systems cannot readily be employed for DHPs without establishing in model compounds the effect these substituents have on the photoswitching efficiency.

Experimental Section

The synthesis for **5**, **6**, and **8**, their spectroscopic characterization, and checks for purity are described in the Supporting Information. Ground-state spectra were obtained with Varian Cary 1 or 5 spectrometers, while fluorescence spectra at room and low temperatures were measured with a PTI QM-2 spectrofluorimeter.[61] Fluorescence lifetimes were determined using a Ti:sapphire laser/Hamamatsu streak camera system previously described.[62] Samples for the nanosecond laser flash photolysis experiments[63] were excited either with an Excimer laser at 308 nm, a Nd:Yag laser at 266, 355, or 532 nm, or by using a OPO tunable laser with excitation wavelengths above 420 nm. Fluorescence quantum yields were measured[64] using $Ru(bipy)_3Cl_2$ as a primary standard,[30] and compound **2** as a secondary standard. Ring opening quantum yields were measured using ferrioxalate actinometry as a primary standard,[33,34,65] or **1** as a secondary standard.

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Supporting Information Available: Tables S1 and S2 show ϵ values for the DHPs, and Figure S1 shows the transient absorption spectra for **2** and **3**. Details of the experimental procedures are also included (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(61) Details on the spectroscopic techniques and methods are given in the Supporting Information.

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