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Photophysical studies on the photochromism of *trans*-10b,10c-dimethyldihydropyrene

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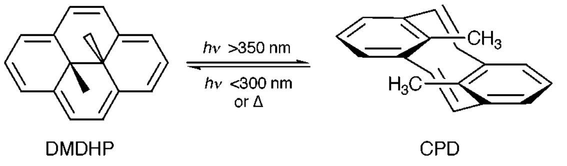
Photophysical studies on the photochromism of *trans*-10b,10c-dimethyldihydropyrene showed that several transients, including the triplet excited state of the cyclophanediene, were observed.

Dimethyldihydropyrene derivatives and their isomeric cyclophanes can be interconverted photochemically. Once the less stable isomer is formed photochemically it reverts back to the more stable form in a thermal reaction.[1] In the case of *trans*-10b,10c-dimethyldihydropyrene (DMDHP, Scheme 1), the cyclophanediene (CPD) is the less stable isomer by 3 kcal mol^{-1}.[2]

Photochromic molecules have considerable potential as optical switches.[3–5] Dimethyldihydropyrene derivatives are photochromic and have been synthetized with sophisticated multiple switching sites.[6,7] However, photophysical studies have mostly been limited to irradiation with broadband light sources. Although theoretical studies have discussed the possible intermediates involved in the isomerization reaction,[2,8] experimentally no studies have been reported on the detection of reactive intermediates. The latter is the subject of this report.

DMDHP was synthesized as previously described.[9] Its absorption spectrum extends up to 650 nm,[10] and when excited (PTI QM-2 fluorimeter) at 470 nm its fluorescence centered at 640 nm was observed. The energy for the S$_1$ state is 44 kcal mol^{-1},[11] and its geometry is similar to that of the ground state since no wavelength shift was observed between the emission maximum and the absorption maximum at the longest wavelength. The CPD absorption is shifted to the blue because this molecule is less conjugated than DMDHP and the S$_1$ energy is higher than 80 kcal mol^{-1}.

Laser flash photolysis[12] was employed to obtain the transient spectra for DMDHP. A flow cell was used to ensure that a fresh solution was irradiated for each laser pulse. Irradiation of DMDHP at 355 nm led to a bleaching at wavelengths longer than 300 nm and the detection of transients in the 250–320 nm region (Fig. 1). No transient signals were detected between 550 and 650 nm. Upon excitation, DMDHP is transformed into transients with higher molar absorptivities in the UV region of the spectrum and loss of absorption in the visible region. For delays longer than 70 ns the transient spectrum had a maximum at 280 nm (transient **I**) and an isosbestic point was observed at 310 nm (inset Fig. 1). The latter suggests that at long delays only DMDHP and **I** were present. At very short delays (< 50 ns) a transient at 310 nm was detected (transient **II**). The transient kinetics showed a short- and a long-lived component (Fig. 2). The lifetimes for these components were the same for the decay at 280–290 nm and the growth at 340 nm, indicating that **I** and **II** reformed DMDHP. Transient **I** did not decay back to the baseline [inset (*a*) in Fig. 2] and the bleaching at 340 nm did not completely recover (≤ 2 ms). This 'permanent' absorption change was assigned to the formation of CPD. The lifetime of **I** was longer than 5 μs and was very dependent on the presence of trace amounts of oxygen. The lifetime for **II** was shorter than the time-resolution of our system (< 12 ns) and the time-profile observed was that of the laser pulse (Fig. 2).



Scheme 1

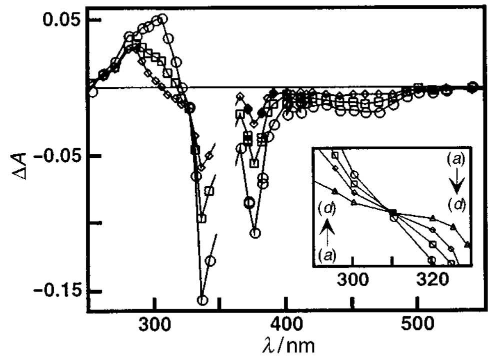


Fig. 1 Transient absorption spectra of DMDHP in cyclohexane at short delays after the laser pulse: (○) 10, (□) 50 and (◇) 70 ns. The inset shows the absorption region close to the isosbestic point at long delays: (*a*) 1, (*b*) 5, (*c*) 10 and (*d*) 15 μs.

CPD, obtained by irradiating DMDHP in MeCN at −40 °C above 550 nm, was excited at 266 nm and −35 °C.[13] At 280 nm bleaching was observed indicating that some CPD reacted. In contrast, at 340 and 470 nm a positive absorption appears suggesting that CPD was isomerized into DMDHP. These results show that the transient phenomena being observed are due to the photochromism of DMDHP.

Quenching studies were performed to obtain information about the chemical nature of **I**. Oxygen readily reacts with **I** [(3.3 ± 0.6) 10^9 M^{-1} s^{-1}]. Quenchers with different triplet energies (E_T) were employed to check if **I** is a triplet excited

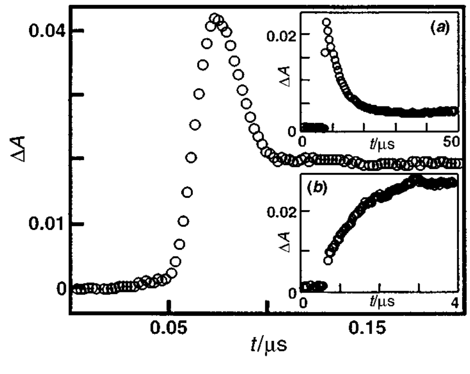


Fig. 2 Kinetic traces for the decay of transient **II** monitored at 290 nm (short time scale). Inset (*a*) shows the decay of transient **I** at 280 nm on a long time scale. Inset (*b*) shows the growth for triplet β-carotene (20 μM) when DMDHP is irradiated.

state. Cyclohexa-1,3-diene (E_T = 52 kcal mol^{-1})[14] or ferrocene (E_T = 38 kcal mol^{-1})[15] did not shorten the lifetime of **I**. However, β-carotene (E_T = 21 kcal mol^{-1})[14] quenched **I**. The triplet β-carotene was observed as a growth at 520 nm [Fig. 2, inset *(b)*] and the quenching rate constant was estimated to be *ca.* 10^{10} M^{-1} s^{-1}. These results show that **I** is a triplet state with an energy between 21 and 38 kcal mol^{-1}.

The quantum yield for the DMDHP to CPD photoisomerization ($\phi_{\mathrm{DMDHP}\rightarrow\mathrm{CPD}}$) was estimated from the magnitude of the'permanent' bleaching ($\tau \geq 2$ ms) at 470 nm using benzophenone [(ϕ_{isc} = 1, $\varepsilon(\mathrm{BP})_{530}$ = 7220 M^{-1} cm^{-1}]^{14} as a standard. Samples in cyclohexane containing benzophenone or DMDHP with matched absorptions at the laser excitation wavelength were excited at different laser energies and the values of ΔA at 530 nm for benzophenone and the bleaching at 470 nm for DMDHP were measured. These values are related by eqn. (1) [$\varepsilon(\mathrm{DMDHP})_{470}$ = 8200 ± 600 M^{-1} cm^{-1}, from *A vs.* [DMDHP] plots].

$$|\Delta A(\mathrm{DMDHP})| = \frac{\varepsilon(\mathrm{DMDHP})_{470}\,\phi_{\mathrm{DMDHP}\rightarrow\mathrm{CPD}}}{\varepsilon(\mathrm{BP})_{530}\,\phi_{\mathrm{isc}}}\,\Delta A(\mathrm{BP}) \quad (1)$$

The recovered value for $\phi_{\mathrm{DMDHP}\rightarrow\mathrm{CPD}}$ (0.03 ± 0.01, three determinations) agrees well with the reported value (0.02).[1]

Based on the quenching by β-carotene and the absorption maximum at 280 nm, we assign **I** to the excited triplet state of CPD. The absorption at 280 nm indicates that, compared to DMDHP, a considerable amount of conjugation was lost, suggesting that the transannular bond was broken. Twisting of the bonds without breaking the transannular bond will not lead to a significant loss of conjugation. For this reason transient **I** cannot be the triplet excited state of DMDHP. The triplet CPD has a biradical character. In this respect, **I** is similar to the triplets of photoenols and xylylenes where these excited states are the biradicals of the corresponding ground state molecules.[16–18] The decay of **I** is probably determined by the rate of intersystem crossing to the singlet biradical which will rapidly form DMDHP or CPD.

The energy for **I** has been bracketed between 22 and 38 kcal mol^{-1} which overlaps with the energy for the transition state for the thermal reversion of CPD to DMDHP (Fig. 3). The triplet and singlet biradical reaction surfaces are likely to be close to the ground state surface and the reaction can proceed diabatically to the ground state surface once intersystem crossing to the singlet biradical occurs. In contrast, the reactivity from the excited singlet DMDHP could occur through a concerted or biradical mechanism. Although the formation of CPD was previously attributed to the reaction of the excited singlet DMDHP[1] it cannot be excluded that some CPD is formed from an excited triplet state with a low quantum yield.

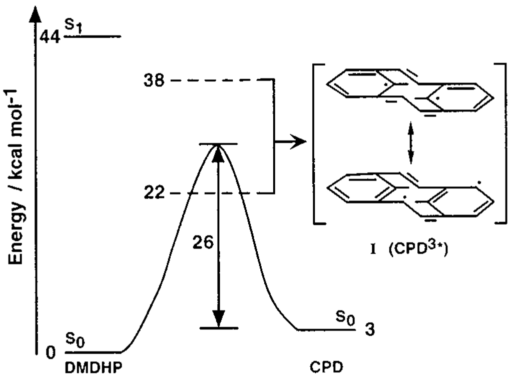


Fig. 3 Diagram representing the thermal conversion between DMDHP and CPD and some of the excited states of these isomers (only two resonance structures for **I** are shown).

Transient **II** cannot be definitely assigned because of its short lifetime. Its spectrum shows a maximum at 310 nm indicating that the DMDHP conjugation has been lost and **II** cannot be the excited singlet or triplet state of DMDHP. In addition, **II** is not the excited singlet state of CPD, since this state is not accessible on energetic grounds from the S_1 of DMDHP. One possibility, which is still speculative, is that **II** corresponds to the singlet biradical of CPD. Since the lifetime for **II** is shorter than the lifetime for triplet CPD, **II** can only be detected at short delays when formed from the excited singlet of DMDHP.

In conclusion, we report for the first time the transients formed in the irradiation of DMDHP. Detailed future studies on the photophysics of DMDHP derivatives will establish the importance of these transients when designing switches with high photoisomerization quantum yields.

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