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Photocyclization of Diphenylamine Studied by Time-Resolved Thermal Lensing. Heat of Reaction, Energetics, and Reactivity of Intermediates

Tadashi Suzuki, Yoshizumi Kajii, Kazuhiko Shibuya, and Kinichi Obi*
Department of Chemistry, Tokyo Institute of Technology, 2-12-1 Ohokayama, Meguro-ku, Tokyo 152
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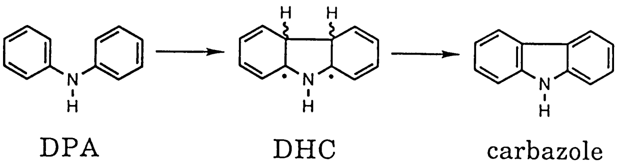
The time-resolved thermal lensing (TRTL) technique was employed to study the photocyclization of diphenylamine (DPA) to form intermediate 4a,4b-dihydrocarbazole (DHC) in methanol solution at room temperature. The heat of reaction, ΔH, was determined to be $(2.6\pm0.2)\times10^2$ kJ mol^{-1} (^{1}DPA→^{1}DHC): The reaction proceeds endothermically. The ring closure step proceeds on the triplet surface (^{3}DPA*→^{3}DHC*). These triplet states are found to be isoenergetic by analyzing the time evolution of the TRTL signal. ^{3}DHC* is located at 21 kJ mol^{-1} above ^{1}DHC. Furthermore, two-color laser flash photolysis experiments have revealed that the photoexcitation of intermediate ^{1}DHC leads to the recovery of parent DPA and therefore inhibits the formation of carbazole.

Photocyclization reactions of diphenylamines have been extensively studied using both continuous wave and pulsed light sources.[1—5] With the irradiation of diphenylamines, such as diphenylamine, *N,N*-diphenylmethylamine, triphenylamine, and several of their derivatives, intramolecular cyclization reactions take place to produce the corresponding carbazoles. Carbazole is the final product of the irradiation of diphenylamine (DPA) in solution.[1] Mass spectrometric analysis revealed that the amounts of molecular hydrogen and carbazole produced are equal.[2] Shizuka et al. carried out triplet-sensitization experiments and found that the cyclization proceeds via the lowest triplet states of diphenylamines.[3] Förster et al. identified the transient species with the absorption maximum at 610 nm observed in the photoexcitation of *N,N*-diphenylmethylamine as the relatively long-lived intermediate 4a,4b-dihydrocarbazole, and found rather large frequency factors[4] for the decay rate constants of triplet diphenylamines of 10^{12}—10^{13} s^{-1}. Recently, the overall reaction scheme of the DPA photocyclization has been proposed by Rahn et al. on the basis of nanosecond laser flash photolysis experiments:[5] The first excited singlet DPA (^{1}DPA*) efficiently yields ^{3}DPA*, which either undergoes cyclization to form triplet dihydrocarbazole (^{3}DHC*) or relaxes to DPA in the ground state (^{1}DPA). Subsequently, ^{3}DHC* relaxes rapidly to the ground state (^{1}DHC). However, the energetics of DHC in the ground and triplet states and the reactivity of the excited singlet state have not been reported due to its instability.

Since the time-resolved thermal lensing (TRTL) method instantaneously detects the time-dependent heat emitted through radiationless deactivation processes of the excited and metastable states, this technique allows us to obtain new information that is not attainable by conventional optical methods such as laser-induced fluorescence, laser flash photolysis, etc. In this paper we have applied this technique to determine the energetics of the photocyclization reaction of DPA. Moreover, the photochemistry of ^{1}DHC has been studied using stepwise two-photon laser flash spectroscopy, which has revealed that the selective excitation of intermediates opens new reaction channels.[6—8] We demonstrate that such a reaction pathway can be controlled by the two-color flash photolysis experiment of DHC as well.



Experimental

A XeCl excimer laser (Lambda Physik LPX105; 308 nm, 100 mJ/pulse, 20 ns pulse duration) served as an excitation light source. The laser beam was focused into a sample cuvette (NSG T-59FL-UV-10; 10 mm light-path length) with a 120-mm focal length lens. Since the intermediate formed upon photoexcitation of DPA has a strong absorption band in the red region (<700 nm), an IR diode laser was used as a probing light source for TRTL signals. The diode laser (Sharp LT024MD), with 30 mW of energy at 780 nm, was driven by an integrated circuit (Sharp IR3C02A) with automatic power control. The IR laser beam was collimated with a 20-mm focal length lens, and traversed the cuvette coaxially to the excitation light after being focused in front of the cuvette with a 30-mm focal lens. A portion of the monitoring light transmitted through a pinhole (Corion 2401; 300 μm diameter) was detected as the lens signals with a combination of a monochromator (Nikon P250) and a photomultiplier (Hamamatsu Photonics R928). The output signal was converted into voltage with a 50- or 500-Ω load resister, amplified by a preamplifier (ORTEC 574), digitized and recorded with a storage oscilloscope (Gould 4074; 400 MHz) or a digital memory (Iwatsu DM901; 10 ns/word, 2 kwords memory) connected with a personal computer (NEC PC9801F2). The TRTL signals were averaged over fifty shots to improve the S/N ratio. The excitation laser energy was varied by a neutral-density linear-wedge filter (Corion 2161) and detected by a photodiode (Hamamatsu Photonics S1336-5BQ), which was calibrated with a pyroelectric detector (Gentec ED100). Conventional flash photolysis experiments were carried out to investigate the kinetics of photoexcited DPA; a Xe flash lamp (Ushio UXL150DS; 150 W) was used as a monitoring light source, synchronously fired with the XeCl excimer laser. In the two-color flash photolysis, a dye laser (Lambda Physik FL3002) pumped by a XeCl excimer laser (Lambda Physik EMG52MSC; 70 mJ, 15 ns) was used as an excitation light source for the reaction intermediate.

Diphenylamine (Tokyo Kasei; zone refined) and methanol (Kanto Chemical Co., Ltd.; GR grade) were used as received. Pyridazine was purified by vacuum distillation. Methanol was used as a solvent. All measurements were carried out at room temperature in a flow system to eliminate the effect of photoproducts. Argon gas (purity 99.95%) saturated with methanol vapor was passed through the sample solution for half an hour before use.

Results and Discussion

Heat of Reaction of DHC Production. Figure 1 shows the transient absorption spectra measured at four different delay times after the laser excitation of DPA at 308 nm. The spectrum immediately after the excitation was corrected for the fluorescence of DPA. The spectra measured at the delay times of 0 and 4.5 μs are assigned to ^{3}DPA* and ^{1}DHC, respectively, after the reported spectra.[5] Bleaching due to the decrease of the DPA concentration was observed at wavelengths below 320 nm. Figure 2 shows the time profile of the transient absorption intensity monitored at 605 nm. This time evolution consists of two components: The decay of ^{3}DPA* (k_T) and the growth of ^{1}DHC (k'_p). The rate constants of k_T and k'_p were determined to be $(1.4\pm0.1)\times10^6$ s^{-1} and $(2.4\pm0.1)\times10^6$ s^{-1}, respectively, with the nonlinear least-squares method. The best fit decay and growth time profiles are shown in Fig. 2 as solid lines. The overall photocyclization reaction to produce ^{1}DHC was completed in 4.5 μs, and the lifetime of the relatively long-lived intermediate, ^{1}DHC, was determined to be 2.4 ms, even at room temperature.

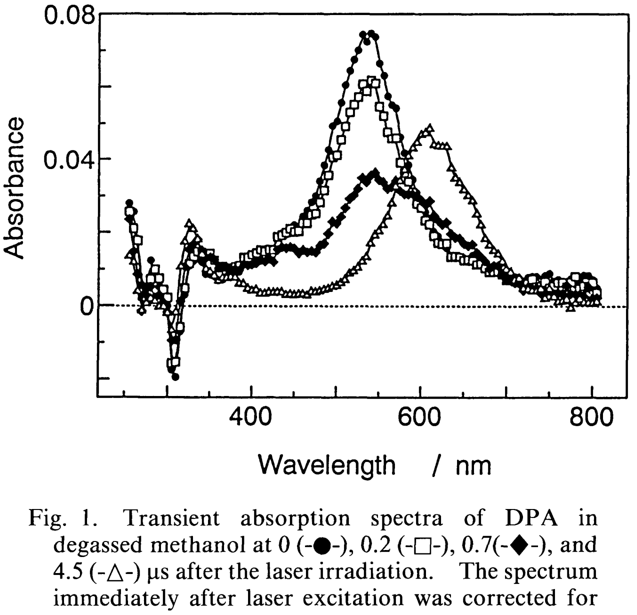


Fig. 1. Transient absorption spectra of DPA in degassed methanol at 0 (-●-), 0.2 (-□-), 0.7(-◆-), and 4.5 (-△-) μs after the laser irradiation. The spectrum immediately after laser excitation was corrected for the fluorescence.

Figure 3 shows the time evolution of the TRTL signals measured for the photoexcitation of DPA, where the time scale is the same as that in Fig. 2. The TRTL signals are composed of steep rise and slow growth after the laser excitation. The steep rise corresponds to the heat released through the nonradiative processes that produce ^{3}DPA*, and the slow one is characterized by the heat released from ^{3}DPA* relaxing to ^{1}DPA and forming ^{1}DHC. The slow component was analyzed with a biexponential rise (vide infra).

As described in the Introduction, quantitative analyses of heat emitted through the nonradiative processes give us calorimetric and kinetic information. The heat conversion efficiency, α, is defined as the ratio of the energy released as heat to the absorbed photon energy,

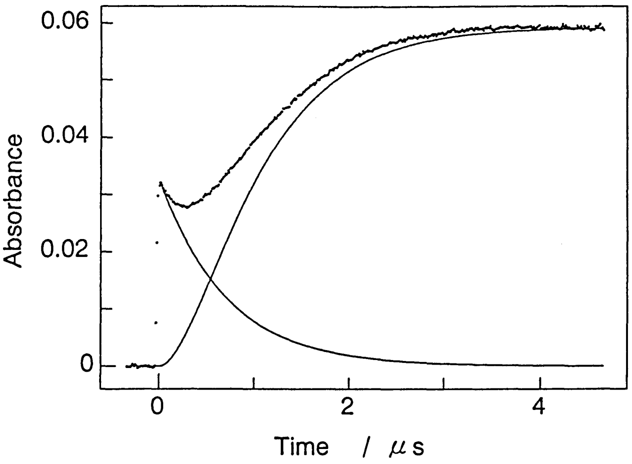


Fig. 2. Time evolution of transient absorption of DPA monitored at 605 nm. The signal is composed of two components: The decay of ^{3}DPA*(k_T=1.4×10^6 s^{-1}) and the growth of ^{1}DHC (k'_p=2.4×10^6 s^{-1}), shown as solid lines. The cyclization reaction to produce ^{1}DHC is completed in 4.5 μs.

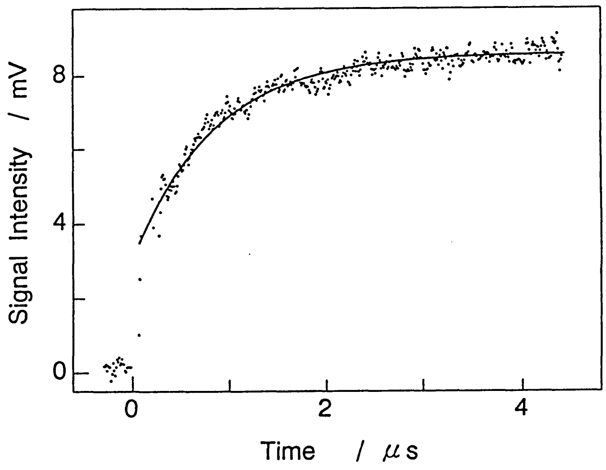


Fig. 3. TRTL signal of DPA. The solid curve shows the best fitting of the heat released through the decay of ^{3}DPA* and the growth of ^{1}DHC. (See text for details.)

$$\alpha=(E_{\mathrm{ex}}-\Sigma\Phi_iE_i)/E_{\mathrm{ex}}, \qquad (1)$$

where E_{ex} denotes the excitation energy; Φ_i and E_i are the quantum yield of and the energy consumed by process i, where i is either fluorescence or chemical reaction. Since photoexcited DPA fluoresces or undergoes photocyclization, the fractional energy Φ_fE_s escapes out of the reaction system and $\Phi_r\Delta H$ is stored in the system as chemical energy, where ΔH is the heat of reaction for the cyclization.

To obtain ΔH, first, we must determine the α value. Figure 4 shows the laser power dependence of the TRTL signals, U_{T}, measured at the delay time of 4.5 μs when the photocyclization is complete. The data follow the best fitted straight lines obtained with the least-squares method, which indicates that multiphoton process does not occur in this system. The slopes of the lines in Fig. 4, $U_{\mathrm{T}}/I_{\mathrm{L}}$, are plotted in Fig. 5 (open squares) against the fraction of the laser light absorbed, $1-10^{-A}$, where A is the absorbance of DPA at 308 nm. Pyridazine was employed as a calorimetric standard, because the α value of pyridazine has been established to be unity.[9] The data for pyridazine measured under the same conditions as for DPA are plotted (open circles) in Fig. 5. From the ratio between these two slopes we determined the α value of DPA to be 0.66±0.03.

Using Eq. 1, the value of ΔH system is given as

$$\Delta H=[(1-\alpha)E_{\mathrm{ex}}-\Phi_{\mathrm{f}}\langle E_{\mathrm{s}}\rangle]/\Phi_{\mathrm{r}}. \qquad (2)$$

We adopted the reported value $\Phi_{\mathrm{f}}=0.11$ in ethanol.[10] Since the fluorescence spectrum covered a wide wavelength range from 310 to 500 nm, we used an averaged energy of fluorescence, $\langle E_{\mathrm{s}}\rangle$, in place of E_{s}: The $\langle E_{\mathrm{s}}\rangle$ value was calculated to be $(2.75\pm0.02)\times10^4$ cm^{-1} from the fluorescence spectrum (the detailed procedure was described in Ref. 6). The quantum yield of the cyclization reaction, Φ_{r}, was determined to be 0.37±0.01 from the flash photolysis experiments carried out under the same experimental conditions as TRTL. The parameters used to estimate Φ_{r} were the ^{3}DPA* quantum yield, $\Phi_{\mathrm{isc}}=0.86$, and the extinction coefficient[5] of ^{3}DPA* at the peak wavelength (530 nm), $\varepsilon_{\mathrm{T}}=1.5\times10^4$ M^{-1}cm^{-1}. Since the extinction coefficient of ^{1}DHC is not reported, we used the reported value of 9-methyl-DHC, $\varepsilon_{\mathrm{H}}=2.1\times10^4$ M^{-1}cm^{-1} at 610 nm.[4] Finally, the heat of reaction, ΔH, was determined to be $(2.6\pm0.2)\times10^2$ kJ mol,$^{-1}$ using Eq. 2. The cyclization reaction is found to be fairly endothermic.

Triplet Energy of DHC. The TRTL technique is suitable to study optically dark states because it detects the heat released through nonradiative processes. We analyzed the time evolution of TRTL signals to determine the energy level of the nonphosphorescent ^{3}DHC* state, which is the precursor of ^{1}DHC. Figure 6 shows the energy diagram of the overall reaction forming ^{1}DHC, adopted from Rahn et al.[5] According to this scheme, the time evolution of TRTL signals is expressed as follows:

$$U(t)/K=A+B\exp(-k_{\mathrm{T}}t)+C\exp(-k'_{\mathrm{p}}t), \qquad (3)$$
$$A=E_{\mathrm{ex}}-\Phi_{\mathrm{f}}\langle E_{\mathrm{s}}\rangle-\Phi_{\mathrm{r}}\Delta H,$$
$$B=\Phi_{\mathrm{r}}(k'_{\mathrm{p}}\Delta H-k_{\mathrm{T}}E'_{\mathrm{T}})/(k'_{\mathrm{p}}-k_{\mathrm{T}})-\Phi_{\mathrm{isc}}E_{\mathrm{T}},$$
$$C=k_{\mathrm{r}}\Phi_{\mathrm{isc}}(E'_{\mathrm{T}}-\Delta H)/(k'_{\mathrm{p}}-k_{\mathrm{T}})$$

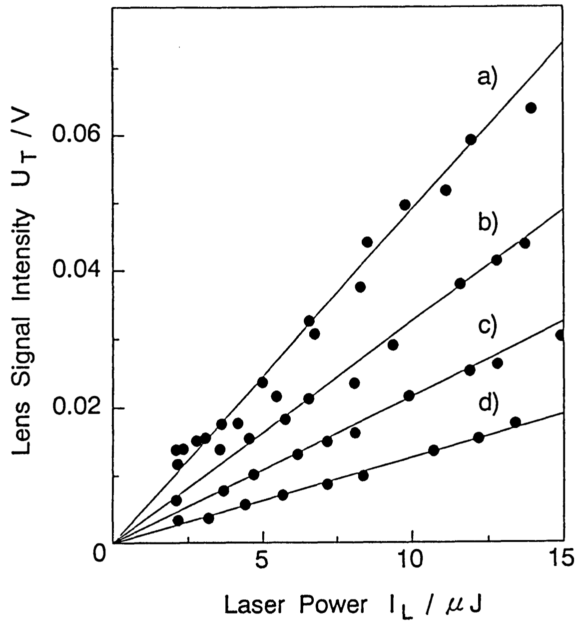


Fig. 4. Laser power dependence of the TRTL signals measured at 4.5 μs at several DPA concentrations: The absorbance at 308 nm are 0.856 (a), 0.401 (b), 0.250 (c), and 0.097 (d). The solid lines are fitted by the least-squares analysis and a linear relationship is maintained below 15 μJ.

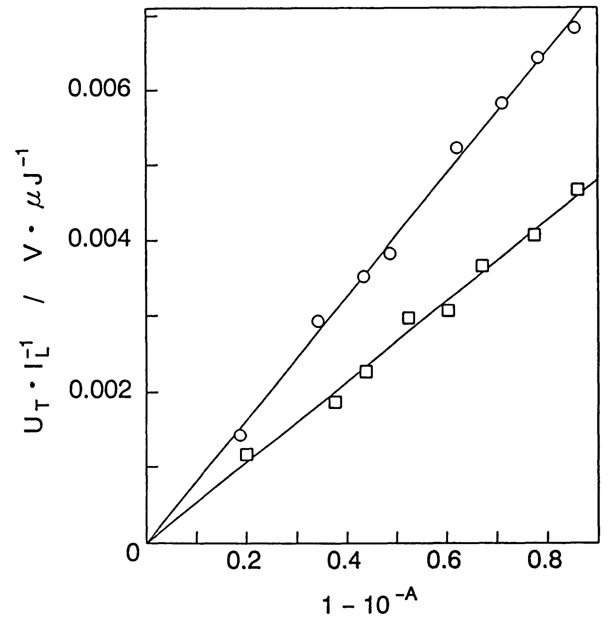


Fig. 5. The relationship of the slope, $U_{\mathrm{T}}/I_{\mathrm{L}}$, to the quantity of light absorbed, $1-10^{-A}$, for DPA (-□-) and pyridazine (-○-).

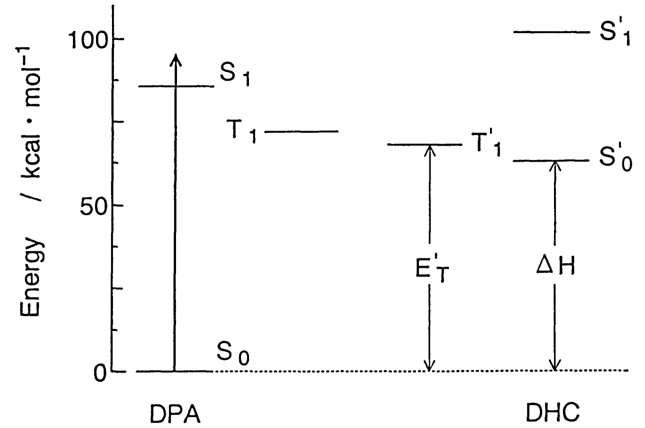


Fig. 6. Energy diagrams of DPA and DHC in methanol solution. ΔH denotes the heat of reaction of ^{1}DHC and E'_T is the energy of ^{3}DHC* relative to DPA in the ground state.

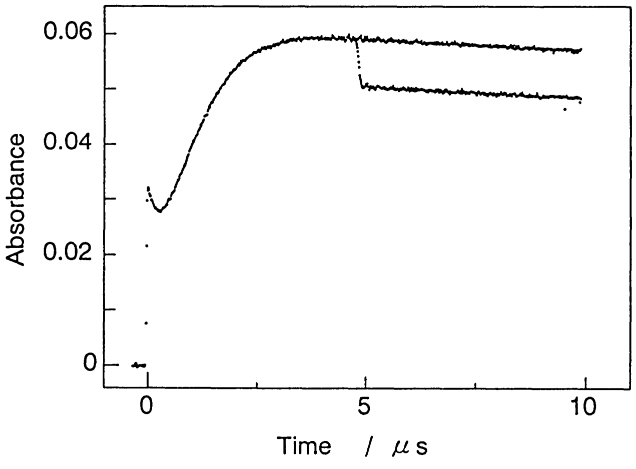


Fig. 7. Time profiles of transient absorption of DPA monitored at 605 nm. The 600 nm dye laser pumped by the excimer laser was fired at 4.8 μs after the photolysis light irradiation. The produced bleaching does not recover.

where K is a constant including the instrumental factor, E'_T is the energy level of ^{3}DHC* relative to DPA in the ground state, and k_r is the cyclization reaction rate constant for ^{3}DPA*→^{3}DHC*. The value of k_r is estimated to be 5.2×10^5 s^{-1} from the available values of k_T, Φ_{isc}, and Φ_r. Here, the first term of Eq. 3 in the right hand side denotes the total energy released as heat with the production of ^{1}DHC. All parameters except E'_T were already obtained above. The measured time profile of the TRTL signals was fitted with Eq. 3, using the energy of E'_T as a fitting parameter. The best fitting shown in Fig. 3 as the solid curve was obtained for $E'_T=(2.8\pm0.2)\times10^2$ kJ mol^{-1}. Since the energy of ^{3}DPA* is reported to be 3.0×10^2 kJ mol^{-1}, we come to the rather surprising conclusion that the reaction proceeds isoenergetically from ^{3}DPA* to ^{3}DHC*.

It is noteworthy that the T$_1$ state of DHC lies near to S$_0$ but not to S$_1$: ΔE(T$_1$–S$_0$) is only 20 kJ mol^{-1}, which is much smaller than ΔE(S$_1$–T$_1$)=138 kJ mol^{-1}. Moreover, DHC has a low-frequency absorption band starting at 750 nm and peaking around 600 nm, which is shifted to red compared with other azaaromatic compounds of similar size. These facts suggest that DHC has a different electronic structure from other azaaromatics like carbazole and acridine. We suppose that DHC has a biradical character in the ground state, which would be located closely to the S$_0$ state. Theoretical studies are necessary to reveal the electronic structure of DHC.

Reactivity of DHC in the Excited Singlet State. To investigate the photodynamics of the excited singlet state of DHC, we carried out two-color flash photolysis. Figure 7 shows the time profiles of the transient absorption intensity monitored at 605 nm. ^{1}DHC was excited with the dye laser at 600 nm, which was fired at 4.8 μs after the excimer laser. The bleaching of ^{1}DHC was observed when the dye laser was fired, and did not recover. This indicates some photochemical reactions take place through S'$_1$. If the S'$_1$ state yields T'$_1$, some part of the bleaching should recover within the T'$_1$ lifetime. However, this is not the case. It is, therefore, concluded that the reaction does not occur through intersystem crossing to T'$_1$. Next, we determined the reaction quantum yield of the excited DHC by using the T–T absorption of zinc tetraphenylporphyrin (ZnTPP) as a standard. The concentration of ZnTPP was adjusted so that the optical density of excited ZnTPP was matched to that of initially excited DHC at the dye laser wavelength. The change in optical density, ΔOD_{DHC} (ν_1), is equal to $\varepsilon_H(\nu_1)\Phi'_r C_{DHC}\, l$, where Φ'_r is the reaction quantum yield of the excited state, C_{DHC} is the excited DHC concentration, and l is the light path length. The optical density of the ZnTPP triplet, $OD_{ZnTPP}(\nu_2)$, was measured at 830 nm under the same excitation conditions as the ΔOD_{DHC} measurement. Then, the reaction quantum yield is as follows,

$$\Phi'_r=\Phi_T\cdot\frac{\Delta OD_{DHC}}{OD_{ZnTPP}}\cdot\frac{\varepsilon_{ZnTpp}}{\varepsilon_H} \tag{4}$$

where Φ_T is the quantum yield of triplet formation. Using the reported values,[11] $\Phi_T=0.95$ and ε_{ZnTPP} (830 nm)=8700 M^{-1}cm^{-1}, the reaction quantum yield, Φ'_r, was determined to be 0.63±0.06.

The optical density difference between the transient absorption spectra with and without firing the dye laser (OD' and OD, respectively) is given as,

$$\begin{aligned}\Delta OD &= OD'-OD\\ &=(\varepsilon_P-\varepsilon_H)[P]\,l.\end{aligned} \tag{5}$$

Here, ε_P is the molar extinction coefficient and [P] the concentration of product in the photolysis of DHC. Figure 8 shows the difference spectrum; that is, ΔOD against wavelength. This spectrum shows the depletion of ^{1}DHC at wavelengths longer than 320 nm and the formation of photoproducts with an absorption

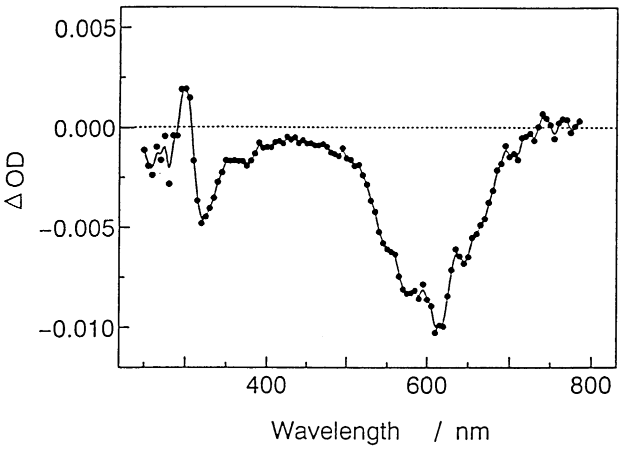


Fig. 8. The difference spectrum. The characteristic peak around 600 nm is identical with that in the absorption spectrum of DHC.

around 300 nm. The extinction coefficient of DHC at 300 nm was estimated to be ca. 10^4 $M^{-1}\,cm^{-1}$ from the transient spectrum measured at 4.5 μs delay time in Fig. 1. The positive ΔOD value at 300 nm suggests that the photoproduct has a larger extinction coefficient than ^{1}DHC. This photoproduct remains alive during the time range of our experimental setup and seems to be a chemically stable species. The plausible photoproducts of DHC are carbazole and DPA. The extinction coefficient of carbazole is 3000 $M^{-1}\,cm^{-1}$ at 300 nm, which is much smaller than that of DHC. Based on Eq. 5, carbazole can be excluded as the main photoproduct. On the other hand, the ε value of DPA is 14000 $M^{-1}\,cm^{-1}$ at 300 nm. Therefore, it is concluded that the main photoproduct is DPA, and the reaction of excited DHC is the cleavage of the photoproduced C–C bond to yield the parent DPA. To form carbazole, two hydrogen atoms must be eliminated as a hydrogen molecule. The hydrogen atoms at the 4a- and 4b-positions in dihydrocarbazole are known to be in the trans position.[12] It is reasonable to conclude that the reaction rate of *trans*-hydrogen elimination is slower than that of the σ-bond cleavage.

In conclusion, we determined the heat of reaction for DPA photocyclization to produce the intermediate DHC to be $(2.6\pm0.2)\times10^2$ kJ mol^{-1}. The energy level of the optically dark state, ^{3}DHC*, was determined to lie at 20 kJ mol^{-1} above the ground state of DHC by analyzing the time evolution of the TRTL signal. We demonstrated that the TRTL technique can be successfully applied to the calorimetric measurements of transient species. DHC excited into the S_1 state mainly undergoes σ-bond cleavage to yield the parent DPA in the ground state, not ^{3}DHC* or carbazole formation. The quantum yield of the reaction was determined to be 0.63 ± 0.06.

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