Biradical Intermediates

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Thermoluminescence Originating from the Singlet Excited State of 1,4-Diarylcyclohexane-1,4-diyls: A Potentially General Strategy for the Observation of Short-Lived Biradicals**

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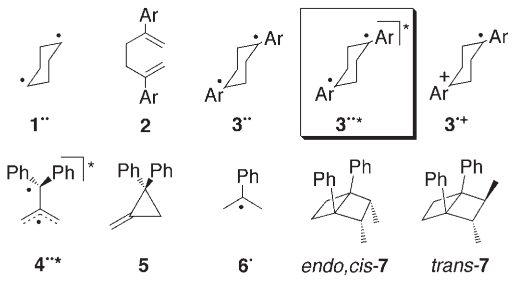
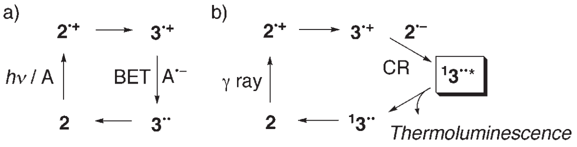
The triplet cyclohexane-1,4-diyl ($^{3}\mathbf{1}^{\cdot\cdot}$, Scheme 1) is a typical example of an organic biradical.[1,2] By using nanosecond absorption spectroscopy on laser flash photolysis, Adam et al.[3] observed the 1,4-diphenylcyclohexane-1,4-diyl biradical ($^{3}\mathbf{3b}^{\cdot\cdot}$), a transient species that plays a key role in the triplet-sensitized photodeazetation reaction of 1,4-diphenyl-2,3-diazabicyclo[2.2.2]oct-2-ene. The *singlet* cyclohexane-1,4-diyl ($^{1}\mathbf{1}^{\cdot\cdot}$) has been proposed as a hypothetical biradical intermediate in pathways for pyrolytic reactions of bicyclo[2.2.0]hexanes and in thermal degenerate Cope rearrangements of 1,5-hexadienes.[1,4] Moreover, the 1,4-diphenyl derivative ($^{1}\mathbf{3b}^{\cdot\cdot}$) has attracted much attention from both the theoretical and experimental standpoint.[4] However, owing to its short lifetime, this intermediate has not been observed in thermally induced Cope rearrangements.



Scheme 1. Ar = 4-XC$_6$H$_4$; X = F (**a**), H (**b**), CH$_3$ (**c**), Cl (**d**), Br (**e**), CH$_3$O (**f**).

Interestingly, the singlet 1,4-diphenylcyclohexane-1,4-diyl biradical ($^{1}\mathbf{3b}^{\cdot\cdot}$) is an intermediate in the acceptor-sensitized degenerate Cope rearrangement of 2,5-diphenyl-1,5-hexadiene (**2b**, Scheme 2a) by photoinduced electron transfer (PET).[5] The transient species $^{1}\mathbf{3b}^{\cdot\cdot}$ is generated by back-electron transfer (BET) from a sensitizer radical anion (A$^{\cdot -}$) to the radical cation $\mathbf{3b}^{\cdot +}$. Although $\mathbf{3b}^{\cdot +}$, stabilized by efficient through-space and through-bond interactions,[6] can be observed with nanosecond absorption spectroscopy on laser flash photolysis, the singlet biradical $^{1}\mathbf{3b}^{\cdot\cdot}$ can not be detected.[5]



Scheme 2. a) Mechanism for the PET degenerate Cope rearrangement of **2**. b) Possible mechanism for TL using **2**. A = acceptor.

Its significance as an important mechanistic intermediate has stimulated thought about new ways to detect $^{1}\mathbf{3b}^{\cdot\cdot}$. One strategy relies on the generation of the excited state of $^{1}\mathbf{3}^{\cdot\cdot}$ ($^{1}\mathbf{3}^{\cdot\cdot}$*), which might be observable by light emission (but not absorption) associated with its conversion into $^{1}\mathbf{3b}^{\cdot\cdot}$. An ideal approach to forming and observing emission from $^{1}\mathbf{3}^{\cdot\cdot}$* is thermoluminescence (TL).[7] In the TL process, an excited-state species is generated by charge recombination (CR), a synonym for BET, between a radical cation and a radical anion pair. In a recent effort, we were able to observe TL originating from the excited state of a 1,1-diphenyl-substituted trimethylenemethane biradical ($^{3}\mathbf{4}^{\cdot\cdot}$*), produced by CR between $\mathbf{4}^{\cdot +}$ and the radical anion of 2,2-diphenyl-1-methylenecyclopropane (**5**).[7,8] Herein, we describe the first observation of $^{1}\mathbf{3}^{\cdot\cdot}$ by using the TL technique and the results of experimental and DFT calculations probing substituent effects on the energy of $^{1}\mathbf{3}^{\cdot\cdot}$*.

Annealing a γ-irradiated methylcyclohexane (MCH) glassy matrix of **2b** (5 mM) from 77 to about 130 K gave rise to an intense TL band at $\lambda_{\mathrm{TL}} = 582$ nm together with weak TL

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bands at $\lambda_{TL} = 306$, 481, and 520 nm (Figure 1). We presumed that the 582-nm emission band was associated with $^{1}\mathbf{3b}^{\bullet\bullet}$.[9] To gain support for this assignment, DFT and time-dependent DFT (TD-DFT) calculations[12] at the UB3LYP/cc-pVDZ level[13] of theory were carried out for $^{1}\mathbf{3b}^{\bullet\bullet}$ and $^{3}\mathbf{3b}^{\bullet\bullet}$. The results show that both structures have chair conformations and that $^{1}\mathbf{3b}^{\bullet\bullet}$ is 1.14 kcal mol^{-1} more stable than $^{3}\mathbf{3b}^{\bullet\bullet}$.[14] Furthermore, TD-DFT calculations suggest that $^{1}\mathbf{3b}^{\bullet\bullet}$ has an electronic-transition band at $\lambda_{calcd} = 623$ nm with an oscillator strength (f) of 0.12, assigned to a HOMO→LUMO transition (Figure 2). In contrast, $^{3}\mathbf{3b}^{\bullet\bullet}$ does not have any electronic-transition band near 600 nm. This result supports the proposal that the 582-nm emission band originates from $^{1}\mathbf{3}^{\bullet\bullet}$*. The unusual red shift of the transition band of $^{1}\mathbf{3b}^{\bullet\bullet}$ compared with that of $\mathbf{6}^{\bullet}$ can reasonably be explained by invoking efficient through-space and through-bond interactions between the two radical components, in a manner similar to that in $\mathbf{3}^{\bullet+}$.[6]

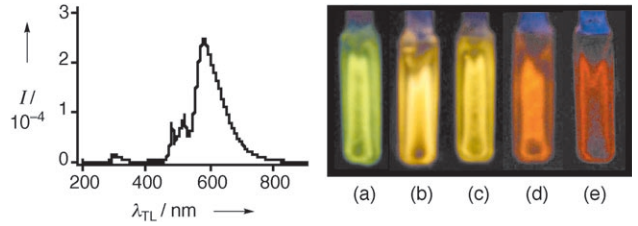

Figure 1. Left: TL spectrum of $^{1}\mathbf{3b}^{\bullet\bullet}$* obtained upon annealing a γ-irradiated MCH glassy matrix containing **2b** (5 mM) from 77 to about 130 K. Right: Photos of TL of $^{1}\mathbf{3a}^{\bullet\bullet}$* (a), $^{1}\mathbf{3b}^{\bullet\bullet}$* (b), $^{1}\mathbf{3c}^{\bullet\bullet}$* (c), $^{1}\mathbf{3d}^{\bullet\bullet}$* (d), and $^{1}\mathbf{3e}^{\bullet\bullet}$* (e). Note that the TL color depends not only on the λ_{TL} value of the major band but also on the width of the TL band including a minor one.

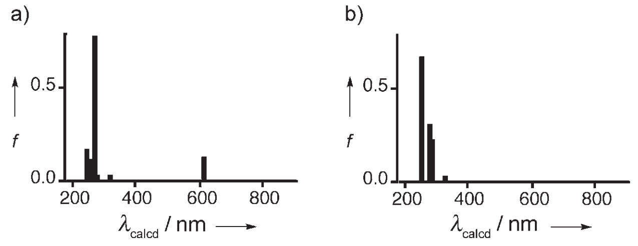

Figure 2. Electronic transitions of a) $^{1}\mathbf{3b}^{\bullet\bullet}$ and b) $^{3}\mathbf{3b}^{\bullet\bullet}$ calculated with TD-DFT at the UB3LYP/cc-pVDZ level.

The validity of this assignment gains further support from the results of TL studies using *endo,cis*- and *trans*-1,4-diphenyl-2,3-dimethylbicyclo[2.2.0]hexane (*endo,cis*-**7** and *trans*-**7**), which are the precursors of dimethyl derivatives of $\mathbf{3}^{\bullet+}$ and $\mathbf{3}^{\bullet\bullet}$ in PET reactions.[15] Both showed intense TL bands at $\lambda_{TL} = 598$ nm, with spectral features that closely resemble the TL spectrum from **2b**. The slight red shift of emission bands derived from these substances compared with those from **2b** (582 nm) is presumably a result of perturbation by the methyl groups.

Substituent effects on electronic-transition energy of the major TL band of **2b** were evaluated. TL from the *para*-substituted derivatives **2a,c–e** appeared at $\lambda_{TL} = 572$, 586, 590, and 592 nm, respectively (Figure 1 and Table 1). TL using **2f** did not exhibit a clear emission peak. The relative transition energies (ΔE_{TL}), based on the absolute transition energy of nonsubstituted $^{1}\mathbf{3b}^{\bullet\bullet}$, correlate well with the radical substituent constants $\sigma^{\bullet}$ [Eq. (1), Figure 3a].[16] This result strongly suggests that the emitting species have radical character. Moreover, the substituent effects on the energy of $^{1}\mathbf{3b}^{\bullet\bullet}$ were successfully reproduced by using TD-DFT calculations. The computed λ_{calcd} values of $^{1}\mathbf{3a,c\text{–}f}^{\bullet\bullet}$* are 625, 634, 641, 644, and 647 nm with corresponding f values of 0.12, 0.14, 0.14, 0.15, and 0.15, respectively (Table 1). A plot of ΔE_{calcd} versus $\sigma^{\bullet}$ gives a favorable correlation [Eq. (2), Figure 3b]. The slope ρ value of −6.87 from a plot of the experimental data closely matches that of −5.73 obtained from treatment of the TD-DFT calculated energies.

Table 1: Observed[a] and calculated[b] TL maxima (λ_{TL} and λ_{calcd}), relative energies (ΔE_{TL} and ΔE_{calcd}), and oscillator strengths (f) of $^{1}\mathbf{3}^{\bullet\bullet}$*.

	λ_{TL} [nm]	ΔE_{TL} [cal mol^{-1}]	λ_{calcd} [nm]	f	ΔE_{calcd} [cal mol^{-1}]
$^{1}\mathbf{3a}^{\bullet\bullet}$*	572	0.858	625	0.12	−0.096
$^{1}\mathbf{3b}^{\bullet\bullet}$*	582	0.00	623	0.12	0.00
$^{1}\mathbf{3c}^{\bullet\bullet}$*	586	−0.335	634	0.14	−0.740
$^{1}\mathbf{3d}^{\bullet\bullet}$*	590	−0.666	641	0.14	−1.201
$^{1}\mathbf{3e}^{\bullet\bullet}$*	592	−0.829	644	0.15	−1.457
$^{1}\mathbf{3f}^{\bullet\bullet}$*	–[c]	–	647	0.15	−1.646

[a] In MCH. [b] Calculations were carried out with TD-DFT at the UB3LYP/cc-pVDZ level. [c] No clear emission peak was observed.

$$\Delta E_{TL} = -6.87\sigma^{\bullet} + 0.20 \tag{1}$$

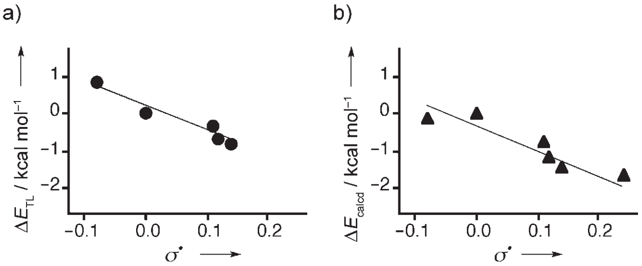

Figure 3. Plots of a) ΔE_{TL} and b) ΔE_{calcd} for $^{1}\mathbf{3}^{\bullet\bullet}$* vs. $\sigma^{\bullet}$.

$$\Delta E_{calcd} = -5.73\sigma^{\bullet} - 0.35 \tag{2}$$

A plausible mechanism for TL emanating from **2** (Scheme 2b) can be constructed based on the results of our recent study using **5**.[7] γ-Irradiation of the MCH glassy matrix containing **2** at 77 K promotes electron transfer that simultaneously produces $\mathbf{2}^{\bullet+}$ and $\mathbf{2}^{\bullet-}$. Owing to the small activation energy for cyclization, $\mathbf{2}^{\bullet+}$ undergoes rapid isomerization to form $\mathbf{3}^{\bullet+}$. Upon annealing, the excited-state biradical $^{1}\mathbf{3}^{\bullet\bullet *}$ is generated by exoergonic CR between $\mathbf{2}^{\bullet+}$ and $\mathbf{3}^{\bullet-}$ and then undergoes emission to form the ground-state biradical $^{1}\mathbf{3}^{\bullet\bullet}$. Finally, **2** is regenerated by bond cleavage in $^{1}\mathbf{3}^{\bullet\bullet}$.

In conclusion, we have designed a unique TL-based strategy that has led to the first successful detection of the singlet biradical $^{1}\mathbf{3}^{\bullet\bullet}$, a significant and controversial species in organic chemistry. TL has high potential as a general method for observing reactive intermediates whose short lifetimes prevent detection by using absorption spectroscopy. Finally, the observation of enormous red shifts of emission bands of biradicals ($^{1}\mathbf{3}^{\bullet\bullet}$) caused by through-space and through-bond interactions, similar to the red shift of absorption bands of radical cations ($\mathbf{3}^{\bullet+}$),[6] is noteworthy as it suggests that small-molecule fluorophores that emit long-wavelength light can be developed. This issue is significant in the field of organic light-emitting diodes.[7]

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[9] The 306-nm emission is assigned to the excited state of **2b** because of its coincidence with the photoluminescence (PL) of **2b** ($\lambda_{\mathrm{PL}} = 308$ nm in MCH glassy matrix, 77 K). Similarly, the 481- and 520-nm emission bands are assigned to the excited state of the cumyl radical skeleton, generated by side reaction(s), owing to their similarity to the cumyl radical ($\mathbf{6}^{\bullet}$) PL ($\lambda_{\mathrm{PL}} = 481$ and 515 nm in MCH glassy matrix, 77 K),[10] which was generated from cumyl alcohol by γ irradiation.

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