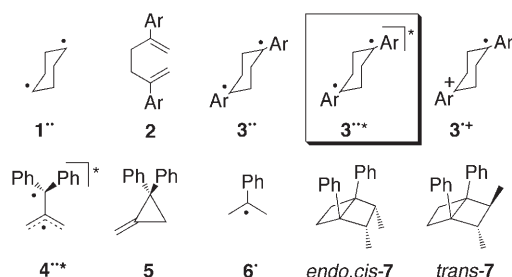


Thermoluminescence Originating from the Singlet Excited State of 1,4-Diarylcyclohexane-1,4-diyls: A Potentially General Strategy for the Observation of Short-Lived Biradicals**

Hayato Namai, Hiroshi Ikeda, Yosuke Hoshi, and Kazuhiko Mizuno*

The triplet cyclohexane-1,4-diyl (**3¹***, Scheme 1) is a typical example of an organic biradical.^[1,2] By using nanosecond absorption spectroscopy on laser flash photolysis, Adam

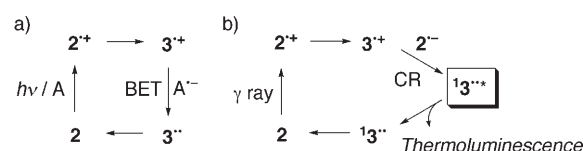


Scheme 1. Ar = 4-XC₆H₄; X = F (a), H (b), CH₃ (c), Cl (d), Br (e), CH₃O (f).

et al.^[3] observed the 1,4-diphenylcyclohexane-1,4-diyl biradical (**3b•**), 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•**) has been proposed as a hypothetical biradical intermediate in pathways for pyrolytic reactions of bicyclo[2.2.0]hexanes and in thermal degenerate Cope rearrange-

ments of 1,5-hexadienes.^[1,4] Moreover, the 1,4-diphenyl derivative (**13b⁺**) 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.

Interestingly, the singlet 1,4-diphenylcyclohexane-1,4-diyl biradical (**13b^{••}**) is an intermediate in the acceptor-sensitized degenerate Cope rearrangement of 2,5-diphenyl-1,5-hexadiene (**2b**, Scheme 2a) by photoinduced electron transfer



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

(PET).^[5] The transient species $^1\mathbf{3b}^{\bullet}$ is generated by back-electron transfer (BET) from a sensitizer radical anion ($\mathbf{A}^{\bullet-}$) to the radical cation $\mathbf{3b}^+$. Although $\mathbf{3b}^+$, stabilized by efficient through-space and through-bond interactions,^[6] can be observed with nanosecond absorption spectroscopy on laser flash photolysis, the singlet biradical $^1\mathbf{3b}^{\bullet}$ can not be detected.^[5]

Its significance as an important mechanistic intermediate has stimulated thought about new ways to detect $^1\mathbf{3b}^{\bullet}$. One strategy relies on the generation of the excited state of $^1\mathbf{3}^{\bullet*}$ ($^1\mathbf{3}^{\bullet*}$), which might be observable by light emission (but not absorption) associated with its conversion into $^1\mathbf{3b}^{\bullet}$. An ideal approach to forming and observing emission from $^1\mathbf{3}^{\bullet*}$ 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 ($^3\mathbf{4}^{\bullet*}$), produced by CR between $\mathbf{4}^+$ and the radical anion of 2,2-diphenyl-1-methylenecyclopropane ($\mathbf{5}$).^[7,8] Herein, we describe the first observation of $^1\mathbf{3}^{\bullet}$ by using the TL technique and the results of experimental and DFT calculations probing substituent effects on the energy of $^1\mathbf{3}^{\bullet*}$.

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 $\lambda_{\text{TL}} = 582$ nm together with weak TL

[*] Prof. Dr. H. Ikeda, Prof. Dr. K. Mizuno
Department of Applied Chemistry
Graduate School of Engineering
Osaka Prefecture University
Sakai, Osaka 599-8531 (Japan)
Fax: (+81) 72-254-9289
E-mail: ikeda@chem.osakafu-u.ac.jp
Homepage: [http://www.chem.osakafu-u.ac.jp/ohka/ohka5/ikeda/
index-e.html](http://www.chem.osakafu-u.ac.jp/ohka/ohka5/ikeda/index-e.html)

Dr. H. Namai, Dr. Y. Hoshi
Department of Chemistry
Graduate School of Science
Tohoku University
Sendai 980-8578 (Japan)

[**] H.I. and K.M. thank the Ministry of Education, Culture, Sports, Science, and Technology of Japan for financial support in the form of a Grant-in-Aid for Scientific Research (19350025) and for that in Priority Areas (Area No. 417) and also Professor M. Ueda (Tohoku University) for his generous assistance. H.I. acknowledges financial support from the Iketani, Shorai, and Mazda Foundations and from the Japan Science and Technology Agency (a Research for Promoting Technological Seeds).



Supporting information for this article is available on the WWW under <http://www.angewandte.org> or from the author.

bands at $\lambda_{\text{TL}} = 306, 481, \text{ and } 520 \text{ nm}$ (Figure 1). We presumed that the 582-nm emission band was associated with $^1\mathbf{3b}^*$.^[9] To gain support for this assignment, DFT and time-dependent

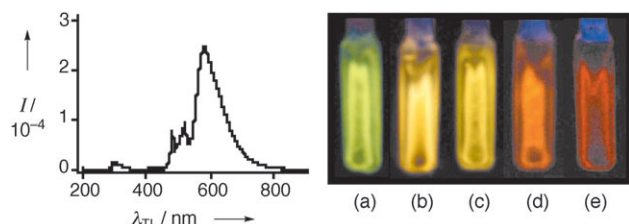


Figure 1. Left: TL spectrum of $^1\mathbf{3b}^*$ obtained upon annealing a γ -irradiated MCH glassy matrix containing $\mathbf{2b}$ (5 mm) from 77 to about 130 K. Right: Photos of TL of $^1\mathbf{3a}^*$ (a), $^1\mathbf{3b}^*$ (b), $^1\mathbf{3c}^*$ (c), $^1\mathbf{3d}^*$ (d), and $^1\mathbf{3e}^*$ (e). 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.

DFT (TD-DFT) calculations^[12] at the UB3LYP/cc-pVDZ level^[13] of theory were carried out for $^1\mathbf{3b}^*$ and $^3\mathbf{3b}^*$. The results show that both structures have chair conformations and that $^1\mathbf{3b}^*$ is $1.14 \text{ kcal mol}^{-1}$ more stable than $^3\mathbf{3b}^*$.^[14] Furthermore, TD-DFT calculations suggest that $^1\mathbf{3b}^*$ has an electronic-transition band at $\lambda_{\text{calcd}} = 623 \text{ nm}$ with an oscillator strength (f) of 0.12, assigned to a HOMO $\rightarrow$ LUMO transition (Figure 2). In contrast, $^3\mathbf{3b}^*$ does not have any electronic-

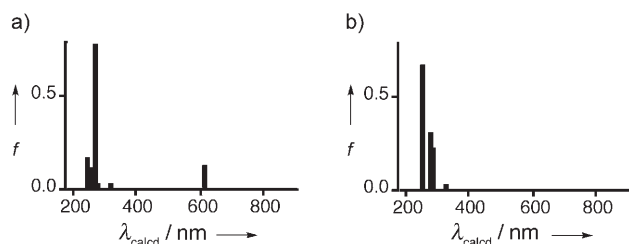


Figure 2. Electronic transitions of a) $^1\mathbf{3b}^*$ and b) $^3\mathbf{3b}^*$ calculated with TD-DFT at the UB3LYP/cc-pVDZ level.

transition band near 600 nm. This result supports the proposal that the 582-nm emission band originates from $^1\mathbf{3b}^*$. The unusual red shift of the transition band of $^1\mathbf{3b}^*$ compared with that of $\mathbf{6}^+$ 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 $\mathbf{3}^+$.^[6]

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*- $\mathbf{7}$ and *trans*- $\mathbf{7}$), which are the precursors of dimethyl derivatives of $\mathbf{3}^+$ and $\mathbf{3}^+$ in PET reactions.^[15] Both showed intense TL bands at $\lambda_{\text{TL}} = 598 \text{ nm}$, with spectral features that closely resemble the TL spectrum from $\mathbf{2b}$. The slight red shift of emission bands derived from these substances compared with those from $\mathbf{2b}$ (582 nm) is presumably a result of perturbation by the methyl groups.

Substituent effects on electronic-transition energy of the major TL band of $\mathbf{2b}$ were evaluated. TL from the *para*-substituted derivatives $\mathbf{2a,c-e}$ appeared at $\lambda_{\text{TL}} = 572, 586, 590, \text{ and } 592 \text{ nm}$, respectively (Figure 1 and Table 1). TL using $\mathbf{2f}$

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 $^1\mathbf{3}^*$.

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

did not exhibit a clear emission peak. The relative transition energies (ΔE_{TL}), based on the absolute transition energy of nonsubstituted $^1\mathbf{3b}^*$, correlate well with the radical substituent constants σ^* [Eq. (1), Figure 3a].^[16] This result strongly

$$\Delta E_{\text{TL}} = -6.87\sigma^* + 0.20 \quad (1)$$

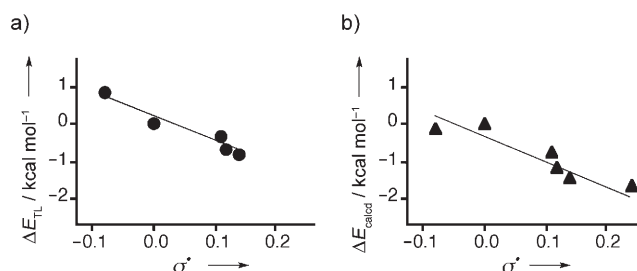


Figure 3. Plots of a) ΔE_{TL} and b) ΔE_{calcd} for $^1\mathbf{3}^*$ vs. σ^* .

suggests that the emitting species have radical character. Moreover, the substituent effects on the energy of $^1\mathbf{3b}^*$ were successfully reproduced by using TD-DFT calculations. The computed λ_{calcd} values of $^1\mathbf{3a,c-f}^*$ 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 σ^* gives a favorable correlation [Eq. (2), Figure 3b]. The slope ρ

$$\Delta E_{\text{calcd}} = -5.73\sigma^* - 0.35 \quad (2)$$

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.

A plausible mechanism for TL emanating from $\mathbf{2}$ (Scheme 2b) can be constructed based on the results of our recent study using $\mathbf{5}$.^[7] γ -Irradiation of the MCH glassy matrix containing $\mathbf{2}$ at 77 K promotes electron transfer that simultaneously produces $\mathbf{2}^+$ and $\mathbf{2}^-$. Owing to the small activation

energy for cyclization, 2^+ undergoes rapid isomerization to form 3^+ . Upon annealing, the excited-state biradical 13^{**} is generated by exoergonic CR between 2^+ and 3^- and then undergoes emission to form the ground-state biradical 13^- . Finally, 2 is regenerated by bond cleavage in 13^- .

In conclusion, we have designed a unique TL-based strategy that has led to the first successful detection of the singlet biradical 13^- , 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 (13^-) caused by through-space and through-bond interactions, similar to the red shift of absorption bands of radical cations (3^+),^[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]

Received: June 9, 2007

Published online: August 17, 2007

Keywords: biradicals · electron transfer · luminescence · photochemistry · reaction mechanisms

- [1] a) J. A. Berson in *Rearrangements in Ground and Excited States, Vol. 1* (Ed: P. de Mayo) Academic, New York, **1980**, pp. 311–390; b) R. A. Caldwell, in *Kinetics and Spectroscopy of Carbenes and Biradicals* (Ed.: M. S. Platz), Plenum, New York, **1990**, pp. 77–116.
- [2] P. S. Engel, *Chem. Rev.* **1980**, *80*, 99–150.
- [3] W. Adam, S. Grabowski, H. Platsch, K. Hannemann, J. Wirz, R. M. Wilson, *J. Am. Chem. Soc.* **1989**, *111*, 751–753.
- [4] a) M. J. S. Dewar, C. Jie, *J. Am. Chem. Soc.* **1987**, *109*, 5893–5900; b) J. J. Gajewski, *Acc. Chem. Res.* **1980**, *13*, 142–148.
- [5] a) T. Miyashi, H. Ikeda, Y. Takahashi, *Acc. Chem. Res.* **1999**, *32*, 815–824; b) H. Ikeda, T. Minegishi, H. Abe, A. Konno, J. L. Goodman, T. Miyashi, *J. Am. Chem. Soc.* **1998**, *120*, 87–95; c) H. Ikeda, T. Minegishi, Y. Takahashi, T. Miyashi, *Tetrahedron Lett.* **1996**, *37*, 4377–4380; d) H. Ikeda, T. Minegishi, T. Miyashi, *J. Chem. Soc. Chem. Commun.* **1994**, 297–298.
- [6] H. Ikeda, Y. Hoshi, H. Namai, F. Tanaka, J. L. Goodman, K. Mizuno, *Chem. Eur. J.* DOI: 10.1002/chem.200700820.
- [7] H. Namai, H. Ikeda, Y. Hoshi, N. Kato, Y. Morishita, K. Mizuno, *J. Am. Chem. Soc.* **2007**, *129*, 9032–9036.
- [8] a) H. Ikeda, H. Namai, N. Kato, T. Ikeda, *Tetrahedron Lett.* **2006**, *47*, 1857–1860; b) H. Ikeda, H. Namai, N. Kato, T. Ikeda, *Tetrahedron Lett.* **2006**, *47*, 1501–1504.
- [9] The 306-nm emission is assigned to the excited state of **2b** because of its coincidence with the photoluminescence (PL) of **2b** (λ_{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 (**6'**) PL (λ_{PL} = 481 and 515 nm in MCH glassy matrix, 77 K),^[10] which was generated from cumyl alcohol by γ irradiation.
- [10] The emission maxima of the excited state benzyl radical is reported to be around 480 and 500 nm in a 3-methylhexane matrix at 77 K. See reference [11].
- [11] M. Irie, M. Shimizu, H. Yoshida, *J. Phys. Chem.* **1976**, *80*, 2008–2014.
- [12] Gaussian 98 (Revision A.11.4), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, **1998**.
- [13] a) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–5652; b) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785–789.
- [14] Details of the calculations are given in the Supporting Information.
- [15] H. Ikeda, T. Takasaki, Y. Takahashi, A. Konno, M. Matsumoto, Y. Hoshi, T. Aoki, T. Suzuki, J. L. Goodman, T. Miyashi, *J. Org. Chem.* **1999**, *64*, 1640–1649.
- [16] J. M. Dust, D. R. Arnold, *J. Am. Chem. Soc.* **1983**, *105*, 1221–1227.