Electronic Supplementary Information

The Lifetime and Efficiency of Triplet–Triplet Fluorescence from the Excited State of a Trimethylenemethane Biradical Determined Using Transient Emission Spectroscopy on Two-color Two-laser Flash Photolysis

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1. Experimental.

1.1 General.

Melting points are obtained with a Yanako (MP-500) and reported uncorrected. Elemental analyses were performed by the Research and Analytical Center at Kanazawa University. ^{1}H and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively, on a Varian Mercury 300 spectrometer. Continuous wave irradiation was carried out at 20 ± 1 °C using a 70-W Rayonet lamp (λ_{EX} = 350 nm).

1.2 Materials and Solvents.

All solvents and chemicals were used without further purification unless otherwise noted. C_6H_6, CH_2Cl_2, and CCl_4 were dried and distilled from CaH_2. THF and ether were purified by passing through GlassContour solvent dispensing systems. MCH was dried over MS4A.

2. General Procedures of Photoreactions

2.1 Trapping reaction of ^{3}**2c**$^{\bullet\bullet}$ with O_2 affording endoperoxide 3 and 1,4-dibenzoylbenzene 4.

An O_2-saturated CH_2Cl_2 (12.5 mL) containing **1c** (78 mg, 0.25 mmol) was irradiated through a Pyrex filter with Rayonet lamp (350 nm, 70 W) at room temperature for 3 h. After removal of the solvent, purification with preparative GPC ($CHCl_3$) afforded **3** (10%) and **4** (25%) with recovery of **1c** (31%).

2.2 Trapping reaction of ^{3}**2c**$^{\bullet\bullet}$ with TCNE affording adducts 5 and 6.

An Ar-saturated CH_2Cl_2 (12.5 mL) containing **1c** (78 mg, 0.25 mmol) and TCNE (64 mg, 0.5 mmol) was irradiated through a Pyrex filter with Rayonet lamp (350 nm, 80 W) at room temperature for 2 h. After removal of the solvents, purification with silica-gel column chromatography (*n*-hexane/EtOAc) followed by preparative GPC afforded **5** (56 mg, 52%) and **6** (33 mg, 31%).

3. The Detail of Kinetic Analyses

3.1. Kinetic analysis of ring-closing process of ^{3}**2c**¨.

A CCl_4 solution containing **1c** (1 mM) was degassed by repeating four freeze (77 K)–pump (10^{-1} mmHg)–thaw (ambient temperature) cycles and sealed at 10^{-1} mmHg at 77 K. Time-dependent change of absorption at 360 nm was traced at 253, 263, 273, 283, and 293 K upon LFP (Table S1). An Arrhenius plot analysis was carried out with eq S1. As a result, E_a = 2.9 kcal mol^{-1} and $A = 5.0 \times 10^7$ were obtained

$$\ln k_{FN} = -\frac{E_a}{RT} + \ln A \qquad \text{(S1)}$$

Table S1. Rate Constant for Decay (k_{DE}) of ^{3}**2c**¨

Temperature / K	k_{DE} / 10^4 s^{-1}
253.0	3.34
263.0	4.56
273.0	5.68
283.0	7.18
293.0	9.54

4. The Results of Quantum Chemical Calculations

Table S2. The Cartesian Coordinates (in Å) of **1c** Optimized by B3LYP/cc-pVDZ. (The sum of electronic and zero-point energies is –962.186159 Hartree. $<S^2>$ = 0.0000)

Atom	Coordinates		
	X	Y	Z
C	–3.490408	–0.307441	–0.091140
C	–2.659990	0.917044	0.232785
C	–3.007918	2.217494	–0.393511
C	–3.384247	2.056078	1.013228
C	–1.194670	0.657320	0.501287
H	–4.433481	1.868538	1.258551
H	–2.831094	2.619308	1.770151
C	–2.920967	3.000654	–1.458484
H	–2.447657	2.654053	–2.380535
H	–3.317483	4.019192	–1.445698
C	–0.412069	0.058049	–0.499819
C	–0.578974	0.979432	1.720184
C	0.774564	0.721619	1.927843
C	0.946566	–0.181153	–0.303735
C	1.563600	0.157071	0.913690
H	–1.167074	1.423568	2.524514
H	1.245170	0.948280	2.885022
H	–0.879513	–0.231178	–1.443005
H	1.523214	–0.661760	–1.094553
C	3.001442	–0.139776	1.227376
C	–4.396062	–0.325601	–1.161187
C	–3.375152	–1.456410	0.710345
C	–4.149084	–2.587729	0.451301
C	–5.173663	–1.459121	–1.419384
C	–5.053677	–2.593803	–0.615553
H	–2.669239	–1.462631	1.543049
H	–4.045301	–3.470224	1.086095
H	–4.492574	0.555577	–1.796945
H	–5.872431	–1.453675	–2.258657
H	–5.657925	–3.479963	–0.819419
O	3.343408	–0.327040	2.387973
C	4.028199	–0.210657	0.131206
C	3.944461	0.541512	–1.052375
C	5.164939	–1.007014	0.354057
C	6.177600	–1.079028	–0.599797
C	4.970792	0.484648	–1.998809
C	6.082471	–0.332378	–1.779882
H	5.232215	–1.561972	1.290244
H	7.048772	–1.712742	–0.422508
H	3.089400	1.196028	–1.223839
H	4.902227	1.083728	–2.908900
H	6.879003	–0.382669	–2.525109

Table S3. The Cartesian Coordinates (in Å) of ^{3}**1c** Optimized by UB3LYP/cc–pVDZ. (The sum of electronic and zero–point energies is –962.088548 Hartree. $<S^2>$ = 2.0003)

Atom	Coordinates		
	X	Y	Z
C	3.274004	–2.048582	0.796989
C	3.060891	–1.288420	2.031379
C	2.660212	–0.705175	0.640851
C	3.655258	–3.176862	0.216658
C	3.503484	0.439921	0.118909
H	3.923240	–0.820760	2.515414
C	1.196681	–0.665778	0.273783
H	2.269654	–1.610669	2.714930
H	4.051056	–4.009338	0.804269
H	3.581320	–3.312704	–0.865173
C	0.181048	–0.459658	1.227336
C	0.812332	–0.832233	–1.070856
C	–0.519834	–0.791257	–1.451757
C	–1.160368	–0.431215	0.867891
C	–1.547667	–0.569610	–0.490438
H	1.582532	–0.982740	–1.830271
H	–0.794741	–0.902781	–2.500559
H	0.448941	–0.329053	2.277409
H	–1.922051	–0.315963	1.638962
C	–2.932785	–0.575344	–0.909422
C	4.808412	0.238619	–0.355439
C	2.990748	1.748453	0.128424
C	3.763984	2.822862	–0.313289
C	5.583830	1.315403	–0.795335
C	5.066073	2.611875	–0.776673
H	1.973986	1.925258	0.483440
H	3.345617	3.831530	–0.296557
H	5.218839	–0.771786	–0.383237
H	6.596718	1.135263	–1.161901
H	5.669864	3.452164	–1.124910
O	–3.175044	–1.252308	–2.024597
C	–4.085001	0.030824	–0.273637
C	–3.974843	1.169742	0.566087
C	–5.384468	–0.475859	–0.550604
C	–6.509920	0.110568	0.018325
C	–5.107933	1.734432	1.138748
C	–6.383726	1.212829	0.872249
H	–5.483065	–1.348873	–1.195918
H	–7.497747	–0.301740	–0.197820
H	–2.996522	1.615549	0.745863
H	–5.001583	2.604415	1.790292
H	–7.268174	1.667481	1.321475

Table S4. The Cartesian Coordinates (in Å) of ^{3}**2c¨** Optimized by UB3LYP/cc–pVDZ. (The sum of electronic and zero–point energies is –962.168700 Hartree. $\langle S^2 \rangle = 2.0517$)

Atom	Coordinates		
	X	Y	Z
C	–3.938871	2.739601	0.625645
C	–2.910880	2.236595	–0.190948
H	–4.438534	2.117033	1.366270
H	–4.243459	3.784381	0.543093
C	–2.526790	0.819282	–0.105176
C	–2.261173	3.096049	–1.094350
H	–2.533687	4.151961	–1.138883
H	–1.499980	2.734403	–1.784072
C	–3.550522	–0.196850	0.175231
C	–1.136767	0.415941	–0.297992
C	–0.058463	1.249516	0.092854
C	–0.803063	–0.832844	–0.887419
C	0.516732	–1.210940	–1.079576
C	1.264135	0.852132	–0.070762
C	1.578765	–0.388715	–0.655686
H	–1.603337	–1.490817	–1.227139
H	0.759182	–2.153154	–1.571991
H	–0.271365	2.213898	0.554183
H	2.061725	1.526680	0.241836
C	2.975991	–0.845971	–0.941543
C	–4.857998	–0.088889	–0.356032
C	–3.267365	–1.321433	0.986533
C	–4.240495	–2.282046	1.254166
C	–5.825437	–1.056749	–0.094588
C	–5.524656	–2.158271	0.713597
H	–2.275040	–1.423163	1.427548
H	–3.996659	–3.131597	1.895429
H	–5.101598	0.756726	–1.000050
H	–6.821260	–0.954568	–0.530878
H	–6.284749	–2.913987	0.920455
O	3.182424	–1.631638	–1.859267
C	4.133091	–0.352774	–0.117067
C	4.023068	–0.020510	1.243470
C	5.399106	–0.316495	–0.726748
C	6.522918	0.077811	–0.004050
C	5.154461	0.354232	1.972773
C	6.403036	0.414261	1.349252
H	5.477067	–0.607650	–1.774665
H	7.498580	0.116043	–0.492565
H	3.056491	–0.083072	1.744311
H	5.059686	0.596548	3.033073
H	7.284610	0.715847	1.918674

Table S5. The Cartesian Coordinates (in Å) of ^{1}**2c¨** Optimized by UB3LYP/cc–pVDZ. (The sum of electronic and zero–point energies is –962.163757 Hartree. $\langle S^2 \rangle = 0.4504$)

Atom	Coordinates		
	X	Y	Z
C	–3.308097	2.907992	0.721141
C	–2.781603	2.181315	–0.345534
H	–3.502365	2.438302	1.685432
H	–3.536413	3.970580	0.611238
C	–2.484003	0.719109	–0.153251
C	–2.528851	2.765700	–1.585063
H	–2.738960	3.824390	–1.753733
H	–2.120222	2.185258	–2.412316
C	–3.601565	–0.167229	0.145864
C	–1.115749	0.271472	–0.273481
C	–0.032599	1.176469	–0.090338
C	–0.775226	–1.068111	–0.625009
C	0.543664	–1.466725	–0.756275
C	1.288271	0.760946	–0.190436
C	1.607215	–0.572931	–0.513365
H	–1.569515	–1.781491	–0.842480
H	0.788456	–2.483686	–1.064357
H	–0.245809	2.216611	0.154486
H	2.084116	1.491274	–0.042235
C	3.001926	–1.071942	–0.719163
C	–4.911975	0.148575	–0.299037
C	–3.448723	–1.343384	0.925901
C	–4.536492	–2.160557	1.221100
C	–5.992688	–0.679295	–0.010704
C	–5.814720	–1.840905	0.749593
H	–2.469374	–1.590786	1.335070
H	–4.387922	–3.050439	1.836300
H	–5.067321	1.047268	–0.896230
H	–6.985206	–0.416957	–0.382851
H	–6.664976	–2.485300	0.980239
O	3.201599	–2.046017	–1.437064
C	4.170026	–0.390382	–0.060198
C	4.091655	0.226762	1.199400
C	5.415700	–0.461224	–0.707385
C	6.548910	0.105416	–0.127826
C	5.233073	0.775907	1.789379
C	6.459998	0.726226	1.123365
H	5.470711	–0.971710	–1.669358
H	7.507979	0.057585	–0.647405
H	3.142746	0.253262	1.736079
H	5.163263	1.240771	2.774776
H	7.349152	1.163985	1.581786

(end)