Supplementary Material for Theoretical Calculations

Synthesis and Photophysical Properties of Conjugated Thioketone, Thioketone *S*oxide (Sulfine), and Related Compounds Incorporated in a Dibenzobarrelene Skeleton

Akihiko Ishii,* Ryota Ebina, Mari Shibata, Yuki Hayashi, and Norio Nakata

Department of Chemistry, Graduate School of Science and Engineering, Saitama University 255 Shimo-okubo, Sakura-ku, Saitama, 338-8570, Japan

Contact: Akihiko Ishii; e-mail: ishiiaki@chem.saitama-u.ac.jp

Contents:

(1) S_0 of ketone 6	••• S2
(2) S_1 of ketone 6	••• S7
(3) S_0 of thicketone 9	••• S10
(4) S_1 of thicketone 9	••• S13
(5) S ₀ of (<i>Z</i>)-sulfine 10	••• S16
(6) S ₁ of (<i>Z</i>)-sulfine 10	••• S20
(7) T_1 of (<i>Z</i>)-sulfine 10	••• S26
(8) (<i>E</i>)-sulfine 10	••• S28
(9) T ₁ (<i>E</i>)-sulfine 10	••• S30
(10) Model compound 18	••• S32
(11) Oxathiirane 19	••• S36
(12) Transition state (TS) from (<i>E</i>)-10 to Oxathiirane 19	••• S37

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Figure S9. ¹ H and ¹³ C NMR spectra of ketone 6.	••• S9
Figure S10. ¹ H and ¹³ C NMR spectra of hydrazone 7.	••• S10
Figure S11. ¹ H and ¹³ C NMR spectra of diazo compound 8.	••• S11
Figure S12. ¹ H and ¹³ C NMR spectra of thioketone 9.	••• S12
Figure S13. ¹ H and ¹³ C NMR spectra of (Z)-sulfine 10	••• S13
Figure S14. ¹ H and ¹³ C NMR spectra of a mixture of (Z)-10 and (E)-10	••• S14



Figure S1. ¹³C NMR data of thiocarbonyl carbons in relevant conjugated thioketones.

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Figure S2. C–S and C–O Bond lengths (Å) of C=S=O groups in conjugated sulfines.

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Figure S3. Plots of Stokes shifts *vs.* (a) standard empirical solvent parameter (E_T^N) and (b) Δf (the Lippert-Mataga plot) for ketone **6**. E_T^N : hexane (0.009), toluene (0.099), CH₂Cl₂ (0.309), MeCN (0.46), and MeOH (0.762). $\Delta f = [(\varepsilon_r - 1)/(2\varepsilon_r + 1)] - [(n^2 - 1)/(2n^2 + 1)]$; e = relative permittivity; n = refractive index: hexane (-0.000), toluene (0.013), CH₂Cl₂ (0.217), MeCN (0.305), and MeOH (0.320)



Figure S4. Decay of emission of ketone **6** in EtOH at room temperature. Excitation (WL = LED04) 470 nm, Emission WL = 515 nm, Time Range = 51 ns, Stop Condition = Peak(2000), Frequency = 5 MHz, Meas. Time = 113.4, Iris = 076, Counting Rate = 0.035% / 0.035%.



Figure S5. Decay of emission of ketone **6** in EtOH at 77 K. Excitation (WL = LED03) 405 nm, Emission WL = 480 nm, Time Range = 51 ns, Stop Condition = Peak(2000), Frequency = 5 MHz, Meas. Time = 1.9, Iris = 076, Counting Rate = 2.896% / 2.884%.



Figure S6. Optical absorption (solid lines) and emission (dotted lines) spectra of sulfine (Z)-10 in various solvents. The heights of emission spectra were adjusted to those of respective optical absorption spectra.



Figure S7. Decay of emission of sulfine (*Z*)-10 in EtOH at room temperature. Excitation (WL = LED04) 470 nm, Emission WL = 520 nm, Time Range = 51 ns, Stop Condition = Peak(1000), Frequency = 5 MHz, Meas. Time = 419.8, Iris = 076, Counting Rate = 0.004% / 0.004%



Figure S8. Decay of emission of sulfine (*Z*)-10 in EtOH at 77 K. Excitation (WL = LED04) 470 nm, Emission WL = 540 nm, Time Range = 51 ns, Stop Condition = Peak(1000), Frequency = 5 MHz, Meas. Time = 4.4, Iris = 076, Counting Rate = 0.808% / 0.774%.



Figure S9. ¹H and ¹³C NMR spectra of ketone 6.



Figure S10. ¹H and ¹³C NMR spectra of hydrazone 7.



Figure S11. ¹H and ¹³C NMR spectra of diazo compound 8.



Figure S12. ¹H and ¹³C NMR spectra of thioketone 9.



Figure S13. ¹H and ¹³C NMR spectra of (Z)-sulfine 10



Figure S14. ¹H and ¹³C NMR spectra of a mixture of (Z)-10 and (E)-10