

1 **Heavy Atom Effect on the Room Temperature Chemiluminescent**
 2 **Phosphorescence of the Tricyclic 1,2-Dioxetanes**

3 CHUNG-WEN SUN¹, SHUN-CHI CHEN^{2,*} and TAI-SHAN FANG^{1,*}

4 ¹Department of Chemistry, National Taiwan Normal University, Taipei 116, Taiwan

5 ²Department of Chemical Engineering, Mingchi University of Technology, Taishan, Taipei 243, Taiwan

6 *Corresponding author: E-mail: scchemts@ntnu.edu.tw; john.sun@bsmi.gov.tw

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7 1,2-Dioxetane tricyclic compound (**1a**) and 5-halo substituted of 1,2-dioxetane tricyclic compounds (**2a**, **3a**) were synthesized from 1,4-
 8 dioxin acenaphthylene compound (**1**) and 5-halo substituted 1,4-dioxin acenaphthylene compounds (**2**, **3**), by reacting with singlet-
 9 oxygen (¹O₂) at 238 K and their chemiluminescent efficiency both in fluorescence and phosphorescence was studied while upon heating
 10 to temperatures between 313-353 K in dichloromethane. The chemiluminescent phosphorescence can be detected along with the chemi-
 11 luminescent fluorescence when compounds (**2a**, **3a**) are decomposed thermally to the corresponding naphthalene diesters (**2b**, **3b**).
 12 Experimental evidences for formation of the dioxetanes **1a**, **2a** and **3a** are the observed chemiluminescence spectra which are consistent
 13 with the photoluminescence spectra of the excited compounds **1b-3b**. Temperature-dependent kinetic measurements reveal an increase of
 14 room temperature chemiluminescent phosphorescence efficiency from triplet chemiexcitation processes due to the internal heavy atom
 15 effect of compound **3a**.

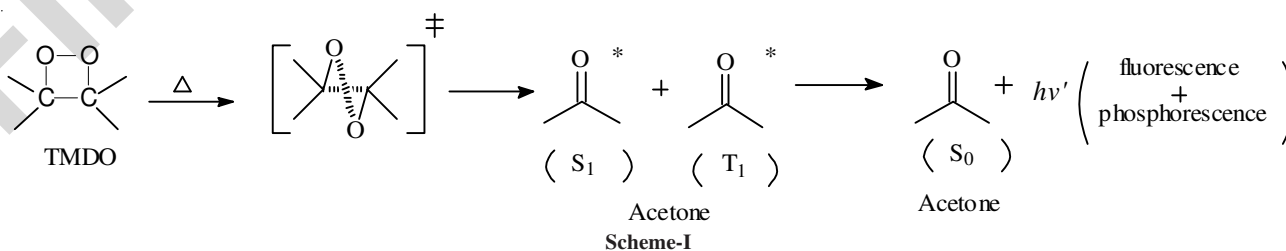
16 **Key Words: Chemiluminescence, Fluorescence, Phosphorescence, Dioxetane, Heavy atom effect.**

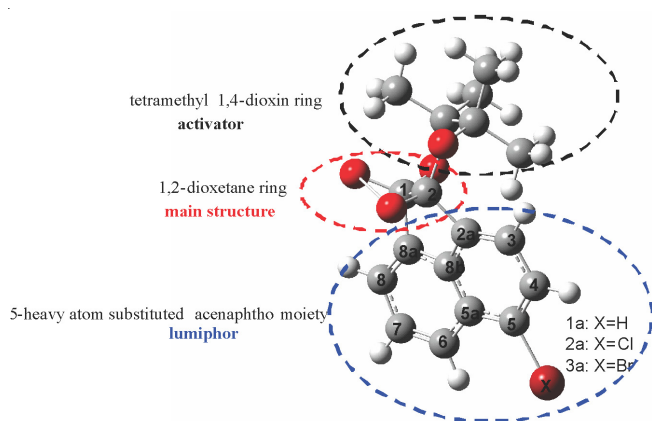
INTRODUCTION

17 Photoluminescence is a type of optical spectroscopy in
 18 which a photoluminescent molecule is promoted to an elec-
 19 tronically excited state by absorption of incident radiation.
 20 Chemiluminescence is a type of optical spectroscopy in which
 21 a chemiluminescent molecule is generated to an electronically
 22 excited state by chemiexcitation reactions. There are few reports
 23 about the room temperature chemiluminescent fluorescence
 24 and phosphorescence. For example, room temperature lumines-
 25 cence is rarely observed from the thermal decomposition of
 26 the simple 1,2-dioxetanes which produce excited carbonyl
 27 compounds. The energy in the form of light is released from
 28 1,2-dioxetanes due to a chemiexcitation reaction during thermal
 29 decomposition. A simple example is the thermal decomposition
 30 of tetramethyl dioxetane (TMDO). In the TMDO structure,

31 the C-O-O-C is a twisted four-membered ring peroxide with
 32 high strain energy, which liberates much energy during thermal
 33 decomposition into two excited carbonyl fragments (singlet
 34 and triplet excited acetone) and then return to the ground state
 35 by chemiluminescence (**Scheme-I**)¹⁻⁵.

36 The molecular structure of TMDO was used as a base
 37 template to design and synthesize compounds (**1a-3a**). The
 38 structure of the 1,2-dioxetane tricyclic compounds (**1a-3a**) are
 39 comprised of three parts. These are the 1,2-dioxetane ring
 40 (main structure), the electron-donor dialkoxy activator
 41 (tetramethyl 1,4-dioxin ring) on one side and the lumiphor (5-
 42 heavy atom substituted acenaphtho moiety) on the other side
 43 (**Scheme-II**). The chloro- and bromo- substituents on the
 44 lumiphor are incorporated to study the internal heavy atom
 45 effect, which is an important factor for the room temperature





Scheme-II

46 chemiluminescent phosphorescence (RTCP) detection of
47 chemiluminescent molecule by experimental measurements.

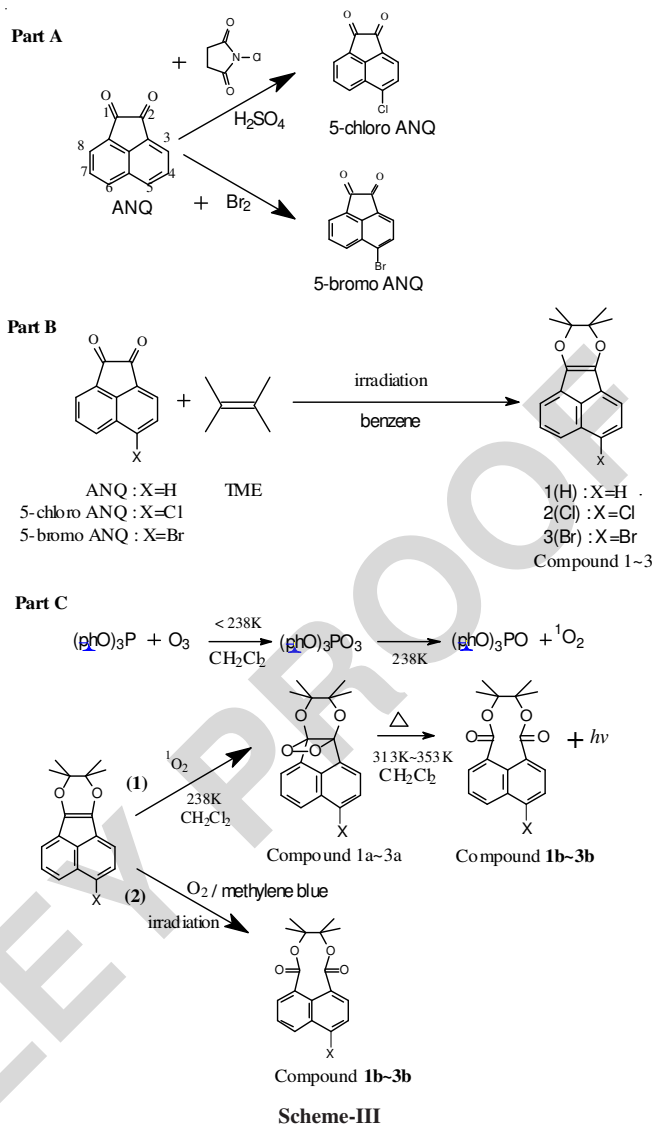
48 It is well known that the 1,2-dioxetane ring with its high
49 strain energy undergoes simultaneous cleavage of both the
50 O-O and C-C bonds during thermal decomposition into two
51 excited intramolecular carbonyl fragments (singlet and triplet
52 excited intramolecular naphthalene diester compounds **1b***-
53 **3b***), which return to the ground state by chemiluminescent
54 fluorescence (CF) and chemiluminescent phosphorescence
55 (CP), respectively⁶⁻⁹.

56 While it is difficult to detect the room temperature ~~chemi-~~
57 ~~luminescent~~ phosphorescence from compounds (**1b-3b**) under
58 nondegassed condition, because of quenching by triplet-oxygen
59 (³O₂), the room temperature chemiluminescent phosphore-
60 scence is detected more easily, because the room temperature
61 chemiluminescent phosphorescence emission derives from the
62 chemiexcitation reactions of 1,2-dioxetanes. It is well known
63 that the internal heavy atom effect can enhance the phosphore-
64 scence. This paper describes the room temperature chemi-
65 luminescent phosphorescence of 1,2-dioxetane tricyclic
66 compound with a 5-heavy atom substituent in the acenaphtho
67 moiety.

EXPERIMENTAL

68 **1,4-Dioxin acenaphthylene, compounds (1-3):** Acena-
69 phthenequinone (ANQ) was obtained from Aldrich. The 5-
70 chloro acenaphthenequinone was synthesized from acenaph-
71 thenequinone and N-chlorosuccinimide (NCS) in concentrated
72 sulfuric acid. The reaction mixture was refluxed for 2 h. The
73 5-bromo acenaphthenequinone was synthesized from acenaph-
74 thenequinone and bromine liquid. The reaction
75 mixture was refluxed for 2 h^{10,11} (**Scheme-III** part A). The
76 compounds (**1-3**) were synthesized by the photo-cycloaddition
77 reaction of acenaphthenequinone (ANQ) with tetramethyl-
78 ethylene (TME) in benzene¹² (**Scheme-III** part B).

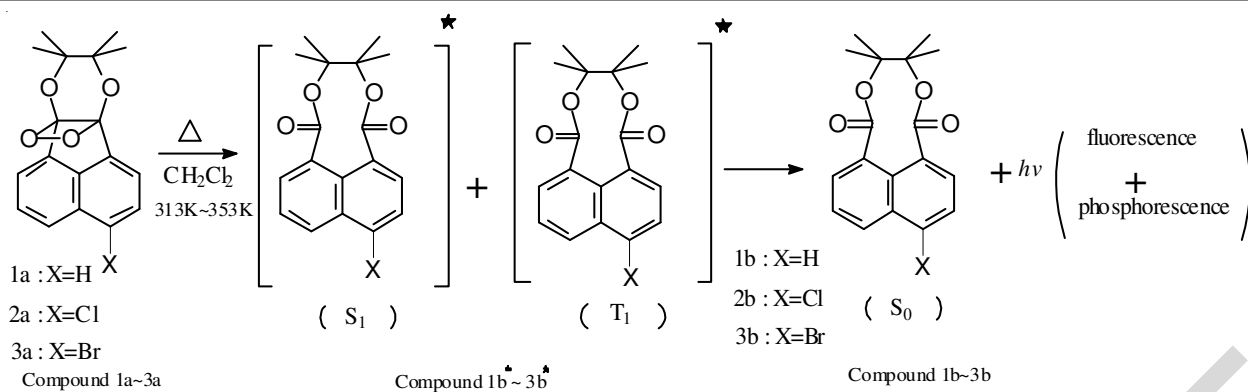
79 **1,2-Dioxetane tricyclic compounds (1a-3a):** Singlet-
80 oxygen oxidation of the 1,4-dioxin compounds (**1-3**) to produce
81 the 1,2-dioxetane tricyclic compounds (**1a-3a**) was carried out
82 using the ozone-triphenyl phosphite procedure given in ref.³.
83 Dioxetane adducts (**1a-3a**) were isolated by ice-chilled *n*-hexane
84 extraction from the low temperature synthesis of ozonized
85 triphenyl phosphite [**Scheme-III** part C(1)].



Scheme-III

86 **Naphthalene diester compounds (1b-3b):** There are two
87 methods to synthesize the naphthalene diester compounds (**1b-**
88 **3b**). (1) The compounds (**1a-3a**) were decomposed thermally
89 to the naphthalene diester compounds (**1b-3b**) (**Scheme-III**
90 part C(1)). (2) The compounds (**1-3**) in benzene solution were
91 irradiated in the presence of photosensitizer methylene blue
92 and purged oxygen [**Scheme-III** part C(2)].

93 **Measurements:** The UV/visible absorption spectra were
94 measured on a Hewlett-Packard diode array spectrophoto-
95 meter. The steady-state emission spectra were obtained using
96 a Cary Eclipsed Spectrofluorimeter equipped with a temper-
97 ature controller. Luminescence lifetimes were measured by a
98 microsecond flash lamp Luminescence Spectrofluorimeter
99 (Cary Eclipse) in a temperature range of 313-353 K. For the
100 temperature-dependent kinetic measurements, the temperature
101 of the sample solution were controlled to within ± 0.5 K with
102 an electronically thermostating single cell and monitored with
103 thermocouples attached to the cell. The room temperature
104 chemiluminescent fluorescence (RTCF) and the room temper-
105 ature chemiluminescent phosphorescence thermal decay of the
106 compounds (**1a-3a**) were determined using a photomultiplier
107 tube.



Scheme-IV

RESULTS AND DISCUSSION

108 The isolated compounds (**1a-3a**) were formed by reacting
109 compounds (**1-3**) with singlet-oxygen (¹O₂) in dichloromethane
110 at 238 K. Thermal decomposition of the 1,2-dioxetanes produce
111 the electronically excited diesters (**1b*-3b***) that decayed by
112 chemiluminescent fluorescence or chemiluminescent phosphorescence
113 to the ground state compounds (**1b-3b**). To avoid
114 triplet-oxygen (³O₂) quenching of the triplet excited states, we
115 used the freeze-pump-thaw method to degas solutions where
116 the compounds (**1b-3b**) are dissolved. Experimental evidences
117 show that the chemiluminescence spectral peaks of the compounds
118 (**1a-3a**) are consistent with that of the photoluminescence
119 spectral peaks of the photoexcited nondegassed and degassed
120 compounds (**1b-3b**). These spectroscopic observations suggest
121 that the compounds (**1a-3a**) thermally decomposed to the
122 excited state of the compounds (**1b*-3b***), with subsequent
123 radiative decay to the ground state of the compounds (**1b-3b**).
124 These processes are shown in **Scheme-IV**.

125 As an example, the UV/visible absorption and photoluminescence
126 spectra of the compound **3b** and the chemiluminescence spectrum
127 of the compound **3a** in dichloromethane are shown in Fig. 1. To compare the three spectra (chemiluminescence,
128 nondegassed and degassed photoluminescence) conveniently, the chemiluminescence and photoluminescence
129 spectral peaks at λ_{max} are normalized to same relative intensity.
130 The experimental results show that the room temperature chemiluminescent fluorescence spectral peak of the compound
131 **3a** at 378 nm is consistent with that of the photoluminescence spectral peaks of the photoexcited nondegassed and degassed
132 compound **3b**. The room temperature chemiluminescent phosphorescence spectral peak of the compound **3a** at 560 nm
133 is consistent with that of the photoluminescence spectral peak of the photoexcited degassed compound **3b**. The photoluminescence
134 spectral peak at 560 nm of the photoexcited nondegassed compound **3b** is not observed due to quenching
135 of the triplet states by triplet-oxygen (³O₂). The lifetimes of the two peaks in the chemiluminescence spectrum of the
136 compound **3a** were measured by monitoring the decays at fixed wavelength. The experimental results show the fluorescence
137 and phosphorescence decay lifetimes of the degassed compound **3b** in dichloromethane are 5.3 and 80 μs, respectively.
138 The chemiluminescence spectral peaks are composed of chemiluminescent fluorescence and chemiluminescent phosphorescence
139 (Fig. 1).

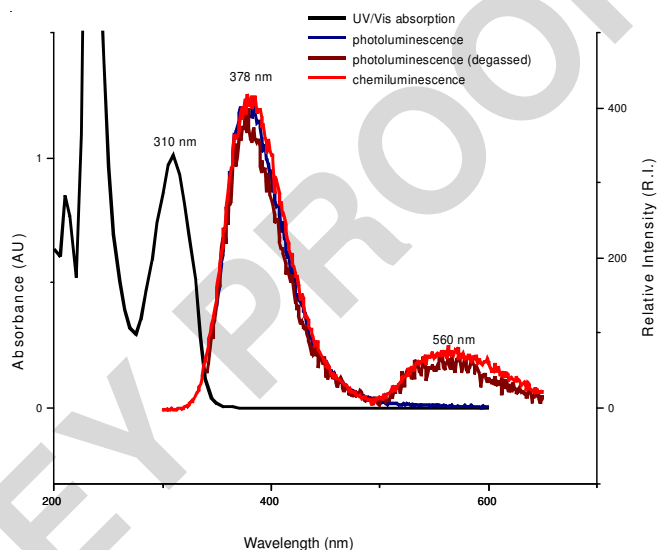


Fig. 1. UV/visible absorption, photoluminescence spectra of the photoexcited compound **3b** and the room temperature chemiluminescent fluorescence and room temperature chemiluminescent phosphorescence spectra of the compound **3a** at 343 K in dichloromethane

151 We observed quite different room temperature chemiluminescent phosphorescence spectra relative intensity between
152 the nondegassed compounds **1a(H)-2a(Cl)-3a(Br)**. It is known that the rate of a spin-forbidden process is enhanced by the
153 presence of an atom of high atomic number. This factor is observed with the room temperature chemiluminescent
154 phosphorescence. The 5-heavy atom substituted acenaphtho moiety of 1,2-dioxetanes shows enhanced nonradiative inter-
155 system crossing from the lowest triplet state, resulting in an increase in the intensity of the phosphorescence. This increase
156 of the room temperature chemiluminescent phosphorescence spectra relative intensity from triplet excited state due to the
157 internal heavy atom substituted is H < Cl << Br (Fig. 2).
158
159
160
161
162
163

164 The photoluminescence spectral peaks of the photoexcited compounds (**1b-3b**) are little shifted toward longer wavelengths
165 as the solvent is changed from the less polar dichloromethane to more polar acetonitrile. The room temperature chemiluminescent
166 fluorescence and room temperature chemiluminescent phosphorescence derive from singlet and triplet *π→π states.
167 An external heavy atom effect was observed with compound **3b** in going from benzene to dichloromethane (Fig. 3). The
168 intensity of phosphorescence of compound **3b** which dissolved in dichloromethane is higher than that dissolved in benzene.
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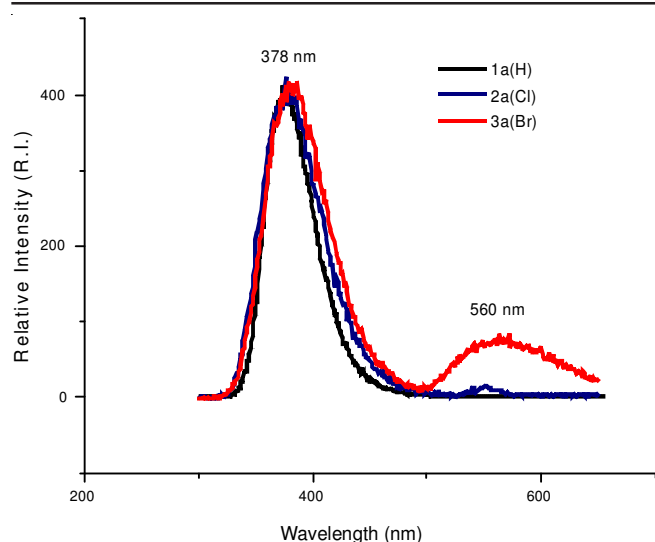


Fig. 2. Chemiluminescence of the compound **1a(H)**-**2a(Cl)**-**3a(Br)** at 343 K in dichloromethane

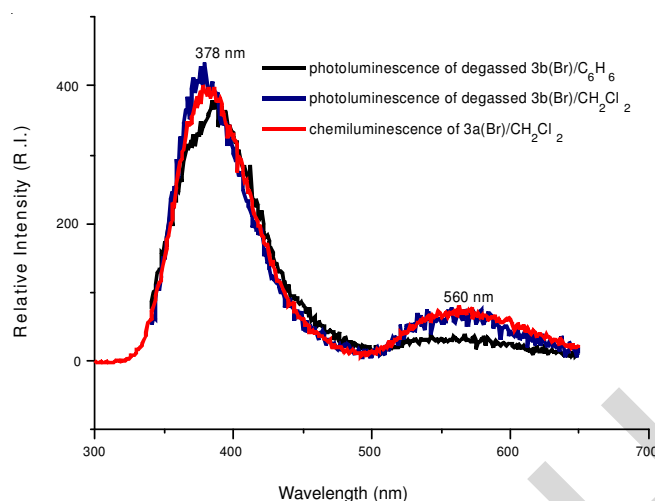
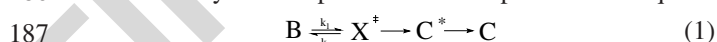


Fig. 3. Photoluminescence spectral peaks of the compound **3b**

174 The ratio ($RI_{\lambda,560\text{ nm}}/RI_{\lambda,378\text{ nm}}$) of the degassed compound **3b** in
175 benzene solvent is 0.10, while this ratio increases to 0.17 in
176 dichloromethane solvent.

177 The rate constants for the decomposition of the compound
178 **3a** was obtained at 10 K increments between 313-353 K by
179 measuring the decay of the chemiluminescence intensity at
180 the maximum wavelength of the chemiluminescence in
181 dichloromethane ($\lambda_{CF,max}$: 378 nm, $\lambda_{CP,max}$: 560 nm). Fig. 4 show
182 the chemiluminescent fluorescence and the chemiluminescent
183 phosphorescence thermal decays of the compound **3a** at 343 K,
184 monitored at 378 and 560 nm, respectively.

185 The overall chemiluminescent mechanism of the 1,2-
186 dioxetane tricyclic compound **3a** can be presented as eqn. 1.



188 where B = 1,2-dioxetane tricyclic compound **3a**; X^\ddagger = the
189 activated complex; C^* = excited intramolecular diester
190 compound **3b***

191 From the Boltzmann distribution eqn. 2

$$192 \quad k = \left(\frac{k_B T}{h} \right) e^{\left(\frac{-\Delta G^\ddagger}{RT} \right)} \quad (2)$$

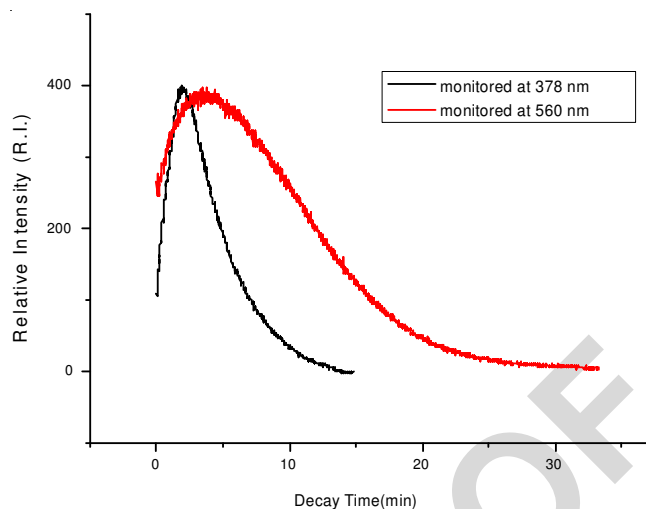


Fig. 4. Chemiluminescent fluorescence and chemiluminescent phosphorescence decay of the compound **3a** at 343 K

where k_B = the Boltzmann constant; h = Planck's constant, 193
 ΔG^\ddagger = the activation free energy of the transition state; R = the 194
gas constant and the Gibbs free energy eqn. 3 195

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \quad (3) \quad 196$$

where ΔH^\ddagger = the activation enthalpy of the transition state; 197
 ΔS^\ddagger = the activation entropy of the transition state, is obtained 198
by the Eyring eqn. 4 using transition-state theory¹³⁻¹⁵. 199

$$\ln \frac{k}{T} = \left(\ln \frac{R}{N_A h} + \frac{\Delta S^\ddagger}{R} \right) - \frac{\Delta H^\ddagger}{RT} \quad (4) \quad 200$$

where N_A = Avogadro's constant; h = Planck's constant. 201

This equation relates $\ln(k/T)$ and $(1/T)$ as a linear function. 202

A plot of $\ln(k/T)$ versus $(1/T)$ gives a straight line with slope 203
($-\Delta H^\ddagger/R$) from which the activation enthalpy of the transition 204
state may be derived. The chemiluminescent fluorescence and 205
chemiluminescent phosphorescence decays from 1,2- 206
dioxetane **3a** was analyzed by eqn. 4. There are two slopes 207

$\left(\frac{\Delta H^\ddagger_{\text{Singlet}}}{R} \right)$, $\left(\frac{\Delta H^\ddagger_{\text{Triplet}}}{R} \right)$ of the Eyring plots corresponding 208

to the chemiluminescent fluorescence decay of compound **3a** 209
at 378 nm and the chemiluminescent phosphorescence decay 210
of compound **3a** at 560 nm, respectively, as shown in Fig. 5. 211
The activation parameters and rates of decomposition for comp- 212
ound **3a** calculated with eqn. 2 are listed in Table-1. 213

TABLE-1
ACTIVATION PARAMETERS AND RATES OF
DECOMPOSITION FOR COMPOUND **3a**

λ_{max} (nm)	ΔH^\ddagger (kcal/mol)	ΔS^\ddagger (cal/mol K)	ΔG^\ddagger (25 °C) (kcal/mol)	k_{25} °C (s ⁻¹)
378 (75.7)	22.2	-5.1	23.7	2.44×10^{-5}
560 (51.1)	15.2	-26.5	23.1	7.6×10^{-5}

The results show that there are two transition excited 214
energy states in the chemiexcitation processes: (1) The transi- 215
tion singlet excited state activation enthalpy ($\Delta H^\ddagger_{\text{Singlet}}$). (2) 216
The transition triplet excited state activation enthalpy 217

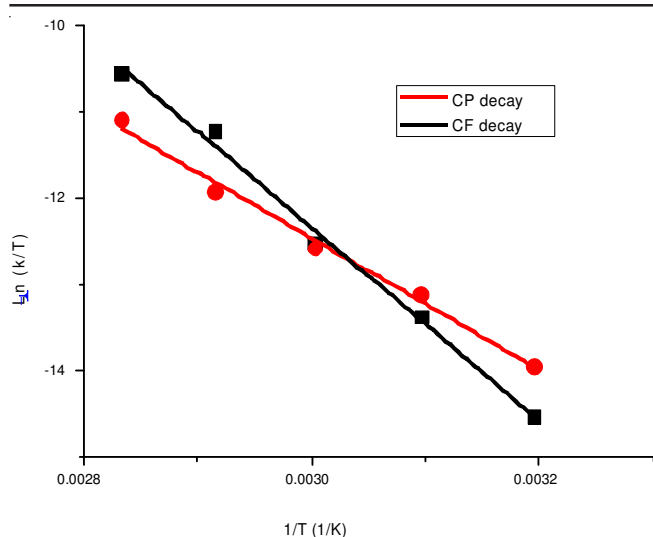


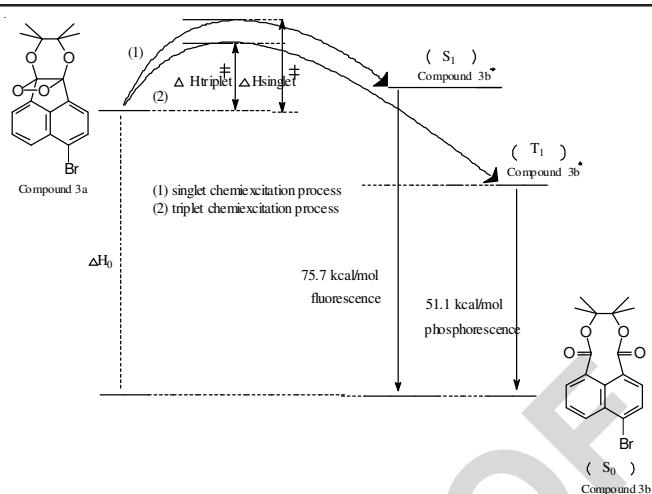
Fig. 5. Eyring plots of the chemiluminescence kinetics of compound **3a**

218 ($\Delta H_{\text{Triplet}}^{\ddagger}$). The singlet excited state activation enthalpy
 219 ($\Delta H_{\text{Singlet}}^{\ddagger}$) of compound **3a** has been determined experimen-
 220 tally to be 22.2 kcal/mol. The triplet excited state activation
 221 enthalpy ($\Delta H_{\text{Triplet}}^{\ddagger}$) of compound **3a** has been determined
 222 experimentally to be 15.2 kcal/mol. The different activation
 223 enthalpies show the chemiluminescent phosphorescence and
 224 chemiluminescent fluorescence arise by competing path in the
 225 decomposition of the dioxetane and the lower enthalpy of
 226 activation results from the lower enthalpy (greater stability)
 227 of the lower lying triplet state. The rate constant of the triplet
 228 state obtained at 298 K is also higher than that of the singlet
 229 state. The different activation enthalpies and different rate
 230 constants seem to be a reasonable explanation that the triplet
 231 state is not formed by way of the singlet state and the chemi-
 232 excitation processes favour the pathway for the formation of
 233 the chemiluminescent phosphorescence.

234 The rate of a spin-forbidden process is enhanced by the
 235 internal presence of bromo-substituent, result the increase of
 236 the relative intensity of the room temperature chemilumines-
 237 cent phosphorescence of compound **3a**. The enhancement of
 238 the phosphorescence of compound **3b** is also observed by the
 239 external heavy atom solvent. The calculations of the room
 240 temperature chemiluminescent fluorescence and the room
 241 temperature chemiluminescent phosphorescence decay time
 242 at variable temperature obtain the activation parameters for
 243 compound **3a**. The enthalpy ($\Delta H_{\text{‡}}$) of reaction for thermal
 244 decompositions of typical dioxetanes have been estimated from
 245 thermal chemical calculations from -69 to -90 kcal/mol¹⁶. The
 246 energy relationship diagram of the compound **3a** thermal
 247 decomposed to compound **3b** can be sketched, if we postulate
 248 the enthalpy of reaction for thermal decomposition of com-
 249 pound **3a** symbol for " $\Delta H_{\text{‡}}$ ". The energy relationship diagram
 250 is showed in Scheme-V.

251 Conclusion

252 The unique feature of this work lies in the observed room
 253 temperature chemiluminescent phosphorescence of the
 254 5-heavy atom substituted acenaphtho lumiphor. In the 1,2-
 255 dioxetane ring of compound **3a** which has high strain energy



Scheme-V

due to the twisted four-membered ring peroxide structure 256
 (C-O-O-C), both the O-O and C-C bonds are cleaved almost 257
 simultaneously during thermal decomposition into two excited 258
 pathways: (1) singlet chemiexcitation processes, (2) triplet 259
 chemiexcitation processes. The internal heavy atom effect of 260
 5-heavy atom substituted is $\text{Br} \gg \text{Cl} > \text{H}$. The transition triplet 261
 excited state activation enthalpy ($\Delta H_{\text{Triplet}}^{\ddagger}$) is lower than the 262
 transition singlet excited state activation enthalpy ($\Delta H_{\text{Singlet}}^{\ddagger}$) 263
 ca. 7 kcal/mol ($\Delta H_{\text{Triplet}}^{\ddagger} < \Delta H_{\text{Singlet}}^{\ddagger}$). We have shown that 264
 the 1,2-dioxetane tricyclic compound-based chemilumines- 265
 cence especially chemiluminescent phosphorescence of 266
 compound **3a**. We continue to investigate these and other 267
 aspects, example as 5-iodo substituted 1,2-dioxetane tricyclic 268
 compound. 269

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