

Scheme-II

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

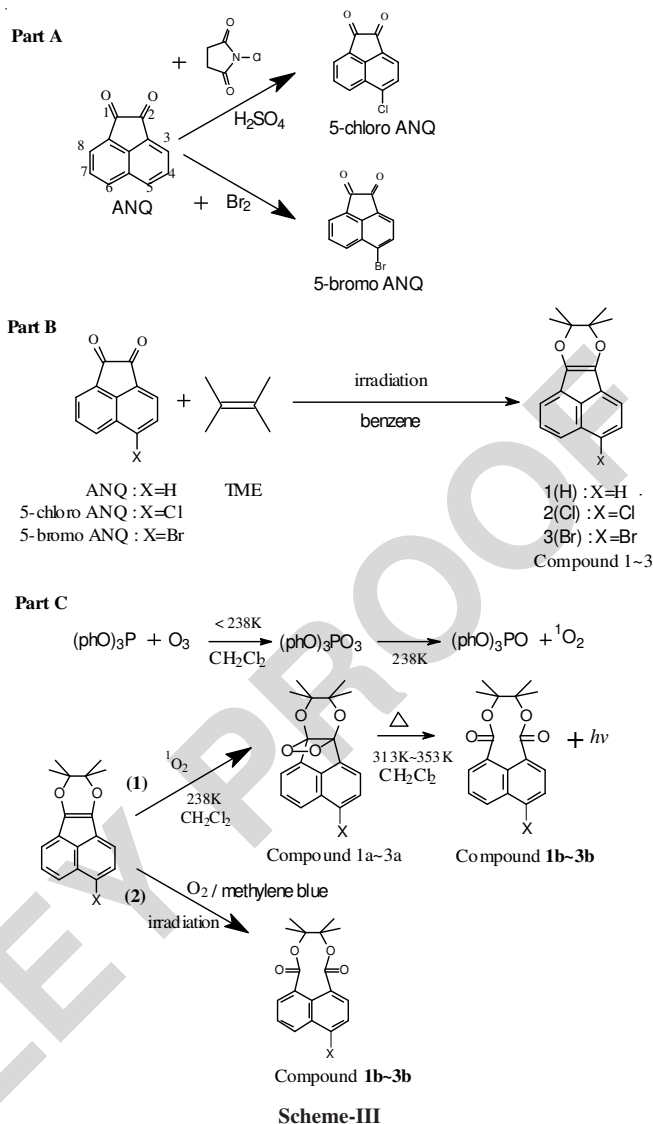
48 It is well known that the 1,2-dioxetane ring with its high  
49 strain energy undergoes simultaneous cleavage of both the  
50 O-O and C-C bonds during thermal decomposition into two  
51 excited intramolecular carbonyl fragments (singlet and triplet  
52 excited intramolecular naphthalene diester compounds **1b\***-  
53 **3b\***), which return to the ground state by chemiluminescent  
54 fluorescence (CF) and chemiluminescent phosphorescence  
55 (CP), respectively<sup>6-9</sup>.

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 (<sup>3</sup>O<sub>2</sub>), 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

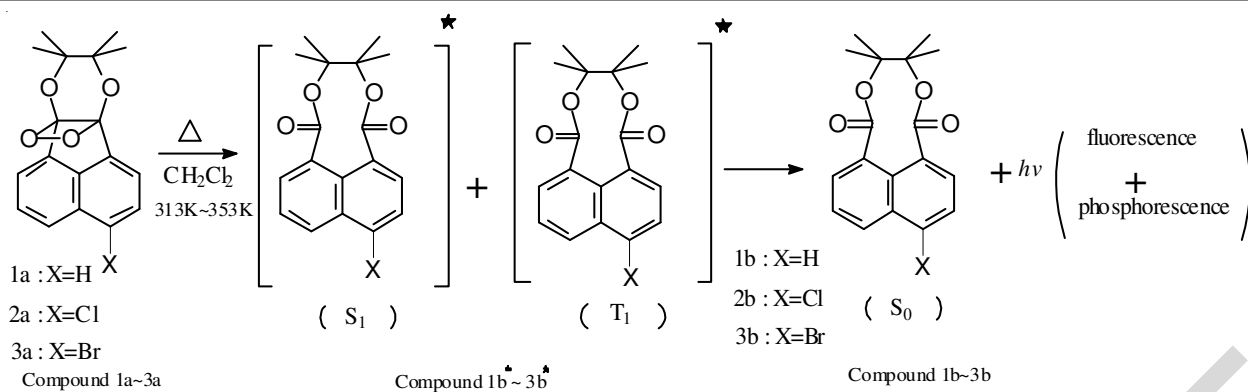
68 **1,4-Dioxin acenaphthylene, compounds (1-3):** Acena-  
69 phthenequinone (ANQ) was obtained from Aldrich. The 5-  
70 chloro acenaphthenequinone was synthesized from acenaph-  
71 thenequinone and N-chlorosuccinimide (NCS) in concentrated  
72 sulfuric acid. The reaction mixture was refluxed for 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<sup>10,11</sup> (**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 benzene<sup>12</sup> (**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.<sup>3</sup>.  
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)].



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  $\pm 0.5$  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 ( $^1\text{O}_2$ ) 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 ( $^3\text{O}_2$ ) 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  $\lambda_{\text{max}}$  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 ( $^3\text{O}_2$ ). 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  $\mu\text{s}$ , respectively.  
138 The chemiluminescence spectral peaks are composed of chemiluminescent fluorescence and chemiluminescent phosphorescence  
139 (Fig. 1).

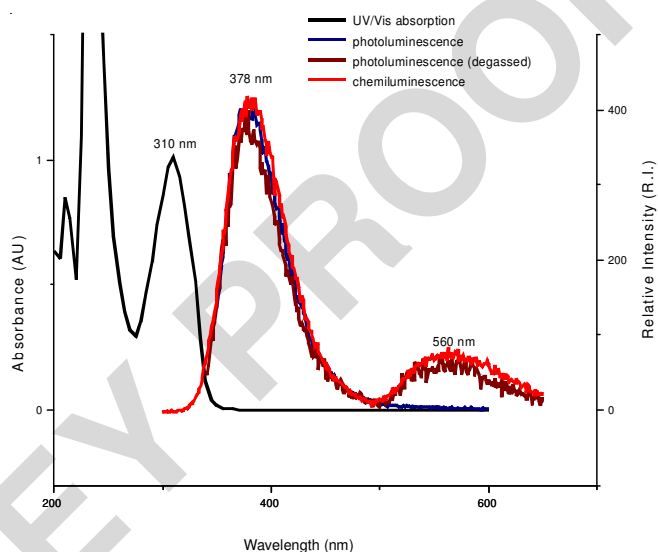


Fig. 1. UV/visible absorption, photoluminescence spectra of the photoexcited compound **3b** and the room temperature chemiluminescent fluorescence and room temperature chemiluminescent phosphorescence spectra of the compound **3a** at 343 K in dichloromethane

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

164 The photoluminescence spectral peaks of the photoexcited  
165 compounds (**1b-3b**) are little shifted toward longer wavelengths  
166 as the solvent is changed from the less polar dichloromethane  
167 to more polar acetonitrile. The room temperature chemiluminescent  
168 fluorescence and room temperature chemiluminescent  
169 phosphorescence derive from singlet and triplet  $^*\pi \rightarrow \pi$  states.  
170 An external heavy atom effect was observed with compound  
171 **3b** in going from benzene to dichloromethane (Fig. 3). The  
172 intensity of phosphorescence of compound **3b** which dissolved  
173 in dichloromethane is higher than that dissolved in benzene.

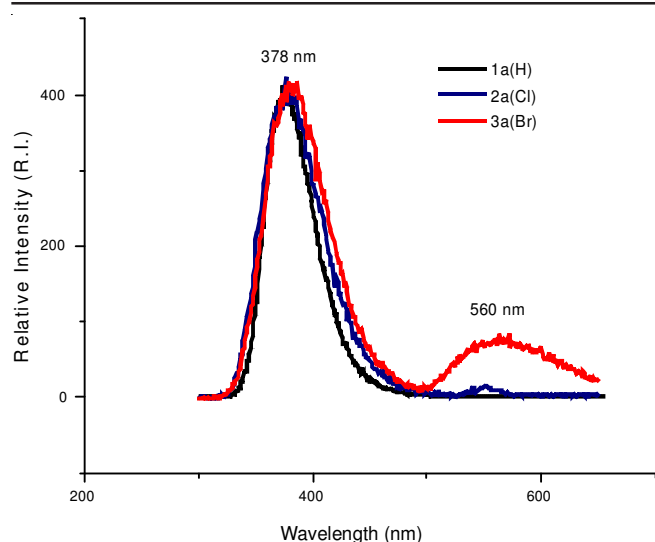


Fig. 2. Chemiluminescence of the compound **1a(H)**-**2a(Cl)**-**3a(Br)** at 343 K in dichloromethane

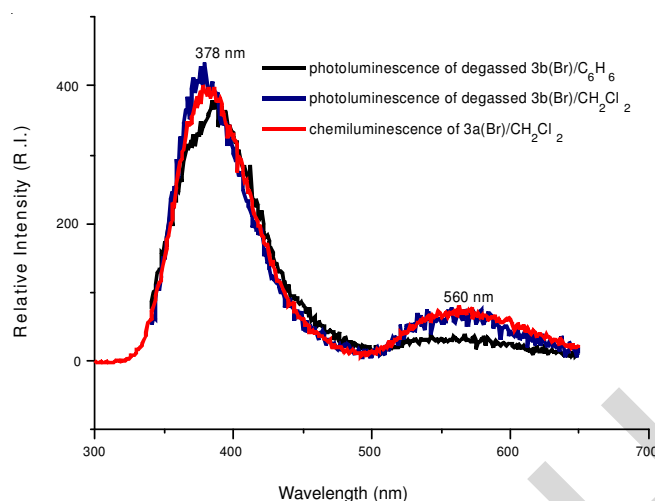
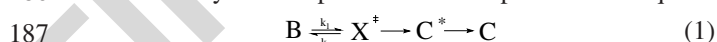


Fig. 3. Photoluminescence spectral peaks of the compound **3b**

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

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

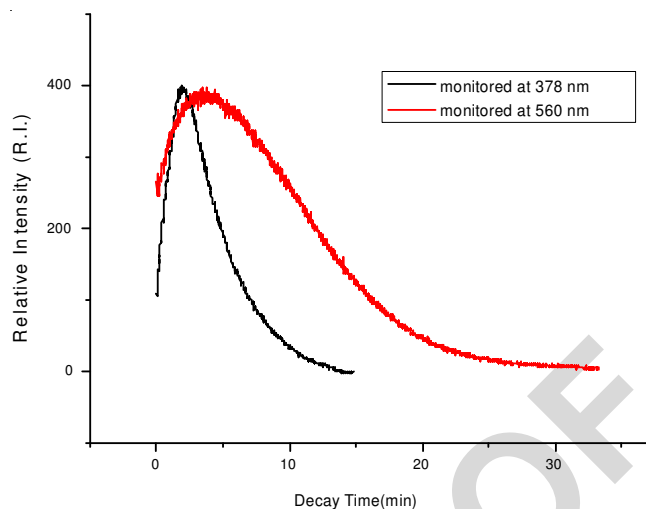


Fig. 4. Chemiluminescent fluorescence and chemiluminescent phosphorescence decay of the compound **3a** at 343 K

where  $k_B$  = the Boltzmann constant;  $h$  = Planck's constant, 193  
 $\Delta G^\ddagger$  = 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  $\Delta H^\ddagger$  = the activation enthalpy of the transition state; 197  
 $\Delta S^\ddagger$  = the activation entropy of the transition state, is obtained 198  
by the Eyring eqn. 4 using transition-state theory<sup>13-15</sup>. 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**

$\lambda_{max}$ (nm)	$\Delta H^\ddagger$ (kcal/mol)	$\Delta S^\ddagger$ (cal/mol K)	$\Delta G^\ddagger$ (25 °C) (kcal/mol)	$k_{25}$ °C (s <sup>-1</sup> )
378 (75.7)	22.2	-5.1	23.7	$2.44 \times 10^{-5}$
560 (51.1)	15.2	-26.5	23.1	$7.6 \times 10^{-5}$

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



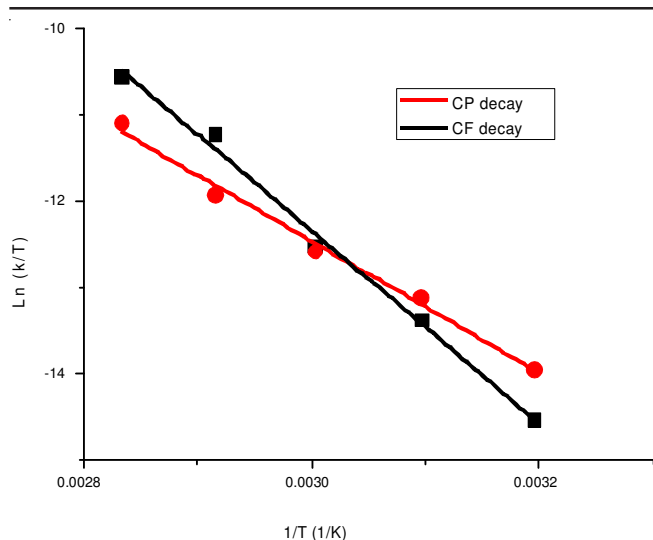


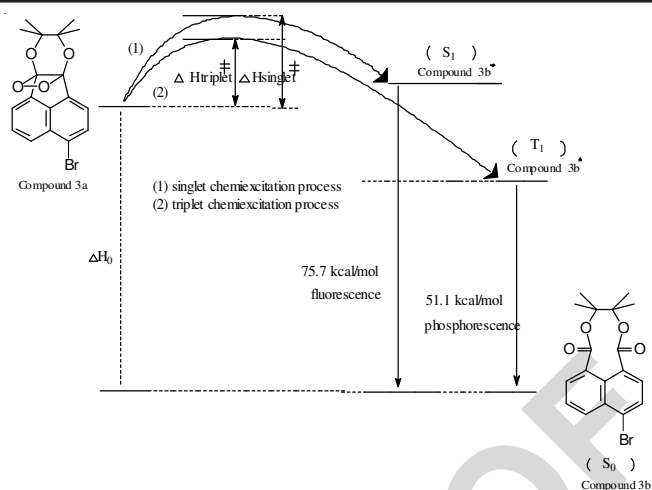
Fig. 5. Eyring plots of the chemiluminescence kinetics of compound **3a**

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 ( $\Delta H^{\circ}$ ) of reaction for thermal  
 244 decompositions of typical dioxetanes have been estimated from  
 245 thermal chemical calculations from -69 to -90 kcal/mol<sup>16</sup>. 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 “ $\Delta H^{\circ}$ ”. 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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