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Ozonation and chemiluminescence of 8,8,9,9-tetramethylaceno[1,2-b]1,4-dioxin. Evidence for dual reaction pathways.

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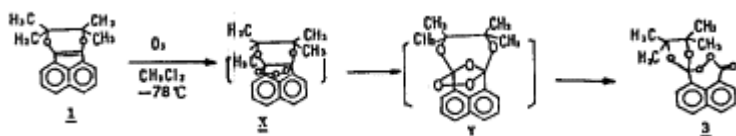
Available online 9 March 2001.

## Abstract

Chemiluminescence and 90% of a highly unusual spiro peroxide **3** were obtained in the ozonation of compound **1** in dichloromethane or methanol.

## Graphical Abstract

Ozonation of **1** in CH<sub>2</sub>Cl<sub>2</sub> or MeOH gave **3** in 90% yield. Chemiluminescence was also observed.



## Article Outline

- References

**Graphical Abstract (in preparation for submitting to Tetrahedron)**

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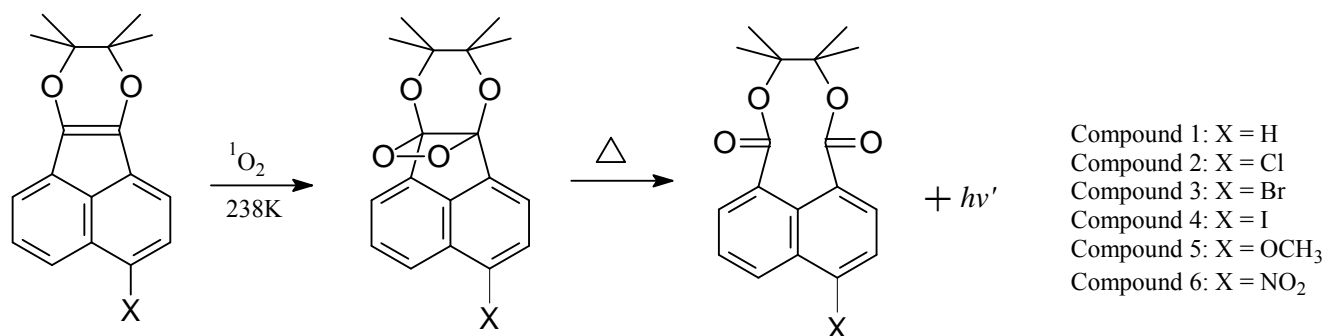
**Study and Revisit on the Chemically  
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(CICSL) of Aromatic Dioxetanes**

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## Study and Revisit on the Chemically Initiated Charge Separation Luminescence (CICSL) of Aromatic Dioxetanes

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### Abstract

Bicyclic dioxetane compounds 1a~6a were synthesized from dioxin compounds 1~6 reacted with singlet oxygen in dichloromethane at 238 K, and studied on their chemiluminescence efficiency in benzene while upon heating to temperatures in between 280~350 K. Direct evidence for the dioxetanes 1a~6a decomposed thermally into electronically excited diester compounds 1b\*~6b\* associated with the ( $\pi^* \rightarrow \pi$ ) emission spectra of diester compounds 1b~6b. These results show that the thermal decomposition ( $n \rightarrow \pi^*$ ) of the dioxetane with the substituted aromatic electron donor display chemically initiated charge separation luminescence (CICSL) of the  $\pi^* \rightarrow \pi$ , in which a charge transfer from an aromatic electron donor to the highly-strained dioxetane ring occurs to induce its decomposition with aromatic diester as a  $\pi^* \pi$  emitter. The activation parameters and chemiluminescence quantum yields are in agreement with the occurrence of a CICSL mechanism in the decomposition of these dioxetanes.

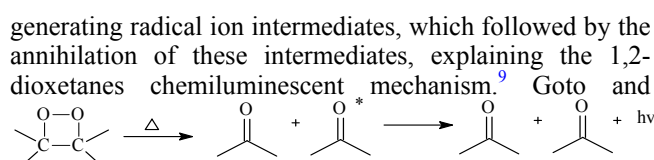
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**Keywords:** Chemiluminescence; Dioxetane; chemically initiated charge separation luminescence (CICSL)

### 1. Introduction

The phenomenon of firefly bioluminescence<sup>1-2</sup> has led to the theoretical<sup>3-4</sup> and practical<sup>5-7</sup> study of the chemiluminescence of 1,2-dioxetanes and has been of interest to chemists for a long time. The high-energy 1,2-dioxetane molecules are the focus of many investigations because of their unique ability to decompose thermally into electronically excited carbonyl products.<sup>2</sup> (see Scheme 1) Although 1,2-dioxetanes have been postulated as reaction intermediates for over 100 years, the thermal decomposition mechanism of these elusive materials is still not clear. It is likely that the effect of structural changes will help elucidate the still-debated mechanism of this reaction. The most common preparation of 1,2-dioxetanes is through the [2 + 2] cycloaddition of singlet oxygen to electron-rich alkenes.<sup>8</sup>

The key concept of the CICSL mechanism suggests that the activated electron in the molecule is transferred,



Scheme 1

Nakamura proposed that indolyl-dioxetane reacted into an excited diester via an exciplex intermediate form.<sup>10</sup> Adam also discussed the CICSL of 1,2-dioxetanes.<sup>11</sup>

The chemiluminescence of ozonization and singlet oxygen oxidation of the dioxin compound 1 was reported several years ago in this laboratory.<sup>12</sup> Based on the aforementioned current interest areas, we used the molecular structure of this compound as a base template to design and synthesize halo-substituted dioxin compounds 2~6. We report the chemiluminescence of compounds 1a~6a by taking the advantage of their dialkoxy-activated double bond, and fused with the high energy, para-position electrophile group substituted naphthalene ring to

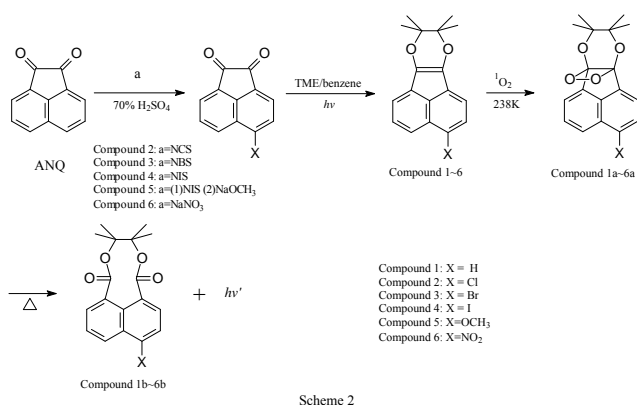
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present some new pieces of evidence in the intramolecular CICSL mechanism.

## 2. Experimental

### 2.1. Materials

Acenaphthenequinone (ANQ, Aldrich) was purified using chromatography and recrystallized several times before being used. para- position electrophile or nucleophile group substituted ANQ (compounds 2~6) were prepared using the method in ref. 13. Compounds 1~6 were synthesized by the photo-Diels-Alder reactions of the para-substituted acenaphthenequinone with tetramethylethylene (TME) in benzene.<sup>14</sup> Singlet oxygen oxidation of the dioxins (1~6) into the dioxetanes (1a~6a) was carried out using the procedure given in ref. 5. Dioxetane adducts (1a~6a) were isolated by ice-chilled n-hexane extraction from low temperature synthesis of ozonized triphenylphosphite for chemiluminescence studies. They were identified by <sup>1</sup>H NMR spectroscopy in CDCl<sub>3</sub> and by their quantitative cleavage to diesters (1b~6b) which were fully characterized. (see Scheme 2)



Scheme 2

### 2.2. Measurements

The absorption spectra were measured on a Hewlett-Packard diode array spectrophotometer. The steady-state emission spectra were obtained using a Cary Eclipsed Spectrofluorimeter equipped with a temperature controller. For the temperature-dependent kinetic measurements, the temperature of the sample solution was controlled to within  $\pm 0.5$  K with an electronically thermostating single cell and monitored with thermocouples attached to the cell. The quantum yields of the chemiluminescence of compounds (2a~6a) were determined using a photomultiplier tube, using compound 1a at the same concentration as the reference. The fluorescence quantum yields of compounds (2b~6b) were determined using the fluorescence spectrum of compound 1b as a reference.

## 3. Results and Discussions

The isolated dioxetane compounds 1a~6a were formed by reacting compounds 1~6 with singlet oxygen in

dichloromethane at 238 K and decomposed thermally into electronically excited diesters 1b\*~6b\* and then fluoresced to the ground state configurations 1b~6b.<sup>12</sup> As an example, the absorption, excitation and fluorescence spectra of diester compound 1b and the chemiluminescence spectra of dioxetane compound 1a in dichloromethane are shown in Fig. 1. Evidence shows that the chemiluminescence spectrum peak of the dioxetane compound 1a at 390 nm is consistent with that of the fluorescence of the excited diester compound 1b.

[Insert Fig. 1 here]

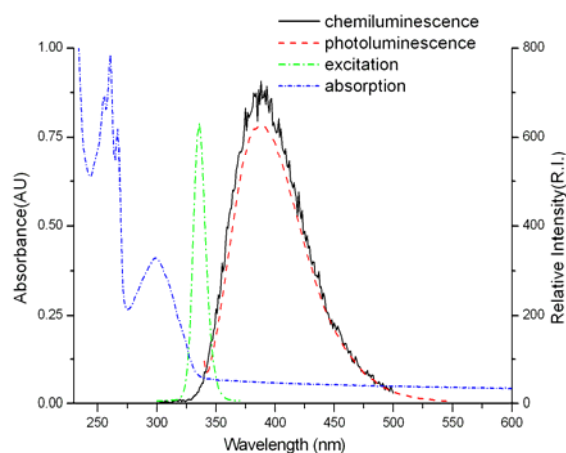


Fig. 1 The chemiluminescence spectrum (black line) of dioxetane compound 1a. The absorption (blue line), excitation (green line) and photoluminescence (red line) of the excited diester compound 1b.

【 $\sigma_p$ : (OCH<sub>3</sub> -0.12; I, 01.8; Br,0.26; Cl,0.24; NO<sub>2</sub>, 0.81) Table 8.2 (ref) ref. (7) Anslyn, Eric V.; Dougherty Dennis A. "Modern Physical Organic Chemistry" 2004,p.446, Table 8.2

The rate constants for the decomposition of dioxetanes were obtained at 313~353 K by measuring the decay of the chemiluminescence intensity. The chemiluminescence decay of compounds 1a~6a was monitored at the maximum value of the fluorescence in dichloromethane and/or benzene, plotted using the Arrhenius equation. There are two different linear equation groups corresponding to compounds 1a~6a respectively, as shown in Fig. 2.

[Insert Fig. 2 here]

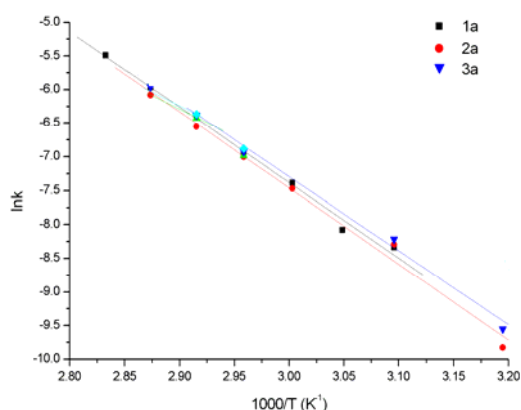


Fig. 2 The Arrhenius plots of the chemiluminescence kinetics of compounds 1a~6a.

Thus, the overall mechanism of dioxetanes can be presented as equation (1).



Where B = dioxetanes;  $X^\ddagger$  = the activated complex;  $C^*$  = the excited diesters. The rate constant equation (2) can be obtained using transition-state theory. The thermal parameters of compounds 1a~6a calculated with equation (2) are listed in Table 1.

$$\ln \frac{k}{T} = \left( \ln \frac{R}{N_A h} + \frac{\Delta S^\ddagger}{R} \right) - \frac{\Delta H^\ddagger}{RT} \quad (2)$$

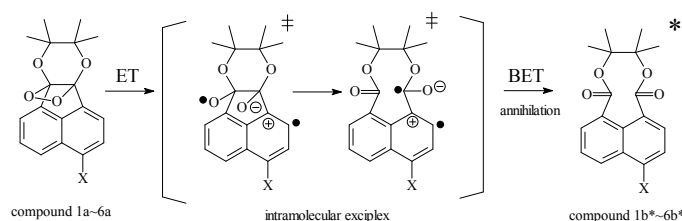
where  $N_A$  = Avogadro's constant ;  $h$  = Planck's constant

Table 1 shows that the energy of activation of the para- position nucleophile group substituted compounds (2a~5a) is lower than electrophile group substituted compound 6a. The O-O bond was cleaved through intramolecular exciplex via electron transfer (ET) into a transition state, as shown in Scheme 3. The nucleophile group on the naphthalene ring of compounds (2a~5a) could stabilize the transition state. The lone pair on the bromo-, chloro-, iodo or methoxy groups resonated to the cation at para- position of naphthalene ring. The CICSLS-type mechanism could be used to explain the result that the activation energy of compound 6a is much higher than that of compounds (1a~5a), as shown in Table 1.

Table 1

The thermodynamic parameters of compound 1a~5a

Compound	Ea (kcal/mol)	$\Delta H^\ddagger$ <sup>b</sup> (kcal/mol)	$\Delta S^\ddagger$ <sup>b</sup> (eu)
1a	22.2	21.5	-8.8
2a	22.4	21.7	-8.4
3a	21.8	21.1	-9.9
4a			
5a			
6a			



Scheme 3

The chemiluminescence quantum yields of dioxetane compounds 1a~6a that decomposed thermally into electronically excited diester compounds 1b\*~6b\*, which then emitted a photon, returning to their ground state configurations 1b~6b, can be calculated by equation (3).<sup>15</sup>

$$\varphi_{rel.CL} = \varphi_{rel.EX} \times \varphi_{rel.FL} \quad (3)$$

$\varphi_{rel.CL}$ : the relative chemiluminescence quantum yields of dioxetane compounds

$\varphi_{rel.EX}$ : the relative formation quantum yields of excited diester compounds

$\varphi_{rel.FL}$ : the relative fluorescence quantum yields of diester compounds

The chemiluminescence quantum yields of compounds 1a~6a and photoluminescence quantum yields of compounds 1b~6b are listed in Table 2. It was inferred that if the activated  $\pi$  electron on naphthalene of compound 1a transferred to generate a radical ion onto one oxygen atom of the 1,2-dioxetane ring, then the O-O bond was cleaved simultaneously through CICSLS. On one side on the 1,2-dioxetane ring, the dialkoxy group was the electron donor. The naphthalene ring was the corresponding electron acceptor (emitter) on the other side of the 1,2-dioxetane. The C-C bond was cleaved through the formation of an intramolecular exciplex, and then annihilated by anion/cation interactions via backward electron transfer (BET). Finally, the excited diesters were

formed from the activated complexes, and emitted a photon to return to the ground state. This is consistent with the intramolecular CICSL mechanism shown in Scheme 3.

Table 2

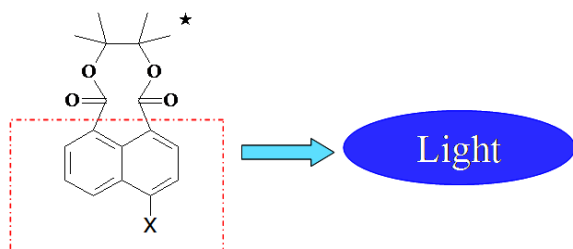
The relative quantum yields of chemiluminescence (1a~5a) and photoluminescence (1b~5b)

Compound	$\Phi_{rel.CL}$	Compound	$\Phi_{rel.FL}$
1a	1.0 <sup>#</sup>	1b	1.0 <sup>#</sup> (390nm max.)
2a	1.3	2b	4.9 (400nm max.)
3a	0.17	3b	3.8 (450nm max.)
4a		4b	
5a		5b	
6a		6b	

#: reference to compound 1a and 1b (~±20% error)

The chemiluminescence quantum yields of dioxetanes were affected by the formation quantum yields of the excited singlet state and the fluorescence quantum yields of compounds (1b~6b). Evidently, both fluorescence quantum yields and chemiluminescence quantum yields were affected by the substituents on the naphthalene ring. As shown in Table 2, the relative quantum yield of fluorescence ( $\Phi_{rel.FL}$ ) is  $5b > 4b > 3b > 2b > 1b > 6b$ . It can be inferred that the iodo-group of compound 4b would enhance the heavy atom effect making the formation of the triplet state more probable whereas the relative chemiluminescence quantum efficiency ( $\Phi_{rel.CL}$ ) is  $5a > 1a > 2a > 3a > 4a > 6a$ . It is also clearly that the chemiluminescence quantum yields were affected by the heavy atom effect of the halo-group on the naphthalene ring. The relative singlet chemiluminescence quantum yield increased with the inductive effect of the chloro-substituents and decreased with the heavy atom effect of the iodo-substituents.

The activation energy was controlled by the activated stability of transient dioxetane. The photo-excited emission frequency was mainly controlled by the naphthalene rigid structure. Hence, the naphthalene structure within the molecule played the role of a chemiluminescent, as shown in Scheme 4.



chemiluminescent emitter

Scheme 4

#### 4. Conclusion

We have shown that the 1,2-dioxetane-based chemiluminescence color is modulated by the intramolecular CICSL mechanism of a dioxetane bearing a substituted-naphthalene group. The change of substituent on the naphthalene emitter causes a change in the color of the dioxetane-based chemiluminescence, and also affects the decomposed reaction activation energies of the dioxetanes. The chemiexcitation process of the CICSL decay was rationalized and described as being mainly due to a particular form of entropic trapping. We continue to investigate these and other aspects of the CICSL mechanism.

#### Acknowledgments

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Study and Revisit on the Chemically Initiated Charge Separation Luminescence (CICSL) of Aromatic Dioxetanes

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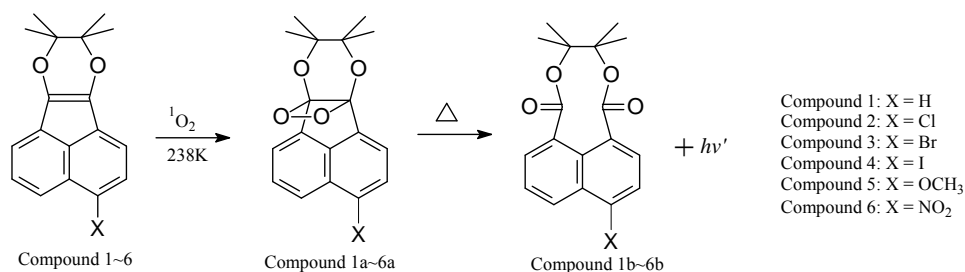
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Chung-Wen Sun (born June 27, 1963) is a PhD candidate student under the supervision of Prof. Tai-Shan Fang in the Department of Chemistry at the National Taiwan Normal University. His main research interest is in study and revisit on the chemically initiated charge separation

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