CHEMISTRY LETTERS, pp. 1231-1234, 1979. Published by the Chemical Society of Japan

PREFERENTIAL CONFORMATION FOR INTRAMOLECULAR EXCIPLEX FORMATION IN CHEMILUMINESCENCE OF THE DIOXETANES, 1-(1-SUBSTITUTED-3-INDOLYL)-6-ARYL-2,5,7,8-TETRAOXABICYCLO[4.2.0]OCTANES

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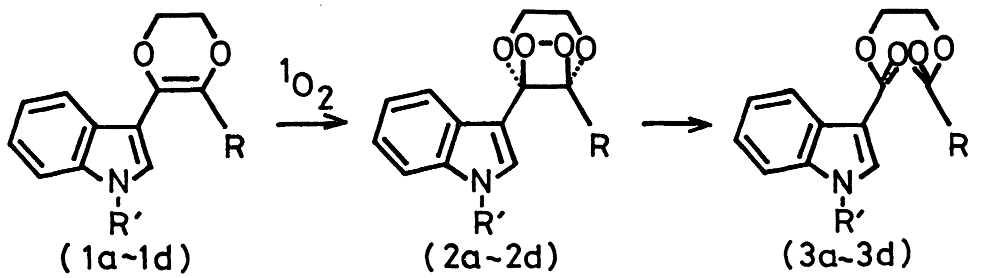
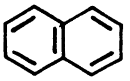
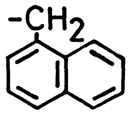
The title dioxetanes give in polar solvents visible chemiluminescence which is proven to be produced from the intramolecular exciplex between two aromatic substituents on the product diesters by comparison of chemiluminescence of the dioxetanes (**2a**-**2d**) and fluorescence of the corresponding diesters (**3a**-**3d**). That decomposition of the dioxetanes gives the corresponding diesters (in a singlet excited state) in a preferential conformation for the formation of intramolecular exciplex is also concluded from the above analysis as well as the examination of conformational effects on the exciplex fluorescence of the diesters, **4** and **5**.

Recent studies on the dioxetane thermolysis have been focused on the relationship between the efficiency of excited singlet state formation and the structure of dioxetane.[1] Accumulated results[2,3] have suggested that dioxetanes which conjugate with an electron-donating and highly fluorescent chromophor give efficient chemiluminescence by changing its O-O bond fission from homolytic to an highly charge-transferred (heterolytic) nature.

Recently we reported[4] that 1-(1-methyl-3-indolyl)-6-phenyl-2,5,7,8-tetraoxabicyclo[4.2.0]octane (**2b**) gave a highly efficient chemiluminescence (CL) in non-polar solvent (λ_{max} 320 nm in hexane, ϕ_{CL}=3.6% and ϕ_S=50%)[5] and the CL spectrum matched exactly with the fluorescence (F) spectrum of the product, diester **3b**, as expected. This ultra-violet CL of efficiently CL compounds so far examined; it corresponds to 94 kcal/mol, which may be close to the maximum value obtainable by dioxetane decomposition ($\sim$100 kcal/mol).[6] In polar solvents, on the other hand, was observed additonal CL at a visible region, λ_{max} 400 nm in CH_2Cl_2. In the previous paper[7] this was attributed to the CL from an intramolecular exciplex formed between the substituents, indole and phenyl groups, of the product (indole group as electron donor),[9,10,11] although only indirect evidence was at hand at that time (solvent and temp. effects, quenching with MeOH, independency to concentration, etc.) since the product showed no exciplex F by uv irradiation. This paper provides direct evidence that the visible CL is produced from the intramolecular exciplex and that the dioxetane decomposition gives the corresponding diester in a preferential conformation for production of the exciplex.

The title dioxetanes **2**[7,8] show two types of CL (Fig 1 and 2); one is at uv and another at visible region.[12] The former is produced from the locally excited state of the lower-energy chromophor in the products **3** (1-methylindole-3-carboxylate for **2a** and **2b**, 1-naphthoate for **2c**, and naphthalene for **2d**) since the CL



	a	b	c	d
R	CH_3	C_6H_5		C_6H_5
R'	CH_3	CH_3	CH_3	

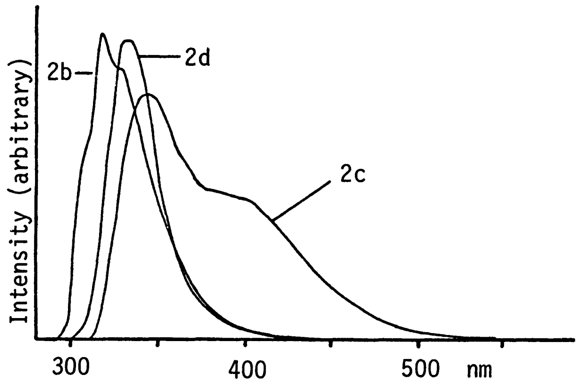


Fig. 1. Chemiluminescence spectra of dioxetanes, **2b**-**2d**, in hexane at room temperature

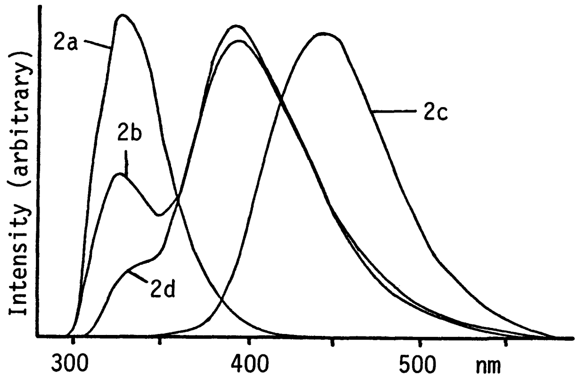


Fig. 2. Chemiluminescence spectra of dioxetanes, **2a**-**2d**, in CH_2Cl_2; **a** at room temp. and **b**-**d** at -10° ∿ -5°C

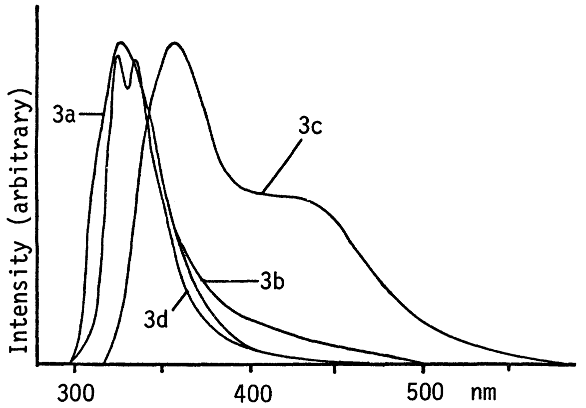


Fig. 3. Fluorescence spectra of diesters **3a**-**3d**, in CH_2Cl_2 at room temp.

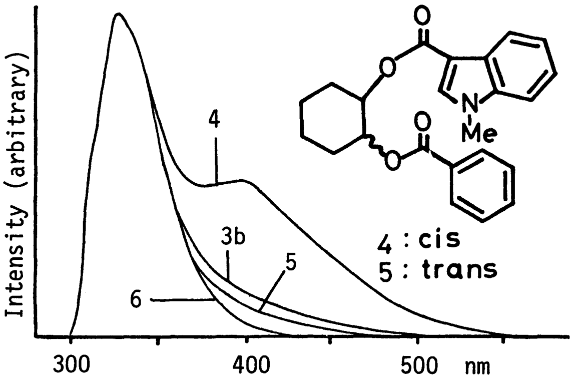


Fig. 4. Fluorescence spectra of diesters **3b**, **4** and **5**, and methyl 1-methylindole-3-carboxylate (**6**) in CH_2Cl_2 at room temperature.

spectra are superimposable with the F spectra of methyl 1-methylindole-3-carboxylate, methyl 1-naphthoate, and naphthalene, respectively. The latter is attributable from the evidence shown later to the intramolecular exciplex between indole and another chromophor attached to the dioxetane ring, and obviously observed more strongly in polar solvents rather than non-polar ones. Dioxetane **2a** does not show visible CL even in CH_2Cl_2 since it has no aryl substituent for acceptance of electron from the indole group to form the charge-transfer (CT) exciplex. Both **2b** and **2d** show visible CL at the same wavelength although uv CL spectra of **2b** and **2d** are different and obviously produced from the locally excited state of 1-methylindole-3-carboxylate and naphthalene, respectively, indicating that the intramolecular exciplex is formed only between two carbonyl fragments produced by dioxetane decomposition and not between indole and the substituent on 1 position of the indole. The dioxetane **2c** having naphthalene substituent on the dioxetane ring shows visible CL even in non-polar solvent, hexane, and uv CL is not observed in CH_2Cl_2 (ϕ_{CL} of the exciplex CL in CH_2Cl_2 is 3.8%, which is comparable to that of uv CL of **2b**). Thus CT interaction between naphthalene and indole is stronger than that between phenyl and indole.

CL products of the dioxetanes, **2a**-**2d**, are diesters, **3a**-**3d**, respectively, which are regarded as the emitter of CL. The F spectra of the diesters, **3a**, **3b**, and **3d**, give only one peak at uv region due to the lower-energy chromophor (1-methylindole-3-carboxylate for **3a** and **3b**, and naphthalene for **3d**) even in polar solvent (CH_2Cl_2). The F spectrum of **3c**, however, shows an additonal peak at 435 nm in CH_2Cl_2 and after subtraction of the F of methyl 1-naphthoate the remaining spectrum matches the CL spectrum of **2c**; polar nature[13] of this F is indicated by dependence of wavelength on solvent polarity, i.e., λ_{max} 390 nm in hexane, 435 nm in CH_2Cl_2, and 455 nm in acetonitrile. Thus, the F due to the intramolecular exciplex is clearly observed in this compound, although it is much weaker than the exciplex CL from **2c**.

Attempted observation of the exciplex F between 1-methylindole-3-carboxylate and benzoate chromophors of diester **3b** by changing solvents and temperatures failed, although thermolysis of the dioxetane **2b** gave the strong exciplex CL. This could be attributed to the conformational difference between excited states produced by the dioxetane thermolysis and by uv irradiation of the diester; the former produces the diester in which two aromatic groups faced

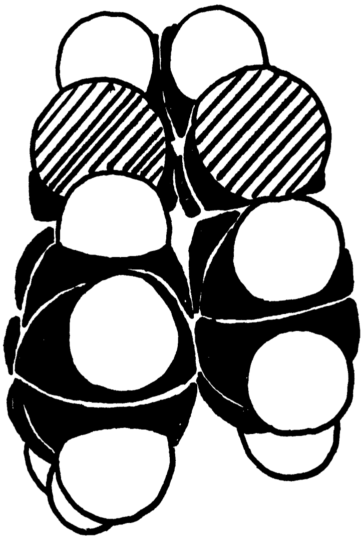


Fig. 5. Conformation model of diester **3b** formed by decomposition of dioxetane **2b**.
Black: C; white: H; shadow: O.

each other preferable for production of the CT complex (Fig 5), whereas in the latter case no such a special conformation is expected. To see the effect of proximity of the two aromatic chromophores, we synthesized compounds 4 and 5, in which indole-3-carboxylate and benzoate chromophores are in 1,2-cis and 1,2-trans orientation, respectively, on a cyclohexane ring. The F spectrum of the cis-diester 4 showed obvious exciplex luminescence at λ_{max} 400 nm in CH_2Cl_2, which matched the CL spectrum of dioxetane 2b. As shown in Fig 4 the exciplex component is decreased in the following order: cis 4 > acyclic 3b > trans 5; ratios of the F efficiency $(\phi_E/\phi_L)^{14}$ of the exciplex and the local chromophore (1-methylindole-3-carboxylate) in CH_2Cl_2 are 1.6, 0.3, and 0.1, respectively.[15] The exciplex F of 5 increases with increasing solvent polarity (ϕ_E/ϕ_L=0.1 in hexane, 1.6 in CH_2Cl_2 and 2.7 in acetonitrile) and is quenched by MeOH ($k_q\tau$ is ca 6.8 M^{-1} at 20°C obtained from Stern-Volmer plot).[7]

These results suggest that the intramolecular exciplex between the 1-methyl-indole-3-carboxylate and the benzoate chromophors can be formed only in the conformation where the chromophores are in a special geometry. This is the reason why the intense CL from the intramolecular exciplex is observed in thermolysis of the dioxetanes; the diester is formed in the most preferential geometry to produce the exciplex.

Acknowledgments —— This work was partly supported by Grant-in-Aid for Special Project Research and Grant-in-Aid for Scientific Research, The Ministry of Education, Science and Culture.

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5. ϕ_{CL} = quantum yield of CL; ϕ_S = quantum yield of singlet excited state.
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12. CL and F spectra were measured under aerobic conditions and uncorrected.
13. T. Okada, T. Fujita, M. Kubota, S. Masaki, N. Mataga, R. Ide, Y. Sakata, and S. Misumi, Chem. Phys. Letters, 14, 563 (1972).
14. ϕ_E = luminescence efficiency of exciplex; ϕ_L = luminescence efficiency of locally excited chromophor.
15. These ratios increase by lowering temperature and are independent of concentration of the esters ($1.8 \times 10^{-4} \sim 4.5 \times 10^{-6}$ M).

(Received August 3, 1979)