I with a comparable efficiency under the same conditions.

This study adds a new class of enzymes to proteases[12] as catalysts used in peptide synthesis.[2] The use of organic solvents instead of water as the reaction medium solves the equilibrium and solubility problems, and lipases, in contrast to proteolytic enzymes, have a broad specificity and do not catalyze secondary hydrolysis[2e] of peptides. We are currently applying the lipase strategy[13] to the synthesis of biologically active peptides.

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(11) Lipase from *Mucor* sp. was obtained from Amano International Enzyme Co. as a powder with a specific activity of 10 units/mg solid. It was dried under vacuum prior to use to lower the enzymatic ester hydrolysis.

(12) Catalysis of peptide bond formation cannot be attributed to a possible presence of proteases in the lipase samples, for both porcine pancreatic and *Mucor* lipases (100 mg/mL) failed to hydrolyze *N*-Ac-L-Phe-L-Leu-NH$_2$ (1 mM) in water (pH 7.8, 5% dimethylformamide) (3-day incubation at 45 °C, assay by HPLC).

(13) Lipases as catalysts in organic solvents appear an evermore useful synthetic methodology which has been successful in regioselective acylations of glycols (Cesti, P.; Zaks, A.; Klibanov, A. M. *Appl. Biochem. Biotechnol.* **1985**, *11*, 401–407) and sugars (Therisod, M.; Klibanov, A. M. *J. Am. Chem. Soc.* **1986**, *108*, 5638–5640) and for stereoselective conversions of alcohols and acids (Kirchner, G.; Scollar, M. P.; Klibanov, A. M. *J. Am. Chem. Soc.* **1985**, *107*, 7072–7076. Langrand, G.; Baratti, J.; Buono, G.; Triantaphylides, C. *Tetrahedron Lett.* **1986**, *27*, 29–32. Margolin, A. L.; Crenne, J.-Y.; Klibanov, A. M. *Tetrahedron Lett.* **1987**, *28*, 1607–1610.

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A New Type of Pericyclic Chemiluminescence

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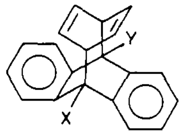
Chemiluminescence and its related bioluminescence involve the generation of light-emitting excited-state molecules by chemical means. The phenomenon and mechanism of chemiluminescence have been subjects of interest to many scientists.[1] In connection with our interest in the chemistry of energy-rich dimers of aromatic hydrocarbons, we have synthesized a number of para,para′ dimers of benzene and substituted anthracenes bearing substituents at the bridgehead positions (**1b–d**).[2] Thermolyses of some of these compounds are chemiluminescent.



1a, X = Y = H
b, X = COOH, Y = H
c, X = Y = COOH
d, X = CH$_3$, Y = H
e, X = CN, Y = H

The formation of excited-state molecules in a chemical reaction is governed by both an energy factor and a probability factor. In the former factor, the energy available from the chemical reaction, the sum of free energy and free energy of activation of the reaction, must exceed the excitation energy of the luminescent product. In the latter factor, there must be a pathway for the product in gaining access to the excited state. We had synthesized the parent dimer **1a** and found that its thermolysis to benzene and anthracene was not chemiluminescent, in spite of the fact that the available energy exceeds the excited energy of anthracene.[2] Since the thermolysis of **1** is symmetry-forbidden as a concerted process, the reaction may proceed via a biradical or biradical-like intermediate **2**. If **1** contains an appropriate substituent at the bridgehead position, such as an electronegative substituent W at the 9-position of the anthryl moiety, the substituent may introduce a polar character into **2** (eq 1). The partial anionic character in the anthryl moiety may proceed further along a reaction pathway which may ultimately lead to the formation of a radical ion pair of benzene radical cation and anthracene radical anion. This pathway may become endoergic as these ions separate to overcome the electrostatic attraction between them (dotted line CS, or charge-transfer surface, in Figure 1). In the meantime, excited anthracene can be formed efficiently from excited **1** in a symmetry-allowed and highly exoergic process, line S, or singlet excited surface.[2] Conceivably, the crossing of these two surfaces may lead to the formation of excited anthracene from the initial polar dissociation of **1**; i.e., introduction of an electron-withdrawing group at the bridgehead of **1** may enhance the probability of chemiluminescence in the thermolysis of these compounds.

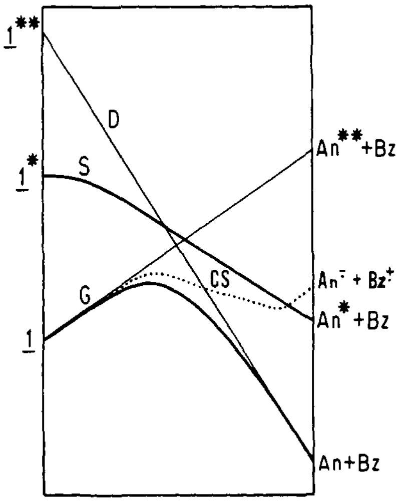
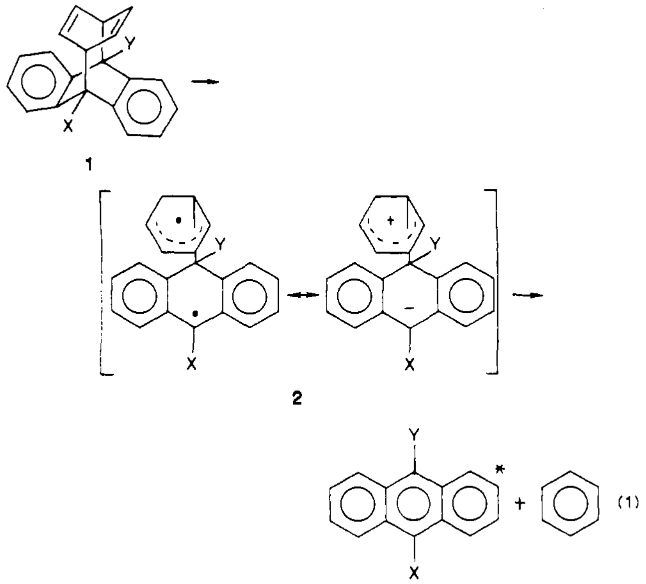


Figure 1. Schematic diagram of the reaction coordinate of thermolysis of **1**.



Our initial goal was to synthesize the cyano derivative **1e**, but our attempts in its synthesis have not been successful. However,

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(1) For some recent reviews and references on chemiluminescence, see: (a) *Chemical and Biological Generation of Excited States*; Adam, W., Cilento, G., Eds.; Academic: New York, 1982. (b) Adam, W.; Platsch, H.; Schmidt, E. *Chem. Ber.* **1985**, *118*, 4385–4403. (c) Handley, R. S.; Stern, A. J.; Schaap, A. P. *Tetrahedron Lett.* **1985**, *26*, 3183–3186. (d) Little, C. B.; Schuster, G. B. *J. Org. Chem.* **1986**, *51*, 2050–2055; Schuster, G. B. *Acc. Chem. Res.* **1979**, *12*, 366–373. (e) Turro, N. J.; Lechtken, P.; Schore, N. E.; Schuster, G.; Steinmetzer, H.-C.; Yetka, A. *Acc. Chem. Res.* **1974**, *7*, 97–105. Lechtken, P.; Breslow, R.; Schmidt, A. H.; Turro, N. J. *J. Am. Chem. Soc.* **1973**, *95*, 3025–3027. (f) White, E. H.; Steinmetz, M. G.; Miano, J. D.; Wildes, P. D.; Morland, R. *J. Am. Chem. Soc.* **1980**, *102*, 3199–3208.

(2) Yang, N. C.; Chen, M.-J.; Chen, P. *J. Am. Chem. Soc.* **1984**, *106*, 7310–7315. Yang, N. C.; Chen, M.-J.; Chen, P.; Mak, K. T. *Ibid.* **1982**, *853*–855.

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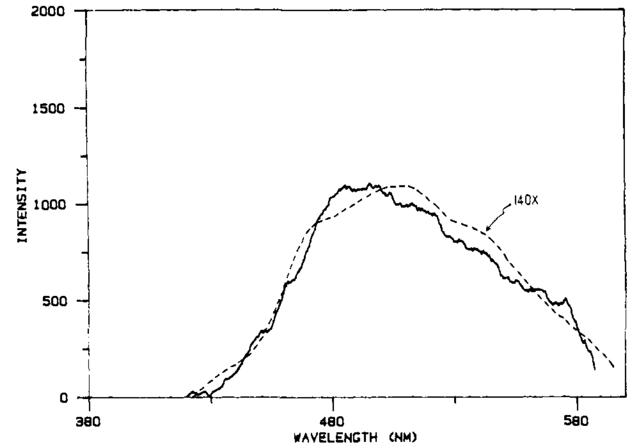
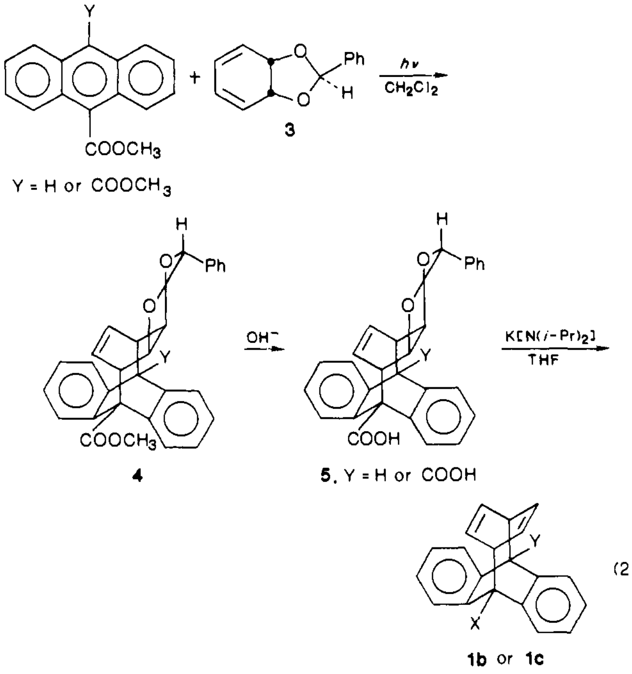


Figure 2. Chemiluminescence spectrum of **1b** at 150 °C (---) and the fluorescence spectrum of solid 9-anthroic acid at 125 °C (—).

we have succeeded in the synthesis of **1b** and **1c** according to eq 2.[3] The gap between the energy level of the radical ions formed and that of excited 9-anthroic acid may be estimated from polarographic measurements[4] and spectroscopic data of the products to be approximately 15 kcal/mol. Thermolyses of these compounds in the solid state at 150 °C are distinctively chemiluminescent,[5] and the presence of air or oxygen has no effect on the luminescence. The chemiluminescence spectrum of thermolysis of **1b** was found to be virtually identical with the fluorescence spectrum of 9-anthroic acid (Figure 2),[6] in agreement with our prediction.



Since the fluorescent state of 9-anthroic acid (0 → 0 band at 388 nm) is red-shifted from that of anthracene (0 → 0 band at 376 nm), the formation of excited anthroic acid in the thermolysis of **1b** may also be due to a more favorable energy factor. To explore this further, **1d** carrying an electron-releasing methyl group was synthesized.[2] The thermolysis of **1d** will yield 9-methylanthracene which exhibits a fluorescent state (0 → 0 band at 388 nm)[7] isoenergetic with that of 9-anthroic acid. However, the result from the thermolysis of **1d** was not detectably different from that of **1a**. Therefore, in contrast to the carboxyl group, an electron-releasing methyl group at the same position exerts no detectable effect on the probability of chemiluminescence of the parent compound.

In conclusion, the pericyclic dissociation of energy-rich dimers of aromatic compounds with appropriate substituents represents a new type of chemiluminescence. These compounds apparently exhibit more desirable handling characteristics in the laboratory for mechanistic studies than chemiluminescent peroxides, such as dioxetanes. The synthesis and thermolysis of compounds related to **1** are actively being pursued in our laboratory in order to probe into the mechanism of chemiluminescence.

Acknowledgment. We acknowledge the generous support from the National Institute of General Medical Sciences and the partial support from the National Science Foundation. We also express our appreciation for the assistance of Professor G. R. Fleming and Scott Courtney in the construction of the chemiluminescence spectrometer, and thank the NSF Instrumentation Program and the National Cancer Institute via The University of Chicago Cancer Research Center (CA-14599) for the NMR instruments used in this work.

Supplementary Material Available: Text consisting of experimental details (2 pages). Ordering information is given on any current masthead page.

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(3) Correct spectral and elemental analyses were obtained for all intermediates, and correct spectral analyses were obtained for **1b–d**. Elemental analyses for **1b–d** were not attempted because of their low thermal stability.

(4) (a) Pysh, E. S.; Yang, N. C. *J. Am. Chem. Soc.* **1963**, *85*, 2124–2130 and references therein. (b) Klemm, L. H.; Kohlik, A. J.; Desai, K. B. *J. Org. Chem.* **1963**, *28*, 625–630. Klemm, L. H.; Kohlik, A. J. *Ibid.* 2044–2049.

(5) The luminescence yield is estimated to be <0.001.

(6) The chemiluminescence spectrometer used in this investigation consists of a UFS-200 flat field spectrograph (Instrument SA, Inc., F/3, 200–800 nm), a DIDA-512G reticon detector head (set at 330–650 nm), and an OMSA ST-110 detector controller (Princeton Instruments, Inc.). The slit of the spectrograph was set at 250 μm, and the resolution was ± 5 nm.

(7) Rice, J.; McDonald, D. B.; Ng, L.-K.; Yang, N. C. *J. Chem. Phys.* **1980**, *73*, 4144–4146.

(8) The amount of energy required to form a 9-methylanthracene radical cation and benzene radical anion may be extrapolated from the polarographic oxidation potential of 9-methylanthracene and polarographic reduction potentials of aromatic compounds (ref 4) to be 4.5 eV or 103.5 kcal/mol. Therefore, their formation is unlikely.

Evidence for the Formation of a $ZnFe_3S_4$ Cluster in *Desulfovibrio gigas* Ferredoxin II

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The electron-transport protein ferredoxin II (Fd II) from *Desulfovibrio gigas* contains an Fe_3S_4 cluster[1] which reacts readily with Fe^{2+} to form the cubane Fe_4S_4 complex.[2] This conversion suggested that the Fe_3S_4 core of Fd II can serve as a precursor for the formation of novel clusters of the MFe_3S_4 type. Indeed, we have demonstrated[3] the formation of $[CoFe_3S_4]^{1+,2+}$. The Fe_3S_4

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(1) Huynh, B. H.; Moura, J. J. G.; Moura, I.; Kent, T. A.; LeGall, J.; Xavier, A. V.; Münck, E. *J. Biol. Chem.* **1980**, *255*, 3242–3244.

(2) Moura, J. J. G.; Moura, I.; Kent, T. A.; Lipscomb, J. D.; Huynh, B. H.; LeGall, J.; Xavier, A. V.; Münck, E. *J. Biol. Chem.* **1982**, *257*, 6259–6267.

(3) Moura, I.; Moura, J. J. G.; Münck, E.; Papaefthymiou, V.; LeGall, J. *J. Am. Chem. Soc.* **1986**, *108*, 349–351.

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