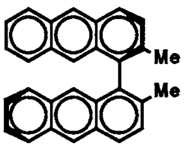
CHEMISTRY LETTERS, pp. 2227-2228 1994.

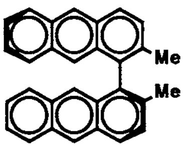
Chiral Discrimination in Exciplex Quenching of 2,2'-Dimethyl-1,1'-bianthryl - N,N-Dimethylaniline System

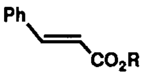
Toshinori NISHIYAMA, Kazuhiko MIZUNO,* Yoshio OTSUJI, and Hiroo INOUE
Department of Applied Chemistry, College of Engineering,
University of Osaka Prefecture, Sakai, Osaka 593

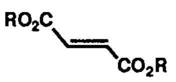
Emission associated with exciplex between (*R*)-(-)- or (*S*)-(+)-2,2'-dimethyl-1,1'-bianthryl (*R*-(-)-**1** or *S*-(+)-**1**) and N,N-dimethylaniline (DMA) was quenched by (+)- and (-)-menthyl cinnamates at room temperature. The chiral exciplexes were discriminated by the two enantiomeric quenchers that interact with the exciplexes in an enantioselective manner.

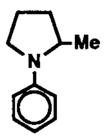
Chiral recognition in excited molecules has received considerable attention in recent years.1) Irie et al. have reported a chiral discrimination in fluorescence quenching of (*R*)-(-)-1,1'-binaphthyl by chiral amines.2) In this system, however, exciplex emission was extremely weak. We now report a chiral recognition in the exciplex quenching3) of the system consisting of *S*-(+)- and *R*-(-)-2,2'-dimethyl-1,1'-bianthryls (*S*-(+)- and *R*-(-)-**1**) and N,N-dimethylaniline (DMA) using (+)- and (-)-menthyl cinnamates ((+)- and (-)-**2**).4)

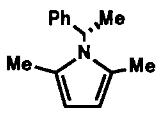

R-(-)-**1**


S-(+)-**1**


(+)-**2**, (-)-**2**


(+)-**3**, (-)-**3**


(+)-**4**, (-)-**4**


(+)-**5**, (-)-**5**

R = (+)- or (-)- menthyl

The fluorescences of *R*-(-)-**1** and *S*-(+)-**1** in benzene was quenched by chiral electron-donating and -accepting molecules **2**-**5**.

Table 1. Fluorescence Quenching of *S*-(+)-**1** by Chiral Quenchers[a)]

Quencher	$[\alpha]_D$	$k_q\tau$ / mol^{-1}dm^3	$k_q\tau$ ratio in enantiomer - pair
(+)-**2**	+48.1	1.25	1.03±0.02
(-)-**2**	-49.5	1.21	
(+)-**3**	+85.2	13.1	1.09±0.03
(-)-**3**	-86.4	14.3	
(+)-**4**	+38.2	12.3	1.02±0.03
(-)-**4**	-38.2	12.5	
(+)-**5**	+24.2	0.53	1.15±0.04
(-)-**5**	-24.9	0.61	

a) [*S*-(+)-**1**] = 1 x 10^{-5} mol dm^{-3} in benzene at 25 °C under argon.

The rates of this fluorescence quenching depended on the structure of the quenchers and also on their chirality. The largest chiral discrimination was found in the fluorescence quenching of *S*-(+)-**1** by the enantiomer pair (+)-**5** and (-)-**5** (Table 1).

Furthermore, when the fluorescence of *R*-(-)-**1** and *S*-(+)-**1** was quenched by electron-donating quenchers (+)-**4** and (-)-**4**, an exciplex emission was observed, showing an isoemissive point at 480 nm. The fluorescence of *R*-(-)-**1** and *S*-(+)-**1** was also quenched by DMA, accompanied by appearance of a strong exciplex emmision. This exciplex emission was quenched by electron-accepting quenchers (+)-**2** and (-)-**2** at different rates. The kqτ values for quenching of the emission associated with the exciplexes systems *R*-(-)-**1**/DMA and *S*-(+)-**1**/DMA by (+)-**2** in various organic solvents are shown in Table 2.[5] The quenching rate of the exciplex emission of the racemic **1**/DMA exciplex system by (+)-**2** showed an intermediate value between those of the optical active **1**/DMA exciplex systems by (+)-**2**. This result strongly suggests that the chiral quenchers **2** interact with the chiral **1**/DMA exciplexes in an enantioselective manner. The enantioselectivity in quenching of the exciplex emission decreased with increasing solvent polarity.

To the best of our knowledge, litte is known about the chiral discrimination in the quenching of chiral exciplexes by chiral quenchers.[6]

Table 2. Quenching of Exciplex [**1** - DMA]* by **2**[a]

Solvent	Exciplex	Quencher	kqτ / $mol^{-1}dm^3$	kqτ ratio in enantiomer - pair
benzene	*S*-(+)-**1**–DMA	(+)-**2**	51.4	1.08±0.02
	R-(-)-**1**–DMA	(+)-**2**	55.6	
	(±)-**1**–DMA	(+)-**2**	53.6	
Bu_2O	*S*-(+)-**1**–DMA	(+)-**2**	36.8	1.07±0.03
	R-(-)-**1**–DMA	(+)-**2**	39.2	
CH_2Cl_2	*S*-(+)-**1**–DMA	(+)-**2**	123	1.02±0.03
	R-(-)-**1**–DMA	(+)-**2**	126	

a) [**1**] = 1 x 10^{-5} mol dm^{-3}, [DMA] = 1.05 mol dm^{-3} at 25 °C under argon.

This work was partially supported by a Grant-in-Aid on Priority-Area-Research 'Photoreaction Dynamics' from the Ministry of Education, Science and Culture, Japan (06239253).

References

1) H. Rau, *Chem. Rev.* **83**, 535 (1983); Y. Inoue, *ibid.*, **92**, 471 (1992).

2) M. Irie, T. Yorozu, and K. Hayashi, *J. Am. Chem. Soc.*, **100**, 2236 (1978).

3) R. A. Caldwell, D. Creed, D. C. DeMarco, L. A. Melton, H. Ohta, and P. H. Wine, *J. Am. Chem. Soc.*, **102**, 2369 (1980).

4) Enantiomer excesses (e.e.), *R*-(+)-**1**=86%, *S*-(-)-**1**=99%, (+)-**4**=99%, (-)-**4** =88%, were determined by HPLC by use of chiral column (chiral cell OD).

5) Triplex emission was not observed under this quenching conditions.

6) T. Masaki, Y. Uehara, S. Yanagida, and C. Pac, 61st National Meeting of the Chemical Society of Japan, Tokyo, March 1991, Abstr., No. 2, 1548.

(Received August 12, 1994)