

gested to resemble that of ionic crystals.¹⁰ Indeed the rate constant for the ultrafast proton transfer observed in the present work (2.0 ± 0.2) ($10^{12} \text{ M}^{-1} \text{ s}^{-1}$) lies between values determined in water ($\sim 10^{11} \text{ M}^{-1}$) and derived in ice (10^{13} – $10^{14} \text{ M}^{-1} \text{ s}^{-1}$).²⁴ Excited-state proton tunneling cannot be excluded.

The present communication has demonstrated the feasibility of ultrafast proton transfer when the reactants are localized in suitable environment. Micellar surfaces provide a convenient means for the reduction in dimensionality, an important and recognized way fast reaction occurs at membrane surfaces^{6,7} and in complex biomacromolecules.

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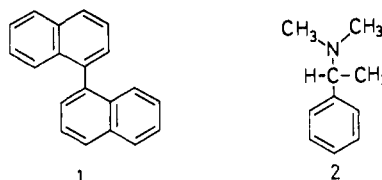
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Steric Effect on Fluorescence Quenching of 1,1'-Binaphthyl by Chiral Amines

Sir:

Although several works have been published recently dealing with steric influence upon fluorescence quenching rates,¹ a satisfactory answer to the question of whether a specific geometry is required for charge-transfer or electron-transfer quenching processes has not yet been given.² Efforts have so far been directed to measuring the quenching rate as a function of substitution on the quenchers or the excited molecules. The conclusions deduced from these experiments have several limitations, since the introduction of substituents implies electronic, as well as steric, changes, which can affect the role of a charge-transfer interaction in the excited state.³ In addition, the imposition of bulky substituents may also produce an effect on the solvation shell and on diffusion rates, which will result in differences in the quenching rate.

In this communication we would like to present unambiguous evidence that specific geometry is required for the fluorescence quenching of 1,1'-binaphthyl (**1**) by *N,N*-dimethyl- α -phenethylamine (**2**) in less polar solvents. Both **1** and **2** are



chiral compounds. The chirality of 1,1'-binaphthyl is molecular in nature.⁴ The use of chiral compounds as excited molecules and quenchers enables one to examine pure steric effect upon the quenching rate without being disturbed by the electronic factor, since enantiomers have inherently the same electronic nature, i.e., oxidation-reduction potential or bulkiness. Chiral sensitizers or quenchers are also useful in photochemical reactions, such as asymmetric inductions⁵ or racemization reactions.^{4,6}

Photoexcited 1,1'-binaphthyl gives a fluorescence around 360 nm. The fluorescence can be quenched by adding *N,N*-dimethyl- α -phenethylamine, the quenching being similar to a typical exciplex-type quenching observed in the naphthalene-triethylamine system.⁷ Figure 1a shows Stern-Volmer plots of a fluorescence quenching of racemic mixture of 1,1'-binaphthyl by enantiomers, (*S*)-(-) and (*R*)-(+)-*N,N*-dimethyl- α -phenethylamines in *n*-hexane. No difference was discerned in the quenching rate. On the other hand, a significant difference in the rates was observed for the quenching of (*R*)-(-)-1,1'-binaphthyl ($[\alpha]_D -190^\circ$) fluorescence by these enantiomers, as shown in Figure 1b and 1c. The ratio of the quenching rates, $k_q(R-S)/k_q(R-R)$, was determined to be 1.90. The difference in the rate clearly indicates that the quenching occurs in the contact pair of an excited molecule and a quencher, and specific orientation is required in the quenching process.

Solvent polarity is believed to alter the quenching mechanism.^{1,8,3,8,9} In nonpolar solvents, exciplex formation is dominant in the quenching process; in polar solvents, quenching by electron transfer in an encounter complex of loose structure dominates. This mechanism was examined by measuring the quenching rate with the two enantiomers as a function of the polarity of solvent. The ratio, $k_q(R-S)/k_q(R-R)$, has a tendency to decrease with increasing solvent polarity as shown in Table I. No noticeable difference was detected in acetonitrile. In 1,2-dichloroethane, however, there is still a significant difference. The Stern-Volmer constant also depends upon the polarity. It increases with increasing solvent polarity, the highest value being observed in acetonitrile. The increase is

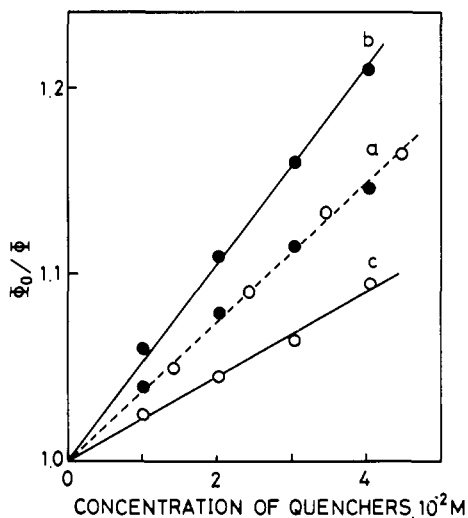


Figure 1. Stern-Volmer plots of the fluorescence quenching of racemic (- - -) and (R)-(-)-1,1'-binaphthyl (—) by (S)-(-)- (●) and (R)-(+)-N,N-dimethyl- α -phenethylamines (○) in *n*-hexane at 22 °C. Concentration of 1,1'-binaphthyl is 1.1×10^{-5} mol/L.

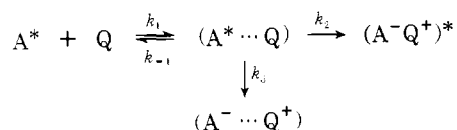
Table I. Solvent Dependence of the Quenching Rate

Solvent	ϵ^a	$k_q(R-S)/k_q(R-R)^b$
<i>n</i> -Hexane	1.89	1.90
Benzene	2.28	1.82
1,2-Dichloroethane	10.4	1.51
Acetonitrile	37.5	1.00

^a Dielectric constant at 20 °C. ^b The ratio of the fluorescence quenching rate of (R)-(-)-1,1'-binaphthyl ($[\alpha]_D -190^\circ$) by (S)-(-)- and (R)-(+)-N,N-dimethyl- α -phenethylamines.

ascribable mainly to an increase in the fluorescence quenching rate, since solvent scarcely alters the fluorescence lifetime of 1,1'-binaphthyl.¹⁰

The above steric and polarity effects upon the quenching rate can be interpreted by the following general scheme:



A^* is 1,1'-binaphthyl in the excited state, Q is *N,N*-dimethyl- α -phenethylamine, $A^* \cdots Q$ is an encounter complex, $(A^-Q^+)^*$ is an exciplex, and $A^- \cdots Q^+$ is an ion pair. The rate constant for fluorescence quenching, k_q , is therefore a function of k_1 , k_{-1} , k_2 , and k_3 .

$$k_q = k_1 \left(\frac{k_2 + k_3}{k_{-1} + k_2 + k_3} \right)$$

We can expect that k_3 is small in less polar solvents but relatively large in polar solvents.³ Therefore in less polar solvents k_2 determines the quenching rate. This process involves geometric and solvent relaxation of the encounter complex to an equilibrium exciplex. The steric effect on the quenching rate in *n*-hexane indicates that specific geometry is required between A^* and Q molecules in the equilibrium exciplex state and the relaxation rate, or the rate of the formation of the exciplex, k_2 , depends on the structure of the two molecules.

On the other hand, in polar solvents quenching is governed by the electron-transfer reaction, the rate constant of which is k_3 . The reaction occurs in the encounter complex in a loose structure. Therefore, the quenching rate is fast and no steric effect was discerned.¹¹ In solvents of medium polarity, the relaxation process is considered to compete with the electron-transfer reaction. The steric effect observed in 1,2-di-

chloroethane is due to the contribution of the exciplex quenching process, not the electron-transfer quenching process.

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Trisection of Reaction Pathways in Automerization of 6-Methylenebicyclo[3.2.1]oct-2-ene

Sir:

A previous study¹ showed that C_3 and C_9 deuterium labels redistributed themselves to C_1 and C_7 , with rate constants k_3 and k_9 , respectively, during pyrolysis of 6-methylenebicyclo[3.2.1]oct-2-ene-3,9,9- d_3 (A, $\blacksquare = CD_2$, Scheme I). The observation that within experimental error $k_3 = k_9$ permitted only three formal mechanisms: (1) $A \rightleftharpoons B$ only (pure Cope rearrangement); (2) $A \rightleftharpoons$ equal amounts of C and D only; (3) any mixture of these two mechanisms, including as a special case mechanism (3a), a mixture of one-third 1 and two-thirds 2, which is indistinguishable from a randomized

Scheme I

