Difference in the Rate of Photo-induced Unimolecular Motion of Chiral Salicylideneamines in the Chiral Crystal Environments

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From the kinetic investigation on the photochromic process of chiral *N*-salicylidene-1-phenylethylamine it was revealed that the rate of unimolecular asymmetric motion was influenced by the neighboring asymmetric crystal environments.

Differences of right and left are of basic importance in both life science and artificial systems. Enantiomers have identical physical properties except the right- and left-direction of rotation of the plane of polarized light, and have identical chemical properties except toward chiral reagents in the solutions.[1] Recently, asymmetric transformations in chiral crystals have received much attention as new synthetic processes or to probe reaction pathways.[2] Here we report the difference of right and left, which concerns the rate of unimolecular motion of chiral molecules in asymmetric crystal environments.

Unimolecular photoreactions of organic crystals have well-studied.[3] Salicylideneamines crystals are one of the constructive samples to define unimolecular dynamic behavior because they exhibit reversible photo-coloration (from yellow to orange), which involves an intramolecular proton transfer from the *o*-hydroxyl group to the imine nitrogen atom in the excited state followed by the intramolecular framework alteration: the resultant photochrome fades thermally in the ground state when they are kept in the dark.[3-5] A first-order reaction is usually due to independent unimolecular alteration of a reactant. By measuring the first-order rate constant (k) of the thermal bleaching reaction of the photochrome derived from salicylideneamine, one can estimate the rate of the framework change or unimolecular motion of the compounds in the ground state. For such a photosensitive Schiff base, we used chiral *N*-salicylidene-1-phenylethylamine (**1**)[6,7] in this study.

Each photo-colored species was obtained by irradiating crystalline salicylideneamine powder with 365 nm light. The thermal fading reaction of the photochrome was followed by reflectance spectrophotometry at 30 °C by measuring the optical density (A_t) at the wavelength at which a maximal decrease occurred in the dark. The final optical density (A_∞) was taken after 10 half-lives. The experimental optical density *vs.* time (t) data were treated with the standard integrated expression, $kt = \ln\{(A_o - A_\infty) / (A_t - A_\infty)\}$, for a first-order process using linear least-squares analysis.[5] All the rate constants for the *R*- and *S*-enantiomers (each: mp 77-78 °C) and the racemic mixture (mp 50-51 °C) of **1** were measured to be identical (k = 7.6 x 10^{-2} s^{-1}); however, the racemic compound (mp 62-63 °C) did not display such photo-induced color-change (molecular motion).

Here, racemic compound consists of crystals in each of which the *R*- and *S*-enantiomers are present in a 1:1 ratio down to the unit cell level, being easy to yield by ordinary recrystallization of an equimolar mixture of enantiomeric isomers, whereas racemic mixture is regarded as a simple 1:1 mechanical mixture or conglomerate of crystals of the two enantiomers (Figure 2). In

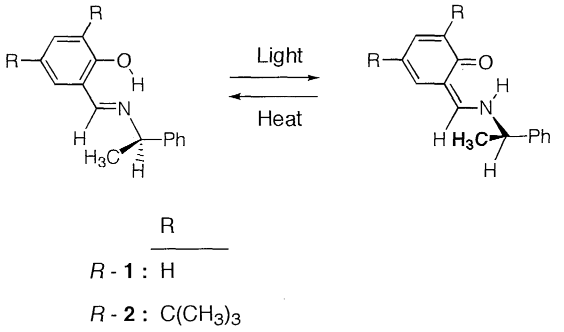

Figure 1. Chemical Structures of (*R*)-*N*-salicylidene-1-phenylethylamine (*R*-**1**) and its photo-colored form. The (*S*)-isomer has the mirror-image structure of the *R*-configuration.

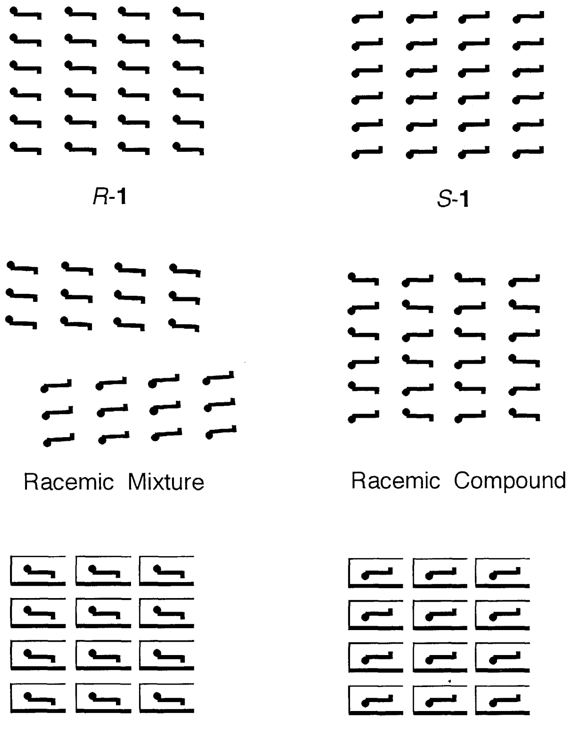

Figure 2. Schematic representation of crystals due to *R*-type, *S*-type, racemic compound, and racemic mixture of chiral *N*-salicylidene-1-phenylethylamine molecules (¬ or ⌐) and their enclathrated crystals into chiral DCA crystal lattice (one-sided braces).

this study the racemic mixture of **1** was prepared by slow evaporation of solvent from a solution of (±)-**1** in ethanol at a temperature below 15 °C; the resultant sample exhibited exactly same mp and IR spectral data to those of the simple 1:1 mechanical mixture of the two enantiomers. The *R*- and *S*-enantiomers, racemic mixture, and racemic compound of **1** showed deservedly identical NMR spectra in $CDCl_3$. This is a new example exhibiting the difference of (photo)chemical properties between a racemic compound and a racemic mixture.

Recently, introduction of bulky *t*-butyl substituents to the 3- and 5-position of salicylideneamines was suggested to enable photosensitive Schiff base crystals to be prepared.[8] The bulky groups were assumed to space out the molecules in the crystal lattice and allow photo-induced motion of the Schiff bases in the solid state. Thus, the racemic compound (mp 99-100 °C) from a mixture of *t*-butyl substituted derivatives (*R*-**2** and *S*-**2**) was prepared to present photo-coloration. The thermal decoloration of the photochrome from the racemic compound went on in two steps and the rate constants were $k_1 = 4.9 \times 10^{-3}$ s^{-1} and $k_2 = 6.1 \times 10^{-4}$ s^{-1}, while the ones for the *R*- and *S*-enantiomers (each: mp 94-95 °C) and the racemic mixture (mp 83-88 °C) of the derivatives were $k_1 = 6.8 \times 10^{-3}$ s^{-1} and $k_2 = 2.5 \times 10^{-4}$ s^{-1}. These results demonstrate that the photo-induced framework alteration occurs in the way to avoid steric crowding between the methyl hydrogens and the azomethine hydrogen and the directed unimolecular motion is not entirely independent from nonbonding interaction with the neighboring chiral molecules. The photo-coloration mechanism in this study is consistent with the previous findings on steric requirements for the photochromism of Schiff bases.[8]

In order to acquire an additional support, each *R*- and *S*-isomer of **1** was incorporated in the crystal lattice cavities formed by chiral deoxycholic acid (DCA).[9] The desired inclusion complex was obtained in 60% yield as pale yellow crystals, which were purified by recrystallization from methanol; the host/guest ratio of the product was determined to be 5 by satisfactory elemental analyses and reasonable intensity ratios of the ^1H NMR peaks. The obtained definite clathrate compounds, [(*R*-**1**)$(DCA)_5$] (mp 169-170 °C) and [(*S*-**1**)$(DCA)_5$] (mp 166-167 °C), were both photosensitive but the rate constants were different each other ($k = 1.3 \times 10^{-2}$ s^{-1} for *R*-**1** and $k = 1.8 \times 10^{-2}$ s^{-1} for *S*-**1**) (Figure 3). In these crystals DCA molecules are not used as chiral reactants but act as host molecules to offer asymmetric rooms or cavities to receive guest molecules.[10] These results clearly show that unimolecular asymmetric motion in the crystals is influenced by the neighboring asymmetric molecular environments.

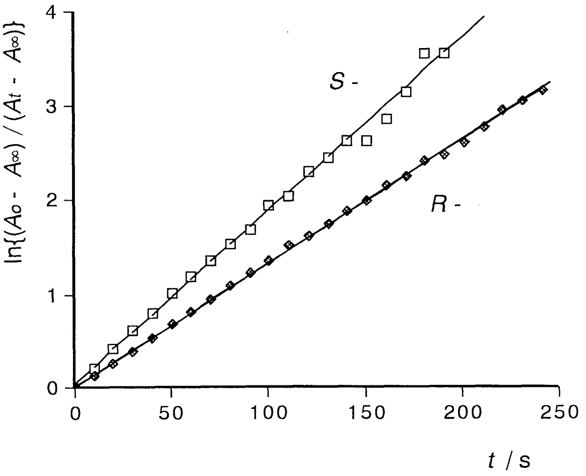

Figure 3. Kinetic plots of optical density decrease for the photochrome derived from [(*R*-**1**)$(DCA)_5$] and [(*S*-**1**)$(DCA)_5$]. The lines show the least-squares linear regression slopes.

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