Photochemistry of Salicylideneaniline Analogue at Low Temperature

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Naphthalene-based salicylideneaniline analogue **2** underwent photochemical cis–trans isomerization in organic glass at low temperature. The lifetime of the photoproduct trans-keto tautomer in glass was similar to that in solution at higher temperature, suggesting the formation of high energy conformer by volume conserving isomerization mechanism.

Salicylideneaniline (SA) and its related compounds are one of typical molecules which undergo excited state intramolecular proton transfer (ESIPT) followed by the deactivation to give cis-keto form ($^1K_{cis}$) and trans-keto ($^1K_{trans}$) form in the ground state. Generally, $^1K_{trans}$ can be observed in transient absorption spectra in microsecond time region. In most cases, $^1K_{trans}$ undergoes thermal trans-to-cis isomerization to give $^1K_{cis}$ followed by very fast re-enolization process (Figure 1).[1,2] The photochemical isomerization pathway of SAs at low temperature has scarcely been reported, since their thermochromic behaviour may interfere the study of the photochemical production of $^1K_{cis}$ and $^1K_{trans}$.

We have recently reported the chromic behaviour of SAs[3] and its naphthyl analogues **1** and **2** (Figure 2)[4] in solution and found that **2** did not exhibit thermochromism, which enables us to detect $^1K_{trans}$ species clearly even at low temperature. Therefore, compound **2** seemed to be a good candidate for the study on the photoisomerization from $^1K_{cis}$ in the excited state to $^1K_{trans}$ in the ground state at low temperature. When only a hydrogen atom is present in the adjacent position of C=C double bond, Hula-twist (HT) mechanisms, proposed by Liu in 1985 at low temperature or congested environment,[5–7] can take place by way of concomitant twisting of the double bond and the adjacent single bond. It is possible that cis–trans photoisomerization of $^1K_{cis}$ in SAs follows a HT pathway at low temperature. The molecules which can take HT mechanism isomerize even in confined environment such as in protein or in organic glass at low temperature, because HT needs much less volume change than that with one bond flip (OBF) mechanism during the isomerization. Here we report the studies on the photochemical isomerization of salicylideneaniline analogues in organic glass at low temperature.

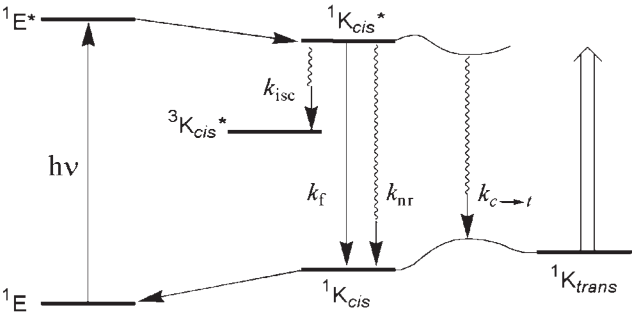

Figure 1. Potential energy diagram for ESIPT followed by deactivation with isomerization from $^1K_{cis}^*$ to $^1K_{trans}$ and reverse tautomerization to ^1E.

1

2

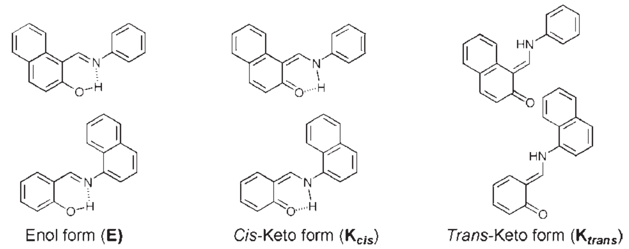

Figure 2. Chemical structure of **1** and **2** and their tautomers.

The transient absorption spectra and the decay curves of **2** (1.5×10^{-4} M) in 2-methyltetrahydrofuran (MTHF) under nitrogen were shown in Figure 3. A peak due to $^1K_{trans}$ was observed at 480 nm at 295 K, of which the intensity (ΔO.D.) was obviously decreased with decreasing temperature, especially between 170 and 110 K, probably because the photochemical isomerization from $^1K_{cis}^*$ to $^1K_{trans}$ is partially suppressed under the melting point of MTHF (mp = 137 K). In organic glass, the transient band for K_{cis} in the excited triplet state ($^3K_{cis}^*$) clearly appeared when the transient spectra were taken in shorter timescale (data not shown). The peak of the transient band for $^3K_{cis}^*$ was observed at 520 nm and therefore, the transient bands for $^3K_{cis}^*$ and for $^1K_{trans}$ overlapped each other at low temperature in organic glass (Figure 3). When the decay curve at 480 nm was monitored in shorter timescale at various temperature, the decrease of the intensity of $^1K_{trans}$ (the longer lived species) and the increase of the intensity of $^3K_{cis}^*$ (the shorter lived species) with decreasing temperature can be observed, suggesting that the intersystem crossing prevails over the isomerization at lower temperature. The lifetime of the shorter lived transient species is 3.3, 5.4, and 36 μs at 170, 140, and 110 K, respectively. However, the band for $^1K_{trans}$ at 480 nm still appeared at 110 K which indicates that the isomerization around the quasi double bond took place even in organic glass. The lifetime of $^1K_{trans}$ increased with decreasing the temperature from 760 μs at 295 K to 1300 μs at 170 K, and remained to be 1300 μs at 140 K and 1200 μs at 110 K (Table 1). Once $^1K_{trans}$ is produced in organic glass at 110 K, the lifetime of $^1K_{trans}$ seems to be much longer than that in solution at 170 K because conformational change from $^1K_{trans}$ to $^1K_{cis}$ should be more difficult in organic glass at lower temperature than in solution at higher temperature. However, the experimental findings that the lifetime of $^1K_{trans}$ at 110 K is almost the same with that at 170 K, suggest that $^1K_{trans}$ in glass at 110 K is less stable than that in solution at 170 K. One of the reasons is that the conformational issue of $^1K_{trans}$ produced in organic glass: One can suppose that a high energy conformer of $^1K_{trans}$ is yielded by isomerization with the volume conserving HT mechanism and the following conforma-

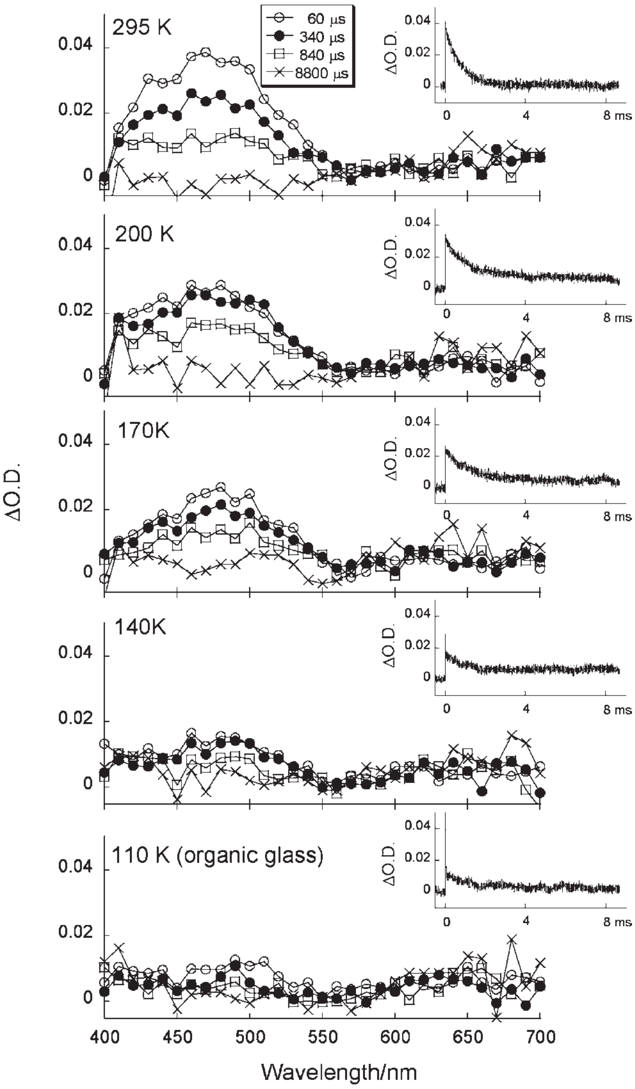

Figure 3. Transient absorption spectra of **2** (1.5×10^{-4} M) on excitation at 308 nm in different temperature in MTHF. Inset: Decay profiles for transient species of **2**, monitored at 480 nm in different temperature in MTHF under nitrogen.

Table 1. The lifetimes of $^1K_{trans}$ and $^3K_{cis}{}^*$ of **2**

T/K	$\tau(K_{trans})/\mu s$	$\tau(^3K_{cis}{}^*)/\mu s$
295	760	
230	810	
200	1200	
170	1300	3.3
140	1300	5.4
110	1200	36

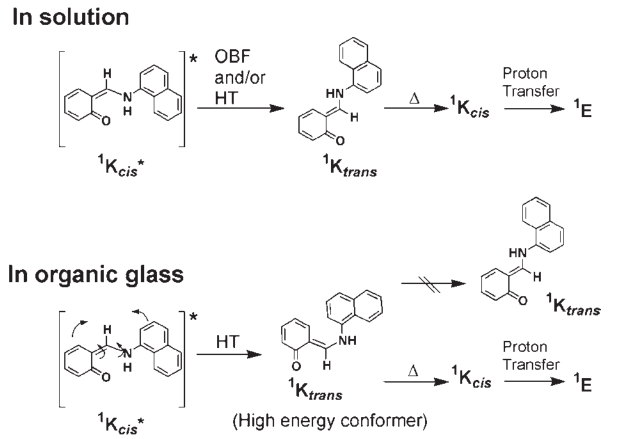

Figure 4. Possible photoisomerization pathways and corresponding products of **2** in solution and in organic glass at low temperature.

tional change to stable conformer of $^1K_{trans}$ is difficult at low temperature (Figure 4). The high energy conformer of $^1K_{trans}$ may easily revert to $^1K_{cis}$ and therefore, one can accidentally observe a similar lifetime at 110 K in glass and at 140–200 K in solution. The photochemical production of the high energy conformer with HT mechanism was suggested in *cis*-1,2-bis-β-naphthylethylene at 77 K.[7]

In conclusion, we have observed isomerization in a naphthyl analogue of salicylideneaniline after ESIPT at low temperature. The lifetime of produced $^1K_{trans}$ in glass at 110 K is similar to that in solution at 140–200 K. Therefore it is suggested that the photochemical isomerization takes place by volume conserving mechanism in confined media to give less stable conformer of $^1K_{trans}$.

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