

Photochromism of Bis Schiff Base *N,N'*-Bis(Salicylidene)-1,2-Cyclohexanediamine

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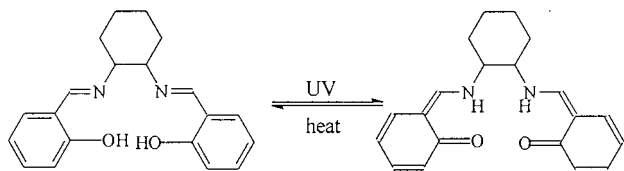
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The photochromism of *N,N'*-bis(salicylidene)-1,2-cyclohexanediamine was studied by time-dependent UV-Vis absorption spectra, fluorescence spectra and INDO/SCI methods. The photo-product was determined to be the two-proton-transferred *cis*-keto form.

A photonic era is approaching and a whole family of functional compounds or material have to be developed to meet the need in the field of high-density information storage, electro- or light-driven information display device, light switching device or nonlinear optical devices. Salicylideneanilines is one of the prospective choices owing to their photo or thermochromism resulting from the intramolecular hydrogen transfer ability.¹⁻³ Although the study on these Schiff bases having been continued for several decades, there is no conclusion on the photochromic mechanism and the structure of the photo-product. We studied the photochromism of *N,N'*-bis(salicylidene)-1,2-cyclohexanediamine (BSC), a barely reported photochromic Schiff base, by time-dependent spectroscopy and some brief results are reported in this letter (Scheme 1).



Scheme 1. Photochromism of BSC.

BSC was synthesized by usual method. The UV-Vis absorption and fluorescence spectra were recorded with Shimadzu UV-3100 recording spectrophotometer and Shimadzu RF-5301 PC spectrofluorophotometer, respectively. All the samples were stored in dark for more than 72 hours before use to diminish the photochromism effected by room light. The concentrations of all the solution are maintained at 5×10^{-5} M. A light source of 125 W xenon lamp with diffraction grating monochromator was used in the photochromism study. For calculation, the geometries of the species possibly involved in the photochromism were optimized firstly by MM2 and further by AM1 method. The electronic transition energy (E , in nm) and corresponding oscillator strength (f) was calculated by INDO / SCI method.

The experimental results show that the UV-Vis spectra of BSC CHCl_3 solution change with irradiation (Figure 1). The original peaks at 253.6 and 318.0 nm decreased and new peaks at 283.5 and 369.2 nm appeared and intensified with irradiation. The new peak centered at 283.5 nm may be attributed to the new generated extended α,β -unsaturated ketones (quinoid

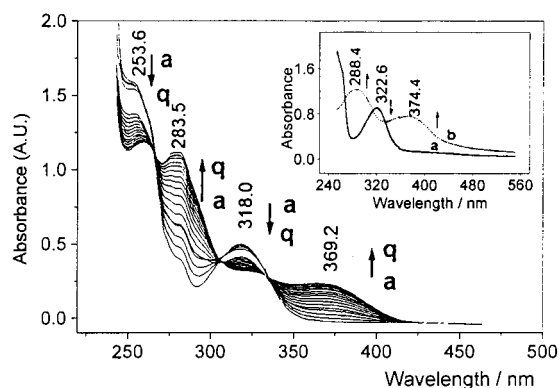


Figure 1. UV-Vis absorption spectral changes for BSC with irradiation (in CHCl_3 , $\lambda_{\text{ex}} = 278$ nm, from a to q each irradiation time 300 s, total: 4800 s. Insert: the spectral changes of CCl_4 solution with irradiation, a: no irradiation; b: irradiation time: 1600 s).

structure, the photo-product, Scheme 1), based upon an empirical equation used in organic chemistry,⁴ by which the absorption of keto-form of BSC ($\pi-\pi^*$ transition only) should be equal to 281 nm. The spectral changes of CCl_4 solution are also studied (briefly shown as the insert spectra in Figure 1) and are found to be similar to that in CHCl_3 solution. The absorption of the BSC CCl_4 solution will be 291 nm by the above equation (agree well with the experimental value 288.4 nm). These results mean that the enol-form of BSC tautomerized to keto-form in photochromism. Another conclusion can be drawn from Figure 1 is that BSC can perform the photochromism more easier in CCl_4 than that in CHCl_3 , based upon the irradiation time needed to effect the spectral changes to the same extent for this two kind of solution.

The time-dependent fluorescence spectra of solid BSC with irradiation are also studied (Figure 2). The original peak at 500 nm decreased and the new peaks at 540 and 563 nm intensified with irradiation. It is found that the major spectral changes occurred within the beginning dozens of seconds of the irradiation, and the photochromism is reversible. A more detailed study shows that the fluorescence spectra converted to the "c" position (insert spectra in Figure 2) after the first excitation (not the original "a" position), then, the photochromism is reversible between the curve c and curve b. The fluorescence intensity difference of curve a and curve c is due to the molecular packing adjustment during the first cycle of photochromism of BSC, by which the distance between BSC molecules was increased in state c than that of state a.⁵

The dynamics of the photochromism of solid BSC studied

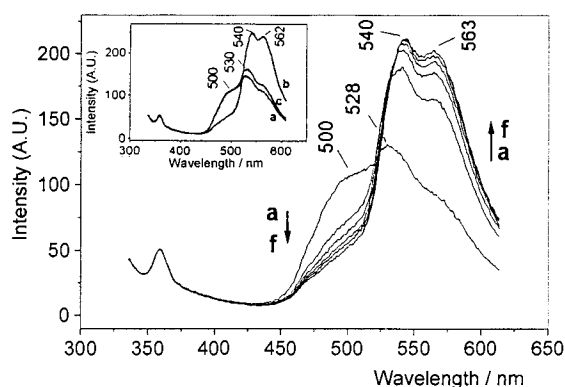


Figure 2. Fluorescence spectral changes for solid BSC with irradiation ($\lambda_{\text{ex}} = 315$ nm, irradiation time: a: 0 s; b: 5 s; c: 10 s; d: 20 s; e: 30 s; f: 60 s. Inset: fluorescence spectra of non-irradiated solid BSC (a), irradiated for 60 s (b) and delay 500 s in dark after irradiation (c) of the first cycle of the photochromism).

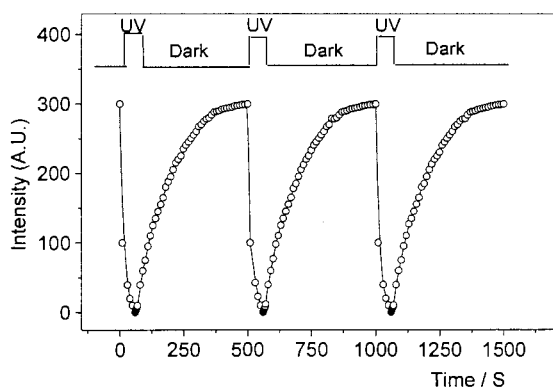


Figure 3. Fluorescence intensity of solid BSC at 500 nm: variations during UV irradiation — thermal decay (store in dark) — UV irradiation cycles. $\lambda_{\text{ex}} = 315$ nm.

by time-dependent fluorescence spectra is summarized in Figure 3. The curve in Figure 3 shows that the decrease of the fluorescence intensity at 500 nm with irradiation will be completed within about 60 seconds. It is needed 500 seconds in

Table 1. Calculated (INDO/SCI) electronic transitions (E , in nm) and oscillator strength (f) of the enol- and the two-proton-transferred *cis*-keto form of BSC. Experimentally (exp.) determined transition energy of BSC in chloroform solution are also included.

Enol-form			Photo-product (<i>cis</i> -keto)		
Calc.		Exp.	Calc.		Exp.
E / nm	f		E / nm	f	
241.0	1.01	237.0	249.0	0.55	-- ^a
249.0	0.10	253.6	294.0	0.73	283.5
273.0	0.16	-- ^a	303.0	0.18	-- ^a
325.0	0.27	319.4	352.0	0.12	369.2

^a For the non-maxima absorption corresponding to the calculated values, please refer to Figure 1.

dark for this decreased peak to revert back to its original intensity. This result shows that the photochromism is reversible.

In order to understand the structure of the photo-product, theoretical chemistry calculations was conducted (only part of the experimental results is listed in Table 1) and the results show that the photo-product as the two-proton-transferred *cis*-keto form.⁶ This conclusion is partly supported by the UV-Vis spectra analysis (*vide supra*). It should be pointed out that the two-proton-transferring is not the necessary result of the photochromism of bis Schiff base. It is only one proton was transferred for some bis Schiff bases.⁷ More detailed results will be released elsewhere and the study about other photochromic Schiff bases is in progress in our laboratory.

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