SHORT PAPER

J. Chem. Research (S), 2000, 416–417

Spectroscopic study on the photochromism of Schiff base *N*-salicylidene-α-methylbenzylamine

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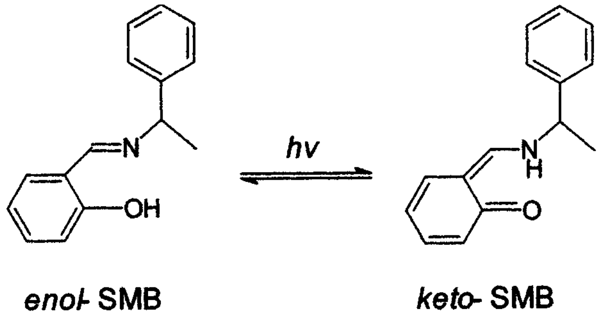
The photochromism of Schiff base *N*-salicylidene-α-methylbenzylamine has been studied by time-dependent UV–Vis absorption and fluorescence spectroscopy.

Photochromic compounds are in the research spotlight for their potential use in high-density information storage systems, information display devices and optical calculation devices, *etc*[1]. Salicylideneanilines are one kind of photochromic compound resulting from excited-state intramolecular proton transfer that have been studied for several decades.[2] Although the information storage device based upon these compounds is said to be able to operate with a single molecule as a storage unit, it is difficult to get a focused beam with a diameter of a few nanometres at this time, so we have to utilise these compounds in an aggregated state. Unfortunately, the photochromism of these compounds was usually restricted in the crystalline state, LB film or in other rigid matrixes.[3,4] We found that *N*-salicylidene-α-methylbenzylamine (SMB), a Schiff base for which the photochromism has not yet been reported, exhibits the photochromism with great speed in the crystalline state. The details are as follows.

The time-dependent UV–Vis absorption spectra of SMB in $CHCl_3$ solution are shown in Fig. 1. The original UV-Vis absorption peaks at 258 nm and 317 nm decreased with irradiation and two new peaks at 288 nm and 372 nm appeared and intensified at the same time. The newly generated peak at 288 nm may be attributed to the keto-form(the photo-product) of SMB[5] (Scheme 1). The isosbestic points in Fig. 1 imply the presence of an equilibrium system in the solution and this is consistent with our knowledge of this kind of Schiff base: the photochromism was caused by excited-state intramolecular proton transfer, no other species participating in this process.



Scheme 1 Photochromism of N-salicylidene-α-methylbenzylamine.

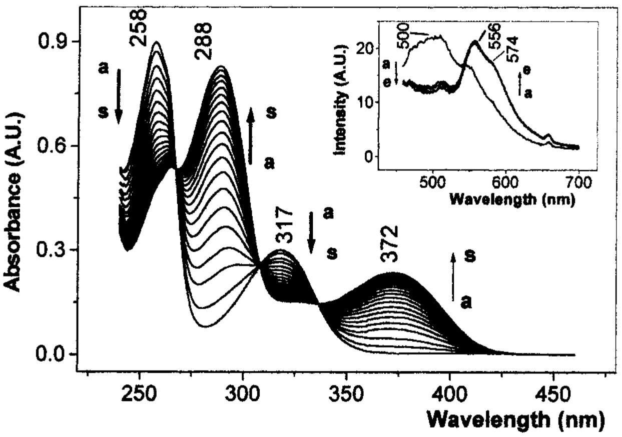


Fig. 1 UV–Vis absorption spectral changes for SMB with irradiation ($CHCl_3$, 5×10^{-5} M. Irradiation wavelength: 280 nm, irradiation time for each curve from a to s: 100 seconds. Insert: fluorescence spectral changes for SMB in crystalline state with irradiation. Excitation wavelength: 438 nm, irradiation time for each curve from a to e: 5 seconds)

The time-dependent fluorescence spectral[6] changes of SMB in $CHCl_3$ show similar changes.

We also studied the time-dependent fluorescence spectra of SMB in the crystalline state (insertion of Fig. 1). The original peak at 500 nm decreased and the fluorescence intensity at 556 nm and 574 nm intensified with irradiation. The spectral changes are so rapid that it is difficult to study them by the usual

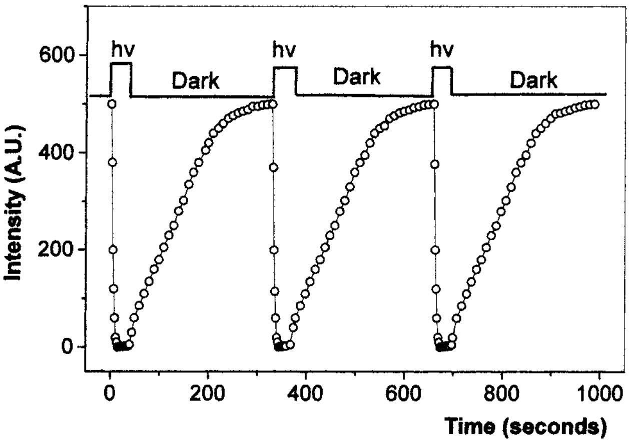


Fig. 2 Fluorescence intensity of crystalline SMB at 500 nm: variation during irradiation-thermal decay (in darkness)-irradiation cycles. Irradiation wavelength: 438 nm.

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[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

time-dependent fluorescence spectroscopy, so we used the “time course” technique to monitor the fluorescence intensity changes at 500 nm during irradiation and thereafter, its thermal decay in darkness (Fig. 2).

The results show that the major fluorescence intensity changes occurred within 5 seconds of irradiation and about 300 seconds was needed for the thermal decay of the irradiated crystalline SMB, and the photochromism is reversible. With AM1 method, the heat of formation of enol- and keto-form (photoproduct) of SMB were determined to be 90.3 kJ mol–$^{-1}$ and 105.8 kJ mol^{-1}, respectively. These calculations may be used to explain the thermal decay of the irradiated SMB, for the photoproduct is thermodynamically unfavorable.

The photochromism of crystalline SMB shows excellent resistance to fatigue. The crystalline SMB can undergo the colouration – bleaching cycles for many times without detectable loss of photochromic activity. This result is due to two reasons. Firstly, the photochromism of SMB does not result from ordered orientation and secondly, SMB molecules are not decomposed by the UV–Vis irradiation. Therefore, there is not fatigue problem for the photochromism of the crystalline SMB, provided that the intensity of the irradiation light is not so strong that the molecules in crystalline SMB are evaporated or decomposed.

The Schiff base SMB will be an information storage medium if its decay process is further restricted by some measures.

Experimental

The UV–Vis absorption and fluorescence spectra were determined with a Shimadzu UV-3100 UV-VIS-NIR recording spectrophotometer and a Shimadzu RF-5301 PC spectrofluorophotometer, respectively. All samples were stored in darkness for more than 24 hours before use to prevent the photo-conversion caused by room light. The $CHCl_3$ solution was degassed with nitrogen before determination of its spectrum.

N-Salicylidene-α-methylbenzylamine (SMB) was synthesized by the condensation of salicylaldehyde with α-methylbenzylamine. The final product was yellow-green crystalline state. M.p. 77–78°C. ^{1}HNMR ($CDCl_3$) δ 1.67 (d, 4H), 4.51 (q, 1H), 7.35 (m, 9H), 8.41 (s, 1H), 13.59 (br, 1H). C, H, N found (%): C, 79.90; H, 6.73; N, 6.20. $C_{15}H_{15}NO$ calculated (%): C, 79.97; H, 6.71; N, 6.22.

This project was supported by the NSFC 29633010.

Received 16 February 2000; accepted 20 August 2000
Paper 00/190

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