Utilization of Crystal Lattice Cavities of Host Deoxycholic Acid for achieving Photochromism of Guest Salicylideneanilines in the Crystal State

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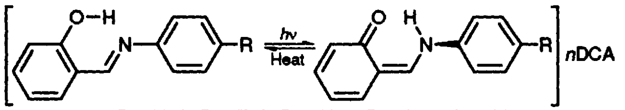
Salicylideneanilines have been easily incorporated in the crystal lattice cavities formed by deoxycholic acid molecules to yield clathrate compounds, which exhibit photochromism irrespective of the photosensitivity of the starting Schiff bases in the crystal state.

Photochromism of solid materials has attracted much attention owing to its scientific interest and technical applications. Salicylideneanilines (SAs) are well-known examples which exhibit either photo- or thermo-chromism in the solid state.[1] Although different mechanisms for the same proton transfer from the hydroxy group to the imine nitrogen have been considered for the photo- and thermo-colouration, the structures of the coloured species are still not established.[1,2] The electronic characteristics of the ring substituents in SAs do not dictate whether the SA crystals exhibit photo- or thermochromism;[3] therefore, the existence of topochemical problems has been suggested for this phenomenon. Recently, we prepared a series of photochromic Schiff bases by the introduction of *tert*-butyl substituents into many non-photochromic SAs;[4] the bulky *tert*-butyl groups were suggested to act as a space-opener, which maintained room for the photoinduced molecular motion of SAs in the crystal lattice. This assumption prompted us to use the crystal lattice cavities of deoxycholic acid (DCA), that is known to form clathrate compounds with a wide variety of organic compounds,[5] to provide the required space for the photoisomerization of the guest SA molecules.

The pure SAs (type **a** compounds) used were prepared by condensation of salicylaldehyde and *p*-substituted anilines (Scheme 1). Synthesis of a DCA–SA complex (type **b** compound) was accomplished by mixing each SA (0.5 mmol) with DCA (3 mmol) in hot methanol (25 ml) for 15 min. Evaporation of the solvent gave the desired complex generally ≥80% yield as pale-yellow crystals, which were recrystallized from methanol. The products exhibited sharp melting points (°C) (**1b**: 182–183, **2b**: 190–192, **3b**: 191–192, **4b**: 192–193, **5b**: 193–194) and the structures were determined to be definite complexes by satisfactory elemental analyses and spectral data. A host : guest molar ratio (*n*), which was monitored by intensity ratios of their ^{1}H NMR peaks, was not affected by the recrystallization. The ratio varied from 4 to 5, depending on the size of ring substituents in the guests.



1; R = H, 2; R = F, 3; R = Cl, 4; R = Br, 5; R = OMe

Scheme 1

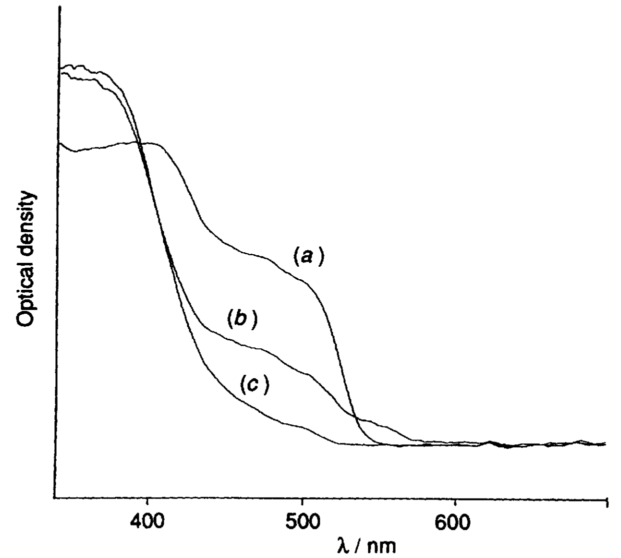


Fig. 1 Reflectance spectra of (*a*) **3a**, (*c*) **3b** and (*b*) photocoloured species (**3b** + *hv*)

When R = F, Cl or OMe, the pure crystalline SA (**2a**, **3a** or **5a**) is not photosensitive; however, the yellow colour of all the clathrate compounds changed to an orange or reddish colour on 365 nm light irradiation (Fig. 1) but returned to the starting yellow colour after placing in the dark. The thermal bleaching reaction of the resultant photochrome was then followed by reflectance spectrophotometry at 30 °C by measuring the optical density at a proper wavelength (λ) where the maximum change of the optical density was observed at regular time intervals. The absorption decrease data were treated with a standard integrated expression for a first-order process using linear least-squares analysis to give two consecutive rate constants (k_1 and k_2)[4] for every photochromic compound (Table 1). The definite wavelengths λ and rate constants for salicylideneaniline **1a** and the bromo derivative **4a** are considerably different from those of the corresponding DCA complexes **1b** and **4b**, respectively. These results are good evidence that the photoisomerization of SA takes place within the channel formed by DCA. In other words, the channel-type cavity is of sufficient size to accommodate SA, and the degree of molecular motion allowed for the guest to change its conformation must be limited within the cavity. These findings are consistent with our previous proposal[4] that the bulky *tert*-butyl substituents in photochromic SAs act as a spacer in the crystal lattice as well as in the mechanism of the photocolouration process, which involves a molecular framework variation owing to a hybrid alteration at the protonated nitrogen atom from sp^2 to sp^3 to generate an *ortho*-quinoid form (Scheme 1).

Regio- and stereo-specific reactions initiated by photohydrogen abstraction by ketones inside the channel of DCA have attracted considerable attention.[6] Since included species are normally considered to be present as single molecules within the cavities, topochemical relations among neighbouring molecules must be simplified. The detailed discussion on

Table 1 Rate constants *k* of thermal fading of photocoloured species measured at optimum wavelength λ at 30 °C

Compound	R	*n*(DCA)	λ/nm	k_1/s^{-1}	k_2/s^{-1}
1a	H	0	511	1.4×10^{-3}	6.0×10^{-5}
1b	H	4	482	1.4×10^{-3}	9.3×10^{-5}
2b	F	4	474	1.0×10^{-3}	2.6×10^{-5}
3b	Cl	4	480	4.3×10^{-4}	2.6×10^{-5}
4a	Br	0	530	6.1×10^{-3}	3.1×10^{-3}
4b	Br	4	476	1.2×10^{-3}	5.7×10^{-5}
5b	OMe	5	486	1.1×10^{-2}	2.3×10^{-4}

the kinetic data of our system will be reported in due course. The DCA molecules in this study may be replaced by other proper host substances.[7]

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