Photochromism of a spirooxazine in the single crystalline phase†

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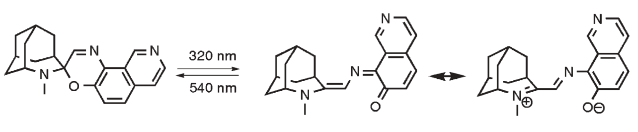
The single crystals of a closed form spirooxazine spiro[azahomoadamantane-isoquinolinoxazine] were found for the first time to undergo photocoloration processes consistent with photochromism in the single crystalline phase.

Photochromic materials have potential applications in destructive and non-destructive optical data storage that arise from the dramatic change in absorption spectra associated with photoisomerization processes.[1–3] The optically-driven changes in electronic structure associated with photochromism can be coupled with emission processes,[4] optical rotation,[5] or magnetic properties,[6] giving rise to non-destructive read–write materials. Challenges associated with incorporating photochromic materials into optical storage technologies arise from creating thermally irreversible photochromic systems that are capable of photoisomerization in the solid state or polymer films. While several classes of photochromic compounds have been reported, compounds that exhibit photochromic activity in the single crystalline phase are extremely rare.[7–9] Diarylethenes have been shown to exhibit photochemically reversible isomerization in the single crystalline phase with very small changes in volume dictated by the "reaction cavity".[9] The investigation of solid state photochemical systems which undergo significant volume changes upon photoisomerization is therefore of great interest toward understanding the structural and energetic requirements for solid-state reactivity.

Spirooxazines and spiropyrans form a class of photochromes that undergo reversible photoinduced isomerization in solution from a colorless closed spirooxazine form (SO) with $\lambda_{max} \sim 350$ nm to a colored photomerocyanine form (PMC) (Scheme 1).[10–12] Delocalization of the π system in the PMC form leads to a bathochromic shift in the absorption spectra to $\lambda_{max} \sim 600$ nm. Investigations into spirooxazine photochromism in confined environments have led to the prediction that spiroooxazines are not likely to undergo photoisomerization in severely constrained environments due to the large volume changes associated with isomerization.[13,14] Herein we report evidence to support the photochemically reversible, thermally irreversible isomerization of a spirooxazine in the single crystalline phase obtained from spiro[azahomoadamantane-isoquinolinoxazine] (**1**).



Scheme 1 Photochromism of **1**.

† Electronic supplementary information (ESI) available: X-ray crystallographic data and spectroscopy of compound **1**. See http://www.rsc.org/suppdata/cc/b4/b417026a/

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Compound **1** was synthesized as an equilibrium mixture of **1a** and **1b** by base-promoted condensation of 7-hydroxy-8-nitrosoisoquinoline with 5-methyl-4-azahomoadamantyl-4-enium iodide[15] in methylene chloride to give a purple microcrystalline solid. The thermal equilibrium state in solution (K_T = [PMC]/[SO]) lies toward the open form ($K_T = 0.17$) in acetonitrile at 298 K relative to parent spirooxazines in which K_T is typically 0.001.[16,17] Steady-state UV irradiation of **1** in solution (280 nm $< \lambda <$ 400 nm) at 298 K leads to an increase in absorption at $\lambda_{max} = 564$ nm, consistent with ring opening to the photomerocyanine form (**1b**) (Fig. 1). The colorability of **1**, defined here as the difference between the photostationary state and the thermal equilibrium state ($\Delta K = K_{UV} - K_T = 9.0$), is extremely large relative to that of the parent spirooxazines ($\Delta K \sim 0.02$)[18] in CH_3CN at 298 K. Thermal relaxation to the equilibrium state occurs with a rate constant three orders of magnitude slower ($k_T = 3.34 \times 10^{-4}$ s^{-1}) than that of the parent spirooxazine spiro[indoline-naphthoxazine] ($k_T = 5.02 \times 10^{-1}$ s^{-1})[19] in CH_3CN at 298 K, consistent with a stabilization of the PMC form. The solution photochemical and thermal behavior of **1a** is therefore characteristic of the larger family of spirooxazines and spiropyrans with a significant enhancement in the colorability and stabilization of the photomerocyanine form.

The effect of constrained media on the photoisomerization and thermal relaxation behavior of **1** was investigated in both polymer films and the microcrystalline state. A polystyrene thin film of **1** (2.1% w/w) cast from a dichloromethane solution exhibited intense coloration upon irradiation with an absorption band at $\lambda_{max} = 578$ nm, a bathochromic shift of 14 nm relative to **1** in

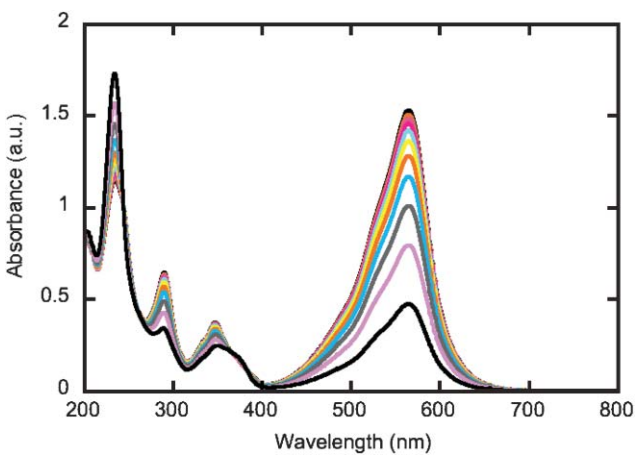

Fig. 1 Time-resolved spectra of steady state UV irradiation (λ_{exc} 250–400 nm) of **1** in acetonitrile (4×10^{-5} M at 298 K).

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acetonitrile. In addition, a shoulder appeared on the blue edge of the band due to either PMC aggregation (H aggregate) or formation of an alternative isomeric PMC form, both of which have been proposed to form in polymer films.[10] Similar to other spirooxazines, the thermal back reaction of **1** in polystyrene was fit to a biexponential function with rate constants $k_1 = 2.28 \times 10^{-4}$ s^{-1} and $k_2 = 2.15 \times 10^{-3}$ s^{-1} at 298 K indicating multiple pathways for reversion to the SO form. In addition, irradiation of **1** in the microcrystalline state leads to coloration followed by thermal reversion on the order of hours upon removal of the light source. Thus, the photoisomerization and thermal relaxation behavior of **1** is consistent with other spirooxazines in partially constrained environments.[20–22]

X-ray quality single crystals of **1a** were obtained by recrystallization from hexane to give colorless monoclinic $P2_1/c$ prisms.[23] The closed form (SO) crystallizes with four molecules in the unit cell in pairs of head-to-tail dimers that sit orthogonal to each other in the crystal lattice (Fig. 2). Intermolecular π–π contacts within each dimer are weak, with an intermolecular mean plane distance of 3.818 Å. Analysis of bond lengths and angles reveals little deviation from typical bond lengths and angles of other spirooxazines.[15,24–26]

Steady state UV irradiation with an Hg-arc lamp of colorless single crystals leads to coloration with no loss of transparency or crystalline order, as determined by X-ray diffraction experiments. In the absence of light at 298 K, the coloration of the single crystal does not decay, indicating that the stability of the photomerocyanine form in the single crystalline phase is extremely high. On the other hand, pulverized single crystals decolorize within hours, indicating that while in the microcrystalline state thermal reversion to the closed form occurs rapidly, consistent with other studies of spirooxazine photoisomerization in the microcrystalline state.[13,20,21] The increased stability of the photomerocyanine form in the crystalline state suggests that photoisomerization is occurring in the single crystalline phase and is not simply a surface effect.[27] Steady state visible irradiation ($\lambda_{ex} > 520$ nm) of photocolored single crystals leads to reversion and rapid decoloration in seconds to regenerate colorless crystals of **1a** ($k_{dec} \sim 10^{-1}$ s^{-1}). The cycle of photoisomerization is photochemically reversible, thermally irreversible, and fatigue resistant, as evidenced by numerous cycles of irradiation (> 10 cycles).

In order to determine the extent of alignment of the photocolored species in the crystalline state, a single crystal of **1a** was irradiated with the UV light from a Kr–Ar mixed-gas ion laser for two hours (λ_{ex} = 333–363 nm) and its absorption band measured as a function of the direction of polarized light before and after UV irradiation. The single crystal was rotated with respect to the polarizer until complete extinction was observed at 45° relative to [100] in (011). This direction was defined as 0° with respect to the polarizer. A very slight change in the intensity of the PMC band was detected as the crystal was rotated with respect to the direction of polarized light (Fig. 3). Thus, polarized absorption spectra of the spirooxazine crystal before and after UV irradiation suggest little anisotropy at polarizer angles of 0° and 90°. This could in principle be due either to a photocolored disordered phase or to head-to-tail packing of **1** in the crystal lattice. The direction of the spirooxazine molecular dipole is not expected to change appreciably in direction after photoisomerization, independent of the conformation of the PMC form. The latter effect would then lead to a cancelling of molecular dipoles and little difference in intensity with polarizer angle, as is observed. Similar results were obtained for all faces of the crystal.

In an attempt to determine the structure of the photogenerated form, a full X-ray data set of **1** was obtained before and after irradiation. The difference Fourier electron density map, defined as the electron density of an irradiated (UV light) single crystal of **1** minus the electron density of a non-irradiated single crystal of **1**, was generated and visualized with the Maxus program (Fig. 4). The electron density difference map exhibits small changes in the vicinity of the azahomoadamantyl group, with little change in other regions of the molecule. This suggests that (i) either the photogenerated form is disordered, (ii) little change in structure occurs upon photoisomerization, or (iii) that the percentage of molecules undergoing conversion under these conditions is not large enough to allow full or partial structure determination. DSC

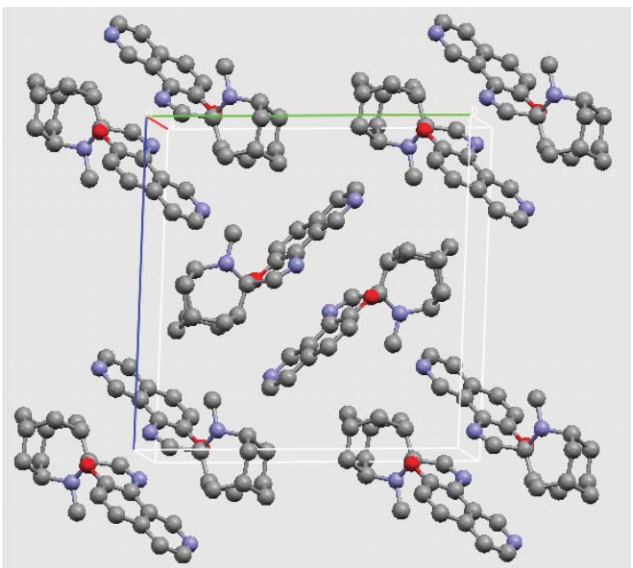

Fig. 2 Packing diagram of spirooxazine **1** as viewed down the *a*-axis.

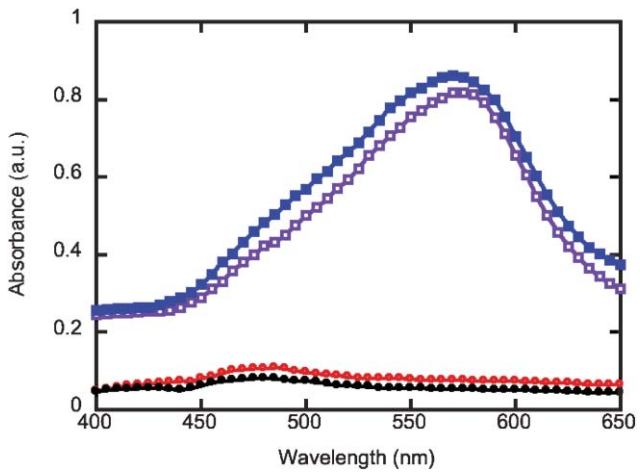

Fig. 3 Polarized absorption spectra of spirooxazine **1** before UV irradiation with the polarizer at 0° (red circles) and 90° (black circles), and after irradiation with the polarizer at 0° (purple squares) and 90° (blue squares) relative to the [011] plane.

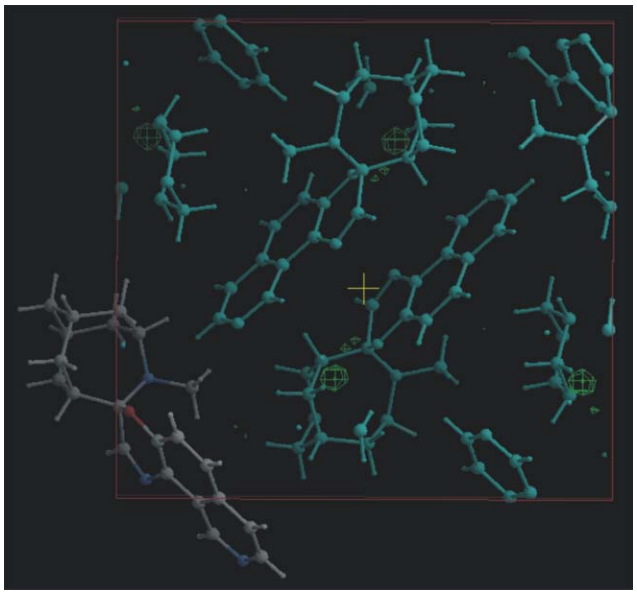

Fig. 4 Fourier electron density difference map showing the electron density of an irradiated (UV light) single crystal of **1a** minus the electron density of a non-irradiated single crystal of **1a** as viewed down the *a*-axis.

experiments on irradiated crystals of **1a** support the latter interpretation. The high optical density of the photocolored form ($\varepsilon \sim 30{,}000$) may in fact preclude high conversion efficiency after initial irradiation, suggesting the need for two-photon conversion experiments.

As topochemical reactions are diffusionless, sufficient space in the "reaction cavity" and sufficient flexibility in the overall crystal packing are required for spatial reorganization to occur. It is possible that in this case, the azahomoadamantyl group provides sufficient free space in the crystal lattice to allow single crystalline phase photoisomerization. Consistent with this is the observation that steady state visible irradiation of single crystals of indolyl analog, spiro[indoline-isoquinolinoxazine], does not lead to photocoloration. Both spirooxazines, however, undergo photoisomerization in the microcrystalline state and in KBr pellets with comparable rates, suggesting that microcrystalline state photoisomerization does not necessarily correlate with single crystalline behavior.

In conclusion, we have synthesized an azahomoadamantyl spirooxazine that undergoes photochemically reversible and thermally irreversible coloration in the single crystalline phase. While investigations of thermal and light-induced isomerization processes for **1** reveal behavior typical of spirooxazines in solution, the thermal reversion in the single crystal is extraordinarily slow, consistent with generation of a PMC form in a constrained environment. Reversible photocoloration in the single crystalline phase was observed only from the closed SO form of **1**, and not from single crystals of other spirooxazines. Future studies will involve structural analysis of the photocolored form generated in the single crystalline phase through two-photon processes and X-ray crystallography.

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