

Photochromism of chromene crystals; a new property of old chromenes†

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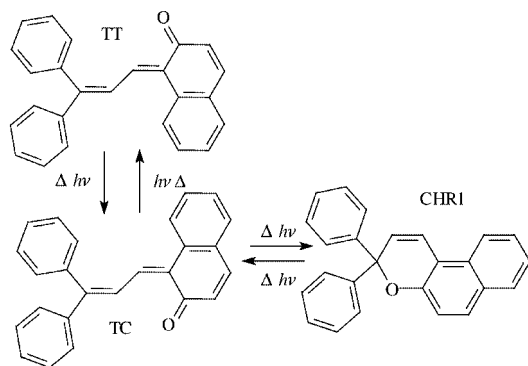
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Of the four chromene compounds; 3,3-diphenyl-5,10a-dihydro-3H-benzo[f]chromene (CHR1), 6-methoxy-2,2-diphenyl-2H-benzo[h]chromene (CHR2), 2,2-diphenyl-2H-benzo[h]chromene (CHR3) and 6,7-dimethoxy-2,2-diphenyl-2H-chromene (CHR4), CHR2–4 exhibited crystalline state photochromism.

Solution and dispersed state photochromism are well known phenomena, however there are relatively fewer examples of crystalline state photochromism.^{1–5} Photochromic crystals are especially unusual, although not unknown,^{3–5} when the photochromism involves large structural changes such as *cis–trans* isomerisation. This is due to the small free volume in a crystal lattice. In the case of spiropyrans and spirooxazines such crystalline photochromism, involving a minimum of two isomerisation steps, has been reported using femtosecond laser pulses where there is a laser fluence threshold that must be reached before any colouration reaction is observed.⁵ Prior to our work, photochromic chromene (CHR) crystals, having a similar photochemistry to the spirooxazines, had not been reported.⁶ The CHR reaction mechanism in solution^{7,8} is shown in Scheme 1 exemplified for CHR1. As can be seen the reaction is complex involving several isomerisation steps.

CHR1–4 were synthesised by Great Lakes Technology using the standard synthetic routes.^{6,9} UV/VIS spectra were measured using a Hewlett Packard HP8452 diode array spectrophotometer in reflectance mode. Macroscopic UV irradiation was carried out using a nitrogen laser at 337 nm (10 nanosecond pulse duration, repetition rate 100 Hz, 0.1 mW pulse^{−1} cm^{−2}) or a 100 W Hg lamp emitting in the visible and UV. HPLC was used to assign CHR2 photochromic reaction products with a reverse phase C-18 column on an HP 1090 chromatograph with a 1:9 ratio of water to acetonitrile at a flow rate of 1 mL min^{−1}



Scheme 1

† Microscopic colour images showing photo-colouration and bleaching are available as electronic supplementary information (ESI). Microscopic images were obtained with a Nikon Eclipse E800 Fluorescence microscope using the microscope's Hg lamp excitation source to photo-convert the crystals. See <http://www.rsc.org/suppdata/cc/b0/b003480k/>

with diode array UV/VIS detection. X-Ray diffraction data¹⁰ were collected before and after 1 h of irradiation of a single CHR2 crystal (0.5 × 0.5 × 0.4 mm) using the nitrogen laser.

After UV irradiation (nitrogen laser or CW source) pale yellow CHR2 crystals turned deep orange. The orange colour was partially photobleachable with visible light, but did not thermally bleach. This is shown in Fig. 1. The non-permanent component of the CHR2 colouration could be cycled between photocoloured and photobleached states.

For CHR2 it is possible to isolate the TT isomer from the TC isomer since it can crystallise in a mixed lattice with the CHR2 form.¹² From solutions of such mixed crystals HPLC retention times were established for the CHR2-form (5.45 min) and the TT isomer (6.55 min). From HPLC on mixtures of the TT, TC and CHR2-form, produced photochemically in acetonitrile, the TC isomer retention time (8.31 min) was also found. The λ_{max} of the TT isomer was blue shifted by only 10 nm with respect to that of the TC isomer. Retention times from HPLC carried out on dissolved photocoloured crystals (nitrogen laser 1 h) showed that the crystals contained a mixture of mainly the CHR2 form, but with TT and TC isomers also present. The integrated absorption/elution time profiles of TT and TC were approximately equal, implying similar fractional conversion to TT and TC if we assume similar extinction coefficients. The overall fraction of photoconversion to TT and TC suggested from this HPLC and separately determined by ¹H NMR was <1% even after prolonged irradiation (nitrogen laser 1 h). Also from X-ray analysis of a single CHR2 crystal we found no detectable increase in the bulk lattice disorder even after prolonged irradiation (nitrogen laser 1 h). We must therefore conclude that under these conditions photoisomerisation is probably not a feature of every lattice site, although this may be because conversion is concentrated at the surfaces by consideration of Beers Law.

Using HPLC on photoconverted and subsequently photobleached CHR2 we found that photobleaching reduces the

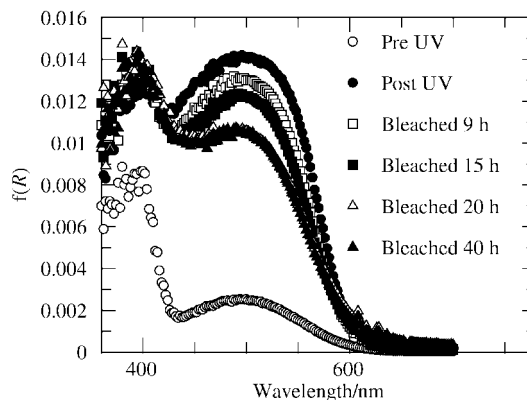


Fig. 1 Diffuse reflectance spectra (Kubelka Munk)¹¹ of CHR2 crystals before and after UV irradiation and during and after photobleaching.

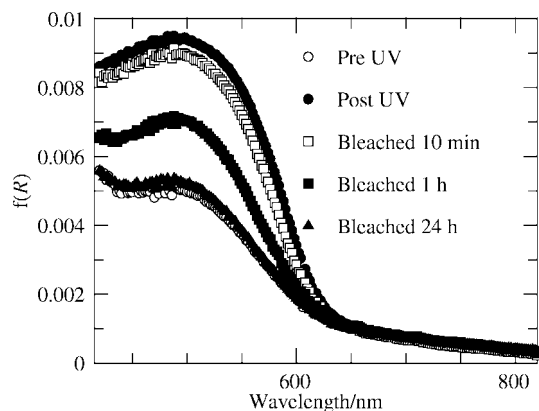


Fig. 2 Diffuse reflectance spectra (Kubelka Munk)¹¹ of CHR3 crystals before and after UV irradiation and during and after photobleaching. For microscopic colour images showing photo-colouration and bleaching see <http://www.rsc.org/suppdata/cc/b0/b003480k/>

proportion of the TC isomer relative to the TT form. The TT isomer is persistent both photochemically and thermally. Conversely CHR3 and CHR4 crystals photo-coloured with UV light could be almost fully photo and thermally bleached back to the CHR-form. This is shown in Figs. 2 and 3.

All of the compounds CHR2–4 could be photoconverted with relatively weak CW UV irradiation sources. For example, photo-colouration was even observed after irradiating the samples with the excitation beam from a standard fluorimeter (Shimadzu RF5300PPC 350 nm). From this we conclude that this colouration reaction is activated by a single photon non-cooperative (no simultaneous excitation of adjacent sites required⁵) solid-state reaction. We also note that CHR1 did not exhibit any photochromism in its the crystalline state.

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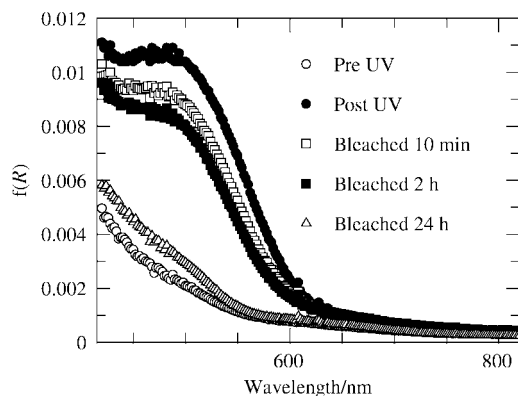


Fig. 3 Diffuse reflectance spectra (Kubelka Munk)¹¹ of CHR4 crystals before and after UV irradiation and during and after photobleaching.

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