

## Facile Irreversible Thermochromism of a Near-infrared Azamethine Chromophore

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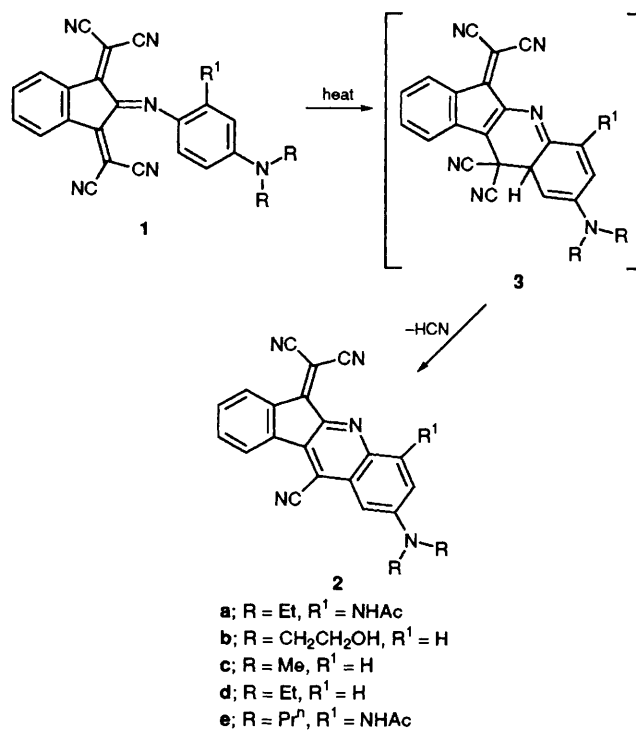
The near-infrared azamethine chromophoric system **1** shows a pronounced colour change on heating, which is due to a facile disrotary electrocyclic reaction followed by a loss of hydrogen cyanide, giving the intense blue chromophore **2**.

Intrinsically thermochromic molecules (*i.e.* chromophores which are chemically altered on heating without the need for an external reagent, and which change colour in the process) are rare.<sup>1</sup> Commercial thermochromic materials thus depend either on liquid crystals or pH indicator dyes which respond to a thermally induced pH change of the environment. Intrinsically thermochromic near-infrared (IR) dyes appear to be unknown and are of interest because they should be capable of thermal activation by a diode laser, and give a colourless to coloured change that could be of use in imaging and data storage. We now describe a thermochromic near-IR chromophore of this type.

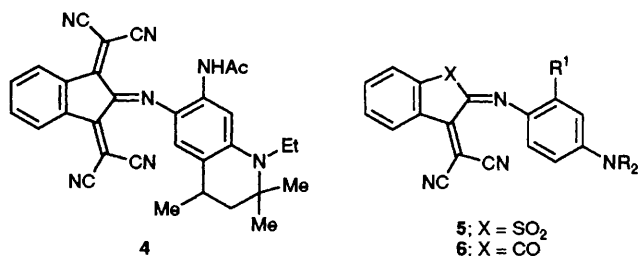
The azamethine dye **1a**<sup>2</sup> has an intense absorption band in the near-IR ( $\lambda_{\max}$  794 nm,  $\epsilon_{\max}$  39 800 dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> in CH<sub>2</sub>Cl<sub>2</sub>), giving near colourless solutions. When heated in *p*-xylene at 135 °C for 1 h, the very pale-green solution turned deep-blue, and on cooling dark crystals of the product **2a** deposited. The solid, obtained in 80% yield, showed  $\lambda_{\max}$  629 nm in CH<sub>2</sub>Cl<sub>2</sub>, and the structure was confirmed by IR, elemental analysis and mass spectrometry (C<sub>26</sub>H<sub>20</sub>N<sub>6</sub>O;  $m/z$  = 432).

The reaction may be presumed to follow the pathway shown in Scheme 1. Thus, a thermally allowed disrotary electrocyclic reaction of the phenylazabutadiene residue of **1a** takes place, giving the cyclised product **3a**, which then loses a molecule of HCN to give the stable conjugated chromophore **2a**. Analogous thermal electrocyclic reactions of phenylbutadienes<sup>3</sup> and phenylazabutadienes<sup>4</sup> are known, but these generally require temperatures of the order of 450 °C in order to proceed. The present case is thus exceptional in its facility, and the relatively low temperatures at which the thermochromic reaction occurs ensures that thermal degradation of the chromophore **2a** does not occur simultaneously.

The generality of the thermochromic process was demonstrated with compounds **1b–e**, all of which reacted smoothly to give **2b–e** respectively on heating in various solvents. The



Scheme 1



products were all blue in colour [ $\lambda_{\text{max}}$  (CH<sub>2</sub>Cl<sub>2</sub>): **2a** 629; **2c** 586; **2d** 595; **2e** 620 nm;  $\lambda_{\text{max}}$  (THF) **2b** 564 nm]. The rate of reaction was strongly dependent on solvent polarity, and for example was particularly rapid in dimethylformamide (DMF). This is demonstrated in Fig. 1 for dye **1e**, reaction occurring readily at room temperature in this solvent. Reactions also took place readily when the dyes were dissolved in cellulose acetate film. However, the derivative **4** was exceptional, and no thermochromic reaction was observed even on heating at 190 °C for 1 h. This can be understood in terms of the steric crowding arising from the 4-methyl group of the tetrahydroquinoline moiety in **4**, which would inhibit cyclisation to a structure of the type **3**.

It appears that both dicyanovinyl residues in dyes **1** are essential for the reaction to proceed. Thus, analogous dye chromophores **5** and **6** showed no corresponding colour change on heating, apart from slow thermal degradation.

The thermochromic process was investigated by thermal analysis for the dye **1b**. This had  $\lambda_{\text{max}}$  745 nm in THF and was converted quantitatively to **2b** on heating in cyclopentanone at 130 °C for 30 min. Differential scanning calorimetry showed that in the solid state **1b** was stable up to 200 °C, but at 201 °C a large exotherm occurred ( $\Delta H = 185 \text{ J g}^{-1}$ ), which was absent on reheating. Thermogravimetric analysis of **1b** showed a

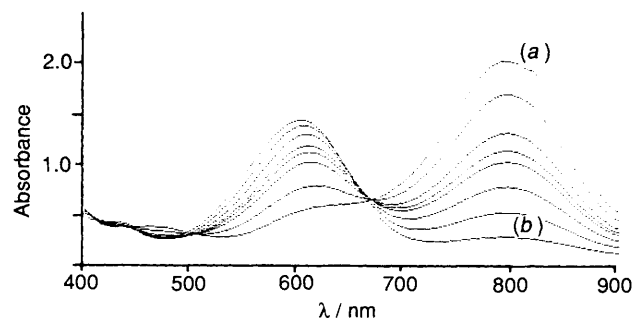


Fig. 1 Conversion of **1e** into **2e** in DMF at 20 °C: (a) zero time; (b) after 60 min

small weight loss at 201 °C corresponding to loss of a molecule of hydrogen cyanide.

Several of the dyes of type **1** absorb at sufficiently long wavelengths to absorb diode laser radiation efficiently. Thus, there is the possibility of using such materials for thermal recording, using a laser as the heat source. Information would then be registered as a coloured image against a colourless or near-colourless background, and the process would be irreversible (see Fig. 1).

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## References

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