

Intramolecular [4 + 4] Photocycloaddition Reactions of the Photochromic Compounds, 3,4-Bis(9-anthrylmethylene)tetrahydrofuran-2,5-dione and its 5-Dicyanomethylene Derivative

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The red and the purple photochromic title compounds undergo intramolecular [4 + 4] photocycloaddition reactions on irradiation with white light to form pale yellow and colourless adducts, respectively, which undergo the reverse reactions thermally or on exposure to ultraviolet light.

Fatigue-resistant thermally stable photochromic fulgides owe their photochromic properties to reversible photochemical electrocyclic reactions.¹ We report on a fulgide **2a** and its related dicyanomethylene derivative **2b** which show photochromism due to intramolecular [4 + 4] cycloaddition reactions and the reverse processes. The reversible photodimerisation of anthracene² and the intramolecular [4 + 4] photocycloaddition reaction of 9-anthroic anhydride³ do not cause major colour changes.

Stobbe condensation of 9-anthrylaldehyde with dimethyl succinate in toluene, in the presence of potassium *tert*-butoxide, followed by cyclisation of the resulting bis(9-anthrylmethylene)succinic diacids by treatment with acetyl chloride, gave a mixture of fulgides from which *E,E*-3,4-bis(9-anthrylmethylene)tetrahydrofuran-2,5-dione **2a** was obtained as red needles, mp > 300 °C (5% yield) after fractional recrystallisation from dichloromethane–toluene. Its stereochemistry was assigned from its NMR spectrum which showed a singlet at δ 8.9 due to the two olefinic hydrogens deshielded by the carbonyl groups, and a simple pattern of highly shielded aromatic signals due to overlapping anthryl groups.

Reaction of the mixture of fulgides with malononitrile and diethylamine in tetrahydrofuran⁴ gave the salt **4**, which was filtered off, dissolved in dichloromethane and treated with acetyl chloride, giving 3*E*,4*Z*-3,4-bis(9-anthrylmethylene)-5-dicyanomethylenetetrahydrofuran-2-one **1b** as purple rhomboids, mp 284–286 °C (40% yield). Its stereochemistry follows from its NMR spectrum which showed a singlet at δ 9.50 due to the olefinic hydrogen deshielded by the dicyanomethylene group, a singlet at δ 7.24 due to the olefinic hydrogen shielded by an anthryl group, and the multiplicity of aromatic signals expected for the non-symmetrical compound. The severely overcrowded helical *E,E*-fulgide **2a** in toluene (λ_{\max} 489 nm ϵ 7

100 dm³ mol⁻¹ cm⁻¹) underwent a facile intramolecular [4 + 4] cycloaddition reaction on exposure to white light to give the pale yellow adduct **3a**. The spectrum of fulgide **2a** (1×10^{-4} mol dm⁻³ solution in toluene) before and after irradiation with white light is shown in Fig. 1. At ambient temperatures in the dark or on irradiation with ultraviolet light, the reverse colour change occurred but the product was mainly the *E,Z*-fulgide **1a**, as established by NMR studies. On exposure to white light, it isomerised to the *E,E*-fulgide **2a** which reformed the photoadduct **3a**. The purple *Z,E*-dicyanomethylene compound **1b** in toluene (λ_{\max} 521 nm ϵ 8 400 dm³ mol⁻¹ cm⁻¹) formed the colourless adduct **3b** on irradiation with white light, presumably by *Z*–*E* isomerisation followed by the [4 + 4] photocycloaddition reaction of the resulting *E,E*-isomer **2b**. The purple colour was restored on irradiation (366 nm) of the solution or on heating the solution to boiling (110 °C). The colourless adduct **3b** was stable at ambient temperatures in the dark. Its NMR spectrum precluded the possibility that an intermolecular cycloaddition reaction had occurred. The spectra of the dicyanomethylene compound **1b** and photoadduct **3b** (1×10^{-4}

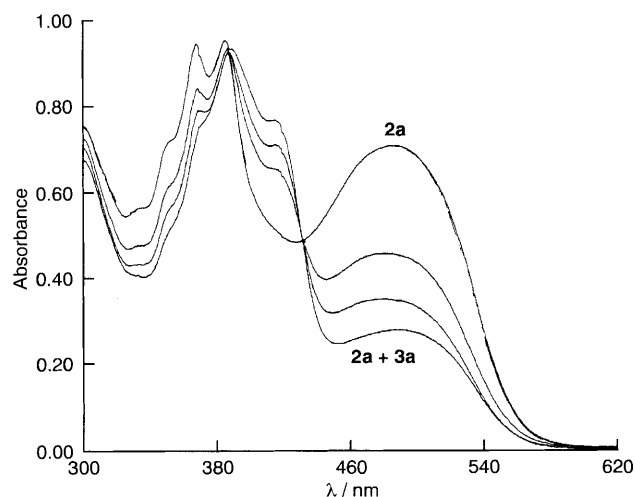
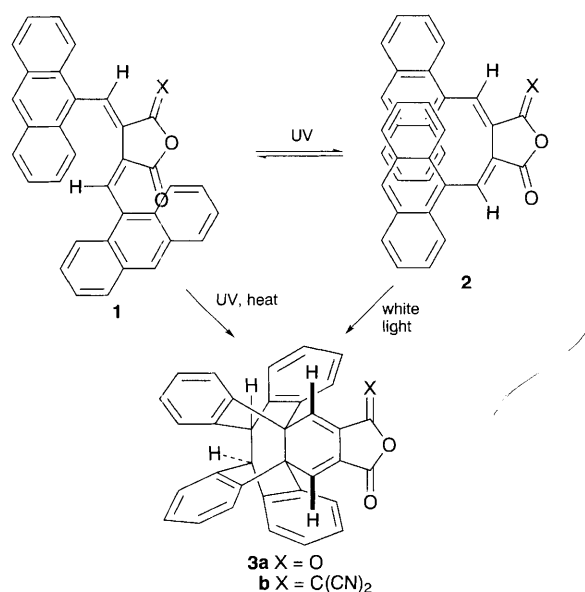
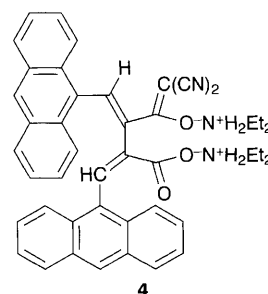


Fig. 1 The spectrum of fulgide **2a** (1×10^{-4} mol dm⁻³ solution in toluene) before and after irradiation with white light

mol dm⁻³ solution in toluene) are shown in Fig. 2. On irradiation (366 nm), *E,E*-fulgide **2a** and *E,Z*-dicyanomethylene derivative **1b** in toluene underwent geometrical isomerisation only. Satisfactory combustion analyses were obtained. NMR studies were carried out on a Bruker, W. M. 360 MHz NMR

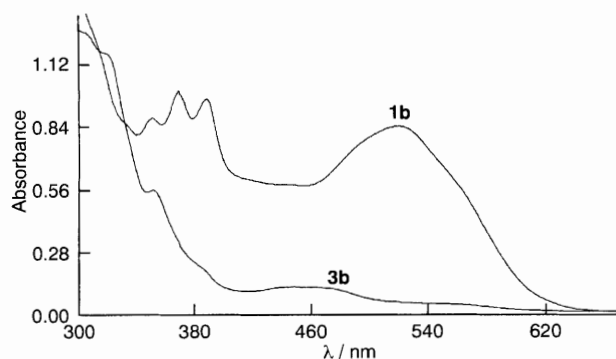


Fig. 2 The spectra of the dicyanomethylene compound **1b** and photoadduct **3b** (1×10^{-4} mol dm⁻³ solution in toluene)

spectrometer. The thermally stable photochromic compound **1b** may be suitable for optical recording.

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