A New Class of Photochromic Compounds exemplified by *E*-5-Dicyanomethylene-4-(dialkyl and dicycloalkyl)methylene[1-(2,5-methyl-3-furyl) and (2-methyl-5-phenyl-3-thienyl)ethylidene]tetrahydrofuran-2-ones

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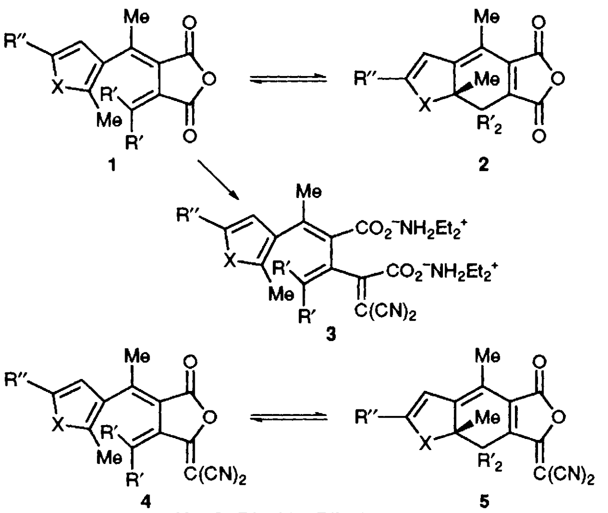
The title photochromic compounds **4** photocyclise to thermally stable blue and infrared active 7-dicyanomethylene-5-oxo-5,7,8,8a-tetrahydro-2-substituted-4,8a-dimethylfuro[3,4-f]benzofurans or benzothiophenes **5** which absorb at longer wavelengths (>100 nm) than the photocyclised compounds **2** from the corresponding photochromic fulgides **1**.

Previous papers[1,2] on heterocyclic fulgides have described the influence of substituent groups and the type of heteroaromatic rings on photochromic properties and have generated interest in the development of infrared active, thermally stable fatigue-resistant photochromic fulgides for reversible optical recording using diode lasers.[3] Suitable compounds with the correct combination of properties are elusive because of problems of rapid fatigue, low quantum efficiencies for bleaching, and difficulties of preparation.

We describe here a simple and convenient method for the preparation of a wide range of new photochromic dicyanomethylene derivatives of fulgides, including infrared active compounds, based upon the method of Moore and Kim[4] for the synthesis of 3-dicyanomethylenephthalide by the base-catalysed condensation of phthalic anhydride with malononitrile.

Replacement of the appropriate carbonyl oxygen of the anhydride ring in photochromic heterocyclic fulgides by the powerful electron-withdrawing dicyanomethylene group causes a major bathochromic shift (>100 nm) of the long-wavelength absorption band of the corresponding coloured forms (Table 1).

The synthesis of compounds **4a–c** is illustrated by that of compound **4a**. 2 equiv. of diethylamine was added dropwise to a stirred solution of equimolar proportions of *E*-isopropylidene[1-(2,5-dimethyl-3-furyl)ethylidene]succinic anhydride **1a** and malononitrile in thf at room temp. After 4 hours, the salt **3a** was filtered off and treated with acetyl chloride, giving *E*-5-dicyanomethylene-4-dicyclopropylmethylene[1-(2,5-dimethyl-3-furyl)ethylidene]tetrahydrofuran-2-one **4a** as bright yellow crystals, mp 153–154 °C (62% yield) after recrystallisation from dichloromethane–light petroleum (1:3). All new compounds were fully characterised. *Z*-Fulgides gave the corresponding *Z*-dicyanomethylene compounds.



a X = O, R′ = Me, R″ = Me
b X = O, R′R′ = cyclopropyl, R″ = Ph
c X = S, R′ = Me, R″ = Ph

Which oxygen is replaced depends on which carbonyl group is more susceptible to nucleophilic attack by the dicyanomethylene anion. Stereochemistries can be deduced from NMR spectra and the photochromic properties of the compounds. *E*-isomers colourise rapidly whereas *Z*-isomers must photoisomerise before photocyclisation can occur. The structure and stereochemistry of the isomer of **4b** has been confirmed by X-ray crystallographic analyses and is shown in Fig. 1.† Of particular interest in this overcrowded structure are the following torsion angles: C(4)–C(7)–C(9)–C(10) −19(2), C(8)–C(7)–C(9)–C(10) 154(1) and C(12)–C(11)–C(15)–C(16) 45(3)°.

The yellow fulgides **1a** and **1b** gave the red 7,7a-dihydrobenzofuran derivatives **2a** and **2b** respectively on irradiation at 366 nm while the yellow dicyanomethylene derivatives **4a** and **4b** photocyclised to the blue compounds **5a** and **5b** respectively.

Table 1 λ_{max} Values for the long wavelength absorption bands of coloured forms after photocyclisation of precursors, illustrating the major bathochromic shifts and solvatochromic effects caused by replacing the appropriate carbonyl oxygen by the dicyanomethylene group

Compound	Solvent	λ_{max}/nm
2a	Toluene	494
	Acetonitrile	507
5a	Toluene	601
	Acetonitrile	665
2b	Toluene	500
5b	Toluene	636
2c	Toluene	546
	Acetonitrile	544
5c	Toluene	669
	Acetonitrile	684

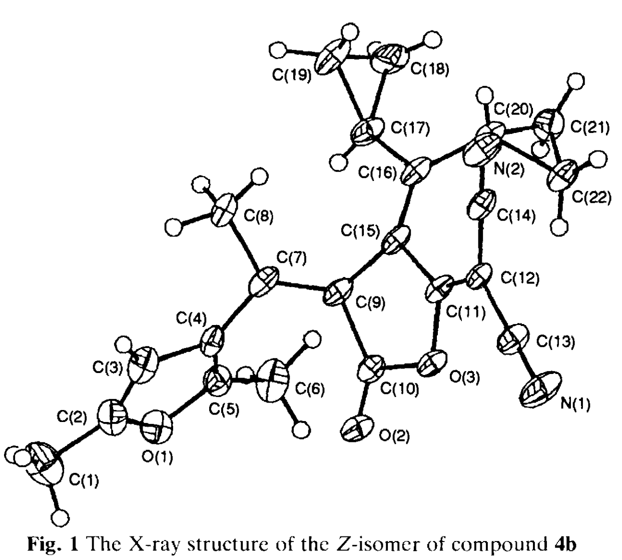


Fig. 1 The X-ray structure of the *Z*-isomer of compound **4b**

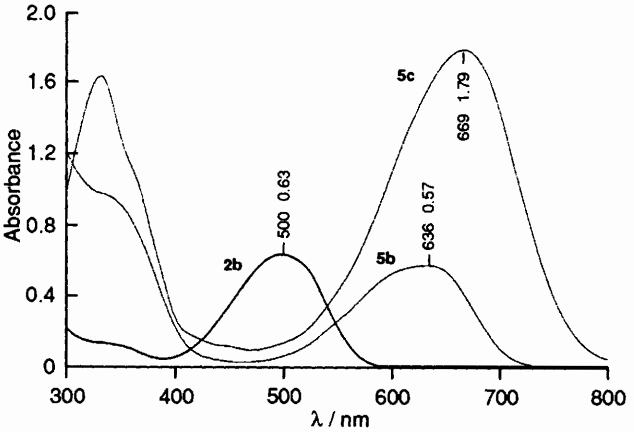


Fig. 2 The spectra of compounds **2b**, **5b** and **5c** (1×10^{-4} mol dm^{-3} solutions in toluene) after irradiation at 366 nm to the photostationary state

Yellow *E*-5-dicyanomethylene-4-isopropylidene[1-(2-methyl-5-phenyl-3-thienyl)ethylidene]tetrahydrofuran-2-one **4c** gave the infrared active green 7,7a-dihydrobenzothiophene derivative **5c** under similar conditions. 7,7a-Dihydrobenzofuran and benzothiophene derivatives **5a–c** are thermally stable but are converted into the respective dicyanomethylenetetrahydrofuranone derivatives **4a–c** on exposure to visible light.

The spectra of compounds **2b**, **5b** and **5c** (1×10^{-4} mol dm^{-3} solutions in toluene), after irradiation at 366 nm to the photostationary state, are shown in Fig. 2 and illustrate the potential of replacing the appropriate carbonyl function in fulgides by a dicyanomethylene group in the molecular design and tailoring of new fatigue-resistant thermally stable photochromic systems.

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Footnote

† *Crystal data*: $C_{22}H_{20}N_2O_3$, M_r 360.4, triclinic, space group $P\bar{1}$, a = 8.31(4), b = 9.22(7), c = 12.88(6) Å, α = 97.0(1), β = 94.8(3), γ = 105.5(1)°, V = 937(9) Å^3, Z = 2, D_c = 1.28 g cm^{-3}. $R1$ = 0.065, wR2 = 0.131 for all 2542 data and 324 parameters. Data were recorded using a FAST TV area detector diffractometer and Mo-Kα radiation. Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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