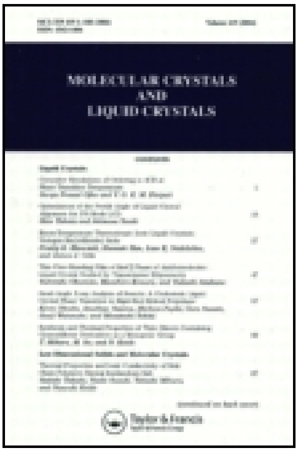

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The Design and Development of New Thermally Stable Infra-Red Active Photochromic Compounds

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THE DESIGN AND DEVELOPMENT OF NEW THERMALLY STABLE INFRA-RED ACTIVE PHOTOCHROMIC COMPOUNDS

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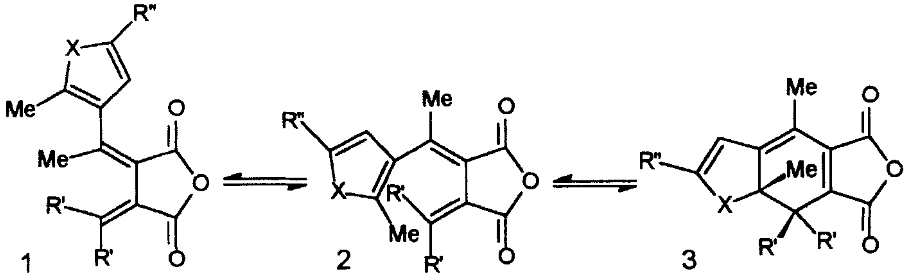
Abstract

E-β-dicyanomethylene-4-alkylidene-3-[1-(substituted-3-furyl or-3-thienyl)-ethylidene)tetrahydrofuran-2-ones, (prepared by base-catalysed condensation of the corresponding E-fulgides with malononitrile, followed by cyclisation with acetyl chloride) undergo base-catalysed cyclisation to photochromic 3-alkylidene-6-amino-7-cyano(substituted-3-furyl or 3-thienyl)-2,3-dihydrobenzofuranones, which photocyclise to compounds having long wavelength absorption band maxima at ca. 750 nm. Charge transfer characteristics in the photochromes are essential for retention of aromatic character in the annelated benzene ring.

One of the remaining challenges in the study of organic photochromic compounds is the molecular design of thermally stable fatigue resistant systems which undergo reversible photoreactions from colourless and infrared inactive to coloured and infrared active. The colourless form should undergo near quantitative conversion into the infrared active form on exposure to ultraviolet light and the infrared active form should undergo photoreversal on irradiation with visible light. Quantum efficiencies for colouring and bleaching should be high. These photochromic systems would have applications in write/read /erase information storage systems and in security printing in which the activated form would be read with the infrared diode laser systems used in compact disc players and bar code readers. If these photochromic compounds could be obtained in optically active forms, non-destructive read out would be possible by taking advantage of the difference in optical rotation between the two forms. This article outlines how these various objectives have been achieved.

Fulgides

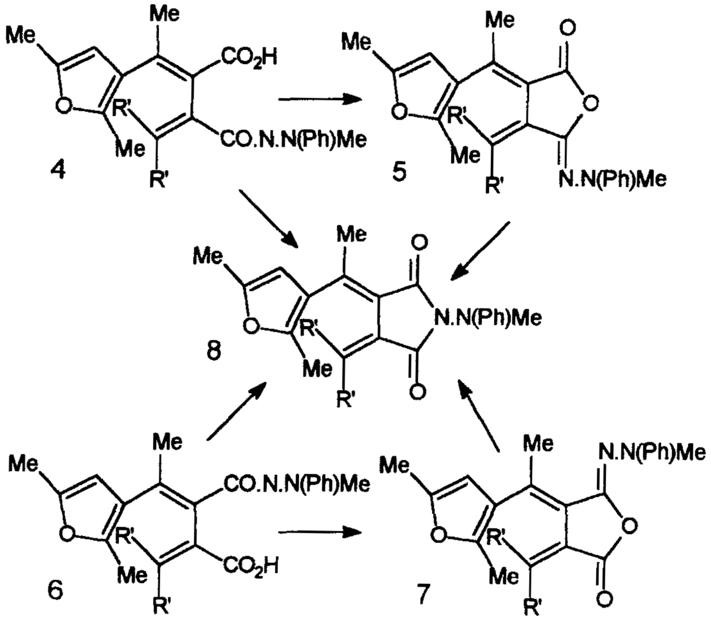


R' = methyl in the **a** series and cyclopropyl in the **b** series

Photochromic fulgides **2** undergo conrotatory photocyclisation to photochrome **3** on exposure to ultraviolet light. The reverse reaction takes place on irradiation with white light. Thermal disrotatory ring opening is prevented by steric interactions.[1]

The absorption spectrum of photochrome **3** shows a marked bathochromic shift when the heteroatom **X** is changed from oxygen to sulphur to nitrogen (with a resulting colour change from red to purple to blue). A large bathochromic effect can be achieved also by making **R** an electron releasing substituent as is shown in the table.[1] Appropriate changes to **X** and **R** result in coloured forms **3**, which absorb above 700 nm. Unfortunately, the large bathochromic shifts are accompanied usually by low quantum efficiencies for bleaching and ready photodegradation.

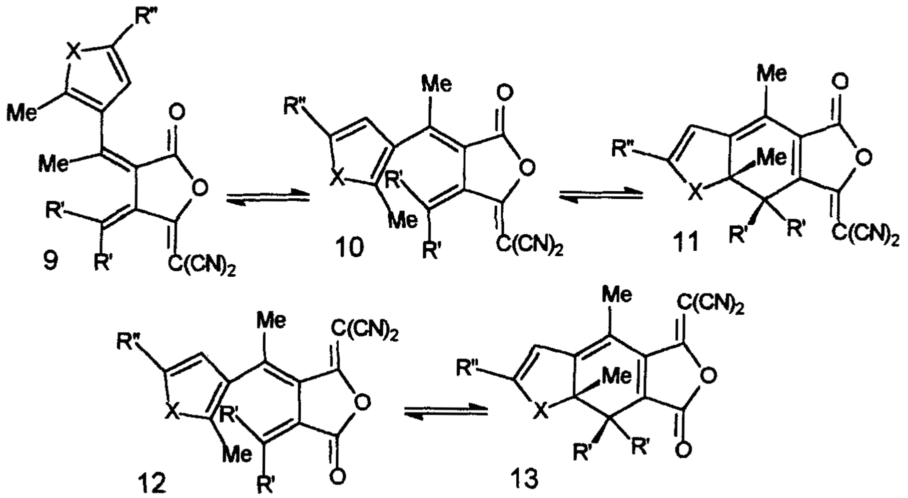
Fulgimides and Isofulgimides



R' = methyl in the **a** series and cyclopropyl in the **b** series

One of the changes to the anhydride ring of fulgides **2** which has been investigated, is the replacement of one of the oxygen atoms by a substituted nitrogen. To distinguish between the two carbonyl groups of the anhydride moiety in unsymmetrical fulgides **2**, we term the carbonyl group which becomes part of the main chromophore in photochrome **3**, as the α carbonyl and the other as the β carbonyl. Replacement of the oxygen of one of these carbonyl groups results in the α or β series of the new photochromic systems respectively. For example, cyclisation of succinamic acid **4b** with dicyclohexylcarbodiimide gives the photochromic α– isofulgimide **5b**. The photochromic β–isofulgimide **7b** is synthesised in a similar manner from the corresponding succinamic acid **6b**. α– and β–Isofulgimides **5b** and **7b** undergo acid-catalysed rearrangements to fulgimide **8b**, which can be obtained directly from succinamic acids **4b** and **6b** by reaction with acetyl chloride. Spectral data are given in the table. Fulgimides are more resistant to hydrolysis than the corresponding fulgides.

5-Dicyanomethylene(substituted-3,4-bismethylene)tetrahydrofuran-2-ones (**10** and **12**) We have reported incorrectly that E-fulgide (**2a**; **X=O**) in dichloromethane, on treatment with malononitrile in the presence of diethylamine, gives a salt, which is cyclised by acetyl chloride at room temperature, to E-α-5-dicyanomethylene-4-isopropylidene-3-[1-(2,5-dimethylfurylethylidene] tetrahydrofuran-2-one (**10a**; **X=O**).[2] We have established that E-fulgide (**2a**; **X=O**) gives photochromic E-β-5-dicyanomethylene-4-isopropylidene-3-[1-(2,5-dimethyl-3-furylethylidene]tetrahydrofuran-2-one (**12a**; **X=O**) which photocyclises to benzofuranone (**13a**; **X=O**). In an analogous sequence of reactions, Z-fulgide (**1a**; **X=O**) yields Z-α-dicyanomethylenetetrahydrofuran-2-one (**9a**; **X=O**), which photoisomerises to the photochromic E-α-furanone (**10a**; **X=O**), which, in turn, photocyclises to the benzofuranone (**13a**; **X=O**). Values for the maxima of the long wavelength absorption bands of photochromes from photocyclisation of α– and β–dicyanomethylenefuranones are shown in the table, to illustrate the large bathochromic shifts which can be attained when a carbonyl oxygen is replaced by the dicyanomethylene group.

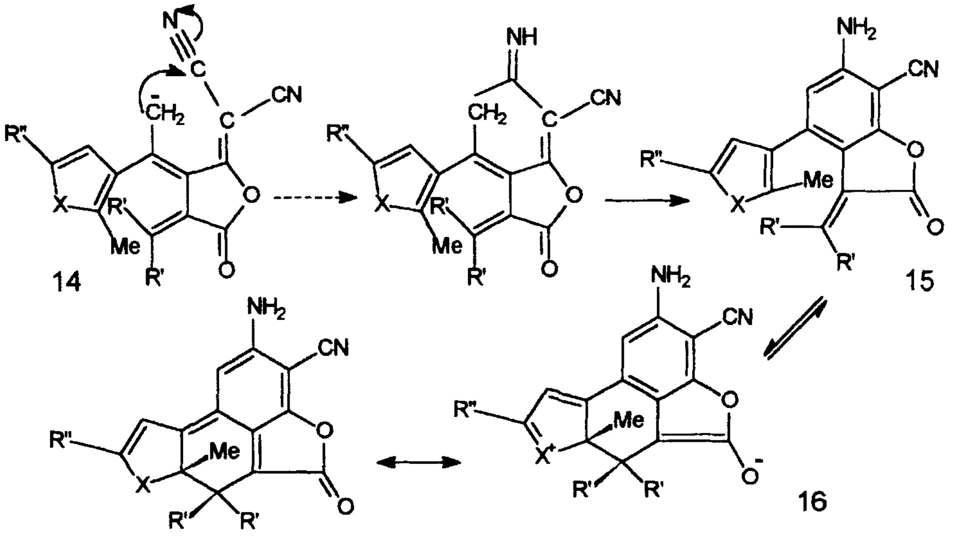


R' = methyl in the **a** series and cyclopropyl in the **b** series

The ρ-Compounds

The anion (**14a**; **X=O**) of E-β-5-dicyanomethylene-4-isopropylidene-3-[1-(2,5-dimethylfurylethylidene] tetrahydrofuran-2-one (**10a**; **X=O**) undergoes further cyclisation to the photochromic 6-amino-7-cyano-4-(2,5-dimethyl-3-furyl)-3-isopropylidene-2,3-dihydrobenzofuran-2-one (**15a**; **X=O**). The corresponding blue-green photochrome (**16a**; **X=O**) is obtained on irradiation of the lactone (**15a**; **X=O**) in toluene at 366 nm. The colour is rapidly reversed on exposure to white light. The long wavelength absorption band of photochrome (**16a**; **X=O**) which extends into the infrared region (λ max. 720 nm) is a consequence of its dipolar character, which is a requirement if aromatic character of the benzene ring in photochrome (**16a**; **X=O**) is to be retained.

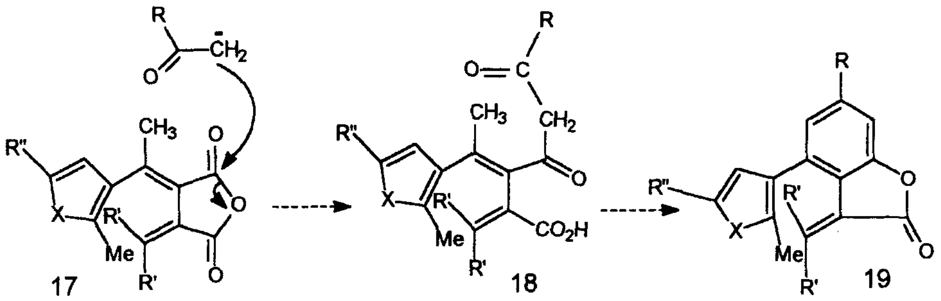
The same principles of molecular tailoring of the **X** and **R"** groups, which has been used so successfully to cause major bathochromic shifts in the long wavelength absorption bands of the photochromes from fulgides and fulgimides and their α– and β–dicyanomethylene derivatives, can be used in this series of compounds also, which we term the ρ–compounds (from the surname of N. Rowles, who first prepared them).



R' = methyl in the **a** series and cyclopropyl in the **b** series

Their exceptional photochromic properties prompted us to devise alternative syntheses which did not involve β-dicyanomethylene derivatives **12**.

For example, ρ-compound (**17b**; **X=O**, **R=Ph**) can be synthesised readily by condensation of E-fulgide (**2b**; **X=O**) with acetophenone in the presence of potassium t-butoxide in toluene, followed by cyclisation of the resulting acid (**18b**; **X=O**) with acetyl chloride.,



R′ = methyl in the **a** series and cyclopropyl in the **b** series

The quantum yield for bleaching can be increased ca. six fold by replacing the isopropylidene group by the adamantylidene group or optically active compounds can be obtained by replacing the isopropylidene group by the 3-methylcyclohexanylidene group, in which the axial methyl group dictates only one of the two helical structures by asymmetric induction. Because of their versatility, ρ compounds are expected to attract the high level of interest which fulgides have enjoyed.

The compounds described in this paper have been fully characterised and their structures and stereochemistry established by X-ray crystallographic analyses for which we thank Professor Michael B. Hursthouse and Mr. David Hughes

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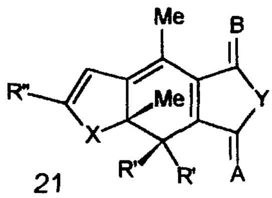

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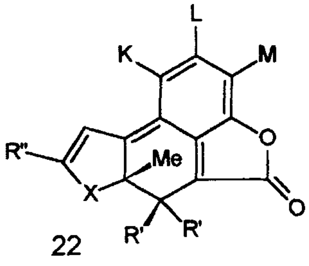

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Table

Spectra characteristics of photochromes **21** and **22**, from the photocyclisation of fulgides, α- and β-isofulgimides, α-and β-dicyanomethylene compounds, and ρ-compounds, respectively, measured for solutions in toluene.

Compound 21, R' = cyclopropyl

X	Y	R"	A	B	λ max./nm.
O	O	Me	O	O	514
S	O	Me	O	O	542
NPh	O	Me	O	O	638
O	N.N(Ph)Me	Me	O	O	527
O	O	Me	O	N.N(Ph)Me	438
O	O	Me	N.N(Ph)Me	O	497
O	O	Me	O	$(C(CN)_2$	594
O	O	Me	$(C(CN)_2$	O	636
S	O	Me	$(C(CN)_2$	O	667
O	S	Me	$(C(CN)_2$	O	681

Compound 22, R' = cyclopropyl

X	Y	R"	K	L	M	
O	O	Me	H	Ph	H	653
O	O	Me	H	NH_2	CN	720
S	O	Ph	H	Ph	H	728
O	O	Ph	H	NH_2	CN	768
S	O	Ph	H	NH_2	CN	776