Thermally stable fatigue resistant near infrared active photochromic compounds, exemplified by 6-amino-7-cyano-3-(dicyclopropylmethylene)-4-(2,5-dimethyl-3-furyl)-benzofuran-2(3*H*)-one

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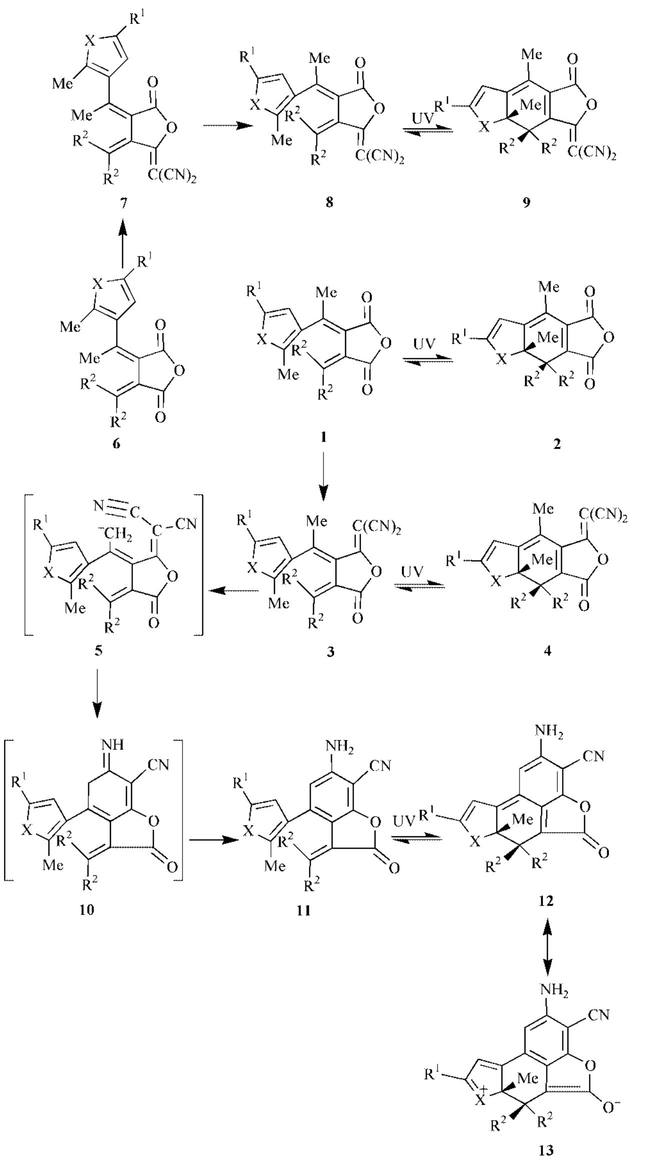
The title pale yellow photochromic compound 11b in toluene, on irradiation at 366 nm, cyclises to the thermally stable infrared active blue–green photochrome, 8-amino-7-cyano-4,4-dicyclopropyl-3a,4-dihydro-6-hydroxy-2,3a-dimethylnaphtho[2,1-*b*]furan-5,6-carbolactone, 12b which has a λ_{max} value of 720 nm for its broad long wavelength absorption band.

E-Fulgides, (*E*)-3-[1-(2,5-dimethyl-3-furyl)ethylidene]-4-isopropylidenetetrahydrofuran-2,5-dione **1a**, (*E*)-3-[1-(2,5-dimethyl-3-furyl)ethylidene]-4-(cyclopropylmethylene)tetrahydrofuran-2,5-dione **1b**, (*E*)-3-[2,5-dimethyl-3-thienyl)-ethylidene-4-isopropylidene tetrahydrofurandione **1c** and (*E*)-3-[2-methyl-5-phenyl-3-thienyl)ethylidene-4-(dicyclopropylmethylene)tetrahydrofuran-2,5-dione **1d** reacted with malononitrile and diethylamine in THF to give exclusively (*E*)-2-dicyanomethylene derivatives **3a–d** which, in toluene, cyclised to photochromes **4a–d** on irradiation at 366 nm. The thermally stable blue photochromes **4a–d** underwent reverse reactions on exposure to white light. Previous papers[1,2] reported erroneously that *E*-fulgides (*e.g.* **1a**) gave the corresponding (*E*)-5-dicyanomethylene derivatives (*e.g.* **8a)** on reaction with malononitrile (1 equiv.) and diethylamine (2 equiv.) in THF, followed by cyclisation with acetyl chloride.



Z-Fulgides **6a–d** gave exclusively the corresponding pale yellow (*Z*)-5-dicyanomethylene derivatives **7a–d** under similar experimental conditions. The latter, in toluene, isomerised to *E*-isomers **8a–d** and cyclised to photochromes **9a–d** on irradiation at 366 nm. The thermally stable blue photochromes **9a–d** underwent reverse reactions to pale yellow *E*-isomers **8a–d** on exposure to white light.

Deprotonation of the methyl group *syn* to the dicyanomethylene group in (*Z*)-2-dicyanomethylene derivative **3b**, by boiling with diisopropylamine in THF, gave anion **5b**, which reacted with the adjacent cyano group to form imine **10b**, which isomerised to 6-amino-7-cyano-3-(dicyclopropylmethylene)-4-(2,5-dimethyl-3-furyl)-1-benzofuran-2(3*H*)-ones **11b**,† obtained as bright yellow crystals (from chloroform–petrol). Its structure was confirmed by X-ray crystallographic analysis (Fig. 1). Amines **11a–d** were prepared in a similar manner.

All new compounds were fully characterised. Spectral data, melting points and yields are given in Table 1.

On irradiation at 366 nm, amines **11a–d** in toluene cyclised to thermally stable blue-green photochromes **12a–d** (Table 2) which underwent the reverse reactions on exposure to white light.

Photochromes **2a–d**, **4a–d**, and **9a–d** showed bathochromic shifts when the push-pull effect is enhanced, as reported for infrared active dyes.[3] Photochromes **12a–d** have increased intramolecular charge-transfer character, due to the tendency to

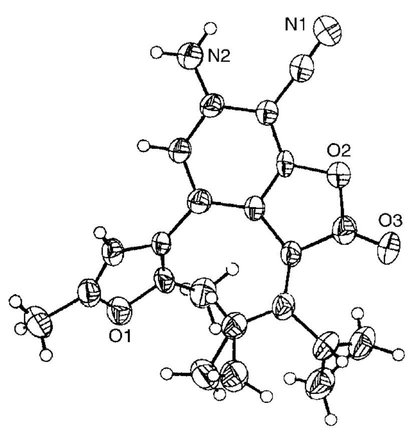


Fig. 1 The X-ray structure of the photochromic compound **11b**.

Table 1 λ_{max} Values for solutions in toluene after photocyclisation, melting points, and yields of photochromic compounds[a]

Compound	**3a**	**3b**	**3c**	**3d**	**7a**	**7b**	**7c**	**7d**	**11a**	**11b**	**11c**	**11d**
λ_{max}/nm	318	323	323	341	353	358	335	333	349	374	348	378
Mp/°C	153–154	155–156	177–178	150–151	184–185	182–183	177–178	151–152	227–229	180–181	212–214	237–238
% Yield	62	62	35	49	39	67	35	90	39	65	31	47

[a] **a** X = O, R^1 = R^2 = Me; **b** X = O, R^1 = Me; R^2 = cyclopropyl; **c** X = S, R^1 = R^2 = Me; **d** X = S, R^1 = Ph, R^2 = cyclopropyl.

Table 2 λ_{max} Values for the long wavelength absorption bands of photochromes in toluene after the photocyclisation of precursors, illustrating the major bathochromic shifts that can be achieved by molecular tailoring[a]

Photochrome	**2a**	**2b**	**2c**	**2d**	**4a**	**4b**	**4c**	**4d**	**9a**	**9b**	**9c**	**9d**	**12a**	**12b**	**12c**	**12d**
λ_{max}/nm	496	514	520	566	601	594	598	653	610	634	642	669	698	720	681	776

[a] **a** X = O, R^1 = R^2 = Me; **b** X = O, R^1 = Me; R^2 = cyclopropyl; **c** X = S, R^1 = R^2 = Me; **d** X = S, R^1 = Ph, R^2 = cyclopropyl.

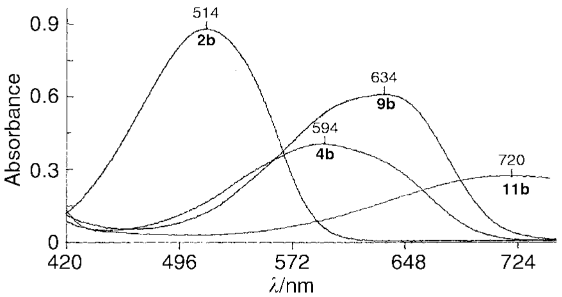


Fig. 2 The spectra of compounds **2b**, **4b**, **9b** and **12b** (1×10^{-4} molar solutions in toluene) after irradiation at 366 nm to the photostationary state.

retain the benzene ring, as indicated by resonance forms **13a–d**, which results in the broad absorption band in the region 750–800 nm. The spectra of coloured forms, thermal stability, fatigue resistance and high efficiencies for colouring and bleaching make the photochromic system based on compounds **11a–d** well suited for optical memory devices and security printing. The major changes in the spectra of these photochromes by molecular tailoring are illustrated in Fig. 2.

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Notes and references

† *Crystal data* for **11b**: $C_{22}H_{20}N_2O_3$, M_r 360.4, monoclinic, space group $P(2)\ 1/c$, a = 9.372(8), b = 11.198(7), c = 17.679(7) Å, β = 101.06 (4)°, V = 18212 A^3, T = 293(2) K, Z = 4, D_c = 1.315 g cm^{-3}, R_1 = 0.0380, wR_2 = 0.0676 for all 2655 points data and 248 parameters. Data were recorded using a FAST TV area detector diffractometer and Mo-Kα radiation. CCDC 182/1692. See http://www.rsc.org/suppdata/cc/b0/b003496g/ for crystallographic files in .cif format.

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