The Intramolecular [2 + 4] Cycloaddition Reaction of *E,E*-9-Anthrylmethylene-[1-(2,5-dimethyl-3-furylethylidene)]succinic Anhydride

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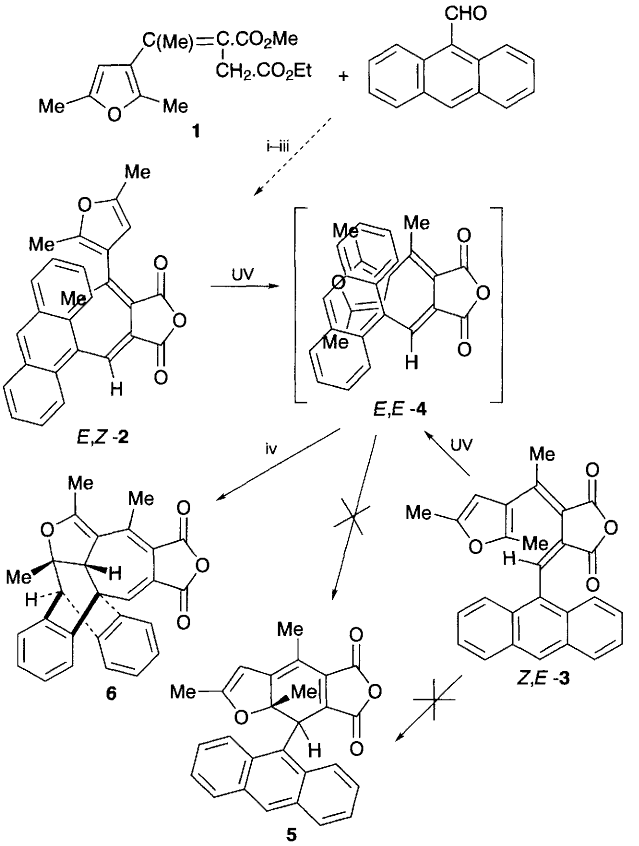
Red and yellow *E,Z*- and *Z,E*-isomers of the title compound isomerise photochemically or thermally to the *E,E*-isomer, which undergoes a [2 + 4] intramolecular cycloaddition reaction at room temperature involving the 4,5-positions of the 2,5-dimethyl-3-furyl group and the 9,10-positions of the anthryl group.

Unlike *E,E*-2,6-dichlorophenylmethylene[1-(2,5-dimethyl-3-furylethylidene)]succinic anhydride, which cyclises thermally and photochemically to a 7,7a-dihydrobenzofuran derivative,[1] *E,E*-9-anthrylmethylene[1-(2,5-dimethyl-3-furylethylidene)]succinic anhydride **4** does not cyclise thermally or photochemically to the *cis*- or *trans*-7,7a-dihydrobenzofuran derivative **5**, but undergoes an irreversible thermal intramolecular [2 + 4] cycloaddition at room temperature to adduct **6**, the structure of which follows from its combustion analysis, mass spectrum and NMR spectrum (Fig. 1) and was confirmed by X-ray crystallographic analyses† (Fig. 2).

Stobbe condensation of equimolar proportions of a 1 : 1 *E*:*Z* mixture of [1-(2,5-dimethyl-3-furylethylidene)]succinic esters **1** with 9-anthraldehyde in toluene in the presence of potassium *tert*-butoxide, followed by hydrolysis of the resulting half-esters with ethanolic KOH to the diacids and cyclisation with acetyl chloride, gave a mixture of *E,Z*- and *Z,E*-9-anthrylmethylene[1-(2,5-dimethyl-3-furylethylidene)]succinic anhydrides **2** and **3**, obtained as red rhomboids and yellow plates, respectively, and adduct **6** as orange needles, after separation by column chromatography on silica gel using a 1 : 4 mixture of diethyl ether and light petroleum (bp 40–60 °C) as eluent, and recrystallisation from chloroform and light petroleum (Table 1; Scheme 1). On melting, **2** and **3** isomerise and form adduct **6**. The stereochemistry of **2** and **3** was established from their ^{1}H NMR spectra.‡



Scheme 1 *Reagents and conditions*: i, Bu^{t}OK, toluene; ii, KOH, ethanol; iii, AcCl, dichloromethane; iv, room temp.

On irradiation (366 nm) at room temperature or on heating at 110 °C, *E,Z*- and *Z,E*-fulgides **2** and **3** in toluene gave adduct **6** in quantitative yield, presumably by isomerisation to *E,E*-fulgide **4** followed by thermal intramolecular [2 + 4] cycloaddition. Molecular modelling (using the Nemesis program)

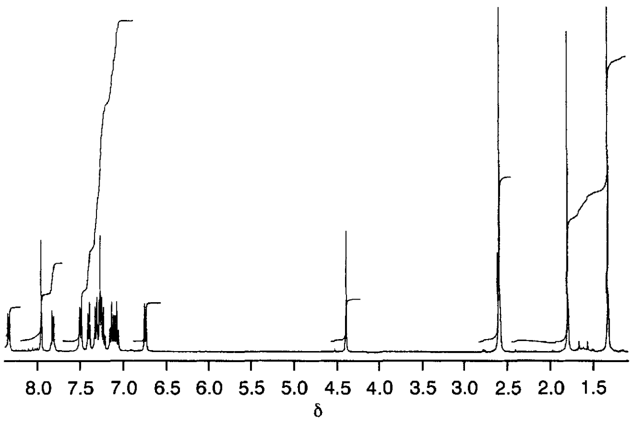


Fig. 1 360 MHz ^{1}H NMR spectrum of adduct **6**

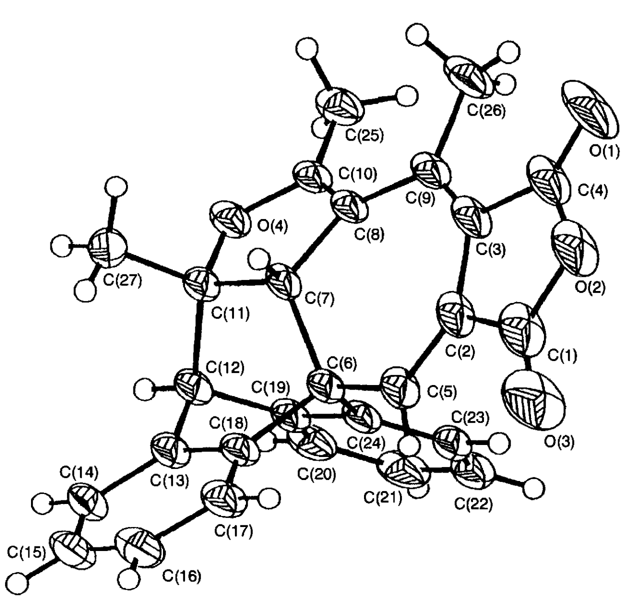


Fig. 2 X-Ray structure of adduct **6**

Table 1 Melting points and spectral data

Compound	Mp/°C	λ_{max}/nm	ε/dm^3 mol^{-1} cm^{-1}
E,Z-**2**	189–190	376, 438	8500, 8300
Z,E-**3**	193–194	388, 438	9340, 7290
Adduct **6**	243–244	396	11 800

indicates that the helical structure of **4**, with the severe molecular overcrowding owing to overlapping furyl and anthryl moieties, facilitates this reaction.

Solutions of **2** and **3** and **6** (1×10^{-4} mol dm^{-3} in toluene) were yellow but the difference in the UV–VIS spectra of *E,Z*- and *Z,E*-fulgides **2** or **3** and adduct **6** (Fig. 3) indicates that **2** and **3** have the potential for irreversible optical recording. Adduct **6** does not undergo the reverse reaction, unlike adducts from the [4 + 4] intramolecular photocycloaddition reactions of *E,E*-bisanthrylmethylenesuccinic anhydride and its dicyanomethylene derivative, which undergoes the reverse reaction on heating.[2]

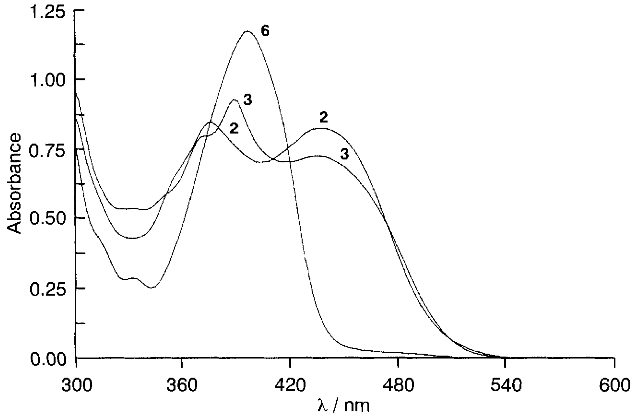


Fig. 3 Absorption spectra of fulgides **2** and **3** and adduct **6** (1×10^{-4} mol dm^{-3} solutions in toluene)

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Footnotes

† *Crystal data* for **6**: $C_{54}H_{40}O_8$, M_r = 816.86, triclinic, space group $P1$, a = 9.200(3), b = 15.471(3), c = 15.957(3) Å, α = 61.65(1), β = 83.00(1), γ = 77.24(1)°, V = 1949.1(8) Å^3, Z = 2, D_x = 1.392 g cm^{-3}, R_1 = 0.091, wR_2 = 0.177 for all 8784 unique data and 567 parameters [R_1 = 0.039 for 2731 data with $I > 2\sigma(I)$]. Data were recorded using a FAST TV area detector diffractometer and Mo-Kα radiation. The structure was solved by direct methods (SHELXS)[3a] and refined using full-matrix least squares methods in SHELX93.[3b] Hydrogen atoms were included in idealised positions with U_{iso} values linked to the U_{equs} of the parent atoms. 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.

‡ *E,Z*-Fulgide **2** showed a singlet at δ 0.70 owing to the methyl in the shielding zone of the anthryl group and a singlet at δ 8.66 owing to the alkenic hydrogen in the deshielding zone of the carbonyl group. *Z,E*-Fulgide **3** showed a singlet at δ 2.76 characteristic of a methyl group in the deshielding zone of a carbonyl group, and a singlet at δ 8.24 indicative of the alkenic hydrogen in the shielding zone of the furyl group.

References

1 H. G. Heller, C. J. Morgan and M. J. Ottaway, *J. Chem. Soc., Perkin Trans. 1*, in the press.

2 H. G. Heller and M. J. Ottaway, *J. Chem. Soc., Chem. Commun.*, 1995, 479.

3 (*a*) G. M. Sheldrick, SHELXS, University of Göttingen, 1986; (*b*) G. M. Sheldrick, SHELX93, University of Göttingen, 1993.