SHORT PAPER

J. Chem. Research (S),
2000, 526–527

Synthesis of 3,4-bis(fluorenylidene)-5-(4-fluorophenylcyanomethylene)tetrahydrofuran-2-one and the X-ray structure of its cyclised form†

Shar S. Al-Shihry

Department of Chemistry, College of Education, King Faisal University,
P.O. Box 1759, Hofuf 31982, Saudi Arabia

The title compound (**4**) cyclizes photochemically or thermally, via an unexpected [1,7] hydrogen shift, to a new stable adduct (**7**), the structure of which was confirmed by X-ray crystallographic analysis.

Replacement of one of the carbonyl groups in heterocyclic fulgides by a dicyanomethylene group causes a major bathochromic shift.[1] A number of new heterocyclic photochromic compounds have been prepared by base-catalysed condensation of the corresponding fulgide with substituted phenylacetonitriles, followed by dehydration.[2]

The condensation of bis(fluorenylidene) succinic anhydride **1** with 4-fluorophenylacetonitrile **2** in the presence of two moles of potassium *t*-butoxide in toluene gave the lactone **4** as the sole product. On irradiation at 366 nm or on heating this cyclizes quantitatively, to the new chiral and thermally stable adduct **7** via the intermediate **6**. Presumably, the formation of **7** from **1** follows the pathway shown in Scheme 1. Extension of conjugation in **6** is expected to lead to the more extended [1,7]-hydrogen shift. However only a [1,5]-hydrogen shift has been encountered previously in such a system *e.g.* in the electrocyclic reaction of the simpler fulgide **1**[3]. The pure adduct **7** was isolated as cubic orange crystals which were suitable for X-ray analyses. The molecular structure of adduct **7** is shown in Fig. 1 while selected bond lengths and angles are given in Table 1.

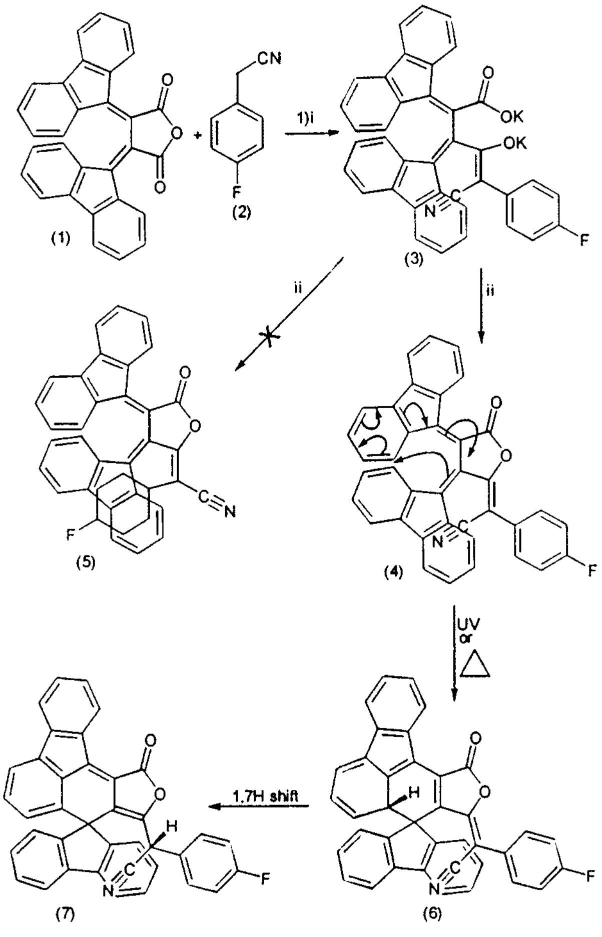
Experimental

Melting points were determined on an electro-thermal apparatus and were uncorrected. ^{1}H NMR spectra were obtained for solutions in $CDCl_3$ with TMS as internal standard using a Bruker DPX 400 SF 400.13 MHz spectrometer. Mass spectra were recorded on a Jeol JMS SX102 spectrometer. Microanalyses were carried out using a Perkin Elmer 2400 analyser.

Bis(fluorenylidene) succinic anhydride **1***:* Fulgide **1** was synthesised according to the literature method it had,[4] m.p. 251–252°C. ^{1}HNMR: δ 8.97–6.78 (16H, m, aromatic protons).

3,4-Bis(fluorenylidene)-5-(4-florophenylcyanomethylene)tetrahydrofuran-2-one **4***:* A mixture of the fulgide **1** and 4-fluorophenylacetonitrile **2** in the presence of 2 mole equivalents of potassium *tert*-butoxide in toluene was kept at room temperature. Cyclization of the resulting disalt **3** with acetyl chloride followed by purification on silica gel column using a 3:7 mixture of diethyl ether and light petroleum (b.p. 40–60°C), and recrystallization from petrol and ether afforded yellow plates of a single isomer, lactone **4** (39% yield), m.p. 310°C decomp. Found: C, 83.95; H, 3.58; N, 2.43%. $C_{38}H_{20}O_2NF$ requires C, 84.28; H, 3.72; N, 2.59%. ^{1}HNMR: δ 8.58–6.12 (20H, m, aromatic protons). Neither TLC, H-NMR or X-ray analysis have revealed the formation of the conjugated byproduct **5**.

Irradiation of the lactone **4***:* Compound **4** (400 mg) in toluene (20 ml) was irradiated at 366 nm for 10 h. Concentration of the solution afforded adduct **7** (85 mg 21%). Recrystallization from boiling ethanol, afforded cubic orange crystals of lactone **7,** m.p. 287–289°C, decomp, λ_{max} 432 nm. Found: C, 84.11; H, 3.63; N, 2.48%. $C_{38}H_{20}O_2NF$ requires C, 84.28; H, 3.72; N, 2.59%). The chemical structure of compound **7** was confirmed by X-ray crystallographic analysis.



Scheme 1 Reagents and conditions: I, *t*-BuOK, toluene; ii, AcCl, dichloromethane, room temperature.

Crystal data for lactone **7** chemical formula: $C_{38}H_{20}NO_2F$, M_r= 541.55, crystal system Triclinic, space group *P*-1, a = 11.4072 (11), b = 11.4616 (11), c = 11.9127 (11) Å, α = 66.966 (2), β = 68.492 (2), γ = 78.333 (2)°, T = 193 (2) K, V = 1330.4 (2) Å, Z = 2, 1.352 mg/m^3, R_1 = 0.0375, wR_2 = 0.0937, for all 6102 unique reflections [$R(F)$ = 3.75%, $wR(F^2)$ = 9.37% for 4186 reflections with $F_o>4\sigma(F_o)$]. The structure was solved by direct methods (SHELXS)[5]. Hydrogen atoms were initially placed in calculated positions but later allowed to refine freely (xyzU). The structure was determined by direct methods with the successful location of many non-hydrogen atoms using the program XS[6]. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

The author would like to thank Dr J. Fitteger, University of Maryland, USA for carrying out the X-ray analysis.

---

* To receive any correspondence.

† This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

Table 1 Selected bond length (Å) and bond angles (°) for adduct **7**

C (7) – C (8)	1.4800 (18)	C (7) – C (9)	1.4986 (17)
C (10) – C (9)	1.3409 (15)	C (10) – C (11)	1.4498 (16)
C (10) – C (26)	1.5230 (15)	C (11) – C (13)	1.3513 (16)
C (24) – C (26)	1.5405 (16)	C (26) – C (38)	1.5271 (17)
C (26) – C (27)	1.5301 (16)		
C (8) – C (7) – H (7)	106.1 (8)	N (8) – C (8) – C (7)	179.84 (16)
C (10) – C (9) – O (9)	112.88 (10)	C (10) – C (9) – C (7)	131.80 (11)
C (25) – C (24) – C (26)	120.00 (10)	C (23) – C (24) – C (26)	123.09 (11)
C (10) – C (26) – C (24)	110.16 (10)	C (27) – C (32) – C (33)	108.41 (11)

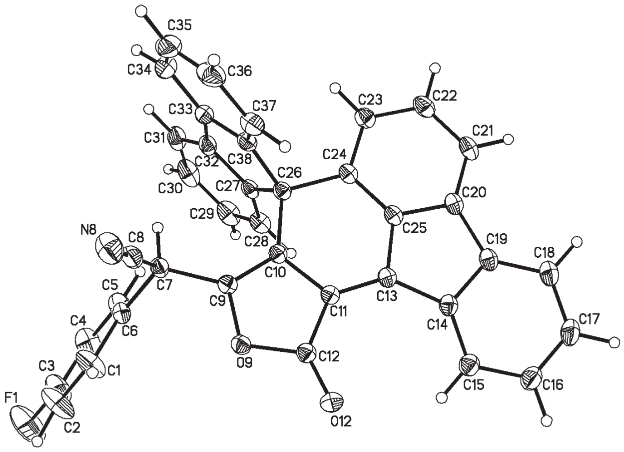


Fig. 1 Atomic numbering schemes for non-hydrogen atoms. Hydrogen atom numbering follows the carbon atom numbers.

Received 9 July 2000; accepted 13 November 2000
Paper 00/427

References

1 H.G. Heller, D. Hughes, M.B. Hursthouse, and K.V. Koh, *J. Chem. Soc. Chem. Commun.* 1994, 2713.
2 S.S. Al-Shihry, *Kuwait J. Sci. Eng.*, in press.
3 R.J. Hart and H.G. Heller, *J. Chem. Soc., Perkin Trans* 1972, **1**, 132.
4 A.M. Asiri, *J. Chem. Res (S)*, 1997, 302.
5 G.M. Sheldrick, SHELXTL/PC. Version 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA, (1994).
6 G.M. Sheldrick, *Acta Crystallagr*, 1990, **A46**, 467–473.