

Synthesis and Photochemistry of 3,6-Difluoro-10,11-benzopentacyclo-[6,4,0.0^{2,7},0^{3,12}.0^{6,9}]dodeca-4,10-diene†

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9,12-Difluoro- and 9,12-dichlorotetracyclo[6.4.2.2^{9,12}.0^{2,7}] hexadeca-2,4,6,13,15-pentaene-10,11-dicarboxylic anhydrides (**2a**) and (**2b**) were prepared by $4\pi_s + 4\pi_s$ photocycloaddition between *cis*-3,6-difluoro- or *cis*-3,6-dichloro-1,2-dihydrophthalic anhydride and naphthalene, respectively. 12,15-Difluoro- and 12,15-dichlorohexacyclo[8.6.0.0^{2,15}.0^{3,8}.0^{9,12}.0^{11,16}]hexadeca-3,5,7-triene-13,14-dicarboxylic anhydrides (**6a**) and (**6b**) were obtained by $2\pi_s + 2\pi_s$ intramolecular photocycloaddition of adducts (**2a**) and (**2b**), respectively. 12,15-Difluorohexacyclo[8.6.0.0^{2,15}.0^{3,8}.0^{9,12}.0^{11,16}]hexadeca-3,5,7,13-tetraene (**7a**) has been synthesized by the electro-oxidative decarboxylation of anhydride (**6a**) and the excited singlet naphthalene has been observed on irradiation of adduct (**7a**), and is presumably formed *via* an adiabatic pathway.

Recently we have been interested in the application of the photocycloaddition of arenes and cyclo-1,3-dienes to the synthesis of energy-rich cage compounds,¹ and intended to synthesize 12,15-dihalogenohexacyclo[8.6.0.0^{2,15}.0^{3,8}.0^{9,12}.0^{11,16}]hexadeca-3,5,7,13-tetraenes (**7**). We now report the synthesis of the difluoride (**7a**) and the photoconversion of compound (**7a**) into excited naphthalene through an adiabatic process.

Results and Discussion

The reaction route for the synthesis of the cage compounds is shown in Scheme 1. There are two noteworthy points in this Scheme. One is the manner of photocycloaddition of naphthalene and *cis*-3,6-dihalogeno-1,2-dihydrophthalic anhydrides (**1a** and **b**). From knowledge of the manner of photocycloaddition between naphthalene and cyclohexa-1,3-diene,^{1b-d} we can expect the formation of $4\pi_s + 4\pi_s$ photocycloadducts (**2a** and **b**) or (**3a** and **b**) and $4\pi_s + 2\pi_s$ cycloadducts (**4a** and **b**) or (**5a** and **b**). However, only photo-allowed $4\pi_s + \pi_s$ adducts (**2a** and **b**) were observed. These are key intermediates for the synthesis of the energy-rich cage compounds (**6a** and **b**), which proceeds by intramolecular $2\pi_s + 2\pi_s$ photocycloaddition. The intramolecular $2\pi_s + 2\pi_s$ photocycloaddition was performed by a photosensitized reaction using xanthone as a triplet sensitizer. In the case of the $4\pi_s + 4\pi_s$ photoadduct, tetracyclo[6.4.2.2^{9,12}.0^{2,7}]hexadeca-2,4,6,10,13-pentaene,^{1b-d} direct irradiation gave naphthalene and a polymer. The other point is the electronic oxidative bisdecarboxylation of the acid anhydride of photoadducts (**2a** and **b**). Technically the addition of hexane to the reaction mixture is important because the two-layered system protects the cage compound (**7**) from further electrolysis. As shown in Table 1, higher pyridine concentration and lower capacitance gave a higher yield of compound (**7a**). We failed to synthesize the dichloride (**7b**) by $\text{Pb}(\text{OAc})_4$ or electro-oxidative bisdecarboxylation.

The u.v. spectra of adducts (**2a**), (**6a**), and (**7a**) are shown in Figure 1. These spectra show almost the same absorption pattern because these compounds have the *o*-xylene system as a common characteristic chromophore.² The ¹³C and ¹H

Table 1. Yield of compound (**7a**) by electrolysis

(6a) (mmol)	Concentration of pyridine in water (%)	Electrical capacitance (mF)	Yield (%) of (7a)
0.47	10	134	3.5
1.32	60	75	23.7
1.30	80	41	42.2

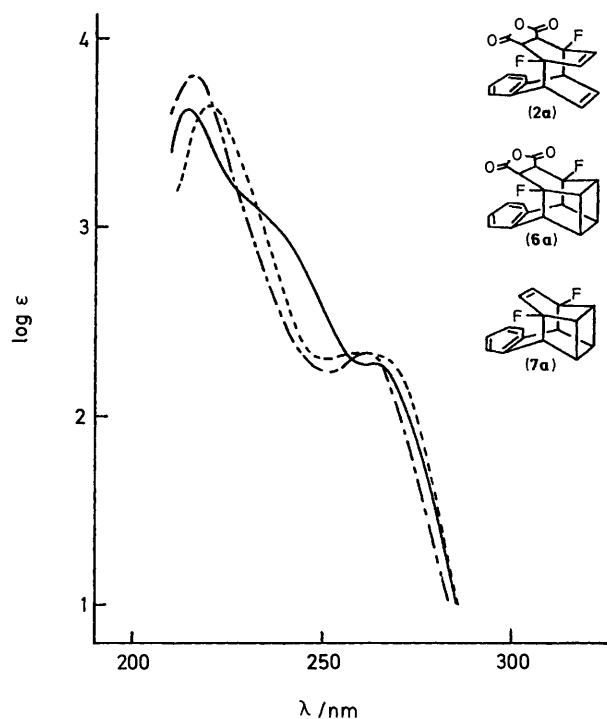
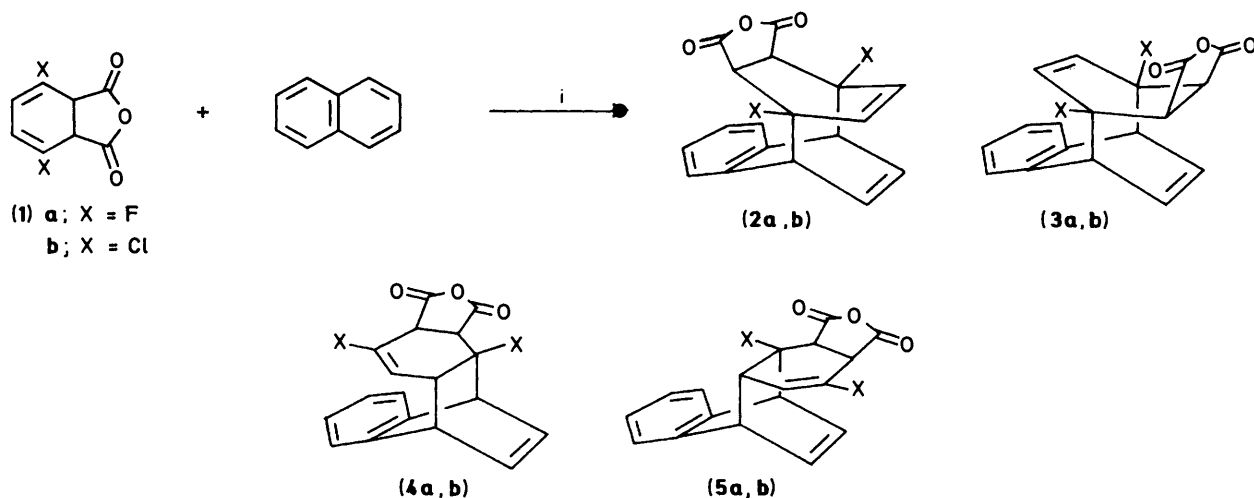


Figure 1. U.v. absorption of compounds (**2a**) (—), (**6a**) (---) and (**7a**) (- - -) in EtOH

n.m.r. spectra of compound (**7a**) in CDCl_3 are shown in Figure 2. The vinyl protons actively couple with adjacent fluorine atoms, and the bridgehead protons also actively couple with adjacent fluorine atoms. Six methine protons on the cage heads

† Systematic name: 12,15-difluorohexacyclo[8.6.0.0^{2,15}.0^{3,8}.0^{9,12}.0^{11,16}]hexadeca-3,5,7,13-tetraene.



Scheme 1.

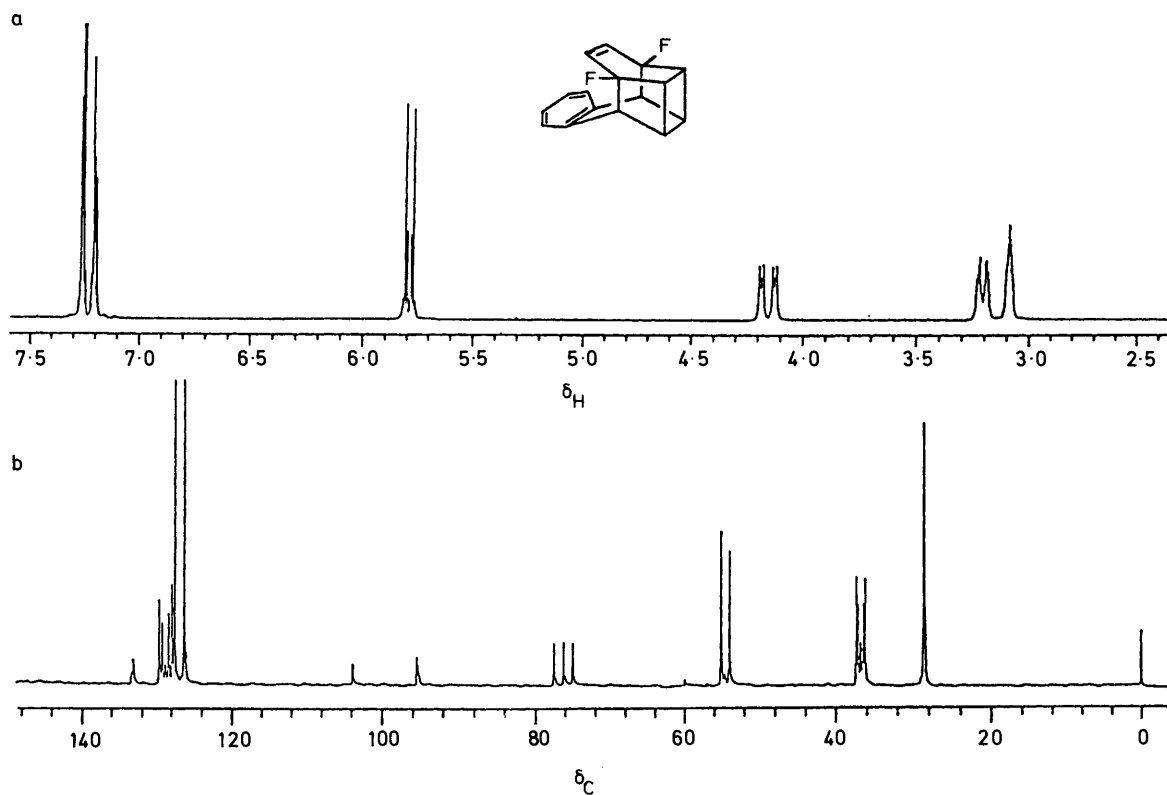
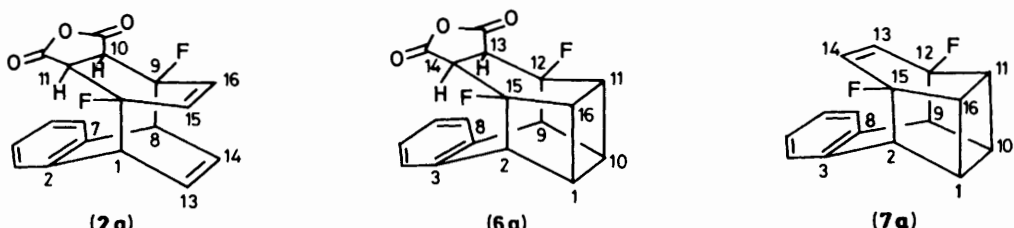


Figure 2. (a) ^1H N.m.r. (500 MHz) spectrum of compound (7a) in CDCl_3 and (b) ^{13}C n.m.r. (100 MHz) spectrum of compound (7a) in CDCl_3 .

appear at δ_{H} 3.20, 3.09, and 4.15. In Table 2 the following features are of interest. The chemical shift of vinyl protons in adduct (7a) is upfield from those in (2a). The methine protons on the acid anhydride moiety of adducts (2a) and (6a) appear at δ ca. 3, upfield from those of compound (1a) (δ 4.35). This high-field shift is reasonably explained in terms of the anisotropy effect of the benzene ring located over these protons. It is informative to test the possibility of a chemiluminescent reaction using this energy-rich system.³ There are several interesting chemiluminescent systems, but a chemiluminescent system which does not contain oxygen atoms is very rare. Unfortunately, we could not observe an emission from a hot solution of adduct (7a) in xylene with or without a fluorescer (rubrene, dibromo-

anthracene, or diphenylanthracene). There is a relatively large energy gap between the ground-state energy surface of adduct (7a) and the excited-state energy surface of naphthalene and it is impossible to jump this energy gap between them to reach the corresponding excited naphthalene by heating the reaction system. However, when compound (7a) was irradiated at 263 nm, efficient fluorescence (Φ 0.22) from naphthalene was observed as shown in Figure 3. This means that there is a smooth energy surface in the excited states between the excited cage compound (7) and the excited naphthalene, and an adiabatic photoreaction occurred efficiently.⁴ This is the first example of the formation of an excited product through an adiabatic process using a pentacyclogene system. Although we

Table 2. Chemical shifts for hydrogens of compounds (2a), (6a), and (7a)


Compound	Chemical shift (δ_H)				
(2a)	4.03 (1- and 8-H)	3.10 (10- and 11-H)	6.63 (13- and 14-H)	6.10 (15- and 16-H)	7.27 (ArH)
(6a)	4.27 (2- and 9-H)	3.02 (13- and 14-H)	3.21 (1- and 10-H)	3.64 (11- and 16-H)	7.23 (ArH)
(7a)	4.16 (2- and 9-H)	5.79 (13- and 14-H)	3.08 (1- and 10-H)	3.21 (11- and 16-H)	7.23 (ArH)

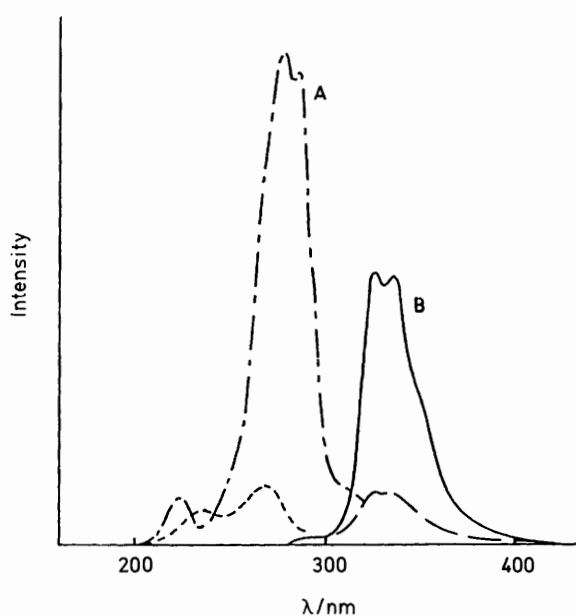


Figure 3. The emission spectrum of compound (7a) (---, $1.1 \times 10^{-5} M$ in EtOH) through an adiabatic mechanism; the excitation spectrum for the emission of compound (7a) at 325 nm (---); the fluorescence spectrum of naphthalene (—, $2.3 \times 10^{-4} M$ in EtOH); and the excitation spectrum for the emission of naphthalene (---) at 325 nm*

expected the formation of hexaprismane derivative (8) by the sensitized irradiation of adduct (7a) with ketones (xanthone or acetone) as sensitizers, we observed the formation of naphthalene instead of (8) (see Scheme 2). We assumed a stepwise bridge C-C bond cleavage by the thermal reaction which

* For our evaluation of the relative quantum yields of the emission of compound (7a), we followed the method of Berlman. The emission spectra of naphthalene and (7a) are observed by irradiation with u.v. light of 263 nm (slit width 5 nm) using ethanol solutions whose concentrations were set to have the same absorbance at 263 nm. The area of emission curve of compound (7a) (curve A) was compared with the area of the naphthalene fluorescence curve (B). We estimated the quantum yield for the adiabatic photoreaction as 0.22 from the ratio of their areas of emission curves (A/B 0.22). See I. B. Berlman, 'Handbook of Fluorescence Spectra of Aromatic Molecules,' Academic Press, New York and London, 1965, p. 14.

consumed almost all stored energy in the system without any visible light emission.

Experimental

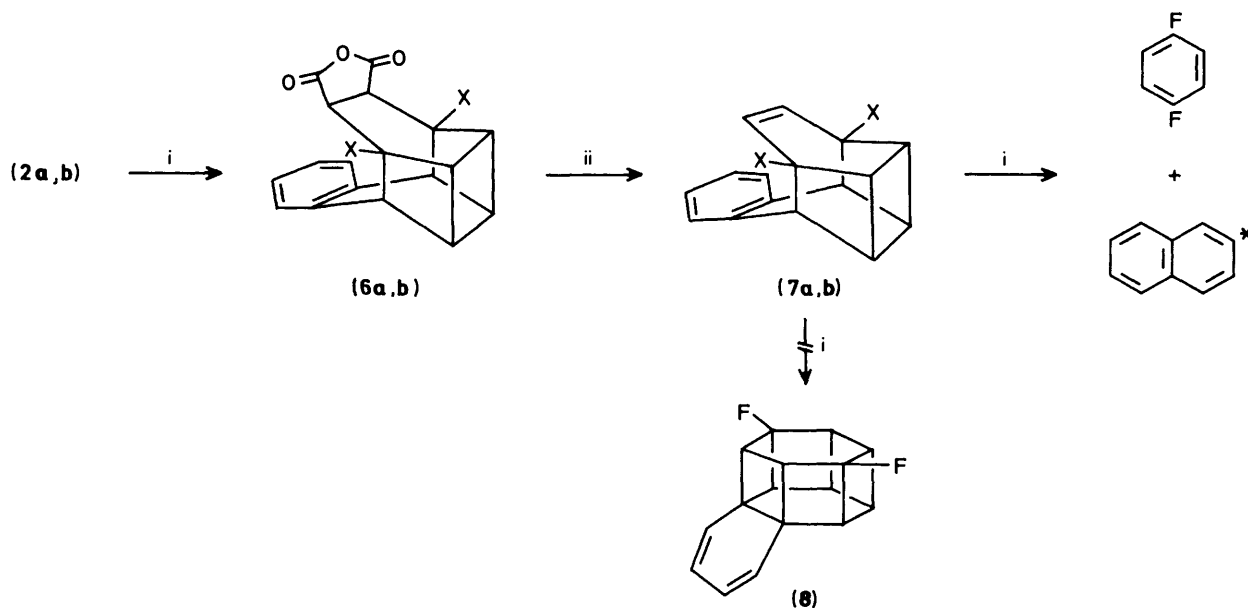
M.p.s were measured with a Yanaco micro melting point apparatus and are uncorrected. 1H N.m.r. spectra were taken on Varian XL-500, Varian XL-360, JEOL FX-100, or JEOL JNMPX 60 spectrometers, for $CDCl_3$ solutions with tetramethylsilane as internal standard. I.r. spectra were recorded on a JASCO IRA-1 spectrometer. U.v. spectra were recorded on a Hitachi model 200-10 spectrometer.

Materials.—*cis*-3,6-Dichloro-1,2-dihydrophthalic anhydride (1b) was prepared by the method of Breslow *et al.*⁵ *cis*-3,6-Difluoro-1,2-dihydrophthalic anhydride (1a) was prepared by a similar method as for compound (1a).

9,12-Difluorotetracyclo[6.4.2.2^{9,12}.0^{2,7}]hexadeca-2,4,6,13,15-pentaene-10,11-dicarboxylic Anhydride (2a).—A solution of naphthalene (5 g, 3.9 mmol) and *cis*-3,6-difluoro-1,2-dihydrophthalic anhydride (1a) (650 mg, 3.5 mmol) in benzene (110 ml) was irradiated with a Ushio 100 Hg high-pressure lamp through a Pyrex filter for 12 h. The solvent was evaporated off under reduced pressure and the residue was chromatographed on silica gel with benzene to give compound (2a) (280 mg, 26%), m.p. 176.5–177 °C (from EtOH); δ_H (60 MHz) 3.10 (m, 2 H), 3.78 (m, 1 H), 4.28 (m, 1 H), 6.10 (m, 2 H), 6.63 (m, 2 H), and 7.27 (4 H, ArH); ν_{max} (Nujol) 1 850 and 1 770 cm^{-1} ; λ_{max} 265 (log ϵ 2.26) and 214 nm (3.63) (Found: C, 68.9; H, 4.0. $C_{18}H_{12}F_2O_3$ requires C, 68.79; H, 3.85%).

9,12-Dichlorotetracyclo[6.4.2.2^{9,12}.0^{2,7}]hexadeca-2,4,6,13,15-pentaene-10,11-dicarboxylic Anhydride (2b).—This was prepared from (1b) by the same method as difluoride (2a): 1.3% yield, m.p. 159–160 °C; δ_H (60 MHz) 3.69 (s, 2 H), 4.38 (m, 2 H), 6.07 (s, 2 H), 6.64 (m, A_2X_2 , 2 H), and 7.15 (s, 4 H); ν_{max} (Nujol) 1 860 and 1 780 cm^{-1} ; λ_{max} (EtOH) 350 (log ϵ 3.74) and 218 nm (4.69) (Found: C, 62.2; H, 3.4. $C_{18}H_{12}Cl_2O_3$ requires C, 62.27; H, 3.48%).

12,15-Difluorohexacyclo[8.6.0.0^{2,15}.0^{3,8}.0^{9,12}.0^{11,16}]hexadeca-3,5,7-triene-13,14-dicarboxylic Anhydride (6a).—Compound (2a) (100 mg, 0.3 mmol) was dissolved in benzene (100 ml), and xanthone (25 mg, 0.13 mmol) was added as a sensitizer. The reaction mixture was irradiated under N_2 at room temperature with a Ushio 100 W Hg high-pressure lamp for 10 h. The solvent was evaporated off under reduced pressure by rotary evaporator. The residue was recrystallized from ethyl



Scheme 2. Reactions: i, *hv*; ii, Electro-oxidative decarboxylation

acetate to give the crude product (**6a**) (80 mg, 80%), m.p. 247—247.5 °C; δ_{H} (360 MHz) 4.27 (m, 2 H), 3.02 (m, 2 H), 3.21 (m, 2 H), 3.64 (m, 2 H), and 7.23 (4 H, ArH) ν_{max} (Nujol) 1 860 and 1 770 cm^{-1} ; λ_{max} (EtOH) 260 (log ϵ 2.34) and 220 nm (3.64) (Found: C, 68.9; H, 3.85. $\text{C}_{18}\text{H}_{12}\text{F}_2\text{O}_3$ requires C, 68.79; H, 3.85%).

12,15-Dichlorohexacyclo[8.6.0.0^{2,15}.0^{3,8}.0^{9,12}.0^{11,16}]hexa-deca-3,5,7-triene-13,14-dicarboxylic Anhydride (**6b**).—This compound was prepared in a similar manner, 66% yield; m.p. 159—160 °C; δ_{H} (60 MHz) 3.41 (m, 6 H), 4.58 (m, 2 H), and 7.28 (4 H, ArH); ν_{max} (Nujol) 1 855 and 1 780 cm^{-1} ; λ_{max} (EtOH) 264 nm (log ϵ 2.47) (Found: C, 62.4; H, 3.35. $\text{C}_{18}\text{H}_{12}\text{Cl}_2\text{O}_3$ requires C, 62.27; H, 3.48%).

12,15-Difluorohexacyclo[8.6.0.0^{2,15}.0^{3,8}.0^{9,12}.0^{11,16}]hexa-deca-3,5,7,13-tetraene (**7a**).—Compound (**6a**) (438 mg, 1.32 mmol) was dissolved in 60% aqueous pyridine (25 ml) containing triethylamine (0.4 ml). Hexane (13 ml) was added to the solution in order to extract products during the reaction. The stirred solution was electrolysed for 10 h (74.6 mF) while cooled in an ice-water-bath (a current of 200 mA was supplied at 35—40 V between the stationary platinum plate electrodes). The hexane layer was separated and the reaction mixture was extracted with hexane (3 × 20 ml). The hexane layers were combined and evaporated. The residue was recrystallized from hexane to give the title compound (**7a**) (75.7 mg, 23.7%), m.p. 138—139 °C (from EtOH); δ_{H} (500 MHz) 3.09 (m, 2 H), 3.20 br d, J 17 Hz, 2 H), 4.15 (br d, J 29 Hz, 2 H), 5.80 (d, J 19 Hz, 2 H, 13- and 14-H), 7.20 (m, A_2X_2 , 2 H, ArH), and 7.26 (m, A_2X_2 , 2 H, ArH); δ_{C} (100 MHz) 28.59, 37.09, 55.10, 100.47, 127.40, 128.72, 129.93, and 134.25; ν_{max} (Nujol) 2 885, 1 480, 1 380, 1 270, 1 105, 1 060, and 890 cm^{-1} ; λ_{max} (EtOH) 261 (log ϵ 2.33) and 216 nm (3.81) (Found: C, 79.6; H, 4.95. $\text{C}_{16}\text{H}_{12}\text{F}_2$ requires C, 79.32; H, 4.99%).

Photoreaction of Difluoride (**7a**).—A benzene (4 ml) solution of compound (**7a**) (22.9 mg, 0.095 mmol) in a quartz cell was irradiated under argon for 6 h using a merry-go-round apparatus with a Toshiba 450 Hg high-pressure lamp through a UV-25 (Toshiba glass filter) aqueous solution of 2,4-dimethyl-1,5-diazacyclohepta-1,4-diene iodate (0.2 g l^{-1} ; 1 cm width)

combination filter system for irradiation at 254 nm. After removal of the solvent, the reaction mixture was analysed by ^1H n.m.r. spectroscopy in CDCl_3 and naphthalene was observed as the sole product.

Sensitized Photoreaction of compound (**7a**).—(a) A solution of compound (**7a**) (20.3 mg, 0.084 mmol) and xanthone (2.7 mg, 0.014 mmol; E_t 74 kcal mol^{-1}) in C_6D_6 (300 μl) was irradiated with a Ushio 100 Hg high-pressure lamp through a Pyrex filter purged with argon, and the reaction was followed by 60 MHz ^1H n.m.r. spectroscopy. Only naphthalene (δ_{H} 7.45) and *p*-difluorobenzene (δ_{H} 6.53) were detected as products.

(b) A solution of compound (**7a**) (28 mg, 0.084 mmol) and acetone (45 mg, 0.78 mmol; E_t 80 kcal mol^{-1}) in C_6D_6 (300 μl) was irradiated with a Ushio 100 W Hg high-pressure lamp under the same conditions as above. Only naphthalene and *p*-difluorobenzene were detected as products.

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