A Nuclear Magnetic Resonance Study of the Photoisomerisation Products of Dimethyl 2-Fluoro-9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate

Ralf Sieckmann*

Lehrstuhl für Organische Chemie 2, Ruhr-Universität Bochum, 44780 Bochum, Germany

Reprinted from

JOURNAL OF CHEMICAL RESEARCH(S)

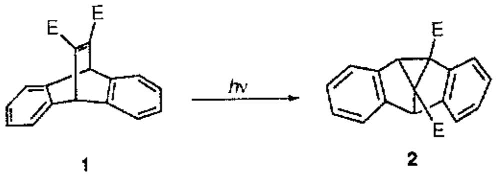
1994

J. Chem. Research (S),
1994, 172–173
J. Chem. Research (M),
1994, 1080–1089

A Nuclear Magnetic Resonance Study of the Photoisomerisation Products of Dimethyl 2-Fluoro-9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate

Ralf Sieckmann*
Lehrstuhl für Organische Chemie 2, Ruhr-Universität Bochum, 44780 Bochum, Germany

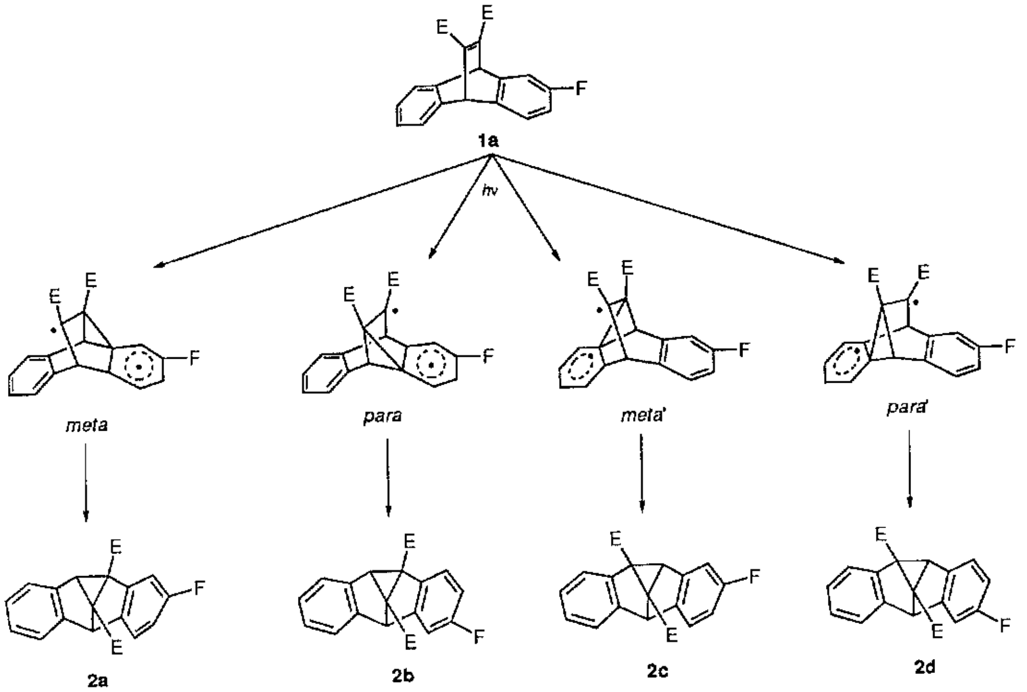
This study deals with the structural assignment of the isomerisation products obtained by the sensitized and direct photolysis of dimethyl 2-fluoro-9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate (**1a**). It is known that the parent compound dimethyl 9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate (**1**) in solution[1] and in the solid state[2] is exclusively converted into dimethyl pentacyclo$[7.7.0.0^{2,16}.0^{3,8}.0^{10,15}]$hexadeca-3,5,7,10,12,14-hexaene-1,2-dicarboxylate (**2**; dimethyl dibenzosemibullvalene-8b,8d-dicarboxylate). Likewise, dibenzobarrelenes with other electron-withdrawing groups at the vinyl position (CN, CF_3, COPh) exclusively form semibullvalenes.[1,3] Even some dibenzobarrelenes with electron-donating groups [Me, $CH_2C(CN)_2$—] can be converted exclusively into the corresponding semibullvalene upon sensitized photolysis.[4,5] The photoisomerisation process of **1** is illustrated in Scheme 1 (with $E = CO_2Me$) and the corresponding photoisomerisation process of **1a** in Scheme 2.



Scheme 1

LIS Studies in ^{1}*H NMR and* ^{19}*F NMR.*—Shift experiments using $Eu(fod)_3$ were run and the bound shift values were found to be in the narrow range for the aromatic protons of unsubstituted and fluoro-substituted benzene rings. With compounds of structure **2a** a doublet of doublets with an *ortho* HF-coupling (9.2 Hz) and a *meta* HH-coupling (2.7 Hz) was shifted farthest downfield and corresponded to the signal for the proton at C-4, whereas for compounds of structure **2b** a first-order doublet of doublets with an *ortho* HH-coupling (8.7 Hz) and a *meta* HF-coupling (5.1 Hz) was shifted.

Compounds of structures **2c** and **2d** show at first view almost identical shifting patterns for most of the protons in the shifted spectrum, *i.e.*, a first-order doublet of doublets with an *ortho* HH-coupling (8.3 Hz) and a *meta* HH-coupling (2.4 Hz) for the proton at C-4. On closer inspection, however, the characteristic proton patterns found suitable for differentiating between **2a** and **2b** are also found to be helpful in the shifted spectra of **2c** and **2d**, which at *ca.* 7 ppm are the only ones not substantially shifted due to their unfavourable steric position at C-14. Thus, isomer **2c** shows a doublet of doublets with an *ortho* HH-coupling and a *meta* HF-coupling, having identical patterns as the most shifted signal of **2b**. Isomer **2d** shows a doublet of doublets with an *ortho* HF-coupling and a *meta* HH-coupling having identical patterns as the most progressive signal of **2a**.



Scheme 2

NMR Results.—The chemical shifts (^{1}H,^{19}F) of the dimethyl fluoropentacyclo$[7.7.0.0^{2,16}.0^{3,8}.0^{10,15}]$hexadeca-3,5,7,10,12,14-hexaene-1,2-dicarboxylates **2a–d** are presented in Table 1 together with those of the parent compound dibenzosemibullvalene dimethyl ester (**2**).

Quantum Yields.—The quantum yields for product formation during the di-π-methane rearrangement upon direct and sensitized irradiation in comparison to the parent compound are shown in Table 4. The first point to note is that the introduction of a fluorine substituent into the benzene moiety of the molecule produces a large degree of chemical deactivation for energy dissipation. Further, in halide-substituted

---

* *Present address:* Baumstrasse 8, 45128 Essen, Germany.

Table 1 ^{1}H and ^{19}F NMR chemical shifts (ppm) of compounds **2** and **2a–d**[a]

X[b]	**2**[c]	**2a**[d]	**2b**[d]	**2c**[d]	**2d**[d]
C-4	7.28(0.34)	7.00(0.33)	7.22(0.33)	7.29(0.32)	7.31(0.32)
C-5	7.14(0.13)	*−117.22(0.16)*	6.81(0.13)	7.14(0.13)*	7.13(0.13)*
C-6	7.11(0.11)	6.83(0.08)	*−115.46(0.11)*	7.10(0.11)*	7.11(0.11)*
C-7	7.19(0.15)	7.11(0.15)	6.88(0.14)	7.29(0.15)	7.18(0.15)
C-9 (d)	5.07(0.36)	5.01(0.35)	5.02(0.35)	5.02(0.34)	5.03(0.34)
C-11	7.19(0.11)	7.35(0.10)	7.17(0.11)	7.09(0.11)	6.87(0.11)
C-12	7.14(0.04)	7.13(0.05)*	7.13(0.06)*	6.79(0.05)	*−115.67(0.13)*
C-13	7.08(0.00)	7.10(0.00)*	7.09(0.00)*	*−117.45(0.05)*	6.75(0.05)
C-14	7.33(0.00)	7.17(−0.01)	7.34(0.00)	7.03(−0.01)	7.19(−0.01)
C-16 (d)	4.51(1.00)	4.50(1.00)	4.49(1.00)	4.45(1.00)	4.45(1.00)
C-1″ (q)[e]	3.74(0.12)	3.75(0.10)	3.74(0.09)	3.75(0.08)	3.74(0.07)
C-2″ (q)[e]	3.89(0.25)	3.90(0.23)	3.89(0.23)	3.89(0.21)	3.89(0.21)

[a]LIS values (relative to the shift of the proton at C-16) are given in parentheses. [b]Numbering of the carbon skeleton starting from the central cyclopropane ester carbon. [c]For comparison and structure assignment. [d]Values in italics are fluorine chemical shifts. [e]Or reversed. *Signal not resolved in the unshifted spectrum.

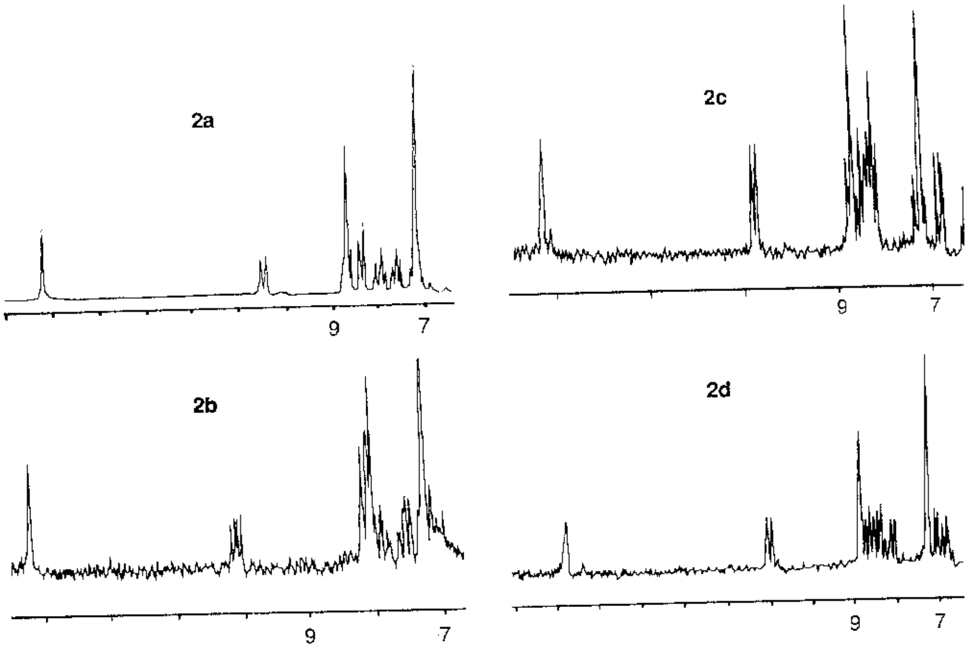


Fig. 1 Results of LIS experiments performed with the photo-isomerisation products

Table 4 Quantum yields of **2a–d** and **2**[a]

	2a	**2b**	**2c**	**2d**	**2a** + **2b**	**2c** + **2d**	Σ(**2a** − **2d**)	**2**
Sens.[b]	0.0258	0.0116	0.0440	0.0252	0.0374	0.0692	0.1066	0.690
Dir.[c]	0.0383	0.0120	0.0497	0.0413	0.0617	0.0910	0.1410	0.650

[a]Concentration 12 μmol l^{-1}. [b]At 366 nm with 25 mmol l^{-1} benzophenone in benzene (corresponding to a 740 μmol l^{-1} sample concentration). [c]At 251 nm in THF.

systems spin–orbit coupling will further enhance the rate of intersystem crossing leading back to the ground state.[6,7] The regioselectivity preferably producing isomers **2c** and **2d** shows that a bridging between the unsubstituted benzene moiety and the vinyl group is more efficient in view of the destabilising effect of the intermediate fluorobenzene radical[2] (see Scheme 2).

Techniques used: Direct and sensitized irradiation, HPLC separation, ^{1}H, ^{13}C and ^{19}F NMR, double-resonance experiments, NOE difference, LIS studies, quantum yield measurements.

References: 13 Schemes: 2 Figure: 1 Tables: 4

Received, 22nd November 1993; Accepted, 14th February 1994
Paper E/3/06925G

References and notes cited in this synopsis

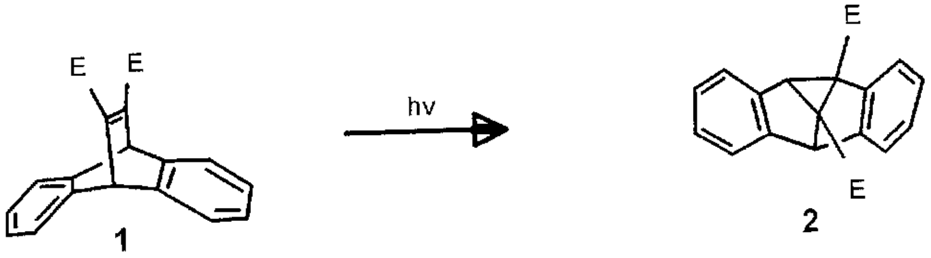
1 E. Ciganek, *J. Am. Chem. Soc.*, 1966, **88**, 2882.
2 J. R. Scheffer, J. Trotter, M. Garcia-Garibay and F. C. Wirego, *Mol. Cryst. Liq. Cryst. Inc. Nonlin. Opt.*, 1988, **156**, 63.
3 N. K. Saxena, M. Maya, P. S. Venkataratami, *Indian J. Chem.* 1975, **13**, 1075; C. V. Kumar, B. A. R. Murthy, S. Lahini, E. Chackeracheri, J. C. Scaiano and V. George, *J. Org. Chem.*, 1984, **49**, 4923.
4 S. J. Christol, R. L. Kaufman, S. M. Opitz, W. Szalecki and T. H. Bindel, *J. Am. Chem. Soc.*, 1983, **105**, 3226.
5 Even the cycloadduct of tetracyanoethylene and 9,10-dihydro-11,12-dimethylene-9,10-ethanoanthracene upon acetone-sensitized photolysis affords the corresponding semibullvalene whereas room-temperature direct photolysis in THF does not result in any photoproduct formation: R. Sieckmann, unpublished results.
6 N. J. Turro, *Modern Molecular Photochemistry*, Benjamin, Menlo Park, 1978, pp. 72–74 and 170–172.
7 R. C. Hahn and R. P. Johnson, *J. Am. Chem. Soc.*, 1975, **97**, 212.

A Nuclear Magnetic Resonance Study of the Photoisomerisation Products of Dimethyl 2-fluoro-9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate

Ralf Sieckmann*
Lehrstuhl für Organische Chemie 2, Ruhr-Universität Bochum, 44780 Bochum, Germany

Introduction

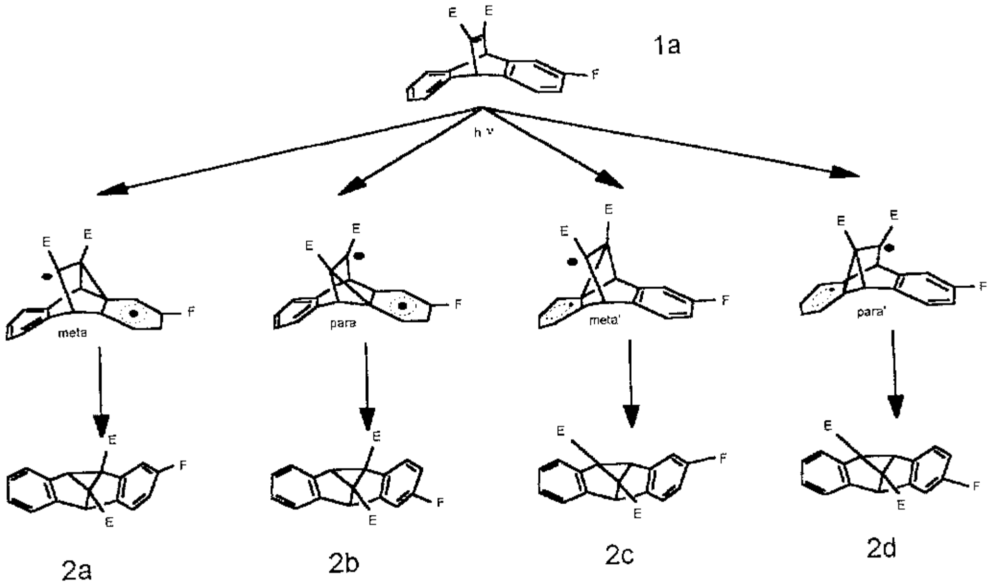
This study deals with the structural assignment of the isomerisation products obtained by the sensitized and direct photolysis of dimethyl 2-fluoro-9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate **1a**. It is known that the parent compound dimethyl 9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate **1** in solution[1] and in the solid state[2] is exclusively converted into dimethyl pentacyclo[7.7.0.0^{2,16}.0^{3,8}.0^{10,15}]hexadeca-3,5,7,10,12,14-hexaene-1,2-dicarboxylate **2** (dimethyl dibenzosemibullvalene-8b,8d-dicarboxylate). Likewise, dibenzobarrelenes with other electron-withdrawing groups at the vinyl position (CN, CF_3, COC_6H_5) exclusively form semibullvalenes.[1,3] Even some dibenzobarrelenes with electron-donating groups (Me, $CH_2C(CN)_2$-) could be exclusively converted into the corresponding semibullvalene upon sensitized photolysis.[4,5] The photoisomerisation process of **1** is illustrated in Scheme 1 (with E=COOMe) and the corresponding photoisomerisition process of **1a** in Scheme 2 .



Scheme 1

---

*Present address: Baumstr. 8, 45128 Essen, Germany



Scheme 2

NMR-Results

The chemical shifts ($^1H,^{19}F$) of the dimethyl fluoropentacyclo[7.7.0.0^{2,16}.0^{3,8}.0^{10,15}]-hexadeca-3,5,7,10,12,14-hexaene-1,2-dicarboxylates (**2a-d**) are presented in Table 1 together with those of the parent compound dibenzosemibullavalenedimethylester (**2**), the corresponding LIS-values being supplemented in parenthesis. The (relative) LIS-values are defined as the difference between the shifted and the unshifted spectrum of a proton H_i (Hz) divded by the difference of the between the shifted and the unshifted spectrum of the proton at C-16 (Hz) both of which proton measured separely at several additions of Eu(fod)$_3$. The carbon chemical shifts of the dimethyl fluoropentacyclo[7.7.0.0^{2,16}.0^{3,8}.0^{10,15}]hexadeca-3,5,7,10,12,14-hexaene-1,2-dicarboxylates **2a-d**) are presented in Table 2 together with those of the parent compound (**2**).

Table 1. ^{1}H and ^{19}F NMR chemical shifts (ppm) of compounds **2** and **2a** - **2d**[a]

X[b]	2[c]	2a[d]	2b[d]	2c[d]	2d[d]
C-4	7.28 (0.34)	7.00 (0.33)	7.22 (0.33)	7.29 (0.32)	7.31 (0.32)
C-5	7.14 (0.13)	*- 117.22 (0.16)*	6.81(0.13)	7.14 (0.13)*	7.13 (0.13)*
C-6	7.11(0.11)	6.83 (0.08)	*-115.46 (0.11)*	7.10 (0.11)*	7.11 (0.11)*
C-7	7.19 (0.15)	7.11 (0.15)	6.88 (0.14)	7.29 (0.15)	7.18 (0.15)
C-9(d)	5.07 (0.36)	5.01 (0.35)	5.02 (0.35)	5.02 (0.34)	5.03 (0.34)
C-11	7.19 (0.11)	7.35 (0.10)	7.17 (0.11)	7.09 (0.11)	6.87 (0.11)
C-12	7.14 (0.04)	7.13 (0.05)*	7.13 (0.06)*	6.79 (0.05)	*- 115.67 (0.13)*
C-13	7.08 (0.00)	7.10 (0.00)*	7.09 (0.00)*	*- 117.45 (0.05)*	6.75 (0.05)
C-14	7.33 (0.00)	7.17 (-0.01)	7.34 (0.00)	7.03 (-0.01)	7.19 (-0.01)
C-16(d)	4.51 (1.00)	4.50 (1.00)	4.49 (1.00)	4.45 (1.00)	4.45 (1.00)
C-1'' (q)[e]	3.74 (0.12)	3.75 (0.10)	3.74 (0.09)	3.75 (0.08)	3.74 (0.07)
C-2'' (q)[e]	3.89 (0.25)	3.90 (0.23)	3.89 (0.23)	3.89 (0.21)	3.89 (0.21)

[a] LIS-values (relative to the shift of the proton at C-16) are given in parentheses.[9]

[b] Numbering of the carbon skeleton starting from the central cyclopropane ester carbon.

[c] For comparison and structure assignment.

[d] Values in italics are fluorine chemical shifts.

[e] Or reversed.

* Signal not resolved in the unshifted spectrum.

Table 2. ^{13}C NMR chemical shifts (ppm) of compounds **2a-2d** and 2[a]

X[b]	2[c]	2a	2b	2c	2d
C-3	133.39	135.37*	130.10	133.32	133.55
C-4	125.75(159)	113.53+	127.13*	125.94	125.94
C-5	126.81(159)	162.32#	113.94+	127.02	127.22
C-6	127.78(159)	114.94+	162.50#	128.03	128.06
C-7	121.21(159)	122.32*	108.80+	121.28	121.58
C-8	149.80	145.44◆	152.00	149.90	149.23
C-9 (d)	55.70(149)	55,11	55,72	55,09	55.59
C-10	149.92	150.01	148.90	145.72◆	152.00
C-11	121.32(159)	121.24	121.51	122.26*	108.95+
C-12	127.52(159)	127.82	127.02	114.48+	162.67#
C-13	126.81(159)	127.03	125.58	162.50#	113.78+
C-14	125.37(159)	125.61	125.58	112.93+	126.40*
C-15	134.59	134.43	134.82	136.70*	130.31◆
C-16 (d)	49.30(173)	49.50	49.01	48.99	48.59
C-1	57.40	57.04	57.50	57.50	57.32
C-2	67.30	68.15	67.94	67.94	67.63
C-1'	168.40	168.03	168.21	168.21	168.40
C-2'	169.20	169.06	168.80	168.80	169.15
C-1''(q)[d]	52.20(148)	52.44	52.34	52.34	52.41
C-2''(q)[d]	52.60(148)	52.92	52.78	52.78	52.86

coupling constants (1st order (CF)): #: ~245 Hz; +: ~24 Hz; *: ~9 Hz; ◆: ~3 Hz.

[a] The carbon chemical shifts of isomers **2a-2d** were assigned by correlation with the corresponding shifts of the parent compound 2 and fluorobenzene.

[b] Numbering of the carbon skeleton starting from the central ester carbon.

[c] For comparison, 1st order coupling constants in parenthesis.

[d] Or reversed.

[e] Or reversed.

Structural Assignment by Nuclear Overhauser Effect difference

The assignment of the benzylic methoxycarbonyl group's position relative to the substituted aromatic ring could be done unequivocally by measuring the nuclear Overhauser difference enhancement (nOe difference) by saturating (i) the transition of the cyclopropane proton at C-16 and (ii) the transition of the dibenzylic proton at C-9, respectively, thereby studying the increased signal pattern in the aromatic region of the neighbouring protons which atoms being only about 0.25 nm and about 0.31 nm, respectively, apart as could be estimated from a FMM. The said measurements were performed with compounds **2a**, **2c** and **2d** and the results are sumarised in Table 3.

Table 3 NOe difference measurements

Photo isomer	saturated transition (ppm)		NOe difference at (ppm)
	δ_H	Proton at	δ_H (multiplicity or coupling constants;Proton)
2a	4.50	C-16	7.17 (m; C-14)
2a	5.01	C-9	7.11 (dd, 8.7 and *5.4* Hz; H_7) 7.35 (m;H_{11})
2c	4.45	C-16	7.03 (dd; *9.2* and 2.7 Hz; H_{14})
2c	5.02	C-9	7.09 (dd;8.7 and *5.4* Hz; H_{11}) 7.29 (dd;H_7)
2d	4.45	C-16	7.19 (dd; 8,7 and *5.4* Hz; H_{14})
2d	5.03	C-9	6.87 (dd;*9.2* and 2.7 Hz; H_{11}) 7.18 (dd;H_7)

1st order HF coupling constants in italics

LIS-studies in ^{1}H NMR and ^{19}F NMR

Furthermore, shift experiments using Eu(fod)$_3$ were run and the bound shift values were found to be in a narrow range for the aromatic protons of the unsubstituted and fluoro-substituted benzene rings. With compounds of structure **2a** a doublet of doublets with an *ortho* HF-coupling (9.2 Hz) and a *meta* -HH-coupling (2.7 Hz) was shifted farthest down field and corresponded to the signal of the proton at C-4 whereas for compounds of structure **2b** a first-order doublet of doublet with an *ortho* HH-coupling (8.7 Hz) and a *meta* HF-coupling (5.1 Hz) was shifted.

Compounds of structures **2c** and **2d** show at first view almost identical shifting patterns for most of the protons in the shifted spectrum i.e. a first-order doublet of doublets with an *ortho* HH-coupling (8.3 Hz) and a *meta* HH-coupling (2.4 Hz) for the proton at C-4. On closer inspection, however, the characteristic proton patterns found suitable for differentiating between **2a** and **2b** are also found to be helpful in the shifted spectra of **2c** and **2d, which** at *ca.* 7 ppm are the only ones not substantially shifted due to their unfavourable steric position at C-14. Thus, isomer **2c** shows a doublet of doublets with an *ortho* HH-coupling and a *meta* HF-coupling, having identical patterns as the most shifted signal of **2b**. Isomer **2d** shows a doublet of doublets with an *ortho* HF-coupling and a *meta* HH-coupling having identical patterns as the most progressive signal of **2a**. The results of the LIS-experiments are shown in Figure 1. The bound shift values (LIS) based on the position of the signal of the cyclopropane proton are reported in table 1. In an analogous way LIS-values were obtained for the fluorine nuclei and, quite unexpectedly, are found to be in the same range as evaluated for the protons for all the isomers except **2d**.

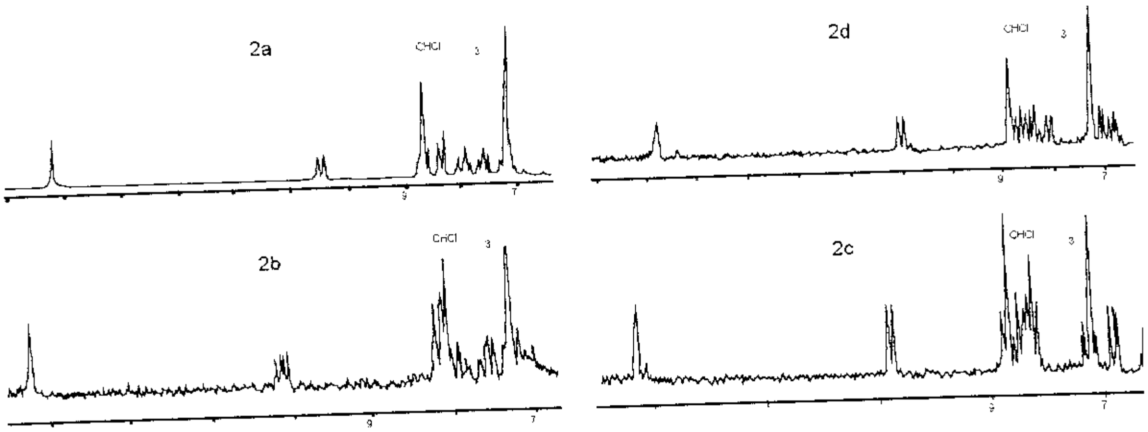


Figure 1. Results of LIS experiments performed with the photoisomerisation products.

Quantum Yields

The quantum yields of the product formation during the di-π-methane rearrangement upon direct and sensitized irradiation in comparison to the parent compound are shown in Table 4.

Table 4 Quantum yields of **2a** - **2d** and **2**^{a}

	2a	**2b**	**2c**	**2d**	2a+2b	2c+2d	Σ(2a-2d)	**2**
sens.^{b}	0.0258	0.0116	0.0440	0.0252	0.0374	0.0692	0.1066	0.690
dir.^{c}	0.0383	0.0120	0.0497	0.0413	0.0617	0.0910	0.1410	0.650

^{a} Concentration 12 μmol l^{-1}. ^{b} At 366 nm with 25 mmol l^{-1} benzophenone in benzene (corresponding to a 740 μmol l^{-1} sample). ^{c} At 251 nm in THF.

The first point to note is that the introduction of a fluorine substituent into the benzene moiety of the molecule produces a large degree of chemical deactivation for energy dissipation i.e., "nuclear motion towards a geometry where the excited-state and the ground-state hyperfaces come close to reach a funnel"[6] (compare Σ (**2a-2d**) to 2). Further, in halide-substituted systems spin-orbit coupling will further enhance the rate of intersystem crossing leading back to the ground state.[6,7] The regioselectivity preferably producing isomers **2c** and **2d** shows that a bridging between the unsubstituted benzene moiety and the vinyl group is more efficient in view of the destabilising effect of the intermediate fluorobenzene radical[2] (see Scheme 2). The regioselectivity found could be also predicted by simple Hückel calculations[8] with a through space parameter of 0.2ß wherein the bond orders of the LUMO could be used to explain why the ratio of **2c** > **2a** ~ **2d** > **2b** shows the same trend.

Experimental

The melting points were corrected and were taken using a Tottoli apparatus (Büchi SA, Swiss). ^1H NMR spectra were recorded on a Bruker WP 80 (80 MHz), Bruker WH 250 (250 MHz) and Bruker AM 400 spectrometer (400 MHz). ^{19}F NMR spectra were run using a Bruker WP 80 spectrometer (75.4 MHz), standard C_6F_6 was set on -163.00 ppm. the ^{13}C NMR spectra were recorded on (A) Bruker WH 90 (22.64 MHz) and (B) Bruker WM 400 (100.61 MHz) spectrometers. The pulse width was 6 µsec for A and 4 µsec for B with a sweep width of 1000 Hz for A and 25,000 kHz for B. The flip angles were 30° and 50°, respectively. The number of scans ranged from 2,000 to 20,000, depending on solubility. The samples were recorded in $CDCl_3$ at ambient temperature applying internal deuterium lock, and are referenced to the central peak (δ = 77.00) corresponding to δ = 0.00 for TMS; the chemical shifts are accurate to at least 0.05 ppm. 1 NOe differences were measured on a Bruker WP 80 spectrometer using solutions of 15 µmol sample in 0.5 ml $CDCl_3$ after degassing with nitrogen for 15 min. in an ultrasonic bath. Shift experiments with $Eu(fod)_3$ (Merck) were performed using a Bruker WP 80 spectrometer and the solvent $CDCl_3$. The procedure of Roth and Rewicki was used to obtain the bound shift values.[9] LIS-values of fluorine nuclei were defined as the difference (Hz) of F_i obtained from the ^{19}F NMR spectrum divided by the difference (Hz) of H at C_{16} obtained from ^1H NMR. The mass spectra were measured on a Varian CH 5 spectrometer. High resolution mass spectra were recorded using a Varian MAT 731 (70 eV) spectrometer. For calculation of the theoretical values the following molecular weight values were used: H: 1.0078, C: 12.0000, N: 14.0031 and F: 18.9984. The IR spectra were recorded on a Perkin-Elmer 257 spectrometer and the UV spectrum using a Perkin-Elmer 402 spectrometer.

Preparative irradiations were run in a Rayonet-Photochemical-Reactor RPR 100 (Southern New England Ultraviolet Company) equipped with RPR 253.7 nm sunlight-phosphor lamps. Analytical and semipreparative separations were conducted with an HPLC device comprising a Waters

M 6000 pump, a Waters UK 6 injector and a LDC UV 254 nm detector. Peak heights and peak areas determinations were performed with a LDC 308 computing integrator. The quantum yields were obtained with an apparatus comprising a HBO 200 lamp and a Bausch & Lomb high-intensity monochromator. The light quanta were measured by a device described by Amrein et al.[10] which was calibrated by ferrioxalate actinometry.[11] The quantum yields were obtained by conversion of less than about 4.5 %.

The synthesis of 2-fluoroanthracene was performed using the sequence of E. D. Bergman et al. comprising Friedel-Crafts acylation, zinc dust reduction, further reduction with P/HI, cyclisation and zinc dust reduction.[12] The purity of the intermediates was monitored by ^{19}F NMR obtaining the following data (in ppm as ddd):
2-(4-fluorobenzoyl)benzoic acid: -106.10; 3-(4-fluorobenzyl) phthalide: -113.02; 2-(4-fluorobenzyl)-benzoic acid: -118.63; [2-fluoro-9,10-anthraquinone: -102.883 (12.4%, reference); 2-fluoro-9-anthrone: -115.55 (70%); 2-fluoro-9-anthranol: - 113.22(17.6%)]; 2-fluoroanthracene: -115.43.

Dimethyl 2-fluoro-9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate **1a** was prepared by subjecting a mixture of 2-fluoroanthracene (2 g; 10.2 mmol) and dimethyl acetylenedicarboxylate (3g; 21.2 mmol) to a thermal treatment at about 200°C for 15 minutes followed by working up as described by Diels and Alder.[13] Yield: 81%; mp 144-145°C (MeOH). MS, high resolution, found 338.0938, required $C_{20}H_{15}O_4F$ 338.095. ^{1}H NMR (acetone-d_6; 400 MHz): 3.76 (s, 6H), 5.66 (s, 1H), 5.69 (s, 1H), 6.78 (ddd, 1H), 7.29 (dd, 1H), 7,46 (dd, 1H), 7.01-7.08 and 7.41-7.48 ppm (AA'BB' , 4H); J_{HF} = 9.4 Hz and 5.3 Hz; J_{HH} = 8.5 Hz and 2.56 Hz. ^{19}F NMR ($CDCl_3$): -118.235 ppm (ddd). ^{13}C NMR ($CDCl_3$): 51.816 (dd, 1C, J_{CF}: 1Hz), 52.247 (d, 1C), 52.247 (q, 2C), 111.297 (d, 1C, J_{CF}=22 Hz), 112.079 (d, 1C, J_{CF}=24 Hz), 123.646 (d, 1C), 123.808 (d, 1C), 124.428 (d, 1C, J_{CF}=8.4 Hz), 125.426 (d, 1C), 125.588 (d, 1C), 139.47 (s,1C, J_{CF}=3Hz), 143.41 (s, 1C, J_{CF}=11 Hz), 145.924 (s; 1C), 146.403 (s, 2C), 147.374 (s, 1C), 160.397 (s, 1C, J_{CF}=245.4 Hz), 165.493 ppm (s, 2C). MS, m/z (relative intensity): 339 (21), 338 (97, M^+), 310 (14), 280 (14), 279 (88), 278 (100), 251 (30), 247 (20), 220 (53), 196 (44). UV (EtOH): 283 (3.32), 276 (3.32), 237 (3.33) 217 nm (4.10).

Photoisomerisation of **1a:**

A solution of **1a** (100 mg; 296 μmol) in dry acetone (350 ml) was irradiated in a quartz vessel which was thoroughly purged with nitrogen prior to and during the reaction while tap water cooled the solution in a Rayonet Photochemical Reactor comprising 16 sunlight phosphor lamps. The irradiation was run until **1** had been completely converted into photoisomers. The solvent was removed *in vacuo* and the photoisomers separated by semipreparative normal phase HPLC (column: C18 on LiChrosorb® Si 100, 5 μm, 150 mm 15.5 mm i.d.; mobile phase: hexane/ether/-MeCN: 95/4/1). Three fractions **2a**, (**2b**,**2c**) and **2d** were separated and the solvents of the first and of the third fraction removed *in vacuo* to yield the corresponding photoisomers. The solvent from the second fraction was also removed and the said sample was again subjected to the above separation. Finally, 20 mg **2a**, 3 mg **2b**, 20 mg **2c** and 15 mg of **2d** were obtained.

2a: m.p.: 130 °C (THF); MS, high resolution, found 338.0938, required 338.095 $C_{20}H_{15}0_4F$. IR(KBr-disk): 3030, 2990, 2940, 1735, 1725, 1620, 1595, 1490, 1440, 1340, 1310, 1300, 1255, 1225, 1175, 1165, 1160, 1090, 1050, 810, 770, 760, 735 cm^{-1}. MS, m/z (relative intensity): 339 (11), 338 (49,M^+), 280 (16), 279 (78), 278 (100), 251 (27), 247 (23), 221 (28), 220 (80), 219 (23), 218 (22), 207 (15).

2b: m.p.: 120 °C (pentane); MS, high resolution, found 338.095, required 338.095 $C_{20}H_{15}0_4F$. IR(KBr-disk): 3010, 2960, 2920, 2850, 1735, 1720, 1598, 1480, 1440, 1335, 1295, 1250, 1230, 1175, 1082, 935, 870, 805, 768, 735 cm^{-1}. MS, m/z (relative intensity): 339 (11), 338 (50, M^+), 279 (91), 278 (100), 251 (51), 247 (15), 221 (34), 220 (94).

2c: m.p.: 117 °C (pentane); MS, high resolution, found 338.0957, required 338.095 $C_{20}H_{15}0_4F$. IR (KBr-disk): 3030, 2920, 1725, 1600, 1480, 1435, 1390, 1300, 1240, 1180, 1090, 1015, 890, 840, 820, 790, 745 cm^{-1}. MS, m/z (relative intensity): 339 (14), 338 (59, M^+), 280 (17), 279 (94), 278 (100), 251 (39), 247 (26), 221 (29), 220 (93), 219 (24), 218 (27), 207 (19).

2d: m.p.: 100 °C (THF); MS, high resolution, found 338.0984, required 338.095 $C_{20}H_{15}0_4F$. IR (KBr-disk): 3060, 2990, 2930, 1735, 1720, 1600, 1480, 1440, 1340, 1310, 1230, 1175, 1090, 1015, 950, 750, 740 cm^{-1}. MS, m/z (relative intensity): 339 (12), 338 (54, M^+), 280 (17), 279 (88), 278 (100), 251 (31), 247 (23), 221 (32), 220 (90), 219 (22), 218 (23).

The author gratefully acknowledges the financial support by the Lehrstuhl für Organische Chemie 2 of the Ruhr-Universität Bochum. He thanks Prof. H. Hemetsberger for his guidance and fruitful discussions, Mr. J. Hartmann, for recording the NMR spectra and Mr. H. Ricken for assistance with HPLC separations.

References

1. E. Ciganek, *J. Am. Chem. Soc.* 1966, **88**, 2882.
2. J. R. Scheffer, J. Trotter, M. Garcia-Garibay, F. C. Wirego, *Mol. Cryst. Liq. Cryst. Inc. Nonlin. Opt.* 1988, **156**, 63-84; .
3. N. K. Saxena, M. Maya, P.S. Venkaratarami, *Indian J. Chem.* 1975, **13**, 1075; C. V. Kumar, B. A. R. Murthy, S. Lahini, E. Chackeracheri, J. C. Scaiano, V. George, *J. Org. Chem.* 1984, **49**, 4923.
4. S. J. Christol, R. L. Kaufman, S. M. Opitz, W. Szalecki, T. H. Bindel, *J. Am. Chem. Soc.* 1983, **105**, 3226.
5. "Even the cycloadduct of tetracyanoethylene and 9,10-dihydro-11,12-dimethylene-9,10-ethanoanthracene [^{1}H-NMR (d_6-acetone): 3.72 (s; 4H), 5.23 (s; 2H), 6.88-7.08 and 7.18-7.38 ppm (AA'BB', 8H] upon acetone-sensitized photolysis affords the corresponding semibullvalene [^{1}H NMR ($CDCl_3$): 2.90 (d, J: 15.2 Hz, 1H), 2.92 (d, 16.6, 1H), 3.30 (d, 16.6, 1H), 3.40 (s,, 1H), 3.78 (d, 15.8, 1H), 4.42 (s,, 1H), 6,90-7.35 ppm (m,, 8H); MS (high intensity) m/z found: 358.1219, required for $C_{24}H_{14}N_4$: 358.1219] whereas room tempe-

rature direct photolysis in THF does not result in any photoproduct formation;" R. Sieckmann, unpublished results.

6. N. J. Turro, *Modern Molecular Photochemistry*, Benjamin Menlo Park, Reading, London, Amsterdam, Don Hills, Sydney, 1978, 72-74 and 170-172.
7. R. C. Hahn, and R. P. Johnson, *J. Am. Chem. Soc.*, 1975, **97**, 212.
8. A. Streitwieser, *Molecular Orbital Theory for Organic Chemists*, 2nd Ed. Wiley, 1962, 135.
9. K. Roth, D. Rewicki, *Kontakte* (Darmstadt), 1978, 9
10. W. Amrein, J. Gloor, K. Schaffner, *Chimia*, 1974, **28**, 175.
11. C. G. Hachard, C. A. Parker, *Proc. R. Soc.*, 1956, **235**, 518.
12. E. D. Bergmann, J. Blum, S. Butanaro, *J. Org. Chem.*, 1961, **26**, 2311.
13. O. Diels, K. Alder, *Justus Liebigs Ann. Chem.*, 1931, **486**, 191.