# Effect of Substituents in the Course of the Photoisomerization of Dimethyl 2,3-Di-X′-9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylates (X′ = Me, MeO, AcO, Cl, F, $CO_2Me$, CN)

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# Effect of Substituents in the Course of the Photoisomerization of Dimethyl 2,3-Di-X′-9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylates (X′ = Me, MeO, AcO, Cl, F, $CO_2Me$, CN)

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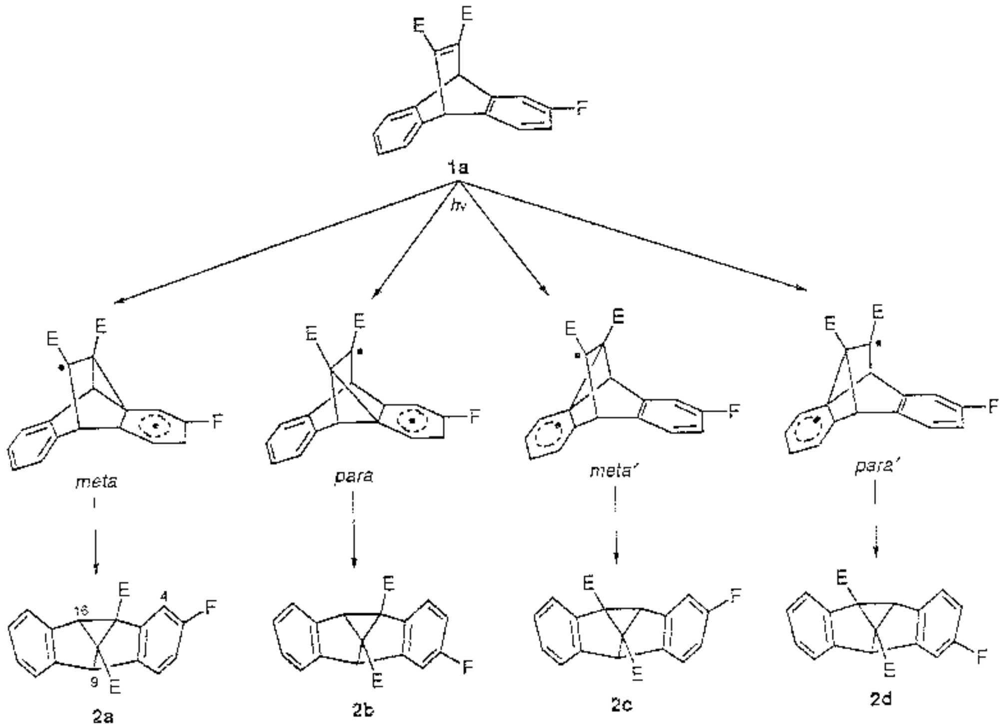
The present study deals with the structural assignment and photochemistry of the isomerization products obtained by the sensitized and direct photolysis of dimethyl 2,3-di-X′-9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate **3** (X′ = Me, MeO, AcO, Cl, F, $CO_2Me$, CN).

It is known that the parent compound dimethyl 9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate 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 (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] A recent study on the photoisomerization products of dimethyl 2-fluoro-9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate (**1a**) has shown that the presence of an electron-withdrawing group on one of the aromatic rings creates a regioselectivity, isomers (**2c**, **2d**) resulting from bridging between the unsubstituted benzene moiety and the vinyl group being preferred.[6] The photoisomerization of **1a** is outlined in Scheme 2 (with E = $CO_2Me$).



Scheme 2

The dimethyl 2,3-di-X-dibenzobarrelene-11,12-dicarboxylates **3a–3g** were synthesized by Diels–Alder addition of dimethyl acetylenedicarboxylate to 2,3-di-X-anthracenes.[7,8]

$^1$H and $^{19}$F NMR shift experiments using $Eu(fod)_3$ were run and the bound shift values were found to be in a close range for the aromatic protons of the unsubstituted and substituted benzene rings. Deviations were only found with substituents containing oxygen because of competitive complexation of the shift reagents with these groups. With compounds of structure **4** a singlet was shifted farthest downfield and corresponded to the signal of the proton at C-4, whereas for compounds of structure **5** a multiplet was shifted. Additional information obtained with **4e** included a doublet of doublets with an *ortho* HF-coupling (10.2 Hz) and a *meta* HF-coupling (7.4 Hz) which was shifted farthest.

Direct and sensitized irradiation of 1 μmol solutions of **3a–3g** in acetone at 300 nm delivered as the sole photoproduct the isomers **4a–4g** and **5a–5g** which could be shown to be photostable. The amount of photoisomers **4** and **5** were evaluated by direct $^1$H NMR analysis in the crude mixture of photoisomers.

The photoreaction of **3a–3g** is sensitized by benzophenone. The relative quantum yield for the parent compound **1** (for comparison) was found to be 0.96 using acetophenone ($E_T = 310$ kJ mol$^{-1}$),[14] 1.00 for benzophenone ($E_T$ 289 kJ mol$^{-1}$)[14] and 0.03 for Michlers ketone ($E_T$ 260 kJ mol$^{-1}$)[14] so that the triplet energy is in the range of 267–276 kJ mol$^{-1}$.

The quantum yields of the benzophenone-sensitized irradiations are higher than those for direct irradiations with the exception of that of the dichloro starting material **3d**. These materials are known to introduce and accelerate intersystem crossing.[15] The remainder of the starting materials

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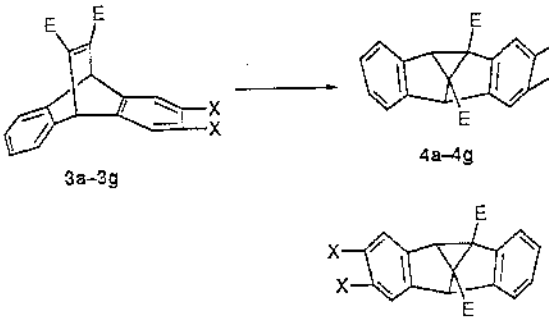
**Table 6** Quantum yields of **4a–4g**, **5a–5g**[a]

| X (substituent) | Isomer **4** |  | Isomer **5** |  | Total |  | Ratio **4** : **5** |  |
|---|---|---|---|---|---|---|---|---|
|  | Dir.[b] | Sens.[c] | Dir.[b] | Sens.[c] | Dir.[b] | Sens.[c] | Dir.[b] | Sens.[c] |
| H[d] (**2**) |  |  |  |  | 0.6480 | 0.6900 | — | — |
| Me (**a**) | 0.0123 | 0.0150 | 0.0123 | 0.0150 | 0.0246 | 0.0300 | 1.00 | 1.00 |
| MeO (**b**) | 0.0097 | 0.0530 | 0.0134 | 0.0550 | 0.0231 | 0.1085 | 0.72 | 0.96 |
| OAc (**c**) | 0.0272 | 0.0520 | 0.0333 | 0.0780 | 0.0605 | 0.1300 | 0.82 | 0.66 |
| Cl (**d**) | 0.0560 | 0.0870 | 0.0810 | 0.0138 | 0.1410 | 0.2250 | 0.69 | 0.63 |
| F (**e**) | 0.0904 | 0.0722 | 0.0875 | 0.0531 | 0.1780 | 0.1250 | 1.03 | 1.36 |
| $CO_2Me$ (**f**) | [e] | 0.2210 | [e] | 0.0501 | [e] | 0.2720 | 4.74 | 4.41 |
| CN (**g**) | 0.3020 | 0.3370 | 0.0450 | 0.0505 | 0.3470 | 0.3870 | 6.71 | 6.67 |

[a]Concentration 12 μmol $l^{-1}$. [b]At 251 nm in THF. [c]At 366 nm with 25 mmol $l^{-1}$ benzophenone in benzene (corresponding to a 740 μmol $l^{-1}$ sample concentration). [d]Parent compound for comparison.[3] [e]Only the ratio of isomers was determined.



**3a–3g**

**4a–4g**

**5a–5g**

X = **a**, Me; **b**, MeO; **c**, OAc; **d**, Cl; **e**, F; **f**, $CO_2Me$; **g**, CN

**Scheme 3**

show pretty well the triplet transition state and an insufficient intersystem crossing from the lowest singlet state. The Stern–Vollmer analysis of the quenching experiments with piperylene gave a straight line which confirms with a triplet state as the photoreactive state.

The ratio of quantum yields of the isomers **4** *vs.* **5** agrees well for sensitized and direct irradiations of Me-, AcO- and Cl-starting materials, whereas it is lower for the fluorine starting material **3e**. Applying the finger-print method of Kasha,[16] that the excited state is the same as the photoreactive state if the ratio of products is the same for direct and sensitized irradiations, it can be concluded that, at least in the former cases with adjacent electron-accepting substituents, the entire photoreaction is present in the triplet state. In the remaining three cases with adjacent electron-donating substituents, at least a portion of the photo rearrangement may proceed through the singlet state.

If one looks at the ratios of regioisomers formed in the direct or sensitized irradiations of the molecules **3a–3g**, the triplet state was found to be the electronic excited state. In the case of the dichloro molecule **3d**, a part of the photoreaction is formed from the excited singlet state. Not considering parent compound **1** and the methyl isomer **3a**, it seems as if the efficiency of intersystem crossing (ISC) goes from an electron donor substituent such as methoxy ($\phi_{ISC}$ 0.21) to an electron acceptor group such as cyano ($\phi_{ISC}$ 0.89). In the same order an increase in the ratio of **4** *vs.* **5** was found. This means that the reaction path initiated by a substituted benzo-vinyl bridging is favoured if electron-withdrawing groups are present. Regioselectivity can be the result of preferential bridging of the vinyl moiety to the benzene or to the substituted benzene ring forming an intermediate as recently outlined and shown in Scheme 2.[6] Another way to explain the regioselectivity could be a preferential return of the said intermediates to the starting material caused by the substituents.

As can be seen from Table 6 the quantum yields for photoisomerization are lower for disubstituted dimethoxycarbonyl dibenzobarrelenes than for the parent compound irrespective of the electron-donating or electron-withdrawing properties of the substituents. The reduced efficiency of the triplet states to react to form products can be the result of enhanced ISC back to the ground state of the starting materials as a consequence of increased spin-orbit coupling caused by the hetero atoms of the substituents. However, the very low quantum yield of the methyl starting material argues against this being the only reason.

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

References: 36

Fig. 1: Results of LIS experiments performed with the photoisomers **4a** and **5a**

Schemes: 3

Tables: 13

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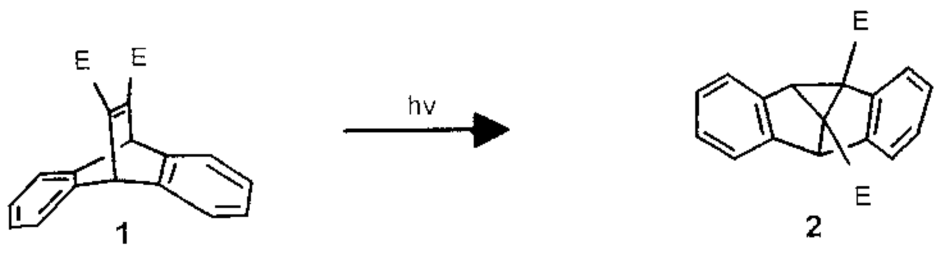
## INTRODUCTION

To study the effect of substituents on the relative reactivity of the triplets in the di-π-methane rearrearrangement double-connected systems - in this case two aryl moieties are connected to one vinyl moiety - such as 5,6-disubstituted dibenzobarrelenes would be useful. Systems of this structure are supposed to react by benzo-vinyl bridging leading to two photoisomers, one as the result of successful interaction of the substituted aryl ring and the other as a consequence of bridging of the unsubstituted ring with the vinyl group. 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 = $CO_2Me$). A recent study on the photoisomerisation products of dimethyl 2-fluoro-9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate **(1a)** has shown that the presence of an electron-withdrawing group on one of the aromatic rings creates a regioselectivity, isomers **(2c, 2d)** resulting from bridging between the unsubstituted benzene moiety and the vinyl group being preferred.[6] The photoisomerisation of **1a** is outlined in Scheme 2 (with E=$CO_2Me$ ).

The present study deals with the structural assignment and with the photochemistry of the isomerisation products obtained by the sensitized and direct photolysis of dimethyl 2,3-di-X'-9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate **3**, which process is outlined in Scheme 3 (with E=$CO_2Me$ and X as defined below ).



**Scheme 1**

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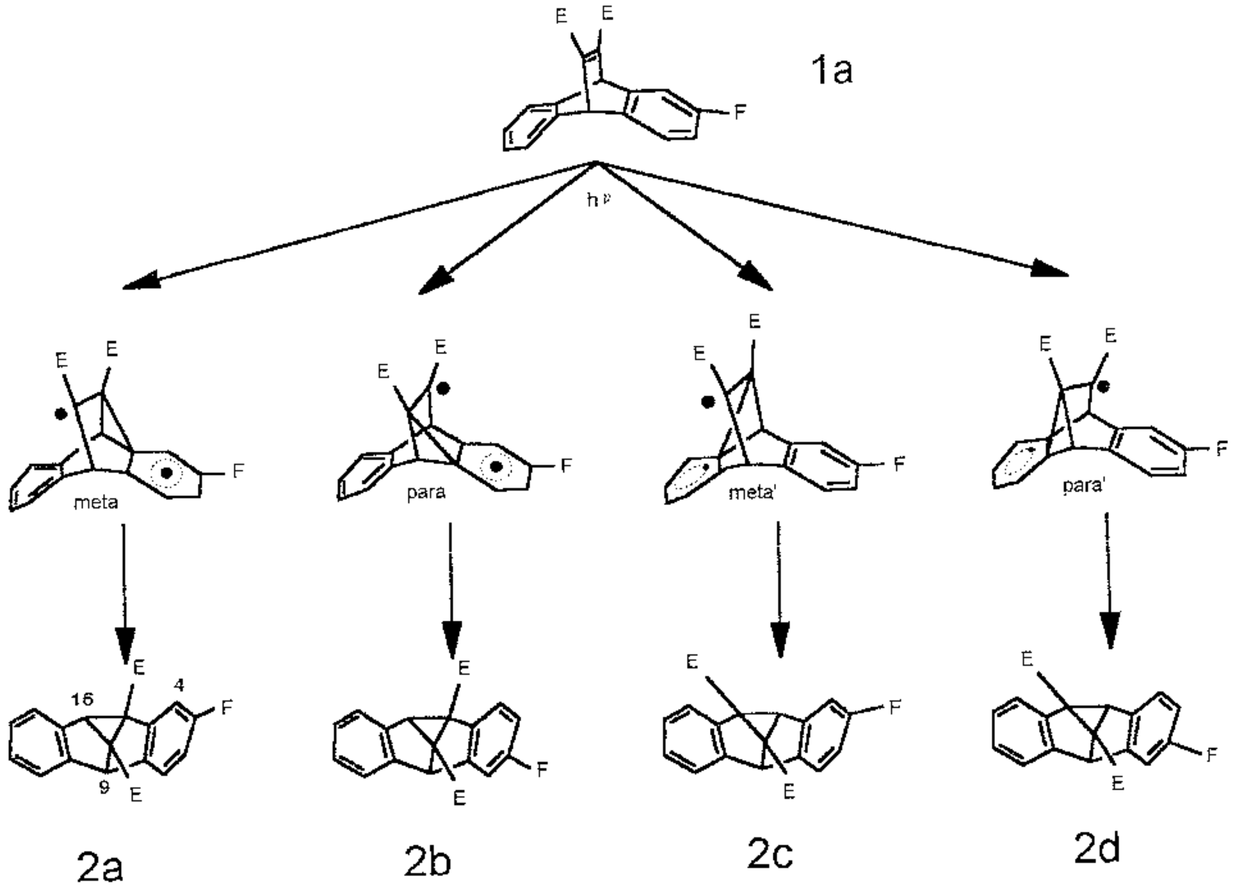
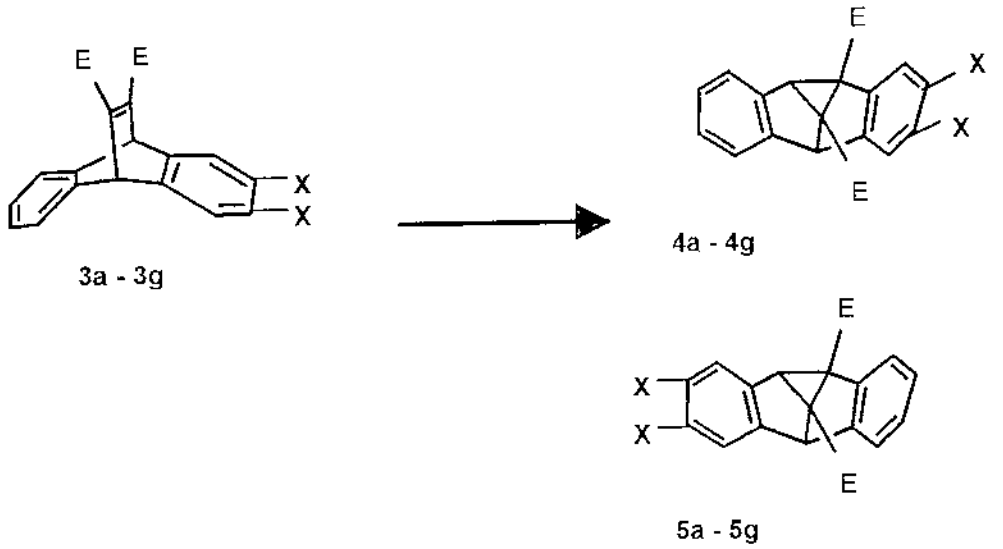


Scheme 2



**X** a: Me, b: MeO, c: OAc, d:Cl, e: F, f: $CO_2Me$, g: CN.

Scheme 3

## RESULTS

### Synthesis of the starting materials and photoisomers

The dimethyl 2,3-di-X-dibenzobarrelene-11,12-dicarboxylates **3a** - **3g** were synthesized by Diels-Alder addition of dimethyl acetylenedicarboxylate to 2,3-di-X-anthracenes.[7] The syntheses of the corresponding anthracenes have been published with the exception of 2,3-difluoroanthracene and 2,3-dicyanoanthracene.[8] 2,3-Difluoroanthracene was obtained by zinc-dust reduction of the corresponding 2,3-difluoro-9,10-anthraquinone, the latter being obtained from 2,3-dichloro-9,10-anthraquinone.[31] 2,3-Dicyanoanthracene was prepared by a multi-step diene synthesis using dicyanoacetylene instead of diethyl acetylenedicarboxylate in the penultimate step of a procedure of Angus and Johnson.[9]

The synthesis of the photoisomers **4a** - **4g** and **5a**- **5g** was performed by sensitized irradiation in acetone with 300 nm lamps to complete conversion of the starting material. The photoisomers were separated by preparative HPLC and were obtained pure with the exception of the dicyano photoisomers **4g** and **5g**.

### NMR Results

The chemical shifts ($^1H$,$^{19}F$) of the dimethyl 5,6-di-X-pentacyclo[$7.7.0.0^{2,16}.0^{3,8}.0^{10,15}$] hexadeca-3,5,7,10,12,14-hexaene-1,2-dicarboxylates **4a-g** are presented in Table 1, the corresponding LIS-values being supplemented in parentheses. The corresponding chemical shifts of the 12,13-isomers **5a-5g** are presented in Table 2. The proton NMR assignments in Tables 1 and 2 have been performed in view of the known data from parent compound **2** and from the monofluoro photoisomers **2a - 2d**.[6] The (relative) LIS-values are defined as the difference (in Hz) between the shifted and the unshifted spectrum of a proton $H_i$ divided by the difference (also in Hz) between the shifted and the unshifted spectrum of the proton at C-16, both protons being measured separately at several additions of $Eu(fod)_3$.[10] The carbon chemical shifts of the dimethyl 5,6-di-X-pentacyclo[7.7.0.$0^{2,16}$.$0^{3,8}$.$0^{10,15}$]hexadeca-3,5,7,10,12,14-hexaene-1,2-dicarboxylates **4a-g** are presented in Table 4 and those of the 12,13-isomers **5a- 5e, 5g** are presented in Table 5 together with those of the parent compound **2**.[6] The carbon chemical shifts of isomers 4 (C-3 to C-8) or of **5** (C-10 to C-15), respectively, were assigned by correlation with the corresponding shifts of *ortho*-di-X-benzenes, a method used to assign molecules comprising *ortho*-di-X-benzene moieties.[11] [The correlation coefficient for **4** exceeded 0.997 for the C-4 to C-7 and was 0.98 for C-8, and for isomer **5** they exceeded 0.998 for the C-11 to C-14 and was 0.985 for the remaining chemical shifts.] The results from incremental calculations of 2-benzyl-1-cyclopropylbenzene were found to be not helpful.

**Table 1** $^1$H and $^{19}$F NMR chemical shifts of compounds **4a-4g**[a]

| X[b] | 4a | 4b | 4c | 4d | 4e[c] | 4f | 4g |
|---|---|---|---|---|---|---|---|
| **C-4** | **7.03(0.34)** | **6.80(0.87)** | **7.11(0.41)** | **7.39(0.32)** | **7.12(0.32)** | **7.67(0.52)** | **7.81(0.33)** |
| **C-5** | | | | | *-139.3(0.18)* | | |
| **C-6** | | | | | *-140.9(0.17)* | | |
| **C-7** | **6.95(0.16)** | **6.69(0.61)** | **7.01(0.23)** | **7.14(0.15)** | **6.97(0.13)** | **7.51(0.34)** | **7.58(0.16)** |
| **C-9(d)** | **5.00(0.35)** | **4.96(1.32)** | **5.00(0.37)** | **5.00(0.35)** | **5.00(0.35)** | **5.09(0.36)** | **5.14(0.35)** |
| **C-11** | **7.18(0.11)** | **f (0.28)** | **f (0.14)** | **f (0.11)** | **7.13(0.13)** | **f (0.13)** | **f (0.11)** |
| **C-12** | **7.11(0.04)** | **f (0.10)** | **f (0.05)** | **f (0.05)** | **7.12(0.05)** | **f (0.05)** | **f (0.05)** |
| **C-13** | **7.07(-0.01)** | **f (0.05)** | **f (0.00)** | **7.08 (0.01)** | **7.14(0.01)** | **f (0.02)** | **7.11(0.00)** |
| **C-14** | **7.35(-0.03)** | **7.35(0.07)** | **7.35(0.00)** | **7.35(0.00)** | **7.35(-0.01)** | **7.33(0.00)** | **7.38(0.00)** |
| **C-16** | **4.47(1.00)** | **4.46(1.00)** | **4.48(1.00)** | **4.51(1.00)** | **4.49(1.00)** | **4.55(1.00)** | **4.67(1.00)** |
| **C-1"** | **3.73(0.08)** | **3.73(0.11)** | **3.73(0.08)** | **3.75(0.11)** | **3.75(0.11)** | **3.75(0.08)** | **3.78(0.11)** |
| **C-2"** | **3.89(0.22)** | **3.89(0.23)** | **3.87(0.20)** | **3.90(0.22)** | **3.89(0.23)** | **3.90(0.19)** | **3.93(0.22)** |
| **C-5'**[d] | **2.17(0.10)** | **3.78(0.60)** | | | | | |
| **C-6'**[d] | **2.17(0.08)** | **3.82(0.58)** | | | | | |
| **C-5"**[e] | | | **2.24(0.12)** | | | **3.84(0.21)** | |
| **C-6"**[e] | | | **2.22(0.11)** | | | **3.87(0.22)** | |

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[a] LIS-values (relative to the shift of the proton at C-16) are given in parentheses.[10,6]

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

[c] Values in italics are fluorine chemical shifts.

[d] Or reversed.

[e] Or reversed.

[f] Signal not resolved in the unshifted spectrum.

Structural Assignment by Nuclear Overhauser Effect Difference

The assignment of the position of the benzylic methoxycarbonyl group relative to the substituted aromatic ring could be done unequivocally by measuring the nuclear Overhauser difference enhancement (nOe difference) by saturating the transition of the cyclopropane proton at C-16, thereby studying the increased signal patterns in the aromatic region of the neighbouring protons.[6] These experiments were performed with the photoisomers **4b**, **4e**, **5e**, **4f** and **5f** , the results of which are summarised in Table 3. With the compounds belonging to structure **4** a multiplet appeared corresponding to the resonance signal at the neighbouring aromatic proton being only ca. 0.25 nm apart as could be estimated from a FMM. In contrast, with photoisomer **5** a singlet appeared, whereas with **5e** a doublet of doublets gave evidence for an *ortho-* and a *meta*-coupling with the fluorine nuclei.

**Table 2** $^1$H and $^{19}$F NMR chemical shifts of compounds 5a-5g$^a$

| X$^b$ | 5a | 5b | 5c | 5d | 5e$^c$ | 5f | 5g |
|---|---|---|---|---|---|---|---|
| C-4 | 7.29(0.34) | 7.30(0.33) | 7.30(0.33) | 7.29(0.33) | 7.29(0.32) | 7.27(0.32) | 7.29(0.31) |
| C-5 | 7.12(0.14) | f (0.24) | f (0.14) | f (0.11) | 7.16(0.13) | 7.14(0.10) | f |
| C-6 | 7.14(0.11) | f (0.12) | f (0.11) | f (0.10) | 7.17(0.10) | 7.14(0.09) | f |
| C-7 | 7.19(0.15) | f (0.12) | f (0.18) | f (0.13) | 7.16(0.14) | 7.18(0.14) | f |
| C-9(d) | 5.01(0.35) | 4.97(0.80) | 5.03(0.35) | 5.02(0.35) | 5.00(0.35) | 5.11(0.35) | 5.19(0.34) |
| C-11 | 6.94(0.11) | 6.69(0.73) | 7.00(0.25) | 7.19(0.12) | 6.95(0.11) | 7.51(0.32) | 7.58(0.12) |
| C-12 | | | | | *-139.3(0.15)* | | |
| C-13 | | | | | *-141.0(0.07)* | | |
| C-14 | 7.10(-0.02) | 6.87(0.35) | 7.11(0.15) | 7.39(-0.01) | 7.12(-0.01) | 7.67(0.18) | 7.74(0.00) |
| C-16 | 4.45(1.00) | 4.43(1.00) | 4.48(1.00) | 4.51(1.00) | 4.42(1.00) | 4.52(1.00) | 4.58(1.00) |
| C-1" | 3.73(0.10) | 3.74(0.15) | 3.73(0.12) | 3.75(0.10) | 3.75(0.10) | 3.75(0.09) | 3.77(0.08) |
| C-2" | 3.88(0.25) | 3.89(0.21) | 3.88(0.24) | 3.88(0.24) | 3.88(0.23) | 3.89(0.23) | 3.91(0.22) |
| C-12'$^d$ | 2.18(0.03) | 3.82(0.54) | | | | | |
| C-13'$^d$ | 2.18(0.03) | 3.79(0.43) | | | | | |
| C-12"$^e$ | | | 2.24(0.10) | | | 3.85(0.21) | |
| C-13"$^e$ | | | 2.23(0.06) | | | 3.87(0.13) | |

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[a] LIS-values (relative to the shift of the proton at C-16) are given in parentheses.[10]

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

[c] Values in italics are fluorine chemical shifts.

[d] Or reversed. [e] Or reversed.

[f] Signal not resolved in the unshifted spectrum.

**Table 3** nOe difference measurements

| Photo-isomer | Saturated transition (ppm). proton at carbon-N° 16 | nOe difference of proton at carbon N° 14 (ppm) $\delta_H$ (multiplicity or coupling constants) |
|---|---|---|
| **4b** | 4.46 | 7.35 (m; 7.5 and 2.5 Hz) |
| **4e** | 4.49 | 7.35 (m; 7.7 and 2.5 Hz) |
| **5e** | 4.42 | 7.12 (*dd*; *10.2* and *7.4* Hz) |
| **4f** | 4.55 | 7.33 (m; 7.5 and 2.6 Hz ) |
| **5f** | 4.52 | 7.67 (s) |

First order HF coupling constants in italics.

## 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 a close range for the aromatic protons of the unsubstituted and substituted benzene rings. The proton NMR (LIS) assignments in Tables 1 and 2 above have been performed in view of the previously published data from parent compound **2** and from the monofluoro photoisomers **2a** - **2d**.[6] Deviations with repect to these data were only found with substituents containing oxygen (MeO, OAc, COOMe) because of competitive complexation of the shift reagents with these groups. With compounds of structure **4** a singlet was shifted farthest downfield and corresponded to the signal of the proton at C-4, whereas for compounds of structure **5** a multiplet was shifted. Additional information obtained with **4e** intended a doublet of doublets with an *ortho* HF-coupling (10.2 Hz) and a *meta* HF-coupling (7.4 Hz) which was shifted farthest. The results of the LIS-experiments of compounds **4a** and **5a** are shown in Fig. 1. The bound shift values (LIS) based on the position of the signal of the cyclopropane proton are reported in tables 1 and 2. In an analogous way LIS-values were obtained for the fluorine nuclei and , quite unexpectedly, were found to be in the same range as those evaluated for the protons.

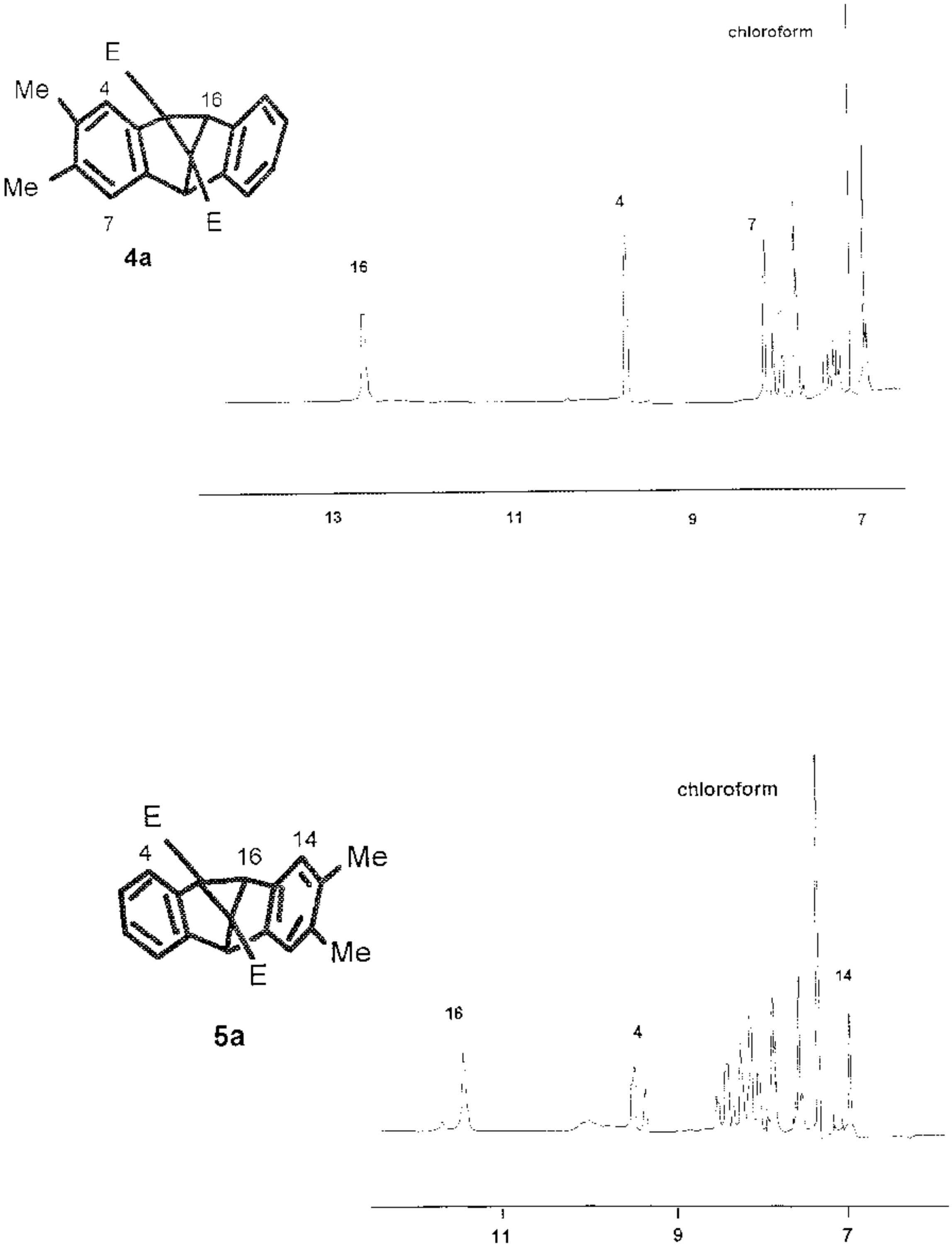

Fig.1 Results of LIS experiments performed with the photoisomers **4a** and **5a**

**Table 4** $^{13}$C NMR chemical shifts (ppm) for compounds **4a-4g** [a]

| X[b] | 4a | 4b | 4c | 4d | 4e[c] | 4f | 4g |
|---|---|---|---|---|---|---|---|
| C-3 | 131.00 | 128.00 | 132.98 | 133.53 | 130.50 | 136.71 | 139.18 |
| C-4 | 126.72 | 109.08 | 121.30 | 127.94 | 115.01 | 127.00 | 131.65 |
| C-5 | 135.25 | 148.54 | 141.04 | 131.04 | 149.71 | 131.13 | 114.63 |
| C-6 | 136.25 | 149.50 | 141.66 | 131.86 | 150.08 | 131.80 | 115.09 |
| C-7 | 121.52 | 104.81 | 116.15 | 123.09 | 110.17 | 124.00 | 126.23 |
| C-8 | 147.62 | 142.01 | 147.64 | 149.57 | 146.00 | 152.51 | 154.44 |
| C-9(d) | 55.38 | 55.56 | 55.38 | 55,32 | 55.42 | 55.65 | 55.50 |
| C-10 | 149.10 | 150.10 | 149.10 | 148.99 | 149.30 | 148.62 | 147.32 |
| C-11 | 121.38 | 121.05 | 121.38 | 121.52 | 121.31 | 121.70 | 121.73 |
| C-12 | 127.85 | 127.46 | 127.85 | 128.13 | 127.87 | 128.21 | 128.83 |
| C-13 | 127.15 | 126.21 | 127.15 | 127.46 | 127.57 | 127.57 | 128,37 |
| C-14 | 125.59 | 125.67 | 125.59 | 125.67 | 125.57 | 125.66 | 126.00 |
| C-15 | 134.59 | 134.64 | 134.59 | 134.46 | 134.39 | 134.46 | 134.13 |
| C-16(d) | 48.74 | 49.28 | 48.74 | 49.53 | 49.27 | 49.53 | 50.31 |
| C-1 | 57.37 | 56.62 | 57.37 | 56.32 | 56.30 | 56.77 | 56.20 |
| C-2 | 67.36 | 67.27 | 67.94 | 67.78 | 67.78 | 68.15 | 68.00 |
| C-1' | 168.82 | 168.57 | 168.08 | 167.57 | 167.95 | 167.52 | 166.49 |
| C-2' | 169.52 | 169.27 | 168.73 | 168.73 | 168.65 | 168.61 | 167.70 |
| C-1''(q)[d] | 52.23 | 52.23 | 52.34 | 52.19 | 52.31 | 52.54 | 52.80 |
| C-2''(q)[d] | 52.74 | 52.65 | 52.63 | 53.01 | 52.76 | 52.92 | 53.95 |
| other C | 19.78 | 55.92 | 167.81 |  |  | 167.73 | 115,33 |
|  | 19.87 | 56.02 | 167.82 |  |  | 167.73 | 115.33 |
| other C |  |  | 20.32;20.32 |  |  | 52.62;52.62 |  |

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[a] The carbon chemical shifts of isomers **4a-4g** were assigned by correlation with the corresponding shifts of the parent compound **2** (table 5 below) and with those of 1,2-di-X-benzenes.[11]

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

[c] Coupling constants (1st order (CF)): C-12,F ca. 248 Hz;C-11,F ca.20 Hz.

[d] Or reversed.

**Table 5** $^{13}$C NMR chemical shifts (ppm) for compounds **5a-5e, 5g** ; **2**[a]

| X[b] | 2 [c] | 5a | 5b | 5c | 5d | 5e[d] | 5g |
|---|---|---|---|---|---|---|---|
| C-3 | 133.39 | 132.22 | 134.65 | 132.97 | 133.37 | 133.22 | 134.18 |
| C-4 | 125.75(159) | 125.79 | 125.82 | 125.91 | 126.00 | 125.92 | 126.00 |
| C-5 | 126.81(159) | 126.73 | 126.67 | 127.19 | 127.46 | 127.17 | 128.37 |
| C-6 | 127.78(159) | 127.76 | 127.70 | 128.13 | 128.37 | 128.08 | 129.00 |
| C-7 | 121.21(159) | 121.21 | 121.06 | 121.38 | 121.54 | 121.31 | 121.73 |
| C-8 | 149.80 | 150.20 | 149.08 | 148.02 | 148.90 | 149.21 | 147.36 |
| C-9(d) | 55.70(149) | 55.41 | 55.56 | 55.38 | 55.17 | 55.28 | 55.50 |
| C-10 | 149.92 | 147.69 | 142.01 | 149.10 | 149.78 | 146.03 | 154.60 |
| C-11 | 121.32(159) | 122.58 | 105.05 | 116.31 | 123.18 | 110.37 | 126.52 |
| C-12 | 127.52(159) | 135.98 | 149.08 | 141.66 | 131.58 | 150.08 | 115.08 |
| C-13 | 126.81(159) | 135.13 | 148.44 | 141.08 | 130.95 | 149.66 | 114.63 |
| C-14 | 125.37(159) | 126.52 | 108.69 | 120.30 | 127.28 | 114.28 | 131.73 |
| C-15 | 134.59 | 133.55 | 128.20 | 133.52 | 134.88 | 130.54 | 140.70 |
| C-16(d) | 49.30(173) | 49.41 | 49.59 | 48.72 | 48.34 | 48.50 | 48.31 |
| C-1 | 57.40 | 57.44 | 57.32 | 57.37 | 57.41 | 57.16 | 56.20 |
| C-2 | 67.30 | 67.42 | 67.57 | 67.94 | 67.45 | 67.67 | 68.00 |
| C-1' | 168.40 | 168.67 | 168.57 | 168.08 | 167.97 | 167.95 | 166.54 |
| C-2' | 169.20 | 169.52 | 169.27 | 168.73 | 168.73 | 168.85 | 167.72 |
| C-1''(q)[e] | 52.20(148) | 52.23 | 52.23 | 52.19 | 52.93 | 52.31 | 52.80 |
| C-2''(q)[e] | 52.60(148) | 52.71 | 52.65 | 52.63 | 52.95 | 52.71 | 53.34 |
| other C |  | 19.63 | 55.93 | 167.81 |  |  | 115.33 |
|  |  |  |  | 167.81 |  |  | 115.33 |
| other C |  | 19.63 | 56.03 | 20.32;20.32 |  |  |  |

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[a] The carbon chemical shifts of isomers **5a-5e and 5g** were assigned by correlation with the corresponding shifts of the parent compound **2** and with those of 1,2-di-X-benzenes.[11]

[b] Numbering of the carbon skeleton starting from the central ester carbon. [c] For comparison.[6]

[d] Coupling constants (1st order (CF)): C-12,F ca. 248 Hz; C-11,F ca. 20 Hz. [e] Or reversed.

## Photorearrangement

Direct and sensitized irradiation of **3a-3g** in acetone of 1 μmol solutions at 300 nm delivered as the sole photoproduct the isomers **4a-4g** and **5a-5g** which could be shown to be photo-stable. The amount of the photoisomers **4** and **5** were evaluated by direct $^1$H NMR analysis of the crude mixture of photoisomers. The signals for the cyclopropane proton of the photoisomers **4** were always found at lower chemical shifts than those of the corresponding photoisomers 5. Since the values obtained this way were less accurate than those from HPLC measurements the ratio results are given in connection with the quantum yield determination.

### Multiplicity studies and quantum yields

The quantum yields for product formations were obtained with an apparatus comprising an HBO 200 lamp and a Bausch and Lomb high intensity monochromator. The light quanta were measured by a device described by Amrein et al.[12] which was calibrated by ferrioxalate actinometry.[13] The quantum yields measured were obtained by conversion of less than 5 % with two exceptions and are collected in Table 6. The photoreaction of **3a** - **3g** is sensitized by benzophenone. The relative quantum yield for the parent compound **1** (for comparison) was found to be 0.96 using acetophenone ($E_T$ = 310 KJ / mole)[14], 1.00 for benzophenone ($E_T$ 289 KJ / mole)[14] and 0.03 for Michlers ketone ($E_T$ 260 KJ / mole)[14] so that the triplet energy is in the range of 267 - 276 KJ / mole. The piperylene concentration of **1** gave a straight line with a slope of 22 and an intercept of one.

**Table 6** Quantum Yields of **4a-4g**, **5a-5g**[a]

| X | Isomer **4** | | Isomer **5** | | Total | | Ratio (4/5) | |
|---|---|---|---|---|---|---|---|---|
| (Substituent) | Dir.[b] | Sens.[c] | Dir.[b] | Sens.[c] | Dir.[b] | Sens.[c] | Dir.[b] | Sens.[c] |
| H[d] (2) | | | | | 0.6480 | 0.6900 | ./. | ./. |
| Me (a) | 0.0123 | 0.0150 | 0.0123 | 0.0150 | 0.0246 | 0.0300 | 1.00 | 1.00 |
| MeO (b) | 0.0097 | 0.0530 | 0.0134 | 0.0550 | 0.0231 | 0.1085 | 0.72 | 0.96 |
| OAc (c) | 0.0272 | 0.0520 | 0.0333 | 0.0780 | 0.0605 | 0.1300 | 0.82 | 0.66 |
| Cl (d) | 0.0560 | 0.0870 | 0.0810 | 0.0138 | 0.1410 | 0.2250 | 0.69 | 0.63 |
| F (e) | 0.0904 | 0.0722 | 0.0875 | 0.0531 | 0.1780 | 0.1250 | 1.03 | 1.36 |
| COOMe (f) | e | 0.2210 | e | 0.0501 | e | 0.2720 | 4.74 | 4.41 |
| CN (g) | 0.3020 | 0.3370 | 0.0450 | 0.0505 | 0.3470 | 0.3870 | 6.71 | 6.67 |

[a] Concentration 12 μmol $l^{-1}$. [b] At 251 nm in THF. [c] At 366 nm with 25 mmol $l^{-1}$ benzophenone in benzene (corresponding to a 740 μmol $l^{-1}$ sample concentration). [d] Parent compound for comparison.[6] [e] Only the ratio of isomers was determined.

Interpretative discussion

The quantum yields of the benzophenone sensitized-irradiations are higher than those for direct irradiations with the exception of that of the dichloro starting material **3d**. The said materials are known to introduce and accelerate intersystem crossing.[15] The remainder of the starting materials show pretty well a triplet transition state and an insufficient intersystem crossing from the lowest singlet state. The Stern-Vollmer analysis of the quenching experiments with piperylene gave a straight line which confirms with a triplet state as the photo reactive state.

The ratio of quantum yields of the isomers **4** *versus* **5** agrees well for sensitized and direct irradiations of Me-, AcO- and Cl-starting materials, whereas it is lower for the fluorine starting material **3e**. Applying the finger-print method of Kasha[16], that the excited state is the same as the photo reactive state if the ratio of products is the same for direct and sensitized irradiations, it can be concluded that, at least in the former cases with adjacent electron-accepting substituents, the entire photoreaction is present in the triplet state. In the remaining three cases with adjacent electron-donating substituents, at least a portion of the photo rearrangement may proceed through the singlet state.

In this connection it should be noted that also the efficiencies of the direct and sensitized irradiations show a surprising trend. These is a remarkable increase in the quantum when going from dibenzobarrelene through ethoxycarbonyl dibenzobarrelene to dimethoxycarbonyl dibenzobarrelene (Table 7 ).

Table 7 Quantum yields of (vinyl(di)substituted) dibenzobarrelenes

| Compound | $\varnothing_{366}$(sens.)[a] | $\varnothing_{251}$(dir.) |
|---|---|---|
| Dibenzobarrelene.[17] | 0.19 | 0.04 |
| Ethoxycarbonyl dibenzobarrelene.[18] | 0.46 | 0.12 |
| Dimethoxycarbonyl dibenzobarrelene.[6] | 0.69 | 0.65 |

[a] Benzophenone in benzene.

This increase is more straight with the direct than with the sensitized irradiations. One explanation of this is that increasing the number of methoxycarbonyl groups in the molecule will enhance the efficiency of intersystem crossing. In addition and likewise, a lowering of the triplet energy may be expected. Using the line of argument put forward by Zimmerman[19] to explain the preference of vinyl-vinyl bonding over benzo-vinyl bonding in benzobarrelene, styrene[20] ($E_T$ = 268 KJ/mol) would be isoconjugated with dibenzobarrelene and ethyl cinnamate[21] ($E_T$ = 240 KJ/Mol) with ethoxycarbonyl dibenzobarrelene. With this lowering of the triplet energy the quantum yield increases to 250%. An ethoxycarbonyl-substituted cinnamic ester would be isoconjugated with **1**. This is cross-conjugated and leads to less stabilisation and an increase in quantum yield of only

150%. A comparable more efficient population of the triplet state with the parent starting material was found for the other starting materials **3a - 3g** and , in fact, no fluorescence could be detected for **3a**, **3e** or **3g.**

The molecules **3a- 3g** comprise three chromophores, namely aromatic, substituted aromatic and vinylic. It is known that two chromophores linked by a methylene group to form a molecular arrangement in same cases show interactions. From the PE spectra of benzobarrelenes it has been concluded that homoconjugative interactions of the π-molecular fragments exist. [22]

Since none of the molecules **3a - 3g** fluorescence there is no real chance to obtain rates. Consequently, this discussion only deals with trends in regioselectivity and quantum yields.

If one looks at the ratios of regioisomers formed in the direct or sensitized irradiations of the molecules **3a - 3g** , the triplet state was found to be the electronic excited state. In the case of the dichloro molecule 3d a part of the photoreaction is formed from the excited singlet state. Not considering parent compound **1** and the dimethyl isomer **3a** it seems as if the efficiency of intersystem crossing is going from an electron donor substituent such as methoxy ($\varnothing_{ISC}$= 0.21) to an electron acceptor group such as cyano ($\varnothing_{ISC}$ = 0.89). In the same order an increase in the ratio of **4** *versus* **5** was found. This implies that the reaction path initiated by a substituted benzo-vinyl bridging is favoured if electron-withdrawing groups are present. Regioselectivity can be the result of preferential bridging of the vinyl moiety to the benzene or to the substituted benzene ring forming an intermediate as recently outlined and shown in Scheme 2.[6] Another way to explain the regioselectivity could be a preferential return of the said intermediates to the starting material caused by the substituents.

A Hammett plot of the logarithm of the ratio of the regioisomers - corresponding to the ratio of substituted benzo-vinyl bridging and unsubstituted benzo-vinyl bridging - *versus* the σ+ or σ-values of Brown and Okamoto[23] and of Biggs and Robinson[24] shows a straight line for electron-withdrawing groups with a positive slope (i.e. $\rho > 0$). The correlation coefficients are 0.997 and 0.999. In contrast thereto, a plot of various σ-values for electron-withdrawing substituents shows no correlation (correlation coefficient -0.730).

Zimmerman observed in a study on the di-π-methane rearrangement of 1,1-diaryl-5,5-diphenyl-3,3-dimethyl-1,4-dienes that a plot of $\log(\varnothing_X/\varnothing_H)$ versus σ-values resulted in a straight line with a negative slope.[25] This regiospecificity was the result of a bond breaking. Zimmerman explained this regiospecifity that the carbinyl carbon becoming more positive or less negative as the π-bond is engendered at this side.

The application of the Hammett plot to *ortho*-disubstituted benzene derivatives need some explanation.[11]First of all, $\sigma_p$ and $\sigma_m$-values for electron-withdrawing groups are of the same order, whereas for electron-donating groups $\sigma_p$-values are substantially more negative.[14] Consequently, it can be expected that a plot of the logarithm of the ratio of the isomers should show a better correlation with the $\sigma_p$-values for electron-withdrawing groups than for electron-donors. A positive σ value signifies that in the bond-forming step a carbinyl carbon is formed which is more negative than the carbon of the aromatic ring. Since electron-withdrawing groups allow a better distribution of the negative charge these groups can be expected to favour bond-forming.

MO-calculations have been used to explain the course of photoreaction.[26] In a number of cases even Hückel calculations are sufficient to show that the bond order control is a means of predicting the route of the photoisomerisation. Hückel calculations on **3b**, **3e** and **3g** allowing a weak through-space interaction between the chromophores have been performed. It was found that in the excited state the bond orders of the HOMO and LUMO are greater for substituted benzo-vinyl than for benzo-vinyl bridging, if electron-withdrawing groups are appended. On the other hand, with donor substituents the bond orders are positive for benzo-vinyl bridging in the LUMO but negative in the HOMO. Thus, the observed regiospecifity is at best explained by the bond orders of the LUMOs which can be compared with the more sophisticated calculations of Houk in the case of the photo rearrangement of benzonorbornadienes.[27,28]

As can be seen from Table 6 the quantum yields for photoisomerisation are lower for disubstituted dimethoxycarbonyl dibenzobarrelenes than for the parent compound irrespective of the electron-donating or electron-withdrawing properties of the substituents . The reduced efficiency of the triplet states to react to form products can be the result of enhanced ISC back to the ground state of the starting materials as a consequence of increased spin-orbit coupling caused by the hetero atoms of the sub-stituents. However, the very low quantum yield of the dimethyl derivatives argues against this being the only reason. Another explanation would be the formation of an electron-transfer species which could offer more efficiently a path back to the ground state of the starting material . An argument for this explanation could be the lowering of the electron affinities for the substituted benzene moieties irrespective of donating or withdrawing substituents.[29] Salisbury et al. have used the ionisation potentials in their study of the di-π-methane rearrangement of 1,1-dicyano-2-methyl-3-R-phenylpropenes to explain the observed reactivities.[30]

## Experimental

The melting points were corrected and were taken using a Tottoli apparatus (Büchi SA, Swiss). $^1$H NMR spectra were recorded on Bruker WP 80 (80 MHz), Bruker WH 250 (250 MHz) and Bruker AM 400 spectrometers (400 MHz); the $^{13}$C NMR spectra were recorded on Bruker WH 90 (22.63 MHz), Bruker WH 250 (62.86 MHz) and Bruker AM 400 spectrometers (100.61 MHz) as all-proton noise decoupled and as fully coupled spectra using CDCl$_3$ set to 77.00 ppm. $^{19}$F NMR spectra were run using a Bruker WP 80 spectrometer (75.4 MHz); standard $C_6F_6$ was set on -163.00 ppm. Nuclear Overhauser Effect 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 with CDCl$_3$ as solvent. The procedure of Roth and Rewicki was used to obtain the bound shift values.[10] LIS-values of fluorine nuclei were defined as the difference (Hz) for $F_i$ obtained from the $^{19}$F NMR spectrum divided by the difference (Hz) for H at $C_{16}$ obtained from $^1$H 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, F: 18.9984 and Cl: 34.9689. The IR spectra were recorded on a Perkin-Elmer 257 spec-trometer and the UV spectra 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 an LDC 308 computing integrator.

Synthesis of starting materials:

2,3-Dimethylanthracene, 2,3-dimethoxyanthracene, 2,3-diacetyloxyanthracene, 2,3-dichloroanthracene and dimethyl anthracene-2,3-dicarboxylate are produced in accordance with previously reported methods.[8]

**2,3-Difluoro-9,10-anthraquinone**

A solution of 2,3-dichloro-9,10-anthaquinone[31] (10g; 36.1 mmol) and dry potassium fluoride (10 g; 172 mmol) in 100g diphenylsulfone was allowed to react under stirring for 16 h in a 250 °C silicon-oil bath. After cooling the reaction mixture and dispersing in water 2,3-difluoro-9,10-anthraquinone was precipitated by acidifying with acetic acid. The work-up procedure with $H_2O_2$ recommended by Russian scientists could not be successfully duplicated.[32] The green to yellow masses could be directly used in the next step after drying. 4.86g ; 55.1% yield. m.p.: 195-196°C (subl.); [195-196°C[32]]. $^1$H NMR ($CDCl_3$): $\delta$ = 7.71-7.93 and 8.18-8.40 (AA'BB', 4H), 8.08 ppm (t, 2H, $J_{HF}$=8.6 Hz). $^{19}$F NMR ($CDCl_3$): $\delta$ = -127.65 ppm (t, J=8.6 Hz). MS, m/z (relative intensity) 244($M^+$, 97), 216 ($(M -CO)^+$, 100), 188($(M- 2\ CO)^+$, 88), 197 (26), 94 (29), 31 (63). IR (KBr-disk): 3030, 2990, 1660, 1615, 1580, 1485, 1325, 1270, 840, 702 $cm^{-1}$. $^{13}$C NMR.[11]

**2,3-Difluoroanthracene**

A suspension of zinc dust (20g) and 2,3-fluoro-9,10-anthraquinone (4.86g, 19.9 mmol) in 200 ml ammonia (5%) was refluxed until the initially dark red solution turned to light green. The solid phase was filtered when cooled. Continuous extraction of the solid phase with toluene for 2 days yielded 2,3-difluoroanthracene (2g) in a 46.9 % yield. m.p.: 178-179°C (EtOH). $^1$H-NMR($CDCl_3$) $\delta$ = 7.38-7.60 and 7.84-8.04 (AA'BB', 4H), 7.65 (t, $J_{HF}$ = 9.8 Hz, 2H), 8.30 ppm (s; 2H). $^{19}$F NMR ($CDCl_3$): $\delta$ = -137.15 ppm (t, J = 9.8 Hz). IR (KBr-disk): 3020, 2890, 1630, 1555, 1480, 1452, 1283, 1190, 1130, 890, 860, 735 $cm^{-1}$. UV (MeOH): 363 (3.78), 340 (3.67), 325 (3.50), 249 (5.13), 222 nm (4.20). MS, m/z (relative intensity): 215 (12, $M^{++1}$), 214 (100, $M^+$). MS-high resolution, found 214.0638, required $C_{14}H_8F_2$ 214.0592.

**1,4,5,8,9,10-Hexahydroanthracene-2,3-dicarbonitrile**

2,3-Bismethylene-1,4,5,8-tetrahydronaphthalene obtained from 2,3-bis(hydroxymethyl)-1,4,5,8-tetrahydronaphthalene (2g, 10.4 mmol) according to a procedure of Angus and Johnson[9] was dissolved in 10 ml THF immediately and dicyanoacetylene (0.7g, 9.2 mmol) was added at -10 °C. The glass flask was sealed stopcock protected with a clamp and the content was stirred at room temperature for 4 hours.. The Diels Alder adduct precipitated as a white powder. After filtration and drying 982 mg (45.5 %) were obtained pure having a m.p. of 218-220°C. $^{1}$H NMR (DMSO-$d_6$/$CDCl_3$): $\delta$ = 2.62 (s, 2H), 2,69 (s, 2H), 3.18 (s, 2H), 5.86 ppm (s, 2H). $^{13}$C NMR (DMSO-$d_6$/$CDCl_3$): $\delta$ = 29.16 (t, 2C), 31.16 (t, 2C), 33.66 (t, 2C), 114.50 (s, CN), 119.74 (s, 2C), 121.56 (s, 2C), 122.68 (s, 2C), 131.84 ppm (s, 2C). IR (KBr-disk): 2990, 2845, 2810, 2780, 2210, 1615, 1430, 1410, 965, 955, 750, 670 cm$^{-1}$. MS, m/z (relative intensity): 235 (18, M$^{+1}$), 234 (100), 130 (61), 128 (52), 91 (53), 78 (58). MS-high resolution, found 234.1157, required $C_{16}H_{14}N_2$ 234.1162.

**Anthracene-2,3-dicarbonitrile**

DDQ (2.97 g; 12.81 mmol) was dissolved in dry benzene (150 ml) and 1,4,5,8,9,10-hexahydroanthracene-2,3-dicarbonitrile (1 g; 4.27 mmol) dissolved in dry benzene (400 ml) was added and the mixture stirred overnight. The solvent was removed *in vacuo* and the dry residue was suspended in dry THF (10 ml). The hydroquinone dissolved almost completely. The anthracene-2,3-dicarbonitrile was suction-filtered and carefully washed with a small amount of THF affording the final product in a yield of 520 mg (53.4%). m.p.: 223°C (subl.). The material is only sparingly soluble in common solvents. Thus, no NMR could be performed. IR (KBr-disk): 3060, 2920, 2230, 1630, 1600, 1510, 1500, 1420, 1410, 1190, 1175, 960, 934, 862, 755 cm $^{-1}$. UV (EtOH): 402 (3.61), 374 (3.68), 321 (4.52), 310 (4.54), 279 (4.96), 258 (4.69), 246 nm (4.67). MS, m/z (relative intensity): 228 (100, M$^{+}$), 201 (20), 175 (10), 101 (8), 51 (6), 39 (4). MS-high resolution, found 228.0686, required $C_{16}H_8N_2$ 228.069.

**Dimethyl 2,3-di-X'-9,10-dihydro-9,10-ethenooanthracene-11,12-dicarboxylates (general procedure)[7]**

2,3-Di-X anthracenes were mixed with dimethyl acetylenedicarboxylate in a molar ratio of 1:1 to 1:3 and heated to about 200°C for 10 to 30 min. After cooling the reaction mixture was dissolved in a small amount of benzene and the Diels-Alder adduct purified by column chromatography using silica gel Si 60, Merck® 70 - 230 mesh.

The synthesis of dimethyl 2,3-dimethyl-9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate **3a**[33] and of dimethyl 9,10-etheno-9,10-dihydroanthracene-11,12-dicarboxylate **1** and the photo product thereof **2**[1] is published elsewhere.

**2,3-Dimethoxy** (X' = 0Me; **3b**): molar ratio: 1:2; m.p. : 149-150°C (MeOH); 63.5% yield; $^{1}$H NMR (acetone-d6): $\delta$ : 3.74 (s, 6H), 3.76(s, 6H), 5.52(s, 2H), 6,89-7.11 and 7.20-7.42 (AA'BB'; 4H) and 7.18 ppm (s, 2H). IR (KBr-disk): 3020, 2970, 2840, 1725, 1635, 1510, 1442, 1328, 1298, 1263, 1215, 1082, 1059, 754 cm$^{-1}$. UV(cyclohexane): 297 (3.52), 277 (3.31), 217 nm

(4.33). MS, m/z (relative intensity): 381 ($M^{++1}$,26), 380 ($M^+$), 322 (23), 321 (90), 320 (32), 238(28). MS-high resolution, found 380.1243, required $C_{22}H_{20}O_6$ 380.1254. $^{13}C$ NMR.[11]

**2,3-Diacetoxy** (X' = OCOMe; **3c**): molar ratio 1:2.13. m.p.: 132-133°C (EtOH); 52.7% yield; $^1H$ NMR: δ : 2.20 (s, 6H), 3.75 (s, 6h), 5.66 (s, 2H), 6.96-7.18 and 7.36-7.58 (AA'BB', 4H), 7.18 ppm (s, 2H). IR (KBr-disk): 2835, 1755, 1700, 1620, 1475, 1458, 1430, 1365, 1335, 1275, 1255, 1205, 1162, 1138, 1105, 1055, 1008, 900, 805, 785, 742 $cm^{-1}$. UV (cyclohexane): 289 (3.36), 260 (3.87), 219 (4.47), 202 nm (4.46). MS. m/z (rel. intensity): 436 (16, $M^+$), 394 (24), 353 (24), 352 (100), 293 (53), 292 (48), 216 (17), 182 (16), 44 (16), 43 (42). MS-high resolution, found: 436.1260, required $C_{24}H_{20}O_8$ 436.1152. $^{13}C$ NMR.[11]

**2,3-Dichloro** (X'=Cl; **3d**): 2,3-dichloroanthracene containing 20% of 2-chloroanthracene[34] was used for the Diels-Alder addition as described above: The reaction mixture was separated with HPLC reverse phase using a C18-column, 150 mm, 15.54 mm i.d., and MeOH/water = 70/30. pure material was obtained after extraction and crystallisation. m.p.: 188 °C (MeOH). 54.6% yield; $^1H$ NMR (acetone-$d_6$): δ : 3.77 (s; 6H), 5.71 (s, 2H), 6.98-7.20 and 7.37-7.59 (AA'BB', 4H), 7.65 ppm (s, 2H). IR (KBr-disk): 2930, 1730, 1630, 1460, 1440, 1370, 1260, 1215, 1110, 1055, 945 $cm^{-1}$. UV (cyclohexane): 296 (3.29), 286.5 (3.33), 264 (3.54), 257 (3.65), 252 (3.70), 222 (4.27), 210 nm (4.61). MS, m/z (relative intensity): 390 (30), 388 (56),330 (76), 329 (73), 328 (100), 270 (39). MS-high resolution, found 380.024, required $C_{20}H_{14}O_4Cl_2$ 380.028. $^{13}C$ NMR.[11]

**2,3-Difluoro** (X'=F; **3e**): molar ratio 1:2; m.p. 108-109°C (EtOH); 5% yield; $^1H$ NMR (acetone-$d_6$): δ: 3.78 (s, 6H), 5.68 (2H), 6.96-7.18 and 7.38-7.60 (AA'BB', 4H, 7.45 ppm (t, J = 8.6 Hz; 2H). $^{19}F$ NMR ($CDCl_3$): δ: -142.55 ppm (t, J= 8.6 Hz). IR (KBr-disk): 3080, 3000, 2950, 2840, 1740, 1715, 1640, 1490, 1460, 1435, 1330, 1300, 1270, 1235, 1205, 1145, 1120, 1055, 1030, 880, 750, 670 $cm^{-1}$. UV (MeOH): 283 (3.41), 277 (3.38), 210 nm (4.45). MS, m/z (relative intensity): 357 (16), 356 (55), 313 (38), 312 (48), 297 (89), 296 (100), 269 (44), 238 (70), 214 (69). MS-high resolution, found 356.0847, required $C_{20}H_{14}O_4F_2$ 356.0902. $^{13}C$ NMR.[11]

**2,3-Dimethoxycarbonyl** (X'=$COOCH_3$; **3f**): molar ratio 1:2; m.p. 156-157°C (EtOH); $^1H$ NMR (acetone-$d_6$): δ: 3.77 (s, 6H), 3.82 (s, 6H), 5.82 (s, 2H), 6.99-7.20 and 7.42-7.63 (AA'BB', 4H), 7.81 ppm (s, 2H). IR (KBr-disk): 2990, 2950, 1737, 1721, 1630, 1435, 1335, 1270, 1205, 1120, 1065, 1025, 790, 755 $cm^{-1}$. UV (cyclohexane): 269 (3.74), 261 nm (3.84). MS, m/z (relative intensity): 437 (17), 436 (60), 377 (66), 376 (100), 176 (29). MS high resolution, found 436.150, required $C_{24}H_{20}O_8$ 436.1152. $^{13}C$ NMR.[11]

**2,3-Dicyano** (X'=CN; **3g**): molar ratio 1:1.5; m.p. 228-229°C (MeOH); 61.4 % yield; $^1H$ NMR (acetone-$d_6$): δ: 3.78 (s, 6H), 5.93 (s, 2H), 7.05-7.23 and 7.45-7.63 (AA'BB', 4H), 8.11 ppm (s, 2H). IR (KBr-disk): 3040, 2990, 2230, 1720, 1630, 1480, 1435, 1285, 1130, 1110, 940 $cm^{-1}$.UV (EtOH) 277 (4.40), 239 (4.41), 210 nm (4.23). MS, m/z (relative intensity): 371 (16), 370 (65), 311 (67), 310 (100), 283 (20), 228 (28). MS high resolution, found 370.0971, required $C_{22}H_{14}O_4N_2$ 370.0950. $^{13}C$ NMR.[11]

**2,3-Dihydroxy** (X'=OH; **3h**): obtained quantitatively from **3c** by hydrolysis with a molar excess of conc. HCl in MeOH at elevated temperature and work up in a *per se* known manner. m.p. 215-216°C (MeOH) $^1H$ NMR (acetone-$d_6$) δ: 3.75 (s; 6H), 5.41 (s, 2H), 6.88-7.08 and 7.28-7.48

(AA'BB', 4H), 6.98 (s; 2H), 7.65 ppm (broad s, 2H). IR (KBr-disk): 3500, 3360, 3060, 3020, 2955, 2840, 1720, 1630, 1500, 1435, 1330-1280, 1210, 1140, 1100, 1060, 930, 865, 830, 780, 750, 680 $cm^{-1}$. UV (MeOH) 297 (3.66), 213 nm (4.49). MS, m/z (relative intensity): 353 (26), 352 ($M^{+}$, 81), 293 (100), 292 (72), 234 (44), 210 (43). MS high resolution, found 352.0940, required $C_{20}H_{16}O_6$ 352.0942. $^{13}C$ NMR.[11]

Preparative Photoisomerisation of **3a-3g**:

General procedure: The reactants were dissolved in dried acetone and 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 irradiations were run until all starting materials were converted which was monitored by HPLC. The solvent was removed *in vacuo* and the photoproduct (mixtures) separated by (semi)preparative HPLC under conditions described below.

Irradiation of dimethyl 9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate (**1**) [for comparison]: A solution of 200 mg **1** in 350 ml acetone was irradiated for 15 min.. The solvent was removed *in vacuo* and the oily residue crystallised from MeOH yielding 190 mg 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**).

**2**: m.p. 98°C (MeOH) [lit.[1] 98-99°C]; yield 95%. IR (KBr-disk): 3030, 2960, 1720, 1480, 1439, 1315, 1295, 1255, 1216, 1083, 945, 768, 745, 690 $cm^{-1}$. MS high resolution, found 320.1055, required $C_{20}H_{16}O_4$ 320.1050.

Irradiation of **3a**: A solution of **3a** (70 mg) in acetone (350 ml) was irradiated for 10 min. A $^{1}H$ NMR analysis of the residue show a ratio of **4a** to **5a** of 48 to 52. The reaction mixture was separated by reversed phase HPLC (column: C18 on LiChrosorb® Si 100, 10 μm, 150 mm, 15.5 mm i.d.; mobile phase: MeOH to Water of 70 to 30. Two fractions were collected which were extracted with pentane yielding 27 mg dimethyl 5,6-dimethylpentacyclo[7.7.0.$0^{2,16}$.$0^{3,8}$.$0^{10,15}$]-hexadeca-3,5,7,10,12,14-hexaene-1,2-dicarboxylate (**4a**) and 29 mg dimethyl 12,13-dimethylpentacyclo[7.7.0.$0^{2,16}$.$0^{3,8}$.$0^{10,15}$]hexadeca-3,5,7,10,12,14-hexaene-1,2-dicarboxylate (**5a**).

**4a**: m.p. 70-72°C (pentane); (KBr-disk): 2950, 1731, 1465, 1435, 1385, 1340, 1315, 1292, 1246, 1210, 1160, 1118, 1099, 1070, 749, 720 $cm^{-1}$. UV(cyclohexane): 292 (3.35), 285 (3.38), 266 (3.54), 203 nm (4.17). MS, m/z (relative intensity): 348($M^{+}$, 52), 289 (100), 288 (93), 251 (23), 230 (36), 215 (25). MS (high resolution), found 348.1378, required $C_{22}H_{20}O_4$ 348.1356.

**5a**: m.p. 161-162°C (pentane); IR (KBr-disk). 2935, 1715, 1428, 1360, 1295, 1230, 1190, 1160, 1079, 1032, 735 cm-1; UV (cyclohexane): 293 (3.25), 286 (3.31), 223 (4.37), 212 nm (4.43).MS, m/z (relative intensity) 348 ($M^{+}$, 52), 289. MS high resolution, found: 348.1343, required $C_{22}H_{20}O_4$ 348.1356.

Irradiation of **3b**: A solution of **3b** (100 mg) in acetone (350 ml) was irradiated for 30 min. A $^{1}H$ NMR analysis of the residue show a ratio of **4b** to **5b** of 30 to 70. The reaction mixture was sepa-rated by normal phase HPLC (column: C18 on LiChrosorb® Si 100, 5 μm, 150 mm, 15.5 mm i.d.; mobile phase: hexane to THF of 52 to 8. The solvent was removed yielding 20 mg dimethyl

5,6-dimethoxypentacyclo[$7.7.0.0^{2,16}.0^{3,8}.0^{10,15}$]hexadeca-3,5,7,10,12,14-hexaene-1,2-dicarboxylate (**4b**) and 60 mg dimethyl 12,13-dimethoxypentacyclo[$7.7.0.0^{2,16}.0^{3,8}.0^{10,15}$]hexadeca-3,5,7,10,12,14-hexaene-1,2-dicarboxylate (**5b**).

**4b**: m.p. 94-95 °C (pentane); IR (KBr-disk): 3040, 2970, 2930, 2800, 1710, 1701, 1598, 1490, 1455, 1425, 1330, 1290, 1228, 1188, 1160, 1100, 1090, 1034, 988, 912, 875, 855, 842, 812, 728, 720 $cm^{-1}$. UV (EtOH): 298.5 nm (3.20).MS, m/z (relative intensity): 381 ($M^{++1}$; 14), 380 (57). MS high resolution, found 380.1267, required $C_{22}H_{20}O_6$ 380.1240.

**5b**: m.p. 142-143oC (pentane); IR(KBr-disk): 3045, 2970, 2920, 2810, 1712, 1708, 1595, 1485, 1450, 1425, 1335, 1265, 1225, 1205, 1155, 1070 $cm^{-1}$. UV (EtOH): 299 nm (3.22). MS, m/z (relative intensity): 381 ($M^{++1}$; 14), 380 (58) MS high resolution, found 380.1222, required $C_{22}H_{20}O_6$ 380.1240.

Irradiation of **3c**: A solution of **3c** (100 mg) in acetone (350 ml) was irradiated for 30 min. A $^1$H NMR analysis of the residue show a ratio of **4c** to **5c** of 33 to 67. The reaction mixture was separated by reversed phase HPLC (column: C18 on LiChrosorb Si 100, 10 µm, 150 mm, 15.5 mm i.d.; mobile phase: MeOH to Water of 60 to 40. Two fractions were collected which were extracted with pentane yielding 30 mg dimethyl 5,6-diacetoxypentacyclo[$7.7.0.0^{2,16}.0^{3,8}.0^{10,15}$]-hexadeca-3,5,7,10,12,14-hexaene-1,2-dicarboxylate (**4c**) and 15 mg dimethyl 12,13-diacetoxypentacyclo[$7.7.0.0^{2,16}.0^{3,8}.0^{10,15}$]hexadeca-3,5,7,10,12,14-hexaene-1,2-dicarboxylate (**5c**).

**4c**: m.p. 80-81°C (pentane): IR (KBr-disk): 2960, 1780, 1740, 1492, 1445, 1378, 1302, 1255, 1215, 1160, 1122, 1080, 1018, 910, 805, 755 $cm^{-1}$, UV (MeOH): 282 (3.17), 275 (3.15), 224 (4.29), 211 nm (4.37). MS m/z (relative intensity): 436 ($M^+$, 36). MS-high resolution, found 436.1156, required $C_{24}H_{20}O_8$ 436.1160.

**5c**: m.p. 215-216°C (pentane); IR (KBr-disk): 2960, 1760, 1720, 1490, 1445, 1375, 1315, 1260, 1220, 1160, 1118, 1018, 905, 820, 755 $cm^{-1}$. UV (MeOH): 281 (3.18), 275 (3.16), 224 (4.29), 211 nm (4.36). MS m/z (relative intensity) 436 ($M^+$, 22), 293 (100). MS high resolution, found 436.1149, required $C_{24}H_{20}O_8$ 436.1160.

Irradiation of **3d**: A solution of **3d** (120 mg) in acetone (350 ml) was irradiated for 35 min. A $^1$H NMR analysis of the residue show a ratio of **4d** to **5d** of 52.8 to 47.2. The reaction mixture was separated by normal phase HPLC (column: C18 on LiChrosorb® Si 100, 5 µm, 150 mm, 15.5 mm i.d.; mobile phase: hexane to THF of 95 to 5. The solvent was removed from the flasks yielding 33 mg dimethyl 5,6-dichloropentacyclo[$7.7.0.0^{2,16}.0^{3,8}.0^{10,15}$]hexadeca-3,5,7,10,12,14-hexaene-1,2-dicarboxylate (**4d**) and 36 mg dimethyl 12,13-dichloropentacyclo[$7.7.0.0^{2,16}.0^{3,8}.0^{10,15}$]hexadeca-3,5,7,10,12,14-hexaene-1,2-dicarboxylate (**5d**).

**4d**: 148°C (pentane); IR (KBr-disk): 2960, 1727, 1465, 1439, 1370, 1305, 1290, 1248, 1215, 1110, 1090, 1055, 955 $cm^{-1}$. UV (cyclohexane): 302 (3.30), 287 (3.37), 277 (3.44), 218 nm (4.49). MS m/z (relative intensity): 390 (23), 388 (35), 329 (100). MS high resolution, found 388.0258, required $C_{20}H_{14}O_4Cl_2$ 388.0280.

**5d**: m.p. 152°C (pentane); IR (KBr-disk): 2950, 1735, 1470, 1460, 1442, 1338, 1295, 1245, 1215, 1171, 1100, 1958, 1010, 935, 890, 765, 740 $cm^{-1}$. UV (cyclohexane): 303 (3.46), 292

(3.55), 233 (4.68), 219 nm (4.69). MS m/z (relative intensity): 390 (30), 388 (46), 329 (100). MS high resolution, found 388.0261, required $C_{20}H_{14}O_4Cl_2$ 388.0280.

Irradiation of **3e**: A solution of **3e** (100 mg) in acetone (350 ml) was irradiated for 30 min. A $^1$H NMR analysis of the residue show a ratio of **4e** to **5e** of 39.8 to 60.2. The reaction mixture was separated by normal phase HPLC (column: C18 on LiChrosorb® Si 100, 5 µm, 300 mm, 15.5 mm i.d.; mobile phase: hexane to THF of 52 to 8. The solvent was removed yielding 15 mg dimethyl 5,6-difluoropentacyclo[7.7.0.0$^{2,16}$.0$^{3,8}$.0$^{10,15}$]hexadeca-3,5,7,10,12,14-hexaene-1,2-dicarboxylate (**4e**) and 30 mg dimethyl 12,13-dimethoxypentacyclo[7.7.0.0$^{2,16}$.0$^{3,8}$.0$^{10,15}$]hexadeca-3,5,7,10,12,14-hexaene-1,2-dicarboxylate (**5e**).

**4e**: m.p. 50-51°C; IR (KBr-disk): 3050, 2925, 2820, 1725, 1720, 1480, 1460, 1425, 1345, 1280, 1235, 1210, 1150 cm$^{-1}$. UV (EtOH): 283 (3.20), 277 (3.18), 208 nm (4.24). MS m/z (relative intensity) 356 ($M^+$, 50), 296 (100) MS high resolution, found 356.0852, required $C_{20}H_{14}O_4F_2$ 356.0856.

**5e**: m.p.125-126°C (THF) IR (KBr-disk): 3050, 2925, 2830, 1725, 1720, 1598, 1480, 1425, 1367, 1335, 1270, 1230, 1212, 1157, 1078, 1032, 1000, 860 cm$^{-1}$. UV (EtOH): 283 (3.15), 278 (3.14) 207 nm (4.19). MS m/z (relative intensity) 357 ($M^{+1}$, 12), 356 (54). MS high resolution, found 356.0805, required $C_{20}H_{14}O_4F_2$ 356.0865.

Irradiation of **3f**: A solution of **3f** (100 mg) in acetone (350 ml) was irradiated for 45 min. A $^1$H NMR analysis of the residue show a ratio of **4f** to **5f** of 84 to 16. The reaction mixture was separated by reversed phase HPLC (column: C18 on LiChrosorb® Si 100, 10 µm, 150 mm, 15.5 mm i.d.; mobile phase: MeOH to water of 55 to 45. Two fractions were collected which were extracted with pentane yielding 50 mg tetramethyl pentacyclo[7.7.0.0$^{2,16}$.0$^{3,8}$.0$^{10,15}$]-hexadeca-3,5,7,10,12,14-hexaene-1,2,5,6-tetracarboxylate (**4f**) and 5 mg tetramethyl pentacyclo-[7.7.0.0$^{2,16}$.0$^{3,8}$.0$^{10,15}$]hexadeca-3,5,7,10,12,14-hexaene-1,2,11,12-tetracarboxylate (**5f**).

**4f**: m.p. 70-71°C (pentane); IR (KBr-disk): 2960, 1742, 1732, 1440, 1355, 1325, 1255, 1215, 1121, 1098, 1061, 825, 770 cm$^{-1}$. UV (MeOH): 212 nm (4.33). MS m/z (relative intensity) 436 ($M^+$, 41), 376 (100). MS high resolution,found 436.1173, required $C_{24}H_{20}O_8$ 436.1152.

**5f**: m.p. 44-45°C (pentane); IR (KBr-disk): 3020, 2960, 1750, 1730, 1440, 1328, 1267, 1212, 1120, 1030 cm$^{-1}$. MS m/z (relative intensity) 436 ($M^+$, 41), 376 (100). MS high resolution, found 436.1173, required $C_{24}H_{20}O_8$ 436.1152.

Irradiation of **3g**: A solution of **3g** (60 mg) in acetone (350 ml) was irradiated for 30 min. A $^1$H NMR analysis of the residue showed a ratio for **4g** to **5g** of 87 to 13. The reaction mixture could not be separated under preparative HPLC conditions. The LIS experiments were thus performed on the crystallized photoproduct mixture of dimethyl 5,6-dicyanopentacyclo-[7.7.0.0$^{2,16}$.0$^{3,8}$.0$^{10,15}$]hexadeca-3,5,7,10,12,14-hexaene-1,2-dicarboxylate (**4g**) and dimethyl 12,13-dicyanopentacyclo-[7.7.0.0$^{2,16}$.0$^{3,8}$.0$^{10,15}$]hexadeca-3,5,7,10,12,14-hexaene-1,2-dicarboxylate (**5g**).

Analytical irradiation of **3h**: A solution of **3h** (2mg) in acetone (5 ml) was irradiated for 5 min. A $^1$H NMR analysis of the dark yellow residue showed neither traces of photoisomers nor of any starting material left so that the photolysis must have produced indefinite fragments.

## LIS-Studies in $^{1}$H NMR and $^{19}$F NMR

**Table 8** Results of LIS-studies on **4a**

| proton at C No[a] | 0 µl[b] | 50 µl[b] | 75 µl[b] | 100 µl[b,e] | LIS[c] |
|---|---|---|---|---|---|
| 16(s) | 4.47 | 8.87 | 10.87 | 12.64 | 1.00 (1.00) |
| 9 (s) | 5.00 | 6.55 | 7.25 | 7.87 | 0.35 (1.00) |
| 1 (s)[d] | 3.73 | 4.09 | 4.25 | 4.38 | 0.08 (1.00) |
| 2 (s)[d] | 3.89 | 4.84 | 5.27 | 5.64 | 0.22 (1.00) |
| 4(s) | 7.03 | 8.50 | 9.17 | 9.74 | 0.34 (1.00) |
| 7(s) | 6.95 | 7.64 | 7.95 | 8.23 | 0.15 (1.00) |
| 11 (m) | 7.18 | 7.74 | 7.93 | 8.23 | 0.09 (0.99) |
| 12 (m) | 7.11 | 7.31 | 7.40 | 7.46 | 0.04 (1.00) |
| 13 (m) | 7.07 | 7.06 | 7.05 | 7.07 | -0.01 (0.95) |
| 14 (m) | 7.35 | 7.19 | 7.16 | 7.12 | -0.03 (0.94) |
| 5 (s), Me | 2.17 | 2.60 | 2.81 | 2.99 | 0.10 (1.00) |
| 6 (s), Me | 2.17 | 2.54 | 2.71 | 2.86 | 0.08 (1.00) |

[a] Multiplicity in parentheses. [b] Amount of $Eu(fod)_3$ dissolved in $CDCl_3$ added to a 500 µl sample solution. [c] Correlation coefficient in parentheses. [d] Or reversed. [e] See fig. 1.

**Table 9** Results of LIS-studies on **5a**

| proton at C No[a] | 0 µl[b] | 40 µl[b] | 80 µl[b] | 110 µl[b,e] | 220 µl[b] | LIS[c] |
|---|---|---|---|---|---|---|
| 16(s) | 4.45 | 7.41 | 9.60 | 11.37 | 15.68 | 1.00 (1.00) |
| 9 (s) | 5.01 | 6.05 | 6.83 | 7.46 | 8.96 | 0.35 (1.00) |
| 1 (s)[d] | 3.73 | 4.05 | 4.29 | 4.48 | 4.86 | 0.10 (1.00) |
| 2 (s)[d] | 3.88 | 4.60 | 5.13 | 5.56 | 6.53 | 0.25 (1.00) |
| 4 | 7.29 | 8.29 | 9.04 | 9.64 | 11.09 | 0.34 (1.00) |
| 5 | 7.12 | 7.49 | 7.77 | 8.03 | 8.62 | 0.14 (1.00) |
| 6 | 7.14 | 7.55 | 7.77 | 7.88 | 8.34 | 0.11 (1.00) |
| 7 | 7.19 | % | 7.96 | 8.24 | 8.90 | 0.15 (1.00) |
| 11 (s) | 6.94 | 7.41 | 7.53 | 7.73 | 8.22 | 0.11 (1.00) |
| 14 (s) | 7.10 | 7.04 | 6.99 | 6.96 | 6.90 | -0.02 (1.00) |
| 12 (s), Me | 2.18 | 2.26 | 2.33 | 2.38 | 2.52 | 0.03 (1.00) |
| 13 (s), Me | 2.18 | 2.26 | 2.33 | 2.38 | 2.52 | 0.03 (1.00) |

[a] Multiplicity in parentheses. [b] Amount of $Eu(fod)_3$ dissolved in $CDCl_3$ added to a 500 µl sample solution. [c] Correlation coefficient in parentheses. [d] Or reversed. [e] See fig. 1.

**Table 10** Results of LIS-studies on **4b**

| proton at C No[a] | 0 µl[b] | 40 µl[b] | 60 µl[b] | 100 µl[b] | 140 µl[b] | LIS[c] |
|---|---|---|---|---|---|---|
| 16(s) | 4.46 | 13.56 | 16.42 | 19.19 | 19.90 | 1.00 (1.00) |
| 9 (s) | 4.96 | 10.01 | 13.32 | 17.32 | 18.39 | 1.32 (1.00) |
| 1 (s)[d] | 3.73 | 4.62 | 4.98 | 5.29 | 5.35 | 0.11 (1.00) |
| 2 (s)[d] | 3.89 | 5.52 | 6.37 | 7.24 | 7.48 | 0.23 (0.99) |
| 4(s) | 6.80 | 12.79 | 15.18 | 17.21 | 17.87 | 0.87 (1.00) |
| 7(s) | 6.69 | 7.64 | 9.99 | 11.74 | 12.23 | 0.61 (1.00) |
| 11 (m) | e | 8.78 | 9.55 | 7.93 | 8.23 | 0.28 (1.00) |
| 12 (m) | e | 7.58 | 7.87 | 7.40 | 7.46 | 0.10 (1.00) |
| 13 (m) | e | 7.27 | 7.37 | 7.53 | 7.60 | 0.05 (0.97) |
| 14 (m) | 7.35 | 7.77 | 7.97 | 8.15 | 8.18 | 0.07 (1.00) |
| 5 (s), OMe | 3.78 | 8.49 | 10.31 | 11.92 | 12.32 | 0.60 (1.00) |
| 6 (s), OMe | 3.82 | 8.70 | 10.49 | 12.01 | 12.39 | 0.58 (1.00) |

[a] Multiplicity in parentheses. [b] Amount of Eu(fod)$_3$ dissolved in $CDCl_3$ added to a 500 µl sample solution. [c] Correlation coefficient in parentheses. [d] Or reversed. [e] Signal not resolved.

**Table 11** Results of LIS-studies on **5b**

| proton at C No[a] | 0 µl[b] | 40 µl[b] | 80 µl[b] | 100 µl[b,e] | 140 µl[b] | LIS[c] |
|---|---|---|---|---|---|---|
| 16(s) | 4.42 | 12.92 | 17.76 | 18.99 | 20.01 | 1.00 (1.00) |
| 9 (s) | 4.97 | 12.00 | 14.77 | 15.27 | 15.66 | 0.80 (0.99) |
| 1 (s)[d] | 3.74 | 4.82 | 5.58 | 5.73 | 5.84 | 0.15 (0.99) |
| 2 (s)[d] | 3.88 | 5.54 | 6.68 | 6.91 | 7.08 | 0.21 (0.99) |
| 4 | e | 9.68 | 11.40 | 11.72 | 12.02 | 0.33 (1.00) |
| 5 | e | 9.20 | 10.49 | 10.73 | 10.92 | 0.24 (0.99) |
| 6 | e | 8.05 | 8.67 | 8.76 | 8.88 | 0.12 (1.00) |
| 7 | 7.28 | 8.05 | 8.67 | 8.24 | 8.88 | 0.10 (1.00) |
| 11 (s) | 6.69 | 12.0 | 16.27 | 7.73 | 17.39 | 0.73 (0.99) |
| 14 (s) | 6.87 | 8.82 | 11.38 | 6.96 | 12.28 | 0.35 (1.00) |
| 12 (s), OMe | 3.79 | 7.80 | 9.80 | 2.38 | 10.44 | 0.43 (1.00) |
| 13 (s), OMe | 3.82 | 8.78 | 11.35 | 11.84 | 12.20 | 0.54 (1.00) |

[a] Multiplicity in parentheses. [b] Amount of Eu(fod)$_3$ dissolved in $CDCl_3$ added to a 500 µl sample solution. [c] Correlation coefficient in parentheses. [d] Or reversed. [e] Signal not resolved.

**Table 12** Results of LIS-studies on **4e**

| proton at C No[a] | 0 μl[b] | 10 μl[b] | 25 μl[b] | 45 μl[b] | 55 μl[b] | LIS[c] |
|---|---|---|---|---|---|---|
| 16(s) | 4.49 | 8.09 | 11.97 | 14.40 | 14.60 | 1.00 (1.00) |
| 9 (s) | 4.99 | 6.28 | 7.62 | 8.46 | 8.55 | 0.35 (1.00) |
| 1 (s)[d] | 3.75 | 4.20 | 4.59 | 4.83 | 4.88 | 0.11 (1.00) |
| 2 (s)[d] | 3.89 | 4.78 | 5.68 | 6.23 | 6.27 | 0.23 (1.00) |
| 4(dd) | 7.12 | 8.32 | 9.54 | 10.32 | 10.39 | 0.32 (1.00) |
| 7(dd) | 6.97 | 7.51 | 8.08 | 8.45 | 8.47 | 0.13 (1.00) |
| 11 (m) | 7.13 |  | 8.05 | 8.40 | 8.55 | 0.13 (1.00) |
| 12 (m) | 7.12 |  | 7.60 | 7.71 | 7.73 | 0.04 (1.00) |
| 13 (m) | 7.14 |  | 7.29 | 7.29 | 7.29 | 0.01 (1.00) |
| 14 (m) | 7.35 |  | 7.31 | 7.30 | 7.30 | -0.01 (0.99) |
| 5 (ddd), F[e] | 138.91 | 138.26 | 137.62 | 137.21 | 137.10 | 0.18 (1.00) |
| 6 (ddd), F[e] | 140.63 | 140.04 | 139.47 | 139.00 | 138.92 | 0.17 (1.00) |

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[a] Multiplicity in parentheses. [b] Amount of Eu(fod)$_3$ dissolved in CDCl$_3$ added to a 500 μl sample solution. [c] Correlation coefficient in parentheses. [d] Or reversed. [e] Negative ppm values.

**Table 13** Results of LIS-studies on **5e**

| proton at C No[a] | 0 μl[b] | 10 μl[b] | 40 μl[b] | 70 μl[b] | LIS[c] |
|---|---|---|---|---|---|
| 16(s) | 4.42 | 6.55 | 11.92 | 14.45 | 1.00 (1.00) |
| 9 (s) | 5.00 | 5.73 | 7.60 | 8.47 | 0.35 (1.00) |
| 1 (s)[d] | 3.75 | 3.93 | 4.46 | 4.66 | 0.09 (1.00) |
| 2 (s)[d] | 3.88 | 4.25 | 5.54 | 6.09 | 0.23 (1.00) |
| 4 | 7.29 | 7.97 | 9.72 | 10.50 | 0.32 (1.00) |
| 5 | 7.16 | 7.48 | 8.15 | 8.48 | 0.13 (1.00) |
| 6 | 7.17 |  | 8.07 | 8.32 | 0.10 (1.00) |
| 7 | 7.16 |  | 8.28 | 8.67 | 0.14 (1.00) |
| 11 (s) | 6.95 | 7.18 | 7.76 | 8.05 | 0.11 (1.00) |
| 14 (s) | 7.12 | 7.07 | 7.02 | 7.01 | -0.01 (1.00) |
| 12 (ddd), F[e] | 139.31 | 139.00 | 138.24 | 137.85 | 0.15 (1.00) |
| 13 (ddd), F[e] | 140.95 | 140.81 | 140.50 | 140.33 | 0.06 (1.00) |

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[a] Multiplicity in parentheses. [b] Amount of Eu(fod)$_3$ dissolved in CDCl$_3$ added to a 500 μl sample solution. [c] Correlation coefficient in parentheses. [d] Or reversed. [e] Negative ppm values.

Photolysis equipment and procedure for quantum yield determinations:

Quantum yields were obtained using a micro bench device similar to that described by Zimmerman.[35] Light from an Osram HBO 200 W high pressure mercury lamp was passed through a Bausch & Lomb Model 33-86-75 high intensity monochromator, entrance slit 5.4 mm and exit slit 3.0 mm, giving a band path of 20 nm at half peak height. Wavelength setting will be given in the following. Samples were irradiated in 1cm x 1 cm quartz cells in an electric actinometer calibrated be ferrioxalate actinometry.[12] The THF, benzene and acetone solutions were degassed for 15 to 30 min. prior to and during photolysis employing deoxygenated nitrogen. After irradiation of the solutions an aliquot with a standard was added. Analysis was performed with HPLC using a Polygosil® Si 60, 5 µm, 250 mm, 4.35 mm i.d., using mixtures of hexane/THF in various ratios as the mobile phase. All runs but three were conducted to a conversion of less than or equal to 4 % and may be taken to be kinetic. All quantum yields were determined from the average of at least three independent runs.

Results:

The results are follows: starting material; concentration (mmol/l); amounts of quanta absorbed (µ-Einstein); conversion of starting material (%); ∅tot; ∅2i; ratio hexane /THF (v/v) used in the HPLC determination.

Direct irradiations were performed at 251 nm using THF. Sensitised irradiations were run at 366 nm using as sensitizer benzophenone (0.239 mol/l) in benzene.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **1**(dir.): | 4.96 | 0.548 | 3.0 | 0.648 ± 0.007 | **2**: 0.648 | | 96:4 |
| **1**(sens): | 3.79 | 0.712 | 4.4 | 0.690 ± 0.020 | **2**: 0.690 | | |
| **3a**(dir.): | 4.73 | 1.591 | 1.2 | 0.025 ± 0.006 | **4a**: 0.013 | **5a**: 0.013 | 98:2 |
| **3a**(sens): | 4.36 | 0.697 | 2.0 | 0.030 ± 0.001 | **4a**: 0.015 | **5a**: 0.015 | |
| **3b**(dir.): | 4.00 | 6.490 | 1.5 | 0.023 ± 0.002 | **4b**: 0.001 | **5b**: 0.013 | 87:13 |
| **3b**(sens): | 4.00 | 2.360 | 2.0 | 0.109 ± 0.003 | **4b**: 0.053 | **5b**: 0.055 | |
| **3c**(dir.): | 4.00 | 1.295 | 1.5 | 0.141 ± 0.008 | **4c**: 0.056 | **5c**: 0.081 | 86:14 |
| **3c**(sens): | 3.73 | 2.293 | 5.5 | 0.225 ± 0.015 | **4c**: 0.087 | **5c**: 0.138 | |
| **3d**(dir.): | 4.40 | 0.547 | 0.8 | 0.178 ± 0.007 | **4d**: 0.090 | **5d**: 0.088 | 95:5 |
| **3d**(sens): | 4.00 | 1.116 | 1.5 | 0.125 ± 0.008 | **4d**: 0.072 | **5d**: 0.053 | |
| **3e** (dir.): | 3.23 | 1.873 | 1.0 | 0.061 ± 0.002 | **4e**: 0.027 | **5e**: 0.033 | hexane/ether/MeCN |
| **3e** (sens): | 3.66 | 1.384 | 2.0 | 0.130 ± 0.009 | **4e**: 0.052 | **5e**: 0.078 | 96/3/1 |
| **3f** (dir): | 3.76 | 1.728 | 4.0 | 0.272 ± 0.011 | **4f**: 0.221 | **5f**: 0.050 | |
| **3g** (dir.): | 3.60 | 1.318 | 4.0 | 0.347 ± 0.011 | **4g** 0.302 | **5g**: 0.045 | 87:13 |
| **3g**(sens): | 3.60 | 1.640 | 6.0 | 0.347 ± 0.003 | **4g**: 0.337 | **5g**: 0.051 | |

Quenching experiments:

Five solutions of **1** (0.045 M) in MeCN of different concentrations of trans-piperylene were degassed with nitrogen and irradiated in a merry-go-round apparatus for 4 min. with 14 RPR 254 nm lamps. The amount of photoisomerisation was determined as described above using HPLC. Quantum yields were determined relative to an unquenched sample $\varnothing_0$. The data are listed as follows: trans-piperylene concentration (μmol/l), $\varnothing_0 / \varnothing$;
13.3, 1.795; 33.0, 2.679; 67.0, 3.254; 133.0, 4.436; 167.0, 4.927.

HMO calculations were performed using standard parameters.[36] For the through-space-interaction a bond integral of 0.2 was used.

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