Selective alkylation by photogenerated aryl and vinyl cation

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Chapter 6 | **Photochemical generation and reactivity of naphthyl cations; *cine* substitution**

Introduction

The research on aryl cation intermediates in organic (photo)chemistry has focussed mainly on phenyl cations[1]. Theoretical and experimental studies have shown that substituents have a decisive effect on the nature (singlet or triplet), and thus on the reactivity, of aryl ions[2]. Recently, density functional theory (DFT) calculations on the singlet-triplet gap in the 1-, and 2-naphthyl cation and in the 9-anthryl cation probed the influence of a larger electronic framework on spin-multiplicity[3].

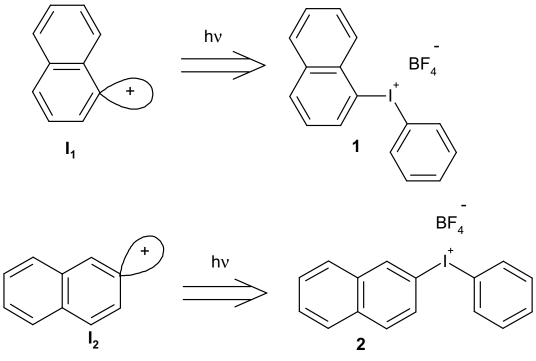
The unsubstituted phenyl cation possesses a singlet, closed shell $\pi^6\sigma^0$ structure. Phenyl cations substituted with electron-donating substituents in the *para* position prefer an open-shell $\pi^5\sigma^1$ structure, with triplet multiplicity[3].

The 1-naphthyl- and 2-naphthyl cations can be considered as phenyl cations bearing an electron-donating substituent. Due to their rigidity they are hampered to adopt the distorted structures normally encountered for singlet, closed shell species. Both effects lower the singlet-triplet gap. In fact, MO calculations[3] indicate that the singlet and triplet form of the naphthyl cations have about the same energy.

Naphthyl cations, and other cationic polyaromatic hydrocarbons, are not only of fundamental chemical interest. They play a relevant role in combustion processes and are present in the interstellar medium[4]. The chemistry of aryl cations and derivatives in the presence of H_2O, CO, NH_3, and especially H_2 and D_2 is subject of a continuous stream of reports[5].

Upon irradiation, vinyl iodonium salts efficiently yield vinyl cations[6]. Likewise, diphenyliodonium salts, commonly used as photo-acid generators in lithography, release phenyl cations upon photolysis[7]. It was therefore anticipated that photolysis of iodonium salts of polynuclear aromatic systems would provide the corresponding cations. The photochemical generation of the 1-naphthyl cation (**I**$_1$) and the 2-naphthyl cation (**I**$_2$), from 1-naphthyl(phenyl)iodonium tetrafluoroborate (**1**) and 2-naphthyl(phenyl)iodonium tetrafluoroborate (**2**) respectively

Chart 1: Naphthyl cations produced from their corresponding iodonium salts.



(Chart 1), and a study of their reactivity are presented. For reasons of comparison, also 1- and 2-naphthyldiazonium tetrafluoroborate and 1-iodonaphthalene were photolyzed.

Results and Discussion

Synthesis

Compounds **1** and **2** were synthesised by reaction of 1- and 2-(4, 4, 5, 5-tetramethyl-1, 3, 2-dioxoborolanyl)naphthalenes with an equimolar amount of (diacetoxy)iodobenzene in the presence of two mole equivalents of hydrogen tetrafluoroborate (in diethyl ether) at -30 °C in dichloromethane. After stirring the reaction mixture for 90 min., *n*-hexane is added which causes the products to crystallise. Repetitive crystallisation at 0 °C from tetrahydrofuran and *n*-hexane gives the pure salts **1** and **2** in 21% and 28% yield, respectively.

Photoproducts

Irradiation of 1-naphthyl(phenyl)iodonium tetrafluoroborate (**1**) in methanol at λ_{exc} = 254 nm yields the product mixture depicted in Scheme 1 [8], in the composition recorded in Table 1. The products are grouped along the various C-I bond cleavage modes. Next to the two leaving groups 1-iodonaphthalene (**3**) and iodobenzene (**6**), and the reductive dehalogenation products benzene (**4**) and naphthalene (**7**), two nucleophilic aromatic substitution products, anisole (**5**) and 1-methoxynaphthalene (**8**), are produced. Further, the Friedel-Crafts type products 1-phenylnaphthalene (**9a**) and 1-(2-, 3-, and 4-iodophenyl)naphthalene (**9b**-**d**) are formed. Intriguingly, 2-phenylnaphthalene (**10a**) and 2- (2-, 3-, and 4-iodophenyl)naphthalene (**10b**-**d**) are produced as well. To the best of our knowledge this pattern of reactivity, commonly referred to as *cine* substitution, has not yet been observed in the aryl(phenyl)iodonium salt chemistry of unsubstituted precursors.

All products are proposed to have been formed via photolytic cleavage of either the phenyl-iodonium (A) or the 1-naphthyl-iodonium (B) bond of **1** (Scheme 2). Both cleavages can occur through homolysis (A1 and B1) or heterolysis (A2 and B2). Homolytic fission of the A bond produces the 1-iodonaphthyl radical cation $\mathbf{I}_3$ and the phenyl radical $\mathbf{I}_4$. Radical cation $\mathbf{I}_3$ can acquire an electron from the solvent and to form **3**. Phenyl radical $\mathbf{I}_4$ will produce **4** by hydrogen atom abstraction. The parent phenyl cation $\mathbf{I}_5$, formed after heterolytic fission of bond A, will be trapped by methanol and form **5**. Alongside $\mathbf{I}_5$, **3** is formed.

Scheme 1: Products of the photolysis of **1** in methanol.

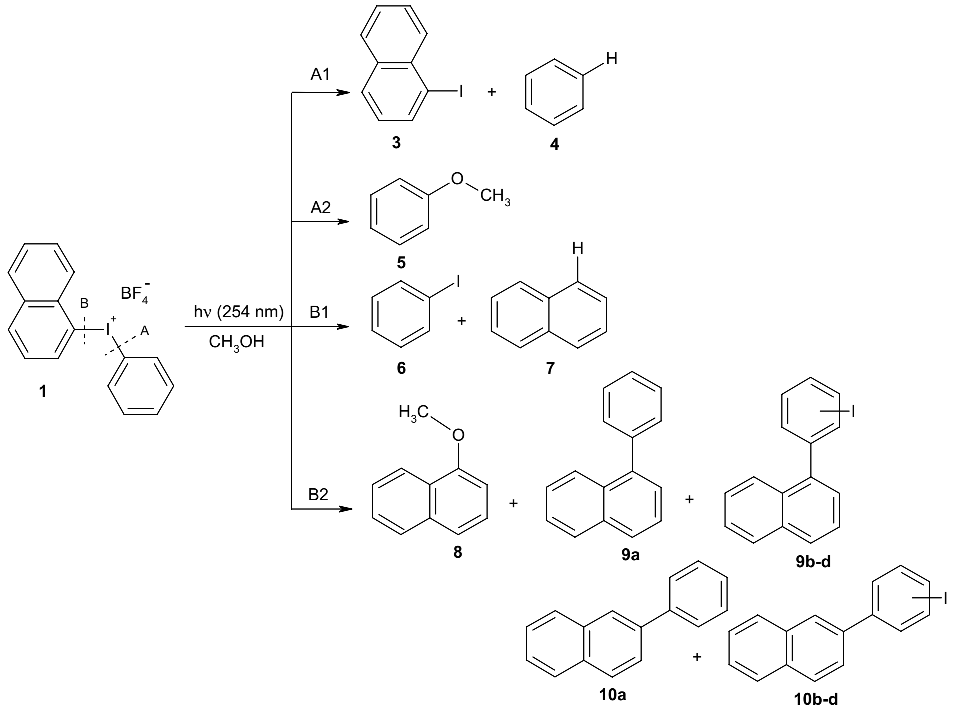


Table 1: Product composition upon photolysis of **1** in methanol at λ_{exc}= 254 nm[a,b] (ca. 4% conversion[c]).

3	**4**	**5**	**6**	**7**	**8**	**9a**	**9b-d**	**10a**	**10b-d**
8[d]	5	3	19	20	19	12	4	2	Traces

a) Percentages of total yield (GC). b) Product composition after 45 minutes of irradiation. c) 1.2% **3** and 2.4% **6** (GC yields relative to internal standard). d) Estimated yield, 1-iodonaphthalene overlaps with the internal standard.

Homolytic cleavage of the B bond gives two intermediates, iodobenzene radical cation **I**$_6$ and naphthyl radical **I**$_7$. These, in turn, produce **6** and **7** by abstraction of an electron and a hydrogen atom from the solvent, methanol, respectively. Upon heterolytic cleavage of bond B, the 1-naphthyl cation **I**$_1$ will be produced next to the leaving group **6**. **I**$_1$ is trapped by methanol to form **8** or by the leaving group iodobenzene to form **9a**, **9b-d**. The mode of formation of the *cine*-substitution products **10a** and **10b-d** will be discussed later.

Prompted by the formation of both **9** and **10** from the 1-naphthyl(phenyl)iodonium salt **1**, the 2-naphthyl(phenyl)iodonium salt **2** was subjected to photolysis under the same reaction con-

Scheme 2: Mechanism of product formation upon photolysis of **1** in methanol.

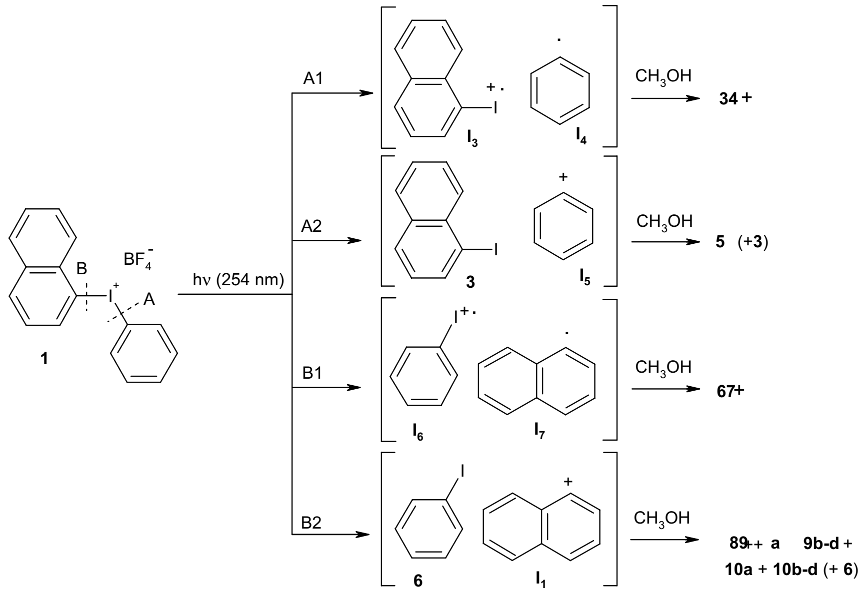


Table 2: Product composition upon photolysis of **2** in methanol at λ_{exc}= 254 nm[a,b] (ca. 10% conversion[c]).

11	4	5	6	7	12	10a	10b-d	9a	9b-d
8[d]	5	2	19	17	16	3	<2	7	Traces

a) Percentages of total yield (GC). b) Product composition after 45 minutes of irradiation. c) 3.0% **11** and 6.8% **6** (GC yields relative to internal standard). d) Estimated yield, 2-iodonaphthalene overlaps with the internal standard.

ditions (methanol, λ_{exc} = 254 nm) (Scheme 3, Table 2). In analogy with the results obtained in the photolysis of **1**, the product mixture consists of the two leaving groups 2-iodonaphthalene (**11**) and iodobenzene (**6**), the reductive dehalogenation products benzene (**4**) and naphthalene (**7**), anisole (**5**), 2-methoxynaphtalene (**12**), the 2-arylnaphthalenes **10a**-**d**, and the *cine*-substitution products **9a**-**d**.

The presence of both **9** and **10** in the photoproduct mixtures of **1** or **2** was confirmed when the the effect of the solvent was studied and the irradiations were carried out in acetonitrile and trifluoroethanol. The leaving groups **3**, **6** and **11** and the reductive dehalogenation product **4** and **7** are formed as before, as are the products resulting from trapping of the phenyl cation $\mathbf{I_5}$ by the solvent. As shown in Scheme 4, in acetonitrile, the naphthyl cation intermediates $\mathbf{I_1}$, and $\mathbf{I_2}$ are trapped by that solvent and fortuitous water (Ritter reaction) yielding the acetanilido products **8**-NHAc and **12**-NHAc. The nucleophilic addition of trifluoroethanol to $\mathbf{I_1}$, and $\mathbf{I_2}$

Scheme 3: Products of the photolysis of **2** in methanol.

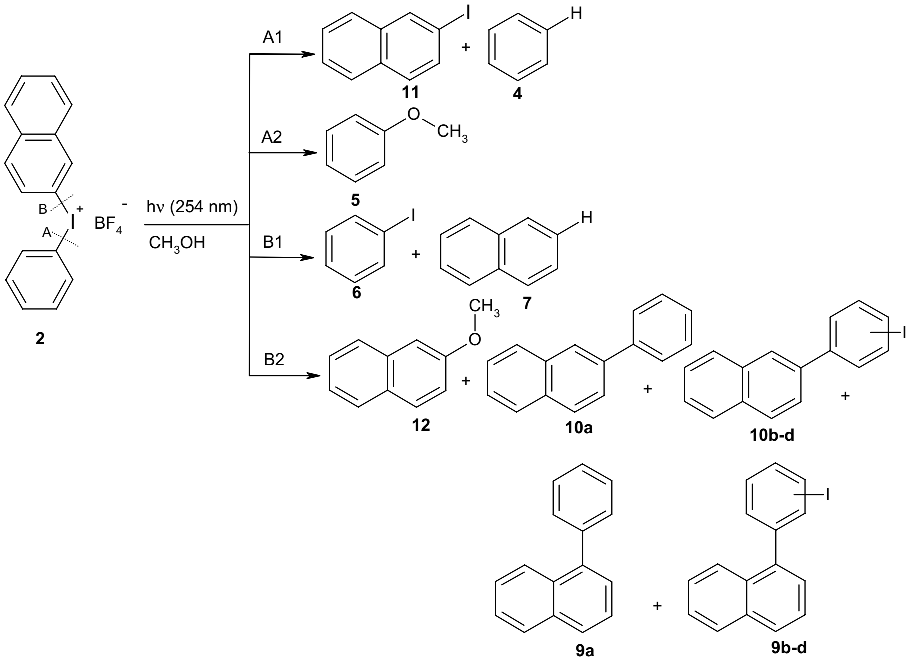


Table 3: Ratios of **8**: **9a-d and 12**: **10a-d** produced upon irradiation of **1** or **2** in various solvents.

Solvent	Ratio **8**: **9a-d** (precursor **1**)	Ratio **12**: **10a-d** (precursor **2**)
Methanol	1:1	1.5:1
Acetonitrile	1:3.3	1:1.1
Trifluoroethanol	1:4.3	1:2.3

yields the trifluoroethoxyethers **8**-OCH_2CF_3 and **12**-OCH_2CF_3, respectively. The Friedel-Crafts type products **9** and **10** are found in all irradiation mixtures.

The ratios in which the nucleophilic substitution products and the Friedel-Crafts products are formed depend on the solvent (Table 3). No *cine* substitution is found for **8** and **12**. Remarkably, the ratio of formation of **9** to **10**, starting from **1** or **2**, also varies with the solvent (Table 4).

Scheme 4: Products of the photolysis of **1** and **2** in acetonitrile and trifluoroethanol (only the products of route B2 are depicted).

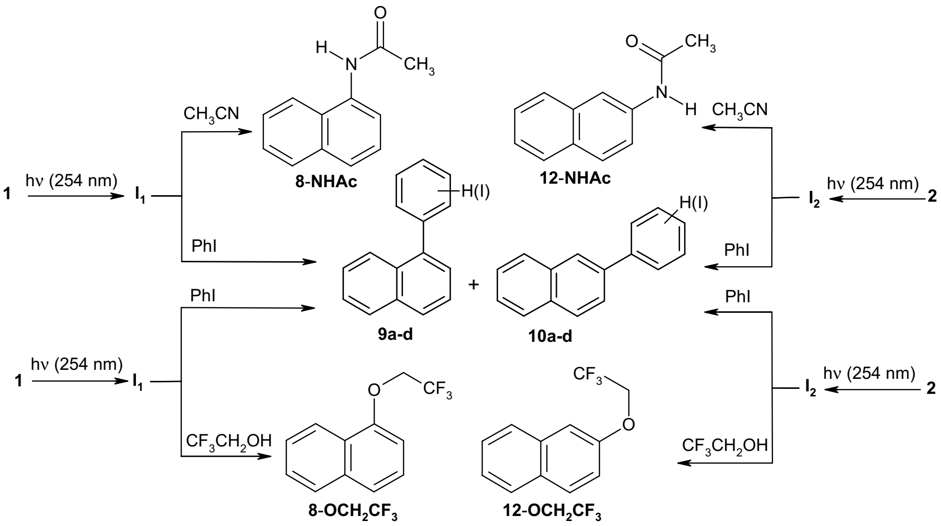


Table 4: Ratios of **9**: **10** produced upon irradiation of **1** or **2** in various solvents.

Solvent	Ratio **9**: **10** (precursor **1**)	Ratio **9**: **10** (precursor **2**)
Methanol	8:1	1.3:1
Acetonitrile	5:1	1:2
Trifluoroethanol	28:1	1:11

The *o*, *m*, *p* ratios of the iodobiaryls **9b**-**d** produced in the photolysis of **1** and **10b**-**d** produced in the photolysis of**2** also vary with the solvent (Table 5). These ratios could not be determined for the products **10b**-**d** in the irradiation of **1** and **9b**-**d** in the irradiation of **2**. They appear in minute amounts and can only be detected on GC-MS.

Table 5: Ratios of **9b**-**d** and **10b**-**d** produced upon irradiation of **1** or **2** in various solvents.

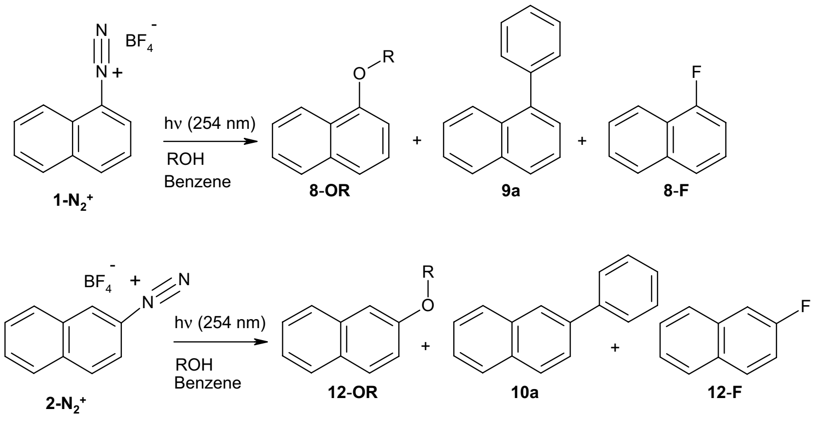
Solvent	Ratio **9b**: **9c**: **9d** (precursor **1**)	Ratio **10b**: **10c**: **10d** (precursor **2**)
Methanol	56:21:23	59:17:24
Acetonitrile	35:22:44	43:25:30
Trifluoroethanol	52:19:30	54:21:25

Only in trifluoroethanol the photolysis of **1** yields a phenylated iodonaphthalene as one of the products. The irradiation of **2** produces another phenylated iodonaphthalene. The identity of these products could not be established rigorously, but it is speculated that they are 1-iodo-2-or

4-phenyl-naphthalene in the photoproduct mixture of **1** and 1-phenyl-2-iodonaphthalene in that of **2**. They are the products of the trapping of the phenyl cation **I**$_5$ by the leaving group **3** or **11** (Scheme 2, route A2) which is only competitive with trapping by the solvent in the non-nucleophilic trifluoroethanol.

To study the effect of the nature of the leaving group on the substitution pattern of the photoproducts, the 1- and 2-naphthyldiazonium tetrafluoroborates **1**-N$_2^+$ and **2**-N$_2^+$ were photolyzed in methanol or trifluoroethanol, in the presence of benzene (Scheme 5). In methanol the photolysis of **1**-N$_2^+$ yields **8**-OR and **9a** in a 1.6:1 ratio, in trifluoroethanol the ratio of **8**-OR to **9a** is 1:1.7. Similar ratios are obtained in the photolysis of **2**-N$_2^+$; in methanol **12**-OR: **10a** = 1.5:1 and in trifluoroethanol **12**-OR : **10a** = 1:1.6. Solely 1- or 2-naphthyl products are formed. No *cine* substitution was observed.

Scheme 5: Products of the photolysis of **1**-N$_2^+$ and **2**-N$_2^+$ in methanol or trifluoroethanol and benzene.



(R = -CH$_3$, -CH$_2$CF$_3$)

Quantum Chemical Calculations

The singlet and triplet naphthyl cations **I**$_1$ and **I**$_2$ and the corresponding 1,2 naphthynes **I**$_8$ (vide infra, Scheme 8) were studied by density functional theory methods in vacuum, and single points in medium, and in methanol, respectively (Table 6, Figure 1)[10]. All optimisations were performed using B3LYP/6-311G(d,p). Next, single point characterisations were carried out using B3LYP/6-311++G(2d,2p). The data in columns 1 and 2 of Table 6 pertain to optimisation in vacuum (column 1) and optimisation after subsequent placement in solvent (column 2). The data in column 3 result from complete optimisation in methanol followed by single point characterisations. For the first time optimisation in a solvent worked at this level of calculation.

Table 6: B3LYP/6-311++G(2d,2p)-calculated energies[a,b] of the singlet and triplet 1,2-naphthyl cations $\mathbf{I}_1$ and $\mathbf{I}_2$ and 1,2-naphthyne $\mathbf{I}_8$, optimised in vacuum and in methanol.

	Vacuum	Rel.	Vacuum→MeOH	Rel.	MeOH	Rel.
$^{1}\mathbf{I}_1$	-385.02153	0	-385.10433	0	-385.10417	0
$^{3}\mathbf{I}_1$	-385.02330	-1.1	-385.10255	1.1	-385.10257	1.0
$^{1}\mathbf{I}_2$	-385.01968	1.2	-385.10290	0.9	-385.10335	0.5
$^{3}\mathbf{I}_2$	-385.02103	0.3	-385.10140	1.8	-385.10144	1.7
$^{1}\mathbf{I}_8$	-384.66696	0	-384.67488	0	-384.67483	0
$^{3}\mathbf{I}_8$	-384.61188	35	-384.60333	45	-384.61931	35

[a] Values absolute (Hartrees) and relative to $^{1}\mathbf{I}_1$ (kcal/mol) for the cations. [b] Values absolute (Hartrees) and relative to $^{1}\mathbf{I}_8$ (kcal/mol) for the naphthynes (1 Hartree = 627.51 kcal/mol).

Comparison of the data in column 1 with those in columns 2 and 3 shows a significant effect of stabilisation of the solvent on the cations. Vacuum-optimised structures that are placed in methanol have energies largely comparable to those of the solvent-optimised structures (columns 2 versus 3). According to the calculations in vacuum, the triplet cations $^{3}\mathbf{I}_1$ and $^{3}\mathbf{I}_2$ are slightly lower in energy than the singlet cations. This situation is reversed when the cations are placed in methanol. The differences are small; the energies of the singlet and triplet species are all within a few kcal/mol of each other. Most earlier reports on the calculated stabilities of $\mathbf{I}_1$ and $\mathbf{I}_2$ in vacuum grant the triplet manifolds the honour of being the lowest in energy, whereas one report finds the singlet cations more stable, albeit also with small differences[3,4b,11]. The near-equal energies ascertain that spin-inversion of the singlet to the triplet cations, or vice versa, is energetically feasible.

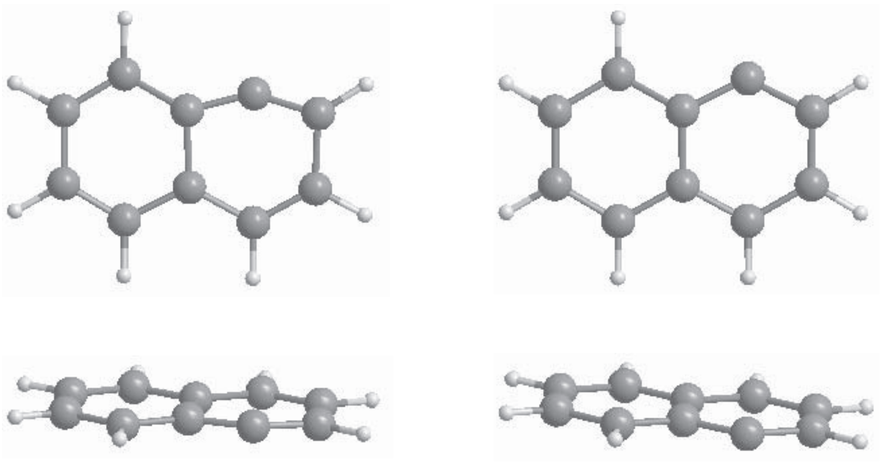
The triplet naphthyne $^{3}\mathbf{I}_8$ is calculated to be significantly less stable than the singlet naphthyne $^{1}\mathbf{I}_8$ in vacuum, in agreement with earlier calculations[12]. This is also the case in methanol.

All structures $\mathbf{I}_1$, $\mathbf{I}_2$ and $\mathbf{I}_8$ but one are calculated to be minima with a C_s symmetry (Figure 1). The exception is the singlet 2-naphthyl cation $^{1}\mathbf{I}_2$. Within the constraints of a C_s symmetry, the structure has one large imaginary frequency, and this structure thus is not a minimum. The real minimum is a distinctly nonplanar structure with C_1 symmetry.

Singlet/ triplet nature of the product-forming intermediates

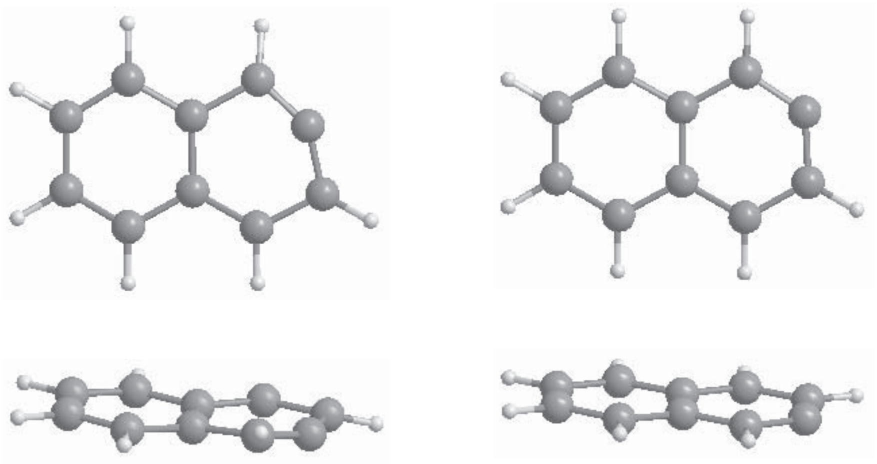
The formation of the nucleophilic substitution products **8** and **12**, and the Friedel-Crafts type products **9** and **10** upon irradiation of **1** and **2** indicate the intermediacy of the naphthyl cations $\mathbf{I}_1$ and $\mathbf{I}_2$, that are trapped by the solvent or by the leaving group iodobenzene (Scheme 2, route B2). It is of interest to know whether these intermediates are of singlet or triplet nature. As discussed in more detail in chapters 2, 3 and 4 of this thesis, diphenyliodonium salt photochemistry may directly form triplet phenyl cations from the triplet excited state, next to singlet phenyl cations from the singlet excited state. For example, singlet excited **1** can give cleavage

Figure 1: Calculated structures (top and side view) of $\mathbf{I}_1$ and $\mathbf{I}_2$.



Cation $^1\mathbf{I}_1$:

Cation $^3\mathbf{I}_1$:



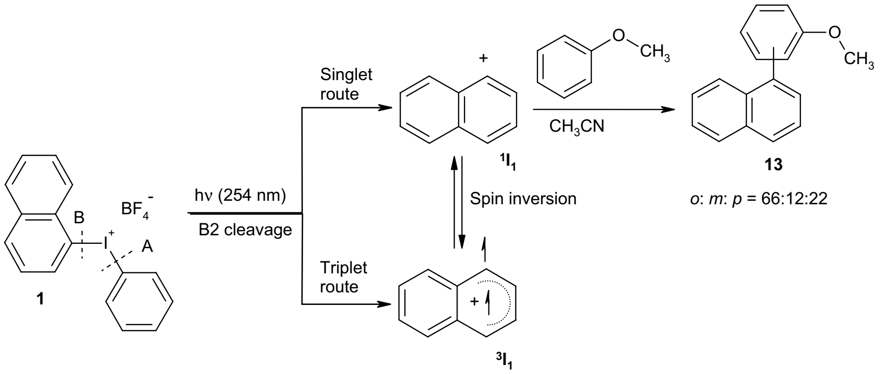
Cation $^1\mathbf{I}_2$:

Cation $^3\mathbf{I}_2$:

of the naphthyl-I bond and yield singlet $^1\mathbf{I}_1$ (Scheme 6, singlet route). Alternatively, due to the heavy atom effect of iodine, it can undergo efficient intersystem crossing to triplet excited **1**, which upon cleavage of the naphthyl-I bond yields triplet $^3\mathbf{I}_1$ (Scheme 6, triplet route). $^1\mathbf{I}_1$ and $^3\mathbf{I}_1$ may interconvert, provided their spin inversion is fast enough to compete with their reactions with nucleophiles.

A fingerprint of the singlet/ triplet nature of the product-forming naphthyl cation $\mathbf{I}_1$ was made by irradiating **1** in acetonitrile/ anisole 1/1 at λ_{exc} = 254 nm (Scheme 6). 1-(2-, 3- and 4-Methoxy-

Scheme 6: Formation of singlet or triplet $\mathbf{I_1}$ and their fingerprint by photolysis of **1** in acetonitrile/anisole.



phenyl)naphthalene (**13**) are formed in an *o*, *m*, *p* ratio of 66:12:22. This ratio is quite similar to the ratio (71:11:17) observed for 2-, 3- and 4-methoxybiphenyl, produced through trapping of the phenyl cation by anisole, formed after heterolytic phenyl-I bond cleavage of **1** (Route A2 in Scheme 2). Moreover, the *o*, *m*, *p* ratio in **13** is practically the same as the ratio obtained with benzenediazonium tetrafluoroborate (68:13:19) and diphenyliodonium tetrafluoroborate (68:12:19) under the same photolysis conditions [13] and with the radiolysis of 1,4-ditritiobenzene in anisole (65:13:22) [14]. The product-forming intermediate in the latter three reactions is a phenyl cation of singlet nature. The results of the photolyses of 1-naphthyldiazonium tetrafluoroborate (**1**-N_2^+) and 1-iodonaphthalene (**3**) in acetonitrile/ anisole 1/1 at λ_{exc} = 254 nm further clarify the picture. The first reaction, which occurs through the singlet naphthyl cation intermediate $\mathbf{^1I_1}$, yields **13** in an *o*, *m*, *p* ratio of 61:15:25, and the second reaction, which occurs through the naphthyl radical intermediate $\mathbf{I_1}$•, produces **13** in an *o*, *m*, *p* ratio of 67:17:16. The ratio obtained with **1**-N_2^+ is similar to that obtained with **1** and to that of the singlet phenyl cation reference reactions[13,14]. The ratio obtained with **3** is unlike that of **1** and **1**-N_2^+, and is reminiscent of the ratio obtained upon irradiation of iodobenzene, which generates a phenyl radical intermediate, in acetonitrile/ anisole 1/1 (75:13:12)[13]. The regioselectivities in the reaction of **1** thus show that both the naphthyl and the phenyl cation intermediate in their singlet state are the product-forming intermediates in the formation of **13** and of 2-, 3- and 4-methoxybiphenyl, respectively.

That the singlet naphthyl cation $\mathbf{^1I_1}$ is the (major) product-forming intermediate, does not necessarily mean that a singlet cation is generated upon photolysis of **1**. The triplet naphthyl cation $\mathbf{^3I_1}$, if formed, may convert to $\mathbf{^1I_1}$ before being trapped by the solvent, provided trapping is slower than spin inversion (see Scheme 6), and provided $\mathbf{^1I_1}$ is of lower energy than $\mathbf{^3I_1}$. The calculated stabilities of the naphthyl cations in methanol assembled in Table 6 indicate that this process is thermodynamically feasible.

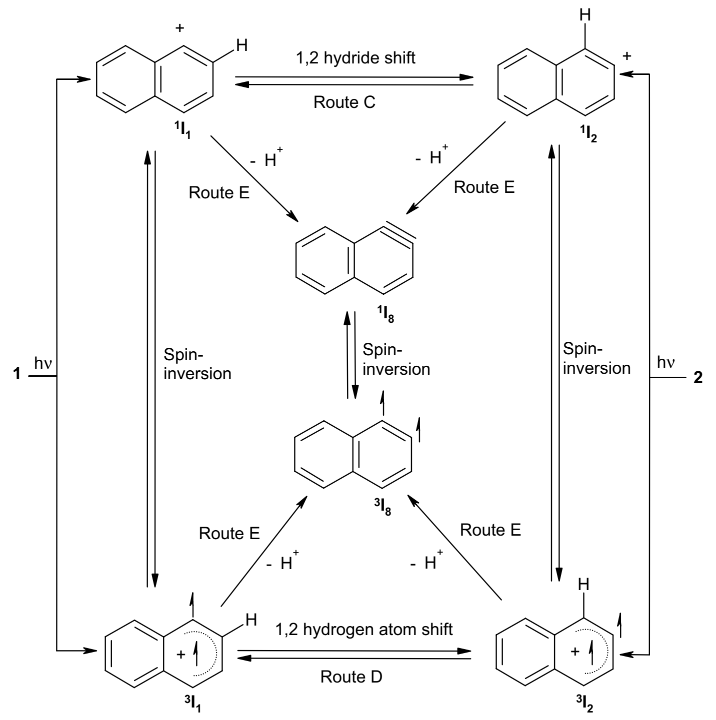
The *o*, *m*, *p* ratios of the iodobiaryls **9b**-**d** and **10b**-**d** formed in the irradiation of **1** and **2** (Table 4) are also fingerprints of the naphthyl cations **I**$_1$ and **I**$_2$, reacting with the leaving group iodobenzene in the solvent cage. Photolysis of diphenyliodonium hexafluorophosphate in acetonitrile produces iodobiaryls in a 73:13:15 ratio, whereas the bromonium and the chloronium salts under these reaction conditions produce halobiaryls in a 53:30:19 and a 48:31:21 ratio, respectively[7b]. In chapter 4 of this thesis, the latter two ratios are attributed to the in-cage attack of a singlet phenyl cation on bromobenzene or chlorobenzene and the ratio for the iodonium salt is reasoned to be the result of the combined reactivity of a singlet and a triplet phenyl cation. The *o*, *m*, *p* ratios of the biaryls **9b**-**d** and **10b**-**d** obtained in the photolyses of **1** and **2** (Table 5) differ from these data. The ratios in methanol and trifluoroethanol are more like the regioselectivity of the diphenylbromonium and -chloronium salt than of the -iodonium salt. They are therefore attributed to the reaction of singlet ^{1}**I**$_1$ and ^{1}**I**$_2$ with iodobenzene. It is not clear why in acetonitrile little or no regioselectivity is found.

The nucleophilic trapping of **I**$_1$ and **I**$_2$ by the solvent (methanol, acetonitrile or trifluoroethanol), producing **8** and **12**, relative to trapping by the leaving group iodobenzene, producing **9** and **10** (Scheme 4, Table 3), shows that the order of the efficiency of the solvents to trap the intermediates is: methanol, acetonitrile, trifluoroethanol. In trifluoroethanol the alkylation of the leaving group outperforms the alkylation of the solvent. The order parallels the nucleophilicities of the solvents[15].

Cine substitution

A number of pathways can be envisioned that may explain the observed *cine* substitution. The singlet 1-naphthyl cation ^{1}**I**$_1$, formed either directly or via the triplet cation, may undergo isomerisation to the singlet 2-naphthyl cation ^{1}**I**$_2$, and vice versa via a 1,2 hydride shift (Scheme 7, route C). Such a shift has been reported for ^{1}**I**$_1$, generated by β-decay of 1,4 ditritionaphthalene: with benzene both in solution and in the gas phase a mixture of 1- and 2-phenylnaphthalene is produced[16,17]. This shift is feasible because the intrinsic energy of the vibrationally excited naphthyl cation, left after expulsion of helium, is sufficient to allow isomerisation. Photolysis of **1** and **2** is not expected to yield vibrationally excited naphthyl cations. Anyhow, if interconversion of ^{1}**I**$_1$ and ^{1}**I**$_2$ takes place, not only 1- and 2-phenylnaphthalene but also 1- and 2-alkoxynaphthalene and the corresponding Ritter products should have been formed. This is not the case, therefore singlet cation isomerisation is not the operative mechanism.

Scheme 7: Interconversion of singlet and triplet naphthyl cations and corresponding naphthynes.



Isomerisation of the triplet naphthyl cations $^{3}\mathbf{I}_{1}$ and $^{3}\mathbf{I}_{2}$, formed directly or via the singlet cations, via a 1,2 hydrogen atom shift opens another route for isomerisation (Scheme 7, Route D). These triplet cations react selectively with the π-nucleophile iodobenzene and not with the n-nucleophiles R-OH and acetonitrile. This would explain why only scrambling of the phenyl naphthalenes is observed and no scrambling of the alkoxynaphthalenes. It also explains why no scrambling occurs with **1**-N_2^+ and **2**-N_2^+: photolysis of unsubstituted diazonium salts only yields singlet cations. It is not clear whether or not a 1,2 hydrogen atom shift in $^{3}\mathbf{I}_{1}$ and $^{3}\mathbf{I}_{2}$ is feasible, in other words what its energy of activation is. A 1,2 hydrogen shift has recently been observed in high temperature gas phase chemistry of naphthyl radicals [18]. In the phenyl radical the shift occurs with an activation energy of 58 kcal/mol[17]. The barrier is probably lower in naphthyl radicals, and even lower in $^{3}\mathbf{I}_{1}$ and $^{3}\mathbf{I}_{2}$ (for which naphthyl radicals may not be a good model) but may be still too high to overcome.

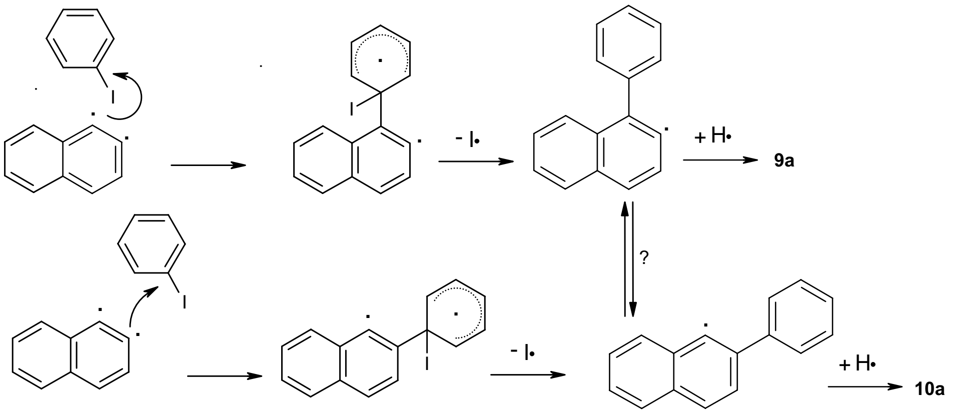
Cine substitution is typically found in alkyne [19] or aryne [20] chemistry. If a 1,2-naphthyne intermediate is accountable for *cine*-product formation in the photolysis of **1** and **2**, the singlet or triplet naphthyl cations $\mathbf{I}_{1}$ and $\mathbf{I}_{2}$ must be prone to lose a β-proton to their environment yielding singlet or triplet naphthyne $^{1}\mathbf{I}_{8}$ and $^{3}\mathbf{I}_{8}$ respectively (Scheme 8, Route E). Aryne formation through an aryl cation intermediate has been reported before in the thermolysis of 2,5-di-*tert*-butyl benzene diazonium acetate in dichloromethane[21]. The acetate counter-ion not only traps the aryl cation intermediate forming the acetate product, but also abstracts a proton forming 2,5-di-*tert*-butylbenzyne. 1,2-Naphthyne has been prepared as an intermediate by 1,2 HX elimination from halonaphthalenes by a strong base[22] and in matrix photodecarboxylation reactions[23]. All naphthynes found in matrix trapping experiments possess a singlet multiplicity. The singlet structure $^1\mathbf{I}_8$ is calculated to be far lower in energy than its triplet spin isomer $^3\mathbf{I}_8$, not only in the gas phase (in agreement with earlier calculations[22]) but also in methanol (Table 6). Still, singlet naphthyne $^1\mathbf{I}_8$ cannot be the *cine* product-forming intermediate. This species is expected to react with methanol to yield predominantly 2-methoxynaphthalene[24], a product not found in the photolysis of **1**. Also no *cine* substitution occurs with diazonium salts **1**-N_2^+ and **2**-N_2^+ which fragment in the singlet excited state producing $^1\mathbf{I}_1$ or $^1\mathbf{I}_2$, which upon proton loss would yield singlet naphthyne $^1\mathbf{I}_8$. On the other hand, the iodonium salts **1** and **2**, which do give *cine* substitution, fragment not only in the singlet but also in the triplet excited state, which yields triplet cation $^3\mathbf{I}_1$ or $^3\mathbf{I}_2$ and after proton loss triplet naphthyne $^3\mathbf{I}_8$. Proton abstraction from the triplet cations $^3\mathbf{I}_1$ and $^3\mathbf{I}_2$, yielding 1,2-naphthyne $^3\mathbf{I}_8$, is thought to be feasible because these species are also formal radical cations, which are known to easily lose a proton, specially from the benzylic position[25,26,27].

An argument in favour of naphthyne as *cine* product-forming intermediate is the variation in the ratio **9**:**10** as function of the solvent (Table 4). Under the photolysis reaction conditions the proton abstraction can only be effected by the solvent. Acetonitrile (779.2 kJ/mol), methanol (754.3 kJ/mol) and trifluoroethanol (700 kJ/mol) differ markedly in their proton-affinity[28]. It is reasonable to expect more aryne- derived product in the better proton-abstracting solvent. Indeed, in the photolyses of **1** in the three solvents, the relative abundance of the *cine* substitution products increases with the proton-affinity of the solvent. In the photolysis of **2**, scrambling is more outspoken than for **1** (Table 4). The triplet 2-naphthyl cation $^3\mathbf{I}_2$, which is a benzylic type radical cation, must be a stronger acid than the 1-naphthyl cation; already in the less basic solvent trifluoroethanol significant scrambling occurs. The photolysis of **2** in methanol yields more scrambled product than expected on the basis of the relative proton affinities. Currently we can offer no explanation for this observation.

An effort to trap naphthyne $\mathbf{I}_8$ in a [4+2] or [2+2] cycloaddition reaction with benzene was in vain. The products of those reactions would be 1,2-naphthobarrelene or dihydrobenzo[a]naphthalene[29], each with molecular mass 204. The photoreaction of **1** in methanol in the presence of benzene (**1**: benzene = 1:20) again produced, next to 1-methoxynaphthalene (**8**), 1- and 2-phenylnaphthalene (**9a**, **10a**) by in-cage reaction of $\mathbf{I}_1$ with iodobenzene and by reaction with benzene. No products with molecular mass 204 other than **9a** and **10a** were detected on GC-MS. An “ene” reaction may also produce **9a** and **10a** from $\mathbf{I}_8$ and benzene[30]. However, there is no reason why $^1\mathbf{I}_8$ should favor the “ene” reaction totally over [4+2] cycloaddition.

Triplet naphthyne $^3\mathbf{I}_8$ supposedly reacts with iodobenzene to form -in the case of ipso attack- an 1-[1'-iodocyclohexadienyl]-2-naphthyl diradical and a 2-[1'-iodocyclohexadienyl]-1-naphthyl diradical (Scheme 8). These distonic diradical intermediates will lose an iodine atom and acquire a hydrogen atom to yield **9a** and **10a**, respectively. The ratio of **9a**:**10a** will be determined by the regioselectivity of the attack of iodobenzene on the 1 or 2 position of $^3\mathbf{I}_8$. In theory, further scrambling may occur through a 1,2 phenyl shift (neophyl type rearrangement) of the 1- and 2-phenyl substituted 2- and 1-naphthyl radicals[31]. The activation energy of this shift is probably too high for efficient competition with the hydrogen atom abstraction, where a strong Csp^2-H bond is formed from a weak Csp^3-H bond of the solvent.

Scheme 8: Ipso-addition of iodobenzene to triplet naphthyne $^3\mathbf{I}_8$, forming **9a** and **10a**.



Conclusion

The 1- and 2-naphthyl cations $\mathbf{I}_1$ and $\mathbf{I}_2$ were generated by photolysis of their iodonium and diazonium salt precursors and their reactivity was studied. The naphthyl cations react (predominantly) through their singlet, closed-shell isomer. With the iodonium salt precursors, which fragment also from the triplet excited state, a contribution of the triplet naphthyl cations to the pattern of reactivity is found. Presumably, under the circumstances investigated, the singlet closed shell naphthyl cations are lower in energy than their triplet isomers.

It appears that, using the naphthyliodonium precursors, the triplet naphthyl cations formed isomerise via a 1,2 hydrogen atom shift or lose a proton to the solvent producing triplet 1,2-naphthyne. These processes lead to the *cine*-substitution patterns found in the photoproduct mixtures. No *cine* substitution occurs upon irradiation of 1- and 2-napthyldiazonium tetrafluoroborate, which generates only the singlet 1-, and 2-napthyl cation.

Experimental Section

Materials

Iodonium salts **1** and **2** were synthesised following a modified literature procedure [32,33]. To a mixture of 0.5 g (diacetoxy)iodobenzene in 25 mL dry dichloromethane at -30 °C, 0.50 mL HBF_4 in diethyl ether 54% wt. is added. The temperature is allowed to rise to 0 °C after which the clear yellow solution is cooled back to –30 °C. Stepwise, over a few min. 0.39 g of commercially available 1- or 2-(4, 4, 5, 5-tetramethyl-1, 3, 2-dioxoborolanyl)naphthalene is added. The reaction mixtures turn dark. After stirring the reaction mixtures for 90 min. at –30 °C the temperature is allowed to rise to 0 °C. *n*-Hexane (40 mL) is added which causes crystallisation. Filtration of the crude products and repetitive crystallisations from dichloromethane and *n*-hexane yield off-white, powdery crystals in 21% and 28% yield, respectively. (**1**: ^{1}H NMR[34] (200MHz, DMSO d_6, δ): 7.3-7.7 (m, 3H), 7.7-8.1 (m, 6H), 8.1-8.4 (d, 2H), 8.9 (s, 1H) and IR[35] (neat): 1000-1100 cm^{-1}, strong (BF_4^-)). (**2**: ^{1}H NMR (200MHz, DMSO d_6) 7.4-7.8 (m, 6H), 7.9-8.1 (d, 2H), 8.1-8.4 (t, 3H); 8.9 (s, 1H) and IR (neat): 1000-1100 cm $^{-1}$, strong (BF_4^-)). Diazonium salts **1**-N_2^+ and **2**-N_2^+ were prepared from commercially available starting materials according to a literature procedure[36]. 1-Iodonaphthalene (**3**) is commercially available. Anisole was distilled under argon to obtain GC purity. Methanol, acetonitrile, trifluoroethanol, and anisole were argon purged prior to their use in the photolysis experiments.

Photochemistry

The photochemical reactions were carried out under argon in quartz tubes equipped with a rubber seal. The starting materials were dissolved at 0.02M in 10 mL solvent. *n*-Decane was used as internal standard. For the experiments where product formation was followed as a function of time of irradiation, the tubes are placed in a merry-go-round apparatus. A Hanau TNN-15/32 low pressure mercury lamp placed in a water cooled quartz tube is used to supply light with a main emission at λ = 254 nm. For product studies, the tubes were placed in a Rayonet Reactor (RPR200) fitted with 7 254 nm or 300 nm lamps. The photolyses of the salts **1**, **2**, **1**-N_2^+ and **2**-N_2^+ in methanol and acetonitrile were followed as a function of time by taking aliquots (0.050 mL sample) and adding them to 0.5 mL water + 0.050 mL diethyl ether. Aliquots from the irradiation mixtures in trifluoroethanol were added to 0.5 mL water + 0.050 mL dichloromethane. The organic layers were analyzed by GC and GC-MS and the assignment of the structures was confirmed by coinjection of commercially available or independently prepared products. After completion of the irradiations, the reaction mixtures were poured in 10 mL water and extracted two times with 5 mL diethyl ether. The combined ether fractions were analyzed by GC and GC-MS.

Photoproducts

The products **3**, **4**, **5**, **6**, **7**, **8**, **8**-OCH_2CF_3, **8**-NHAc, **8**-F, **9a**, **10a**, **12**, **12**-NHAc and **12**-F were identified by means of GC, GC-MS and coinjection with the aid of commercially obtained reference samples. Products **11**[37] and **12**-OCH_2CF_3[38] were synthesised according to literature procedures. The *o*, *m*, *p* biaryl mixtures **9b**-**d**, **10b**-**d** and **13** were prepared by allowing the diazonium salts **1**-N_2^+ or **2**-N_2^+ to react with neat iodobenzene or anisole at 80°C for 6 hrs[9].

Quantum Chemical Calculations

The computations were performed with the Gaussian 03 program, version B3[10]. DFT calculations of the compounds under study were performed with the B3LYP functional [39] as implemented in G03. The total energies were corrected with zero-point energies, obtained at the level of optimisation.

Equipment

UV spectra were recorded at room temperature on a double beam Varian DMS 200 Spectrophotometer, if applicable with pure solvent in the reference cell. ^1H-NMR spectra were recorded on a JEOL 200, using $CDCl_3$ as solvent. As analytical GC a Hewlett-Packard 6890 model was used, equipped with a automatic injector, fitted with a CP-Sil5-CB column (25 m, ø = 0.25 mm, 1.2 μm) using hydrogen as carrier gas. The Flame-Ionisation Detector (FID) was calibrated using commercially available reference chemicals. HP Chemstation was used for the analysis of the analytical data. Mass spectra were measured on a GC-MS set-up consisting of a Hewlett-Packard 5890 series 2 model GC, equipped with a automatic injector, fitted with a AT-5MS column (30 m, ø = 0.25 mm, 0.25 μm) using helium as carrier gas. The GC was coupled to a Finnigan Mat SSQ 710 mass spectrometer, employing electron-impact as the ionisation method. The GC-MS data was analyzed with Xcaliber.

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[8] Under the same reaction conditions as used for the photolysis experiments, upon exclusion of light, **1**, **2**, **1**-N$_2^+$ and **2**-N$_2^+$ are inert.

[9] The assignments of the *o*, *m*, *p* isomers are based on the assumption that the products elude from the GC column in the usual order 1 = *ortho*, 2 = *meta*, 3 = *para*.

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