DOI: 10.1002/ejoc.200700338

Photochemical Generation and Reactivity of Naphthyl Cations: *cine* Substitution

Micha Slegt,[a] Floor Minne,[a] Han Zuilhof,[b] Hermen S. Overkleeft,[a] and Gerrit Lodder*[a]

Keywords: Photochemistry / Naphthyl cations / Spin multiplicity / *cine* substitution / Ab initio calculations

The photochemical solvolyses of naphthalen-1-yl(phenyl)iodonium tetrafluoroborate and naphthalen-2-yl(phenyl)iodonium tetrafluoroborate in methanol regiospecifically yield the naphthalen-1- and -2-yl ethers but afford scrambled 1- and 2-phenylnaphthalene Friedel–Crafts products. It is demonstrated that singlet naphthyl cations account for the formation of the naphthyl ethers, but that the *cine* substitution is most likely to be due to the intermediacy of triplet naphthyl cations. According to the experiments reported here, the singlet naphthyl cations are lower in energy than their triplet isomers. High-level MO calculations for the cations in methanol support this finding.

Introduction

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 pronounced effects on the natures (singlet or triplet), and thus on the reactivities, of phenyl cations.[2] Recently, density functional theory (DFT) calculations on the singlet–triplet energy gaps in the naphthalen-1- and -2-yl cations and in the anthracen-9-yl cation examined 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 their *para* positions prefer open-shell $\pi^5\sigma^1$ structures, with triplet multiplicity.[2a]

The naphthalen-1-yl and naphthalen-2-yl cations can be regarded as phenyl cations bearing electron-donating substituents. Also, their rigidities hamper the cations' abilities to adopt the distorted structures normally encountered for singlet, closed-shell species. Both factors lower the singlet–triplet energy gaps. In fact, the MO calculations in ref.[3] indicate that the singlet and triplet forms of the naphthyl cations have about the same energies.

Naphthyl cations, and other cationic polyaromatic hydrocarbons, are not only of fundamental chemical interest. They also play relevant roles 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 the subject of many 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 should provide the corresponding cations. The photochemical generation of the naphthalen-1-yl cation (**I$_1$**) and the naphthalen-2-yl cation (**I$_2$**), from naphthalen-1-yl(phenyl)iodonium tetrafluoroborate (**1**) and naphthalen-2-yl(phenyl)iodonium tetrafluoroborate (**2**), respectively, and a study of their reactivities are presented (Scheme 1). For reasons of comparison, naphthalen-1- and -2-yldiazonium tetrafluoroborates (**1**-N_2^+ and **2**-N_2^+) and 1-iodonaphthalene (**3**) were also photolysed. The singlet/triplet natures of the photogenerated naphthyl cations were investigated by the fingerprint method reported in the accompanying paper.[8]

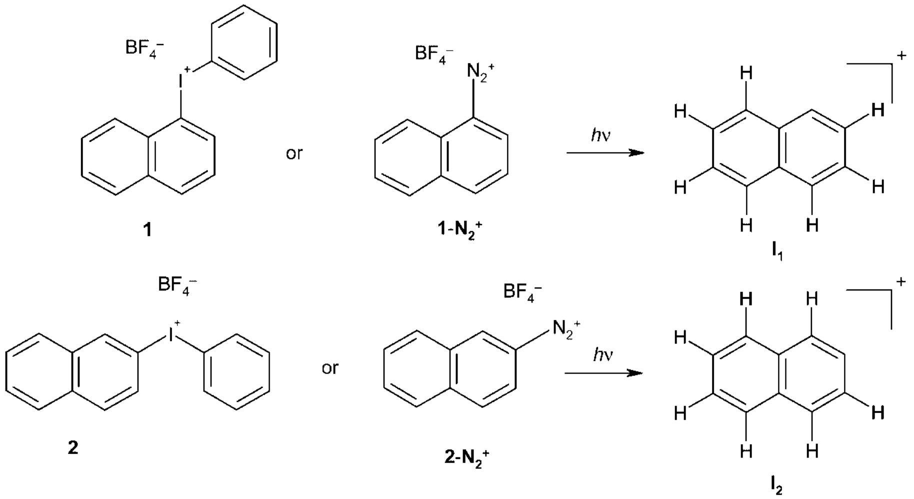
Results and Discussion

Synthesis

Compounds **1** and **2** were synthesised by treatment of 1- and 2-(4,4,5,5-tetramethyl-1,3,2-dioxoborolanyl)naphthalene with equimolar amounts of (diacetoxy)iodobenzene in the presence of two mol equivalents of hydrogen tetrafluoroborate (in diethyl ether) at –30 °C in dichloromethane. After the reaction mixtures had been stirred for 90 min, *n*-hexane was 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%

---

[a] Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University,
P. O. Box 9502, 2300 RA Leiden, The Netherlands
E-mail: lodder@chem.leidenuniv.nl
[b] Laboratory of Organic Chemistry, Wageningen University,
Dreijenplein 8, 6703 HG Wageningen, The Netherlands

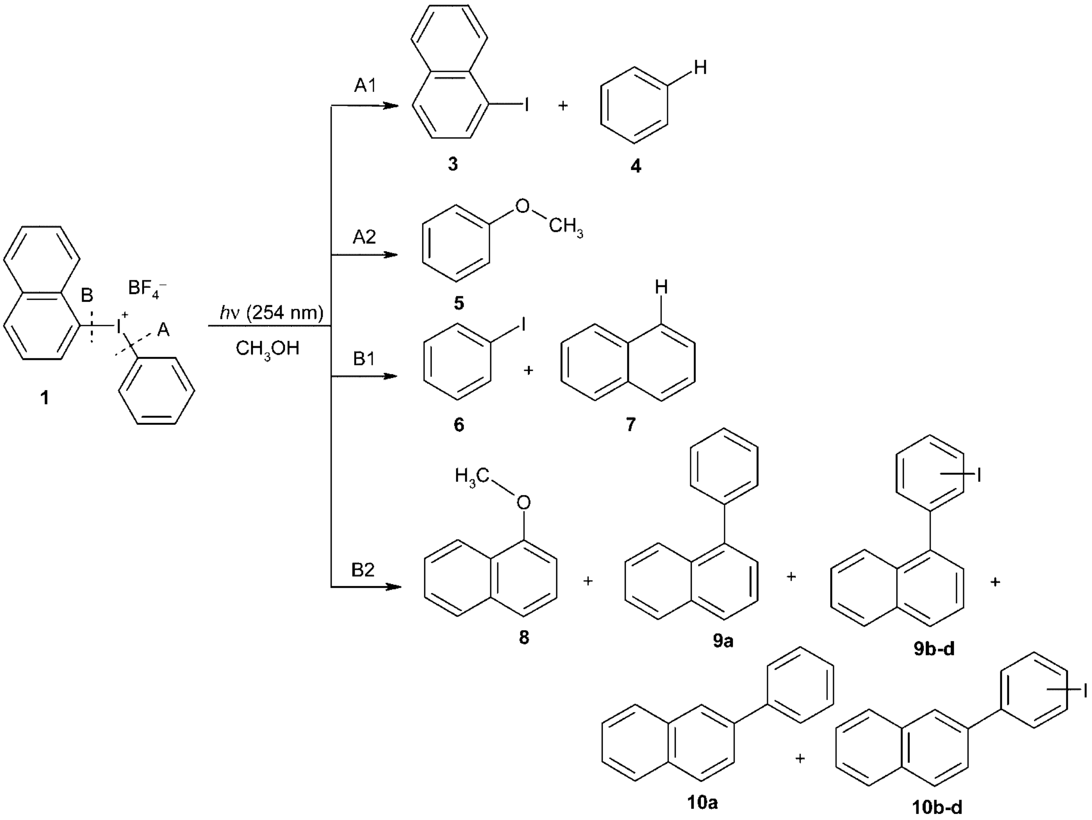


Scheme 1.

yields, respectively. Diazonium salts **1**-N_2^+ and **2**-N_2^+ were synthesized by a literature procedure.[9]

Photoproducts

Irradiation of naphthalen-1-yl(phenyl)iodonium tetrafluoroborate (**1**) in methanol at λ_{exc} = 254 nm yielded the mixture of products depicted in Scheme 2,[10] in the composition recorded in Table 1. Examination of the product concentrations as a function of time of irradiation revealed that all products are primary photoproducts. 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. Furthermore, the Friedel–Crafts-type products 1-phenylnaphthalene (**9a**) and 1-(2-, 3- and



Scheme 2. Products of the photolysis of **1** in methanol.

4-iodophenyl)naphthalene (**9b–d**) are also 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 only been observed in the aryl(phenyl)iodonium salt chemistry of *ortho*-unsubstituted precursors if a strong base is present.[11]

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 min of irradiation. [c] 1.2% **3** and 2.4% **6** (GC yields relative to internal standard). [d] Estimated yield; the signal of 1-iodonaphthalene overlaps with the internal standard.

It is proposed that all products were formed through photolytic cleavage of either the phenyliodonium (A) or the naphthalen-1-yliodonium (B) bond of **1** (Scheme 3). 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 (**I$_3$**) and the phenyl radical (**I$_4$**). Radical cation **I$_3$** can acquire an electron from the solvent and form **3**. Phenyl radical (**I$_4$**) will produce **4** by hydrogen atom abstraction. The parent phenyl cation (**I$_5$**), formed after heterolytic fission of bond A, is trapped by methanol and forms **5**. Alongside **I$_5$**, **3** is formed. In principle, the phenyl cation (**I$_5$**) may also be trapped by the leaving group 1-iodonaphthalene (**3**), and form **9a** via *ipso* substitution. In that case, however, a non-*ipso* substitution product, a phenylated iodonaphthalene, should also be formed, but such a product is only formed in trifluoroethanol as solvent (vide infra). In methanol, unlike in trifluoroethanol, trapping of **I$_5$** by the leaving group apparently cannot compete with its trapping by the nucleophilic solvent.

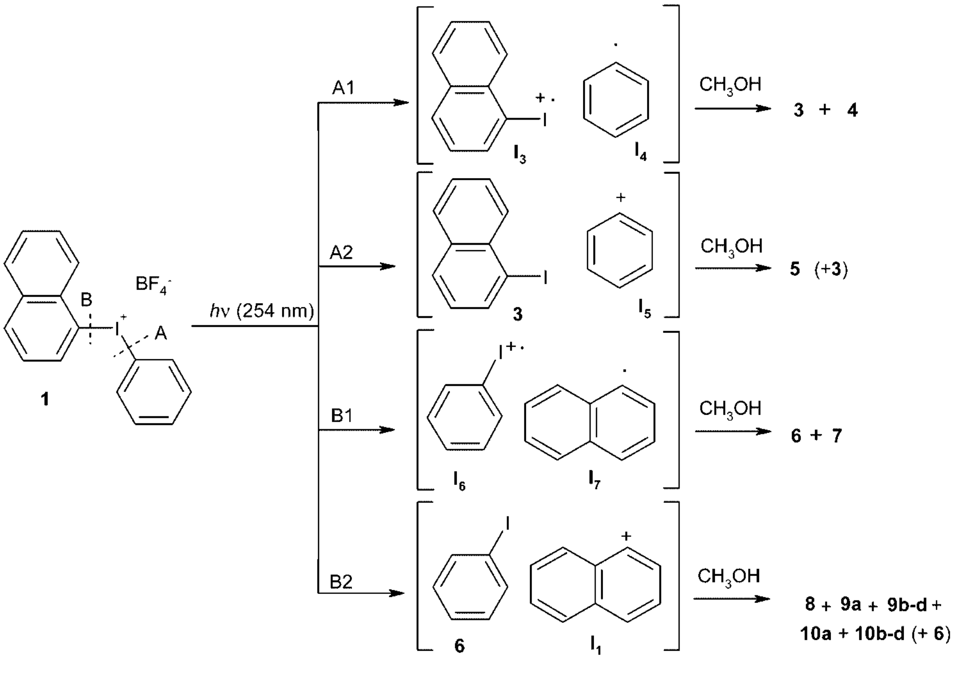
Homolytic cleavage of the B bond gives two intermediates: iodobenzene radical cation (**I$_6$**) and naphthyl radical **I$_7$**. These, in turn, produce **6** and **7** through abstraction of an electron and a hydrogen atom, respectively, from the methanol solvent. Upon heterolytic cleavage of bond B,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

Prompted by the formation of both **9** and **10** from the naphthalen-1-yl(phenyl)iodonium salt **1**, we subjected the naphthalen-2-yl(phenyl)iodonium salt **2** to photolysis under the same conditions (methanol, λ_{exc} = 254 nm; Scheme 4, Table 2). In analogy with the results obtained in the photolysis of **1**, the mixture of primary products consists of the two leaving groups 2-iodonaphthalene (**11**) and iodobenzene (**6**), the reductive dehalogenation products benzene (**4**) and naphthalene (**7**), anisole (**5**), 2-methoxynaphthalene (**12**), the 2-arylnaphthalenes **10a–d** and the *cine*-substitution products **9a–d**.

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	1	7	traces

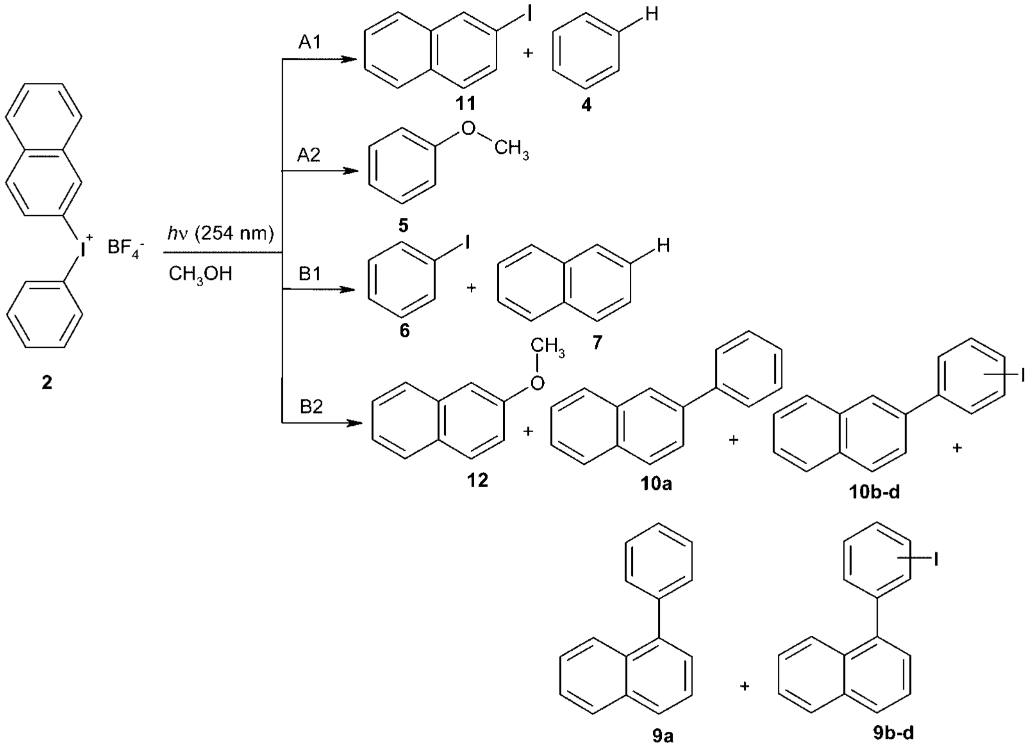
[a] Percentages of total yield (GC). [b] Product composition after 45 min of irradiation. [c] 3.0% **11** and 6.8% **6** (GC yields relative to internal standard). [d] Estimated yield; the signal of 2-iodonaphthalene overlaps with the internal standard.



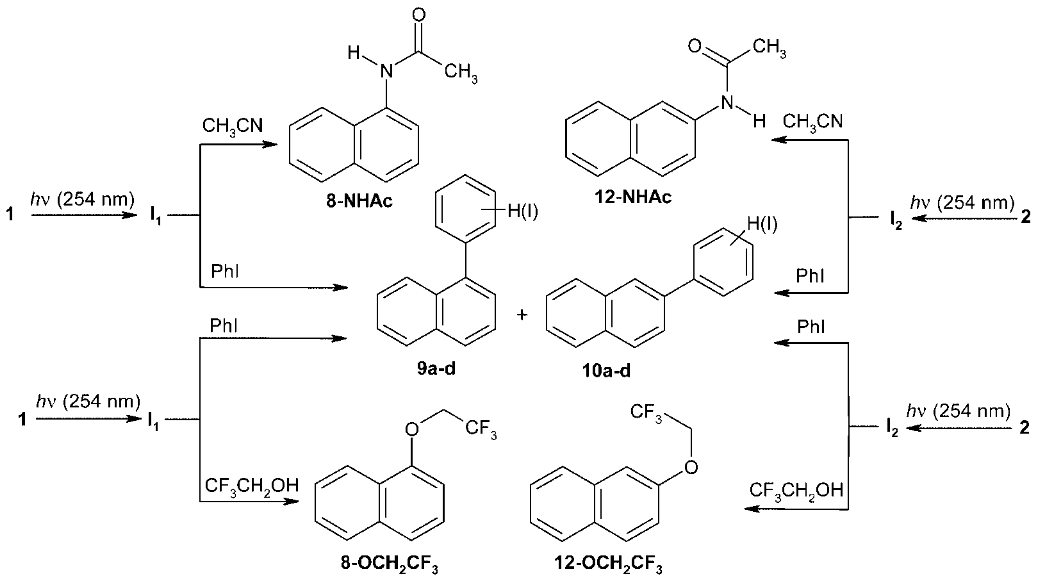
Scheme 3. Mechanism of product formation upon photolysis of **1** in methanol.

Both **9** and **10** were also observed in the photoproduct mixtures of **1** or **2** when the effect of the solvent was studied and the irradiation was carried out in acetonitrile and trifluoroethanol. The leaving groups **3**, **6** and **11** and the reductive dehalogenation products **4** and **7** are formed as before, as are the products C_6H_5NHAc and $C_6H_5OCH_2CF_3$ resulting from trapping of the phenyl cation (**I$_5$**) by the solvent. As shown in Scheme 5, in acetonitrile the naphthyl cation intermediates **I$_1$**, and **I$_2$** are trapped by that solvent and adventitious water (Ritter reaction), yielding the acetanilido products **8**-NHAc and **12**-NHAc. The nucleophilic additions of trifluoroethanol to **I$_1$** and **I$_2$** yield the trifluoroethoxy ethers **8**-OCH_2CF_3 and **12**-OCH_2CF_3, respectively. The Friedel–Crafts-type products **9** and **10** are found in all irradiation mixtures. No *cine* substitution is found in the production of **8** and **12**.

Only in trifluoroethanol does the photolysis of **1** yield a phenylated iodonaphthalene as one of the products. The



Scheme 4. Products of the photolysis of **2** in methanol.



Scheme 5. Products of the photolysis of **1** and **2** in acetonitrile and trifluoroethanol (only the products of Route B2 are depicted).

irradiation of **2** produces another phenylated iodonaphthalene. The identities 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 groups **3** or **11** (cf. Scheme 3, Route A2), which is only competitive with trapping by the solvent in the nonnucleophilic trifluoroethanol.

The ratios in which the nucleophilic substitution products **8** and **12** and the Friedel–Crafts products **9** and **10** are formed depend on the solvent (Table 3). The ratios of formation of **9** to **10**, starting from **1** or **2**, also vary with the solvent (Table 4), as do the *o*/*m*/*p* ratios of the iodobiaryls **9b–d** produced in the photolysis of **1** and of **10b–d** produced in the photolysis of **2** (Table 5).[12] The last of these ratios could not be determined for the products **10b–d** in the irradiation of **1** and **9b–d** in the irradiation of **2**. These products appear in minute amounts and can only be detected by GC-MS.

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

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	1.8:1
Acetonitrile	5:1	1:2
Trifluoroethanol	28:1	1:11

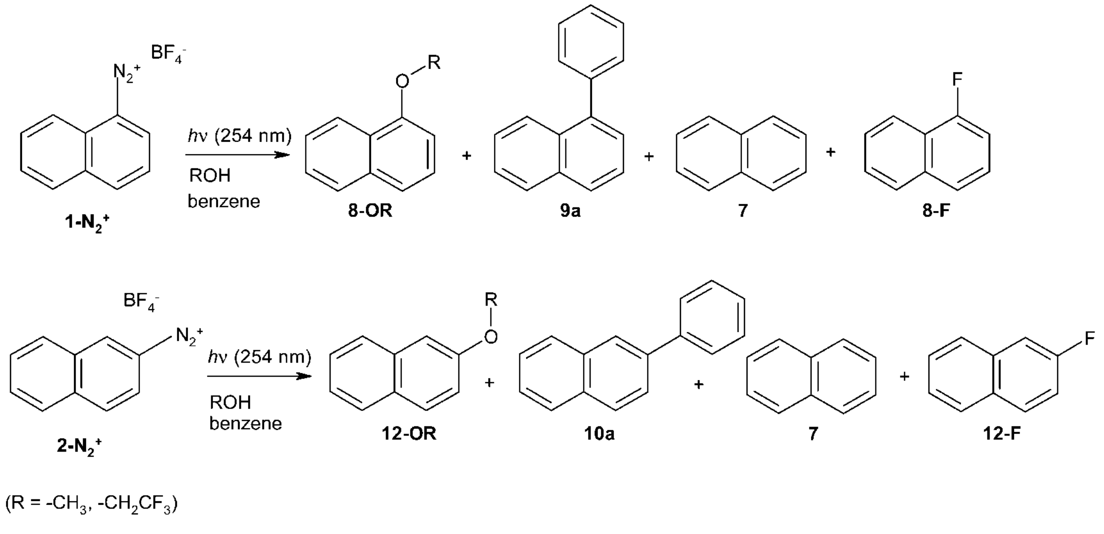
Table 5. Ratios of **9b/9c/9d** and **10b/10c/10d** produced upon irradiation of **1** or **2** in various solvents.

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

To study the effects of the natures of the leaving groups on the substitution patterns of the photoproducts, the naphthalen-1- and -2-yldiazonium tetrafluoroborates **1**-N_2^+ and **2**-N_2^+ were photolysed in methanol and in trifluoroethanol, in the presence of benzene (Scheme 6).[10] In methanol, the photolysis of **1**-N_2^+ yields **8**-OR and **9a** in a ratio of 1.6:1, while 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. The formation of the reduction product **7** and the Schiemann products **8-F** and **12-F** was confirmed by GC-MS. Solely naphthalen-1- or -2-yl products are formed. No *cine* substitution was observed.

The formation of **8-F** and **12-F** from **I$_1$** and **I$_2$** occurs through abstraction of fluoride from the BF_4^- counterion[13,14] and in the case of trifluoroethanol as solvent possibly also partly through abstraction of fluoride from the solvent.[15] Although the amounts of **8-F** and **12-F** in the reaction mixtures could not be quantified, because their GC peaks overlap with that of naphthalene, in trifluoroethanol not significantly more F product was produced than in methanol. This indicates that fluoride abstraction from trifluoroethanol is not a significant reaction pathway for naphthyl cations **I$_1$** and **I$_2$**. β-Silicon-stabilized phenyl cations, generated from their triflate in trifluoroethanol, do not yield products derived from fluoride abstraction.[16]

Remarkably, the iodonium tetrafluoroborate salts **1** and **2** do not yield the naphthyl fluorides **8-F** and **12-F**, whereas the diazonium tetrafluoroborate salts **1**-N_2^+ and **2**-N_2^+ do



Scheme 6. Products of the photolysis of **1**-N_2^+ and **2**-N_2^+ in methanol or trifluoroethanol and benzene.

(see Schemes 2 and 4 vs. Scheme 6). We suggest that in the (polar) nucleophilic solvents used, the iodonium salts form diaryl-λ^3-iodane complexes with the solvent: [Ar-I-Ph·solvent]$^+$$BF_4^-$.[17,18] Excitation of these solvent-coordinated complexes results in the formation of the naphthyl cations (**I_1** or **I_2**), iodobenzene, and a solvent molecule within a solvent cage: [**I_1** or **I_2** PhI solvent]BF_4^-. The unstable and short-lived naphthyl cations react with the nearby solvent and iodobenzene in the cage, yielding **8-** and **12-OMe**, **-OCH_2CF_3**, **-NHAc** and **9** and **10**, and not with the further removed BF_4^- anion, thus not yielding **8-F** and **12-F**. This interpretation is supported by results of the photolysis of phenanthren-9-yl(phenyl)iodonium tetrafluoroborate.[19] This salt does not give the Schiemann product 9-fluorophenanthrene in methanol, but does so in trifluoroethanol. In the less nucleophilic TFE, λ^3-iodane formation is less important and the BF_4^- can now compete with other nucleophiles for the photogenerated phenanthren-9-yl cation, which is more stable and thus longer-lived than the naphthyl cations **I_1** and **I_2**.

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. To study the role of solvent effects, the structures were optimized at the B3LYP/6-311G(d,p) level of theory both in vacuo and in a dielectric medium resembling methanol.[20] Subsequently, single-point calculations were performed at the B3LYP/6-311++G(2d,2p) level of theory, in vacuo on the "in vacuo" structures (Table 6, column 2), in the dielectric medium on the "in vacuo" structures (Table 6, column 4), and in the dielectric medium on the "in solvent" structures (Table 6, column 6), respectively. This approach allows a separate evaluation of the solvent effects on both the geometries and the energies of the resulting structures. 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 naphthalen-1- and -2-yl cations **I_1** and **I_2** and 1,2-naphthyne **I_8**, optimised in vacuo and in methanol.

	Vacuum	Rel.	Vacuum→MeOH	Rel.	MeOH	Rel.
$^1I_1$	–385.02153	0	–385.10433	0	–385.10417	0
$^3I_1$	–385.02330	–1.1	–385.10255	1.1	–385.10257	1.0
$^1I_2$	–385.01968	1.2	–385.10290	0.9	–385.10335	0.5
$^3I_2$	–385.02103	0.3	–385.10140	1.8	–385.10144	1.7
$^1I_8$	–384.66696	0	–384.67488	0	–384.67483	0
$^3I_8$	–384.61188	35	–384.60333	45	–384.61932	35

[a] Absolute values (Hartrees) and values relative to **$^1I_1$** (kcal mol^{-1}) for the cations. [b] Absolute values (Hartrees) and values relative to **$^1I_8$** (kcal mol^{-1}) for the naphthynes (1 Hartree = 627.51 kcal mol^{-1}).

Comparison of the data in column 2 with those in columns 4 and 6 shows a significant effect of stabilisation of the solvent on the cations. Vacuum-optimised structures that are placed in methanol have energies largely similar to those of the solvent-optimised structures (columns 4 vs. 6). According to the calculations in vacuo, the triplet cations **$^3I_1$** and **$^3I_2$** 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^{-1} of each other. Most earlier reports on the calculated stabilities of **I_1** and **I_2** in vacuo place the triplets energetically below the singlet structures, whereas in contrast one report finds the singlet cations to be more stable, albeit also only with small differences.[3,4b,21] The near-equal energies demonstrate that isomerization of the singlet to the triplet cations, or vice versa, is energetically feasible.

The triplet naphthyne **$^3I_8$** is calculated to be significantly less stable than the singlet naphthyne **$^1I_8$** in vacuo, in agreement with earlier calculations.[22] This is also the case in methanol.

Three of the four **I_1** and **I_2** structures are calculated to be minima with C_s symmetry (Figure 1). The exception is the singlet naphthalen-2-yl cation (**$^1I_2$**). Within the constraints of C_s symmetry, the structure has one large imagi-

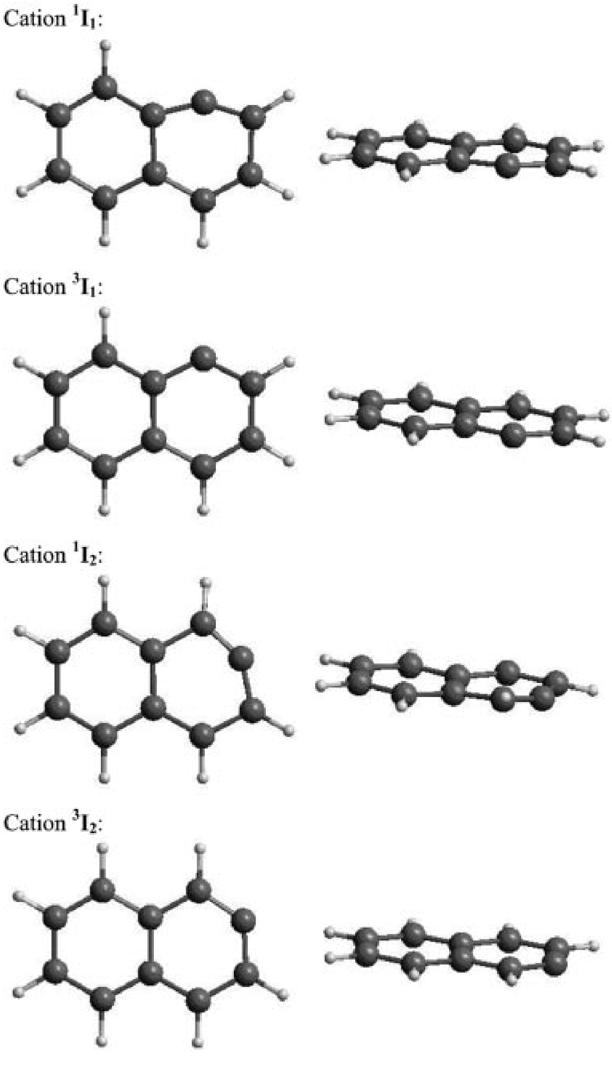


Figure 1. Calculated structures (top and side view) of **I_1** and **I_2**.

nary frequency, and this structure is therefore not a minimum. The real minimum is a distinctly nonplanar structure with C_1 symmetry (e.g., the H atom at C-1 adjacent to the formally positively charged carbon atom is pointing slightly upwards, as can be seen in the side view of $^1\mathbf{I_2}$ in Figure 1).

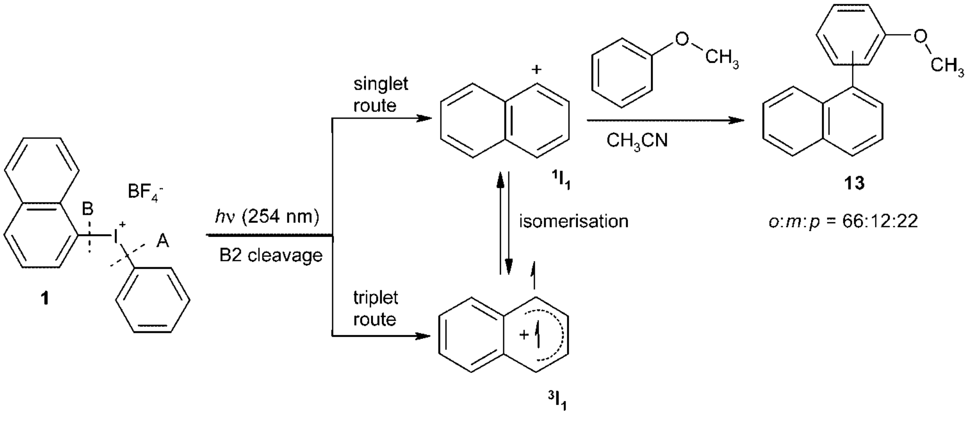
Singlet/Triplet Natures of the Product-Forming Intermediates

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 $\mathbf{I_2}$, which are trapped by the solvent or by the iodobenzene leaving group (Scheme 3, Route B2). It is of interest to know whether these intermediates are of singlet or triplet natures. Irradiation of diphenyliodonium salts may yield triplet phenyl cations from the triplet excited state, together with singlet phenyl cations from the singlet excited state.[8] Here, singlet excited **1** might give cleavage of the naphthyl-I bond and yield singlet $^1\mathbf{I_1}$ (Scheme 7, singlet route). Alternatively, because of the heavy atom effect of iodine, it can undergo efficient intersystem crossing to give triplet excited **1**, which upon cleavage of the naphthyl-I bond yields triplet $^3\mathbf{I_1}$ (Scheme 7, triplet route). $^1\mathbf{I_1}$ and $^3\mathbf{I_1}$ may interconvert, provided that their spin inversion is energetically feasible and 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 7) by the method described in the accompanying paper.[8] 1-(2-, 3- and 4-Methoxyphenyl)naphthalenes **13** were 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 by anisole of the phenyl cation $\mathbf{I_5}$, formed after heterolytic phenyl–I bond cleavage of **1** (Route A2 in Scheme 3). Moreover, the *o*/*m*/*p* ratio in **13** is practically the same as the ratios obtained for the photolyses of benzenediazonium tetrafluoroborate (68:13:19) and diphenyliodonium tetrafluoroborate (68:12:19) under the same reaction conditions[8] and also for the radiolysis of 1,4-ditritiobenzene in anisole (65:13:22).[23] The product-forming intermediate in the last three reactions is a phenyl cation of singlet nature. The results of the photolyses of naphthalen-1-yldiazonium tetrafluoroborate (**1**-N_2^+) and 1-iodonaphthalene (**3**)[10] in acetonitrile/anisole (1:1) at λ_{exc} = 254 nm further clarify the picture. The first reaction, which, like those of other aryl diazonium salts,[24] presumably occurs through the singlet naphthyl cation intermediate $^1\mathbf{I_1}$, yields **13** in an *o*/*m*/*p* ratio of 61:15:25. The second reaction, which occurs through the naphthyl radical intermediate $\mathbf{I_1}^{\cdot}$,[25] 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 seen in singlet phenyl cation reactions.[8,23] The ratio obtained with **3** is unlike that observed with **1** and **1**-N_2^+, but is reminiscent of the ratio obtained upon irradiation of iodobenzene, which generates the phenyl radical as an intermediate, in acetonitrile/anisole (1:1; *o*/*m*/*p* ratio 75:13:12).[8] The regioselectivities in the reaction of **1** thus show that both the naphthyl and the phenyl cation intermediates in their singlet states are the product-forming intermediates in the formation of **13** and of 2-, 3- and 4-methoxybiphenyl, respectively.

That the singlet naphthyl cation $^1\mathbf{I_1}$ is the (major) product-forming intermediate does not necessarily mean that a singlet cation is generated upon photolysis of **1**. The triplet naphthyl cation $^3\mathbf{I_1}$, if formed, may convert into $^1\mathbf{I_1}$ before being trapped by the solvent, provided that trapping is slower than spin inversion (see Scheme 7), and also provided that $^1\mathbf{I_1}$ is of lower energy than $^3\mathbf{I_1}$. 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**/**9c**/**9d** produced in the irradiation of **1** and of **10b**/**10c**/**10d** produced in the irradiation of **2** (Table 5) are also fingerprints of the naphthyl cations $\mathbf{I_1}$ and $\mathbf{I_2}$, 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 produce halobiaryls in 53:30:19 and 48:31:21 ratios, respectively, under these reaction condi-



Scheme 7. Formation of singlet or triplet $\mathbf{I_1}$ and their fingerprinting by photolysis of **1** in acetonitrile/anisole.

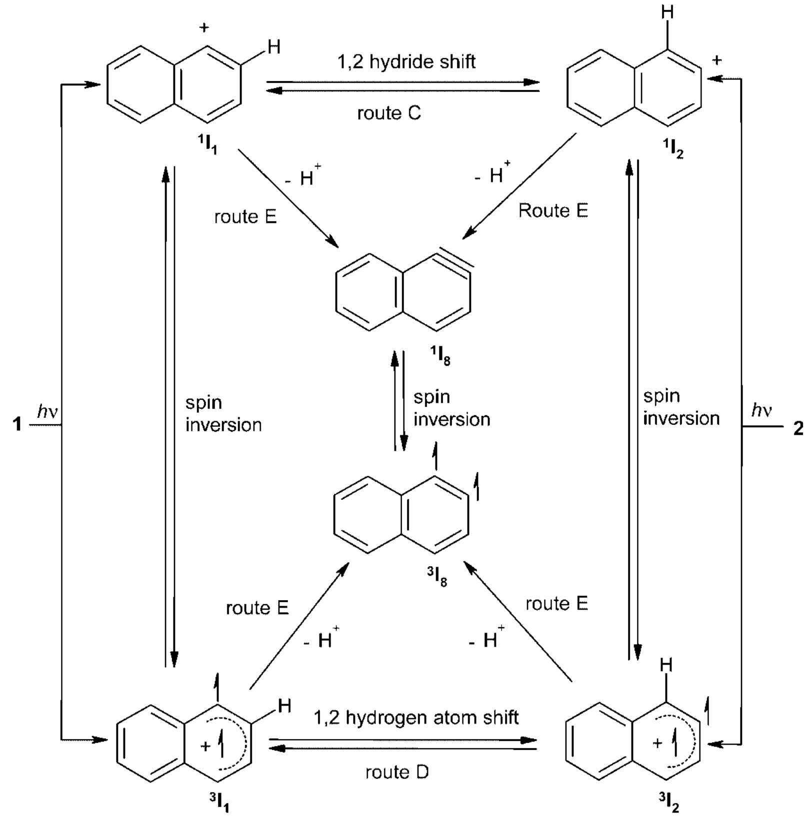
tions.[7b] The *o*/*m*/*p* ratios of the biaryls **9b–d** in the irradiation of **1** and of **10b–d** in the irradiation of **2** (Table 5) in methanol and trifluoroethanol more closely correspond to the regioselectivities of the diphenylbromonium and -chloronium salts, which supposedly react through a singlet phenyl cation, than to that of the -iodonium salt, which reacts both through a singlet and through a triplet phenyl cation. They are therefore attributed to substantial formation of singlet $^1\mathbf{I}_1$ and $^1\mathbf{I}_2$, through initially formed $^3\mathbf{I}_1$ and $^3\mathbf{I}_2$ and the subsequent reaction with iodobenzene. It is not clear why little or no regioselectivity is found in acetonitrile.

The nucleophilic trapping of $\mathbf{I}_1$ and $\mathbf{I}_2$ by the solvent (methanol, acetonitrile or trifluoroethanol), producing **8** and **12**, relative to trapping by the leaving group iodobenzene, producing **9** and **10** (Scheme 5, Table 3), shows that the order of the efficiency of the solvents in trapping 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.[26]

cine Substitution

A number of pathways that may explain the observed *cine* substitution can be envisioned. The singlet naphthalen-1-yl cation ($^1\mathbf{I}_1$), formed either directly or via the triplet cation, may undergo isomerisation to the singlet naphthalen-2-yl cation ($^1\mathbf{I}_2$), and vice versa through a 1,2 hydride shift (Scheme 8, Route C). Such a shift has been reported for $^1\mathbf{I}_1$, 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.[27,28] This shift is feasible because the energy of the vibrationally excited naphthyl cation, left after expulsion of helium, is sufficient to allow isomerisation. Photolysis of **1** and **2** would not be expected to yield vibrationally excited naphthyl cations. Anyhow, if interconversion of $^1\mathbf{I}_1$ and $^1\mathbf{I}_2$ were to have taken 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 and therefore singlet cation isomerisation is not the operative mechanism.

Isomerisation of the triplet naphthyl cations $^3\mathbf{I}_1$ and $^3\mathbf{I}_2$, formed directly or via the singlet cations, through 1,2 hydrogen atom shifts, opens another route for isomerisation (Scheme 8, Route D). These triplet cations react with the π-nucleophile iodobenzene and not with the n-nucleophiles R-OH and acetonitrile. This would explain why only scrambled phenylnaphthalenes and no scrambled alkoxynaphthalenes are observed. It would also explain 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 1,2 hydrogen atom shifts in $^3\mathbf{I}_1$ and $^3\mathbf{I}_2$ are kinetically feasible (in other words, what their energies of activation are). A 1,2 hydrogen shift has recently been observed in high-temperature gas-phase chemistry of naphthyl radicals.[29] In the phenyl radical the shift occurs



Scheme 8. Interconversion of singlet and triplet naphthyl cations and corresponding naphthynes.

with an activation energy of 58 kcal mol^{-1}.[29] 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 still be too high to overcome.

cine substitution is typically found in alkyne[30] or aryne[11,31] chemistry. If a 1,2-naphthyne intermediate is responsible for the formation of the *cine* products in the photolysis of **1** and **2**, the singlet or triplet naphthyl cations $\mathbf{I_1}$ and $\mathbf{I_2}$ must be prone to losing β-protons to their environments, yielding singlet or triplet naphthynes $^1\mathbf{I_8}$ and $^3\mathbf{I_8}$, respectively (Scheme 8, Route E). Aryne formation through an aryl cation intermediate has been reported previously in the thermolysis of 2,5-di-*tert*-butylbenzenediazonium acetate in dichloromethane.[32] The acetate counterion not only traps the aryl cation intermediate, forming the acetate product, but also abstracts a proton to form 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[33] and in matrix photodecarboxylation experiments.[34] All naphthynes found in matrix trapping experiments possess singlet multiplicities. 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 would be expected to react with methanol to yield predominantly 2-methoxynaphthalene,[35] 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 to produce $^1\mathbf{I_1}$ 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 states.[7] The latter process would yield triplet cations $^3\mathbf{I_1}$ 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 formally also radical cations, which are known to lose protons easily, especially from their benzylic positions.[36–38]

An argument in favour of naphthyne as a *cine* product-forming intermediate is the variation in the **9**:**10** ratio as a 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^{-1}), methanol (754.3 kJ mol^{-1}) and trifluoroethanol (700 kJ mol^{-1}) differ markedly in their proton affinities.[39] It is reasonable to expect more aryne-derived product in the better proton-abstracting solvent. Indeed, in the photolyses with **1** in the three solvents, the relative abundances of the *cine* substitution products increase with the proton affinities of the solvents. In the photolysis of **2**, scrambling is more prevalent than for **1** (Table 4). The triplet naphthalen-2-yl cation ($^3\mathbf{I_2}$), which is a benzylic-type radical cation, must be a stronger acid than the naphthalen-1-yl 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.

To substantiate the possible occurrence of *cine* substitution via naphthyne $\mathbf{I_8}$ as intermediate we tried to trap it in [4 + 2] or [2 + 2] cycloaddition reactions with benzene. The efforts were in vain. The products of those reactions would be 1,2-naphthobarrelene or dihydrobenzo[*a*]naphthalene,[40] each with molecular mass 204. The photoreaction of **1** in methanol in the presence of benzene (**1**:benzene = 1:20) produced, together with 1-methoxynaphthalene (**8**), 1- and 2-phenylnaphthalene (**9a**, **10a**), by in-cage reactions between $\mathbf{I_1}$ and iodobenzene and by reaction with benzene. No products of molecular mass 204 other than **9a** and **10a** were detected by GC-MS. An "ene" reaction may also produce **9a** and **10a** from $\mathbf{I_8}$ and benzene.[41] However, there is no reason why $\mathbf{I_8}$ should favour the "ene" reaction totally over [4 + 2] cycloaddition.

Conclusions

The naphthalen-1- and -2-yl cations $\mathbf{I_1}$ and $\mathbf{I_2}$ were generated by photolysis of their iodonium and diazonium salt precursors and their reactivities were studied. The naphthyl cations react (predominantly) through their singlet, closed-shell isomers. With the iodonium salt precursors, which also fragment from the triplet excited state, a contribution of the triplet naphthyl cations to the patterns of reactivity was found. Presumably, under the circumstances investigated, the singlet closed-shell naphthyl cations are lower in energy than their triplet isomers.

It appears that, with use of the naphthyliodonium precursors, the triplet naphthyl cations formed isomerise through 1,2 hydrogen atom shifts or lose protons 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 naphthalen-1- and -2-yldiazonium tetrafluoroborates, which generates only the singlet naphthalen-1- and -2-yl cations.

Experimental Section

Materials: Iodonium salts **1** and **2** were synthesised by a modified literature procedure.[42,43] HBF_4 (0.50 mL) in diethyl ether (54 wt.-%) was added at –30 °C to (diacetoxyiodo)benzene (0.5 g) in dry dichloromethane (25 mL). The temperature was allowed to rise to 0 °C, after which the clear yellow solution was cooled back to –30 °C. Stepwise, over a few min. commercially available 1- or 2-(4,4,5,5-tetramethyl-1,3,2-dioxoborolanyl)naphthalene (0.39 g) was added. The reaction mixtures turned dark. After the reaction mixtures had been stirred for 90 min at –30 °C, the temperature was allowed to rise to 0 °C. *n*-Hexane (40 mL) was added, causing crystallisation. Filtration of the crude products and repeated crystallisations from dichloromethane and *n*-hexane yielded off-white, powdery crystals in 21% and 28% yields, respectively. {**1**: ^{1}H NMR[44] (200 MHz, [D$_6$]DMSO): δ = 7.3–7.7 (m, 3 H), 7.7–8.1 (m, 6 H), 8.1–8.4 (d, 2 H), 8.9 (s, 1 H) ppm. IR[45] (neat): $\tilde{\nu}$=1000–1100 cm^{-1}, strong (BF_4^-)}. {**2**: ^{1}H NMR (200 MHz, [D$_6$]DMSO): δ = 7.4–7.8

(m, 6 H), 7.9–8.1 (d, 2 H), 8.1–8.4 (t, 3 H); 8.9 (s, 1 H) ppm. IR (neat): $\tilde{\nu}$=1000–1100 cm^{-1}, strong (BF$_4^-$)}. Diazonium salts **1**-N$_2^+$ and **2**-N$_2^+$ were prepared from commercially available starting materials by a literature procedure.[9] 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 fitted with rubber seals. The starting materials were dissolved at 0.02 M in the solvent (10 mL). *n*-Decane was used as internal standard. For the experiments in which product formation was followed as a function of irradiation time, the tubes were placed in a merry-go-round apparatus. A Hanau TNN-15/32 low-pressure mercury lamp placed in a water-cooled quartz tube was 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 seven 254 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 water (0.5 mL) and diethyl ether (0.050 mL). Aliquots from the irradiation mixtures in trifluoroethanol were added to water (0.5 mL) and dichloromethane (0.050 mL). The organic layers were analysed by GC and GC-MS and the assignments of the structures were confirmed by coinjection of commercially available or independently prepared products. After completion of the irradiations, the reaction mixtures were poured into water (10 mL) and extracted twice with diethyl ether (5 mL). The combined ether fractions were analysed by GC and GC-MS. The photolysis of **3** in acetonitrile/anisole (1:1) was followed as a function of time by taking samples (0.050 mL). The samples were analysed by GC and GC-MS. After completion of the irradiation the reaction mixture was analysed by GC and GC-MS.

Photoproducts: The products **3**, **4**, **5**, **6**, **7**, **8**, **8**-OCH$_2$CF$_3$, **8**-NHAc, **8**-F, **9a**, **10a**, **12**, **12**-NHAc and **12**-F were identified by GC, GC-MS and coinjection with the aid of commercially obtained reference samples. Products **11**[46] and **12**-OCH$_2$CF$_3$[47] were synthesised by 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 h.[12]

Quantum Chemical Calculations: The computations were performed with the Gaussian 03 program, version B3.[20] DFT calculations for the compounds under study were performed with the B3LYP functional[48] 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 with a double beam Varian DMS 200 spectrophotometer, if applicable with pure solvent in the reference cell. ^{1}H NMR spectra were recorded on a JEOL 200 instrument, in 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) with hydrogen as carrier gas. The Flame-Ionisation Detector (FID) was calibrated with 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) with helium as carrier gas. The GC was coupled to a Finnigan Mat SSQ 710 mass spectrometer, with electron impact as the ionisation method. The GC-MS data were analysed with Xcaliber.

---

[1] a) P. J. Stang, in *Dicoordinated Carbocations* (Eds.: Z. Rappoport, P. J. Stang), Wiley, Chichester, UK, **1997**, p. 451; b) M. Hanack, L. R. Subramanian, in *Methoden Org. Chemie* (Ed.: M. Hanack), Thieme, Stuttgart, Germany, **1990**, vol. E19C, p. 249; c) M. Winkler, W. Sander, *J. Org. Chem.* **2006**, *71*, 6357–6367.

[2] a) J. N. Harvey, M. Aschi, H. Schwarz, W. Kock, *Theor. Chem. Acc.* **1998**, *99*, 95–99; b) M. Aschi, J. N. Harvey, *J. Chem. Soc. Perkin Trans. 2* **1999**, 1059–1062; c) B. Guizzardi, M. Mella, M. Fagnoni, A. Albini, *J. Org. Chem.* **2001**, *66*, 6353–6563; d) S. Milanesi, M. Fagnoni, A. Albini, *Chem. Commun.* **2003**, 216–217; e) S. Protti, M. Fagnoni, M. Mella, A. Albini, *J. Org. Chem.* **2004**, *69*, 3465–3467.

[3] K. K. Laali, G. Rasul, G. K. Prakash, G. A. Olah, *J. Org. Chem.* **2002**, *67*, 2913–2918.

[4] a) V. Le Page, Y. Keheyan, T. P. Snow, V. M. Bierbaum, *J. Am. Chem. Soc.* **1999**, *121*, 9435–9446; b) D. Ascenzi, P. Bassi, P. Francheschi, O. Hadjar, P. Tosi, M. Di Stefano, M. Rosi, A. Sgamellotti, *J. Chem. Phys.* **2004**, *121*, 6728–6737.

[5] a) T. P. Snow, V. Le Page, Y. Keheyan, V. M. Bierbaum, *Nature* **1998**, 259–260; b) V. Le Page, Y. Keheyan, V. M. Bierbaum, T. P. Snow, *J. Am. Chem. Soc.* **1997**, *119*, 8373–8374; c) V. Le Page, Y. Keheyan, T. P. Snow, V. M. Bierbaum, *Int. J. Mass Spectrom.* **1999**, *185/186/187*, 949–959; d) Y. Keheyan, *Chem. Phys. Lett.* **2001**, *340*, 405–412; e) S. Petrie, D. K. Bohme, *Top. Curr. Chem.* **2003**, *225*, 37–75; f) M. Di Stefano, M. Rosi, A. Sgamellotti, *Future Gener. Comput. Syst.* **2004**, *20*, 807–819.

[6] a) R. Gronheid, G. Lodder, M. Ochiai, T. Sueda, T. Okuyama, *J. Am. Chem. Soc.* **2001**, *123*, 8760–8765; b) R. Gronheid, G. Lodder, T. Okuyama, *J. Org. Chem.* **2002**, *67*, 693–702; c) T. Okuyama, G. Lodder, Nucleophilic Vinylic Substitution and Vinyl Cation Intermediates in the Reactions of Vinyl Iodonium Salts, *Advances in Physical Organic Chemistry*, vol. 37 (Eds.: T. Tidwell, J. P. Richard), Elsevier Science Ltd., Amsterdam, **2002**.

[7] a) J. L. Dektar, N. P. Hacker, *J. Org. Chem.* **1990**, *55*, 639–647; b) J. L. Dektar, D. V. Leff, N. P. Hacker, *J. Org. Chem.* **1991**, *56*, 2280–2282; c) T. Kitamura, in *CRC Handbook of Organic Photochemistry and Photobiology*, 2nd ed. (Eds.: W. M. Horspool, F. Lenci), CRC Press LLC, Boca Raton, Fl: **2004**, Chapter 110.

[8] M. Slegt, H. S. Overkleeft, G. Lodder, *Eur. J. Org. Chem.* **2007**, 5364–5375; following paper.

[9] a) T. Kuokkanen, J. Palokangas, M. Talvensaari, *J. Phys. Org. Chem.* **2000**, *13*, 452–460; b) T. Kuokkanen, J. Palokangas, M. Talvensaari, *J. Phys. Org. Chem.* **2001**, *14*, 618–624.

[10] Under the same reaction conditions as used for the photolysis experiments, upon exclusion of light, **1**, **2**, **1**-N$_2^+$, **2**-N$_2^+$ and **3** are inert.

[11] a) T. Akiyama, Y. Imasaki, M. Kawanisi, *Chem. Lett.* **1974**, 229–230; b) T. Kitamura, M. Yamane, K. Inoue, M. Todaka, N. Fukatsu, Z. Meng, Y. Fujiwara, *J. Am. Chem. Soc.* **1999**, *121*, 11674–11679.

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

[13] S. M. Gasper, C. Devadoss, G. B. Schuster, *J. Am. Chem. Soc.* **1995**, *117*, 5206–5211.

[14] H. Eustathopoulos, J. Court, J. M. Bonnier, *J. Chem. Soc. Perkin Trans. 2* **1983**, 803–807.

[15] P. S. J. Canning, K. McCrudden, H. Maskill, B. Sexton, *Chem. Commun.* **1998**, 1971–1972.

[16] Y. Himeshima, H. Kobayashi, T. Sonada, *J. Am. Chem. Soc.* **1985**, *107*, 5286–5288.

[17] a) T. Okuyama, T. Takino, K. Sato, M. Ochiai, *J. Am. Chem. Soc.* **1998**, *120*, 2275–2282 and references cited therein; b) G. F. Koser, *Aldrichimica Acta* **2001**, *34*, 89–102.

[18] λ^3-Iodanes are also the reactive species in the photolysis of vinyl iodonium tetrafluoroborates in methanol and (to a lesser extent) in TFE; see ref.[6a–6b].

[19] M. Plugge, Leiden University, unpublished results.

[20] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman Jr, Montgomery, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D, Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, L. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challa-Combe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, *Gaussian 03, Revision B.3*, Gaussian, Inc., Pittsburgh, PA, **2003**.

[21] a) P. Du, F. Salama, G. H. Loew, *Chem. Phys.* **1993**, *173*, 421–437; b) K. Fujiwara, A. Harada, J. Aihara, *J. Mass Spectrom.* **1996**, *31*, 1216–1220.

[22] a) R. R. Squires, C. J. Cramer, *J. Phys. Chem. A* **1998**, *102*, 9072–9081; b) J. Cioslowski, A. Szarecka, D. Moncrieff, *Mol. Phys.* **2003**, *101*, 1221–1225.

[23] G. Angelini, Y. Keheyan, M. Speranza, *Helv. Chim. Acta* **1988**, *71*, 107–119.

[24] S. M. Gasper, C. Devadoss, G. B. Schuster, *J. Am. Chem. Soc.* **1995**, *117*, 5206–5211.

[25] a) D. R. Augood, J. I. G. Cadogan, D. H. Hey, G. H. Williams, *J. Chem. Soc.* **1953**, 3412–3417; b) R. L. Dannley, E. C. Gregg, R. E. Phelps, C. B. Coleman, *J. Am. Chem. Soc.* **1954**, *76*, 445–448.

[26] a) S. Minegishi, S. Kobayashi, H. Mayr, *J. Am. Chem. Soc.* **2004**, *126*, 5174–5181; b) *Advances in Chemistry: Nucleophilicity*, J. M. Harris, S. P. MacManus, American Chemical Society, Washington, **1987**.

[27] G. Angelini, Y. Keheyan, E. Lilla, G. Perez, *Radiochim. Acta* **1990**, *51*, 173–176.

[28] Y. Keheyan, R. Bassanelli, *Radiat. Phys. Chem.* **1996**, *47*, 465–468.

[29] a) M. A. Brooks, L. T. Scott, *J. Am. Chem. Soc.* **1999**, *121*, 5444–5449; b) R. F. C. Brown, *Eur. J. Org. Chem.* **1999**, 3211–3222.

[30] a) T. Okuyama, M. Fujita, *Acc. Chem. Res.* **2005**, *38*, 679–686; b) M. Fujita, W. H. Kim, Y. Sakanishi, S. Fujiwara, T. Okuyama, Y. Ohki, K. Tatasumi, Y. Yoshioka, *J. Am. Chem. Soc.* **2004**, *126*, 7548–7558.

[31] H. H. Wenk, M. Winkler, W. Sander, *Angew. Chem. Int. Ed.* **2003**, *42*, 502–528.

[32] R. W. Franck, K. Yanaga, *Tetrahedron Lett.* **1966**, *25*, 2905–2909.

[33] H. Gilman, N. N. Crounce, S. P. Massie, R. A. Benkeser, S. M. Spatz, *J. Am. Chem. Soc.* **1945**, *67*, 2106–2108.

[34] a) J. Lohmann, *J. Chem. Soc. Faraday Trans. 1* **1972**, 814–824; b) T. Sato, A. Niino, A. Yabe, *J. Phys. Chem. A* **2001**, *105*, 7790–7798.

[35] a) *Studies in Modern Chemistry: Carbenes, Nitrenes and Arynes*, T. L. Gilchrist, C. W. Rees, Nelson Press, London, **1969**, chapter 8, pp. 103–119; b) *Reactive Intermediates in Organic Chemistry*, N. S. Isaacs, John Wiley & Sons Ltd., London, **1973**, chapter 7, pp. 408–419.

[36] L. A. Deardurff, M. S. Alnajjar, D. M. Camaioni, *J. Org. Chem.* **1986**, *51*, 3686–3693.

[37] Loss of the other β proton, the non-benzylic 3-H proton, from $\mathbf{I_2^3}$, yielding 2,3-naphthyne, is unlikely.

[38] L. A. Huck, P. Wan, *Org. Lett.* **2004**, *6*, 1797–1799.

[39] *NIST Chemistry Webbook, NIST Standard Reference Database Number 69* (Eds.: W. G. Mallard, P. J. Linstrom), National Institute Of Standards and Technology, Gaitherburg, MD, 20899, March **2003** (http://webbook.nist.gov).

[40] a) H. E. Zimmerman, C. O. Bender, *J. Am. Chem. Soc.* **1970**, *92*, 4366–4376; b) M. Jones, R. H. Levin, *J. Am. Chem. Soc.* **1969**, *91*, 6411–6415.

[41] E. K. Fields, in *Organic Reactive Intermediates* (Ed.: S. P. McManus), Academic Press, New York, **1973**, p. 486.

[42] M. Ochiai, M. Toyonari, T. Nagaoka, D.-W. Chen, M. Kida, *Tetrahedron Lett.* **1997**, *38*, 6709–6712.

[43] M. Caroll, V. W. Pike, D. A. Widdowson, *Tetrahedron Lett.* **2000**, *41*, 5393–5396.

[44] B. R. Kaafarani, H. Gu, A. A. Pinkerton, D. C. Neckers, *J. Chem. Soc. Dalton Trans.* **2002**, 2318–2321.

[45] P. J. Stang, *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 274–285.

[46] J. Schmidlin, M. Huber, *Ber. Dtsch. Chem. Ges.* **1910**, *43*, 2834.

[47] H. Suzuki, T. Matuoka, I. Ohtsuka, A. Osula, *Synthesis* **1985**, 499–500.

[48] P. J. Stephens, F. J. Devlin, C. F. Chabalowski, M. J. Frisch, *J. Phys. Chem.* **1994**, *98*, 11623–11627.

Received: April 17, 2007