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Homolytic vs Heterolytic Paths in the Photochemistry of Haloanilines

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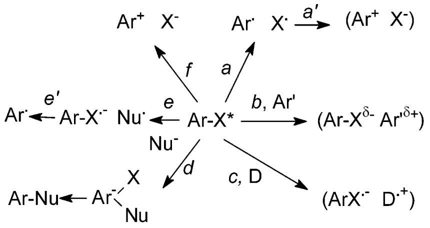
Abstract: The photochemistry of 4-haloanilines and 4-halo-*N*,*N*-dimethylanilines has been studied in apolar, polar aprotic, and protic solvents. Photophysical and flash photolysis experiments show that the reaction proceeds in any case from the triplet state. It is rather unreactive in apolar media, the highest value being $\Phi = 0.05$ for the iodoanilines in cyclohexane. Changing the solvent has little effect for iodoanilines and for the poorly reacting bromo analogue, while it leads to a variation of over 2 orders of magnitude in the quantum yield for the chloro and fluoro derivatives. The triplets have been characterized at the UB3LYP/6-31G(d) level of theory, evidencing a deformation and an elongation (except for C−F) of the C−X bond. Homolytic fragmentation is in every case endothermic, but calculations in acetonitrile solution show that heterolytic cleavage of C−Cl and C−Br is exothermic. Experimentally, the occurrence of heterolytic fragmentation has been monitored through selective trapping of the resulting phenyl cation by allyltrimethylsilane. Heterolytic dechlorination occurs efficiently in polar media (e.g., $\Phi = 0.77$ in MeCN), while debromination remains ineffective due to the short lifetime of the triplet. Heterolytic defluorination is efficient only in protic solvents ($\Phi = 0.48$ in MeOH), in accord with calculations showing that in the presence of an ancillary molecule of water fragmentation is exothermic due to the formation of the strong H−F bond. The energy profile for both homo- and heterolytic dissociation paths has been mapped along the reaction coordinates in the gas phase and in acetonitrile. The conditions determining the efficiency and mode of dehalogenation have been defined. This is significant for devising synthetic methods via photogenerated phenyl cations and for rationalizing the photodegradation of halogenated aromatic pollutants and the phototoxic effect of some fluorinated drugs.

Introduction

The photochemistry of aryl halides has been the subject of extensive investigation and has revealed many mechanistically interesting facets,[1] besides the environmental application for the degradation of persistent pollutants of this class. Different paths have been envisaged for the observed photoreactions and are indicated in Scheme 1.[2]

Scheme 1



Homolysis (path a) has some synthetic potential, for the preparation of biaryls, in particular in the intramolecular version for the construction of polycyclic systems.[2b,3] The viability of this path appears to be strictly determined by thermochemistry. C−X bond cleavage in the triplet state[4] is exothermic for iodo- and bromobenzenes and is probably moderately endothermic for chlorobenzenes, though there has been some controversy about the correct value of the Ph−Cl bond dissociation energy.[5] On the contrary, the largely endothermic homolysis of the aryl−fluorine bond does not take place. The decrease of the triplet energy in naphthalenes and in higher arenes makes cleavage unlikely. A variation of this path is cage electron transfer within the primarily formed radical pair leading to the ion pair in an indirect way (path a′).[6]

In other cases, the reaction proceeds from a (hetero)excimer (path b)[4b,5,7] or from an exciplex (e.g., with an aliphatic amine[8]

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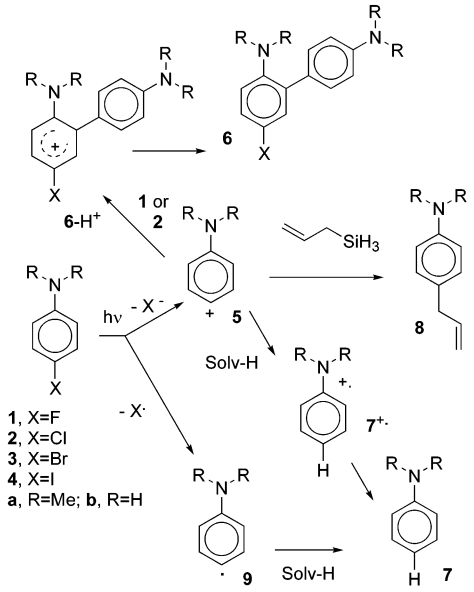
or with an aniline,[9] path c) rather than directly from the excited state.

Interaction of an excited aryl halide with a nucleophile leads either to substitution via the $\mathrm{S_N}$2Ar* mechanism (path d) or to electron transfer (path e).[10] In the latter case, the resulting radical anion may fragment (path e′) to give the aryl radical, which in turn may initiate a chain process ($\mathrm{S_{RN}}$1 mechanism).[11]

In contrast, unimolecular heterolytic cleavage (path f) has been rarely invoked in the photochemistry of aromatics. Actually, until recently heterolytic dehalogenation leading to nucleophilic photosubstitution via an $\mathrm{S_N}$1Ar* mechanism had been proposed only in a couple of cases.[12,13] In the last few years, however, considerable evidence about the photo*heterolysis* of halogenated phenols,[14,15] anisoles,[16] and anilines[17,18] in water as well as of 2-propylchlorobenzene in trifluoroethanol[19] has appeared. Our group found that with chloroanilines the reaction is efficient in polar organic solvents and affords a smooth entry to aryl cations.[20] This adds a synthetic perspective, because these otherwise hardly accessible intermediates[21] can be exploited in a variety of arylation reactions, in particular of alkenes and arenes, which offer a convenient access to functionalized anilines.[22]

The available evidence, mainly obtained with 4-chloroaniline, suggests that heterolytic cleavage proceeds efficiently from the triplet state and forms the triplet phenyl cation. However, under suitable conditions also 4-fluoroaniline cleaves,[20a,22d] which is intriguing in view of the high energy of the aryl−fluorine bond. Furthermore, it is not known to what extent homolytic cleavage competes in different haloanilines and in different media. These facts motivated a comprehensive examination of the photochemistry of haloanilines, based on the determination of product distribution and photophysical experiments in various solvents, as well as on computational studies both in the gas phase and in acetonitrile solution in the frame of DFT theory and the C-PCM (conductor version of PCM) solvation model.

Scheme 2



Results

Photochemistry. The halides examined were the fluoro-, chloro-, bromo-, and iodoanilines (**1**−**4**), as both *N*,*N*-dimethyl derivatives (**1a**−**4a**) and nonmethylated derivatives (**1b**−**4b**). It was previously found that chloroanilines **2a**,**b** are poorly photoreactive in apolar solvents while their irradiation in a polar solvent such as acetonitrile gives diphenyldiamines **6** accompanied by some anilines **7**. These products were rationalized as arising from cation **5** via electrophilic attack of the starting compound or, respectively, reduction. A product of structure **6** was formed also from fluoroaniline **1a**. However, in the presence of alkenes the reaction was diverted to arylation of the latter substrates. This reaction was particularly efficient when using allyltrimethylsilane, in which case allylanilines **8** became by far the major product (81% **8a** and 4% **7a** from **2a** in MeCN).[22a] On the other hand, anilines **7** may result from homolytic cleavage via radical **9**. Therefore, we decided to use the reaction with the allylsilane for the specific "titration" of the aryl cation and to explore the medium dependence of the reaction.

The irradiation of anilines **1**−**4** was carried out in a series of solvents of differing polarity and proticity (cyclohexane, dichloromethane, acetonitrile, methanol, and trifluoroethanol), and the experiments were repeated in the same solvents in the presence of 1 M allyltrimethylsilane. The product distribution and quantum yield of the reaction were determined (see Scheme 2 and Tables 1 and 2).

Fluoroaniline **1a** reacted quite sluggishly in cyclohexane or dichloromethane and only slightly more efficiently in acetonitrile; in the last case diphenyldiamine **6a** and amine **7a** were the main products. The reaction was much faster in alcohols,

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Table 1. Photochemistry of Some Haloanilines in Various Solvents

substrate	X	R	solvent	$\Phi_{-1\text{ or }2}$	yield of **6**, %	yield of **7**, %
1a	F	Me	C_6H_{12}	<0.005		80
			CH_2Cl_2	0.01		65
			MeCN	0.05	65	32
			MeOH	0.55	15	82
			CF_3CH_2OH	0.30	55	23
2a	Cl	Me	C_6H_{12}	0.003[a]		80
			CH_2Cl_2	0.2	15	65
			MeCN	0.87[a]	58	38
			MeOH	0.95[a]	8	87
			CF_3CH_2OH	0.50[a]	46	40

[a] From ref 20b.

Table 2. Photochemistry of Some Haloanilines in Various Solvents in the Presence of Allyltrimethylsilane (1 M)

	solvent	**a**, R = Me Φ_8	 Φ_7	**b**, R = H Φ_8	 Φ_7
1, X = F	C_6H_{12}		0.003		
	CH_2Cl_2		0.01		
	MeCN	0.04	<0.005	<0.01	
	MeOH	0.48	0.06	0.24	0.02
	CF_3CH_2OH	0.28		0.22	
2, X = Cl	C_6H_{12}		0.02		0.02
	CH_2Cl_2	0.16	0.03	0.08	0.01
	MeCN	0.77	0.04	0.39	0.04
	MeOH	0.68	0.18	0.36	0.10
	CF_3CH_2OH	0.55		0.22	0.01
3, X = Br	C_6H_{12}	0.001	0.001	0.001	0.001
	CH_2Cl_2	0.002	0.003	<0.001	0.001
	MeCN	0.003	0.001	0.001	0.001
	MeOH	0.02	0.004	0.01	0.01
	CF_3CH_2OH	0.05	<0.001	0.03	<0.001
4, X = I	C_6H_{12}	0.01	0.04	0.01	0.03
	CH_2Cl_2	0.02	0.04	0.01	0.04
	MeCN	0.02	0.03	0.02	0.03
	MeOH	0.03	0.04	0.02	0.03
	CF_3CH_2OH	0.03	0.02	0.025	0.02

with reduction to amine **7a** predominating in methanol and formation of diamine **6a** predominating in trifluoroethanol (Table 1). In acetonitrile as well as in the alcohols allylaniline **8a** became the major product in the presence of allyltrimethylsilane, though the overall quantum yield of the starting material decomposition remained the same as in the neat solvents (Table 2). Fluoroaniline **1b** followed a parallel pattern, with a slightly lower reaction quantum yield than **1a** under the same conditions.

Chloroanilines **2a**,**b** were again almost photostable in cyclohexane, but significantly photoreactive in dichloromethane, and reached the maximal value of photoreaction in acetonitrile, with diamines **6** as the main products, and in methanol (in the latter case, reduction to **7** predominated, Table 1). Also in this case, the overall quantum yield of photodecomposition changed little in the presence of the silane, where the main products became allylanilines **8** (Table 2).

With bromoanilines **3a**,**b** the quantum yield remained low under all of the conditions examined, with a moderate increase from some parts per thousand in cyclohexane to some percent in the alcohols and further some increase in the yield of allylanilines **8** (see Table 2).

Iodoanilines **4a**,**b** were more reactive than the bromo derivatives with a quantum yield of decomposition of ca. 5% under all of the conditions examined and anilines **6** as the main products. Only in trifluoroethanol the proportion slightly shifted in favor of allylated **8** (see Table 2).

Table 3. Selected Photophysical Parameters for Haloanilines **1**−**4** in Various Solvents

substrate	X	R	solvent	Φ_F	τ_F, ns	τ_T, μs
1a	F	Me	C_6H_{12}	0.14	2.8	1
			MeCN	0.23	5	
			MeOH	0.20	3.9	
1b	F	H	C_6H_{12}	0.16	2.1	
			MeCN	0.19	2.7	
			MeOH	0.19	2.8	
2a	Cl	Me	C_6H_{12}	0.024	0.7	0.3
			MeCN	0.026	0.8	
			MeOH	0.026	0.7	
2b	Cl	H	C_6H_{12}	0.012	0.6	
			MeCN	0.019	0.5	
			MeOH	0.019	0.5	
3a,**b**	Br	Me, H	C_6H_{12}, MeCN, MeOH	<0.001	<0.1	
4a,**b**	I	Me, H	C_6H_{12}, MeCN, MeOH	<0.001	<0.1	

Emission Properties. The emission of the above haloanilines was examined in fluid solution in apolar, polar, and protic media. The fluoro derivatives **1** exhibited a moderate fluorescence, with ca. 20% efficiency and a lifetime of some nanoseconds (see Table 3), with a limited effect of the nature of the solvent. With the chloroanilines **2** both Φ_F and τ_F decreased by up to 1 order of magnitude with respect to those of the fluorinated analogues.[23]

Fluoro- and chloroanilines also exhibited phosphorescence in a glassy matrix at 77 K, both polar (EPA) and apolar (3-methylpentane), with λ_{max} values around 425−435 nm.[24] The triplet energies (E_T) evaluated from the edge of the phosphorescence spectrum are reported in Table 5.

On the other hand, with both bromo- and iodoanilines **3** and **4** both fluorescence at room temperature and phosphorescence in a glassy matrix were very weak.

Transients. Laser excitation of a cyclohexane solution of fluoroanilines **1a**,**b** produced a transient with a concentration-dependent lifetime (1 μs or below in a 10^{-4} M solution), which was quenched in oxygen-saturated solutions. All of these characteristics closely matched those of the parent anilines **7a**,**b**,[25] and the transient was confidently assigned to the triplet state (Figure 1, Table 3). In acetonitrile the shape and lifetime of the transient changed little, although in the case of **1a** a fraction (<20%) of the signal around 460 nm persisted for a longer time.

In alcohols, on the other hand, the above transient was completely superseded by a different, intense absorption. With 1×10^{-4} M **1a** in MeOH, a persistent (>10 μs) absorption with maxima at 430, 450, and 480 nm was observed (Figure 2a). The transient was similar in *i*-PrOH. An additional feature in TFE was a further absorption with maxima at 400 and 420 nm (Figure 2b).

The results were quite similar to those of the other fluorinated aniline **1b** with the difference that the transients were blue-

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(23) The present results compare well with literature data obtained under some of the above conditions; see: Koutek, B.; Musil, L.; Soucek, M. *Collect. Czech. Chem. Commun.* **1985**, *50*, 1753.

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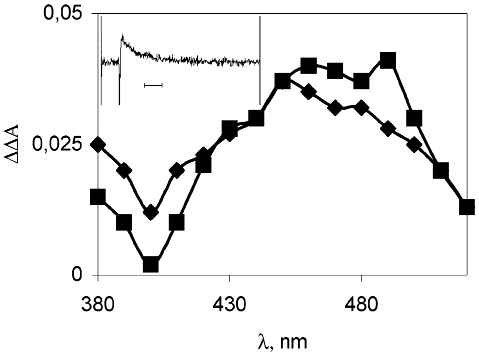

Figure 1. Transient absorption upon flashing fluoroaniline **1a** in cyclohexane (◆) and acetonitrile (■). Inset: decay of the absorption at 450 nm in cyclohexane, time unit 1 μs.

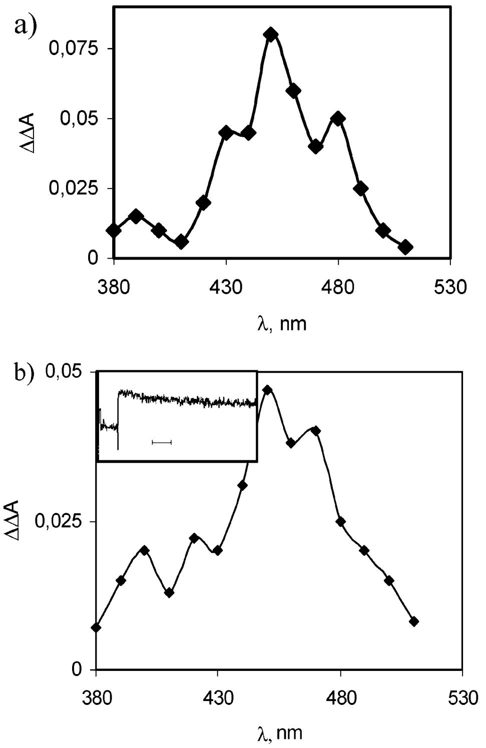

Figure 2. Transient absorption 1 μs after flashing fluoroaniline **1a** in methanol (a) and trifluoroethanol (b). Inset: decay of the absorption at 450 nm in TFE, time unit 10 μs.

shifted by ca. 20 nm (e.g., $\lambda_{\max} = 425$ nm in methanol) and the persistent absorption in alcohols was even longer lived ($\tau =$ ca. 100 μs).

With the chloroanilines **2a**,**b** flash photolysis experiments had been previously carried out in various solvents both by Othmen et al.[17a] and by us.[20b] They revealed the triplet in cyclohexane (see Table 3) and a persistent absorption closely matching that observed with **1a**,**b** in methanol. Flashing **2a**,**b** in TFE likewise gave results similar to those of the fluoro derivatives. A difference between the chloro- and fluoroanilines was that with the former derivatives the end-of-pulse absorption had a maximum at 430 nm and evolved into a persistent absorption extending from 340 to 510 nm, similar to that observed in alcohols, whereas with **1a**,**b** the triplet was observed. Experiments in the presence of 1 M allyltrimethylsilane were then carried out and showed that the long-lived transient was suppressed with both chloro- and fluoroanilines.

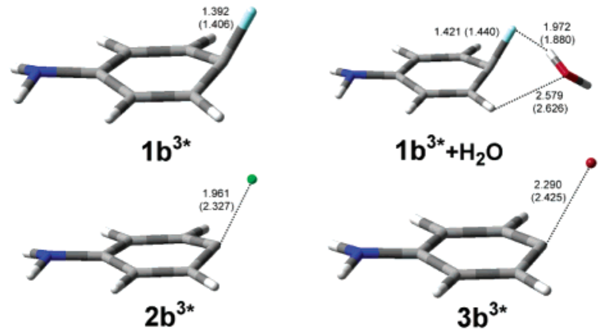

Figure 3. Triplet state of haloanilines **1b**−**3b**. Bond lengths (Å) at UB3LYP/6-31G(d) and UB3LYP-C-PCM/6-31G(d) (in parentheses) are reported.

As for the bromo- and iodoanilines, only weak signals were observed in the region 370−410 nm, with little difference in the solvent tested.

Irradiation in a frozen solution was also explored, with negative results. As an example 1 h of irradiation of the glass obtained from a 1×10^{-4} M solution of chloroaniline **2a** in EtOH at 90 K led neither to a significant change of the absorption spectrum nor to the formation of a permanent photoproduct as determined by HPLC analysis.

Thermochemistry of the Homolytic and Heterolytic Dissociation Processes in the Gas Phase and Acetonitrile Solution. It was vital for the rationalization of the above data that the viability of homolytic or heterolytic fragmentation of the haloanilines was evaluated. Cleavage of the weak carbon−iodine bond (63.7 kcal/mol in iodobenzene)[26] was expected, but in the case of the other halides a prediction of the feasibility and of the mode of fragmentation was not obvious. As is illustrated in the Discussion, the photochemical reaction proceeded from the triplet state. Accordingly, the structure and the reactivity of triplet haloanilines were examined at the UB3LYP/6-31G(d) level of theory. This method had been previously shown to be well suited for triplets and when applied to the haloanilines actually reproduced the experimental C−X bond dissociation energy data (see the Supporting Information). The optimized triplet states in the gas phase and acetonitrile solution of compounds **1b**−**3b** (by the C-PCM solvation model) were characterized by the out-of-plane deformation of the C_4 atom and of the C_4–X bond (see Figure 3).

As it appears from Table 4, the C−F bond in triplet **1b**^{3*} was only slightly elongated (2.5% in the gas phase, 3.5% in MeCN). The elongation of the C−Cl bond in **2b**^{3*} was more marked in the gas phase (11.3%) and increased strongly in MeCN bulk (32.1%), while C−Br in **3b**^{3*} was severely stretched already in the gas phase (19.6%; 27.1% in MeCN).

Furthermore, the C_4–F bond in **1b**^{3*} had a polar character with roughly equal opposite charges (0.25−0.30) on fluorine and C_4 atoms, and the charges did not vary in MeCN with respect to the gas phase. On the contrary, the negative charge on the chloro atom increased markedly in **2b**^{3*} on going from the gas phase to MeCN (up to −0.505) and was not counterbalanced by a charge on C_4 (−0.06 and +0.03 in the two cases), most of the positive charge being localized on the amino group. The bromoaniline triplet was similar to the chloro analogue in this respect.

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Table 4. Triplet State of Haloanilines **1b**−**3b** [at UB3LYP/6-31G(d)]

aniline	d_{C-X},[a] Å	E_T, kcal/mol	d_{C-X},[b] Å	charge(C_4)[b]	charge(X)[b]
1a, $H_2NC_6H_4F$	1.355	78.0	1.392 (1.406)	+0.258 (+0.238)	−0.290 (−0.315)
1b, $H_2NC_6H_4Cl$	1.762	72.2	1.961 (2.327)	−0.06 (+0.03)	−0.197 (−0.505)
1c, $H_2NC_6H_4Br$	1.915	68.0	2.290 (2.434)	+0.013 (+0.032)	−0.303 (−0.458)
1a, $H_2NC_6H_4F{\cdot}H_4O$			1.421[c]	+0.237[c]	−0.300[c]

[a] In the ground state. [b] In the gas phase; values in parentheses were taken in MeCN. [c] In the presence of one molecule of water in MeCN.

Table 5. Computed (B3LYP) Electronic Energies (kcal/mol) for the Triplet States of Haloanilines and Homo- and Heterolytic Fragmentation[a]

	E_T		ΔE(vacuum)	ΔE(MeCN)		ΔE(vacuum)	ΔE(MeCN)
1b, $H_2NC_6H_4F$	78.0	$H_2NC_6H_4\bullet + F\bullet$	51.5	52.0	$H_2NC_6H_4^+ + F^-$	149.1	9.1
2b, $H_2NC_6H_4Cl$	72.2	$H_2NC_6H_4\bullet + Cl\bullet$	21.3	23.4	$H_2NC_6H_4^+ + Cl^-$	81.1	−31.4
3b, $H_2NC_6H_4Br$	68.0	$H_2NC_6H_4\bullet + Br\bullet$	18.3	18.8	$H_2NC_6H_4^+ + Br^-$	74.5	−34.6
1b, $H_2NC_6H_4F{\cdot}H_2O$	78.0	$H_2NC_6H_4\bullet + F\bullet + H_2O$	39.0	37.0	$H_2NC_6H_4^+ + HF + OH^-$	103.7	−4.6

[a] Solvent effect calculation; see the Experimental Section.

The thermochemistry of both homolytic and heterolytic fragmentations (eqs 1 and 2) was then evaluated by calculating the potential energy change associated with these processes.

$$4\text{-}H_2NC_6H_4\text{-}X^{3}* \rightarrow 4\text{-}H_2NC_6H_4\bullet + X\bullet \qquad (1)$$

$$4\text{-}H_2NC_6H_4\text{-}X^{3}* \rightarrow 4\text{-}H_2NC_6H_4^{+} + X^{-} \qquad (2)$$

The key results are summarized in Table 5. With bromoaniline, homolytic fragmentation is moderately endothermic in the gas phase (18.3 kcal/mol), while the heterolytic process is largely so (74.5 kcal/mol). Shifting the calculation to an acetonitrile solution (with optimization of both reactants and adducts in acetonitrile bulk) left the homolytic process unchanged, while making heterolysis a markedly exothermic reaction (−34.6 kcal/mol). Essentially the same situation was encountered with chloroaniline. On the other hand, the strong carbon−fluorine bond was not as easily cleaved. The homolytic reaction was strongly endothermic in the gas phase (51.5 kcal/mol) as well as in acetonitrile (52.0 kcal/mol). Heterolytic fragmentation was extremely endothermic in the gas phase, and although dramatically dropping from 149.1 to 9.1 kcal/mol, it remained unfavorable in a polar aprotic solvent such as acetonitrile.

The experimentally noted effect of protic solvents on the photochemistry of fluoroanilines suggested also taking into consideration proticity. To model the specific interaction with the triplet excited state of fluoroaniline, we added an ancillary water molecule H-bonded to the fluorine atom. As it appears from Table 4 (last entry) and Figure 3, the characteristics of triplet **1b**^{3}***** were only scarcely affected by the presence of water. However, in this case additional cleavage modes involving a molecule of water could be considered (eqs 3 and 4).

$$4\text{-}H_2NC_6H_4\text{-}F^{3}*\cdots H_2O \rightarrow 4\text{-}H_2NC_6H_4\bullet + HF + HO\bullet \qquad (3)$$

$$4\text{-}H_2NC_6H_4\text{-}F^{3}*\cdots H_2O \rightarrow 4\text{-}H_2NC_6H_4^{+} + F^{-}\cdots H_2O \qquad (4)$$

Table 5 shows that the homolytic cleavage according to eq 3 remained strongly endothermic both in the gas phase (39.0 kcal/mol) and in acetonitrile solution (37.2 kcal/mol), but heterolysis according to eq 4 became slightly but clearly exothermic in acetonitrile (−4.6 kcal/mol), due to the determining contribution of the strong H-bonding involving fluorine anion and water.

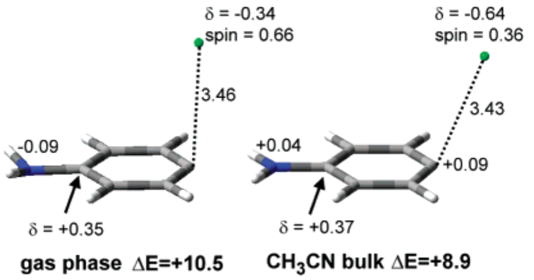

Figure 4. Geometries, Mulliken charges (with hydrogen charges summed into heavy atoms), and spin densities of triplet chloroaniline **2b** at a 3.4 Å C−Cl bond length in the gas phase (left) and in acetonitrile (right). Bond lengths are in angstroms and energies in kilocalories per mole.

Energetics of the Fragmentation Processes along the C···X Reaction Coordinate. A detailed mapping of the fragmentation process was carried out both in the gas phase and in MeCN by 0.1 Å increments of the C−X bond length and optimization at each point. Starting with the chloroaniline triplet, for which homolytic cleavage is slightly less endothermic in the gas phase (21.3 kcal/mol vs 23.4 kcal/mol for heterolysis), the scan showed a rather uniform increase in the potential surface.

The *homolytic* mode of the reaction could be recognized through the structure of the intermediates. At 10.51 kcal/mol, the bond was essentially broken (d_{C-Cl} = 3.461 Å; see Figure 4, left) and the chlorine atom had slightly increased the charge (−0.336) and strongly the spin (0.663), while the charge on C_4 was unchanged (+0.05).

The result was quite different in MeCN bulk. In this case, *heterolytic* cleavage occurred at a comparable elongation of the C−Cl bond as in the gas-phase dissociation process above (d_{C-Cl} = 3.427 Å; see Figure 4, right). The energy had increased by 8.98 kcal/mol, and this involved localization of the charge (−0.638) rather than of the spin (0.357) at the chlorine atom, while the organic moiety had a geometry quite similar to that we previously calculated for triplet 4-aminophenyl cation,[22a] with an almost planar structure. The charge was mainly located on the C_1–NH_2 moiety, not on C_4 (+0.089).

The dissociation process of the fluoroaniline triplet presented a more complex energy profile. In the gas phase, strongly endothermic (51.5 kcal/mol) dissociation proceeded via a transition state (30.7 kcal/mol, **TS-1b** in Figure 5) with the fluorine atom between C_4 and C_3 (C_4–F = 2.106 Å, C_3–F =

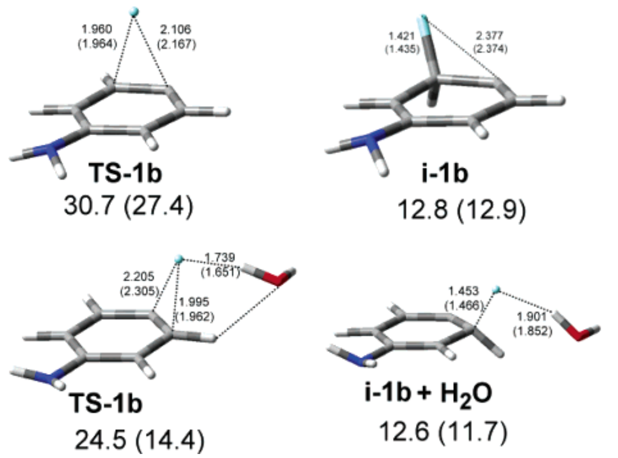

Figure 5. TS and intermediate involved in C−F bond cleavage of triplet fluoroaniline **1b** (top) and in the complex with one molecule of water (bottom) in the gas phase at the UB3LYP/6-31G(d) level. Stationary points optimized in MeCN bulk (in parentheses) have been optimized at the UB3LYP-C-PCM/6-31G(d) level of theory. Bond lengths are in angstroms and energies in kilocalories per mole.

1.96 Å). Such a TS is not directly connected to free products, but along the reaction coordinate there is an additional minimum (12.8 kcal/mol, **i-1b**) with the fluorine atom bonded at C_3 (C_4–F = 2.377 Å, C_3–F = 1.421 Å). The presence of a molecule of water only marginally affected the path followed toward homolytic dissociation (39.0 kcal/mol) through a transition state (24.5 kcal/mol, C_4–F = 2.205 Å, C_3–F = 1.995 Å, F−H = 1.739 Å, **TS-1b** + H_2O) and a minimum (C_4–F = 2.380 Å, C_3–F = 1.453 Å, H−F = 1.901 Å, **i-1b** + H_2O).

In neat MeCN both transition-state and minimum geometries for fluorine transfer from C_4 to C_3 were similar (respectively, 27.39 kcal/mol, C_4–F = 2.167 Å, and C_3–F = 1.964 Å and 12.87 kcal/mol, C_4–F = 2.374 Å, C_3–F = 1.435 Å; see Figure 5), but now the thermochemistry of heterolysis was only slightly endothermic (by 9.1 kcal/mol).

The geometry of the intermediates was similar also when a water molecule was added (see Figure 5, bottom), but heterolytic fragmentation according to eq 4 was now *exothermic* (by 4.6 kcal/mol). We were unable to locate a further TS between the minimum (**i-1b** + H_2O) and a separated triplet aniline cation−$F^-\cdots H_2O$ complex. However, it was clear that a molecule of water assisted C−F fragmentation, as shown by the increased C_4–F (2.305 Å) and decreased H−F (1.651 Å) distances both in transition state **TS-1b** + H_2O and in intermediate **i-1b** + H_2O (C_4–F = 2.380 Å, C_3–F = 1.466 Å, H−F = 1.852 Å; see Figure 5). Furthermore, the path was now more favorable and both structures had now a lower energy (**TS-1b** + H_2O, 14.4 kcal/mol; **i-1b** + H_2O, 11.71 kcal/mol).

Discussion

Excited State Involved. In the case of aniline, as with many other aromatic substrates, the sum of the fluorescence quantum yield and phosphorescence quantum yield in the glass at low temperature ($\Phi_F + \Phi_P$) comes close to unity. In fluid solution, the fluorescence lifetime is much shorter than the natural lifetime.

Among the presently considered compounds (Table 1), fluoroanilines **1a**,**b** both fluoresce and (in the glassy state) phosphoresce with similar intensity as parent anilines **7a**,**b**.

Scheme 3

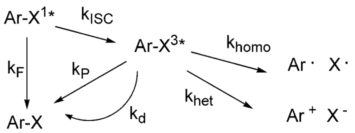

Table 6. Some Kinetic Parameters for the Excited States of Anilines **7** and Haloanilines **1**−**4**

	k_{ISC}, s^{-1}	k_d, s^{-1}	k_{het}, s^{-1}	k_{homo}, s^{-1}
7, X = H	$2.5 \times 10^{8\,a}$	7×10^5		
1, X = F	$2.5 \times 10^{8\,b}$	1×10^6	$<1 \times 10^5$ (MeCN) 1×10^6 (MeOH)	$<1 \times 10^5$
2, X = Cl	$3 \times 10^{9\,b}$	3×10^7	3×10^7 (MeCN, MeOH)	$<1 \times 10^5$
3, X = Br	$>1 \times 10^{10}$	$>1 \times 10^8$		
4, X = I	$>1 \times 10^{10}$	$>1 \times 10^8$		$>5 \times 10^6$

[a] From ref 24c. [b] From ref 23 [see also the reported value for PhCl, k_{ISC} = ca. 1×10^9 s^{-1} (Ichimura, T.; Mori, Y. *J. Chem. Phys.* **1973**, *58*, 288)].

Previous studies established that in fluid solution the main decay path for the singlet is intersystem crossing (ISC) to the triplet state, both for parent aniline (ca. 80%)[25] and for the chloro derivative (ca. 95%),[17a,20b] and for the fluoroanilines both Φ_F and τ_F are close to those of the parent compound. Thus, the main path of decay from the singlet is ISC, and k_{ISC} (see Scheme 3) is evaluated as $(2-5) \times 10^8$ s^{-1} for the fluoroanilines, $(1.3-2) \times 10^9$ s^{-1} for the chloroanilines, and $>1 \times 10^{10}$ s^{-1} for the bromo and iodo analogues, where fluorescence is too short lived to be detected (Table 6).

The triplet is clearly revealed by the T−T absorption in flash photolysis (Figure 1) for the chloro- and fluoroanilines, with a lifetime of 1 μs or less for dilute solutions in apolar solvents (Table 3). A similar transient is not detected with either the bromo or the iodo analogues. Since there is no reason to expect a dramatic decrease of the absorbance, this indicates efficient depopulation of the triplet due to a heavy atom effect (T_1 to S_0, $k'_{ISC} \cong k_d$ more than an order of magnitude larger than in the previous cases).

As for the photochemical reaction, this is efficient ($\Phi \geq 0.5$) only in polar solvents with the chloroanilines and only with protic solvents with the fluoro derivatives (see Table 2). With these substrates, no parallel change occurs in the photophysical parameters of the singlet excited state (which if anything lives longer in polar or protic solvents; see Table 3). Thus, the singlet is not involved in the photoreaction, which proceeds only from the triplet state. Indeed, the triplet becomes too short lived to be detected in the media where these substrates react. A fortiori, any photochemical reaction involves the triplet state with the bromo and iodo derivatives, for which S_1–T_1 intersystem crossing is even faster.

Flash photolysis data support this representation. Under conditions where the haloanilines react efficiently, the triplet (Figure 1) is substituted by a long-lived transient (Figure 2). The long-wavelength part of such a transient is, in accord with previous reports,[17a,20b] attributed to radical cation $\mathbf{7}^{\bullet+}$. The short-wavelength part is attributed to the adduct cation **6-H**$^+$ (Scheme 2).[20b,21d] The latter part is more important in TFE (and from **2** also in MeCN), where indeed **6** is the main product.

Quantitative Determination of Heterolytic Cleavage. We previously supplied chemical trapping evidence that dechlorination of 4-chloroanilines **2a**,**b** gives triplet 4-aminophenyl cation **5**.[20b,22a] The selective electrophilic reactivity of this intermediate supports its role, although direct detection fails, apparently due to spectroscopic characteristics. This species adds efficiently to π nucleophiles such as alkenes and (hetero)-aromatics, but not to σ nucleophiles such as water or methanol, as has been computationally and experimentally documented.[20a] The cation is in part reduced through hydrogen transfer from the solvent via **7**$\bullet^+$ and in part adds to the starting material (Scheme 2).

In the presence of a sufficient amount of a π nucleophile, the cation is trapped. This approach has been employed in this work for titrating the cation formed from haloanilines **1**−**4** under various conditions. Allyltrimethylsilane has been chosen, since elimination of the electrofugal Me_3Si^+ group leads to a single product, allylaniline **8**, which is easily gas chromatographically determined. As shown in Table 2, product **8** is formed efficiently from chloroanilines in polar solvents and from the fluoro derivatives in protic solvents. Under such conditions, the long-lived transients are not observed, apparently due to quenching of their precursor, phenyl cation **5** (see Scheme 2). On the contrary, the inefficient dechlorination of **2a**,**b** in cyclohexane is not affected in the presence of the alkene and the products remain anilines **7a**,**b**. Thus, under these conditions the homolytic path via **9** is followed both for chloroanilines and for analogously behaving bromo- and iodoanilines (see Table 2).

Structure and Homolysis of Haloaniline Triplets. The lowest lying triplet of haloanilines **1b**−**3b** is in every case characterized by a strong out of plane deformation of the halogen atom. Previously, an out of plane shift of the fluorine atom in triplet fluorobenzene was indicated by the SINDO1 method.[27] Our calculations at the UB3LYP/6-31G(d) and UB3LYP-C-PCM/6-31G(d) levels of theory (for the gas phase and acetonitrile solution, respectively) confirm such evidence. In addition, our data suggest that such a deformation is accompanied by elongation of the C−X bond. This is small in fluoroaniline (from 1.355 Å for the singlet ground state to 1.392 and 1.406 Å for the triplet state in the gas phase and in acetonitrile solution, respectively), while it is conspicuous for both cloroaniline (2.327 Å) and bromoaniline (2.425 Å) in acetonitrile (see Table 4).

Noteworthy is the bulk solvent effect on C−X elongation for the cloroaniline triplet. The bond distance increases by 0.20 Å in the gas phase and by 0.56 Å in acetonitrile solution. The deformation initiates the path toward homolysis, although the barrier on the potential energy surface (PES) remains significant for both chloroaniline and bromoaniline triplets (21.3 and 18.3 kcal/mol in the gas phase, essentially unchanged in MeCN). Cleavage is expected to be easier in iodoaniline in view of the much lower (by ca. 15 kcal/mol) bond strength. On the contrary, with the fluoro analogue elongation of the bond is small and does not increase in acetonitrile, homolysis remaining highly unfavorable in both cases (Table 4).

Mapping the surface for the chloroaniline triplet in the gas phase shows no transition state, but a smooth increase of the energy, with increasing spin, not charge, localization on the chloro atom (Figure 4). With fluoroaniline, the strong endothermicity of C−F homolysis (51.5 kcal/mol) leads to an interesting change in the path, and the fluorine atom migrates to position 3 and reaches, after passing a transition state, a minimum with a carbene configuration (see the structure **i-1b** in Figure 5). In this case, calculations referred to acetonitrile as the medium show no important change with respect to those referred to the gas phase.

Experimentally, an indication for the homolytic path can be obtained from the photolysis in cyclohexane. With chlorobenzene it has been found that homolysis is efficient in this solvent, with a limiting value of $\Phi = 0.5$ at infinite dilution, though the actual values at a reasonable concentration are lower due to the chemically unproductive formation of an exciplex.[28] The reaction has been attributed to internal conversion of the $\pi\pi^*$ triplet to a close-lying, repulsive $\pi\sigma^*$ triplet,[29] as supported by ab initio UHF calculations.[30]

With the present haloanilines, homolysis is, as expected, negligible with the fluoro derivative and inefficient with the other derivatives, since the triplet energy is lower than that of halobenzenes. This is in accord with the straightforward correlation between efficiency and the difference between excited-state energy and bond strength generally observed with haloarenes and with the calculated endothermicity of the process (Table 5). In the event, Φ_{homo} decreases from chloro (0.02) to bromo (0.002) derivatives and increases to iodo derivatives (0.05). This is due to the balance between competing processes from T_1, homolysis and heavy-atom-induced intersystem crossing to S_0, the rate of both increasing with atomic weight. In every case $k_{\mathrm{homo}} < k'_{\mathrm{ISC}}$ (Scheme 3). With iodoanilines, $k_{\mathrm{homo}} \cong 0.05k_{\mathrm{d}}$; thus, $>5 \times 10^6\ \mathrm{s}^{-1}$, with that of the bromo derivatives at least an order of magnitute lower.

Triplet Heterolysis. Calculations at the UB3LYP/6-31G(d) level show that triplet heterolysis in the gas phase is a strongly endothermic process for fluoro-, chloro-, and bromoanilines, and the barrier on the PES for such a process is quite high (149.1, 81.1, and 74.5 kcal mol^{-1}, respectively). However, evaluation by C-PCM stationary point optimization of the acetonitrile bulk effect evidences a strong change in both triplet chloroaniline structure (as discussed above) and PES profile. In detail, the optimized triplet in MeCN shows not only a more elongated C−Cl bond, but also an increased anionic character of the chlorine atom with respect to that in the gas phase (from −0.197 to −0.505). The corresponding positive charge resides essentially on the amino group.

Mapping the cleavage shows no transition state, but a smooth increase of energy accompanied by localization of the charge on the chloro atom. When the C−Cl distance is stretched to 3.4 Å, the organic moiety attains a planar configuration very close to that of the final product, phenyl cation. The moderate barrier encountered (ca. 9 kcal/mol) and the strong exothermicity of the overall process (−31 kcal/mol) clearly indicate the feasibility of the heterolytic process. This is supported both by the increase of the reaction efficiency with solvent polarity (for **2a**, $\Phi = 0.2$ in CH_2Cl_2, 0.85 in MeCN, 0.97 in MeOH, and 0.5 in CF_3CH_2OH, with a decrease in the last solvent presumably because H-bonding by the acidic alcohol limits the electron

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donation from the amino group) and by the essentially complete trapping of the cation by the allylsilane to produce **8** (except in good hydrogen donating MeOH, where reduction still competes with a 20% proportion). The role of solvation in allowing detachment of the oppositely charged fragments is also indicated by nonreactivity of **2a** in rigid ethanol glass, where the ions apparently recombine. The dramatic change of $\Phi_{-\mathbf{2}}$ in polar solvents while the endothermicity of homolysis remains unchanged (Table 5) ensures that the process occurring is heterolytic fragmentation directly from the triplet, not electron transfer after homolysis (path f, not path a′, in Scheme 1).

Path a′ is probably involved with iodoanilines ($\Phi_{-\mathbf{4}}$ low and solvent independent, though the proportion of product **8** grows somewhat in polar solvents), while the tendency of bromoanilines to heterolysis in polar solvents is barely detectable since the fast decay of the triplet cuts photochemistry to low values ($\Phi_{-\mathbf{3}} = 0.002$ to 0.02; see Table 2).

On the other hand, examination of fluoroanilines shows no change parallel to that of the chloro analogues in MeCN (and actually the quantum yield remains low). In fact, calculations support that the fragments, triplet phenyl cation and fluoride anion, are greatly stabilized in comparison to those in the gas phase, but remain at a higher energy on the PES with respect to the bonded triplet state (9.1 kcal mol^{-1}). However, when both bulk (acetonitrile) and specific interactions with a protic medium, which has been computationally modeled by an ancillary water molecule added to the reactive system ($H_2NC_6H_4F{\cdot}H_2O$), are taken into account, calculations do show a noteworthy change. A transition state still remains, but the activation energy is lowered (14.4 kcal/mol), and although the path still goes over a minimum with the fluorine atom essentially bonded to C_3 (**i-1b** + H_2O), the final products, viz., the phenyl cation and the fluoride anion hydrogen bonded to the water molecule, are stabilized with respect to the triplet state by −4.6 kcal/mol. Thus, the experimentally observed efficient defluorination in alcohols (up to $\Phi = 0.5$) is not merely due to the increased polarity of the medium, but is the result of synergism with the strong H-bonding interaction (eq 4). Once again, trapping by allylsilane is unambiguous evidence for the involvement of phenyl cation in protic media.

Conclusion

The photochemistry of haloanilines proceeds via the triplet state and exhibits a varied pattern. The course of the reaction changes from the inefficient (ca. 5%), solvent-independent homolytic cleavage of iodoaniline to the efficient (ca. 50% or more) heterolytic cleavage observed in polar solvents with chloroaniline and in protic solvents with fluoroaniline. Formation of the strong H−F bond plays a key role in the last case, as supported by both experimental and computational evidence. On the other hand, the heavy atom effect decreases the triplet lifetime and thus limits the efficiency of homolytic fragmentation also for relatively weak C−Br and C−I bonds.

Heterolytic fragmentation and S_N1Ar^* reactions are quite efficient with chloroanilines and fluoroanilines under appropriate conditions. Literature reports[13,14,16] and ongoing experiments suggest that conditions can be found for extending such reactions to further aryl halides, at least with electron-donating substituted derivatives, and their scope may be larger than it now appears from the literature. The smooth generation of a phenyl cation via photoheterolysis of halides complements the formation of such intermediates from diazonium salts and, differently from that case,[31] leads exclusively to the triplet state, the reactions of which are characterized by a high selectivity, in contrast to the unselective reactions of singlet phenyl cations. Photoheterolysis of the aryl−Cl and aryl−F bonds appears to be a convenient method for the smooth generation of aryl cations and allows exploitation of the chemistry of these as yet scarcely investigated intermediates.[21] Addition of aryl cations to alkenes, aromatics, and heterocycles is a synthetically promising method.[20,22]

Furthermore, the rationalization of the structure and reactivity of triplet haloanilines is significant for applications such as the photochemical decontamination of aryl halides as pollutants in water,[32a] for phototochemical applications in nanotechnology,[32b] and for understanding the efficient ($\Phi = 0.5$) heterolytic defluorination of several fluoroquinolone drugs in water,[33] which is probably the cause of the disturbing phototoxic side effect of those antimicrobic agents.

Experimental Section

General Procedures. The haloanilines either were commercial samples or were prepared by *N*-methylation[34] or ring iodination[35] according to published procedures. The other reagents (of commercial origin) were distilled or recrystallized before use. For the irradiations, spectroscopic grade solvents were used as received.

Photochemical Reactions. Irradiations were carried out by using 5 mL portions of the haloaniline solutions in quartz tubes. The tubes were capped after being flushed with argon for 15 min and externally irradiated by means of six 15 W phosphor-coated lamps (center of emission 310 nm) for an appropriate time in a merry-go-round apparatus. The conversion was limited to 20%. Product formation was assessed by GC and HPLC on the basis of calibration curves with dodecane as the internal standard. Allylanilines **8** have been previously characterized.[22a] The light flux for quantum yield determination was measured by ferrioxalate actinometry. Irradiations in a glassy matrix were carried out in a quartz cuvette immersed in an Oxford DN104 liquid nitrogen cryostat kept at 90 K.

Photophysical Measurements. Fluorescence spectra and lifetimes were measured by means of an Edinburgh Instruments F900 single-photon-counter instrument. Phosphorescence spectra were measured at 77 K by means of an Aminco Bowman SPF instrument fitted with a rotating phosphoroscope.

Flash Photolysis. The laser flash photolysis studies were carried out by using the fourth (266 nm) harmonics of a Q-switched Nd:YAG laser (model HY 200, JK Laser Ltd. Lumonics). This delivered 3 mJ pulses with a duration of ca. 10 ns. The monitor system, arranged in cross-beam configuration, consisted of a laser kinetic spectrophotometer (model K 347, Applied Photophysics) fitted with a 200 W Xe arc lamp, an F/3.4 monochromator, and a five-stage photomultiplier. The signals were captured by a Hewlett-Packard 54510A digitizing oscilloscope, and the data were processed on a 286-based computer system using software developed by Prof. C. Long (Dublin).

Computational Details. The B3LYP method was chosen due to its viability for computing PESs for organic reactions involving open shell

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species, including radical cations, and has been successfully tested.[36] UDFT methods and in particular UDFT with hybrid functionals (such as B3LYP) have been proved to provide a basis for a reasonable description of biradical species,[37,38] or systems with high biradical character. Furthermore, the suitability of DFT for reliably describing hydrogen-bonded systems has been the subject of many investigations,[39] and such methods have proven useful for studying hydrogen-bonded complexes.[40] The B3LYP functional in particular is highly effective, at least as long as an appropriate basis set is used.[41] Therefore, the level of theory chosen for the optimization of all the stationary points in our investigation [UB3LYP/6-31G(d)] appears to be a proper choice. All calculations were carried out using the Gaussian 94[42] and Gaussian 98[43] program packages.

To confirm the nature of the stationary points, vibrational frequencies (in the harmonic approximation) were calculated for all the optimized structures and used, unscaled, to compute the zero-point energies. The computed relative (to the lowest triplet state) electronic energies for transition structures and products are listed in Table 5.

The contribution of bulk solvent effects to the potential energy was calculated via the self-consistent reaction field (SCRF) method using C-PCM[44] employing the HF parametrization by Barone's united atom topological model (UAHF),[45] as implemented in Gaussian 98. Such a model includes the nonelectrostatic terms (cavitation, dispersion, and repulsion energy) in addition to the classical electrostatic contribution. The former terms, unlike the latter one, always give a positive contribution to the solvation energy, but this is much less important than the electrostatic term. For all PCM-UAHF calculations, the number of initial tesserae per atomic sphere was set to 60 as in the default.

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Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

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