J. Org. Chem. **2001,** *66,* 6353−6363

Generation and Reactivity of the 4-Aminophenyl Cation by Photolysis of 4-Chloroaniline

Benedetta Guizzardi, Mariella Mella, Maurizio Fagnoni, Mauro Freccero, and Angelo Albini*

Department of Organic Chemistry, University of Pavia, Via Taramelli 10, 27100 Pavia, Italy

albini@chifis.unipv.it

Received May 7, 2001

4-Chloroaniline and its *N*,*N*-dimethyl derivative are photostable in cyclohexane but undergo efficient photoheterolysis in polar media via the triplet state and give the corresponding triplet phenyl cations. CASSCF and UB3LYP calculations show that the 4-aminophenyl triplet cation has a planar geometry and is stabilized by >10 kcal mol^{-1} with respect to the slightly bent singlet. The triplet has a mixed carbene−diradical character at the divalent carbon. This species either adds to the starting substrate forming 5-chloro-2,4′-diaminodiphenyls (via an intermediate cyclohexadienyl cation) or is reduced to the aniline (via the aniline radical cation) in a ratio depending on the hydrogen-donating properties of the solvent. Transients attributable to the triplet aminophenyl cation as well as to the ensuing intermediates are detected. Chemical evidence for the generation of the phenyl cation is given by trapping via electrophilic substitution with benzene, mesitylene, and hexamethylbenzene (in the last case the main product is a 6-aryl-3-methylene-1,4-cyclohexadiene). Relative rates of electrophilic attack to benzene and to some alkenes and five-membered heterocycles are measured and span over a factor of 15 or 30 for the two cations. The triplet cation formed under these conditions is trapped by iodide more efficiently than by the best π nucleophiles. However, in contrast to the singlet cation, it does not form ethers with alcohols, by which it is rather reduced.

Aryl cations[1] are potentially useful synthetic intermediates, but their chemical behavior is poorly known at present. This is mainly because of their limited accessibility. The dediazoniation of diazonium salt normally occurs under reducing conditions,[2] and thus useful reactions such as the Gomberg−Bachmann synthesis of biaryls and the Meerwein arylation of alkenes involve aryl radicals rather than cations.[2,3] The phenyl cation and some of its derivatives have been generated by decay of tritium-marked benzenes,[4] by solvolysis of some perfluoroalkylsulfonic aryl esters,[5] and by solvolytic cyclization of (trifluoromethanesulfonyl)oxydienynes[6] as well as by carrying out under controlled conditions the thermal[7] or photochemical (in solution[8] or in matrix[9a−c]) decomposition of diazonium salts. Quite recently, the phenyl cation has been shown to be among the products from the photolysis of bromo- and iodobenzene in matrix at 4 K.[9d]

From the evidence available, phenyl cations are highly reactive and indiscriminate reagents, behaving both as electrophiles and as radical hydrogen abstractors. However, the conditions required for their generation via the noncatalyzed decomposition of diazonium salts limit the choice of experimental parameters and the other methods have a purely mechanistic interest. The scope of their reactivity and the possibility of synthetic application have thus not been examined. It has been recently proposed that some electron-donating substituted haloaromatics undergo heterolytic photoinduced fragmentation[10,11] and

---

* Corresponding author. Fax: +39-0382-507323.

[1] (a) Stang, P. J. In *Dicordinated Carbocations*; Rappoport, Z., Stang, P. J., Eds.; Wiley: New York, 1997; p 451. (b) Hanack, M.; Subramanian, L. R. In *Methoden Org. Chemie*; Hanck, M., Ed.; Thieme: Stuttgart, Germany, 1990; Vol. E19C, p 249.

[2] (a) Galli, C. *Chem. Rev.* **1988**, *88*, 765. (b) Zollinger, H. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 141. (c) Metger, J. O. In *Methoden Org. Chemie*; Regitz, M., Giese, B., Eds.; Thieme: Stuttgart, Germany, 1989; Vol. E19A, p 121. (d) The distinction of the mechanistic alternatives between heterolytic decomposition of the diazonium cation to yield the phenyl cation and catalyzed (e.g. Sandmayer) decomposition to yield the phenyl radical has been first clearly formulated by Waters.[2e] (e) Waters, W. A. *J. Chem. Soc.* **1942**, 266.

[3] (a) Hey, D. H. In *Advances in Free Radical Chemistry*; Williams, G. H., Ed.; Academic Press: New York, 1980; Vol. 2, p 47. (b) Rondesvedt, C. S. *Org. React.* **1976**, *24*, 225. (c) Ghosez, A.; Giese, B.; Zipse, H. In *Methoden Org. Chemie*; Regitz, M., Giese, B., Eds.; Thieme: Stuttgart, Germany, 1989; Vol. E19A, p 1216.

[4] (a) Speranza, M. *Chem. Rev.* **1993**, *93*, 2933. (b) Hrusák, J.; Schröder, D.; Iwata, S. *J. Am. Chem. Soc.* **1993**, *115*, 2015. (c) Filippi, A.; Lilla, G.; Occhiucci, G.; Sparapani, C.; Ursini, O.; Speranza, M. *J. Org. Chem.* **1995**, *60*, 1250. (d) Speranza, M. In ref 1a, p 157. (e) Shchepina, N. E.; Nefedov, V. D.; Toropova, M. A.; Avrorin, V. V.; Lewis, S. B.; Mattson, B. *Tetrahedron Lett.* **2000**, *41*, 5303.

[5] (a) Himeshima, Y.; Kobayashi, H.; Sonoda, T. *J. Am. Chem. Soc.* **1985**, *107*, 5286. (b) Apeloig, Y.; Arad, D. *J. Am. Chem. Soc.* **1985**, *107*, 5285. (c) Subramanian, L. R.; Hanack, M.; Chang, L. W.; Imhoff, M. A.; Schleyer, P. v. R.; Effenberger, F.; Kurtz, W.; Stang, P. J.; Dueber, T. E. *J. Org. Chem.* **1976**, *41*, 4099. (d) Laali, K.; Szele, I.; Yoshida, K. *Helv. Chim. Acta* **1983**, *66*, 1710.

[6] (a) Holweger, W.; Hanack, M. *Chem. Ber.* **1984**, *117*, 3004. (b) Bleckmann, W.; Hanack, M. *Chem. Ber.* **1984**, *117*, 3021. (c) Hanack, M.; Rieth, R. *Chem. Ber.* **1987**, *120*, 1659.

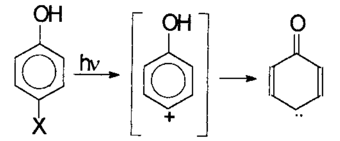
[7] (a) Romsted, L. S.; Zhang, J.; Zhang, L. *J. Am. Chem. Soc.* **1998**, *120*, 10046. (b) Chauduri, A.; Loughlin, J. A.; Romsted, L. S.; Yao, J. *J. Am. Chem. Soc.* **1993**, *115*, 8351. (c) Swain, C. G.; Sheats, J. E.; Harbison, K. G. *J. Am. Chem. Soc.* **1975**, *97*, 783. (d) Bergstrom, R. G.; Landells, R. G. M.; Wahl, G. W.; Zollinger, H. *J. Am. Chem. Soc.* **1976**, *98*, 3301.

[8] (a) Zollinger, H. *Diazochemistry I*; VCH: New York, 1995. (b) Gasper, S. M.; Devadoss, C.; Schuster, G. B. *J. Am. Chem. Soc.* **1995**, *117*, 5206. (c) Steenken, S.; Askokkuna, M.; Maruthamuthu, P.; McClelland, R. A. *J. Am. Chem. Soc.* **1998**, *120*, 11925.

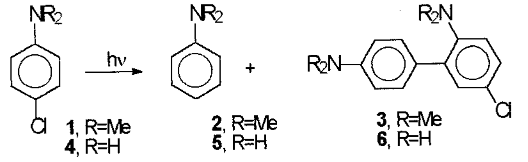
[9] (a) Ambroz, H. B.; Kemp, T. J. *J. Chem. Soc., Perkin Trans. 2* **1980**, 768. (b) Ambroz, H. B.; Kemp, T. J. Prybytniak, G. K. *J. Photochem. Photobiol., A* **1997**, *108*, 149. (c) Ambroz, H. B.; Kemp, T. J. *Chem. Soc. Rev.* **1979**, *8*, 353. (d) Winkler, M.; Sander, W. *Angew. Chem., Int. Ed. Engl.* **2000**, *39*, 2014. (e) Cox, A.; Kemp, T. J.; Payne, D. R.; Symons, M. C. R.; de Moira, P. P. *J. Am. Chem. Soc.* **1978**, *100*, 4779. (f) Ambroz, H. B.; Kemp, T. J. *J. Chem. Soc., Perkin Trans. 2* **1969**, 1420.

10.1021/jo0104680 CCC: $20.00

Scheme 1



Scheme 2



this may be a potentially more versatile source of aryl cations, as it is the case for the better known generation of vinyl cations by photoheterolysis of vinyl halides.[12] The reaction has been studied in detail for the case of halophenols (mostly in water), where however deprotonation leads to a further different intermediate, a carbene (see Scheme 1).[11] We report in the following that 4-chloroaniline and its *N*,*N*-dimethyl derivative undergo efficient photodechlorination and that useful arylation reactions via the corresponding phenyl cation can be obtained in this way.[13]

Results

Photodecomposition of Chloroanilines. Irradiation of *N*,*N*-dimethyl-4-chloroaniline (**1**, 0.05 M) in acetonitrile caused decomposition of the substrate with evolution of hydrogen chloride and formation of *N*,*N*-dimethylaniline (**2**) and of a lesser amount of 5-chloro-2,4′-bis(dimethylamino)biphenyl (**3**) (see Scheme 2, Table 1). The irradiation could be carried out to high (>85%) conversion (see Table 1). The photodecomposition took place in various solvents (alcohols, perfluoroalcohols, ethyl acetate, chlorinated hydrocarbons)[14] with essentially the same course, although the ratio between products **2** and **3** and the irradiation time required for reaction changed significantly. In particular, the photoreaction of compound **1** was much slower in cyclohexane (compare the quantum yield measurements below).

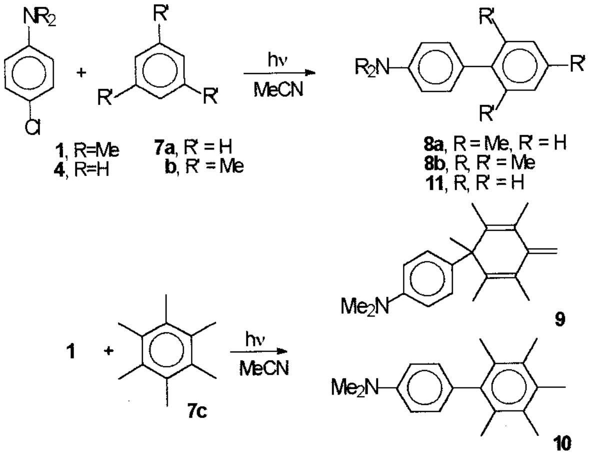
4-Chloroaniline (**4**) was likewise photoreactive. Aniline (**5**) and 5-chloro-2,4′-diaminobiphenyl (**6**) were the products, similarly to the case of the *N*,*N*-dimethyl derivative **1** (Scheme 2, Table 1). Hydrogen chloride was evolved during the reaction, and particularly with **4**, this caused partial precipitation of the amine hydrochloride. Some of the irradiations, particularly in the presence of acid-sensitive traps (see below), were thus carried out in the presence of 0.1 M triethylamine or by stirring solid potassium carbonate in the irradiation vessel. This caused no major change in the product distribution.

Table 1. Products from the Irradiation of Chloroanilines 1 and 4[a]

aniline	additive	products (% yield)
1	none	**2** (47), **3** (30)
1	**7a**[b]	**2** (20), **3** (11), **8a** (44)
1	**7b**[b]	**2** (12), **3** (5), **8b** (65)
1	**7c**[c]	**2** (12), **3** (5), **9** (40), **10** (18)
1	NaI, 0.05 M[d]	**2** (5), **15** (60)
4	none	**5** (45), **6** (31)
4	**7a**[b]	**5** (21), **6** (9), **11** (40)
4	NaI, 0.05 M[d]	**5** (5), **16** (51)

[a] By irradiation of a 0.05 M solution of the anilines in MeCN for 1 h in the case of **1** and 2 h in the case of **4**; conversion was ca. 85% except when otherwise noted. In the case of **4** a solution containing 0.1 M triethylamine was irradiated to avoid crystallization of the hydrochlorides; similar results were obtained by stirring solid potassium carbonate in the reaction vessel. [b] 1 M. At 0.1 M the yield of adducts such as compounds **8** or **11** did not exceed 10%. [c] In this case a 5×10^{-3} M solution of **1** in the presence of 5×10^{-2} M **7c** was irradiated. [d] At ca. 50% conversion.

Scheme 3



Reaction with Arenes. When aniline **1** was irradiated (310 nm) in acetonitrile containing 1 M benzene (**7a**), the amount of the above-mentioned products was strongly reduced and the biphenylamine **8a** was formed in 43% yield (Scheme 3, Table 1). In a 0.1 M benzene solution compound **8a** was a minor product and the yields of products **2** and **3** only slightly diminished with respect to neat acetonitrile. With 1 M mesitylene (**7b**) the corresponding biphenylamine **8b** was again the main product.

Experiments with hexamethylbenzene (**7c**) required some modification, due to the limited solubility of this compound in acetonitrile. Satisfactory trapping was obtained by irradiating a 5×10^{-3} M solution of **1** in the presence of 5×10^{-2} M **7c**. Under these conditions two new products were formed, and their spectroscopic properties allowed us to assign the structure of the triene **9** to the major one and that of the diphenyl derivative **10** to the minor one.

Nonmethylated aniline **4** reacted in a way similar to **1** and gave biphenylamine **11** in the presence of benzene.

The reaction with arenes could be carried also in other solvents. Thus, biphenylamine **8a** was obtained by irradiation of **1** in ethyl acetate containing 1 M benzene provided that the irradiation was twice as long as in acetonitrile, as well as by irradiation in neat benzene,

---

(10) (a) Zhang, G.; Wan, P. *J. Chem. Soc., Chem. Commun.* **1994**, 19. (b) Yang, N. C.; Huang, A.; Yang, D. H. *J. Am. Chem. Soc.* **1989**, *111*, 8060. (c) Othmen, K.; Boule, P. *Bull. Environ. Contam. Toxicol.* **1997**, *59*, 924. (d) Hori, K.; Sonoda, T.; Harada, M.; Yamazaki-Nishida, S. *Tetrahedron* **2000**, *56*, 1429.

(11) (a) Durand, A. P.; Brown, R. G.; Worrall, D.; Wilkinson, F. *J. Chem. Soc., Perkin Trans. 2* **1998**, 365. (b) Grabner, Richard, C.; Köhler, G. *J. Am. Chem. Soc.* **1994**, *116*, 11470. (c) Bonnichon, F.; Grabner, G.; Guyot, G.; Richard, C. *J. Chem. Soc., Perkin Trans. 2* **1999**, 1203. (d) Arnold, B. R.; Scaiano, J. C.; Bucher, G. F.; Sander, W. *J. Org. Chem.* **1992**, *57*, 6469.

(12) Lodder, G. In ref 1a, p 377.

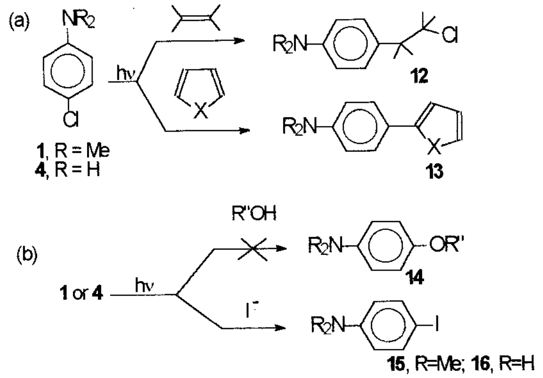
(13) Preliminary communication: Fagnoni, M.; Mella, M.; Albini, A. *Org. Lett.* **1999**, *1*, 1299.

(14) In solvents of low polarity the chloridrate of the aniline precipitated out during irradiation unless the acidity set free was buffered (see below the reactions with **4**).

Table 2. Quantum Yield of Reaction and Products Formed by Irradiation of Chloroanilines 1 and 4 (Low-Conversion Runs)

	N,*N*-dimethyl-4-chloroaniline (**1**)				4-chloroaniline (**4**)			
solvent	Φ_r	$\Phi_{\mathbf{2}}$	$\Phi_{\mathbf{3}}$	Φ_{other}	Φ_r	$\Phi_{\mathbf{5}}$	$\Phi_{\mathbf{6}}$	Φ_{other}
MeCN	0.87	0.5	0.33		0.44	0.23	0.17	
MeCN, 1 M C_6H_6	0.78	0.19	0.07	0.36 (**8a**)	0.45	0.04	0.03	0.33 (**11**)
MeCN, 0.02 M NaI	0.92	0.08	<0.01	0.81 (**15**)	0.70	0.05		0.6 (**16**)
MeOH	0.95	0.83	0.08		0.50	0.45	0.03	
CF_3CH_2OH	0.50	0.2	0.23		0.25	0.15	0.06	
i-PrOH	0.90	0.85	<0.01		0.60	0.48	0.06	
t-BuOH	0.70	0.37	0.3		0.29	0.08	0.17	
AcOEt	0.50	0.29	0.14		0.13	0.1	0.02	
C_6H_6	0.05			0.03 (**8a**)	0.03			0.02 (**11**)
C_6H_{12}	0.03	0.02			0.02	0.02		

Scheme 4



albeit in this case the reaction was so slow as to make the reaction unpractical for preparative purposes.

Besides the benzene derivatives discussed above, several other substrates were efficiently arylated during the photodecompostion of the chloroanilines **1** and **4**. In particular alkenes gave either β-chloroalkylarenes (**12**) or vinyl or allylarenes while five-membered heterocycles gave arylheterocycles (**13**) (see Scheme 4a). The preparative scope and the mechanism of such reactions are discussed separately.[15]

Reaction in Alcohols and in the Presence of Salts. As mentioned above, irradiation of anilines **1** or **4** in alcohols led to the same products as in acetonitrile, though with a change in the ratio. In methanol and in 2-propanol the proportion of dehalogenated anilines **2** and **5** increased (see Table 1 as well as the quantum yield data in Table 2). In *tert*-butyl alcohol and in trifluoroethanol the product distribution was essentially the same as that in MeCN, with some increase of self-arylation in one case (**4** in *tert*-BuOH; see Table 2). However, with all of the alcohols tested the corresponding alkoxyanilines **14** were formed at most in trace amounts (see Scheme 4b).

Addition of some salts had a major effect. Thus, irradiation of either **1** or **4** in acetonitrile containing 0.05 M NaI gave 4-iodoanilines **15** and **16** as by far the main products, at least at a moderate conversion (see Scheme 4b and Table 1).

Reaction Quantum Yield. The decomposition quantum yield of anilines **1** and **4** was measured in low (<20%) conversion experiments. Representative results are reported in Table 2. The quantum yield was dependent on the structure (in MeCN $\Phi = 0.87$ for **1** and 0.44 for **4**; see Table 2) and on the solvent (a decrease by a factor >20 in going from MeCN to cyclohexane) but essentially independent from the presence of additives. As an example, the reaction quantum yield for **1** in the presence of benzene, 1-hexene, or pyrrole up to 1 M very little changed (within 10%) with respect to neat acetonitrile, despite the fact that under these conditions a major change in the product distribution occurred, since the main products became **8a**, **12** (mixture of the two regioisomers), and **13** (X = NH) respectively, in the place of **2** and **3** obtained in the absence of the additives. Also in the presence of salts the effect was generally small. The reaction quantum yield for chloroaniline **1** in acetonitrile containing NaI little changed (5%), while it increased significantly (by ca. 40%) in the case of compound **4**.

Competition Experiments. The above results suggested to compare the relative efficiency of the arylation reactions with various substrates in direct competition experiments. Since substitution of a iodo for a chloro atom was efficient already at low iodide concentration (down to 2×10^{-3} M), we found it expedient to compare the formation of iodoanilines with that of arylated organic substrates at 1 M concentration of the organic trap and varying the concentration of iodide in the appropriate range (over at least 1 order of magnitude). In this way the bulk properties of the medium were varied as little as possible, since the amount of the apolar trap remained constant and the concentration of the added salt was small. The competition experiments were carried out at low (<20%) conversion and in the presence of a small amount (5×10^{-3} M) of triethylamine. This low concentration ensured that no acid-catalyzed process intervened while barely enhancing the yield of anilines **2** and **5**.

The substrates chosen were benzene, 1-hexene, and 2,3-dihydrofuran as a representative enol ether as well as two heteroaromatic substrates, viz. pyrrole and thiophene. A doubly reciprocal plot of the iodoaniline formed vs the iodide concentration was found to be linear in every case giving two families of straight lines with common intercept for chloroanilines **1** and **4**, respectively (shown in Figure 1 for the case of compound **1**). The intercept/slope ratios from such plots are reported in Table 3.

Photophysical Experiments. Chloroanilines **1** and **4** showed a well-detectable phosphorescence in a glassy matrix. Both the form of the spectrum (λ_{max} 425 nm) and the efficiency of the emission were similar to those observed for the corresponding nonhalogenated anilines **2** and **5** (λ_{max} 405 nm) and underwent no major change in passing from a polar (ether−pentane−alcohol) to an apolar (3-methylpentane) glass.

Nanosecond laser flash photolysis experiments were carried out, again in comparison with nonhalogenated

---

[15] For the trapping with alkenes see the accompanying article. With heterocycles see: Guizzardi, B.; Mella, M.; Fagnoni, M.; Albini, A. *Tetrahedron* **2000**, *56*, 8691.

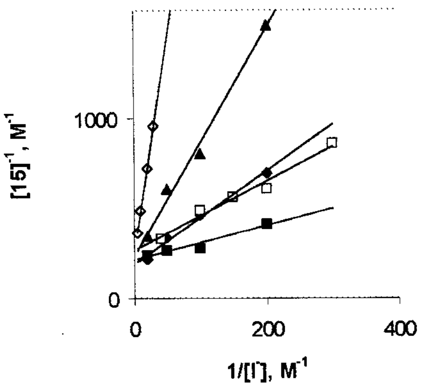


Figure 1. Double reciprocal plot of *N*,*N*-dimethyl-4-iodoaniline (**15**) formed vs sodium iodide concentration by irradiation of *N*,*N*-dimethyl-4-chloroaniline (**1**) in the presence of 1 M additives: (■) benzene; (◇) pyrrole; (□) thiophene; (◆) 1-hexene; (▲) 2,3-dihydrofuran. The intercept vs slope ratios obtained from this plot are reported in Table 3. Similar plots are obtained in the case of 4-chloroaniline (**4**).

Table 3. Formation of Iodoanilines vs Alkyl- or Arylanilines in Competition Experiments in Acetonitrile

	dimethylaniline **1**		aniline **4**	
substrate	intercept/ slope, M[a]	relative to benzene	intercept/ slope, M[b]	relative to benzene
1-hexene	73.4	2.2	19.9	5.5
2,3-dihydofuran	39.1	4.2	18.8	5.8
benzene	163.3	1	109.5	1
pyrrole	10.4	16.3	3.5	31.3
thiophene	132.7	1.2	126	.87

[a] From the plot in Figure 1. [b] From a plot analogous to that in Figure 1 (not shown) using aniline **4** in the place of **1**.

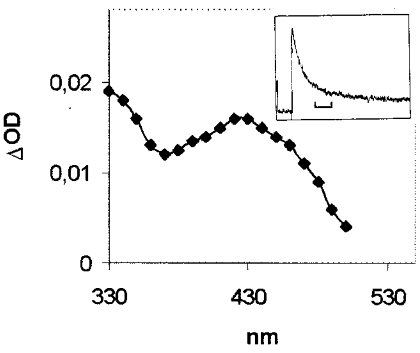


Figure 2. Transient observed 200 ns after flashing (266 nm) a 1 × 10^{-4} M solution of *N*,*N*-dimethyl-4-chloroaniline (**1**) in cyclohexane (inset, decay at 460 nm, time unit 1 μs).

substrates. Aniline (**2**) in cyclohexane showed a conspicuous transient absorption with maximum in the visible at 450 nm and a lifetime of ca. 2 μs. This has been previously observed and assigned to the T−T absorption.[16] In acetonitrile the same transient was observed with a similar intensity and lifetime. The lifetime of the transient decreased upon increasing the concentration, with a stronger effect in C_6H_{12} than in MeCN.

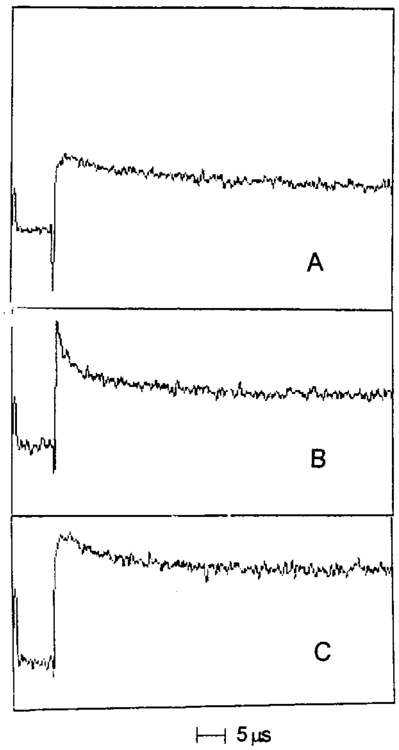


Figure 3. Oscilloscope traces at 390 (A), 430 (B), and 480 (C) nm after flashing (266 nm) a 2 × 10^{-4} M solution of *N*,*N*-dimethyl-4-chloroaniline (**1**) in acetonitrile

The introduction of a chlorine atom did not change the situation in cyclohexane, where chloroaniline **1** showed a transient absorption in the same wavelength range as nonchlorinated **2** (see Figure 2), again with some decrease in the lifetime at higher concentration. However, in acetonitrile the result was completely different. The end-of-pulse absorption (50 ns) was a strong band peaking at 430 nm which evolved into further intense and persistent absorptions at both shorter and longer wavelength (τ several tenths of microseconds) (see decay profiles and spectra in Figures 3 and 4). Parallel results were obtained with the nonmethylated chloroaniline **4**. A similar behavior was observed in all of the polar solvents used, with some change in the wavelength distribution. In particular in methanol and 2-propanol the persistent transient corresponded to the long-wavelength part of the spectrum in acetonitrile (Figure 5). In the presence of 0.3 or 0.6 M mesitylene, on the contrary, the long-lived transient at 460 nm was much reduced and a different transient appeared, with the strongest absorption around 350 nm (Figure 6).

Computational Results. Since the 4-aminophenyl cation was suspected to be an intermediate in the above reactions, calculations were carried out to determine the structure of such species. The singlet and triplet states of the $H_2NC_6H_4^+$ cation were optimized by the standard (U)B3LYP method, using 6-31G(d) and 6-311+G(d,p) basis sets. The computed relative electronic energies for $H_2NC_6H_4^+$ singlet ($^1A'$) and triplet ($^3B_2$) states and the relative Gibbs free energies obtained from gas-phase vibrational frequencies are listed in Table 4.

To check the viability of such a single-determinant approach and to describe the nature of the singlet and triplet $H_2NC_6H_4^+$, CASSCF calculations with an active space comprising eight electrons in eight active orbitals were then performed. The active space consisted of six π orbitals, the nitrogen lone pair (p_N), and the σ orbital located at the divalent carbon atom (C_1 in Figure 7). It was found that in the case of $^3B_2$ state the CASSCF wave function was well described by the ground-state reference

---

[16] Previtali, C. M. *J. Photochem.* **1985**, 233.

Table 4. Electronic Energies and Gibbs Free Energies (kcal mol^{-1}) for Single and Triplet States

			ΔE		ΔG(298 K), 1 atm	
species	state	pt group	CASSCF^a	(U)B3LYP^b	CASSCF^a	(U)B3LYP^b
$NH_2C_6H_4^+$	$^1A'$	C_s	16.12^b	10.92^b (9.84)^c	15.29^{b,d}	10.09^{b,d} (9.01)^{c,d}
	$^3B_2$	C_{2v}	0.00	0.00 (0.00)^c	0.00	0.00 (0.00)

^{a} CASSCF(8,8)76-31G(d). ^{b} (U)B3LYP/6-31G(d). ^{c} (U)B3LYP/6-311+G(d,p). ^{d} Adding the thermal correction to Gibbs free energy computed from frequency calculation at the (U)B3LYP/6-31G(d) level of theory.

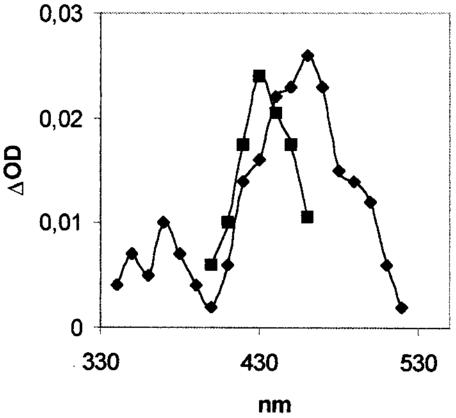


Figure 4. Transient observed 50 ns (■) and 1 μs (◆) after flashing (266 nm) a 2 × 10^{-4} M solution of *N*,*N*-dimethyl-4-chloroaniline (**1**) in acetonitrile.

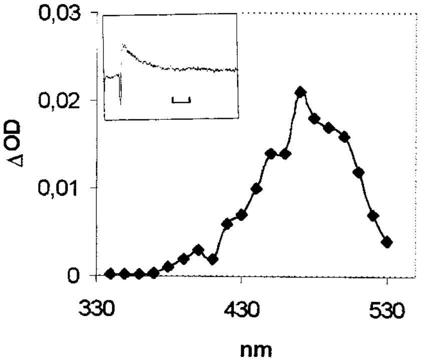


Figure 5. Transient observed 200 ns after flashing (266 nm) a 2 × 10^{-4} M solution of *N*,*N*-dimethyl-4-chloroaniline (**1**) in methanol (inset, decay at 460 nm, time unit 0.5 μs).

determinant, while the $^1A'$ state was poorly described by any single configuration. Clearly, a balanced comparison of the geometries and nature of the two states could only be obtained through a multiconfigurational approach.

Both methods agreed in establishing that the triplet state was more stable than the singlet state in the gas phase by at least 10 kcal mol^{-1}. (U)B3LYP/6-31G(d) underestimated such a gap in comparison to the CASSCF/6-31G(d) (16.12 kcal mol^{-1}) method by 5.2 kcal mol^{-1}. Such a result agreed with previous investigations[25] focused on this aspect where it had been recognized that B3LYP underestimated the S−T gap by 2−4 kcal mol^{-1}. On the other hand one has to keep in mind the possible limitation of the CASSCF approach concerning the quantitative energy assessment of different states, due to the missing dynamic correlation energy term. Further efforts toward the exact computation of the triplet−singlet gap were not carried out, since the main aim of this work was rather to allow an appreciation of the wave functions involved and of the nature of the two states to facilitate the rationalization of the observed chemistry. At any rate it was checked that the extension of the basis set from 6-31G(d) to 6-311+G(d,p) at the (U)B3LYP level of theory slightly reduced the gap (from 10.92 to 9.84 kcal mol^{-1}; see Table 4, values in parentheses). Inclusion of nonpotential energy terms and entropy did not modify the energy gap, as demonstrated by an identical gap in the Gibbs free energies (see ΔG in Table 4).

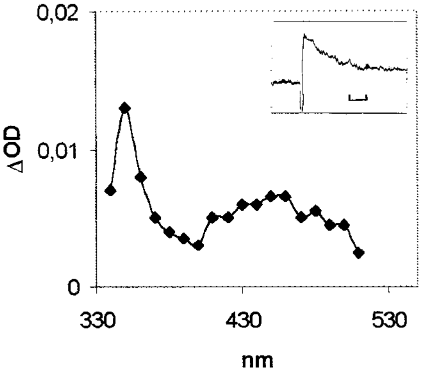


Figure 6. Transient observed 480 ns after flashing (308 nm) a 2 × 10^{-4} M solution of *N*,*N*-dimethyl-4-chloroaniline (**1**) in acetonitrile containing 0.3 M mesitylene (inset, decay at 350 nm, time unit 1 μs).

The geometry of the two states as obtained by both methods is depicted in Figure 7, and the corresponding charge and spin densities are reported in Table 6. To facilitate the discussion on the chemical properties of the cation, the key orbitals Φ4 and Φ5 and their contribution to the two states are depicted in Figure 8

Discussion

Photoinduced Cleavage. 4-Chloroanilines **1** and **4** undergo efficient photodecomposition in a variety of polar

---

(17) Othmen, K.; Boule, P. *J. Photochem. Photobiol., A* **1999**, *121*, 161.

(18) Bunce, N. J.; Bergsma, J. P.; Bergsma, M. D.; De Graaf, W.; Kumar, Y.; Ravanal, L. *J. Org. Chem.* **1980**, *45*, 3708.

(19) Othmen, K.; Boule, P.; Szczepanik, B.; Rotkiewicz, K.; Grabner, G. *J. Phys. Chem. A* **2000**, *104*, 9525.

(20) Miller, G. C.; Crosby, D. G. *Chemosphere* **1983**, *12*, 1217. Szczepanik, B.; Latowski, T. *Pol. J. Chem.* **1997**, *71*, 807.

(21) Kouteck, B.; Musil, L.; Velek, J.; Soucek, M. *Collect. Czech. Chem. Commun.* **1985**, *50*, 1985.

(22) (a) Bunce, N. J. In *CRC Handbook of Organic Photochemistry and Photobiology*; Horspool, W. M., Song, P. S., Eds.; CRC Press: Boca Raton, FL, 1994; p 1181. (b) Bunce, N. J.; Gallacher, J. C. *J. Org. Chem.* **1982**, *47*, 1955. (c) Sammes, P. G. In *The Chemistry of the Carbon−Halogen Bond*; Patai, S., Ed.; Wiley: New York, 1973; Part II, Chapter 11. (d) Lodder, G.; Cornelisse, J. In *The Chemistry of the Carbon−Halogen Bond*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1995; Supplement D, Chapter 29. (e) Grimshaw, J.; de Silva, A. P. *Chem. Soc. Rev.* **1981**, *10*, 181. (f) D'Auria, M.; De Luca, B.; Mauriello, G.; Racioppi, R. *J. Chem. Soc., Perkin Trans 1* **1998**, 271. (g) Mangion, D.; Arnold, D. R. *Can. J. Chem.* **1999**, *77*, 1655.

(23) Arnold, D. R.; Wong, P. C. *J. Am. Chem. Soc.* **1977**, *99*, 3363. Ichimura, T.; Mori, Y. *J. Chem. Phys.* **1973**, *58*, 288.

(24) Nicolaides, A.; Smith, D. A.; Jensen, F.; Radom, L. *J. Am. Chem. Soc.* **1997**, *119*, 8083−8088.

(25) (a) Aschi, M.; Harvey, J. N. *J. Chem. Soc., Perkin Trans. 2* **1999**, 1059. (b) Mendez, F.; Garcia-Garibay, M. A. *J. Org. Chem.* **1999**, *64*, 7061.

Table 5. Fractional Population γ_i for the Eight Active Orbitals for Single and Triplet States from the CAS-SCF (8,8)/6-31G* Level of Theory

state	$\Phi1(\pi)$	$\Phi2(\pi)$	$\Phi3(\pi)$	$\Phi4(p_N)$	$\Phi5(\sigma$ at divalent $C_1)$	$\Phi6(\pi^*)$	$\Phi7(\pi^*)$	$\Phi8(\pi^*)$
$^1A'$	1.96	1.94	1.89	1.46	0.54	0.11	0.06	0.03
$^3B_2$	1.96	1.92	1.90	1.00	1.00	0.07	0.097	0.034

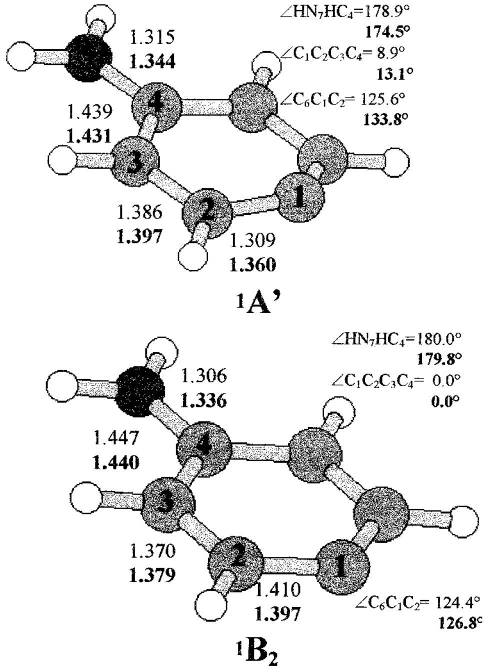


Figure 7. Bond lengths (Å), angles (∠; in deg), and dihedral angles (∠; in deg) for singlet ($^1A'$) and triplet ($^3B_2$) 4-aminophenyl cation as obtained by B3LYP/6-31G(d) (bold characters) and CASSCF(8,8)/6-31G(d) (plain characters) calculations.

Table 6. Mulliken Charges (with Hydrogens Summed into Heavy Atoms) and Spin Density for Single and Triplet States

	$^1A'$		$^3B_2$		$^3B_2$: UB3LYP
atom	CASSCF	B3LYP	CASSCF	UB3LYP	(spin density)
C_1	0.133	0.162	0.121	0.138	1.340
C_2	0.073	0.150	0.083	0.086	−0.134
C_3	0.100	0.048	0.092	0.097	0.242
C_4	0.346	0.425	0.368	0.379	0.083
N_7	0.176	0.016	0.160	0.115	0.350

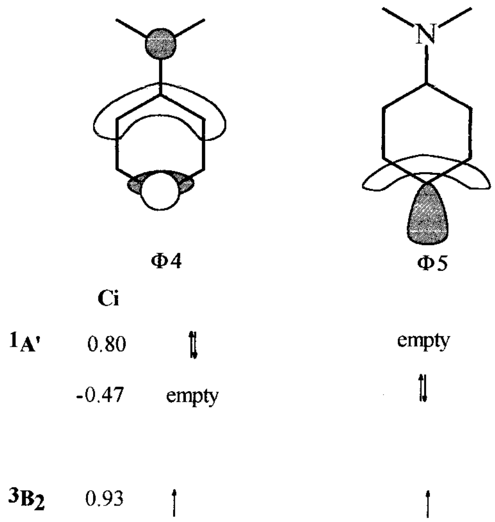


Figure 8. Schematic depiction of the nature of triplet ($^3B_2$) and singlet ($^1A'$) 4-aminophenyl cation. The coefficients (C_i) of the triplet state lowest eigenvector and the coefficients of the two main electronic configurations for the singlet state of 4-aminophenyl cation are reported. In the case of the singlet, the most important configuration has two spin-coupled electrons in a π orbital (Φ4) and an empty σ orbital (Φ5). The second most important configuration involves double excitation of the above electrons from the π orbital (Φ4) to the σ orbital (Φ5).

organic solvents. Although the photoreaction of **4** in water (to give 4-aminophenol and 2,4′-diamino-5-chlorobiphenyl) has been previously reported,[17] this result is somewhat surprising particularly when the rather high quantum yields, 0.84 and 0.44 for **1** and **4,** respectively, in MeCN and the strong solvent effect are considered. Such an effect of the solvent polarity on the photoreaction efficiency has not previously observed for halobenzenes; e.g., fragmentation of chlorobenzene occurs efficiently in cyclohexane.[18] However, a known exception is that of halophenols, which are photoreactive only in alcohols or water,[11] and after the submission of this work a report by Othmen et al.[19] appeared showing that chloroanilines **1** and **4** fragment in water and in polar organic solvents but not in *n*-hexane.

The present study shows that aminoarylation reactions occur efficiently upon irradiation of chloroanilines in the presence of various substrates. Thus, the reaction has some synthetic interest and recognizing the mechanism of fragmentation is important not only for the photodegradation of chloroanilines and phenols, which has motivated previous studies,[10c,11,17,19,20] but also for exploring new mild C−C bond-forming reactions.

The initiating photochemical step involves C−Cl bond fragmentation. Various pieces of evidence support that the cleavage proceeds from the triplet. Thus, the intersystem crossing efficiency for both chlorinated and nonchlorinated anilines such as **1**, **2**, **4**, and **5** has been estimated to be around 0.9 and to be little affected by the solvent.[21] This precludes the possibility of a role of an excited singlet in an efficient reaction such as the present one. Furthermore, the reaction quantum yield increases by a factor >20 in going from cyclohexane to acetonitrile. There is no corresponding decrease in the fluorescence lifetime (actually reported to *increase* by a factor of ca. 2 from isooctane to MeCN),[21] while there is a major change in the transients observed. Thus, in cyclohexane a short-lived transient is observed with both **1** or **4** (τ in the microsecond range). The spectra are very similar to those that the nonchlorinated anilines **2** and **5** exhibit in both polar and apolar solvents (as well as that shown by 4-chlorophenol in cyclohexane)[11b] and are confidently assigned to the T−T absorption in accordance with Othmen et al.[19]

On the other hand, in all of the polar solvents tested such transients are substituted by a strong transient at 430 nm, which clearly cannot be attributed to the same species and gives place to further long-lived and intensive signals (τ in the tenths of microseconds range). Thus, the triplet undergoes a fast decomposition in polar solvents, and actually there is a reverse relationship between the efficiency of the photoreaction and solvent polarity (see

Table 2). This notion is strengthened by the demonstration by Othmen et al. that T−T energy transfer from $\mathbf{4}^{3*}$ is more that 1 order of magnitude slower in ethanol than in *n*-hexane.[19]

As for the mode of fragmentation, the body of data accumulated on the photoreactions of haloaromatics has been rationalized in terms of a homolytic fragmentation (eq 1).[18,21,23]

$$\mathrm{Ar{-}Cl} + h\nu \rightarrow \mathrm{Ar}^{\bullet} + \mathrm{Cl}^{\bullet} \qquad (1)$$

$$\mathrm{Ar{-}Cl} + h\nu \rightarrow \mathrm{Ar}^{+} + \mathrm{Cl}^{-} \qquad (2)$$

However, the present reaction appears to involve a heterolytic cleavage (eq 2). This is supported by the consideration of the thermodynamics of the process and of the solvent effect. Indeed, it is unlikely that triplet **1** or **4** ($E_T = 72$ kcal mol^{-1}, as evaluated from the phosphorescence spectrum) undergoes cleavage of the C−Cl bond (BDE $\approx$ 85−91 kcal mol^{-1}) with an equal to or greater efficiency than the more energetic triplet chlorobenzene ($E_T \approx 82$ kcal mol^{-1}), while it has been consistently observed that the photohomolysis quantum yield decreases, as one may expect, with the excited-state energy.[22a] When the cleavage is homolytic, it occurs also in an apolar medium (e.g. for chlorobenzene $\Phi_r = 0.42$ when 0.02 M in cyclohexane; the yield is somewhat concentration dependent)[18] while **1** and **4** have Φ_r ca. 0.02 in cyclohexane and quantum yields are high only in a polar medium.

The $\pi\pi^*$ S_1 of **1** and **4** has an internal charge-transfer character, as indicated by the bathochromic shift in going from isooctane to MeCN (1700 cm^{-1}),[21] and this reasonably holds also for the emitting triplet, again a $\pi\pi^*$ state as indicated by the phosphorescence shape and intensity. In the case of the homolysis of chlorobenzene, the possible intermediacy of a nonemitting, somewhat higher-lying $\sigma\sigma^*$ state has been considered.[23] We have no support for the role of such a state in the fragmentation of anilines. It appears that a polar medium is determining for the efficiency of the cleavage by increasing the CT character of the excited state and stabilizing the ionic fragments. In particular, this is indicated by the requirement of at least a moderately polar environment (with ethyl acetate, $\epsilon = 6$, Φ_r is about a half of the maximum value, reached by all solvent with $\epsilon > 12$) and by the fact that with the strongly polar but significantly acidic trifluoroethanol as the solvent Φ_r markedly decreases, indicating that lessening CT through amino group protonation disfavors the efficiency of the C−Cl bond cleavage.

There is little precedent for such a strong solvent polarity effect on a photochemical reaction, but we see no other explanation for the unusual solvent dependence. The behavior appears to be typical of chlorophenols (where the reaction requires protic, not merely polar, solvents)[11] and of chloroanilines, as reported also by Othmen et al.[19]

Structure of the Aminophenyl Cation. The proper choice of the method was an obviously important issue. In the frame of density functional theory the B3LYP method appeared to be a good choice, because, while being computationally affordable, it has been used for the parent phenyl cation[24,25a] and shown to fairly well account for the singlet−triplet splitting[25a,26] and to yield very similar geometries as those obtained by the RCCSD(T)-(full)/6-31G(d) and CASSCF(6,7)/6-31G(d) methods. We confirmed that in the case of the parent cation the ground-state reference determinant contributed more than 90% (the coefficient of the lowest eigenvector is 0.94 and 0.95 for the singlet and triplet state, respectively).[27] Therefore, in that case a single-determinant reference wave function such as B3LYP is fairly adequate to provide a correct description of the molecular characteristics.[27]

However, in the case of the 4-aminophenyl cation this is reasonable only for the $^3B_2$ state for which the CASSCF wave function is described for more than 90% by the reference determinant and no individual excited configuration contributes significantly. On the other hand, the $^1A'$ state of the amino-substituted cation is poorly described by any single configuration. Therefore, it is not surprising that the geometric parameters (in Figure 7) and charges (in Table 6) determined by the two methods are in excellent agreement only for the $^3B_2$ state of 4-aminophenyl cation.

Both methods recognize the triplet as the lowest energy state by at least 10 kcal mol^{-1} in the gas phase, in accord with a previous evaluation.[25] Both the ring an the nitrogen atom remain planar in the triplet, while the singlet has the nitrogen slightly pyramidalized and C_1 slightly bent out of plane and puckered (Figure 7).

Chemical Reactions of the Aminophenyl Cation. Consideration of the chemistry observed both in neat solvent and in the presence of a trap offers alternate evidence for the structure of the intermediate. The reaction quantum yields in the presence of increasing concentrations of the traps do not differ from those observed in neat solvent. Furthermore, Φ remains the same also in dilute solutions of the chloroaniline, where quenching of the short-lived triplet is excluded. Thus the present reaction does not involve electron-transfer quenching of the excited aniline or formation of an exciplex, as in other arylation processes,[22c−e,g] but rather trapping of an intermediate arising directly from the triplet state. The structure of the final products in the reactions with benzene and methylbenzenes implies the intermediacy of an electrophilic species and is best accounted for by an aryl cation (**17**) reacting through the usual addition−elimination mechanism via the cyclohexadienyl cation **18** (Scheme 5). Thus, electrophilic substitution takes place both with benzene (**7a**) and with mesitylene (**7b**), with no competing hydrogen abstraction in the latter case (the proportion of aniline is lower with **7b** than with **7a**). This again disproves a role of an aryl radical. Most notably the reaction with hexamethylbenzene (**7c**) involves ring attack. The methylenecyclohexadiene **9** and the pentamethylbenzene **10** are the expected products from the fragmentation of the cyclohexadienyl cation **18′**. Indeed a 1-alkyl-4-methylenecyclohexadiene and a 1-alkylpentamethylbenzene are formed in a similar yield in the alkylation of **7c** by alkyl halides and $AlCl_3$.[28]

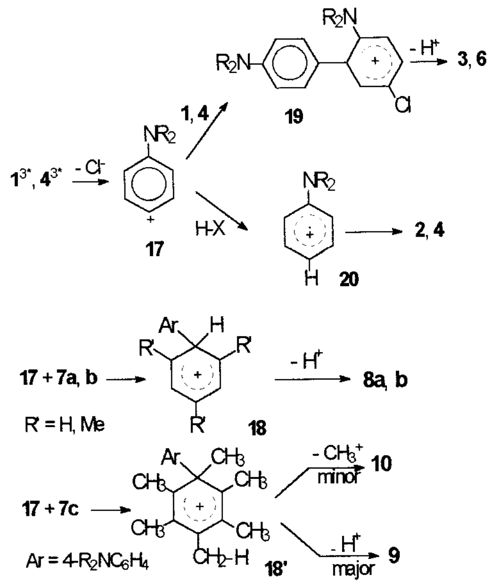
---

(26) Hrusak, J.; Schroder, D.; Iwata, S. *J. Chem. Phys.* **1997**, *106*, 7541−7549.

(27) The correctness of (U)B3LYP method choice in studying unsubstituted phenyl cation is corroborated by CASSCF(6,7)/6-31G(d) results performed by one of us (M.Fr.) in the frame of a comprehensive study of substituted phenyl cations, including the solvent effect. These will be submitted in due course.

(28) (a) Mindl, J.; Sebastiani, G. V. *Collect. Czech. Chem. Commun.* **1987**, *52*, 2936. (b) See also: Shubin, V. G.; Tabatskaya, A. A.; Darendayaev, B. G.; Korchagina, D. V.; Koptyung, V. A. *Zh. Org. Khim.* **1970**, *6*, 2072. Hünig, S.; Schilling, P. *Chem. Ber.* **1975**, *108*, 3355. (c) For an analogy in the gas phase, see: Attinà, M.; Cacace, F.; de Petris, G.; Fornarini, S.; Giacomello, P. *J. Am. Chem. Soc.* **1985**, *107*, 2297.

Scheme 5



The observed aromatic substitution occurs with some selectivity. This has been studied by means of competition experiments. In neat MeCN, the corresponding anilines and biphenyldiamines are formed (eq 3).

$$\mathbf{1}\ (\text{or } \mathbf{4}) \rightarrow \mathbf{2}\ (\text{or } \mathbf{5}) + \mathbf{3}\ (\text{or } \mathbf{6}) \quad \text{rate } k_{\text{MeCN}} \tag{3}$$

$$\mathbf{1}\ (\text{or } \mathbf{4}) + \text{I}^- \rightarrow \mathbf{15}\ (\text{or } \mathbf{16}) \quad \text{rate } k_{\text{I}} \tag{4}$$

$$\mathbf{1}\ (\text{or } \mathbf{4}) + \text{trap} \rightarrow \text{trapping product(s)} \quad \text{rate } k_{\text{Tr}} \tag{5}$$

In the presence of iodide the iodoanilines **15** or **16** are obtained (eq 4). In the presence of an aromatic substrate, and analogously with heteoaromatics and alkenes ("traps"), trapping products are formed (e.g. **8a** from **1** and benzene; see eq 5). In the presence of both iodide and trap, the amount of iodoaniline **15** (or **16**) formed in a given amount of time is expressed by eq 6 if, as we suggest, all of the products arise from the same intermediate.

$$[\mathbf{15}] = K\frac{k_{\text{I}}[\text{I}^-]}{k_{\text{MeCN}} + k_{\text{I}}[\text{I}^-] + k_{\text{Tr}}[\text{trap}]} \tag{6}$$

In the reciprocal form and by consideration of only experiments at 1 M trap, where, as it appears from Table 2, trapping is efficient and $k_{\text{Tr}}[\text{trap}] > k_{\text{MeCN}}$, eq 6 modifies to eq 7.

$$[\mathbf{15}]^{-1} \cong K^{-1}\left(1 + \frac{k_{\text{Tr}}[\text{trap}]}{k_{\text{I}}[\text{I}^-]}\right) \tag{7}$$

Figure 1 shows the verification of eq 7 for a range of traps and the appropriate range of iodide concentrations. This allows one to evaluate the ratio $k_{\text{I}}/k_{\text{Tr}}$ as reported in Table 3.

As it appears from Table 3, the organic substrates tested react with the aryl cations from 3.5 to 165 times slower than iodide. Among organic traps, thiophene is essentially as reactive as benzene while pyrrole is 31 times more reactive than benzene in the case of the amino cation derived from **4** and 16 times with the dimethylamino cation from **1**. This reflects, though in a compressed range, the known order of reactivity with electrophiles with these substrates and is roughly proportional to the ionization potentials. Likewise, an enol ether as 2,3-dihydrofuran is a more efficient trap than a simple alkene.

With this mechanism, it is expected that, in the absence of a purposely added trap, cation **17** attacks activated substrates such as the starting anilines yielding the biphenyldiamines **3** and **6**.

Reduction to anilines **2** and **4** is competitive with the above reactions. This depends on the hydrogen-donating properties of the solvent. The ratio biphenyldiamine/reduced aniline is ca. 1 or larger in acetonitrile, *tert*-butyl alcohol, or trifluoroethanol, while it is reduced to 0.1 with better hydrogen donors such as 2-propanol or methanol (down to 0.01 with **1** in 2-propanol).

Transient Attribution. The transients observed can be rationalized within this framework. In polar solvents, differently from cyclohexane, the triplet is too short-lived for detection. The intensive end-of-pulse transient (λ_{max} 430 nm; see Figure 3) is attributed to cation **17** resulting from dechlorination. The same identification has been given by Othmen et al., though these author refers to this species as a (protonated) carbene (see above).[19] The absorption fits with that observed by photolysis of 4-(dialkylamino)phenyldiazonium salts in glass at low temperature[9a−c] and identified as the triplet phenyl cation also on the basis of EPR measurements.[9e,f] In contrast, a previous search for this cation by photolysis of 4-(dialkylamino)phenyldiazonium tetrafluoborate at room temperature had revealed only a *weak* transient in the picosecond time scale in this spectral region.[8b] This is not in contrast with the present results, since direct photolysis of the diazonium salt generates the singlet cation, while dechlorination of triplet chloroaniline gives the triplet species (see further below).

Evolution of the primary intermediates leads to long-lived (>10 μs in MeCN) transients in two spectral regions, around 340−370 and around 460 nm. We suggest that the first one corresponds to the cyclohexadienyl cation **19** formed by addition of the 4-aminophenyl cation **17** to the starting aniline. The stabilization by the amino group explains the persistence of this species.

On the other hand, hydrogen transfer from the solvent generates radical cation **20**. The longer-wavelength transient is quite similar in shape to the spectrum observed by Mariano upon electron transfer from dimethylaniline to 1,4-dicyanobenzene (λ_{max} 430−470 nm in MeOH−MeCN).[29] Under the present conditions (organic solvent, weak laser power) the radical cation is not formed by photoionization of the anilines, although this may be the case under different circumstances.[30] This is shown by the fact that no radical cation is formed from nonchlorinated aniline **2** under these conditions. Since no easy reduction path is available, this species is quite long-lived under the present case.

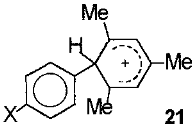
Consistently with this identification, little if any transient absorption is observed below 430 nm upon flash photolysis in methanol (Figure 5) or 2-propanol, while the long-wavelength band corresponding to the radical cation (somewhat red-shifted and markedly shorter-lived)

---

(29) Zhang, X.; Yeh, S. R.; Hong, S.; Freccero, M.; Albini, A.; Falvey, D. E.; Mariano, P. S. *J. Am. Chem. Soc.* **1994**, *116*, 4211.

(30) Latowski, T. *Ann. Soc. Chim. Pol.* **1966**, *40*, 231. Latowski, T. *Ann. Soc. Chim. Pol.* **1968**, *42*, 99.

is apparent: in alcohols, reduction to the aniline strongly predominates over formation of the biphenyldiamines (see further below). Conversely, in the presence of mesitylene, where attack to the aromatic is the dominant process, the two above transients are substituted (only the 470 nm transient is detected as a weak signal) by a different absorption with a maximum at 350 nm (τ 2 μs; see Figure 6). This is similar in shape to the transient observed by Steenken and McClelland upon photolysis of phenyldiazonium tetrafluoborates in the presence of the same trap and attributed to the cyclohexadienyl cation **21** (X = H).[8c] In our case the corresponding amino-substituted derivative (**21**, X = NMe$_2$ ≡ **18**, R = Me) is formed and since the amino group is not conjugated, no major difference is expected on the spectrum of the cation or on its persistence (explaining the much shorter lifetime with respect to stabilized **19**). Indeed, according to Steenken and McClelland[8c] the spectrum of the (4-methoxyphenyl)cyclohexadienyl cation (**21**, X = OMe, λ_{max} 356 nm in hexafluoropropanol) was only slightly different from that of the parent cation (**21**, X = H, λ_{max} 350 nm).



21

Spin-Dependent Chemistry of the Cation. What is perhaps unexpected in the chemistry reported above is the selectivity. Electrophilic attack to (hetero)arenes and alkenes and hydrogen abstraction are consistent with the "intuitively" expected reactivity of aryl cations. Less obvious is that, while being efficiently trapped by iodide to give iodoanilines (ca. 90% at [I$^-$] = 0.02 M), cation **17** does not react with σ neutral nucleophiles. Strikingly, only trace amounts of alkoxyanilines **14** have been detected in the irradiation we carried out in various alcohols. This should be compared with the previous reports on the photodecomposition of diazonium salts in alcohols. Steenken and McClelland obtained both a biphenyl and an ether by photodecomposition of phenyldiazonium tetrafluoborates in hexafluoropropanol containing 0.05−0.5 M benzene derivatives (eq 8),[8c] apparently indicating competition between the attack at the π and at the σ nucleophile (quite a weak one in this case). Schuster obtained substituent-dependent results from the photolysis of 4-substituted phenyldiazonium tetrafluoroborates in trifluoroethanol.[8b] With dialkylamino derivatives the ethers accounted for ca. 90% of the products (eq 9), whereas with the 4-acetyl derivatives reduction was by far the main process (>90%, eq 10) and the ether was formed in traces. As indicated in the equations, this was rationalized as being due to fast ISC induced by the keto group in the last case.

$$C_6H_5N_2{}^+BF_4{}^- \xrightarrow[(CF_3)_2CHOH,\ Ar'H]{h\nu} C_6H_5{}^+ \rightarrow C_6H_5Ar' + C_6H_5OCH(CF_3)_2 \quad (8)$$

$$4\text{-}R_2NC_6H_4N_2{}^+BF_4{}^- \xrightarrow[CF_3CH_2OH]{h\nu} 4\text{-}R_2NC_6H_4{}^+\,(S) \rightarrow 4\text{-}R_2NC_6H_4OCH_2CF_3 \quad (9)$$

$$4\text{-}MeCOC_6H_4N_2{}^+BF_4{}^- \xrightarrow[CF_3CH_2OH]{h\nu,\ ISC} 4\text{-}MeCOC_6H_4{}^+\,(T) \rightarrow 4\text{-}MeCOC_6H_5 \quad (10)$$

This led to the triplet state of the aryl cation which abstracted hydrogen from the solvent. In the other cases, the singlet excited state of the diazonium salt underwent dediazoniation before ISC leading to the singlet cation and the ether from it.

It has been well established in the present and in previous studies[10d,25,27,31] that the singlet is the lowest state with the parent phenyl cation, but the energy ordering depends on the substituent. As mentioned above, the triplet is markedly lower in energy (by >10 kcal mol^{-1}) with the 4-amino-substituted derivative. Under such conditions ISC is expected to be slow, as suggested by the computed energy difference between the triplet cation and the minimum energy crossing point with the singlet surface (9.1 kcal mol^{-1}).[25a] It may well be that, analogously to what happens with isoelectronic phenylnitrene,[32] for which a similar situation applies, the chemical reaction (expected to involve essentially no activation energy) proceeds from the first formed spin state before ISC. Thus, the aminophenyl cation reacts from the *singlet* state when generated in this state by photolysis the diazonium salt, while heterolysis of chloroanilines proceeds, as indicated above, from the triplet state and leads to *triplet* phenyl cation.

The above computational results offers a clue for understanding the contrasting chemistry. The analysis of the CI wave function (Ψ) for $^3B_2$ state can be carried out in terms of the coefficient of the lowest eigenvector, or equivalently of populations of the active orbitals (γ_i, in Table 5). In this case, a single configuration dominates Ψ. In fact, the highest coefficient (C_i) is >0.93. This is reflected in the values of the fractional populations γ_i, which are close to 0, 1, and 2 respectively for the eight active orbitals (Table 5). The σ and a π orbitals (Φ4, Φ5; see Figure 8 with the corresponding C_i) are both singly occupied. The triplet state can be viewed as a classical triplet carbene, with the electrons in orthogonal spaces. However, the electron in the σ space is highly localized while the electron in the π space is delocalized on the ring and on the nitrogen atom. This consideration is based on CASSCF data and is also supported by UB3LYP spin density data (see Table 6) showing that the N atom has the second highest spin density (0.35). Therefore, the $^3B_2$ state has a 65% diradical, 35% carbene character at divalent C$_1$ atom. As for charge distribution, CASSCF and UB3LYP data are very similar (see Table 2) and the highest positive charge is on the C$_4$ atom (+0.37). Thus, the $^3B_2$ state involves no cation at C$_1$ and it is not surprising that it does not react with a neutral σ nucleophile, while it easily adds to a π nucleophile behaving as an electrophilic radical.

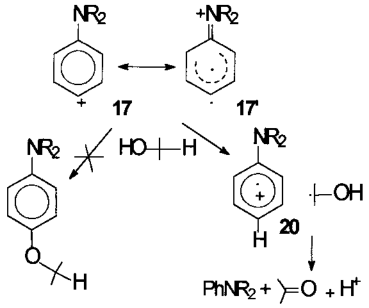
Contrary to $^3B_2$ state, the singlet 4-aminophenyl cation ($^1A'$) cannot be properly described by a single-determi-

---

[31] Dill, J. D.; Schleyer, P. v. R.; Binkley, J. S.; Seeger, R.; Pople, J. A.; Haselbach, E. *J. Am. Chem. Soc.* **1976**, *98*, 5428. Dill, J. D.; Schleyer, P. v. R.; Pople, J. *J. Am. Chem. Soc.* **1977**, *99*, 1. Castenmiller, W. A. M.; Buck, H. M. *Rec. Trav. Chim. Pays-Bas* **1977**, *96*, 207. Vincent, M. A.; Radom, L. *J. Am. Chem. Soc.* **1978**, *100*, 3306. Gamba, A.; Simonetta, M.; Suffritti, G.; Szele, I.; Zollinger, H. *J. Chem. Soc., Perkin Trans. 2* **1980**, 492. Alcock, N. W.; Greenhough, T. J.; Hirst, D. M.; Kemp, T. J.; Payne, D. R. *J. Chem. Soc., Perkin Trans. 2* **1980**, 8. Tasaka, M.; Ogata, M.; Ichikawa, H. *J. Am. Chem. Soc.* **1981**, *103*, 1885. Schleyer, P. v. R.; Kos, A. J.; Raghavachari, K. *J. Chem. Soc., Chem. Commun.* **1983**, 1296. Butcher, V.; Costa, M. L.; Dyke, J. M.; Ellis, A. R.; Morris, A. *Chem. Phys. Lett.* **1988**, *153*, 309. Schleyer, P. v. R.; Jiao, H.; Glukhotsev, M. N.; Chandrasekhar, J.; Kraka, E. *J. Am. Chem. Soc.* **1994**, *116*, 10129.

[32] Platz, M. S. *Acc. Chem. Res.* **1995**, *28*, 487.

Scheme 6

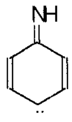


nant approach such as B3LYP. Thus, this question will be addressed on the basis of CASSCF data. There are two large coefficients in the lowest CI engenvector, respectively 0.81 and −0.47 (see Figure 8). Correspondingly, the populations of the active orbitals Φ4 and Φ5 are 1.46 and 0.54 (see Table 5). The most important configuration has the 8 electrons in four orbitals, three π and the p_N, while the σ orbital on C_1 (Φ5) is empty. However, the second configuration has a role, and results from double excitation from Φ4 to Φ5, both electrons being promoted from the p_N to the σ orbital. The first configuration corresponds the conventional representation of a phenyl cation with an empty σ orbital ($\pi^6\sigma^0$) while the latter one emphasizes the important singlet carbene character (planar sp^2-hybridized carbon, filled σ, and empty p orbital) of this species. Even if the charge is delocalized also in this case, the singlet carbene character supports that addition to σ nucleophiles is easy. This is not relevant in the present case since, as shown above, with chloroanilines ISC precedes heterolysis and leads directly to the triplet phenyl cation.

Thus, photolysis of an aminophenyldiazonium salt in alcohols yields an aminophenyl ether, since the singlet excited diazonium salt decomposes to the singlet phenyl cation, while only reduced aniline is obtained from the heterolysis of chloroaniline, via the triplet phenyl cation. As discussed above, this species has a radical−carbene character, indicated in Scheme 6 through mesomeric formula **17′**, and hydrogen abstraction is fast in neat alcohols (e.g. the intermediate radical cation **20**, see Scheme 6, is formed within 1 μs in MeOH; see Figure 3). This leaves no room for ether formation, and the rate for such process is at least 2 orders of magnitude slower than that of hydrogen transfer from the activated alcoholic C−H. In accordance with this mechanism, photoreduction of the chloroanilines is less efficient both in α trisubstituted *tert*-butyl alcohol and in electron-poor trifluoroethanol, but then it is the attack on anilines to give products **3** and **6** which competes and not ether formation (see Table 2).

While an uncharged σ nucleophile is ineffective, a charged species such as bromide or iodide does trap the cation also in the triplet state. Indeed, iodide is a better trap than the best π nucleophile, pyrrole, reacting 10 or 3.5 times faster respectively with the two cations considered. In the case of aniline **4** (not with the more reactive **1**), there is also a moderate increase in the quantum yield of reaction, contrary to what observed with all the other additives. It is possible that in this case a further path via electron transfer to the triplet contributes to the decomposition of the chloroaniline adding to the usual unimolecular fragmentation. Therefore, while the ratios in Table 3 give the order of π nucleophiles, a quantitative comparison with the rate of reaction with anions is premature, since the mechanism may be not be exactly the same in that case.

It should also be noted that the chemical results obtained with chloroaniline **4**, both as far as the product distribution and as far as the relative rates are concerned, differ very little from what found with the corresponding *N*,*N*-dimethyl derivative **1**. Presumably, the aminophenyl cation reacts with both hydrogen donors and π nucleophiles faster than it deprotonates. Actually, there is no need to invoke carbene **22** as an intermediate since *triplet* cation **17** has a carbene−diradical character which fully explains the observed chemistry. Since some of the arylations discussed here and in the accompanying paper[15] may have some synthetic significance, this is a relevant point since it leads to the expectation that both N-alkylated and nonalkylated anilines may be used as a substrates for photochemical reactions of this type.



22

Conclusion

The present data show that the 4-amino derivatives of the elusive phenyl cation are efficiently generated in solution by photoheterolysis of 4-chloroaniline and its dimethyl derivative in moderately polar or polar solvents. Under these conditions the triplet cation is generated. CASSCF and UB3LYP calculations show that this species has a mixed carbene−diradical character and very little positive charge at C_1. In accordance with this representation, it reacts with π nucleophiles but not with neutral σ nucleophiles. Importantly from the synthetic point of view, irradiation of chloroanilines offers a smooth and versatile method for the arylation of arenes. As discussed separately, the arylation of alkenes can be carried out similarly and offers a variety of synthetically useful paths.[15] Furthermore, preliminary studies show that photoinduced arylations are not limited to haloanilines but can be extended to other electron-donating substituted aromatics.[33]

Experimental Section

General Methods. *N*,*N*-4-chlorodimethylaniline (**1**, prepared by methylation of the aniline) and the other reagents (of commercial origin) were distilled or recrystallized before use. For the irradiations, spectroscopic grade solvents were used as received.

Preparative Irradiations. In a typical experiment a solution of 780 mg of aniline **1** or 625 mg of aniline **4** (0.05 M) in 100 mL of acetonitrile (containing a trap when required) was irradiated for 3 h in an immersion well apparatus fitted with a high-pressure mercury arc (125 W, water-cooled through a quartz jacket) after 15 min of flushing with argon and maintaining a slow gas flux during the irradiation. In the experiments with acid-sensitive substrates anhydrous potassium carbonate (2 g) was added and the solution magnetically stirred during the experiment. In an alternative procedure, irradiations were carried out by using 20 mL portions of the same solutions in a number of quartz tubes which were capped after flushing with argon for 15 min and externally irradiated

---

[33] Unpublished from the present laboratory.

by means of 6 × 15 W phosphor-coated lamps for 3 h in a merry-go-round apparatus. In this case, the solution was made 0.1 M in triethylamine when a buffer was required. The progress of the reaction was monitored by GC and GC/MS. The traps used are listed in Table 1.

Products Isolation and Identification. The irradiated solution was evaporated under reduced pressure and the residue chromatographed on silica gel 60 HR by eluting with cyclohexane−ethyl acetate mixtures. The products were obtained as solids or oils from the fractions (by repeating the chromatography in the case of unsatisfactory separation) and characterized by elemental analysis, GC/MS, and NMR as detailed in the following.

4-Arylanilines **8a**,[34] **8b**,[35] and **11**[36] and iodoanilines **15** and **16** were previously reported and were recognized either by comparison with an authentic sample or by comparison of the spectral properties. ^{1}H and ^{13}C NMR spectra were recorded with a 300 MHz spectrometer, and the chemical shifts are reported relative to TMS. The structure of new compounds were deduced from the results of ^{1}H, ^{13}C, DEPT-135, and 2D-correlated experiments. The GC-MS analyses were performed using a DB-5 column, 30 m × 0.25 mm with film thickness 0.25 μm. The carrier was helium at 0.6 mL/min. The total run time was 30 min with the initial oven temperature 80 °C (4 min.), rising at a rate of 10 °C/min to 250 °C.

***N*,*N*-Dimethyl-2-(4′-(dimethylamino)phenyl)-4-chloroaniline (3)** formed as a colorless oil which solidifies on standing, mp 40−42 °C (lit.[37] oil). Anal. Found: C, 77.82; H, 7.83; N, 10.05. Calcd for $C_{16}H_{19}N_2Cl$: C, 77.87; H, 7.76; N, 10.19. NMR: δ_H ($CDCl_3$) 2.55 (s, 6H, NMe$_2$), 3.05 (s, 6H, −NMe$_2$), 6.9 (d, J = 8 Hz, 1H), 6.72 and 7.45 (AA′XX′, 4H, aromatics), 7.14 (dd, J = 2, 8 Hz, 2H), 7.18 (dd, J = 2 Hz, 1H); δ_C ($CDCl_3$) 40.4 (NMe$_2$), 43.1 (NMe$_2$), 112.3 (CH), 118.6 (CH), 126.3, 126.5 (CH), 128,9, 129.0 (CH), 130.9 (CH), 135.8, 149.4, 149.8. GC/MS: t_R 11.21 min; m/z 274 (100), 276 (33), 259 (25).

2-(4′-Aminophenyl)-4-cloroaniline (6) was obtained as an oil.[38] Anal. Found: C, 65.85; H, 5.10; N, 12.72. Calcd for $C_{12}H_{11}N_2Cl$: C, 65.91; H, 5.07; N, 12.87. NMR: δ_H ($CDCl_3$) 3.9 (4H, broad, exch, NH$_2$), 6.68 (1H, dd, J = 8, 1.5 Hz), 6.79 and 7.25 (4H, AA′XX′, aromatics), 7.08 (2H, m,); δ_C ($CDCl_3$) 115.2 (CH), 116.3 (CH), 122.9, 127.4 (CH), 128.1, 129.4, 129.7 (CH), 129.8 (CH), 142.2, 145.7.

6-(4′-(Dimethylamino)phenyl)-3-methylene-1,2,4,5,6-pentamethylcyclohexadiene (9) was obtained as a mixture with ***N*,*N*-dimethyl-4-(2,3,4,5,6-pentamethylphenyl)aniline (10)** in a 3:2 ratio. The assignment of proton and carbon signals for each compound resulted from 2D-NOESY and 2D-HSQC NMR experiments. NOE correlations allowed the attribution of methyl signals and proved the position of the methylene group in cyclohexadiene derivative. Then the carbon signals were completely attributed on the basis of ^{1}H−^{13}C correlations. **9**: NMR δ_H ($CDCl_3$) 1.45 (*s*, 3H, CH$_3$-6), 1.55 (*s*, 6H, CH$_3$-1 and CH$_3$-5), 1.9 (*s*, 6H, CH$_3$-2 and CH$_3$-4), 2.95 (*s*, 6H, −NMe$_2$), 5.0 (bs, 2H, CH$_2$-3), 6.7 and 7.08 (4H, AA′XX′, aromatics). The following cross-peaks were found in the NOESY spectrum: 5.0 with 1.9; 7.08 with 1.43 and 1.55; 1.55 with 1.9. NMR: δ_C ($CDCl_3$) 14.5 (CH$_3$-2 and CH$_3$-4), 16.6 (CH$_3$-1 and CH$_3$-5), 21.8 (CH$_3$-6), 40.5 (NMe$_2$), 49.7 (C-6), 102.7 (CH$_2$-3), 112.6 (CH), 124.2, 127.9 (CH), 132.1, 132.3, 138.4, 142.5. GC/MS: t_R 18.42 min; m/z 281 (48), 266 (85), 251 (100), 237 (15), 146 (15). **10**: NMR δ_H ($CDCl_3$) 2.01 (s, 6H, CH$_3$-2 and CH$_3$-6), 2.25 (*s*, 6H, CH$_3$-3 and CH$_3$-5), 2.3 (*s*, 3H, CH$_3$-4), 3.05 (s, 6H, −NMe$_2$), 6.9 and 7.02 (4H, AA′XX′, aromatics). The following cross-peaks were found in the NOESY spectrum: 7.02 with 2.01; 2.01 with 2.25. NMR: δ_C ($CDCl_3$) 16.7 (CH$_3$-4), 18.3 (CH$_3$-2 and CH$_3$-6), 30.8 (CH$_3$-3 and CH$_3$-5), 40.6 (NMe$_2$), 112.2 (CH), 126.5, 130.1 (CH), 131.9, 132.3, 133.5, 140.1, 142.5. GC/MS: t_R 19.16 min; m/z 267 (100), 252 (20), 237 (8).

Low-Conversion Experiments. Low-conversion experiments were carried out for quantum yields measurements (Table 2) and competition experiments (Table 3). The solutions (5 mL) were prepared and irradiated under the same conditions as in the preparative experiments in a merry-go-round apparatus. Alternatively, 2 mL portions were irradiated in spectrophotometric couvettes by means of a 200 W focalized high-pressure mercury arc (interference filter, λ_{tr} 313 nm). In every case the conversion was limited to 20%. Product formation was assessed by GC and HPLC. The light flux was measured by ferrioxalate actinometry.

Emission Measurements. Emission spectra were measured by means of an Aminco Bowman spectrofluorometer, fitted by a rotating phosphoroscope for phosphorescence measurements (made at 77 K).

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 monochormator, 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). The experiments with excitation at 308 nm (excimer laser) were carried out at the Department of Chemistry of the University of Perugia. We thank Prof. F. Elisei for assistance in these measurements.

Calculations. The singlet (^{1}A′) and triplet (^{3}B$_2$) states of the $H_2NC_6H_4^+$ cation were optimized by the standard (U)-B3LYP method, using 6-31G(d) and 6-311+G(d,p) basis sets, as implemented in the Gaussian 94 program.[39] Both states were characterized by harmonic frequency calculations at B3LYP/6-31G(d) level. To confirm the nature of the stationary points and to produce theoretical parameters, vibrational frequencies (in the harmonic approximation) were calculated by B3LYP/6-31G(d) and used with no scaling for computing the zero point energies and their contributions to Gibbs free energies. CASSCF(8,8)/6-31(d) calculations were carried out, and the active space consisted of six π orbitals, the nitrogen lone pair (p$_N$), and the σ orbital located at the divalent carbon atom.

Acknowledgment. Partial support of this work by the CNR and MURST, Rome, is gratefully acknowledged.

Supporting Information Available: Complete computational results in the form of tables of *Z*-matrixes with the computed total energies. This material is available free of charge via the Internet at http://pubs.acs.org.

JO0104680

---

[34] Brune, H. A.; Erte, J. *Liebigs Ann. Chem.* **1980**, 928.

[35] Häfelinger, G.; Hack, F.; Wentermayer, G. *Chem. Ber.* **1978**, *111*, 1323.

[36] Dyall, L. K. *Aust. J. Chem.* **1964**, *17*, 419.

[37] Bellavita, V. *Gazz. Chim. It.* **1935**, *65*, 632.

[38] Badger, G.; Drewer, R. J.; Lewis, G. E. *Aust. J. Chem.* **1964**, *17*, 1036.

[39] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*, revision E.3; Gaussian, Inc.: Pittsburgh, PA, 1995.