Photodissociation of *N*-Arylmethylanilines: A Laser Flash Photolysis, Fluorescence, and Product Analysis Study[1]

M. G. Siskos,[†] A. K. Zarkadis,*,[†] S. Steenken,[‡] and N. Karakostas[†]

Department of Chemistry, University of Ioannina, 451 10 Ioannina, Greece, and Max-Planck-Institut für Strahlenchemie, 45470 Mülheim, FRG

Increased phenylation in the molecular series PhCH$_2$NHPh **(1)**, Ph$_2$CHNHPh **(2)**, and Ph$_3$CNHPh **(3)** has two important consequences on the photophysical/photochemical behavior: (i) decrease in the fluorescence quantum yields (cyclohexane), Φ_f = 0.115, 0.063, 0.001 (λ_{exc} = 254 nm) and 0.164, 0.089, 0.019 (λ_{exc} = 290 nm), respectively, and (ii) increase in the quantum yield (MeCN) of the photodissociation products PhCH$_2$•, Ph$_2$CH•, and Ph$_3$C•, $\Phi_{radical}$ = 0.16, 0.25, 0.65 (λ_{exc} = 248 nm) and (not measured), 0.18, 0.29 (λ_{exc} = 308 nm), respectively. As the C–N bond progressively weakens in the series **1**, **2**, **3** (bond dissociation enthalpy: 52, 48, 39 kcal/mol, respectively), the C–N fission channel becomes obviously more favorable and competes effectively with fluorescence. The involved intermediates PhCH$_2$•, Ph$_2$CH•, Ph$_3$C•, and PhNH• were identified using laser flash photolysis (248 and 308 nm). Product analysis (lamp irradiation) gives as main products aniline and (i) 1,1-diphenylethane and *o*- and *p*-benzylaniline for **1**, (ii) 1,1,2,2-tetraphenylethane for **2**, (iii) Ph$_3$CH and 9-Ph-fluorene for **3**; all these compounds are formed from the above radicals through coupling or H-abstraction reactions.

Introduction

Studies on ground-state substituent effects and structure–reactivity relationships lie in the center of extensive efforts to understand and predict chemical transformations.[2] Concerning particularly the fundamental bond-homolysis process, considerable progress has been achieved in rationalizing the factors which govern the readiness of a molecule to undergo bond fission,[3] distinguishing between electronic and steric contributions.[2–4]

Substituent effects in photodissociations are even more complex due to the additional involvement of excited states, and the focus of current experimental[5] and theoretical studies[6] aims to identify the excited states involved, the primary fragments (radicals, ions, etc.), and decipher their interconversions via electron-transfer reactions (ET).

Especially Michl et al.[6a,b] formulated conditions which facilitate the homolytic photodissociation of a benzylic bond: (1) large local excitation energy, (2) weak σ bond, (3) excitation into the triplet state, or efficient intersystem crossing, and (4) σ-bond perpendicular to the plane of the local excited system. On the basis of this model we could recently[7] explain the high efficiency (Φ(Ph$_3$C•) = 0.6–0.8) of the photodissociation of the C–N bond in Ph$_3$CNHPh, **3**; this molecule has a weak C–N σ bond (39 kcal/mol)[7] and a local chromophore (aniline)[8] with high excitation energy ($E_{singlet}$ > 90 kcal/mol, $E_{triplet}$ > 70 kcal/mol).[9]

In the present report we describe our photochemical studies on two systems with very closely related structures, Ph$_2$CHNHPh **(2)** and PhCH$_2$NHPh **(1)**, where we

* Corresponding author. Tel: (+30 651) 98 379. 98398, Fax: (+30 651) 45840. E-mail: azarkad@cc.uoi.gr.
† University of Ioannina.
‡ Max-Planck-Institut für Strahlenchemie.

(1) Zarkadis, A. K.; Siskos, M. G.; Georgakilas, V.; Steenken, S.; Karakostas, N.; Garas, S. K. Partly presented at the XVIIIth International Conference on Photochemistry, Warsaw, August 3–8, 1997.
(2) See, for example: The First Century of Physical Organic Chemistry (IUPAC Special Issue). *Pure Appl. Chem.* **1997**, *69*, 211–292.
(3) *Substituent Effects in Radical Chemistry*; Viehe, H. G., Janousek, Z., Merenyi, R., Eds.; NATO ASI Series C, Mathematical and Physical Sciences, D. Reidel Pub.; Vol. 189, 1986. Sustmann, R.; Korth, H.-G. *Adv. Phys. Org. Chem.* **1990**, *26*, 131. Jiang, Xi-Kui, *Acc. Chem. Res.* **1997**, *30*, 283.
(4) Ziegler, K. *Angew. Chem.* **1949**, *61*, 168. Rüchardt, C.; Beckhaus, H.-D. *Top. Curr. Chem.* **1985**, *130*, 1. Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165. Hansch, C.; Hoekman, D.; Gao, H. *Chem. Rev.* **1996**, *96*, 1045. Neumann, W. P.; Uzick, W.; Zarkadis, A. K. *J. Am. Chem. Soc.* **1986**, *108*, 3762.
(5) (a) Cristol, S. J.; Bindel, T. H. *Org. Photochem.* **1983**, *6*, 327. (b) Kropp, P. J. *Acc. Chem. Res.* **1984**, *17*, 131. (c) Smirnov, V. A.; Plotnikov, V. G. *Russ. Chem. Rev.* **1986**, *55*, 929. (d) Das, P. K. *Chem. Rev.* **1993**, *93*, 119. (e) Johnston, L. J. *Chem. Rev.* **1993**, *93*, 25. (f) Wilson, R. M.; Schnapp, K. A. *Chem. Rev.* **1993**, *93*, 223. (g) Scaiano, J. C.; Johnston, L. J. *Org. Photochem.* **1989**, *10*, 309. (h) Wagner, P.; Park, B.-S. *Org. Photochem.* **1991**, *11*, 227. (i) Pincock, J. A. *Acc. Chem. Res.* **1997**, *30*, 43. (j) McGowan, W. M.; Hilinski, E. F. *J. Am. Chem. Soc.* **1995**, *117*, 9019. (k) Dreyer, J.; Peters, K. S. *J. Phys. Chem.* **1996**, *100*, 15156.

(6) (a) Michl, J.; Bonacic-Koutecky, V. *Electronic Aspects of Organic Photochemistry*; Wiley-Interscience: New York, 1990; p 138, 292, 374. Klessinger, M.; Michl, J. *Excited States and Photochemistry of Organic Molecules*; Verlag Chemie: Weinheim, 1995; p 348. (b) Michl, J.; Balaji, V. In *Computational Advances in Organic Chemistry: Molecular Structure and Reactivity*; Ögretir, C., Csizmadia, I. G., Lang, E. A., Eds.; NATO ASI Series, Vol. 330, Kluwer: Dordrecht, 1991; p 323. (c) Larson, J. R.; Epiotis, N. D.; McMurchie, L. E.; Shaik, S. S. *J. Org. Chem.* **1980**, *45*, 1388. (d) Zimmerman, H. E. *J. Am. Chem. Soc.* **1995**, *117*, 8988. (e) Formosinho, S. J.; Arnaut, L. G. *Adv. Photochem.* **1991**, *16*, 67. (f) Bernardi, F.; Olivucci, M.; Robb, M. A. *Chem. Soc. Rev.* **1996**, 321.
(7) Siskos, M. G.; Zarkadis, A. K.; Steenken, S.; Karakostas, N.; Garas, S. K. *J. Org. Chem.* **1998**, *63*, 3251.
(8) The energy of the lowest excited state of various (triarylmethyl)-anilino derivatives is reported to be localized on the anilino chromophore: Manring, L. E.; Peters, K. S. *J. Phys. Chem.* **1984**, *88*, 3516. Herz, M. L. *J. Am. Chem. Soc.* **1975**, *97*, 6777. Cremers, D. A.; Cremers, T. L. *Chem. Phys. Lett.* **1983**, *94*, 102. Spears, K. G.; Gray, T. H.; Huang, D. *J. Phys. Chem.* **1986**, *90*, 779. Geiger, M. W.; Turro, N. J.; Waddel, W. H. *Photochem. Photobiol.* **1977**, *25*, 15.
(9) For PhNH$_2$:[9a] $E_{singlet}$ = 95.1 kcal/mol (nonpolar solvents), 91.8 kcal/mol (polar) and $E_{triplet}$ = 71.0 kcal/mol (polar). For PhNMe$_2$: $E_{singlet}$ = 91.5 kcal/mol (nonpolar) and 89.6 kcal/mol (polar) and $E_{triplet}$ = 75.8 kcal/mol (polar). (a) Murov, S. L.; Carmichael, I.; Hug, G. L. *Handbook of Photochemistry*, 2nd ed.; Marcel Dekker: New York, 1993.

keep the anilino chromophore as in **3** and change systematically through consecutive phenyl elimination (from **3** to **1**) only the C−N bond strength. The bond dissociation enthalpy (BDH) decreases in the order **1**, **2**, **3** (52, 48, 39 kcal/mol, respectively)[7,10] as a consequence of increased phenyl substitution. How such a variation of a ground-state property (BDH) is reflected in the photochemical/photophysical behavior of compounds **1**, **2**, and **3**? The intention of this paper is to give experimental data using laser flash photolysis (LFP), fluorescence spectroscopy, and product analysis and attempt a first approach to this question.

Experimental Section

Materials. Compounds **2** and **3** has been prepared according to literature procedures.[11] *N*-Benzylaniline (Aldrich, 99%) has been used as received. Aniline and *N*-methylaniline (Aldrich) were purified by vacuum distillation before use. Acetonitrile, hexane, cyclohexane, propanol-2 (Merck), and *n*-BuCl (Fluka) were of spectroscopic grade.

Instruments. Fluorescence emission and excitation spectra were obtained on a Spec Fluorolog instrument. Fluorescence lifetimes were measured with a time-correlated single-photon counter (nanosecond range) in cyclohexane ($\lambda_{exc} = 290$ nm, $OD_{290nm} = 0.53$/cm). The sample were excited at 290 nm with a sparck lamp (PRA 510C), filled with hydrogen gas (0.6 bar), operated at 6 kV.

Gas chromatographic analyses and separations were conducted on a Hewlett-Packard 5890, Series II, FID gas chromatograph with an OV-1701, 15 m capillary column and a Siemens 1 mV recorder (injector 200 °C, detector 300 °C, column temperature 70−280 °C, 8 °C/min). The hydrogen production was measured on a Varian 1400 WLD gas chromatograph with a 3.5 m charcoal column at 70 °C and argon as the carrier gas (42 mL/min). GC-MS analyses were performed on a SSQ 700 EI instrument with the same column, under identical conditions.

Photochemical Experiments (Product Analyses). Photochemical reactions were run with a Philips HPK-125 W lamp (medium pressure) at 20 °C in special quartz cuvettes. The photolysis solutions were purged with argon before they were irradiated.

Laser Flash Photolysis Experiments. Solutions of the corresponding substrates (A/cm ~0.8−1.6) were deoxygenated by bubbling with argon and photolyzed at 20 °C in a flow system (Suprasil quartz cell) using 20-ns pulses (0.3−100 mJ) of 248 nm light (KrF*) from a Lambda Physik EMG 103MSC excimer laser or 308-nm light (XeCl*) from Lambda Physik EMG150E laser.[7,12]

Table 1. Absorption (ν_a^{max}, 10^3 cm^{-1}) and Fluorescence (ν_f^{max}, 10^3 cm^{-1}) Peaks of the Aniline Derivatives, Fluorescence Lifetimes (τ_f, ns), and Fluorescence Quantum Yields (Φ_f) in Cyclohexane at 25 °C

sample	ν_a^{max} $^1L_a \leftarrow {}^1A$ ($^1L_b \leftarrow {}^1A$)	ν_f^{max} at $\lambda_{ex} = 290$ nm	τ_f ($\lambda_{ex} = 290$ nm)	Φ_f $\lambda_{ex} = 290$ nm ($\lambda_{ex} = 254$ nm)
PhNH$_2$	42.74 (34.82)	31.08	3.69[a]	0.17[18] (0.11)[19]
PhNHMe	41.36 (33.94)	30.45	3.42[22b]	0.18[b] (0.10)
1	41.25 (34.01)	30.38	3.11	0.164 (0.115)
2	40.68 (34.25)	30.57	not measured	0.089 (0.063)
3	42.12 (shoulder)	30.56	1.90	0.019 (0.001)

[a],[b] The following values are reported in the literature: (a) 4.34,[22a] 3.9,[18] 4.42;[23] (b) 0.13,[23a] 0.119[22a].

Quantum Yields. Quantum yields of the radical production were determined[7] by measuring the initial absorbance of the corresponding radical Ph$_3$CH•, Ph$_2$CH•, and PhCH$_2$• at $\lambda_{max} = $ 334 ($\epsilon = 3.6 \times 10^4$ M^{-1} cm^{-1}),[12b] 332 ($\epsilon = 4.4 \times 10^4$ M^{-1} cm^{-1}),[12b] and 318 nm ($\epsilon = 8.8 \times 10^3$ M^{-1} cm^{-1}),[13] respectively. The initial absorbance (A) of the hydrated electron at 600 nm produced by photolysis of an aqueous solution of KI under identical conditions (the same optical density at 248 nm, OD = 1.0/cm) was used as the reference for the 248-nm laser photolysis, while the initial absorbance of Aberchrome-540 at 494 nm was used for the 308-nm laser photolysis.[14] The measurements were carried out by varying the laser power (0−40 mJ/pulse) and plotting the absorbance versus the laser power.[15] We used values of $\epsilon_{e-(aq)} = 1.33 \times 10^4$ M^{-1} cm^{-1} at 600 nm[16] and ϵ(Aberchrome 540) $= 8.2 \times 10^3$ M^{-1} cm^{-1} at 494 nm.[14] The quantum yield for the formation of the hydrated electron was taken as 0.29, a value obtained by product analysis following 254-nm irradiation[17] and for Aberchrome 540 as 0.2.[14]

Fluorescence quantum yields were measured by comparison with values reported for aniline: $\Phi_f = 0.17$ ($\lambda_{exc} = 290$-nm)[18] and $\Phi_f = 0.11$ ($\lambda_{exc} = 254$-nm)[19] in cyclohexane solutions (OD$_{290 nm} = 0.25$/cm, OD$_{254 nm} = 0.60$/cm).

Pulse Radiolysis Experiments. A 3-MeV Van der Graaf electron accelerator was used as radiation source. Dosimetry was performed with a N$_2$O-saturated 10 mM KSCN aqueous solution, taking $G_{(OH)} = 6.0$ and $\epsilon_{(SCN)2-} = 7600$ dm^3 mol^{-1} cm^{-1} at 480 nm.[20]

Results and Discussion

1. Absorption and Fluorescence Spectra. Absorption, fluorescence excitation, and fluorescence emission spectra of **1**−**3** were obtained in cyclohexane at 298 K (see Table 1). All absorption (and fluorescence excitation) spectra show the two typical aniline bands which are attributed to the $^1L_b \leftarrow {}^1A$ (~290 nm) and $^1L_a \leftarrow {}^1A$ (~240 nm) transitions and correspond to the S_1 and S_2 states,

(10) Based on the known BDH of the C−N bond in H$_3$CNHPh (68.9 kcal/mol)[10a] and the calculated difference of ~30 kcal/mol in the BDH's between H$_3$C−H (105 kcal/mol)[10b] and Ph$_3$C−H (75 kcal/mol),[10c−e] we arrive at a value of ~39 kcal/mol for the BDH in Ph$_3$CNHPh, not considering, however, possible steric effects which should decrease the BDH even more. Similarly, based on the BDH of Ph$_2$CH−H (84 kcal/mol)[10b] we find a value of 48 kcal/mol for the C−N bond of **2**, and based on the BDE of PhCH$_2$−H (88 kcal/mol)[10b] we find 52 kcal/mol for **1**. (a) Colussi, A. J.; Benson, S. W. *Int. J. Chem. Kinet.* **1978**, *10*, 1139.; For a critical review, see: Batt, L.; Robinson, G. N. *The Chemistry of the Functional Groups, Suppl. F*; Patai, S., Ed.; Wiley-Intersience: Chichester, 1982; Part 2, p 1035. (b) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493. (c) Breslow, R.; Grant, J. L. *J. Am. Chem. Soc.* **1977**, *99*, 7745. See, however, for a discussion of the trityl stabilization energy: (d) Beckhaus, H.-D.; Dogan, B.; Schuetzer, J.; Hellman, S.; Rüchardt, C. *Chem. Ber.* **1990**, *123*, 137. (e) Increased values for the BDH for C−H (81 kcal/mol) of Ph$_3$CH were reported: Bordwell, F. G.; Cheng, J.-P.; Ji, G.-Z.; Satish, A. V.; Zhang, X. *J. Am. Chem. Soc.* **1991**, *113*, 9790.

(11) Siskos, M. G.; Garas, S. K.; Zarkadis, A. K.; Bokaris, E. P. *Chem. Ber.* **1992**, *125*, 2477.

(12) (a) Faria, J. L.; Steenken, S. *J. Am. Chem. Soc.* **1990**, *112*, 1277. (b) Bartl, J.; Steenken, S. Mayr, H.; McClleland, R. A. *J. Am. Chem. Soc.* **1990**, *112*, 6918. (c) McClleland, R. A.; Kanagasabapathy, V. M.; Steenken, S. *J. Am. Chem. Soc.* **1988**, *110*, 6913.

(13) Claridge, R. F. C.; Fischer, H. *J. Phys. Chem.* **1983**, *87*, 1960.

(14) (a) Heller, H. G.; Langan, J. R. *J. Chem. Soc., Perkin Trans. 2* **1981**, 341. (b) Wintgens, V.; Johnston, L. J.; Scaiano, J. C. *J. Am. Chem. Soc.* **1988**, *110*, 511.

(15) (a) McClelland, R. A.; Banait, N.; Steenken, S. *J. Am. Chem. Soc.* **1989**, *111*, 2929. (b) Wintgens, V.; Jonson, L.; Scaiano, J. C. *J. Am. Chem. Soc.* **1988**, *110*, 511.

(16) Hug, G. L. *Natl. Stand. Ref. Data Ser.* **1981**, *69*, 1.

(17) Jortner, J.; Ottolenghi, M.; Stein, G. *J. Phys. Chem.* **1962**, *66*, 2029, 2037, 2042; **1964**, *68*, 247.

(18) Perichet, G.; Chapelon, R.; Pouyet, B. *J. Photochem.* **1980**, *13*, 67.
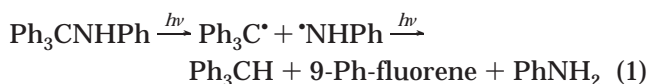
(19) Malkin, Ya. N.; Ruziev, Sh.; Pigorov, N. O.; Kuz′min, V. A. *Bull. Akad. USSR, Ser. Chem.* **1987**, *36*, 51.

(20) Jagannadham, V.; Steenken, S. *J. Am. Chem. Soc.* **1988**, *110*, 2188.

respectively.[21] The differences in the Stokes shifts are almost identical ($\Delta\nu \approx 3.7 \times 10^3$ cm^{-1}, see Table 1), indicating that the intramolecular charge-transfer character is similar for all the compounds in both the fluorescence S$_1$ state and the ground state.[21,22] In all cases the excitation spectra are found to be identical to the corresponding absorption spectra.
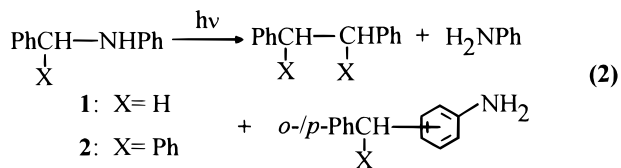
The fluorescence quantum yields and fluorescence lifetimes were measured and are listed also in Table 1, along with those of PhNH$_2$ and PhNHMe for comparison. Both are influenced by the bulkiness of the *N*-alkyl group and tend to decrease as the phenyl substitution increases (from **1** to **3**). The fluorescence quantum yields of all compounds decrease considerably on excitation into the S$_2$ ($\lambda_{exc} = 254$ nm) relative to S$_1$ ($\lambda_{exc} = 290$ nm) state, which indicates that photoinduced chemical transformations in S$_2$ takes place, as found out by Köhler and Getoff for aniline itself.[23]

2. Product Studies. (a) Ph$_3$CNHPh (3). Recently,[7] we reported a detailed product analysis study of the stationary photolysis of **3** in MeCN and hexane, both with lamp and laser light (248 and 308 nm), see Experimental Section. The main products identified were PhNH$_2$, Ph$_3$CH, and 9-Ph-fluorene (eq 1). T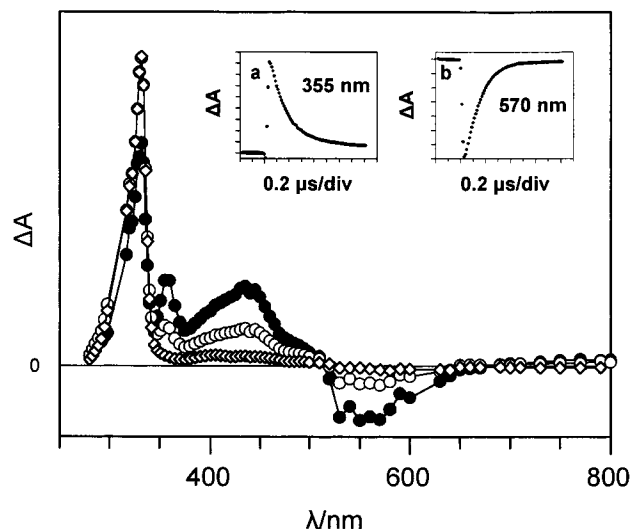heir formation is explained through a homolytic C−N bond cleavage of **3** according to reaction 1. These results were supported through the indentification of Ph$_3$C$^{\bullet}$ and PhNH$^{\bullet}$ using LFP and ESR.[7]

$$\text{Ph}_3\text{CNHPh} \xrightarrow{h\nu} \text{Ph}_3\text{C}^{\bullet} + {}^{\bullet}\text{NHPh} \xrightarrow{h\nu}$$
$$\text{Ph}_3\text{CH} + \text{9-Ph-fluorene} + \text{PhNH}_2 \quad (1)$$

(b) PhCH$_2$NHPh (1) and Ph$_2$CHNHPh (2). Irradiation (lamp, see Experimental Section) of either **1** or **2** in MeCN solution (0.3 mM) leads to the formation of 1,2-diphenylethane and 1,1,2,2-tetraphenylethane, respectively (the corresponding dimerization products of the benzyl and diphenylmethyl radicals), and aniline. Additionally, in the case of **1**, almost equivalent amounts of *o*- and *p*-benzylaniline (traces of *o*- and *p*-diphenylmethylaniline in the case of **2**) were formed, well-known coupling products of the benzyl and anilino radicals.[24] Obviously, as in the photolysis of **3**, the primary step is a photoinduced C−N bond homolysis followed by radical recombination reactions, see reaction 2. Ring subsitution and formation of the *ortho* and *para* derivatives is less effective with Ph$_2$CH$^{\bullet}$ than with PhCH$_2$$^{\bullet}$, probably because of the larger steric requirements of the first. The

Figure 1. Transient absorption spectra obtained upon 248-nm laser photolysis of an argon-saturated acetonitrile solution (0.55 mM) of **2**. Spectra were recorded at times (●) 60 ns, (○) 200 ns, and (◇) 750 ns after the pulse. In the insets are shown (a) the decay of the Ph$_2$CH$^{\bullet*}$ radical at 355-nm and (b) its emission at 570 nm.

products were identified by comparison of GC retention times using authentic samples and/or GC/MS analyses and are the same also in the nonpolar solvent hexane.

Since N−H bond breaking is a well-known photoprocess for aniline derivatives,[7,22−26] hydrogen gas formation was checked; no significant amounts were detected (see Experimental Section).

3. Laser Flash Photolysis Experiments. (a)[7] Ph$_3$CNHPh, 3. This compound photolyzes very efficiently with 248- and 308-nm laser light in MeCN under argon, giving Ph$_3$C$^{\bullet}$ with quantum yields $\Phi = 0.65$ and 0.29, respectively. The second fragment is the anilino radical as described in detail in a previous paper.[7] Secondary transient products were also formed, like Ph$_3$C$^+$ and 4a,4b-dihydro-9-phenylfluorenyl radical (DHPF$^{\bullet}$), derived from Ph$_3$C$^{\bullet}$ by absorption of a second photon (two-photon process).

(b) Ph$_2$CHNHPh, 2. The transient absorption spectrum obtained by 248-nm laser photolysis (see Figure 1) of **2** in MeCN, 60 ns after the pulse, was characterized by a strong absorption peak at $\lambda_{max} = 330$ nm. This peak decayed in oxygen-saturated solution ([O$_2$] = 8.2 mM)[9a] with rate constant $k = 1.8 \times 10^9$ M^{-1} s^{-1} and assigned to Ph$_2$CH$^{\bullet}$ on the basis of the identity of its spectrum to that reported in the literature[12b,27] and the excellent agreement of the kinetic data (a value of $k = 1.7 \times 10^9$ M^{-1} s^{-1} was reported for the reaction of Ph$_2$CH$^{\bullet}$ with oxygen).[12b,27] Additionally, other weaker absorption bands at $\lambda_{max} = 355$ and 435 nm and a weak negative signal in the 520−600 nm region (light emission) were observed.

(21) Sarkar, S. K.; Kastha, G. S., *Specrochim. Acta, Part A* **1992**, *48*, 1611.

(22) (a) Saito, F.; Tobita, S.; Shizuka, H. *J. Photochem. Photobiol. A* **1997**, *106*, 119. (b) Saito, F.; Tobita, S.; Shizuka, H. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 4177.
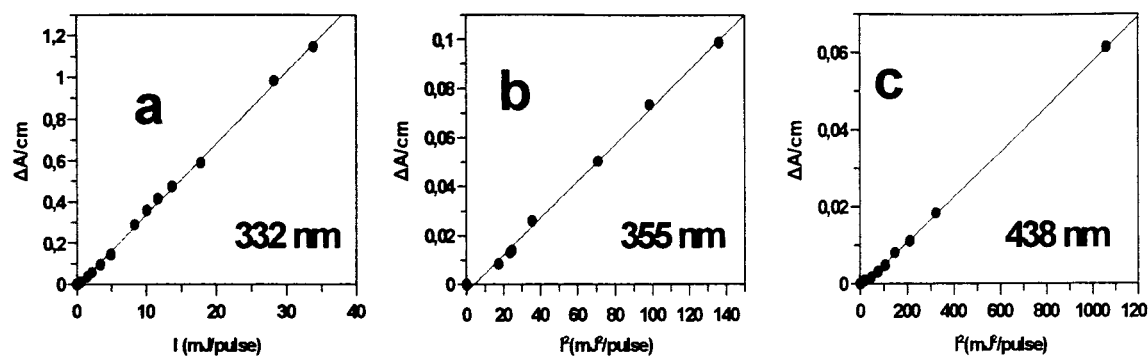
(23) (a) Köhler, G., *J. Photochem.* **1987**, *38*, 217. (b) Köhler, G.; Getoff, N. *J. Chem. Soc., Faraday Trans. 1* **1980**, *76*, 1576. (c) Köhler, G.; Rosicky, C.; Getoff, N. In *Excited States in Organic Chemistry and Biochemistry*; Pullman, B., Goldblum, N., Eds.; Reidl: Dordrecht, 1977; p 303.

(24) Ogata, Y.; Takagi, K. *J. Org. Chem.* **1970**, *35*, 1642.

(25) (a) Qin, L.; Tripathi, N. R.; Schuler, R. H. *Z. Naturforsch.* **1985**, *40a*, 1026. (b) Land, E. J.; Porter, G. *Trans. Faraday Soc.* **1963**, *59*, 2027. (c) Malkin, Ya. N.; Ruziev, Sh.; Pigorov, N. O.; Kuz'min, V. A. *Bull. Akad. USSR, Ser. Chem.* **1987**, 51. (d) Leyva, E.; Platz, M. S.; Niu, B.; Wirz, J. *J. Phys. Chem.* **1987**, *91*, 2293. (e) Wagner, B. D.; Ruel, G.; Lusztyk, J. *J. Am. Chem. Soc.* **1996**, *118*, 13.

(26) (a) Malkin, J. *Photochemical and Photophysical Properties of Aromatic Compounds*; CRC: Boca Raton, FL, 1992: p 117, 201. (b) Malkin, Ya. N.; Kuz'min, V. A. *Russ. Chem. Rev.* **1985**, *54*, 1041.

(27) (a) Bronberg, A.; Schmidt, K. H.; Meisel, D., *J. Am. Chem. Soc.* **1985**, *107*, 8381. (b) Hadel. K. M.; Platz, M. S.; Scaiano, J. C., *J. Am. Chem. Soc.* **1984**, *106*, 283.

Figure 2. Dependence of the yield of Ph$_2$CH$^{\bullet}$ (at 332 nm, a), Ph$_2$CH$^{\bullet*}$ (at 355 nm, b), and Ph$_2$CH$^+$ (at 435 nm, c) measured by the increase of the corresponding absorbance (ΔA) as a function of the laser power I (a) or square laser power I^2 (b, c) in the photolysis (308-nm laser light) of **2** in MeCN under argon (a, b) or oxygen (c).

The absorption at 355 nm is attributed to the excited state of diphenylmethyl radical (Ph$_2$CH$^{\bullet*}$) and the broad negative signal at 520−600 nm to its fluorescence (first excited electronic state, D$_1$), as described in the literature.[28] This assignment is further supported by the fact that the rate constants of the decay of both the absorption at 355 nm (inset a, Figure 1) and the emission at 570 nm (inset b) have exactly the same value ($k = 6.8 \times 10^6$ s^{-1}) and both could be removed with oxygen. The peak at 435 nm was decayed in an oxygen-saturated solution with a rate constant $k = 4.1 \times 10^6$ s^{-1}, the same as that measured previously for Ph$_2$CH$^+$ under argon in the same solvent MeCN ($k = 4.0 \times 10^6$ s^{-1},[12c,29] 4.3×10^6 s^{-1} [28]). This band was not present when the photolysis was carried out in the presence of 1−5% H$_2$O, where only the bands of the two radicals Ph$_2$CH$^{\bullet}$ and Ph$_2$CH$^{\bullet*}$ remained. Therefore this absorption band (435 nm) is attributed to the ionic species Ph$_2$CH$^+$.
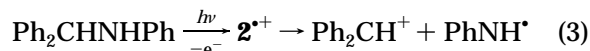
The same spectrum was obtained by irradiating with 308-nm laser light, the only difference being the increased intensity of the transient absorption corresponding to Ph$_2$CH$^{\bullet*}$ (355 nm) and its fluorescence (520−600 nm) relative to that of Ph$_2$CH$^{\bullet}$, a reasonable observation in view of the increased absorption of Ph$_2$CH$^{\bullet}$ at 308 nm and the consequently more efficient reexitation to Ph$_2$CH$^{\bullet*}$.

The signal intensity of Ph$_2$CH$^{\bullet}$ (332 nm) was found to increase linearly with the 308-nm (or 248 nm) laser power (Figure 2a), indicating a monophotonic process (photohomolysis of the C−N bond). In the case of Ph$_2$CH$^{\bullet*}$ (355 nm) the signal amplitude follows a quadratic dependence on the 308-nm (or 248-nm) laser power, reflecting the need of the second photon for the excitation of Ph$_2$CH$^{\bullet}$ (Figure 2b), as has been already reported in the literature.[30]

Concerning the band at 435 nm (attributed to the Ph$_2$CH$^+$), a two-photon process was also found (Figure 2c); the measurements (248 and 308 nm) were carried out in an oxygen-saturated solution in order to remove the broad absorption with λ_{max} at 355 nm corresponding to the excited radical Ph$_2$CH$^{\bullet*}$. This two-photon process excludes a direct photoheterolysis of the C−N bond or photoionization of Ph$_2$CH$^{\bullet}$ as the origin of the Ph$_2$CH$^+$ formation. The latter process was studied in detail by

Faria and Steenken[30] using the "tandem pulse" laser technique, and it was found that two photons are required for the ionization of Ph$_2$CH$^{\bullet}$ radical in MeCN with 308-nm light.

However, an alternative possible way to produce Ph$_2$CH$^+$ is the photoionization of the parent compound **2** to the corresponding radical cation **2**$^{\bullet+}$, followed by fragmentation to Ph$_2$CH$^+$ and PhNH$^{\bullet}$ (reaction 3). The fragmentation of **2**$^{\bullet+}$ to Ph$_2$CH$^+$ was demonstrated by a pulse radiolysis study of **2** (4.2 mM solution in *n*-BuCl), where the absorption of Ph$_2$CH$^+$ at ca. 431 nm was observed 3 μs after the pulse.

$$\text{Ph}_2\text{CHNHPh} \xrightarrow[-e^-]{h\nu} \textbf{2}^{\bullet+} \rightarrow \text{Ph}_2\text{CH}^+ + \text{PhNH}^{\bullet} \quad (3)$$

Actually, photoionization of aromatic amines with concomitant fragmentation is a very common behavior,[22,23,26] owing to their low ionization[31] or oxidation potentials.[32] Because the optical detection of the photo-ejected electron is impossible in MeCN,[33] we performed the experiment in deoxygenated 2-PrOH/H2O (2:3) mixture and obtained the spectrum shown in Figure 3. In addition to the radical Ph$_2$CH$^{\bullet}$ absorbing at 332 nm, a broad peak at 500−800 nm was observed, which followed a clear quadratic dependence from the laser power (Figure 3, inset) and was efficiently removed by O$_2$ and N$_2$O; it was therefore identified as due to e$^-_{aq}$. The same dependence was also found previously by the formation of Ph$_2$CH$^+$ in MeCN (Figure 2c); Ph$_2$CH$^+$, however, cannot be observed here (2-Pr/H$_2$O 2/3) due to its high reactivity with the nucleophilic solvent (a lifetime of about ∼80 ps was calculated previously[12b,30] in H$_2$O/EtOH 1/3 for this cation).

The same radicals (Ph$_2$CH$^{\bullet}$, Ph$_2$CH$^{\bullet*}$, and PhNH$^{\bullet}$) were observed on photolysis (248 nm) of **2** in cyclohexane. However, Ph$_2$CH$^+$, the ionization product, was not detected in the nonpolar solvent, as expected.

(c) PhCH$_2$NHPh, 1. Irradiation of an argon-saturated solution of **1** in MeCN with 248-nm laser light results in the spectrum shown in Figure 4a. The spectrum is

(28) Scaiano, J. C.; Tanner, M.; Weir, D. *J. Am. Chem. Soc.* **1985**, *107*, 4396.

(29) MacClelland, R. A.; Kanagasabapathy, V. M.; Banait N. S.; Steenken, S. *J. Am. Chem. Soc.* **1989**, *111*, 3966.

(30) Faria, J. L.;Steenken, S. *J. Phys. Chem.* **1993**, *97*, 1924. Adam, W.; Oestrich, R. S. *J. Am. Chem. Soc.* **1992**, *114*, 6031.

(31) Farrell, P. G.; Newton, J. *J. Phys. Chem.* **1965**, *69*, 3506. Vedeneyev, V. I.; Gurvich, L. V.; Kondrat'yev, V. N.; Medvedev, V. A.; Frankevich, Ye. L. *Bond Energies, Ionization Potentials and Electron Affinities*; Edward Arnold Publishers: London, 1966; p 170.
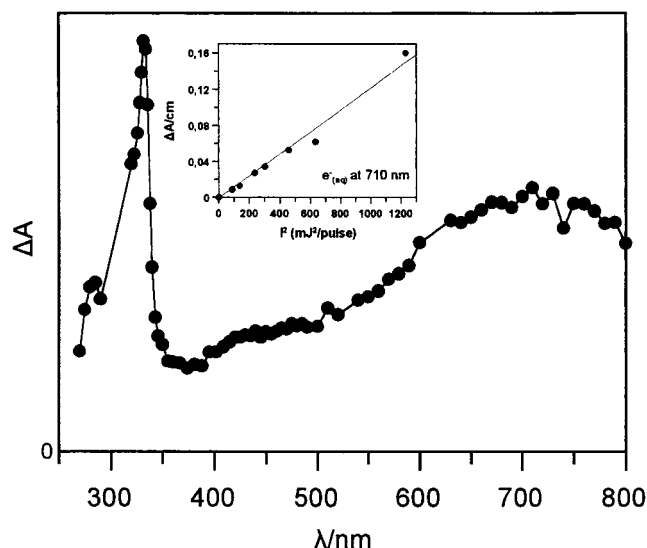
(32) (a) Jonsson, M.; Lind, J.; Eriksen, T. E.; Merenyi, G. *J. Am. Chem. Soc.* **1994**, *116*, 1423. (b) Jonsson, M.; Lind, J.; Merenyi, G. Eriksen, T. E. *J. Chem. Soc., Perikin Trans. 2* **1995**, 67.

(33) Hirata, Y.; Mataga, N.; Sakata, Y.; Misumi, S. *J. Phys. Chem.* **1983**, *87*, 1493. Hirata, Y.; Takimoto, M.; Mataga, N. *Chem. Phys. Lett.* **1983**, *97*, 569.

Figure 3. Absorption spectra recorded 250 ns after flash photolysis of a 0.47 mM solution of **2** in 2-Pr/H$_2$O (2/3) under argon with 308-nm laser light. Inset: yield of e$^-_{aq}$ (measured at 710 nm) as a function of the square laser power I^2, see text.
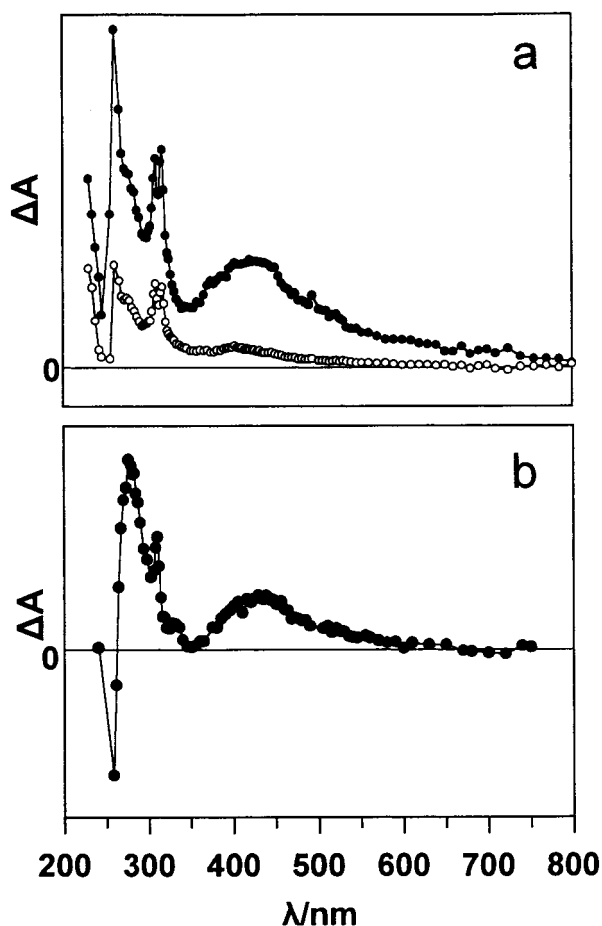
Figure 4. (a) Absorption spectra recorded (●) 45 ns and (○) 5 μs after flash photolysis of a solution of **1** (0.082 mM) in MeCN (argon saturated), with 248-nm laser light. (b) Absorption spectrum obtained in oxygen-saturated solution, 45 ns after the laser pulse.

characterized by a sharp and intensive peak at 264 nm, a shoulder at ca. 279 nm, two weaker and almost equal by intense peaks at 309 and 318 nm, and a broad

absorption band in the region 350−800 nm with a maximum at ca. 430 nm.

In an oxygen-saturated solution the bands at 264 and 318 nm were completely removed, indicating a species of radical character. The remaining spectrum recorded on the same delay time as under argon (Figure 4b) consists from an intense absorption band at 279 nm (shoulder under argon), a sharp but weaker band at 309 nm (reduced to 1/3 relative to that obtained under argon), and a broad band extended (in this case) between 300 and 650 nm, with the maximum at ca. 430 nm. The amplitude of this broad band was decreased ca. 3 times and its decay became slower.

The absorptions at 264, 309, and 318 nm are assigned to PhCH$_2^{\bullet}$ on the basis of its well-known absorption spectrum (maxima at 264, 309, and 318 nm)[13,34] and its reaction with oxygen. The peak at 309 nm is assigned to the anilino radical also on the basis of its well-known absorption spectrum (maximum at 309 nm)[7,22,25] and the observation that it persists[25e] in an oxygen atmosphere (reduced, however, to 1/3 of that obtained under argon).

The broad absorption peak (350−800 nm) should correspond to at least to two superimposed transient species with maxima in the same region (∼430 nm). One of them, extending to 800 nm under argon, disappears in oxygen atmosphere (probably the triplet state of **1**) and the second extending to 650 nm (Figure 4b) is unaffected by oxygen and probably corresponds to a cationic species.

This second band shows the same decay profile ($k_{obs} \approx 5 \times 10^5$ s^{-1}) as the band at 279 nm (oxygen atmosphere) and therefore is assigned to the same species. Since the spectrum is similar to that produced by irradiating **1** in 2-PrOH/H$_2$O (1/4) under O$_2$ (two bands with maxima at 279 and 435 nm, see Figure 5a), or with pulse radiolysis (Figure 5b), it is attributed to the corresponding radical cation **1**$^{\bullet+}$. A reasonable assignment to PhCH$_2^+$ can be excluded, since this species has an absorption maximum at 305 nm.[35]

To distinguish between **1**$^{\bullet+}$ and a possible triplet state we conducted the irradiation (248 nm) in cyclohexane, to avoid the photoionization process leading to **1**$^{\bullet+}$. We obtained the transient spectrum shown in Figure 6a, where in addition to the three sharp bands belonging to PhCH$_2^{\bullet}$ at 259, 308, and 315 nm (a small blue-shift is observed in a nonpolar solvent), a broad absorption band with maximum at ca. 440 nm is also observed. This band, which is produced monophotonically, decayed exponentially with a lifetime of 0.59 ms,[36] disappears in oxygen, and is quenched by 2,3-dimethylbuta-1,3-diene with a rate constant of $k^T_q = 6.4 \times 10^9$ M^{-1} s^{-1}, comparable to that of the quenching of the aniline triplet state under the same conditions ($k^T_q = 1.3 \times 10^{10}$ M^{-1} s^{-1}),[22b] and therefore can be attributed to the triplet state of **1**. The

(34) (a) Meisel, D.; Das, P. K.; Hug, G. L.; Bhattacharyya, K.; Fessenden, R. W. *J. Am. Chem. Soc.* **1986**, *108*, 4706. (b) Christensen, H. C.; Sehested, K.; Hart, E. J. *J. Phys. Chem.* **1973**, *77*, 983. (c) McAskill, N. A.; Sangster, D. F. *Aust. J. Chem.* **1977**, *30*, 2107. (d) Tokumura, K.; Udagawa, M.; Ozaki, T.; Itoh, M. *Chem. Phys. Lett.* **1987**, *141*, 558.

(35) Fujisaki, N.; Comte, P.; Gäumann, T. *J. Chem. Soc., Chem. Commun.* **1993**, 848.

(36) The lifetime of 0.59 μs measured for the T$_1$ state of **1** (cyclohexane) is much less than that of PhNH$_2$ in the same solvent, 3.3 μs;[22b] a lifetime of 2.8 μs[7] has been measured for the T$_1$ of PhNH$_2$ in MeCN, 1.2 μs[36a] in benzene and 4.3 μs[36b] in dioxane. (a) Malkin, Ya. N.; Ruziev, Sh.; Kuz'min, V. A. *J. Gen. Chem. USSR* **1987**, *57*, 560. (b) Shimamori, H.; Sato, A. *J. Phys. Chem.* **1994**, *98*, 13481.
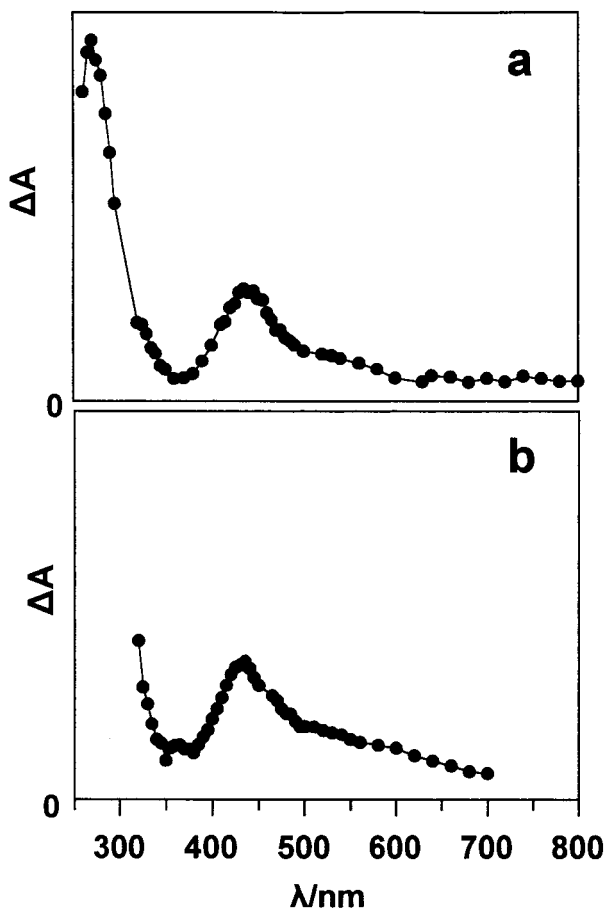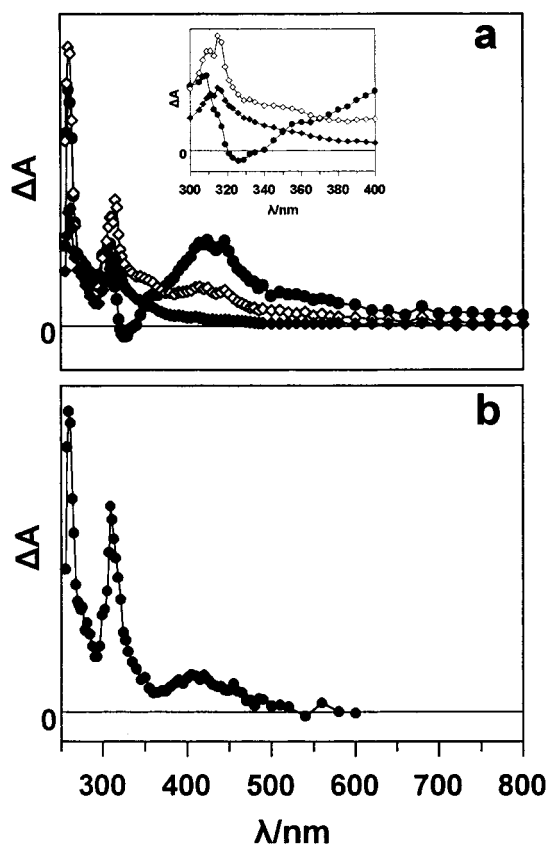
Figure 5. (a) Absorption spectrum obtained on 308-nm LFP of a 4.7 mM solution of **1** in 2-Pr/H2O (1/4) under oxygen 1 μs after the pulse. (b) Absorption spectrum obtained on pulse radiolysis of **1** (6.1 mM in *n*-BuCl) under oxygen 1 μs after the pulse.

Figure 6. (a) Transient absorption spectra obtained upon 248-nm laser photolysis of an argon-saturated cyclohexane solution (0.55 mM) of **1**. Spectra were recorded at times (●) 40 ns, (◇) 600 ns, and (◆) 15 μs after the pulse. The inset displays the 300−400 nn area of the spectrum two times enlarged. (b) The absorption spectrum obtained in oxygen atmosphere about 750 ns after the laser pulse.

Figure 7. Plot of the first-order rate constant (k_{obs}) for the decay of the T_1 of **1** at 440 nm versus the 2,3-dimethylbuta-1,3-diene concentration in cyclohexane at 20 °C.

rate constant (k^T_q) was determined by monitoring the transient $T_n \leftarrow T_1$ absorption as a function of the quencher concentration (Figure 7; $r = 0.999$). The decay of the triplet state is accompanied by an increase in the maximum optical density of the PhCH$_2$• radical at 259, 308, and 315 nm, indicating that the triplet decays in part through C−N bond homolysis; the well-known spectrum[7,22,25] of the second fragment PhNH• is clearly observed when the LFP experiment was conducted under an oxygen atmosphere. Under these conditions PhCH$_2$• and the triplet state were removed (Figure 6b).
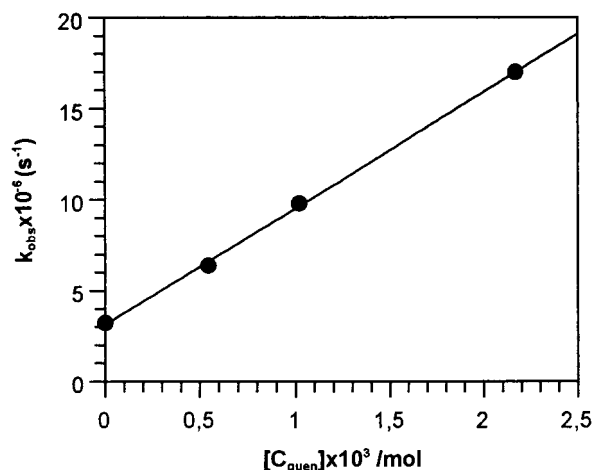
4. Quantum Yields. Table 2 shows the quantum yields (see Experimental Section) of the PhCH$_2$•, Ph$_2$CH•, and Ph$_3$C• radicals, formed upon 248- and 308-nm LFP of the corresponding compounds **1**, **2**, and **3** in argon-saturated solutions (MeCN), together with the values of the bond dissociation enthalpies (BDH)[7,10] of the corresponding C−N bonds. A decrease of the BDH's is accompanied by an increase of the quantum yields of the radical formation.

5. Conclusions. In summary, we have shown that increased phenylation and progressive weakening of the C−N bond in the series **1**, **2**, and **3** (52, 48, 39 kcal/mol, respectively) affects both the photophysical and the photochemical behavior of the compounds.

The fluorescence quantum yields Φ_f (Table 1) decrease in the same order irrespective of the excitation wavelengths (254 or 290 nm) corresponding roughly to the S$_2$

and S$_1$ excited states; the Φ_f values are smaller on excitation to S$_2$ indicating the occurrence of an irreversible chemical process arising from S$_2$. The latter observation has been also made for PhNH$_2$ and attributed to the N−H photodissociation.[23] In the case of compounds **1−3**, however, since the C−N bond is much weaker than the N−H (ca. 83 kcal/mol),[10a] C−N bond fission (and not N−H) obviously occurs leading to radical formation

Table 2. Quantum Yields for the Formation of the Radicals PhCH$_2^{\bullet}$, Ph$_2$CH$^{\bullet}$, and Ph$_3$C$^{\bullet}$ (in MeCN under Argon)

compd	BDH (kcal/mol)	$\Phi_{radical}$ (248 nm)	$\Phi_{radical}$ (308 nm)
1	52	0.16	*a*
2	48	0.25	0.18
3	39	0.65	0.29

a Not able to be measured because PhCH$_2^{\bullet}$ absorbs at 308 nm (laser wavelength) and disturbs its absorption signal.

(PhCH$_2^{\bullet}$, Ph$_2$CH$^{\bullet}$, Ph$_3$C$^{\bullet}$, and PhNH$^{\bullet}$); the fact that no H$_2$ was produced (see Experimental Section) is an additional evidence against N–H bond cleavage. The same tendency follows the fluorescence lifetimes. In contrast, the non-benzylic derivatives PhNH$_2$ and PhNHMe do not show any significant difference either in Φ_f or τ_f (Table 1).

On the contrary, the quantum yields (MeCN) of the photodissociation products PhCH$_2^{\bullet}$, Ph$_2$CH$^{\bullet}$, and Ph$_3$C$^{\bullet}$ (Table 2) increase as the C–N bond becomes weaker (**1** > **2** > **3**), and the values are larger in the case of the higher energy excitation into the S$_2$ state (λ_{exc} = 254 nm). This means that the photodissociation occurs even in S$_2$, in line with the decreased Φ_f values measured on excitation to S$_2$ relative to those measured on excitation into the S$_1$ state. Product analysis (see above) confirms the photodissociation process, giving as main products aniline and dimerization and H-abstraction products originating from the free radicals (PhCH$_2^{\bullet}$, Ph$_2$CH$^{\bullet}$, Ph$_3$C$^{\bullet}$, and PhNH$^{\bullet}$). These were identified by LFP as the primary products of the photohomolytic process.

As the C–N bond progressively weakens in the series **1**, **2**, and **3** the C–N fission channel becomes obviously more favorable and competes effectively with fluorescence. This indicates dissociation originating from the singlet state, although in the case of compound **1** we identified the triplet state (Figure 6) as the dissociating state giving PhCH$_2^{\bullet}$; pressumably both are involved in the dissociation process. Here we should note the debate[19,23] regarding the responsible excited state(s) for the N–H photodissociation in PhNH$_2$; Malkin et al.[19] considered that photodissociation occurs mainly from the T$_1$ state, while Köhler and Getoff[23b] and Saito, Tobita, and Shizuka[22b] concluded that most of the formation of PhNH$^{\bullet}$ takes place from the S$_1$ state.

The above results clearly demonstrate the effect of the variation of a ground-state property (BDH) in processes involving excited states and agree nicely with Michl's[6a] theoretical predictions. Michl pointed out that, in the case of a photodissociating bond, keeping all other parameters constant (electronegativity difference, excitation energy, same local chromophore as occurs in our model compounds **1**, **2**, and **3**), a weakening of the bond strength lowers the excitation energy of the responsible excited state;[37,38] this minimizes the barrier needed to be overcome for the transition from the bound "local" excited state (in **1**, **2**, and **3**, the "local" chromophore is considered to be the anilino group)[8] to that repulsive excited state of the bond (C–N in **1**, **2**, and **3**) which finally leads to its full dissociation. The reduction of the BDH down the series **1**, **2**, and **3** minimizes the above barrier in the same order and makes the C–N dissociation channel more favorable, thus facilitating the C–N bond cleavage at the expense of radiative deactivations such as fluorescence (see Tables 1 and 2). Moreover, excitation energies and bond strengths are linearly related as shown by Pearson a few years ago.[38]

An alternative interpretation of the decreased values Φ_f attributed to increased intersystem crossing as the nonplanarity of the lone pair on nitrogen increases[21,39] cannot be excluded, although the constant Stokes shifts (Table 1) down the series **1**, **2**, and **3** do not support any significant geometry variation around the nitrogen atom.

Summary. Progressive phenylation in the molecular series PhCH$_2$NHPh, Ph$_2$CHNHPh, and Ph$_3$CNHPh reduces the C–N bond strength (BDH = 52, 48, 39 kcal/mol, respectively) and has two important consequences on the photophysical/photochemical behavior: (i) decrease in the fluorescence quantum yields (cyclohexane) Φ_f = 0.115, 0.063, 0.001 (λ_{exc} = 254-nm) and 0.164, 0.089, 0.019 (λ_{exc} = 290-nm), respectively, and (ii) increase in the quantum yield (MeCN) of the photodissociation products PhCH$_2^{\bullet}$, Ph$_2$CH$^{\bullet}$, and Ph$_3$C$^{\bullet}$ $\Phi_{radical}$ = 0.16, 0.25, 0.65 (λ_{exc} = 248-nm) and (not measured), 0.18, 0.29 (λ_{exc} = 308-nm), respectively. As the C–N bond progressively weakens, a C–N fission channel becomes obviously more favorable and competes effectively with fluorescence. The results demonstrate the reflection of the variation of a ground-state property (BDH) in the excited-state behavior (Φ_f, τ_f, $\Phi_{radical}$) of the aniline derivatives **1**, **2**, and **3**. Work is in progress to study more examples and quantify the above relationship.

(37) Michl, J. *Acc. Chem. Res.* **1990**, *23*, 127.
(38) Pearson, R. C. *J. Am.Chem. Soc.* **1988,** *110*, 2092.
(39) Lim, E. C.: Chakrabarti, S. K. *J. Phys. Chem.* **1967**, *47*, 4726. Adams, J. E.; Mantulin, W. W.; Huber, R. J. *J. Am.Chem. Soc.* **1973,** *95*, 5477. Watson, F. H., Jr.; El-Bayoumi, M. A. *J. Chem. Phys.* **1971**, *55*, 5464.