

Photodissociation of *N*-(Triphenylmethyl)anilines: A Laser Flash Photolysis, ESR, and Product Analysis Study¹

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

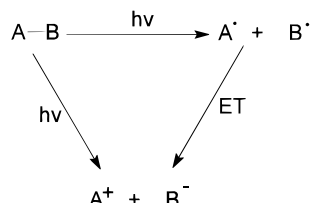
Department of Chemistry, University of Ioannina, 451 10 Ioannina, Greece, and Max-Planck-Institut für Strahlenchemie, Mülheim, FRG

Received October 17, 1997

N-(Triphenylmethyl)anilines (Ph₃C-NHPh-R, R = H, *o*-Me, *m*-Me, *p*-Me, *p*-CPh₃), upon photolysis with 248- and 308-nm laser light, as well as by lamp irradiation with 254-nm light in acetonitrile and hexane solutions, undergo exclusively C–N bond homolysis to give the triphenylmethyl radical in a monophotonic process. Product analysis gives as main products Ph₃CH, 9-Ph-fluorene, and PhNH₂. The quantum yields for the formation of Ph₃C• are high (0.6–0.8, 248-nm excitation) and independent of the solvent. This effective homolytic dissociation results from the low electronegativity difference between the carbon and nitrogen atoms constituting the bond to be broken, the low bond dissociation enthalpy of the C–N bond, the high excitation energy of the local chromophore (aniline), and probably from a favorable alignment of the C–N bond in a plane perpendicular to the anilino chromophore (due to the large steric requirements of the trityl group), thus enabling an effective hyperconjugative interaction with it. The above dissociation competes effectively with heterolytic cleavage, which is the pathway dominating, e.g., in the photolysis of Ph₃C–Cl in MeCN under the same conditions. At high pulse intensities the trityl radicals formed above are excited by a second photon leading to either electrocyclicization to 4a,4b-dihydro-9-phenylfluorenyl radical (DHPF•), or photoionization to Ph₃C⁺, the latter only in MeCN and only on 248-nm photolysis. A new intermediate (9-Ph-4a*H*-fluorene) on the way to the final product 9-Ph-fluorene is identified resulting from electrocyclicization, supporting a mechanism proposed earlier. The optical measurements are supported by ESR studies (irradiation with 254-nm light).

Introduction

The photodissociation of the benzylic carbon–heteroatom bond (C–X, X = Hal, OCOR, OR, ⁺SR₂, PO₃H[−], [−]NR₃) of molecules in solution has been the focus of extensive product and time-resolved spectroscopic studies,² as well as of theoretical considerations.^{3,4,5b} Despite the many-sided consequences in mechanistic and applied photochemistry (photochromic materials, dyes, photoprotection techniques, etc.), the fundamental question of the responsible excited states, the nature of the primary fragments (radicals, ions), and their interconversion via electron transfer (ET) is far from being settled.^{5,6b,7,8}



Especially Michl et al.³ pointed out the essential role which is played by the electronegativity difference (δ_{AB})

of the atoms making up the bond to be broken, with respect to the energy and the shape of the first excited singlet (S₁) and triplet (T₁) state; while S₀ and T₁ remains almost unchanged as δ_{AB} increases, the energy and shape of S₁ rapidly approaches that of T₁ and the two differ very little and merge in the fully dissociated limit. In the special case of a tritopic dissociation of a σ bond (like the C–N bond in CH₃–NH₂), both S₁ and T₁ states acquire similar, dissociative states.^{3a} Furthermore, Michl et al.³ formulated conditions which facilitate the homolytic photodissociation of a benzylic bond: e.g., (1) a large local excitation energy, (2) a weak σ bond, (3) excitation into the triplet state, or efficient intersystem crossing, (4) σ bond perpendicular to the plane of the local excited system.

We have decided to concentrate our studies on the photochemistry (248- and 308-nm laser light) of the

(3) (a) Michl, J.; Bonacic-Koutecky, V. *Electronic Aspects of Organic Photochemistry*; Wiley-Interscience, **1990**, pp 138, 292, 374. (b) Michl, J.; Balaji, V. In *Computational Advances in Organic Chemistry: Molecular Structure and Reactivity*; Ögretir, C., Csizmadia, I. G., Lang, E. A., Eds.; Kluwer: Dordrecht, 1991; NATO ASI Series, Vol. 330, p 323; (c) Michl, J. *Acc. Chem. Res.* **1990**, *23*, 127.

(4) Larson, J. R.; Epiotis, N. D.; McMurchie, L. E.; Shaik, S. S. *J. Org. Chem.* **1980**, *45*, 1388.

(5) (a) McGowan, W. M.; Hilinski, E. F. *J. Am. Chem. Soc.*, **1995**, *117*, 9019. (b) Zimmerman, H. E. *J. Am. Chem. Soc.* **1995**, *117*, 8988. (c) Pincock, J. A. *Acc. Chem. Res.* **1997**, *30*, 43.

(6) (a) Faria, J. L.; Steenken, S. *J. Am. Chem. Soc.* **1990**, *112*, 1277. (b) Bartl, J.; Steenken, S. Mayr, H.; McClelland, R. A. *J. Am. Chem. Soc.* **1990**, *112*, 6918. (c) Jagannadham, V.; Steenken, S. *J. Am. Chem. Soc.*, **1988**, *110*, 2188. (d) Faria, J. L.; Steenken, S. *J. Phys. Chem.* **1993**, *97*, 1924. (e) McClelland, R. A.; Kanagasabapathy, V. M.; Steenken, S. *J. Am. Chem. Soc.* **1988**, *110*, 6913.

(7) Gaillard, E.; Fox, A. M.; Wan, P. *J. Am. Chem. Soc.* **1989**, *111*, 2180.

(8) (a) Manring, L. E.; Peters, K. S. *J. Phys. Chem.* **1984**, *88*, 3516. (b) Peters, K. S.; Li, B. *J. Phys. Chem.* **1994**, *98*, 401. (c) Dreyer, J.; Peters, K. S. *J. Phys. Chem.* **1996**, *100*, 15156.

* 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) (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) Sciano, J. C.; Johnston, L. J. *Org. Photochem.* **1989**, *10*, 309.

Table 1. Spectroscopic Absorption Data of 1a–e in MeCN^a

1

R	H	<i>o</i> -Me	<i>m</i> -Me	<i>p</i> -Me	<i>p</i> -Ph ₃ C
1	a	b	c	d	e
λ_{\max} (nm)	236	236	240	240	265
$\log \epsilon$ (M ⁻¹ cm ⁻¹)	4.23	4.21	4.12	4.16	4.08

^a They show an additional shoulder at 300–310 nm ($\log \epsilon \sim 3.3 \text{ M}^{-1} \text{ cm}^{-1}$).

N-(triphenylmethyl)aniline derivatives **1a–e**, keeping in mind Michl's "spirit": a low δ_{CN} (nitrogen is the closest of the first row elements to carbon), a weak central C–N σ bond ($\sim 39 \text{ kcal/mol}$),⁹ and a local chromophore (aniline)^{8a,10a} with high excitation energy ($E_{\text{singlet}} > 90 \text{ kcal/mol}$, $E_{\text{triplet}} > 70 \text{ kcal/mol}$).¹⁰ While the absorption spectra of **1a–e** are the sum of the methylene-isolated phenyl and anilino chromophores (see Table 1), the fluorescence spectra which we obtained in hexane are characteristic of the anilino chromophore (emission at $\lambda_{\max} \approx 330 \text{ nm}$).^{10b} The main justified objection to relating our system to Michl's approach would presumably be the "nonpure" $\pi\pi^*$ character of the lowest excited states (S_1 , T_1), due to the perturbing effect of the lone pair on nitrogen. However, in aniline¹¹ this contribution seems to be rather small ($\sim 22\%$), and S_1 and probably S_2 remain in fact $\pi\pi^*$ states.^{11a,12}

The photodissociation of the C–N bond in benzylic compounds has recently attracted much attention, but most studies concern ammonium salts,^{2a,d} where the C–N bond already possesses considerable ground-state carbocation–dipole character ($\text{R}_3\text{C}^+\cdots\text{NR}'_3$)¹³ due to the increased electronegativity of the ammonium group. There do exist also some product studies¹⁴ apart from the classical papers by Lewis and Lipkin^{14a} and Porter and Stracham.^{14b,15b}

(9) On the basis of the known BDH of the C–N bond in $\text{H}_3\text{C–NHPH}$ (68.9 kcal/mol)^{9a} and the calculated difference of $\sim 30 \text{ kcal/mol}$ in the BDH's between $\text{H}_3\text{C–H}$ (105 kcal/mol)^{9b} and $\text{Ph}_3\text{C–H}$ (75 kcal/mol),^{9c,47} we arrive at a value $\sim 39 \text{ kcal/mol}$ for the BDH in $\text{Ph}_3\text{C–NHPH}$, not considering, however, possible steric effects which should decrease the BDH even more. (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-Interscience, 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 for a discussion of the trityl stabilization energy: (d) Beckhaus, H.-D.; Dogan, B.; Schuetzler, J.; Hellman, S.; Ruchardt, C. *Chem. Ber.* **1990**, *123*, 137. (e) Similarly, on the basis of the difference in the BDH's between $\text{H}_3\text{C–H}$ (105 kcal/mol)^{9b} and $\text{PhCH}_2\text{–H}$ (88 kcal/mol),^{9b} we find for the BDH of the C–N bond in $\text{PhCH}_2\text{–NHPH}$ $\sim 56 \text{ kcal/mol}$.

(10) The energy of the lowest excited state of various (triarylmethyl)-anilino derivatives is reported to be localized on the anilino chromophore.^{8a,10a} For PhNH_2 , $E_{\text{singlet}} = 95.1 \text{ kcal/mol}$ (nonpolar solvents), 91.8 kcal/mol (polar) and $E_{\text{triplet}} = 71.0 \text{ kcal/mol}$ (nonpolar), 76.6 kcal/mol (polar); for PhNMe_2 , $E_{\text{singlet}} = 91.5 \text{ kcal/mol}$ (nonpolar), 89.6 kcal/mol (polar) and $E_{\text{triplet}} = 75.8 \text{ kcal/mol}$ (polar).³⁵ (a) 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.; Waddell, W. H. *Photochem. Photobiol.* **1977**, *25*, 15. (b) We measured the fluorescence spectra of the compounds PhNHMe , PhNHCH_2Ph , PhNHCHPh_2 , and PhNHCPH_3 (**1a**) (0.05 mM in hexane, excitation at 240 and 300 nm) and found emissions at λ_{\max} 328, 332, 327, and 327 nm, respectively, typical values for the anilino chromophore.^{10a}

(11) (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. (c) Saito, F.; Tobita, S.; Shizuka, H. *J. Photochem. Photobiol. A*, **1997**, *106*, 119. (d) Saito, F.; Tobita, S.; Shizuka, H. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 4177.

Certainly, with the aniline chromophore there is the risk of introducing additional complications into the system due to the well-known tendency of the aniline function to photoionize in polar solvents, usually water, or to break the N–H bond in nonpolar solvents.^{11,15}



We present here a laser flash photolysis (LFP) and electron spin resonance (ESR) study, supported by product analysis, on the aniline derivatives **1**. Our data indicate that compounds **1** undergo clean homolytic photodissociation to trityl radical, in both polar (acetonitrile) and nonpolar solvents (hexane), with high quantum yields, competing effectively with other possible pathways, such as heterolysis or photoionization. This photobehavior follows nicely Michl's predictions. In sharp contrast, we obtained (see Figure 1c) under the same conditions (MeCN/248-nm laser) a ratio $[\text{Ph}_3\text{C}^\bullet]:[\text{Ph}_3\text{C}^+] \approx 1:1.4$ by the photodissociation of $\text{Ph}_3\text{C–Cl}$, not very different than in diarylmethyl chlorides;^{16a} to be noted here is the large δ_{CCl} and the strengthening of the C–Cl bond ($\sim 60 \text{ kcal/mol}$)^{16b} compared to C–N.

Experimental Section

Materials. The synthesis of *N*-(triphenylmethyl)aniline derivatives **1a–e** has been described previously.^{17,18} They were purified by recrystallization (twice) from methanol or a mixture of methanol and CHCl_3 . The triphenylmethyl chloride (Merck) was recrystallized from hexane by adding drops of acetyl chloride. Ph_3CH (Fluka) was recrystallized from ligroin, 9-Ph-fluorene (9-Ph-flH) was prepared from the corresponding carbinol,¹⁹ and 9-Ph-fl-NHPh from the 9-Ph-fl-Cl and aniline.²⁰ Acetonitrile (MeCN), hexane, cyclohexane, ethanol, tetrachloromethane (Merck), and *n*-butyl chloride (Fluka) were spectroscopic grade and used as received.

Instruments. Fluorescence spectra (uncorrected) were obtained on a Spex Fluorolog. Electron spin resonance spectra were obtained on a Varian E-109 spectrometer. Gas chromatographic analyses and separations were conducted on a

(12) The spectrum is recorded 18 μs after the pulse to avoid T–T absorptions of the triplet state^{12a} of aniline (lifetime of the triplet state is 1.2 μs in benzene and 4.3 μs in dioxane;^{12b} we found 2.8 μs in MeCN). (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.

(13) Boyd, S. L.; Boyd, R. J.; Bessonette, P. W.; Kerdraon, D. I.; Aucoin, N. T. *J. Am. Chem. Soc.* **1995**, *117*, 8816.

(14) (a) Lewis, G. N.; Lipkin, D. *J. Am. Chem. Soc.* **1942**, *64*, 2801. (b) Porter, G.; Stracham, E. *Trans. Faraday Soc.* **1958**, *54*, 1595. (c) Ogata, Y.; Takagi, K. *J. Org. Chem.* **1970**, *35*, 1642. (d) Ratcliff, M. A.; Kochi, J. K. *J. Org. Chem.* **1972**, *37*, 3268. (e) Bekowies, P. J.; Albrecht, A. C. *J. Phys. Chem.* **1971**, *75*, 431. (f) Shi, M.; Okamoto, Y.; Takamuku, S. *J. Chem. Res. (S)*. **1990**, 346.

(15) (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.; Lusztzyk, J. *J. Am. Chem. Soc.* **1996**, *118*, 511.

(16) (a) A ratio 1: 1.6 was reported for $\text{Ph}_2\text{CH–Cl}$ by Steenken and co-workers.^{6b} (b) From $\Delta H_f(\text{Ph}_3\text{C–Cl})_{\text{gas}} = 53.3 \text{ kcal/mol}$, $\Delta H_f(\text{Cl})_{\text{gas}} = 29.9 \text{ kcal/mol}$,^{16c} and $\Delta H_f(\text{Ph}_3\text{C}^\bullet)_{\text{gas}} = 84.5 \text{ kcal/mol}$,^{9d} a value of 61 kcal/mol is obtained for the BDH of the C–Cl bond in $\text{Ph}_3\text{C–Cl}$. This is reasonable in view of the reported values of 64 kcal/mol for $\text{Ph}_2\text{CH–Cl}$,^{6b} and 72.2 kcal/mol for $\text{PhCH}_2\text{–Cl}$.^{9b} (c) *NIST Standard Reference Database 25*; Lias, S. G., Liebman, J., Lewin, R. D., Kafafi, S. A., Eds.; 1994; Version 2.0.

(17) Siskos, M. G.; Tzerpos, N. I.; Zarkadis, A. K. *Bull. Chem. Soc. Belg.* **1996**, *105*, 759.

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

(19) Schuler, R. H.; Hartzell, A. L.; Behar, B. *J. Phys. Chem.* **1981**, *85*, 192.

(20) Kliegl, A. *Ber. Dtsch. Chem. Ges.* **1905**, *38*, 284.

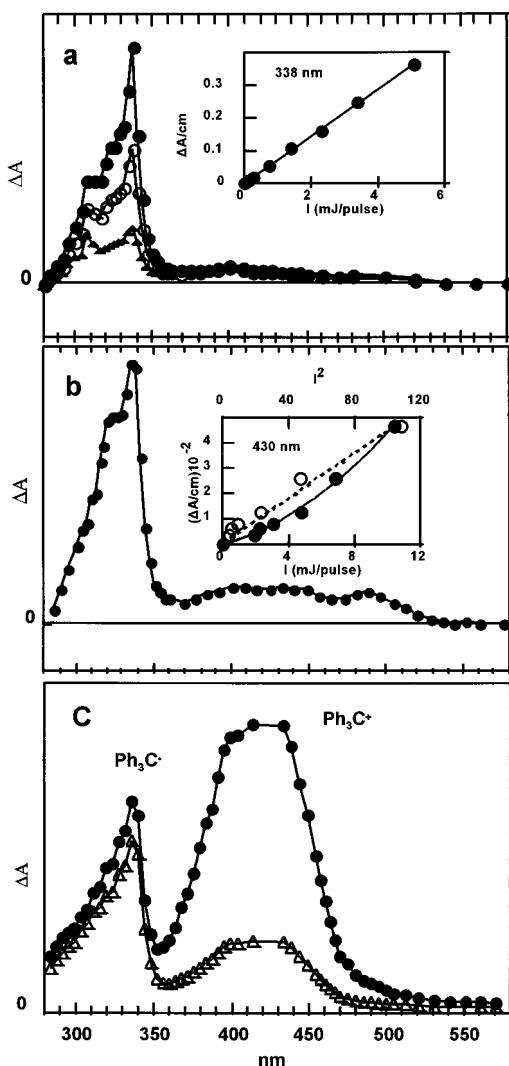


Figure 1. Absorption spectra obtained on 248-nm LFP in MeCN: (a) 0.3 mM **1a** in oxygen-saturated solution recorded at ●, 85 ns; ○, 170 ns; and ▲, 350 ns after the pulse. Inset: yield of trityl radical (ΔA_{338}) as a function of the laser energy (under argon); see the text. (b) 0.1 mM **1d** under argon recorded at 70 ns. Inset: yield of trityl radical as a function of the laser power I (full circles) and I^2 (open circles); see text. (c) 0.7 mM $\text{Ph}_3\text{C}-\text{Cl}$ under argon: ●, 200 ns; △, 14 μs .

Siechromat or Hewlett-Packard 5890, Series II or Varian 3700, FID gas chromatograph with an OV-1 (10 m) or an SE-54 (35 m) or an OV-1701 (15 m) and RTX-1701 (15 m) capillary column (injector, 200 °C; detector, 300 °C; column temperature, 70–280 °C, 8 or 10 °C/min). The hydrogen production was measured on a Varian 1400 WLD gas chromatograph with a 3.5 m charcoal column at 70 °C using argon as carrier gas (42 mL/min). GC-MS analyses were performed on a SSQ 700, EI instrument, using the same conditions and columns.

Photochemical Experiments (Product Analyses). Photochemical reactions were run with a Philips HPK-125 W medium-pressure mercury vapor lamp at 20 °C in special quartz cuvettes. The photolysis solutions (concentration ~ 0.1 mM) were purged with argon or oxygen before they were irradiated. The same quartz cuvettes were used also for the reaction with the 248-nm (KrF*) or 308-nm (XeCl*) excimer laser. The photolyses at 254-nm were performed with a Haraeus TNN-8 W low-pressure mercury lamp.

Laser Flash Photolysis Experiments. Solutions of the corresponding substrates ($A/\text{cm} \sim 1.0$) 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

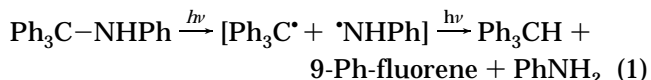
nm light (KrF*) from a Lambda Physik EMG 103MSC excimer laser or 308-nm light (XeCl*) from a Lambda Physik EMG150E laser.^{6a,b,d}

Quantum Yields. These were determined²¹ by measuring the initial absorbance of Ph_3C^* at $\lambda_{\text{max}} = 334$ nm. The initial absorbance 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. The measurements were carried out by varying the laser intensity (0–10 mJ/pulse) and plotting the absorbance versus the laser dose.^{21,22b} We used values of $\epsilon_{e-(\text{aq})} = 1.33 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ at 600 nm²³ and $\epsilon(\text{Ph}_3\text{C}^*) = 3.6 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ at 334 nm.^{6a,b} 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.²⁴ The accuracy of this method is not better than ± 0.1 .

Pulse Radiolysis Experiments. A 3-MeV Van der Graaf electron accelerator was used as radiation source. Dosimetry was performed with N_2O -saturated 10 mM KSCN aqueous solution taking $G(\text{OH}) = 6.0$ and $\epsilon_{(\text{SCN})^{2-}} = 7600 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ at 480 nm.^{6c}

Results and Discussion

1. Product Studies. (a) **In Acetonitrile.** Product studies were performed in MeCN solution under argon in quartz cells (lamp irradiation, see Experimental Section). The photoconversion of **1a** (colorless) is very effective (about 90% in 6 min) and the solution turns bright red. At ca. 10% consumption of **1a** the major products were found to be Ph_3CH , 9-Ph-fluorene, and aniline in an approximately 1:1:2 ratio, using gas chromatographic and GC-MS analyses (comparison with authentic samples). These products inform at first instance of a homolytic C–N bond cleavage (see also LFP experiments later) leading to formation of the radicals Ph_3C^* (appearance of bright yellow color) and PhNH^* . Actually, the first two products (Ph_3CH and 9-Ph-fluorene) have been identified since the early studies of trityl radical chemistry^{25–27} (see, however, ref 28) in terms of the well-known photoproducts of the trityl radical (eq 1). Aniline could be generated from the anilino radical through hydrogen atom abstraction, see later.



Under oxygen atmosphere the product that was identified almost quantitatively was $\text{Ph}_2\text{C}=\text{O}$. Benzophenone

(21) Wintgens, V.; Jonson, L.; Scaiano, J. C. *J. Am. Chem. Soc.* **1988**, *110*, 511. Cozens, F. L.; Mathivanan, N.; McClelland, R. A.; Steenken, S. *J. Chem. Soc., Perkin Trans. 2*, **1992**, 2083.

(22) (a) McClelland, R. A.; Banait, N.; Steenken, S. *J. Am. Chem. Soc.* **1986**, *108*, 1757. (b) McClelland, R. A.; Banait, N.; Steenken, S. *J. Am. Chem. Soc.* **1989**, *111*, 2929.

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

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

(25) (a) Gomberg, M.; Cone *Ber. Dtsch. Chem. Ges.* **1904**, *37*, 3545; **1906**, *39*, 1469, 2967. (b) Gomberg, M. *Chem. Rev.* **1924**, *1*, 91.

(26) (a) Schlenk W.; Herzenstein A., *Ber. Dtsch. Chem. Ges.* **1911**, *44*, 3541. (b) Schmidlin J.; Garcia-Banus A., *Ber. Dtsch. Chem. Ges.* **1912**, *45*, 1344. (c) Bowden S. T.; Jones J. J. *J. Chem. Soc.* **1928**, 1149. (d) Berlin K. D.; Sturm G. P. *J. Chem. Soc.* **1964**, 2275. (e) Lewis, H. G.; Owen, E. D. *J. Chem. Soc.* **1967**, 422.

(27) (a) Letsinger R. L., Collat R., Magnusson M. *J. Am. Chem. Soc.* **1954**, *76*, 4185. (b) Wilson, R. M.; Schnapp, K. A.; Hannemann, K.; Ho, D. M.; Memarian, H. R.; Azadnia, A.; Pinchas, A. R.; Figley, T. M. *Spectrochim. Acta*, **1990**, *46A*, 551. (c) Engel, P. S.; Chen, Y.; Wang, C. *J. Org. Chem.* **1991**, *56*, 3073.

(28) Actually, they^{26,27a} photolyzed concentrated solutions of the α , p -dimer of the Ph_3C^* , where Ph_3C^* itself constitutes the minor component.^{28a,42e} (a) Lankamp, H.; Nauta, W. Th.; MacLean, C. *Tetrahedron Lett.* **1968**, 249.

is known as a decomposition product (thermal or photochemical)^{29c,d} of trityl peroxide or trityl hydroperoxide (oxidation products of Ph₃C[•]). Small amounts (<3%) of PhOH, PhCH=O, and PhNO₂ were also produced.

Analysis of the photochemical products formed by irradiation of **1a** with the 248- and 308-nm laser light (50–200 shots, under argon) in MeCN solution indicated the same products: PhNH₂, Ph₃CH, and 9-Ph-fluorene.

(b) In *n*-Hexane. The mixture of photoproducts obtained by lamp irradiation ($\lambda > 290$ nm) of **1a** in hexane has the same composition as in the case of the photolysis in MeCN, the only difference being the formation of the imine Ph₂C=NPh (traces).³⁰

At very low conversion (~3%), the oxygenated products Ph₂C=O, Ph₃COH, PhOH, and aniline are the major components identified (GC), in line with the assumption of a primary photolysis of the C–N bond and formation of the radical Ph₃C[•]. Obviously, under this low conversion the small concentration of the trityl radicals formed does not allow for an effective photoconversion to the final products according to eq 1, so only oxidation products, obtained on exposing the samples to the air, were obtained.

By pulsed irradiation (248 and 308 nm) no imine was detected, the other products being the same as in MeCN. By the 308-nm photolysis an increased amount of 9-Ph-fluorene (GC) was measured and its characteristic absorption spectrum with λ_{\max} at 266, 293, and 303 nm was observed, identical with that of an authentic sample. It is interesting to note here (308 nm, 0.1 mM) that no new photoproducts are formed even after ~90% consumption of the starting material **1a**. Under oxygen atmosphere Ph₂C=O is again the main product.

These results show the formation³⁰ of hydrogen gas to be insignificant (<2%) for low conversions of **1a** (<10%).

2. Identification of the Photochemically Produced Transients by Laser Flash Photolysis (LFP)

(a) Acetonitrile. On 248-nm laser photolyses in deoxygenated and oxygenated acetonitrile solution (OD₂₄₈ \cong 1.0/cm), *N*-tritylaniline **1a** undergoes at room temperature very efficient homolysis ($\Phi = 0.65$), leading to the formation of the well-known^{6,31–34} triphenylmethyl radical ($\lambda_{\max} = 337$ nm); see Figure 1a. In addition, very weak absorption bands were apparent at $\lambda_{\max} = 400, 440,$ and 486 nm. Irradiating the other aniline derivatives **1b–e** under the same conditions gave almost identical transient spectra. In Figure 1b is shown the absorption spectrum obtained by photolysis of the aniline derivative **1d** (R = *p*-Me), which is characterized by increased absorption maxima at 400, 440, and 486 nm. The

absorptions at 337 and 486 nm were affected by purging the solution with oxygen (Figure 1a) and they decayed in saturated solutions ([O₂] = 9.1 mM)³⁵ with rate constants $k = 6.8 \pm 0.2 \times 10^8$ and $1.3 \pm 0.4 \times 10^8$ M⁻¹ s⁻¹, respectively, typical values for scavenging of benzyl radicals by oxygen.²⁹ In contrast, the signals observed at 400–440 nm show no difference in the decay rate in argon and in oxygen atmosphere ($k \cong 2 \times 10^5$ s⁻¹).

In a water/MeCN mixture (4:1) of **1a**, only the decay of the absorption at 400–440 nm was accelerated (reaction with H₂O), while with the strong nucleophile azide N₃⁻ a rate constant of 3.2×10^9 M⁻¹ s⁻¹ was found. We assign the transient at 400–440 nm to the trityl cation Ph₃C⁺ on the basis of the similarity of its absorption spectrum to that reported in the literature^{6,22} (to compare see also Figure 1c) and its nonreactivity with oxygen. This assignment is further supported by the reactivity of this species with the strong nucleophile N₃⁻; a rate constant $k = 4.1 \times 10^9$ M⁻¹ s⁻¹ was measured previously^{6,22} for the reaction of Ph₃C⁺ with the same nucleophile.

The transient absorbing at 486 nm must be a radical species because of the 10-fold acceleration of its decay rate in the presence of oxygen, and on the basis of the identity of its absorption spectrum with the literature spectrum,^{6a,31b,f} it is assigned to the 4a,4b-dihydro-9-phenylfluorenyl radical (DHPF[•]), the proposed^{6a,31b,f} cyclization product of the photoexcited Ph₃C[•] radical (see Scheme 1). Similar conclusions were drawn also in a recent product study on the photolysis of (triphenylmethyl)diethylamine.^{14f}

The dependence of the intensities of the above absorptions was studied by varying the laser doses in the range ~0–10 mJ/pulse (248 nm) with the use of filters placed in the beam, using deoxygenated solutions. A linear dependence was found for the absorption at 337 nm, indicating that the formation of the radical Ph₃C[•] is a monophotonic process (Figure 1a, Scheme 1a), and a quadratic dependence was found for the signals at 400–440 and 486 nm, showing a biphotonic pathway leading to the trityl cation (Scheme 1e, or 1i,j) and DHPF[•] radical (Scheme 1b), respectively. The biphotonic processes are particularly clear in the cases of the photolysis of **1c** and **1d**, where relatively strong absorptions in the range of 400–500 nm were obtained (see, for example, Figure 1b). In the other cases, the signals are too weak (see, for example, Figure 1a) to make an unambiguous assignment, the other disturbing factor being here the overlap-

(29) The rate constants $k = 2.36 \times 10^8$ ^{29a} and 3.16×10^8 M⁻¹ s⁻¹^{29b} are given for the reaction of O₂ with PhCH₂[•] and Ph₂MeC[•] radicals, respectively. (a) Maillard, B.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1983**, *105*, 5095. (b) Howard, J. A.; Chenier, J. H. B.; Yamada, T. *Can. J. Chem.* **1982**, *60*, 2566. (c) A lower limit of 4.8×10^7 M⁻¹ s⁻¹ was found for the rate constant of the reaction of the Ph₃C[•] with O₂: Bodner, G. S.; Gladysz, J. A.; Nielsen, F. M.; Parker, V. D. *J. Am. Chem. Soc.* **1987**, *109*, 7023. (d) Neckers, D. C.; Linden, S.-M.; Williams, B. L.; Zakrzewski, A. *J. Org. Chem.* **1989**, *54*, 131. (e) Akaba, R.; Kamata, M.; Itoh, H.; Nakao, A.; Goto, S.; Saito, K.; Negishi, A.; Saguragi, H.; Tokumaru, K. *Tetrahedron Lett.* **1992**, 7011.

(30) The amount of the imine increases on prolonged irradiation (conversion of **1a** >30%, lamp irradiation) and evolution of hydrogen gas was then observed, which continues (increasing linearly with the irradiation time) even after all the starting material has been consumed. It was also found that irradiation of the imine alone under the same conditions also gives H₂. We are currently investigating this interesting phenomenon.

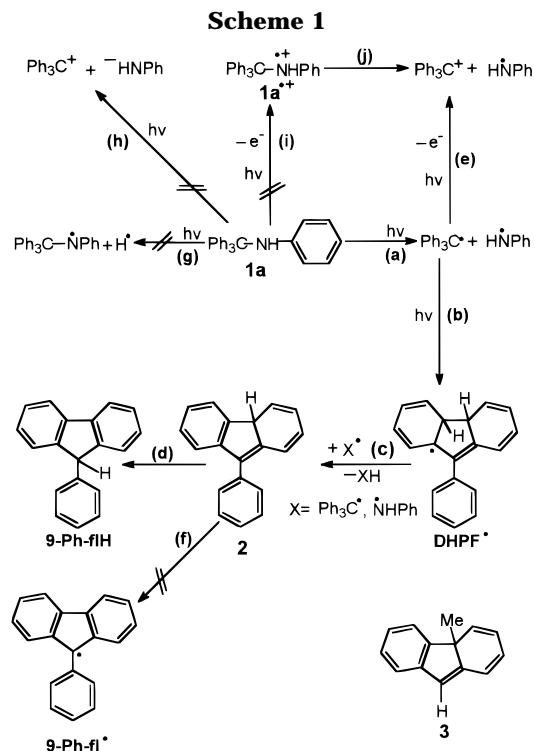
(31) (a) Bromberg, A.; Schmidt, K. H.; Meisel, D. *J. Am. Chem. Soc.* **1984**, *106*, 3056. (b) Bromberg, A.; Schmidt, K. H.; Meisel, D. *J. Am. Chem. Soc.* **1985**, *107*, 83. (c) Bromberg, A.; Meisel, D. *J. Phys. Chem.* **1985**, *89*, 2507. (d) Meisel, D.; Das, P. K.; Hug, G. L.; Bhattacharyya, K.; Fessenden, R. W. *J. Am. Chem. Soc.* **1986**, *108*, 4706. (f) Schmidt, J. A.; Hillinski, E. F. *J. Am. Chem. Soc.* **1988**, *110*, 4036.

(32) (a) Luckhurst, G. R.; Ockwell, J. N. *Tetrahedron Lett.* **1968**, 4123. (b) Fox, M. A.; Gaillard, E.; Chen, C.-C. *J. Am. Chem. Soc.* **1987**, *109*, 7088. (c) Ruberu, S. R.; Fox, M. A. *J. Phys. Chem.* **1993**, *97*, 143. (d) Fox, M. A.; Dulay, M. T.; Krosley, K. *J. Am. Chem. Soc.* **1994**, *116*, 10992; (e) Johnston, L. J.; Scaiano, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 2349.

(33) (a) Grellmann, K.-H.; Sherman, G. M.; Linschitz, H. *J. Am. Chem. Soc.* **1963**, *85*, 1881. (b) Linschitz, H.; Grellmann, K.-H. *J. Am. Chem. Soc.* **1964**, *86*, 303. (c) Lopez, D.; Boule, P.; Lemaire, J. *Nouv. J. Chem.* **1980**, *4*, 615. (d) Gawinecki, R.; Boszczyk, W.; Rasala, D.; Bak, T. *J. Photochem. Photobiol. A: Chem.* **1993**, *71*, 133.

(34) (a) Lewis, G. N.; Lipkin, D.; Magel, T. T. *J. Am. Chem. Soc.* **1944**, *66*, 1579. (b) Ting, L. C.; Weissmann, S. I. *J. Chem. Phys.* **1954**, *22*, 21.

(35) Murov, S. L.; Carmichael, I.; Hug, G. L. *Handbook of Photochemistry*, 2nd ed.; Marcel Dekker: New York, 1993.



ping absorptions due to anilino radical ($\lambda_{\text{max}} \approx 400$ nm, see discussion below) and DHPF^{•+} (absorption at 420–520 nm, $\lambda_{\text{max}} = 486$ nm). To remove some PhNH[•] and DHPF^{•+}, we measured in saturated oxygen solution (**1d**, MeCN) the dose dependence of the signal intensity of Ph₃C⁺ at 438 nm (delay times of 62 and 370 ns after the pulse) and found again a biphotonic process. In general we observe saturation to take place starting with doses of ca. 10 mJ/pulse.³⁶

A slightly different picture is obtained by irradiating **1a** with 308-nm laser light. While we observe again the absorptions at 337 and 486 nm previously assigned to Ph₃C[•] and the DHPF^{•+} radicals, respectively, the broad signal at 400–440 nm corresponding to Ph₃C⁺ is absent; instead a very weak absorption at 377 nm appears (see discussion later); in Figure 2 a representative spectrum obtained by the photolysis of **1a** is displayed. None of the decays of the three absorbances was affected by addition of the strong nucleophile N₃⁻, indicating absence of carbocations. The pathways leading to Ph₃C[•] and DHPF^{•+} are again mono- and biphotonic processes, respectively. In contrast to the 248-nm photolysis (see above), the increased signal intensity at 486 nm (owing to the stronger absorption of the trityl radical at 308 nm than at 248 nm) facilitates the biphotonic processes.

(b) In *n*-Hexane as Solvent. Laser excitation (248 nm) of **1a** in hexane leads to an absorption spectrum almost identical with that of Figure 2, indicating the formation of Ph₃C[•] ($\lambda_{\text{max}} = 337$ nm), DHPF^{•+} ($\lambda_{\text{max}} = 486$ nm), and the unknown intermediate with the very weak absorption at ca. 377 nm.

Irradiation with 308-nm light produces the spectrum displayed in Figure 3. It is similar to that obtained in MeCN (see Figure 2), showing, however, two new

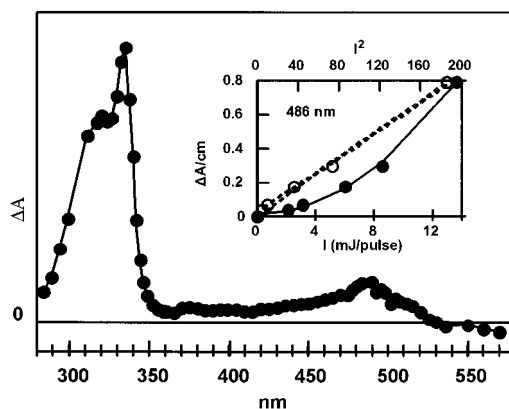


Figure 2. Absorption spectrum obtained on 308-nm LFP of 1.1 mM **1a** in MeCN under argon recorded at 280 ns after the pulse. Inset: yield of DHPF^{•+}, as a function of the laser power I (full circles) and I^2 (open circles); see the text.

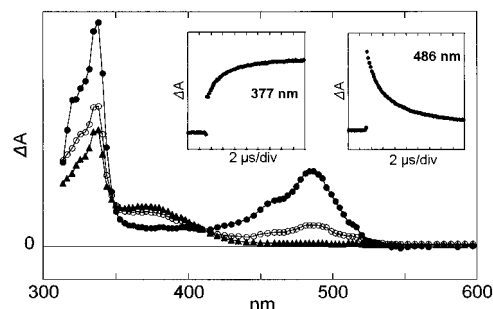


Figure 3. Absorption spectrum obtained on 308-nm LFP of 1.7 mM **1a** in hexane under argon ●, 50 ns; ○, 5 μs; and ▲, 80 μs after the pulse. Insets are as follows: decay of DHPF^{•+} radical at 486 nm, and buildup of transient **2** at 377 nm.

characteristics: first, the increased intensities at 377 and 486 nm and, second, the isosbestic points at 350 and 414 nm. The process leading to the absorptions at 337 and 486 nm was found (in both the 248- and 308-nm excitations) to be clearly mono- and biphotonic, respectively. The decay at 486 nm ($k_{\text{obs}} = 1.4 \pm 0.3 \times 10^6 \text{ s}^{-1}$) is accompanied by the increase at 377 nm ($k_{\text{obs}} = 1.7 \pm 0.3 \times 10^6 \text{ s}^{-1}$), both processes showing similar (dose-dependent) rate constants (laser dose ≈ 35 mJ/pulse, $\text{OD}_{308} = 1.03/\text{cm}$) indicating conversion of DHPF^{•+} radical to a species absorbing at 377 nm, see insets in Figure 3. The 377 nm absorption remains unaffected by saturation with O₂ (regarding only its growth kinetics, while the yield is clearly reduced as expected due to the reaction of DHPF^{•+} with O₂) and, as mentioned before (in MeCN), also with N₃⁻, which means that the unknown species is not of cationic or radical nature. This intermediate is not the final product 9-Ph-fluorene (see product analysis), which absorbs at shorter wavelengths, but must be a neutral, nonradical species arising by way of the DHPF^{•+} radical to the end product 9-Ph-fluorene.

Letsinger et al.^{27a} discussed the possible involvement of the cyclic polyene 9-Ph-4aH-fluorene **2** in the above transformation, produced by H-abstraction from DHPF^{•+} and subsequent aromatization (Scheme 1c), and Fox et al.^{32b,c} made similar assumptions for the case of the photocyclization of perchlorinated analogues (perchlorotriphenylmethyl radical), not providing, however, any definitive spectroscopic identification. The only compound structurally related to **2** that we found in the literature is the unstable hydrocarbon 4a-methyl-4aH-

(36) For an analysis of the intensity dependence on product formation in laser flash photolysis experiments see: (a) Lachish, U.; Schafferman, A.; Stein, G. *J. Chem. Phys.* **1976**, *64*, 4205. (b) Nikogosyan, D. N.; Angelov, D. A.; Oraevsky, A. A. *Photochem. Photobiol.* **1982**, *35*, 627.

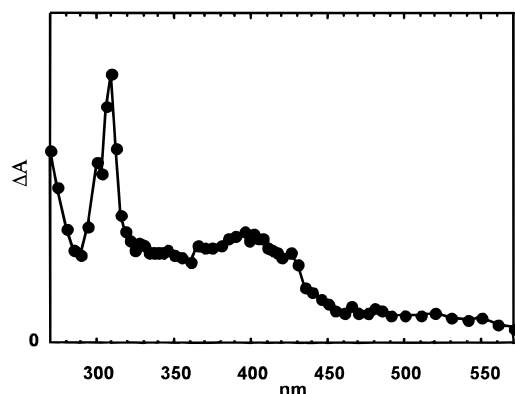


Figure 4. Absorption spectrum obtained on 248-nm LFP of 0.3 mM PhNH₂ in MeCN under argon recorded at 18 μs after the pulse.

fluorene **3**^{37a} (see Scheme 1) having $\lambda_{\text{ma}} = 371$ nm and $\epsilon_{371} = 4900 \text{ M}^{-1} \text{ cm}^{-1}$ in ethanol.

Meisel and his co-workers^{31b} calculated for DHPF• $\epsilon_{480} = (1.5 \pm 0.1) \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$. On the basis of this value and assuming a clean transformation of DHPF• to the species absorbing at 377 nm, not unreasonable in view of the observed isobestic points at 350 and 414 nm, we arrive at a value of $\epsilon_{377} = 5100 \pm 300 \text{ M}^{-1} \text{ cm}^{-1}$ for the unknown species, very close to that of **3**. We therefore suggest that the intermediate absorbing at 377 nm is compound **2**.^{37b} An allylic shift of a hydrogen atom of **2** accompanied by aromatization can explain the conversion to the final product 9-Ph-fluorene (Scheme 1d).

A species which is missing in the above presentation is the anilino radical PhNH•. It must be the second fragment generated by the photolytic C–N bond homolysis, as also the product analysis (formation of PhNH₂, eq 1) indicates. PhNH• is a well-known radical having absorption maxima at $\lambda_{\text{max}} = 308$ nm ($\epsilon = 3500 \text{ M}^{-1} \text{ cm}^{-1}$) and 401 nm ($\epsilon = 1250 \text{ M}^{-1} \text{ cm}^{-1}$)^{15a} in water, not different from those in hexane, cyclohexane,^{15b} heptane,^{15c} or benzene/di-*tert*-butyl peroxide.^{15d} In Figure 4 is shown the absorption spectrum of the anilino radical obtained by 248-nm laser photolysis¹² of PhNH₂ in MeCN. It possesses $\lambda_{\text{max}} = 309$ and 398 nm and shows an intensity ratio in agreement with the mentioned reports.^{12,15} Assuming an equimolar formation of the radicals PhNH• and Ph₃C• produced immediately after the laser pulse, we must expect a signal intensity ratio 1:12 at 309 nm and 1:32 at 398 nm with respect to the absorption at 337 nm, which corresponds to Ph₃C•. This implies that the absorptions of the anilino radical at 309 and 398 nm are very weak and overlap with those of the trityl radical at 337 nm and the trityl cation at 400–440 nm, respectively. However, looking at the transient absorption spectra in Figures 1a,b, 2, and 3 we see in every case a shoulder at 309 nm which becomes clearer under oxygen (Figure 1a). While Ph₃C• reacts rapidly with O₂ (see above), PhNH• as an aminyl radical is less reactive^{15e} and becomes observable at longer delay times.

3. 9-Ph-fl• Participation? A further point which should be addressed with respect to the photoconversion of the trityl radical is whether the 9-phenyl-9-fluorenyl radical (9-Ph-fl•) and its dimer are involved. Even since

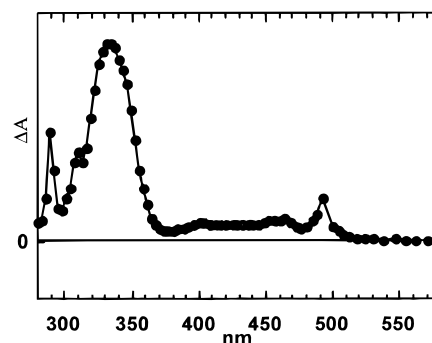
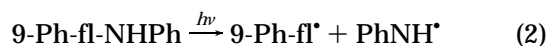


Figure 5. Absorption spectrum obtained on 248-nm LFP of 2.8 mM 9-Ph-fl-NHPh in MeCN under argon 170 ns after the pulse.

the early days of the history of Ph₃C• its decoloration^{25a} in direct sunlight is reported, followed by its decomposition²⁶ to Ph₃CH and 9,9'-diphenyl-9,9'-difluorenyl (the dimer of 9-Ph-fl•).³² The fact^{32b,c} that also perchlorotriptyl radical leads photochemically to perchlorinated 9-Ph-fl•, makes a closer investigation necessary.

We generated for this reason 9-Ph-fl• by irradiating 9-Ph-fl-NHPh in MeCN with 248-nm light, see Figure 5, which we interpret in terms of reaction 2 occurring.



As expected, 9-Ph-fl• is unaffected by N₃⁻ but, to our surprise, also by O₂.³⁸ Furthermore, we obtained the same spectrum in the nonpolar solvent hexane, thus eliminating the possibility of having produced the corresponding cation 9-Ph-fl⁺, whose spectrum³⁹ resembles that of 9-Ph-fl•, at least in the characteristic region of 450–500 nm. Moreover, the spectrum in Figure 5 is very similar to the literature spectrum of the 9-mesitylfluorenyl radical⁴⁰ and to a spectrum assigned earlier by Lewis^{34a} to 9-Ph-fl•. Comparing the spectrum of 9-Ph-fl• (Figure 5) with that obtained by the photolysis of **1a** (Figures 1a and 2), formation of 9-Ph-fl• by the photolysis of **1a** can be excluded. The 9-Ph-fl• absorptions in the region 450–500 nm are ca. 10 nm red-shifted with respect to those of DHPF• and possess additional absorptions below 300 nm (at 272 and 287 nm, a small additional peak at 310 nm should belong to the PhNH• radical produced by the C–N bond homolysis, eq 2). Moreover, the decay of DHPF• increases by ca. 1 order of magnitude in the presence of O₂ ([O₂] = 9.1 mM),³⁵ while that of 9-Ph-fl• remains unchanged. Additional support for these observations arises from the fact that upon irradiation of Ph₃C• in the cavity of an ESR spectrometer (see ESR studies below) its spectrum disappears, but is not replaced by that of 9-Ph-fl•.

4. Quantum Yields. In Table 2 are presented the quantum yields for the formation of Ph₃C• radical upon 248-nm irradiation of **1a–e** in MeCN and other solvents. These values were determined²¹ by measuring the initial absorbance at $\lambda_{\text{max}} = 334$ nm (see Experimental Section).

(38) 9-Ph-fl• reacts slowly⁴⁰ with O₂ and obviously in a time scale longer than 100 μs used in our measurements.

(39) (a) Allen, D. M.; Owen, E. D. *J. Chem. Soc. Chem. Commun.* **1971**, 848. (b) McClelland, R. A.; Mathivanan, N.; Steenken, S. *J. Am. Chem. Soc.* **1990**, *112*, 4857. (c) Cozens, F.; Robert, J. L.; McClelland, R. A.; Steenken, S. *Angew. Chem. Internat. Ed.* **1992**, *104*, 753; Van Tamelen, E. E.; Cole, T. M., Jr. *J. Am. Chem. Soc.* **1971**, *93*, 6158.

(40) Chandross, E. A.; Sheley Jr, C. F. *J. Am. Chem. Soc.* **1968**, *90*, 4345.

(37) (a) Neuhaus, D.; Rees, W. C. *J. Chem. Soc. Chem. Commun.* **1983**, 318. (b) An additional phenyl group at the 9-fluorenyl position has no any appreciable effect on the UV absorption spectrum, because it is substantially twisted out of the fluorene ring plane.⁴⁰

Table 2. Quantum Yields for the Formation of the Radical Ph₃C• (under Argon)

1	solvent	$\Phi(\text{Ph}_3\text{C}^\bullet)$	1	solvent	$\Phi(\text{Ph}_3\text{C}^\bullet)$
a	MeCN	0.65	c	MeCN	0.80
a	hexane	0.71	d	MeCN	0.64 (0.61) ^a
a	EtOH	0.61	e	MeCN	0.57
b	MeCN	0.67			

^a Under oxygen.

The high quantum yields ($\Phi \approx 0.6$ – 0.8) indicate an efficient homolytic photodissociation of the C–N bond of the aniline compounds **1**. The quantum yield for the formation of Ph₃C• (photolysis of **1d**) was measured also in MeCN solution saturated with O₂, and only a slightly smaller value of 0.61 was found, not different, however, than that under argon (0.64) within the experimental error. This indicates that the dissociation proceeds faster than the quenching of the photoexcited state of **1d** with O₂.⁴¹ It is noteworthy that the N–H photodissociation in PhNH₂ proceeds to 80% via the triplet state.¹¹

5. ESR Studies. To provide additional evidence for the very effective C–N bond rupture and formation of the radical Ph₃C• upon irradiation of the *N*-tritylaniline derivatives **1**, ESR spectroscopy was applied. Upon irradiating a solution of **1** in hexane in the cavity of the ESR spectrometer with a low-pressure mercury lamp (see Experimental Section, main emission at 254 nm), we observe a spectrum [$g = 2.0026$, $a^{\text{H}}_{\text{ortho}}(6\text{H}) = 2.54$ G, $a^{\text{H}}_{\text{meta}}(6\text{H}) = 1.13$ G, $a^{\text{H}}_{\text{para}}(3\text{H}) = 2.77$ G] identical with the well-known^{42b–e} spectrum of the Ph₃C• radical. It is interesting that no signal was detected if we irradiated with a high-pressure mercury lamp, which has strong emissions at the wavelength of the maximum absorbance of the trityl radical (337 nm). Obviously, a fast destruction of the radical takes place due to the above-described photocyclization to 9-Ph-fluorene such that the steady-state concentration is insufficient for an observable ESR signal. A further confirmation of this conclusion was the fact that upon producing Ph₃C• in the cavity with 254-nm light and subsequently changing the light source to the high-pressure mercury lamp, the signal disappeared rapidly. Here it is worth to note that we do not observe any change of the signal to that of 9-Ph-fl•, in line with the conclusions (no formation of 9-Ph-fl•) reached above by the LFP studies.

These results represent a clear demonstration of how easily erroneous conclusions can be drawn about the involvement of free radicals in photochemical processes when the photochemical behavior of the radicals themselves is unknown and when taking into account that photolysis is one of the most common methods for generating free radicals.

Here we note that **1** dissociates thermally (decalin/205 °C) to Ph₃C• (ESR).^{17,18}

6. Mechanistic Considerations. In summary, we have shown that the aniline derivatives **1a–e** undergo very efficient (see Table 2) homolysis on irradiation with 248- or 308-nm laser light, leading to Ph₃C• and PhNH• in a monophotonic pathway in both polar (MeCN) and

nonpolar (hexane) solvents. In a second step trityl radical is excited and forms the DHPF• radical (in a biphotonic process relative to the parent **1a**, which is more effective with 308- than with 248-nm light), in agreement with the suggestion by Meisel and co-workers.^{31a,b} Moreover, we identified Ph₃C• only in the polar medium MeCN and only by photolysis with 248-nm laser light (biphotonic process relative to the **1a**).

To explain the results we propose the mechanistic scheme outlined in Scheme 1. The easy photochemical C–N bond homolysis in compounds **1a–e** is not surprising if we consider the high excitation energy localized on the anilino chromophore^{8a,10} either in its singlet (>90 kcal/mol)¹⁰ or triplet (>70 kcal/mol)¹⁰ state and the low bond dissociation enthalpy (BDH) of the corresponding bond C–N, which is estimated to be ~39 kcal/mol.⁹ The weakness of this bond dictates in fact the high efficiency of the C–N bond homolysis and competes effectively with the common photochemical property of aromatic amines,¹¹ which is the dissociation of the N–H bond. The BDH of the N–H bond in *N*-methylaniline, Ph(Me)N–H, which should be not very different from that in **1**, is 83.3 kcal,^{9a} more than twice that of the corresponding C–N bond. Thus, the bond scission of the N–H bond in **1a–e** (Scheme 1 g) should be very unfavorable and was not observed in the LFP experiments,⁴³ a fact corroborated by the ESR studies⁴³ and the product analysis (absence of hydrogen gas evolution in hexane).

The high quantum yields for trityl radical formation ranging from 0.57 to 0.8 (Table 2) do not reflect any significant differentiation in the photodissociation abilities of the various derivatives **1a–e**, if one considers the accuracy (10%) of the measurements. Although aniline-ring substitution does not seem to affect the C–N bond strength,⁴⁴ a small steric effect may be present due to bulkiness of the trityl group in **1**. However, the “propeller”-shaped trityl group forces the C–N bond to approach a perpendicular plane with respect to the aniline’s plane (as space-filling models show), and this is more obvious in the case of the *o*-Me and *m*-Me substituents. The latter has as a consequence a better hyperconjugative interaction of the bond being broken (C–N) with the excited π -system and therefore (see introduction)³ a more effective dissociation. The last point is related once again to Michl’s ideas³ and the role of the small electronegativity difference (δ_{CN}) in promoting homolysis (in **1a–e**, Figure 1a,b), as contrasted by Ph₃C–Cl (Figure 1c), where heterolysis of the C–Cl bond is the dominant process (increased δ_{CCl}).

We believe the data do not allow one to consider the effect described by Malkin,^{12a} where *o*-Me, *m*-Me, and *p*-Me aniline derivatives have a more effective isc ($S_2 \rightarrow T_2$) and a higher quantum yield on photodissociation of their N–H bond with respect to unsubstituted aniline, as related to our results; the deviations in the measured quantum yields (Table 2) are too insignificant to account for such an effect.

(43) In the case of a N–H photohomolysis we would expect the formation of a nitrogen-centered radical (Ph₃C–N•–Ph) (Scheme 1g). Such radicals should give ESR spectra with different g -values and hyperfine splittings than Ph₃C•: Siskos, M. G.; Zarkadis, A. K. unpublished results. Moreover, the absorption spectrum of the radical Me–N•–Ph displays λ_{max} at 314 and 400 nm,^{15b,e} different than we observe on the photolysis of **1a–e**.

(44) Ring substitution in aniline does not affect its N–H bond strength: (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. Perkin Trans. 2* **1995**, 67.

(41) Similar cases are known in the literature, see for example: Mizuno, K.; Ichinose, N.; Otsuji, Y. *J. Am. Chem. Soc.* **1985**, *107*, 5797.

(42) (a) Gomberg, M. *Ber. Dtsch. Chem. Ges.* **1900**, *33*, 3150. (b) Maki, A. H.; Allendoerfer, R. D.; Danner, J. C.; Keys, R. T. *J. Am. Chem. Soc.* **1968**, *90*, 4225. (c) Sinclair, J.; Kivelson, D.; *J. Am. Chem. Soc.* **1968**, *90*, 5075. (d) Kulkarni, S. V.; Trapp, C. *J. Am. Chem. Soc.* **1970**, *92*, 4801. (e) Neumann, W. P.; Uzick, W.; Zarkadis, A. K. *J. Am. Chem. Soc.* **1986**, *108*, 3762.

The formation of DHPF[•] (Scheme 1b) is rationalized³¹ in terms of an electrocyclic ring closure of the excited Ph₃C[•], resulting from an increased twist angle of the phenyl rings out of the central molecular plane, in contrast to Ph₂CH[•], where no intramolecular photochemistry was observed.^{6b,d,31,45} The biphotonic process leading to the DHPF[•] that we observed in the LFP experiments is consistent with this proposal. DHPF[•] decays rapidly to the cyclic polyene hydrocarbon **2**, probably through a hydrogen atom abstraction by the PhNH[•] or Ph₃C[•] radical (Scheme 1c). This is probably a very facile process since the C_{aliph}-H bond strength of the cyclohexadienyl radical, a simplified analogue to DHPF[•], is only ca. 25 kcal/mol,⁴⁶ considerably weaker than the BDH of the aniline N-H bond (89.1 kcal/mol)^{44,47} or of the triphenylmethane C-H bond (75 kcal/mol).^{8c,47} This hydrogen atom abstraction is probably the reason for the relatively shorter decay time (<10 μs) obtained in our LFP experiments for DHPF[•] versus those of Meisel (>100 μs).^{31b} Fox and co-workers^{32b} found for the perchlorinated-DHPF[•] ~22 μs, which is, however, more stable than DHPF[•]. The identification of the intermediate **2** (see above) is the first strong evidence for the electrocyclization mechanism of the excited Ph₃C[•]. Concomitant rearrangement of **2** (Scheme 1d) to the final product 9-Ph-flH through an allylic shift and aromatization is a well-known reaction of such cyclohexadienyl systems, catalyzed by acids, bases, or via free radicals.^{27a,c,48} Another conceivable possibility of transforming **2** to 9-Ph-fl[•] (Scheme 1f) could be excluded (see above), and this radical could not be identified either by LFP or by ESR.

Now, it remains to address the occurrence of the trityl cation Ph₃C⁺. There exist at least three possible paths for its formation; the first one is the formation of Ph₃C⁺ through a direct photoheterolysis of the C-N bond (Scheme 1h). In the literature^{2a,5,6b,7,8} there is a long-lasting discussion on the very early processes and the nature of the formed intermediates after excitation of a substrate and particularly about the competition between homolysis and heterolysis. In the case of compounds **1**, although the heterolytic C-N bond dissociation enthalpy is estimated to be lower (~13 kcal/mol)⁴⁹ than the homolytic one (~39 kcal/mol),⁹ we found a biphotonic process leading to the formation Ph₃C⁺; a direct heteroly-

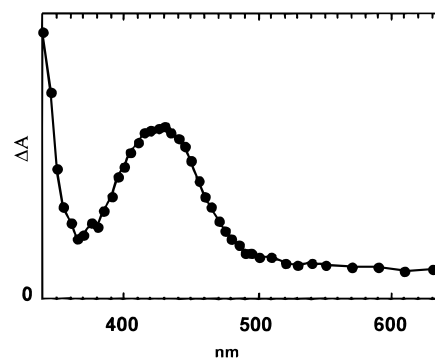


Figure 6. Absorption spectrum obtained on pulse radiolysis of 2.8 mM **1a** in *n*-BuCl under argon 600 ns after the pulse.

sis leading to Ph₃C⁺ and PhNH⁻ would be a monophotonic process.

Second, the photoionization of Ph₃C[•] to Ph₃C⁺ in water with 248- or 308-nm laser light is a well-documented process,^{6a} consuming another photon and making the overall process biphotonic, as we also observed in MeCN (Scheme 1e). The fact that we do not see carbocation formation upon irradiating with 308-nm (4.03 eV) in MeCN can be attributed to the lower solvation power of Ph₃C⁺ in MeCN than in H₂O.⁵⁰ In contrast, the 5 eV energy provided by the 248-nm photons compensates for the missing energy and photoionization takes place. From this point of view, it is reasonable that Ph₃C⁺ was not observed in hexane, neither with 248- nor with 308-nm light. Meisel and co-workers^{31b} also failed to see carbocation formation upon irradiating with 347-nm laser light (3.57 eV) in MeCN and cyclohexane.

A third way to produce Ph₃C⁺ is, however, the photoionization of the parent molecule **1a** to the anilinium radical cation **1a**^{•+} (Scheme 1i) with subsequent fragmentation to give Ph₃C⁺ and PhNH[•] (Scheme 1j). Actually, photoionization of aromatic amines with concomitant fragmentation is a very common property¹¹ owing to their low ionization⁵¹ or oxidation potentials.⁴⁴ While direct photoionization is favored in polar media (usually in water)⁵² and is less studied, the sensitized photoinduced electron transfer in amines is currently a very active area of research.⁵³ To clarify the possibility of the participation of **1a**^{•+}, a pulse radiolysis study of **1a** was undertaken and we obtained the absorption spectrum shown in Figure 6, which coincides with the spectrum of Ph₃C⁺. Also it is identical with the spectrum obtained by irradiation of **1a** in MeCN/CCl₄ (248-nm laser),⁵⁴ while irradiation with 254-nm light (lamp) failed to give an ESR signal (hexane/CCl₄). Apparently, here (pulse ra-

(45) Arnold, B. R.; Scaiano, J. C.; McGimpsey, W. G. *J. Am. Chem. Soc.* **1992**, *114*, 9978. Scaiano, J. C.; Tanner, M.; Weir, D. *J. Am. Chem. Soc.* **1985**, *107*, 4396.

(46) This derives from the enthalpy liberated (-25 kcal/mol) by the formation of the cyclohexadienyl radical via hydrogen atom addition to benzene.^{9b,49d} See also: Schaffer, F.; Beckhaus, H.-D.; Rieger, H.-J.; Rüdhardt, C. *Chem. Ber.* **1994**, *127*, 557. Gerst, M.; Morgenthaler, J.; Rüdhardt, C. *Chem. Ber.* **1994**, *127*, 691.

(47) Increased values for the BDH of aniline N-H (92.0 kcal/mol) and for C-H (81 kcal/mol) of Ph₃CH were reported: Bordwell, F. G.; Cheng, J.-P.; Ji, G.-Z.; Satish, A. V.; Zhang, X. *J. Am. Chem. Soc.* **1991**, *113*, 9790.

(48) Tzerpos, N. I.; Zarkadis, A. K.; Kreher, R. P.; Repas, L.; Lehnig, M. *J. Chem. Soc. Perkin Trans. 2* **1995**, 755.

(49) On the basis of the calculated C-N homolytic BDH (39 kcal/mol)⁹ for Ph₃C-NHPh, the redox potentials $E_{ox}(PhNH^{\bullet}) = -0.992$ V in DMSO (vs ferrocene/ferrocinium ion)^{47,49a} and $E_{1/2}(Ph_3C^+) = -0.133$ V in sulfolane (vs ferrocene/ferrocene couple),^{49b,c} and using Wayner and Parker's method,^{49d} we calculate ~13 kcal/mol for the heterolytic bond dissociation enthalpy of Ph₃C-NHPh. One should note here that this value is not in the solvent used (MeCN); see ref 51b for a comment about the uncertainties in using redox potentials obtained in DMSO, H₂O, MeCN, sulfolane. (a) Bordwell, F. G. *Acc. Chem. Res.* **1993**, *26*, 510. (b) Arnett, E. M.; Venimadhavan, S.; Amarnath, K. *J. Am. Chem. Soc.* **1992**, *114*, 5598. (c) Arnett, E. M.; Flowers III, R. A. *Chem. Soc. Rev.* **1993**, *9*. (d) Wayner, D. D. M.; Parker, V. D. *Acc. Chem. Res.* **1993**, *26*, 287. (e) Saveant, J.-M. *Acc. Chem. Res.* **1993**, *26*, 455.

(50) (a) For a critical discussion of the role of the solvation energy in heterolytic dissociations and photoionizations, see ref 6a,b and references therein. (b) Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*; Verlag Chemie, Weinheim, 1990; p 31.

(51) 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 Publ.: London, 1966; p 170.

(52) Köhler, G.; Getoff, N. *J. Chem. Soc., Faraday Trans. 1* **1980**, *76*, 1576.

(53) (a) Gaillard, E. R.; Whitten, D. G. *Acc. Chem. Res.* **1996**, *29*, 292, and references therein. (b) Zhang, X.; Yeh, S.-R.; Hong, S.; Freccero, M.; Albini, A.; Falvey, D. E.; Mariano, P. S. *J. Am. Chem. Soc.* **1994**, *116*, 4211.

(54) Photolysis of aromatic amines in CCl₄ leads to primary formation of radical cations on nitrogen,^{54a,b} whereas CCl₄^{•+} decomposes in $\tau < 18$ ps.^{54c} (a) Budyka, M. F.; Alfimov, M. V. *Russ. Chem. Rev.* **1995**, *64*, 705, and literature cited therein. (b) Shimamori, H.; Musasa, H. *J. Phys. Chem.* **1995**, *99*, 14359. (c) Chateaufneuf, J.; Luszyk, J.; Ingold, K. U. *J. Org. Chem.* **1990**, *55*, 1061.

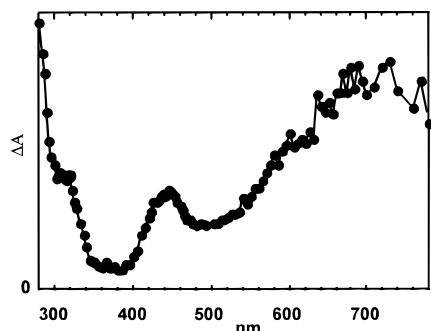


Figure 7. Absorption spectrum obtained on 248-nm LFP of 0.1 mM PhCH₂NHPH in H₂O/2-PrOH (4:1) under argon 300 ns after the pulse.

diolysis) the radical cation **1a**^{•+} fragmentates quickly to give Ph₃C⁺ and PhNH[•] (Scheme 1j) and can therefore not be observed in the time scale of our pulse radiolysis experiments (≥500 ns). The C–N bond in **1a**^{•+} is very weak (ca. –3 kcal/mol)⁵⁵ and apparently a very fast dissociation makes its detection (if it is formed) impossible. Nevertheless, these two experiments show that if photoionization of **1** takes place, then formation of the trityl carbocation occurs.

Direct photoionization of aromatic amines is facilitated in water.^{11,52} Therefore we irradiated (248 nm) **1a** in a mixture *i*-PrOH/H₂O (3:4) and we recorded the same spectrum as in MeCN (see Figure 1a,b) with an additional weak broad peak at 500–800 nm which can be efficiently removed by O₂ and N₂O and is therefore assigned^{6a,d} to e⁻_{aq}. The formation of e⁻_{aq} obeys a biphotonic pathway, as in all the cases outlined above where Ph₃C⁺ was produced, so we still cannot decide whether the electron is photoejected from Ph₃C[•] (Scheme 1e) or from **1a** (Scheme 1i,j). The radical cation **1a**^{•+} is also here undetectable, despite the much shorter time scale of the LFP experiment (≥20 ns).

To examine if compounds of the type **1** are able to undergo photoionization in our LFP experiments, we chose to study *N*-benzylaniline, PhCH₂–NHPH, which is structurally analogous to **1** but possesses a stronger C–N bond (~56 kcal/mol),^{9e} making the corresponding radical cation (PhCH₂NHPH)^{•+} more persistent than **1a**^{•+}. Indeed, irradiating PhCH₂–NHPH under the same conditions (248-nm/ *i*-PrOH/H₂O), we observed the spectrum shown in Figure 7. The broad absorption at 440 nm is assigned to the corresponding radical cation (PhCH₂–NHPH)^{•+} on the basis of its nonreactivity with oxygen and its absorption spectrum⁵⁶ (obtained via sensitized photoinduced electron transfer). The strong absorption at 500–800 nm is due to e⁻_{aq}, which is produced in a biphotonic process. However, when we irradiated PhCH₂–NHPH in MeCN with 308-nm laser light, we observed the same spectrum with λ_{max} at 440 nm corresponding to (PhCH₂NHPH)^{•+}, and once again we measured for its formation a biphotonic process. The absorption spectrum of the solvated electron e⁻_{aq} cannot be observed in

MeCN.^{6d,57} Summarizing, *N*-benzylaniline can be ionized even in MeCN with 308-nm photons, and this should hold also for *N*-tritylanilines **1** which must have ionization potentials not higher than *N*-benzylaniline. This makes possible, at least it does not exclude, the formation of the trityl cation through dissociation of **1a**^{•+}.

Now, the fact that we do not see any Ph₃C⁺ by the photolysis of **1a** under the same conditions (308-nm/ MeCN, see above) indicates probably that, although **1a** is able to ionize in MeCN (308-nm) to **1a**^{•+}, this is not the way leading to Ph₃C⁺, but the fast dissociation of the excited state of **1a** produces preferable Ph₃C[•] and PhNH[•] (Scheme 1a) and in a second step trityl radical undergoes photoionization to Ph₃C⁺ (Scheme 1e). This is presumably a consequence of the consecutive biphotonic nature of the photoionization of these aniline derivatives; the excited state of **1a** is, because of the fast homolysis (Scheme 1a), too short living to be ionized by a second photon, and this in contrast to benzylaniline, where its triplet state absorption is longer living and observable in the LFP experiment.⁵⁸

Electron transfer from Ph₃C[•] to PhNH[•] leading to Ph₃C⁺ and PhNH⁻, although thermochemically feasible,⁵⁹ would be a monophotonic process for the formation of Ph₃C⁺ and is thus also eliminated as a possible way.

7. Summary. The present work describes an effective and selective homolytic photodissociation of the C–N bond in *N*-tritylanilines **1**, leading exclusively to the formation of Ph₃C[•] (high quantum yields). This is in contrast to Ph₃C–Cl, where homolysis and heterolysis occur in a ratio 1:1.4, respectively, in line with Michl's theoretical analysis. In addition, a detailed mechanistic scheme is proposed for the photoionization of Ph₃C[•] to Ph₃C⁺ and its photoconversion to 9-Ph-fluorene (MeCN). A new intermediate (9-Ph-4*a*H-fluorene **2**) going from Ph₃C[•] to the final product 9-Ph-fluorene is identified for the first time (hexane) and supports the mechanism proposed earlier.^{30,34} Furthermore, because the trityl group belongs to the classical amino-protecting groups in the synthesis of polyfunctional molecules and particularly in peptide synthesis,⁶⁰ its potential function as photodeprotective^{61,62} group is, after the above results, of great interest.

Acknowledgment. We thank Bundesministerium für Forschung und Technologie (Germany) and General Secretariat for Research and Technology (Greece) for a grant (Grant No. 6BOA1A) and Dr. K. Hildenbrand and Dr. C. Borsarelli (MPI für Strahlenchemie, Mülheim) for reading the draft.

JO9719261

(57) 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.

(58) Siskos, M. G.; Zarkadis, A. K.; Steenken, S. Unpublished results.

(59) On the basis of the redox potentials of the trityl carbocation and anilino anion,⁴⁹ we find an exergonic conversion (ca. –26 kcal/mol).

(60) Zervas, L.; Theodoropoulos, D. M. *J. Am. Chem. Soc.* **1956**, *78*, 1359; Barlos, K.; Gatos, D.; Kallitsis, J.; Papaphotiou, G.; Sotiriou, P.; Wenqing, Y.; Schäfer, W. *Tetrahedron Lett.* **1989**, *30*, 3947.

(61) Schelhaas, M.; Waldmann, H. *Angew. Chem.* **1996**, *108*, 2192.
(62) Pillai, V. N. R. *Org. Photochem.* **1987**, *9*, 225.

(55) The radical cation **1a**^{•+} would be also very instable, at least judging from the ca. –3 kcal/mol BDH of its C–N bond.^{55a} (a) Taking approximately the oxidation potential of the *N*-methylaniline (~0.7 V vs SCE),^{55b} which is between that of aniline and dimethylaniline,^{44a} to be the "same" as that of **1a**, the calculated BDH of the C–N bond in **1a**,⁹ and the appropriate thermochemical cycle,^{49d,e} we arrive at a BDH of ca. –3 kcal/mol for **1a**^{•+}. (b) Galus, Z.; Adams, R. N. *J. Phys. Chem.* **1963**, *67*, 862.

(56) Lucian, A. L.; Burton, R. D.; Schanze, K. S. *J. Phys. Chem.* **1993**, *97*, 9078.