

# C-N vs. C-C Bond Photodissociation in *N*-(*tert*-butyldiphenylmethyl)aniline

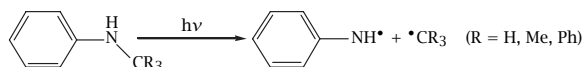
Stylianos Garas, Michael G. Siskos, and Antonios K. Zarkadis<sup>†</sup>

*Department of Chemistry, University of Ioannina, 451 10 Ioannina, Greece*

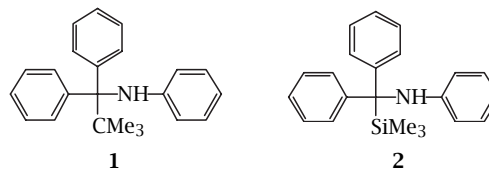
**ABSTRACT.** The direct photolysis of the title aniline compound  $\text{Ph}_2(\text{Me}_3\text{C})\text{C-NHPh}$  in acetonitrile with 248 nm laser light results in the dissociation of the C-N bond giving the corresponding (*tert*-Bu)diphenylmethyl radical **1a**<sup>•</sup> and the anilino radical  $\text{PhNH}^{\bullet}$  detectable by *ns*-laser flash photolysis (LFP) and ESR spectroscopy. The same radical **1a**<sup>•</sup> is also produced from the corresponding (*tert*-Bu)diphenylmethyl chloride  $\text{Ph}_2(\text{Me}_3\text{C})\text{C-Cl}$  either photolytically in MeCN through C-Cl bond homolysis or pulse radiolytically in THF; the (*tert*-Bu)diphenylmethyl cation is also detected, however, at shorter time scales because of its high reactivity in the solvent MeCN. At higher laser pulse intensities the radical **1a**<sup>•</sup> is reexcited by a second photon leading through electrocyclization to the 4a,4b-dihydro-9-*tert*-butylfluorenyl radical (DHBF<sup>•</sup>) and finally to fluorenyl products. Product analyses of steady state photolyses using GC and GC-MS gave as principal products (*tert*-Bu)diphenylmethane, aniline and various 9-substituted fluorenyl derivatives, corroborating further the primary C-N bond cleavage and the formation of the radicals **1a**<sup>•</sup> and  $\text{PhNH}^{\bullet}$ . Other conceivable dissociation pathways leading to the C-CMe<sub>3</sub> or N-H bond rupture were not observed.

## 1. INTRODUCTION

The photodissociation of the benzylic bond C-X (X = Hal, <sup>+</sup>OH<sub>2</sub>, OCOR, OR, <sup>+</sup>SR<sub>2</sub>, <sup>-</sup>PO<sub>3</sub>H, <sup>+</sup>NR<sub>3</sub>, CR<sub>3</sub> etc.) of molecules in solution continues to be the focus of extensive product and time-resolved spectroscopic [1] as well as of theoretical studies [2]. The reason lies not only in the fundamental problem of the competition between homolytic and heterolytic C-X splitting [1b, 3], but also in the many-sided consequences in applied photochemistry (photochromic materials, photodeprotection techniques, photoaffinity labels, photoacid and photobase generation, photodegradation of biomolecules and pollutants etc.). In general, fundamental questions regarding the responsible excited states, the nature of the primary fragments (radicals, ions) and their interconversion *via* electron transfer (ET), the role of substituent effects etc. are far from being settled [1-3].



In our recent work on *N*-substituted anilines we showed both experimentally [4a-4c] and theoretically [2c], how the systematic introduction of radical stabilizing substituents R affects the photodissociation efficiency of the central C-N bond, namely that the photodissociation quantum yield increases in a predictable way as the substituent stabilizing power increases [5].



In the present paper we describe our photochemical studies on *N*-(*tert*-butyldiphenylmethyl)benzenamine **1**, and show that photodissociation of only the C-N (and not of the C-CMe<sub>3</sub>) bond takes place, as contrasted to both the C-N and the C-Si bond cleavage of the Si-analogue **2** [4a]. The work is a combination of Laser Flash Photolysis (LFP), Pulse Radiolysis, ESR Spectroscopy, Fluorescence and product analysis studies.

## 2. EXPERIMENTAL SECTION

*N*-(*tert*-butyldiphenylmethyl)benzenamine **1** was synthesized as previously described [4a]. Acetonitrile, hexane, cyclohexane (Merck), and *n*-BuCl (Fluka) were of spectroscopic grade.

**Fluorescence measurements.** Absorption spectra were obtained with a Perkin-Elmer Lambda-16 spectrophotometer and fluorescence spectra measurements using a Perkin-Elmer Model LS-50B fluorescence spectrometer at 25 ° (corrected spectra). Fluorescence quantum yields were determined by comparison with the reported fluorescence quantum yield of aniline in cyclohexane at 20 °C  $\Phi_f = 0,17$  ( $\lambda_{\text{exc}} = 290\text{-nm}$ ) [6a], and  $\Phi_f = 0,11$  ( $\lambda_{\text{exc}} = 254\text{-nm}$ ) [6b]. Fluorescence lifetime measurements were carried out using the single-photon counter FL900 (Edinburgh Instruments.)

<sup>†</sup>E-mail: azarkad@cc.uoi.gr

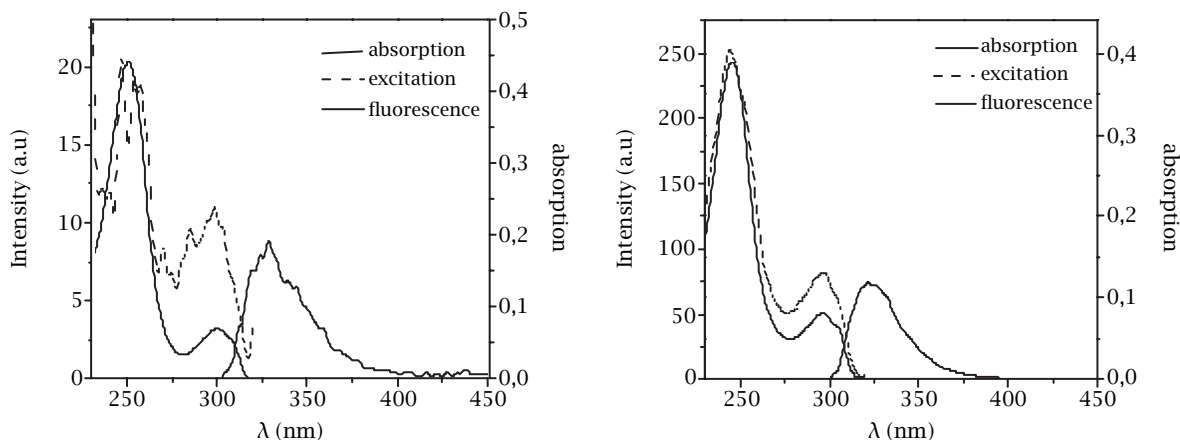


Figure 1. Absorption, fluorescence (solid lines) and fluorescence excitation (broken line) spectra of **1**; in cyclohexane (right), and in MeCN (left) at 298 K.

#### Photochemical experiments (product analyses).

A solution of the aniline derivative **1** ( $A/cm \sim 2.0$  at 254-nm, concentration 0.57 mM) in benzene and MeCN purged with argon was irradiated directly with a Philips HPK-125 W medium pressure mercury vapor lamp in special quartz cuvettes at 25 °C. The progress of the reaction was monitored by GC, and the reaction was stopped when **1** was consumed (> 90%). The photoproducts were analysed by GC and GC/MS and were characterized by comparison using authentic samples. Gas chromatographic analyses and separations were conducted on a Siechromat or Varian 3700, FID gas chromatograph with a SE-54 (25 m) capillary column (Injector: 200 °C, Detector: 300 °C, column temperature: 70–280 °C, 8 °C/min or 10 °C/min). GC-MS analyses were performed on a SSQ 700, EI instrument, using the same conditions and columns.

**Laser flash photolysis experiments.** Solutions of the corresponding substrates ( $A/cm \sim 1.0$  at 248) were deoxygenated by bubbling with argon and photolysed at 25 °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 [4a, 4b, 4d].

**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  $G(OH) = 6.0$  and  $\epsilon_{(SCN)_2^-} = 7600 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  at 480 nm.

**ESR measurements.** ESR spectra were measured on a Varian E-109 spectrometer. The  $g$  values were determined by using DPPH as reference ( $g = 2.0037$ ).

### 3. RESULTS AND DISCUSSION

**Absorption and fluorescence spectra.** Figure 1 shows the absorption, fluorescence and fluorescence

excitation spectrum of the aniline derivative **1** in cyclohexane (Figure 1, right) and acetonitrile (Figure 1, left) solution. As in the case of the aniline itself, there are two absorptions bands appeared, one at 245 nm and the other at 296 nm which can be assigned to the  ${}^1L_b \leftarrow {}^1A$  and  ${}^1L_a \leftarrow {}^1A$  transitions, respectively, (cyclohexane). A small red-shift is observed in the polar solvent MeCN (249 and 298-nm, respectively), attributed to an increase in the dipole moment upon excitation, well-known behavior of anilines [8]. Comparison of the fluorescence excitation and absorption spectrum shows that both spectra are identical concerning the absorption maxima. They show, however, a different intensity ratio due to the decrease of the fluorescence quantum yield when the energy of the excitation light reaches the second absorption band [8b, 8c]. The data are summarized in Table 1.

**Product studies.** The photoconversion of **1** is very effective (> 90% in a few minutes), while the solution color turned from colorless to bright red. The major products found are depicted in Scheme 1 and identified using gas chromatographic and GC-MS techniques (see experimental section). The products  $Ph_2(tert\text{-}Bu)CH$  and  $PhNH_2$  are indicative of a primary homolytic cleavage of the C-N bond producing the radicals  $Ph_2C^{\bullet}(CMe_3)$  and  $PhNH^{\bullet}$  (see also LFP experimental confirmation later).

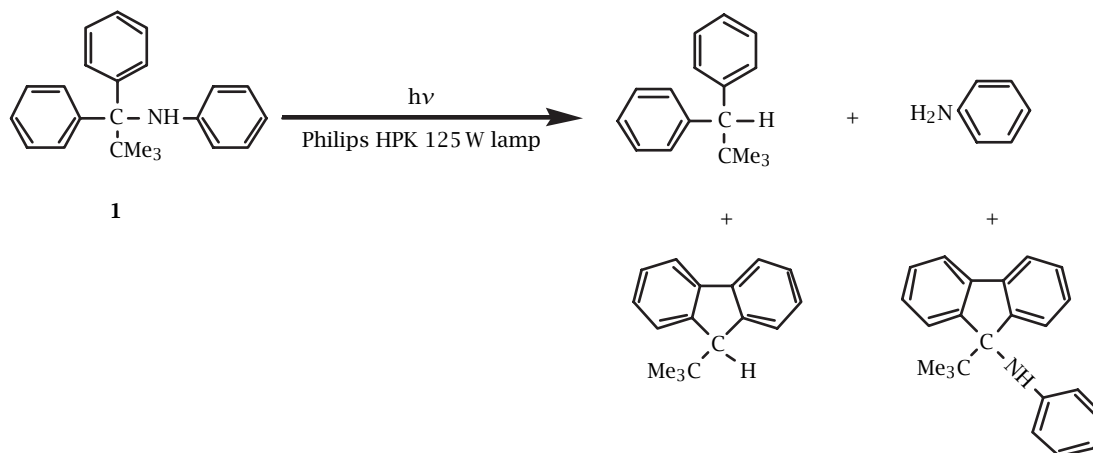
The fluorenyl derivatives are well-known secondary photoproducts derived from the photocyclization reaction of steric crowded diphenylmethyl radicals like the  $Ph_2C^{\bullet}(CMe_3)$  [4b, 7, 10g]. Traces of  $PhN=NPh$  are also detected. On the other hand, no products like  $Ph_2CH-NHPh$ ,  $Ph_2C=NPh$  or  $Ph_2CH_2$  were found (use of authentic samples) which would refer to a possible C-CMe<sub>3</sub> cleavage.

**Transient absorption spectra.** Figure 2 shows the transient absorption spectra obtained upon 248-nm

Table 1. Absorption and emission wavelength maxima, fluorescence lifetimes ( $\tau_f$ ) and quantum yields ( $\Phi_f$ ).

	Hexane		Cyclohexane		MeCN		
	$\lambda_{\max}$ (nm) (log $\epsilon$ )	$\lambda_{\max}$ (nm) (log $\epsilon$ )	$\Phi_f$	$\lambda_{\max}$ (fluor.) (nm)	$\lambda_{\max}$ (nm) (log $\epsilon$ )	$\Phi_f$	$\lambda_{\max}$ (fluor.) (nm)
PhNH <sub>2</sub>	234 (3,96)		$\Phi_{290} = 0,17^a$		239 (3,99)	$\Phi_{290} = 0,15^a$	330
	287 (3,32)	234	$\Phi_{254} = 0,11^b$		288 (3,26)	$\tau_f = 3,57 \text{ ns}^a$	
		287	$\tau_f = 4,34 \text{ ns}^c$	322			
PhNHMe	234 (4,16)		$\Phi_{290} = 0,12^c$		235 (4,30)	$\Phi_{290} = 0,17^d$	
	295 (3,55)	242	$\tau_f = 3,42 \text{ ns}^c$		296 (3,39)	$\tau_f = 4,6 \text{ ns}^d$	
		295		328			
1	244 (4,26)		$\Phi_{290} = 0,038$		249 (4,20)	$\Phi_{290} = 0,003$	329
	295 (3,45)	245 (4,14)	$\Phi_{254} = 0,027$		298 (3,40)	$\Phi_{254} = 0,003$	
		296 (3,46)	$\tau_f = 0,81 \text{ ns}$	328		$\tau_f \ll 1 \text{ ns}$	

<sup>a</sup> Ref. [6a], <sup>b</sup> Ref. [11b], <sup>c</sup> Ref. [11c, 11d], <sup>d</sup> Ref. [11e].



Scheme 1.

LFP of a MeCN solution ( $5,2 \times 10^{-4}$  mol/lit) of **1** at 298 K under argon atmosphere. One absorption band is observed in the region 420–550 nm with maximum at 485 nm and a shoulder at 455 nm, a second broad signal at 300–350 nm peaking up at 309 and 330 nm and a third sharp absorption at 270 nm. The band at 485 nm has a lifetime of about  $6 \mu\text{s}$  and disappears within  $7,5 \mu\text{s}$  after the pulse. The bands at 270 and 330 nm remain fairly constant, while the sharp peak at 309 nm decays faster than that at 330 nm changing thus the shape of the whole absorption band at 300–350 nm in later time windows. All the above absorption bands are quenched by oxygen ten times faster ( $k_{\text{obs}} = 3,6 \times 10^6 \text{ s}^{-1}$ ) than under argon. The only exception is the transient at 309 nm that is less affected by oxygen and its sharp absorption peak appears more pronounced (see Figure 2b). Based on the product anal-

yses described above and the reactivity against oxygen, all these bands can be tentatively assigned to radical species. Triplet states of aniline compounds are less probable because they are usually quenched by oxygen ca. 10 times faster than radical reactions (for example, the triplet state of *p*-CF<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-NH-CHPh<sub>2</sub> is quenched by oxygen with  $k_q = 5,8 \times 10^7 \text{ s}^{-1}$  [15]) and show absorptions with maxima at ca. 420–440 nm [4c, 11d].

What is now the identity of these transient species? First of all, the radicals Ph<sub>2</sub>C•(CMe<sub>3</sub>) and PhNH• formed by the dissociation of the C-N bond are expected. The anilino radical PhNH• is a well-studied radical [4b, 9] and shows sharp maxima at 270, 309 and a weaker broad band at 400 nm ( $\epsilon_{309} = 3500 \text{ M}^{-1} \text{ cm}^{-1}$  and  $\epsilon_{400} = 1250 \text{ M}^{-1} \text{ cm}^{-1}$ ). Because of its low extinction coefficient PhNH• is expected to contribute little to the transient absorption spectrum. So, we can

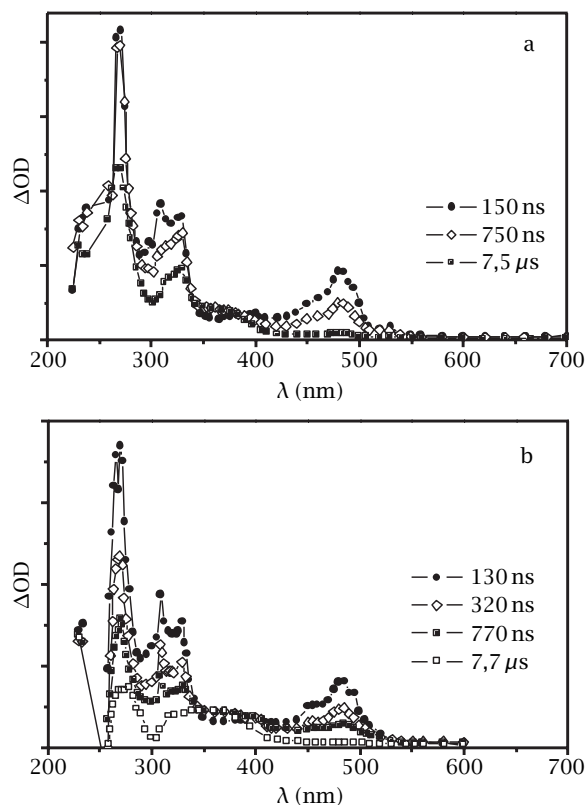


Figure 2. Transient absorption spectra observed on 248 nm laser excitation of a 0,52 mM solution of **1** in  $\text{CH}_3\text{CN}$ : a) under argon atmosphere 150 ns ( $\bullet$ ), 0,75  $\mu\text{s}$  ( $\diamond$ ), 7,5  $\mu\text{s}$  ( $\blacksquare$ ) after the pulse and b) under  $\text{O}_2$  atmosphere 130 ns ( $\bullet$ ), 0,32  $\mu\text{s}$  ( $\diamond$ ), 0,77  $\mu\text{s}$  ( $\blacksquare$ ) and 7,7  $\mu\text{s}$  ( $\square$ ) after the pulse.

with confidence assign the little sharp peak at 309 nm to the anilino radical, a fact strengthened by the observed sluggishness of this transient against  $\text{O}_2$ ; as an “electrophilic” radical  $\text{PhNH}^\bullet$  is known to be less reactive against  $\text{O}_2$  compared with carbon centered radicals [4b,9d-9e].

The absorption range around 330 nm and the decay rate constant in  $\text{O}_2$  is typical [4a, 10] for diphenylmethyl radicals, so that a good starting point is to assign this absorption to the second expected radical  $\text{Ph}_2\text{C}^\bullet(\text{CMe}_3)$ . Decisive in this assignment is the independent generation of this radical using two different methods. First through reductive dissociation of the C-Cl bond of the corresponding chloride  $\text{Ph}_2(\text{CMe}_3)\text{C-Cl}$  using the pulse radiolysis technique, and secondly through direct laser photolysis of the same chloride.

Irradiation of a THF solution (saturated with argon) of  $\text{Ph}_2(\text{CMe}_3)\text{C-Cl}$  with 3 MeV electron pulses (400-ns duration) gave the transient spectrum shown in Figure 3. It consists of a broad absorption maximum in the range of 300 to 345 nm with a small tail ex-

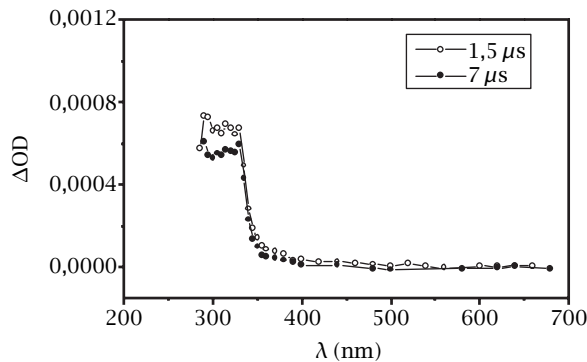
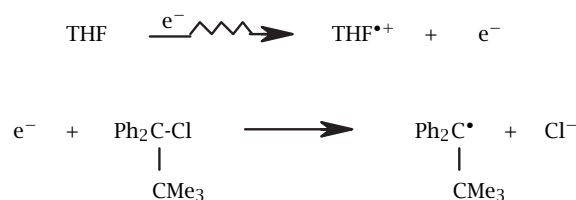


Figure 3. Transient absorption spectra observed on pulse radiolysis of a 2,3 mM solution of **1** in THF 1,5  $\mu\text{s}$  ( $\circ$ ) and 7  $\mu\text{s}$  ( $\bullet$ ) after the pulse.



Scheme 2.

tended until 450 nm (we are unable to go to wavelengths lower than 300 nm due to the high absorption of parent compound imposed through the high concentration needed, 2.3 mM). The similarity of this spectrum to that of Figure 2 is remarkable as far as the wavelength region 300–350 nm is considered. The standard pulse radiolytic reactions [10a] leading to  $\text{Ph}_2\text{C}^\bullet(\text{CMe}_3)$  are depicted in Scheme 2.

Alternatively, the radical was produced also photochemically from  $\text{Ph}_2(\text{CMe}_3)\text{C-Cl}$  in MeCN (under argon). It is well known that the diarylmethyl halides undergo efficient homolysis and heterolysis in acetonitrile to yield the corresponding radicals and cations [4b, 10a, 10d]. In Figure 4 the absorption spectrum resulting from 248-nm laser photolysis of the chloride in acetonitrile (1.1 mM) is shown. The spectrum is very similar (i) to that produced *via* pulse radiolysis (Figure 3) as far as the region 290–350 nm concerns, and (ii) to that described in Figure 2 derived from the photolysis of **1**. It is evident that in all three cases we deal with the same radical  $\text{Ph}_2\text{C}^\bullet(\text{CMe}_3)$ .

In a more detailed description, the spectra in Figure 2 (photolysis of **1**) and Figure 4 (photolysis of the chloride) contain the same bands at 270 nm, 300–350 nm and 485 nm, the only difference being, as expected, the absence in Figure 4 of the small absorption peak at 309 nm attributed previously to the anilino radical. It seems that the peak at 270 nm and the broad absorption at 300–350 nm belong to the same transient

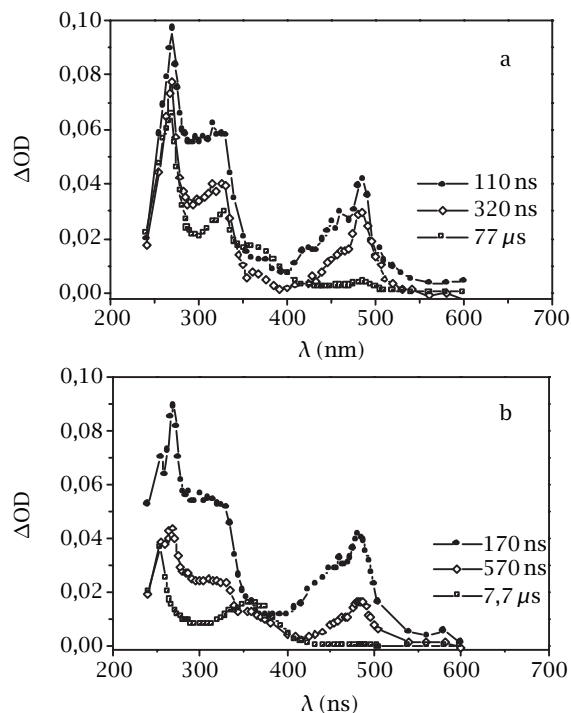
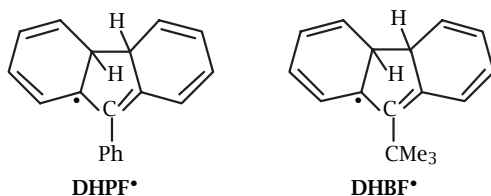


Figure 4. Transient absorption spectra observed on 248 nm laser excitation of a 1,13 mM solution of  $\text{Ph}_2(\text{CMe}_3)\text{C-Cl}$  in  $\text{CH}_3\text{CN}$ ; a) under argon atmosphere 110 ns ( $\bullet$ ), 0,32  $\mu\text{s}$  ( $\diamond$ ) 77  $\mu\text{s}$  ( $\blacksquare$ ) after the pulse, and b) under  $\text{O}_2$  atmosphere 170 ns ( $\bullet$ ), 0,57  $\mu\text{s}$  ( $\diamond$ ) and 7,7  $\mu\text{s}$  ( $\blacksquare$ ) after the pulse.

( $k_{\text{obs}} \approx 5.1 \times 10^4 \text{ s}^{-1}$  at 325 and 272 nm, monophotonic generation) and the band at 485 nm with the shoulder at 455 nm corresponds to a different radical species because of its faster decay ( $k_{\text{obs}} = 1.5 \times 10^5 \text{ s}^{-1}$  at 485 nm) and biphotonic formation. The radical character of all of them is confirmed also by their increased reactivity in oxygen-saturated solution, Figure 4b ( $k_{\text{obs}} \approx 2.3 \times 10^6 \text{ s}^{-1}$ ). The



first species is attributed to the  $\text{Ph}_2\text{C}^+(\text{CMe}_3)$  radical and the second at 485 nm should correspond to the 4a,4b-dihydro-9-*tert*-butylfluorenyl radical (DHBF $\bullet$ ) due to its similarity to the 4a,4b-dihydro-9-phenyl-fluorenyl radical (DHPF $\bullet$ ) spectrum [4a]. Latter is formed through an electrocyclization reaction caused by reexcitation of triphenylmethyl radical by a second photon [4b], and is a well-known property of steric hindered diphenyl-

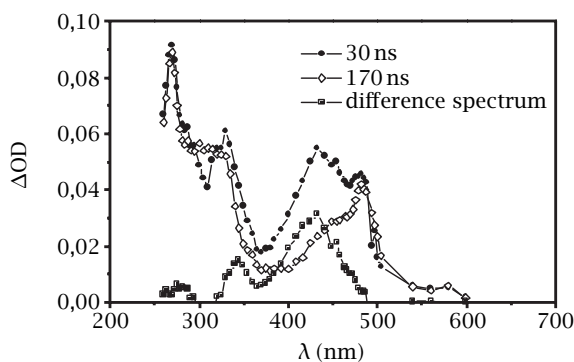


Figure 5. Transient absorption spectra observed on 248 nm laser excitation of a 1,13 mM solution of  $\text{Ph}_2(\text{CMe}_3)\text{C-Cl}$  in  $\text{CH}_3\text{CN}$  under  $\text{O}_2$  atmosphere 30 ns ( $\bullet$ ), 170 ns ( $\diamond$ ) after the pulse and their difference ( $\blacksquare$ ).

methyl radicals [4b,7,10g]. Additional support for this assignment comes from the product analyses where  $\text{Ph}_2\text{CH}(t\text{-Bu})$  and fluorenyl derivatives like the 9-*tert*-butyl-fluorene were identified. Similar assignments were made also in a recent study concerning the photochemistry of  $\text{Ph}_3\text{C-NHPh}$  and derivatives [4b,4c].

At this point the question regarding the nonoccurrence of the cation  $\text{Ph}_2\text{C}^+(\text{CMe}_3)$  by the photolysis of the chloride  $\text{Ph}_2(\text{CMe}_3)\text{C-Cl}$  must be considered. It is namely expected, from the experience with other diphenylmethyl [10a] or triphenylmethyl chlorides [4b], that both photohomolysis and photoheterolysis should occur in polar solvents like MeCN. In Figure 4 we have not any indication about the formation of such carbocationic species which would be unreactive against oxygen. However, looking at the absorption spectrum in a shorter time window, 30 ns after the laser pulse, an additional broad band is observed in the region of 400–450 nm that disappears rapidly in MeCN ( $k_{\text{obs}} = 2.7 \times 10^7 \text{ s}^{-1}$  at 433 nm), characteristic rate constants of carbocationic species. Subtracting the remaining spectrum at 170 ns (when the peak at  $\sim 430$  nm was totally disappeared) from the spectrum at 30 ns, a clear absorption spectrum is revealed in the range of 360–480 nm with maximum at 433 nm (see Figure 5), typical for arylmethyl carbocations [10a,10i]. We assign this last absorption band to the missed  $\text{Ph}_2\text{C}^+(\text{CMe}_3)$  cation and attribute its higher reactivity, compared to  $\text{Ph}_2\text{C}^+\text{Me}$  ( $k_{\text{obs}} = 1.8 \times 10^6 \text{ s}^{-1}$  [10h]), to the higher twisting of the Ph rings out of the carbocationic plane imposed through the bulkiness of the *t*-Bu group. The twisting makes  $\text{Ph}_2\text{C}^+(\text{CMe}_3)$  unstable and therefore more reactive towards nucleophiles [10i].

**ESR spectroscopy.** In our earlier work [4a] we presented ESR data of the radical  $\text{Ph}_2\text{C}^+(\text{CMe}_3)$  obtained in the cavity of an ESR instrument through direct photolysis of **1**, obviously after C-N bond cleavage took

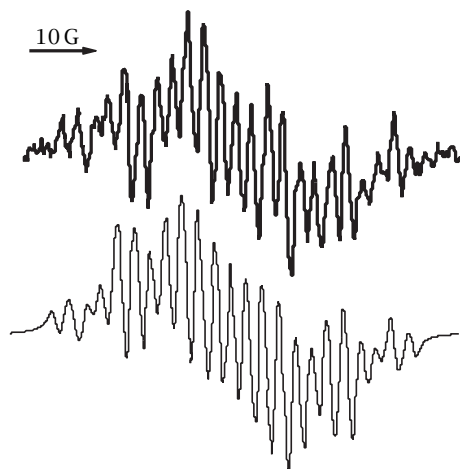
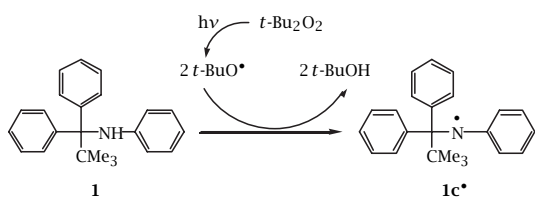


Figure 6. Experimental (a) ESR spectra of  $1c^{\bullet}$  and (b) computer-simulation using the coupling constants reported in the text. The experimental spectrum was obtained after irradiation of a solution of **1** in  $t\text{-Bu}_2\text{O}_2$  with a high pressure Hg-lamp at  $20^\circ\text{C}$ .

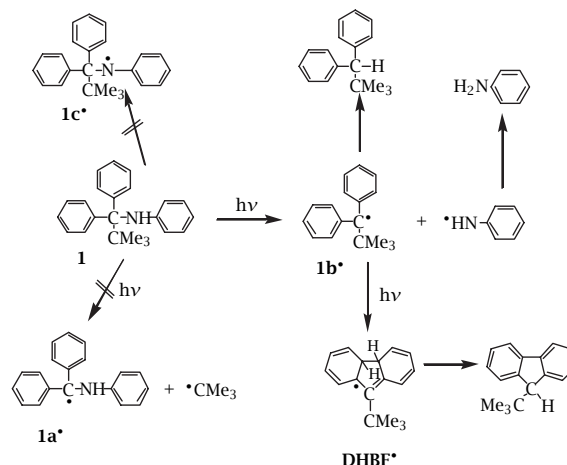
place. An alternative conceivable fragmentation, that of the  $\text{C-CMe}_3$  bond could be excluded, because the expected fragment radical  $\text{PhNH-C}^{\bullet}\text{Ph}_2$  gives a completely different ESR spectrum, as we showed, generating it through the C-Si photodissociation of the Si-analogue compound **2** [4a].

In order to search for a possible N-H photodissociation, not uncommon in anilines [11], we generated the aminyl radical  $1c^{\bullet}$  by irradiation of **1** in  $t\text{-Bu}_2\text{O}_2$  using a high pressure Hg lamp (Hanau 150 W) directly in the cavity of the ESR machine; the  $t\text{-BuO}^{\bullet}$  radical formed



photolytically abstracts the only one available hydrogen atom from the N-H group. The ESR spectrum thus recorded is depicted in Figure 6 together with its computer simulation. The spectrum was analyzed in terms of a coupling constant of 9.29 G (triplet) due to the nitrogen, two triplets attributed to the *p*- and *o*-hydrogens (7.61 and 5.53 G, respectively), and a smaller triplet due to the two *m*-hydrogens (1.98 G). The *g*-factor was found as 2.0044, characteristic of N-centered radicals.

Evidently, the spectrum of  $1c^{\bullet}$  is different from that obtained by the photolysis of **1**, supporting the product analysis and LFP results presented above, i.e., it is the



Scheme 3.

C-N bond which primary dissociates and not the C-C or the N-H one.

#### 4. CONCLUSIONS

Summarizing the results, we have shown that the photophysical properties (absorption and fluorescence spectra) of the aniline derivative **1** are dominated by the anilino chromophore showing comparable to the aniline itself absorption and emission maxima.

The photochemical behavior is pictorially summarized in Scheme 3. Compound **1** undergo primarily C-N homolysis on irradiation with 248-nm laser light in MeCN leading to  $1b^{\bullet}$  and  $\text{PhNH}^{\bullet}$ . The C-N bond homolysis is not surprising if we consider the high excitation energy localized on the anilino chromophore either in its singlet ( $> 90$  kcal/mol) [12] or triplet state ( $> 70$  kcal/mol) [12] and the low bond dissociation enthalpy (BDH) of the dissociating bond C-N; this should be  $< 45$  kcal/mol if we consider the BDH of the C-N bond in  $\text{Ph}_2\text{C}(\text{Me})\text{-NHPh}$ , which is estimated in the range of 45 kcal/mol [13], and the increased steric demands of the *tert*-Bu group in **1** compared to the Me group in  $\text{Ph}_2\text{C}(\text{Me})\text{-NHPh}$ . The weakness of this bond favors C-N bond homolysis and competes effectively with the dissociation of the N-H bond, which is a common photochemical property of aromatic amines [11a]. The BDH of the N-H bond in N-methylaniline,  $\text{Ph}(\text{Me})\text{N-H}$ , which should be not very different from that in **1**, is 83.3 kcal/mol [14]. Thus, the bond scission of the N-H bond in **1** should be very unfavorable and was not observed in the LFP experiments, a fact corroborated by the ESR studies and product analyses. The other possible pathway, a primary photoheterolysis of the C-N bond leading to  $\text{Ph}_2\text{C}^+(\text{CMe}_3)$  should be excluded, because latter was not detected in the *ns*-LFP experiments. In contrast, the cation was detected by the photolysis of the more polar C-Cl bond in  $\text{Ph}_2(\text{CMe}_3)\text{C-Cl}$ .

In a second step  $\text{Ph}_2\text{C}^*(\text{CMe}_3)$  is reexcited and forms the **DHBF** $^*$  radical in agreement with earlier work done by us [4b] and others [10e, 10f, 10g] on triphenylmethyl and diphenylmethyl radicals. Thus, the fluorenyl end-products are derived from **DHBF** $^*$  through typical radical H-abstraction or coupling reactions analog to  $\text{Ph}_3\text{C}^*$ . Also in a similar way the final photoproducts  $\text{Ph}_2\text{CH}(\text{CMe}_3)$  and  $\text{PhNH}_2$  could be explained as occurring from **1b** $^*$  and  $\text{PhNH}^*$ .

An alternative conceivable fragmentation, that of the weak C-CMe<sub>3</sub> bond leading to the stabilized radicals **1a** $^*$  and  $^*\text{CMe}_3$  could also be excluded on the basis of (i) the ESR data (**1a** $^*$  gives a completely different ESR spectrum [4a]), (ii) the LFP spectrum of **1a** $^*$  (produced through photolysis or radiolysis of **2** [15]) showing a red-shifted absorption spectrum compared to **1b** $^*$ , and (iii) the nonoccurrence of photoproducts indicative of a C-CMe<sub>3</sub> bond cleavage, such as  $\text{Ph}_2\text{CH-NHPh}$ ,  $\text{Ph}_2\text{C=NPh}$  or  $\text{Ph}_2\text{CH}_2$ . This is in contrast to the Si-analogue **2**, where both the C-N and C-Si bond fragmentations take place [4a, 15]. The C-C bond is generally considered as a "hard" bond and possess higher lying  $\sigma^*_{\text{C-C}}$  antibonding orbitals in respect to  $\sigma^*_{\text{C-Si}}$ . This probably makes the population of  $\sigma^*_{\text{C-C}}$  energetic unfavorable and renders the C-C bond resistant to photocleavage reactions, as we recently shown theoretically [16].

#### ACKNOWLEDGMENTS

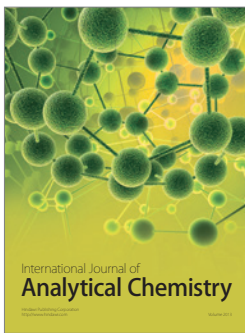
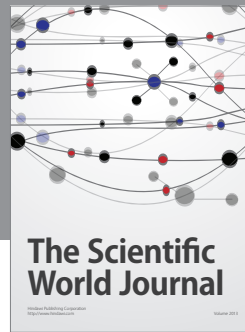
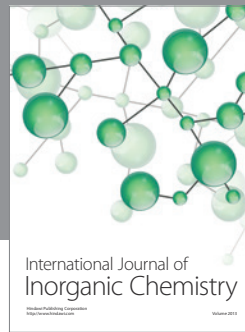
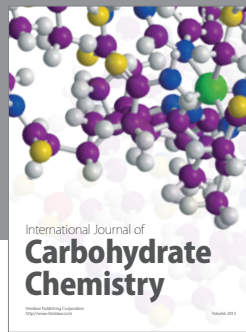
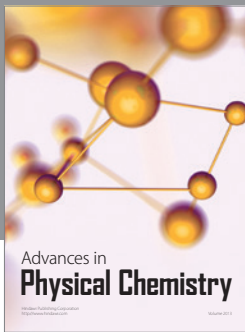
We thank Prof. S. Steenken, Max-Planck-Institut für Strahlenchemie, Mülheim, Germany for enabling us to obtain the LFP and pulse radiolysis spectra, and Dr. G. Pistolis, N. C. S. R. "Democritos," Athens, for fluorescence spectra, the General Secretariat for Research and Technology (Greece) for a grant (Grant No. 6BOA1A). A. K. Z. and M. G. S. thank the Deutscher Akademischer Austauschdienst (Germany) for a Fellowship and the Research Committee of the University of Ioannina for a grant (62/609).

#### REFERENCES

- [1] (a) S. J. Cristol and T. H. Bindel, *Org. Photochem.* **6** (1983), 327; (b) S. A. Fleming and J. A. Pincock, *Organic Molecular Photochemistry* (V. Ramamurthy and K. S. Schanze, Eds.), Marcel Dekker, New York, 1999, pp. 211-283, and references cited therein.
- [2] (a) J. Michl and V. Bonacic-Koutecky, *Electronic Aspects of Organic Photochemistry*, Wiley-Interscience, 1990, p. 138, 292, 374; (b) J. R. Larson, N. D. Epitotis, L. E. McMurchie, and S. S. Shaik, *J. Org. Chem.* **45** (1980), 1388; (c) M. F. Budyka, T. S. Zyubina, and A. K. Zarkadis, *J. Molec. Struct. (THEOCHEM)* **594** (2002), 113.
- [3] (a) W. M. McGowan and E. F. Hilinski, *J. Am. Chem. Soc.* **117** (1995), 9019; (b) H. E. Zimmerman, *J. Phys. Chem. A.* **102** (1998), 5616; (c) J. A. Pincock, *Acc. Chem. Res.* **30** (1997), 43.
- [4] (a) M. G. Siskos, S. K. Garas, A. K. Zarkadis, and E. P. Bokaris, *Chem. Ber.* **125** (1992), 2477; (b) M. G. Siskos, A. K. Zarkadis, S. Steenken, N. Karakostas, and S. K. Garas, *J. Org. Chem.* **63** (1998), 3251; (c) M. G. Siskos, A. K. Zarkadis, S. Steenken, and N. Karakostas, *J. Org. Chem.* **64** (1999), 1925.
- [5] A. K. Zarkadis, M. F. Budyka, M. G. Siskos, E. Ragga, G. Pistolis, and S. Steenken, 2nd Mediterranean Meeting on Photochemistry, Giardini Naxos, Sicily, 28th June - 2nd July 2003.
- [6] (a) G. Perichet, R. Chapelon, and B. Pouyet, *J. Photochem.* **13** (1980), 67; (b) Ya. N. Malkin, Sh. Ruziev, N. O. Pigorov, and V. A. Kuz'min, *Bull. Akad. USSR, Ser. Chem.* **36** (1987), 51.
- [7] (a) M. Gomberg, *Chem. Rev.* **1** (1924), 91; (b) W. Schlenk and A. Herzenstein, *Ber. Dtsch. Chem. Ges.* **44** (1911), 3541; (c) J. Schmidlin and A. Garcia-Banus, *Ber. Dtsch. Chem. Ges.* **45** (1912), 1344; (d) S. T. Bowden and J. J. Jones, *J. Chem. Soc.* (1928), 1149; (e) K. D. Berlin and G. P. Sturm, *J. Chem. Soc.* (1964), 2275; (f) H. G. Lewis and E. D. Owen, *J. Chem. Soc.* (1967), 422; (g) R. L. Letsinger, R. Collat, and M. Magnusson, *J. Am. Chem. Soc.* **76** (1954), 4185; (h) R. M. Wilson, K. A. Schnapp, K. Hanne-mann, D. M. Ho, H. R. Memarian, A. Azadnia, A. R. Pinchas, and T. M. Figley, *Spectrochim. Acta* **46A** (1990), 551; (i) P. S. Engel, Y. Chen, and C. Wang, *J. Org. Chem.* **56** (1991), 3073.
- [8] (a) S. K. Sarkar and G. S. Kastha, *Spectrochim. Acta Part A* **48** (1992), 1611; (b) G. Köhler and G. Getoff, *J. Chem. Soc., Faraday Trans. I* **76** (1980), 1576; (c) C. Dubroca and P. Lozano, *Chem. Phys. Lett.* **24** (1974), 49.
- [9] (a) E. J. Land and G. Porter, *Trans. Faraday Soc.* **59** (1963), 2027; (b) L. Qin, N. R. Tripathi, and R. H. Schuler, *Z. Naturforsch.* **40A** (1985), 1026; (c) E. Leyva, M. S. Platz, B. Niu, and J. Wirz, *J. Phys. Chem.* **91** (1987), 2293; (d) B. D. Wagner, G. Ruel, and J. Lusztyk, *J. Am. Chem. Soc.* **118** (1996), 511; (e) M. Canle, J. A. Santaballa, and S. Steenken, *Chem. Eur. J.* **5** (1999), 1192.
- [10] (a) J. Bartl, S. Steenken, H. Mayr, and R. A. McClelland, *J. Am. Chem. Soc.* **112** (1990), 6918; (b) J. L. Faria and S. Steenken, *J. Phys. Chem.* **97** (1993), 1924; (c) R. A. McClelland, V. M. Kanagasabapathy, and S. Steenken, *J. Am. Chem. Soc.* **110** (1988), 6913; (d) J. Dreyer and K. S. Peters, *J. Phys. Chem.* **100** (1996), 15156; (e) A. Bromberg, K. H. Schmidt, and D. Meisel, *J. Am. Chem. Soc.* **107** (1985), 83; (f) J. A. Schmidt and E. F. Hilinski, *J. Am. Chem. Soc.* **110** (1988), 4036; (g) D. Meisel, P. K. Das, G. L. Hug, K. Bhattacharyya, and R. W. Fessenden, *J. Am. Chem. Soc.* **108** (1986), 4706; (h) E. Ragga, PhD Thesis, University of Ioannina, Greece, in

- preparation; (i) H. Mayr, B. Kempt, and A. R. Ofial, *Acc. Chem. Res.* **36** (2003), 66; (j) R. A. McClelland, in *Reactive Intermediate Chemistry*, (R. A. Moss, M. S. Platz, and M. Jones Jr., Eds.), Wiley, NY, 2004, pp. 3–40.
- [11] (a) J. Malkin, *Photochemical and Photophysical Properties of Aromatic Compounds*, CRC, Boca Raton, FL, 1992, p. 117, 201; (b) Ya. N. Malkin and V. A. Kuz'min, *Russ. Chem. Rev.* **54** (1985), 1041; (c) F. Saito, S. Tobita, and H. Shizuka, *J. Photochem. Photobiol. A* **106** (1997), 119; (d) F. Saito, S. Tobita, and H. Shizuka, *J. Chem. Soc., Faraday Trans.* **92** (1996), 4177; (e) S. Tobita, K. Ida, and S. Shiobara, *Res. Chem. Intermed.* **27** (2001), 205.
- [12] S. L. Murov, I. Carmichael, and G. L. Hug, *Handbook of Photochemistry*, 2nd ed., Marcel Dekker, Inc., New York, 1993.
- [13] Based on the known BDE of the C-N bond of H<sub>3</sub>C-NHPh (68.9 kcal/mol) [13a] and the calculated difference of 24 kcal/mol in the BDE's between H<sub>3</sub>C-H (105 kcal/mol) [13b, 13c] and Ph<sub>2</sub>C(Me)-H (81 kcal/mol) [13b], (a) A. J. Colussi and S. W. Benson, *Int. J. Chem. Kinet.* **10** (1978), 1139; (b) D. F. McMillen and D. M. Golden, *Ann. Rev. Phys. Chem.* **33** (1982), 493; (c) J. Berkowitz, G. B. Ellison, and D. Gutman, *J. Phys. Chem.* **98** (1994), 2744.
- [14] A. J. Colussi and S. W. Benson, *Int. J. Chem. Kinet.* **10** (1978), 1139, for a critical review see: L. Batt and G. N. Robinson, in *The Chemistry of the Functional Groups*, Suppl. F (S. Patai, Ed.), Part 2, Wiley-Interscience, Chichester, 1982, p. 1035.
- [15] S. Garas, PhD-Thesis, University of Ioannina, in preparation.
- [16] (a) J. C. Giordan and J. H. Moore, *J. Am. Chem. Soc.* **105** (1983), 6541; (b) J. Michl, *Acc. Chem. Res.* **23** (1990), 128; (c) M. F. Budyka, T. S. Zyubina, and A. K. Zarkadis, *J. Molec. Struct. (THEOCHEM)* **668** (2004), 1.





**Hindawi**

Submit your manuscripts at  
<http://www.hindawi.com>

