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# Comparative Study of Ionization of Benzidine and Its Derivatives by Free Electron Transfer and One-Electron Oxidation

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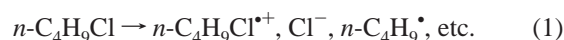
The bimolecular electron transfer from primary aromatic amines to the parent radical cation of a nonpolar solvent results in the synchronous formation of an amine radical cation as well as an anilino radical. The interesting observation is that the yield of the anilino radical is not very significant. The upper limit for the direct formation of anilino radical is about 20%. This could be due to additional delocalization of electrons essentially reducing destabilization of the cation radical in their twisted form. The results were supported by pulse radiolysis reactions carried out in aqueous solution. Benzidine and *o*-tolidine reactions were carried out at pH 7 and 13 with various radicals,  $\bullet\text{OH}$ ,  $\text{O}^{\bullet-}$ , and  $\bullet\text{N}_3$ , to determine the yields of radical cations and anilino radicals. The molar absorptivity calculated in aqueous solution was used to determine the actual yield in nonpolar solvent after free electron transfer (FET). The above results were supported by quantum chemical calculations.

## Introduction

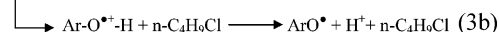
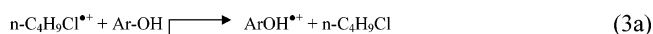
Understanding the ionization behavior of molecules is difficult due to their complexity. In the case of photoionization, the excited states can play a significant role.<sup>1–4</sup> Aromatic amines, because of their low ionization potentials ( $I_g \sim 7.5$  eV) and high reduction potential ( $E^\circ = 1$  V vs NHE), have been examined rather frequently to elucidate the ionization mechanism in the liquid phase.<sup>5–8</sup> Aromatic amines and phenols are often used as antioxidants.<sup>9,10</sup> The former is exploited in chemical industry as a constituent in dyestuffs and later for their role in flavonoids, polyphenols, etc. in foods and beverages. The main reasons for their use as antioxidants is the relatively weak N–H and O–H bond, and because of this, these compounds act as H atom donors in radical reactions. The bond dissociation energy<sup>11,12</sup> for primary and secondary amine is 80–85 kcal mol<sup>–1</sup>, whereas for phenols,<sup>13,14</sup> it is 88 kcal mol<sup>–1</sup>. Because of the fact that amines and phenols have low IP and a weaker N–H/O–H, bond they can undergo oxidation reactions and/or H atom transfer reactions rather easily.<sup>9</sup> To study these processes, time-resolved kinetic techniques are often employed for characterizing the transients.

Recently, Brede et al. have done exhaustive studies on the ionization of the aforementioned compounds in nonpolar solvents<sup>15–20</sup> because the ionization processes in polar (aqueous) solution are more complex. The intricacy of their work is that by using nonpolar solvents they could distinguish radical cations and radicals based on free electron transfer (FET) reactions.

Parent radical cations of nonpolar solvents such as *n*-alkanes and alkyl chlorides are very efficient electron acceptors. Hence, they are being used as universal tools for the generation of solute radical cations. For example in chlorobutane (*n*-C<sub>4</sub>H<sub>9</sub>Cl), the following reactions occur:<sup>15–20</sup>



This type of reaction, termed FET, is well studied by pulse radiolysis. It is suggested that the reaction in eqs 1 and 2 is governed by diffusion kinetics.<sup>15–20</sup> But recently, it has been shown that a real electron jump occurs in the range of tens of femtoseconds.<sup>15,16,21,22</sup> This is justified by showing the formation of a radical cation and phenoxyl radical in comparable amounts. Further using fs and ns lasers, it has been shown that they can lead to different products than that obtained by pulse radiolysis through eqs 1 and 2.<sup>21</sup> Formation of an identical yield of radical cation and radical in the case of phenols is explained as



In reaction 3, it is implied that FET occurs during the rotation of the OH group which has a frequency of around 10<sup>13</sup> Hz.<sup>15</sup> In the course of the rotation, the molecular situation could be understood in terms of two structures, that is, a plane structure and a twisted one in which OH group twisted 90° out of the plane. Under such a scenario, two possibilities exist in which the radical cation is conjugated and the other one in which it is localized on oxygen. The latter has more probability to deprotonate to give the radical (route 3b). Based on these observations, the formation of an identical yield of the aniline radical and cation is explained due to the rotation of the N–H group in aromatic amines.<sup>11,12</sup>

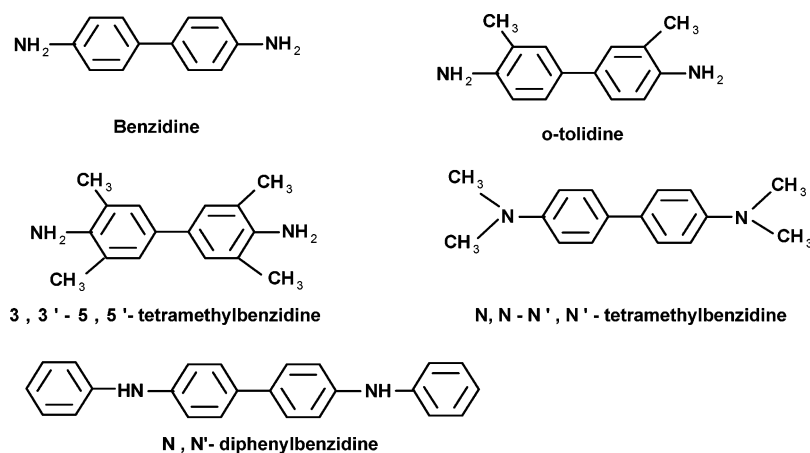
The question arises whether or not the above-mentioned effect applies for higher (or long chain) amines and in particular for benzidine, *o*-tolidine, 3,3'-5,5'-tetramethyl benzidine (TMB), *N,N,N',N'*-tetramethylbenzidine (N-TMB) and *N,N'*-diphenyl benzidine (DPB) (Scheme 1) where conjugation is extended. The main objective of this work is 2-fold. First, we determine

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## SCHEME 1



whether FET reactions in a nonpolar solvent and classical one-electron oxidation reactions in aqueous solution lead to different results if there are no pH effects involved. Having established this, we further probe the effect of counterions on the decay kinetics and in turn on the formation of the end products. Aside from details of aforementioned objectives, free radical reactions of these compounds are also probed for comparative studies. The experimental results are justified using theoretical calculations.

### Experimental Section

Benzidine (Fluka), *o*-tolidine (Fluka), 3,3',5,5'-tetramethylbenzidine (Aldrich), *N,N,N',N'*-tetramethylbenzidine (Sigma), *N,N'*-diphenylbenzidine (Aldrich), *n*-chlorobutane (Riedel-de Haën), and sodium azide (Aldrich) were used as received. The pH was adjusted using phosphate buffer and NaOH solutions. Highly pure water (Millipore), with a resistivity greater than 18.0 MΩ·cm, was used throughout. IOLAR grade N<sub>2</sub> and N<sub>2</sub>O gas (purity ≥ 99.99%) used for purging solutions were obtained from Indian Oxygen Limited. All solutions were prepared just before the experiments and kept in the dark to avoid any photochemical reactions. All experiments were carried out at ambient temperature close to 27 °C.

**Pulse Radiolysis Data Analysis.** Pulse radiolysis experiments were performed with high-energy electron pulses (50 and 500 ns durations) of an electron linear accelerator. The absorbed dose per pulse measured was 10 Gy for the 50 ns pulse and 11 and 47 Gy for the 500 ns pulse, corresponding to transient concentrations of around  $6 \times 10^{-6}$  mol dm<sup>-3</sup>. Details of the pulse radiolysis setup are reported elsewhere.<sup>23</sup> An aerated  $1 \times 10^{-2}$  mol dm<sup>-3</sup> KSCN solution was used for dosimetry, and the (SCN)<sub>2</sub><sup>•-</sup> radical was monitored at 475 nm. The absorbed dose per pulse was calculated<sup>24</sup> assuming  $G\epsilon$  [(SCN)<sub>2</sub><sup>•-</sup>] =  $2.6 \times 10^{-4}$  m<sup>2</sup> J<sup>-1</sup> at 475 nm.

### Results and Discussion

**Pulse Radiolysis Studies in *n*-Chlorobutane.** The interaction of ionizing radiation with nonpolar solvents results in the generation of sigma-type radical cations which are metastable in the nanosecond time scale.<sup>25</sup> This metastability of parent radical cations can be exploited for the generation of solutes radical cation provided the ionization potential of the solute is lower than the parent solvent.

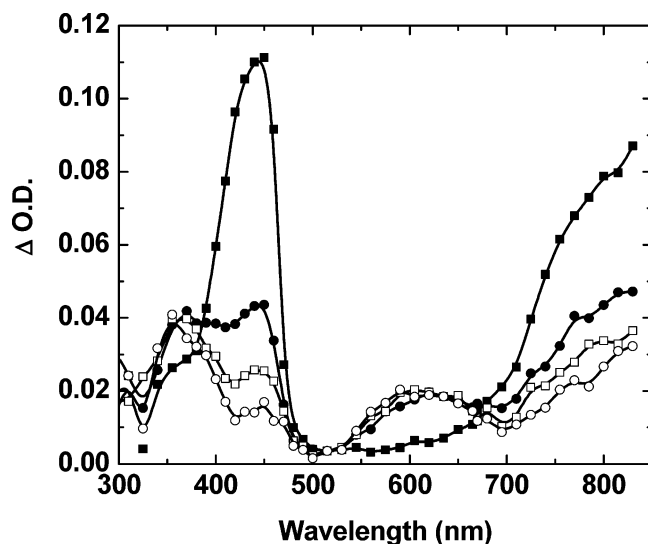
Figure 1 shows the time-resolved absorption spectrum obtained in N<sub>2</sub>-bubbled solution containing  $1 \times 10^{-2}$  mol dm<sup>-3</sup> benzidine in *n*-C<sub>4</sub>H<sub>9</sub>Cl immediately after the 500 ns electron

pulse. It is pertinent to mention here that similar spectrum features were obtained when a 50 ns electron pulse was employed. The parent radical cation of the solvent absorbed in the wavelength region 300–700 nm with a maximum at around 550 nm has a life time of about 150 ns in the absence of any solute.<sup>17,18</sup> Under our experimental conditions, *n*-C<sub>4</sub>H<sub>9</sub>Cl<sup>•+</sup> could not be detected. However, the growth of the transient formed from FET of *n*-C<sub>4</sub>H<sub>9</sub>Cl<sup>•+</sup> to benzidine showed a broad absorption spectrum in the wavelength region 275–850 nm.

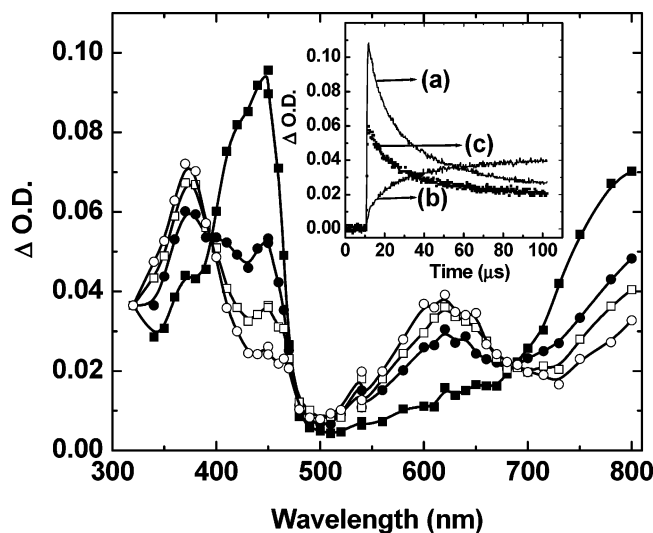
It can be seen from Figure 1 that the transient optical spectrum shows a sharp absorption maximum at  $\lambda_{\text{max}} = 450$  nm and a broad absorption at wavelengths higher than 700 nm just after the electron pulse. Two other absorption maxima at 370 and 620 nm develop with time, whereas absorption due to the transient shows a maximum at 450 nm and at wavelengths higher than 700 nm decreases. At first glance, it appears that, as the bands showing a maximum at 450 nm and at wavelengths higher than 700 nm decrease, the concomitant increase in the growth of the transient having a maximum at 370 and 620 nm occurs. However, a closer look shows that after 20 μs the absorption maxima at 370 and 620 nm do not change significantly in spite of the fact that the decay of the transient having a maximum at 450 and at wavelengths higher than 700 nm occurs.

On comparing the transient absorption bands with those reported in the literature in aqueous solution<sup>26,27</sup> the transient bands at 450 nm and at wavelengths higher than 700 nm were assigned to the radical cation and at 370 and 620 nm were assigned to the 4-(4'-aminophenyl) anilino radical. It is reported that the radical cation has a small absorption in the wavelength region 520–620 nm<sup>27</sup> because of its low molar absorptivity.

Figure 2 shows the time-resolved absorption spectrum obtained after electron pulse irradiation of an air-saturated solution containing  $1 \times 10^{-2}$  mol dm<sup>-3</sup> benzidine in *n*-C<sub>4</sub>H<sub>9</sub>Cl. The observed spectrum shows similar features as that obtained in the N<sub>2</sub>-bubbled solution. However, a closer look clearly shows that the yield of the transient increases significantly at 370 and 620 nm. It is known that in *n*-C<sub>4</sub>H<sub>9</sub>Cl the overall radical concentration is very high because the primarily formed quasisolvated electrons react dissociatively with the solvent.<sup>17,18</sup> This leads to the formation of butyl radicals. Carbon-centered radicals react with aminyls with diffusion controlled rates. In the presence of oxygen, butyl radicals get converted to butyl peroxy radicals which are less reactive.<sup>18</sup> This could be the reason for observing a higher yield of aniline radicals in oxygenated solution. Kinetic plots at various wavelengths under different conditions are shown in the inset of Figure 2.



**Figure 1.** Transient absorption spectrum of  $1 \times 10^{-2}$  mol  $\text{dm}^{-3}$  benzidine in  $n\text{-C}_4\text{H}_9\text{Cl}$  under  $\text{N}_2$  saturated condition:  $\blacksquare$  1.5  $\mu\text{s}$ ,  $\bullet$  20  $\mu\text{s}$ ,  $\square$  40  $\mu\text{s}$ , and  $\circ$  80  $\mu\text{s}$ . Dose = 47 Gy/pulse.



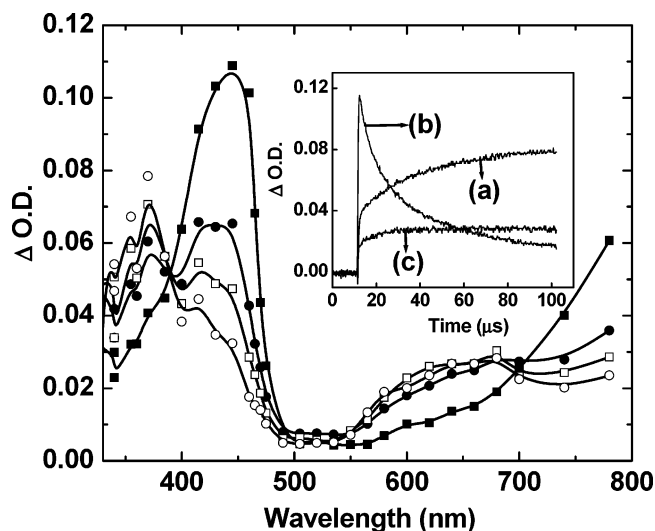
**Figure 2.** Transient absorption spectrum of  $1 \times 10^{-2}$  mol  $\text{dm}^{-3}$  benzidine in  $n\text{-C}_4\text{H}_9\text{Cl}$  under air saturated condition:  $\blacksquare$  3  $\mu\text{s}$ ,  $\bullet$  18  $\mu\text{s}$ ,  $\square$  40  $\mu\text{s}$ , and  $\circ$  80  $\mu\text{s}$ . Inset: Kinetic traces at (a) 450 nm, (b) 620 nm, and (c) 750 nm. Dose = 47 Gy/pulse.

Figure 3 shows the time-resolved absorption spectrum obtained on pulse irradiation of a  $\text{N}_2$ -bubbled solution containing  $1 \times 10^{-2}$  mol  $\text{dm}^{-3}$  *o*-tolidine in  $n\text{-C}_4\text{H}_9\text{Cl}$ . The spectral features are similar to that observed for benzidine. Based on the results obtained for benzidine, the observed bands are assigned to the radical cation (445 nm) and anilino radical (375 and 625 nm) which were further confirmed by doing one-electron oxidation reactions in aqueous solution (vide infra). The decay kinetics and growth of the transients at different wavelengths are shown in the inset of Figure 3. On comparing the results with that obtained for benzidine, it appears that the increase in the electron density in the benzene ring has no effect on the stability of the radical cation. The only difference observed was that the anilino radical spectrum has become little broader.

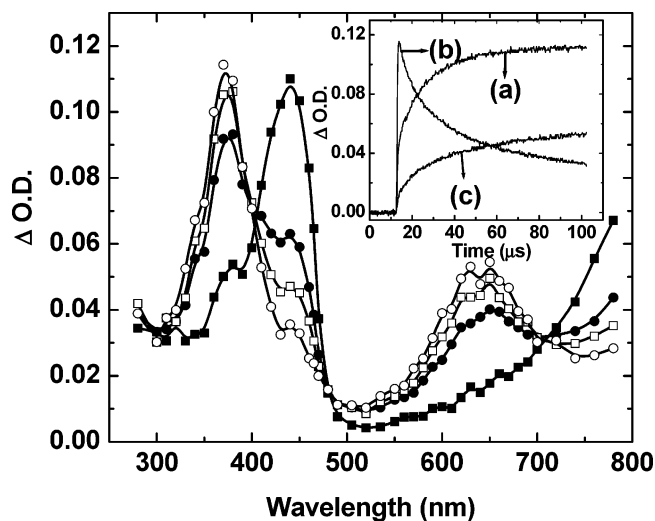
The decay of the radical cation could be due to the reaction<sup>25</sup>



where R denoted either the benzene or toluene ring for benzidine and *o*-tolidine, respectively. It can be noticed that though the



**Figure 3.** Transient absorption spectrum of  $1 \times 10^{-2}$  mol  $\text{dm}^{-3}$  *o*-tolidine in  $n\text{-C}_4\text{H}_9\text{Cl}$  under  $\text{N}_2$  saturated condition:  $\blacksquare$  2.5  $\mu\text{s}$ ,  $\bullet$  20  $\mu\text{s}$ ,  $\square$  40  $\mu\text{s}$ , and  $\circ$  80  $\mu\text{s}$ . Inset: Kinetic traces at (a) 370 nm, (b) 445 nm, and (c) 680 nm. Dose = 47 Gy/pulse.

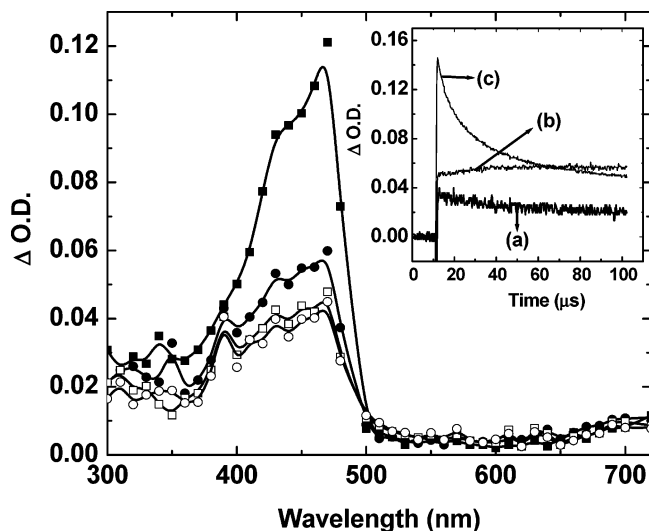


**Figure 4.** Transient absorption spectrum of  $1 \times 10^{-2}$  mol  $\text{dm}^{-3}$  *o*-tolidine in  $n\text{-C}_4\text{H}_9\text{Cl}$  under air saturated condition:  $\blacksquare$  2.5  $\mu\text{s}$ ,  $\bullet$  20  $\mu\text{s}$ ,  $\square$  40  $\mu\text{s}$ , and  $\circ$  80  $\mu\text{s}$ . Inset: Kinetic traces at (a) 375 nm, (b) 445 nm, and (c) 625 nm. Dose = 47 Gy/pulse.

radical cation decay occurs while there is no significant growth of the anilino radical within the same time scale. As no growth was observed in the wavelength region 520–620 nm and also at 370 nm, it appears that radical cation undergoes some other reaction paths.

Figure 4 shows the transient absorption spectrum obtained in an  $\text{O}_2$ -bubbled solution of  $1 \times 10^{-2}$  mol  $\text{dm}^{-3}$  *o*-tolidine in  $n\text{-C}_4\text{H}_9\text{Cl}$  after electron pulse irradiation. It can be seen from the figure that the yield of the transient having maxima at 375 and 625 nm increases enormously in the presence of  $\text{O}_2$  as compared to that obtained in a  $\text{N}_2$  bubbled solution (Figure 3). A clear isobestic point at 475 nm shows the transformation of one species to the other. The formation kinetics of various transients is shown in the inset of Figure 4. On comparing the decay of radical cations under  $\text{N}_2$ -bubbled and  $\text{O}_2$ -bubbled conditions (inset Figures 3 and 4), it can be noted that there is no significant change in the kinetics of the decay of the radical cations in the presence of  $\text{O}_2$ . Also, under identical experimental conditions, the yield of the radical cations is almost similar. The increase in the yield at 370 and 625 nm is probably due to the same reasons as explained above for benzidine.



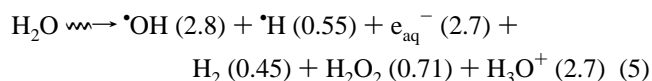


**Figure 5.** Transient absorption spectrum of  $1 \times 10^{-2} \text{ mol dm}^{-3}$   $N,N,N',N'$ -tetramethylbenzidine in  $n\text{-C}_4\text{H}_9\text{Cl}$  under  $\text{N}_2$  saturated condition: ■ 2.5  $\mu\text{s}$ , ● 30  $\mu\text{s}$ , □ 60  $\mu\text{s}$ , and ○ 80  $\mu\text{s}$ . Inset: Kinetic traces at (a) 360 nm, (b) 390 nm, and (c) 470 nm. Dose = 47 Gy/pulse.

**Ionization of  $N,N,N',N'$ -Tetramethylbenzidine (N-TMB) and  $N,N'$ -Diphenylbenzidine (DPB).** As N-TMB has no H atom at the heteroatom, ionization of N-TMB should result in the amine radical cation only. Indeed on electron pulse irradiation of a solution of  $1 \times 10^{-2} \text{ mol dm}^{-3}$  of N-TMB in  $n\text{-C}_4\text{H}_9\text{Cl}$ , only radical cations absorbing in the wavelength region 330–500 nm with an absorption maximum at 450 nm was observed. No transient formation was observed in the 500–650 nm range showing that the anilino radical is not getting formed. This shows that the anilino radical is not getting formed when the heteroatom is substituted with methyl groups (Figure 5). However, it appears that some transient formation occurs in the wavelength region 350–400 nm. By analogy this transient can be assigned to carbon centered radical as no growth was observed in the wavelength region 500–650 nm (results not shown). Due to the low solubility ( $5 \times 10^{-4} \text{ mol dm}^{-3}$ ) of DPB in  $n\text{-C}_4\text{H}_9\text{Cl}$ , the spectrum obtained was very weak due to low absorbance. Nevertheless it showed the presence of the radical cation and the nitrogen-centered radical (results not shown).

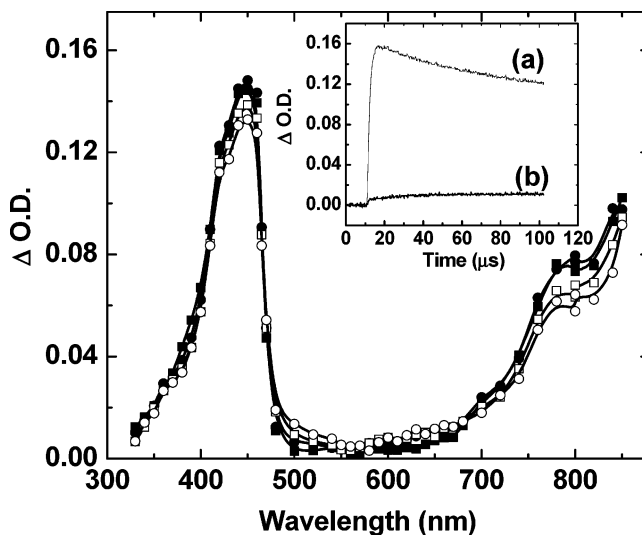
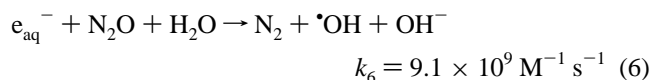
**Radiolytic Studies in Aqueous Solution.** To get more information about the transients' spectroscopic properties, experiments were carried out in aqueous solution under the experimental conditions where specifically only one type of the transient can be generated.

On irradiation of an aqueous solution the following primary species are formed<sup>28,29</sup>



where the numbers in parentheses represent the G-values, the number of species formed per 100 eV of energy absorbed. Total radical concentrations in this study were  $\sim 6\text{--}8 \mu\text{M}$  per pulse.

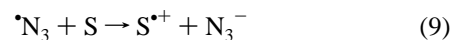
The reaction of only hydroxyl radicals was achieved by presaturating the solutions with  $\text{N}_2\text{O}$ , which quantitatively converts the hydrated electron,  $e_{\text{aq}}^-$ , to this radical<sup>29</sup>



**Figure 6.** Time-resolved absorption spectrum of  $1 \times 10^{-4} \text{ mol dm}^{-3}$   $o$ -tolidine under  $\text{N}_2\text{O}$  saturated condition at pH 7.8: ■ 4.0  $\mu\text{s}$ , ● 30  $\mu\text{s}$ , □ 60  $\mu\text{s}$ , and ○ 80  $\mu\text{s}$ . Inset: Kinetic traces at (a) 450 nm and (b) 640 nm. Dose = 11 Gy/pulse.

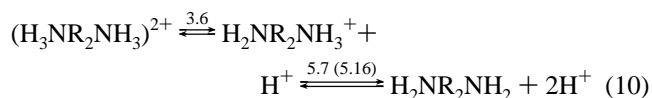
Due to slow reaction for  $\text{H}^+$  scavenging,  $\text{N}_2\text{O}$  saturation ultimately doubles the amount of hydroxyl radicals by scavenging electrons.

When electron-transfer conditions were desired, the azide radical was formed according to reaction 8 and used



Reaction 9 is specific, and it is suggested that one can get almost 100%  $\text{S}^{\cdot+}$  by choosing the conditions properly,<sup>30</sup> that is, at a pH that is significantly different than that of  $\text{pK}_a$  of radical cation at which its de-protonation does not occur.

Benzidine has two  $\text{pK}_a$  at 3.6 and 5.7, whereas for  $o$ -tolidine the second  $\text{pK}_a$  is at 5.16.<sup>31</sup>



where R denotes either the benzene or toluene ring for benzidine and  $o$ -tolidine, respectively. Therefore, most of the work was carried out at pH much away from the  $\text{pK}_a$  of the parent compound. Figure 6 shows the transient absorption spectrum obtained on pulse irradiation of  $\text{N}_2\text{O}$  saturated solution containing  $1 \times 10^{-4} \text{ mol dm}^{-3}$   $o$ -tolidine at pH 7.8. The observed transient spectrum showed a maximum at a wavelength of 450 nm and a monotonous increase at wavelengths higher than 650 nm. The bimolecular rate constant for the formation of the transient and other spectral properties are compiled in Table 1. It can be seen that transient absorption spectrum does not decay significantly within the time window of our experiment. A closer look at the transient spectra shows that there is marginal increase in the absorption in the wavelength region 500–620 nm. Therefore, the decay kinetics of the transient was monitored at different wavelengths. The results are shown in the inset of Figure 6. It can be noted that under the identical time scales there is a slight decay of the radical cation with a concomitant increase in the absorbance at 640 nm. As the  $\cdot\text{OH}$  radical is electrophilic in nature, it can add as well as oxidize the

**TABLE 1: Kinetics and Absorption Characteristics of the Transient Produced by the Reactions of Various Free Radicals with *o*-Tolidine**

radicals	pH	$\lambda_{\max} (\text{N}^{\bullet+})$ nm	$\epsilon (\text{N}^{\bullet+})$ dm <sup>3</sup> mol <sup>-1</sup> cm <sup>-1</sup>	$k_2$ dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>	$\lambda_{\max} (\text{N}^{\bullet})$ nm	$\epsilon (\text{N}^{\bullet})$ dm <sup>3</sup> mol <sup>-1</sup> cm <sup>-1</sup>	$k_2$ dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>
•OH	7.8	450	24100	$8.2 \times 10^9$			
O <sup>•-</sup>	13				390/620	18960/5520	$4.7 \times 10^9$
•N <sub>3</sub>	7.8	450	28850	$8.9 \times 10^9$	630	2160	
•N <sub>3</sub>	13				390/630	18410/5680	$7.4 \times 10^9$

compound. Therefore, reactions were carried out with a specific one-electron oxidant, the •N<sub>3</sub> radical.

Figure 7 shows the transient absorption spectrum obtained on pulse irradiation of N<sub>2</sub>O saturated solution containing  $1 \times 10^{-4}$  mol dm<sup>-3</sup> *o*-tolidine,  $5 \times 10^{-2}$  mol dm<sup>-3</sup> N<sub>3</sub><sup>-</sup> at pH 7.8. The observed transient spectrum shows four bands at different wavelengths. The absorption maximum at 450 nm and absorbance at wavelengths higher than 700 nm decrease with time with a concomitant increase in the absorption maximum at wavelength 375 nm and in the wavelength region 480–680 nm. The kinetic profiles are shown in the inset of Figure 7. The bimolecular rate constant and other spectral properties of the transients are compiled in Table 1. On comparing the transient absorption spectrum with that obtained on the •OH reaction (Figure 6), it appears that the •N<sub>3</sub> radical produces distinctly two different transients on reaction with *o*-tolidine. However, the yield of the transient generated just after the electron pulse is almost similar at wavelengths of 450 and above 700 nm in both cases. This shows that the •OH radical lead to the formation of only one transient species, that is, the radical cation of *o*-tolidine. The surprising observation is the distinct formation of another transient in the case of •N<sub>3</sub> radical reaction. It is known in literature that the radical cation of aromatic compounds reacts with negative ions in reaction 4 and undergoes a neutralization reaction.<sup>25</sup> During this process, they form a radical. We presume that a similar process is occurring in the presence of N<sub>3</sub><sup>-</sup>. Identical yields of the radical cation in the case of the •OH and •N<sub>3</sub> radicals confirmed the earlier results that the •OH radical lead to the formation of a radical cation after elimination of water.<sup>26</sup> The results can be summarized as



The molar absorptivity and other spectral parameters of the transients are compiled in Table 1. It is pertinent to mention here that H-atom reaction at pH 2 with *o*-tolidine results only in a very weak absorption in the UV region. Thus any contribution from its transient reaction products toward absorption in the UV–visible region can be neglected.

As mentioned above, radical cation undergoes neutralization reaction and subsequently generate a radical. Therefore, to get a better idea about the spectral characteristics of the anilino radical, we have tried to determine the p*K*<sub>a</sub> of the radical cation. A typical case for *o*-tolidine is shown in the inset of Figure 8. The p*K*<sub>a</sub> of the semioxidized species was calculated to be 10.7. The reactions can be written as



where R<sub>2</sub> is toluene ring. Therefore, the reaction of O<sup>•-</sup> radical with *o*-tolidine was studied at pH 13. Figure 8 shows the transient absorption spectrum obtained at pH 13 on pulsing N<sub>2</sub>O saturated  $1 \times 10^{-4}$  mol dm<sup>-3</sup> *o*-tolidine. The observed transient spectrum showed two bands having absorption maxima at 375 and 625 nm. The formation kinetics of the bands at 375 and

625 nm was almost similar. At pH 7 and 13, the *G*(•OH) and *G*(O<sup>•-</sup>) under these conditions are taken as 5.5 and 6.0, respectively, for spectral parameter calculations and compiled in Table 1. At pH 13, the following reaction occurs:

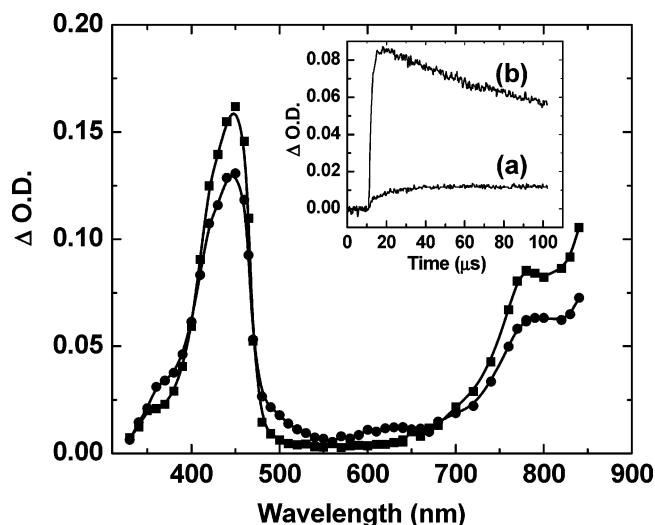


The transient spectrum obtained on pulsing an N<sub>2</sub>O-saturated solution of  $2 \times 10^{-4}$  mol dm<sup>-3</sup> benzidine at pH 7 and 13 showed spectral features similar to that reported in the literature<sup>26</sup> (result not shown). The reaction of a specific one-electron oxidant, •N<sub>3</sub>, with benzidine also showed the spectral features similar to that obtained on reaction of •OH at pH 7.

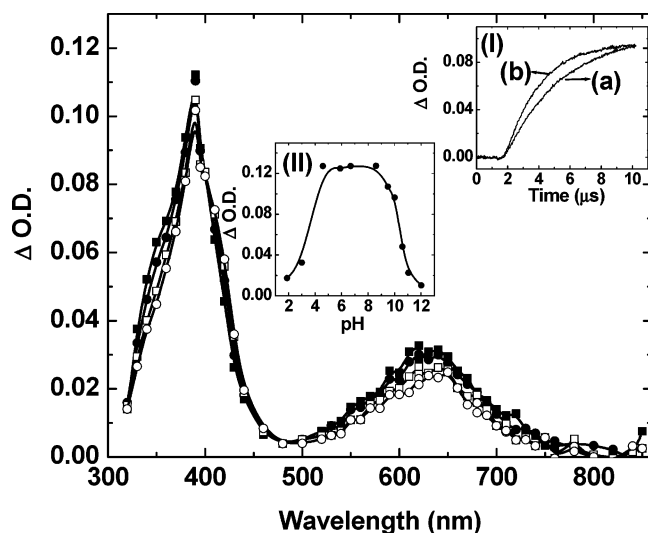
The main aim of the present study is to identify the possibility of the formation of the anilino radical in addition to the radical cation just after the electron pulse. For this, the ratio of absorbance at 450 nm to that at 370 and 620 nm obtained in *n*-C<sub>4</sub>H<sub>9</sub>Cl are compared with the results obtained in aqueous solution under specific one electron oxidation conditions. The advantage with benzidine and *o*-tolidine is that their radical cation is stable. In addition they mimic the presence of a hetero group similar to that present in phenol, aniline, and diphenyl amine.<sup>11,12,25</sup> The results are compiled in Table 2. It can be seen that the ratios are higher in aqueous solution. The factors that can increase the yield of the anilino radical are neutralization of radical cation with Cl<sup>-</sup> in *n*-C<sub>4</sub>H<sub>9</sub>Cl solution. Whereas in aqueous solution, the pH of the solution can have profound affect on the yield of the anilino radical if the working pH is close to the p*K*<sub>a</sub> of the radical cation. FET reactions are generally done in chlorinated solvents. Thus, it was not possible to completely avoid the neutralization reaction. Therefore, attempts were made to measure the ratio as close as possible after the electron pulse in *n*-C<sub>4</sub>H<sub>9</sub>Cl. Whereas for aqueous solutions, it was achieved by selecting the working pH so that the possibility of the formation of an anilino radical due to deprotonation is significantly low. The ratio of absorbances at just after the electron pulse and at 80 μs for benzidine and *o*-tolidine in *n*-C<sub>4</sub>H<sub>9</sub>Cl and water are compiled in Table 2. It is pertinent to mention here that in *n*-C<sub>4</sub>H<sub>9</sub>Cl the kinetics for electron-transfer gross reaction is five times faster than the experimental time resolution. From the observed results, it can be extrapolated that the yield of the radical cation might be higher at time scales where FET takes place. Though, it is not possible to comment on the rate constant of FET, nevertheless, this does not affect the overall conclusion that the yield of the radical cation is much higher than that of the anilino radical just after the electron pulse.

On comparing radical cation spectra of *o*-tolidine obtained just after the electron pulse in *n*-C<sub>4</sub>H<sub>9</sub>Cl and aqueous solution (Figures 3 and 6), it can be seen that the spectral features are almost similar in *n*-C<sub>4</sub>H<sub>9</sub>Cl and in aqueous solution. This clearly shows that though with time anilino radical yield increases in *n*-C<sub>4</sub>H<sub>9</sub>Cl solvent due to the neutralization reaction there was no significant yield of anilino radical just after the pulse.

There are various routes by which benzidine and *o*-tolidine radical cation can decay; among them most significant are the formation of a dimer radical cation, deprotonation (eq 3b), and neutralization (eq 4) reaction.<sup>12</sup> It is suggested that in the case



**Figure 7.** Time-resolved absorption spectrum of  $1 \times 10^{-4}$  mol  $\text{dm}^{-3}$  *o*-tolidine and  $5 \times 10^{-2}$  mol  $\text{dm}^{-3}$  sodium azide under  $\text{N}_2\text{O}$  saturated condition at pH 7.8: ■ 6.0  $\mu\text{s}$  and ● 70  $\mu\text{s}$ . Inset: Kinetic traces at (a) 640 nm and (b) 780 nm. Dose = 11 Gy/pulse.



**Figure 8.** Time-resolved absorption spectrum of  $1 \times 10^{-4}$  mol  $\text{dm}^{-3}$  *o*-tolidine under  $\text{N}_2\text{O}$  saturated condition at pH 13: ■ 8.0  $\mu\text{s}$ , ● 30  $\mu\text{s}$ , □ 60  $\mu\text{s}$ , and ○ 80  $\mu\text{s}$ . Inset I: Formation kinetic traces at 380 nm (a)  $5 \times 10^{-5}$  mol  $\text{dm}^{-3}$  and (b)  $1 \times 10^{-4}$  mol  $\text{dm}^{-3}$  *o*-tolidine. Inset II: Plot of  $\Delta \text{O.D.}$  vs pH at 450 nm. Dose = 11 Gy/pulse.

**TABLE 2: Ratio of Absorbances of Radical Cation and Anilino Radical at Various Times**

amine	just after the pulse		after 80 $\mu\text{s}$	
<i>o</i> -tolidine in aqueous solution	$\text{OD}_{450}/\text{OD}_{370}$	4.81	$\text{OD}_{450}/\text{OD}_{370}$	4.5
	$\text{OD}_{450}/\text{OD}_{620}$	36.0		
<i>o</i> -tolidine in $n\text{-C}_4\text{H}_9\text{Cl}$	$\text{OD}_{450}/\text{OD}_{370}$	2.70	$\text{OD}_{450}/\text{OD}_{370}$	0.41
	$\text{OD}_{450}/\text{OD}_{620}$	10.89	$\text{OD}_{450}/\text{OD}_{620}$	1.37

of aromatic amines a dimer radical cation, formed by reaction between the radical cation and parent compound, in reality represents a charge-transfer complex and exists in equilibrium.<sup>11,12</sup> However, the rate constant for the neutralization reaction (eq 4) is generally greater than the dimerization rate constant at least by 1 order of magnitude.<sup>11,12</sup> Thus, the contribution of deprotonation and neutralization is comparatively more than the dimerization reaction in the decay of the radical cation. It can be seen that the delayed increase in absorbance of anilino radical is significantly higher than that just after the pulse. Although, due to the superimposition of transients generated by electron-

transfer, eq 3, with subsequent conversion of the radical cation into radical according to eqs 3b and 4 it is difficult to judge the ratio of transients. However, on the basis of the results obtained in aqueous solution, one can calculate the ratio of the transients and conclusively draw the above conclusions.

At this juncture, it would be worthwhile to compare our results with the somewhat similar results obtained by Brede et al.<sup>11,12,15–20</sup> in the case of aromatic amines and phenols. It is suggested that FET in nonpolar solvents, where negligible solvation of ions and almost complete lack of an activation barrier, makes it possible the electron jump from the solute to solvent radical cation in very first encounter. The electron jump without any barrier was suggested to occur in time scales of  $\leq 10^{-15}$  s.<sup>32,33</sup> As the vibrational spectroscopy encompassing the molecular oscillations (deforming, bending) falls in this time scale only,<sup>34</sup> one can visualize that the possible different conformers of a molecule persist with different  $n$  or  $\pi$  electron distribution in the HOMO ground state. Therefore, in the time range of hundreds of femtoseconds, the  $n$  electron of the nitrogen atom fluctuates between planar and perpendicular conformers. In the planar case, the  $n$  electrons are distributed over the entire molecule, whereas in the perpendicular structure, the electrons are localized at the heteroatom. A similar situation can be visualized for aromatic amines.<sup>11,12</sup> The bending motion is centered at the amine nitrogen which carried three bonds and a lone electron pair as per  $\text{sp}^3$  hybridization. It is suggested that one can presume similar planar and perpendicular conformers for primary and secondary aromatic amines. It is pertinent to mention here that one-electron oxidation reactions of phenols failed to generate radical cations due to the fact that the oxidation reaction is coupled with proton transfer. This has always led to the generation of the phenoxyl radical at least in the pH range 0–14.<sup>13,14</sup>

Although polar solvents are more complex compared to nonpolar solvents for studying radical cations, because of inherent properties of polar solvent such as hydrogen bonding, even then one can study the formation of radical cations by selecting proper experimental conditions. In aqueous solution, this can be achieved by changing the pH of the solution. Thus, the solvation state of the ions is the deciding parameter. In the thermodynamic equilibrium, benzidine and *o*-tolidine can exist in mesomeric states where the  $\pi$  electrons and the lone electron pairs are in resonance. Our results show that the synchronous generation of the radical cation and radical depends on strong delocalization of electrons through aromatic system leading to stabilization of the radical cation. The present results show that if the radical cation exists in constrained conformer it is bound to release a proton to form a radical. Benzidine is a simple dimer of aniline. Thus, by analogy, a similar situation should prevail in it. However, it was observed that the life time of radical cation increases drastically in benzidine compared to that of aniline or diphenyl aniline. These observations might have importance as aromatic amines are widely used in industry.

**Theoretical Consideration.** Quantum chemical calculations were made to better understand the observed low experimental yields of the deprotonated radical immediately after irradiation. Density functional theory (DFT), namely gradient corrected B3LYP and BH&HLYP,<sup>37–40</sup> was used as implemented in the Gaussian 03 program package.<sup>41</sup> BH&HLYP was used to avoid possible over delocalization of unpaired electrons in symmetric radical cations because it was shown<sup>42,43</sup> that the BH&HLYP method leads to correct localization of the unpaired electron in such cases, contrary to B3LYP. This discrepancy arises from the apparent inability of B3LYP and several other DFT



TABLE 3: DFT BH&HLYP/6-31G(d) Calculated Quantum Chemical Data<sup>a</sup>

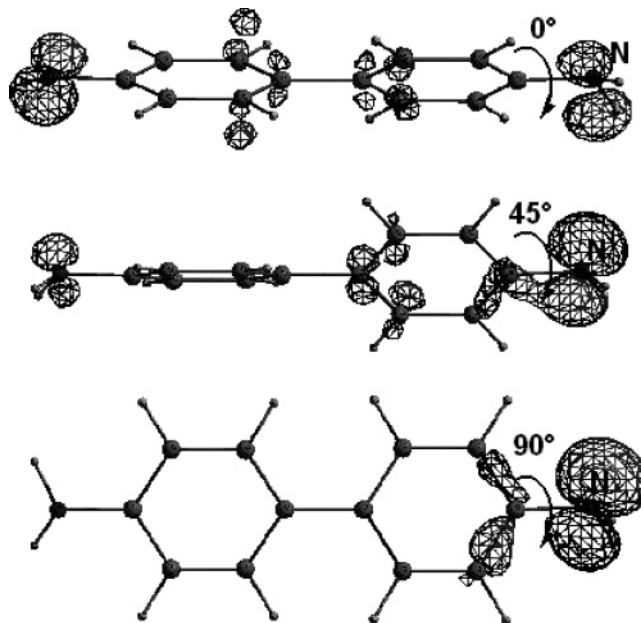
solute	$\nu_{\text{Rot}} (\text{cm}^{-1})$	$t_{\text{Rot}} [10^{-15}\text{s}]$	$\nu_{\text{oscil}} (\text{cm}^{-1})$	$t_{\text{Osci}} [10^{-15}\text{s}]$	$E_a (\text{S})$	$E_a (\text{CR})$	$\Delta E$	$\Delta Q$
benzidine	264	126	3584	9.3	4.87	17.4	14.2	0.149
Ph-NH <sub>2</sub>	268	124	3585	9.3	5.71	39.8	30.8	0.304

<sup>a</sup> Frequencies (scale factor  $f = 0.96$ ) of polar NH<sub>2</sub>-group rotation and valence N-H vibration oscillations,  $t$ -times of one motion; activation energy (kcal mol<sup>-1</sup>) for NH<sub>2</sub>-group rotation of the singlet  $E_a(\text{S})$  and cation radical  $E_a(\text{CR})$  states;  $\Delta E$  (kcal mol<sup>-1</sup>) – energy difference between radical cations at the stable (planar) and the transition (perpendicular) geometries of singlet ground state;  $\Delta Q$  – additional positive mulliken atomic charge on nitrogen after ionization.

functionals to localize the unpaired electron and from the tendency to favor delocalized structures in radical cations where localization of unpaired electrons is expected.<sup>44</sup>

According to the proposed model,<sup>24</sup> the low-frequency vibrations of molecule, such as intramolecular rotations causing slow (in comparison with electron motion) changes of the molecular structure, can lead in some cases the drastic change in the distribution of  $n$  electrons from heteroatoms and  $\pi$  electrons from aromatic rings. Though such changes of electron distribution cause only small (a few kcal mol<sup>-1</sup>) destabilization of molecules in their singlet ground state, it can lead to very strong destabilization of molecules in their radical cation state. The reason for the destabilization of the radical cation is the localization of electrons. Although electrons tend to be in the most possible delocalized distribution in the stable molecular structure, the localization of electron forces destabilization of molecule. The larger is the degree of localization, the stronger is destabilization of radical cation, reducing essentially dissociation energy for deprotonation or radical building. As follows, immediate formation of the deprotonated radical (anilino radical in our case) could be expected. Otherwise, the better the electron is delocalized through molecule, the more stable the radical cation will be. Now we try to apply the proposed model of simultaneous formation of both the radical cation and deprotonated radical to the case of benzidine to understand the low yields of the anilino radical in comparison with those for aniline. The calculated parameters for benzidine were compared with those for aniline, which have shown<sup>11,12</sup> direct formation of amine radical cations as well as aminyl radicals, in comparable amounts. The calculated quantum chemical parameters are given in Table 3.

The calculated parameters with the BH&HLYP method are in quantitative agreement with those calculated with B3LYP.<sup>11</sup> At the singlet state, both benzidine and Ph-NH<sub>2</sub> have a low-frequency rotational (torsion) vibration, which is about 30 times slower than valence N-H vibrations. Because of the relative low activation energy, these torsion vibrations may have free rotation at room temperature. The activation energy for intramolecular rotation of the NH<sub>2</sub> group is only slightly smaller in the case of benzidine. The optimized most stable structure of benzidine has aromatic rings slightly rotated out of plane (30° and 13° for the singlet and cation radical, respectively). Nevertheless, due to the favorable symmetry, the  $n$  electron from nitrogen is completely delocalized through whole aromatic system (Figure 9). Due to the change of the molecular structure through torsion vibration, a drastic change in the electron distribution should occur, leading to localization of the  $n$  electron at the NH<sub>2</sub> group close to the perpendicular position relative to the aromatic ring. However, the calculated energy difference  $\Delta E$  between radical cations at their stable ground state (planar) and the transition (perpendicular) geometry differs essentially (14.2 and 30.8 kcal mol<sup>-1</sup> for benzidine and Ph-NH<sub>2</sub>, respectively). This difference, namely  $E_a(\text{CR})$ , is even larger for optimized stable and transition structures of cation radicals (17.4 and 39.8 kcal mol<sup>-1</sup>). That occurs apparently due to a smaller deviation from the molecular plane at the optimized cation



**Figure 9.** Change of the electron distribution of  $n$ -molecular orbital from nitrogen in dependence on intramolecular rotation of NH<sub>2</sub> group. radical structure leading to a better delocalization of the electron and additional stabilization of the cation radical. Additionally, the larger delocalization of electrons in the case of benzidine is supported by the calculated change of the Mulliken atomic charge on nitrogen by ionization. Thus, after electron transfer from the neutral molecule, the nitrogen atom becomes positively charged, 0.304 in the case of Ph-NH<sub>2</sub> and only 0.149 in the case of benzidine. As follows, the radical cation of benzidine in the transition (perpendicular) geometry will be less destabilized than the radical cation of Ph-NH<sub>2</sub>. On the contrary, the stable cation radical will be additionally stabilized due to delocalization of the  $n$ -electron through the two aromatic rings. As a consequence, the relative amount of the stable cation radical and anilino radical should be shifted to favor the cation radical. All of this can explain the observed experimentally low (about 20%) yield of the anilino radicals.

## Conclusions

The present study clearly highlights the differences of the reaction channel paths involved in FET and one-electron oxidation reactions. The observed differences could be due to the molecular oscillations in the molecule that subsequently govern the product of chemical reaction. In the case of *o*-tolidine and benzidine, the radical cation is probably resonance stabilized. This could be the reason for its long life time. In benzidine and *o*-tolidine, because of the conjugated ring, it appears that distortion of the molecular geometry at the heteroatom bond does not lead to a significant destabilization of the radical cation. This results in a low yield of the deprotonated radical.

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