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# Photoinduced Oxygen Uptake of Diphenylamines in Solution and Their Ring Closure Revisited

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The photochemistry of diphenylamine (DPA), *N*-methyldiphenylamine (MeDPA), and triphenylamine (TPA) was studied in solution at room temperature. The major photoprocess was cyclization, and the quantum yields were $\Phi_{cyc} = 0.02-0.6$. The photoinduced oxygen uptake/consumption, studied in air-saturated acetonitrile-water or methanol-water, was efficient. Three subsequent transients, the polyphenylamine triplet state, the 4a,4b-dihydrocarbazole triplet state, and its labile ground state, were accessible by laser flash photolysis prior to carbazole formation. Their yields were determined and compared with the $\Phi_{cyc}$ values. Oxygen can reduce or enhance $\Phi_{cyc}$ since one step, quenching of the polyphenylamine triplet state, blocks cyclization and one step, scavenging of dihydrocarbazole, favors cyclization since it competes successfully with the back-reaction to the substrate. The former is dominant for DPA in solvents with low and high polarity and the latter is dominant for MeDPA preferentially in nonpolar solvents as well as for TPA in all solvents.

## Introduction

Polyphenylamines, such as diphenylamine (DPA), *N*-methyldiphenylamine (MeDPA), and triphenylamine (TPA) are photochemically accessible and thus the subject of intensive studies.[1−19] The main photoreaction is cyclization, which takes place intramolecularly, and the obvious product is the corresponding carbazole (Scheme 1). Polyarylamines show fluorescence, and the quantum yield ($\Phi_f$) is much lower than that of intersystem crossing ($\Phi_{isc}$). For example, MeDPA in nonpolar media has $\Phi_{isc} = 0.86$ and $\Phi_f = 0.04$.[9−12] The ring closure contains a cascade of reactions, and one rather unique property of the polyphenylamines is a deactivation route via consecutive population of the triplet states of both the amine and the dihydrocarbazole, as has been first shown for TPA.[9] A modified triplet state mechanism operates for the photoionization of DPA, when the two pulse method is applied.[16] Time-resolved photoacoustic calorimetry in methanol has supported the pathway via the two triplet states.[18,19]

UV irradiation of DPA yields carbazole in the presence of oxygen and both carbazole and tetrahydrocarbazole in its absence. The photoinduced oxygen uptake in donor−acceptor systems frequently converts oxygen into $H_2O_2$, whereby the hydroperoxyl/superoxide ion radical ($HO_2^\bullet/O_2^{\bullet-}$) is an important intermediate.[20−22] This radical is also formed in the intramolecular photocyclization of 2-benzoylpyridine in an air-saturated solution.[23] The effects of amine structure, oxygen, and nature of the solvent on the quantum yield ($\Phi_{cyc}$) of ring closure are complex. The mechanism for MeDPA in nonpolar media has been intensively studied by Grellmann et al. (Scheme 2): $\Phi_{cyc} = 0.4-0.6$ and $0.01-0.06$ under air and in the absence of oxygen, respectively.[3,4,7−12] The spectral and kinetic properties of *N*-methyl-4a,4b-dihydrocarbazole and *N*-methyltetrahydrocarbazole are well-characterized,[7−12] but the assignment of the observed intermediate had earlier been questioned.[5,6] The photoproducts of parent DPA in methanol are likewise carbazole and tetrahydrocarbazole, albeit the mechanism differs partly.[13] $\Phi_{cyc} = 0.37$ and a triplet lifetime of ca. 1 μs for DPA in oxygen-free methanol indicates that cyclization is a relatively slow process.[13] However, the values for MeDPA and TPA lifetimes in oxygen-free methanol are as short as 20 and 50 ns, respectively.[19] The absence of oxygen yields a low $\Phi_{cyc}$ value also for TPA in nonpolar media.[7] For a better understanding of the relationship between the polyphenylamine structure as a gateway to the function of photoinduced ring closure, further investigation in solvents of different polarities is required.

Here, the photoinduced oxygen uptake/consumption of DPA, MeDPA, and TPA was examined in air-saturated mixtures with water. The reaction of oxygen with the dihydrocarbazoles yielded hydrogen peroxide and carbazoles. Moreover, their photochemistry in solvents of low and high polarity was studied by time-resolved and steady state techniques. This work aims toward a completion of the experimental results in solvents of any polarity and a consistent interpretation. The effects of solvents and oxygen on the quantum yield $\Phi_{cyc}$ of ring closure and the kinetics of the two triplet states and the dihydrocarbazole intermediate are outlined.

## Experimental Procedures

DPA, MeDPA, TPA, and most of the solvents were used as received (EGA, Sigma, Acros). Acetonitrile was Uvasol quality (Merck), methylcyclohexane (MCH) was purified by distillation, and water was from a Millipore (milliQ) system. The absorption spectra were monitored on a UV−vis spectrophotometer (HP, 8453). The molar absorption coefficients of DPA and TPA in cyclohexane were $\epsilon_{282} = 1.7 \times 10^4$ and $\epsilon_{300} = 2.4 \times 10^4$ M$^{-1}$ cm$^{-1}$, respectively.[5] *N*-Methylcarbazole, the stable product of MeDPA, has characteristic peaks at 230, 260, 295, and 343 nm with $\epsilon_{343} = 5.8 \times 10^3$ M$^{-1}$ cm$^{-1}$ in nonpolar media and $4 \times 10^3$ M$^{-1}$ cm$^{-1}$ in ethanol.[9,13] The molar absorption coefficient of carbazole is $\epsilon_{343} = 5.8 \times 10^3$ M$^{-1}$ cm$^{-1}$.[5] Carbazoles can also be generated from aromatic amines electrochemically.[24] For photoconversion, the 254 nm line of a low pressure Hg lamp was used. Alternatively, a 1000 W Xe−Hg lamp and a monochromator were used for irradiation at 270−313 nm. HPLC

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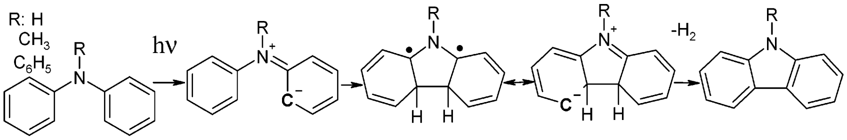
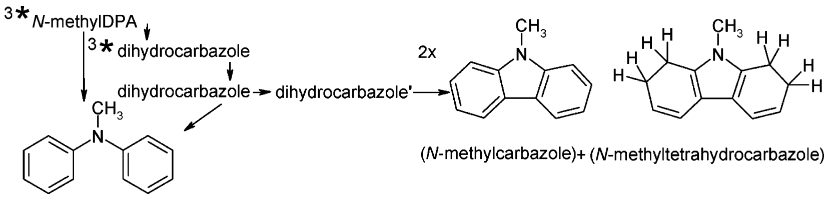
**SCHEME 1**



**SCHEME 2**



analyses were performed on a reversed phase N-5-$C_{18}$ column (0.8 mL $min^{-1}$) with MeOH-water (2:3) as the eluent. The educts versus primary products had retention times (min) of 18.4 versus 17.8, 20.2 versus 19.6, and 22.1 versus 21.2 for DPA, MeDPA, and TPA, respectively. $\Phi_d$ and $\Phi_{cyc}$ values were determined using the uridine actinometer $\Phi = 0.0018$.[25] The photoconversion can also be monitored by fluorescence, as carbazoles have a higher $\Phi_f$ value than DPA derivatives.[26] The excitation spectra of the educt and photoproduct are distinctly different (not shown). The fluorescence, however, was found to be less suited than the absorption method.

The oxygen concentration was measured by a Clark electrode (Hansatech). The relative yield of oxygen consumption was determined from the slope of the oxygen concentration versus irradiation time.[22] The oxygen concentration in aqueous solution prior to photolysis was 0.27 mM, and the signal increased only by ca. 20% when mixed with acetonitrile or methanol (1:1 vol). The aqueous solutions were unbuffered. An excimer laser (Lambda Physik, EMG 201 MSC, pulse width of 20 ns, energy <100 mJ) was used for excitation at 308 nm. Alternatively, $\lambda_{exc} = 248$ nm was used, but for the sake of consistency, the (more or less similar) data are not presented. The absorption signals were measured with two digitizers (Tektronix 7912AD and 390AD), and an Archimedes 440 computer for data handling was used as in previous work.[22] The yields were measured using optically matched solutions, and the experimental error was ±15%. All measurements refer to 24 °C.

## Results and Discussion

**Photoconversion.** The UV spectra of DPA, MeDPA, and TPA exhibited characteristic changes upon continuous UV irradiation. Examples for irradiation at 280 nm of MeDPA in air- and argon-saturated acetonitrile are shown in Figure 1. The absorbance of the MeDPA educt at 280 nm decreased upon irradiation, whereas the absorbances at 260 or 300 nm increased markedly. The quantum yields $\Phi_d$ of substrate decomposition and $\Phi_{cyc}$ of conversion into the major product were determined from plots of the UV changes (Figure 2) or plots of the HPLC chromatogram signals as a function of the time of irradiation at 280 nm. The $\Phi_{cyc}$ values were found to be equal to $\Phi_d$ in various cases. This demonstrates the minor role of side products. Nevertheless, prolonged irradiation can cause degradation. Alternatively, irradiation at 313 nm (Figure 3a) or 254 nm could be used, but the results are limited to a low conversion due to large absorption of the carbazole photoproduct at these wavelengths. On the other hand, photoconversion can be achieved by 308 nm pulses (Figure 3b). Thus, an irradiation source of low intensity is not a necessary precondition.

The $\Phi_{cyc}$ values for DPA in air-saturated cyclohexane, benzene, acetonitrile, and methanol-water are small but much larger under argon (Table 1). This is in contrast to the cases of MeDPA and TPA, where $\Phi_{cyc}$ is generally lower under argon than under air. $\Phi_{cyc}$ <0.01 was found only for MeDPA in MCH, cyclohexane, or *n*-hexane in the absence of oxygen.[5,6,9,10] These values are more than 10 times smaller than under air. $\Phi_{cyc}$ values in benzene are reported for the first time, and in other solvents, only a few were found in the literature.

**Reaction Scheme in the Absence of Oxygen.** Polyphenylamines show fluorescence (e.g., $\Phi_f = 0.04$) for MeDPA in nonpolar solvents and acetonitrile.[9,17] Decay of the excited singlet state ($^{1*}$A) leads via intersystem crossing to the lowest triplet state ($^{3*}$A) (Scheme 3). This points to a moderate lifetime of the excited singlet state. The $^{3*}$A state (lifetime: $\tau^{A}_{T}$) decays by intersystem crossing, step 1, or by ring closure, step 2. Under appropriate conditions, the cyclization occurs via two consecutively populated triplet states.[11] The second intermediate is the triplet state of 4a,4b-dihydrocarbazole ($^{3*}$B), which decays into its ground state $B_0$, step 3. The triplet lifetimes of DPA, MeDPA, and TPA in methanol are $\tau^{B}_{T} = 1.3$, 0.6, and 0.4 $\mu$s, respectively, and the level of $^{3*}$B is 14−15 kcal $mol^{-1}$ below that of $^{3*}$A and ca. 5 kcal $mol^{-1}$ above $B_0$.[19]

Decay of the labile $B_0$ takes place by reactions 4−6. First-order kinetics is due to sequences 4 and 5 into carbazole plus tetrahydrocarbazole (C-$H_4$) or by back-reaction 6 into the educt, respectively. Reaction 4 leads to a modified dihydrocarbazole (C′-$H_2$), which has no detectable absorption. Reaction 5 from C′-$H_2$ to carbazole and C-$H_4$ has been suggested for MeDPA in nonpolar solvents.[11−13] Another possibility could be a decay of $B_0$ via reaction 4′. In fact, such a second-order decay component has been reported,[16] but this was found to take place only at high $B_0$ concentrations and changes into a first-order law when the laser intensity is lowered.

**Reactions in the Presence of Air.** Oxygen interferes threefold: it quenches $^{3*}$A, $^{3*}$B, and $B_0$ (reactions 7−9, respectively (Scheme 3)).[10,12] Reaction 7 is the usual triplet quenching and may produce singlet molecular oxygen. Reaction 8 has been observed for TPA, where the lifetime at room temperature is largest.[7,12] In principle, the quenching of $^{3*}$B by oxygen could also directly yield carbazole and $H_2O_2$. This does not change the overall pattern but can be excluded for MeDPA since the yield of $B_0$ changes less than twice, whereas $\tau^{B}_{T}$ changes 10-fold on going from air to argon (Tables 2 and 3). In reaction 9, hydrogen peroxide is the second product. It may be formed in two dehydrogention steps: the first yields superoxide $O_2^{\bullet -}$ and the corresponding carbazole radical and the second converts both into $H_2O_2$ and carbazole. A corresponding $O_2$-mediated sequence

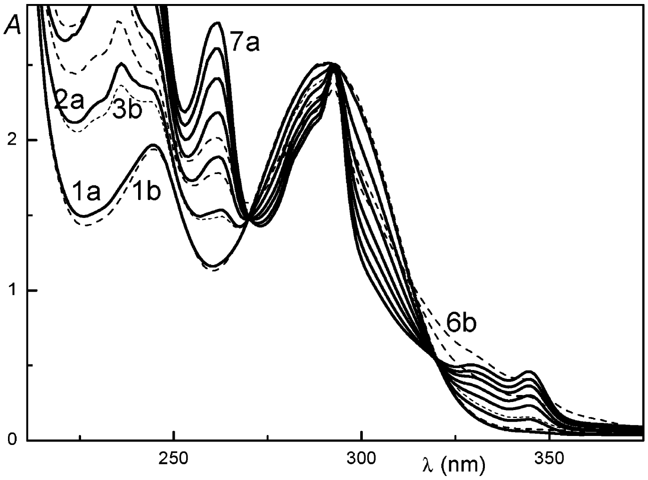


**Figure 1.** Absorption spectra of MeDPA in air-saturated (a: solid lines) and argon-saturated (b: dashed lines) acetonitrile after irradiation times of 0, 10, 20, 30, 40, 50, and 60 s (1−7, respectively) at $\lambda_{irr} = 280$ nm.

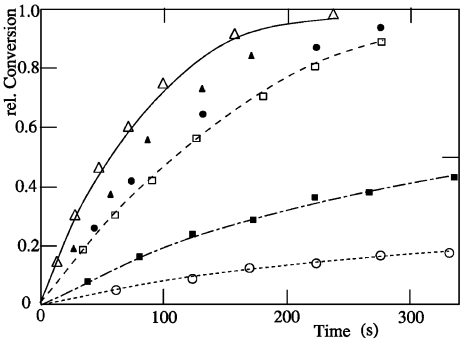


**Figure 2.** Conversion using absorbance as a function of the irradiation time for DPA (circles), MeDPA (triangles), and TPA (squares) in argon-saturated (solid symbols) and air-saturated (open symbols) acetonitrile, $\lambda_{irr} = 280$ nm.

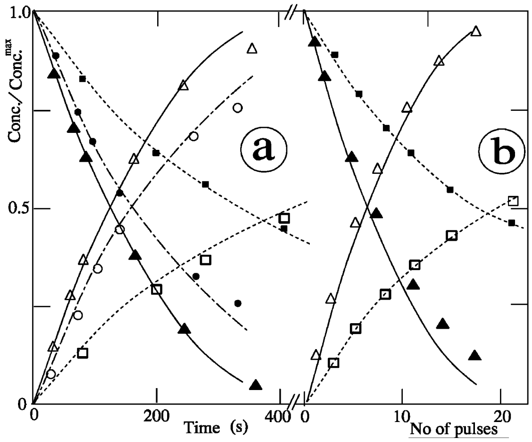


**Figure 3.** Conversion using relative concentrations as a function of (a) the time of irradiation at 313 nm and (b) the number of 308 nm pulses (10 mJ) for DPA (circles), MeDPA (triangles), and TPA (squares) in argon-saturated acetonitrile; solid and open symbols refer to substrate and major product, respectively.

**TABLE 1: Quantum Yield $\Phi_{cyc}$ of Cyclization**[a]

| | DPA | | MeDPA | | TPA | |
|---|---|---|---|---|---|---|
| solvent | air | argon | air | argon | air | argon |
| cyclohexane | 0.03 | 0.30 | 0.60 | 0.01 | 0.23 | 0.04 |
| benzene | 0.03 | 0.25 | 0.52 | 0.12 | 0.22 | 0.08 |
| acetonitrile | 0.04 | 0.22, 0.2[b] | 0.45 | 0.28 | 0.20 | 0.09 |
| MeOH-water[c] | 0.05 | 0.28 | 0.48 | 0.22 | 0.18 | 0.04 |

[a] Using $\lambda_{irr} = 280$ nm. [b] Ethanol. [c] 1:1 vol at pH 7.

**TABLE 2: Yield and Lifetime of the Triplet States**[a]

| compound | solvent | gas | $\Delta A_{510}$ | $\Delta A_{430}$ | $\tau^{A}_{T}$ ($\mu$s) | $\tau^{B}_{T}$ ($\mu$s) |
|---|---|---|---|---|---|---|
| DPA | cyclohexane | air | 0.3 | *b* | 0.02 | |
| | | argon | 0.3 | *b* | 1 | |
| | acetonitrile | air | 0.4 | *b* | 0.08 | |
| | | argon | 0.3 | *b* | 1 | |
| MeDPA | cyclohexane | air | *b* | 0.2 | <0.01 | 0.1 |
| | | argon | *b* | 0.2 | <0.01 | 1 |
| | acetonitrile | air | *b* | 0.18 | <0.01 | 0.05 |
| | | argon | *b* | 0.22 | 0.02 | 0.6 |
| TPA | cyclohexane | air | 0.2 | *b* | 0.02 | 0.08 |
| | | argon | 0.3 | 0.3 | 0.05 | 0.5 |
| | acetonitrile | air | 0.12 | *b* | 0.02 | 0.12 |
| | | argon | 0.25 | 0.25 | 0.05 | 0.5 |

[a] Using $\Delta A_{610} = 1$ for MeDPA in air-saturated cyclohexane as a reference for $\Delta A_{430}$ and $\Delta A_{510}$ and $\lambda_{exc} = 308$ nm. [b] Not measurable within 10 ns.

**TABLE 3: Yield of Ground State 4a,4b-Dihydrocarbazole ($B_0$) Formation**[a]

| | DPA | | MeDPA | | TPA | |
|---|---|---|---|---|---|---|
| solvent | air | argon | air | argon | air | argon |
| cyclohexane | 0.03 | 0.26 | 0.62 | 1.0 | 0.20 | 0.90 |
| benzene | 0.03 | 0.29 | 0.56 | 0.90 | 0.25 | 0.85 |
| acetonitrile | 0.03 | 0.26 | 0.60 | 0.85 | 0.22 | 0.75 |
| MeOH-water[b] | 0.05 | 0.25 | 0.55 | 0.80 | 0.18 | 0.65 |

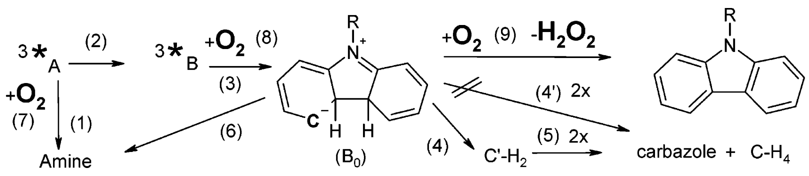
[a] $\Delta A_{610}/\Delta A_{610}^{max}$ using MeDPA in air-saturated cyclohexane as reference and $\lambda_{exc} = 308$ nm. [b] 1:1 vol at pH 7.

has been suggested by Bortolus et al.[23] for closure into the pyrrole ring.

Examples of the photoconversion of oxygen in $H_2O_2$ are shown in Figure 4. The oxygen concentration decreases with irradiation time, and the quantum yield was obtained from the slope of the linear dependence. $\Phi_{O_2} = 0.5$ for MeDPA in air-saturated acetonitrile-water or methanol-water, 1:1. For DPA and TPA, $\Phi_{O_2} = 0.06$ and 0.22, respectively, and for diclofenac (2-(2,6-dichloroanilino)phenylacetic acid), which is structurally similar to DPA, no oxygen uptake was found here or previously.[27] The changes to higher $\Phi_{O_2}$ values in the order DPA, TPA, and MeDPA are in full agreement with $\Phi_{cyc}$ values in air-saturated methanol-water of 0.05, 0.18, and 0.5, respectively (Table 1).

**Transients upon Pulsed Excitation.** Excitation of the amines by 308 nm laser pulses produces the $^{3*}$A state, which has a maximum around 520 nm, and the dihydrocarbazole ground-state $B_0$, which has a maximum around 610 nm and a minor band in the 330−400 nm range. This is shown in Figures 5−7 for DPA, MeDPA, and TPA, respectively. The *T*−*T* absorption

**SCHEME 3**



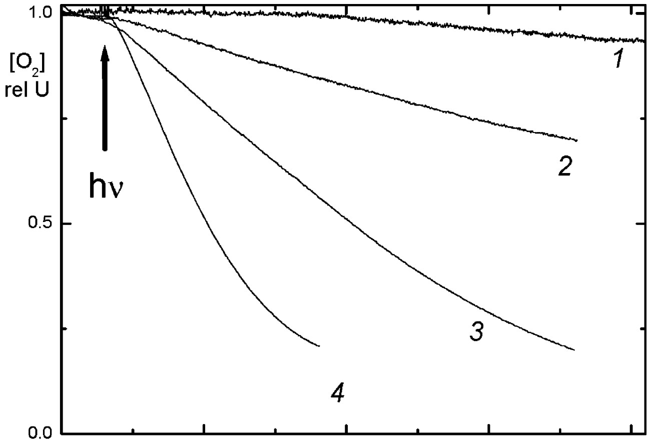


**Figure 4.** Plots of the oxygen concentration as a function of irradiation time, indicated by an arrow, $\lambda_{irr} = 280$ nm, for diclofenac (curve 1), DPA (curve 2), TPA (curve 3), and MeDPA (curve 4) in 1:1 mixtures of acetonitrile with water, pH 7.

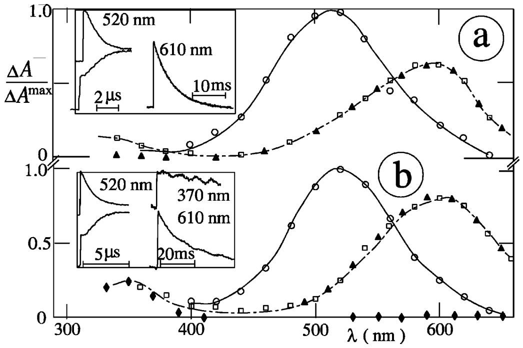


**Figure 5.** Transient absorption spectra of DPA in argon-saturated (a) cyclohexane and (b) acetonitrile at 20 ns (○), 10 $\mu$s (□), 1 ms (▲), and 0.1 s (◆) after the 308 nm pulse; insets: kinetics at 370, 520, and 610 nm.

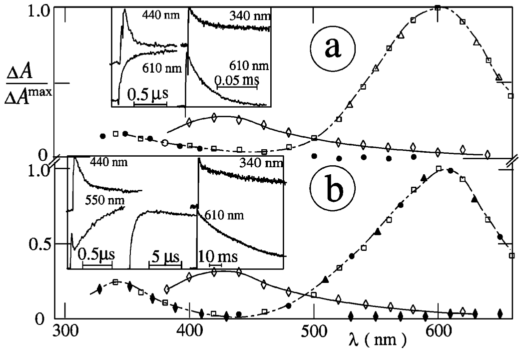


**Figure 6.** Transient absorption spectra of MeDPA in (a) air-saturated and (b) argon-saturated acetonitrile at 0.1 $\mu$s (◇), 1 $\mu$s (△), 10 $\mu$s (□), 0.1 ms (●), 1 ms (▲), and 0.1 s (◆) after the 308 nm pulse; insets: kinetics at 340, 440, 550, and 610 nm.

maximum of $^{3*}$A of DPA in methanol is at 530 nm, $\epsilon_{530} = 1.5 \times 10^4$ M$^{-1}$ cm$^{-1}$.[13] The molar absorption coefficients for $^{3*}$A of DPA are (1−3) × $10^4$ in various solvents, and the $\epsilon_{430}$ value for $^{3*}$B is slightly lower.[13] For MeDPA in MCH, values at the maxima of $\epsilon_{540} = 2.6 \times 10^4$ and $\epsilon_{610} = 2.1 \times 10^4$ M$^{-1}$ cm$^{-1}$ are known for $^{3*}$A and B$_0$, respectively.[9,12]

In most cases, the lifetime of the $^{3*}$A state is rather short even if oxygen is excluded (e.g., $\tau^{A}_{T} \leq 50$ ns (Table 2)); only for DPA in the absence of oxygen is $\tau^{A}_{T} = 1$ $\mu$s. The spectra in Figure 5b of DPA in acetonitrile resemble those in methanol.[15]

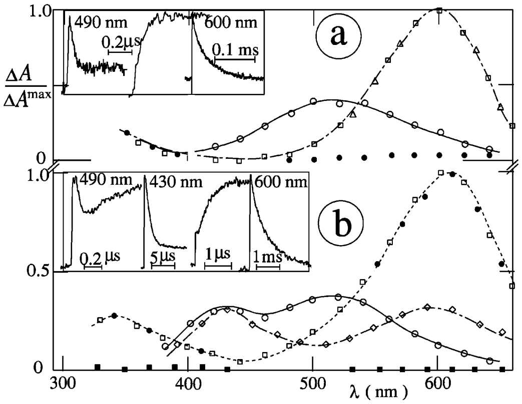


**Figure 7.** Transient absorption spectra of TPA in (a) air-saturated and (b) argon-saturated acetonitrile at 20 ns (○), 0.1 $\mu$s (◇), 1 $\mu$s (△), 10 $\mu$s (□), 0.1 ms (●), and 10 ms (■) after the 308 nm pulse; insets: kinetics at 430, 490, and 600 nm.

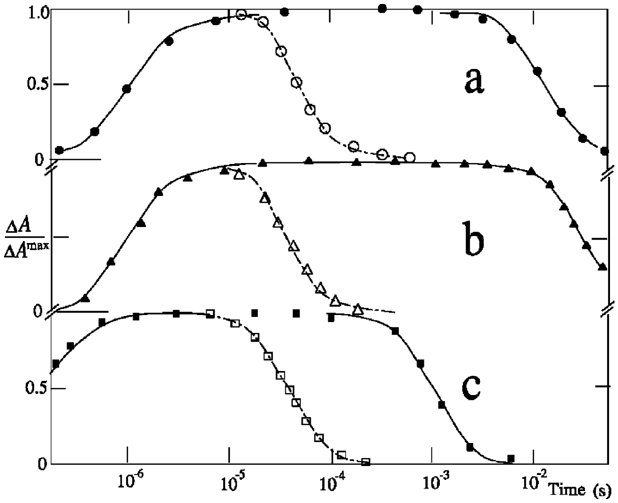


**Figure 8.** Semilogarithmic plots of the time dependence of the transient absorption at 610 nm after the 308 nm pulse for (a) DPA, (b) MeDPA, and (c) TPA in air-saturated (open symbols) and argon-saturated (solid symbols) acetonitrile.

An interesting detail is the observation of the $^{3*}$B triplet state, which has a maximum around 430 nm.[7,9−13] In oxygen-free methanol, $\tau^{B}_{T} = 1.6$, 0.6, and 0.4 $\mu$s has been reported for DPA, MeDPA, and TPA, respectively.[19] The subsequent species with a maximum at 610 nm is due to the stronger absorbing ground-state B$_0$. For TPA in argon-saturated acetonitrile (Figure 7b) or cyclohexane,[7] the $^{3*}$B state (lifetime: $\tau^{B}_{T}$) is formed from the $^{3*}$A state and decays into B$_0$. The $^{3*}$A triplet state in the case of MeDPA was observed around 550 nm (Figure 6b), where fluorescence does not interfere under our conditions, in contrast to shorter wavelengths.

The kinetics of formation and decay of B$_0$ of DPA, MeDPA, and TPA in air- and argon-saturated acetonitrile is shown in Figures 8a−c, respectively. The yield and decay of B$_0$ depend strongly on both the oxygen concentration and the structure. Examples of the intensity dependence of the yield of B$_0$ under optically matched conditions are shown in Figure 9, and the values in four selected solvents are compiled in Table 3. The yield of B$_0$ in an air-saturated solution should be proportional to $\Phi_{cyc}$ since step 9 converts each molecule in the B$_0$ state into carbazole (see Scheme 3). In fact, $\Phi_{cyc}$ and the normalized yield of B$_0$ in Tables 1 and 3 are comparable. This, however, is only fulfilled in air-saturated solution. Oxygen also reacts with the $^{3*}$A and the $^{3*}$B states. Examples in air- and argon-saturated

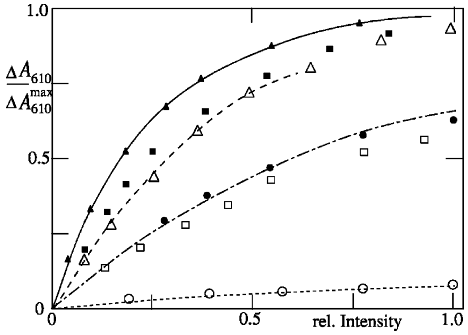


**Figure 9.** Plots of the transient absorption at 610 nm and after ca. 10 μs as a function of the intensity of the 308 nm pulse for DPA (circles), MeDPA (triangles), and TPA (squares) in argon-saturated (solid symbols) and air-saturated (open symbols) acetonitrile.

**TABLE 4: Lifetime $\tau^{B}_{0}$ of Ground State 4a,4b-Dihydrocarbazole (in ms)[a]**

| | DPA | | MeDPA | | TPA | |
|---|---|---|---|---|---|---|
| solvent | air | argon | air | argon | air | argon |
| cyclohexane | 0.07 | 6 | 0.4 | 20[b] | 0.03 | 0.9 |
| benzene | 0.06 | 3 | 0.06 | 30[b] | 0.06 | 0.7 |
| acetonitrile | 0.05 | 12[b] | 0.05 | 25[b] | 0.04 | 1.1 |
| MeOH-water[c] | 0.1 | 2 | 0.14 | 30[b] | 0.06 | 0.8 |

[a] Using MeDPA in air-saturated cyclohexane as reference and $\lambda_{exc}$ = 308 nm. [b] Second-order decay component at high laser intensity. [c] 1:1 vol at pH 7.

acetonitrile are shown for MeDPA (Figure 6a,b) and TPA (Figure 7a,b). The rate constant of quenching the triplet of MeDPA in MCH is $k_7 = 3 \times 10^{10}$ $M^{-1}$ $s^{-1}$.[12] The reactivity is lower for DPA in acetonitrile-water (1:1), $k_7 = 4 \times 10^{9}$ $M^{-1}$ $s^{-1}$.[16] A consequence of the first quenching step 8 is a lower yield ($\Delta A_{610}/\Delta A_{610}^{max}$) of $B_0$ (see Table 3).

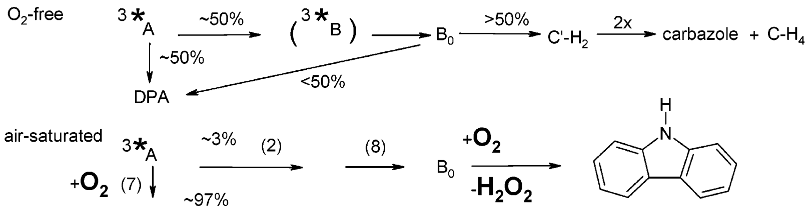
The decay of $B_0$ in the presence of traces of oxygen follows first-order kinetics throughout. The lifetimes ($\tau^{B}_{0}$) are compiled in Table 4. For TPA and MeDPA in oxygen-free hexane, $\tau^{B}_{0}$ = 0.5 and 16 ms, respectively.[2] A consequence of the last quenching step 9 is $\tau^{B}_{0} \leq 0.1$ ms under air versus a much longer lifetime (or half-life) under argon. For a case with $\tau^{B}_{0} = 0.1$ ms and an oxygen concentration of 2.0 mM, $k_9 = 5 \times 10^{6}$ $M^{-1}$ $s^{-1}$ can be estimated, which is close to the value for MeDPA in MCH.[10] It should be noted that in $O_2$-free solutions, $\tau^{B}_{0}$ and $\Phi_{cyc}$ are not correlated since the latter is only large when $k_6$ is small with respect to $k_4$ and/or $k_5[B_0]$. It is also worth mentioning that the zwitterionic nature of $B_0$ has been confirmed by calculations, showing a positive partial charge at the nitrogen atom.[19] A similar zwitterionic intermediate with a maximum around 600 nm and first-order decay kinetics has been reported for the cyclization of aryl vinyl ethers.[28]

**Photoprocesses of DPA.** For parent DPA, $\Phi_{isc} = 0.4$ in cyclohexane and 0.6−0.9 in methanol.[5,13,19] The proposed pathway at room temperature involves the DPA triplet state and $B_0$ (see Scheme 4). $\Phi_{cyc} = 0.1$ in argon-saturated nonpolar solvents, and in methanol, $\Phi_{cyc} = 0.4$[15,19] rather than 0.1.[1] No indication of the $^{3*}B$ triplet state could be observed in this work. Nevertheless, a short-lived $^{3*}B$ state is likely, and conversion of $^{3*}A$ via $^{3*}B$ to $B_0$ has indeed been observed at low temperatures.[9] The triplet lifetime is relatively long when oxygen is excluded (Figure 5a and Table 2). $\Phi_{cyc}$ is well below unity, and $1 - \Phi_f - \Phi_{cyc} = 0.3{-}0.5$. This could be ascribed to back-step 6, which however, does not block the bond cleavage since the yield of $B_0$ is similar to $\Phi_{cyc}$ (Tables 1 and 3). A back-reaction prior to $B_0$ formation is therefore proposed. This step prior to ring closure is isc from $^{3*}A$,[13] whereas isc from $^{3*}B$ into the DPA educt is also possible but less likely.

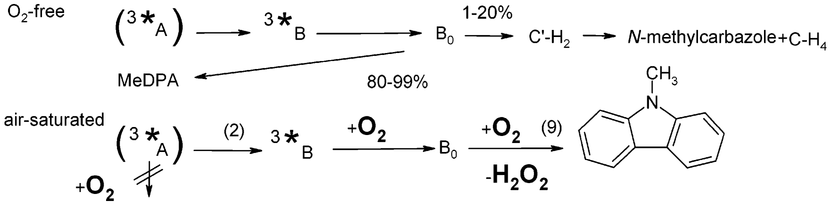
For DPA in air-saturated solvents of low and large polarity, quenching step 7 is the obvious reason for the low yield of $B_0$ of 0.02−0.05 (Table 3), which is in agreement with the low $\Phi_{cyc}$ value (Table 1). The efficiency of step 7 only for DPA is due to the previously mentioned long lifetime of the $^{3*}A$ triplet state of ca. 1 μs in the absence of oxygen (Table 2). Under air, less than 5% of the excited molecules can populate $B_0$ via reactions 2 and 8.

**Photoprocesses of MeDPA.** The proposed pathway involves the triplet and ground state of $B_0$ (see Scheme 5). For MeDPA $\Phi_{isc} = 0.9$ in solvents of low and large polarity.[5,19] The MeDPA/MCH/oxygen-free case has kinetically been characterized by $k_6 = 21{-}35$ $s^{-1}$ and $k_4 = 1.2$ $s^{-1}$.[10] The $^{3*}A$ triplet state has been observed at low temperatures, and $\tau^{A}_{T} = 20$ ns was extrapolated at room temperature.[18] $B_0$ is efficiently populated, but the photoconversion is inefficient since the back-reaction 6 is 20−30 times faster than step 4. Moreover, the product analysis of *N*-methylcarbazole is known in great detail.[11,12] The modified dihydrocarbazole C′-$H_2$ is lacking a zwitterionic structure and has therefore a much lower absorbance. Concerning tetrahydrocarbazoles, it should be recalled that the most stable C-$H_4$ structure (after rearrangement) has been identified by NMR.[11,12] The yield of $B_0$ is also high for MeDPA in polar solvents (Figure 6), but the $k_6/k_4$ ratio is smaller. The strong increase to $\Phi_{cyc}$ =

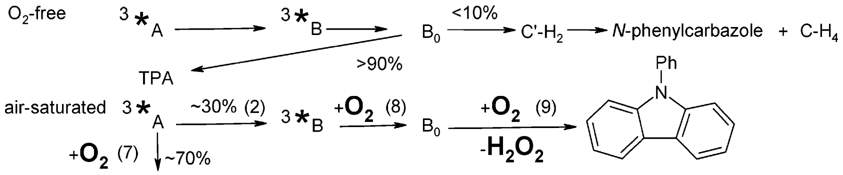
**SCHEME 4**



**SCHEME 5**



**SCHEME 6**



0.12 in benzene demonstrates that the unique case $\Phi_{cyc} = 0$ for MeDPA in nonpolar solvents is due to the large $k_6/k_4$ ratio. Thus, in any other solvent, the difference in $\Phi_{cyc}$ due to *N*-substitution is smaller.

The MeDPA/MCH/oxygen case has $k_9 = 8 \times 10^5$ M$^{-1}$ s$^{-1}$, and the plot of $\Phi_{cyc}$ versus the oxygen concentration has a maximum.[10] Quenching step 8 is not efficient in solvents of medium and large polarity, and oxygen has therefore only a small effect on the yield of $B_0$ (Table 2). The oxygen effect on $\Phi_{cyc}$ for MeDPA is a result of the low $k_6$ versus $k_9[O_2] = 1.5 \times 10^3$ s$^{-1}$ value in air-saturated solvents.

**Photoprocesses of TPA.** The sequence from $^{3*}$A to $^{3*}$B and via $B_0$ to *N*-phenylcarbazole is illustrated in Scheme 6. TPA constitutes a case that can be called the general mechanism because all intermediates are detectable. Moreover, $\Phi_{isc} = 0.9-0.98$ in solvents of low and large polarity.[15,19] A consequence of the presented data is a larger absorption coefficient for $B_0$, and a lower limit of $\epsilon_{610} = 3 \times 10^4$ M$^{-1}$ cm$^{-1}$ is now postulated. This is based on the spectra in Figure 7b, $\epsilon_{500} = 1.5 \times 10^4$ M$^{-1}$ cm$^{-1}$, and 75% yield of $B_0$.

Decay of $B_0$ under argon mainly leads back to the TPA educt since the yield of $B_0$ is close to unity and $\Phi_{cyc}$ is close to zero (Tables 1 and 3). The triplet lifetimes are $\tau^A_T = 50$ ns and $\tau^B_T = 500$ ns (Table 2). Thus, they are not too short, and quenching steps 7 and 8 are moderate but cannot be ignored. Step 7 reduces both the yield of $B_0$ and the yield of $\Phi_{cyc}$ and has a contribution of 60−80% with respect to step 2.

## Conclusion

The photocyclization of three polyphenylamines was reexamined based on yields that were obtained by time-resolved and steady state photochemical means. Carbazole was the major photoproduct, and the other products under argon and air were the corresponding tetrahydrocarbazole and $H_2O_2$, respectively. The pathway led from the substrate triplet via the dihydrocarbazole triplet to the ground-state dihydrocarbazole ($B_0$) and then to the carbazole/tetrahydrocarbazole products. The conditions for changes in $\Phi_{cyc}$ by structure and environmental factors were described. The triplet lifetime is longest for parent DPA, and quenching of this triplet state by oxygen blocks the route via the second triplet state to $B_0$ and further into carbazole. In contrast, for MeDPA, the route to $B_0$ is not greatly affected by oxygen, and the yield of *N*-methylcarbazole is generally high and only low for the special oxygen-free case in nonpolar media, where the back-route into MeDPA is too fast. The larger $\Phi_{cyc}$ value for TPA under air than under argon is due to quenching by oxygen of the decay of $B_0$, which compensates favorably for triplet quenching into TPA. The proposed mechanism is in agreement with the general properties of the photorelaxation of these specific amines.

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