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Energetics of photocyclization of polyphenylamines and assignment of the intermediate: A time-resolved photoacoustic calorimetric study

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The photocyclization reactions of diphenylamine (DPA), N-methyldiphenylamine (MDPA) and triphenylamine (TPA) have been studied in methanol solvent through nanosecond/microsecond flash photolysis and time-resolved photoacoustic calorimetry (TRPAC). It is confirmed for all the amines that the long-lived dihydrocarbazole intermediate (^{1}XDHC^0) is formed through a cascade of processes. However, DPA behaves differently from the other two members of the series so far as the rates of the individual processes are concerned. The quantum yield of triplet formation and the quantum yield of the photocyclization of the amine triplet have been estimated for the DPA system. In conjugation with the experiments, theoretical calculations, employing AM1-SCI method, have been performed to propose a structure for the intermediate. For all the amines, the intermediate has been proposed to be of zwitterionic nature in the ground state. The enthalpies of formation of the intermediate (^{1}XDHC^0) from MDPA and TPA have been determined experimentally to be around 51 kcal mol^{-1} and the values agree well with the calculated ones.

Introduction

Since the works of Parker and Barnes,[1] the oxidative photo-cyclization of arylamine/s to carbazole/s has been the subject of extensive research.[2–14] Upon irradiation, diphenylamine (DPA), N-methyldiphenylamine (MDPA) and triphenylamine (TPA) undergo an oxidative photocyclization reaction leading to the formation of the corresponding carbazoles as the final product. The most challenging part of the studies of these reactions is to find a plausible reaction mechanism for the complex multi-step reactions and to assign the nature and structure of the long-lived intermediates (XDHC), unsubstituted or substituted dihydrocarbazole, depending on the amine. The authors have employed mostly the flash photolytic technique to identify the different intermediates and to determine the rates of the individual reactions through which the total photoprocess proceeds. Although the multi-step reaction mechanism as proposed by Rahn et al.[3] is accepted, in general, as the most plausible pathway for the photocyclization process, there is still a lack of completeness in the studies, particularly, in respect of the energetics of the reactions. It has been observed that the photophysical parameters of DPA differ remarkably from those of MDPA and TPA, leading to a marked difference in the rate constants of the individual steps of the photocyclization reaction for DPA compared with those of the other two members of the series. So far as the energetics of the reaction is concerned, we have only two reports in the literature, one from Suzuki et al. for DPA using a time-resolved thermal lensing (TRTL) technique[11] and the other from our group for TPA using time-resolved photoacoustic calorimetry (TRPAC).[13]

There is a long-standing controversy regarding the nature of the long-lived intermediate that has a typical broad T–T absorption band at around 610 nm. While Suzuki et al. proposed a biradical structure for it in its ground state,[11] Grell-mann et al. proposed a zwitterionic structure, although they

have not ruled out the possibility of the biradical structure.[4–7] Again, Shizuka et al. proposed that the "610 nm" transient differs from the intermediate ^{1}XDHC^0 for DPA.[9,10] Only recently,[13] we have established experimentally that, for TPA, the long-lived intermediate is not a biradical. From a comparison of the experimental and the calculated parameters of TPA, we have further established that the intermediate is of zwitterionic character with a partial positive charge on the nitrogen atom. In this report, we intend to present comprehensively our experimental and theoretical results on all three members of the series. It is noted that MDPA and TPA behave very similarly with regard to their reactivities. However, DPA differs in terms of reaction rates and reaction quantum yields.

Experimental

DPA, MDPA and TPA were of the best quality products available from Aldrich. DPA and TPA were purified by vacuum sublimation followed by recrystallization from ethanol. MDPA was used as received after checking its purity spectroscopically. Spectroscopic grade methanol (Merck) was used as received. 2-Hydroxybenzophenone (HBP, Aldrich) was used as a reference for the TRPAC experiments as before.[13]

A Shimadzu UV-2100 spectrophotometer and a Spex Flu-orolog 2 spectrofluorimeter were used for the absorption and fluorescence measurements respectively. Although reported elsewhere,[13] we will reproduce the main points regarding the instrumentation. This is particularly important since there are some modifications for the DPA system.

The flash photolysis set-up comprises a Spectra Physics Quanta-Ray GCR-130 Nd-YAG laser, an Applied Photo-physics LKS 60 laser flash photolysis spectrometer and a Hewlett-Packard Infinium Oscilloscope (500 MHz, 1 Gsa s^{-1}). For MDPA and TPA, the samples were excited with the

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third harmonic (355 nm, 8 ns FWHM) of the laser. Since there is hardly any absorption of DPA at 355 nm, we used the fourth harmonic (266 nm) of the laser. The monitoring light was produced by a 150 W pulsed Xe lamp. The detection of the transient species in the range 300–650 nm was made with a Hamamatsu photomultiplier (model 1P-28). The sample solutions were prepared with absorbance within 0.1–0.2 at the excitation wavelength and were degassed with dry nitrogen prior to their use in the flash experiments.

The photoacoustic calorimetry apparatus follows the front-face irradiation design described elsewhere.[13–15] The solutions were pumped through a 0.11 mm thick cell at a flow rate of 1 mL min^{-1} with an SSI chromatography pump (model 300) and irradiated with an unfocussed (area of the laser beam at the cell surface being ≈ 0.5 cm^2) N$_2$ laser (PL 2300 from PTI) working at a frequency of 2 Hz. The laser energy was a little less than 1 mJ pulse^{-1}. The acoustic waves generated by the non-radiative processes following light absorption in the cell were detected with a high frequency Panametrics transducer, preamplified with a Panametrics ultrasonic preamplifier (model 5676), captured by the transient recorder (Tektronix DSA 601) and transferred to a PC for data analysis. For MDPA and TPA we used a 2.25 MHz transducer and for DPA, because of the slow reaction rates, we used a 0.5 MHz transducer. For each of the sample, reference and pure solvent an average of 100 acoustic waves were collected. Four sets of averaged waves for each of the sample, reference and solvent were used for data analysis at a given laser intensity, and four laser intensities were employed in each experiment. The different laser intensities used in the experiment were obtained by interposing filters with transmissions in the range 30 to 100%. As oxygen was found to have a strong effect on the PAC signal, the experiments were performed under an atmosphere of constant purging with solvent-saturated N$_2$. Before going through the TRPAC we confirmed that the PAC signal was linear with the concentration of the sample, at least up to a concentration of the solution with absorbance = 0.3 (correlation coefficient $\geqslant 0.99$). However, for the TRPAC experiments we used sample solutions with absorbance $\simeq 0.1$. The absorbances of the reference solutions were the same as those of the sample solutions within the limit of the experimental error.

Although, less precise than *ab initio* calculations involving extended basis sets with extensive configuration interaction (CI), the semi-empirical molecular orbital methods have already established their utility in explaining the structures, energetics and reactivities of different molecular systems in different electronic states. These methods are particularly useful for large molecular systems. The methods provide acceptable approximations to give results quite close to the experimental findings.[13,16–20] In the present calculations, we have used the commercial package, Hyperchem 5.01 (Hypercube Inc., Canada). The energies of the various electronic states of the different species (the amines and different possible structures of the intermediate, ^{1}XDHC^0) have been calculated for the optimized structures using the AM1-SCI method.

Results and discussion

Flash photolysis

The flash photolysis and the TRPAC experiments substantiate the following scheme (Scheme 1) as proposed by Rahn *et al.*[3] Results of our flash photolysis experiments on the amines in methanol corroborate the literature data in general with some exceptions for DPA in terms of the reaction rate constants. In general, the photoexcited amine (^{1}A*) forms its triplet (^{3}A*) in the first step (step I). The amine triplet has a broad T–T absorption band with a maximum at around 530 nm. ^{3}A* then forms the triplet of the intermediate (^{3}XDHC*) (step II)
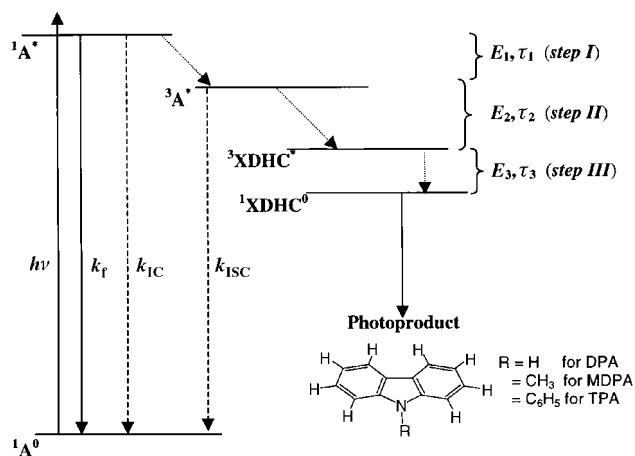
Scheme 1 Different steps in the photoreaction of the amines.

which eventually forms the corresponding long-lived ground state species (^{1}XDHC^0) (step III). ^{3}XDHC* has a T–T absorption band peaking at around 420 nm while ^{1}XDHC^0 has a very broad absorption with a maximum at around 610 nm. In degassed methanolic solution and at ambient temperature, ^{3}A* has lifetimes of 20 and 50 ns for MDPA and TPA respectively. For both these amines, ^{3}XDHC* has a much longer lifetime than that of ^{3}A*. The lifetimes of ^{3}XDHC* have been determined to be 580 and 380 ns respectively for the two amines. It is interesting to note that the rates of the individual processes (step II and step III) are grossly comparable for MDPA and TPA. However, the rate of step II is an order of magnitude faster than step III for these two amine systems. In sharp contrast, these rates are markedly different for DPA under similar experimental conditions. ^{3}DPA* is much longer-lived than ^{3}MDPA* and ^{3}TPA* and now the rates of step II and step III are of the same order of magnitude. This makes the accurate determination of the rate constants for the individual steps difficult. There is also the problem of overlap of the absorption bands responsible for the different species. Being aware of the fact that the 610 nm absorption of ^{1}XDHC^0 is contaminated by the 530 nm absorption band of ^{3}A*, we monitored the growth of the ^{1}XDHC^0 at 640 nm to minimize the ^{3}A* contamination. From our flash photolysis experiment, we determined the lifetimes of ^{3}A* and ^{3}XDHC* for DPA as 800 and 1300 ns respectively in degassed methanol solution. Although, the DPA triplet decay time, as determined by us, is supported by others,[3,11] for the intermediate triplet, the data differs from the literature.[3,11] For all the amines, ^{1}XDHC^0, responsible for the 610 nm absorption, is quite long-lived, in the range of hundreds of microseconds. ^{1}XDHC^0 finally gives the photoproduct, the carbazole derivative. For our TRPAC experiments this species is sufficiently long-lived to serve as the dump. The kinetic data for step II and step III, determined from our flash photolysis experiments, have been summarized in Table 1.

Photoacoustic calorimetry

Quantum yield of triplet amine formation. In TRPAC the acoustic wave, generated by the heat released in the non-radiative processes following electronic excitation, is analysed. The experimental wave (E-wave) of the sample is compared with that of the pressure transducer (T-wave). The T-wave is obtained with the calorimetric reference (in our case, HBP), in the same solvent absorbing the same fraction of light as the sample and releasing it as thermal energy in a time much shorter than the transducer oscillation frequency. The phase and amplitude differences between the T- and E-waves allow simultaneous determination of the thermal energy released by the transients (E$_i$) and their lifetimes (τ_i). Typical background-corrected sample and reference signals for MDPA in methanol are shown in Fig. 1.

Table 1 Rate constants (s^{-1}) of the individual steps for the photoreaction of the amines in degassed methanolic solution measured by flash photolysis

| Reaction | Monitoring process | Rate constants[a]/s^{-1} | | |
		DPA	MDPA	TPA
Step II	Decay of ^{3}A* at 530 nm	1.3×10^6	5.0×10^7	2.0×10^7
	Growth of ^{3}XDHC* at 420 nm	1.2×10^6	5.4×10^7	2.0×10^7
Step III	Decay of ^{3}XDHC* at 420 nm	7.7×10^5	1.7×10^6	2.6×10^6
	Growth of ^{1}XDHC^0 at 610 nm[b]	8.0×10^5	1.9×10^6	2.6×10^6

[a] The data incorporates a 10% error associated with the method. [b] For DPA, the monitoring wavelength was 640 nm to minimize contamination from ^{3}A* absorption.

For MDPA and TPA, we interpret the waves of the N$_2$-saturated samples with three sequential exponents, following the flash photolysis results. The first one for the formation of the ^{3}A* (step I), the second one corresponding to the formation of the intermediate in its triplet state (^{3}XDHC*) (step II) and the third one for its decay to ^{1}XDHC^0 (step III) as described in Scheme 1. Each decay step is described by two parameters: the lifetime of the transient (τ) and the fraction of thermal energy released (ϕ) within that time window. Convolution of the reference waves with the parameters of the kinetic model for the decay of the transient species gives the calculated E-wave. The appropriateness of the kinetic model and its parameters in describing the observed E-wave can be evaluated by the difference (termed as residual) between the amplitudes and phases of the observed (E-) and calculated (C-) waves at each decay time (Fig. 1). For all the amines, the formation of ^{3}A*, following the excitation, is faster than the time resolution of our experimental set-up, and we arbitrarily set the lifetime of the first exponential decay to $\tau_1 = 1$ ns. Smaller values of τ_1 do not change the other parameters in the deconvolution. For MDPA and TPA, the second and third exponential components are set from the τ_2 and τ_3 values as determined from the flash experiments corresponding to step II and step III and given in Table 1. We have also verified the time windows for the individual steps independently by fixing τ_1 and τ_3 and allowing τ_2 to be adjusted by the Marquardt's algorithm employed in the deconvolution process. The τ_2 values that we get for good fits correspond well with the flash results.
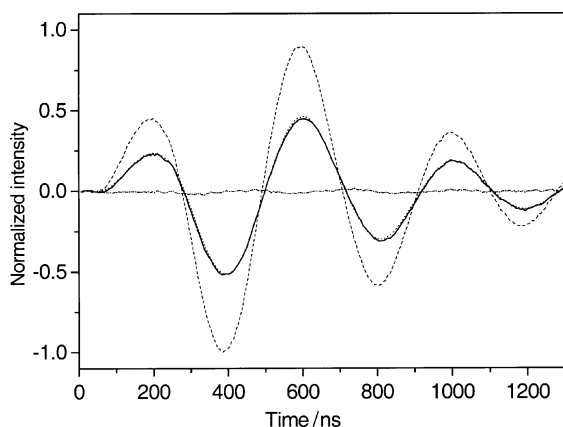

Fig. 1 Typical sample photoacoustic wave (E-wave, ——), reference wave (T-wave, – – –), calculated wave (C-wave, · · ·) and the residual (– · – · –). The calculated wave, C-wave, was obtained with three sequential decays with lifetimes $\tau_1 = 1$ ns, $\tau_2 = 20$ ns and $\tau_3 = 580$ ns. Residual = (C-wave) − (E-wave). For details see text. The E- and T-waves were corrected for the background signal and normalized. The normalization factor is the reciprocal of the largest absolute value of the T-wave. The sample (MDPA), reference (HBP) and solvent (methanol) data were obtained under the following experimental conditions: irradiation at 337 nm of N$_2$-saturated solutions with a filter with 72% transmittance; absorbance of 0.10 for both sample and reference solutions; solution flow rate of 1 mL min^{-1}.

In spite of the fact that the photoreaction (from photoexcited state to ^{1}XDHC^0) of DPA is very similar to those of MDPA and TPA, involving three stages, we could not analyse our TRPAC waves with three exponents. This is probably because of the slowness and also the proximity of the rates of step II and step III. Because of the long lifetime of ^{3}A*, there should be a considerable overlap of the time windows for the thermal energies to evolve from the two individual steps. This makes it hard to resolve the total heat released into the individual components corresponding to the two steps. Considering the thermal energies coming out from these two steps together, we interpreted the photoacoustic waves with two sequential exponents, using the values $\tau_1 = 1.0$ ns and $\tau_2 = 1300$ ns.

The fractions of laser energy released by each system were measured at four laser intensities. The first fraction was found to vary with laser intensity. We plotted this fraction as a function of laser intensity and obtained linear correlation coefficients greater than 0.96. The difference was assigned to transient–transient absorption and was corrected by extrapolating the fraction of energy released to zero laser intensity. From this *laser intensity corrected* value of the first fraction of the released heat, the quantum yields of triplet formation (ϕ_T) were determined for all the amines from eqn. (1).[14]

$$\phi_T = \{(1 - \phi_0)E_{hv} - \phi_F E_S\}/E_T \qquad (1)$$

ϕ_0 being the *laser intensity corrected* value of the first fraction of the released heat, ϕ_F, the fluorescence quantum yield, E_{hv}, the energy of the exciting radiation and E_S and E_T, the energy of the first excited singlet and the lowest triplet states. For our purpose, we have used the well established literature values of the energies of the first excited singlet (E_S) and the lowest triplet (E_T) states and also fluorescence quantum yields (ϕ_F). The determined ϕ_T and the values of the parameters we used for the determination are given in Table 2.

It is clear from the table that although the triplet yield (ϕ_T) is almost unity for MDPA and TPA in methanol, it is much less for DPA in the same solvent. The ϕ_T values for the former two amines agree well with the literature reports.[8,21,23] It is pertinent to mention here that unlike MDPA and TPA, the literature data for the triplet yield (ϕ_T) of DPA is quite scattered, ranging from 0.32 to 0.89.[3,23–25] The ϕ_T value determined by our TRPAC technique is lower than that reported

Table 2 Triplet quantum yield (ϕ_T) determined from TRPAC and the literature values of the energies of the S$_1$ (E_S) and T$_1$ (E_T) states and the fluorescence quantum yields (ϕ_F) of the three amines used for the determination of ϕ_T. The energies are in kcal mol^{-1}

Parameter	DPA	MDPA	TPA
ϕ_T	0.57 ± 0.06	0.95 ± 0.06	0.98 ± 0.06
E_s	88.9[a]	90.2[b]	86.5[a]
E_T	72.0[b]	70.3[b]	70.0[a,b]
ϕ_F	0.05[c]	0.04[b,d]	0.05[a]

[a] Ref. 21. [b] Ref. 8. [c] Ref. 2. [d] Ref. 22.

by Rahn et al.[3] (0.86 in methanol) but closer to the values reported by Lamola and Hammond[23] (0.38 in benzene) and by Sveshnikova and Snegov[24] (0.47 in 1-butanol). As the fluorescence quantum yield of DPA is of the same magnitude as that for MDPA and TPA, a lower ϕ_T value for the DPA compared to the values for the other two systems points to an additional reaction pathway from the S_1 state of DPA that is absent in the other two systems. Although, we did not notice any absorption representative of a new species (undefined so far for the system) within the wavelength range of our flash photolysis experiments, probably photoionization of DPA through the dissociation of the hydrogen attached to the nitrogen is responsible for the lower value of ϕ_T for DPA.

Enthalpies and quantum yields of reaction. It is known that at room temperature and in degassed solutions, the cyclization reaction for the formation of $^3XDHC^*$ from $^3A^*$ is quantitative ($\phi_R \simeq 1.0$) for MDPA and TPA.[7] So, E_2 and E_3 (refer to Scheme 1) were estimated from the other two fractions of heat released in the other two exponents ($E_2 = \phi_2 E_{hv}$, $E_3 = \phi_3 E_{hv}$).[13,14] After obtaining the energies involved in each of the three steps, it is easy to determine the enthalpy of reaction (ΔH_R) for the formation of the stable intermediate, $^1XDHC^0$, from the ground state amines. Table 3 presents the energies involved in step II (E_2) and step III (E_3) during the photoproduction of $^1XDHC^0$ and also ΔH_R, as determined by TRPAC, for both MDPA and TPA.

Table 3 reveals that the enthalpy of reaction (ΔH_R) for the formation of $^1XDHC^0$ in methanol solvent is nearly the same (~ 51 kcal mol^{-1}) for both MDPA and TPA. As will be discussed in a forthcoming section dealing with the theoretical results, there is very good agreement between the experimental and calculated enthalpies of reaction for the formation of the stable intermediate from MDPA and TPA. This gives strong support for our calculations. For DPA, however, Suzuki et al. have reported ΔH_R to be 62.1 kcal mol^{-1}.[11] A large difference in ΔH_R for DPA compared with the other two members of the series is rather surprising. Our calculation also does not support a large difference in the ΔH_R value for DPA from those for MDPA and TPA. Since there are no literature data for ϕ_R for the DPA system for a cross-check, it seems that an error in their estimated ϕ_R possibly led to an error in the estimation of ΔH_R. For DPA, we could not determine E_2 and E_3 individually for two reasons. Firstly, as already discussed, we could not resolve the thermal energies coming out of the two steps and, secondly, the quantum yield of the cyclization reaction (ϕ_R) is not known. After establishing the validity of the method of calculation to calculate ΔH_R for MDPA and TPA, we have extended the same method of calculation to the DPA system and using the calculated value of ΔH_R, we have determined ϕ_R for DPA in the following way.

Considering that in degassed solution, $^3A^*$ deactivates via two routes (i) returning to the ground state of the amine (DPA) with a quantum yield of ϕ_{ISC} and (ii) forming the intermediate, with a quantum yield of ϕ_R, one can write the following relation.

$$\phi_R + \phi_{ISC} = 1 \tag{2}$$

$^3A^*$, initially forms the intermediate in the triplet state ($^3XDHC^*$), the latter then passes to its stable form ($^1XDHC^0$) (steps II and III respectively in Scheme 1). However, since there is no other way of deactivation of $^3XDHC^*$ but its decay to $^1XDHC^0$, we can safely consider the quantum yield of step III as unity. Again, considering the thermal energy received by the transducer in the second time window (for a bi-exponential treatment of the acoustic waves in the case of DPA) as the sum of the heat released in steps II and III, one gets the following equation from the energy balance condition.

$$\phi E_{hv} = \phi_{ISC} E_T + \phi_R (E_T - E_{INT}) \tag{3}$$

where E_{hv}, E_T and E_{INT} are the energies of the exciting radiation, $^3A^*$ and $^1XDHC^0$ respectively and ϕ is the fraction of heat released during the second time window. With an experimental value of 0.60 for ϕ, 84.82 kcal mol^{-1} for E_{hv}, 72.0 kcal mol^{-1} for E_T (see Table 2) and 51.39 kcal mol^{-1} for E_{INT} (from the calculation, see Table 5), we estimate the value of ϕ_R to be 0.41. Although this value is not so far from the value of 0.37 reported by Suzuki et al.,[11] this difference is responsible for the deviation in their ΔH_R value for DPA from our experimentally determined values for MDPA and TPA.

Assignment of the stable intermediate $^1XDHC^0$. Apart from the energetics of the photocyclization, the other interesting aspect of the study of this reaction with these amines lies in establishing the nature of the stable intermediate, $^1XDHC^0$, responsible for the 610 nm absorption. From their observation with the DPA system, that $^3XDHC^*$ lies closer to its S_0 state and not its S_1 state, Suzuki et al. tentatively proposed that the intermediate might have a biradical character in the ground state.[11] However, there is no direct experimental evidence in favor of the proposition. In a recent report we have established from both experiment and theoretical calculation,[13] at least for TPA, that $^1XDHC^0$ is not a biradical but has a zwitterionic character. We have also applied the same techniques to the other two members, viz., DPA and MDPA, of the series.

From the experimental point of view, a biradical with a very long lifetime should be very sensitive to quenching by spin trapping agents like 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) and N-tert-butyl-α-phenylnitrone (PBN).[26,27] For all the amines in the present study, $^1XDHC^0$ has a very long lifetime, of the order of hundreds of microseconds. However, our flash experiments with both the spin traps, viz., DMPO and PBN, reflected no change in the lifetime of the 610 nm band corresponding to $^1XDHC^0$. We have further tried with a conjugated triene, viz., 1,6-diphenyl-1,3,5-hexa-triene, to see whether there is any quenching in the lifetime of $^1XDHC^0$ since the biradicals are susceptible to addition reactions with these substrates. The negative results with all our quenching experiments clearly negate the biradical nature of the intermediate in its ground state.

To assign the structure of the intermediate $^1XDHC^0$, we have calculated the energies of the electronic states for all reasonable structures. The one that explains the experimental findings best is the trans isomer (with the two central hydrogens in a trans arrangement) with a zwitterionic character. The skeleton is shown in Fig. 2. Although Linschitz and Grellmann also proposed a zwitterionic nature for the intermediate without any experimental or theoretical support, they conjectured that the two central hydrogens would be in the cis configuration.[5] For all the three systems, however, we have found that the trans isomer is more stable than the cis isomer.

It is revealed that in the ground state the nitrogen atom acquires a reasonable positive charge while all the carbon atoms, particularly, C_5, C_3 and C_1 (or C_8, C_{10} and C_{12})

Table 3 The amount of energy involved in step II (E_2) and step III (E_3) during the photoreaction of MDPA and TPA (see Scheme I) and the enthalpy of reaction (ΔH_R) for the formation of $^1XDHC^0$ in methanol solvent. The energies are in kcal mol^{-1}

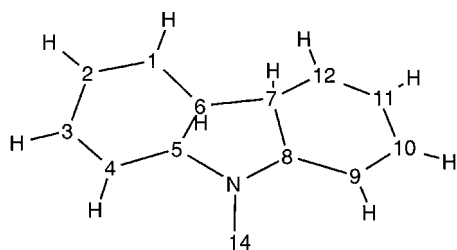| Parameters	MDPA	TPA
E_2	13.8 ± 1.0	14.9 ± 1.0
E_3	5.5 ± 0.6	3.9 ± 0.6
ΔH_R	51.0 ± 1.5	51.2 ± 1.5

Fig. 2 Skeleton of the ground state structure of the intermediate, ^{1}XDHC^0. Only the carbon atoms are numbered. 14 represents H for DPA, methyl carbon for MDPA and phenyl carbon for TPA. Charges on the atoms have been dropped in the figure as the negative charge has been calculated to be delocalized (see Table 4).

acquire partial negative charges. Table 4 gives the net charges on the atoms comprising the skeleton of the intermediate for DPA, MDPA and TPA.

We have simulated the electronic spectrum of the intermediate for all the amine systems under study. All of them show a strong absorption (oscillator strength, $f \approx 0.33$) within the range 633.3 to 643.6 nm corresponding to the 0–0 transition of $S_0 \to S_1$. Experimentally, a strong absorption band with a broad maximum in the range 610–620 nm is observed for all the systems, justifying the acceptability of our assigned structure for the transient. We have also calculated the ground state energy of the amines from their optimized geometries. From the difference in the ground state energies (or in the enthalpy of formation) of the amines and the intermediate (^{1}XDHC^0) we have estimated the enthalpy of reaction (ΔH_R) for the formation of ^{1}XDHC^0 from the amines during the photoreaction.

Table 5 lists the calculated values of ΔH_R as well as the absorption energies ($S_0 \to S_1$) corresponding to the intermediate for all the amines. A comparison of the strong absorp-

Table 4 Net charges on different atoms of the ^{1}XDHC^0 skeleton

Atom (see Fig. 2)	Net charge DPA	MDPA	TPA
C_1	−0.154 924	−0.156 289	−0.157 976
C_2	−0.129 259	−0.128 447	−0.127 901
C_3	−0.153 060	−0.158 045	−0.162 153
C_4	−0.085 703	−0.081 198	−0.080 966
C_5	−0.223 373	−0.228 071	−0.213 062
C_6	−0.017 471	−0.015 094	−0.016 082
C_7	−0.017 318	−0.016 304	−0.015 868
C_8	−0.223 551	−0.220 944	−0.213 423
C_9	−0.085 876	−0.082 062	−0.080 634
C_{10}	−0.152 892	−0.156 744	−0.162 351
C_{11}	−0.129 303	−0.129 236	−0.127 501
C_{12}	−0.155 040	−0.155 487	−0.158 232
N	+0.050 622	+0.095 292	+0.131 026
C_{14}[a]	+0.243 295	+0.000 918	−0.115 392

[a] C_{14} represents H for DPA, methyl carbon for MDPA and phenyl carbon for TPA. For numbering see Fig. 2.

Table 5 Calculated values of ΔH_R (kcal mol^{-1}), $S_0 \to S_1$ absorption position (nm) and corresponding oscillator strength (f) for the three amines

Parameter	DPA	MDPA	TPA
ΔH_R	51.39	48.94	50.71
$S_0 \to S_1$ absorption[a]	633.3	645.0	643.6
Oscillator strength[b] (f)	0.32	0.32	0.33

[a] The calculated absorption corresponds to the 0–0 transitions only, while the observed absorption spectrum leads also to transitions to higher vibrational levels. [b] For all the amines the calculated $S_0 \to S_1$ transition has reasonably high oscillator strength, justifying the strong absorption observed for the species in this wavelength region.

tion observed for the intermediates with the calculated $S_0 \to S_1$ energies and a very good agreement between the experimental reaction enthalpies (Table 3) with the calculated ones (Table 5) enable us to unhesitatingly assign the structure of the intermediate to a zwitterionic one with a partial positive charge on the nitrogen centre as described above.

Conclusion

We confirm the proposition of Rahn et al.[3] that for DPA, MDPA and TPA the long lived intermediate ^{1}XDHC^0 is formed through a cascade of processes during the photoreaction of the amines. TRPAC study reveals that the formation of the intermediate from the amine is an endothermic process, the endothermicity being ~ 51 kcal mol^{-1} in methanol solution. For DPA, we have determined the quantum yield of formation of the amine triplet and the quantum yield of the cyclization reaction. From the good agreement between the calculated and the experimental results, the structure of the intermediate (^{1}XDHC^0) has been assigned for all the amine systems. The present work establishes that for all members of the present series, the intermediate is zwitterionic in the ground state with a partial positive charge on the nitrogen centre.

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