

## Kinetics of the photoconversion of diphenylamine in $\beta$ -cyclodextrin environments

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### Abstract

Photochemical conversion of diphenylamine (DPA) to carbazole (CAZL) has been studied fluorometrically in aerated aqueous and aqueous  $\beta$ -cyclodextrin ( $\beta$ -CD) environments. The fluorophore forms a 1:1 inclusion complex with  $\beta$ -CD. The quantum yield of the photoreaction is found to remain unaltered in both the environments. However, estimation of the rate constants for the photochemical conversion of DPA to CAZL in the two environments reveals that within the CD environment, rate of the photoreaction is affected remarkably. This has been rationalized from the restriction in the intramolecular rotation for accessing the reaction centres responsible for the photocyclization process. This has also been corroborated from a comparison of the cavity diameter of the  $\beta$ -CD and the optimized geometry of DPA obtained from the semiempirical (AM1-SCI) calculation. © 2000 Elsevier Science S.A. All rights reserved.

*Keywords:* Diphenylamine;  $\beta$ -cyclodextrin; Carbazole; Photoconversion

### 1. Introduction

The UV irradiation on diphenylamine (DPA) and its derivatives in air-equilibrated solutions is known to yield primarily carbazole and its derivatives, which is formed via the photoexcited state of the amine [1–8]. Bowen and Eland [1] reported that the photocyclization of DPA involves a different state from the original excited state and further found mass spectrometrically that the amount of molecular hydrogen produced is comparable to that of carbazole formed. On the basis of flash-excitation studies Linschitz et al. [4,5] proposed that the photocyclization of DPA occurs through the triplet state, and the triplet transient converts to another transient, having an absorption maximum at 610 nm, which is the intermediate (a closed-ring polar structure) in the reaction. However, from theoretical consideration, Shizuka et al. concluded that the 610 nm transient cannot be assigned to the intermediate for CAZL formation [7]. From their laser flash photolysis experiments with DPA in methanol, Rahn et al. [8] were able to establish two deactivation routes of  $^3\text{DPA}^*$ ; ring closure to form dihydrocarbazole (DHC) triplet state and intersystem crossing to the DPA ground state.

Suzuki et al. [9] have recently studied the photocyclization of DPA in methanol solution by time-resolved thermal lensing technique. In the same work, using two-color laser flash photolysis, they have shown that the photoexcitation of intermediate  $^1\text{DHC}$  leads to the recovery of parent DPA inhibiting the formation of CAZL. From a study of the photoconversion of 1-(*N*-ethylanylino)cyclohexene and its derivatives, Grellmann et al. invoked a zwitterionic transient intermediate [10,11]. Thus, different authors have proposed different detailed mechanisms for the overall photochemical reaction, of course, all involving the triplet state. The photoreaction has already been applied for the synthesis of many organic compounds including the ellipticines [12].

Cyclodextrins are interesting microvessels capable of embedding appropriately sized fluorophores and thus providing restriction in space and a reduced polarity in the near vicinity of the chromophore [13–16]. The resulting supramolecules serve as excellent miniature models of enzyme-substrate complexes [17]. The space restriction within the CD cavity and lowering of micropolarity are shown to influence a number of photophysical/photochemical processes [18–21].

In the present paper, we have studied the photocyclization reaction of DPA in aqueous and aqueous  $\beta$ -CD solutions using the fluorometric technique. Without going into the mechanistic aspect, we have endeavored, here, to look at the

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effect of encapsulation of the reactant into the  $\beta$ -CD cavity on the reaction kinetics.

## 2. Experimental

Diphenylamine and carbazole (both from Aldrich) were purified following the procedures as mentioned elsewhere [22,23].  $\beta$ -Cyclodextrin was procured from Fluka and used as received. Triple distilled water was used for the preparation of experimental solutions. All the experiments were performed with air equilibrated solutions. The  $\beta$ -CD solutions were prepared by sonication. All the experimental solutions were prepared in dark room to avoid any photochemical transformation beforehand. For the preparation of the aqueous solutions of known concentrations of DPA and CAZL, we started with a standard and dilute solution of the fluorophore in ethanol; and then further diluting them to make 1% ethanolic water solutions. For the kinetic studies, the solutions were prepared directly in water without adding ethanol and these solutions were prepared by matching their absorbencies with those of the previous solutions (containing 1% ethanol).

Shimadzu MPS 2000 spectrophotometer and Spex Fluorolog spectrofluorimeter were used for the absorption and fluorescence measurements. For the geometry optimization of DPA, we have used the semiempirical AM1-SCI method supported by the Hyperchem 5.01 package from Hypercube Inc., Canada. Application of the AM1 method in getting the reliable structural data has already been established [24–27]. We have considered the single electronic transitions for all the configurations, to be specific 1 1 1 configurations, within the arbitrarily set energy window of 13 eV from the ground state.

## 3. Results and discussion

The absorption spectra of aqueous solutions of DPA and CAZL (concentration  $1.5 \times 10^{-6}$  M) have been shown in Fig. 1. DPA yields an absorption spectrum with a broad and unstructured band with maximum at  $\sim 280$  nm ( $\epsilon = 20,600 \text{ M}^{-1} \text{ cm}^{-1}$ ). CAZL, on the contrary, yields a distinctly structured band with a maximum at  $\sim 292$  nm ( $\epsilon = 16,000 \text{ M}^{-1} \text{ cm}^{-1}$ ). The experimental values of the molar extinction coefficients are in agreement with the earlier reports [28,29]. It is interesting to see that although the molar extinction coefficients of the two molecular systems are different at their respective absorption maxima; they are nearly same at 292 nm. Hence, the excitation wavelength has been set to 292 nm for the study of the photocyclization reaction of DPA.

The fluorescence spectra of both the solutions were taken (it is important to point out here, that the portion of the DPA solution used for the absorption study must not be used for the emission studies as an appreciable portion of the photo-

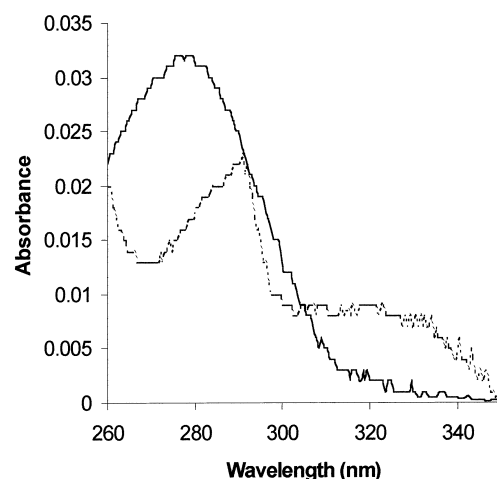


Fig. 1. Absorption spectra of CAZL (...) and DPA (—) in aqueous solutions (concentration of the solutions  $1.5 \times 10^{-6}$  M).

chemical reaction has already been taken place. So a fresh part from the stock solution, kept in dark, must be used). While, DPA yielded a broad and unstructured fluorescence spectrum with a maximum at  $\approx 390$  nm, CAZL spectrum was structured with a maximum at  $\approx 358$  nm. The fluorescence quantum yields of DPA and CAZL were estimated to be 0.06 and 0.21, respectively against quinine sulphate solution in 0.1 N  $\text{H}_2\text{SO}_4$  ( $\phi = 0.54$ ) [30].

There was hardly any change in the absorption spectrum of the DPA solution on addition of  $\beta$ -CD to it. However, the same solution in the presence of  $\beta$ -CD, showed a small but gradual increase in the fluorescence yield associated with a clear hypsochromic shift with an increase in the  $\beta$ -CD concentration. Presence of an isoemissive point (Fig. 2) at 388 nm confirms the formation of a 1:1 complex between the fluorophore and  $\beta$ -CD. A gradual shortening of the FWHM for the emission band with an increase in the  $\beta$ -CD concentration also points to the inclusion of DPA within the CD

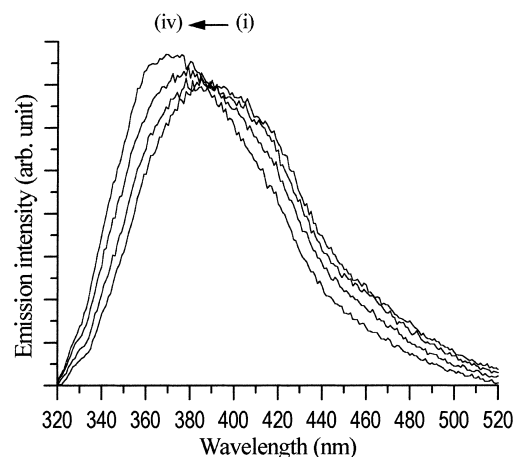


Fig. 2. Fluorescence spectra of DPA (at zero time) in aqueous  $\beta$ -CD solutions. The different  $\beta$ -CD concentrations from (i) to (iv) are: 0, 0.25, 0.75 and 1.5 mM (concentration of DPA is  $1.5 \times 10^{-6}$  M).

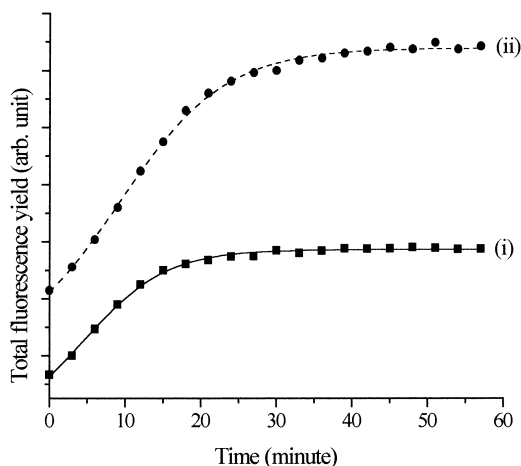


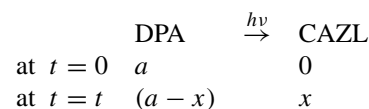
Fig. 3. Plot of total fluorescence of the DPA vs. time in (i) aqueous and (ii) 1.5 mM  $\beta$ -CD medium (concentration of DPA is  $1.5 \times 10^{-6}$  M).

cavity. It reflects that the fluorophore is experiencing a less polar environment within the  $\beta$ -CD cavity as similar band narrowing has been observed in less polar solvents.

On keeping the aqueous solution of DPA, exposed to the 292 nm radiation, the fluorescence spectrum changes with time. Gradually the DPA fluorescence is transformed into the structured fluorescence of CAZL, the peak maximum moving from 390 to 358 nm. This is associated with an increase in the fluorescence yield. Thus, monitoring the total fluorescence yield with time provides a convenient way to study the course of the photoconversion of DPA to CAZL. Fig. 3 represents plots of total fluorescence of the reacting system in aqueous and in aqueous  $\beta$ -CD solutions with time. The figure clearly shows that the photoconversion reaction is quite slow (time range in minutes). It is also important to notice that the time required for levelling of the fluorescence is greater for the  $\beta$ -CD solution reflecting that in this environment the reaction is slower compared to that in the aqueous solution. It is pertinent to mention here that in the  $\beta$ -CD solution, all the DPA molecules are supposed to be complexed with  $\beta$ -CD as the concentration of the latter is three orders of magnitude higher than that of DPA.

For the determination of the rate constant for the photochemical conversion of DPA to CAZL in absence and in the presence of  $\beta$ -CD, let us have a look to the relevant equations.

At  $t=0$  (i.e., initially), the total fluorescence corresponds to the total amount of DPA present in the system. As time passes (under continuous irradiation), DPA concentration is decreased and equimolar amount of CAZL is formed. Thus,



where  $x$  is the moles of DPA reacted or moles of CAZL formed. Considering first order reaction (final plots validate the first order nature of the reaction), we can write,

$x = a(1 - e^{-kt})$ ,  $k$  being the first order reaction rate constant. Thus, concentration of DPA and CAZL after time  $t$  (from the start of the reaction) becomes  $ae^{-kt}$  and  $a(1 - e^{-kt})$ , respectively,  $a$  being the initial concentration of DPA. Interestingly, for the present case, both the reactant (DPA) and the photoproduct (CAZL) are excited by the exciting radiation at 292 nm and they emit independently depending on their instantaneous concentrations. We can correlate the total fluorescence at any instant of time with the fractional light absorption by the components [31] as:

$$\phi_t = \phi_{\text{CAZL}} I_{\text{CAZL}} + \phi_{\text{DPA}} I_{\text{DPA}} \quad (1)$$

where  $\phi_t$ ,  $\phi_{\text{CAZL}}$ ,  $\phi_{\text{DPA}}$  represent the fluorescence quantum efficiencies of the reaction mixture, pure carbazole and pure diphenylamine.  $I$ 's are the fractional light absorbed by the species represented by the subscript ( $I = I_0 (1 - e^{-2.303\epsilon cl})$ ,  $I_0$  being the incident light intensity and  $l$ , the optical path length, which for our case was 1 cm). Introducing and assuming the molar extinction coefficients of DPA and CAZL to be equal (discussed earlier) and incorporating the concentration terms from the kinetic scheme mentioned earlier we arrive at the following final expression:

$$\log \left[ \phi_{\text{CAZL}} - \frac{\phi_t}{2.303 I_0 l a \epsilon} \right] = - \frac{kt}{2.303} + \log(\phi_{\text{CAZL}} - \phi_{\text{DPA}}) \quad (2)$$

Plot of the left hand term against time yielded straight lines (Fig. 4) in both aqueous and aqueous  $\beta$ -CD solutions from the slope of which we extracted the values of the rate constant for the photochemical reaction. In homogeneous aqueous and microheterogeneous  $\beta$ -CD environments they are 0.083 and 0.050  $\text{min}^{-1}$  respectively. Although the absolute values of the rate constants will depend on the intensity of the light source, under the same experimental condition, the relative value of them in the two systems (aqueous and aqueous  $\beta$ -CD solution) is experimentally valid.

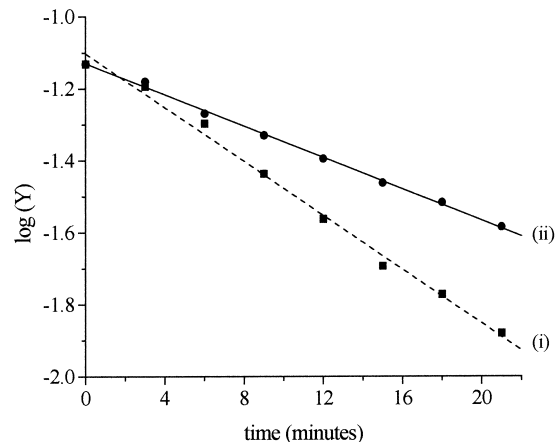


Fig. 4. Plot of  $\log(Y)$  vs. time in (i) aqueous and (ii) 1.5 mM  $\beta$ -CD solution ( $Y = [\phi_{\text{CAZL}} - (\phi_t/2.303 I_0 l a \epsilon)]$ , for detail see text).

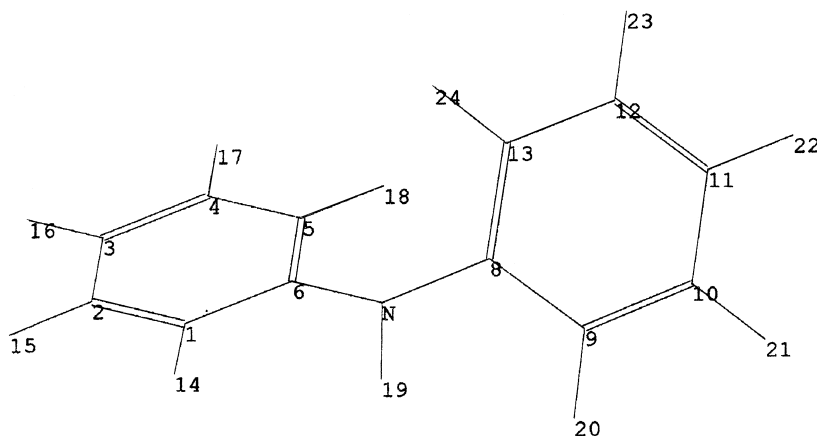


Fig. 5. Optimized geometry of DPA.

Using the same equation at long times of irradiation of DPA (after attainment of the levelling of fluorescence, see Fig. 3) and adopting the derived rate constant, we have determined the quantum yields of the photoreaction in both aqueous and aqueous  $\beta$ -CD solutions. The value of the quantum yield in both the media was estimated to be 0.11 and the value was found to be indifferent to the  $\beta$ -CD concentration. The quantum yield for the photoreaction derived by us is consistent with the values reported by Bowen and Eland [1].

The zero time fluorescence study of DPA in the absence and in the presence of  $\beta$ -CD and the associated narrowing of the fluorescence band in the presence of  $\beta$ -CD, clearly demonstrates the formation of an inclusion complex of DPA with  $\beta$ -CD. It also reveals that the probe remains embedded within the CD cavity even in the photoexcited state where the photochemical reaction is supposed to take place. The ground state optimized geometry of DPA is given in Fig. 5 which shows that the molecule is non-planar and the two benzene planes are at an angle of  $52^\circ$  with each other. Thus, it is evident that an intramolecular rotation is essential for the molecule to be planar which is a requirement for the formation of the closed ring intermediate,  $^1$ DHC (dihydrocarbazole) [9], for the photocyclization process. The distance from one end to cover both the carbon centres responsible for the cyclization process is only 6.23 Å. The cavity diameter of  $\beta$ -CD is, however, known to be around 7.00 Å [14,32]. The inclusion complex is, thus, believed to keep both the carbon centres within the  $\beta$ -CD cavity. The intramolecular rotation of the reactant (DPA) to make a planar geometry is, thus, restricted within the cyclodextrin environment, resulting in slowing down of the overall reaction. Thus, we believe that CD-imposed steric rigidity might be the principal cause for the lowering of the photochemical reaction rate. However, since no reactant molecule is permanently blocked for the reaction,  $\beta$ -CD inclusion has no effect on the final quantum yield of the photochemical reaction.

Although we started with an intention not to deal with the mechanistic aspects in the present paper, the comparative

results of the photoconversion process points to the mechanistic proposition that an intramolecular rotation is essential for the photocyclization process. Furthermore, a remarkable lowering in the reaction rate, when the probe is encapsulated within  $\beta$ -CD, indicates that this intramolecular rotation is, probably, the rate determining step for the concerted process.

#### 4. Conclusion

The present study gives rise to the following points:

1. DPA forms a 1:1 inclusion complex with  $\beta$ -CD in aqueous solution.
2. The quantum yield of the photochemical conversion of DPA to CAZL is not modified in the  $\beta$ -CD environment.
3. Within the  $\beta$ -CD environment, the intramolecular rotation of DPA is restricted, and hence, the rate constant of the photocyclization process is lowered.

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