Twisted intramolecular charge transfer of \( p\-N,N\)-dimethylamino-benzaldehyde in cyclodextrin environments

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Twisted intramolecular charge transfer (TICT) of \( p\-N,N\)-dimethylamino-benzaldehyde (DMABA) has been studied in different aqueous cyclodextrin (\( \alpha \)-, \( \beta \)- and \( \gamma \)-) environments. The fluorophore forms 1:1 complexes with all the three cyclodextrins (CD). The TICT emission is extremely weak in pure water but it is enhanced as the probe is encapsulated within the cyclodextrin cavities. The relative enhancement of the emission from the TICT species to the locally excited (LE) species is maximum in the \( \alpha \)-CD environment and minimum in the \( \gamma \)-CD environment. This differential enhancement of the two emission bands in different aqueous CD solutions has been explained on the basis of the polarity factor. It has been suggested that the polarity of the microenvironment is the principal controlling factor for the TICT process.

The twisted intramolecular charge transfer (TICT) phenomenon in solutions, though discovered only in early seventies\(^1\), has received immense attention due to its application in laser dyes, isomerisation of polyenes and thodopsin, molecular switching devices, charge separation in photochemical energy utilisation, etc.\(^2\), and has been the subject of several recent studies\(^1\-18\). The studies are mostly confined to the \( p\-N,N\)-dimethylaminobenzene compounds although work on some other types of molecules is also being carried out increasingly\(^12\). As the process involves molecular motion alongwith charge separation, it is expected that the environmental viscosity and polarity will have remarkable influence on the process. However, literature reports indicate that the viscosity of the medium is the controlling factor only when the rotating groups are large and/or the viscosity of the environment is very high\(^12,17\). In the cases of \( p\-N,N\)-dimethylaminonitriile (DMABN) and \( p\-N,N\)-dimethylaminobenzaldehyde (DMABA), where the rotating group is small, the viscosity effect of the medium is expected to be small or negligible\(^12\). In these cases the two important factors likely to affect the TICT process are: (i) the polarity of the environment and (ii) the spatial restriction for the relative movement of different parts of the fluorescent probe.

Cyclodextrins (CDs) are interesting microvessels capable of embedding appropriately sized fluorophores. They provide a reduced polarity as well as a restriction in space in the near vicinity of the chromophore\(^19\-24\). This space restriction and/or lowering of micropolarity influences a number of photophysical/photochemical processes including the TICT\(^9\-15\). Selecting \( \alpha \-\beta \-\gamma \) CDs with radii approximately 4.5, 6.5 and 8.0 Å respectively, one can provide a controlled steric restriction for the encaged probe alongwith a reduction in the polarity of the microenvironment around it. Thus, the study of the TICT process in the CD environments provides a way to answer the question whether the process is governed by the polarity or by the steric rigidity around the probe. While Lyapustina \textit{et al.}\(^14\) inferred that the spatial restriction experienced by the guest molecule within the CD cavity is the main factor to affect the TICT state formation, Eisenthal \textit{et al.}\(^3,4\) and Bhattacharyya \textit{et al.}\(^9,10\) suggested that the TICT state formation is exclusively controlled by the polarity factor. In the concluding communication of our series of investigations of TICT in aqueous cyclodextrin environments, we report here the outcome of our systematic study with another TICT probe, DMABA, which is reported to exhibit dual liminescence in the polar solvents\(^19\).

**Materials and Methods**

DMABA (Aldrich) was purified by vacuum sublimation followed by recrystallisation from 90% ethanol. The purity of the compound was checked using spectroscopic methods as well as TLC. \( \alpha \)-, \( \beta \)- and \( \gamma \)-CDs (all from Aldrich) were used as received. Triply distilled water was used for the preparation of
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the solutions. The solutions were sonicated well for the steady-state equilibrium for the complexation process to be attained. Although degassing of the solutions did not produce any difference in the basic observations, the reports are for the deaerated solutions; the degassing was done by bubbling dry nitrogen.

A Shimadzu MPS 2000 absorption spectrophotometer and a Spex Fluorolog fluorimeter were used to record the absorption and emission spectra respectively. For the time resolved experiments the time-correlated single photon counting technique was adopted and a nitrogen flashlamp of nanosecond duration (Edinburgh Instruments, 199 fluorescence spectrometer) was used as the excitation source.

Results and Discussion

The absorption spectra of aqueous 1x10^{-5} mol dm^{-3} DMABA solution as a function of cyclodextrin concentration are shown in Fig. 1. Irrespective of the \( \alpha \), \( \beta \) or \( \gamma \)-CD used, on the addition of the CD to the aqueous solution, the absorption maximum shows a bathochromic shift indicating that the probe is experienced less polarity in the CD environment. This has been established independently from the observation of a blue shift in the absorption band as the polarity of the solvent is reduced (for solvents like water, methanol, chloroform and cyclohexane the maxima are at 358, 342, 337 and 325 nm respectively).

The existence of an isosbestic point (at 355 nm) in the absorption spectra of DMABA in aqueous \( \alpha \)-CD solutions confirms the formation of a one-to-one complex between the fluorophore and the CD. In \( \beta \) and \( \gamma \)-CD environments no such isosbestic point could be detected. For the latter system, however, a 1:1 probe-CD complexation is conceived and the association constant is evaluated from the fluorescence study.

The equilibrium constant for the process,

\[
\text{DMABA} + \gamma\text{-CD} \rightleftharpoons \text{complex}
\]

can be given by,

\[
K = \frac{[\text{complex}]}{[\text{DMABA}][\gamma\text{-CD}]} \quad \cdots \quad (1)
\]

Denoting [complex] as \( C_c \), [DMABA] as \( C_d \) and [\( \gamma\text{-CD} \)] as \( C_{cd} \), one can write

\[
K = \frac{C_c}{C_d C_{cd}} \quad \cdots \quad (2)
\]

The fluorescence quantum yield of a DMABA solution containing \( \gamma \)-CD can be written as,

\[
\phi = \frac{\phi_c I_d + \phi_d I_c}{I_d + I_c} \quad \cdots \quad (3)
\]

where, \( \phi_i \) s are the quantum yields for the individual \( i^{th} \) species. Again,

\[
I_d = \frac{\phi_d \epsilon_d C_d}{I_c = \epsilon_c C_c} \quad \cdots \quad (4)
\]

Combining equations (2), (3) and (4), we arrive at

\[
\left( \frac{\phi - \phi_d}{\phi_d} \right)^{-1} = \left( \frac{\phi_c - 1}{\phi_d - 1} \right)^{-1} + \left( \frac{\phi_c - 1}{\phi_d - 1} \right)^{-1} \frac{\epsilon_d}{K_c C_{cd}} \quad \cdots \quad (5)
\]

The experimental data yielded a straight line when
was plotted against \(1/C_{cd}\) (Fig. 2) substantiating the one-to-one complexation between the fluorophore and the \(\gamma\)-CD. Since the addition of \(\gamma\)-CD to the DMABA solution does not change the absorbance significantly, we assume that \(\varepsilon_{d} = \varepsilon_{c}\) and, thus, the association constant comes out to be 13.5 mol\(^{-1}\) dm\(^{3}\).

The low value of the binding constant is rationalised on the basis of the large cavity size of the \(\gamma\)-CD compared to the dimension of the probe. The interaction of the fluorophore with the \(\gamma\)-CD is also corroborated by an enhancement of its fluorescence lifetime in the presence of \(\gamma\)-CD.

For the \(\beta\)-CD solution neither absorption nor emission studies could establish the 1:1 complexation between the probe and the CD. Similar deviations of the complexes from 1:1 stoichiometry have been reported by several groups\(^{2,24-26}\). Two possibilities are proposed for this deviation. Firstly, more than one guest molecule can be accommodated within a single CD cavity. Secondly, due to the space restriction, more than one type of complexes, each having a 1:1 stoichiometry, may be formed. The following discussion establishes the second possibility in the present case and leads us to propose two distinct complexes. The complexes, similar to those reported for the DMABN — \(\beta\)-CD system\(^{10}\), are : one with the DMABA completely enclosed within the CD cavity and the other with a part of the fluorophore projecting out of the cavity.

The slight increase in the absorbance is, presumably, due to the detergent action of the CD and is attributed to the additional dissolution of DMABA adsorbed on the surface of the walls of the container\(^{1,24,25}\).

In contrast to the absorption spectra, on addition of the CDs, the emission spectra of aqueous DMABA show a remarkable change (Fig. 3). It is observed that in the water solution the emission quantum yields of both the non-polar (LE, \(\approx 400\) nm) (the term non-polar is often used for the blue edge emission when such dual liminescence occurs and the term reflects that the form responsible for this emission is less polar
than the other form but does not necessarily represent its actual dipole moment) and the TICT emission (>500 nm) are extremely low. This is probably due to the dissipation of the energy of the excited species to the ground and/or low lying triplet states through the stabilised TICT state, very similar to that proposed for DMABN. Our recent laser induced optoacoustic spectroscopic (LIOAS) study on the probes DMABN and DMABA in different solvents has revealed that the quantum yield of the internal conversion (IC) increases with an increase in the solvent polarity, substantiating the energy dissipation to the ground state more through the TICT singlet. With the addition of the CDs, the yield as well as the lifetime of both the emissions increase, but the rate of enhancement of two emission bands is different for different CD solutions. While the rate of enhancement of the TICT band is highest for α-CD followed by that for β- and γ-CD, the same for the LE emission is in the reverse order. Thus, the relative fluorescence enhancement (RFE = TICT/LE) for the probe — CD complex is in the order: α- > β- > γ-. Of course, the enhancement of the bands is accompanied by hypsochromic shifts.

The increase in the LE emissions in the CD solutions is too large to be explained by the primitive proposition of the dissolution of the fluorophore molecules adsorbed on the walls of the container due to the detergent action of the CDs.

Formation of a 1:1 complex in the case of the DMABA — α-CD system, as confirmed by the isosbestic point, does not necessarily mean that the probe, DMABA, is entirely encaged within the α-CD core. Had it been so, then one would not except an enhancement in the TICT luminescence with an increase in the α-CD concentration due to the unfavourable non-polar environment and/or steric restriction imposed by the small core of the α-CD. Thus, it seems that a part of the molecule remains within the small α-CD cavity and the rest is projected out towards the polar aqueous environment. In such a position, the probe experiences a polarity intermediate between that of the CD core and the bulk water. From our recent study of the TICT in encapsulating microheterogeneous phases we propose that the dimethylamino (DMA) group faces the aqueous phase and is thus free to twist.

Because of the intramolecular charge transfer, the TICT state has a large dipole moment (see later) and the species is expected to be stabilised more with an increase in the solvent polarity. This has two consequences. Firstly, the lowering of the energy of the TICT state reduces the energy barrier between the locally excited Frank-Condon excited state (LE) and the stabilised TICT state (Fig. 4) favouring the LE → TICT transition and leading to the formation of the TICT species to a greater extent. Following the second consequence, stabilisation of the TICT state decreases the energy gap between the TICT state and the higher vibrational levels of the ground state. According to the energy gap law, this would lead to an enhancement in the non-radiative decay from the TICT state to the ground state. Thus, on going from a higher to a lower polarity, the energy of the TICT state will increase resulting in an increase in

![Fig. 4 - Relative energies (schematic) of the LE and the TICT states in nonpolar and polar solvents.](image)

<table>
<thead>
<tr>
<th>CD Solution</th>
<th>LE (ns)</th>
<th>TICT (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-CD</td>
<td>0.96</td>
<td>0.91</td>
</tr>
<tr>
<td>β-CD</td>
<td>0.99</td>
<td>1.01</td>
</tr>
<tr>
<td>γ-CD</td>
<td>0.96</td>
<td>1.05</td>
</tr>
</tbody>
</table>

Table 1 — Lifetimes (τ, nanoseconds) of the LE (at 400 nm) and the TICT (at 500 nm) species of DMABA in different CD solutions
the activation energy for the TICT process. Thus, the LE → TICT transition should decrease along with a blue shift of the TICT emission band. In the present experiment, as we go from aqueous to the cyclodextrin solutions, the polarity of the microenvironment around the fluorophore is reduced and, as expected, a gradual blue shift is observed in both the LE as well as the TICT bands along with an enhancement in the LE emission. A similar hypsochromic shift was also observed by Kosower and Dodiuk. The blue shift of the TICT band is, however, much more compared to that of the LE emission establishing that the TICT species is reasonably more polar than the LE species.

The partial encagement of the fluorophore in the α-CD cavity explains the enhancement of both the emissions considering a reduction in the polarity of the microenvironment around the probe. The time-resolved results also corroborate this. The lifetime values of both the LE and the TICT species are found to increase in both α- and β-CD solutions (Table 1). Due to the very low fluorescence yield of the TICT emission in the γ-CD solution, the lifetime value of this band could not be extracted reliably. However, the lifetime of the LF emission was found to increase when the fluorophore was embedded within the γ-CD cavity. Based on the earlier discussion the increase in the lifetime of the LE species is ascribed to the restriction in the TICT formation in the less polar CD environments while that of the TICT species is ascribed to the reduction in the non-radiative transition from the TICT state to the lower levels due to the energy gap restriction imposed by the less polar CD environments. To ascertain whether or not there is any parent-daughter relationship between the LE and the TICT emission in the β-CD solution, we examined the excitation spectra of the LE (at 400 nm) and the TICT (at 500 nm) emissions. It was observed that the excitation spectra monitoring the former is blue shifted compared to that of the latter (Fig. 5). This distinct difference in the two excitation spectra indicates that these emissions essentially originate from the two different sets of complexes having absorption maxima at 353 nm and 359 nm respectively. The steady-state study, thus, indicates that the LE and the TICT emissions in the presence of β-CD are due to different sets of the ground state DMABA—β-CD complexes. The excitation spectral study was not extended to the α- and γ-CD solutions as the existence of the ground state uncomplexed and complexed species is already confirmed in both these environments.

Another interesting point is that although the concentration of the probe is same in both the α- and β-CD systems, the emission yield and the lifetime corresponding to the LE band are greater in the latter system. On the other hand, both the parameters for the TICT species are higher in α-CD system. This reflects that in the β-CD environment all the probe molecules are not aligned in a fashion as they are in the α-CD environment. The greater extent of the

[Fig. 5 - Excitation spectra of aqueous solution of DMABA containing 8 mmol dm⁻³ β-CD monitored at (i) LE (400 nm) and (ii) TICT (500 nm) bands.]

[Fig. 6 - The proposed structures of the different DMABA—CD complexes [(a) DMABA—α-CD, (b) DMABA—β-CD and (c) DMABA—γ-CD].]
TICT enhancement in the α-CD compared to that in the β-CD solution led us to suggest that some of the probes are unable to undergo TICT process in that β-CD environment. This situation arises when some of the fluorophores are totally encapsulated into the hydrophobic CD cavity where the TICT formation is severely hindered. In such a condition one should expect an enhancement in the LE emission yield as well as the corresponding lifetime as consistent with the observation. In γ-CD environment, the lifetime of the LE emission is more than that in other CDs. This is attributed to the marked depression in the non-radiative deactivation through the TICT formation.

Thus, the steady-state and the time resolved studies of the TICT process of DMABA in the smaller α- and the relatively spacious β- and γ-CD environments prove that the microscopic polarity around the probe governs the process. The study also establishes two types of complexes for β-CD — probe system (Fig. 6(b). In one, the molecule DMABA is totally encapsulated inside the cavity, which produces enhanced LE emission and in the other, the molecule is partially is partially enclosed giving rise to an enhanced TICT emission.

One relevant question that may arise here is that since the DMABA molecule is not entirely free inside the β-CD cavity the suppression of the TICT yield in the β-CD solution may not be due to the reduced polarity but due to the restriction imposed on the molecular motion by the finite size and shape of the cavity.

This point can be resolved from our observations in the more spacious γ-CD (diameter 8.0 Å) environment. Addition of the γ-CD to an aqueous DMABA solution increases the LE emission yield considerably with very little enhancement in the TICT emission band (Fig. 3(c)). This large enhancement in the LE emission yield cannot be explained by the detergent action of the CD (see before). So, the reason lies with the reduction of the main non-radiative path of the LE state, i.e., the formation of the TICT state in the γ-CD environment. Had the space restriction provided by the CD cavity been the governing factor for the TICT formation, one would have expected more TICT emission from the probe in the γ-CD environment as compared to that in the β-CD, since the cavity size of the former is much greater than that of the β-CD, providing a greater allowance for the twisting of the dimethylamino group relative to the rest of the molecule. However, inappreciable amount of the TICT emission in the γ-CD, which arises probably due to the incorporation of some water molecules within the large cavity, negates this possibility.

The RFE [relative fluorescence enhancement (TICT/LE)] for the probe — CD complex is in the order: α → β → γ-CD. This can be explained by the consideration of the location of the probe molecule in different environments. DMABA forms 1:1 complexes with α- and γ-CD. In the latter case, the microenvironment around the fluorophore is basically nonpolar, but, for the former complex, the environment is neither nonpolar nor as highly polar as that of water; it lies in between. So the RFE is expected to be higher for aqueous solution of α-CD than that for the γ-CD solution. In the presence of the β-CD, however, DMABA forms two types of complexes: one of them viz., the totally embedded fluorophore within the CD cavity, is incapable of yielding the TICT emission, while the other one, viz., the partially encaged one, can do so. Thus, in the aqueous β-CD solution, the RFE value lies between the values obtained for the other two CD solutions.

To substantiate the polarity dependence of the TICT process further, we have studied the process in DMABA as a function of ET (30) in a series of p-dioxane — water mixtures. Of the different polarity parameters available we have chosen ET (30) since it represents the microscopic polarity around the probe molecule more truly than the others. Fig. 7 presents the variation of the TICT/LE fluorescence ratio of the fluorophore against ET (30).

The figure shows that with an increase in the solvent polarity [ET(30)], the intensity ratio (TICT/LE) increases initially and then decreases gradually passing through a maximum at ET (30) ~ 38.5. An extension of the earlier discussion dictates that the solvent polarity affects the formation and the decay channels of the TICT state quite oppositely. In the highly polar solvents with large ET (30) values, stabilisation of the TICT state is so good that due to the proximity of this stabilised state and the low lying states, the non-radiative decay is favoured very much and one hardly expects any TICT emission. As pointed out earlier, a recent photoacoustic study re-
veals an increase in the quantum yield for the internal conversion (IC) process with an increase in the solvent polarity. A reduction in the polarity of the medium destabilises the TICT state resulting in an increase in the energy gap between the TICT state and the low lying states, in effect, enhancing the TICT emission. But so far as the formation channel is concerned, the effect of the solvent polarity is, qualitatively, the reverse. The destabilisation of the TICT state is associated with an increase in the activation barrier for the LE → TICT conversion (see Fig. 4). If the polarity at the near vicinity of the fluorophore is too low, this barrier becomes sufficiently high to inhibit the LE → TICT transition. This eventually reduces the TICT fluorescence yield. So the LE emission increases in the less polar environment because of the restriction in the non-radiative decay channel to govern the TICT yield. But, after a certain value of the polarity parameter, $E_T(30)$, there occurs a reversal of the predominancy amongst the channels and the decay of the TICT state is facilitated due to the non-radiative energy dissipation. Thus, the plot shows a maximum at some intermediate polarity, $E_T(3s) = 38.5$.

Conclusion

The systematic study of the TICT process of the fluorophore, DMABA, in different aqueous cyclodextrin environments, in conjunction with the experiments in the dioxane — water mixed solvent establishes that the TICT process depends exclusively on the polarity of the microenvironment around the fluorophore.

Acknowledgement

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References