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# Dual emission from 4-dimethylaminobenzonitrile in cyclodextrin derivatives

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## Abstract

Dual fluorescence of 4-dimethylaminobenzonitrile (DMABN) in the presence of hydroxypropyl-β-cyclodextrin (HP-β-CD) and dimethyl-β-cyclodextrin (DM-β-CD) in aqueous media is reported. Equilibrium constants for the formation of inclusion complexes between DMABN and CD-derivatives are calculated for the ground as well as the excited states. Two maxima are observed in the excitation spectra, indicating the presence of two absorbing species. Fluorescence lifetimes of these complexes are also reported in addition to their ICD spectra. Based on the experimental observations, it is concluded that while the more polar TICT emission originates from the aqueous exterior, LE emission occurs predominantly from the complexed molecule. Higher order complexes are not observed. Absence of hydrogen bonding and a 'tighter fit' with the CD derivatives are the main factors responsible for this. ©2000 Elsevier Science S.A. All rights reserved.

*Keywords:* 4-Dimethylaminobenzonitrile; Dual emission; Hydroxypropyl-β-CD; Dimethyl-β-CD complexes; Lifetime; ICD spectra

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## 1. Introduction

*para*-Dimethylaminobenzonitrile is a prototype of molecules exhibiting twisted intramolecular charge transfer (TICT) behaviour. In polar media these molecules emit dual fluorescence from conformationally distinct, excited singlet states [1,2]. The high-energy band (LE band) is emitted by the locally excited planar conformation and the low-energy band (TICT band) is emitted by a state in which the electron-donating moiety of the molecule is perpendicular to the electron-accepting moiety. The maximum position of the TICT band is particularly sensitive to the polarity of the microenvironment. Different mechanisms have been presented in the literature to explain this phenomenon [3–6]. Among these, the 'twisted intramolecular charge transfer' model pioneered by Grabowski [3] has received widespread attention. According to this model, a 90° twist of the dimethylamino group with respect to the phenyl ring is considered to have occurred in the CT state of DMABN and hence the dimethylamino group is assumed to be electronically decoupled from the rest of the molecule due to the 'minimum overlap rule' [6].

The intramolecular charge transfer (ICT) from the LE state to the CT state in the singlet excited state is also investigated [7] for the model compounds, namely, 4-dialkylaminobenzonitriles (DRABN) and 4-dialkylamino-2,6-dimethylbenzonitriles (RDB) (R=methyl, ethyl, *n*-propyl) in toluene as a function of temperature by photostationary and time resolved experiments which establish that the efficiency of the ICT reaction, is enhanced by an increase in the size of the dialkylamino group as well as by the presence of the two extra methyls in the phenyl ring.

Recently it is reported [8–10] that the amino and benzonitrile moieties for a series of 4-aminobenzonitriles are not in fact decoupled in the CT state. In the proposed planar intramolecular charge transfer (PICT) model, it is assumed that the relaxed CT state has an essentially planarized structure, with a less pyramidal amino nitrogen atom and different bond lengths than in the LE state, resulting in a larger dipole moment [7,11]. With DMABN and a series of 4-(dialkylamino)benzonitriles, having alkyl groups ranging from ethyl (DEABN) to *n*-decyl (DDABN), dual fluorescence is observed in a variety of solvents, even in nonpolar alkanes such as cyclohexane and *n*-hexane [9]. These observations show that a polar solvent is not necessary for the appearance of ICT in these systems.

The dual fluorescence of DMABN and DEABN has been studied in aqueous solutions of α- and β-cyclodextrins by Turro et al. [12]. Fluorescence parameters (peak maximum, lifetime and relative intensity) have been measured and are found to be consistent with the formation of complexes between probe and CD. TICT in the presence of α-, β- or γ-CDs also have been examined for DMABN

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[12–15], 4-dimethylaminobenzaldehyde (DMABA) [16] and 4-dimethylaminobenzoic acid (DMABOA) [17]. For the same TICT fluorophore, the TICT behavior shows a CD cavity size dependence [13–15], while for the same CD, the TICT behavior varies appreciably with the TICT fluorophore [14,16,17]. The correlation of the ratio of TICT to normal band of 4-dimethylaminobenzoic acid (DMABOA) [17] in aqueous α-CD solutions is opposite to that in pure organic solvents, which is explained in terms of the different TICT behavior in aqueous solution. These observations have provided two routes in the ground state to modify and even control the TICT process through the formation of a CD inclusion complex. Dimethylaminobenzoyl-appended CDs are synthesized [18] and are used as fluorescent chemosensors [19].

In this work, we report the results of our studies on the dual emission of DMABN in two CD derivatives namely, HP-β-CD and DM-β-CD, which provide interesting contrast to the previously reported works on DMABN in β-CD [12–15]. While DM-β-CD is more hydrophobic than β-CD, HP-β-CD is actually more hydrophilic than β-CD. Both DM-β-CD and HP-β-CD are not discrete compounds but a mixture of hydroxypropylated/methylated derivatives with an average degree of substitution 6 and 1.8/glucose unit, respectively. They are used after recrystallization from water. Though, this situation is not ideal for quantitative measurements, it caused no major problems as long the material has a consistent composition and gives reproducible results.

## 2. Experimental

### 2.1. Materials

2-Hydroxypropyl-β-CD (DS 6, randomly hydroxypropylated/gift sample from Cerestar, USA) and dimethyl-β-CD (DS 1.8, non-recrystallizable, randomly methylated/gift sample from Wacker-Chemie, Germany) were used after recrystallization from water. Positive-ion Fast Atom Bombardment Mass spectra of HP-β-CD and DM-β-CD showed a relatively symmetric peak distribution around the average molecular weight of the main product (approximately 1493 and 1342, respectively). DMABN was prepared by the procedure given in the literature [20], recrystallized using hexane and the purity of the DMABN was checked by its characteristic mp and also by gas chromatography. All the solvents used in this study were of HPLC grade. In all the experiments, doubly distilled water was used to make stock solutions. All the solutions were freshly prepared before each measurements.

### 2.2. Method of preparation CD complexes

Stock solution of DMABN ($1\times10^{-3}$ M) was prepared by weighing known amount of DMABN, dissolved in water with sonication. 0.1 ml of this stock solution was transferred into a 10 ml volumetric flask, the respective CD (from $1\times10^{-2}$ M freshly prepared stock solution in water) is added, diluted to 10 ml with water and stirred for 6 h to ensure equilibrium in complexation.

Absorption and emission spectra were recorded using JASCO 7800 UV/Vis spectrophotometer and JASCO FP 770 spectrofluorometer respectively. The excitation wavelength was fixed as 300 nm unless specified otherwise and the slits for the excitation and emission monochromators were both 5 nm. The scan rate was 100 nm/min. Solid state emission spectra were recorded on HITACHI F 4500 fluorescence spectrophotometer. The excitation and emission monochromator slit widths were both 2.5 nm with a scan speed of 240 nm/min. The fluorescence lifetimes were measured in a IBH 5000 Single-photon counting instrument. Circular dichroism spectra was recorded using JASCO J600 spectropolarimeter.

### 2.3. Calculation of equilibrium constants

Equilibrium constants ($K_f$) for the formation of the (1:1) complexes in the ground state were calculated using the Benesi–Hildebrand method [21,22] employing the equation

$$\frac{1}{\Delta I}=\frac{1}{A}\times\frac{1}{K_f[\mathrm{CD}]_0}+\frac{1}{A} \tag{1}$$

where, '$\Delta I$' is change in fluorescence intensity upon addition of CD, '$A$' is the instrumental factor.

$K_f$ (e.s.), the true equilibrium constants in the excited state are calculated from Eq. (4). The free energies of the excited states of DMABN and their complexes with CDs are calculated by the following equation,

$$G_{ex}=G_{gd}+\Delta E$$

$$G_{ex}=G_{gd}+h\nu \tag{2}$$

where '$\Delta E$' is an excitation energy, '$G_{ex}$' and '$G_{gd}$' are the free energy of the excited and ground states, respectively, in the free or the complexed form and '$\nu$' is the frequency of the absorbed light. A photon energy of fluorescence light is usually used for calculation of $\Delta E$.

The free energy changes at the complexation of DMABN with CDs in a ground state are calculated by the following thermodynamic relationship

$$\Delta G_{gd}=-RT\ln K_{gd} \tag{3}$$

The free energy changes at the complexation in the excited state [23] can also be calculated by the following equation:

$$\Delta G_{ex}=G_{ex}(\text{complex})-G_{ex}(\text{free})$$

$$\Delta G_{ex}=\Delta G_{gd}-h\nu_1+h\nu_2 \tag{4}$$

Here, '$\nu_1$' and '$\nu_2$' are the frequencies of the absorbed lights of free and complexed compounds, respectively.

## 3. Results

### 3.1. Studies with DM-β-CD

When the concentration of DM-β-CD is increased the absorbance (at 297 nm) of DMABN increases without any shift in the $\lambda_{max}$ and no isosbestic point is observed. In the emission spectra of DMABN in the presence of DM-β-CD in aqueous solution (Fig. 1 ), two emission maxima are observed, one at 370 nm and the other at 520 nm. The lower wavelength emission, known as the localized emission (LE), is due to the planar conformation of the DMABN molecule and the higher wavelength emission is from the twisted intramolecular charge transfer state (TICT emission) [13–15]. Upon encapsulation into the DM-β-CD cavity, the fluorescence intensities of both the peaks are enhanced and hypsochromic shifts are observed. The LE and TICT peaks are shifted to 341 and 490 nm, respectively in the presence of $7\times10^{-3}$ M DM-β-CD.

The equilibrium constants for the formation of inclusion complexes between DMABN ($1\times10^{-6}$ M) and DM-β-CD are calculated for the ground [21,22] as well as the excited states [23] and are given in Table 1 (Fig. 2a).

Since the host–guest equilibrium does not reach a steady state in the fluorescence lifetime, which is too fast compared with diffusion rate of molecules, $K_f$ (g.s) value for the ground state complex is calculated from the 370 nm emission [23]. $K_f$ (e.s), the true equilibrium constants in the excited state are calculated from Eq. (4). Scheme 1 shows the calculated free energy levels in the ground and excited states.

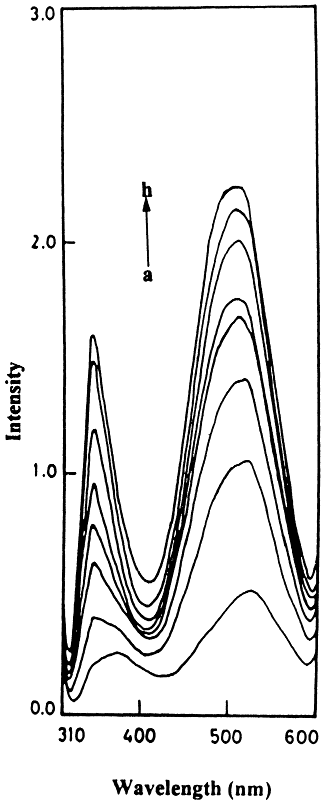


Fig. 1. Fluorescence spectra ($\lambda_{ex}$=300 nm) of DMABN ($5.3\times10^{-5}$ M) in aqueous and in the presence of DM-β-CD. [DM-β-CD]=(a) 0, (b) $1\times10^{-3}$ M, (c) $2\times10^{-3}$ M, (d) $3\times10^{-3}$ M, (e) $4\times10^{-3}$ M, (f) $5\times10^{-3}$ M, (g) $6\times10^{-3}$ M, (h) $7\times10^{-3}$ M.

Table 1
Complex formation constants ($K_f$, $M^{-1}$) of inclusion complexes of DMABN with CD derivatives

| CD | $K_f$ (g.s.)[a] | $K_f$ (e.s.)[a] | $K_f$ (e.s.)[b] |
|---|---|---|---|
| DM-β-CD | 390 | $7.1\times10^{-3}$ | 1.50 |
| HP-β-CD | 446 | 37.5 | 74.2 |
| β-CD[c] | 1025 (302)[d] | – | – |

[a] $K_f$ values calculated from 370 nm emission.
[b] $K_f$ values calculated from 520 nm emission.
[c] From [24].
[d] Value reported from absorption spectra.

From the data in Table 1, it is clear that both DM-β-CD and HP-β-CD form weaker complexes with DMABN, when compared to β-CD. Also, complex stability decreases in both the excited states, compared to the ground state. The stability decreases more significantly in the LE state than in the TICT state.

The excitation spectra of DMABN in the presence of DM-β-CD (monitored at the two emission maxima) are recorded and are shown in Fig. 3. A change in the excitation spectrum of the complex is observed when the emission wavelength is changed. For the emission maximum of 350 nm two peaks are observed in the excitation spectra, one at 285 nm and the other at 234 nm and for the 490 nm emission, the peaks are shifted to 305 and 247 nm, respectively.

The emission spectra at different excitation wavelengths in the presence of DM-β-CD are also recorded. By shifting the excitation wavelength i.e., from 290 to 330 nm, the intensity of the TICT emission shows no change whereas the intensity of LE emission is reduced with an increase in excitation wavelength.

At very low concentration of DMABN ($1\times10^{-6}$ M), only the emission from LE state is observed. When the concentration of the DM-β-CD increases, the intensity of the LE emission increases and no TICT emission is observed (Fig. 4i). When the substrate concentration is increased to $1\times10^{-5}$ M, (Fig. 4ii) along with LE emission, the TICT emission is also observed. Upon addition of DM-β-CD, emission intensities of both the bands are enhanced, but enhancement in TICT is less compared with LE emission. With a further increase in the concentration of DMABN to $5.3\times10^{-5}$ M, (Fig. 4iii) both emissions are enhanced and compared with LE, the enhancement is higher in TICT emission. It is pertinent to note here that when the concentration of DMABN is very low (i.e. $1\times10^{-6}$ M), only LE band is observed and an increase in concentration of free DMABN (uncomplexed) causes an increase in intensity of TICT band (Fig. 4i–iii and Fig. 7i–iii). The variations in intensity as a function of the concentration of DM-β-CD at two different emission maxima for all the three different concentrations of DMABN are shown in Fig. 5.

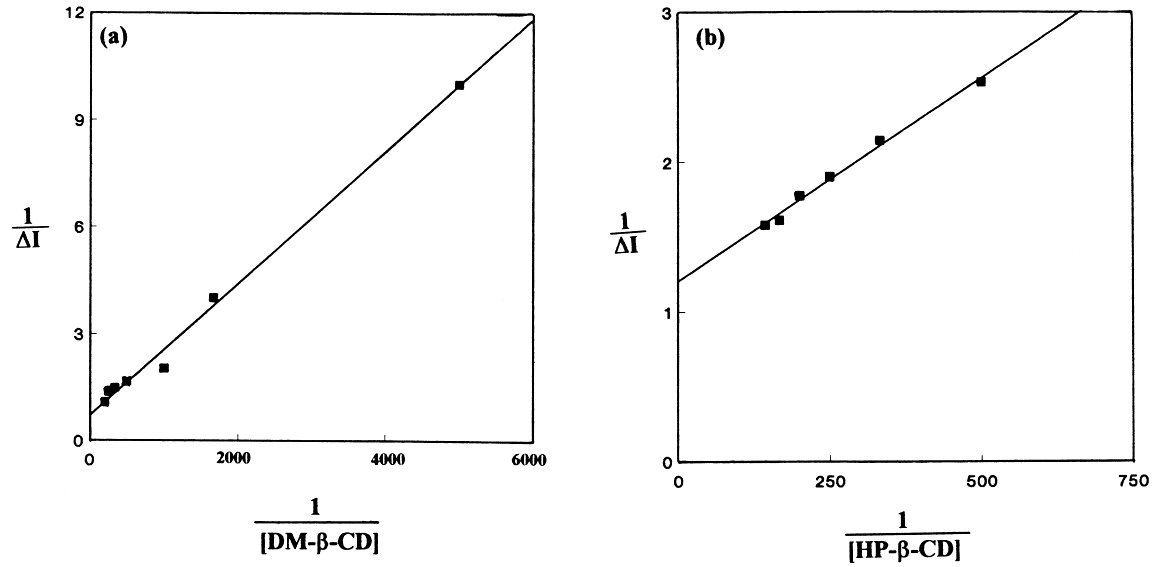
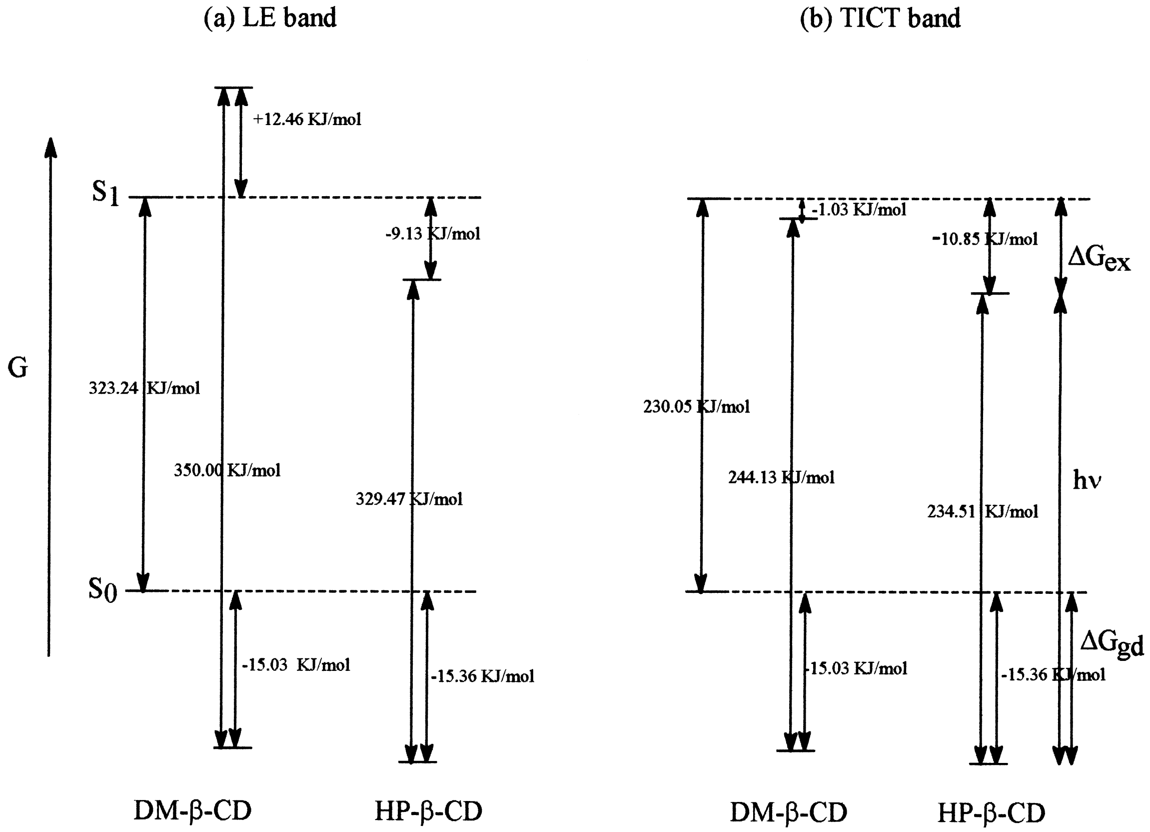


Fig. 2. Benesi–Hildebrand plot for the formation of 1:1 inclusion complex of DMABN ($1\times10^{-6}$ M) in the presence of (a) DM-β-CD and (b) HP-β-CD.



Scheme 1.

### 3.2. *Studies with HP-β-CD*

Upon addition of HP-β-CD, both absorbance as well as the fluorescence intensities of DMABN (Fig. 6) are increased and no shift is observed in the absorption spectra. Upon encapsulation within HP-β-CD, the $\lambda_{max}$ for emission gets shifted to 363 and 510 nm for the LE and TICT emissions, respectively. The shift, however, is lesser compared to DM-β-CD. The equilibrium constants for the formation of inclusion complexes of DMABN ($1\times10^{-6}$ M) with HP-β-CD in the ground and the excited states are calculated and are given in Table 1 (Fig. 2b).

The excitation spectra at two different emission wavelengths i.e., at 350 and 490 nm in the presence of HP-β-CD

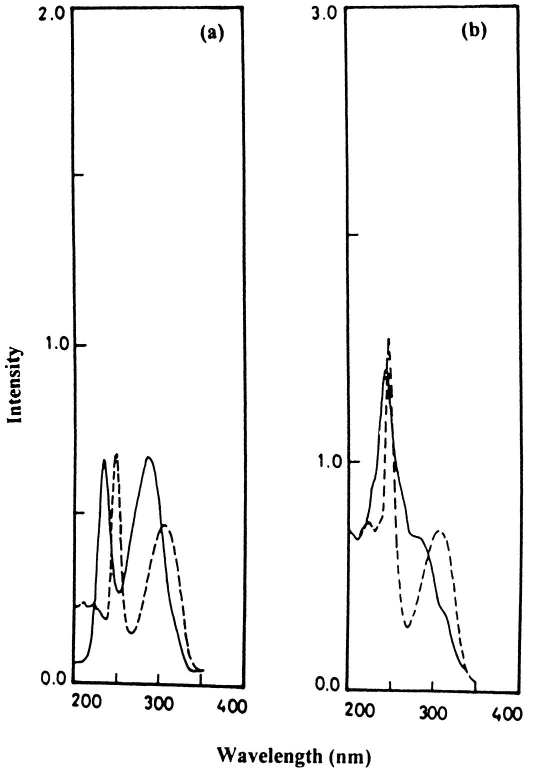


Fig. 3. Excitation spectra of DMABN ($1\times10^{-5}$ M) in the presence of (a) DM-β-CD ($1\times10^{-2}$ M) at 490 nm (- - -) and at 350 nm (—) and (b) in the presence of HP-β-CD ($1\times10^{-2}$ M) at 490 nm (- - -) and at 350 nm (—).

are recorded (Fig. 3). Two excitation maxima are observed, one at 244 and the other one at 280 nm for the emission maxima of 350 nm for the complexed DMABN. Similarly for the 490 nm emission, the excitation spectrum gives two peaks at 246 and 305 nm. The emission spectra of DMABN are recorded at different excitation wavelength. With an increase in the wavelength of excitation, both emissions are decreased in intensity and a red shift is observed in the LE emission.

When the concentration of DMABN is $1\times10^{-6}$ M, only LE is observed and no TICT emission is observed (Fig. 7i), as in the case of DM-β-CD. When the concentration of DMABN is increased to $1\times10^{-5}$ M, TICT emission is also observed along with LE emission. By the addition of HP-β-CD, both emissions are enhanced (Fig. 7ii) and compared with Fig. 7a, the emission intensity of LE is less. At very high concentration of DMABN ($7.5\times10^{-5}$ M) the TICT emission is enhanced in the presence of HP-β-CD, whereas the intensity of the LE emission is also increased but the increase is much less compared to the increase of TICT emission intensity (Fig. 7iii). The intensity variation as a function of concentration of HP-β-CD for the three different concentrations of DMABN are shown in Fig. 5.

The solid state emission spectra of DMABN in the free state and complexed with β-CD and HP-β-CD are recorded and are given in Fig. 8. Only one emission is observed around 360 nm in the case of β-CD complex whereas in the presence of HP-β-CD both emissions are observed. TICT emission is shifted to 475 nm and non-polar emission is observed at 400 nm.

The fluorescence lifetimes of DMABN in the presence of DM-β-CD and HP-β-CD are given in Table 2. $\tau_1$ represents the TICT lifetime and $\tau_2$ represents the lifetime of DMABN from the LE state. $\tau_2$ value is affected significantly by the

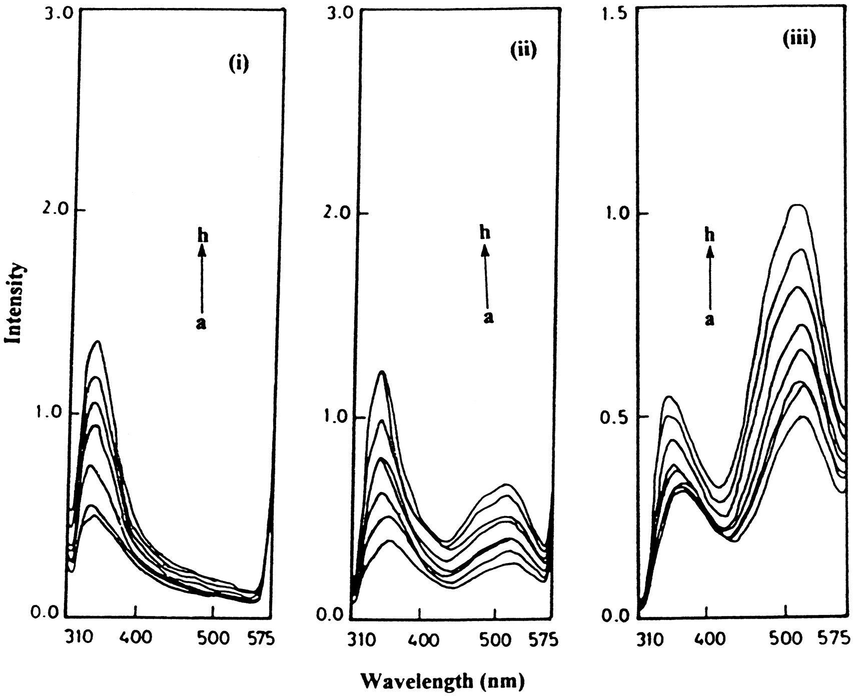


Fig. 4. Concentration variation of DMABN in the presence of DM-β-CD. [DMABN]=(i) $1\times10^{-6}$ M, (ii) $1\times10^{-5}$ M, (iii) $5.3\times10^{-5}$ M and [DM-β-CD]=(a) 0, (b) $1\times10^{-3}$ M, (c) $2\times10^{-3}$ M, (d) $3\times10^{-3}$ M, (e) $4\times10^{-3}$ M, (f) $5\times10^{-3}$ M, (g) $6\times10^{-3}$ M, (h) $7\times10^{-3}$ M. $\lambda_{ex}$=290 nm.

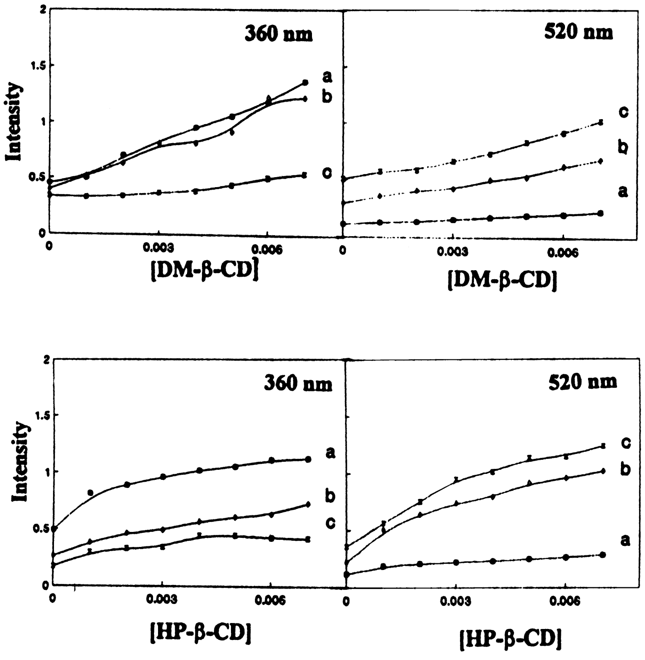


Fig. 5. The variation of intensity as a function of concentration of DM-β-CD (Top) and HP-β-CD (bottom) for the different substrate concentrations at two different wavelengths. [DMABN]=(a) $1\times10^{-6}$ M, (b) $1\times10^{-5}$ M, (c) $5.3\times10^{-5}$ M for DM-β-CD and (a) $1\times10^{-6}$ M, (b) $1\times10^{-5}$ M, (c) $7.5\times10^{-5}$ M for HP-β-CD system.

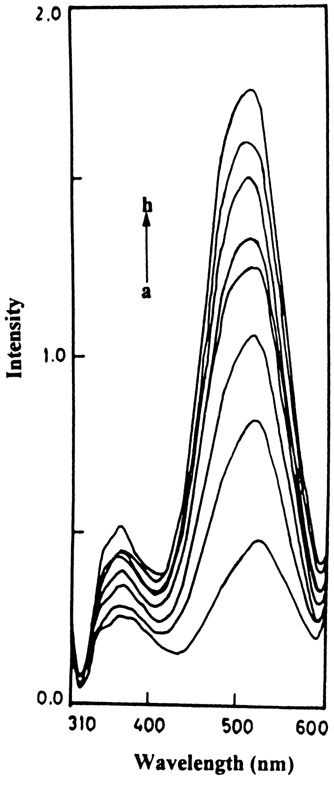


Fig. 6. Emission spectra ($\lambda_{ex}$=300 nm) of DMABN ($5.3\times10^{-5}$ M) in aqueous solution and in the presence of various concentrations of HP-β-CD. [HP-β-CD]=(a) 0, (b) $1\times10^{-3}$ M, (c) $2\times10^{-3}$ M, (d) $3\times10^{-3}$ M, (e) $4\times10^{-3}$ M, (f) $5\times10^{-3}$ M, (g) $6\times10^{-3}$ M, (h) $7\times10^{-3}$ M.

Table 2
Lifetimes of DMABN in different environments

| Medium | $\tau_1$ (ns) | $\tau_2$ (ns) |
|---|---|---|
| DM-β-CD | 4.93 | 0.22 |
| HP-β-CD | 2.32 | 0.24 |
| Toluene[a] | 3.10 | 0.016 |
| α-CD[b] | 3.26 | – |
| β-CD[b] | 2.43 | – |
| $H_2O$[b] | 1.82 | – |

[a] Literature data from [7].
[b] From [12].

presence of both CD derivatives (Table 2) though, however, $\tau_1$ is not affected very much.

The induced circular dichroism spectra for α-, β-, γ-CDs, DM-β-CD and HP-β-CD are given in Fig. 9. The magnitude of molar ellipticity is larger in the case of β-CD and its derivatives, lesser with α-CD and the least in γ-CD. ICD spectra is also recorded in the presence of 1-adamantanol (an exogeneous guest, which shows remarkable binding ability into β-CD cavity) and is given in Fig. 10.

## 4. Discussion

The dual emission of DMABN in the presence of α-, β- and γ-CDs are reported by various groups [12–16,24]. It is proposed that 1:1 complexes are formed with α-CD and this is confirmed by the presence of an isosbestic point in the absorption spectra [12]. For β- and γ-CDs, in addition to 1:1 complex, higher order complexes are also proposed [25]. In the emission spectra, the LE emission is highly intense compared to the TICT emission in the presence of β- and γ-CDs. Two excitation maxima are observed at two different emission wavelengths. The peaks are observed at 295 and 306 nm in β-CD and at 302 and 312 nm in the case of γ-CD when monitored at the LE and TICT bands, respectively. These results clearly indicate that two sets of complexes are formed which absorb at two different wavelengths. Hence, in addition to the normal 1:1 complex, a 2:2 complex (homodimer) is also proposed [25] and this is supported by studies of guest concentration variations.

In the present study employing CD derivatives, namely, DM-β-CD and HP-β-CD also, both the emission peaks of DMABN are shifted to lower wavelengths indicating that the molecule now resides in a different environment. The shift is largest in the case of DM-β-CD reflecting its greater hydrophobicity. Also, compared to β-CD, the blue shift in the LE emission is maximum in DM-β-CD.

It is relevant to note here that stronger complexes are formed in the case of β-CD, in comparison with CD derivatives (Table 1). Also the complexes with DM-β-CD and HP-β-CD are much more weaker in the excited state than in the ground state of DMABN. Tight fitting of the guest inside the host and absence of hydrogen bonding to stabilize the polar excited states in the CD derivatives may be responsible

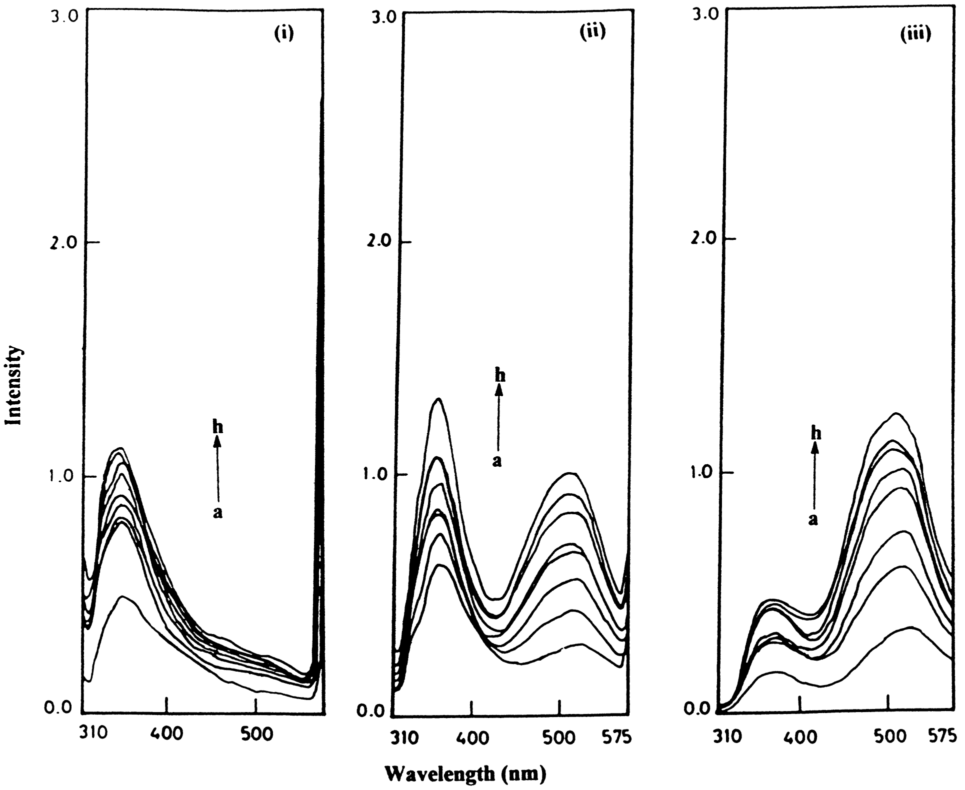


Fig. 7. Fluorescence spectra for the variation of concentration of DMABN in the presence of HP-β-CD. [DMABN]=(i) $1\times10^{-6}$ M, (ii) $1\times10^{-5}$ M, (iii) $7.5\times10^{-5}$ M and [HP-β-CD]=(a) 0, (b) $1\times10^{-3}$ M, (c) $2\times10^{-3}$ M, (d) $3\times10^{-3}$ M, (e) $4\times10^{-3}$ M, (f) $5\times10^{-3}$ M, (g) $6\times10^{-3}$ M, (h) $7\times10^{-3}$ M. $\lambda_{ex}$=290 nm

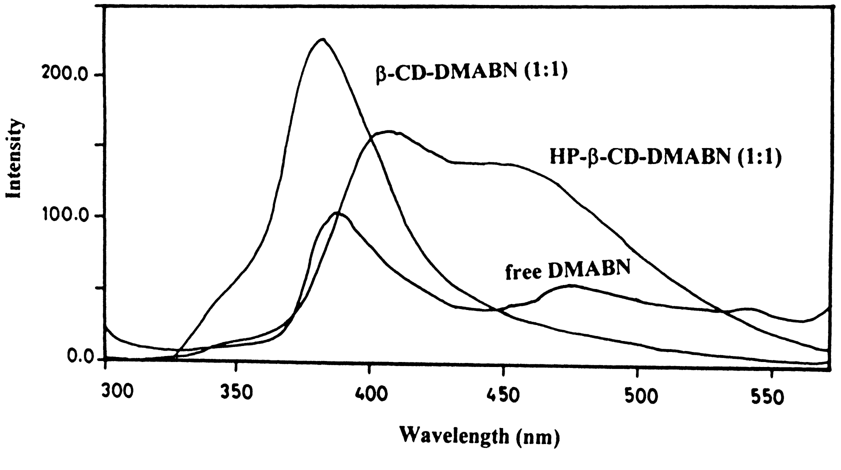


Fig. 8. Solid state emission spectra ($\lambda_{ex}$=300 nm) of free DMABN, β-CD-DMABN and HP-β-CD-DMABN (1:1) complexes.

for this observation. It is likely that the presence of methoxy groups in the rim of DM-β-CD suppresses the formation of hydrogen bonds between the substrate and DM-β-CD and also between two CDs. This is also responsible for the decrease in the amount of higher order complexes. The intensity of the LE band is significantly enhanced, compared to that of the TICT emission. This may be attributed to the much more fitter and tighter binding with the two CD derivatives which makes it difficult for DMABN to twist, so that TICT is reduced compared to LE state.

### *4.1. Concentration variations*

In polar solvents, it has been reported that the fluorescence spectrum is unaffected by changes in concentration of DMABN. However, in nonpolar solvents, the fluorescence spectrum has varied significantly with the concentration of DMABN [26] which exerts a long-range electrostatic interaction, playing the role of a polar solvent. In addition, a short-range dipolar interaction to form a loose 1:1 or 1:*n* ‘self-complex’, between the polar excited and ground-state

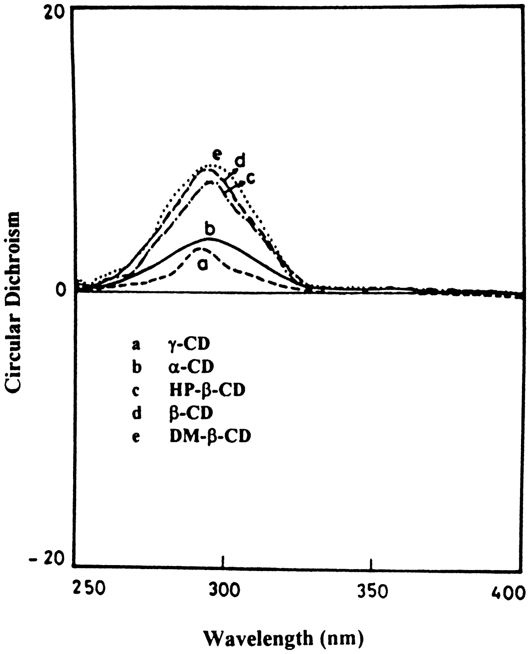


Fig. 9. ICD spectra of DMABN ($3\times10^{-4}$ M) in the presence of cyclodextrins. [α-CD]=$2.55\times10^{-3}$ M, [β-CD]=$1.82\times10^{-3}$ M, [γ-CD]=$2.03\times10^{-3}$ M, [DM-β-CD]=$2.52\times10^{-3}$ M and [HP-β-CD] =$4.41\times10^{-3}$ M.

DMABN molecules has also proposed by Nakashima et al. [25]. Neither ground-state association nor excimer formation is detected. With polar solvents, while the long-range interactions are negligible, the short-range interactions are weaker.

In the present study with water as solvent, when the concentration of DMABN is very low, solvation is extensive. This makes the twisting to TICT state more difficult, resulting only in LE band. With further increase in the concentration of DMABN the short-range interactions as discussed by Nakashima et al. [25] become more pronounced, thus weakening the solvent shell around the DMABN molecule. Twisting to TICT state now becomes smoother and TICT band has also appeared in the emission spectrum.

The concentration of the substrate is also varied in order to gain an insight into the type of complexes with CD derivatives. With very low solvent polarity [27], CDs contribute appreciably to the different emission spectrum at different concentration of the substrate. At very low concentration of the substrate even with high concentrations of DM-β-CD as well as HP-β-CD, no TICT emission is observed and only at moderate and at high concentrations of the substrate, TICT emission is significant. Thus, the shape of the emission spectra is largely dependent on the concentration of DMABN (Figs. 4 and 7).

The results provide interesting contrast to earlier reports [25] of DMABN with β-CD, wherein increase in the concentration of DMABN, caused an increase in the ratio of the intensity of LE band to that of the TICT band. It is proposed that the species which exhibits an intense LE band and which increase at higher concentration of the guest is a 2:2 complex.

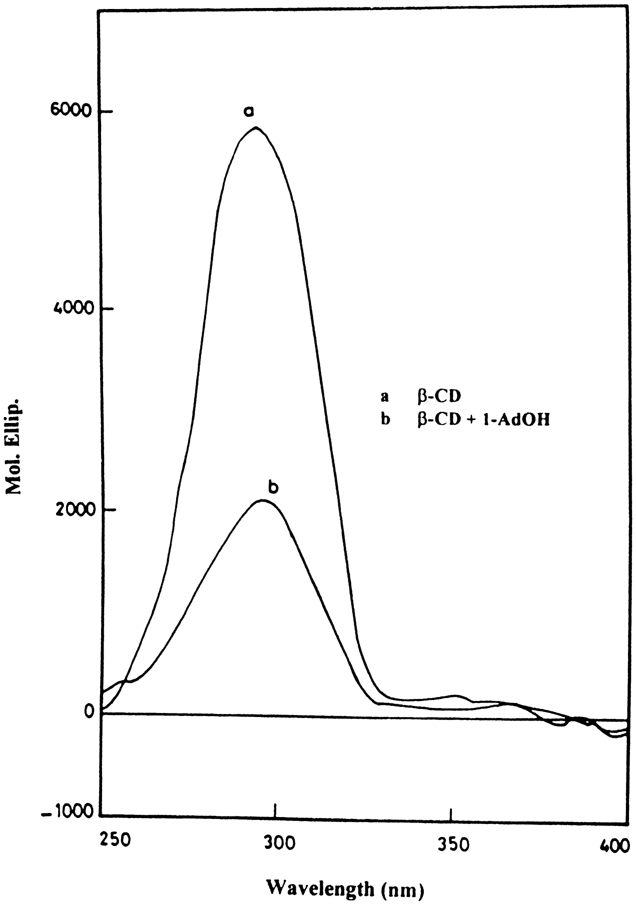


Fig. 10. Variation in molar ellipticity in the ICD spectra of DMABN ($3\times10^{-4}$ M) in the presence of (a) β-CD ($1.82\times10^{-3}$ M) and (b) β-CD+1-AdOH ($1.96\times10^{-3}$ M).

In the present study, with both DM-β-CD and HP-β-CD, an increase in the concentration of DMABN causes a reverse trend, i.e., the ratio of the intensities of the TICT band to LE band increases. Obviously, this indicates that no 2:2 complex is formed with these CD derivatives. Also, the driving force (which is not discussed earlier) for 2:2 complex formation is not significant with CD derivatives. This prompted us to propose that hydrogen bonding between two β-CD molecules in the complexed state may have contributed significantly to the formation of 2:2 complexes.

Excitation spectra also lends support to the observation that there are two absorbing species present. It is observed that the excitation spectrum monitored at the 'non-polar' emission maximum is hypsochromically shifted (285 and 280 nm in DM-β-CD and HP-β-CD, respectively) compared with that monitored at the TICT emission (305 nm in both). This indicates that the emissions are essentially due to two different sets of complexes having absorption maxima at 302 and 312 nm.

### 4.2. Lifetime studies

The lifetime of TICT state ($\tau_1$) is not very different compared to the data reported in solvents [10,12] which indicates that not all molecules are included into the CD cavity. While some of the molecules are included, the rest remain in the aqueous exterior. It is likely that the TICT state, being more polar, prefers to remain in the aqueous solution. This conclusion is also supported by the concentration dependence studies of DMABN in the presence of both CDs. At low concentration of DMABN, most of the substrate molecules are included into the CD cavity, thereby making twisting to TICT state more difficult. Thus, only emission from LE state is observed. As the concentration of the DMABN increases, the percentage of DMABN present in the aqueous exterior increases. It is also relevant to recall that there is a dynamic equilibrium between CD-complexed and free DMABN. The resultant increase in the amount of DMABN in aqueous exterior, with an increase in the concentration of DMABN, is attributed to the increase in TICT emission at the expense of LE emission. This conclusion is also supported by $K_f$ values (Table 1). With both DM-β-CD and HP-β-CD, $K_f$ values for the excited states are lower compared to ground state complex.

In contrast, the lifetime of the LE state in CD exhibits a tenfold increase compared to that in toluene medium, suggesting that the molecule now is in the complexed form.

Solid state emission spectra of DMABN, 1:1 complexes of β-CD and HP-β-CD are also reported (Fig. 8). Only LE emission is observed in free solid DMABN as well as 1:1 β-CD-DMABN complexes. In the solid form, no polar environment is available. Twisting is also difficult in the solid form as well as in 1:1 β-CD complexes resulting in only LE emission. However, with HP-β-CD-DMABN solid complexes, both LE (red shifted) and TICT emissions are present. As the HP-β-CD itself is more hydrophilic in character, the molecule now finds itself in a polar environment and TICT emission is observed at 475 nm in the solid state emission spectra.

### 4.3. Circular dichroic studies

To gain an insight into the orientation of the guest molecules inside the CD cavity circular dichroic studies have been employed. The signs of the ICD spectra of the CD-DMABN complexes are positive in all the CDs in the wavelength region of the electronic transition, indicating that the long axis of the arene guest is parallel to the axis of the CD cavity (axial inclusion). The magnitude of induced circular dichroism is significant with β-CD, DM-β-CD as well as HP-β-CD and is the least with γ-CD. This is in accordance with the tightness of fit between the host and the guest. However, with α-CD, the ICD value is only marginally higher than γ-CD and significantly lower than β-CDs indicating that DMABN is not included fully into the α-CD cavity. The increase in polarity upon excitation may be attributed to the decrease in inclusion into the hydrophobic CD cavity.

Addition of 1-adamantanol causes a decrease in the magnitude of the molar ellipticity in the ICD spectra (Fig. 10) and this can be construed as additional support that axial inclusion of DMABN has taken place into the β-CD cavity.

## 5. Conclusion

The results presented above, amply demonstrate that the binding behaviour of DMABN into DM-β-CD and HP-β-CD are significantly different from β-CD and provide interesting insight into the factors responsible for complexation. Along with evidences from lifetime and CD data, the results indicate that while TICT emission occurs from the aqueous exterior, LE emission is predominantly from the complexed molecule. This rules out partial inclusion (or) incomplete penetration as well as formation of higher order complexes, which are significant with unmodified α-, β- and γ-CDs. Absence of hydrogen bonding and a tighter fit with HP-β-CD and DM-β-CD are attributed to these interesting observations.

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