

Fluorescence quenching of benzimidazoles by chlorinated methanes

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Fluorescence quenching of benzimidazole (BI), 2-methylbenzimidazole (MBI), 5, 6-dimethylbenzimidazole (DMBI), 1-ethyl-2-methylbenzimidazole (EMBI), 2, 5, 6-trimethylbenzimidazole (TMBI), 2-phenylbenzimidazole (PBI) and 1-ethyl-2-phenylbenzimidazole (EPBI) by CH_2Cl_2 , CHCl_3 and CCl_4 have been studied in cyclohexane, methanol and acetonitrile and the values of k_q have been determined. Correlation of $\log k_q$ versus electron affinity (EA) of the quencher clearly indicates that deactivation of the excited state of BI's by above quenchers proceeds through the formation of charge transfer type complex. The high value of k_q in more polar acetonitrile as compared to that in non-polar cyclohexane could be due to the stability of charge transfer complex in acetonitrile as compared to that in cyclohexane. The static quenching component can be described by the sphere of action model with a radius of 1 nm for BI and TMBI. The quenching efficiencies of CCl_4 is nearly unity, 0.36 to 10^{-2} for CHCl_3 and 10^{-3} to 10^{-2} for CH_2Cl_2 respectively.

Micelles have often been used as mimicking agents for biomembranes and different types of reactions have been studied in micelles to understand similar reactions occurring in biologically active systems¹⁻⁴. This is because different kind of molecules get solubilized and get bound at different positions of the micelles, having different environments. Molecules in aqueous micelles get distributed in micellar and aqueous phases and the distribution depends upon their binding constants to the micelles. The partition coefficients can be determined from the changes observed in either the absorption or fluorescence spectra. Sometimes, it becomes very difficult to do so because the changes observed in the spectral characteristics are negligible, for example, the absorption and fluorescence spectra of benzimidazoles⁵⁻⁷ (BI's) in aqueous medium are not different from those noticed in aqueous sodium dodecyl sulphate (SDS) micelles^{8,9}. Under these circumstances, the preference fluorescence quenching method can be used to find the amount of solute present in any one phase. The assumption¹⁰ involved in this process of fluorescence quenching is that the quencher molecules are soluble only in one of the two phases and thus quenches the fluorescence of the molecules present in that phase. The fluorescence intensity of the fluorophore present in the other phase is not affected by the quencher.

The present study deals with the fluorescence quenching of benzimidazole (BI), 2-methylbenzimidazole (MBI), 5, 6-dimethylbenzimidazole (DMBI),

1-ethyl-2-methylbenzimidazole (EMBI), 2, 5, 6-trimethylbenzimidazole (TMBI) 2-phenylbenzimidazole (PBI) and 1-ethyl-2-phenylbenzimidazole (EPBI) by methylene chloride, chloroform, and carbon tetrachloride. This is because our recent study^{8,9} has indicated that the spectral characteristics of benzimidazoles do not change very much both in band maxima and intensity in SDS micelles. Thus the partitioning of BI's in micellar solutions or determination of binding constants to SDS micelles poses a big problem. Since chlorinated methanes get solubilized in the core of SDS micelles (or their solubility in water is nearly negligible), the fluorescence quenching by these molecules (specially CHCl_3 and CCl_4) can be used to find the partitioning of the BI's between aqueous and micellar phases and thus the binding constants. We have used three different kinds of solvents; cyclohexane, pure non-polar (similar to core of SDS), acetonitrile (polar but aprotic) and methanol (polar and protic).

Materials and Methods

BI, MBI, EMBI, DMBI, TMBI, PBI and EPBI (Aldrich) were purified according to the procedure mentioned in our earlier paper⁶. Analytical grade cyclohexane (Sisco), acetonitrile (E. Merck) and methanol (BDH) were further purified as suggested in literature¹¹. Spectrograde CH_2Cl_2 , CHCl_3 and CCl_4 were used as such.

Absorption spectra were recorded on Shimadzu spectrophotometer 190 UV. equipped with 135U

Table 1—Quenching rate constants (k_q) by different quenchers in different solvents, excited singlet state energy (E_{S^*}) and ionisation potentials of benzimidazoles

Compound	E_{S^*} (eV)	IP_D (eV)	k_q ($dm^3 mol^{-1} s^{-1}$)							
			Cyclohexane				Methanol			
			τ^* (ns)	CH_2Cl_2 $\times 10^{-7}$	$CHCl_3$ $\times 10^{-9}$	CCl_4 $\times 10^{-9}$	τ^* (ns)	CH_2Cl_2 $\times 10^{-7}$	$CHCl_3$ $\times 10^{-9}$	CCl_4 $\times 10^{-9}$
BI	4.36	8.5	5.7	—	1.5	10.2	4.33	0.46	1.2	14.8
MBI	4.33	8.24	—	—	—	—	3.74	0.46	2.5	16.2
EMBI	4.28	8.36 ^a	5.0	1.2	2.7	11.7	5.4	0.2	1.39	12.0
DMBI	4.21	8.17	4.9	0.6	3.96	10.1	6.6	0.17	2.0	11.0
TMBI	4.18	7.88 ^a	5.56	3.1	7.1	8.2	4.76	1.1	4.3	12.6
PBI	3.91	8.73 ^a	1.98	2.52	0.33	4.0	3.5	0.6	0.16	4.2
EPBI	3.87	8.63 ^a	2.0	2.0	0.46	4.7	3.84	0.4	0.18	3.3

	E_{S^*} (eV)	IP_D (eV)	Acetonitrile			
			τ^* (ns)	CH_2Cl_2 $\times 10^{-7}$	$CHCl_3$ $\times 10^{-9}$	CCl_4 $\times 10^{-9}$
BI	4.36	8.5	3.5	—	2.7	20.5
MBI	4.33	8.24	3.7	0.16	5.1	19.4
EMBI	4.28	8.36 ^a	4.26	0.45	3.9	17.0
DMBI	4.21	8.17	5.5	0.86	4.1	16.6
TMBI	4.18	7.88 ^a	5.12	1.6	6.6	13.9
PBI	3.91	8.73 ^a	2.0	0.55	0.3	9.5
EPBI	3.87	8.63 ^a	2.15	0.51	0.3	11.3

a = this work.

chart recorder. Fluorescence characteristics were measured on scanning spectrofluorimeter, fabricated in this laboratory (details are available elsewhere)¹². Fluorescence decay lifetimes of PBI, EPBI and TMBI in different solvents at 300K were determined with the nanosecond single photon counting spectrofluorimeter (model SP-70/80) supplied by Applied Photophysics (APP) England, using nitrogen in the flash lamp, whereas hydrogen was used for molecules like BI, MBI, EMBI and DMBI. The electronic processing equipment and multichannel analyser were from Ortec and Norland respectively. The software for deconvolution, supplied by APP, was used for calculating the fluorescence lifetimes. The computer system was CPM based vector-3 model. In all the cases, the fluorescence decay observed followed single exponential decay giving good chi square values (1.0 ± 0.2) and nice Dublin-Watson parameters. The values of lifetimes are listed in Table 1. The concentrations of the BI's used vary between $1-2 \times 10^{-5} M$, where as those of $CHCl_3$ and CCl_4 varied from 0.001 to 0.4M. CH_2Cl_2 is a very poor quencher and thus very high concentration (9.2 M)

has to be used to get any meaningful fluorescence quenching.

Results and Discussion

Absorption spectra

The absorption spectra of all the BI's in cyclohexane, acetonitrile and methanol at various concentrations of $CHCl_3$ and CCl_4 do not change i.e. the band shapes and full band width at half the absorbance remain the same. This indicates that no complex formation between benzimidazoles and $CHCl_3$ and CCl_4 are occurring in the ground state. Whereas in case of CH_2Cl_2 , a small red shift in absorption spectra of BI's are noted. This is not due to the ground state complex formation but because of solvent effect as very high concentration (9.2 M) of CH_2Cl_2 is used. Corrections have been applied to the fluorescence intensities of BI's in high concentration of CH_2Cl_2 .

Fluorescence spectrum

The fluorescence spectra of all the BI's in three different solvents at various concentrations of chlorinated methanes were recorded. It has been

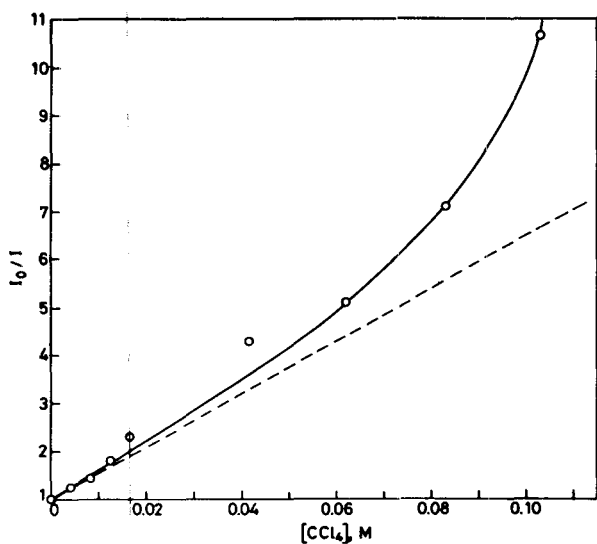


Fig. 1.—Plot of I_0/I versus $[CCl_4]$. $[BI] = 2 \times 10^{-5} M$, solvent, methanol

observed that the fluorescence intensity of the fluorophore decreases with the increase in quencher concentration, without appearance of any other new fluorescence band. The fluorescence band shape and full width at half the maximum intensity did not change. Further, the fluorescence intensity, as well as, the absorbance of any solution containing highest concentration of quencher did not change when the spectrum was recorded after the experiment was carried out once. This indicates that no detectable photoproduct is formed under our experimental conditions. This could be due to very small amount of quencher (less than $0.4 M$) used and duration time used for exciting the sample. Dichloromethane was the exception since the concentration of quencher used was $9.2 M$. Even at such a high concentration of CH_2Cl_2 , the results obtained were similar to those observed in case of $CHCl_3$ and CCl_4 . Further, the Stern-Volmer plot for CH_2Cl_2 as a quencher, is linear and thus indicates that no ground state or contact complex between the fluorophore and CH_2Cl_2 is formed even at such a high concentration of quencher.

The Stern-Volmer plot of the fluorescence quenching of BI in cyclohexane by CCl_4 is shown in Fig. 1. The plot is linear upto $0.01 M$ concentration of CCl_4 and positive deviation from Stern-Volmer plot is observed if the concentration of CCl_4 is greater than $0.01 M$. Similar observations were also noticed for TMBI and PBI ($[CCl_4] > 0.04 M$). The simple Stern-Volmer equation is

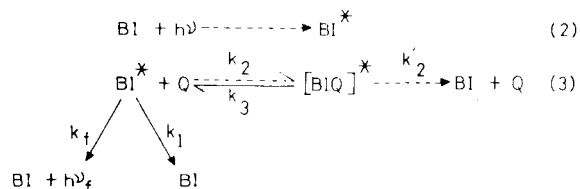
$$I_0/I = 1 + K_{sv}[O] = 1 + k_q\tau^0[Q] \quad \dots (1)$$

where I and I_0 are the fluorescence intensities of the fluorophore with and without the quencher Q , $K_{sv} =$

$k_q\tau^0$ is the Stern-Volmer constant, k_q is the second order quenching rate constant and τ^0 is the lifetime of the fluorophore in the absence of quencher. Similar plots were observed for other quenchers using different fluorophores and different solvents. The values of k_q thus obtained are compiled in Table 1.

Of all the benzimidazoles used, BI has the highest first singlet state energy and its absorption spectrum, can interfere with that of CCl_4 . So this molecule was selected to study the effect of excitation wavelength on the fluorescence quenching. Three different excitation wavelengths (276, 280, 285 nm) were used for all the quenchers in different solvents. It has been found that the values of K_{sv} obtained in a given solvent are not different from each other within experimental errors, e.g. in acetonitrile as solvent and CCl_4 as quencher, the $\lambda_{exc} = 276$ nm, $K_{sv} = 111 M^{-1}$; $\lambda_{exc} = 280$ nm, $K_{sv} = 110 M^{-1}$ and $\lambda_{exc} = 285$ nm, $K_{sv} \approx 115 M^{-1}$. These results indicate that no distinct complex formation between CCl_4 and BI in the ground state is observed and excitation energy has no effect on the fluorescence quenching of these fluorophores. As said earlier, this is also manifested from the study of absorption spectrum of BI. But these results are different from those of anthracene and CCl_4 where it has been shown that the photo products are formed¹³⁻¹⁵.

The fluorescence quenching of BI's by these molecules can be represented by Scheme 1.



Scheme 1

where BI, Q and $h\nu$ represent the fluorophore, quencher and the light quantum. BI^* and $[BIQ]^*$ are the excited states of the fluorophore and encounter complex between BI^* and Q respectively, k 's are reaction rate constants, k_f and k_1 are rate constants for the radiative and non-radiative processes. The apparent quenching rate constant k_q for the collisional quenching process can be given by $k_q = \gamma k_2$, where γ is the efficiency of the quenching reaction, which is given by $k'_2/(k_3 + k'_2)$. γ approaches unity if $k_3 \ll k'_2$ (quenching process is very fast) or it approaches k'_2/k_3 , when every encounter between BI^* and Q does not result in quenching i.e. the value of $k_q = k_2$ in the former case and $k_2k'_2/k_3$ in the latter case.

It is also clear from the absorption spectra of BI's and the quencher that the energy transfer from BI^* 's

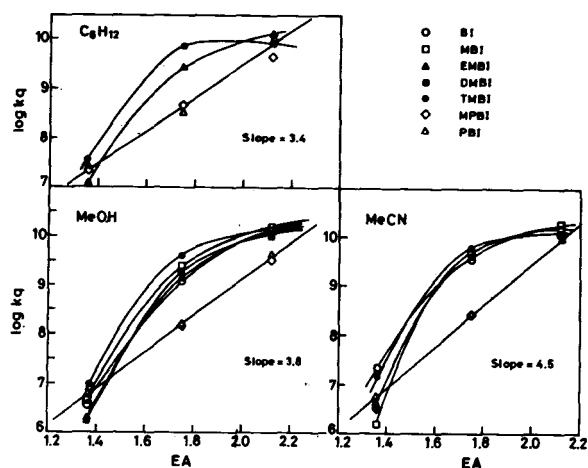


Fig. 2—Plot of $\log k_q$ versus electron affinity of the donors

to the quencher is an endothermic process. This is further manifested from the fact that k_q is independent of the wavelength of excitation. Thus in these cases where the quencher possesses no low lying excited singlet state, which can be populated by dipole-dipole resonance transfer of energy from excited BI*'s, the two molecules must approach one another at least to distances where the mutual interaction of the species is effective. This means that the rate of first step should be controlled by the diffusion process. Thus the maximum value of $k_q = k_2$ should be equal to k_{diff} , determined by using modified form of Stokes-Einstein relation¹⁶ ($8RT/2000n$, n is the viscosity of the medium, R is a gas constant, T in Kelvin) as 1.47×10^{10} , 2.7×10^{10} and $1.6 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ respectively in cyclohexane, acetonitrile and methanol.

The data of Table 1 clearly indicate that fluorescence quenching rate constants for BI's by CCl_4 in all the solvents are nearly equal to k_{diff} , i.e. every collision between the excited BI and CCl_4 in all the solvents, are effective in quenching the fluorescence of BI, (PBI and EPBI are being exception) whereas the quenching efficiency of CHCl_3 is only 0.1 ± 0.03 and that of CH_2Cl_2 is two to three order of magnitude less than the diffusion controlled. The quenching efficiency of all the quenchers in all the solvents for PBI and EPBI are less than that observed for methyl substituted molecules. (γ of CCl_4 and CHCl_3 for PBI and EPBI are 0.38 and 0.44; 0.1 and 0.1 respectively). The quenching rates even in the case of CH_2Cl_2 are considerably faster than can be accounted for chemical quenching (for example, the rate constant of quenching of alkyl radicals with CCl_4 does not exceed 10^4 - $10^5 \text{ M}^{-1} \text{ s}^{-1}$, see ref. 17). Thus the quenching is believed to proceed via an intermediate donor-acceptor exciplex between the

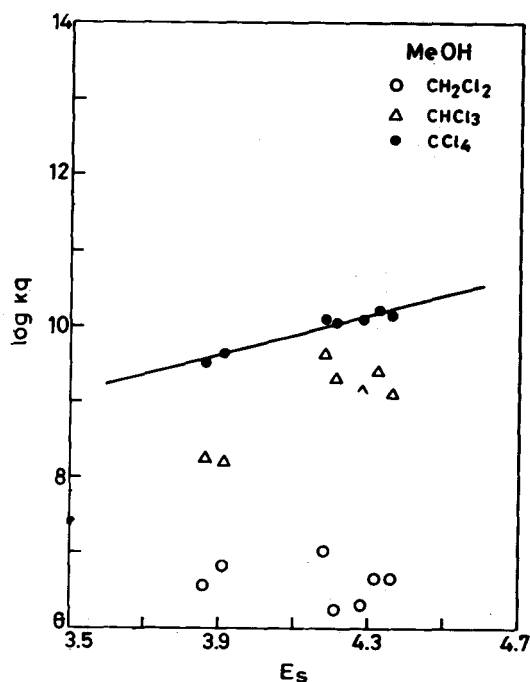


Fig. 3—Plot of $\log k_q$ versus first excited singlet state energy of the benzimidazoles

excited BI's and the halomethane molecules. Higher singlet state energy of the quencher than the fluorophore (i.e. non-classical energy transfer) and negligible overlap of the donor fluorescence spectra and acceptor absorption spectra further manifest the formation of exciplex¹⁸. Klein *et al.*¹⁴ developed a model in which the formation rate constant of this complex was considered as the rate determining step in the excitation quenching process. The equation derived is

$$\ln k_q \propto -(\text{IP}_D - \text{EA}_A - C - P - E_s)/k_b T \quad \dots (4)$$

where k_q is the quenching rate constant, IP_D is the ionisation potential of the donor, EA_A is the electron affinity of the acceptor, C is the Coulomb energy, P is the polarisation energy of the separated charges, E_s is the energy of the first excited singlet state of the fluorophore and k_b is the Boltzmann constant.

In order to verify the above mechanism, we have adopted two procedures:

(i) We selected one fluorophore and varied the quenchers. Under these conditions Eq. (4) reduces to Eq. (5)

$$k_q \propto \exp [(E_s + \text{const})/k_b T]$$

$$\log k_q = \text{const} + E_s/2.303 k_b T \quad \dots (5)$$

Although we had only three quenchers, we had plotted $\log k_q$ versus E_s (Fig. 2). As expected a linear relation has been observed for PBI and EPBI, whereas curved plots are observed for all other BI's

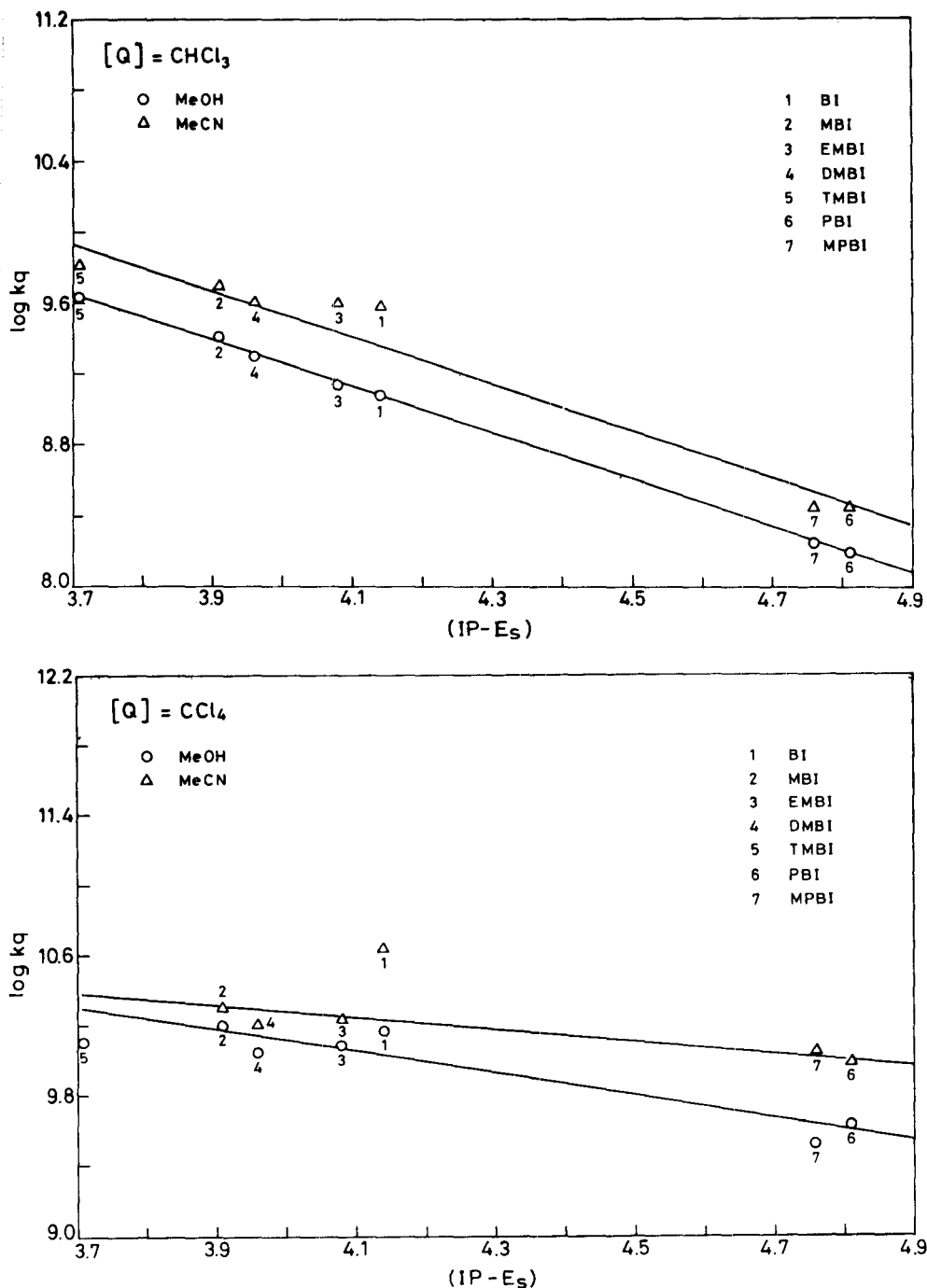


Fig. 4—Plot of $\log k_q$ versus $IP-E_s$, (a) $Q = CHCl_3$, (b) $Q = CCl_4$

and curves are levelling off to a diffusion controlled rate constant. A similar behaviour has also been observed in the case of fluorescence quenching of aromatic molecules by inorganic ions¹⁹⁻²² as well as, for aromatic amines by halomethanes²³. The slopes observed for PBI and EPBI are nearly similar and the values observed in cyclohexane, methanol and acetonitrile are 3.2 eV^{-1} , 3.7 eV^{-1} and 4.2 eV^{-1} respectively. The linear correlation suggests that

other variables except EA_A are practically constant. The above results are consistent with the fact that the values of the quenching rate constant are limited by the electron affinity of the quencher so long as these values are less than diffusion controlled limit. Once the value of k_q is equal to k_{diff} , k_q will be independent of EA_A . The values of slopes so obtained in each solvent are much less than the theoretical value [i.e. $1/(2.303 k_b T) = 16.78 \text{ eV}^{-1}$ at 298 K]. This, therefore, suggests

that though the direction of the rate constant indicates charge transfer character in the complex, such transfer is probably not a complete one-electron transfer at the transition state or in the complex. Our results are similar to those observed by Loutfy and Somershell²⁴, Encinas *et al.*¹⁵ and Goswami *et al.*²³. (ii) Equation (4) reduces to (6) if we choose different fluorophores and one quencher.

$$\ln k_q \propto [-(IP_D - E_s - \text{const})/k_b T]$$

or

$$\log k_q = \text{const} + (E_s - IP_D)/2.303 k_b T \quad \dots (6)$$

The singlet state energy of all the benzimidazoles were calculated by taking the average of long wavelength band maximum of absorption spectrum and short wavelength band maximum of fluorescence spectrum in cyclohexane. This is because in this solvent, the interactions between the solvent and the fluorophore is minimum. These values are compiled in Table 1.

The ionisation potential data for all the benzimidazoles are not available, except for BI, MBI and DMBI (i.e. 8.50, 8.24 and 8.17 eV respectively)²⁵. With the limited data available, it is clear that we cannot assume that IPs are constant for these benzimidazoles. However in the absence of IP_D values, $\log k_q$ versus singlet state energy of the fluorophores for CH_2Cl_2 , $CHCl_3$ and CCl_4 in all the three solvents are plotted in Fig. 3. As regards CCl_4 -induced fluorescence quenching is concerned the k_q values in all the solvents are nearly diffusion controlled except for phenyl substituted benzimidazoles, which are nearly half of k_{diff} . Thus it is difficult to draw any definite conclusion. But no linear correlation is observed between $\log k_q$ and singlet state energy for other quenchers in three solvents. This is because the value of k_q increases for even those molecules whose singlet state energy is less than that of BI.

Most of the main departures from correlation between $\log k_q$ and E_s can be explained in terms of IP_D of the donors. For example, from limited data available regarding IP_D , it is apparent that IP_D decreases with increase in methyl groups on benzimidazole moiety. We have tried to plot $\log k_q$ versus $(IP_D - E_s)$ for three benzimidazoles (BI, MBI, DMBI) for $CHCl_3$, using methanol as solvent in Fig. 4. This quencher is selected because k_q observed in this case is neither too close to k_{diff} nor very small that large concentration of quencher is required. Though the number of compounds is small, a reasonable straight line is obtained. Assuming that a similar dependence of k_q will be observed for other

fluorophores, $IP_D - E_s$ values have been determined corresponding to $\log k_q$. Using E_s , IP_D for the four benzimidazoles (EMBI, TMBI, PBI and EPBI) have been determined and compiled in Table 1. Using these values of IP_D (so determined) and E_s , $\log k_q$ versus $(IP_D - E_s)$ have been plotted in Fig. 4 for $CHCl_3$ and CCl_4 in other solvents. A reasonably good linear correlation is noticed for each case. These plots suggest that (1) IP_D determined in this manner for other BI's are not far from actual values and (ii) C and P values are constant for these systems in each solvent. The second point seems to be alright because the structure of the fluorophores are similar to each other and they are only distinguished by the presence of methyl or phenyl groups. The conclusion (1) also seems to be alright considering the following points. (a) The data of Table 1 show that IP_D decreases with increase in methyl groups and increases with the presence of phenyl groups on the BI. This could be because the methyl groups are electron donating and will increase the charge density on the BI moiety, thus decreasing the IP_D , whereas phenyl group acts as an electron withdrawing and thus increases the IP_D . Similar results have also been observed in other alkyl substituted aromatic compounds²⁶. (b) Further the pK_a values^{5,6} for the protonation reaction of alkyl and aryl substituted BI's also substantiate the fact that the charge density on the tertiary nitrogen atom increases with methyl substituents and decreases with aryl substituents.

In general, it has been found that the efficiency of the quencher increases with the increase in polarity of the solvent if the charge transfer complex is formed as an intermediate²⁷⁻³⁰. This has been explained by the fact that encounter complex (AQ)* leads to the formation of free ions ($A^+ + Q^{*-}$ or $A^{+*} + Q^-$) in polar solvents and to ($A^+ \cdots Q^{*-}$ or $A^{+*} \cdots Q^{*-}$) in nonpolar solvents. In medium polar solvents, the two rate constants compete with each other. The results are consistent with the above explanation that the efficiency of formation of free ions or ion pairs are more in acetonitrile than in cyclohexane or methanol. Nearly similar results observed in methanol and cyclohexane (even though the former is nearly as polar as acetonitrile) suggests that the presence of hydrogen bonding between the fluorophore and solvent molecule may hinder the transfer of charge from fluorophore to quencher. The above results thus suggest that the quencher has an affinity for electrons. The electrons can be donated either by the π -cloud of aromatic ring or by the lone pair of the tertiary nitrogen atom. The latter seems to be more plausible. This is because protonation is the extreme step in hydrogen bonding. The pK_a value for the protonation

of *ter*-nitrogen atom increases with increase in the number of electron donating methyl groups.

When dichloromethane is used as an electron acceptor, increase in fluorescence intensity as well as shift in fluorescence band maximum of the donor molecule is observed when concentration of CH_2Cl_2 is more than 5M and this can be explained in terms of a change in the rate of unimolecular photoprocesses induced by the change in solvent. At very high concentration of CH_2Cl_2 its effect as a solvent (and the decrease in k_q due to the decrease in the polarity) is more significant than the change in the quencher concentration (i.e. $k_q [\text{Q}]$ decreases with increase in $[\text{Q}]$). Similar dependence has also been observed in other molecules^{15,23,31}.

Fluorescence quenching at high CCl_4 concentration

Departure from linearity observed in the Stern-Volmer plot (Fig. 1) at high concentration of CCl_4 in case of BI and TMBI and PBI can be explained with the help of static quenching. There are two mechanisms.

Model I: Ground state complex formation

In this model, the fluorophore forms complex with the quencher in the ground state and thus depleting the concentration of free fluorophores. This model is rejected on the ground that no changes are observed in the absorption spectra of all the molecules with increase in quencher concentration and K_{SV} is independent of the wavelength of excitation.

Model II: Franck and Vavilov³¹ have suggested that instantaneous fluorescence quenching results at those instances in a randomly distributed system when a quencher happens to reside within a "sphere of action" with a volume of V/N_{av} and radius of R i.e. $V/N_{av} = 4/3 R^3$, surrounding the fluorophore at the time of excitation. N_{av} is the Avogadro's number. The Stern-Volmer equation can be written as

$$I_0/I = (1 + K_{SV} [\text{Q}]) e^{W[\text{Q}]} \quad \dots (7)$$

where W is a constant, from which the radius of active sphere 'R' can be calculated, using the following relation

$$R = [400 W]^{1/3} \quad \dots (8)$$

Using the values of K_{SV} , determined from the linear portion of Stern-Volmer plot and taking different values of W , Stern-Volmer curves are generated as a function of $[\text{CCl}_4]$. It has been found that the radius of sphere of action for quenching by CCl_4 are 1 nm, 1 nm and 0.6 nm for the fluorophores BI, TMBI and PBI respectively. These radii are larger for BI and TMBI than the value of 0.5 to 0.6 nm, which can be estimated

as the sum of the radii of BI, TMBI and CCl_4 , but smaller than that of PBI and CCl_4 (~ 0.8 nm). These results can be explained as follows. It has been well established that the first excited singlet state⁷ of BI and methyl substituted BI's is degenerate possessing both π^* and charge transfer state (CT). The CT state is lower in energy if electron donating group is present on benzo ring and electron withdrawing group is present on the imidazole ring^{6,7}. On the other hand, in the case of PBI, the lowest energy transition is of $\pi \rightarrow \pi^*$ and charge migration is completely delocalized on the whole molecule. This suggests that in molecules BI and TMBI, the first excited singlet state possesses enough CT character and thus can interact with the quencher molecule over a longer distance as compared to PBI.

In conclusion the fluorescence quenching rate constant of BI's by the halomethanes is reasonably well described by means of diffusion controlled mechanism of the quenching reaction. CCl_4 is the most efficient, CH_2Cl_2 is very weak and CHCl_3 is intermediate in quenching. Such an order of quenching ability is parallel with the order of electron affinity of the chloromethanes. Therefore, the initiation of quenching is perhaps related with the partial charge transfer from excited BI's to the chloromethanes and thus forming a non-fluorescent charge transfer complex. The stability of this complex increases with the increase in polarity of the solvent. Sphere of action model plays the main role in quenching the fluorescence at high concentration of CCl_4 .

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