Hydrogen Bonding Probe: Effect of Polarity

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ABSTRACT

Millions of compounds have been found in literature that show solvatochromic shift in absorption and /or emission spectra due to hydrogen bonding. Almost all of them are sensitive to the polarity of the medium as well. A large number of fluorophores show quenching of emission intensity on hydrogen bonding, while in case of a few increments in fluorescence is observed. However a hydrogen bonding probe, Dibenzo [a,c] phenazine, that cannot sense the polarity of the environment, has been reported which is unique in this respect. This probe can determine only the hydrogen bonding donating capacity of a solvent irrespective of its polarity.

Keywords: Hydrogen Bonding; Excited State; Polarity

Introduction

Hydrogen bonding (HB) has been key of interest for more than a century due to its importance and prevalence in numerous biological structures and reaction pathways. The unique properties of water, as solvent and biological medium, are due to the tetrahedral hydrogen bond network. However recent theoretical studies reveal that hydrogen bond is not present in supercritical water (Schienbein & Marx, 2020). Especially in biological sciences, it is perhaps the most abundant weak chemical interaction. It is involved in three-dimensional structure of DNA, RNA, secondary structure of proteins etc and mechanistic pathway of many enzyme catalysed reactions. Isotope-edited IR spectroscopy has recently been used to probe the HB environment of individual bases in DNA duplexes (Fick *et al*., 2021). Even atmospheric chemistry use HB network as a probe to characterise the nature of glycerol-water aerosols (Weeraratna *et al*., 2021). The identification of these interactions are manifested on the photophysical properties of the fluorophores involved there in. However, HB can broadly be classified into two categories: a) ground state HB in and b) excited state HB. The HB interaction of any fluorophore both in ground and excited state can be identified by solvatochromic effect on absorption and fluorescence spectra. This implies that depending on nature of the solvent, whether it is polar / nonpolar and protic / nonprotic, the peak position, shape and intensity changes.

Review of literature

Conditions Required for HB Formation and Solvatochromic Effects

In high school studies, students learn about HB as an electrostatic interaction between a hydrogen atom, which forms a covalent bond with an electronegative element such as N, O, or F and another electronegative element that may be Cl, Br etc. The first hydrogen atom is known as hydrogen bond donor and the later electronegative atom is called hydrogen bond acceptor. HB can be inter- or intra- molecular, that change various physic-chemical properties of a molecule viz. melting point, boiling point, acidity, basicity etc.

Although the charge separation and consequently the charge distribution were first identified in the ground state (S_0), sometimes the effect is enhanced in the excited state (S_1, S_2 ...). The change in the charge distribution pattern is reflected by an enhancement of dipole moment in the excited state (μ_e) compared to ground state (μ_g). This is called intra-molecular charge transfer. Molecules showing such transition contain distinct donor (D) and acceptor (A) moieties. The highest occupied molecular orbital (HOMO) is mainly localised on D and lowest unoccupied molecular orbital (LUMO) has mainly acceptor character (Rohatgi-Mukherjee, 1978).

When solvent interaction comes into effect, the situation becomes a bit complicated. Two cases may arise:

Case I: If $\mu_g < \mu_e$, change from a nonpolar to a polar solvent increases the solvent interaction and get greater stabilisation in the excited state, resulting in a bathochromic or red shift of absorption spectra. Such characteristics are observed for $\pi \rightarrow \pi^*$ transitions, as the charge separation occurs in an enhanced region (figure 1).
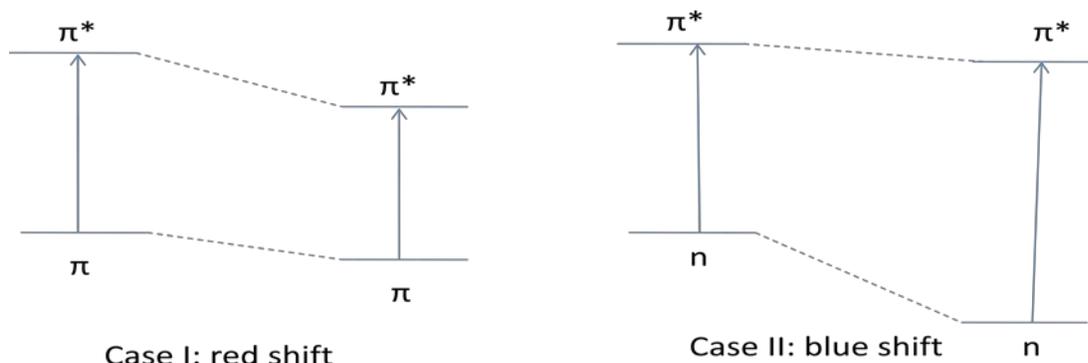

Case I: red shift   Case II: blue shift

Figure 1: Energy Level Rearrangement on Solvation (Rohatgi-Mukherjee, 1978)

Case II: If $\mu_g > \mu_e$, the ground state is more stabilised in polar solvents. For $n \rightarrow \pi^*$ transitions, non-bonding lone pair of an heteroatom like N, O remain hydrogen bonded in the ground state. This gives more stability to ground state and excited state is not much stabilised as promotion of nonbonding electrons to π^* orbital reduces the hydrogen bonding forces in the excited state. This results in a hypsochromic shift in changing from nonpolar to a polar solvent (figure 1).

Types of HB

Conventionally two kinds of HB are possible: in-plane HB and out of plane HB. In-plane HB is the classical type of HB that occurs with the non-bonding lone pair of any donor and electron deficient hydrogen atom. While out of plane HB occurs with the π^* orbital of the donor that is perpendicular to the molecular plane. Theoretical studies revealed that these two kinds of HB with a same fluorophore vary in HB length and also HB strength. Beside the classical HB, recently π-hydrogen bonding used as a probe to understand the reactivity of differently substituted benzenes towards nitration (Galabov *et al.*, 2019).
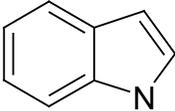
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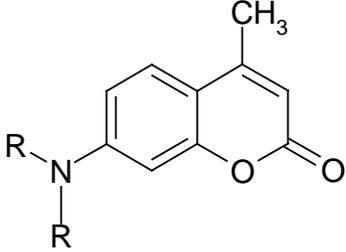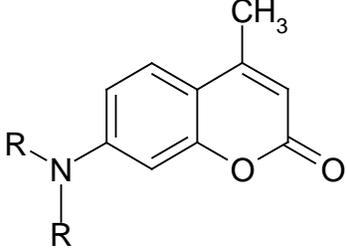
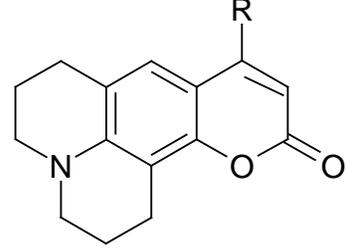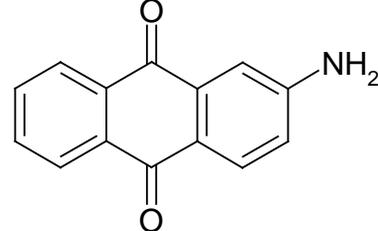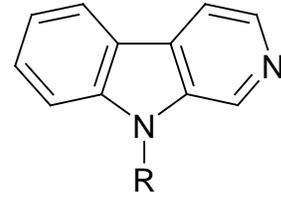### Simultaneous Polarity and Hydrogen Bond Sensor

In literature millions of compounds are there that can sense the dielectric of the solvent involved. They are used in various unknown environments to detect the polarity. These polarity probes may behave differently when kept in protic environment. For some compounds the emission intensity decreases in protic medium while some compounds show enhanced fluorescence (Han & Zhao, 2011).

Fluorescence Quenching on Hydrogen Bonding

There are several classes of compounds and their derivatives that are found to be very suitable for analysing solute-solvent interactions in the ground and excited state. Few of them are listed in Table 1. The compounds listed are sensitive to polarity of the solvent and mostly show red shift on switching from nonpolar to polar solvent. In presence of polar protic solvents, HB occurs even in the ground state. On photoexcitation that HB strength may increase or decrease

Table 1: Structure of Different Fluorophores Showing Quenching on Hydrogen Bonding (Han & Zhao, 2011)

Sceletal fluorophore	Structure
Indole derivatives (eg. Tryptophan)	
Carbazole derivatives	
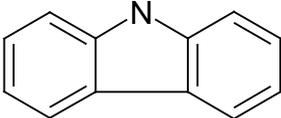
Fluorenone derivatives	
Aminocoumarin derivatives (flexible)	
Rigid coumarin derivatives	
Aminoanthraquinone derivatives	
Harmane derivatives	
Phthalimide derivatives	
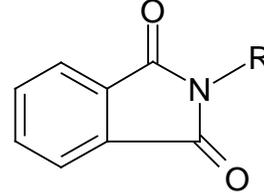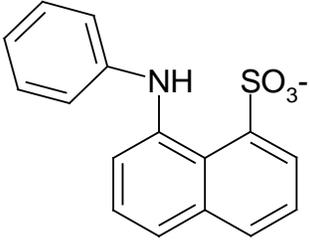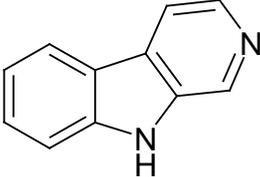
Aminonaphthalene	
β-carbolines	
Diazines: pyridazine, pyrimidine, pyrazine	
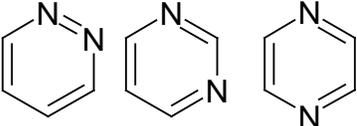
depending on the nature of the compound. In most of the reported cases the emission intensity decreases in protic solvents due to predominant non-radiative transition from S_1 state as it becomes more stable. The HB in protic solvents induces internal conversion and hence quantum yield decreases.

Fluorescence Enhancement on Hydrogen Bonding

There are some compounds where HB with the fluorophore enhances the fluorescence (figure 2). The proposed mechanism suggests that internal conversion and intersystem crossing, both nonradiative channels are stopped. This mechanism named 'close proximity effect' happens if the first two excited states (singlet as well as triplet) are very close apart due to their structure. On changing to polar protic solvents the energy states interchange their positions. In nonpolar solvents the nπ* state was the first excited singlet state, having lower quantum yield. After rearrangement of the energy levels the ππ* becomes the S_1 and hence fluorescence quantum yield increases (Han *et al.*, 2008; Sikorska *et al.*, 2004).

Figure 2: Compounds having increased fluorescence on hydrogen bonding (Han *et al.*, 2008; Sikorska *et al.*, 2004)

Polarity Insensitive Hydrogen Bonding Probe

The fluorescent probes discussed above are unable to differentiate between dielectric of the medium and its hydrogen bonding capacity. A very few probe, viz, dibenzo[a,c]phenazine (DBPZ) (figure 3) (Dey *et al.*, 2007) have been proved to sense only the HB donating capacity of the solvent . The precursor phenazine molecule exhibits almost no change in absorption spectra with different solvents of varying polarity and hydrogen bonding capacity.
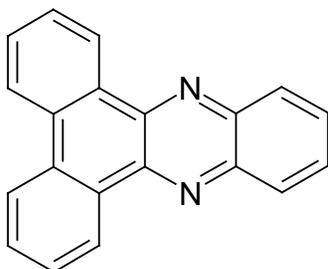

Figure 3: Dibenzo[a,c]Phenazine: Polarity Insensitive Polarity Probe (Dey *et al.*, 2007)

Phenazine shows only ~ 30nm blue shift in fluorescence spectra in water compared to acetonitrile. This indicates that the first excited singlet state of phenazine is of $n\pi^*$ character (Choudhury & Basu, 2005). The fluorescence maxima of phenazine remains same in acetonitrile and in ethanol but only quantum yield increases in the later. Thus, the parent phenazine molecule is not very much informative about the dielectric and the hydrogen bonding capacity of its environment. Beside this there are quite a large number of small organic molecules that show significant variation in their dipole moments on photoexcitation and hence may be used as a polarity sensor (Aaron *et al.*, 1995; Carvalho *et al.*, 2000).

However, DBPZ is such a molecule that has unchanged absorption spectra in solvents of different polarity, e.g. cyclohexane (ε ~2), acetonitrile (ε ~37), methanol (ε ~24) and up to a certain concentration of water (ε = 80). In cyclohexane and acetonitrile, having widely different polarity, the fluorescence maxima and the fluorescence quantum yield of DBPZ show no change. This observation leads to the conclusion that DBPZ cannot sense the polarity of its surrounding environment. However, emission spectra of DBPZ change drastically in hydrogen bond donating solvents. The fluorescence maximum shows bathochromic shift with increase in quantum yield as the hydrogen bond donating capacity of the medium increases. These spectroscopic changes are function of the hydrogen bond donating capacity of the solvents and also the steric effects around the hydrogen bonding site. Though trifluoroethanol has greater hydrogen bond donor capacity than water, (Kamlet *et al.*, 1983) water shows higher quantum yield as it can approach towards the probe more easily, due to its smaller size than the bulkier trifluoroethanol.

The dipole moment of DBPZ is much greater in first excited singlet state compared to the

ground state. So hydrogen bond in the excited state is much stronger than in the ground state. However the molecule remains insensitive to the environment polarity due to its peculiar structure. The two bulky phenyl rings in 'a' and 'c' position make the lone pair of the phenazine nitrogens inaccessible to solvents. Only small hydrogens of the solvent can interact with the lone pair of the nitreogen and build hydrohen bond. This can be proved from ^{1}H NMR study (Dias & Liu, 1990). Excited state hydrogen bonding is reflected from the shortening of hydrogen bond length in the higher state (Parthasarathi, Subramanian & Sathyamurthy, 2006).

Conclusion

Although hydrogen bonding is the most fundamental weak force active in biological medium, most of the probes used to detect hydrogen bonding is also affected by the polarity of the medium. Thus, the photochemical properties shown by those probes are blended with both dielectric and hydrogen bonding capacity of the medium. However Dibenzo[a,c]phenazine is reported to be the polarity insensitive hydrogen bonding probe. The structure of the molecule makes the lone pair of nitrogen unavailable to other atoms except hydrogen.

Acknowledgement

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