

Molecule of the Month

Molecular-Chameleon: Solvatochromism at its Iridescent Best!

Photon Rao

Reichardt's dye A, shows spectacular solvatochromism having solutions coloured red in methanol, violet in ethanol, blue in isopropyl alcohol, green in acetone and greenish-yellow in anisole.

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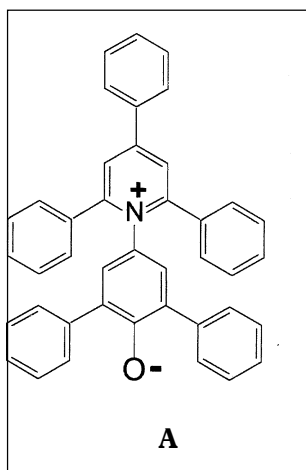
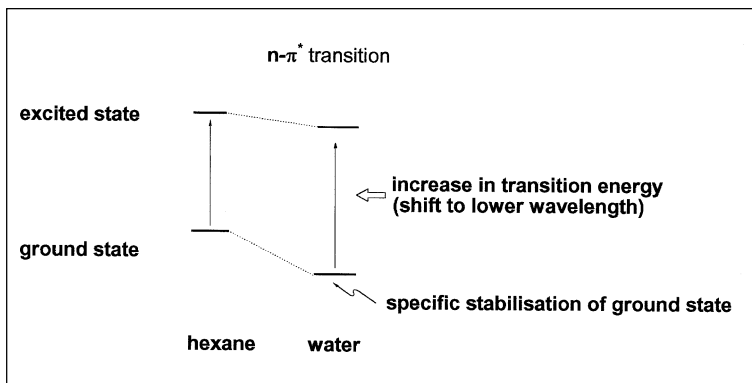
The electronic absorption spectrum of a molecule often depends on the solvent used. The change in position (and, sometimes, intensity) of the UV/Vis band accompanying a change in the polarity of the medium is called solvatochromism. The phenomenon has its origins in intermolecular solute-solvent interactions, such as hydrogen bonding, ion-dipole, dipole-dipole, etc. If the interactions preferentially stabilize either the ground state or the excited state involved in the electronic transition, pronounced solvatochromism is observed. Let us consider two specific examples.

The $n \rightarrow \pi^*$ transition of the keto group shifts towards shorter wavelength (blue-shift) if solvent polarity is increased. In hexane, acetone absorbs at 279 nm, whereas the same absorption moves to 264.5 nm in water. In contrast, the $\pi \rightarrow \pi^*$ transition in alkenes or arenes shifts towards longer wavelength (red-shift) when solvent polarity is raised. For example, the compound para-N,N-diethylaminonitrobenzene absorbs at 364 nm in cyclohexane but at 431 nm in water.

The above changes are easy to interpret. The ground state of a carbonyl compound is highly stabilized by water because of hydrogen bonding involving the carbonyl oxygen lone pair. In the $n \rightarrow \pi^*$ excited state, an electron is removed from the lone pair and promoted to a π^* orbital. As a result, this state can no longer form an efficient hydrogen bond with water. The excited state is also



Figure 1a



less polar, since the electron density is shifted from oxygen towards the less electronegative carbon. The net result is that the transition energy is higher in water (*Figure 1a*), compared to that in a non-polar solvent (which has negligible effect on both the ground and excited states). The opposite shift observed in alkenes and arenes can be understood by considering the polarity of the molecular states. In the ground state, these molecules are not polar. However, in the excited state, significant polarization of the electron density occurs. This is especially the case in the 'push-pull' system mentioned above (see *Box 1*). Polar solvents preferentially stabilize the excited state, resulting in a large red-shift in the absorption maximum (*Figure 1b*).

The above examples of solvatochromism are so well documented that assignment of $n-\pi^*$ and $\pi-\pi^*$ transitions are often confirmed

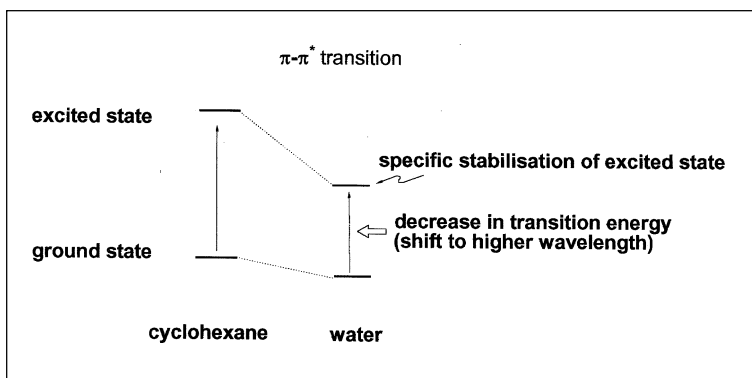


Figure 1b

Box 1

Compounds containing donor and acceptor functionalities in conjugation are called push-pull systems. Substituted ethylenes bearing electron-withdrawing groups on one carbon atom and electron-donating groups on the other are called push-pull ethylenes. Typical electron withdrawing substituents include the cyano and the nitro groups, while methylthio, N,N-dimethylamino groups are examples of common electron donating substituents. Aromatic compounds containing donor and acceptor functionalities in conjugation can form a part of push-pull systems. These systems have interesting chemical and spectral properties.

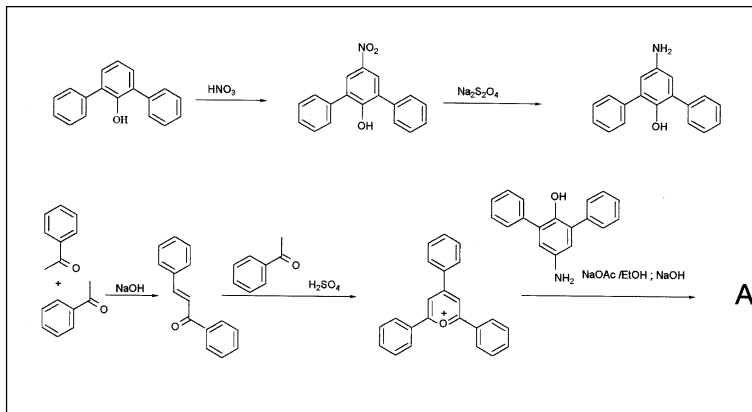
by these solvent induced spectral shifts. Conversely, the magnitude of shifts can be used to quantify the polarity of a solvent or solvent mixture. For such applications, molecules which show very large solvatochromism are needed.

The most spectacular solvent effects have been observed for dipolar meropolymethine dyes. And, to date, the betaine dye **A**, a pyridinium-N-phenoxide betaine, holds the *world record* in solvatochromism. The dramatic effect can be demonstrated without sophisticated instrumentation. The solution colour of **A** is *red* in methanol, *violet* in ethanol, *green* in acetone, *blue* in isopropyl alcohol, and *greenish yellow* in anisole. In quantitative terms, the experimentally observed blue shift as the solvent is changed from diphenyl ether to water is 350 nm, which corresponds to 28 Kcal/mole. Note that the absorption shifts to shorter wave length in a polar solvent. (Why?)

For a dye endowed with such a wonderful property the synthesis remains extremely simple. Two components are needed for making this molecule. One of them, 4-amino-2,6-diphenylphenol is obtained by a nitration, followed by reduction (*Scheme 1*). In a separate reaction, a chalcone is prepared through condensation of acetophenone with an equivalent of benzaldehyde. The chalcone is further condensed with another molecule of acetophenone



Scheme 1



using concentrated sulfuric acid to obtain a symmetric triphenylpyrelium salt. The salt and the aminophenol on coupling yields the dye in question (*Scheme 1*).

The dramatic solvent dependence of the absorption spectrum of **A** naturally finds many uses in chemistry. Determining the polarity of a given solvent is a very important question for practicing chemists. In the industry it is important to find out whether impurities are present in bulk-solvents. The sensitive colour of the dye gives a quick indication of the purity of solvents. In the laboratory, polarity is an invaluable parameter for physico-chemical studies in solution. An accurate approach to determine solvent polarity uses solvatochromism of **A**.

Compound **A** is sold commercially as Reichardt's dye. Its most common use is for the determination of solvent polarity. It is also used as a molecular probe in the study of micelle-solution interface, microemulsions and phospholipid bilayers.

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Suggested Reading

- ◆ C Reichardt. *Solvents and Solvent Effects in Organic Chemistry*. VCH. Weinheim, 1988.
- ◆ B R Osterby and R D McKelvely, *J. Chem. Edu.* Vol. 3. p.260, 1996.