

| Problem # 25% of total | Question | #.1 | #.2 | #.3 | #.4 | Total |
|---------------------------|----------|-----|-----|-----|-----|-------|
| | Points | 3 | 3 | 4 | 1 | 11 |

Problem #: Molecular sensors

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In 2019, Anandhan *et al.* conducted research on a molecule in hopes of developing a molecular sensor: (Z)-3-(4-(4,5-diphenyl-1H-imidazol-2-yl)phenyl)-2-phenylacrylonitrile. This molecule, which will be denoted as **A** henceforth, exhibited several interesting properties, including solvatochromism, which is when the colour of a compound changes depending on its solvent. Its structure is shown below:

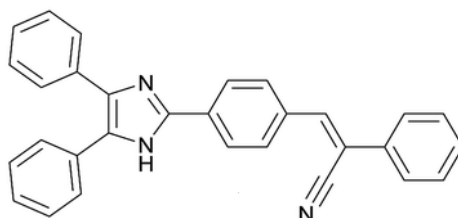


Fig 1.1: Structure of A

When the researchers placed the compound **A** in various solvents ranging from dioxane to DMSO, the following UV spectra were obtained and plotted on the same axes as shown below:

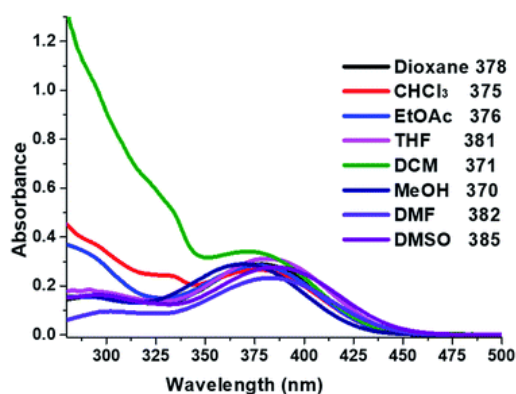


Fig 1.2: UV-Vis spectrum in different solvents

- #.1) Identify the 2 electronic transitions giving rise to each of the peaks at each wavelength shown in Figure 1.2. By considering the allowed and forbidden transitions, match the wavelength of each peak to the corresponding transition.

$n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions. By symmetry considerations, $n \rightarrow \pi^*$ is a forbidden transition while $\pi \rightarrow \pi^*$ is an allowed transition. Hence, the peak at 370–385 nm corresponds to the $\pi \rightarrow \pi^*$ transition while that at 281–305 nm corresponds to $n \rightarrow \pi^*$.

0.5 points for each correctly identified electronic transition. (Total 1 point)

1 point each for each correct pairing. [Accept within the range above] (Total 2 points)

Solvatochromism can be attributed to the changes in energy levels of molecular orbitals due to the interactions with solvents.

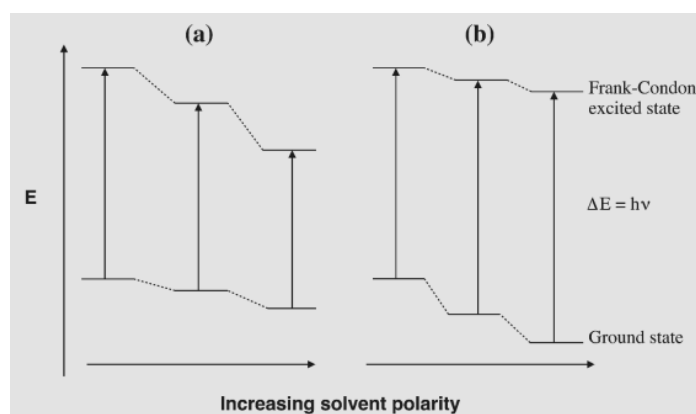


Fig 1.3: Energy level variations

Two examples of solvatochromism are shown above, with the energy levels changing accordingly to give different trends with solvent polarity increasing.

- #.2) By considering the diagrams above, explain if **(a)** or **(b)** corresponds to compound **A**'s behaviour with different solvents. Therefore, explain if the dipole moment of the molecule increases or decreases when it is in the excited state.

(a) corresponds to the behaviour above. The UV-vis transition energy shifts to lower energy and hence a longer wavelength as the solvent polarity is increased.

The dipole moment in the excited state increases. If the dipole moment of the molecule increases upon excitation, then a more dipolar solvent (like DMSO) will stabilise the excited state more than the ground state.

1 point for correct identification of (a).

0.5 points for reasonable explanation in terms of the energy of the transition.

1 point for correct identification of dipole moment increasing.

0.5 points for reasonable explanation in pointing out the stabilisation effect of polar/dipolar solvents.

Next, the researchers varied the pH of the solutions and noticed that (1) decreasing the pH shifted the absorption peaks to shorter wavelengths, while (2) increasing the pH shifted the absorption peaks to longer wavelengths as shown below:

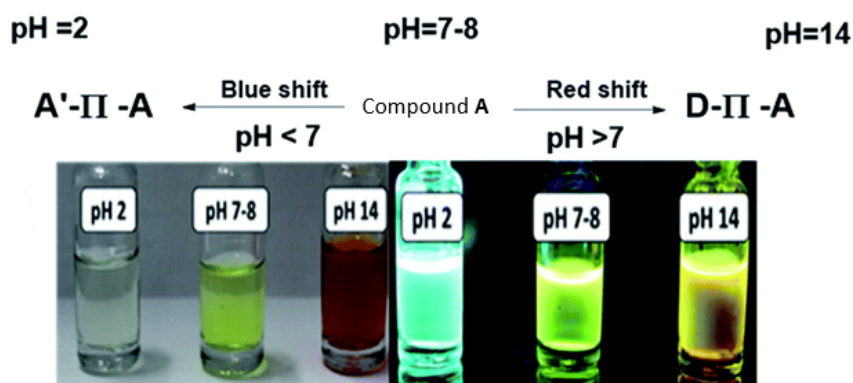


Fig 1.4: Colour of compound A at different pH values

- #.3) By considering the structure of compound **A** as seen in Figure 1, in terms of the electronic transitions of the molecules **and** any inter/intramolecular charge transfer which may occur, explain why the peak at about 305 nm disappeared as pH increased and the shifting of the absorption peak to shorter wavelengths.

The nitrogen atom in the imidazole ring is protonated and hence there is no electron pair to undergo the $n \rightarrow \pi^*$ transition. This peak corresponds to 305 nm and hence disappears.

The blue shift was obtained due to absence of lone pairs in the imidazole ring which in turn prevents the charge transfer and hence causing there to be two acceptor groups, hence causing the energy gap to rise and hence a blueshift.

Notice that the D in the structure above refers to donors and A refer to acceptors. The diagram below illustrates the idea of how intramolecular charge transfers can lead to a blue or red shift:



2 points for correct identification of $n \rightarrow \pi^*$ transition disappearing and attributing it to the peak at 305 nm.

Partial credits:

- 1 point if an idea of a transition disappearing was written
- 0.5 points if it was pointed out that the nitrogen atom in the imidazole ring was protonated and makes the lone pair unavailable.

2 points for correct identification of the absence of lone pairs contributing to the inability of an electron donor-acceptor complex to form OR preventing intramolecular charge transfer. (Blue part not needed)

Partial credits:

- 1 point for alluding to the presence of an electron donor-acceptor complex
- 1 point for correctly identifying that intramolecular charge transfer cannot occur.
- 1 point if explanation is correct, but identified intermolecular charge transfer instead.

- #.4) Hence, propose a use for compound **A** based on the experiment conducted in Figure 1.4.

(Molecular) pH sensor, pH indicator, etc.

1 point for a reasonable suggestion for the function of A based on its pH properties.