Answer on Question #54375 – Chemistry – General chemistry

Question:

Explain the following using an example in each case:

i) the effect of inter molecular hydrogen bonding on the infrared spectra

of the compounds, and

ii) the effect of conjugation on $\pi \rightarrow \pi^*$ transition.

Answer:

i) Hydrogen bonding is ubiquitous in nature. It is involved in the most basic and important chemical and biological phenomena. The strength of hydrogen bonds lies between van der Waals forces and covalent bonds. Although not a true chemical bond, a hydrogen bond is sufficiently strong and directional to become the driving force for molecules to assemble into delicate architectures in supramolecular chemistry, molecular recognition, and self-assembly. The strength of hydrogen bonds is in the range of energies that permits rapid association and dissociation under ambient conditions. Such rapid hydrogen bond dynamics are important in a wide variety of systems, such as the properties of water and biological recognition.3 Hydrogen bonding has been studied extensively in many contexts since the birth of the concept in the early 1900s. Hydrogen bonds can be separated into two categories: intermolecular hydrogen bonds in which the hydrogen bond donor and acceptor are in different molecules and intramolecular hydrogen bonds in which the donor and acceptor are in the same molecule.In general, intramolecular hydrogen bonds form five-, six-, or seven-membered rings, where the geometric restrictions make them relatively weak compared to intermolecular hydrogen bonds involving the same type of donor and acceptor. Because of geometrical constraints, intramolecular hydrogen bonds cannot form with the optimal geometry compared to the intermolecular ones, creating the possibility that the donor of an intramolecular hydrogen bond can form an additional intermolecular hydrogen bond with an appropriate acceptor located on another molecule. A special type of hydrogen bond will form under these conditions.

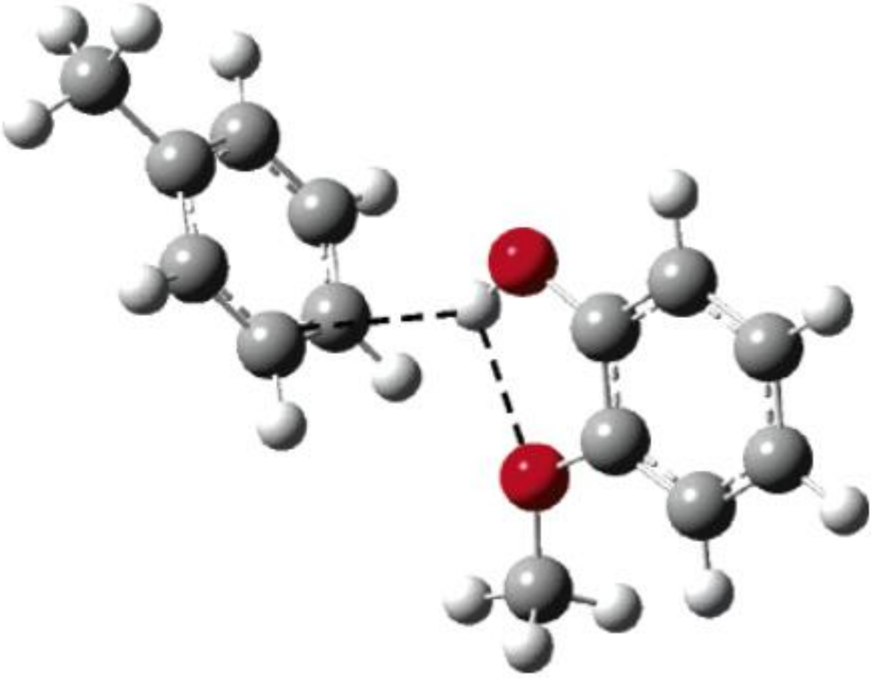

Fig. 1. Structure of the intra-intermolecular hydrogen-bonded complex of 2-methoxyphenol and toluene in the isolated state calculated with DFT at the B3LYP/6-31+G(d,p) level.

This type of hydrogen bond involves three centers, one donor, and two acceptors. There is another type of three-centered hydrogen bond with one acceptor and two donors, which is common when the acceptor has two electron lone pairs; e.g., in a molecule such as water, the oxygen can be the acceptor for two hydrogen donors on two other water molecules. The “intra-intermolecular hydrogen bond” discussed above has a single donor with two acceptors. This type of threecentered hydrogen bond, which is also called “bifurcated”, plays important roles in many chemical and biological systems, e.g., chiral molecular recognition, proteins,RNA,DNA, and carbohydrates. Kinetic studies of the formation and dissociationof this type of hydrogen bond in liquid solutions are challenging because of its ultrafast time scale.

ii)

For molecules that possess π bonding as in alkenes, alkynes, aromatics, acyl compounds or nitriles, energy that is available can promote electrons from a π Bonding molecular orbital to a π Antibonding molecular orbital. This is called a $\pi \rightarrow \pi^*$ transition. The energy difference for such a transition to occur will depend upon the atoms π bonded to each other, other atoms attached as well as the relationship between two or more π bonds within the molecule. π bonds between two carbon atoms will have a different a $\pi \rightarrow \pi^*$ transition compared to π bonds between a carbon and an Oxygen atom (a carbonyl) or a π bond between a carbon atom and a nitrogen atom (a nitrile). This is because there will be a different energy gap between the π Bonding and Pi Antibonding molecular orbital energy states. Other atoms such as Hydrogen(as in an aldehyde) or another SP^3 carbon(as in a ketone) that would be bonded to one of the π bonded atoms in the molecule would also cause the energy of transition to vary. Thegreater the energy of transition the shorter the wavelength of UV or visible radiation will have to be for electrons to be promoted from the bonding to the antibonding state. Every group of atoms with Pi bonding will have a different wavelength where maximum abosrption will take place. This is called the "Lambda Max", the wavelength where maximum absorption takes place, and the group of atoms with the π bonding is called a "chromaphore". Each chromaphore will have a different energy of transition between the bonding and antibonding molecular orbitals for which the electron transition takes place. For example, alkenes and non-conjugated polyenes will have lamda max absorbances that are below 200 nanometers(nm). Such a short wavelength which indicates a larger energy of transition is because such chromaphore molecules have $\pi \rightarrow \pi^*$ transitions