

# **Qualitative studies of cis-trans Equilibrium in o-Halophenols: a perspective based on UV-Visible Spectroscopy**

A dissertation submitted in the partial fulfillment of  
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May, 2024

# DECLARATION

I declare that the thesis entitled “**Qualitative studies of cis-trans Equilibrium in o-Halophenols: a perspective based on UV-Visible Spectroscopy**” has been prepared by me under the supervision of **Dr. Ritesh Dubey** from **Department of Chemistry, School of Engineering, University of Petroleum & Energy Studies, Dehradun, India.**

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# CERTIFICATE

I certify that, **Shefali Sheron** has prepared her project entitled “**Qualitative studies of cis-trans Equilibrium in o-Halophenols: a perspective based on UV-Visible Spectroscopy**” for the award of **B.Sc. (Hons) Chemistry**, under my guidance. She has carried out the work at the **Department of Chemistry, School of Engineering, University of Petroleum & Energy Studies, Dehradun, India.**

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# PLAGIARISM CERTIFICATE

I, **Shefali Sheron**, hereby certify that the research dissertation titled “**Qualitative studies of cis-trans Equilibrium in o-Halophenols: a perspective based on UV-Visible Spectroscopy**” submitted for the partial fulfillment of a B.Sc. degree from University of Petroleum Energy & Studies, Dehradun, India is an original idea and has not been copied/taken verbatim from anyone or from any other sources.

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# Abstract

This thesis investigates the conformational equilibria of ortho-halophenols, with a particular focus on their behavior in UV-Vis spectroscopy. Phenol and its derivatives, ortho-halophenols, possess unique structural characteristics and molecular interactions that have profound implications across diverse scientific disciplines, including organic chemistry and material science.

The historical context provided in this study underscores the foundational research conducted by pioneers like Linus Pauling in 1936. These early investigations laid the groundwork for understanding the cis-trans equilibrium in phenols. Subsequent studies by Alwin W. Baker and others further elucidated the influence of halogen substitution on this equilibrium, revealing distinct cis-trans ratios and conformational energy differences for different halogens.

Experimental methodologies, including infrared (IR) spectroscopy, nuclear magnetic resonance (NMR) spectroscopy, and UV-Vis spectroscopy, have been pivotal in characterizing the conformational preferences of ortho-halophenols. UV-Vis spectroscopy, in particular, emerges as a powerful tool for probing electronic transitions within molecules. The choice of solvent in these experiments plays a critical role in minimizing solvent effects and ensuring the accuracy of spectral interpretation.

The results obtained from UV-Vis spectroscopy experiments provide intriguing insights into the conformational dynamics of phenol and various ortho-halophenols. Phenol and ortho-fluorophenol exhibit distinctive spectral features, including two distinct peaks in their UV spectra, indicative of the presence of both cis and trans conformers in solution. The observed blue shift in ortho-fluorophenol's spectrum can be attributed to the electron-withdrawing nature of fluorine, whereas the red shift observed in ortho-chlorophenol, ortho-bromophenol, and ortho-iodophenol spectra is influenced by resonance and hyperconjugation effects.

In conclusion, this thesis offers valuable insights into the conformational dynamics of ortho-halophenols and their behaviour in UV-Vis spectroscopy. These findings deepen our understanding of intramolecular interactions and electronic transitions in these compounds, with implications for a wide range of scientific applications. Future research endeavors could explore additional halogen substitutions and solvent effects to further enhance our comprehension of these intriguing molecular systems.

Overall, this study contributes to the ongoing dialogue surrounding the structural properties and molecular behavior of ortho-halophenols, enriching our knowledge of these compounds and their potential applications in various scientific domains.

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# CHAPTER 1

## INTRODUCTION

### 1. Introduction

#### 1.1 Historical perspective:

Phenol, a simple aromatic compound consisting of a benzene ring bonded to a hydroxyl group, exhibits interesting symmetry properties due to its molecular structure. The molecular structure of phenol possesses inherent symmetry due to its planar aromatic ring and the presence of the hydroxyl group. The benzene ring exhibits a high degree of symmetry, with all carbon-carbon bonds and carbon-hydrogen bonds being equivalent. However, the introduction of the hydroxyl group disrupts this symmetry to some extent. In the outlook of IR, the Symmetry considerations play a crucial role in analyzing these vibrational modes. The symmetry of the molecule affects the selection rules for vibrational transitions, leading to characteristic peaks in the IR spectrum [14]. In phenol, understanding the symmetry properties of phenol is not only important for theoretical purposes but also has practical implications in various fields including organic chemistry, material science, and pharmaceuticals.

Ortho-halophenols (2-halophenols), a class of compounds derived from phenol by substitution with a halogen atom at the ortho position, exhibit distinctive properties due to both their structural characteristics and the introduction of halogen atoms. Ortho-halophenols are akin to phenol but with a halogen atom (fluorine, chlorine, bromine, or iodine) replacing a hydrogen atom at the ortho position of the aromatic ring. This substitution disrupts the molecule's symmetry and leads to changes in its chemical and physical properties in contrast to phenol [15].

There is an interesting study on the infrared absorption of organic compounds given by Pauling in 1936 which discuss about the possibility of cis trans equilibrium in Halophenols. In phenols the decrease in carbon atom's effective radius due to hybridization change from  $sp^3$  to  $sp^2$  is attributed to an increase in double-bond character, favouring a planar equilibrium configuration of phenol in its ground electronic state. This character results from quinonoid resonance structures and Kekule-type structures, placing the hydrogen atom in the molecular plane. This leads to two equivalent configurations with the hydrogen of the OH group being on one side of the other of the C–O bond. i.e. cis form and trans form. Usually, cis form is more stable than the trans form [2]. Phenols generally exhibit a plane of symmetry due to the symmetrical arrangement of carbon atoms in the benzene ring so it shows a distinct OH peak. However, the addition of halogen atoms affects the symmetry of the molecule. In 1958, Alwin W Baker, investigated the change in OH frequencies due to the presence of halogens. According to the sequence  $F > Cl > Br > I$ , trans isomers are destabilized in relation to cis isomers. This destabilization could be caused by one of the non-bonding electron pairs'  $sp^2$  type orbitals certainly overlaps a halogen's rehybridized orbital, causing a repulsive interaction when the oxygen bonds rehybridize due to conjugation with the ring. He confirmed Pauling's observation of cis configuration being more stable than trans configuration by 2 to 3 kcal./mole. He observed that except o-fluorophenol all o-halophenols showed 2 distinct peaks [3]. Which leads us to question the if halogen hydroxyl interaction in halophenols is repulsive or attractive? It was illustrated in 1965 when o-trifluoromethyl phenol showed a repulsive interaction

where major OH peak at  $3624\text{ cm}^{-1}$  and a minor shoulder peak at  $3605\text{ cm}^{-1}$ . This confirmed the presence of dominating cis form and minor trans form in solution. The above stated experiments were conducted in carbon tetrachloride solution under IR region. In 1965 A.W. Baker observed the enthalpy of intermolecular halogen hydroxyl shows weak interaction between fluorine and hydrogen, but it was weaker than the interaction between hydrogen and any of the other three heavier halogens (Cl, Br, I). This leads us to study the behaviour of o-fluorophenol [4].

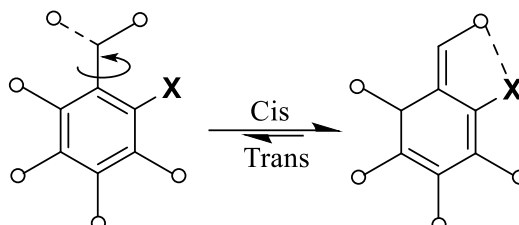


Figure 1. Schematic representation of cis-trans equilibrium

### 1.2 Recent studies:

From theoretical studies conducted in 2015 o-fluorophenol stands out as it exhibits very little intramolecular hydrogen bonding compared to other 2-halophenols like o-chlorophenol, o-bromophenol, and o-iodophenol. In IR spectroscopy Zumwalt and Badger observed only one band in the near IR spectrum of 2-fluorophenol, indicating that there is no clear distinction between cis and trans forms in the spectrum. In NMR studies, o-fluorophenol showed only one band in the near IR spectrum, suggesting that the cis and trans forms of o-fluorophenol may overlap in the spectrum. The NBO analysis reveals a very small delocalization interaction energy between the lone pair of the halogen and the sigma antibonding O-H orbital in o-fluorophenol compared to other compounds, indicating weak interactions. Additionally, a microwave study observed only transitions due to the cis conformer in o-fluorophenol, but noted that there could be up to 20% of the trans form present [12]. Computation Study revealed that the interactions in o-fluorophenol do not reach a zero value, suggesting the absence of a bond critical point between O-H and F indicating no intramolecular hydrogen bond. Additionally, theoretical study shows fluorine in o-fluorophenol does not have a steric effect on the ortho OH proton, unlike other halogens. The only direct effect the fluorine has on the OH proton chemical shift is due to its electric field.

### 1.3 Current work:

This research work deals with a straightforward and efficient method to observe the behaviour of cis-trans equilibrium in o-halophenols by UV-Vis Spectroscopy.

# CHAPTER 2

## Experimental Background

### 2. Characterization:

#### 2.1 IR studies

Extensive research has been conducted on the conformational preferences and intramolecular hydrogen bonding interactions in 2-halophenols, utilizing a variety of experimental techniques and theoretical calculations. Pauling's early work in 1936 investigated the infrared (IR) spectra of phenol, o-chlorophenol, and 2,4,6-trichlorophenol, providing insights into their conformational equilibria and strengths of hydrogen bonding. For instance, in o-chlorophenol, the IR data revealed two peaks at  $7050\text{ cm}^{-1}$  (trans) and  $6910\text{ cm}^{-1}$  (cis), with an intensity ratio of about 1:10. This ratio indicates a preference for the cis conformer, which is stabilized by  $1400\text{ cal/mol}$  due to an attractive interaction between the partially shielded proton and the chlorine atom [2].

Following Pauling's work, Baker (1958) and Robinson et al. (1972) conducted further IR studies to quantify the cis/trans ratios and conformational energy differences ( $\Delta E$ ) for various 2-halophenols in both the gas phase and non-polar solvents such as carbon tetrachloride ( $\text{CCl}_4$ ). The key data obtained include the O-H stretching frequencies for the cis and trans bands, as well as the cis/trans intensity ratios: 2-fluorophenol ( $<1/20$ ), 2-chlorophenol (1/56), 2-bromophenol (1/38), and 2-iodophenol (1/13.5). The  $\Delta E$  values (kcal/mol) from IR data were also reported, such as 2-chlorophenol ( $3.6 \pm 0.3$  in vapour,  $1.4 \pm 0.6$  in  $\text{CCl}_4$  solution), 2-bromophenol ( $2.6 \pm 0.5$  in vapour,  $1.7 \pm 0.4$  in  $\text{CCl}_4$  solution), and 2-iodophenol ( $3.0 \pm 0.3$  in vapour,  $1.2 \pm 0.2$  in  $\text{CCl}_4$  solution) [3,8].

Compound	Cis/Trans Ratio	$\Delta E$ (kcal/mol)
2-Fluorophenol	$<1/20$	N/A
2-Chlorophenol	1/56	$3.6 \pm 0.3$ (vapor), $1.4 \pm 0.6$ ( $\text{CCl}_4$ solution)
2-Bromophenol	1/38	$2.6 \pm 0.5$ (vapor), $1.7 \pm 0.4$ ( $\text{CCl}_4$ solution)
2-Iodophenol	1/13.5	$3.0 \pm 0.3$ (vapor), $1.2 \pm 0.2$ ( $\text{CCl}_4$ solution)

Table 1: Cis/Trans Ratios and Conformational Energy Differences ( $\Delta E$ ) in 2- Halophenols

Carlson et al. (1972) obtained  $\Delta E$  values from observing the OH torsional vibrations in the gas phase and cyclohexane solution, reporting values (in kcal/mol) of 1.6 (F), 1.6 (Cl), 1.5 (Br), and 1.3 (I) for the vapour phase, and 1.4 (F), 1.6 (Cl), 1.6 (Br), and 1.5 (I) in cyclohexane solution [7].

Compound	$\Delta E$ (kcal/mol) - Vapor	$\Delta E$ (kcal/mol) - Cyclohexane Solution
2-Fluorophenol	1.6	1.4
2-Chlorophenol	1.6	1.6
2-Bromophenol	1.5	1.6
2-Iodophenol	1.3	1.5

Table 2: Conformational Energy Differences ( $\Delta E$ ) in 2-Halophenols from OH Torsional Vibrations

## 2.2 NMR studies

Nuclear magnetic resonance (NMR) spectroscopy has also been employed to study the conformational equilibria of 2-halophenols. In a recent study, the authors determined the concentration dependence of the  $^1\text{H}$  chemical shifts of the OH proton in various 2-halophenols and related compounds in  $\text{CDCl}_3$  and DMSO solvents. By comparing the observed chemical shifts at infinite dilution to those calculated using the CHARGE model, they estimated the cis/trans ratios, which indicated substantial cis conformer populations, especially for the heavier halophenols: 65% cis for 2-fluorophenol, 76% cis for 2-chlorophenol, 71% cis for 2-bromophenol, 85% cis for 2-iodophenol [12].

Several computational studies have complemented the experimental work by providing theoretical estimates of the conformational energy differences and hydrogen bonding strengths. For instance, Mobli (2009) calculated  $\Delta E$  (trans - cis) values (in kcal/mol) using density functional theory (DFT): 3.9 for 2-fluorophenol, 4.3 for 2-chlorophenol, and 4.6 for 2-bromophenol. The authors of the recent study also obtained  $\Delta G$  (trans - cis) values (in kcal/mol) at the MP2/aug-cc-pVTZ level, showing a small preference for the cis conformer: 2.5 for 2-fluorophenol, 3.2 for 2-chlorophenol, 3.4 for 2-bromophenol, and 3.7 for 2-iodophenol [10].

## 2.3 Limitations in current methodologies

Despite the extensive research, there is still significant variation in the reported enthalpy/free energy differences and cis/trans ratios, likely due to the different experimental methods, computational levels, and solvent environments employed. Nevertheless, these studies have provided valuable insights into the interplay between intramolecular hydrogen bonding, conformational preferences, and substituent effects in the 2-halophenol series.

While previous research has provided valuable insights into cis-trans isomerism of o-halophenols, there are limitations that call for further investigation: Most studies focused on IR spectroscopy, which can be sensitive to both cis and trans forms but may not always provide clear distinction, particularly for o-fluorophenol where the isomers might overlap. Research primarily explored the impact of chlorine, bromine, and iodine, with less emphasis on fluorine's unique behaviour. Studies conducted in carbon tetrachloride (non polar) solution may differ in polar solvents or in the solid state, potentially leading to variations in observed interactions

# CHAPTER 3

## Methodology

### 3.1 Principles of UV Spectroscopy

UV-visible spectroscopy is a fundamental analytical technique used to investigate the electronic structure of molecules. It relies on the absorption of ultraviolet and visible light by molecules, leading to electronic transitions between different energy levels. The absorption of light occurs when the energy of the incident photons matches the energy difference between electronic states in the molecule. This absorption is quantified by measuring the intensity of light absorbed as a function of wavelength.

### 3.2 Electronic Transitions

There are two primary types of electronic transitions observed in UV-Vis spectroscopy that are relevant to our investigation of o-halophenols:

- $\pi$ - $\pi^*$  Transitions: These transitions involve the excitation of an electron from a bonding  $\pi$  orbital (formed by the overlap of p orbitals) to an anti-bonding  $\pi^*$  orbital. In conjugated systems, such as the benzene ring in o-halophenols, these transitions are particularly important. The extent of conjugation within a molecule influences the energy required for such transitions, and the specific wavelength absorbed falls within the UV-visible region.
- n- $\pi$  Transitions: These transitions involve the excitation of an electron from a non-bonding n orbital (lone pair orbital) to an anti-bonding  $\pi^*$  orbital. These transitions generally require higher energy than  $\pi$ - $\pi^*$  transitions and often occur in the UV region. In o-halophenols, the lone pair on the oxygen atom of the hydroxyl group can participate in n- $\pi^*$  transitions.

### 3.3 Navigating the Spectrum: Blue Shifts, Red Shifts, and Solvent Selection

The observed shifts in wavelength ( $\lambda$ ) within a UV-Vis spectrum hold valuable information about the electronic transitions occurring within a molecule. Here, we will explore two key types of shifts and the role of solvent selection:

- Blue Shift: A blue shift refers to a decrease in wavelength ( $\lambda$ ) and an increase in energy (E) of the absorbed light. This can occur when a molecule undergoes a structural change that increases the energy gap between its ground and excited states. For example, the introduction of an electron-withdrawing substituent like fluorine in o-fluorophenol can



stabilize the ground state compared to phenol. This requires higher energy light (shorter wavelength) to achieve the same electronic transition, resulting in a blue shift.

- **Red Shift:** Conversely, a red shift signifies an increase in wavelength ( $\lambda$ ) and a decrease in energy ( $E$ ) of the absorbed light. This can occur when a molecule undergoes a structural change that decreases the energy gap between its ground and excited states. For example, some o-halophenols with bulkier halogens (Cl, Br, I) might exhibit a red shift compared to phenol due to hyperconjugation. Hyperconjugation involves the interaction of electrons in  $\sigma$  bonds with the  $\pi$  system of the benzene ring, potentially stabilizing the excited state.
- Solvent selection plays a crucial role in UV-Vis spectroscopy. Polar solvents can interact with the solute molecule through dipole-dipole interactions. If these interactions stabilize the ground or excited state, they can influence the observed wavelength shift. Choosing a non-polar solvent like chloroform minimizes these interactions and allows for a more accurate interpretation of the intrinsic electronic transitions within the o-halophenol molecules.

By understanding these concepts of electronic transitions, shifts, and solvent effects, we can effectively utilize UV-Vis spectroscopy to decipher the electronic landscape of o-halophenols and gain deeper insights into their unique behavior.

### **3.4 Materials and Sample Preparation**

Commercially available o-chlorophenol, o-bromophenol, o-iodophenol, o-fluorophenol, and phenol were chosen as samples for this study. To investigate the effect of halogen substitution on cis-trans equilibrium, these compounds with varying halogen groups (Cl, Br, I, F) were selected.

All chemicals were used without further purification unless otherwise specified. Chloroform (HPLC grade) was chosen as the solvent due to its suitability for UV spectroscopy and minimal interaction with the o-Halophenol compounds.

The o-Halophenol samples were prepared by dissolving a known amount of each compound in chloroform to create solutions with concentration ranging from  $10^{-2}$  to  $10^{-6}$  M. The solutions were then subjected to UV spectroscopy to record their absorption

# CHAPTER 4

## Results and Discussion

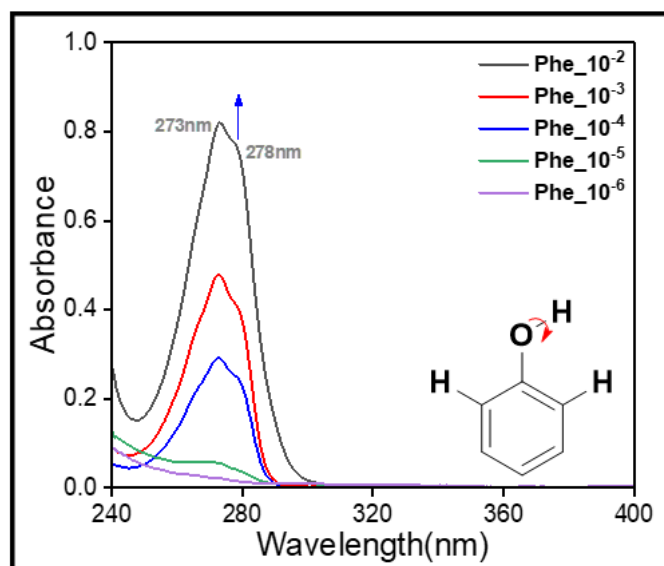
### 4.Experimental analysis:

#### 3.1 UV-visible studies

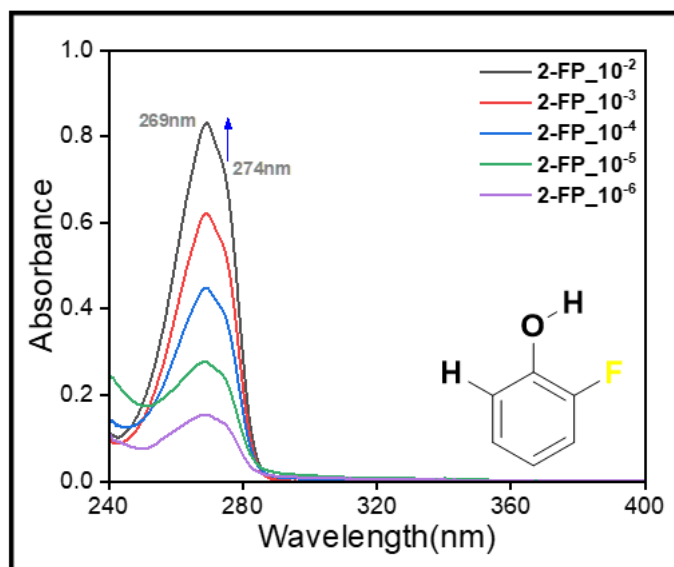
As part of this thesis, UV-vis spectroscopy has been employed to further investigate the conformational equilibria of phenol and o-halophenols in chloroform solution. After performing the experiment, we were surprised by the experimental data, which revealed strong absorption at a specific wavelength for various electronic transitions. This suggests the presence of two distinct components in the solution. Samples were prepared at concentrations ranging from  $10^{-2}$  to  $10^{-6}$  M, and the UV-vis spectra were recorded using chloroform as the reference solvent.

#### Phenol and 2-Fluorophenol:

For phenol and 2-fluorophenol having two chemical phenomena has been observed in UV spectra. In phenol, a major peak was observed at 273 nm (assigned to the major trans conformer) and shoulder peak observed at 278 nm (assigned to the minor cis conformer). Similarly, 2-fluorophenol exhibited peaks at 269 nm (major trans) and 274 nm (minor cis).



(a)



(b)

Figure 2. UV-spectra of Phenol (a) and 2-Fluorophenol (b) at  $10^{-2}$  to  $10^{-6}$  M concentration.

The surprising similarity in the intensity of the shoulder peaks between phenol and o-fluorophenol can be attributed to the size of both hydrogen (H) and fluorine (F) atoms. Despite the slight difference in size ( $0.4 \text{ \AA}$  for H and  $0.5 \text{ \AA}$  for F), their electron configuration plays a key role. Both elements possess only one valence shell, resulting in a strong pull of electrons towards the nucleus. In hydrogen, this pull is due to the single proton.

In fluorine, although there are more electrons, the additional ones occupy a higher energy shell (2s and 2p orbitals) and offer minimal shielding to the nucleus. This strong nuclear attraction in both elements compresses their electron cloud, leading to their comparable size and a minimal steric hindrance to hydrogen bonding with the benzene ring in o-fluorophenol. This explains why the presence of fluorine does not significantly alter the intensity of the shoulder peak associated with the cis isomer.

#### **Blue Shift in 2-Fluorophenol:**

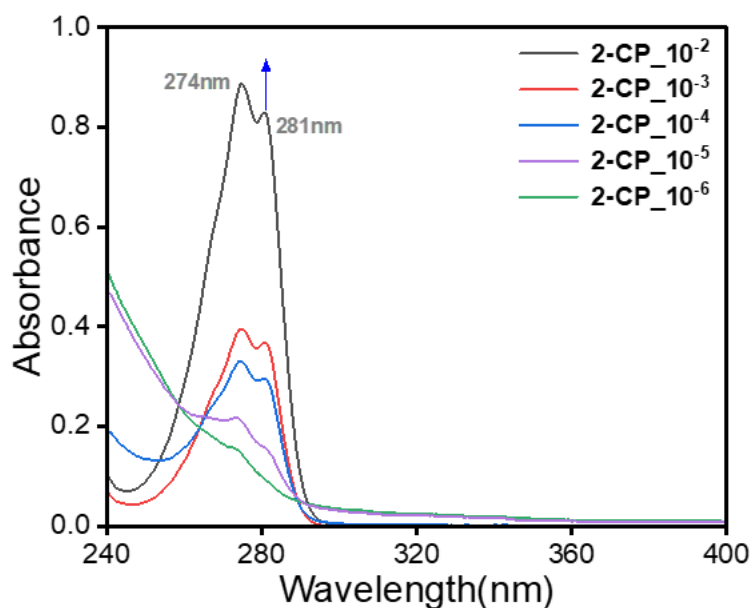
The difference in wavelength between phenol and o-fluorophenol, though seemingly small at 4 nm, signifies a significant electronic transition shift. This blue shift in o-fluorophenol can be attributed to the electron-withdrawing nature of fluorine. Fluorine's electronegativity pulls electron density towards itself, stabilizing the ground state of the molecule. This larger energy gap between the ground and excited state requires higher energy light (shorter wavelength) to achieve the electronic transition, resulting in the observed blue shift.

#### **Heavy halogen atoms:**

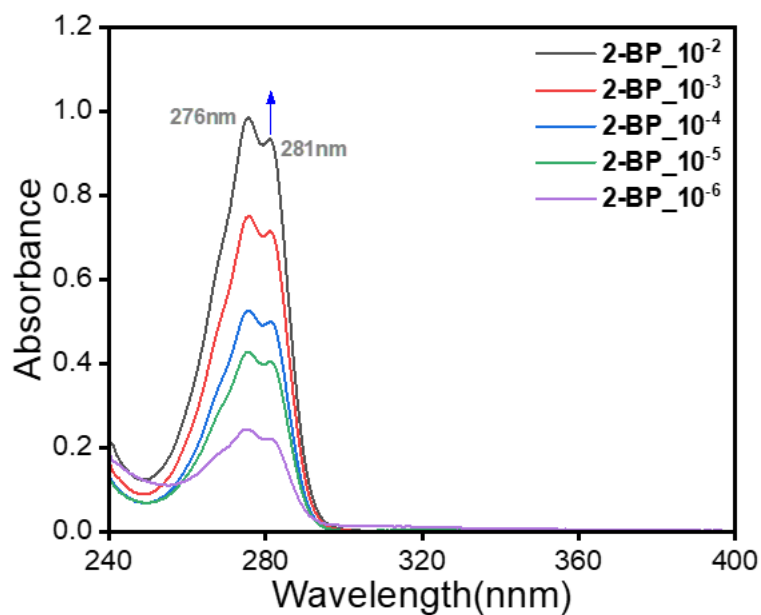
#### **2-Chlorophenol, 2-Bromophenol, and 2-Iodophenol:**

As per the previous studies the introduction of heavy halogen atoms (Cl, Br, I) in ortho position on phenols are making impactful difference in the context of cis-trans equilibria.

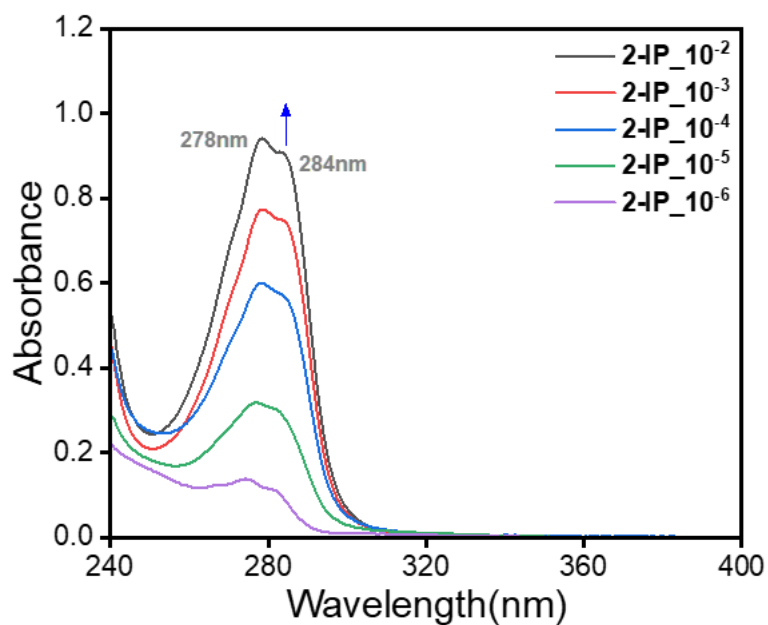
In UV analysis, the presence of two distinct and prominent peaks indicates the existence of two conformers in solution, with one being more abundant than the other. The appearance of the second peak (minor) becomes more pronounced as we move down the halogen family, indicating an increase in size and ellipticity of the p-orbital of the halogen atom. This suggests a specific type of behaviour or non-covalent interactions (intramolecular hydrogen bond) that are influencing the formation of a particular conformer. Additionally, this distinction arises from the interplay between resonance and steric effects. Phenols inherently display  $\pi$ - $\pi^*$  transitions in UV-Vis due to the interaction between the lone pairs on the oxygen atom of the hydroxyl group (OH) and the pi ( $\pi$ ) electron system of the benzene ring. However, the presence of bulkier halogen atoms (Cl, Br, and I) introduces a steric hindrance. This hindrance disrupts the coplanarity between the OH group and the benzene ring, hindering resonance in the trans isomer. Consequently, the cis and trans isomers exhibit distinct electronic transitions, resulting in the observed two distinct peaks.



(a)



(b)



(c)

Figure 3. UV-spectra of 2-Chlorophenol (a), 2-Bromophenol (b) and 2-Iodophenol (c) at  $10^{-2}$  to  $10^{-6}$  M concentration.

The position of major and minor peaks of 2-chlorophenol, 2-bromophenol and 2-iodophenols are 274 nm, 276 nm, 278 nm (major peak) and 281 nm, 281 nm, 284 nm (minor peak) respectively.

Unlike o-fluorophenol, o-chlorophenol, o-bromophenol, and o-iodophenol display a red shift in their UV-Vis spectra. Conversely, o-chlorophenol, o-bromophenol, and o-iodophenol exhibit a **red shift** compared to phenol. This can be explained by the

combined effects of resonance and hyperconjugation. While the steric hindrance from the bulkier halogens disrupts the coplanarity in the trans isomer, it also enhances hyperconjugation, a phenomenon where electrons in  $\sigma$  bonds (C-H bonds adjacent to the OH group) interact with the  $\pi$  system of the benzene ring. This additional electron donation can further stabilize the excited state, particularly in the cis isomer. The net effect can be a red shift compared to phenol, where hyperconjugation is less pronounced.

The UV-vis data complement the previously reported IR and NMR studies, as well as computational investigations, in elucidating the effects of halogen substitution on ortho position leads the intramolecular hydrogen bonding and conformational behaviour of these systems.

#### **Solvent effect:**

Different solvents were used for the experimental analysis but chloroform was the most suitable solvent due to its non polar nature. The minimizes the interaction between ground or excited state and provides better interpretation for compound which lies in lesser wavelengths.

# CHAPTER 5

## Future Prospect

The successful application of UV-vis spectroscopy in this research opens doors to exciting future avenues for investigating cis-trans equilibria and electronic transitions in o-halophenols. Here's an expanded look at the suggested future directions:

### 1. Quantitative Analysis with UV-Vis:

- **Develop calibration curves:** By measuring the absorbance of solutions with known cis/trans ratios at specific wavelengths, we can establish calibration curves. These curves will allow us to determine the cis/trans ratio of unknown samples based on their absorbance in the UV-vis spectrum.
- **Explore chemometrics:** Techniques like multivariate analysis can be employed to analyze complex UV-vis data containing contributions from both cis and trans isomers. This could involve principal component analysis (PCA) to identify underlying factors influencing the spectra and partial least squares (PLS) regression to build robust models for quantitative analysis.
- **Comparison with other methods:** The cis/trans ratios obtained from UV-vis can be compared with those derived from established techniques like IR spectroscopy and NMR spectroscopy. This comprehensive comparison would validate the accuracy and reliability of the UV-vis method.

### 2. Advanced Theoretical Calculations:

- **Refine computational models:** Existing computational models can be further refined by incorporating higher levels of theory and considering specific solvent environments. This will provide more accurate predictions of electronic transitions and their dependence on halogen substitution.
- **Explore time-dependent density functional theory (TD-DFT):** This advanced computational approach can simulate the absorption of light by molecules, providing detailed information about excited state properties and electronic transitions. This can be particularly valuable in understanding the subtle differences between cis and trans isomers in o-halophenols.
- **Investigate halogen-aromatic interactions:** Utilize computational methods to explore the nature and strength of halogen-aromatic interactions in o-halophenols. This can provide insights into the steric and electronic effects that influence the conformational preferences.

### 3. Solvent Effects and their Influence:

- **Investigate a range of polarities:** The current study employed chloroform, a non-polar solvent. Expanding the investigation to solvents with varying polarities (from highly polar to non-polar) will reveal how solvent interactions with the solute (o-halophenols) affect the cis-trans equilibrium and electronic transitions.
- **Hydrogen bonding interactions:** Polar solvents can participate in hydrogen bonding with the OH group in o-halophenols. This might influence the populations of cis and

trans isomers by affecting the intramolecular hydrogen bonding within the molecule itself.

- Solvatochromic effects: Study how the solvent environment influences the position and intensity of absorption bands in the UV-vis spectra. This can provide insights into the specific interactions between o-halophenols and different solvents.

#### **4. Applications in Material Science:**

- Design functional materials: The understanding of cis-trans equilibria and their dependence on halogen substitution can be used to design new functional materials. For instance, materials with specific optoelectronic properties could be tailored by controlling the cis/trans ratios in o-halophenol derivatives.
- Liquid crystals: O-halophenols with tunable cis-trans equilibria have the potential to be utilized in liquid crystal displays. By manipulating the halogen substitution and solvent environment, the phase transition behavior of these materials can be controlled, leading to the development of new display technologies.
- Supramolecular assemblies: The self-assembly of o-halophenols into ordered structures can be influenced by the interplay between cis-trans equilibria and intermolecular interactions. This knowledge can be applied to design novel supramolecular assemblies with specific functionalities for applications in catalysis, sensing, and drug delivery.

By pursuing these future directions, researchers can gain a deeper understanding of the structure-property relationships in o-halophenols. This knowledge can pave the way for the development of novel materials with tailored properties and functionalities for various technological advancements



# CHAPTER 6

## Conclusion

This research has successfully employed UV-vis spectroscopy to investigate the cis-trans equilibrium in o-halophenols and provided valuable insights into the interplay between halogen substitution and electronic transitions. The key findings of the study are summarized below:

- **Distinct Conformational Behavior of o-Fluorophenol:** Unlike heavier halogens (Cl, Br, I), fluorine exhibits minimal steric hindrance due to its small size and electron configuration. This allows o-fluorophenol to retain a significant population of the cis isomer, similar to phenol. The UV-vis spectra of phenol and o-fluorophenol show a shoulder peak attributed to the cis isomer, with a surprising similarity in intensity.
- **Electronic Transitions and Substituent Effects:** The introduction of fluorine leads to a blue shift in the UV-vis spectrum compared to phenol. This can be attributed to the electron-withdrawing nature of fluorine, which stabilizes the ground state and requires higher energy light for electronic transitions.
- **Impact of Bulky Halogens:** Heavier halogens (Cl, Br, I) introduce a more pronounced steric effect, disrupting the coplanarity between the OH group and the benzene ring in the trans isomer. This hinders resonance and favors the formation of the cis isomer. The UV-vis spectra of o-chlorophenol, o-bromophenol, and o-iodophenol display two distinct peaks, with the minor peak corresponding to the cis isomer becoming more prominent as the halogen size increases.
- **Red Shift and Hyperconjugation:** The UV-vis spectra of o-chlorophenol, o-bromophenol, and o-iodophenol also exhibit a red shift compared to phenol. This can be explained by the interplay between steric hindrance and hyperconjugation. While steric hindrance disrupts resonance in the trans isomer, it also enhances hyperconjugation, stabilizing the excited state, particularly in the cis isomer. The net effect leads to a red shift compared to phenol.

### Overall Significance:

This study demonstrates the effectiveness of UV-vis spectroscopy in complementing existing IR, NMR, and computational investigations of o-halophenols. By analyzing the electronic transitions and their dependence on halogen substitution, we gain a deeper understanding of the factors influencing cis-trans equilibria and the unique behavior of o-fluorophenol. The findings contribute to a more comprehensive picture of the structure-property relationships in this class of important organic compounds.

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