

## ARTICLE

**Synthesis and Characterization of 4,4'-Dibromoazobenzene**

Ranran Zhen Wei Lu\* Yun Zhou Minzhen Feng Ya Wang

College of Chemistry, Chongqing Normal University, Chongqing, 400000, China

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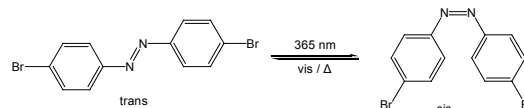
Photoisomerism

## ABSTRACT

Azobenzene molecules show excellent application potential in many fields due to their photoisomerization properties. Azobenzene molecules will gradually change from trans-structure to cis-structure under the irradiation of UV. In this paper, we have synthesized 4,4'-dibromoazobenzene molecules and characterized their photoisomerization properties. We found that with the extension of UV time, the trans absorption peak at 343 nm decreased significantly, while the cis absorption peak at 435 nm showed an upward trend. Furthermore, photoisomerization of azobenzene is not a first-order reaction.

**1. Introduction**

Azobenzene molecules and their derivatives refer to aromatic compounds containing a functional structure of -N=N- in the molecule. In 1858, Johann<sup>[1]</sup> discovered a diazotization reaction that could be used to synthesize azobenzene compounds. Under the specific wavelength of light radiation, azobenzene molecules will have obvious photochromism. This phenomenon is because azobenzene molecules have two geometric isomers. They can be converted to each other under the stimulation of a specific wavelength of light. This phenomenon is called photoisomerism. Azobenzene molecules can undergo trans to cis conversion under the irradiation of ultraviolet light, and cis to trans conversion can be achieved under the irradiation or heating of visible light (Figure 1).

**Figure 1.** Photoisomerization of azobenzene

The classic methods for preparing azobenzene are azo coupling reaction, Mills reaction, and Wallach reaction. The azo coupling reaction is a nucleophilic reaction with short reaction time and high yield<sup>[2]</sup>. Primary aromatic amines initially diazotized at low temperatures before reacting with electron-rich phenol. Diazonium salts are weak electron systems and are prone to reactions in electron-rich systems<sup>[3]</sup>. This reaction needs to be performed in an acidic environment<sup>[4]</sup>. The reaction of aromatic nitroso derivatives and aniline in glacial acetic acid is the Mills reaction<sup>[5]</sup>. Aromatic nitroso derivatives can be prepared from aromatic methyl hydroxylamine by t-butyl hypochlorite oxidation. This oxidation reaction needs

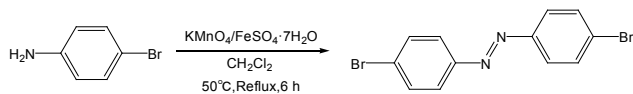
\*Corresponding Author:

Wei Lu,

College of Chemistry, Chongqing Normal University, Chongqing, 400000, China;

Email:

to be carried out in a dilute solution at  $-78\text{ }^{\circ}\text{C}$  to prevent excessive oxidation. For the Wallach reaction, there is an explanation of the reaction mechanism. Azobenzene oxide is first protonated, dehydrated, and isomerized, and then attacked by nucleophiles. After rearrangement, azobenzene products are obtained<sup>[6]</sup>. In this paper, 4,4'-dibromoazobenzene is prepared from 4-bromoaniline by the method of primary oxidizing amines to azo by  $\text{KMnO}_4$  supported on  $\text{Fe(II)SO}_4$  (Figure 2) benzene. The trans to cis conversion was achieved under UV light at 365 nm.



**Figure 2.** Synthesis of 4,4'-dibromoazobenzene

## 2. Experiment

### Synthesis of 4,4'-dibromoazobenzene

Pour equal amounts of  $\text{KMnO}_4$  (5 g) and  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  (5 g) in a mortar and lightly grind (to prevent oxidation of ferrous ions) to obtain the oxidant. 4-Bromoaniline (1.75 g, 1 mmol) was placed in a 250 mL round bottom flask, dissolved in dichloromethane, and a homogeneous mixture of oxidant (10.0 g) was added thereto. The mixture was refluxed for 6 h. The reaction mixture was cooled to room temperature and filtered through celite. The residue was washed with  $\text{CH}_2\text{Cl}_2$  (3 x 15 ml) and ether (3 x 15 ml). The resulting solution was dried over anhydrous sodium sulfate. The solvent was removed and purified by column chromatography (basic alumina, 200-300 mesh, n-hexane: ethyl acetate = 4: 1). Vacuum drying box at  $60\text{ }^{\circ}\text{C}$  for 6h. An orange-red solid was obtained (87% yield).  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.80 (d,  $J = 8.68\text{ Hz}$ , 4H,  $\text{H}^2$ ), 7.66 (d,  $J = 8.68\text{ Hz}$ , 4H,  $\text{H}^1$ ).

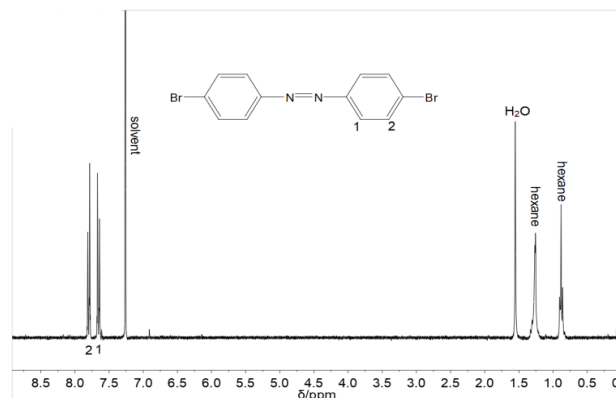
### UV irradiation experiment

Use a volumetric flask to accurately configure 4, 4'-dibromoazobenzene with a concentration of  $3 \times 10^{-5}\text{ mol/L}$  ethyl acetate solution. Add 1 ml of the ethyl acetate solution in 1.5 ml centrifuge tubes. The tubes were irradiated with 450 nm LED blue light for 30 min in order to convert all cis-azobenzene molecules into trans. The tubes were irradiated with a 365 nm UV lamp in a dark box, and a solution was taken every 1 minute for UV-vis spectrophotometry.

## 3. Results and discussion

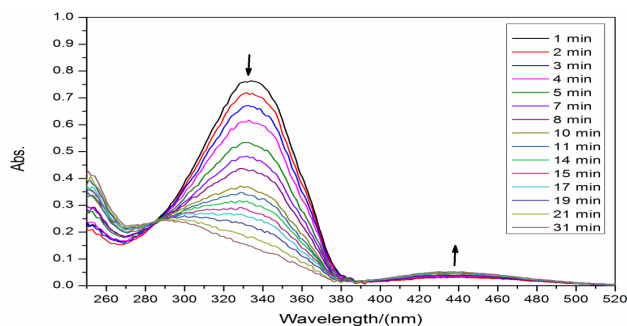
The  $^1\text{H NMR}$  (Figure 3) of the product showed that the ratio of the integrated values of 1 and 2 was 0.99: 1. This result is consistent with the theoretical value. Therefore, 4, 4'-dibromoazobenzene can be prepared by the method of

oxidizing primary amine to azo by  $\text{KMnO}_4$  supported on  $\text{Fe(II)SO}_4$ .



**Figure 3.**  $^1\text{H NMR}$  spectrum of 4, 4'-dibromoazobenzene ( $\text{CDCl}_3$ , 300 MHz, 298 K)

Figure 4 shows the UV-vis absorption spectrum of 4,4'-dibromoazobenzene. From the image, we found that with the increase of the 365 nm UV lamp irradiation time, the absorption peak at 343 nm gradually decreased, while the absorption peak at 435 nm showed an upward trend.



**Figure 4.** UV-vis absorption spectrum of 4,4'-dibromoazobenzene

Under UV radiation at 365 nm, 4,4'-dibromoazobenzene will undergo a  $\pi\text{-}\pi^*$  transition, and its structure will change from trans to cis. The absorption at the wavelength of 343 nm corresponds to the trans structure, and the absorption at the wavelength of 435 nm corresponds to the cis structure. The formula for the first-order reaction is as follows:

$$\ln(c_0) - \ln(c_t) = Kt \quad (1)$$

$$\text{Then through Lambert-Beer law } A = \epsilon bc \quad (2).$$

Where  $c$  is the solution concentration,  $K$  is the reaction rate constant,  $\epsilon$  is the molar absorptance, and  $b$  is the cuvette thickness<sup>[7]</sup>. Wherein the molar absorptance, cuvette thickness, and reaction rate constant are all quantitative,

and we can derive that:

$$\ln(A_0) - \ln(A_t) = Kt \quad (3)$$

Substitute Figure 4 data into the formula and find that the value of K is constant. This result indicates that the reaction is a first-order reaction.

#### 4. Conclusion

In this paper, we successfully synthesized 4,4'-dibromoazobenzene molecules via  $\text{KMnO}_4$  and  $\text{Fe}(\text{II})\text{SO}_4 \cdot 7\text{H}_2\text{O}$  and characterized their photoisomerization properties. We found that with the extension of UV light irradiation time, the trans absorption peak at 343 nm decreased significantly, while the cis absorption peak at 435 nm showed an upward trend. The photoisomerization of azobenzene is not a first-order reaction.

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