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The investigation of crystal structure, spectroscopic and thermal properties of *p*-(*p*-acetylphenylazo)-*o*-allylphenol and *p*-(*p*-bromphenylazo)-*o*-allylphenol

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Abstract

The two new azo dyes *p*-(*p*-acetylphenylazo)-*o*-allylphenol (compound **I**) and *p*-(*p*-bromphenylazo)-*o*-allylphenol (compound **II**) have been synthesized and studied by FT-IR, UV–VIS, ^{1}H NMR, ^{13}C NMR techniques, elemental analysis, X-ray structure analysis and TG, DTG, and DTA analyses. Compound **I** crystallizes in the monoclinic space group P21/c with $a = 19.6130(15)$ Å, $b = 7.3586(6)$ Å, $c = 21.4752(15)$ Å, $\alpha = 90.00°$, $\beta = 101.413(6)°$, $\gamma = 90.00°$, $Z = 8$, $V = 3038.1(4)$ Å^3 and the molecules are linked by two intermolecular O···O hydrogen bonds. There are two independent molecules in the asymmetric unit of compound **I**. Compound **II** crystallizes in the monoclinic space group Cc with $a = 4.7194(7)$ Å, $b = 24.597(2)$ Å, $c = 12.2241(16)$ Å, $\alpha = 90.00°$, $\beta = 96.509(11)°$, $\gamma = 90.00°$, $Z = 4$, $V = 1409.9(3)$ Å^3 and the molecules are linked by O···N and C–H···O intermolecular hydrogen bonds. They are characterized by UV–VIS, FT-IR, ^{1}H NMR, ^{13}C NMR techniques, elemental analysis, TG, DTG, and DTA analyses.

Keywords: Azo dyes; X-ray; UV–VIS; IR; NMR; Thermal analysis

1. Introduction

Azo compounds have caused great interest in organic synthesis. In the class of the dye molecule, azo compounds are an important kind of organic colorants and consist of at least a conjugate chromophore azo group and two or more aromatic rings. The color of azo dyes is mainly due to the interaction of the azo group and incident light. Azo dyes are widely used in textiles, printing, cosmetics, drugs, foods coloring, and other consumer goods [1,2]. They are also used extensively in laboratories as either biological stains or *pH* indicators [2]. They can also be used as materials for non-linear optics and for storage of optical information in laser disks [3]. Recently, many noteworthy studies have shown that some azo compounds possess excellent optical memory and photoelectric properties [4,5]. The X-ray and spectroscopic investigations are revealing the relationship between molecular structure, solid state packing arrangements and dye performance characteristics.

In this study, the molecular and crystal structure of *p*-(*p*-acetylphenylazo)-*o*-allylphenol and *p*-(*p*-brompheny-lazo)-*o*-allylphenol were identified by the spectroscopic techniques such as UV–VIS, IR, ^{1}H NMR, ^{13}C NMR, determined by X-ray diffraction method, elemental and thermal analysis techniques.

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2. Experimental

2.1. Synthesis

The *p*-phenylazo-*o*-allylphenol dyes synthesized with azo-coupling reactions of substituted benzenediazonium salts and *o*-allylphenol are shown in Scheme 1. Substituted anilines were diazotized using sodium nitrite in the presence of hydrochloric acid followed by coupling with *o*-allylphenol substrate to produce *p*-phenylazo-*o*-allylphenol dyes **I** and **II** in good yield.

The diazotization reactions were carried out in an identical manner, and one representative description of the method will be given [6]. *p*-Acetylaniline (1.64 g, 0.012 mol) was dissolved in water (50 mL) containing 6 mL of 5 N HCl. The clear solution was cooled to 0 °C in an ice bath. To this solution was added dropwise $NaNO_2$ (0.83 g, 0.012 mol) dissolved in water (15 mL) at 0 °C maintaining the temperature of the mixture below 5 °C. This mixture was stirred for 1 h at 0 °C and *o*-allylphenol (3.00 g, 0.02 mol) dissolved of aqueous NaOH (0.80 g, 0.02 mol) was added dropwise to this prepared solution. The addition was accomplished quickly and the temperature was not permitted to rise above 5 °C. Following the addition of *o*-allylphenol, the solution became bright red and a red precipitate was collected by suction filtration. Red solid was washed with water (50 mL) and ethanol (50 mL). It was then recrystallized from hot ethanol and dried under vacuum at 50 °C for 6 h and its purity was examined by thin-layer chromatography. Single crystals were grown by slow evaporation of reaction mixture at room temperature. Elemental analyses are in good agreement with the molecular formula proposed for these compounds. *Caution*: prolonged heating in excess of 90 °C may lead to the decomposition of diazo linkage. Yield for compound **I**: 68%. Mp.113 °C. Elemental analysis, found (calculated for $C_{17}H_{16}N_2O_2$, compound **I**), C: 72.42% (72.86%), H: 5.07% (5.71%), N: 9.34% (9.99%). Yield for compound **II**: 78%. Mp.105 °C. Elemental analysis, found (calculated for $C_{15}H_{13}BrN_2O$, compound **II**): 55.76% (56.78%), H: 3.95% (4.10%), N: 8.20% (8.83%).

2.2. Physical measurements

IR spectra of compounds **I** and **II** were recorded in the region of 4000–400 cm^{-1}, using a Mattson 1000 FT-IR Spectrometer (KBr pellets). Absorption spectra in chloroform were determined on a Unicam UV–VIS Spectrometer. ^1H NMR and ^{13}C NMR data were acquired on a Bruker AC 200 Spectrometer. TG, DTG and DTA curves were recorded simultaneously on Rigaku TG 1810 thermal analyzer combined with a TAS 100 thermogravimetric analyzer. The experiments were performed in nitrogen atmosphere (80 mL/min) with a heating rate of 10 °C/min from room temperature to 1000 °C in platinum crucibles. Elemental analyses were recorded by TUBITAK Atal Laboratories.

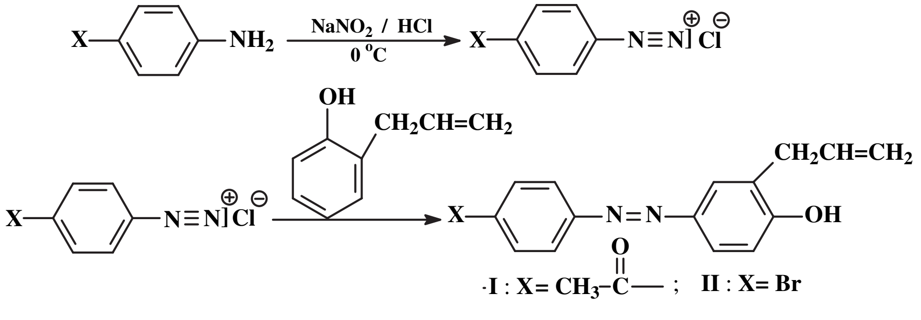
2.3. Crystal structure analysis

Crystals suitable for X-ray work were cut to the size of $0.17 \times 0.44 \times 0.50$ mm for compound **I** and $0.14 \times 0.35 \times 0.50$ mm for compound **II**. X-ray diffraction data were collected on a STOE IPDS II diffractometer with graphite monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) at 293 K. A summary of crystallographic data, experimental details, and refinement results for compounds **I** and **II** are given in Table 1.

3. Result and discussion

3.1. Description of the crystal structure

The molecular structure of compound **I** is shown in Fig. 1 with the atom numbering scheme. The compound consists of two phenyl rings (C1 to C6 and C7 to C12), and an azo frame (C4–N1–N2–C7). The phenyl rings adopt a *trans*-configuration about the azo functional group as observed in crystals of the other azo compounds. The *p*-(*p*-acetylphenylazo)-*o*-allylphenol **I** molecules are linked into zigzag chains by O1B–H1B···O2A and O1A–H1A···O2B hydrogen bonds, with O···O distances of 2.713(3) Å and 2.717(3) Å, respectively (Table 2). There are two independent molecules



Scheme 1.