

Short Note

4,4'-Bis[4-(4'-hydroxyphenyl)phenylazo]diphenyl Ether

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Abstract: 4,4'-Bis[4-(4'-hydroxyphenyl)phenylazo]diphenyl ether (**3**) was prepared by diazotization coupling of 4,4'-oxy dianiline (**1**) and biphenyl-4-ol (**2**). The synthesized compound (**3**) was characterized by elemental analysis, UV-Visible, FTIR and ¹H-NMR (nuclear magnetic resonance) spectroscopic studies.

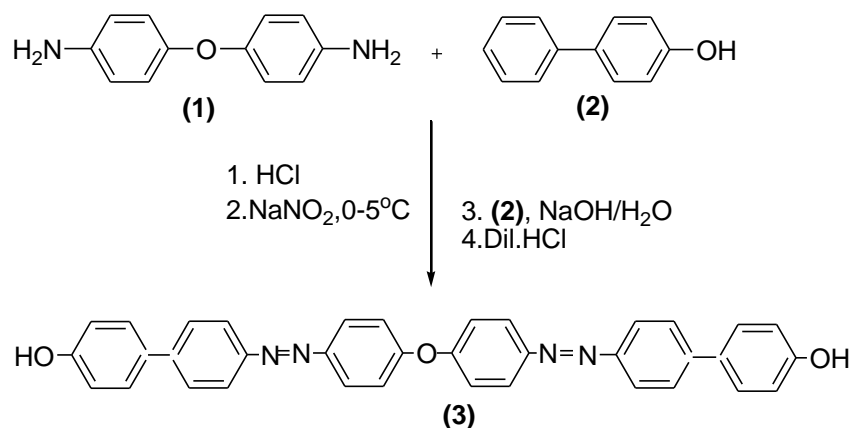
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1. Introduction

Recently, azobenzene and its derivatives have attracted considerable attention based on their extraordinary physical and chemical properties, such as bright colors, good stability, low flammability, and rapid reversible photo-isomerization. These compounds can exist in either cis or trans configuration [1–4]. Upon exposure to ultraviolet (UV) radiation, trans to cis configuration change in azobenzenes is evident from UV-vis spectrum. However, these compounds are changed back to trans state, when exposed to visible light or heat. This type of photo-isomerization is responsible for the change in geometry, absorption spectra, and dipole moments of the azo based compounds [5–8]. Aromatic azo compounds are widely used in the chemical industry as dyes, pigments [6–8], food additives [9], indicators [10], radical reaction initiators [11] and therapeutic agents [12,13]. In addition, azobenzenes have shown promising applications in photo-optical media [14], photo-switches [15], photo-mechanical systems [16], micro patterning [17], nonlinear optical media [18], molecular shuttles, [19] nanotubes, [20] and in the manufacture of protective eye glasses and filters [21]. Moreover, the light induced reversible isomerization of azobenzenes between cis and trans forms makes them excellent candidates to modulate the relative movement of different moieties; thus leads to the development of light driven motors [22].

2. Results

In this work, new bis-azo-diol has been synthesized successfully by diazotization coupling reaction given in Scheme 1.



Scheme 1. Synthesis of 4,4'-bis[4-(4'-hydroxyphenyl)phenylazo]diphenyl ether (3).

3. Discussion

The synthesis of bis-azo-diol was carried out by diazotization coupling reaction of aromatic amine and coupling agent [23]. Diazotization was carried at low temperature between 0–5 °C using ice bath as diazonium salts decompose to liberate nitrogen up to 10 °C. Aromatic diamine used was 4,4'-oxydianiline and the coupling agent was biphenyl-4-ol. The synthesized compound was characterized by m.p., % yield and elemental analysis. The structure of the synthesized compound was determined by UV-Vis, FTIR, and ^1H -nuclear magnetic resonance (NMR) spectroscopic analysis.

Elemental analysis of the synthesized compound (3) provided evidence of its successful synthesis as the formula derived on the observed values was in good agreement with the expected formula.

The UV spectrum was recorded in THF and showed maxima at 350 nm which was mainly because of azo group in the compound showing strong absorption maximum due to π - π^* transitions in trans state of azo moiety. A weak maximum was also observed around 420 nm which was due to a cis band rise due to n - π^* transitions [24,25]. The molar extinction coefficient (ϵ) was calculated to be $32387 \text{ cm}^{-1} \cdot \text{M}^{-1}$ at λ_{max} 350 nm.

The FTIR spectrum of compound (3) exhibited a broad band at 3407 cm^{-1} (range, 3200 – 3400 cm^{-1}) [21], which indicated the presence of OH group. A weak band at 3152 cm^{-1} (range, 3050 – 3150 cm^{-1}) owing to C–H stretching of phenyl group was also observed. The FTIR spectrum also showed a sharp band at 1581 cm^{-1} (range, 1630 – 1550 cm^{-1}) due to azo group. A strong band, assigned to the out of plane C–H bending vibrations of p-substituted phenyl ring appeared at 840 cm^{-1} .

For further analysis, an NMR study of the monomer was also carried out using DMSO as a solvent. In a study of ^1H -NMR, disappearance of the signal for the NH_2 group and appearance of OH signal at 9.55 ppm was observed showing conversion of diamine into the azo diols. The doublets in the spectrum confirmed the presence of aromatic groups in the compound. J values were also calculated which indicated that ortho coupling is in operation [25].

4. Experimental Section

4.1. General Information

4,4'-Oxydianiline and sodium nitrite, were bought from Fluka Switzerland. DMSO, biphenyl 4-ol, H_2SO_4 , HCl and NaOH were purchased from Merck (Munich, Germany). Tetrahydrofuran (THF) was acquired from Riedel de Haën Germany, and was distilled and dried freshly as per requirement for using standard methods. Thin layer chromatography was performed using pre-coated Kieselgel 60-HF₂₅₀ TLC plates.

The melting point was attained on melting point apparatus, Mel-Temp, Mitamura Riken Kogyo, Inc. Tokyo Japan using open capillary tubes. The elemental analysis was obtained from

LECO CHNS-932 (Isomass Scientific Inc., Calgary, AB, Canada). The solid state Fourier Transform infrared spectra were recorded on a Thermo Scientific Nicolet-6700 FTIR (Thermo Scientific, Madison, WI, USA). The UV-visible spectra of the compound were acquired on a 1601-Schimidzu in THF and H₂SO₄, using quartz cells. ¹H-NMR spectral analysis of compound was determined in DMSO solvent by using Bruker Advance ultra-shield 300 MHz (LabX, Carnation, WA, USA) digital NMR instrument using TMS as internal reference.

4.2. Synthesis of 4,4'-Bis[4-(4'-hydroxyphenyl)phenylazo]diphenyl Ether(3)

4,4'-Oxydianiline (7.2g, 36mmol) was dissolved in a 250 mL beaker containing a warm HCl solution (27 mL of 37%, 328 mmol in 50 mL water). Temperature of solution was lowered to 0–5 °C using an ice bath. The reaction mixture was strongly stirred till fine crystals of aromatic diamine hydrochloride were separated out. A cold sodium nitrite solution (7.45 g, 108 mmol) in 10 mL water was slowly added while stirring the mixture. The coupling reagent biphenyl 4-ol (12.25 g, 72 mmol) was dissolved in NaOH (32.87 g, 821 mmol in 100 mL water) and ice cooled in a separate beaker. Azotized solution was slowly added to this solution. The reaction mixture was acidified afterwards by 10 % H₂SO₄ solution. The resulted precipitates were filtered using Buchner funnel. Precipitates were dissolved in 10 % NaOH and precipitated again by 10 % H₂SO₄. Later, precipitates were recrystallized in ethanol/methanol to get the pure compound.

Compound (3): C₃₆H₂₆O₃N₄· 0.25 H₂O, Yield 78%, m.p. 223–225 °C, yellowish brown, solid, Elemental analysis: calcd (C 76.24, H 4.71, N 9.88), found (C 76.21, H 4.56, N 9.80). UV-Visible: λ_{max} (nm) 350. FTIR (cm^{−1}): 3407 (OH), 3152 (aromatic C-H), 1581 (N = N), 1148 (C-O-C), 840 (Biphenyl C-H bend), ¹H-NMR (DMSO-*d*₆, 300 MHz) 9.55 (OH, s), 7.55 (4H, d, *J* 8.1), 7.49 (4H, d, *J* 7.5), 7.47(4H, d, *J* 8.7), 7.38 (4H, d, *J* 8.1), 7.27 (4H, d, *J* 7.5), 6.86(4H, d, *J* 8.7).

5. Conclusions

Diazotization coupling reaction was applied successfully to synthesize a new bis-azo-diol (3). The reaction occurred in a short time and under simple reaction conditions. The melting point observed was around 225 °C and product synthesized was 78% in yield. The spectroscopic data confirmed the structure of the product (3).

Supplementary Materials: The following are available online at <http://www.mdpi.com/1422-8599/2016/4/M914>.

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Author Contributions: Zareen Akhter and Rahima Rahman conceived and designed the experiments; Rahima Rahman performed the experiments and analyzed the data; Asghari Gul contributed in manuscript writing.

Conflicts of Interest: The authors declare no conflict of interest.

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