

Synthesis and Characterization of Monomer to Design a System of Optical Materials

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Abstract

Quinoline forms the key skeletal component of a number for important natural products and active compounds. Despite a tremendous amount of research pertaining to the derivatization of quinoline, very few general synthetic routes are described in the literature starting from quinoline or tetra hydroquinone, and it is very simple synesthetic road we designed from the quinoline our monomer 6-Bromoquinaldine. The monomer structure of resulting was confirmed by UV, FTIR, NMR, and TGA, hence it used in our work as block in a main monomer in the polymers designed and applied in our work in chemical sensor and solar cell this study open new path for our future work and other works.

Keywords: 6-bromoquinoline; Amino Quinoline; Synthesis; Characterization

Introduction

Recently explored a new synthetic strategy for the synthesis of 6-bromo-1,2,3,4-tetrahydroquinoline and 3,6,8-tribromoquinoline based on the bromination reaction of substituted or unsubstituted 1,2,3,4-tetra hydro quinoline, good starting materials with functionality on both rings of quinoline. The direct halogenation of quinoline and tetra hydroquinoline seems the most attractive; however, it is still a challenging strategy as haloquinolines are also the best precursors of many other derivatives [1]. In previous publications, brominated tetra hydro-quinoline was transformed into their respective derivatives. The quinoline moiety forms the key skeleton of several natural-product and pharmacologically-active compounds, displaying a broad spectrum of biological activities [2]. We have investigated a new strategy for the poly functionalization of quinoline via nitration of bromo-quinolines referring to the fact that the nitro group has commonly activated adjacent

bromo groups for nucleophilic substitution. Quinolines (also called as benzo-pyridine and 1-azanaphthalene) are heterocyclic aromatic organic compounds with one nitrogen atom. It has a bicyclic structure, consisting of a benzene ring fused to the 2, 3-positions of the pyridine ring. Quinoline is a weak tertiary base and it can form a salt with acids. It is generally more reactive towards both electrophiles and nucleophiles [3]. The synthesis of quinoline derivatives has been of considerable interest in organic and medicinal chemistry since a number of drugs and natural products contain this heterocyclic moiety. Quinolines and their derivatives have been receiving more attention by researchers especially in the pharmaceutical fields, due to their wide-range of biological activities, such as anti-malarial, anti-hypertensive, anti-asthmatic, anti-bacterial, and anti-inflammatory activities. Fluoro-quinolones are popular and widely used antibacterial drugs. In addition, quinoline has also been used in the study of bio-organic and bio-organometallic pro-

cesses. Quinoline-containing anti-malarial drugs are a mainstay of treatments against malaria [4]. Quinine, a derivative of quinoline, is found naturally in plants as alkaloids. 8-Hydroxyquinoline is an important chelating agent and quinoline is used in the synthesis of rubber chemicals, dyes, and flavoring agents. Xu, *et al.* [5] prepared the monomer of derivative quinine (6-Bromoquinaldine) as main block on their work. Other industrial applications include their use as polymers, catalysts, corrosion inhibitors, and preservatives in our work Scheme 1 the synthetic routes of 6-Bromoquinaldine.

Characterization

IR spectra have performed on a Perkin Elmer Model 882 infrared spectrometer in the range of 4000 to 500 cm^{-1} . $^1\text{H-NMR}$ spectra were a Bruker AMX-500 spectrometer at 400 MHz, with tetra methyl silane (TMS) as the reference and CDCl_3 as a solvent. The absorbance as a function of wavelength was measured using a Lambda 35 UV-vis spectrophotometer with 1 cm square quartz cell. Differential scanning calorimetric (DSC) was performed on a TA instruments DSC 900 equipped with a liquid nitrogen cooling accessory (LNCA) unit under continuous nitrogen gas, the scan rate was $10^\circ\text{C}/\text{min}$. Thermo gravimetric analysis (TGA) of samples (15-25 mg) was carried out using a TA instruments TGA 2050 thermo gravimetric analyzer with a heating rate of $10^\circ\text{C}/\text{min}$ from 0 to 1000°C under continuous nitrogen gas. The thermal degradation temperature (Td) was defined as the temperature of 5% mass loss. The fluorescence spectra were obtained on a PerkinElmer LS 55 spectrometer. The electro spray ionization mass spectra were determined by LCQ Fleet spectrometer (Thermo Fisher). Scans were collected at a resolution of 1 cm^{-1} scanning from 4000 to 500 cm^{-1} .

Synthesis of 6-bromoquinaldine

To a 100 mL three-necked bottle added hydrochloric acid (22.5 mL), distilled water (22.5 mL), 4-bromoaniline (1.5 g), and stirring at 95°C until dissolved to the mixture acetic acid (0.5 mL) was added slowly, followed by addition of iodine/potassium KI (0.132 g), iodine I_2 (0.05 g). Then over 1 h a mixture of toluene (10 mL) and croton aldehyde (1.5mL) was added drop wise, and the formed mixture was refluxed at 100°C for 6 h. Precipitate the product, the sample was cleared by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 1:6) to afford 6-Bromoquinaldine [6]. FTIR (KBr) ν (cm^{-1}) (C-H) 3432, (C-N), 1303, (C=C) 1596 (C-Br) 632. $^1\text{H-NMR}$ (400 MHz,) δ 8.23 - 8.09 (m), 8.03 - 7.87 (m), 7.78 (d, J = 2.1 Hz), 7.76 - 7.50 (m), 7.37 - 7.04 (m), 7.00 (d, J = 17.7

Hz), 6.59 (d, J = 8.5 Hz), 2.92 (s), 2.77 (s), 2.60 (s), 2.45 - 2.36 (m), 2.07 (s), 1.91 (s), 1.70 (s), 1.46 - 1.19 (m), 1.15 - 0.24 (m), 0.17 - -0.00 (m), -0.05 (s), -0.13 (s).

Scheme 1: The synthetic route of 6-Bromoquinaldine.

Results and Discussion

Optical properties-UV-Vis spectroscopy

UV-vis spectra of 6-Bromoquinaldine is 232 nm and 323 nm absorption attributable to bromine at quinoline ring, the peak position relative to the bromine and croton aldehyde aniline blue shift, which indicated that the synthesise was successful.

Figure 1: UV-vis absorbance spectra of 6-Bromoquinaldine.

Fourier transform infrared spectroscopy FTIR

Fourier Transform Infrared Spectroscopy FTIR of 6-Bromoquinaldine the characteristic main beak at 3432 cm^{-1} that are attributed to the C-H vibration, at other hand the peak at 1384 to the C-C stretching vibration-Nat 1303 cm^{-1} and at 632 cm^{-1} to the C-Br stretching =C-H at 829 cm^{-1} .

$^1\text{H-NMR}$ characterization

The $^1\text{H-NMR}$ of 6-Bromoquinaldine, all the characteristic signals of at $\delta \approx 7.5\text{-}9.3$ ppm associate to the quinoline and a peak at $\delta \approx 2.5$ ppm belongs to the C-Brand $\delta \approx 1.5$ to the CH_3 .

Figure 2: IR spectra of 6-Bromoquinaldine.

Figure 3: ¹HNMR spectra of 6-Bromoquinaldine.

Thermo gravimetric analysis TGA

Thermo Gravimetric Analysis TGA using thermo gravimetric analysis (TGA) under nitrogen at a heating rate of 10°C·min⁻¹. The results are presented in figure 4. The thermal decomposition temperatures (Td, 5 wt% loss) the Tg 6-Bromoquinaldine was 134°C.

Figure 4: Thermal gravimetric analysis TGA of 6-Bromoquinaldine.

Conclusion

We have highlighted recent progress towards the synthesis of the monomer 6-Bromoquinaldine designed and prepared successfully. Our work has opened new road for the novelty of new synthesis useful for designer system in the future applied in many application we used the monomer in our privies work as main block and applied in the field of chemical sensor and solar cell.

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