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Synthesis and optical properties of new alkylated pyridinium halides



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ABSTRACT

Three pyridinium salts were prepared effectively under ultrasonic irradiation. The prepared compounds were characterized by their spectral (IR, NMR) data. The optical properties were measured in water as a solvent at different concentrations. The optical characteristics of these compounds were examined by using the UV-vis spectrophotometer. The results indicate that all compounds exhibit high transmittance in the visible light spectrum. The absorption coefficient and the optical energy gap were determined for each sample. Measurement of refractive index and dispersion relation were investigated.

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1. Introduction

Recently, organic materials are intensively investigated due to their wide range of applications in electronics. The investigation of the optical constants such as refractive index, extinction coefficient and dielectric constant of the materials are important for designing of new materials. Optical constants give information for technological applications in the field of photonics technology like optical communication. Furthermore, the changes in refractive index are important for controlling optical properties of organic materials [1,2].

Pyridine and its derivatives can be used as non-linear optical. The ring of pyridine is considered as cationic bonding sites and nitrogen as proton acceptor. Optical properties of pyridine compounds are very important for different applications. They have the main role in optical communication, image and signal processing [2]. The optical transmission of 1-ethyl-2, 6-dimethyl-4-hydroxy pyridinium halide in solution was studied by UV-vis-NIR instrument and it was found in the range 275–1100 nm [3]. The addition of halides to pyridinium compounds modifies the arrangement and their chemical structures [4]. The effect of alkyl chain length, on physical properties including refractive index of polysubstituted pyridinium liquids has been studied [5]. A series of pyridinium and quinolinium salts show high hyper-polarizabilities and good transparencies in the visible region of the spectrum by using hyper-Rayleigh scattering in solution [6].

Pyridinium salts exhibit maximum absorption at 327–337 nm in different organic solvents as counter ions [7]. Moreover, the increase of alkyl chain length of substituted aryl pyridinium salts leads to decrease of thermal stability. The unsubstituted

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pyridinium cations illustrate non-luminescence compared with substituted pyridinium ring with alkyl groups in the position 2,4, and 6, which induced it for UV luminescence [8].

Amalia Pana and coworkers investigate the optical properties of pyridinium ionic liquids and the emission properties of these compounds were tested in solution [9]. The optical properties and morphology of pyridinium ionic liquids were investigated by Scanning electron microscopy, UV-vis, X-ray diffraction, and photoluminescence spectroscopy [10]. The absorption spectrum of pyridinium salts with alkyl bromides indicates that *ortho*-bromine group make shift to red wavelength [11]. The spectral data (UV-vis and FTIR) of 3-hydroxy pyridinium tartarate were measured [12]. Nagapandiselvi and coworkers demonstrate the optical properties of 2-carboxy pyridinium dihydrogen phosphate by UV-vis-NIR, FT-NMR, FTIR, and fluorescence techniques [13].

The spectroscopic properties of 1-methyl-4-[2-(4-hydroxyphenyl) ethenyl] pyridinium dihydrogenphosphate have been measured by spectral techniques. The measurements of refractive indices for 1-butylpyridinium tetrafluoroborate, 1-butyl-3-methylpyridinium tetrafluoroborate, and 1-butyl-4-methylpyridinium tetrafluoroborate, with methyl and ethyl alcohols indicate that the pyridinium compounds in methyl alcohol have higher refractive index than the compounds in ethyl alcohol [14]. The absorption spectra and functional groups of 2-[2-(4-Diethylamino-phenyl)-vinyl]-1-methyl-pyridinium naphthalene-2-sulfonate (DESNS) were investigated by UV-vis-NIR and FTIR spectroscopic techniques, respectively [15]. Also, the spectral data for substituted styryl-pyridinium salts by UV-vis spectral analysis showed strong absorption band higher than 400 nm [16].

Rajalakshmi and coworker investigate the optical and mechanical properties of 2-Aminopyridinium 4-methylbenzoate dihydrate [17]. It was found that the energy band and refractive index equal 2.9 eV and 1.4, respectively at 1200 nm. Optical properties of single crystals the semi-organic non-linear zinc tris (thiourea) sulphate was investigated [18]. On the other hand, UV-vis spectroscopy is benefit to find transmittance, absorption and reflectivity of solutions and thin films [19,20]. The aim of this work is to investigate the optical properties of three alkylated-2-bromo-pyridinium halides prepared under ultrasonic irradiation.

2. Experimental procedure

IR spectrum were recorded with a Nicolet is 10 Thermo scientific as potassium bromide pellets and frequencies were reported in cm⁻¹. H NMR spectra were determined with a JEOL spectrometer at 500 MHz. The chemical shifts are expressed in the δ scale using tetramethylsilane as a reference. TLC was performed on Merck Kiesel gel; 60-F254 plates and the spots were detected by UV light absorption. Optical spectra in UV-vis region were recorded with a UV/visible spectrophotometer (UV-1800 SHIMADZU, Japan) by using 1 cm path length cuvettes at room temperature.

2.1. 1-Methyl-2-bromo-pyridinium iodide 2a

2-Bromo-pyridine (1.0 ml, 10.5 mmol) was dissolved in 2 ml CH_2Cl_2 , followed by the addition of iodomethane (0.783 ml, 12.5 mmol). The resulting mixture was sonicated for 15 min at room temperature. water 20 ml was added The reaction mixture was extracted with CH_2Cl_2 (50 ml \times 3), and the organic layer was washed with water (50 ml), dried over Na_2SO_4 and concentrated in vacuo to afford a yellow product (2.1 g, 88%). ¹H NMR (500 MHz, $CDCl_3$): 9.31 (d, J = 6.9 Hz, 1H), 8.62–8.66 (m, 2H), 8.44 (m, 1H), 1.71 (s, 3H).

2.2. 1-Benzyl-2-bromo-pyridinium chloride 2b

2-Bromo-pyridine (1.0 ml, 10.5 mmol) was dissolved in 2 ml CH₂Cl₂, and then benzyl chloride (1.59 ml, 12.5 mmol) was added. The resulting mixture was sonicated for 15 min at room temperature. The reaction mixture was extracted with CH₂Cl₂ (50 ml × 3), and the organic layer was washed with water (50 ml), dried over Na₂SO₄ and concentrated in vacuo to afford colorless product (3.0 g, 90%) ¹H NMR (500 MHz, CDCl₃): δ 9.25 (d, J = 7.0 Hz, 2H), 8.78 (d, J = 7.0 Hz, 2H), 7.58 (d, J = 3.75 Hz, 2H), 7.41 (m, 3H), 3.45 (s, 2H).

2.3. 1-Allyl-2-bromo-pyridinium bromide 2c

2-bromo-pyridine (1.0 ml, 10.5 mmol) was dissolved in 2 ml CH₂Cl₂, and then allyl bromide (1.15 ml, 10.5 mmol) was added. The resulting mixture was sonicated for 15 min at room temperature. The reaction mixture was extracted with CH₂Cl₂ (50 ml \times 3), and the organic layer was washed with water (50 ml), dried over Na₂SO₄ and concentrated in vacuo to afford colorless oily product (2.8 g, 86%). ¹H NMR (500 MHz, CDCl₃): 9.30 (d, J = 6.9 Hz, 1H), 8.62–8.68 (m, 2H), 8.45 (m, 1H), 6.41–6.60 (m, 1H), 5.97–6.21 (m, 2H), 5.86 (d, J = 6.0 Hz, 2H).

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