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Photophysical studies of fused phenanthrimidazole derivatives as versatile π-conjugated systems for potential NLO applications

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ABSTRACT

Two new heterocyclic imidazole derivatives consists of π-conjugated system attached to a phenanthrimidazole moiety have been synthesized in moderate yield by the condensation of 1,10-phenanthroline-5,6-dione with substituted aromatic aldehydes and 4-methoxyaniline in the presence of ammonium acetate in ethanol medium. The photophysical properties of these imidazole derivatives were studied in several solvents. These derivatives were evaluated concerning their solvatochromic properties and molecular optical nonlinearities. Their electric dipole moment (μ) and hyperpolarizability (β) have been calculated theoretically and the results indicate that the extension of the π-framework of the ligands has an effect on the NLO properties of these imidazole derivatives. The non-zero tensor components of these imidazole derivatives reveal that they possess potent non-linear optical (NLO) behavior. The energies of the HOMO and LUMO levels and the molecular electrostatic potential (MEP) energy surface studies have exploited the existence of intramolecular charge transfer (ICT) within the molecule.

1. Introduction

New material properties can be achieved, when new conjugated systems are composed by different heterocyclic nuclei, which allow the fine tuning of important photophysical properties. As a result of the optical and conductive properties, conjugated materials containing thiophene, imidazole and phenanthroline heterocycles have found many applications [1].

Aryl-imidazo-phenanthrolines play important role in materials science and medicinal chemistry due to their optoelectronic properties [2–4]. They are used as ligands for the synthesis of metal complexes of ruthenium(II), copper(II), cobalt(II), nickel(II), manganese(II), iridium(III) and several lanthanides for nonlinear optical (NLO) applications. They are important building blocks for the synthesis of proton, anion and cation sensors. They have diverse biological applications such as probes of DNA structure and new therapeutic agents due to their capacity to bind or interact with DNA [4].

Our approach to design new π-conjugated systems for several potential optical applications is based on the use of six membered aromatics and imidazoles in the conjugation pathway, combined with electron deficient heterocycles such as phenanthroline. These nuclei act as an acceptor group due to the deficiency of electron density on the ring carbon atoms. These imidazole derivatives exhibit high thermal stabilities making them interesting for several applications in materials chemistry [5,6]. Hence there is considerable interest in the synthesis of new materials with large optical nonlinearities by virtue of their potential use in device applications related to telecommunications, optical computing, optical storage, and optical information processing [7–10]. Herein we focussed the synthesis, photophysical and theoretical studies of some novel arylimidazophenanthroline derivatives (**1** and **2**) and shown as potential candidates for NLO materials by virtue of their high harmonic generation.

2. Experimental

2.1. Materials and methods

1,10-Phenanthroline-5,6-dione has been synthesized and purified according to the reported literature procedure [11]. Benzaldehyde, 4-fluorobenzaldehyde, 4-methoxyaniline and all the other reagents have been purchased from S.D. fine chemicals and used without further purification for the synthesis of these imidazole derivatives reported here (Scheme 1) [12–20].

NMR spectra have been recorded on a Bruker 400 MHz NMR instrument (Figs. 1 and 2). UV–vis absorption and fluorescence spectra have been recorded on Perkin Elmer spectrophotometer Lambda35 and Perkin Elmer LS55 spectrofluorimeter, respectively. Fluorescence spectra were corrected from the monochromator

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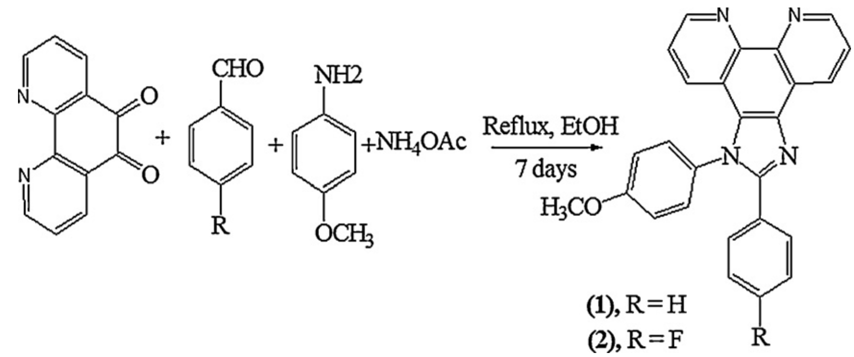

Scheme 1. Synthesis of imidazole derivatives (**1**) and (**2**).

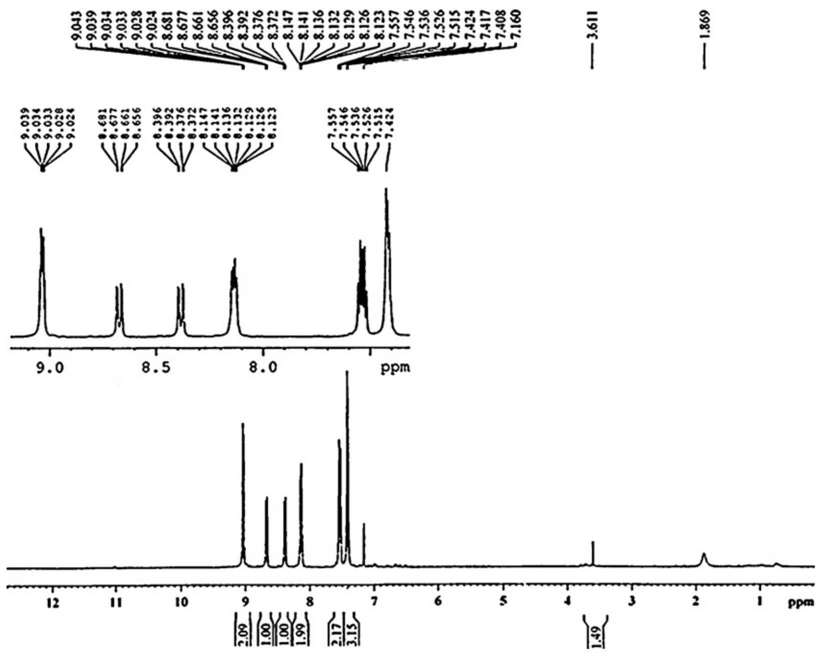

Fig. 1. ^{1}H NMR spectrum of imidazole derivative (**1**).

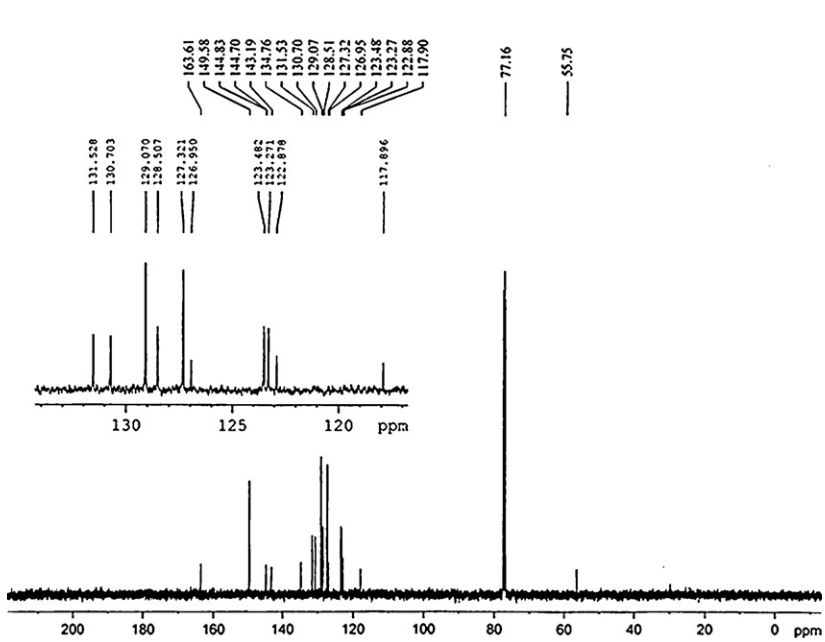

Fig. 2. ^{13}C NMR spectrum of imidazole derivative (**1**).