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Journal of Molecular Structure 873 (2008) 5–16

Journal of
MOLECULAR
STRUCTURE

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Synthesis, characterization, structural optimization using density functional theory and superoxide ion scavenging activity of some Schiff bases

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Received 3 October 2006; received in revised form 30 January 2007; accepted 1 February 2007
Available online 2 March 2007

Abstract

Four Schiff bases, 2-[(4-nitro-phenylimino)-methyl]-phenol (NPIMP-2), 4-[(4-nitro-phenylimino)-methyl]-phenol (NPIMP-4), (1*H*-indol-3-ylmethylene)-(4-nitro-phenyl)-amine (IYNPA), (3-nitro-benzylidene)-(4-nitro-phenyl)-amine (NBNPA) with experimental clue of binding with superoxide ion have been synthesized by the condensation of *p*-nitroaniline with *o*-hydroxy benzaldehyde, *p*-hydroxy-benzaldehyde, indole-3-carboxaldehyde and *m*-nitrobenzaldehyde respectively. These were characterized by IR, ^{1}H NMR, CHN, mass spectroscopy and UV–visible spectroscopy. The Schiff bases thus synthesized exhibited evidence for their binding with superoxide ion in the form of a high intensity charge transfer band beyond 500 nm in their respective UV–vis spectra on the addition of two drops of N/10 NaOH to their respective 10^{-2} M solutions in DMSO. On further addition of two drops of N/10 HCl solution, the charge transfer band vanished and the original spectral pattern of the Schiff bases in DMSO was observed. Out of the four Schiff bases, the binding of NPIMP-4 with O_2^- was observed to be reversible throughout both the cycles of measurements, but the remaining Schiff bases, namely NPIMP-2, IYNPA and NBNPA were found to show reversibility in only one cycle. The variable temperature ^{1}H NMR (RT-175 °C) in DMSO-d_6 revealed reversible intramolecular proton transfer in NPIMP-2 and NPIMP-4 leading to existence of several tautomeric structures. Besides these synthetic and spectroscopic studies, the density functional theory (DFT) calculations were performed for two Schiff bases i.e., NPIMP-2 and NPIMP-4. These calculations provided some important information about the relative stability of various tautomeric forms of NPIMP-2 and NPIMP-4.

Keywords: Superoxide ion; Schiff base; DFT; Variable temperature NMR

1. Introduction

The Schiff bases form a promising area of research due to their wide spectrum applications, particularly as corrosion inhibitors [1], catalysts for activation of small molecules [2,3] and in biological systems [4–11]. Besides these applications, Schiff bases derived from the condensation of oligosalicyaldehyde and a variety of aromatic amines have been exploited as carriers of metal ions found in the industrial waste water [12]. The Schiff bases in their polymeric form like polyazomethine ether have been found to be potential candidate and as non-linear optical (NLO) materials [13]. Metal complexes specially the mononuclear and dinuclear complexes of Cu(II) and Zn(II) derived from Schiff bases have been used as working models of the active site of SOD enzyme by many workers [14–17]. Interestingly, no Schiff base itself has been found to be effective against the superoxide ion so far. Literature reports of various applications of Schiff bases and our earlier interest in the field [17,18] prompted us to synthesize some Schiff bases with complimentary groups and to study them as

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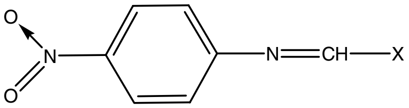
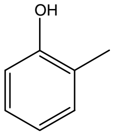
doi:10.1016/j.molstruc.2007.02.031

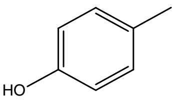
possible superoxide ion scavengers. Out of the four Schiff bases reported in this communication, NPIMP-4 was already reported in the literature [13] as a potential NLO material in its polymeric form. But its reported synthesis [13] involved a longer time duration (12 h) and use of an obnoxious solvent i.e., DMF, while the present study involved a much shorter time (4 h) and use of an unharmful solvent i.e., ethyl acetate for its synthesis. The general structure of the synthesized Schiff bases may be given as follows,



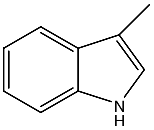
where X =



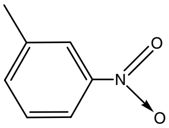
NPIMP-2



NPIMP-4



IYNPA



NBNPA

The Schiff bases being reported in the present communication are likely to exist in various tautomeric forms hence in order to have a deeper insight about the structural details, we performed density functional theory calculations on two Schiff bases i.e., NPIMP-2 and NPIMP-4. The density functional theory has been used by several workers in recent years in order to solve the mechanistic details of various chemical/biochemical reactions [19]. The existence of various tautomeric forms and their relative stability in a number of biochemically important systems has been established using density functional theory earlier [20,21].

2. Experimental

2.1. Apparatus

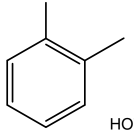
Melting points were obtained on a capillary melting point apparatus and are uncorrected. The IR Spectra of Schiff bases as their mull in nujol were recorded on JASCO-FTIR Spectrophotometer. The ^{1}H NMR Spectra were recorded on JEOL AL 300 FT NMR spectrometer. Chemical shifts are reported in δ values in the units of ppm relative to the tetramethylsilane (TMS) as the internal standard. Besides the room temperature (RT) spectra the variable temperature ^{1}H NMR spectra have also been recorded in the temperature range RT-50 °C in $CDCl_3$ and RT-175 °C in DMSO-d_6 for two Schiff bases i.e., NPIMP-2 and NPIMP-4. The same procedure for the remaining two Schiff bases i.e., IYNPA and NBNPA was not successful as these were insoluble in $CDCl_3$ and decomposed in DMSO-d_6 at higher temperatures. The UV–vis spectra were obtained using a computer controlled Specord-200 spectrophotometer.

2.2. Reagents and chemicals

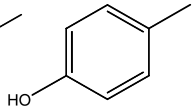
p-Nitroaniline was obtained from SISCO research laboratory, Mumbai, India. Sodium hydroxide pellets were purchased from Qualigens, Mumbai, India, while other required chemicals were obtained from Aldrich and were used as such without any further purification. Ethyl acetate used as solvent for the synthesis of Schiff bases was purchased from E. Merck (India) Limited. The dimethyl sulphoxide (DMSO) of spectroscopic grade was purchased from Central Drug House (P) Ltd., Delhi.

2.3. Preparation of Schiff bases

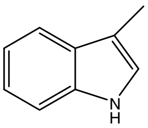
For the preparation of Schiff bases, a general procedure was adopted. In this procedure 4.0 mmol of *p*-nitroaniline was dissolved in 50 ml of ethyl acetate. To this solution, 4.0 mmol of respective aldehyde solution in ethyl acetate was added with constant stirring over a time period of 10 min, followed by their boiling under reflux for 4 h. After refluxing, the contents of the respective round bottom flasks were poured in four different petridishes. The solvents were allowed to evaporate at room temperature which led to micro-crystalline products followed by their recrystallisation from alcohol-water mixture 40:60 v/v. The synthesis of the Schiff bases in the present study can be expressed conveniently through as follows (Scheme 1) where X =



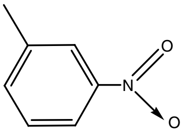
NPIMP-2



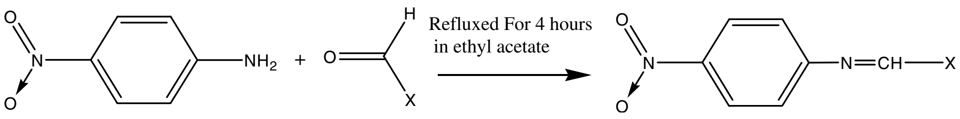
NPIMP-4



IYNPA



NBNPA



Scheme 1. General method for the preparation of Schiff bases.