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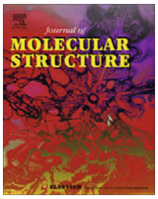

X-ray crystallographic study of 3-Oxo-2-{[4-(thiazol-2-ylsulfamoyl)-phenyl]-hydrazono}-butyric acid ethyl ester and its application in the solvent assisted naked eye sensing of Hg(II)

K.K. Upadhyay [a,*], Shalini Upadhyay [a], Kamlesh Kumar [b], Rajendra Prasad [a]

[a] Department of Chemistry, Faculty of Science, Banaras Hindu University, Varanasi UP 221005, India
[b] Department of Chemistry, IITK, Kanpur, India

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ABSTRACT

The 3-Oxo-2-{[4-(thiazol-2-ylsulfamoyl)-phenyl]-hydrazono}-butyric acid ethyl ester (OSPBE) was studied through single crystal structure analysis revealing some interesting supramolecular architectural patterns. The N(3)–N(4) bond length of OSPBE was found to be 1.36 Å matching well with reported N–N bond length in the literature and hence clearly proved that it is the keto form of OSPBE which is stable. Full structural optimization of OSPBE using density functional theory (DFT) at the HCTH407/6-31G** level also proved that the keto form of OSPBE is stable. The UV–Vis absorption peaks for OSPBE predicted by the time dependent DFT at B3LYP/6-311G** level matched quite well with the experimentally observed UV–Vis bands for OSPBE. The OSPBE was successfully tested as the naked eye sensor for Hg(II) as its chloride salt at the millimolar level in dimethylsulfoxide. A color change from red orange to olive green was observed on addition of 1.0 equiv. of Hg(II) to the 1.0×10^{-3} M DMSO solution of the chemosensor. The role of DMSO in the sensing process appears to be the crucial one because the intramolecular charge transfer (ICT) band of OSPBE in DMSO observed at 489 nm did not appear in the UV–Vis spectrum of OSPBE in nujol. The UV–Vis and ^{1}H NMR titrations revealed that formation of six membered 1:1 chelate between OSPBE and Hg(II) along with reversible supramolecular association of DMSO with NH at N-2 position in OSPBE may be responsible for its Hg(II) sensing. No sensing for other d^{10} metal ions like Zn(II) and Cd(II) were observed with OSPBE under similar conditions. Besides DMSO, some other polar aprotic solvents like DMF and acetone having X=O (where X = C) also produced similar type of color change on the addition of 1.0 equiv. of Hg(II) to their respective 1.0×10^{-3} M OSPBE solutions. Nevertheless, polar aprotic solvent like acetonitrile not having X=O or non-polar aprotic solvent like chloroform no color change was observed under similar conditions.

1. Introduction

Life processes involve multiple ions. The cations and anions play active roles in various life processes [1–4]. They play key role in the form of active sites of different kind of enzymes [5] and as co-factors in good number of enzymes [6]. Owing to their pivotal role in biological processes their qualitative and quantitative determinations to the level of high accuracy and sensitivity are needed. Although several instrumental methods are available for the detection of ionic species at very low concentration level but these methods require costly instrumentation and wastes of time in the pretreatment of sample [7]. The naked eye sensing of ionic species with suitable colorimetric chemosensor have been coming up for last few years [8]. These methods are convenient, easy to handle and they do not require costly instrumentation. Present study is a part of our continuous effort in the field of designing and evaluation of chemosensors for cations and anions [9–11]. The important role of Zn(II) in several enzymes [13] as well as notorious roles of Cd(II) and Hg(II) towards our ecosystem [14,15] prompted us to perform present study. Although a variety of chemosensors for the naked eye sensing of Hg(II) have been reported in the literature [16,17] but the present chemosensor has its worth in terms of its easy designing as well as its cost effectiveness.

The chemosensor being reported under present study is although well documented in the literature decades back [18,19] but its full characterization was never done. Nevertheless, no one used it for the sensing purposes prior to us. We synthesized the 3-Oxo-2-{[4-(thiazol-2-ylsulfamoyl)-phenyl]-hydrazono}-butyric acid ethyl ester (OSPBE) through literature procedure [20] and developed its crystals of suitable sizes from X-ray diffraction (XRD) view point. The full characterization of OSPBE was done by XRD studies along with other spectroscopic data including mass determination. Density functional theory calculations were

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* Corresponding author. Tel.: +91 542 2307321x101.
E-mail address: drkaushalbhu@yahoo.co.in (K.K. Upadhyay).

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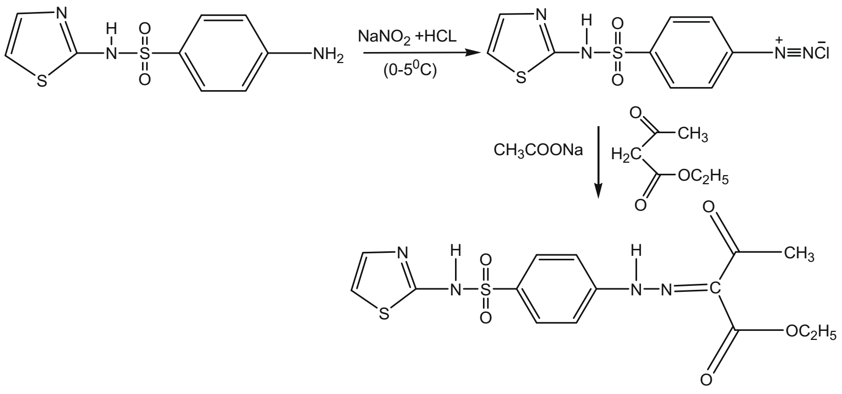

Scheme 1.

performed on OSPBE at HCTH407/6-31G** [21] level to fix the position of hydrogen atoms in its X-ray structure. Time dependent DFT calculations at B3LYP/6-311G** [22] were done to find out various UV–Vis transitions of OSPBE. The assistance of a polar aprotic solvent like DMSO towards sensing is a one of the rarely observed phenomenon for anions [23] as well as for cations and only a few research papers have been published so far [24].

2. Experimental

2.1. Apparatus

Melting point was recorded on a capillary melting point apparatus and is uncorrected. The IR spectra were recorded in KBr on Varian 3100 FT-IR Spectrophotometer. The NMR spectral studies along with titrations were performed on JEOL AL 300 FT NMR spectrometer. The chemical shifts are reported in δ values in the units of ppm relative to the tetramethylsilane (TMS) as the internal standard. The UV–Vis spectral studies along with titrations were performed on UV-1700 pharmaspec UV–Vis spectrophotometer.

2.2. Reagents and chemicals

The sulfathiazole was purchased from Sigma (USA) and used without further purification. The sodium nitrite and sodium acetate both were purchased from Qualigens Fine Chemicals, Mumbai. Ethyl acetoacetate was purchased from Spectrochem Pvt. Ltd., Mumbai. Hydrochloric acid was purchased from Central Drug House (P) Ltd., Delhi. The chloroform, DMF, acetone, acetonitrile and DMSO of spectroscopic grade were purchased from Central Drug House (P) Ltd., Delhi.

2.3. Reaction scheme

The 3-Oxo-2-{[4-(thiazol-2-ylsulfamoyl)-phenyl]-hydrazono}-butyric acid ethyl ester (OSPBE), $C_{15}H_{16}N_4O_5S_2$ (Registry number 49752-93-4) was synthesized according to literature procedure as follows:

Synthesis: The sulfathiazole 2 mmol (510.64 mg) was dissolved in 2 ml conc. HCl and sodium nitrite ~4 mmol (300 mg) dissolved in 10 ml distilled water were cooled separately on crushed ice. Later on cooled $NaNO_2$ solution was added to sulfathiazole solution with constant stirring and maintaining ice cooled temperature. The resulting yellow color solution was added to the ~2 mmol of aqueous solution of 1-carbethoxypropanone-2 followed by addition of 3 g of sodium acetate in small portions. The stirring was further continued for 2 h maintaining the temperature of the reaction vessel between 0 and 5 °C. After 2 h the resulting colored solids were filtered on Buchner funnel followed by their washing with water, ethanol and finally by diethyl ether. The crude product was recrystallized from water–ethanol (50% v/v) mixture and dried in vacuo. The entire synthetic processes have been shown conveniently as Scheme 1.

Yield = 78%.

M.P. = 170 °C.

IR data (KBr) (cm^{-1}): 3453(ν_{N-H} of $-HN-N{=}C\!<$), 3151(ν_{N-H} of $NHSO_2$),2921(ν_{C-H}), 1684($\nu_{>C=O}$ of $COOC_2H_5$), 1583 ($\nu_{>C=O}$ of $COCH_3$), 1533($\nu_{>C=N\,+\,\nu C-H\text{ aromatic ring}}$), 1425(NH bending vib), 1303, 1144 (ν_{SO2}), 666(ν_{C-S}).

^{1}H NMR data (DMSO-d_6): 12.68(1H, –NH at N-2), 11.55(1H, NH at N-3), 6.80–7.79 (6H, Ar–H), 4.28–4.32(2H, CH_2), 2.40(3H, CH_3 of C_2H_5), 1.25–1.30(3H, CH_3).

^{1}H NMR data ($CDCl_3$): 12.67(1H, NH at N-3), 12.33(1H, –NH at N-2), 6.52–7.95(6H, Ar–H), 4.35–4.42(2H, CH_2), 2.49(3H, CH_3 of C_2H_5), 1.24–1.56(3H, CH_3).

^{13}C NMR data (DMSO-d_6): 193.76($>C{=}O$), 162.20[C(OEt)=O], 145.33($>C{=}C<$), 136.34, 133.36, 127.48, 124.30, 115.85, 114.72, 108.01(aromatic C), 61.27($>CH_2$), 25.17 ($-OCH_2C^*H_3$), 13.76($-CH_3$).

Mass (M+H): 397.2.

2.4. X-ray diffraction studies

Crystals of OSPBE of suitable sizes from XRD point of view were developed by layering its supersaturated solution in chloroform with diethyl ether and leaving for few days. A crystal of suitable size was selected from the mother liquor and immersed in paraffin oil, and then it was mounted on the tip of a glass fiber and cemented using epoxy resin. Single-crystal X-ray data were collected at 100 K on a Bruker SMART APEX CCD diffractometer using graphite-monochromated MoKα radiation (λ = 0.71073 Å). The linear absorption coefficients, scattering factors for the atoms, and the anomalous dispersion corrections were taken from International Tables for X-ray Crystallography. The data integration and reduction were processed with SAINT [25] software. An empirical absorption correction was applied to the collected reflections with SADABS [26] using XPREP [27] The structure was solved by the direct method using SHELXTL [28] and was refined on F^2 by full-matrix least-squares technique using the SHELXL-97 [29] program package. For all the cases non-hydrogen atoms were refined anisotropically. The hydrogen atoms were geometrically fixed and treated as riding atoms using SHELXL default parameters. The crystal and refinement data for OSPBE are collected in Table 1.

2.5. Density functional theory (DFT) calculations

The partial and full geometry optimization of OSPBE were done by density functional theory on 6-31G** basis set. The functional HCTH407 was used for the geometry optimization. Furthermore,