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Synthesis, crystallographic, spectral, and spectrophotometric studies of proton transfer complex of 1,2-dimethylimidazole with 3,5-dinitrobenzoic acid in different polar solvents

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ABSTRACT

The molecular interaction between 1, 2-dimethylimidazole (DMI) and 3,5-dinitrobenzoic acid (DNBA) has been investigated in methanol at room temperature. The stoichiometry of the synthesized CT complex was found to be 1:1 using the straight line method of Benesi–Hildebrand equation. The structure of the resulting CT complex was isolating and characterized using X-ray crystallography, FTIR and ^{1}H NMR spectroscopic techniques. The thermal composition and stability of the CT complex were analyzed using thermogravimetric and differential thermal analysis (TGA and DTA). UV–visible spectrophotometric technique was used to the determine the various important physical parameters such as formation constant (K_{CT}), molar extinction coefficient (ε_{CT}), energy of interaction (E_{CT}), ionization potential (I_D), resonance energy (R_N), free energy (ΔG°), oscillator strength (f) and transition dipole moment (μ_N). The effect of polarity of the solvent and concentration of acceptor on these parameters have been investigated. The results indicate that charge transfer complex (CTC) is more stable in less polar solvent due to the high value of the formation constant. A polymeric network through hydrogen bonding interaction between neighboring moieties was observed. This has also been attributed to the formation of 1:1 type CT complex.

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1. Introduction

The study of the proton transfer interaction between organic molecules has been a great deal of interest. Also, the study of this complexation may be useful in understanding the donor–acceptor interactions and the mechanism of their action. The charge transfer complex has been involved resonance with a transfer of charge from donor to acceptor [1,2]. The intermolecular hydrogen bonding (N^+—H—O^-) also plays an important role in transfer of charge from the donor to the acceptor molecule [3]. Charge transfer complexes are well known to take a part in many chemical reactions such as substitution, addition and condensation [4,5]. The synthesized CT complex was obtained from the weak bond interaction between donor and acceptor molecules [6–10]. Theory of charge transfer complex was first introduced by Mulliken [9]. Mulliken considers the complex as a hybrid resonating between the non-polar structure and polar one resulting, the transfer of one electron from a donor to an acceptor molecule [11]. Mulliken's charge-transfer has been widely and successfully applied to the interpretation of various properties of electron donor-acceptor complexes such as their stabilities, geometrical structures and spectroscopic, electric and magnetic properties [12–22].

Charge transfer complexation is of a great importance in biochemical and bioelectrochemical energy transfer processes [23]. The charge transfer complexes play the important roles in many biological systems such as drug action, enzyme catalysis, ion transfers through lipophilic membranes [24], drug acceptor binding mechanism [25], DNA-binding, antibacterial, antifungal, and insecticides [26–30]. Furthermore, the research application of charge transfer complexes is in many fields like photo catalysts [31], dendrimers [32], non-linear optical materials and electrical conductivity [33], solar energy storage [34], organic semiconductors [35] as well as in studying redox processes [36]. The $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ molecular complexes of DNBA with o-tolidine, p-toluidine, piperazine, quinuclidine and many other organic donors were investigated spectrophotometrically [37–41].

In this paper, DMI and DNBA were selected because they are

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chemically active compounds. The DNBA is a strong organic acid, which readily forms 3,5-dinitrobenzoate anion when co-crystallized with organic imidazole bases by transferring an H atom forming salt-like adducts. These types of adducts have been formed via the nitro and carboxylate groups such as N—H···O and O—H···O interactions (Scheme 1) [39]. On the other hand, we have also selected DMI as a good organic base because it can rapidly form cation facilitates a strong attraction with the benzoate anion of DNBA through intermolecular hydrogen bonding (N^+—H···O^-). The study of interaction between DMI and DNBA is one of the most important aspects to determine the molecular structure of the resulting complex and discovering and developing its important significance i.e., analysis of some drugs in pure form [10]. The most special significance to investigate the interaction between DMI and DNBA to know the binding power of the imidazole derivative with organic acceptor DNBA because imidazole derivatives have occupied a unique place in the field of medicinal chemistry. The high therapeutic properties of the imidazole related drugs have encouraged the medicinal chemists to synthesize a large number of novel chemotherapeutic agents. On the basis of various literature surveys imidazole derivatives shows various pharmacological activities [42].

The nature and structure of the synthesized CT complex have been characterized using spectroscopic techniques such as FTIR, ^{1}H NMR, TGA-DTA, UV—Visible studies and single X-ray crystallography.

2. Experimental

2.1. Materials

DMI and DNBA were purchased from Sigma—Aldrich Chemical Company (USA) with a stated purity of greater than 98% and these were used without any further purification. The solvents ethanol, methanol and acetonitrile were obtained from Merck Chemical Company and were used without any modification. The methanol was used for the synthesis of resulting CT complex.

2.2. Synthesis of solid CT complex

The 1:1 solid CT complex was obtained by mixing a saturated solution of DMI (0.19226 g, 2 m mol) and DNBA (0.42424 g, 2 m mol) in methanol. The reaction mixture was stirred continuously for about 3 hours and left standing overnight at room temperature. After filtration the solid CT complex was separated as needle shape crystals and dried under vacuum over anhydrous calcium chloride for 24 hours. Solvent evaporation was controlled by covering the beaker with porous aluminium foil. The crystals of good quality were obtained after a period of five days in methanol at room temperature. The synthesized1:1 CT complex [$(DMI)^+(DNBA)^-$] was characterized by elemental analysis (theoretical values are given in brackets): $C_{12}H_{12}N_4O_6$ (M.W. = 308.26 g, M.P. = 132 °C); C, 46.75% (46.78%); H, 3.92% (3.94%); N, 18.17% (18.21%).

2.3. Single crystal growth

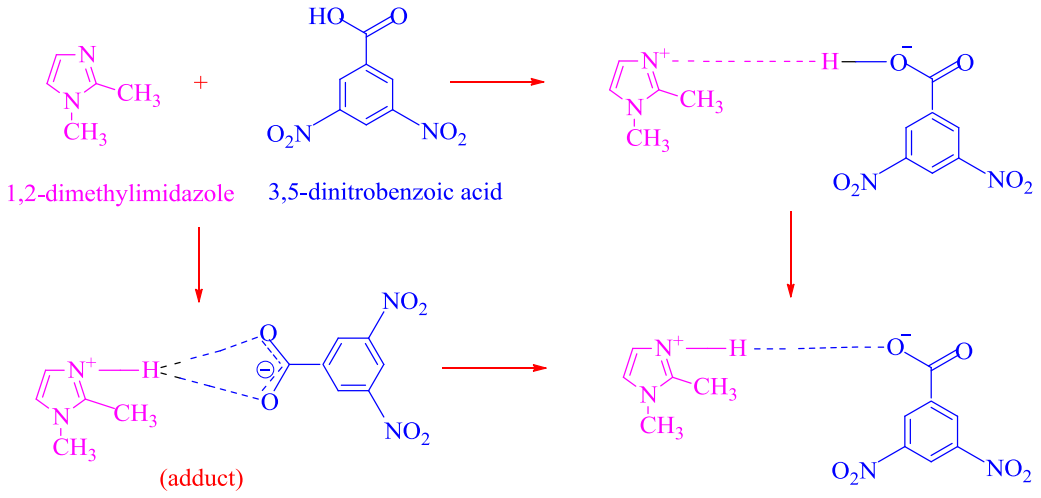
A saturated solution of the synthesized title CT complex [$(DMI)^+(DNBA)^-$] was prepared by dissolving in methanol. Then the solution was filtered through a whatmann: 41 grade filter paper to remove the suspended impurities. The clean filtrate was kept unperturbed in a dust free chamber for one week. Transparent, light yellow, needle shaped crystals were harvested on the last day of the week.

2.4. Preparation of standard stock solutions

Standard stock solutions of DMI (10^{-2} M) and DNBA (10^{-2} M) were prepared by dissolving 0.04806 g and 0.10606 g each in separate volumetric flasks of 50 ml using methanol as a solvent. A solution of fixed concentration (1×10^{-4} M) of the donor was prepared in a 25 ml volumetric flask by diluting 10^{-2} M solution. Solutions of various concentrations of acceptor (1×10^{-4} M, 1.2×10^{-4} M, 1.5×10^{-4} M, 2×10^{-4} M, 2.5×10^{-4} M and 3×10^{-4} M) were prepared in different 25 ml volumetric flask by diluting 10^{-2} M solution with the same solvent. Several other solutions were also prepared in various polar solvents using the same procedure.

2.5. Instrumental

The synthesized proton transfer CT complex was characterized using standard techniques such as FTIR, TGA-DTA, powder XRD, ^{1}H NMR, UV—visible and single crystal X-ray analysis. The electronic spectra were recorded in the region 500—200 nm using UV—Visible (λ-25) spectrophotometer with a 1 cm quartz cell path length. The infrared spectra were recorded with the help of Perkin Elmer FT-IR Spectrometer (Spectrum Two) using the KBr pellets, evacuated to



Scheme 1. Proton transfer mechanism of the reaction between DMI and DNBA.

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