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Characterization of dinaphthosulfoxide molecule

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ABSTRACT

Dinaphthosulfoxide has been synthesized, and confirmed by the experimental methods. The geometrical optimization of the two isomers of the molecule in their ground state was studied using density functional theory. Then, NMR and IR spectra were calculated for the optimized configurations. Analyzing the hydroxyl features in the NMR data and that of sulfoxide in IR spectra, the experimental observables are found to be in agreement with the properties of the syn isomer.

1. Introduction

Synthesis of naphthol based compounds has attracted considerable interest due to their involvement in chemical, biophysical and medicinal applications. Binol, which has been used in the synthesis of new alternative drugs [1,2], is the simplest molecular constitution as two naphthol planes are connected through a carbon-carbon bond. The molecule tends to build complexes with alkali metal ions through oxygen donors in its hydroxyl groups. Being a chiral molecule, it has been used to obtain ligands for asymmetric catalysis and molecular recognition [3,4]. The nonlinear optical properties of some polyanions of binol have also been investigated by means of density functional theory [5].

More active ligand blocks in comparison with the activity of binol can be attained if the naphthol block is bridged by sulfur, or sulfur groups. Hence, an increase in supramolecular chemistry is provided by the properties of sulfur atom [6]. There are such three binol derivative molecules, namely dinaphthosulfide (DNS), dinaphthosulfoxide (DNSO) and dinaphthosulfone (DNSON).

DNSpodands have been synthesized and used in complex building with divalent metal atoms [7,8]. DNS based macrocyclic ligands, which are classified by their cavities, also make complexes with metal ions [9]. In this context, DNS-appended diamides build stable complexes with Hg^{2+} due to strong $S{-}Hg^{2+}$ attraction [10]. An amido conjugate of benzimidazole of DNS has the properties of selective recognition of Ag^{+} ion [11]. A diacid containing DNS has been used to obtain polymeric structure via polyphosphorylation reaction [12]. The similar polymerization in the latter study has been realized by replacing DNS with DNSON [13]. Beyond that, a diamine containing aliphatic units with DNSON has also been synthesized to obtain a specific macrocyclic ligand [14].

The sulfoxide groups in molecules have wide range of therapeutic functions [15]. The ligands containing sulfoxide group in cancer drugs provide more effective results in carrying ruthenium to DNA [16]. Also, the luminescence properties of sulfur bridged chromophores are enhanced by oxidizing sulfide to sulfoxide [17]. Considering the importance of the molecules involving sulfoxide, the research on the title molecule is very limited. The only work is that DNSO diester has been prepared by the oxidation of DNS diester, leading to the synthesis of new aza crowns under microwave radiation [18], to the best of our knowledge.

We report an experimental and theoretical study on *plain* DNSO molecule. It was directly synthesized on the contrary that a sulfoxide involving molecule was usually prepared by oxidation of sulfide unit existed in the molecule. DNSO was confirmed by the experimental spectra. Then, a complete description of the structural properties of DNSO through its consistency with the spectroscopic observables has been presented by quantum chemical simulation methods.

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2. Experimental

All starting reagents were commercially provided and used without any further purification. The melting point was measured with Gallenkamp apparatus. The ^{1}H and ^{13}C-NMR spectra were recorded on Varian 300 MHz and Varian 75.5 MHz, respectively. The IR spectrum of the compound in the range of 450–4000 cm^{-1} was measured by Perkin–Elmer Spectrum Quant Version 10.4 which allows direct measurement in solid phase without any sample preparation, such as KBr pellet or Nujol.

DNSO molecule was synthesized by adapting Friedel–Crafts Method [19], as shown in Fig. 1. 2-naphthol (10.78 g, 75 mmol) was stirred in dichloromethane, in cold. Anhydrous aluminum chloride (4.99 g, 37 mmol) suspension in dichloromethane was added drop wise into the naphthol suspension in half an hour. Then, thionyl chloride (2.7 ml, 37 mmol) in dichloromethane was again added drop wise as the mixture stirred. The reaction was stopped at the end of 48 h as the process was controlled by TLC (2:1 hexane/ethyl acetate). The mixture was awaited in ice-water for twelve hours. The precipitate was removed and dried. Finally, it was crystallized from ethanol. The product was in light brown color and formed by 10% yield. The melting point was observed at 178 °C. IR (cm^{-1}) 3375, 3338, 3060, 1619, 1028, 1000, 969, 958, 933, 862, 815, 774, 746, 720, 678, 667, 653. ^{1}H NMR (300 MHz, DMSO-d$_6$δ ppm) 10.20 (s, 2H), 8.52 (d, J = 8.6 Hz, 2H), 7.73 (d, J = 8.7 Hz, 4H), 7.38 (t, J = 7.7 Hz, 2H), 7.23 (t, J = 7.4 Hz, 2H), 7.17 (d, J = 8.9 Hz, 2H), and ^{13}C NMR (75.5 MHz, DMSO-d$_6$δ ppm) 157.22(C), 135.91(C), 130.94, 129.29(C), 129.05, 127.47, 125.19, 123.57, 118.67, 112.96(C).

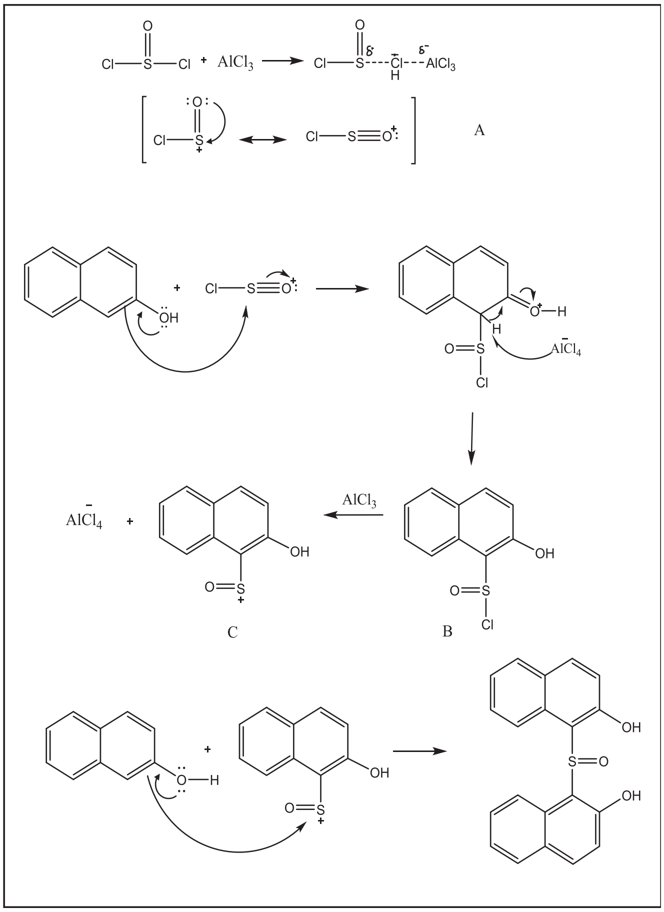

Fig. 1. Reaction mechanism.

The relatively high values of J-coupling values in the NMR data indicate that the vicinal dihedral angles are small according to Karplus equation [20]. The J-coupling values for the doublets and the triplets are close to each other in their own classes but they are different. This is possibly due to the different carbon-carbon bond lengths and π-bond localizations in the naphthol rings. Therefore, we prefer DFT method for the investigation of the molecular formation of DNSO molecule.

3. Computational details

The calculations were performed using Becke3-Lee-Yang-Parr (B3LYP) exchange correlation functional method and 6-311G ++ (2d,p) basis set. Minimal basis sets were successively used in the processes before the final optimization. The molecular structures of DNS and the two isomers of DNSO were optimized in their ground state. Then, the NMR spectra and the IR spectra were calculated for the optimized geometries using the same method and the same basis set. GIAO method was adopted to acquire theoretical ^{1}H and ^{13}C-NMR shifts, which were converted to the tetramethylsilane scale. The IR spectra were scaled by the factor 0.9613 due to the theoretical miscalculations [21,22]. The vibrational modes were assigned by observing the animation property of the frequency calculations provided with Gaussian 09 package and adopting a specific nomenclature [23].

4. Results and discussion

4.1. Reaction mechanism

The reaction mechanism leading to DNSO is depicted in Fig. 1. The electrophile (A) is obtained by reacting thionyl chloride with Lewis acid $AlCl_3$. The product gains resonance stability as a result of the bonding between sulfide and unpaired electron couples on oxygen.2-naphthol is then attacks to (A) to produce the stable product (B). $AlCl_3$ removes chlorine attached to sulphoxide group in (B), and the sulphoxide cation (C) is acquired. The product (C) is attacked by 2-naphthol. The final product is therefore obtained.

4.2. Molecular configuration

To obtain information on the molecular properties such as isomeric structure, polarity and reactivity, DNSO is investigated in the framework of density functional theory. We started the calculations with the optimization of DNS because its theoretical addressing as a single molecule has not been encountered in the literature. The optimized structure of DNS which has the symmetry of point group C_2 is shown in Fig. 2. The geometry appears in anti isomeric configuration, and its selected parameters are given in Table 1.

The hydroxyls, as the agile members of the functional group, determine the isomeric structures of DNSO. The isomerization/enantiomerization pathways depending on the orientation of the hydroxyls in binol have earlier been investigated [24]. Following the lines in the latter work, the two possible isomeric structures marked as the syn-DNSO and the anti-DNSO are optimized. They are shown in Fig. 3a and b, and their selected geometrical parameters are given in Table 1. These isomers are symmetrical as their form obtained in point group C_2. Yet, it has to be pointed out that the minimum energy easily may fall into a local minimum which ends up in an asymmetrical configuration. We have obtained the symmetrical forms of the molecule by varying dihedral angles O2–S–C2–C3, C2′–S–C2–C3 and O1–C1–C2–S with small increments, and optimizing the structure in every step.