Synthesis, Structural Characterization and DTA/TG Studies of a Schiff Base

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(Altın / Received: 03.04.2017, Kabul / Accepted: 17.08.2017, Online Yayınlanma / Published Online: 13.10.2017)

Keywords
Sulphonamides, DTA/TG, Theorical 1H NMR studies

Abstract: Our study contains a novel sulfonyl hydrazide. For this, N’-((1H-pyrrol-2-yl)methylene)-N-methylbenzenesulfonohydrazide were synthesized. The structures of this new compound was characterized by elementary analysis, 1H NMR, 13C NMR, FT-IR, DTA/TG. Also this study is contain performed on optimized geometry at the B3LYP/6.311+G**level for this organic compounds.

Yeni Bir Schiff Bazının Sentez, Yapışsal Karektarizasyon, 1H NMR ve DTA/TG Çalışması

Anahtar Kelimeler
Sülfonamidler, DTA/TG, Teorik 1H NMR çalışma


1. Introduction

Sulphonamides are the first group of drugs used to treat infections [1-3]. Usage areas have decreased after the first world war for bacteral resistance. However, the use of these compounds in pharmaceutical mixtures has increased their usefulness again. For example, Sulphadoxine-primetamine mixture is currently used in the treatment of malaria.

Also the mixture of sulfisoxazole-erythromycin is effective in ear infections, sulfamethoxathirpermethoprim (Co-trimoxazole, Bactrim, Seprtin) mixture are used in pneumonia, intestinal and urine infections. In recent years, rapidly developing computer-aided drug designs suggest that sulphonamides may have very different biological activities. Indeed, in 1998 Sildenafil Citrate (Viagra) [4,5], in 1999 protease Amprenavir [6,7], which is an inhibitor and used in the treatment of HIV, has been exported to the market. Besides these features, degradation steps in thermal processes are easily traceable. Schiff bases are some of the most widely used in this area.

Schiff bases are also used as catalysts, pigments and dyes, as polymer stabilisers, and intermediates in organic synthesis (8).

We have synthesized a new sulfonyl hydrazone compound (Schiff’s base) due to its wide use in the health sector. Subsequently, we were characterised its structure by the FT-IR, 1H NMR, 13C NMR, DTA/TG, and elemental analysis techniques. Also this compound's performed on optimized geometry at the B3LYP/6.311+G**level and HOMO - LUMO were calculated by the GAUSSIAN G03 software. The 1H NMR chemical shifts of the compound were calculated by using the GIAO (Gauge Invariant Atomic Orbital) method in DMSO phases. All measured results were compared with the experimental data. The general reaction of N’-((1H-pyrrol-2-yl)methylene)-N-methylbenzenesulfonohydrazide are given in Figure 1.

Figure 1. The general reaction schemes of N’-((1H-pyrrol-2-yl)methylene)-N-methylbenzenesulfonohydrazide
2. Material and Method

2.1. Physical measurements

The spectrophotometric measurements were made with the devices specified below; Mattson 1000 FT-IR (ATR) spectrometer, Bruker 400 MHz NMR spectrometer, Perkin Elmer Diamond TG/DTA thermal analyzer opti melt 3 hot stage.

2.2. General procedure for the synthesis

2.2.1. Synthesis of \( \text{N}^-\text{((1H-pyrrol-2-yl)methylene)}\text{-N-methylbenzenesulfonohydrazide} \)

A solution N-methylbenzenesulfonohydrazide (50 mmol) in 5 ml THF is mixed with a solution of 2-pyrrol carbaldehyde in 5 ml THF and stirred at 0 °C for all day. The product is crystallised from ethanol three times. This resulted in a musty green solid which is stable at normal conditions and soluble in DMSO and DMF. Its details are as follows:

N’-((1H-pyrrol-2-yl)methylene)-N-methylbenzenesulfonohydrazide: Musty green needles (EtOH) yield 62%; mp 125 °C (disintegration); FT-IR y max 3099(ν(CH) aromatic), 2870(ν=CH(CH3)), 2818(ν(CH3)), 1636(ν(C=O)), 1537(ν(C-C) aromatic), 1449(δ(C-H) aromatic in plane), 1335(ν=SO2), 1265 ν(C=O), 1152(ν=SO2), cm⁻¹[9,10]; \( ^{1}H\) NMR (DMSO d6, 400 MHz), \( ^{13}C\) NMR (DMSO d6, 100 MHz), \( ^{13}C\) NMR (DMSO d6, 400 MHz), δ: 6.15(0H, s, 31H'), 12.10(1H, s, 31H'), 5.79 (1H,d, J=4 Hz), 7.39 (1H, d, 10H'), 7.59 (1H,d, J=4 Hz), 8.80 (1H, t, J=4 Hz), 7.10 (1H, s, 7H'), 8.60 (1H, t, J=2 Hz), 7.59 (3H, d, J=18,20 Hz), J=4 Hz). The proton number in the gaussian program is given as H': δ: 6.13.09 (1H,s, 31 H'), 12.24 (1H,s,31 H'), 11.92 (1H, s, 22 H'), 8.60 (1H, t, 9H'), 7.88 (1H, d, 8H'), 6.80 (1H, d, 10H'), J=4 Hz).

The optimized figure of N’-((1H-pyrrol-2-yl)methylene)-N-methylbenzenesulfonohydrazide is given in Figure 3. Also \( ^{1}H\) NMR spectrum of N’-((1H-pyrrol-2-yl)methylene)-N-methylbenzenesulfonohydrazide is given in Figure 3.

3. Results and Discussion

The report presented, the synthesis and spectral characterisation of the N’-((1H-pyrrol-2-yl)methylene)-N-methylbenzenesulfonohydrazide thermal decomposition and theoretical Gaussian \( ^{1}H\) NMR studies. The N’-((1H-pyrrol-2-yl)methylene)-N-methylbenzenesulfonohydrazide molecule was optimized B3LYP 6.311 G (d,p) basis set. The optimized figure of N’-((1H-pyrrol-2-yl)methylene)-N-methylbenzenesulfonohydrazide (C\(_{12}\)H\(_{13}\)N\(_{3}\)SO\(_{2}\)) is given in Figure 2.

As given in the experimental section, all \( ^{1}H\) NMR, \( ^{13}C\) NMR and FT-IR data are consistent with our expectations.
Figure 3. The $^1$H NMR spectrum of N'-(1H-pyrrol-2-yl)methylene)-N-methylbenzenesulfonohydrazide

Figure 4. HOMO, LUMO and ESP map of The N'-(1H-pyrrol-2-yl)methylene)-N-methylbenzenesulfonohydrazide.

3.1. Thermal studies

The DTA / TG diagram shows that the compound is slightly moist. Thus, in the $^1$H NMR diagram of the compound, very low-intensity ethyl alcohol peak is observed. This is followed by endothermic melting peak observed at around 136 °C. The intense peak at 334 °C indicates that the decay has reached the highest point at this temperature. At this point, approximately 31% of the compound is degraded.

Based on this evidence, we can say that the imine bond is broken and the amine compound remains.
The calculations show that the pyrrole aldehyde fraction accounts for 31% of the compound.

In the second part of the cleavage, the -CH₃NHNH₂ group may be separated from the main molecule. This peak observed at 522 °C. This fraction also accounts for 17% of the compound. The remainder of the compound may be referred to as benzene sulphonic acid. The temperature at which this compound begins to decompose strongly is approximately 870 °C [14-17].

The DTA/TG curves of the compound is shown in Figure 6.

![Figure 6. The DTA/TG diagram of N'-(1H-pyrrol-2-yl)methylene)-N-methylbenzenesulfonohydrazide](image)

4. Conclusion

In conclusion, 1 N'-(1H-pyrrol-2-yl)methylene)-N-methylbenzenesulfonohydrazide was synthesized, and its theoretical studies and DTA/TG studies were evaluated. From the thermal decomposition of compound C₁₂H₁₃N₃SO₂ takes place in three stages. These complexes theoretical ¹H NMR studies were calculated using DFT/6.311(d,p) method. Comparasion of the experimental and the calculated data were in good agreement. We are planning to continue our studies by synthesizing new complexes from N'-(1H-pyrrol-2-yl)methylene)-N-methylbenzenesulfonohydrazide molecule.

References