Nuclear Magnetic Resonance Spectral Study of 2′,4′-Difluoroacetophenone by Density Functional Theory Comparison with Experiments

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ABSTRACT

The 2′,4′-difluoroacetophenone (DFAP) molecule has been characterized by Nuclear magnetic resonance (NMR) spectroscopy. Density functional theory (DFT) calculation using B3LYP have been performed to investigate the molecular structure and ^{1}H and ^{13}C chemical shifts of the title molecule. The obtained results show that the calculated NMR chemical shifts are in a good agreement with experimental data.

Introduction

Acetophenone is one of the most typical aromatic carbonyl, which shows interesting photochemical properties [1, 2]. Acetophenones are exhibit interesting physicochemical and biological properties. They are found in nature [3, 4] and they can also be obtained by means of diverse synthesis procedure [5, 6]. Antibacterial activity can be mentioned among its biological properties. A recent study has linked the antibacterial activity of twenty acetophenones with their structure characteristics by electronic and topological indices [7].

Acetophenone has also been found that diazinium salts with dihydroxyacetophenone skeleton possess antimicrobial activity and that complexes between p-substituted acetophenone and benzoylhydrazones have antifungal activity [8, 9]. On the other hand, substituted acetophenones are employed as synthesis reagents of several organic reactions. The complicating capacity of metallic ions exerted by flavonoids has been investigated in several reaction media and working conditions. Acetophenone is used to create fragrances that correspond to almond, cherry, honeysuckle, jasmine and strawberry.

Material and Measurements

The sample DFAP in the liquid form was purchased from the Lancaster Chemical Company, (UK) with a purity of greater than 97% and it was used as such without further purification. ^{1}H and ^{13}C NMR spectra were recorded in dmso-d6 solvent on AV500 - Bruker FT-NMR Spectrometer.

Computational Details

Entire calculations were carried out for DFAP with Gaussian 09W program package [10] using the Becke's three-parameter (B3) hybrid functional with Lee-Yang-Parr (LYP) correlation functional [11, 12] with the standard 6-311G(d,p) basis set. gauge independent atomic orbital (GIAO) ^{1}H and ^{13}C chemical shift calculations of the title molecule were done by the same method.

Results and Discussion

Molecular geometry

The optimized molecular structure of DFAP was shown in Fig. 1 by B3LYP/6-311G(d,p) level of theory. It has three substituents, CF, C=O and CH3 group attached to benzene ring. The crystal structure of the DFAP is not available in the literature till now by NMR study.
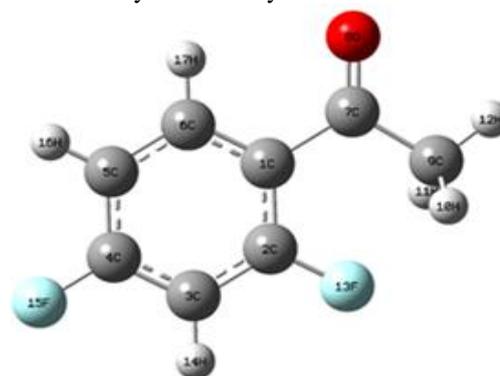

**Figure 1. Molecular structure of DFAP with atom numbering.**

NMR spectral analysis

Gauge independent atomic orbital (GIAO) ^{1}H and ^{13}C chemical shift calculations on DFAP were done by B3LYP/6-311G(d,p) method. The isotropic shielding values of tetramethylsilane (TMS) were used to calculate the chemical shifts. The experimental and theoretical values of ^{1}H and ^{13}C NMR spectrum given in Table 1. The observed ^{1}H and ^{13}C NMR spectra of the compound DFAP is given in the Fig. 2.

There are three hydrogen atoms attached to the benzene ring in DFAP molecule. [1]H chemical shifts of DFAP were obtained by complete analysis of their NMR spectra and interpreted critically in an attempt to quantify the possible different effects acting on the shielding constant of protons.

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Table 1. The experimental and calculated ^{1}H and ^{13}C chemical shifts (ppm) with respect to TMS of DFAP.

^{13}C Assignment	Experimental	Calculated	^{1}H Assignment	Experimental	Calculated
C1	27	36	H10	2.9	3.6
C2	78	85	H11	6.9	5.6
C3	108	112	H12	7	7.8
C4	112	121	H14	7.2	8.0
C5	135	140	H16	8.1	8.6
C6	163	167	H17	8.3	9.2
C7	166	175			
C9	171	182			
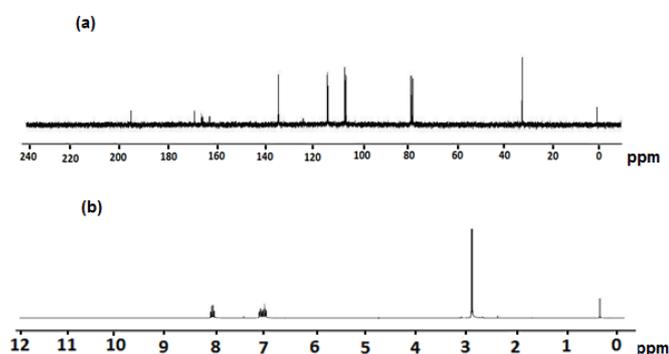
Figure 2. Experimental (a) ^{13}C NMR and (b) ^{1}H NMR spectrum of DFAP.

The hydrogen atoms H14, H16 and H17 present in the benzene ring shows NMR peaks in the normal range of aromatic hydrogen atoms and are assigned to 7.2, 8.1 and 8.3 ppm. The electron donating effect of methyl group is most pronounced on the chemical shifts of the ring protons H14. The methyl group protons are put into the up filed at 2.9, 6.9 and 7 ppm shows that these protons are under high magnetic shielding.

The aromatic carbons chemical shift values range from 100 to 150 ppm [13,14]. There are eight aromatic carbons in title compound. Six are present in benzene ring, one is present in carbonyl group and another is present in methyl group. The six benzene ring carbon chemical shift values range from 27 to 163 ppm in the experimental spectrum and 36 to 167 ppm in theoretical analysis. Comparing the chemical shift positions of ring carbon atoms with that of methyl carbon atom (C9), the down field chemical shift (171 ppm) of C9 is due to the electron donating effect of methyl group. The theoretical chemical shift evaluation slightly deviated from the experimental assessment are due to the theoretical calculations were carried out in the liquid phase.

Conclusion

The experimental and theoretical spectroscopic analysis of DFAP using NMR from the DFT calculation. The chemical shifts were compared with experimental data in dmso-d6 solvent, showing a very good agreement both for proton (^{1}H) and Carbon (^{13}C) NMR.

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