SAÜ. Fen Bil. Der. 17. Cilt, 3. Sayı, s. 357-362, 2013 SAU J. Sci. Vol 17, No 3, p. 357-362, 2013

Adipik asit üzerine ab initio hesaplamaları

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07.01.2013 Geliş/Received, 09.07.2013 Kabul/Accepted

ÖZET

6-31G(d) temel seti ile yoğunluk fonksiyonu teorisi (B3LYP) ve Hartree-Fock (HF) method kullanılarak geometrik optimizasyon, titreşim spektrumları ve ^{13}C NMR, ^{1}H NMR kimyasal kayma hesaplamaları gerçekleştirilmiştir. Bu metodlar adipik asitin yapısal karakterizasyonunda uygulanmış olan bir araç olarak önerilmiştir, bu nedenle IR ve NMR deneysel verilerin yorumlanmasında faydalı destekler sağlanmıştır. Parametreler hesaplanan ve deneysel ^{13}C NMR, ^{1}H NMR kimyasal kayma değerlerinin ve IR datalarının linear korelasyon grafikleri ilişkilendirilmiştir.

Anahtar Kelimeler: DFT, HF,^{13}C NMR ve ^{1}H NMR spectrum, IR spectrum, GIAO, yapı aydınlatılması,

Ab initio calculations on adipic acid

ABSTRACT

Geometric optimization, vibrational spectra and GIAO (gauge including atomic orbital) ^{13}C NMR, ^{1}H NMR chemical shift calculations were carried out by using Hartree-Fock (HF) method and density functional method (B3LYP) with the 6-31G(d) basis set. These methods are proposed as a tool to be applied in the structural characterization of adipic acid, thus providing useful support in the interpretation of experimental NMR data and IR data. Parameters were related to the linear correlation plot of computed data versus experimental ^{13}C NMR, ^{1}H NMR chemical shifts values and IR data.

Keywords: DFT, HF,^{13}C NMR and ^{1}H NMR spectra, IR spectra, GIAO, structure elucidation,

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1. INTRODUCTION

Molecular recognition studies of mono and dicarboxylic acids are of great importance due to their versatile appearance in many biologically active molecules, such as ibuprofen, aspirin, various antibiotics, amino acids, prostaglandins, and also in biotin, folic acid, bile acids, bilirubin, etc. [1]

Adipic acid was the subject of early studies of the effect of additives on individual crystal faces of molecular crystals [2,3] with the influence of surfactants on hydrophilic and hydrophobic faces being observed [4].

Infrared and Raman spectroscopies can be useful in the study of hydrogen bonds in the mixed organic-inorganic crystals. The aim of the present work is to describe and characterize the molecular structure, vibrational properties of adipic acid and GIAO (gauge including atomic orbital) ^{13}C NMR, ^{1}H NMR chemical shift calculations on adipic acid.

A number of papers related to adipic acid are already available. The conformations, energies, and intramolecular hydrogen bonds in dicarboxylic acids were presented by Nguyen, Hibbs and Howard [1].Furthermore, molecular structure and vibrational spectraof glutaconic acid were calculated by Y. Atalay et al. [5].

Density functional theory calculations are reported to provide excellent vibrational frequencies of organic compounds if the calculated frequencies are scaled to compensate for the approximate treatment of electron correlation, for basis set deficiencies and for the anharmonicity [6,7]. Rauhut and Pulay [8] calculated the vibrational spectra of thirty one molecules by using B3LYP method with 6-31G(d) basis set. In their work, they calculated vibrational frequencies of twenty smaller molecules whose experimental vibrational frequencies are well assigned, and derived transferable scaling factors by using least-square method. The scaling factors are successfully applied to other eleven larger molecules. Thus, vibrational frequencies calculated by using the B3LYP functional with 6-31G(d) basis can be utilized to eliminate the uncertainties in the fundamental assignments in infrared and Raman vibrational spectra [9].

A number of papers have recently appeared in the literature concerning the calculation of NMR chemical shift (c.s.) by quantum-chemistry methods [10-15]. These papers indicate that geometry optimization is a crucial factor in an accurate determination of computed NMR chemical shift. Moreover, it is known that the DFT (B3LYP) method adequately takes into account electron correlation contributions, which are especially important in systems containing extensive electron conjugation and/or electron lone pairs [14]. However, considering that as molecular size increases, computing-time limitations are introduced for obtaining optimized geometries at the DFT level, it was proposed that the single-point calculation of magnetic shielding by DFT methods was combined with a fast and reliable geometry-optimization procedure at the molecular mechanics level [14].

The gauge-including atomic orbital (GIAO) [16,17] method is one of the most common approaches for calculating nuclear magnetic shielding tensors. It has been shown to provide results that are often more accurate than those calculated with other approaches, at the same basis set size [18]. In most cases, in order to take into account correlation effects, post-Hartree-Fock calculations of organic molecules have been performed using (i) Møller-Plesset perturbation methods, which are very time consuming and hence applicable only to small molecular systems, and (ii) density functional theory (DFT) methods, which usually provide significant results at a relatively low computational cost [19]. In this regard, DFT methods have been preferred in the study of large organic molecules [20], metal complexes [21] and organometallic compounds [22] and for GIAO ^{13}C c.s. calculations [18] in all those cases in which the electron correlation contributions were not negligible.

In previous publication, J. Housty, M. Hospital had worked X-ray diffraction (XRD) of adipic acid [23]. As well as, ^{13}C NMR, ^{1}H NMR spectra, vibrational spectra of adipic acid [24]. The best of our knowledge, no estimates of theoretical results for adipic acid have been reported so far. In this work, we have calculated the vibrational frequencies, GIAO (gauge including atomic orbital) ^{13}C NMR, ^{1}H NMR chemical shifts of adipic acid in the ground state to distinguish the fundamental frequencies from the experimental vibrational frequencies, GIAO (gauge including atomic orbital) ^{1}H NMR and ^{13}C NMR chemical shift calculations and geometric parameters, by using the HF and DFT (B3LYP) method. These calculations are valuable for providing insight into the ^{1}H NMR and ^{13}C NMR spectrum, vibrational spectrum and molecular parameters.

2. COMPUTATIONAL METHODS

The molecular structures of adipic acid in the ground state (in vacuo) is optimized B3LYP with 6-31G(d) basis set. The geometry of the title compounds, together with that of tetramethylsilane (TMS) is fully optimized. ^{1}H NMR and ^{13}C NMR chemical shifts are calculated within

GIAO approach [16,17] applying B3LYP and HF method [25] with 6-31G(d) [26] basis set. The theoretical NMR ^1H and ^{13}C chemical shift values were obtained by subtracting the GIAO calculated [27,28]. ^1H and ^{13}C isotropic magnetic shielding (I.M.S.) of any X carbon atom, to the average ^{13}C IMS of TMS: $CS_x=IMS_{TMS}-IMS_x$. Additionally, vibrational frequencies for adipic acid are calculated with these methods and then scaled by 0.8929 and 0.9613, respectively. Molecular geometry is restricted and all the calculations are performed by using Gauss-View molecular visualisation program [29] and Gaussian 98 program package on personal computer [30].

3. RESULTS AND DISCUSSION

3.1. Geometrical Structure

J. Housty, M. Hospital [23]determined the crystal structure of adipic acid.The dicarboxylic acid, adipic acid (HO2C(CH2)4COOH) crystallizes in the space group $P2_1/c$ with a=10.01 Å, b=5.15 Å, c= 10.06 Å,
β= 136.75, Z=2. Molecules are linked in infinite chains, parallel to the a axis, by hydrogen bonds involving adjacent carboxylic acid groups. These chains are held together by van der Waals forces and close contacts between oxygens and hydrogens of adjacent aliphatic carbons [23].

The optimized geometric parameters (bond lengths and angles) by HF and B3LYP with 6-31G(d) as the basis set are listed in Table 1,and experimental geometric parameters of adipic acid have referred to experimental geometric parameters of glutaconic acid [31] for compared with theoretical results.For the optimized geometric parameters, various methods including HF method estimates some bond lengths well to some extent [5,32-34]. We noted that the experimental results belong to solid phase and theoretical calculations belong to gaseous phase.

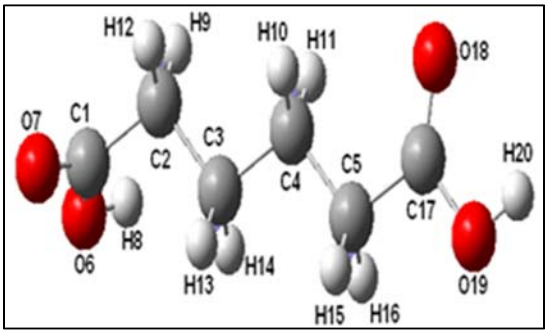

Figure 1. The theoretical geometric structure of adipic acid.

Table 1. Selected optimized and experimental geometries of adipic acid in the ground state

Parameters	Exp.*	Calculated	
		HF	B3LYP
		6-31G(d)	
Bond lengths (Å)			
C(1)-C(2)	1.501	1.5148	1.5232
C(2)-C(3)	1.501	1.5371	1.5421
C(3)-C(4)	1.501	1.5288	1.533
C(4)-C(5)	1.501	1.5255	1.5297
C(5)-C(17)	1.501	1.5073	1.5141
C(1)-O(7)	1.223	1.1816	1.2042
C(17)-O(18)	1.223	1.1876	1.2109
C(1)-O(6)	1.278	1.3381	1.3655
C(17)-O(19)	1.278	1.3305	1.3566
Bond angles (°)			
C(17)-O(19)-H(20)	111(2)	108.2694	106.0995
H(15)-C(5)-H(16)	106(2)	105.8736	105.4241
C(17)-C(5)-H(15)	107(1)	107.539	107.9032

*: Taken from reference [31]. Bondlengths in angstrom, and bond angles in degrees.

3.2. Vibrational Spectra of Adipic Acid

We have not found theoretical results for the adipic acid in the literature and an experimental vibrational spectrum of adipic acid has been taken by http://www.aist.go.jp [24]. We have calculated the theoretical vibrational spectra of adipic acid by using B3LYP and HF method with 6-31G(d) basis set. We have compared our calculation of adipic acid with their experimental results. Theoretical and experimental results of adipic acid are shown in Table 2. The vibrational bands' assignments have been made by using Gauss-View molecular visualisation program [29]. To make comparison with experiment, we present correlation graphic in Figure 2 based on the calculations. As we can see from correlation graphic in Figure 2 experimental fundamentals are in better agreement with the scaled fundamentals and are found to have a good correlation for B3LYP than HF. As can be seen from Table 2, the O-H vibrations of adipic acid have been calculated by using HF and B3LYP method with 6-31G(d) basis set at 3676, 3619 cm^{-1} and 3591, 3543 cm^{-1}, respectively; these bands were experimentally observed at 3033, 2963 cm^{-1} [24]. The CH_2 experimental asymmetric and symmetric stretch bands of adipic acid were observed at 2952, 2672 cm^{-1}, that have been calculated with HF and B3LYP at 2950, 2850 cm^{-1}, 3012, 2904 cm^{-1}, respectively, in Table 2. In the literature the C=O asymmetric and symmetric stretch were only observed at 1698 cm^{-1}, but using HF and B3LYP method with 6-31G(d) basis set is found to be at 1847 cm^{-1}, 1815cm^{-1} and 1811 cm^{-1}, 1776 cm^{-1}, respectively. As can be seen from the Table 2, there is a good agreement between experimental and theoretical vibration results for O-H, C-H, C=O and the others.

Table 2. Comparison of the observed and calculated vibrational spectra of adipic acid

Assignments	FT–IR* with KBr (cm^{-1})	Calculated (cm^{-1})	
		HF	B3LYP
		6-31G(d)	
O-H str.	3033	3676	3591
O-H str.	2963	3619	3543
CH_2 asym. str.	2952	2950	3012
CH_2 asym. str.	2932	2923	2984
CH_2 asym. str.	2919	2889	2948
CH_2 sym. str.	2879	2880	2936
CH_2 sym. str.	-	2873	2929
CH_2 sym. str.	2766	2862	2919
CH_2 sym. str.	2672	2850	2904
C=O str.	-	1847	1811
C=O str.	1698	1815	1776
CH_2 bend.	1464	1476	1476
CH_2 bend.	1429	1440	1434
CH_2 twist.	1409	1388	1386
CH_2 twist.	1357	1346	1357
C-H, O-H rock.	1316	1315	1318
CH_2 wag.	-	1301	1297
CH_2 wag.	1282	1293	1290
CH_2 twist. + O-H rock.	-	1279	1277
CH_2 rock. + O-H rock.	-	1241	1262
CH_2 twist. + O-H rock.	-	1231	1230
O-H rock.	1196	1190	1176
O-H rock.	-	1159	1123
CH_2 twist.	-	1058	1107
C-C str.	-	1038	1046
C-C str.	-	1011	1037
CH_2 wag.	929	902	1015
C-C str.	903	866	894
C-C str.	-	857	855
CH_2 rock.	-	777	774
HO-OC-C wag.	737	720	-
CH_2 rock.	-	708	712
O-H rock.	691	632	691
OH-C=O bend.	-	618	653
OH-C=O bend.	525	602	607
O-H rock.	517	504	504
CH_2, O-H bend.	-	469	475
O-H bend.	-	446	466
CH_2, O-H rock.	-	425	424

*: Taken from reference [24].

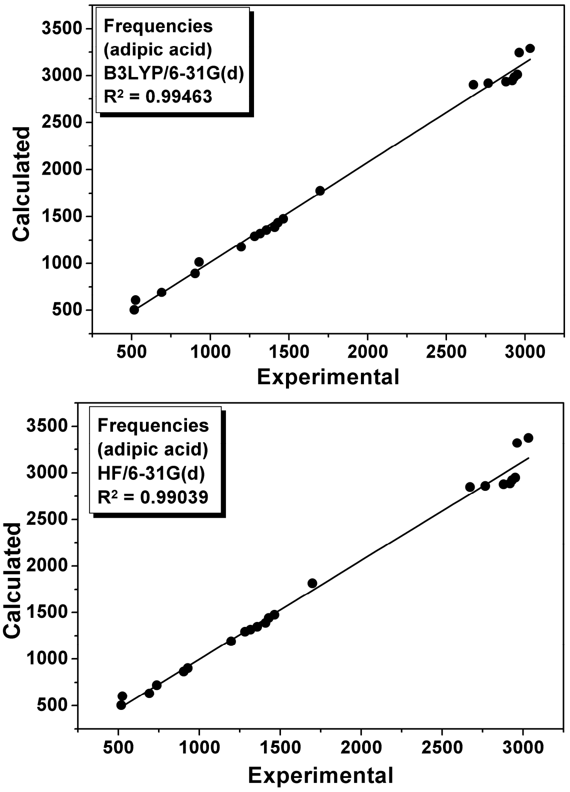

Figure 2. Correlation graphics of calculated and experimental frequencies of adipic acid.

3.3 NMR Spectra of Adipic Acid

GIAO calculations with X-Ray geometry lead to more accurate chemical shifts compared to B3LYP optimized geometry. We have calculated the theoretical chemical shift values of adipic acid by using B3LYP and HF method with 6-31G(d) basis set. The ^{1}H and ^{13}C chemical shift values (with respect to TMS), calculated for the optimized structures adipic acid and experimental ^{1}H and ^{13}C chemical shift values [24] shown in Table 3. The molecular structure of adipic acid can be seen dicarboxylic acids. Therefore, the chemical shift values of C1 and C17 were observed to be 174.28 ppm, (in the DMSO-d_6) for adipic acid [24]. Herein the chemical shift values of C1 has been calculated at 166.1731 ppm and 157.8160 ppm by using HF and B3LYP method with 6-31G(d) basis set for adipic acid, respectively (Table 3). Similarly, the chemical shift values of C17 has been calculated at 171.1619 ppm and 161.6951 ppm by using HF and B3LYP method with 6-31G(d) basis set for adipic acid, respectively (Table 3). However, the chemical shift value of H8 and H20 was found to be 12.00 ppm (in the DMSO-d_6) for adipic acid [24].These values have been calculated at 5.2205 ppm and 5.8786 ppm (for HF method with 6-31G(d) basis set), at 5.3334 ppm and 5.5097 ppm (for B3LYP method with 6-31G(d) basis set) shown in Table 3.These values are apporatiate for dicarboxylic acids carbons and protons [35].As can be seen from the Table 3, there is a good agreement between experimental and theoretical ^{1}H NMR and ^{13}C NMR chemical shifts results for adipic acid. This analysis is supported by the correlation plots obtained from the chemical shift data calculated at HF and B3LYP level with 6-31G(d) basis set (see Figure 3 and Table 3).

Figure 3 shows that the correlation plot of the ^{1}H and ^{13}C chemical shift values (with respect to TMS), calculated at HF and B3LYP level with 6-31G(d) basis set versus the corresponding experimental data shown in Table 3.As we can see from correlation graphic in Figure 3 experimental ^{1}H and ^{13}C chemical shift values are in better agreement with the theoretical ^{1}H and ^{13}C chemical shift values and are found to have a good correlation for B3LYP than HF.

Table 3. Theoretical and experimental ^{13}C and ^{1}H isotropic chemical shifts (with respect to TMS, all values in ppm) for adipic acid ($C_6H_{10}O_4$) (all calculations performed with the 6-31G(d) basis set)

Atom	Experimental* (ppm) NMR (DMSO-d_6)	Calculated chemical shift (ppm)	
		HF/6-31G(d)	B3LYP/ 6-31G(d)
C1	174.28	166.1731	157.8160
C2	33.35	35.2261	38.2804
C3	24.00	23.3213	29.0738
C4	24.00	22.9315	27.3101
C5	33.35	30.8221	32.3787
C17	174.28	171.1619	161.6951
H8	12.00	5.2205	5.3334
H9	2.210	1.8253	2.0671
H10	2.210	1.6942	1.6752
H11	1.501	1.6435	1.6379
H12	1.501	2.2662	2.0926
H13	1.501	1.5555	1.6746
H14	1.501	1.0868	1.2320
H15	2.210	2.2559	2.3172
H16	2.210	2.1539	2.2324
H20	12.00	5.8786	5.5097

*:Taken from reference [24].

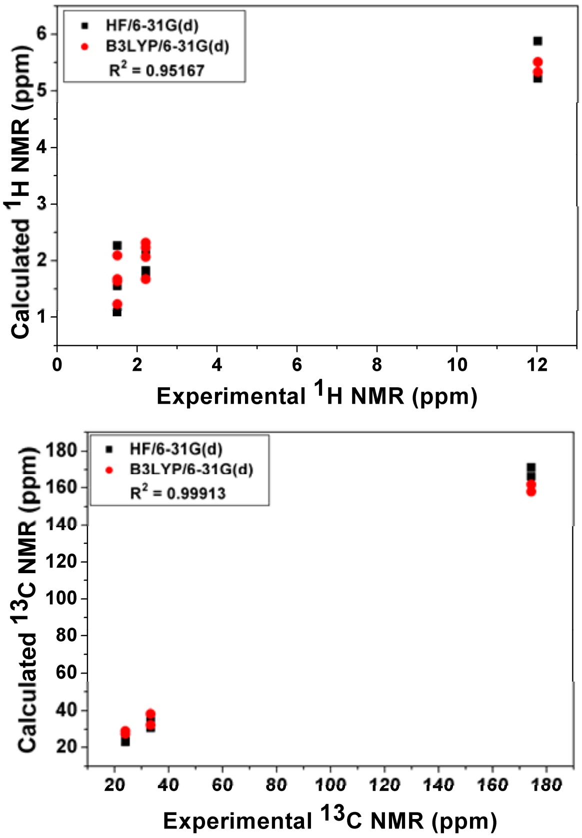

Figure 3. Correlation plot of calculated versus experimental ^{1}H and ^{13}C NMR chemical shift, at the HF and B3LYP level with 6-31G(d) basis set for adipic acid.

4. CONCLUSIONS

In this work, we have calculated the geometric parameters, vibrational frequencies and ^{1}H and ^{13}C chemical shift values of adipic acid by using B3LYP and HF method with 6-31G(d) basis set.In particular, the results of B3LYP method has shown better fit to experimental data than HF in evaluating ^{1}H and ^{13}C chemical shift values. Likewise, B3LYP method seems to be appropriate than HF method for the calculation of vibrational frequencies of adipic acid.As well as, very economical in respect of computational resources density functional calculations would be more suitable for studying typical chemical molecules, especially take into account that large basis sets are required for NMR properties prediction [36].

To test the different theoretical approaches (HF, DFT/B3LYP) reported here, computed and experimental ^{1}H and ^{13}C chemical shifts in the DMSO-d_6 [24] of adipic acid were compared. More commonly, however, the NMR spectrum is used in conjunction with other forms of spectroscopy and chemical analysis to determine the structures of complicated organic molecules.

Acknowledge : This study was supported by Sakarya University Scientific Research Projects Commission (Proje No:2012-50-01-024)

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