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STUDY OF THE SPECTROSCOPIC AND PHOTOCHEMICAL PROPERTIES OF SEVERAL NAIL POLISHES USING THE QUANTUM-CHEMICAL AND EXPERIMENTAL METHODS

Abstract: *In this Research, a study of the photochemical properties of a set of nail polishes (Butyl acetate (BA), adipic acid (AA)) has been conducted using the Time-Independent Density Functional Method DFT/B3LYP(6-331++g(2d.p)) as well as the Time-Dependent Density Functional Method TD-DFT/b3lyp(6-311++G(2d.p)) by finding UV-Vis and IR quantum and experimental spectra of these compounds. The quantum yield has been calculated as well as fluorescence and phosphorescence yield, the Absorption Energy which excites compound particles, and the activation energy and light wavelengths which the particles absorb.*

Key words: *quantum yield, fluorescence, phosphorescence, density functional theory, absorption energy, activation energy.*

ИССЛЕДОВАНИЕ СПЕКТРОСКОПИЧЕСКИХ И ФОТОХИМИЧЕСКИХ СВОЙСТВ НЕСКОЛЬКИХ ЛАКОВ ДЛЯ НОГТЕЙ С ИСПОЛЬЗОВАНИЕМ КВАНТОВО-ХИМИЧЕСКИХ И ЭКСПЕРИМЕНТАЛЬНЫХ МЕТОДОВ

Аннотация: *В этом исследовании было проведено исследование фотохимических свойств набора лаков для ногтей (бутилацетат (BA), адипиновая кислота (AA)) с использованием функционального метода, независимого от времени, DFT / B3LYP (6-331 г (2d)..p)) а также Зависящий от времени функциональный метод плотности TD-DFT / b3lyp (6-311 G (2d.p)) путем нахождения возбужденном состояниях, так и в ультрафиолетовых, видимых и инфракрасных квантовых и экспериментальных спектрах этих соединений. Был рассчитан квантовый выход, а также выход флуоресценции и фосфоресценции, энергия поглощения, которая возбуждает составные*

частицы, и энергия активации и длины волны света, которые частицы поглощают.

Ключевые слова: *квантовый выход, флуоресценция, фосфоресценция, теория функционала плотности, энергия поглощения, энергия активации.*

1. Introduction

Photochemistry is the branch of chemistry involved in the study of the chemical effects of light. Chemical reactions triggered by the exposure of energy in the form of light are called “Photochemical reactions.” Due to the absorption of light new transitional excited states emerge which differ greatly from the original molecules in their physical and chemical properties. The different types of photochemical reactions includephotode composition ; photosynthesis ; photooxidation ; photopolymerization. Photochemistry plays a big and necessary role in a variety of different industries like the production of medical and beauty products: with beauty products being one of the prime example of the application of chemistry in modern daily life, and with chemical products that are of importance to the beauty and skincare industry drawing the public attention and piquing their interest in the most recent years.

Due to chemical compounds being of the essence for the production of beauty products we, in a previously conducted research, have studied the structural, electronic, spectroscopic and photochemical properties of the following components of nail polish (formaldehyde, isopropanol, ethyl acetate) elaborately [1]. As for this study, we discussed the photochemical and spectroscopic properties of other products, specifically butyl acetate and adipic acid. In the previous studies the electronic state was observed and spectrophotometric analysis conducted for both ethyl acetate and butyl acetate, and, as a result, their ionization energy determined and compared to experimental results achieved through (MP2/aug-cc-pVTZ) [2]. The microwave spectrum for butyl acetate was also studied on a quantum level [3], and the kinetic and thermodynamic aspects to the creation of excited butyl acetate researched utilizing hydrogen pyridinium sulfate and using the density functional theory [4]. The photodecomposition of butyl acetate, too, was studied under visible and ultraviolet

frequencies using titanium dioxide and graphene oxide as a photocatalyst [5], and of the same compound in a gaseous phase inside a cyclical reactor using semiconductors (TiO2. Pt/TiO2 WO3/TiO2) [6].

As for adipic acid: as well as being integral in the beauty product industry it is considered an important industrial medium used mainly in the production of industrial organic products (skin nylons, lubrication products, adhesives, pesticide, dyes, food additives, medicine…etc.). It is derived from the oxidation of cyclic hexanol and cyclic hexanon using nitric acid or potassium permanganate, or from the oxidation of cyclic hexanol using ammonium chlorochromate and silica gel under ultrasonic waves [7].

The structural properties of the original state of adipic acid have also been studied, and the compound described on a quantum level with the protonic nuclear magnetic resonance spectrum 1H-NMR, the carbonic nuclear resonance spectrum 13C-NMR and the infrared spectrum FT-IR using density functional theory (B3LYP) with the basis set 6-31G(d) and the Hartree-Fock (HF) method. The values acquired have been compared with the experimental values [8].

From the previous studies it was noted that numerous studies have been conducted on the described compounds, but never were the properties of the compounds studied spectroscopically or photochemically, like fluorescence, phosphorescence, absorption and excitation energies necessary for the reaction to occur, as well as the quantum yield fluorescence and phosphorescence yield, which is what has been done in this study.

2. Research Aims:

This research aims to determine the photochemical properties of butyl acetate (BA) and adipic acid (AA), finding the quantum yield as well as fluorescence and phosphorescence yield; absorption and excitation energies; the light wavelength which the particles absorb; the infrared spectrum (IR), visible and ultraviolet spectrum (UV-Vis) quantum-chemically; in hope to define safety conditions for light-exposed nail polish (radiation frequency, radiation magnitude and radiation period)

3. The Quantum-chemical Method:

The methods used are (DFT/B3LYP(6-311++G(2d.p))), which is the time-independent density functional theory developed by A.D.Becke [9] and C. Lee, W. Yang and G.

Parr [10], and Time-dependent density functional (TD-DFT/B3LYP(6-311++G(2d.p))) represents the basis valence group used within the framework of this method, (2d.p) represents the polarity, and (++) represent the diffusion functions used.oxide as metal carrier.2013, J Membr Sci 430:188–195

4. Calculations:

Calculations are carried out of two programs (Gaussian09, Gauss View6) [11].

Absorption energy for a particle exposed to light is defined by the difference between the total electronic energy of the particle in the original state (before exposure to the light) and the total electronic energy of the particle in the excited state (after exposure to the light)

$$\varepsilon_{\text{Absorption}} = E_i\,(\text{optimized ground state}) - E_i\,(\text{excited states})$$

As for calculating the wavelength of absorbed light:

$$\varepsilon_{\text{Absorption}} = h\nu_{\text{Absorption}} = h\,\frac{c}{\lambda_{\text{Absorpton}}} \quad \Rightarrow \quad \lambda_{\text{Absorption}} = \frac{hc}{\varepsilon_{\text{Absorption}}}$$

c: Speed of light

$$c = 3\times 10^{10}\ \text{cm}\times\text{s}^{-1} = 3\times 10^{17}\ \text{nm}\times\text{s}^{-1}$$

h: Planck's constant

$$\begin{aligned} h &= 6.626\times 10^{-27}\ \text{erg}\times\text{s} \\ &= 6.626\times 10^{-27}\times 10^{-7} = 6.626\times 10^{-34}\ \text{J}\times\text{s} \\ &= 6.626\times 10^{-27}\times 0.624\times 10^{12} = 4.1346\times 10^{-15}\ \text{eV}\times\text{s} \end{aligned}$$

Emission energy through fluorescence is calculated by determining the first excited state singlet energy:

$$\varepsilon_{\text{Fluorescence}} = E_i\,(\text{optimized gruond state}) - E_i\,(\text{optimized first excited singlet state})$$

And the wavelength through fluorescence is calculated using:

$$\lambda_{\text{Fluorescencs}} = \frac{hc}{\varepsilon_{\text{Fluorescence}}}$$

Emission energy through phosphorescence is calculated by determining the excited first triplet state energy:

$$\varepsilon_{\text{Phosphorescenc}} = E_i\,(\text{optimized gruond state}) - E_i\,(\text{optimized first excited triplet state})$$

And the wavelength through phosphorescence is calculated using:

$$\lambda_{\text{Phosphorescencs}} = \frac{hc}{\varepsilon_{\text{Phosphorescence}}}$$

The energy absorbed by the particle to reach the excited state (to change the electronic and structure of the particle leading to the reaction) is calculated using the formula:

$$\varepsilon_{\text{Activation}} = \varepsilon_{\text{Absorption}} - \varepsilon_{\text{Emissionn}}$$

The quantum yield is calculated using:

$$\phi = \frac{\varepsilon_{\text{Activation}}}{\varepsilon_{\text{Absorption}}}$$

Bond energy ΔEb for particle M is calculated using:

$$\Delta E_b\,(M) = E_{i\ (\text{optimized Molecule})} - \sum_{A=1}^{N} E_{i\ (\text{optimized Atom})}$$

Where Ei: Total electronic energy

5. Results and Discussion:

Nail polish is one the most essential beauty products and is used by the majority of women. This product is comprised of many compounds such is (Butyl acetate, adipic acid…etc.).

In the first step the effects of light on this compound was studied by analyzing its electronic, spectroscopic, and photochemical properties.Table (1) shows the electronic properties of butyl acetate in a liquid form with ethanol used as solvent before and after exposure to light

Table 1: electronic properties of butyl acetate (bond energy ΔEb, energy gap Egap, Diople moment μp) in a liquid form using ethanol as a solvent before and after exposure to light.

Property	before exposure to light.	after exposure to light.	E_{rel} (E_{rel} %)
ΔE_b (eV)	-84.7522	-79.9592	(-4.793) (-5.655%)
E_{gap} (eV)	7.7079	4.1559	(-3.6725) (-47.64%)
μ_p (Debye)	2.7048	4.0354	(+1.3306) (+49.19%)

From table 1 we can extrapolate that exposing butyl acetate to light resulted in:

1. Reduction in the blocked field, which indicates an increase in the effectiveness of butyl acetate.

2. Increase in the Dipole moment, which indicates the increased polarity of butyl

Photochemical Property	ε_{Abs} (eV)	$\varepsilon^{F}_{Emission}$ (eV)	ε_{Activ} (eV)	$\varepsilon^{ph}_{Emission}$ (eV)	ε_{In} (eV)	Φ^{Fluore} (eV)	$\Phi^{phospho}$ (eV)	Φ (eV)
BA	5.9762	2.2986	3.6776	0.1649	3.2408	0.3846	0.0275	0.6153
AA	5.9641	5.2301	0.7340	0.9184	7.0307	0.8769	0.1539	0.1230

acetate.

Table (2) shows the electronic properties of Adipic acid in a liquid form with ethanol used as solvent before and after exposure to light.

Table 2: electronic properties of Adipic acid (bond energy ΔEb, energy gap Egap, Dipole moment μp) in a liquid form using ethanol as a solvent before and after exposure to light.

Property	before exposure to light.	after exposure to light.	E_{rel} (E_{rel} %)
ΔE_b (eV)	-88.9171	-83.2871	(-5.63) (-6.33%)
E_{gap} (eV)	7.7137	7.1759	(-0.53) (-6.97%)
μ_p (Debye)	0.0000	0.0000	0.0000

From table 2 we can extrapolate that exposing Adipic acid to light resulted in: Reduction in the blocked field, which indicates an increase in the effectiveness of Adipic acid.

In the second step absorption energy $\boldsymbol{\varepsilon_{Abs}}$, fluorescence emission energy $\boldsymbol{\varepsilon^{F}_{Emission}}$, phosphorescence emission energy $\boldsymbol{\varepsilon^{ph}_{Emission}}$, the quantum yield Φ, intersystem crossing $\boldsymbol{\varepsilon_{In}}$, fluorescence yield $\boldsymbol{\Phi}^{\mathrm{Fluro}}$, and phosphorescence yield $\boldsymbol{\Phi}^{\mathrm{phospho}}$ for both butyl acetate and adipic acid have been calculated, as expressed in table 3.

Table 3: photochemical properties of the studied compounds

From table 3 we can extrapolate that AA was more sensitive to light than BA as: To excite dissolved butyl acetate we have needed to expose to light with the energy:

$$\boldsymbol{\varepsilon}_{\mathbf{Absorption}} \geq 5.9762\ \mathrm{eV}$$

So the wavelength of light necessary to excite butyl acetate dissolved in ethanol:

$$\lambda_{Absorption} \leq 207.55 \text{ nm}$$

To excite dissolved adipic acid we have needed to expose to light with the energy:

$$\varepsilon_{Absorption} \geq 5.9641 \text{ eV}$$

So the wavelength of light necessary to excite adipic acid dissolved in ethanol:

$$\lambda_{Absorption} \leq 207.97 \text{ nm}$$

As for the more reactive substance: Butyl acetate proved to be more reactive than AA as proven with the excitation energy.

In the last step absorption of these compounds to visible and ultraviolet radiation has been tested, which has shown that butyl acetate has an absorption peak (1) (figure 1) at (167.89 nm) due to the transition ($\sigma \rightarrow \sigma^*$), an absorption peak (2) at (179.54 nm) due to the transition ($\pi \rightarrow \pi^*$), and an absorption peak (3) at (210.37 nm) due to the transition ($\pi \rightarrow \pi^*$).The experimental spectrum, figure 2, has shown a peak an absorption peak (1) at (230 nm) due to the transition ($\pi \rightarrow \pi^*$).

In adipic acid figure 3 shows an absorption peak at (177.85 nm) due to the transition ($\pi \rightarrow \pi^*$). an absorption peak (2) at (209.8 nm) due to the transition ($\pi \rightarrow \pi^*$).

The experimental spectrum, figure 4, has shown a peak an absorption peak (1) at (215nm) due to the transition ($\pi \rightarrow \pi^*$).

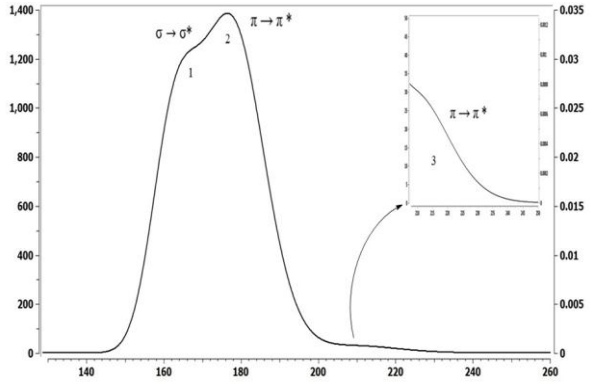

Figure 1: UV-Vis quantum spectrum for butyl acetate.

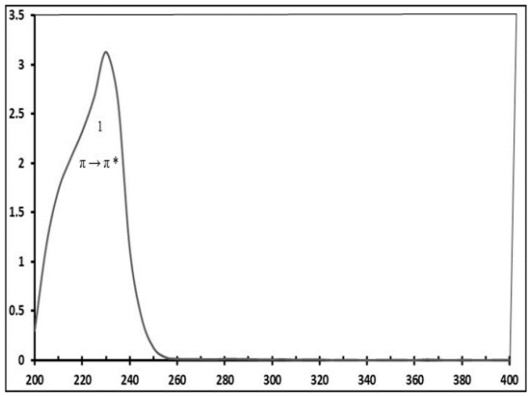

Figure 2: UV-Vis experimental spectrum for butyl acetate.

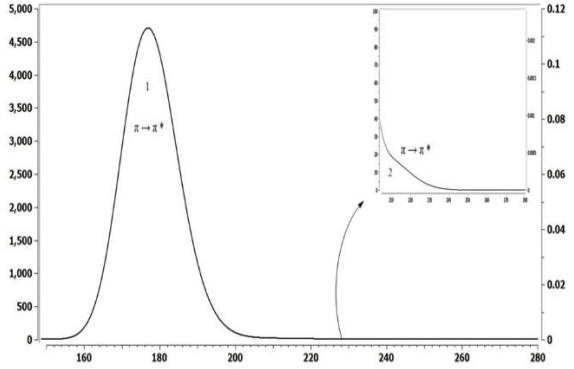

Figure 3: UV-Vis quantum spectrum for adipic acid.

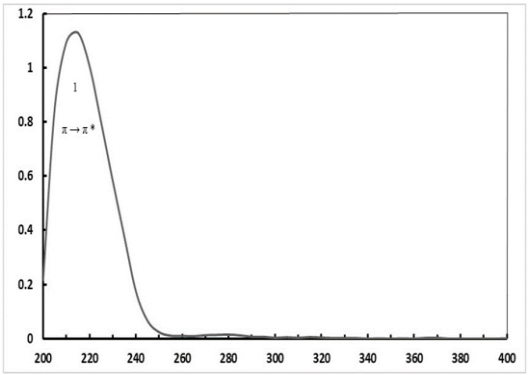

Figure 4: UV-Vis experimental spectrum for adipic acid.

Absorption of these compounds to infrared light has also been studied as is shown in the following quantum and experimental figures.

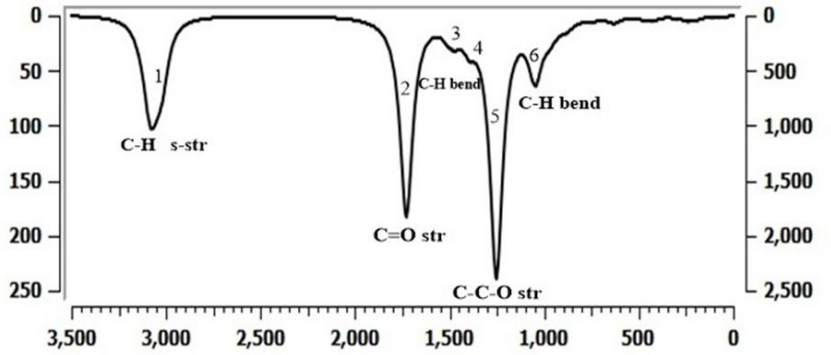

Figure 5: infrared spectrum of butyl acetate calculated quantum chemically

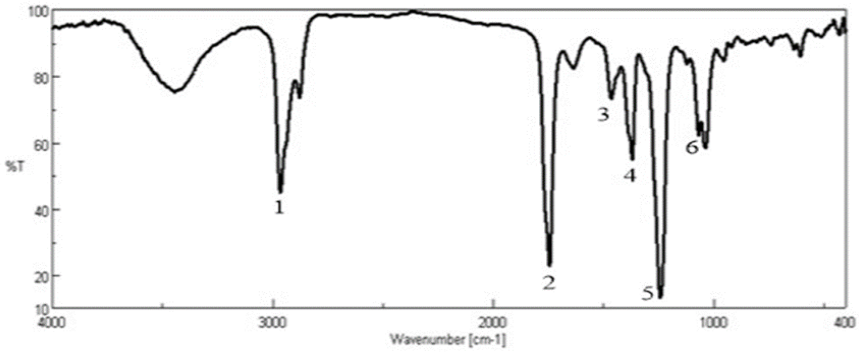

Figure 6: experimental Infrared spectrum of butyl acetate

Table 4: comparison between resonance frequencies for the most prominent butyl acetate functional groups both quantum chemically and xperimentally.

Functionl Group	Peak number	Wave number	
		Calc	Exp
C-H s-str	1	3009	2965
$C = O$ str	2	1729	1744

C-H bend	3	1468	1463
C-H bend	4	1394	1368
$C-C-O$	5	1253	1241
C-H bend	6	1044	1067

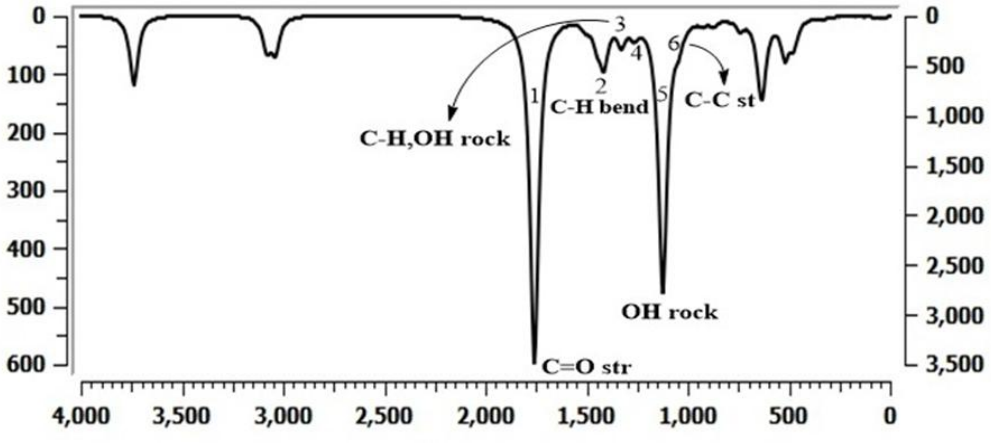

Figure 7: infrared spectrum of adipic acid calculated quantum chemically

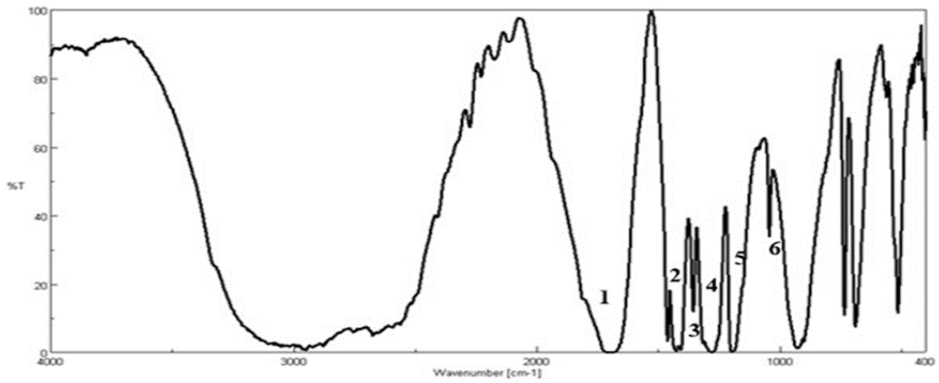

Figure 8: experimental Infrared spectrum of adipic acid

Table 5: comparison between resonance frequencies for the most prominent adipic acid functional groups both quantum chemically and experimentally.

Functionl Group	**Peak number**	**Wave number**			
		This work		**Ref [8]**	
		Calc	**Exp**	**Calc**	**Exp**
C=O str	1	1758	1675	1776	1698
C-H bend	2	1414	1427	1434	1429
C-H,OH rock	3	1327	1356	1318	1316
C-H bend	4	1276	1276	1290	1316
OH rock	5	1123	1196	1176	1196
C-C st	6	1045	1044	1046	-

6. Conclusions:

1-The effects of light on a number of nail polish components (butyl acetate, adipic acid) has been observed by studying the structural and electronic properties in the ground, and the singlet and triplet excited states of these components.The quantum yield has been calculated as well as fluorescence and phosphorescence yield, absorption and excitation energy for the particles. also the IR and UV-Vis spectra for both BA and AA quantum chemically

2-and experimentally. It was noted that the compound most sensitive to light is AA while BB was determined to be more photochemically more active.

3-Light sensitivity for each of the compounds was by finding the light wavelength which its particles absorbs.

References:

1) Edrees.L,Kodlaa.A,Ali.A, **Quantum-Chemical Study of Photochemical Effect of some Nail polish components,**Jornal of Al Baath University,Vol.41(2019) pp. 1-28.

2) ´Smiałek.M.A, Guthmuller.J, MacDonald.M.A , Zuin.L,Delwiche.J, Hubin-Franskin.M.J, Lesniewski.T, Mason.N.J, Limão-Vieira.P, **Photoelectron spectroscopy of a series of acetate and propionate esters**, Journal of Quantitative Spectroscopy & Radiative Transfer,Vol. 200 (2017) pp206–214.

3) Attig.T, Sutikdja.L.W, Kannengießer. R, Kleiner. I,Stahl.W, **The microwave spectrum of n-butyl acetate,** Journal of Molecular Spectroscopy,Vol .284-285 (2013) pp 8–15.

4) Tankov.I, Yankova.R, **Quantum mechanical and reaction dynamics investigation of butyl acetate synthesis in the presence of pyridinium hydrogen sulfate,** Journal of Molecular Liquids,Vol. 278 (2019) pp183–194.

5) Mull.b, Möhlmann.L Wilke.O, **Photocatalytic Degradation of Toluene, Butyl Acetate and Limonene under UV and Visible Light with Titanium Dioxide-Graphene Oxide as Photocatalyst,** Environments ,Vol.4 **(2017)** pp 1- 9.

6) Keller.V, Bernhardt.P, Garin.F, **Photocatalytic oxidation of butyl acetate in vapor phase on TiO2, Pt/TiO2 and WO3/TiO2 catalysts,** Journal of Catalysis ,Vol 215 (2003) pp 129–138.

7) LIN Z-P., **A Convenient and Efficient Protocol for the Synthesis of Adipic Acid Catalyzed by ACC/Silica Gel under Ultrasound Irradiation,** Journal of Chemistry**,**Vol.9(2012)pp.1035-1035.

8) Çetin1.M , Başoğlu1.A, Avcı .D,Atalay.Y, **Ab initio calculations on adipic acid**, SAU J. Sci. Vol .17(2013),pp 357- 362.

9) Becke A.D., **Density-functional exchange-energy approximation with correct asymptotic behavior**, Physical Review A,Vol.38 (1988) pp3098-3100.

10) Le C.,Yang W., Parr R.G., **Development of the Colle-Salvetti correlation-energy formula into a functional of the electrondensity**, Physical Review B, Vol 37(1988) pp785-789.

11) Frisch M.J., et.al: **GAUSSIAN 09**, Revision 02,Gaussian,Inc.,Wallingford CT, (2009).