Int. J. Bio-Inorg. Hybr. Nanomater., 10(3): 165-171, Autumn 2021

Contribution of the effective factors on the conformational properties of the halogenated derivatives of Vinyl azide and Vinyl isocyanate

H. Fallah[1], H. Atabaki[2], L. Moharrery[3**], N. Hasanzadeh[4], H. Yahyaei[5]*

[1] Department of Chemistry, Arak Branch, Islamic Azad University, Arak, Iran
[2] Department of Chemistry, Arak Branch, Islamic Azad University, Arak, Iran
[3] Department of Chemical Engineering, Robat Karim Branch, Islamic Azad University, Tehran
[4] Department of Chemistry, Ahvaz Branch, Islamic Azad University, Ahvaz, Iran
[5] Department of Chemistry, Zanjan Branch, Islamic Azad University, Zanjan, Iran

Received: 14 March 2021; Accepted: 17 May 2021

ABSTRACT: In this research, the contributions of effective factors on the structural and conformational properties of the halogenated derivatives of Vinyl azides and Vinyl isocyanates, Formyl azides, and Formyl isocyanates have been investigated using the methods of initial quantum mechanics computations. For this purpose, the quantum method of LC-ωPBE/ with 6-311+G** basis set has been used on the conformational behavior of halogenated derivatives of Vinyl azides and Vinyl isocyanates including Fluoro vinyl azide (compound 1), Chloro vinyl azide (compound 2), Bromo vinyl azide (compound 3), Fluoro vinyl isocyanate (compound 4), Chloro vinyl isocyanate (compound 5), and Bromo vinyl isocyanate (compound 6). Also, quantum computations methods were studied on the Formyl azide (compound 7) and Formyl isocyanate (compound 8). The following parameters were examined in this study: compounds stability, enthalpy, entropy, Gibbs free energy, calculated energy between cis and trans-forms, structural parameters and conformational behavior of compounds. Obtained results indicated that trans-form is the more stable form between cis and trans-forms of compounds 1 to 6 and also, the cis-forms are more stable between two compounds, 7 and 8. The stability of cis or trans-forms of compounds 1 to 8 was analyzed using the evaluation of factors and effects mentioned above.

Keywords: *Electrostatic interaction; Halogenated derivatives; Initial method.*

INTRODUCTION

The initial method (Ab initio) can get the molecule's structure, properties, and energy based on the quantum mechanics principles and having its wave function. Stabilization energy from electron transfers, orbital populations, and orbital deviation from the standard quantity can be calculated in the NBO method [1-3]. Molecular simulation makes possible the analysis of complex systems properties using the computational method. Their results are processors of the obtained information from chemical experiments, but in some cases, they can lead to the prediction of unseen chemical phenomena [4]. The studies review shows that investigation of the share of influential factors on the structural and conformational properties of compounds 1 to 8 is different from

---

(*) Corresponding Author - e-mail: (*) h-atabaki@iau-arak.ac.ir
(**) leilamoharrery@yahoo.com

each other so that Gibbs free energy difference in the equilibrium of their cis and trans-forms has a contrary sign [5,6]. Concerning this issue, no case has been reported about the influential factors such as stabilization energy from electron transfers, electro comfort effects from dipole moments interaction, steric effects [7], and the resultant of these impacts on the structural and conformational properties of this system, so far.

The energies from electron transfers in the dynamic behavior of the following compounds have been investigated in this article: Formyl azides with molecular formula CO=CH-N=N=N, Formyl isocyanates with molecular formula CO=CH-N=C=O, Vinyl azide with molecular formula CH_2=CH-N=N=N, cis, trans and transition conformations of Vinyl azide and its halogenated derivatives CH_2=CX-N=N=N (X= F, Cl, Br), Vinyl isocyanate with molecular formula CH_2=CH-N=C=O, and cis, trans, and transition state conformations of Vinyl isocyanate and its derivatives CH_2=CX-N=C=O (X= F, Cl, Br). Also, the structural and conformational properties of Formyl azides and Formyl isocyanates have been compared with Vinyl azides, Vinyl isocyanates, and their halogenated compounds using the LC-ωPBE/6-311+G** computational method.

COMPUTATIONAL METHOD

The LC-ωPBE/6-311+G** method is the most used computational method in this article. In an Ab initio calculation for a system, contrary to the semi-empirical computational method, a correct Hamiltonian is used and tried to get an answer without using the experimental data. The Ab initio method is expressive of a complicated method to solve the molecular orbitals based on the basic principles and can lead to a reasonable definition from the Schrödinger equation solution. Afterward, a basis set is selected to complete the method in a convenient direction. The method and basis set are unique for each specific application and may be unusable for another application. This method is used to investigate the small molecules and is one of the most valid available methods, which has utilized a highly limited number of approximations. This method has particular features, that its predictions have been expressed based on the quantum first principles like essential constants, light speed, electron charge, and Planck constant [8-13]. In this method, we get to the Roothan integrals by the Schrodinger equation solution. If we solve all of these multi-electron multi-center integrals and get the answer without any manipulation and approximation, we will operate Ab initio. Although simple hypotheses are considered, we can obtain the exact solution in this method. The Ab initio methods are of great importance among other methods. Determination of the precise electron wave functions for molecules is hard work. An appropriate pattern can be chosen for the molecular electron wave functions with Ab initio methods, and calculations can be performed without further approximations or experimental data. Therefore, the approximation is placed based on the pattern in the Ab initio calculations. This matter will affect the validity of the results so that improper pattern selection leads to incorrect and deceptive results [14-17].

Hypotheses of Ab initio quantum chemistry

Three important hypotheses in the Ab initio quantum chemistry are as follows:

1. The nucleus is assumed static compared to electron mobility. When two electronic states are placed so close to each other, this assumption can be considered unreliable.
2. The basis series shows molecular orbitals.
3. Electron correlation is considered theoretical on some levels.

Steps of an Ab initio computation are as follows:

- Reading the entrance and calculating the geometry.

We need a molecular geometry to perform an Ab initio calculation. Energy and gradient calculation is conducted for any computational geometry at the geometry optimization time.

- Determination of the basis series

The next step is the determination of the base series. At the geometry optimization period, we should start with a relatively weak basic set like STO-3G or 3-21G for organic compounds. Then, we use the optimized geometry as an initial geometry and apply the better basis series.

- Calculation of the nucleus repulsion energy

After determining the molecular geometry and an appropriate basis series, the program evaluates the nucleus repulsion energy. This energy is equal to:

$$E_n = \sum \frac{Z_A Z_B}{R_{AB}}$$

ZA and ZB are the atomic numbers of A and B, and R_{AB} is the distance between A and B atoms. This energy will be added to the evaluated electron energy of the Hartree-Fock theory.

- Integrals calculation

The calculation of integrals that include all phrases in the Hamiltonian system and basis series functions is essential. There are one and two-electron phrases. The number of one electron phrases is relatively simple, and there are n_2 of them, which n is the number of basis functions. The number of two-electron expressions is more than n4, and these calculations are the first required parts in each Ab initio program.

- Determination of the electron configuration

We have to characterize the total charge of the molecule and plurality in the data. Therefore, the total number of electrons in the molecule can be counted correctly, and the electron configuration is determined.

- Creation of the initial guess

In this part, a series of approximate molecular orbitals are selected as the first guess to create the molecular orbitals. Then, they are filled in ascending order of their energy until all electrons are used. There are several methods for the initial guess of orbitals. In Gaussian and many other programs, the assumption for the first-row atoms and some other atoms is the performance of a reformed semi-empirical method like INDO or CNDO.

- Performing the self-consistent field (SCF) repetition (electron energy calculation)

Solving the molecular orbitals and total energy should be performed repetitively by starting from the initial guess. Molecular orbital cannot be optimized unless the experienced field by electron, namely the answer, is specified. This method is known by the name self-consistent field method, and the Hartree-Fock energy is obtained through this method (or density function energy with DFT).

The total energy is gained by the sum of nucleus repulsion energy and electron energy. The total electron energy will be evaluated in each step of the iteration process, which can be depicted below:

$$E = 2\sum h_i + \sum (2J_{ij} - K_{ij})$$

or

$$E = 2\sum \lambda_i + \sum (2J_{ij} - K_{ij})$$

The first sum expression is on i, and the second sum is on all i and j separate pairs. λ_i is the orbital energy.

$$h_i = \left\langle \Phi_i / h / \Phi_j \right\rangle$$
$$J_{ij} = \left\langle \Phi_i \Phi_j / \Phi_i \Phi_j \right\rangle$$
$$K_{ij} = \left\langle \Phi_i \Phi_j / \Phi_i \Phi_j \right\rangle$$

The h_i is the one-electron integral, and K_{ij} and J_{ij} are coulomb and interchange integrals of two-electron integrals, respectively.

- Performing the electron density analysis

In electron density analysis, the electron density of the whole molecule is divided among all orbitals and atoms in several ways. Atomic charges, dipole moments, multipole moments, and other properties can be calculated in this method.

- Next steps

The next step can include the following processes: calculating the advanced Hartree-Fock correlation energy by computation of the first derivatives of energy considering the atomic coordinates or optimizing the geometry by calculating the second derivatives of energy toward the atomic coordinates and earning the vibrational frequencies.

RESULTS AND DISCUSSION

In this project, the impressive factors of the structural and conformational properties of the halogenated derivatives of Vinyl azides, the halogenated derivations

Table 1. Thermodynamic parameters calculation of enthalpy and Gibbs free energy (Kcal/mol) and entropy (cal/mol.K) for cis, transition state, and trans structures of compounds 1 to 3 using the computational levels of LC-ωPBE/6-311+G**

LC-ωPBE/6-311+G**										
	ZPE	EO	H	S	G	ΔZPE	ΔEo	ΔH	ΔS	ΔG
Geometries										
(F-AZ) 1-cis	0.048720	-341.232861	-341.226479	75.199	-341.262208	0.00	0.00	0.00	0.00	0.00
1-trans	0.048549	-341.233568	-341.227074	76.244	-341.263301	-0.10	-0.44	-0.37	1.04	-0.68
1-cis→[TS]‡→5-trans	0.048498	-341.227940	-341.222313	71.572	-341.256319	-0.13	3.08	2.61	-3.62	3.69
(Cl-AZ) 2-cis	0.047361	-701.496850	-701.490205	77.684	-701.527116	0.00	0.00	0.00	0.00	0.00
2-trans	0.047255	-701.498371	-701.491631	78.879	-701.529109	-0.06	-0.95	-0.89	1.19	-1.25
2-cis→[TS]‡→6-trans	0.047180	-701.493001	-701.487125	73.915	-701.522244	-0.11	2.41	1.93	-3.76	3.05
(Br-AZ) 3-cis	0.046684	-2815.174121	-2815.167255	80.611	-2815.205556	0.00	0.00	0.00	0.00	0.00
3-trans	0.046599	-2815.176008	-2815.169037	82.325	-2815.208152	-0.05	-1.18	-1.11	1.71	-1.62
3-cis→[TS]‡→7-trans	0.046585	-2815.170703	-2815.164639	76.539	-2815.201005	-0.06	2.14	1.64	-4.07	2.85

of Vinyl isocyanates, Formyl azide, and Formyl isocyanate have been investigated by the LC-ωPBE/6-311+G** computational method. The obtained results from calculations indicated that the various factors affect the thermodynamic parameters, which are discussed below.

Conformational behavior study of Vinyl halo azides

All halogenated molecules such as Fluoro vinyl azide, Chloro vinyl azide, and Bromo vinyl azide are more stable in the trans-state. Also, the amount of energy can be considered here. Considering that it has more power, the trans mode is more in the halogenated Vinyl azide molecules. According to the above results, effects and factors that have been used for Vinyl azide and Vinyl isocyanate compounds can be applied for compounds 1 to 3 following this research and the obtained results can be utilized in the subsequent works. The findings from calculations at theoretical levels of LC-ωPBE/6-311+G** indicate that trans modes of Vinyl halo azide compound 1-3 are more stable than the relevant cis modes.

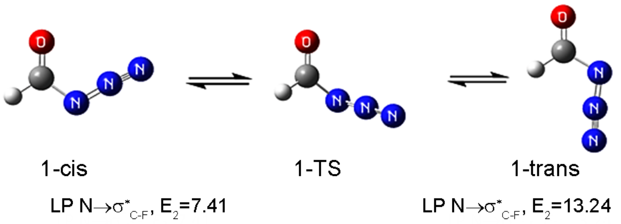


Fig. 1. Schematic diagram of the conformational equilibrium of cis, transition state, and trans-Fluoro vinyl azide

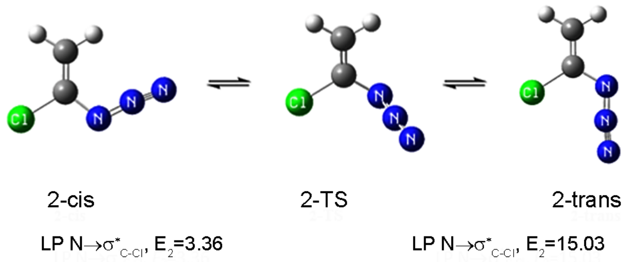


Fig. 2. Schematic diagram of the conformational equilibrium of cis, transition state, and trans-Chloro vinyl azide

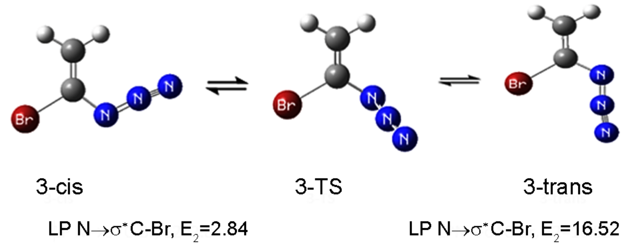


Fig. 3. Schematic diagram of the conformational equilibrium of cis, transition state, and trans-Bromo vinyl azide

Figs 1, 2 and 3 display the conformational equilibrium of Fluoro vinyl azide, Chloro vinyl azide, and Bromo vinyl azide compounds schematically.

Conformational behavior review of Vinyl halo isocyanates

The results from calculations at the theoretical levels of LC-ωPBE/6-311+G** about Fluoro, Chloro, and Bromo vinyl isocyanate compounds show that the trans-forms of Vinyl halo isocyanates [10]. are more

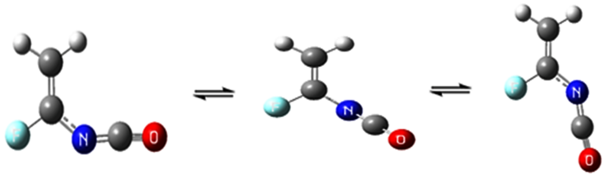
Table 2. Thermodynamic parameters calculation of enthalpy, Gibbs free energy, and entropy for cis, transition state, and trans structures of Fluoro vinyl isocyanate, Chloro vinyl isocyanate, and Bromo vinyl isocyanate

LC-ωPBE/6-311+G**

	ZPE	EO	H	S	G	ΔZPE	ΔEo	ΔH	ΔS	ΔG
Geometries										
(F-CO) 4-cis	0.048956	-345.135817	-345.129277	77.088	-345.165904	0.00	0.00	0.00	0.00	0.00
4-trans	0.049026	-345.137630	-345.131128	76.577	-345.167513	0.04	-1.13	-1.16	-0.51	-1.00
4-cis→[TS]‡→4-trans	0.048826	-345.134936	-345.129178	72.980	-345.163853	-0.08	0.55	0.06	-4.10	1.28
(Cl-CO) 5-cis	0.047559	-705.399413	-705.392537	80.629	-705.430846	0.00	0.00	0.00	0.00	0.00
5-trans	0.047735	-705.402025	-705.395272	79.139	-705.432874	0.11	-1.63	-1.71	-1.49	-1.27
5-cis→[TS]‡→5-trans	0.047537	-705.399439	-705.393428	75.439	-705.429271	-0.01	-0.01	-0.55	-5.19	0.98
(Br-CO) 6-cis	0.046925	-2819.076829	-2819.069741	83.595	-2819.109460	0.00	0.00	0.00	0.00	0.00
6-trans	0.047115	-2819.079642	-2819.072684	82.056	-2819.111672	0.11	-1.76	-1.84	-1.53	-1.38
6-cis→[TS]‡→6-trans	0.046757	-2819.076825	-2819.071364	74.335	-2819.106683	-0.10	0.00	-1.01	-9.26	1.74

stable than the respective cis forms. According to the above results and in the proceeding of this research, the mentioned effects and factors that have been used for Vinyl azide and Vinyl isocyanate compounds can be applied for compounds 4 to 6, and obtained results can be utilized in the future works.

Table 2 indicates thermodynamic parameters calculation of enthalpy and Gibbs free energy (kilocalorie per mole) and entropy (calorie per mole per Kelvin) at 298 oK and 1 atmosphere for cis, transition state, and trans structures of Fluoro vinyl isocyanate, Chloro vinyl isocyanate, and Bromo vinyl isocyanate using the computational levels of LC-ωPBE/6-311+G**.



4-cis 4-TS 4-trans

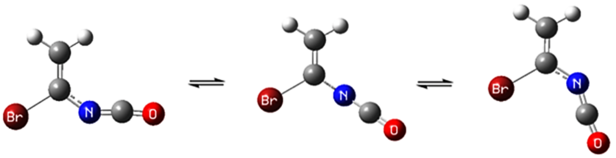
LP N→σ^*_{C-F}, E_2=15.38 LP N→σ^*_{C-F}, E_2=20.21

Fig. 4. Schematic diagram of the conformational equilibrium of cis, transition state, and trans-Fluoro vinyl isocyanate

5-cis 5-TS 5-trans

LP N→σ^*_{C-Cl}, E_2=2.09 LP N→σ^*_{C-Cl}, E_2=20.86

Fig. 5. Schematic diagram of the conformational equilibrium of cis, transition state, and trans-Chloro vinyl isocyanate



6-cis 6-TS 6-trans

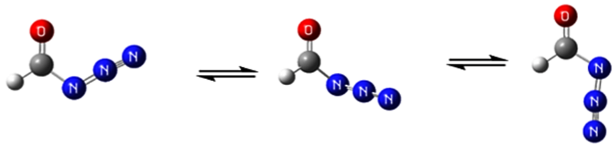
LP N→σ^*_{C-Br}, E_2=0.00 LP N→σ^*_{C-Br}, E_2=22.52

Fig. 6. Schematic diagram of the conformational equilibrium of cis, transition state, and trans-Bromo vinyl isocyanate

Figs 4, 5 and 6 schematically represent the conformational equilibrium of Fluoro vinyl isocyanate, Chloro vinyl isocyanate, and Bromo vinyl isocyanate compounds, respectively.

Conformational study of Formyl azides and Formyl isocyanates

The results from calculations at the theoretical levels of LC-ωPBE/6-311+G** for Formyl azide and Formyl isocyanate have been presented in Table 3. These findings show that the cis forms of Formyl azide and Formyl isocyanate are more stable than the relevant trans-forms. All these studies have been performed at



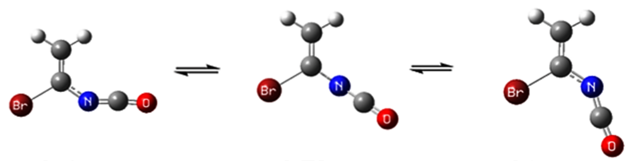
7-cis 7-TS 7-trans

LP N→σ*C-Br, E_2=2.84 LP N→σ*C-Br, E_2=16.52

Fig. 7. Schematic diagram of the conformational equilibrium of cis, transition state, and trans-Formyl azide

Table 3. Thermodynamic parameters calculation (enthalpy and Gibbs free energy in Hartree unit and entropy (calorie per mole per Kelvin) for cis and trans structures of Formyl azide and Formyl isocyanate

	LC-ωPBE/6-311+G**									
	ZPE	EO	H	S	G	ΔZPE	ΔEo	ΔH	ΔS	ΔG
Geometries										
7-cis	0.033251	-277.968122	-277.962783	68.746	-277.995446	0.00	0.00	0.00	0.000	0.00
7-trans	0.032680	-277.961977	-277.956459	69.077	-277.989280	-0.39	3.86	3.97	0.331	3.87
7-cis→$[TS]^{\ddagger}$→7-trans	0.032280	-277.949865	-277.944938	67.151	-277.976843	-0.61	11.46	11.20	-1.595	11.67
8-cis	0.033350	-281.865059	-281.859515	70.324	-281.892928	0.00	0.00	000	0.000	0.00
8-trans	0.032919	-281.862582	-281.856830	71.015	-281.890572	-0.27	1.55	1.68	0.691	1.48
8-cis→$[TS]^{\ddagger}$→8-trans	0.032781	-281.860961	-281.855945	67.971	-281.888240	-0.38	2.57	2.24	-2.353	2.94



8-cis 8-TS 8-trans

LP N→$\sigma^*_{C\text{-}Br}$, E_2=0.00 LP N→$\sigma^*_{C\text{-}Br}$, E_2=22.52

Fig. 8. Schematic diagram of the conformational equilibrium of cis, transition state, and trans-Formyl isocyanate

the temperature of 298 oK and the pressure of 1 atmosphere.

Schematic diagrams of the conformationals equilibirium of cis and trans-Formyl azide and Formyl isocyanate have been shown in Figs 7 and 8.

REFERENCES

[1] Krol, M.C.; Altona, C.J.M. (1990). The anomeric effect: Ab-initio studies on molecules of the type X- CH_2-O-CH3. J. Comput. Chem., 11(7), 765-790.

[2] Bouchy, A.; Rouusy, G. (1977). Geometrical and electronic structures of two conformers of vinyl isocyanate by microwave spectroscopy. J. Mol. Spedrosc., 68(1), 156-165.

[3] Dewar, M.J.S.; Zeobisch, E.J.E.; Hely, F.; Stewart, J.J.P. (1985). Development and use of quantum mechanical molecular models. 76. AM1: a new general purpose quantum mechanical molecular model. J. Am. Chem. Soc., 107(13), 3902-3909.

[4] Hoffmann, R. (1963). An extended Hückel theory. I. hydrocarbons. J. Chem. Phys., 39(6), 1397-1412.

[5] Hoffmann, R. (1964). Extended Hückel Theory. II. σ Orbitals in the Azines. J. Chem. Phys., 40(9), 2745.

[6] Wolfsberg, M.; Helmholz, L. (1952). The spectra and electronic structure of the tetrahedral ions MnO4-, CrO4--, and ClO4-. J. Chem. Phys., 20(5), 837-843.

[7] Slater, J.C. (1930). Atomic shielding constants. Phys. Rev., 36(1), 57.

[8] Hehre, W.J.; Stewart, R.F.; Pople, J.A. (1969). Self-consistent molecular-orbital methods. Use of Gaussian expansions of Slater-type atomic orbitals. J. Chem. Phys. 51(6), 2657-2664.

[9] Gerry, M.C.L.; Thomson, J.C.T.; Sugden, M. (1966). Microwave Spectrum of Silyl Isocyanate. Nature, 211(5051), 846-847.

[10] Duckett, J.A.; Robiette, G.; Mills, I.M. (1976). The two-dimensional anharmonic oscillator: The microwave spectrum of silyl isocyanate, SiH3NCO. J. Mol. Spectrosc., 62(1), 34-52.

[11] Hocking, W.H.M.; Gerry, C.L.J. (1976). The microwave spectrum of cyanogen isocyanate (NCNCO). J. Mol. Spectrosc., 59(3), 338-354.

[12] Nobes, R.H.; Pople, J.A.; Radom, L.; Handy, N.C.; Knowles, P.J. (1987). Slow convergence of the møller-plesset perturbation series: the dissociation energy of hydrogen cyanide and the electron affinity of the cyano radical. Chem. Phys. Lett., 138(5), 481-485.

[13] Schlegel, H.B. (1988). Møller-Plesset perturbation theory with spin projection, The Journal of Physical Chemistry. J. Phys. Chem., 92(11),

3075-3078.

[14] Allinger, N.L. (1976). Calculation of molecular structure and energy by force-field methods, Advances in physical organic chemistry. Adv. Phys. Org. Chem., 13, 1-82.

[15] Allinger, N.L. (1977). Conformational analysis. 130. MM2. A hydrocarbon force field utilizing V1 and V2 torsional terms. J. Am. Chem. Soc., 99(25), 8127-8134.

[16] Gilbert, T.M. (1998). Ab initio prediction of ring strains enthalpies of cyclic amine-boranes. Tetrahedron Lett, 39(50), 9147-9150.

[17] Sundaralingam, M. (1968). Some aspects of stereochemistry and hydrogen bonding of carbohydrates related to polysaccharide conformations. Biopolymers, 6(2), 189-213.

AUTHOR (S) BIOSKETCHES

Hengameh Fallah, PhD., Department of Chemistry, Arak Branch, Islamic Azad University, Arak, Iran, *Email:Hengameh.fallah@yahoo.com*

Hooshang Atabaki, Assistant Professor, Department of Chemistry, Arak Branch, Islamic Azad University, Arak, Iran, *Email: h-atabaki@iau-arak.ac.ir*

Leila Moharrery, Assistant Professor, Department of Chemical Engineering, Robat Karim Branch, Islamic Azad University, Tehran, *Email: leilamoharrery@yahoo.com*

Neda Hasanzadeh, Assistant Professor, Department of Chemistry, Ahvaz Branch, Islamic Azad University, Ahvaz, Iran, *Email: nhzadeh_212@yahoo.com*

Hooriye Yahyaei, Assistant Professor, Department of Chemistry, Zanjan Branch, Islamic Azad University, Zanjan, Iran, *Email: Hooriye_yahyaei@yahoo.com*