Journal of Physical and Theoretical Chemistry
of Islamic Azad University of Iran, 6 (2) 139-144; Summer 2009
(J.Phys.Theor.Chem. IAU Iran)
ISSN: 1735-2126

Kinetics and mechanism of intramolecular Cyclization of (R)-undeca-7,8-dien-2-yne "a DFT study"

M. R. Zardoost,[1] S. R. Emamian,[1] S. A. Siadati,[4] M. R. Gholami[2,3] and H. Aghaie[2,*]

[1] Ph.D. Student, Department of Chemistry, Science and Research Branch, Islamic Azad University, Tehran, Iran
[2] Department of Chemistry, Science and Research Branch, Islamic Azad University, Tehran, Iran
[3] Department of Chemistry, Sharif University of Technology, P.O. Box 11365-9516, Tehran, Iran
[4] Department of Chemistry, Ghaemshahr Branch, Islamic Azad University, Ghaemshahr, Iran

ABSTRACT

A theoretical study of the kinetic and mechanism of intramolecular cyclization of (R)-undeca-7,8-dien-2-yne was performed using DFT methods at B3LYP and B3PW91 levels of theory using 6-311g, 6-311g*, 6-311G**, 6-311+G, 6-311++G and 6-311++G** basis sets. Equilibrium molecular geometries and harmonic vibrational frequencies of the reactant, transition state and product were calculated. The considered rate constants and activation thermodynamic parameters were calculated. It was demonstrated that the obtained results for all calculations were nearly independent to basis sets at B3PW91 level. These calculations showed that the reaction proceeds through asynchronous concerted mechanism.

Keywords: Allene, Cyclization; DFT, Reaction mechanism

INTRODUCTION

A typical organic reaction proceeds in a special mechanism. There may be many proposed mechanisms for a typical organic reaction experimental methods have many instrumental limitations such as trapping the intermediates or transition states in confirming the mechanism that reactions proceed from it. Computational methods can make confirming the mechanism easier, cheaper and exacter computational details.

Recently much attention has been paid to the chemistry of allenes [1, 2]. An intramolecular ene reaction for the formation of an alicyclic ring is a useful tool in organic synthesis [3-10].

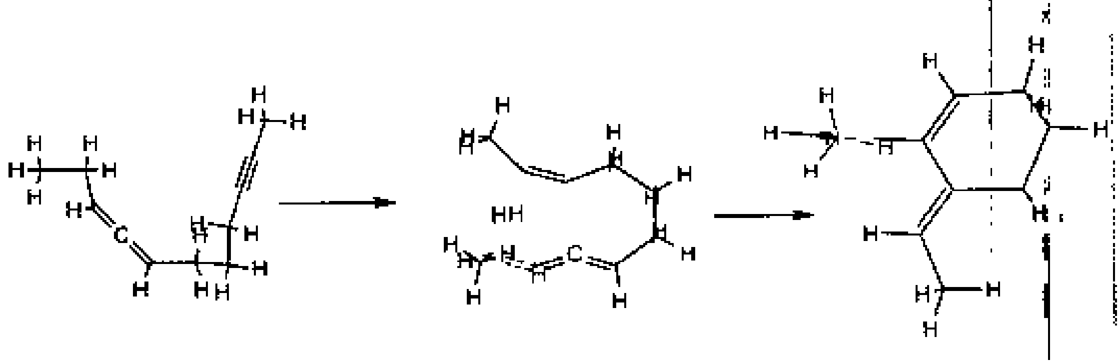
During the course of the reaction two contiguous stereo centers are generated often with a high degree of stereo control, which is of immense synthetic applicability [11]. The presence of an activating substituent in the reactant usually reduces the reaction temperature and increases the possibility of controlling the stereoselectivity [9-12]. Various models have been proposed [16-18] to predict the stereoselectivity of this reaction for the formation of a five membered ring. The most modified model proposed by Houk *et al.* [18], predicts successfully the ratio of the diastereumeric products formed in the case of unactivated reactants. But the model is inadequate in the case of activated enophiles [18].

---

[*] Corresponding author: hn_Aghaie@yahoo.com

This is due to the assumption of a rigid transition state, and the predictions using this, differ greatly from what is experimentally observed. This discrepancy clearly indicates that the actual transition state is relatively flexible. Intramolecular ene reaction can be classified into six different categories [19, 20]. The nomenclature of these classes depends on the binding site of the tether between the ene and the enophile moiety.

G. K. Das et al performed a theoretical study on effect of the hybridization of the hetro-atom present at the tether on the selectivity of the (3, 4) ene Cyclization [21]. In this paper the transition states (TSs) of suitable examples of intramolecular ene reactions with activating substituents have been investigated using a semi-empirical quantum mechanical method. In this work we do a detailed investigation on kinetics and mechanism of cyclization ene reaction.



Scheme 1. Cyclization of (R)-undeca-7.8-dien-2-yne to (E)-6-ethylidene-1-((Z)-prop-1-enyl)cyclohex-1-ene.

COMPUTATIONAL DETAILS

The structures corresponding to the reactants, TS, intermediate and product were optimized and electronic structures and harmonic vibrational frequencies of all stationary points along the reaction pathway were calculated using Gaussian 03 computational package [22] with DFT method at B3LYP and B3PW91 levels.

Some authors [23-25] recommend employing pure functional instead of the hybrid version to describe these type of reactions. The superiority of the BLYP over the more general B3LYP method is not clear and, in particular, the calculation of the reaction pathway, so we have chosen the B3LYP and B3PW91 functional. Optimization of geometries of the stationary points on the potential energy surfaces were performed using Beck's there-parameter hybrid exchange functional with the correlation functional of Lee ,Yang, Parr (B3LYP) [26-27] and Beck's there-parameter hybrid exchange functional with the correlation functional of Perdew-Wang91 [28-30] with the 6-311g [31-32], 6-311g* [33-34] , 6-311g** [33-34] , 6-311+G, 6-311++g [33-34] and , 6-311++g** [33-34] basis sets. The synchronous transit guided quasi Newton (STQN) method [35-36] was used to locate the TS. The intrinsic reaction coordinate (IRC) method of Fukui [37-38] developed by Gonzalez and Schlegel [39-40] was applied in order to check and obtain the profiles connecting the TS to the two associated minima of the proposed mechanism. The natural bond orbital (NBO) analysis [41-42] was applied to determine the charge changes occurring in the studied process. All minimum and transition state structures are verified by vibrational frequency analysis.

The activation energies and Arrhenius factors were computed using eqns. (1) and (2), respectively, which were derived from the transition state theory [43-44].

$$E_a = \Delta H^{\neq} + RT \qquad (1)$$

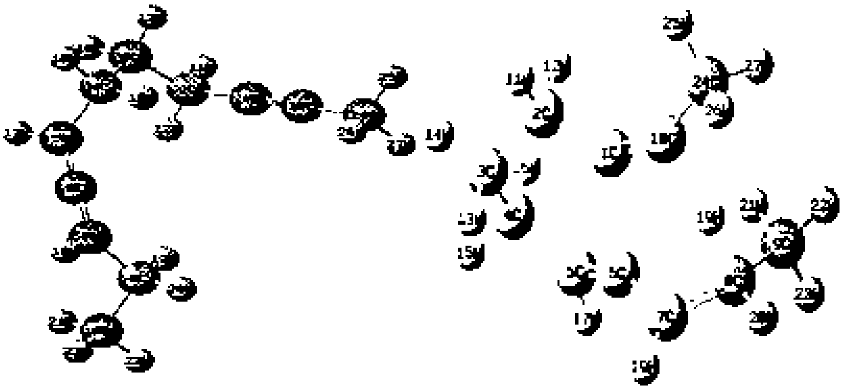
$$A = (ek_BT/h)\exp(\Delta S^{\neq}(T)/R) \qquad (2)$$

RESULTS

Scheme (2) shows the optimized structures of reactants, TS, and intermediate with the selected geometrical parameters at the $B_3LYP/6\text{-}311g^{**}$ shown in Table 1. Throughout this paper, all inter nuclear distances are in angstroms and all angles are in degrees.

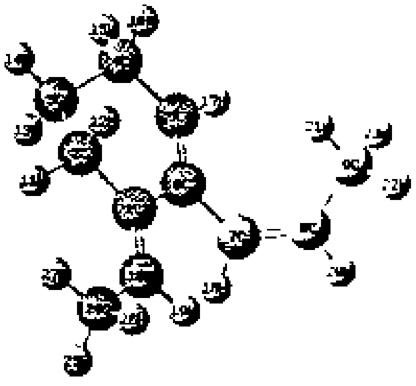
Table 1. Key geometrical parameters of the reactant, TS and product at the B3LYP/6-311G** level of theory

	Reactant	TS	Product
C1-C6		2.197	1.482
C5-C6	1.306	1.320	1.349
C6-C7	1.306	1.360	1.486
C7-C8	1.513	1.433	1.337
C1-C10	1.204	1.249	1.346
	1.248	1.093	**C8-H19**
1.086	1.507		**C10-H19**



Reactant

Transition state



Product

Scheme 2. Optimized geometries of reactant. TS and product for the studied reaction at the B3LYP/6-311G** level.

The bond lengths and angles of the transition state, TS, were calculated using the B3LYP and B3PW91 level of the theory using 6-311g, 6-311g*, 6-311g**, 6-311+G, 6-311++g, and 6-311++g** basis sets. The mechanism is initiated with the C8-H19 bond cleavage and C1-C6 and C10-H19 bond formation. According to Table 1 the transition structure has a breaking C8-H19 bond distance of 1.248 angstrom and forming C1-C6 bond distance of 2.197 angstrom and forming C10-H19 bond distance of 1.507 angstrom. The Pauling relation [45] was used to determine the C8-H19 bond cleavage. The charge difference related partial bond orders, and the values of 0.77, 0.30, and 0.50 were obtained for C8-H19. C1-C6, and C10-H19, respectively. The obtained partial bond orders indicate that 23% of C8-H19 bond is broken, whereas C1-C6 and C10-H19 have 30% and 50% reaching to the transition state, TS.

Table 2 shows the charge distribution in the reactant. TS and the charge difference between TS and reactant (Δcharge) by means of NBO analysis. The results at the TS indicate that a small negative charge developed on C6 which demonstrates C1-C6 bond formation is faster than shows that electron donor groups at C1, C5, C7, and C8 accelerate the reaction. However, at C10 position opposite result is observed.

B3LYP/6-311G** results for the reaction path are shown in Fig 1. This figure demonstrates the energy as a function of the reaction coordinate, and represents the minimum energy path, which connects the reactant to the intermediate through the saddle point.

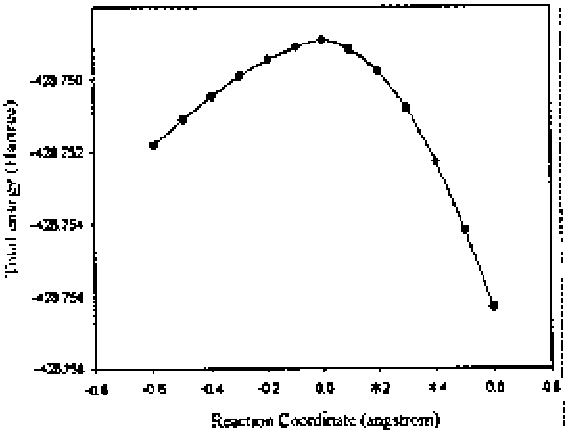


Fig.1. Schematic energy profile of the potential energy surface for the studied reaction at B3LYP/6-311G** level of theory.

The imaginary frequency for the transition structure was calculated to confirm the TS at B3LYP and B3PW91 levels of theory. Table 3 and Table 4 present $\Delta G^{\circ,\neq}$, $\Delta H^{\circ\neq}$, $\Delta S^{\circ\neq}$, E_a, and Arrhenius factor for the reaction. The Gibbs free energy barrier for the TS formation, is 43.752 kcal mol^{-1} and 40.087 kcal mol^{-1} at B3LYP/6-311++G** and B3PW91/6-311++G**, respectively. As can be seen in Table 3 the results are slightly dependent on the basis sets at B3LYP level of the theory, which means the discrepancy found in the $\Delta G^{\circ,\neq}$, comes from the reactants [46]. Using the most reliable energy barrier for this reaction calculated by the B3LYP/6-311++G (d, p) method, it is possible to estimate a TST rate coefficient of 5.24 × 10^{-20} s^{-1} at 298.15 K in gas phase. But as can be seen in Table 4 the results are nearly independent on the basis sets at B3PW91 level of the theory. It seems B3PW91 level gives results that are more reliable than B3LYP results.

CONCLUSION

Cyclization of (R)-undeca-7,8-dien-2-yne to (E)-6-ethylidene-1-((Z)-prop-1-enyl)cyclohex-1-ene was studied by two levels of the Density Functional theory using different basis sets. It was verified that E_a of the reaction was dependent to basis sets slightly. The E_a calculated for the reaction in gas phase by the B_3LYP/6-311++G** is 38.956 kcal . mol^{-1} meaning formation is energetically feasible to occur. The calculated rate constants, does not show any considerable change in different basis sets.

The extent of broken and formed bonds in transition state shows that asynchronous concerted mechanism has occurred for the undeca-7,8-dien-2-yne Cyclization. The charge analysis shows that electron donor groups at C1, C5, C7, and C8 accelerate the reaction. However, at C10 position opposite result is observed.

Table 2. Distributed NBO charges on the reactant and TS at the B3LYP/6-311G** level of theory for first path (the numbering of atoms is like that in scheme 2)

H19	C10	C8	C7	C6	C5	C1	
0.19864	-0.02075	-0.37914	-0.26452	0.07374	-0.27352	-0.02555	**Reactant**
0.22801	-0.12567	-0.33713	-0.21520	0.00218	-0.23890	-0.01129	**TS**
-0.02937	0.10492	-0.04201	-0.04932	0.07156	-0.03462	-0.01426	**ΔCharge**

Table 3. Theoretical kinetic and activation parameters for cyclization ENE reaction of undeca-7,8-dien-2-yne in gas phase at 298.15 K at B3LYP level

6-311++G**	6-311++G	6-311+G	6-311G**	6-311G*	6-311G	B3LYP
43.752	44.187	43.918	41.876	44.116	44.584	$\Delta G^{\circ\neq}(k\ cal\ mol^{-1})$
38.364	35.906	38.935	38.619	38.847	38.818	$\Delta H^{\circ\neq}(kcal\ mol^{-1})$
-18.073	-17.713	-16.711	-10.925	-17.676	-19.337	$\Delta S^{\circ\neq}(cal\ mol^{-1}K^{-1})$
38.956	34.498	39.528	39.211	39.439	39.411	$E_a(k\ cal\ mol^{-1})$
9.277	9.356	9.575	10.540	9.364	9.001	$\log A$

Table 4. Theoretical kinetic and activation parameters for for cyclization ENE reaction of undeca-7,8-dien-2-yne in gas phase at 298.15 K at B3PW91 level

6-311++G	6-311+G	6-311G*	6-311G	B3PW91
40.087	40.135	40.311	40.299	$\Delta G^{\circ,\#}(k\ cal\ mol^{-1})$
35.165	35.200	34.895	35.251	$\Delta H^{\circ,\#}(kcal\ mol^{-1})$
-16.505	-16.554	-18.164	-16.932	$\Delta S^{\circ,\#}(cal\ mol^{-1}K^{-1})$
35.757	35.792	35.488	35.843	$E_a(k\ cal\ mol^{-1})$
9.620	9.609	9.257	9.527	$\log A$

REFERENCES

[1] (For reviews, see: a) The Chemistry of Allenes (Ed.: S. R. Landor), Vol. 1, Academic, London, 1982; b) Modern Allene Chemistry (Eds.: N. Krause, A. S. K. Hashmi), Vol. 1, 2, Wiley-VCH, Weinheim, 2004; c) S. Ma, Palladium-Catalyzed Two- or Three-Component Cyclization of Functionalized Allenes in Palladium in Organic Synthesis (Ed.: J. Tsuji), pp. 183 – 210, Spring, Berlin, Heidelberg, 2005; d) R. Zimmer, C. U. Dinesh, E. Nandanan, F. A. Khan, Chem. Rev. 2000, 100, 3067 – 3125; e) S. Ma, Chem. Rev. 2005, 105, 2829 – 2872; f) S. Ma, Acc. Chem. Res. 2003, 36, 701 – 712; g) L. K. Sydnes. Chem. Rev. 2003, 103, 1133 – 1150; h) D. Lentz, J. Fluorine Chem. 2004, 125, 853 – 861; i) N. Krause. A. Hoffmann-Röder, Tetrahedron, 2004, 60, 11671 – 11 694.

[2] For some of the most recent publications, see: a) H. Ohno, H. Hamaguchi, M. Ohata, S. Kosaka, T Tanaka, J. Am. Chem. Soc. 2004, 126, 8744–8754; b) K. Fumiko, H. Kumio, Chem. Pharm. Bull. 2004, 52, 95 – 103; c) J. Franzen, J. Loftstedt, J. Falk, J. E. BOckvall, J. Am. Chem. Soc. 2003, 125, 14 140 – 14 148; d) S. Kang, Y. Ha, B. Ko, Y. Lim, J. Jung, Angew. Chem. 2002, 114, 353 – 355; Angew. Chem. Int. Ed. 2002, 41, 343 – 345. e) K. Lee, D. Seomoon, P. Lee, Angew. Chem. 2002, 114, 4057 – 4059; Angew. Chem. Int. Ed. 2002, 41, 3901 – 3903. f) K. M Brummond, H. Chen, P. Sill. L. You, J. Am. Chem. Soc. 2002. 124, 15 186 – 15 187; g) B. M Trost, C. Jakel, B. Plietker, J. Am Chem. Soc. 2003, 125, 4438–4439; h) J. Huang. R. P. Hsung. J. Am. Chem. Soc. 2005, 127, 50 – 51; i) K. Chang, D. K. Rayabarapu, F. Yang, C. Cheng, J. Am. Chem. Soc. 2005, 127, 126 – 131.

[3] H. M. R. Hoffmann. Angew. Chem. , Int. Ed. Engl., 8, 1969, 556.

[4] W Oppolzer, K. K. Mahalanabis, K. Battig, Helv. Chim. Acta, 60, 1977, 2388.

[5] W. Oppolzer. C. Robbiani, K. Battig, Helv. Chim. Acta, 63, 1980, 2015.

[6] W. Oppolzer, K. Battig, Tetrahedron Lett., 1982, 4669.

[7] W. Carruthers, in Cycloaddition reactions in Organic Synthesis, Pergamon Press, Oxford, 1990, Chapter 5.

[8] T. K. Sarkar, B. K. Ghorai, S. K. Nandy, B. Mukherjee, Tetrahedron Lett., 35, 1944, 6903.

[9] T. K. Sarkar, B. K. Ghorai, S. K. Nandy, B. Mukherjee. A. Banerji, J. Org. Chem., 35, 1997, 6903.

[10] T. K. Sarkar, B. Mukherjee, S. K. Ghorai, Tetrahedron, 54, 1998, 3243.

[11] J. T. Williams, P. S. Bahia, B. M. Kariuki, N. Spencer, D. Philp, J. S. Snaith, J. Org. Chem. 71, 2005, 2460.

[12] B. B. Snider, Acc. Chem. Res., 13, 1980, 426.

[13] B. B. Snider, E. A. Oeutsch, J. Org. Chem , 47, 1982, 745.

[14] L. F. Tietze, Y. Beifub, Synthesis, 1988, 359.

[15] K. Maruaka, Y. Hoshino, T. Shirasaka, H. Yamamoto, Tetrahedron Lett., 29, 1988, 3967.

[16] W. Oppolzer. C. Robbiani, Helv. Chim. Acta, 63, 1980, 2010.

[17] R. J. Loncharich, K. N. Houk, J. Am. Chem Soc., 109, 1987, 6947.

[18] B. E. Thomas IV. R. J. Loncharich, K. N. Houk, J. Org. Chem., 57, 1992, 1354.

[19] K. Mikami, M. Shimizu, Chem. Rev. 92, 1992, 1021.

[20] (a) H. Ohmura, G D. Smyth, K. Mikami, J. Org. Chem. 64, 1999, 6056; (b) K. Mikami, H Ohmura. J. Yamanaka, J. Org. Chem. 68, 2003, 1081.

[21] K. Chakrabarty, S. Roy, S. N. Gupta, G. K Das, J. Mol. Struct. (Theochem) 901, 2009, 44.

[22] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T Vreven, K. N. Kudin, J. C Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 2003.

[23] C. J. Cramer, J. J Nash, R. R. Squires, Chem. Phys. Lett. 277, 1997, 311.

[24] P. R. Schreiner, J. Am. Chem. Soc. 120, 1998, 4184.

[25] M. Prall, A. Wittkapp, P. R. Schreiner, J. Phys. Chem. A 105, 2001, 9265.

[26] A. D. Becke, *Phys. Rev. A*. 38, 1988, 3098.

[27] C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B*. 371, 1988, 785.

[28] J. P. Pedrew, K. Burke, Y. Wang, Phys. Rev. B 54, 1996, 16533.

[29] J. P. Pedrew, Electronic Structure of Solids' 91, Ed. P. Ziesche, H. Eschring (Akademie Verlag, Berlin, 1991) 11.

[30] K. Burke, J. P. Pedrew, Y. Wang, Electronic Density Functional Theory: Recent Progress and New Directions, Ed. J. F. Dobson, G. Vignale, M. P. Das (Plenum, 1998).

[31] A. D. McLean, G. S. Chandler, *J. Chem. Phys*. 72, 1980, 5639.

[32] R. Krishnan, J. S. Binkley, R. Seeger, J. A. Pople, *J. Chem. Phys*. 72, 1980, 650.

[33] G. A. Petersson, M. A. Al-Laham, *J. Chem. Phys*. 94, 1991, 6081.

[34] G. A. Petersson, A. Bennett, T. G. Tensfeldt, M. A. Al-Laham, W. A. Shirley, J. Mantzaris, J. *Chem. Phys*. 89, 1988, 2193.

[35] C. Peng, P. Y. Ayala, H. B. Schlegel, M. J. Frisch, *J. Comp. Chem* 17, 1996, 49.

[36] C. Peng, H. B. Schlegel, *Israel J. Chem*. 33, 1994, 449.

[37] K. Fukui, J. Phys. Chem. 74, 1970, 4161.

[38] K. Fukui, Acc. Chem. Res. 14, 1981, 363.

[39] C. Gonzalez, H. B. Schlegel, *J. Phys. Chem*. 94, 1990, 5523.

[40] C. Gonzalez, H. B. Schlegel, *J. Chem. Phys*. 90, 1989, 2154.

[41] A. E. Reed, L. A. Curtiss, F. Weinhold, *Chem. Rev*. 88, 1988, 899.

[42] J. E. Carpenter, F. Weinhold, J. Mol. Struct. (*Theochem*). 169, 1988, 41.

[43] S. Glasstane, K. J. Laidler, H. Eyring, *The Theory of Rate Processes*, McGraw-Hill, New York, 1941.

[44] K. J. Laidler, *Theories of Chemical Reaction Rates*, McGraw-Hill, New York, 1941.

[45] L. Pauling, J Am. Chem. Soc. 9, 1947, 542.

[46] M. C. L. Scaldaferri, A. S. Pimentel, Chem. Phys. Lett. 470 (2009) 203

NOTICE TO AUTHORS

1. General Policy

a) The Journal of Physical and Theoretical Chemistry Islamic Azad University of Iran (J.Phys. & Theo.Chem.I.A.U.Iran) is published quarterly by Science and Research Campus, Islamic Azad University of Iran . Research Papers in the fields of Physical and Theoretical Chemistry may be submitted by scientists from all over the world.

b) The paper submitted to this journal should not have been published previously, except in the form of a brief preliminary communication,nor submitted to another journal.

c) Manuscripts will be considered for publication in the form of articles, preliminary communications, notes and reviews .The decision to accept a contribution rests with the Editorial Committee of the J.Phys. & Theo.Chem.I.A.U.Iran. The work should be original or a through review by an authoritative person in a pertinent field.

d) If any figure(s), illustration(s), table(s) or extended quotation(s), etc. are to be from material(s) previously published, the author(s) should secure reproduction permission from the copyright owner.

e) Submission of a manuscript implies that the author(s) agree to transfer copyright to the J.Phys. & Theo..Chem.I.A.U.Iran when the manuscript is accepted for publication .Reproduction of the text, figures or table of this journal is allowed only by permission of the Editorial Committee

f) The author(s) are responsible for the originality and accuracy of their own manuscript, table(s) and figure(s).

2. Instructions to authors for the preparation of manuscript

a) Manuscripts must be submitted in English .They must be typewritten in Microsoft Word 2000 (all version), double-spaced, on good quality A4 paper. Authors are requested to reserve margin of at least 3 cm at the top and bottom of each page and at least 3 cm on the left and right-hand side page .

b) Original drawings of formulas, schemes and figures should be furnished together with the manuscripts

c) Manuscripts should be arranged in a minimum length and should be subdivided into labeled sections (e.g. Abstract, Introduction, Experimental, Results and Discussion, Conclusion, Acknowledgement and References).A current issue of J.Phys. & Theo.Chem.I.A.U IRAN should be consulted.

d) The title of an article should reflect concisely the purpose and findings of the work and be brief and clear as much as possible. Abbreviations, Symbols, Chemical Formulas, References, and Footnotes should be also avoided at the Title page. At least two keywords should be introduced by the author(s) .The name and surname of the author(s) and their appropriate address(s), the name and address of Institution(s) where the work was performed. Footnotes may be added to indicate the current mailing address(s) of the author(s).

e) Following the title page, a brief summary of the work (abstract) should be considered and must not exceed 200 words. It should be self-explanatory and intelligible without references to the text.

f) The total number of pages of an essay must not exceed 10 pages

g) The IUPAC rules and SI units should be considered.

h) Equations, figures and tables should be numbered.

i) Literature references should be abbreviated according to conventions of Chemical Abstract Service Source Index, published by the American Chemical Society and numbered in order in which they are cited in the text. Footnotes which are intended to complement the text should be marked by an asterisk.

j) The E-mail address of the corresponding Author should be given as a footnote to the first page

3. Submission

Manuscripts should be sent in four copies, one original and three copies, to the Editorial address, together with a covering letter signed by the author to whom correspondence should be addressed at following:

Editorial Office of **J.Phys. & Theo.Chem.I.A.U.Iran**
Science and Research Campus, Poonak, Hessarak, Tehran, Iran

Tel: +98 21 44865777
Fax: +98 21 44865767
Email: jptc@srbiau.ac.ir