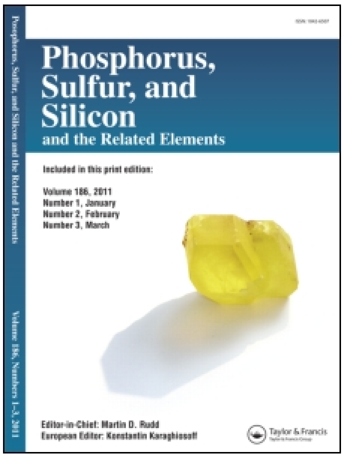
This article was downloaded by:
On: *28 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Ab Initio Study of the Dehydrogenation of 3-Pyrroline, 2,5-Dihydrofuran and 2,5-Dihydrothiophene

Davood Nori-Shargh[ab]; Abolfazl Shiroudi[c]; Reza Naeem-Abyaneh[d]; Maryam Nozari[d]
[a] Chemistry Department, Graduate Faculty,Arak Branch, Islamic Azad University, Arac, Iran [b] Chemistry Department, Science and Research Campus, Islamic Azad UniversityHesarak, Pounak, Tehran, Iran [c] Chemistry Department, Science and Research Campus, Islamic Azad,University Hesarak,Pounak, Tehran, Tehran, Iran [d] Chemistry Department, Graduate Faculty Arak Branch, Islamic Azad University, Arak, Iran

Online publication date: 21 December 2010

To cite this Article Nori-Shargh, Davood , Shiroudi, Abolfazl , Naeem-Abyaneh, Reza and Nozari, Maryam(2005) 'Ab Initio Study of the Dehydrogenation of 3-Pyrroline, 2,5-Dihydrofuran and 2,5-Dihydrothiophene', Phosphorus, Sulfur, and Silicon and the Related Elements, 180: 2, 435 — 442

To link to this Article: DOI: 10.1080/104265090517145

URL: http://dx.doi.org/10.1080/104265090517145

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Phosphorus, Sulfur, and Silicon, 180:435–442, 2005
Copyright © Taylor & Francis Inc.
ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426509051714

Ab Initio Study of the Dehydrogenation of 3-Pyrroline, 2,5-Dihydrofuran and 2,5-Dihydrothiophene

Davood Nori-Shargh
Chemistry Department, Graduate Faculty, Arak Branch, Islamic Azad University, Arak, Iran and Chemistry Department, Science and Research Campus, Islamic Azad, University Hesarak, Pounak, Tehran, Iran

Abolfazl Shiroudi
Chemistry Department, Science and Research Campus, Islamic Azad, University Hesarak, Pounak, Tehran, Iran

Reza Naeem-Abyaneh
Maryam Nozari
Chemistry Department, Graduate Faculty, Arak Branch, Islamic Azad University, Arak, Iran

*The nature of the transition state structures of the decomposition of 3-pyrroline (**1**), 2,5-dihydrofuran (**2**) and 2,5-dihydrothiophene (**3**) were investigated using ab initio Molecular Orbital (MO) and Density Factional Theory (DFT) methods. The energy barrier of the decomposition of compound **1** is smaller than compound **2** and compound **2** is smaller than compound **3**. The energy barriers for the decomposition of compounds **1–3** are 46.20, 50.17, and 61.34 kcal mol^{-1}, respectively, which is calculated by B3LYP/6-31G* //HF/6-31G* level of theory. Which is in good agreement with reported experimental data. Contrary to the previously reported data, the distance between the* cis*-2-and-5-hydrogen atoms in compound **1** is greater than compound **2**. The transition-state structures of the decomposition of compounds **1–3** are formed by interaction of the* cis*-2-and-5-hydrogen atoms. Also, the rings of compounds **1–3** in the transition state structures are puckered.*

Keywords Ab initio calculations; decomposition; dehydrogenation; dihydrofuran; dihydrothiophene; molecular modeling; pyrroline

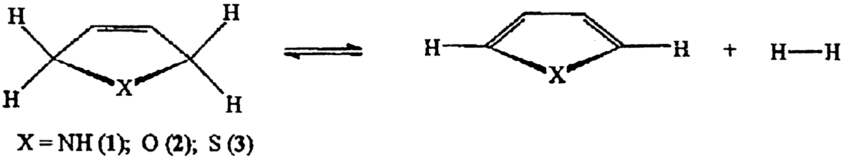
INTRODUCTION

The kinetic thermal decomposition of 3-pyrroline (**1**), 2,5-dihydrofuran (**2**) and 2,5-dihydrothiophene (**3**) have been studied perviously.[1–4] The

Received May 4, 2004; in final form July 27, 2004.

Address correspondence to Davood Nori-Shargh, Chemistry Department, Graduate Faculty, Arak Branch, Islamic Azad University, Arak, Iran. E-mail: nori_ir@yahoo.com

decomposition involves the intramolecular elimination of molecular hydrogen. In compound **2**, it has been suggested that the mechanism of the reaction involves hydrogen atom elimination from the C2 and C5 carbon atoms in the ring by means of six central transition states.[1] A similar mechanism has been shown to be predominate in the thermal decomposition of cyclopentene.[5] An analogous transition state was involved for the decomposition of cyclohexa-1,4-diene, in which the formation of free radicals was shown to be energetically unfavorable.[6] Wellington et al. have mentioned that the *cis*-2-and-5-hydrogen atoms distances in compounds **1–3** is 3.00, 3.45, and 3.90 Å, respectively. They believed that the smaller distance between eliminated hydrogen atoms in compound **1** is one of the reasons for the smaller barrier energy for the decomposition of compound **1**. However, because bond length of C—N (1.462 Å) in compound **1** is longer than C—O (1.407 Å) in compound **2**, the distance of the *cis*-2-and-5-hydrogen atom in compound **2** is greater than compound **1**. Consequently, it seems that other factors affect the decomposition of compound **2**. The main goal of this work is to understand the influence of the affective factors on the transition–state structures of the decomposition of compounds **1–3** to molecular hydrogen, related diene heterocyclic compounds, and barrier heights of these reactions (see Scheme 1). To gain further insight on this subject, we have investigated the ground state and transition state structures of compound **1–3** by performing MO and DFT using the Gaussian 98 package of programs.[7,11] Successful application of DFT-based methods have broadened the applicability of the computational methods and now represent an interesting approach for determining activation barrier and molecular energies.[7–10] The B3LYP functional method combines Becke's three-parameter exchange function with the correlation function of Lee et al.[7,8]



X = NH (1); O (2); S (3)

SCHEME 1

CALCULATION

Ab initio calculation were carried out using HF/6-31G*//HF/6-31G*, MP2/6-31G*//HF/6-31G*, and B3LYP/6-31G*//HF/6-31G* level of theory with the Gaussian 98 package of programs,[11] was implemented on a Pentium-PC computer with 500 MHZ processor. Initial structure geometries of compounds **1–3** were obtained by a molecular mechanics program PC-MODEL (88.0)[12] and for reoptimization of geometries, we used the PM3 method of MOPAC 6.0 computer program was used.[13,14] Energy minimum geometries were located by minimizing the energy with respect to all geometrical coordinates and without imposing any symmetry constraints.

The GAUSSIAN 98 program was finally used to perform ab initio calculations at the HF/6-31G* level in order to obtain the energy-minimum structures and MP2/6-31G*//HF/6-31G* and B3LYP/6-31G*//HF/6-31G* methods for single-point energy calculations.

The nature of the stationary points for the configurations of compounds **1–3** was determined by means of the number of imaginary frequencies. For minimum state structures only real frequency values, and in the transition state only single imaginary frequency values, were accepted.

The structure of the transition state geometries was located using the optimized geometries of the equilibrium structures according to the procedure Dewar et al.[15] These structures were then reoptimized by the QST2 subroutine at the HF/6-31G* level. The vibrational frequencies of ground states and transition states were calculated by the FREQ subroutine.

RESULTS AND DISCUSSION

Corrected Zero-Point (ZPE^b) and total electronic (E_{el}) energies (where $E_0 = E_{\text{el}} + ZPE^b$) for compounds **1–3**, as calculated at the ab initio HF/6-31G* level are given in Table I. For single-point energy calculations both ab initio MP2/6-31G*//HF/6-31G* and the DFT methods (B3LYP/6-31G*//HF/6-31G*) were used.

Representative structural parameters for ground states and transition structures of compounds **1–3**, as calculated by HF/6-31G* level of theory, are given in Table II. Theoretical calculations provide structural parameters for isolated molecule at 0K. Therefore, theoretical calculations are not reported, in principal, to reproduce the experimental values quantitively.[16] Nevertheless, it is possible to carry out ab initio calculations at the Hartree-Fock, from which many properties and structures can be obtained with an accuracy that is competitive with experiments.[17–20]

HF/6-31G* results show that the distances between the *cis*-2-and-5-hydrogen atoms in compounds **1–3** is 3.524, 3.939, and 3.525 Å, respectively. The distance between the cis-2-and-5-hydrogen atoms in

TABLE I Calculated Energies (in Hartree) for Ground State and Transition State Structures of the Dehydrogenation of 3-Pyrroline (1), 2,5-dihydrofuran (2), and 2,5-dihydrothiophene (3)

	Method										
	HF/6-31G*//HF/6-31G*				MP2/6-31G*//HF/6-31G*			B3LYP/6-31G*//HF/6-31G*			
Geometry	ZPE^b	E_{el}	E_o	$\Delta E_o{}^a$	E_{el}	E_o	$\Delta E_o{}^a$	E_{el}	E_o	$\Delta E_o{}^a$	Exp.
1(GS)	0.103801	−209.955853	−209.852052	0.000000 (0.000000)	−210.623412	−210.519611	0.000000 (0.000000)	−211.346817	−211.243016	0.000000 (0.000000)	
1 (TS)	0.095953	−209.837936	−209.741983	0.110069 (69.069398)	−210.542068	−210.446115	0.073496 (46.119474)	−211.265340	−211.169387	0.073629 (46.202933)	(44.6)[c]
2 (GS)	0.091623	−229.786625	−229.695002	0.000000 (0.000000)	−230.465844	−230.374221	0.000000 (0.000000)	−231.213988	−231.122365	0.000000 (0.000000)	
2 (TS)	0.083667	−229.660966	−229.577291	0.117711 (73.864829)	−230.377388	−230.293721	0.080500 (50.514555)	−231.126079	−231.042412	0.079953 (50.171307)	(48.3)[c]
3 (GS)	0.088443	−552.455803	−552.367360	0.000000 (0.000000)	−553.086454	−552.998011	0.000000 (0.000000)	−554.202995	−554.114552	0.000000 (0.000000)	
3 (TS)	0.079803	−552.311539	−552.231736	0.135624 (85.105416)	−552.981369	−552.901566	0.096445 (60.520201)	−554.096609	−554.016806	0.097746 (61.336592)	(55.0)[c]

Numbers in parenthesis are the corresponding ΔE values in kcal mol^{-1}.

[a] Relative to the best configuration.

[b] Corrected by multiplying by a scaling factor (0.9135).

[c] See ref. [4].

TABLE II HF/6-31G*-Calculated Structural Parameters for the Ground State and Transition State Structures of the Dehydrogenation Reaction of 3-Pyrroline (1), 2,5-dihydrofuran (2), and 2,5-dihydrothiophene (3). Bond Lengths are in (Å) and (°)

Compound	**1**		**2**		**3**	
State	(GS)	(TS)	(GS)	(TS)	(GS)	(TS)
Bond lengths (Å)						
$r_{1\text{-}2}$	1.500	1.395	1.407	1.354	1.829	1.759
$r_{2\text{-}3}$	1.498	1.429	1.504	1.420	1.504	1.420
$r_{3\text{-}4}$	1.339	1.356	1.314	1.360	1.316	1.363
$r_{2\text{-}7}$	1.107	1.529	1.087	1.527	1.084	1.555
$d_{6\text{-}7}$	3.524	1.052	3.525	1.015	3.939	0.995
Torsion angles (°)						
$\theta_{1\text{-}2\text{-}3}$	105.3	105.6	104.7	107.6	105.6	109.0
$\theta_{2\text{-}3\text{-}4}$	111.1	106.2	109.6	105.1	117.1	110.4
$\theta_{2\text{-}1\text{-}5}$	107.2	101.1	111.4	101.8	94.6	84.0
$\theta_{1\text{-}2\text{-}7}$	108.2	89.3	109.7	87.0	110.0	87.6
$\theta_{2\text{-}7\text{-}6}$	60.0	111.1	56.6	110.8	54.8	115.9
Torsion angles (°)						
$\phi_{1\text{-}2\text{-}3\text{-}4}$	1.8	23.7	0.0	21.7	0.0	28.0
$\phi_{2\text{-}3\text{-}4\text{-}5}$	0.0	0.0	0.0	0.0	0.0	0.0
$\phi_{4\text{-}5\text{-}1\text{-}2}$	2.9	37.4	0.0	34.5	0.0	36.2
$\phi_{1\text{-}2\text{-}7\text{-}6}$	−37.9	−34.7	−35.4	−35.7	−45.6	−43.6
$\phi_{2\text{-}7\text{-}6\text{-}5}$	0.0	0.0	0.0	0.0	0.0	0.0

compound **3** is greater than compound **1** and **2**. Consequently, in the transition-states structure of the dehydrogenenation of compound **3**, the ring must be more folded than the transition state structures of compounds **1** and **2**. This fact may be a reason for the higher energy barrier of the decomposition of compound **3** in comparison to compounds **1** and **2**. The energy barrier for dehydrogenation of compound **1** is 69.07, 46.12, and 46.20 kcal mol^{-1}, as calculated by HF/6-31G*//HF/6-31G*, MP2/6-31G*//HF/6-31G*, and B3LYP/6-1G*// HF/6-31G* levels of theory, respectivel (see Figure 1). MP2/6-31G*// HF/6-31G*- and B3LYP/6-31G*//HF/6-31G*-calculated energy barrier for dehydrogenation of compound **1** is in agreement to the reported experimental data (44.6 kcal mol^{-1})[4] than the HF/6-31G*//HF/6-31G* results.

The dehydrogenation energy barrier of compound **3** is 85.11, 60.52, and 61.34 kcal mol^{-1}, as calculated by HF/6-31G*//HF/6-31G*, MP2/6-31G*//HF/6-31G*, and B3LYP/6-31G*//HF/6-31G* levels of theory, respectively. MP2/6-31G*//HF/6-31G* calculated energy barriers is in good agreement to reported experimental data (55.0 kcal mol^{-1}).[4]

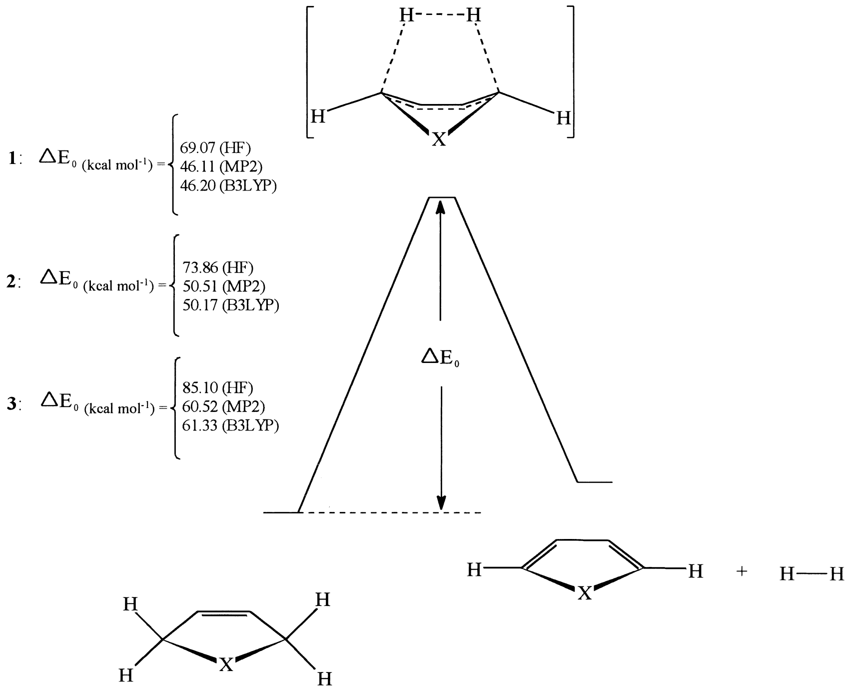


FIGURE 1 Calculated HF/6-31G*//HF/6-31G*, MP2/6-31G*//HF/6-31G*, and B3LYP/6-31G*//HF/6-31G* profile for decomposition of compounds **1–3**.

In compounds **1** and **2**, the distances between the *cis*-2-and-5-hydrogen atoms is 3.524 and 3.525 Å, respectively, was calculated by HF/6-31G*//HF/6-31G* level of theory. These values are almost equal and do not affect the energy barriers of molecular hydrogen eliminations.

The calculated structural parameters for the transition structures of compounds **1–3** revealed that the ring puckering in compound **3** is greater than compound **1**, and compound **1** is greater than compound **2**. The torsion angle of ϕ_{1234} in the transition state structures of compounds **1–3** is 23.7, 28.0, and 21.7 Å, respectively, as calculated by the HF/6-31G* level of theory. It seems the ring folding in the transition state structure of compound **2** is greater than compound **1** and in compound **1** is greater than compound **2**. Also, the aromatic character in pyrrole is more than furan and furan is more than thiophene. Consequently, it can be concluded that the aromatic character of the transition state structure of compound **1** is more than compound **2**, and in compound **2** is more than compound **3**. Therefore, the energy of the transition state structure of compound **1** is lower than compound **2**, and compound **2** is lower than compound **3**, in comparision to the ground state structures of compounds **1–3**.

CONCLUSION

Ab intio and density functional theory calculations provide a picture from both structural and energetic points of view for the decomposition of compounds **1–3**. The results calculated by HF/6-31G*//HF/6-31G*, MP2/6-31G*//HF/6-31G*, and B3LYP/6-31G*//HF/6-31G* levels of theory show that the barrier height of the decomposition of compound **1** is lower than compound **2**, and compound **2** is lower than compound **3**. The reason of this fact may be the greater resonance stabilization in the transition structure of compound **1**, compared to in comparison **2** and **3**. Also, in the ground state structure of compound **1**, the distance between the *cis*-2-and-5-hydrogen atoms is smaller than that in compounds **2** and **3**, and may be this fact facilitate the molecular hydrogen elimination from compound **1**. Also, the greater aromatic character in the transition state structure of the compound **1** facilitate the molecular hydrogen elimination, compared to compounds **2** and **3**.

REFERENCES

[1] C. A. Welligton and W. D. Walters, *J. Am. Chem. Soc.*, **83,** 4888 (1961).
[2] T. L. James and C. A. Wellington, *J. Chem. Soc.*, (A), 2398 (1968).
[3] A. L. Thomas and C. A. Wellington, *J. Chem. Soc.*, (A), 2895 (1969).
[4] C. A. Wellington, T. L. James, and A. C. Thomas, *J. Chem. Soc.*, (A), 2897 (1969).
[5] J. F. Baldwin, *Tetrahedron Let.*, 2953 (1966).
[6] S. W. Benson and R. Shaw, *Trans. Faraday. Soc.*, **63,** 985 (1967).
[7] D. Becke, *J. Chem. Phys.*, **98,** 5648 (1993).
[8] C. Lee, W. Yang, and R. G. Paw, *Phys. Rev.*, **37,** 785 (1988).
[9] W. J. Hehrie, L. Radom, P. V. R. Schleyer, and J. A. Pople, *Abinitio Molecular Orbital Theory* (Wiley, New York, 1986).
[10] J. M. Seminario and P. Politzer (Eds.), *Modern Density Function Theory, A Tool Chemistry*, Elsevier, Amsterdam, 1995.
[11] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrazewski, J. A. Montgomery Jr., R. E. Startmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malik, A. D. Rabuck, K. Raghavachar, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanyakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, and J. A. Pople, GAUSSIAN 98 (Revision A.3), Gaussian Inc., Pittsburgh PA, USA (1998).

[12] Serena Software, Box 3076, Bloomington, IN, USA.

[13] J. J. P. Stewart, *J. Comput. Chem.,* **10**, 221 (1989).

[14] J. J. P. Stewart, QCPE 581, Department of Chemistry, Indiana University, Bloomington, IN, USA.

[15] M. J. S. Dewar, E. F. Healy, and J. J. P. Stewart, *J. Chem. Soc.*, *Farady Trans*., **80,** 227 (1984).

[16] F. Freeman, A. Phornvoraunt, and W. J. Hehre, *J. Phys. Org. Chem*., **11,** 831 (1998).

[17] T. M. Gillbert, *Tetrahedron Lett*., **39,** 9147 (1998).

[18] M. Remko, P. D. Lyne, and W. G. Richards, *Phys. Chem. Chem. Phys*., **1,** 5353 (1999).

[19] A. D. Striland and R. A. Caidwell, *J. Phys. Chem*., **97,** 13394 (1993).

[20] I. Arnason, G. K. Thorarinson, and E. Matern, *J. Mol. Struct*. (*Theochem*), **91,** 454 (1998).