

# DFT calculations on the retro-ene reactions, part II: allyl *n*-propyl sulfide pyrolysis in the gas phase

M. Izadyar<sup>a</sup>, M.R. Gholami<sup>a,\*</sup>, M. Haghgu<sup>b</sup>

<sup>a</sup>Department of Chemistry, Sharif University of Technology, Azadi Ave., 11365-9516 Tehran, Iran

<sup>b</sup>Islamic Azad University, Branch of Hamedan, Hamedan, Iran

Received 24 January 2004; revised 26 July 2004; accepted 29 July 2004

## Abstract

The mechanism and kinetic aspects of the retro-ene reaction of the Allyl *n*-propyl sulfide and its deuterated derivative were studied using four different types of density functional theory methods with eight different levels of the basis sets. The activation energies were determined at 550.65 K. As a consequence of our calculations, a transition state is concluded that consists of a polar six-center cyclic structure. We found that the combination B3PW91/6-311++G\*\* produces activation energy values closer to the experimental ones, but the simpler combination B3LYP/6-31G\* produces excellent values too in less time. Our calculations show that the activation parameters obtained from the B3 methods are better than those obtained using the BLYP method. The mechanistic studies on the reaction show that the reaction proceeds through an asynchronous concerted mechanism. Theoretical calculations indicate that the reaction displays a kinetic isotope effect of 2.86 at 550.65 K.

© 2004 Elsevier B.V. All rights reserved.

**Keywords:** Allyl *n*-propyl sulfide; Retro-ene reaction; Step-wise; Asynchronous concerted mechanism; DFT calculations; Kinetic and mechanism; Activation parameters

## 1. Introduction

The mechanism of the retro-ene reactions has been the subject of the most heated and controversies in the recent years [1–13]. Both experimental data and theoretical calculations indicate that the reaction occurs through a concerted mechanism. Although in some cases, step-wise mechanisms involving diradical intermediates are only slightly less favorable [7–13]. However, it is not straightforward to be sure which mechanism is favored in different conditions.

In the last two decades, the identification of the geometry and energetic of the transition state (TS) has become a very popular tool for studying the reactions mechanism [14]. However, it is not always possible to compute these properties, reliably. The size of the molecule is a key

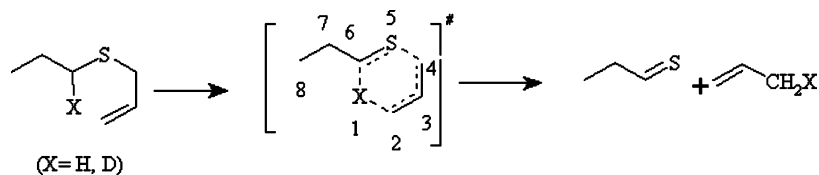
parameter in selecting a computational method. The semi-empirical methods are perhaps the most widely used ones due to their capacity to handle a large molecule [15,16]. Using the moderate standard basis sets, the conventional ab initio method (HF), has been extensively applied for studying the ene and retro-ene reactions [17,18]. As density functional theory (DFT) has considerably evolved from its solid-state physical origin to extensive application to the chemical systems [19–21], its applicability to nearly large systems of interest cannot be overlooked. The speed of DFT calculations as compared to the HF and post HF methods makes them ideal for using for fairly large organic systems.

In the present work, we have utilized the DFT methods using different basis sets to study the concerted and step-wise paths of the retro-ene reactions of Allyl *n*-propyl sulfide (APS) and its deuterated derivative (1-d1-APS).

G. Martin and M. Roperro [22] studied APS and 1-d1-APS experimentally at 543.15–673.15 K. Their results proved that the reactions to be homogeneous, unimolecular and should obey the first-order rate law. The decomposition of these allyl sulfides leads to the formation of propene,

\* Corresponding author. Tel.: +98-216165301; fax: +98-216012983/6005718.

E-mail addresses: gholami@sharif.edu (M.R. Gholami), izadyar@mehr.sharif.edu (M. Izadyar).



Scheme 1.

*n*-propyl thioaldehyde and corresponding deuterated products through six-center TS (Scheme 1).

The empirical rate coefficients for the APS and 1-d1-APS have been reported to be satisfied by the following Eqs. (1) and (2), respectively.

$$k_H(s^{-1}) = 10^{11.52 \pm 0.16} \exp[(-157 \pm 2) \text{ kJ mol}^{-1}/RT] \quad (1)$$

$$(k_H/k_D) = 2.7 \pm 0.2 (T = 281^\circ \text{C}) \quad (2)$$

Here we are going to determine which combination between the theoretical DFT methods and basis sets is more precise and fast enough for calculating accurate activation energy. With this in mind and the aim of understanding the performance of DFT methods in the kinetic studies, we report the kinetic and activation parameters for the APS pyrolysis.

## 2. Computational details

The structures corresponding to the reactant, TS and the products for the reaction were optimized using the GAUSSIAN 98 computational package [23] with DFT methods. The exchange functionals were the Becke (B) and the Becke three-parameter hybrid (B3) [24], the correlation functionals were the Lee–Yang–Parr (LYP) [25], the Perdew–Wang 91 (PW91) [26] and the Perdew 86 (P86) [27]. Basis sets were 6-31G\*, 6-31G\*\*, 6-31+G\*\*, 6-31++G\*\*, 6-311G\*, 6-311G\*\*, 6-311+G\*\* and 6-311++G\*\* [28]. The calculations were carried out on a AMD/Athlon, AT/AT dual processors computer.

The synchronous transit-guided quasi-Newton method as implemented by Schlegel and co-workers [29] was used to locate the TS. The intrinsic reaction coordinate method [30] was applied in order to check and obtain the profile connecting the TS to the two associated minima of the proposed mechanisms.

Vibrational frequencies for the points along the reaction path were determined to provide an estimation of the zero point vibrational energy (ZPVE). These calculations confirmed the nature of the stationary points as minima with the real frequencies and the TS with only one imaginary frequency.

The enthalpy, entropy and Gibbs free energy of the reaction were evaluated from the B3LYP/6-31G\* data at 298.15 K. The kinetic and activation parameters were also determined in the temperature ranges of the retro-ene reaction.

The activation energy,  $E_a$ , and the Arrhenius factor,  $A$ , were computed using the Eqs. (3) and (4), respectively, which have been derived from the transition state theory [31,32]:

$$E_a = \Delta H^\ddagger(T) + RT \quad (3)$$

$$A = (eK_B T/h) \exp(\Delta S^\ddagger(T)/R) \quad (4)$$

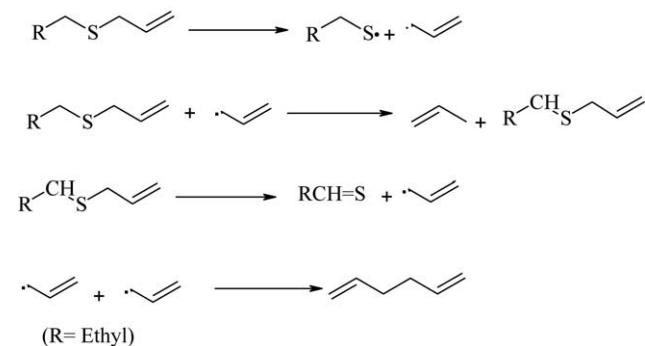
The natural bond orbital (NBO) analysis, which was suggested by Reed et al. [33,34] could be applied to determine the charges at the stationary points through the reaction.

## 3. Results and discussion

Two possible mechanisms have been suggested for the retro-ene reaction of APS in the gas phase: a free-radical reaction and concerted process. The first one may be started by the cleavage of the C4–S5 bond according to Scheme 2 following by a step-wise mechanism (for atom numbering see Scheme 3). The second possibility is a direct unimolecular splitting through six-center cyclic TS. The concerted reaction proceeds through the X1–C2 bond formation and C4–S5 bond cleavage, yielding the propene and *n*-propyl thioaldehyde.

The C4–S5 bond breaking is the rate-determining step in the former mechanism. The C4–S5 bond dissociation energy could be considered as the activation energy of this process from an energy point of view.

After full geometry optimization of the probable radicals, their energies were calculated by the unrestricted B3LYP (UB3LYP) level of the theory using the 6-311++G\*\*



Scheme 2.

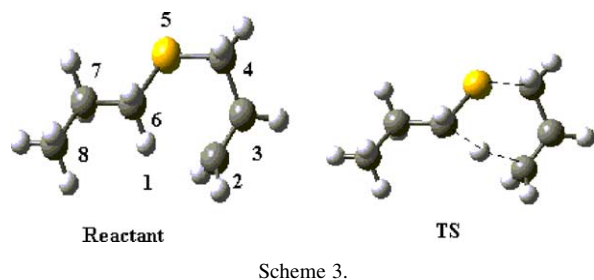


Table 1  
Calculated total energies in hartree for some probable radicals at the UB3LYP/6-311++G\*\* level ( $T=550.65$  K)

$C_3H_5$	$C_3H_5S$	$C_3H_7$	$C_3H_7S$
-117.27	-515.44	-118.50	-516.74

basis set. The results are shown in Table 1. Activation energy is found to be  $314.03 \text{ kJ mol}^{-1}$  for the APS pyrolysis. It is obvious that, it is much greater than the experimental value; so the step-wise mechanism is rejected. This brought our attention to the latter mechanism and the concerted mechanism was fully investigated.

During the retro-ene reaction, the X1–C2, C3–C4 and S5–C6 bond lengths decrease, whereas the X1–C6, C4–S5 and C2–C3 bond lengths increase.

Selected geometric parameters for the reactant and the TS are reported in Table 2, according to atom numbering on Scheme 3. The comparison between the H1–C2 and C4–S5 bond lengths in the TS with the same one in the reactant indicates that the H1–C2 bond formation occurs faster than the C4–S5 bond splitting. Accordingly, the new bond formation occurs via a slightly asynchronous mechanism in the concerted reaction.

The B3LYP/6-31G\* results for the reaction path is shown in Fig. 1. This figure demonstrates the energy including the ZPVE and thermal correction as a function of the reaction coordinate, H1–C2 bond length. It also

represents the minimum energy path, which connects the reactant to the products passing through the saddle point.

Table 3 shows the charge distribution in the reactant and the TS using the NBO analysis. The results at the TS indicate that a small positive charge developed on the H1 atom, while the C2 atom supports the electronic excess. The positive character of the H1 atom allows it to be attracted by negative character of C2 atom at the TS, which confirms the cyclic TS. On the other hand, the positive characters of the C3 and C4 atoms demonstrate that the H1–C2 bond formation is faster than the C4–S5 bond cleavage. This supports the asynchronous character of the reaction mechanism.

Imaginary vibrational frequencies for the TS were calculated. High magnitudes of these frequencies show that this point is associated with the light atom movement of H1 in the TS.

Dipole moments changes through the retro-ene reaction justify the greater polarity of the TS relative to the reactant. Considering the increase of the dipole moments from the reactant through the TS, one can confirm that the charge symmetry decreases for the TS in comparison to the reactant. This could be another reason for the existence of the concerted mechanism.

Thermodynamic properties for the reaction using the B3LYP/6-31G\* level of the theory are reported in Table 4. Calculated values show that the pyrolysis reaction is an endothermic process ( $\Delta H > 0$ ), the global process is spontaneous ( $\Delta G < 0$ ) and the entropy changes through the reaction is positive ( $\Delta S > 0$ ).

Calculated kinetic and activation parameters for the reaction at 550.65 K are listed in Tables 5 and 6, using the Eqs. (3) and (4). A comparison between the calculated activation energies shows that the  $E_a$  obtained from the B3PW91/6-311++G\*\* and B3LYP/6-31G\* are in good agreement with the experimental value. Considering the time cost for the calculations, the total time for computing

Table 2  
Selected geometric parameters for the Allyl *n*-propyl sulfide (R) and the TS in the gas phase, using the 6-31G\* basis set (distances in angstrom and dihedrals in degree)

Parameters	B3LYP (R/TS)	BLYP (R/TS)	B3PW91 (R/TS)	B3P86 (R/TS)
H1–C2	3.01/1.31	3.06/1.33	2.98/1.27	2.94/1.27
C2–C3	1.33/1.42	1.34/1.43	1.33/1.42	1.33/1.42
C3–C4	1.51/1.38	1.52/1.39	1.51/1.38	1.50/1.38
C4–S5	1.83/2.38	1.86/2.43	1.82/2.31	1.82/2.31
S5–C6	1.84/1.70	1.86/1.72	1.83/1.69	1.82/1.69
C6–C7	1.53/1.52	1.54/1.54	1.53/1.52	1.52/1.51
C7–C8	1.53/1.53	1.54/1.54	1.53/1.53	1.52/1.53
H1–C2–C3	79.89/99.37	79.67/99.57	79.60/99.91	80.24/100.01
C2–C3–C4	127.31/119.59	127.45/119.86	127.04/119.09	126.87/118.99
C3–C4–S5	117.60/98.18	117.74/97.56	117.44/98.33	117.27/98.34
C4–S5–C6	100.22/100.31	100.21/99.75	100.16/101.32	99.96/101.16
H1–C2–C3–C4	51.29/63.28	51.38/63.26	51.69/62.26	51.60/62.43
C3–C4–S5–C6	-73.86/44.68	-74.11/44.70	-73.92/48.20	-73.25/48.67

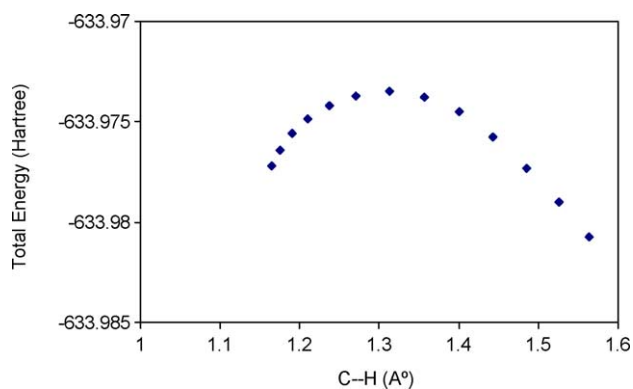


Fig. 1. Schematic energy profile of the PES for the APS pyrolysis (X=H) at the B3LYP/6-31G\* level.

Table 3

Distributed NBO charges on the APS and the TS at the B3LYP/6-311++G\*\* level

	H1	C2	C3	C4	S5	C6	C7
APS	0.24	-0.44	-0.23	-0.62	0.19	-0.58	-0.47
TS	0.26	-0.59	-0.22	-0.45	0.06	-0.53	-0.48

Table 4

Thermodynamic parameters for the reaction using the B3LYP/6-31G\* method at 273.15 K (X=H)

$\Delta H$ (kJ mol <sup>-1</sup> )	$\Delta S$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$\Delta G$ (kJ mol <sup>-1</sup> )
27.71	166.88	-22.04

Table 5

Calculated kinetic and activation parameters for the pyrolysis of APS at 550.65 K using the B3P86/B3PW91 methods (X=H,  $E_a$ ,  $\Delta H^\ddagger$  in kJ mol<sup>-1</sup> and  $\Delta S^\ddagger$  in J mol<sup>-1</sup> K<sup>-1</sup>)

Basis set	$E_a$	$\Delta H^\ddagger$	Log A	$-\Delta S^\ddagger$
6-31G*	152.32/154.50	147.74/149.92	11.70/11.97	26.07/20.85
6-31G**	150.44/152.54	145.86/147.97	11.85/11.87	23.11/22.76
6-31+G**	151.04/153.27	146.46/148.69	11.74/11.77	25.18/24.62
6-31++G**	151.07/153.33	146.49/148.75	11.75/11.78	25.05/24.51
6-311G*	152.22/154.41	147.64/149.84	12.01/12.02	20.19/19.84
6-311G**	150.24/152.32	145.66/147.74	12.01/12.03	20.05/19.81
6-311+G*	150.54/152.64	145.96/148.06	11.98/11.99	20.64/20.45
6-311++G*	150.56/158.84	145.99/154.26	11.99/11.96	20.48/21.03

Experimental values for the APS pyrolysis reaction taken from Ref. [22]:  $E_a = 157 \pm 2$  kJ mol<sup>-1</sup>, log A = 11.52 ± 0.16 (R=H).

Table 6

Calculated kinetic and activation parameters for the pyrolysis of APS at 550.65 K using the BLYP/B3LYP methods, respectively (X=H,  $E_a$ ,  $\Delta H^\ddagger$  in kJ mol<sup>-1</sup> and  $\Delta S^\ddagger$  in J mol<sup>-1</sup> K<sup>-1</sup>)

Basis set	$E_a$	$\Delta H^\ddagger$	Log A	$-\Delta S^\ddagger$
6-31G*	129.35/156.68	124.77/152.10	11.84/12.24	23.30/24.02
6-31G**	127.44/154.75	122.86/150.17	12.01/11.94	20.17/21.37
6-31+G**	128.64/155.66	124.06/151.08	11.88/11.82	22.68/23.73
6-31++G**	128.58/155.64	124.00/151.06	11.89/11.83	22.47/23.58
6-311G*	130.09/156.96	125.52/152.38	12.15/12.10	17.42/18.38
6-311G**	127.61/154.65	123.03/150.07	12.16/12.10	17.24/18.36
6-311+G**	128.39/155.25	123.82/150.67	12.13/12.07	17.72/18.91
6-311++G**	128.44/155.29	123.87/150.71	12.14/12.08	17.66/18.85

Experimental values for the APS pyrolysis reaction taken from Ref. [22]:  $E_a = 157 \pm 2$  kJ mol<sup>-1</sup>, log A = 11.52 ± 0.16 (R=H).

the frequency calculations at the TS using the B3PW91/6-311++G\*\* and B3LYP/6-31G\* are 37382 and 3959 s, respectively. So, it is better to use the quick and accurate B3LYP/6-31G\* method. This choice is accordance with the previous studies [5,13,35–37]. Nearly large differences in activation energies between the BLYP and the other DFT methods shows that the inclusion of the correlation of three-parameter hybrid functional is essential for describing this reaction quantitatively. Therefore, the matching of the theoretical and experimental values is remarkable.

Calculated activation energy of 159.25 kJ mol<sup>-1</sup> for deuterated APS pyrolysis at the B3LYP/6-311++G\*\* level confirmed that the X atom (H or D) transfer plays an important role in the reaction progress.

The magnitude of the calculated kinetic isotope effect for the reaction is 2.87 at 550.65 K, which indicates that the hydrogen is transferred extensively in the TS.

Some organic reactions such as acetates [38] and isopropyl carbonate pyrolysis [39], which proceed through the six-center cyclic TS, possess a value of  $2.7 \pm 0.2$  at 554.15 K and 2.6 at 673.15 K for deuterium kinetic isotope effect, respectively. Calculated value of 2.87 in this study is another reason for hydrogen migration in the TS and confirmed the concerted molecular mechanism.

A comparison between the calculated activation energy and the expected value for the bond dissociation energy of C<sub>3</sub>H<sub>5</sub>SC<sub>2</sub>H<sub>4</sub>CH<sub>2</sub>-H ( $E_a = 154$  kJ mol<sup>-1</sup> for the APS pyrolysis, whereas bond dissociation energy is

Table 7

Calculated activation energy for some retro-ene reactions at the B3LYP/6-31G\* level

Reactant	$E_a$ (kJ mol <sup>-1</sup> )	Reference
AllSAll	122.76	[8]
APS	156.68	This work
ABS	155.19	[37]
AMS	134.30	[40]

464 kJ mol<sup>-1</sup>) reveals that the reaction is highly concerted. More over calculated negative activation entropy indicates that APS pyrolysis proceeds through a concerted cyclic TS, which has been postulated experimentally [22].

Calculated activation energy for some gas phase retro-ene reactions of allylic organo-sulfur compounds are listed in Table 7. Diallyl sulfide (AllSAll) retro-ene reaction possesses the lowest activation energy that indicates that hydrogen atom at the TS has more acidic character than those in allyl *n*-butyl sulfide (ABS), allyl *n*-propyl sulfide (APS) and allyl methyl sulfide (AMS). The acidic character of the movable hydrogen is a consequence of the electronic effects of the substituent groups. *N*-propyl and *n*-butyl substituents induce a similar electron-donating effect. Therefore, the activation energy for the ABS and APS pyrolysis are nearly equivalent. The reported activation energy value for the AMS pyrolysis is less than APS and ABS ones which can be interpreted as a smaller electron-donating effect of methylene relative to the *n*-propyl and *n*-butyl substituents.

#### 4. Conclusion

The mechanism of the gas phase pyrolysis reaction of APS was examined at the DFT level and a valid reaction channel was established.

- The concerted and step-wise pathways for the system were calculated. The concerted mechanism is more favorable than the step-wise pathway.
- An analysis of the atomic charges suggests that the extension of the C4–S5 bond with the initial migration of the H1 atom at the TS can be seen as a driving force for the pyrolysis process. The positive charge appearing on the H1 atom at the TS allows it to be attracted by the negative character of C2 atom.
- The transition structure geometries obtained by different combination methods/basis sets present only slight structural differences.
- An analysis and comparison of the calculated and experimental kinetic and activation parameters confirm the validity of the theoretical approaches. A good quantitative agreement between the theoretical and experimental results is achieved at the B3PW91/6-311 + +G\*\* level.
- The calculated  $E_a$  with the combination B3LYP/6-31G\* is almost good. So, the use of the expensive basis set 6-311 + +G\*\* at the B3PW91 level is unnecessary for this type of calculation.
- APS retro-ene reaction can be described as an asynchronous concerted process.

#### Acknowledgements

The authors thank Dr M. R. Saeedi (Sharif University of Technology) and N. Zamani (Education Organization of Tehran), M. Harati (Sharif University of Technology), Dr A. H. Jahangir (Sharif University of Technology, Department of Computer Engineering) and B. Shirvani (Education Organization of Charmahal Wa Bakhteary) for helpful comments.

#### References

- J. Dubac, A. Laporterie, Chem. Rev. 87 (1987) 319.
- W. Oppolzer, V. Snieckus, Angew. Chem. Int. Ed. Engl. 17 (1978) 476.
- H.M.R. Hoffman, Angew. Chem. Int. Ed. Engl. 8 (1969) 556.
- S.N. Wang, C.A. Winkler, Can. J. Res. 21 (1943) 97.
- M.R. Gholami, M. Izadyar, J. Phys. Org. Chem. 16 (2003) 153.
- C.H. Dupuy, C.A. Bishop, C.N. Goeders, J. Am. Chem. Soc. 83 (1961) 2151.
- M.J. Molera, J.A. Lopez, J. Am. Chem. Soc. 54 (1958) 127.
- A.T. Blades, Can. J. Chem. 31 (1953) 418.
- J.A.L. Quiros, M.J. Molera, J. Am. Chem. Soc. 50 (1954) 851.
- A. Viola, J.J. Collins, J. Chem. Soc., Chem. Commun. 1980; 1247.
- J.D. Price, R.P. Johnson, Tetrahedron Lett. 26 (1985) 2499.
- S. Masamune, Tetrahedron Lett. 1965; 945.
- M.R. Gholami, M. Izadyar, Chem. Phys. 301 (2004) 45.
- K.N. Houk, J. Gonzalez, Y. Li, Acc. Chem. Res. 28 (1995) 81.
- H.B. Schlegel, in: K.P. Lawley (Ed.), Ab Initio Methods in Quantum Chemistry, Wiley, New York, 1987 pp. 249–286.
- B. Jursic, J. Mol. Struct. (Theochem.) 427 (1998) 165.
- B. Jursic, Z. Zdravkovski, J. Mol. Struct. (Theochem.) 309 (1994) 249.
- R.J. Loncharich, K.N. Houk, J. Am. Chem. Soc. 109 (1987) 6947.
- W. Kohn, L.J. Sham, Phys. Rev. 140 (1965) 1133.
- P. Hehenberg, W. Kohn, Phys. Rev. 136 (1964) 864.
- S. Borman, C & E News 1990; 22.
- G. Martin, M. Roper, Int. J. Chem. Kinet. 14 (1982) 605.
- M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery, R.E. Stratmann, 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. Pomelli, C. Adamo, S. Clifford, J. Chertski, G.A. Petersson, P.Y. Ayala, Q. Morokuma, K. Cui, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Ciolowski, J.V. Ortiz, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, J.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M.W. Gills, B. Johnson, W. Chen, M.W. Wong, J.L. Andres, M. Head-Gordon, E.S. Replogle, J.A. Pople, GAUSSIAN 98, Revision A.9, Gaussian Inc., Pittsburgh PA, 1998.
- A.D. Becke, Phys. Rev. A 38 (1988) 3098.
- C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 7885.
- J.P. Perdew, Y. Wang, Phys. Rev. B 45 (1992) 13244.

- [27] J.P. Perdew, Phys. Rev. B 33 (1986) 8822.
- [28] W.J. Hehre, L. Random, P.V.R. Schlegel, J.A. Pople, *Ab Initio Molecular Orbital Theory*, Wiley, New York, 1986.
- [29] H.B. Schlegel, C. Peng, P.Y. Ayala, M.J. Frisch, J. Comput. Chem. 17 (1996) 49.
- [30] K. Fukui, J. Phys. Chem. 74 (1970) 4161.
- [31] S. Glasstone, K.J. Laidler, H. Eyring, *The Theory of Rate Processes*, McGraw-Hill, New York, 1941.
- [32] K.J. Laidler, *Theories of Chemical Reaction Rates*, McGraw-Hill, New York, 1941.
- [33] A.E. Reed, L.A. Curtiss, F. Weinhold, Chem. Rev. 88 (1988) 899.
- [34] A.E. Reed, R.B. Weinstock, F. Weinhold, J. Chem. Phys. 78 (1983) 4066.
- [35] M.R. Gholami, M. Izadyar, J. Mol. Struct. (Theochem.) 672 (2004) 61.
- [36] L.J. Rodriguea, R. Anez, E. Ocando-Mavarez, J. Mol. Struct. (Theochem.) 536 (2001) 53.
- [37] M. Izadyar, A.H. Jahangir, M.R. Gholami, J. Chem. Res (s) 2004, in press.
- [38] D.J. Curtin, D.B. Kellom, J. Am. Chem. Soc. 75 (1953) 6011.
- [39] D.B. Bigley, C.M. Wren, J. Chem. Soc. Perkin Trans. 2 (1972) 1744.
- [40] G. Martin, M. Roperio, R. Avila, In the 10th International Symposium on Organic Chemistry of Sulfur (Abstracts of Reports), Bangor 1982 pp. A024.