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Ab Initio and DFT studies, NBO and NICS analysis of the structures and thermodynamic properties of the decomposition ([2+2] elimination) of 3-halo-2,3-dihydrophosphinine

Hossein Shirani Il Beigi*[,a] and Peyvand Ghanbarpour[b]

[a]*Young Researchers and Elites Club, Najafabad Branch, Islamic Azad University, Njafabad, Iran*
[b]*Young Researchers and Elites Club, Urmia Branch, Islamic Azad University, Urmia, Iran*

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Abstract: Decomposition of 3-fluoro2,3-dihydrophosphinine(**1**),3-chloro2,3-dihydrophosphinine(**3**), 3-bromo2,3-dihydrophosphinine(**5**) to phosphininewas investigated using ab initio Molecular Orbital (MO)and Density Functional Theory (DFT).For all HX(X=F, CL, Br)elimination reactions examined here,transition states have a four-centeredtransition structure. Study on the B3LYP/6-311+G** level of theoryrevealed that the required energy for the decompositionof compounds**1**, **3** and **5** to phosphinineis 31.23,28.91and 25.13(kcal mol^{-1}), respectively. HF/6-311+G**// B3LYP /6-311+G** calculated barrier height for the decomposition of compounds**1**, **3** and **5** to phosphinineare 58.62, 38.30, and 31.27(kcal mol^{-1}), respectively. Also, MP2/6-311+G**// B3LYP /6-311+G** results indicate that the barrier height for the decompositionof compounds**1**, **3** and **5** to phosphinineare47.86, 48.41, and 43.92 (kcal mol^{-1}), respectively.NaturalBond Orbital (NBO) population analysis and Nuclear Independent Chemical Shift (NICS) results showed that, reactants are non-aromatic but products of elimination reaction are aromatic, C-H and C-X bonds are broken and H-X bond is appear.

Keywords: DFT-B$_3$LYP, NBO, NICS, 3-Halo-2,3-dihydrophosphinine.

Introduction

Decomposition mechanism of 3-halo-2,3-dihydrophosphinines to phosphinine was investigated using ab initio Molecular Orbital (MO) and Density Functional Theory (DFT).The experimental study of the kinetic of dissociation process of 3-halo-2,3-dihydrophosphinines, showed that thedecomposition reactionof 3-halo-2,3-dihydrophosphinine is a unimolecular process (Scheme **1**) [1].

In this work, ab initio molecular orbital (MO),[2-6] DFT (B$_3$LYP) methods[7-8] and NBO analysis[9-12] were performed for the investigation of the pyrolysis reactions of 3-fluoro2,3-dihydrophosphinine(**1**),3-chloro2,3-dihydrophosphinine(**3**) and 3-bromo2,3-dihydrophosphinine(**5**) to phosphinine.

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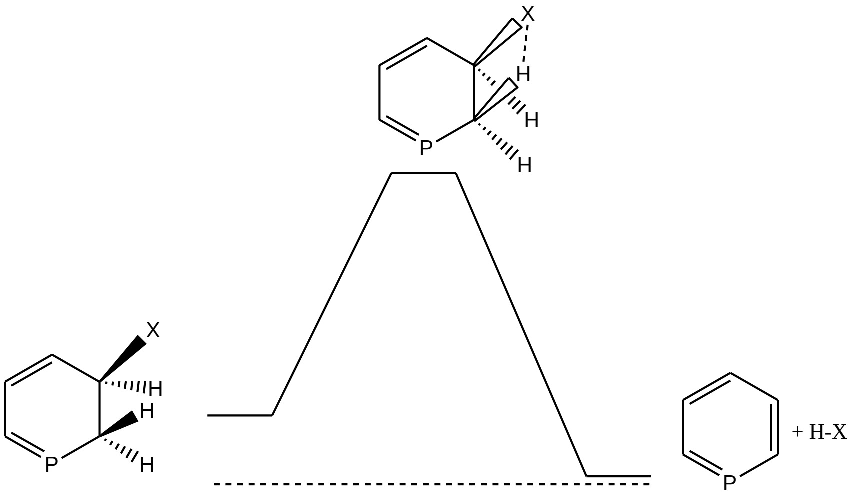
*Corresponding author. Tel: +983312441236; E-mail: shiranihossein@gmail.com

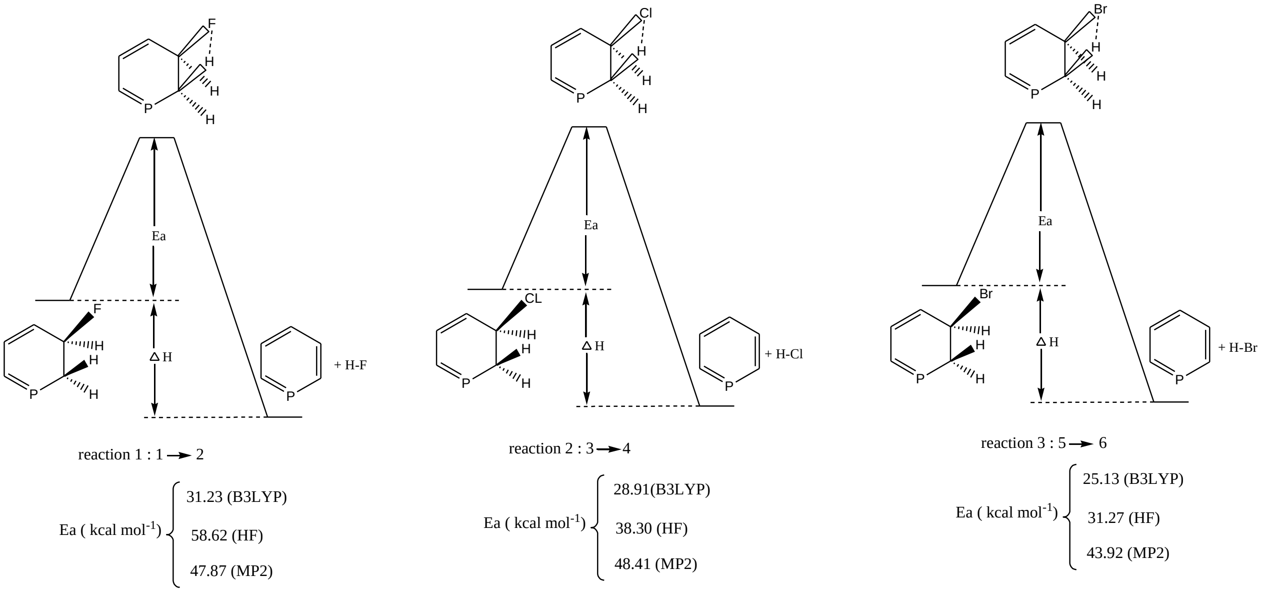


Scheme 1: X = F (**1**), CL (**3**) and Br (**5**)

Results and discussion

Zero point (*ZPE*) and total electronic (E_{el}) energies ($E_0 = ZPE + E_{el}$) for the energy minimum and energy maximum geometries of the decomposition of compound **1**, **3** and **5** to phosphinine as calculated on the B3LYP/6-311+G**//B3LYP/6-311+G** level of theory. For single-point energy calculations, both HF/6-311+G**// B3LYP /6-311+G**andMP2/6-311+G**// B3LYP /6-311+G**method were used and are given in Table **1**.

Studies on the B3LYP/6-311+G**, HF/6-311+G**// B3LYP /6-311+G**, and MP2/6-311+G**// B3LYP /6-311+G** of theory show that the barrier height of the decomposition of the compound **1** to phosphinine (reaction 1) is 31.23, 58.62and47.86 kcal mol^{-1}, respectively. These calculation results for compound **2** revealed that the barrier height of reaction 2 is 28.91, 38.30, and 48.41kcal mol^{-1}, respectively. Also, barrier height of reaction 3 is 25.13, 31.27, and 43.92 kcal mol^{-1}, respectively (Scheme **2**).



Scheme 2: B3LYP, HF and MP2 energy diagram of decomposition of compounds **1**, **3** and **5**.

It is well known that the strength of C-X bonds decreases, while the bond length increases with the size of halide atom. The lengths of C-F, C-CL and C-Br bonds determined were found to be 1.54, 1.92 and 2.14 Å, respectively, in agreement with energetic behaviorand other experimental data [13, 14].

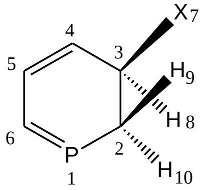


Figure 1:

C2-C3 bond lengths in reactants are greater than transition states and products in reactions 1-3 that showed that C2=C3 double bond formed in products (Table **2**). Also, Natural Bond Orbital (NBO) data revealed that electron population of C2-C3 bond in reactants is similar to single bond but in products is double bond (Table **3**).

Table1: Calculated Electronic Energies (E_{el}), Zero-Point Energies (*ZPE*) and Relative Energies ΔE_0 (in Hartree) for the energy minima structures of compounds **1-6** and transition structures of reactions 1–3

Method	B3LYP/6-311+G**				HF/6-311+G**// B3LYP /6-311+G**			MP2/6-311+G**// B3LYP /6-311+G**		
Geometry	*ZPE*	E_{el}	E_0	ΔE_0	E_{ele}	E_0	ΔE_0	E_{el}	E_0	ΔE_0
1	0.113	-347.654	-347.643	0.000 (0.000)^b	-347.776	-347.686	0.000 (0.000)^b	-348.823	-348.762	0.000 (0.000)^b
2	0.102	-347.876	-347.984	-0.032 (-28.388)^b	-347.825	-347.784	-0.082 (-26.684)^b	-348.895	-348.773	-0.059 (-32.376)^b
[1→2]$^\#$	0.099	-347.553	-347.364	0.052 (31.23)^b	-347.677	-347.578	0.106 (56.466)^b	-348.737	-348.617	0.071 (40.949)^b
3	0.122	-708.624	-708.643	0.000 (0.000)^b	-708.864	-708.718	0.000 (0.000)^B	-709.873	-709.715	0.000 (0.000) ^{b}
4	0.103	-708.157	-708.176	-0.856 (-34.684)^b	-708.854	-708.726	-0.083 (-29.059) ^{b}	-709.827	-709.783	-0.054 (-29.744) ^{b}
[3→4]$^\#$	0.101	-708.874	-708.073	0.039 (28.941)^b	-708.776	-708.642	0.054 (39.371) ^{b}	-709.752	-709.671	0.073 (43.063) ^{b}
5	0.131	-2827.071	-2825.967	0.000 (0.000)b	-2824.662	-2820.541	0.000 (0.000)b	-2820.675	-2820.541	0.000 (0.000)^b
6	0.102	-2827.135	-2825.026	-0.056 (-32.932)	-2824.751	-2820.682	-0.0448 (-29.364) ^{b}	-2820.725	-2820.674	-0.084 (-26.720) ^{b}
[5→6]$^\#$	0.099	-2827.027	-2825.942	0.046 (25.13) ^{b}	-2824.616	-2820.552	0.0534 (33.596) ^{b}	-2820.625	-2820.654	0.096 (38.993) ^{b}

[b] Numbers in parenthesis are the corresponding ΔE values in kcalmol^{-1}.

Table 2: Selected B3LYP/6-31+G** calculated bond lengths in angstrom for the energy minima structures of compounds **1-6** and transition structures of reactions 1–3

Bonds	1	[1→2]	2	3	[3→4]	4	5	[5→6]	6
C3-X7	1.407	1.995	-	1.894	2.694	-	2.048	2.894	-
C2 -H9	1.098	1.284	-	1.069	1.187	-	1.075	1.184	-
C2-C3	1.565	1. 495	1.338	1.584	1.469	1.371	1.559	1.468	1.393

Table 3: Selected B3LYP/6-31+G** calculated bond populations for the energy minima structures of compounds **1-6** and transition structures of reactions 1–3

Selected Bonds	Occupancy		
	Reactant	Transition state	Product
C3 – F7	1.986(σ)	–	–
C2 –C3	1.974(σ)	1.952(σ)	1.928(σ)&1.667(π)
C2–H9	1.963(σ)	1.736(σ)	–
C3 – Cl7	1.932(σ)	–	–
C2 –C3	1.907(σ)	1.991(σ)	1.910(σ)& 1.605(π)
C2 –H9	1.965(σ)	1.727(σ)	–
C3 – Br7	1.930(σ)	–	–
C2 –C3	1.938(σ)	1.960(σ)	1.951(σ)& 1.627(π)
C2 –H9	1.931(σ)	1.813(δ)	–

In order to understand the reason for the lower barrier height of reaction 3 in comparison to reaction 1 and 2, we have carried out natural charge (from NBO calculations)distribution for the ground state structures of compounds**1**, **3**, **5**andthe transition state structures of reactions 1–3.

Consequently, for such a drastic change in the charge distribution of halide and hydrogen atoms in the transition state structures of reactions 1, 2 and 3, the formation of the transition structure of reaction 3 is more favorable than reactions1 and 2, because of the larger variation of the charge distribution of the Br atom in the transition state structure of reaction 3.

Value of C2-C3-H9-X7 dihedral angles in transition state showed the planar structure for transition state. This form is the best structure for H-X dissociation. Internal dihedral angels in the heterocyclic structures of reactants and products revealed that reactants are non-planar (non-aromatic) but products are planar and aromatic (Table **1**). Natural Bond Orbital (NBO) population analysis and Nuclear Independent Chemical Shift (NICS) [15] results have a good agreement with calculated structural parameters.

At this point, it seems useful to remember some useful aspects concerning the NBO analysis, which was effectively used in this work. In the NBO analysis, the electronic wave functions are interpreted in terms of a set of occupied Lewis and a set of unoccupied non-Lewis localized orbitals. The delocalization of electron density between occupied Lewis-type (bond or lone pair) NBO orbitals and formally unoccupied(Anti-bond or Rydberg) non-Lewis NBO orbitals corresponds to a stabilizing donor-acceptor interaction, which is taken into consideration by examining all possible interactions between filled (donor) and empty(acceptor) orbitals and then evaluating their energies by second order perturbation theory.

Accordingly, the delocalization effects (or donor-acceptor charge transfers) can be estimated from the presence of off diagonal elements of the Fock matrix in the NBO basis. NBOs closely correspond to the picture of localized bonds and lone pairs as basicunits of the molecular structure so that is possible to conveniently interpretab initio wave functions in terms of the classical Lewis structure concepts by transforming these functions to NBO form. The interactions due to electron delocalization are generally analyzed by selectinga number of bonding and anti-bonding NBOs, namely, those relevant to the analysis of donor and acceptor properties. As a result, the NBO programsearches for an optimal natural Lewis structure, which has the maximum occupancy of its occupied NBOs, and in general agrees with the pattern of bonds and lone pairs of the standard structural Lewis formula. However, these orbitals suffer from small departures from the idealized Lewis structure, caused by interactions among them, which are known as hyperconjugative or stereoelectronic interactions. Therefore, the new orbitals are more stable than pure Lewis orbitals, stabilizing the wave function and giving a set of molecular orbitals equivalent to canonical molecular orbitals.

For each donor NBO (i) and acceptor NBO (j), the stabilization energy (E_2) associated with i→ j delocalization is explicitly estimated by following equation [11]:

$$E_2 = \Delta E_{ij} = q_i \frac{F^2_{(i,j)}}{ej\text{-}ei}$$

where q_i is the *ith* donor orbital occupancy, ε_i and ε_j are diagonal elements (orbital energies), and $F_{(i,j)}$ are off-diagonal elements, respectively, associated with the NBO Fock matrix.

Table 4: Selected B3LYP/6-31+G** calculated atomic charge for the energy minima structures of compounds **1-6** and transition structures of reactions 1–3

Selected Atoms	Natural Charge		
	Reactant	Transition state	Product
C3	-0.347	-0.338	0.050
C3	0.785	0.090	-0.347
F7	-0.407	-0.073	-0.553
H9	0.309	0.343	0.785
C3	-0.333	-0.307	0.078
C3	-0.330	0.047	-0.349
CL7	-0.009	-0.584	-0.447
H9	0.373	0.307	0.377

C3	-0.338	-0.308	0.748
C3	-0.383	0.038	-0.333
Br7	-0.073	-0.550	-0.043
H9	0.374	0.303	0.390

The NBO analysis of donor–acceptor interactions showed that the resonance energy $\pi_{C2-C3} \rightarrow \pi^*_{C4-C5}$and $\pi_{C2-C3} \rightarrow \pi^*_{N1-C6}$delocalization in phosphinine as product are 22.81 and 17.88 $kcal.mol^{-1}$, respectively. These electronic transitions disappear in reactant; therefore C-C bond in reactant is a single bond.

Nuclear Independent Chemical Shift (NICS) results at GIAO/B3LYP/6-311+G** level of theory revealed that phosphinine cycle is aromatic but all reactants are non-aromatic. NICS values in ring center, 0.5 and 1 angstrom upper than ring center are present at Table **5**. Nuclear Independent Chemical Shift (NICS) results showed that reactants are non-aromatic but products of elimination reaction are aromatic.

Table 5: Calculated NICS values at GIAO/B3LYP/6-311+G** and Magnetic susceptibilities at CSGT/B3LYP/6-311+G** level of theory for the energy minima structures of compounds **1-6** and transition structures of reactions 1–3

Compounds	X=F			X=CL			X=Br		
	1	1→4	4	3	3→4	4	5	5→1	1
NICS(0)	4.141	0.4404	-1.75	4.851	5.415	-7.311	3.173	7.887	-7.880
NICS(0.5)	-	-0.031	-0.447	-	4.358	-0.140	-	7.338	-10.017
NICS(1)	-	-4.471	-10.151	-	4.154	-10.318	-	5.185	-10.488
χ	-44.058	-44.10	-54.831	-57.137	-34.03	-74.808	-11.547	-40.30	-88.455

Theoretical Foundations

In this chapter we give the basic concepts of the non-relativistic quantum-mechanic theory, based on the information given in several books [16–19].The Schrodinger equation describes the wave function of a system:

$$H\,\Psi(\mathbf{r}, t) = i\hbar \frac{\partial \Psi(r,t)}{\partial t} \quad (1)$$

in this equation, *H* is the *Hamiltonian operator*, Ψ(*r*, *t*) is the wave function, ħ is the Planck's constant. The product of Ψ with its complex conjugate (Ψ*Ψ, often written as $|\Psi|^2$) is interpreted as the probability distribution of the particles of the system. The Hamiltonian consists of kinetic and potential energy terms:

$$H = T + V \quad (2)$$

The stationary eigenstates can be obtained from a solution of the simplified time independent Schrodinger equation:

$$H\,\Psi(r) = E\,\Psi(r) \quad (3)$$

Where *E* is the energy of the system. For a molecular system, Ψ is a function of the positions of the electrons and the nuclei within the molecule, which we will designate as *r*and *R*, respectively. The kinetic energy is a summation of ∇^2 over all the particles in the molecule:

$$T = -\frac{\hbar^2}{2}\sum_k \frac{1}{m_k}\left(\frac{\partial^2}{\partial x_k^2} + \frac{\partial^2}{\partial y_k^2} + \frac{\partial^2}{\partial z_k^2}\right) = -\hbar^2 \sum_k \frac{1}{m_k}\frac{1\nabla_k^2}{2} \quad (4)$$

And the potential energy results from the Coulomb interaction between each pair of charged entities:

$$V = \frac{1}{4\pi\varepsilon_0}\left(-\sum_i \sum_\alpha \frac{Z_\alpha e^2}{r_{i\alpha}} + \sum_i \sum_{j<i} \frac{e^2}{r_{ij}} + \sum_\alpha \sum_{\beta<\alpha} \frac{Z_\alpha Z_\beta e^2}{r_{\alpha\beta}} \quad (5)\right.$$

Where $r_{i\alpha}$ is the distance between the ith electron and the αth nucleus, $r_{ij}$the distance between the ith and jth electrons, $R_{\alpha\beta}$the distance between the nuclei α and β, e the charge of electron, and $Z_\alpha$the atomic number for atom α. In the Equation 5 the first term corresponds to electron-nuclear attraction, the second to electron-electron repulsion, and the third to nuclear-nuclear repulsion. Then we can write the Hamiltonian in the representation of atomic units as

$$H = -\sum_i \frac{\nabla_i^2}{2} - \sum_\alpha \frac{1}{M_\alpha}\frac{\nabla_\alpha^2}{2} - \sum_i \sum_\alpha \frac{Z_\alpha e^2}{r_{i\alpha}} + \sum_i \sum_{j<i} \frac{e^2}{r_{ij}} + \sum_\alpha \sum_{\beta<\alpha} \frac{Z_\alpha Z_\beta e^2}{r_{\alpha\beta}} \quad (6)$$

Where M_α is the mass of nucleus α.

The term ab initio is donated to estimation that is derived directly from theoretical principles, with no inclusion of experimental data. The most ordinary type of ab initio computation is called Hartree-Fock (HF), in which the primary approximation is called the mean field approximation .This means which the columbic electron – electron repulsion is not clearly taken into account, however, its average influence is comprised in the computation. In general, Ab initio method is available in macro model program. It is important to select a level which is well parameterized for the molecular system under survey. Accurate geometry coordinates and energy parameters are specifically significant in molecular systems since they control conformational inter conversions. Low-energy structures found on each surface were chosen and subjected to unrestrained quantum mechanical minimization utilizing HF/3-21G SCRF [20]. As a mean-field theory of solvent reaction to the solute electrostatic field, the dielectric continuum model removes the need for averaging over solvent configurations in salvation computations. Because of this powerful feature, the model has investigated to be particularly useful in biophysical applications and molecular modeling, even when applied to parameterized representations of the molecular charge distributions. (The reader is referred to a review by Sharp and Honig for a detailed discussion of the features of the model and its applications [21].

Another review by Tomasi and Persico[22] provides additional details regarding applications to *ab initio* computations. To assess the model's limitations however, it has been necessary to couple it to the most accurate representation attainable of solute charge distributions. This has been the central principle behind the development of all SCRF methods presently in utilize. These methods in general enable a quantum mechanical representation of a solute to be coupled to a dielectric continuum model of the solvent, so enabling *ab initio* solution phase computations to be carried out. The effect of the solvent continuum is depicted by a caused surface charge distribution placed at the solute-solvent dielectric boundary. The total quantum mechanical energy of the system can be inscribed as

$$E_s^{QM} = \langle \Psi^s | H^\circ | \Psi^s \rangle + \frac{1}{2} [\langle \Psi^s | H' | \Psi^s \rangle + H''] \quad (7)$$

where the gas phase Hamiltonian $H°$ is the one electron interaction with the reaction field is , the nuclear interaction with the reaction field is H', the nuclear interaction with the reaction filed is H'', and the solution phase wave function is Ψ^s. In the specific implementation conversed byTannor*etal*[23] and Marten *et al* [24]. The quantum mechanical charge density achieved from a solution to the gas phase or "free molecule" problem $H'= H''=0$ is depicted by a set of point charges centered on the atoms. The magnitude of the charges is computed by fitting the Coulomb potential they produce on a grid some finite distance from the molecule, to the full molecular electrostatic potential. This process is commonly referred to as electrostatic potential *(ESP)* fitting. The point charges are then utilized to solve the dielectric continuum problem. The source of the reaction field is represented as an induced surface polarization charge and is utilized to generate a first iteration of the H', H'' terms in the Hamiltonian. The modified quantum mechanical problem is solved to produce a new molecular charge density and the process is reiterated until convergence.

Conclusion

Ab initio HF, MP2, and B3LYP density functionaltheory calculations provide a picture from structural, energetic, and natural charge distributions points of view for the decomposition mechanismof compound **1**, **3** and **5** to phosphinine and HX(X=F, CL, Br).

B3LYP/6-311+G**//B3LYP/6-311+G**, HF/6-311+G**// B3LYP /6-311+G**, and MP2/6-311+G**// B3LYP /6-311+G** results reveal that a lower barrier height for reaction 3 than that of reactions 1 and 2. These results are justified by natural charge distributionvalues, calculated structural parameters and NBO results analysis in the ground-state structure of compounds**1**, **3** and **5**and transition state structures of reactions 1–3. NBO analysis revealed that resonance energies in products are greater than reactants. Therefore, number of conjugated π bond increased in products.Also, NICS results showed that reactants are non-aromatic but products are aromatic compounds.In conclusion, the calculated data could be considered as fairly acceptable and useful information from the QSAR point of view in the corresponding organic compounds, which are further confirmed by the corresponding energetic and structural results generated by the NBO analysisand NICS results.

Theoretical Methods

Ab initio calculations were carried out using B3LYP/6-311+G**, HF/6-311+G**// B3LYP/6-311+G**, and MP2/6-311+G**// B3LYP /6-311+G** levels of theory with the GAUSSIAN 98 package of programs [25] implemented on a Pentium–PC computer with a 7300 MHz processor. Initial estimation of the structural geometry of the compound 1, 3 and 5 were obtained by a molecular mechanic program PCMODEL (88.0) [26] and for further optimization of geometry, we used the PM3 method of the MOPAC 7.0 computer program [27]. The GAUSSIAN 98 package of programs were finally used to perform ab initio calculations at the B3LYP/6-311+G** level. Energy-minimum molecular geometries were located by minimizing energy, with respect to all geometrical coordinates without imposing any symmetrical constraints. The nature of the stationary points for compound 1, 3 and 5 and transition state structures has been fixed by means of the number of imaginary frequencies. For minimum state structure, only real frequency values, and in the transition-state, only single imaginary frequency values were accepted.The structures of the moleculartransition state geometries were located using the optimized geometriesof the equilibrium molecular structures according to the Dewarprocedure (keyword SADDLE). These geometry structures were reoptimized by the QST2 subroutine at the B3LYP/6-311+G** level. For further optimization, TS subroutine was used. The vibrational frequencies of ground states and transition states were calculated by FREQ subroutine.

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