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Ab initio and DFT studies on structure and stability of aliphatic aldoxime molecules

P. Kolandaivel*, K. Senthilkumar

Department of Physics, Bharathiar University, Coimbatore 641 046, India

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Abstract

Molecular structure and conformational stability of *anti* and *syn* conformers of some aliphatic aldoxime molecules $\text{RCH}=\text{NOH}$ ($\text{R} = \text{H}, \text{CH}_3, \text{NH}_2, \text{OH}, \text{F}$) have been studied by employing the ab initio and density functional theory (DFT) methods. The molecular geometries were optimized employing the MP2, BLYP, B3LYP levels of theory of ab initio and DFT methods implementing 6-31G* basis set. The geometrical parameters of *anti* and *syn* conformers of aldoximes have been discussed in the light of lone pair electrons presented in the atoms. The maximum hardness principle was used to study the conformational stability of the oxime molecules. The role of lone pair electrons in the chemical hardness values has been studied. The Mullikan population analysis has been performed to study the stability of the bond in the oxime molecules. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Aldoximes; Ab initio; Density functional theory; Principle of maximum hardness; Mullikan population analysis

1. Introduction

Oximes, oxime ethers and oxazines are found to be an important substrates in stereoselective carbon–carbon bond forming reactions. The oxime molecules play an important role in Beckmann rearrangement reaction. The aldoxime molecules $\text{RHC}=\text{NOH}$ ($\text{R} = \text{CH}_3, \text{NH}_2, \text{OH}, \text{F}$), are of a special interest since they are considered as prototype molecules for the general imine system $\text{R}_1\text{R}_2\text{C}=\text{NX}$, and are isomers of an important peptide system [1]. The quantum chemical calculations [2–5] and considerable number of experimental studies [6–10] on the structure of aldoximes have been reported. Since these molecules have more than one conformer, the quantum chemical

calculations for the conformational analysis of the oximes are very interesting and have received a lot of attention among theoretical chemists. Recently, the molecular structure and rotational potential energy surfaces of *E* and *Z* geometrical isomers of propionaldehyde oxime have been studied using the ab initio and density functional theory (DFT) methods [11], and arrived the following conclusions: (1) the determination of N–O bond length, i.e. adjacent to the atom with lone pair electrons is a difficult problem both in ab initio and DFT methods; and (2) the chemical hardness values of propionaldehyde oxime were unable to indicate the most stable conformer of the molecule. An attempt has been made to study the chemical hardness and chemical potential of isomers of $\text{XC}(\text{O})\text{X}$ ($\text{X} = \text{F}, \text{Cl}$), $\text{C}_2\text{H}_3\text{NO}$ and HCNC molecules and the hardness profiles of hydrogen bonding systems, $\text{HF}\cdots\text{HCN}$, $\text{HF}\cdots\text{HCl}$ and $\text{CH}_3\text{OH}\cdots\text{H}_2\text{O}$

* Corresponding author. Fax: +91-422-422387.

E-mail address: ponkvel@bharathi.ernet.in (P. Kolandaivel).

[12]. Similar types of studies have also been reported in the literature [13,14]. In most of the cases, the chemical hardness is found to be a good indicator for predicting the most stable isomer. The same conclusion, that the minimum energy conformer has the maximum hardness value, was obtained for the SiC_2 molecule [15]. Another interesting study on isomer stability using the maximum hardness principle (MHP) was made by us [16] and concluded that the MHP could not able to predict the stability of most of the positional isomeric molecules, because of the variation in the chemical potential and external potential, but for the most of geometrical isomers, the MHP was able to predict the most stable conformer of the molecules.

Nguyen and Ha [17] have studied the aldoximes by ab initio SCF techniques, employing the double-zeta (DZ) basis set. From the above study it was observed that the $\text{CH}_3\text{CH}=\text{NOH}$, $\text{FCH}=\text{NOH}$ oximes are more stable in *syn* conformer and $\text{NH}_2\text{CH}=\text{NOH}$, $\text{OHCH}=\text{NOH}$ oximes are more stable in *anti* conformer. The chemical hardness values have been calculated using the orbital energies of SCF techniques, and show that the *anti* conformer of $\text{CH}_3\text{CH}=\text{NOH}$ and $\text{NH}_2\text{CH}=\text{NOH}$ molecules are found to be more stable, and the same predict that the *syn* conformer of $\text{OHCH}=\text{NOH}$ and $\text{FCH}=\text{NOH}$ molecules are found to be more stable, which is one of the reasons for the present study. Goodman et al. [18,19] have studied the role of lone pairs in internal rotation barriers and concluded that oxygen σ lone pairs play an important role in controlling barrier heights. In the present investigation the emphasis have been given to study the role of lone pair electrons in determining the bond lengths and bond angles adjacent to the atoms having lone pair electrons. An attempt has also been made to study the role of lone pairs in chemical hardness and stability of the conformations.

2. Computational procedure

The computations were performed with GAUSSIAN 94 program [20]. The geometry of *anti* and *syn* conformers of all the considered aldoxime molecules were optimized using second order Møller–Plesset perturbation theory [21] and DFT methods. In DFT method, Becke's exchange functional [22] combined

with the gradient corrected functional of Lee–Yang–Parr (LYP) [23] and Becke's three-parameter exact exchange functional [24] combined with gradient corrected functional of LYP [23] were used by implementing the 6-31G* basis set. The same basis set was used for the MP2 level of theory also. The DFT parameters chemical hardness (η) and chemical potential (μ) have been calculated using the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) energies determined by the MP2/6-31G* level of theory. The chemical hardness (η) and chemical potential (μ) can also be expressed with an orbital basis as

$$\eta = \frac{I - A}{2} \quad \mu = -\frac{I + A}{2}$$

Where $I = -E_{\text{HOMO}}$ and $A = -E_{\text{LUMO}}$: I and A are the ionization potential and electron affinity of the molecules.

3. Results and discussion

Formaldoxime $\text{CH}_2=\text{NOH}$ and the *anti* and *syn* conformers of aldoximes $\text{RCH}=\text{NOH}$ ($\text{R} = \text{CH}_3$, NH_2 , OH , F) were optimized employing MP2/6-31G* level of theory of ab initio method and BLYP/6-31G*, B3LYP/6-31G* levels of theory of DFT method. The optimized structural parameters are presented in the Table 1 along with the microwave data for formaldoxime and acetaldehyde oxime molecules. The geometrical arrangements and labelling of atoms for the formaldoxime and *anti*, *syn* conformers of aldoximes are presented in Fig. 1.

The calculated geometrical parameters of formaldoxime are found to be in good agreement with the microwave data [6]. Nguyen and Ha [17] have calculated the bond angle $\theta(\text{N2O3H4})$ employing the DZ basis sets in the SCF method as, 106.7° but the experimental value is found to be 102.7° . In the present study the above angle is found to be 101.9° at MP2/6-31G* and 101.3° , 102.4° at BLYP/6-31G*, B3LYP/6-31G* levels of theory, respectively. The other structural parameters of formaldoxime in the above levels of theory are found to be in good agreement with the experimental values. The calculated bond lengths and bond angles of *anti* and *syn* conformers of acetaldoxime are found to be in good agreement with the

Table 1
Optimized geometrical parameters of aldoximes. (bond length in Å, bond angle in degrees)

Geometrical parameters ^a	HCH=NOH				CH ₃ CH=NOH												
	MP2		BLYP		B3LYP		Expt. ^b		MP2		BLYP		B3LYP		Expt. ^b		
	<i>Anti</i>	<i>Syn</i>	<i>Anti</i>	<i>Syn</i>	<i>Anti</i>	<i>Syn</i>	<i>Anti</i>	<i>Syn</i>	<i>Anti</i>	<i>Syn</i>	<i>Anti</i>	<i>Syn</i>	<i>Anti</i>	<i>Syn</i>	<i>Anti</i>	<i>Syn</i>	
(X = H,C)																	
R(C1–N2)	1.284	1.287	1.273	1.276	1.289	1.286	1.293	1.290	1.279	1.276	1.276	1.276					
R(N2–O3)	1.411	1.431	1.402	1.408	1.417	1.417	1.442	1.439	1.411	1.410	1.408	1.408					
R(O3–H4)	0.973	0.982	0.970	0.962	0.973	0.973	0.981	0.981	0.970	0.970	0.956	0.956					
R(C1–H5)	1.083	1.093	1.086	1.082	1.087	1.092	1.097	1.102	1.089	1.094	1.085	1.085					
R(C1–X6)	1.088	1.099	1.091	1.087	1.496	1.493	1.511	1.506	1.501	1.497	1.504	1.506					
R(X6–H7)	–	–	–	–	1.094	1.091	1.104	1.100	1.097	1.093	1.090	1.094					
R(X6–H8)	–	–	–	–	1.094	1.095	1.104	1.101	1.097	1.098							
R(X6–H9)	–	–	–	–	1.091	1.095	1.100	1.101	1.093	1.098							
<i>θ</i> (C1N2O3)	109.9	110.7	111.2	110.2	109.8	110.0	110.5	110.4	110.9	110.9	110.2	110.2					
<i>θ</i> (N2O3H4)	101.9	101.3	102.4	102.7	101.4	101.7	100.7	101.0	102.0	102.2	102.7	102.7					
<i>θ</i> (H5C1N2)	116.3	116.3	116.7	115.6	113.3	120.2	113.0	120.8	113.5	120.4	115.6	121.8					
<i>θ</i> (X6C1N2)	122.8	123.6	123.1	121.8	125.6	119.3	126.9	119.7	126.4	120.0	126.4	119.3					
<i>θ</i> (H7X6C1)	–	–	–	–	110.3	109.9	110.6	110.5	110.5	110.4	109.4	108.8					
<i>θ</i> (H8X6C1)	–	–	–	–	110.2	110.7	110.6	110.9	110.5	110.8							
<i>θ</i> (H9X6C1)	–	–	–	–	111.0	110.7	111.2	110.9	111.1	110.8							

Geometrical parameters ^a	NH ₂ CH=NOH						OHCH=NOH						FCH=NOH					
	MP2		BLYP		B3LYP		MP2		BLYP		B3LYP		MP2		BLYP		B3LYP	
	<i>Anti</i>	<i>Syn</i>	<i>Anti</i>	<i>Syn</i>	<i>Anti</i>	<i>Syn</i>	<i>Anti</i>	<i>Syn</i>	<i>Anti</i>	<i>Syn</i>	<i>Anti</i>	<i>Syn</i>	<i>Anti</i>	<i>Syn</i>	<i>Anti</i>	<i>Syn</i>	<i>Anti</i>	<i>Syn</i>
(X = N,O,F)																		
R(C1–N2)	1.292	1.287	1.299	1.295	1.285	1.280	1.288	1.282	1.295	1.286	1.280	1.274	1.274	1.274	1.280	1.280	1.266	1.265
R(N2–O3)	1.436	1.430	1.463	1.452	1.432	1.423	1.436	1.424	1.463	1.445	1.431	1.417	1.408	1.417	1.427	1.435	1.399	1.407
R(O3–H4)	0.972	0.972	0.979	0.980	0.968	0.969	0.972	0.972	0.979	0.981	0.968	0.969	0.973	0.973	0.982	0.981	0.970	0.970
R(C1–H5)	1.086	1.090	1.094	1.099	1.087	1.091	1.083	1.086	1.092	1.095	1.084	1.088	1.082	1.086	1.092	1.096	1.084	1.088
R(C1–X6)	1.377	1.389	1.389	1.399	1.376	1.387	1.347	1.353	1.259	1.365	1.343	1.350	1.341	1.339	1.354	1.349	1.336	1.333
R(X6–H7)	1.014	1.016	1.022	1.025	1.013	1.015	0.980	0.978	0.988	0.987	0.977	0.975	–	–	–	–	–	–
R(X6–H8)	1.011	1.014	1.020	1.023	1.010	1.013	–	–	–	–	–	–	–	–	–	–	–	–
R(X6–H9)	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
<i>θ</i> (C1N2O3)	108.1	108.8	108.4	109.2	109.0	109.7	107.4	109.3	107.5	110.1	108.1	110.5	111.5	108.5	112.3	109.5	112.6	110.1
<i>θ</i> (N2O3H4)	101.1	101.1	100.4	100.4	101.6	101.6	101.7	101.2	101.1	100.6	102.3	101.8	101.2	101.3	100.7	100.7	101.8	101.9
<i>θ</i> (H5C1N2)	115.8	122.2	115.7	122.9	115.9	122.3	118.6	125.3	118.6	126.0	118.7	125.3	120.4	127.2	119.9	127.7	120.4	127.1
<i>θ</i> (X6C1N2)	126.4	120.6	127.3	120.9	127.0	121.3	126.7	120.6	127.2	120.7	126.8	121.1	125.0	118.1	125.8	118.1	125.2	118.5
<i>θ</i> (H7X6C1)	113.7	112.3	113.7	112.5	114.3	113.1	105.9	106.7	105.4	106.4	106.3	107.2	–	–	–	–	–	–
<i>θ</i> (H8X6C1)	115.8	113.9	115.9	113.9	116.5	114.5	–	–	–	–	–	–	–	–	–	–	–	–
<i>θ</i> (H9X6C1)	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–

^a Labelling of atoms is shown in Fig. 1.

^b Experimental values taken from Refs. [6,10,25].

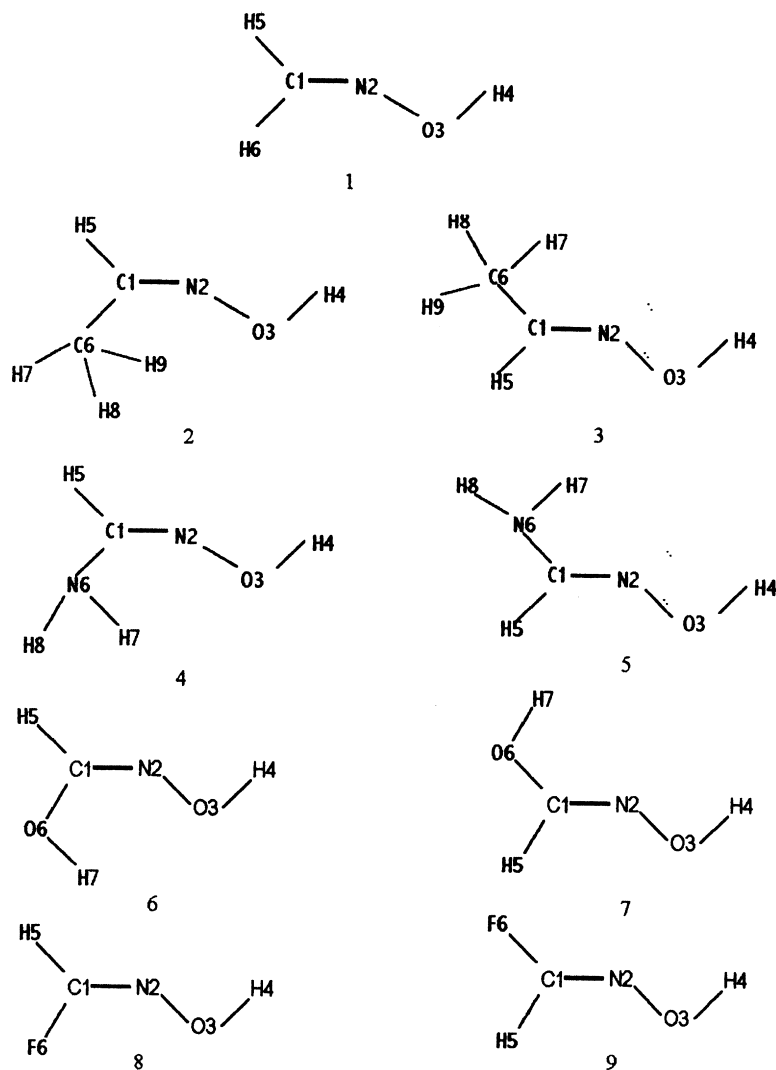


Fig. 1. Optimized geometrical arrangements and labelling of atoms of formaldoxime and the *anti* and *syn* conformers of the aldoximes.

experimental values [10,25]. The B3LYP/6-31G* level of theory of DFT method produced the bond lengths and bond angles much better than the MP2/6-31G* and QCISD/6-31G* [26] levels of theory and the differences between the theory and experiment is found to be very less. In the case of other aldoximes, except the bond length R(N2–O3) all the bond lengths are approximately same for *anti* and *syn* conformers. The large difference for N–O bond length (~ 0.01 Å) has been observed for the OHCH=NOH oxime in all the considered levels of theory of ab initio and DFT methods. It is noted that the B3LYP/6-31G* level of

theory of DFT method predicted the N–O bond length as 1.41 Å (approximately) for all the oxime molecules, which is in good agreement with the mean value of N–O bond length in the gas phase of oxime molecules. So the bond length adjacent to the atoms having lone pair electrons can be described better in B3LYP/6-31G* level of theory of DFT method.

It was observed that both the ab initio and DFT methods predict approximately the same bond angles for *anti* and *syn* conformer of aldoximes except the bond angles $\theta(\text{H5C1N2})$, $\theta(\text{X6C1N2})$ (X = C, N, O, F) and $\theta(\text{CNO})$. It is very interesting to study the

differences in $\theta(\text{CNO})$ angle between the *anti* and *syn* conformers of aldoximes. The above bond angle difference is found to be in the order for molecules as $\text{FCH}=\text{NOH} > \text{OHCH}=\text{NOH} > \text{NH}_2\text{CH}=\text{NOH} > \text{CH}_3\text{CH}=\text{NOH}$. This bond angle change is due to the lone pair electrons presented in the atoms of the molecules. In the case of $\text{FCH}=\text{NOH}$ oxime the above difference is found to be 3, 2.8 and 2.5° at MP2/6-31G*, BLYP/6-31G* and B3LYP/6-31G* levels of theory, respectively, and the *anti* conformer has the higher value of $\theta(\text{CNO})$ angle. This may be due to the fact that in the *anti* conformer the F and O atoms are in the same plane, and the repulsion between the lone pair electrons of the above atoms is more. Gilli et al. [27] has noted that the CNO angle of oximes are confined to a narrow interval ($111\text{--}114^\circ$). Glaser and Streitwieser [28] have obtained the CNO angle of E acetaldoxime isomer as 109.9° . In the present investigation MP2/6-31G* and DFT methods of higher levels of theory have predict the CNO angle very accurately than the lower levels of theory.

The angle $\theta(\text{H5C1N2})$ is found to be higher for the *syn* conformers compared with the *anti* conformers of all the considered aldoximes, and the difference is approximately 7° . The same difference has been noted for the angle $\theta(\text{X6C1N2})$, but the *anti* conformer has higher value. These bond angles differences are due to the attractions and repulsions of NOH group and the substitution groups of aldoximes. More specifically, the lone pair electrons present in the N, O atoms of NOH group attract the H atoms and repel the N, O and F atoms present in the substitution group due to the presence of lone pair electrons in the above atoms. These attraction and repulsion have changes the $\theta(\text{H5C1N2})$ and $\theta(\text{X6C1N2})$ angles. The same trend has been observed both in theoretical [11] and experimental [7,8] works of the propionaldehyde oxime molecule. Vejislava Paophristic et al. [18,19] have studied the role of lone pair electrons in internal rotational barriers of dimethyl ether (DME), protonated dimethyl ether (PDME), methanol and their sulfur analogs employing the combined natural bond orbital, symmetry decomposition of the barrier height and relaxation analysis, and demonstrated that the oxygen lone-pairs play an important role in controlling barrier heights and geometry of the system. In the case of DME the difference in angle $\theta(\text{H}_p\text{CO})$ between EE (eclipsed–eclipsed) and SS (staggered–

staggered) conformer was 4.5° whereas in the case of PDME the difference is very small (0.4°). The lone pair electrons in oxygen atom were tied up in the oxygen-proton bond in PDME, and so it leads to the small significance of the lone pair electrons in the structure and barrier height. The same fact has been observed in the methyl alcohol also in which the change in bond angle $\theta(\text{COH})$ between E and S conformers was 3.9° . In the present study the change in bond angles $\theta(\text{H5C1N2})$, $\theta(\text{X6C1N2})$ in all the aldoximes and $\theta(\text{CIN2O3})$ in $\text{FCH}=\text{NOH}$ aldoxime are due to the lone pair electrons presented in the constituent atoms. All the above studies describe only the quantitative explanation for the role of lone pair electrons in geometry and rotational barrier heights. The qualitative explanation and the adequate theories for the role of lone pair have to be developed for the better understanding of the chemical bond between the atoms having lone pair electrons.

Table 2 presents the total energy, dipole moment, and rotational constants of aldoximes determined by MP2/6-31G*, BLYP/6-31G* and B3LYP/6-31G* levels of theory. The total energy values which were calculated by the Nguyen Ha [17] using the DZ basis set at SCF theory show that the *syn* conformers of $\text{CH}_3\text{CH}=\text{NOH}$, $\text{FCH}=\text{NOH}$ oximes and *anti* conformers of $\text{NH}_2\text{CH}=\text{NOH}$ and $\text{OHCH}=\text{NOH}$ oximes were found to be more stable form. The crystallographic study of $\text{NH}_2\text{CH}=\text{NOH}$ oxime show that the *anti* conformer is the most stable form [9], and the ab initio SCF calculations employing lower level of theory show that the *anti* conformer of $\text{OHCH}=\text{NOH}$ is the most stable form [29]. In the present study, the MP2/6-31G*, BLYP/6-31G* and B3LYP/6-31G* levels of theory predict that the *anti* conformer of $\text{NH}_2\text{CH}=\text{NOH}$, $\text{OHCH}=\text{NOH}$ and $\text{FCH}=\text{NOH}$ molecules are found to be stable form and the relative energies between the conformers are given in Table 2. The *syn* conformer of $\text{CH}_3\text{CH}=\text{NOH}$ molecule is found to be the minimum energy structure at BLYP/6-31G* and B3LYP/6-31G* levels of theory and the relative energies are -0.40 and -0.39 kcal/mol, respectively, at the same time MP2/6-31G* level of theory favours the *anti* conformer, but the relative energy is very small (0.057 kcal/mol). The microwave data has predicted the *syn* conformer as the minimum energy structure with the relative energy as 1.47 kcal/mol [10,25]. In the present investigation, the ab initio

Table 2
Total energy E (in Hartree), Relative energy ΔE (in kcal/mol), Chemical hardness η (in eV), Chemical potential μ (in eV), Dipole moment μ_M (in Debye) and Rotational constants R_A , R_B , R_C (in GHz) of aldoximes (values given in parentheses are calculated from orbital energies taken from Ref. [17])

Parameters	HCH=NOH			CH ₃ CH=NOH						NH ₂ CH=NOH					
				MP2		BLYP		B3LYP		MP2		BLYP		B3LYP	
	MP2	BLYP	B3LYP	Anti	Syn	Anti	Syn	Anti	Syn	Anti	Syn	Anti	Syn	Anti	Syn
$-E$	169.31029	169.76716	169.80827	208.48433	208.48424	209.06178	209.06242	209.13078	209.13140	224.51492	224.50907	225.11460	225.10971	225.17309	225.16800
$\Delta E(E_{anti}-E_{syn})$	—	—	—	0	0.06	0	−0.40	0	−0.39	0	3.67	0	3.07	0	3.19
η	7.58 (7.10)	—	—	7.46 (7.49)	7.50 (7.42)	—	—	—	—	7.41 (7.07)	7.30 (6.95)	—	—	—	—
μ	−3.95	—	—	−2.95	−2.81	—	—	—	—	−2.03	−2.14	—	—	—	—
μ_M	0.627	0.087	0.130	0.900	1.071	0.552	0.599	0.556	0.613	2.167	2.131	1.948	1.868	1.935	1.865
R_A	66.51	66.15	68.68	17.02	45.13	16.85	44.67	17.28	45.91	18.79	51.57	18.46	50.87	19.05	52.69
R_B	11.82	11.52	11.81	6.67	4.23	6.42	4.13	6.57	4.22	6.98	4.41	6.76	4.31	6.91	4.40
R_C	10.03	9.81	10.08	4.94	3.96	4.79	3.88	4.90	3.96	5.11	4.08	4.97	3.99	5.09	4.08

Parameters	OHCH=NOH						FCH=NOH					
	MP2		BLYP		B3LYP		MP2		BLYP		B3LYP	
	Anti	Syn	Anti	Syn	Anti	Syn	Anti	Syn	Anti	Syn	Anti	Syn
$-E$	224.35813	224.35146	224.98894	224.98358	245.03719	245.03169	268.33076	268.32842	269.00082	268.99808	269.04186	269.03963
$\Delta E(E_{anti}-E_{syn})$	0.0	4.19	0.0	3.36	0.0	3.45	0.0	1.47	0.0	1.71	0.0	1.39
η	7.77 (7.62)	7.63 (7.67)	—	—	—	—	7.85 (7.69)	7.77 (7.77)	—	—	—	—
μ	−3.39	−2.65	—	—	—	—	−3.28	−3.36	—	—	—	—
μ_M	0.577	0.851	0.914	1.017	0.920	1.022	1.508	1.322	1.004	1.103	1.084	1.182
R_A	19.22	55.86	18.81	55.32	19.45	57.16	20.69	61.99	20.52	61.69	21.14	63.94
R_B	7.32	4.50	7.14	4.39	7.30	4.50	6.76	4.40	6.52	4.30	6.71	4.40
R_C	5.30	4.16	5.18	4.07	5.31	4.17	5.10	4.10	4.95	4.02	5.09	4.12

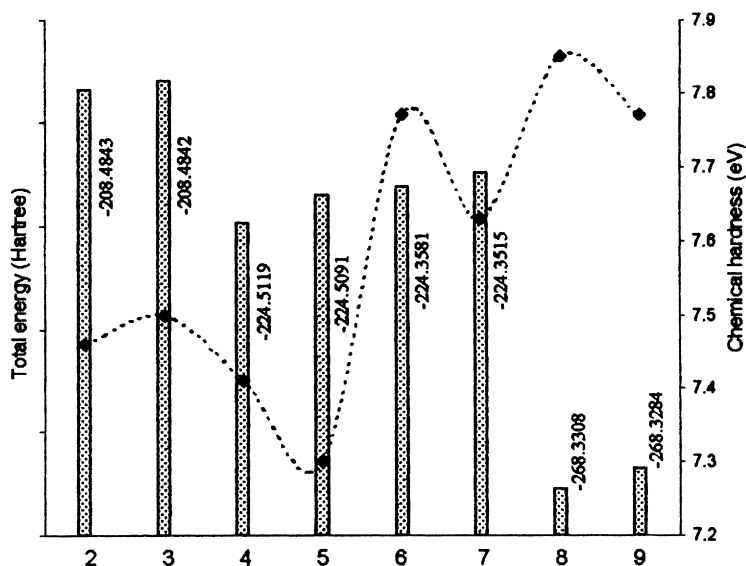


Fig. 2. Plot of the total energy and the chemical hardness calculated at the MP2/6-31G* level for the aldoximes: (□) total energy, (...) chemical hardness. In x-axis, numbers refer to the labels for oximes used in Fig. 1.

and DFT methods predict that the *anti* conformer of FCH=NOH oxime has the minimum energy and the relative energies are found to be 1.47, 1.71, 1.39 kcal/mol at MP2/6-31G*, BLYP/6-31G* and B3LYP/6-31G* levels of theory, respectively. The DZ basis set at the SCF theory has predicted that the *syn* conformer of FCH=NOH oxime is to be most stable form and the relative energy is -2.19 kcal/mol [17]. It is obvious that the lower level of theory could not able to predict the correct form.

The chemical hardness (η) and chemical potential (μ) have been calculated for formaldoxime and aldoximes using the orbital energies of the MP2/6-31G* level of theory and are presented in Table 2. So far no conclusive results have been arrived for the MHP and conformational stability. The most recent study reveals that the MHP able to predict the conformational stability for the geometrical isomers and the same could not able to predict for the positional isomers [16]. Nguyen and Ha have calculated the orbital energies and compared with the orbital energies obtained by photo-electron spectra of CH₂=NOH and CH₃CH=NOH molecules [17]. The total energies and chemical hardness for the *anti* and *syn* conformers of aldoximes have been plotted in the Fig. 2. For all the aldoximes except acetaldoxime

molecule, the chemical hardness able to predict the minimum energy structures. Even for acetaldoxime the energy differences between the *anti* and *syn* conformer is found to be very minimum and the chemical hardness difference is also very minimum. Again it has been confirmed that the MHP could able to predict the minimum energy structure of geometrical isomer.

In the present investigation, the interest has been shown to study the role of lone pairs in the conformational stability of a molecule. For the above purpose the three higher lying molecular orbitals energies were studied and were compared with the values of Nguyen and Ha and the experimental values. The calculated values agree well with the experimental values. The two lower ionization potentials which represent n-ionization (lone pair) and Π ionization (C=N) for the aldoxime molecules. The lowest ionization potential is due to Π ionization, and is represented as HOMO of the oxime molecules. The half of the gap between HOMO and LUMO represents the chemical hardness of the molecule. The chemical hardness and chemical potential were arises due to Π ionization and Π orbital of the oxime molecules except for the NH₂CH=NOH oxime where LUMO is σ orbital. It has been observed that LUMO of

Table 3
Charges of individual atoms in aldoxime molecules

Atomic charges ^a (X = H,C, N,O,F)	HCH=NOH		CH ₃ CH=NOH				NH ₂ CH=NOH				OHCH=NOH				FCH=NOH			
	MP2	B3LYP	MP2		B3LYP		MP2		B3LYP		MP2		B3LYP		MP2		B3LYP	
			<i>Anti</i>	<i>Syn</i>	<i>Anti</i>	<i>Syn</i>	<i>Anti</i>	<i>Syn</i>	<i>Anti</i>	<i>Syn</i>	<i>Anti</i>	<i>Syn</i>	<i>Anti</i>	<i>Syn</i>	<i>Anti</i>	<i>Syn</i>	<i>Anti</i>	<i>Syn</i>
C1	−0.13	−0.13	0.05	0.10	0.05	0.10	0.31	0.32	0.22	0.24	0.40	0.42	0.27	0.31	0.43	0.45	0.30	0.32
N2	−0.11	−0.10	−0.15	−0.17	−0.15	−0.16	−0.24	−0.25	−0.21	−0.23	−0.23	−0.27	−0.19	−0.23	−0.20	−0.19	−0.16	−0.16
O3	−0.61	−0.50	−0.62	−0.61	−0.51	−0.51	−0.65	−0.62	−0.54	−0.52	−0.66	−0.61	−0.55	−0.51	−0.59	−0.61	−0.49	−0.50
H4	0.46	0.41	0.46	0.45	0.41	0.41	0.46	0.45	0.41	0.41	0.47	0.46	0.42	0.41	0.47	0.47	0.42	0.42
H5	0.20	0.16	0.20	0.20	0.15	0.14	0.21	0.21	0.15	0.15	0.22	0.22	0.17	0.17	0.22	0.22	0.17	0.15
X6	0.20	0.15	−0.52	−0.53	−0.48	−0.49	−0.87	−0.85	−0.71	−0.71	−0.70	−0.70	−0.56	−0.56	−0.34	−0.34	−0.23	−0.23
H7	–	–	0.20	0.20	0.18	0.17	0.41	0.37	0.35	0.33	0.50	0.47	0.44	0.41	–	–	–	–
H8	–	–	0.20	0.18	0.18	0.16	0.37	0.36	0.32	0.32	–	–	–	–	–	–	–	–
H9	–	–	0.17	0.15	0.15	0.16	–	–	–	–	–	–	–	–	–	–	–	–

^a Labeling of atoms is shown in Fig. 1.

$\text{NH}_2\text{CH}=\text{NOH}$ oxime molecule is found to be higher than the LUMO of other aldoximes. Since the corresponding change has been occurred in the HOMO, the net chemical hardness value is found to be in the same range as in other oximes. It is important to note that the n-ionization due to the lone pair electrons are not involved in the calculation of the chemical hardness values. As observed in the results, the type of orbitals (σ or Π) and the role of lone pairs have no significant contribution to the chemical hardness and chemical potential values. In DME, the steric contact and the simultaneous rotation of methyl group increases the COC angle and in-turn increases the σ lone pair P character, which made significant contribution to the internal rotational barriers. But in the present case, the lone pair electrons have present only in the few atoms, which did not affect the chemical hardness and chemical potentials of the molecules. Still it may be an interesting subject if one could explore the relevant informations for the atomic chemical hardness using the lone pairs.

The calculated dipole moments for the aldoximes at MP2/6-31G*, BLYP/6-31G* and B3LYP/6-31G* levels of theory are presented in Table 2. The calculated dipole moment values for formaldoxime and anti, *syn* conformers of acetaldoxime at MP2/6-31G* level of theory are 0.63D and 0.90D, 1.07D, respectively, which were agrees well with the experimental values obtained from the stark effect [10,25,30]. The BLYP/6-31G* and B3LYP/6-31G* levels of theory underestimated the dipole moment values. In general for all the considered aldoximes, the dipole moment calculated by DFT methods are found to be lower than the values calculated by the MP2 method. The calculated rotational constants R_A , R_B , and R_C of the aldoximes were summarized in the Table 2. Theoretical rotational constants of formaldoxime and acetaldoxime agree well with the experimental values obtained by the microwave data [6,10,25].

Table 3 provides the charge of the individual atoms of aldoximes calculated by the MP2 and B3LYP methods. The tabulated values show that the atomic charges calculated by the MP2/6-31G* and B3LYP/6-31G* levels of theory are found to be approximately same. In general the atomic charges of individual atoms are strongly affected by the different substituents. The two lone pair electrons of oxygen atom in NOH group attract more charges from the

hydrogen atom to form a bond. So the oxygen atom has more negative charges than the other atoms. The net atomic charge of the nitrogen, oxygen and hydrogen atoms in the NOH group are found to be only very small differences for the different substitutions. Nguyen and Ha reported that the ionization potentials are strongly affected by the substitution [17]. The single lone pair electrons of the nitrogen atom attract less energy from the carbon atom (C1) during the bond formation. Generally the n-ionization (due to lone pairs) is very stronger than the Π ionization (which is found in the $\text{C}=\text{N}$ bond). It is very interesting to study the charge of nitrogen (N2) and oxygen (O3) atoms, which are playing dominant role in the structure of aldoximes. In the case of $\text{FCH}=\text{NOH}$ oxime the above two atoms are more negatively charged in the *anti* conformers compared with *syn* conformer. For all the other aldoximes the above atoms are more negative in the *syn* conformer compared with the *anti* conformer. So the lone pair electrons contribute to the chemical binding.

4. Conclusions

The ab initio and DFT studies have been performed on aliphatic aldoxime molecules to obtain the molecular structure and conformational stability of the molecules. Bond length adjacent to the atoms having lone pair electrons described better in B3LYP/6-31G* level of theory of DFT method. The geometrical parameters, especially related with N and O atoms have show some marked differences between *anti* and *syn* conformers of aldoximes due to the lone pair electrons. Maximum hardness principle could able to predict the stable conformation of aldoximes. The n-ionization, which is due to the lone pair electrons do not have any significant contribution to the chemical hardness values.

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