Int. J. Mol. Sci. **2006**, *7*, 289-319

International Journal of
Molecular Sciences
ISSN 1422-0067

www.mdpi.org/ijms/

A Quest for the Origin of Barrier to the Internal Rotation of Hydrogen Peroxide (H_2O_2) and Fluorine Peroxide (F_2O_2)

Dulal C. Ghosh

Department of Chemistry, University of Kalyani, Kalyani-741235, India
Email: dcghosh1@rediffmail.com, Fax: +91-33 25828282

Received: 2 July 2006 / Accepted: 24 July 2006 / Published: 25 August 2006

Abstract: In order to understand the structure-property relationship, SPR, an energy-partitioning quest for the origin of the barrier to the internal rotation of two iso-structural molecules, hydrogen peroxide, H_2O_2, and fluorine peroxide, F_2O_2 is performed. The hydrogen peroxide is an important bio-oxidative compound generated in the body cells to fight infections and is an essential ingredient of our immune system. The fluorine peroxide is its analogue. We have tried to discern the interactions and energetic effects that entail the nonplanar skew conformation as the equilibrium shape of the molecules. The physical process of the dynamics of internal rotation initiates the isomerization reaction and generates infinite number of conformations. The decomposed energy components faithfully display the physical process of skewing and eclipsing as a function of torsional angles and hence are good descriptors of the process of isomerization reaction of hydrogen peroxide (H_2O_2) and dioxygen difluoride (F_2O_2) associated with the dynamics of internal rotation. It is observed that the one-center, two-center bonded and nonbonded interaction terms are sharply divided in two groups. One group of interactions hinders the skewing and favours planar cis/trans forms while the other group favours skewing and prefers the gauche conformation of the molecule. The principal energetic effect forcing the molecules into the nonplanar gauche form is the variation "O–O' bond energy with torsion in both the molecules. It is demonstrated that the barrier is not a regional effect rather it is made by the conjoint action of all one- and two-center bonding and nonbonding interactions comprising the entire framework of the molecule. The present study claims to reveal one amazing feature of non-bonded interactions. Computed results of nonbonding interactions demonstrate that the nature of interaction between two formally positively charged non-bonding H atoms ($H^{\delta+}$----$H^{\delta+}$) is not always repulsive and it is attractive as well; the nature of the non-bonding interaction between formally negatively charged atom ('O') and formally positively charged ('H') atom, ($O^{\delta-}$----$H^{\delta+}$), is not always attractive but repulsive too; it is also demonstrated

that the nature of the nonbonding interaction between strongly electronegative atoms, ($F^{\delta-}$---$F^{\delta-}$), is not always repulsive and it may be attractive as well.

Keywords: Origin of Barrier, Energy partitioning, QSPR–QSAR descriptors, Hydrogen peroxide therapy.

1. Introduction

Hydrogen peroxide has been used as an antiseptic and anti-bacterial agent for many years. Recent researchers are amazed with many benefits of hydrogen peroxide and a new therapy called 'hydrogen peroxide therapy' has evolved with time. It is also opined that hydrogen peroxide, produced within individual body cell, is essential for life to fight infection. Bio-oxidative therapies are small amounts of diluted ozone and or hydrogen peroxide for the prevention and treatment of disease. Adherents consider it as one of the greatest healing miracles of all time. It is even considered as a potential anti-cancer drug in alternative medical system [1-4]. It is widely accepted that the property and structure are intimately related. There is no unique single effect, which determines equilibrium structure of a molecule. However, quantum chemical descriptors like symmetry type and energies of the frontier orbitals ($\varepsilon_{HOMO,}\varepsilon_{LUM}$), energy gap between frontier orbitals, global hardness, global softness, chemical potential and electronegativity are invoked to relate structure and property of molecules. Although there is no unique correlation of structure and properties, the structure and property are webbed together. Present day science has gone to the molecular level to understand the mechanism of drug action, bacterial activity, mechanism of body's defense and immune systems. Scientists are now in search of molecular descriptors as mathematical values that describe the shape and activity and properties of molecules. This efforts generates QSPR and QSAR modules which are integral to the rationale of drug design cycle. The QSPR and QSAR assume that the bio-physico-chemical activity is correlated with the chemical structure. However, to predict the structure and property relationship, it is essential that the electronic structure of a molecule and the forces operating there are properly explored. Although there are efforts to correlate the properties and reactivity of a molecule in terms of its equilibrium shape, a molecule hardly exists in its static equilibrium structure. The physical process of the dynamics of internal rotation initiates the isomerization reaction and generates infinite number of conformations. Some energy barrier to internal rotation separates the isomers. The quest for origin of the barrier to the internal rotation of molecules is an ever enticing and intriguing problem of theoretical chemistry. Although the present day quantum chemistry can measure the barrier height very accurately, the origin and the development of the barrier are still eluding [5,6,7]. The conformations have critical effect on bioactivity and reactivity on the stereo chemical outcome of many reactions. Thus, an understanding of the relative energies and the mechanism of the evolution of conformational populations will enable more reasonable predictions concerning reactivity, stereochemistry, and product distribution in reaction [8]. Thus information as to the origin of barrier to internal rotation within a molecule is of interest to theoretical, experimental and biological chemists. It appears from the survey of literature on the origin of barrier to internal rotation of molecules that majority of workers believe that it is a regional effect and barrier originates from some mystic reason. The physical process

of generation of Cis ⟷ Trans and Staggered ⟷ Eclipsed conformers is in fact a rotational isomerization process and can be viewed as resulting from reorganization and redistribution of electron density among the atoms in a molecule, so that the total number of electrons is conserved even though there may be an intramolecular charge transfer process [9,10]. Thus the physical process of the dynamics of internal rotation initiates the isomerization reaction, which generates infinite number of conformations between the extreme conformations stated above. We [11] have demonstrated, by a density partitioning analysis, that no new force is appearing during the physical process of evolution of molecular conformations rather the forces responsible for molecular binding and antibinding are deciding the conformational behaviour. The efficacy of Pople's [12,13] approximate SCF theory to compute the conformational isomers is well demonstrated [14,15]. It was also demonstrated that, in the context of study of molecular conformations of hydrogen peroxide, that Pople's approximate method, compared to *ab initio* methods, was more reliable in computing the conformational isomers [16-19]. However, in the present day scenario of computational chemistry, the sophisticated methods can be easily invoked to calculate the barrier heights very accurately. But, perhaps, Pople's approximate SCF method is the only method that provides with a scope of decomposition of the total energy into one- and two-center components and such components can be further decomposed into meaningful physical components. Although, more recently, there are also claims of partitioning the total SCF energy into one- and two center components in ab initio methods [20], but such fuzzy atom dissection of total energy appears to calculate the total one- and two-center interaction energies only and decomposition of such energy terms into meaningful physical components are, probably, yet to be furnished [20]. We have recently demonstrated that the Pople's energy partitioning scheme can be invoked in the significant elucidation of the origin of the barrier to the physical process of inversion [21,22] and intramolecular rotation [23,24], and such an effort is a meaningful venture. In the present venture, we shall invoke the energy partitioning scheme of Pople in the elucidation of the origin of barrier to internal rotation of hydrogen peroxide (H_2O_2) and its analogue fluorine peroxide (F_2O_2). It is well known to the chemists that both hydrogen peroxide and fluorine peroxide have two barriers –cis barrier and trans barrier, and the equilibrium conformations are non-planar skew conformation instead of expected trans form. The fact that the equilibrium geometries of the molecules are not the trans form rather a non-planar skew form, is itself an intriguing phenomenon and a clear departure from a normal behaviour of the phenomenon of structural isomerism of chemistry. But why the preferred conformations of the molecules are the non-planar gauche forms and not the usual trans forms and also the origin of barrier are required to be completely elucidated. It seems that there is yet no theoretical correlation of the preferred conformations and the origin of barrier of the instant molecules. In the above premise, we propose to make a detailed study of the elucidation of the origin of barrier and justifying the preferred conformations of the hydrogen peroxide and fluorine peroxide molecules in terms of the energy partitioning analysis in the present investigation.

2. Method of Computation

2.1 Coordinate System

The Z-axis is made coincident with the 'O–O' bond of both the molecules and we start with the eclipsed (cis) form of the molecule and then keeping one 'O–H' / 'O–F' bond fixed we rotate the other 'O–H' / 'O–F' bond through certain dihedral angle to generate a new conformation and the process of torsion is continued up to 180° till the trans conformation is generated. We follow the geometry optimization technique, GOT, and the geometric parameters of all the generated conformations are optimized invoking Pople's [12] approximate self-consistent field method. Standard parameters [13] and STO basis set are used. The coulomb and overlap integrals are evaluated through the explicit formulae laid down by Roothaan [25]. The total energy, the gross atomic charges are computed for each conformation at its optimized geometry. The energy-partitioning program is then invoked to decompose the total energy of each conformation according to the following scheme.

2.2 Necessary Algorithm

The energy-partitioning algorithm due to Pople [13], Fischer and Kollmar [26]

The total energy of a system is

$$E = \sum_{A} E_A + \sum_{A} \sum_{A<B} E_{AB} \quad (1)$$

where E_A are monatomic terms and E_{AB} are diatomic terms. Fischer and Kollmar [26] decomposed further the monatomic terms E_A and the diatomic terms E_{AB} into physically meaningful components as follows:

The physical components of the one-center terms are:

$$E_A = E^U_A + E^J_A + E^K_A \quad (2)$$

where E^U_A, E^J_A and E^K_A are total monatomic orbital energy, electron- electron repulsion energy, and non -classical exchange energy respectively.

The physical components of the two-center terms are:

$$E_{AB} = E^R_{AB} + E^V_{AB} + E^J_{AB} + E^K_{AB} + E^N_{AB} \quad (3)$$

The superscripts characterize the physical nature of the energy terms. The monatomic terms E^U_A, E^J_A and E^K_A and the diatomic terms E^R_{AB} , E^V_{AB} ,E^J_{AB} , E^K_{AB} , E^N_{AB} can be conveniently classified as one electronic energies and electronic interaction energies as follows: The explicit expressions are laid down below:

The explicit formulae of one– center terms are:

$$E^U_A = \sum_{\mu \in A} P_{\mu\mu} U_{\mu\mu} \quad (4)$$

where E^U_A is the total one-electron energy, $P_{\mu\mu}$'s are elements of bond order matrix and $U_{\mu\mu}$ is the one–

electron energy of μ th atomic orbital, AO, in the isolated atom.

$$E^J_A = ½ (P_A^2 \gamma_{AA}) \quad (5)$$

$$\text{where } P_A = \Sigma P_{\mu\mu} \quad \mu \in A \quad (6)$$

and γ_{AA} is electron-electron repulsion between the two electron of the same atom A. E^J_A is the repulsion of electrons on atom A.

The non-classical exchange energy E^K_A is

$$E^K_A = -1/4\, \gamma_{AA} \Sigma \Sigma P^2_{\mu v} \quad \mu \in A, v \in A \quad (7)$$

where γ_{AA} is the electron-electron repulsion between two electrons on atom A and $P_{\mu v}$ are elements of charge density and bond order matrix.

The physical meaning and explicit formulae of the two-center terms are as follows:

The two-center resonance term, E^R_{AB}

$$E^R_{AB} = \Sigma \Sigma P_{\mu v} \beta_{\mu v} S_{\mu v} \quad \mu \in A , v \in B \quad (8)$$

where $S_{\mu v}$ is the overlap of the STO's μ and v, $\beta_{\mu v}$ is a parameter which is dependent on the types of orbital μ and v . The $P_{\mu v} S_{\mu v}$ are the components of overlap population.

The E^R_{AB} mathematically and physically signifies the contribution of the resonance integrals to the energy of the A–B bond and is the principal feature of covalent bond.

The two-center potential attractions:

$$E^V_{AB} = –P_A .V_{AB} – P_B V_{BA} \quad (9)$$

where V_{AB} is the potential of an electron on atom A in the field of nucleus B and V_{BA} is the potential of an electron on atom B in the field of nucleus A.

We use the definition

$$P_A = \Sigma P_{\mu\mu} \quad \mu \in A$$

where $P_{\mu\mu}$ are elements of density matrix already stated above.

The two-center coulomb repulsion term, E^J_{AB} is

$$E^J_{AB} = P_A P_B \gamma_{AB} \quad (10)$$

γ_{AB} is the electronic repulsion between an electron on atom A and an electron on atom B;

The two-center exchange interaction term, E^K_{AB} is

$$E^K_{AB} = -1/2\ \gamma_{AB} \sum_{\mu \varepsilon A} \sum_{\nu \varepsilon B} P^2_{\mu\nu} \quad (11)$$

The Nuclear Repulsion Energies, E^N_{AB}

$$E^N_{AB} = Z_A Z_B / R_{AB} \quad (12)$$

where Z_A and Z_B are the nuclear charges of atoms A and B respectively, and R_{AB} is the distance between two nuclei and E^N_{AB} is thus representing the nuclear-nuclear repulsion energy of the nuclei A and B.

We further note that the sum the three terms $E^J_{AB} + E^N_{AB} + E^V_{AB}$ is the net electrostatic effect. We may further note that E^K_A and E^K_{AB} are the corresponding one-center and two-center terms for the electronic exchange interactions. The term E^K_{AB} defines the total non-classical exchange energy arising out of quantum mechanical exchange effect between electrons of A and B.

3. Results and Discussion

3.1 Hydrogen Peroxide, H_2O_2

Hydrogen peroxide, H_2O_2, is one of the chemical systems whose conformational isomerism are most widely studied. The molecule is iso-electronic with ammonia borane and ethane but structurally different from the formers. Experimentally [27,28] the molecule has a non-planar gauche [29] conformation about midway between the less stable planar trans and cis isomers. The molecule has two barrier heights to internal rotation via either the cis or the trans conformations. The height of the barrier is quite unusually high [7,30]. The physical process of conformational isomerism of the hydrogen peroxide molecule occurs by either clock wise or anti clockwise rotation of one part of the molecule with respect to the other part around the 'O–O' bond. The optimized geometric parameters of all the generated conformations are presented in Table 1 with the corresponding dihedral angles. The computed total energy, the gross atomic charges are presented in the Table 2. The calculated the one- and two-center bonding and nonbonding interaction energies and their physical components of each conformation and are presented as a function of torsional angle in Tables 3 - 7. The computed data are plotted in diagrams extensively for a better understanding of the position exhibited by the relevant numerical values of the physical quantities.

The total energy is plotted, as a function of dihedral angles, in Figure 2 and this is in fact the potential energy diagram of the hydrogen peroxide molecule. Table 2 and Figure 2 demonstrate that the preferred conformation of hydrogen peroxide is the nonplanar gauche or skew form; the dihedral angle i.e. angle between planes contained by H–O–O and O–O–H parts ,of the minimum energy conformation is 88.3^0; the length of the 'O–O' bond is shorter than the experimental bond length. We have depicted the equilibrium geometry of the molecule in Figure 1. While the Figure 1 is compared with experimental equilibrium conformation depicted by Douglas [3] et al, it is evident that, except 'O–O' bond length, the Figure 1 is the nice representation of the equilibrium conformation of hydrogen

peroxide molecule. From Table 2 and Figure 2 it is also evident that the hydrogen peroxide has three extreme conformations–cis, trans, and gauche corresponding to the dihedral angles of 0^0, 180^0 and 88.3^0 having the stability order – gauche > trans > cis. Figure 2 distinctly demonstrates that the minimum energy conformation of the molecule is non- planar gauche form and the trans form is closer than the cis form to the gauche form. This reveals that the molecule has two barrier heights –cis barrier and trans barrier; and since the trans form is closer to the gauche form, the trans barrier should be smaller than the cis barrier. The evaluated trans barrier is 2.23 kcal/mole and the cis barrier is 5.13 kcal/mole. The corresponding experimental [1,2] values are 1.1 and 7.0 kcal/mole. Veillard [17] pointed out that the best *ab initio* calculation on hydrogen peroxide is the calculation of Kaldor and Shavit [7] and the corresponding barrier heights evaluated by this calculation are 2.2 and 11.8 kcal/mole. One more important aspect to note in the connection of torsional dynamics of the molecule is the charge density reorganization as a function of dihedral angle. As torsion starts from the eclipsed cis form, the charge density on O atom starts decreasing and that on H atom starts increasing and the trend continues till the conformation is nearing the equilibrium gauche form is reached and thereafter the trend of the noted charge density reorganization takes a turn and it is reversed and ultimately the charge density on O atoms is maximum and that on H atoms is minimum at the trans form. This two opposite trend of charge density reorganization on the atoms of hydrogen peroxide molecule within the range of the two extreme conformations seems to have bearing on the choice of energy minimum conformation.

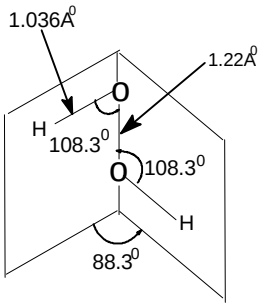

Figure 1. The optimized equilibrium geometry of H_2O_2.

Table 1.The optimized structural parameters of H_2O_2 as a function of dihedral angles.

Angle of torsion (θ) (degrees)	O–O (A^0)	O–H (A^0)	∠HOO (degree)
0(cis)	1.22	1.034	108.9
20	1.22	1.036	108.8
40	1.22	1.037	108.5
60	1.22	1.038	108.3
80	1.22	1.039	108.3
88.3	1.22	1.036	108.3
100	1.22	1.038	106.5
120	1.22	1.038	106.2
140	1.22	1.039	105.9
160	1.22	1.039	105.7
180(trans)	1.22	1.034	108.3

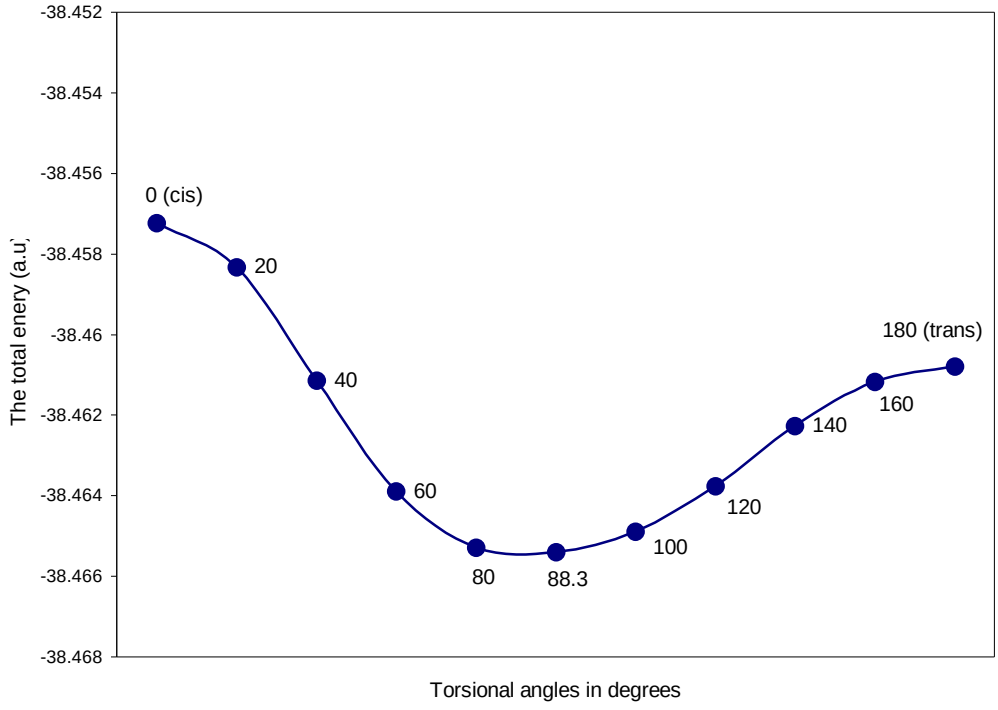

Figure 2. Plot of total energy of hydrogen peroxide molecule as a function of torsional angles

Table 2. The total energy (a .u), gross atomic charge distribution of H_2O_2 as a function of torsional angles.

Torsional angles (θ) in degrees	Total Energy	q (O)	q (H)
0 (cis)	-38.45722	6.1209	0.8791
20	-38.45833	6.1192	0.8808
40	-38.46114	6.1161	0.8839
60	-38.46388	6.1135	0.8865
80	-38.46528	6.1129	0.8870
88.3	-38.46540	6.1136	0.8864
100	-38.46489	6.1156	0.8844
120	-38.46375	6.1202	0.8798
140	-38.46226	6.1260	0.8739
160	-38.46116	6.1307	0.8693
180 (trans)	-38.46078	6.1326	0.8674

The quest for the barrier to internal rotation in terms of the decomposed energy components and the rationale of the skew form as the equilibrium conformation of the hydrogen peroxide molecule:

We have noted that the hydrogen peroxide molecule has three extreme conformations– gauche (equilibrium), cis and trans; energetically the trans form is closer than cis form to the equilibrium gauche form and accordingly the trans barrier is smaller than the cis barrier. In order to understand the physics of the intramolecular interactions, the types of interactions and there are to be identified. An examination of the structure of the molecule reveals the following interactions in the molecule:

(i) Two one-center interactions – one on O atoms and the other on H atoms,

(ii) Two bonding interactions– 'O–O' bond and 'O–H' bond,

(iii) Two nonbonding interactions–'H------H' and 'H-----O',

The two-center bonding interactions:

The 'O---O' and 'O---H' bonding interactions and their physical components as a function of torsional angles are presented in Tables 3 and 4 respectively. The total energy of the 'O---O' bond are plotted as a function of torsional angles in Figure 3. The total energy of the 'O—H' bond is plotted as a function of torsional angle in Figure 4. We also note here a surprising result that the two bonded interactions have opposite effect on the matter of choice of the preferred conformation. Table 3 demonstrates that the 'O—O' bond energy is minimum at the gauche conformation and maximum at the cis conformation. Figure. 3 beautifully depicts that, as torsion starts, the energy of 'O—O' bond sharply declines and reaches the minima at the gauche conformation and then it turns and peaks up to reach the next maxima at the trans conformation. A closer look into the Table 3 reveals that the most crucial components of binding and anti binding, the E^R_{AB} and E^K_{AB} terms, work in concert while the electrostatic effects mutually cancel each other at all conformations. From Table 3, we find that the difference of 'O–O' bond energy between gauche and trans forms is -0.03034 a.u, that between gauche

and cis forms is -0.03135a.u. It appears that this large difference of energy of the 'O----O' bond of trans and gauche conformations decides the equilibrium geometry not in favour of the trans conformation rather in favour of nonplanar skew conformation. The trans conformation is usually the energy-preferred isomer of such compound under the normal circumstances. Thus the rationale of the nonplanar skew conformation as the equilibrium conformation of hydrogen peroxide molecule most probably lies in the variation of the 'O---O' bond energy as a function of internal rotation around 'O---O' bond. Or in other words, the factors which decide the nonplanar skew form as the equilibrium geometry of hydrogen peroxide molecule, the 'O—O' bonded interaction seems to play the major role and forces the molecule to be nonplanar. Since the 'O—O' bonded interaction accelerates the process of skewing, this interaction tends to decrease the energy of the gauche conformation and hence tends to increase the gap in energy between the extreme conformations, which ultimately goes to increase the heights of the barriers. From Table 4 we see just the opposite effect created by the 'O---H' bonded interaction on the conformational preference of the hydrogen peroxide molecule. The 'O---H' bond energy is maximum at the gauche form and minimum at the eclipsed (cis) form and hence this energetic effect hinders the physical process of skewing. Figure. 4 beautifully depicts that if torsion starts either from cis or from trans isomer, the 'O---H' bond energy sharply peaks up with increasing torsion and reaches maxima at the gauche form. Thus the 'O---H' bonded interaction as a function of torsional angles thus does not decide equilibrium geometry either in favour of trans or in favour of gauche conformations. But since the difference between cis and gauche, and that between trans and gauche are –0.00556 a.u, -0. 00167 a.u respectively, the effect 'O—H' bonded interaction is over compensated by the 'O—O' bonded interaction to settle the geometry in favour of nonplanar skew form. Since the 'O---H' bonded interaction hinders skewing, it goes to increase the energy of the skew form compared to those of trans and cis isomers and hence the effect tends to decrease the energy gap between the extreme conformations and hence tends decrease the barrier heights.

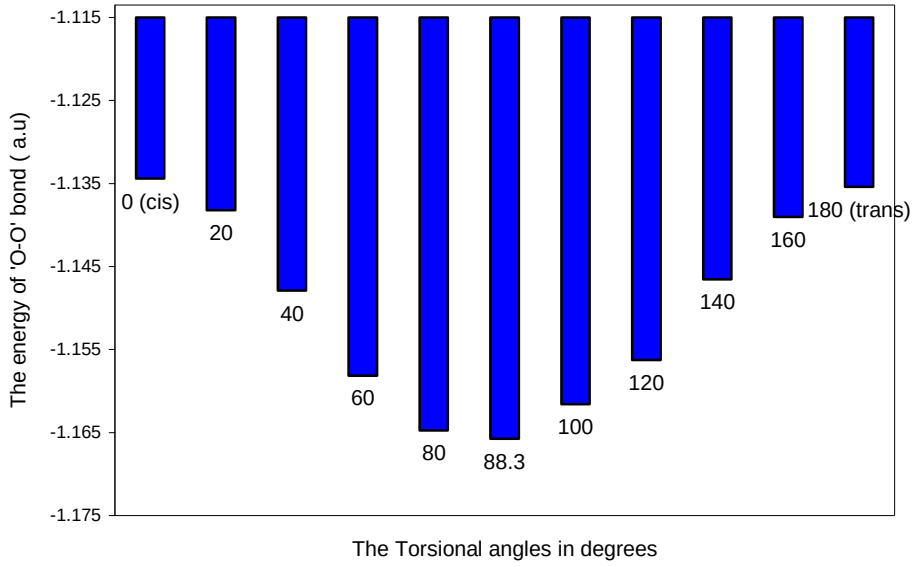

Figure 3. Plot of 'O-O' bond energy as a function of torsional angle in Hydrogen Peroxide

Table 3. The (O—O) bonding interactions and its decomposed components (a.u) in Hydrogen Peroxide with torsion.

Angle of torsion (θ) in degrees	E^J	E^N	E^V	E^K	E^R	E_{Total}
0 (cis)	15.91141	15.61476	-31.19410	-0.21828	-1.24820	-1.13441
20	15.90245	15.61476	-31.18532	-0.21855	-1.25157	-1.13823
40	15.88630	15.61476	-31.16948	-0.21924	-1.26023	-1.14789
60	15.87288	15.61476	-31.15631	-0.21990	-1.26957	-1.15814
80	15.86996	15.61476	-31.15344	-0.22024	-1.27578	-1.16474
88.3	15.87327	15.61476	-31.15669	-0.22024	-1.27686	-1.16576
100	15.88354	15.61476	-31.16677	-0.21971	-1.27342	-1.16160
120	15.90754	15.61476	-31.19031	-0.21921	-1.26903	-1.15625
140	15.93793	15.61476	-31.22009	-0.21848	-1.26067	-1.14655
160	15.96217	15.61476	-31.24382	-0.21801	-1.25414	-1.13904
180 (trans)	15.97208	15.61476	-31.25352	-0.21778	-1.25096	-1.13542

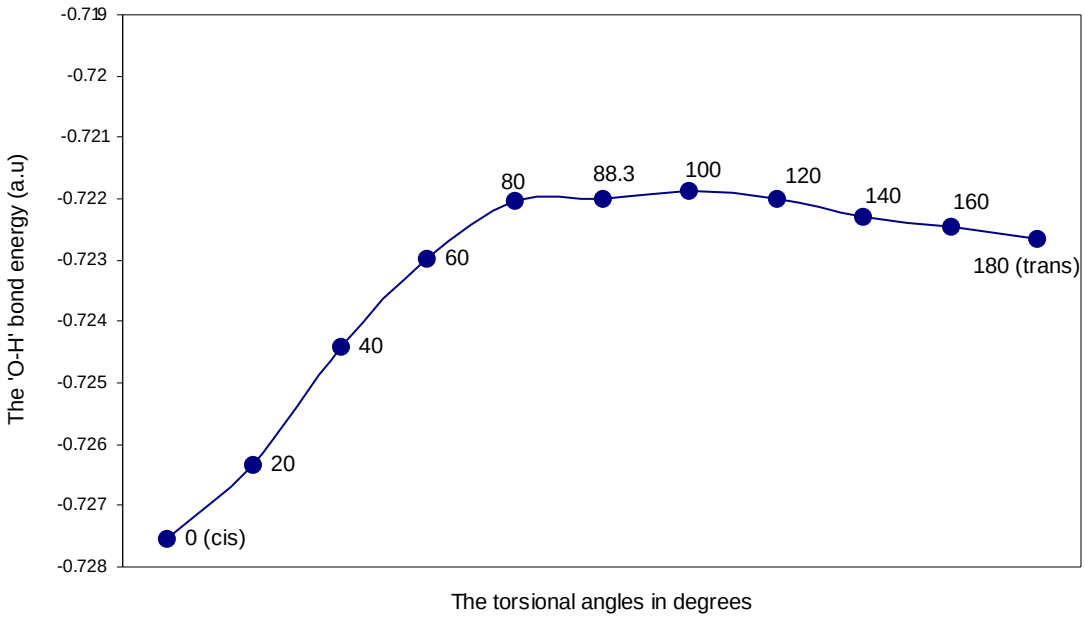

Figure 4. Plot of total 'O-H' bond energy of Hydrogen Peroxide as a function of torsional angles.

Table 4. The (O—H) bonding interactions and its decomposed components (a. u) in Hydrogen Peroxide with torsion.

Angle of torsion (θ) in degrees	E^J	E^N	E^V	E^K	E^R	E_{Total}
0 (cis)	2.55283	3.07061	-5.40644	-0.22832	-0.71623	-0.72755
20	2.55349	3.06467	-5.40288	-0.22806	-0.71356	-0.72634
40	2.55942	3.06173	-5.40647	-0.22797	-0.71113	-0.72442
60	2.56401	3.05878	-5.40878	-0.22786	-0.70914	-0.72299
80	2.56358	3.05582	-5.40627	-0.22768	-0.70749	-0.72204
88.3	2.56201	3.05582	-5.40478	-0.22764	-0.70740	-0.72199
100	2.55891	3.05875	-5.40388	-0.22790	-0.70774	-0.72186
120	2.54750	3.05878	-5.39300	-0.22753	-0.70774	-0.72199
140	2.53478	3.06173	-5.38296	-0.22718	-0.70865	-0.72228
160	2.52316	3.06170	-5.37190	-0.22664	-0.70879	-0.72247
180 (trans)	2.52022	3.06468	-5.37121	-0.22660	-0.70970	-0.72266

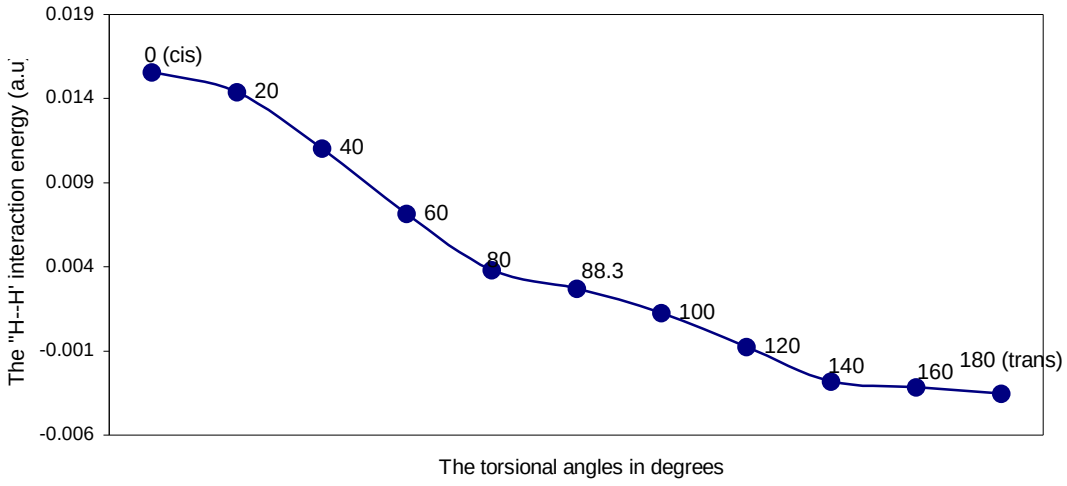

Figure 5. Plot of 'H---H' nonbonding interaction energy as a function of torsional angles in Hydrogen Peroxide.

Table 5. The 'H….H ' non-bonding interaction (a.u) in Hydrogen Peroxide with torsion.

Angle of torsion (θ) in degrees	E^J	E^N	E^V	E^K	E^R	E_{Total}
0 (cis)	0.21388	0.27849	-0.48660	-0.00177	0.01156	0.01556
20	0.21276	0.27586	-0.48312	-0.00149	0.01038	0.01439
40	0.20631	0.26526	-0.46682	-0.00088	0.00718	0.01105
60	0.19600	0.25015	-0.44219	-0.00028	0.00349	0.00717
80	0.18398	0.23424	-0.41482	-0.00000	0.00042	0.00382
88.3	0.17893	0.22806	-0.40372	-0.00001	-0.00058	0.00273
100	0.17470	0.22362	-0.39506	-0.00016	-0.00185	0.00125
120	0.16414	0.21221	-0.37313	-0.00067	-0.00325	-0.00073
140	0.15635	0.20482	-0.35780	-0.00146	-0.00473	-0.00282
160	0.15102	0.19994	-0.34746	-0.00212	-0.00454	-0.00316
180 (trans)	0.14937	0.19861	-0.34441	-0.00239	-0.00469	-0.00351

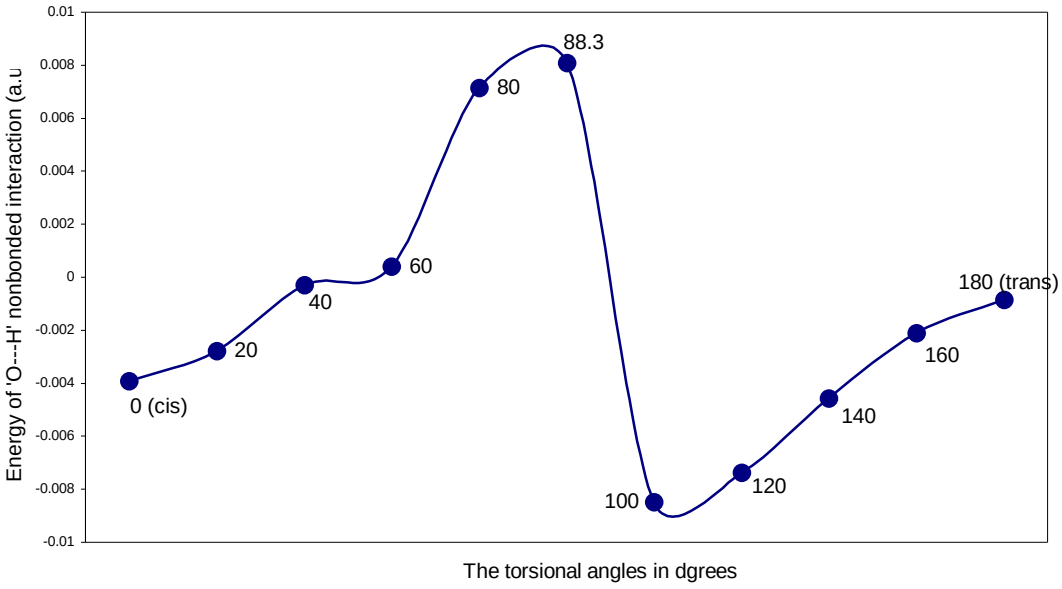

Figure 6. Plot 'O---H' nonbonding interaction as a function of torsional angles in Hydrogen Peroxide.

Table 6. The 'O----H ' non-bonding interaction (a.u) in Hydrogen Peroxide with torsion.

Angle of torsion (θ) in degrees	E^J	E^N	E^V	E^K	E^R	E_{Total}
0 (cis)	1.54113	1.72512	-3.26385	-0.00145	-0.00487	-0.00392
20	1.54614	1.72791	-3.27145	-0.00174	-0.00364	-0.00278
40	1.55299	1.73040	-3.28050	-0.00243	-0.00018	-0.00028
60	1.55812	1.73183	-3.28684	-0.00311	0.00401	0.000401
80	1.55926	1.73217	-3.28828	-0.00345	0.00746	0.00716
88.3	1.55831	1.73217	-3.28737	-0.00345	0.00843	0.00809
100	1.57236	1.75172	-3.32050	-0.00317	0.00848	-0.00848
120	1.56830	1.75513	-3.32005	-0.00250	0.00824	-0.00736
140	1.56692	1.76390	-3.32759	-0.00148	0.00632	-0.00457
160	1.56174	1.76622	-3.32499	-0.00062	0.00446	-0.00211
180 (trans)	1.56145	1.76930	-3.32783	-0.00026	-0.00350	-0.00084

Table 7. The Partitioned components of one-center energies (a.u) on O and H atoms in Hydrogen Peroxide with torsion.

Angle of torsion (θ) in degrees		E^U	E^N	E^K	E_{Total}
0 (cis)	O	-30.88718	15.48207	-2.11602	-17.52113
	H	-0.56148	0.28978	-0.14489	-0.41659
20	O	-30.87981	15.47336	-2.11456	-17.52101
	H	-0.56258	0.29091	-0.14546	-0.41713
40	O	-30.86588	15.45764	-2.11157	-17.51981
	H	-0.56456	0.29297	-0.14649	-0.41808
60	O	-30.85435	15.44459	-2.10884	-17.51860
	H	-0.56621	0.29469	-0.14734	-0.41886
80	O	-30.85220	15.44175	-2.10780	-17.51825
	H	-0.56657	0.29506	-0.14753	-0.41904
88.3	O	-30.85527	15.44496	-2.10811	-17.51902
	H	-0.56616	0.29464	-0.14732	-0.41884
100	O	-30.86622	15.45495	-2.10980	-17.52107
	H	-0.56490	0.29332	-0.14666	-0.41824
120	O	-30.88852	15.47830	-2.11348	-17.52370
	H	-0.56195	0.29027	-0.14514	-0.41682
140	O	-30.91689	15.50788	-2.11851	-17.52752
	H	-0.55822	0.28643	-0.14321	-0.4150

(Table 7 continued)

160	O	-30.93918	15.53148	-2.12257	-17.53027
	H	-0.55524	0.28338	-0.14169	-0.41355
180	O	-30.94835	15.54111	-2.12428	-17.53152
trans	H	-0.55403	0.28214	-0.14107	-0.41296

The two-center nonbonding interactions:

The two-center nonbonding interactions and their physical components of 'H---H' and 'O---H' atom pairs are presented in Tables-5 and 6 respectively; the nonbonding interactions are plotted as a function of torsional angles in Figures 5 and 6 respectively. A look at the Tables reveals that the two nonbonding interactions have opposite effect on the process of conformational isomerism and in deciding the preferred conformation of hydrogen peroxide molecule. Let us discuss the interactions one by one.

The 'H---H' nonbonding interaction:

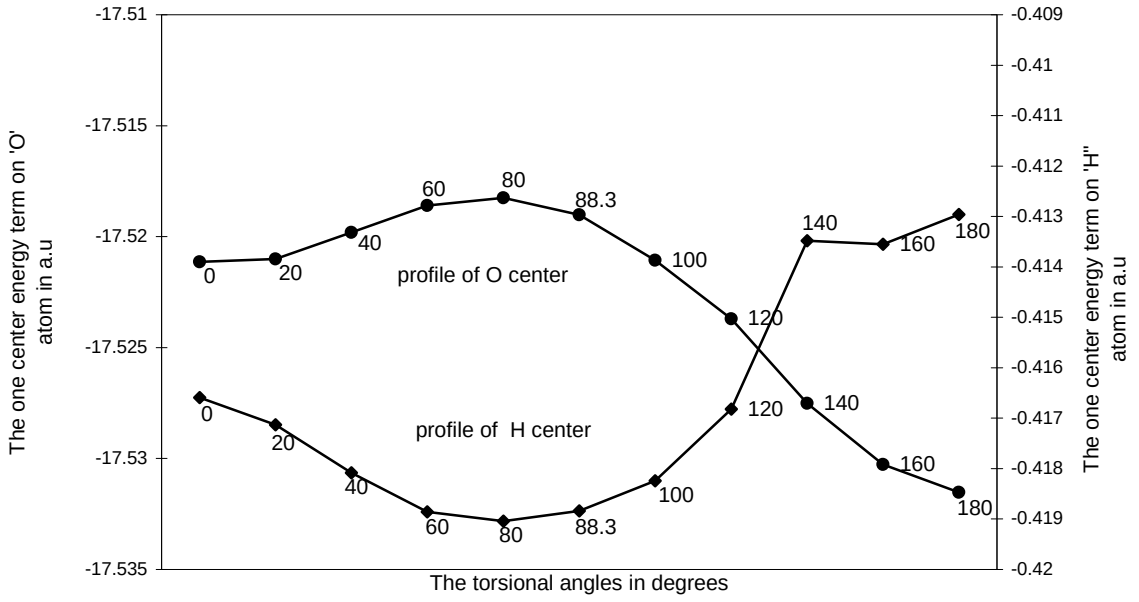

Figure 7. Plot of the one-center energy terms on 'O' and 'H' atoms of hydrogen peroxide as a function of torsional angles

Table 5 demonstrates that the nature of the 'H---H' nonbonding interaction in hydrogen peroxide molecule is both attractive and repulsive. The 'H---H' nonboded interaction is repulsive at cis and gauche conformations but attractive at the trans conformation. Thus the trans conformation is the preferred conformation by the action of this nonbonding interaction. Computed results show that if torsion is started from cis conformation, the 'H---H' nonboded interaction starts decreasing

monotonically to reach the minima at the trans form. It is also distinct from the nature of energy profile in Figure 5 that the 'H---H' nonbonded interaction declines monotonically with progressive torsion if started from the cis isomer and reaches at the minima at the trans isomer. From the computed data of nonboded 'H----H' interaction of hydrogen peroxide molecule we see that the 'H---H' nonboded interaction is not always repulsive although the gross atomic charges on the atoms are positive (Table 2). The nature of variation of the 'H---H' nonbonding interaction with dihedral angles is internally consistent in terms of its physical components. After the analysis of computed data and the nature of the energy profile, we may conclude that 'H---H' nonbonding interaction hinders skewing. If torsion is started from the cis form, the skewing is favoured and accelerated and the 'H---H' nonbonding interaction tends to increase the height of the cis barrier as because the effect tends to decrease the energy of the gauche form compared to that of the cis form. However, if torsion is started from the trans form, skewing will be hindered and this 'H---H' nonbonding interaction will tend to increase the energy of the gauche form and decrease the energy of the trans form and hence the difference in energy of the gauche form and the trans form, the trans barrier, is increased.

The 'O---H' nonbonding interaction:

From Table 6 it is evident that the total nonbonding 'O----H' interaction is attractive at cis and trans conformations but repulsive at the equilibrium gauche conformation. It is also apparent that cis is more preferred than the trans by this nonbonding interaction. However, Figure.6 reveals an interesting feature of the 'O---H' nonbonding interaction. As the torsion starts from the cis conformation, the nonboded interaction sharply peaks up and reaches maxima around the gauche conformation and thereafter it sharply declines to reach the minima at a nonplanar conformation at the torsional angle around 100^0 and thereafter the profile takes a turn and peaks up and reaches the next maxima at the trans conformation. It transpires from the nature of the profile of 'O---H' that there is a deep well in the energy profile diagram and the well resides around the dihedral of 100^0 measured from the cis conformation. Although this 'O--- H' nonbonding interaction is repulsive at the gauche or minimum energy conformation of the molecule at the dihedral angle of 88.3^0, Figure 6 demonstrates that the potential well of 'O---H' nonboded interaction occurs at conformations very near the equilibrium form. This result is a clear indication that 'O---H' nonbonding interaction strongly favours skew conformation of the hydrogen peroxide molecule compared to the trans or cis forms. Thus this result is suggestive that, in addition to the effect of the 'O----O' bonding interaction, the 'O—H' nonbonding interaction also has a role in deciding the equilibrium shape of the hydrogen peroxide molecule. Since the 'O—H' nonboded interaction is repulsive at the gauche conformation, it is apparent that the torsion from either the cis or the trans conformation is hindered and hence the 'O—H' nonboded interaction tends to increase the energy of the gauche form compared to the cis or trans form and hence tends to decreases both cis and trans barrier. We may point out one revealing feature of the nonboded interaction that, although the computed charge distribution suggests that the gross atomic charge on O atom is always negative and that on H atom is positive, still the interaction between such atom pair is not always attractive as may be qualitatively suggested. Thus the possibility of electrostatic model of calculating preferred conformations of molecules is completely ruled out.

The one-center components:

The computed one-center energies and their physical components as a function of torsional angles are presented in Table 7 are drawn in Figure 7. From Tables- 7 and Figure 7 we note a very revealing feature of the two one-center energetic effects in the molecule. The one-center energy of 'O' atoms is lowest at the trans form and highest at the gauche form; as torsion starts from the eclipsed form, the profile of the energy of the 'O' center begins to increase and the process continues monotonically to assume the energy peak at a conformation close to the gauche form; thereafter the profile takes a turn and decreases sharply and steadily to assume the minimum value at the trans form. Thus the one-center energetic effect on 'O' atoms of hydrogen peroxide tends to hinder the physical process of skewing and favours the trans form most. Since the O-center energetic effect tends to increase the energy of the equilibrium gauche form and decrease the energy of both cis and trans forms, and since both the cis and trans forms lie above the gauche form in energy level diagram, this one-center 'O' atom effect tends to decrease the height of both cis and trans barriers. But the one- center energetic effects on 'H' atoms have just opposite effect that is exhibited by that on 'O' atom centers. Table 7 and Figure 7 demonstrate that the 'H' centers have minimum energy at gauche form and maximum energy at the trans form. Computed data demonstrate that as torsion begins from the cis form, the energy profile of 'H' centers starts decreasing monotonically and reaches the minima at the gauche form and thereafter it takes a turn and increase steadily to reach the maxima at the trans form. Thus the energetic effect on 'H' centers accelerates the process of skewing and since this effect tends to decrease the energy of the gauche form compared to that of cis and trans form, it increases the height of the barrier. It is also dissentingly demonstrated by the computed results that, since the pattern of variation of the two one-center energy profiles as a function of torsional angles bear a mirror image relationship to each other, the two one–center energetic effects in hydrogen peroxide molecule has opposite effect to decide the preferred conformation and the barrier height of the molecule. The energetic effect on 'O' atom centers favours trans form while that on 'H' centers favours the process of skewing and the gauche form as the equilibrium conformation of the hydrogen peroxide molecule.

We have seen above that the energy decomposition faithfully displays the physical process of skewing and eclipsing as a function of torsional angle and hence is a good descriptor of the process of isomerization reaction of hydrogen peroxide associated with the dynamics of internal rotation.

We have just discussed above the effects of one-center, and two-center bonded and nonboded interactions in terms of the decomposed one– and two– center energy components upon the conformational isomerism of hydrogen peroxide molecule. From the results of analysis it can be concluded that the one-center effect on 'H' atom, two-center 'O---O' bonded interaction and two-center 'O—H' nonboded interactions conjointly and simultaneously decide the equilibrium geometry of the hydrogen peroxide molecule in favour of skew or gauche form compared to the trans form. However, two-center 'O---O' bonded interaction has the major role to play in deciding the equilibrium conformation of the molecule. The one-center, two center bonded and nonboded interactions occur in pairs but the components of each pair act in opposite direction in deciding the preferred conformation and the barrier heights of the molecule.

3.2 Fluorine Peroxide, F_2O_2

Fluorine peroxide or dioxygen difluoride is also, like hydrogen peroxide, a non-planar [31] molecule with a dihedral angle of 87.5^0 and hence should have two barriers–cis barrier and trans barrier. The fluorine peroxide molecule is well known to be a very difficult problem [32–39] for standard *ab initio* method. While barriers have not been experimentally measured, they are expected to be higher than those of hydrogen peroxide. We have taken up the present study of this system with a view to explore whether the partitioned energy components can monitor the physical process of conformational isomerism generated by the dynamics of internal rotation around the 'O--O' bond of the molecule. We also propose to discern the interactions and energetic effects that entail the nonplanar skew conformation as the equilibrium shape of the molecule. The geometric parameters of each generated conformation are optimized and total energy is computed and then the total energy of each conformation is decomposed according to the algorithm discussed above. The evaluated quantities are presented in tables. The theoretical quantities are plotted in diagrams whenever it is felt necessary for a better visualization of the physical situation. The description of various tables are and figures as follows:

Table 8: the optimized geometric parameters and total energy as a function of torsional angles; The potential energy diagram of the molecule is the Figure 8.

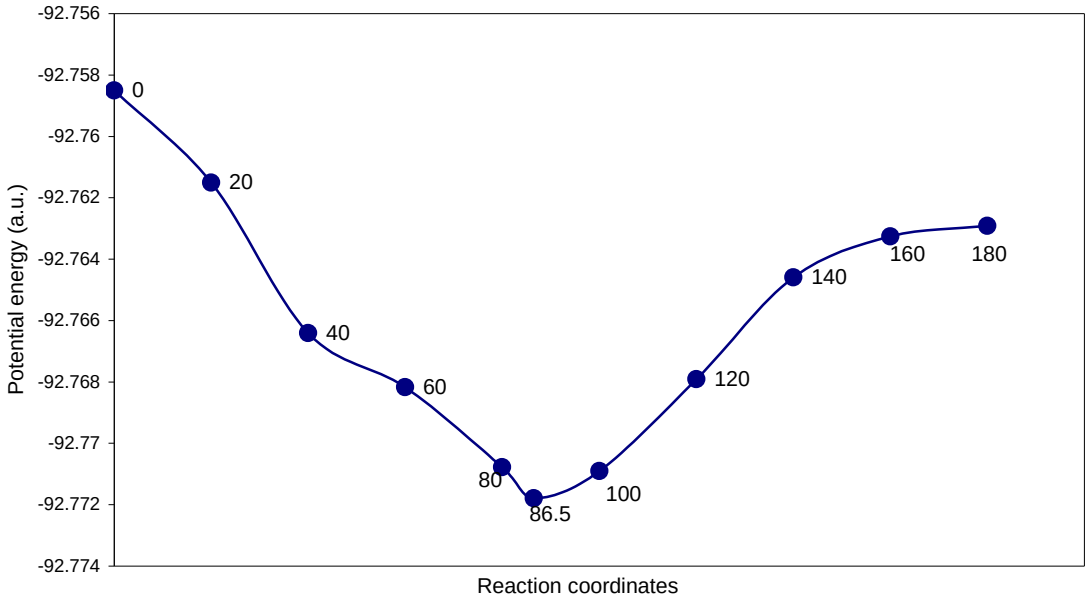

Figure 8. Plot of potential energy as a function of torsional angles in fluorine peroxide.

Table 8. The optimized Structural parameters and the total energy of O_2F_2 as a function of torsional angles

Angle of torsion (θ, degrees)	O–O (A^0)	O–F (A^0)	∠FOO (degree)	Total energy (a.u)
0(cis)	1.22	1.18	109.0	-92.7585
20	1.22	1.18	108.6	-92.76151
40	1.22	1.18	108.5	-92.76641
60	1.22	1.18	108.4	-92.76817
80	1.22	1.18	108.4	-92.77078
86.5	1.22	1.18	108.3	-92.77179
100	1.22	1.18	108.2	-92.7709
120	1.22	1.18	108.0	-92.76791
140	1.22	1.18	107.8	-92.76459
160	1.22	1.18	107.7	-92.76326
180(trans)	1.22	1.18	106.9	-92.76291

The two-center 'O–O' and 'O–F' bonded interactions and their physical components as a function of torsional angles are presented in Tables 9 and 10 and are drawn in figures 9 and 10 respectively.

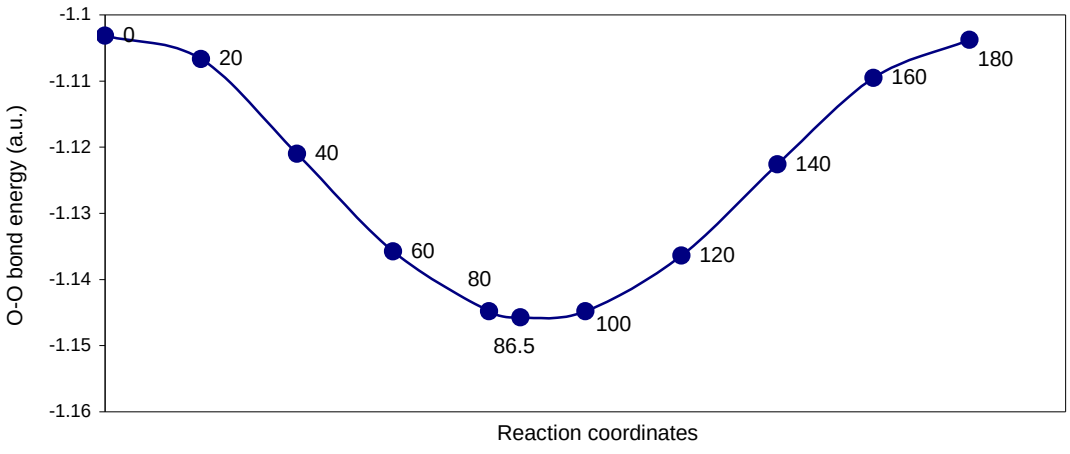

Figure 9. Plot of 'O-O' bond energy (a.u)as a function of torsional angles in fluorine peroxide.

Table 9. The two-center 'O–O' bonding interaction and their physical components (a.u) in O_2F_2 molecule.

Angle of torsion (degrees)	E^J	E^N	E^V	E^K	E^R	E (O – O)
0	14.99701	15.61476	-30.28450	-0.21060	-1.21983	-1.10316
20	14.98779	15.61476	-30.27520	-0.21096	-1.22312	-1.10670
40	14.96508	15.61476	-30.25225	-0.21256	-1.23603	-1.12099
60	14.94054	15.61476	-30.22744	-0.21414	-1.24950	-1.13577
80	14.92515	15.61476	-30.21186	-0.21497	-1.25789	-1.14480
86.5	14.92252	15.61476	-30.20920	-0.21503	-1.25876	-1.14571
100	14.92265	15.61476	-30.20933	-0.21480	-1.25809	-1.14480
120	14.93427	15.61476	-30.22109	-0.21367	-1.25066	-1.13638
140	14.95472	15.61476	-30.24178	-0.21201	-1.23830	-1.12260
160	14.97323	15.61476	-30.26048	-0.21050	-1.22655	-1.10954
180	14.97831	15.61476	-30.26562	-0.21000	-1.22121	-1.10376

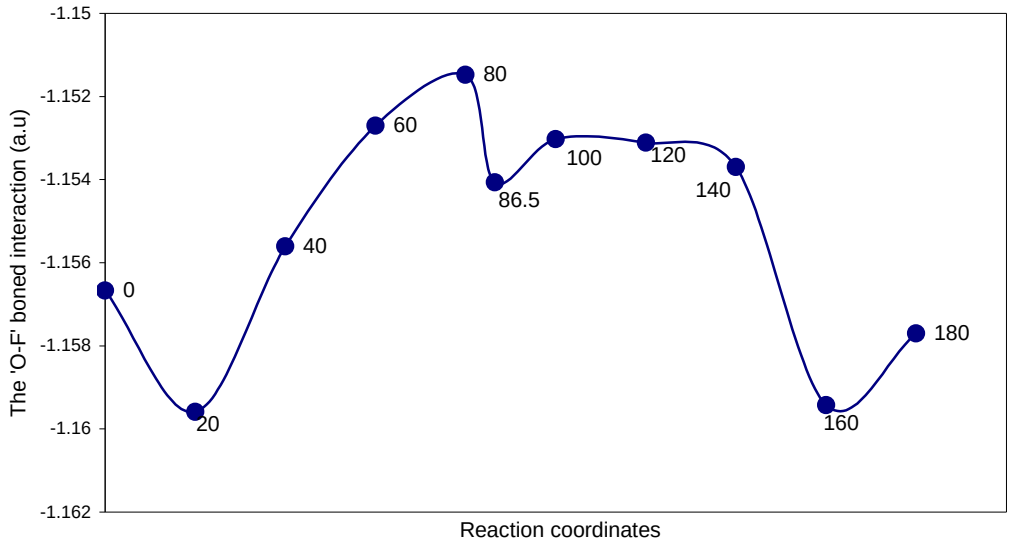

Figure 10. Plot of 'O-F' bonding interaction(a.u) in fluorine peroxide as a function of torsional angles.

Table 10. The two-center 'O–F' bonding interaction and their physical components (a.u) in O_2F_2 molecule.

Angles of torsion (degrees)	E^J	E^N	E^V	E^K	E^R	E (O – F)
0	18.47503	18.83479	-36.97840	-0.21876	-0.26932	-1.15667
20	18.47439	18.83472	-36.97814	-0.21892	-1.27163	-1.15959
40	18.47219	18.83478	-36.97603	-0.21843	-1.26812	-1.15561
60	18.46986	18.83484	-36.97414	-0.21800	-1.26526	-1.15270
80	18.46846	18.83484	-36.97293	-0.21780	-1.26406	-1.15148
86.5	18.46793	18.83479	-36.97261	-0.21781	-1.26636	-1.15407
100	18.46778	18.83469	-36.97215	-0.21785	-1.26550	-1. 15303
120	18.46913	18.83471	-36.97341	-0.21807	-1.26547	-1.15311
140	18.47110	18.83480	-36.97494	-0.21835	-1.26631	-1.15370
160	18.47285	18.83476	-36.97693	-0.21862	-1.27150	-1.15943
180	18.47343	18.83475	-36.97723	-0.21863	-1.27002	-1.15770

The two-center 'O---F' and 'F---F' nonboded interactions and their physical components as a function of torsional angles are presented in Tables 11 and 12 and are drawn in figure 11 respectively.

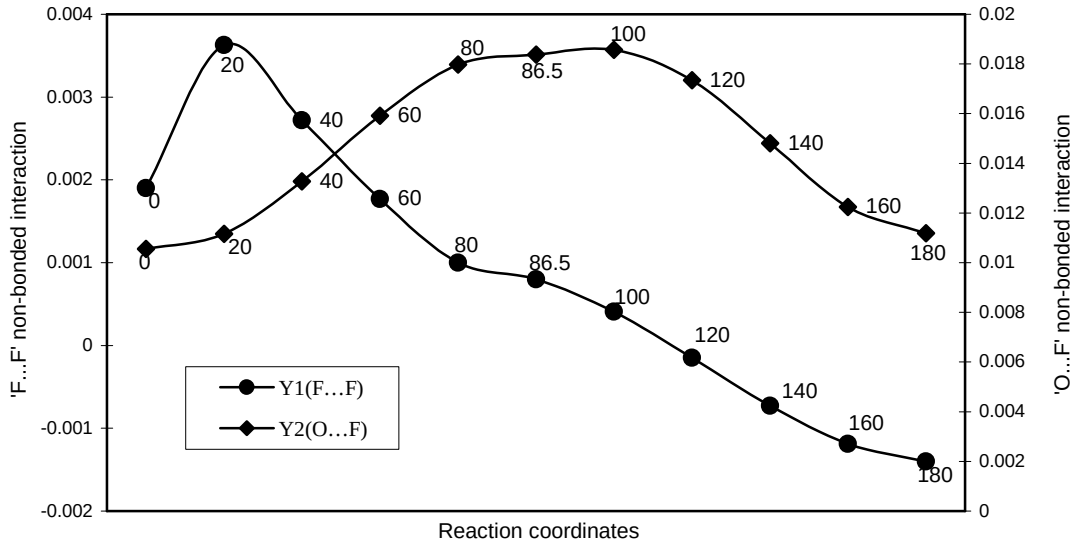

Figure 11. Plot of 'F...F' and 'O...F' non-bonding interaction energies (a.u) as a function of torsional angles in fluorine peroxide.

Table 11. The two-center 'O----F' nonbonding interaction and their physical components (a.u) in O_2F_2 molecule.

Angle (degree)	E^J	E^N	E^V	E^K	E^R	E (O----F)
0	11.35484	11.37403	-22.72726	-0.00268	0.01163	0.01056
20	11.38287	11.40249	-22.78372	-0.00286	0.01238	0.01116
40	11.38838	11.40963	-22.79651	-0.00339	0.01516	0.01327
60	11.39405	11.41684	-22.80954	-0.00394	0.01850	0.01592
80	11.39314	11.41684	-22.80874	-0.00428	0.02102	0.01798
86.5	11.40049	11.42401	-22.82326	-0.00431	0.02146	0.01838
100	11.40744	11.43117	-22.83765	-0.00424	0.02156	0.01875
120	11.42248	11.44566	-22.86675	-0.00382	0.01978	0.01735
140	11.43807	11.46022	-22.89671	-0.00317	0.01640	0.01481
160	11.44670	11.46750	-22.91246	-0.00259	0.01310	0.01224
180	11.50568	11.52655	-23.03028	-0.00231	0.011538	0.01118

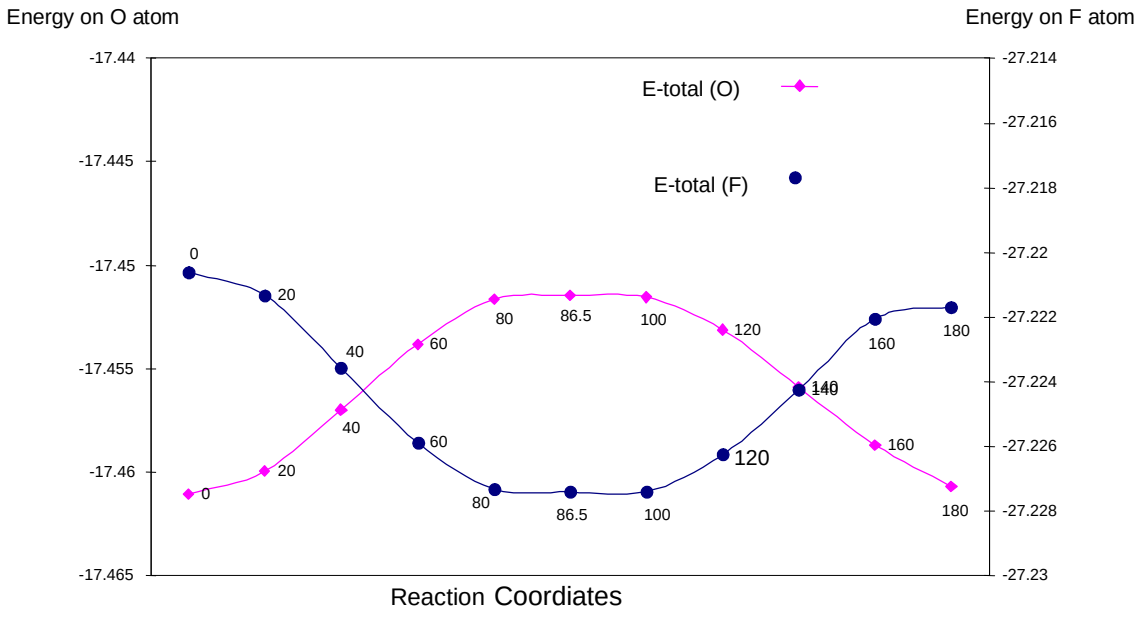

Figure 12. Plot of the one-center energies (a.u) on 'O' and 'F' atom centers as a function of torsional angles in fluorine peroxide

Table 12. The two-center 'F---F' nonbonding interaction and their physical components (a.u) in O_2F_2 molecule.

Angle of torsion (degree)	E^J	E^N	E^V	E^K	E^R	E (F----F)
0	13.25494	13.04062	-26.29378	-0.00160	0.00172	0.00190
20	13.11500	12.89617	-26.0095	-0.00122	0.00316	0.00360
40	12.49931	12.27473	-24.77267	-0.00078	0.00212	0.00272
60	11.69137	11.46525	-23.15543	-0.00034	0.00089	0.00177
80	10.86469	10.64529	-21.50883	-0.00008	-0.00007	0.00100
86.5	10.62738	10.41123	-21.03749	-0.00006	-0.00027	0.00080
100	10.16482	9.95815	-20.12190	-0.00010	-0.00056	0.00041
120	9.60835	9.41914	-19.02654	-0.00036	-0.00073	-0.00015
140	9.21064	9.03963	-18.24946	-0.00077	-0.00075	-0.00073
160	8.97035	8.81296	-17.78260	-0.00115	-0.00074	-0.00119
180	8.92889	8.77469	-17.70291	-0.00131	-0.00076	-0.00140

The two one-center energy and their physical components on 'O' and 'F' atoms as a function of torsional angles are presented in Tables 13 and 14 respectively.

Table 13. The One-center energy and its physical components (a.u) of 'O' atom in F_2O_2 molecule .

Angle of torsion (degree)	E^U	E^J	E^K	E-total (O)
0	-30.01181	14.59213	-2.04136	-17.46105
20	-30.00353	14.58349	-2.03991	-17.45995
40	-29.98211	14.56124	-2.03611	-17.45698
60	-29.95901	14.53732	-2.03213	-17.45381
80	-29.94439	14.52249	-2.02975	-17.45165
86.5	-29.94209	14.52006	-2.02942	-17.45146
100	-29.94190	14.52007	-2.02972	-17.45155
120	-29.95228	14.53138	-2.03221	-17.45312
140	-29.97086	14.55118	-2.03622	-17.45590
160	-29.98796	14.56911	-2.03984	-17.45869
180	-29.99364	14.57413	-2.04118	-17.46069

Table 14. The One-center energy and its physical components (a.u) of 'F' atom in F_2O_2 molecule.

Angle of torsion (degree)	E^U	E^J	E^K	E-total (F)
0	-47.65292	23.52328	-3.09099	-27.22062
20	-47.66415	23.53484	-3.09200	-27.22132
40	-47.69464	23.56556	-3.09450	-27.22358
60	-47.72680	23.59800	-3.09710	-27.22589
80	-47.74717	23.61854	-3.09869	-27.22732
86.5	-47.74923	23.62065	-3.09883	-27.22741
100	-47.74965	23.62107	-3.09884	-27.22741
120	-47.73466	23.60600	-3.09760	-27.22627
140	-47.70818	23.57941	-3.09546	-27.22424
160	-47.68243	23.55371	-3.09333	-27.22205
180	-47.67638	23.54765	-3.09296	-27.22168

From Table 8 it is evident that the minimum energy equilibrium conformation of the molecule is not the trans isomer but a nonplanar skew conformation in between the cis and trans conformers with the dihedral angle of 86.5^0 between the FOO and OOF planes. But it evident that the trans isomer is more preferred than the cis isomer. The computed equilibrium geometry is very near to the experimental [31] geometry with regard to the dihedral angle between the FOO and OOF planes. Like its precursor, the molecule has two barriers- cis barrier and trans barrier and the cis barrier should be larger than the trans barrier. The computed values of the cis barrier and trans barrier are 8.34kcal/mole and 5.57 kcal/mole respectively. It is to be noted the barrier magnitudes of F_2O_2 are considerably larger than the corresponding barriers of H_2O_2. Figure 8 distinctly portrays the stability conditions of the three extreme conformational isomers of the molecule. The minimum is at the gauche form, the first and second maxima are at the trans and the cis conformations respectively; the preference of trans isomer compared to the cis is also straightforward in the diagram.

Energy partitioning analysis and the quest for the origin of the torsional barrier:

The total number of bonding and nonbonding interactions of fluorine peroxide molecule can be identified as follows:

(i) Two 'O–O' and 'O–F' bonding interactions bonds;

(ii) Two 'O----F' and 'F-----F' nonbonding interactions;

(iii) Two different one-center interactions –one on 'O' atoms and the second on 'F' atoms.

Two-center bonding interactions:

The two-center 'O–O' bonding interaction:

From analysis of the computed results in Table 9 it becomes transparent that as the torsion starts from the cis form, the 'O–O' bonded interaction begins to decrease and reaches its minimum at the gauche conformation and thereafter it turns with continued torsion and reaches the second maxima at the trans form. Thus it is evident that the 'O–O' bonded interaction accelerates the process of skewing and tends to select the nonplanar gauche form as the equilibrium conformation of the molecule. It is also evident from the numerical results that the trans form is preferred than the cis form by the 'O–O' bonded interaction. The stability conditions of the generated conformations due to the dynamics of internal rotation are more transparent in Figure 9. Analysis of computed data in Table 9 shows that the variations of the energy of the 'O---O' bond is internally consistent in terms of the variation of its physical components with internal rotation. The E^R and E^K terms principally determines the bond energy variation with torsion.

A comparative analysis of the profile of the 'O–O' bonding interaction (Figure 9) vis-à-vis the potential energy diagram (Figure 8) reveals that the 'O–O' bonding interaction dances with the tune of the dynamics of internal rotation as depicted by the total energy of the fluorine peroxide molecule. Since the profile of 'O–O' bonded interaction mimics the potential energy diagram, this energy component can be a descriptor of the physical process of the conformational isomerism of the molecule.

The difference of the 'O–O' bonded interaction between cis and gauche is -0.04255 a.u and that between gauche and trans is –0. 04195 a.u; hence it may be concluded that this large gap in energy difference between the pairs of extreme conformers forces the molecule to be nonplanar. Or in other words, it can be said that it is apparent that the principal factor responsible for the non-planarity of the equilibrium conformation of the fluorine peroxide molecule is the change in 'O–O' bonded interaction with torsion. More over, since this bonding interaction tends to stabilize the gauche form compared to cis or trans forms, it, eventually, increases the heights of the rotation barriers of the molecule.

The two-center 'O–F' bonding interaction:

From analysis of the computed results in Table 10 it is transparent that as the torsion starts from the cis form, the 'O–F' bonded interaction begins to increase and reaches its maximum at the gauche conformation and thereafter it turns with continued torsion and reaches the second minima at the trans form. Thus the effect of 'O–F' bonded interaction is to hinder the physical process of skewing. It is also evident from Table 10 that the effect of the 'O–F' bonded interaction tends to stabilize the trans isomer more compared to the cis isomer and apparently it makes the gauche conformation most unstable. Comparing the numerical values in Tables-9 and 10 it is at once evident that 'O–F' and 'O–O' bonding interactions act in opposition to select the preferred conformation of the molecule. A close look at the nature of the profile of 'O–F' bonding interaction as a function of torsional angle in Figure 10 reveals that the effect of the 'O–F' bonding interaction is anomalous in the matter of selecting the preferred conformation of the molecule. The nature of the profile of the 'O–F' bonding interaction shows that torsion, started either from the cis or from the trans isomer of the molecule, symmetrically favours skewing at the initial stage; but after a short interval of torsion, the skewing is highly opposed

by this effect. Thus the gauche form is not the preferred conformation of 'O–F' bonded interaction in F_2 O_2 molecule. More over, since 'O–F' bonded interaction tends to increase the energy of the gauche form, compared to that of trans and cis forms, it tends to reduce the heights of the torsional barriers of F_2 O_2 molecule. It is also revealed from the comparison of the Figure 10 with Figure 8 that the 'O–F' bond energy curve has no resemblance whatsoever with the potential energy diagram. It, therefore, transpires that the 'O–F' bond energy does not dance with the tune of the conformational isomerism of the fluorine peroxide molecule.

The two-center nonbonding interactions:

(i) 'O----F'
(ii) 'F-----F'

(i): 'O-------F' ; the two center 'oxygen----fluorine' nonbonding interaction

From Table 11, we see that the nature of the 'O---F' nonbonding interaction is repulsive in all conformations and the trans isomer is energetically favoured than the cis isomer while the gauche form is least favoured by this interaction. It is to be noted that, since from Table 8 it is evident that $\angle$ OOF angle is changing with the internal rotation around the 'O---O' bond, the distance of separation between a pair of the nonbonded 'O' and 'F' atoms is not constant of internal rotation. It is apparent from the geometric parameters from Table 8 and also from an analysis of the nuclear-nuclear repulsion energy component, E^N from Table 11 that the distance between these two nonbonded atoms is shortest at the trans form and longest in the cis form. The nature and magnitude of the interaction between these two-nonbonded atoms are justified in terms of the physical components. The profile of the nonbonded 'O----F' interaction as a function of torsional angle in Figure 11 nicely displays the behaviour; as the torsion starts from either the cis or the trans isomer the 'O---F' nonbonding interaction starts increasing like a monotone increasing function and reaches its peak at the gauche conformation and then it turns and starts decreasing monotonically until the trans or cis form is reached. An analysis of the data in Table 11 and the energy profile in Figure 11 shows that the 'O---F' non-boded interaction hinders skewing and prefers the cis form compared to the trans form while the gauche form is least favoured. Since the nonbonding 'O---F' interaction tends to increase the energy of the gauche form compared to that of cis and trans form, it goes to decrease the heights of the torsional barriers of the fluorine peroxide molecule. However, a comparison of the nature of the curves in Figures. 8 and 11 reveals that the profile of 'O---F' is the mirror image of the potential energy curve. Hence it is transparent that the nonbonded 'O---F' interaction behaves symmetrically with the physical process of conformation isomerism due to the internal rotation around the 'O---O' bond in fluorine peroxide molecule and the nonbonding 'O---F' interaction component alone can be used as a descriptor of the physical process of internal rotation in the molecule.

(ii): 'F-----F' ;. The two-center fluorine ---fluorine nonbonding interaction

From Table 12 we discover a very amazing feature of the nonbonding interaction that the nature of the interaction between two strongly electronegative atoms is not always repulsive. From Table 12 it is evident that the nature of 'F---F' interaction is attractive in the trans isomer and repulsive in the other

two extreme conformers–cis and gauche and the trans isomer is the most favoured of all conformations by this energetic effect in the molecule. The above noted nature of variation of the 'F----F' nonbonding interaction as a function of torsion is straightforward from the Figure11 which nicely displays the nature of variation of the 'F---F' interaction with the evolution of molecular conformations. It is distinct from the curve that if torsion is started from the cis isomer, the 'F---F' interaction energy increases in the next short interval; however, after the process of torsion is past an angle of 20^0, the interaction energy decreases steadily till the absolute minimum is reached at the trans conformation of the molecule. The curve further reveals that the gauche form is more favoured than the cis form by this 'F---F' nonbonding interaction. The comparative study of the profiles in Figure12 and 8 reveals that this 'F---F' nonbonding interaction energy component does not follow the physical process of conformational isomerism due to the dynamics of internal rotation in fluorine peroxide molecule.

A differential contribution to the magnitudes of the barrier heights by the 'F---F' nonbonding interaction is imminent from the study of the nature variation of this interaction as a function of torsional angle. Since this 'F---F' nonbonding interaction effect tends to stabilize the trans form more than the gauche form, it goes to decrease the magnitude of the trans barrier. On the other hand, since the effect goes to stabilize the gauche form more compared to the cis form, it tends to increase the cis barrier. The nature of the interaction between two strongly electronegative fluorine atoms is attractive in the trans form of fluorine peroxide molecule – a fact itself is intriguing and requires to be fully elucidated. The physical components of energy mainly responsible for binding and anti binding effect between atoms are the exchange (E^K) and resonance (E^R) terms. From Table 12 it is evident that the sum the coulomb repulsion (E^J) and the nuclear-nuclear repulsion (E^N) is just offset by the electron-nuclear attraction term (E^V) and the binding or anti binding effect is decided by the resultant effect of the exchange (E^K) and resonance (E^R) terms in almost all conformations. A closer look at the Table 12 reveals that the exchange term, E^K is negative in all conformations while the resonance term, E^R is positive in conformations nearing the cis isomer but it declines in conformations approaching the trans conformation where it is minimum. Therefore the nature of variation of the nonbonding 'F---F' interaction is internally consistent and is justified in terms of the physical components of the energetic effect.

One-center interactions:

From an analysis of numerical results in Table 13 and 14 it is evident that the one-center interactions on 'O' atoms and 'F' atoms have just opposite effect in the matter of selection of the preferred conformation and contribution to the barrier heights of the molecule. From Table 13 we see that as the torsion starts from the cis isomer, the one-center energy on 'O' atoms begins to increase and reaches maxima at the gauche isomer and thereafter it takes a turn and starts decreasing and reaches a second minima at the trans form. It is also evident that the preferred conformation of the one center energetic effect on 'O' atoms is the cis isomer. But from Table 14 we see that as the torsion starts from the cis form, the one–center energy on 'F' atom starts decreasing and reaches minima at the gauche form, then it turns and starts increasing and reaches the second maxima at the trans form. It is evident that the preferred conformation of the one-center energetic effect on 'F' atoms is the gauche conformation. The noted differential nature of variation of the one-center energetic effects on 'O' and 'F' atoms are transparent from their profiles in Figure12. The nature of the profiles reveals that the two

one-center energetic effects are internally consistent and symmetric about gauche conformation and one curve is the mirror image of the other. A comparative analysis of the potential energy diagram (Figure 8) and Figure 12 reveals at once that the profile of 'F' center mimics the potential energy curve while the profile of 'O' center is its mirror image. Thus it is evident that one-center energetic effects in F_2O_2 dance with the tune of the dynamics of internal rotation and express the glimpses of conformational behaviour that correlates nicely with the potential energy diagram. It may be concluded that the one-center energetic effects may be used as the descriptor of the structural isomerism generated by the internal rotation around 'O–O' bond in the fluorine peroxide molecule. We have noted above that the one-center effect on 'O' atoms tends to hinder the torsion and increase the energy of gauche form compared to the cis or trans form and hence tends to reduce the barrier height. On the other hand, the one-center effect on 'F' atoms tends to decrease energy of the gauche form compared to that of cis or trans form and hence goes to reduce the barrier height.

4. Conclusion

The notion of an inherent chemical reactivity of a molecule implies that its reactivity is predetermined by its structure. The single molecule reactivity concepts developed by Fukui [40] and Pearson [41] have been successful in rationalizing many chemical reactions and intrinsic chemical reactivity of a molecule on the basis of its own electronic structure. Fukui [40] relied upon the symmetry species of and electron density distribution in frontier orbitals, the HOMO and LUMO. Pearson [41] put forward his HSAB principle and enunciated empirical rules of reaction between molecules on the basis of their intrinsic hard soft nature. The hardness, initially a qualitative concept, has now been put on sound quantum mechanical basis and the concept is further sublimated by enunciation of maximum hardness principle. Hardness provides with a better picture due to the maximum hardness principle and can be used as a QSAR model for predicting biological activity of any compound [42]. But structures are no static. The rotation dynamics has to be fully explored in order to understand the chemical reactivity in relation to structures of molecules. We have just discussed above the energy partitioning analysis of the physical process of conformational isomerism of the hydrogen per oxide, H_2O_2 and fluorine peroxide, F_2O_2molecules. The hydrogen per oxide, H_2O_2 is well known for its biological activity and use in medicine. The molecules are iso-structural and have identical conformational behaviour under the dynamics of internal rotation around 'O–O' bond. Results reveal that the decomposed energy components faithfully display the physical process of skewing and eclipsing as a function of torsional angles during the process of isomerization reaction of both the molecules. We have tried to explore how the one-center and the two-center bonding and nonbonding interactions in the molecule evolve with the dynamics of internal rotation and how the energetic effects determine the barrier heights and decide the matter of preferred conformation of the molecule. The interaction terms are sharply divided in two groups. One group of interactions hinders the skewing and favours planar cis/trans forms while the other group favours skewing and prefers the gauche conformation of the molecule. However, all the energetic effects are found to be good descriptors of the process of isomerization reaction of hydrogen peroxide and fluorine peroxide molecules associated with the dynamics of internal rotation. The principal energetic effect forcing the molecules into the gauche form is the variation "O–O' bond energy with torsion in both the molecules.

It is demonstrated that the barrier is not a regional effect rather it is made by the conjoint action of all one- and two-center bonded and nonbonded interactions comprising the entire framework of the molecule. We have discovered one amazing feature of non-bonding interactions. We have seen that the nature of interaction between two formally positively charged non-bonded H atoms is not always repulsive and it is attractive as well. The present calculation further reveals that the nature of the non-bonding interaction between formally negatively charged atom ($O^{\delta-}$) and formally positively charged ($H^{\delta+}$) atom is not always attractive but repulsive too. It is also discovered that the nature of the nonbonding interaction between strongly electronegative atoms (i.e. $F^{\delta-}$----$F^{\delta-}$) is not always repulsive and it may be attractive as well. This noted nature of non-bonding interactions between '$H^{\delta+}$---- $H^{\delta+}$', '$O^{\delta-}$---- $H^{\delta+}$', and '$F^{\delta-}$----$F^{\delta-}$' is quite justified in terms of the decomposed physical components of the interaction energies. It is also evident that the barrier does not originate from a particular region of the molecule rather the origin and development of barrier involves the entire skeleton of the molecule.

References

1. Greenwood, N.N.; Earnshaw, A.; *Chemistry of the Elements*, 2nd eds.,Butterworth–Heinemann, Oxford, U.K., 1997.
2. March, J.; *Advanced Organic Chemistry*, 4th eds., Wiley, New York, 1992.
3. Hess, W.T.; Hydrogen Peroxide, in Kirk–Other Encyclopaedia of Chemical Technology, 4th Ed., Wiley, New York, Vol. 13, 961-995, 1995.
4. CA Cancer Jclin. 1993 Jan-Feb; 43 (1): 47-56, " Questionable Methods of Cancer Management: Hydrogen Peroxide and other ' hyper oxygenation' therapies." PMID 8422605.
5. Pitzer, R. M. The barrier to Internal Rotation in Ethane. *Acc. Chem. Res.* **1983**, *16*, 207-210.
6. Lowe, J. P. *Prog. Phys. Chem.* **1968**, *6*,1; (ibid), The Barrier to Internal Rotation in Ethane: A Qualitative, Intuitively Useful Explanation Emerges from a Comparision of Different Theoretical Approaches. *Science* **1973**, *179*, 527-532.
7. Schleyer, P.v.R.; Kaupp, M. ; Hampel, F.; Bremer, M. and Mislow, K. Relationships in the Rotational Barriers of All Group 14 Ethane Congeners $H_3X–YH_3$ (X, Y= C, Si, Ge, Sn, Pb). Comparison of ab Initio Pseudopotential and All-Electron results. *J. Am. Chem. Soc.* **1992,** *114*, 6791-6797..
8. Freeman, F.; Tsegai, Z. M.; Kasner, M. L. and Hehre, W. A Comparison of the ab initio Calculated and Experimental Conformational Energies of Alkyl Cyclohexanes. *J. Chem. Educ.* **2000**, *77***,** 661–667.
9. Cárdenas-Jirón, G. I and Toro-Labbé, A.; Hardness Profile and Activation Hardness for Rotational Isomerization Process 2. The Maximum Hardness Principle. *J. Phys. Chem.* **1995**, *99*, 12730-12738.
10. Cárdenas-Jirón, G. I.; Labsen, J; Toro-Labbé, A.; Hardness Profile and Activation Hardness for Rotational Isomerization Process .1. Application to Nitrous Acid and Hydrogen Persulfide. 2. *J. Phys. Chem.* **1995**, *99*, 5325-5330.
11. Ghosh, D. C. and Rahman, M. A Study of the Origin of Barrier to Internal Rotation of Molecules. *Chem. Environ. Res.* **1996**, *5*, 73-88.
12. (a) Pople, J.A.; Santry, D.P.; Segal,G.A. Approximate Self-Consistent Molecular Orbital Theory. I

Invariant Procedure. *J. Chem. Phys.* **1965**, *43*, S129-S135.
(b) Pople, J.A.; Santry, D.P.; Segal,G.A. Approximate Self-Consistent Molecular Orbital Theory.II Calculation With Complete Neglect of Differential Overlap. *J. Chem. Phys.* **1965**, *43*, S136-S 151

13. Pople, J. A.; Beveridge, D. L. Approximate Molecular Orbital Theory, McGraw-Hill Book Company, 1970.
14. Gordon, M. S. Molecular Orbital Study of Internal Rotation. *J. Am. Chem. Soc.* **1969**, *91*, 3122-3130.
15. Ghosh, D. C. Density Functional and Frontier Orbital Study of the Physical Process of Conformational Isomerism of Ethane. *J. Indian Chem. Soc.* **2002**, *79*, 240-248.
16. Pederson, L. ; Morokuma, K. *Ab Initio* Calculations of Barriers to Internal Rotations of CH_3 CH_3, CH_3NH_2, CH_3OH, N_2 H_4, H_2O_2 and NH_2 OH. *J. Chem. Phys*. **1967**, *46*, 3941–3947.
17. (a) Fink, W. H and Allen, L. C. Origin of Rotational Barriers I. Many-Electron Molecular Orbital Wave Functions for Ethane, Methyl Alcohol, Hydrogen Peroxide. *J. Chem. Phys.* **1967,** *46*, 2261-2275.
(b) ibid, Origin of Rotational Barriers II. Methyl amine and Improved Wave Functions for Hydrogen Peroxide. *J. Chem. Phys.* **1967,** *46*, 2276–2284.
18. Kaldor, U; Shavitt, I. LCAO–SCF Computations for Hydrogen Peroxide. *J. Chem. Phys.* **1966**, *44*, 1823-1829.
19. Palke, W. E. ; Pitzer, R. M. On the Internal Rotation Potential in H_2O_2. *J. Chem. Phys.* **1967**, *46*, 3948-3950.
20. Salvador, P.; Mayer, I. Energy Partitioning for "fuzzy atoms. *J. Chem. Phys.* **2004**, *120*, 5046.
21. Ghosh, D. C. ; Jana, J. and Biswas, R. Quantum Chemical Study of the Umbrella Inversion of the Ammonia Molecule. *Int. J. Quantum Chem*. **2000**, *80*, 1-26.
22. Ghosh, D. C. ; Jana , J. and Bhattacharya, S. Density Functional and Molecular Orbital Study of Physical Process of Inversion of Nitrogen Trifluoride (NF_3) Molecule. *Int. J. Quantum Chem*. **2002,** *87*, 111-134.
23. Ghosh , D. C. and Bhattacharya, S. Molecular Orbital and Density Functional Study of the Formation, Charge Transfer, Bonding and the Conformational of the Boron Trifluoride (BF_3) and Ammonia (NH_3) Donor-Acceptor Complexe. *Int. J. Mol. Sci.* **2004**, *5*, 239-264.
24. Ghosh, D. C. A Density Functional and Molecular Orbital study of the Methylamine Conformers *Internet. Elect. J. Mol. Design* **2005**, *4*, 31-58.
25. Roothaan, C. C. J. A Study of Two-Center Integrals Useful in Calculation on Molecular Structure *J. Chem. Phys.* **1951,** *19*, 1445-1457.
26. Fischer , H. and Kollmar, H. Energy Partitioning with the CNDO Method. *Theor. Chim. Acta.* **1970**, *16*,163-184.
27. Hunt, R.H.; Leacock, R. A.; Peters, C. W and Hecht, K. T. Internal Rotation of Hydrogen Peroxide: The Far-Infrared Spectrum and the Determination of the hindering Potential. *J. Chem. Phys.* **1965**, *42*, 1931-1946.
28. Oelfke, W. C.; Gordy, W. Millimeter-Wave Spectrum of Hydrogen Peroxide. *J. Chem. Phys*. **1969**, *51*, 5336-5343.
29. Douglas, B.; Mc Daniel, D.; Alexander, J. 'Concepts and Models of Inorganic Chemistry', 3rd

Edition, John Wiley & Sons, Inc. New York, 1994.
30. Dunning, Jr, T. H.; Winter, N. W. Theoretical Determination of the Barriers to Internal Rotation in Hydrogen Peroxide. *J. Chem. Phys.* **1975,** *63*, 1847-1855.
31. Jackson, R. H. *J. Chem. Soc.* **1962**, 4585-4592.
32. Amos, R. D.; Murray, C. W.; Handy, N. C. Structure and Vibrational FOOF and FONO using Density Functional Theory. *Chem. Phys. Letts.* **1993**, *202*, 489-494.
33. Scuseria, G. E. Analytic Ebaluation of Energy Gradients for the Singles and Doubles Coupled Cluster Method Including Perturbative Triple Excitations: Theory and Apllication to FOOF and Cr_2. *J. Chem. Phys*. **1991**, *94*, 442-447.
34. Allen Clabo Jr., D..; Schaefer III, H. F. Fluorine Peroxide (F_2O_2): A Continuing Problem for Normally Reliable Theoretical Methods. *Int. J. Quantum Chem.* **1987,** *31*, 429-433.
35. Mack, H. G.; Oberhammer, H. An Improved ab inition Structure for Fluorine Peroxide. *Chem. Phys. Lett.* **1988**, *145*, 121-124.
36. Lee, T. J.; Rice, J.E.; Scuseria, G.E. and Schaefer III, H. F. *Theor. Chim. Acta* **1989**, *75*, 81.
37. 37. Rohlfing, C. M ; Hay, P. J. Structure and Bonding of F_2O_2. *J. Chem. Phys.* **1987**, *86*, 4518-4522.
38. 38. Ahlrichs, R.; Taylor, P. R. The Structure of F_2O_2; Theoretical Predictions and Comparison with F_2 and F_2 O. *Chem. Phys.* **1982**, *72*, 287-292.
39. Raghavachari, K.; Trucks, G. W. Highly Correlated Systems. Structure and Harmonic Force Field of F_2O_2. *Chem. Phys. Lett*. **1989**, *62*, 511-516.
40. Fukui, K.; Role of Frontier Orbitals in Chemical Reactions. *Science* **1982,** *218*, 747-754.
41. Pearson, R. G.; Hard and Soft Acids and Bases. *J. Am. Chem. Soc.* **1963**, *85*, 3533-3539.
42. Pasha, F.A.; Srivastava, H.K.; Singh, P.P. QSAR Study of Estrogens with the Help of PM3–based Descriptors. *Int. J. Quantum Chem.* **2005**, *104*, 87-100.