Potential Energy Surfaces of 1-Phenyl-1,2-propandione-1-oxime and Its Tautomers

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Potential energy surfaces are found for 1-phenyl-1,2-propandione-1-oxime (**1**) and its four tautomers, *i.e.*, 1-nitroso-1-phenyl-1-propen-2-ol (**2**), 1-nitroso-1-phenyl-2-propanone (**3**), 2-hydroxy-1-phenyl-propenone oxime (**4**) and 3-nitroso-3-phenyl-propen-2-ol (**5**). Calculations are carried out at the Hartree-Fock (HF), Density Functional Theory (B3LYP) and the second-order Moller-Plesset perturbation (MP2) levels of theory using 6-31G* and 6-311G** basis sets. Five conformers, with no imaginary vibrational frequency, are obtained by free rotations around three single bonds of **1**: Ph-C(NOH)C(O)CH$_3$, PhC(NOH)-C(O)-CH$_3$ and PhC(N-OH)C(O)CH$_3$. Similarly, eight structures with no imaginary vibrational frequency are encountered upon rotations around three single bonds of **2**: Ph-C(NO)C(OH)CH$_3$, PhC(N-O)C(OH)CH$_3$ and PhC(NO)C(-OH)CH$_3$. In the same manner, six minima are found through rotations around three single bonds of **3**: Ph-CH(NO)C(O)CH$_3$, PhCH(-NO)C(O)CH$_3$ and PhCH(NO)-C(O)CH$_3$. Two minima are also found through rotations around four single bonds of **4**: Ph-C(NOH)C(OH)CH$_2$, PhC(N-OH)C(OH)CH$_2$, PhC(NOH)-C(OH)CH$_2$ and Ph-C(NOH)C(-OH)CH$_2$. Finally, two minima are found through rotations around four single bonds of **5**: Ph-CH(NO)C(OH)CH$_2$, PhCH(-NO)C(OH)CH$_2$, PhCH(NO)-C(OH)CH$_2$ and PhCH(NO)C(-OH)CH$_2$. Inter-conversion within the above sets of conformers (of **1**, **2**, **3**, **4** and **5**) are probed through scanning (one and/or two dimensional) and/or QST3 techniques. The order of the stability of global minima encountered is: **1** > **3** > **2** > **4** > **5**. Hydrogen bonding appears significant in tautomers **2** and **4**.

Key Words: *Ab initio*, DFT, Tautomerization, 1-Phenyl-1,2-propandione-1-oxime, 1-Nitroso-1-phenyl-1-propen-2-ol, 1-Nitroso-1-phenyl-2-propanone, 2-Hydroxy-1-phenyl-propenone oxime, 3-Nitroso-3-phenyl-propen-2-ol.

INTRODUCTION

In organic chemistry the compounds containing the >C=N–OH grouping derived from the aldehydes and ketones by condensing them with hydroxylamine are known as oximes generally oximes may be changed to the corresponding amide derivatives by treatment with various acids. This reaction better known as Beckmann rearrangement[1]. Since oximes have

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more than one conformer, the experimental and quantum chemical calculations for their conformational analysis are very interesting and have received a lot of attention among experimental and theoretical chemists[2]. For instance, the microwave spectrum of *n*-butyraldehyde oxime was observed in the frequency region 26.5-40 GHz, where four rotational conformers were found to exist in the gas phase; among these, two conformers belonged to the (E)-geometrical isomer and the other two to the (Z)-geometrical isomer. The 2-nitrosophenol derivatives are also in tautomeric equilibrium in solution[3,4] with quinonemono-oxime but nitroso form predominates[5]. Buraway *et al.*[3] have shown that in hexane, CCl_4, $CHCl_3$, Et_2O, benzene, ethanol and water the 2-nitrosophenol was observed only as nitroso tautomer. In all the solvents the compound studied exhibits the characteristic band of nitroso group. In disagreement with the above experiment, Jaffe[6] MO calculations have shown that the oxime form of 2-nitrosophenol should be more stable by 4 kcal/mol. *Ab initio* results for the total energies of both tautomers with intramolecular hydrogen bond indicate that the nitroso tautomer is more stable than the oxime tautomer by 10.29 and 5.69 kcal/mol at HF/6-31G and HF/6-31G* level, respectively[7]. In another incident, the tautomeric and conformational equilibrium of acenaphthenequinonemonooxime was studied by liquid and solid state NMR spectroscopy and *ab initio* calculations. The compound studied exists in the solid state as an oxime tautomer. However, in solution both the oxime and the nitroso tautomeric forms are present. *Ab initio* 6-31G (d,p) calculations in agreement with the experimental data predict the oxime tautomer to be more stable[8]. Yet in another study, all the possible carbonyl-nitroso, enol-nitroso and carbonyl-oxime conformations of glyoxalmono-oxime and all the rotamers of carbonyloxime tautomer of 1-methyl and 2-methylglyoxalmonooximes have been theoretically investigated; where the fully linear carbonyl-oxime conformer has been found to be the most favoured one over the enol-nitroso and carbonyl-nitroso conformations[9].

Oxime compounds are used as antidotes for nerve agents. A nerve agent inactivates acetyl cholinesterase molecules by phosphonylation of the molecule. Moreover, compounds capable of nitroso-oxime equilibria often show specific biological activities[10,11]. To carry out such biological functions, biomolecules must adopt definite conformational forms. Again, this makes the study of oxime tautomeric conformations of prime importance and worthy of receiving attentions[12-17]. In particular, the biologically active 1-phenyl-1,2-propandione-1-oxime, **1**, has electron donor atoms consisting of carbonyl oxygen and oxime nitrogen, which enable it to act as a mono- or bidentate ligand in metal complexes[18]. To date, no report has appeared on conformational energy surface of **1** and its tautomers. In this paper, conformational energy surface, are reported for 1-phenyl-1,2-propandione-1-oxime and its tautomers at the Hartree-Fock (HF), DFT (B3LYP) and the second-order Moller-Plesset perturbation (MP2) levels of theory, using 6-31G* and 6-311G** basis sets.

EXPERIMENTAL

Rotational energy profile around all the single bonds of **1, 2, 3, 4** and **5** (Figs. 1-5), are determined using *ab initio* HF calculation and STO-3G basis-sets. Calculations are performed *via* the Gaussian 98 system of programs[19]. Several optimizations are carried out for **1, 2, 3, 4** and **5**. Each at a constant dihedral angle, starting from 0° to 360° with ten degrees increments. All the other structural parameters are allowed to vary and be optimized. The geometrical structures, corresponding to the ground states and transition states are investigated at HF/STO-3G level of theory. To assess the performance of this approach, all species are computed at higher levels. Consequently, the STO-3G outputs are used as inputs for the HF/6-31G* calculations and the HF/6-31G* outputs are inputted for HF/6-31G**. The Hartree-Fock method usually works well for frequency predictions and geometry optimizations, but its utility for calculating conformational energy is questionable[20]. Hence, the necessity of investigating the effects of the electron correlations on the order of the magnitude of relative energies of the conformers arises. So, further post Hartree-Fock (MP2) single point calculations are performed on optimized geometries obtained through HF/6-31G* and HF/6-311G**[21]. Finally, the geometry reoptimizations are carried out using the Density functional theory (DFT) in the form of Becke's three parameters functional hybrid method[22]. This is with the Lee, Yang and Parr correlation functional ((B3LYP)/6-31G*) and (B3LYP)/6-311G**)[23].

Transition state geometries are investigated by QST3 technique. In each case, two optimized conformers along with their speculated transition state are inputted. In order to confirm the nature of the stationary species and evaluate the rotational activation energy barriers around each bond, frequency calculations (using the keyword: FREQ) are carried out for ground and transition states at both HF and DFT levels. The energy values are corrected with zero point vibrational energy to eliminate known systematic errors in calculations. All the structures appeared to correspond to local minima, since frequency calculations yield only positive values at the equilibrium geometries. All the structures are considered to be true transition states by having only one imaginary frequency. Also the reaction path followed by IRC to confirm transition states related to the corresponding minimums[24,25].

RESULTS AND DISCUSSION

In this paper, HF, MP2 and DFT methods, with 6-31G** and 6-311G** basis sets, are employed for investigating the tautomeric and conformational equilibria of 1-phenyl-1,2-propandione-1-oxime (**1**, Table-1), 1-nitroso-1-phenyl-1-propen-2-ol (**2**, Table-2), 1-nitroso-1-phenyl-2-

TABLE-1

HF(6-31G* AND 6-311G** BASIS SETS), B3LYP (6-31G* AND 6-311G** BASIS SETS) AND MP2 (6-31G* AND 6-311G** BASIS SETS) THERMODYNAMIC DATA FOR FIVE ROTOMERS OF 1-PHENYL-1,2-PROPANDIONE-1-OXIME, 1 (1_{Min1}, 1_{Min2}, 1_{Min3}, 1_{Min4} AND 1_{Min5}) SHOWING: THE SUM OF ELECTRONIC AND THERMAL ENERGIES (E), THE SUM OF ELECTRONIC AND THERMAL ENTHALPIES (H), AS WELL AS THE SUM OF ELECTRONIC AND THERMAL GIBBS FREE ENERGIES (G)

Rotomers of 1		HF		B3LYP		MP2	
		6-31G*	6-311G**	6-31G*	6-311G**	6-31G*	6-311G**
$1_{Min 1}$	E	-549.960603	-550.105431	-553.323199	-553.472554		
	H	-549.959659	-550.104487	-553.322255	-553.471610	-551.800134	-552.088888
	G	-550.009280	-550.153420	-553.372872	-553.522447		
$1_{Min 2}$	E	-549.970934	-550.105431	-553.333156	-553.482908		
	H	-549.969990	-550.104487	-553.332212	-553.481964	-551.809992	-552.088889
	G	-550.018549	-550.153420	-553.381613	-553.531664		
$1_{Min 3}$	E	-549.975149	-550.109838	-553.335641	-553.486139		
	H	-549.974205	-550.108894	-553.334697	-553.485194	-551.818044	-552.091891
	G	-550.022625	-550.157434	-553.384096	-553.534721		
$1_{Min 4}$	E	-549.966112	-550.099615	-553.334457	-553.482943		
	H	-549.965167	-550.098671	-553.333513	-553.481999	-551.808648	-552.086843
	G	-550.013360	-550.147036	-553.382263	-553.530787		
$1_{Min 5}$	E	-549.973364	-550.108104	-553.332526	-553.483302		
	H	-549.972420	-550.107160	-553.331581	-553.482357	-551.809791	-552.088625
	G	-550.021239	-550.156014	-553.381627	-553.532285		

TABLE-2

HF (6-31G* AND 6-311G** BASIS SETS), B3LYP (6-31G* AND 6-311G** BASIS SETS) AND MP2 (6-31G* AND 6-311G** BASIS SETS) THERMODYNAMIC DATA FOR EIGHT ROTOMERS OF 1-NITROSO-1-PHENYL-1-PROPEN-2-OL, 2 (2_{Min1}, 2_{Min2}, 2_{Min3}, 2_{Min4}, 2_{Min5}, 2_{Min6}, 2_{Min7} AND 2_{Min8}) SHOWING: THE SUM OF ELECTRONIC AND THERMAL ENERGIES (E), THE SUM OF ELECTRONIC AND THERMAL ENTHALPIES (H), AS WELL AS THE SUM OF ELECTRONIC AND THERMAL GIBBS FREE ENERGIES (G)

Rotomers of 2		HF		B3LYP		MP2	
		6-31G*	6-311G**	6-31G*	6-311G**	6-31G*	6-311G**
2_{Min1}	E	-549.935569	-550.069804	-553.305144	-553.454644		
	H	-549.934625	-550.068860	-553.304199	-553.453700	-551.7770362	-552.0568573
	G	-549.982724	-550.117285	-553.352634	-553.502381		
2_{Min2}	E	-549.689213	-550.062906	-553.298221	-553.448072		
	H	-549.688987	-550.061962	-553.297227	-553.447128	-551.7689024	-552.0492903
	G	-549.739877	-550.110301	-553.346100	-553.496090		
2_{Min3}	E	-549.945179	-550.080068	-553.312073	-553.462071		
	H	-549.944235	-550.079129	-553.311129	-553.461127	-551.7849738	-552.0652023
	G	-549.992318	-550.127602	-553.359536	-553.509839		
2_{Min4}	E	-549.937523	-550.072645	-553.305033	-553.455278		
	H	-549.936579	-550.071700	-553.304089	-553.454334	-551.77718	-552.0577787
	G	-549.984708	-550.120078	-553.352654	-553.502999		
2_{Min5}	E	-549.943747	-550.077284	-553.334456	-553.482943		
	H	-549.942803	-550.076340	-553.333512	-553.481998	-551.7881436	-552.0669052
	G	-549.990284	-550.123998	-553.382260	-553.530787		
2_{Min6}	E	-549.693676	-550.058479	-553.31433	-553.451491		
	H	-549.692732	-550.057535	-553.31399	-553.450552	-551.7763939	-552.0445518
	G	-549.740999	-550.106069	-553.36203	-553.499871		
2_{Min7}	E	-549.946012	-550.080407	-553.315488	-553.464724		
	H	-549.945067	-550.079463	-553.314544	-553.463780	-551.787050	-552.066419
	G	-549.993309	-550.128230	-553.362877	-553.512291		
2_{Min8}	E	-549.932227	-550.066908	-553.297280	-553.446936		
	H	-549.931283	-550.065963	-553.296336	-553.445992	-551.769828	-552.050268
	G	-549.980895	-550.115907	-553.345535	-553.495461		

TABLE-3

HF(6-31G* AND 6-311G** BASIS SETS), B3LYP (6-31G* AND 6-311G** BASIS SETS) AND MP2 (6-31G* AND 6-311G** BASIS SETS) THERMODYNAMIC DATA FOR SIX ROTOMERS OF 1-NITROSO-1-PHENYL-2-PROPANONE, **3** (3_{Min1}, 3_{Min2}, 3_{Min3}, 3_{Min4}, 3_{Min5}, **3** AND 2_{Min6}) SHOWING: THE SUM OF ELECTRONIC AND THERMAL ENERGIES (E), THE SUM OF ELECTRONIC AND THERMAL ENTHALPIES (H), AS WELL AS THE SUM OF ELECTRONIC AND THERMAL GIBBS FREE ENERGIES (G)

Rotomers of 3		HF		B3LYP		MP2	
		6-31G*	6-311G**	6-31G*	6-311G**	6-31G*	6-311G**
$3_{Min\,1}$	E	-549.951331	-550.081722	-553.309432	-553.455692	-551.7849389	-552.0616778
	H	-549.950380	-550.080782	-553.308488	-553.454748		
	G	-550.000407	-550.130895	-553.359347	-553.505692		
$3_{Min\,2}$	E	-549.953518	-550.085726	-553.309136	-553.455676	-551.7862284	-552.062929
	H	-549.952574	-550.082782	-553.308191	-553.454731		
	G	-550.002552	-550.132968	-553.359818	-553.505691		
$3_{Min\,3}$	E	-549.952321	-550.082919	-553.308559	-553.454838	-551.7858823	-552.0631092
	H	-549.951376	-550.081974	-553.307615	-553.453898		
	G	-550.001299	-550.131831	-553.358751	-553.504939		
$3_{Min\,4}$	E	-549.951575	-550.081582	-553.308314	-553.454117	-551.7859174	-552.0616054
	H	-549.950631	-550.080638	-553.307370	-553.453173		
	G	-550.000018	-550.130135	-553.357731	-553.503866		
$3_{Min\,5}$	E	-549.949270	-550.079655	-553.308229	-553.454362	-551.7838841	-552.0603675
	H	-549.948325	-550.078711	-553.307285	-553.453418		
	G	-549.998020	-550.128367	-553.358060	-553.504288		
$3_{Min\,6}$	E	-549.950374	-550.080351	-553.307679	-553.452622	-551.7843739	-552.0603156
	H	-549.949429	-550.079407	-553.305835	-553.451678		
	G	-549.998767	-550.128857	-553.357348	-553.503211		

TABLE-4

HF(6-31G* AND 6-311G** BASIS SETS), B3LYP (6-31G* AND 6-311G** BASIS SETS) AND MP2 (6-31G* AND 6-311G** BASIS SETS) THERMODYNAMIC DATA FOR TWO ROTOMERS OF 2-HYDROXY-1-PHENYL-PROPENONE OXIME, **4** (4_{Min1}, 4_{Min2}) SHOWING: THE SUM OF ELECTRONIC AND THERMAL ENERGIES (E), THE SUM OF ELECTRONIC AND THERMAL ENTHALPIES (H), AS WELL AS THE SUM OF ELECTRONIC AND THERMAL GIBBS FREE ENERGIES (G)

Rotomers of 4		HF		B3LYP		MP2	
		6-31G*	6-311G**	6-31G*	6-311G**	6-31G*	6-311G**
$4_{Min\,1}$	E	-549.940140	-550.081496	-553.303350	-553.460168	-551.777134	-552.069021
	H	-549.939196	-550.080552	-553.302406	-553.459223		
	G	-549.987923	-550.129219	-553.352010	-553.509372		
$4_{Min\,2}$	E	-549.945316	-550.086007	-553.310985	-553.467241	-551.786273	-552.071781
	H	-549.944371	-550.085063	-553.310041	-553.466297		
	G	-549.991342	-550.132158	-553.357777	-553.514154		

TABLE-5

HF(6-31G* AND 6-311G** BASIS SETS), B3LYP (6-31G* AND 6-311G** BASIS SETS) AND MP2 (6-31G* AND 6-311G** BASIS SETS) THERMODYNAMIC DATA FOR TWO ROTOMERS OF 3-NITROSO-3-PHENYL-PROPEN-2-OL, **5** (5_{Min1}, 5_{Min2}) SHOWING: THE SUM OF ELECTRONIC AND THERMAL ENERGIES (E), THE SUM OF ELECTRONIC AND THERMAL ENTHALPIES (H), AS WELL AS THE SUM OF ELECTRONIC AND THERMAL GIBBS FREE ENERGIES (G)

Rotomers of 4		HF		B3LYP		MP2	
		6-31G*	6-311G**	6-31G*	6-311G**	6-31G*	6-311G**
$5_{Min\,1}$	E	-549.923878	-550.060857	-553.281941	-553.429164	-551.756209	-552.048917
	H	-549.922934	-550.059913	-553.280997	-553.429705		
	G	-549.971534	-550.108682	-553.330924	-553.471627		
$5_{Min\,2}$	E	-549.920849	-550.057592	-553.279621	-553.431649	-551.755934	-552.051741
	H	-549.919905	-550.056648	-553.278677	-553.430705		
	G	-549.968928	-550.105852	-553.328431	-553.480756		

propanone (**3**, Table-3), 2-hydroxy-1-phenyl-propenone oxime (**4**, Table-4) and 3-nitroso-3-phenyl-propen-2-ol (**5**, Table-5) (Figs. 1-5). These compounds along with the calculated energy barriers, separating the low energy conformers, as well as the transition states in their inter-conversion pathways. In order to determine the barrier of internal rotations of different tautomers, we have calculated the electronic energies of the molecules as a function of the angle of the rotation about all the single bonds.
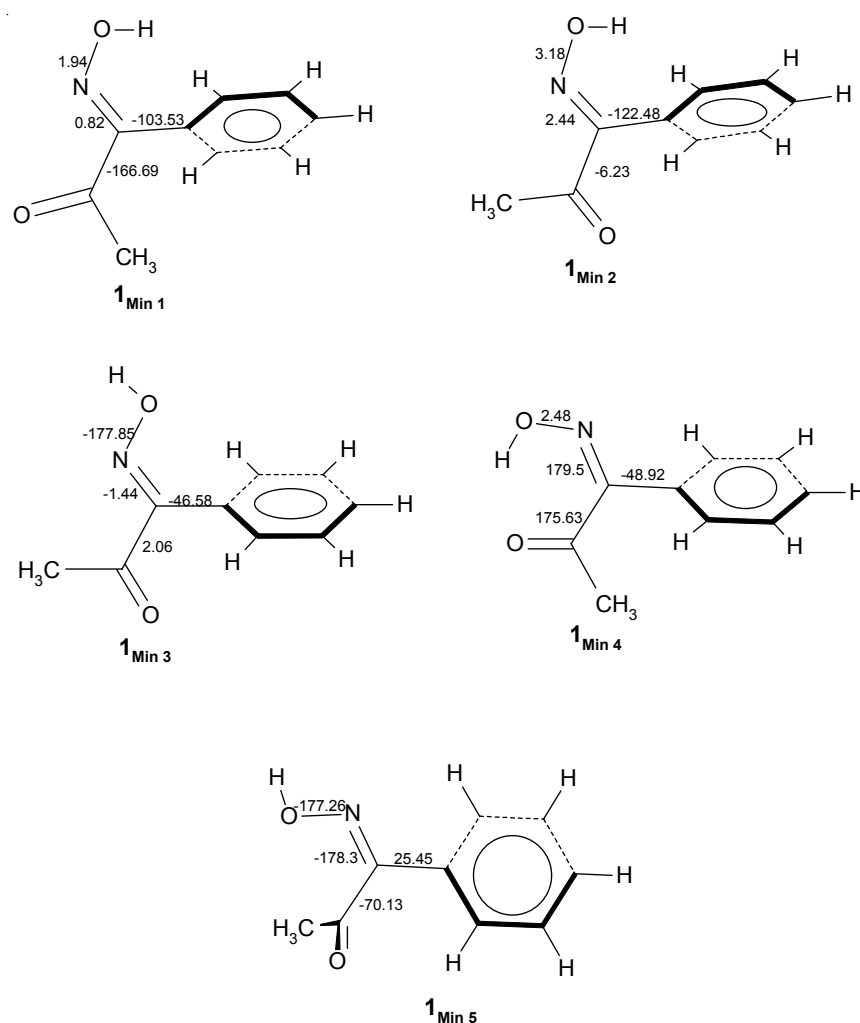
Fig. 1. Final optimized geometrical parameters (dihedral angles) of five conformers of 1-phenyl-1,2-propandione-1-oxime (**1**), obtained through DFT(B3LYP/6-311G**) calculations
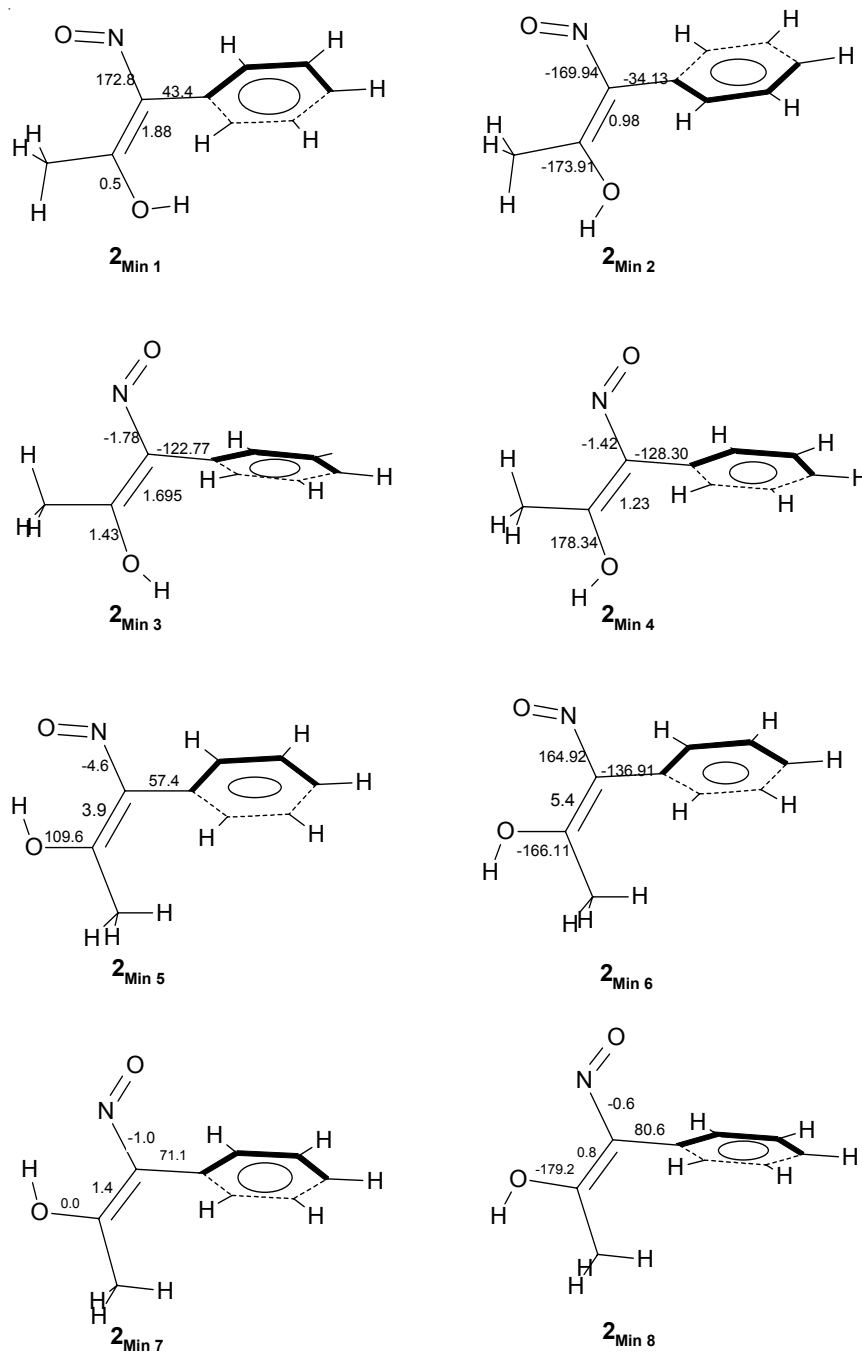
Fig. 2.   Final optimized geometrical parameters (dihedral angles) of eight
conformers of 1-nitroso-1-phenyl-1-propen-2-ol (**2**), obtained by
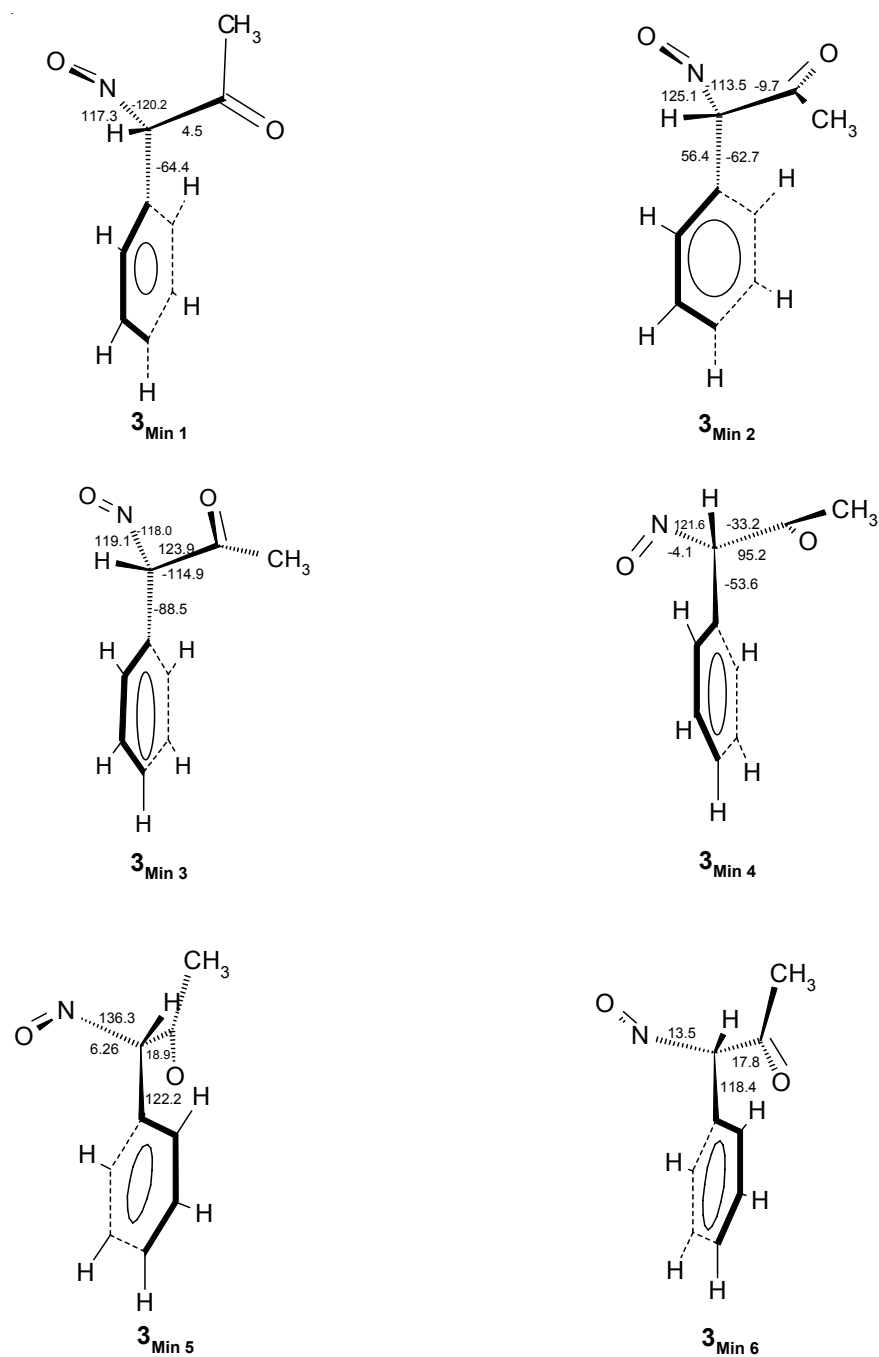DFT (B3LYP/6-311G**) calculations

Fig. 3. Final optimized geometrical parameters (dihedral angles) of six conformers of 1-nitroso-1-phenyl-2-propanone (**3**), obtained by DFT (B3LYP/6-311G**) calculations
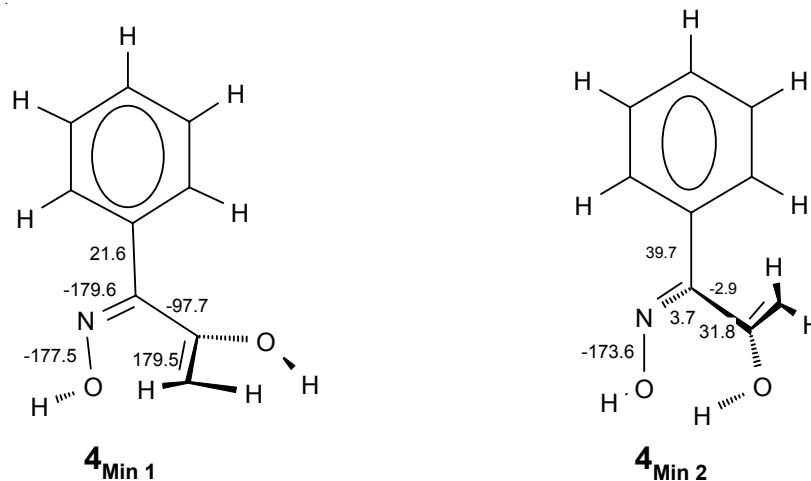
Fig. 4.   Final optimized geometrical parameters (dihedral angles) of two
          conformers of 2-hydroxy-1-phenyl-propenone oxime (**4**),
          obtained by DFT (B3LYP/6-311G**) calculations
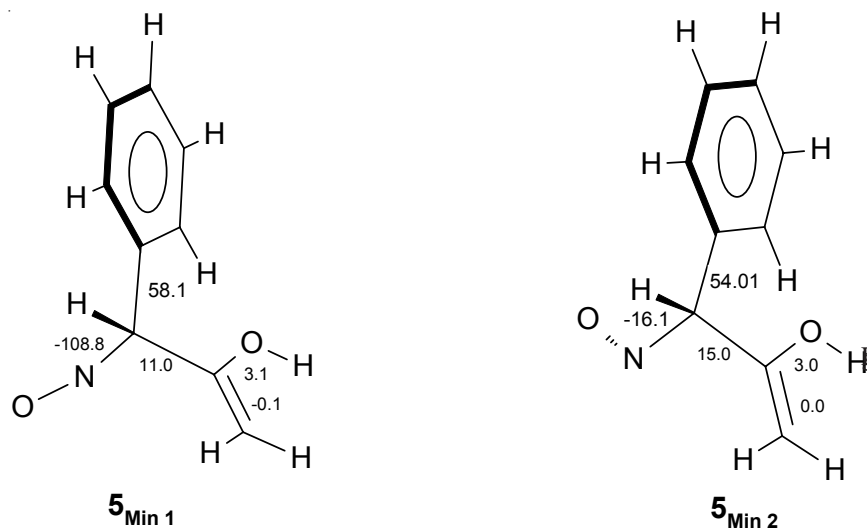

Fig. 5.   Final optimized geometrical parameters (dihedral angles) of two
          conformers of 3-nitroso-3-phenyl-propen-2-ol (**5**), obtained by
          DFT (B3LYP/6-311G**) calculations

The final optimized geometric structural parameters of conformers of
1, 2, 3, 4 and **5** are obtained by DFT (B3LYP/6-311G**) calculations (Figs.
1-5). The results show five rotomers (1_{Min1}, 1_{Min2}, 1_{Min3}, 1_{Min4} and 1_{Min5}) to
be important for conformational description of **1** (Fig. 1). Eight conform-

ers (2_{Min1}, 2_{Min2}, 2_{Min3}, 2_{Min4}, 2_{Min5}, 2_{Min6}, 2_{Min7} and 2_{Min8}) turn out to be significant for conformational account of **2** (Fig. 2). Six conformers (3_{Min1}, 3_{Min2}, 3_{Min3}, 3_{Min4}, 3_{Min5} and 3_{Min6}) are essential for conformational picture of **3** (Fig. 3). Two conformers (4_{Min1} and 4_{Min2}) appear to be important for conformational description of **4** (Fig. 4). Two rotomers (5_{Min1} and 5_{Min2}) are found significant for description of **5** (Fig. 5).

Thermodynamic data of **1, 2, 3, 4** and **5** are calculated at HF (6-31G* and 6-311G**), B3LYP (6-31G*, 6-311G**) and single point MP2 (6-31G*, 6-311G**) (Tables 1-5). These data include the sum of electronic and thermal energies (E), the sum of electronic and thermal enthalpies (H), as well as the sum of electronic and thermal Gibbs free energies (G). All the seven levels of theory show 1_{Min3} to have smaller E_r, H_r and G_r, than those of all the conformers scrutinized (Table-6). Hence, they are set at zero, while the E_r, H_r and G_r of other conformers are adjusted accordingly.

A discrepancy is encountered between HF, MP2 and B3LYP in calculating the global minimum for conformers of **2**. On one hand, hydrogen bonding between oxygen and hydrogen (O—H---O) is observed in 2_{Min5} which is suggested by B3LYP and MP2 methods (with 6-31G* and/or 6-311G** basis sets) to be the global minimum for conformers of **2**. The parameters involved in this hydrogen bonding are quite reasonable with the O—H distance of 0.960 Å and H---O distance of 1.746 Å and with the corresponding ∠ O—H---O motif angle of 106.1° (Fig. 2, Table-6). On the other hand, hydrogen bonding between nitrogen and hydrogen (O—H---N) is observed in 2_{Min7} which is suggested by the less complicated HF methods (with 6-31G* and/or 6-311G** basis sets) to be the global minimum for conformers of **2**. The parameters involved in this hydrogen bonding are also quite reasonable with the O—H distance of 0.954 Å and H---N distance of 2.111 Å and with the corresponding ∠ O—H---N motif angle of 111.2° (Fig. 2, Table-6).

Conversely, no discrepancy is encountered between HF, MP2 and B3LYP in calculating the global minima for conformers of **1, 3, 4**, or **5** tautomers. All the employed methods show 1_{Min4} to be the global minimum of **1** (Fig. 1, Table-6). Hydrogen bonding between oxygen and hydrogen (O—H---O) is observed in 1_{Min4}. The parameters involved in this hydrogen bonding are: the O—H distance = 0.950 Å, H---O distance = 1.790 Å and the corresponding ∠ O—H---O motif angle = 142.4°. This conformer does not immerge as the global minimum of 1, due to the steric effects involved between its *ortho*-hydrogens and the β-CH_3 (Fig. 1, Table-6). Similarly, all the employed methods show 4_{Min2} to be the global minimum of **4** (Fig. 4, Table-6). Hydrogen bonding between oxygen and hydrogen (O—H---O) is observed in 4_{Min2}. The parameters involved in this hydrogen bonding are: the O—H distance = 0.942 Å, H---O distance = 1.805 Å and the correspon-

TABLE-6

RELATIVE ENERGIES (E_r), ENTHALPIES (H_r) AND GIBBS FREE ENERGIES (G_r) FOR 23 CONFORMERS OF THE SCRUTINIZED TAUTOMERS (**1-5**) *via* HF, B3LYP AND MP2 (kcal/mol). THE GLOBAL MINIMUM, **1**$_{Min\ 3,}$ DATA (E_r, H_r AND G_r) ARE SET AT ZERO; WHILE THOSE OF THE OTHER 22 CONFORMERS ARE ADJUSTED ACCORDINGLY

Confor-mers	Energies	HF (kcal/mol)		B3LYP (kcal/mol)		MP2 (kcal/mol)	
		6-31G*	6-311G**	6-31G*	6-311G**	6-31G*	6-311G**
1$_{Min\ 1}$	E	9.13	2.77	7.81	8.52		
	H	9.13	2.77	7.81	8.52	11.24	1.88
	G	8.37	2.52	7.04	7.70		
1$_{Min\ 2}$	E	2.64	2.77	1.56	2.03		
	H	2.64	2.77	1.56	2.03	5.05	1.88
	G	2.56	2.52	1.56	1.92		
1$_{Min\ 3}$	E	0.00	0.00	0.00	0.00		
	H	0.00	0.00	0.00	0.00	0.00	0.00
	G	0.00	0.00	0.00	0.00		
1$_{Min\ 4}$	E	5.67	6.41	0.74	2.01		
	H	5.67	6.41	0.74	2.00	5.90	3.17
	G	5.81	6.52	1.15	2.47		
1$_{Min\ 5}$	E	1.12	1.09	1.95	1.78		
	H	1.12	1.09	1.96	1.78	2.18	2.05
	G	0.87	0.89	1.55	1.53		
2$_{Min\ 1}$	E	24.84	25.12	19.14	19.76		
	H	24.84	25.12	19.14	19.76	25.73	21.98
	G	25.04	25.19	19.74	20.29		
2$_{Min\ 2}$	E	29.71	29.45	23.48	23.89		
	H	29.71	29.45	23.51	23.89	30.84	26.73
	G	29.87	29.58	23.84	24.24		
2$_{Min\ 3}$	E	18.81	18.68	14.79	15.10		
	H	18.81	18.68	14.79	15.10	20.75	16.75
	G	19.02	18.72	15.41	15.61		
2$_{Min\ 4}$	E	23.61	23.34	19.21	19.37		
	H	23.61	23.34	19.21	19.36	25.64	21.41
	G	23.79	23.44	19.73	19.91		
2$_{Min\ 5}$	E	19.70	20.43	0.74	2.01		
	H	19.70	20.43	0.74	2.01	18.76	15.68
	G	20.29	20.98	1.15	2.47		
2$_{Min\ 6}$	E	27.31	32.23	13.37	21.74		
	H	27.31	32.23	12.99	21.74	26.13	29.71
	G	28.01	32.23	13.85	21.87		
2$_{Min\ 7}$	E	18.28	18.47	12.65	13.44		
	H	18.28	18.47	12.65	13.44	19.45	15.98
	G	18.40	18.33	13.31	14.07		

Confor-mers	Energies	HF (kcal/mol)		B3LYP (kcal/mol)		MP2 (kcal/mol)	
		6-31G*	6-311G**	6-31G*	6-311G**	6-31G*	6-311G**
$2_{Min\ 8}$	E	26.93	26.94	24.07	24.60		
	H	26.93	26.94	24.07	24.60	30.26	26.12
	G	26.19	26.06	24.20	24.64		
$3_{Min\ 1}$	E	14.95	17.64	16.45	19.11		
	H	14.95	17.64	16.45	19.10	20.77	18.96
	G	13.94	16.65	15.53	18.22		
$3_{Min\ 2}$	E	13.57	15.13	16.63	19.12		
	H	13.57	16.39	16.63	19.12	19.96	18.17
	G	12.60	15.35	15.23	18.22		
$3_{Min\ 3}$	E	14.32	16.89	16.99	19.64		
	H	14.33	16.89	16.99	19.64	20.18	18.06
	G	13.38	16.07	15.90	18.69		
$3_{Min\ 4}$	E	14.79	17.73	17.15	20.09		
	H	14.79	17.73	17.15	20.09	20.16	19.00
	G	14.19	17.13	16.54	19.36		
$3_{Min\ 5}$	E	16.24	18.94	17.20	19.94		
	H	16.24	18.94	17.20	19.94	21.44	19.78
	G	15.44	18.24	16.34	19.10		
$3_{Min\ 6}$	E	15.55	18.50	17.55	21.03		
	H	15.55	18.50	18.11	21.03	21.13	19.81
	G	14.97	17.93	16.78	19.77		
$4_{Min\ 1}$	E	21.97	17.78	20.26	16.30		
	H	21.97	17.78	20.26	16.30	25.67	24.72
	G	21.78	17.70	20.13	15.91		
$4_{Min\ 2}$	E	18.72	14.95	15.47	11.86		
	H	18.72	14.95	15.47	11.86	19.94	12.62
	G	19.63	15.86	16.52	12.91		
$5_{Min\ 1}$	E	32.17	30.74	33.70	35.75		
	H	32.17	30.74	33.70	34.82	35.04	33.23
	G	32.06	30.59	33.37	39.59		
$5_{Min\ 2}$	E	34.07	32.78	35.15	34.19		
	H	34.07	32.78	35.15	34.19	34.58	32.95
	G	33.69	32.37	34.93	33.86		

ding O—H---O motif angle = 114.5º. Finally, no hydrogen bonding is observed in any conformer of **3** and/or **5**; indicating the higher significance of hydrogen bonding in stabilizing tautomers **2** and/or **4**. The lack of H-bonding in **3** and/or **5** is translated into the higher similarity between the energies of their corresponding rotomers (Table-6).

Free rotations around three single bonds (-) of **1**: Ph-C(NOH)C(O)CH$_3$, PhC(NOH)-C(O)CH$_3$ and PhC(N-OH)C(O)CH$_3$, give five energy minima conformers (**1$_{Min1}$, 1$_{Min2}$, 1$_{Min3}$, 1$_{Min4}$** and **1$_{Min5}$**; Fig. 1). Similarly, rotations around three single bonds of **2**: Ph-C(NO)C(OH)CH$_3$, PhC(N-O)C(OH)CH$_3$ and PhC(NO)C(-OH)CH$_3$, give eight structures (**2$_{Min1}$, 2$_{Min2}$, 2$_{Min3}$, 2$_{Min4}$, 2$_{Min5}$, 2$_{Min6}$, 2$_{Min7}$** and **2$_{Min8}$**; Fig. 2) with no imaginary vibrational frequency. In the same manner, six minima (**3$_{Min1}$, 3$_{Min2}$, 3$_{Min3}$, 3$_{Min4}$, 3$_{Min5}$** and **3$_{Min6}$**; Fig. 3) are found for **3** through rotations around Ph-CH(NO)C(O)CH$_3$, PhCH(-NO)C(O)CH$_3$ and PhCH(NO)-C(O)CH$_3$ bonds. Two minima (**4$_{Min1}$** and **4$_{Min2}$**) are found through rotations around four single bonds of **4**: Ph-C(NOH)C(OH)CH$_2$, PhC(N-OH)C(OH)CH$_2$, PhC(NOH)-C(OH)CH$_2$ and Ph-C(NOH)C(-OH)CH$_2$ (Fig. 4). Similarly, two minima (**5$_{Min1}$** and **5$_{Min2}$**) are found through rotations around four single bonds of **5**: Ph-CH(NO)C(OH)CH$_2$, PhCH(-NO)C(OH)CH$_2$, PhCH(NO)-C(OH)CH$_2$ and PhCH(NO)C(-OH)CH$_2$ (Fig. 5).

Inter-conversion pathways of the five conformers of **1** are probed through scanning (one and/or two dimensional) and/or QST3 (B3LYP/ 6-311G**) techniques (Fig. 6). The same treatments are adopted for the eight conformers of **2** (Fig. 7), the six conformers of **3** (Fig. 8), the two conformers of **4** and the two conformers of **5** (Fig. 9).
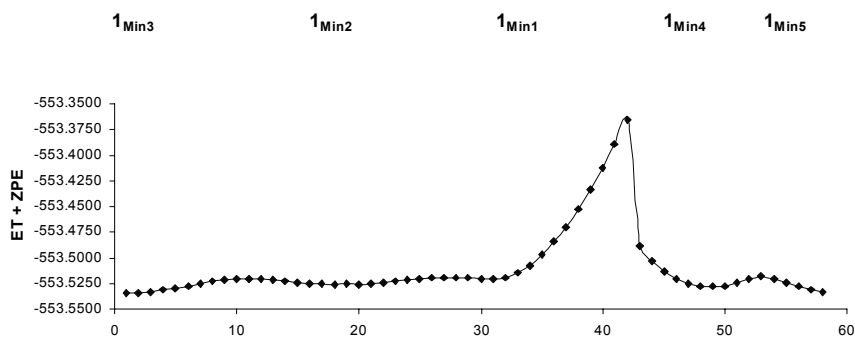

Fig. 6.   The least energetic pathway (among 24 possible routs; B3LYP/6-311G** level of theory) for inter-conversions of five conformers of **1**; probed through scanning (one and/or two dimensional) and/or QST3 techniques)

Rotations around single bonds render several conformers as minima for each tautomer. The lowest possible energy paths are selected for inter-conversions of these conformers. Two dimensional scans are employed for the transition states not reachable through simple rotations around one bond. Search for a transition structure between E and Z conformers of **1** (and/or **2**) is carried out using the STQN (B3LYP/ 6-311G**) method. This option
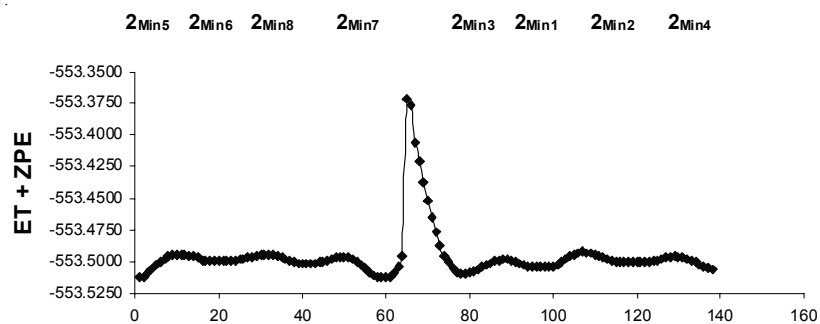
Fig. 7.   The least energetic pathway, for inter-conversions of five conformers of 1-nitroso-1-phenyl-1-propen-2-ol, 2 (B3LYP/6-311G** level of theory) probed through scanning (one and/or two dimensional) and/or QST3 techniques)
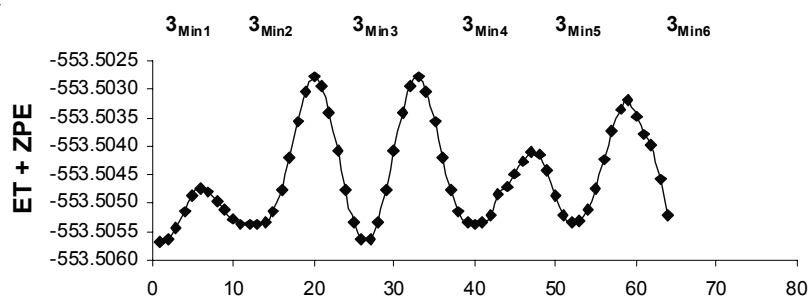

Fig. 8.   The least energetic pathway, for inter-conversions of five conformers of 1-nitroso-1-phenyl-2-propanone, 3 (B3LYP/6-311G** level of theory) probed through scanning (one and/or two dimensional) and/or QST3 techniques)
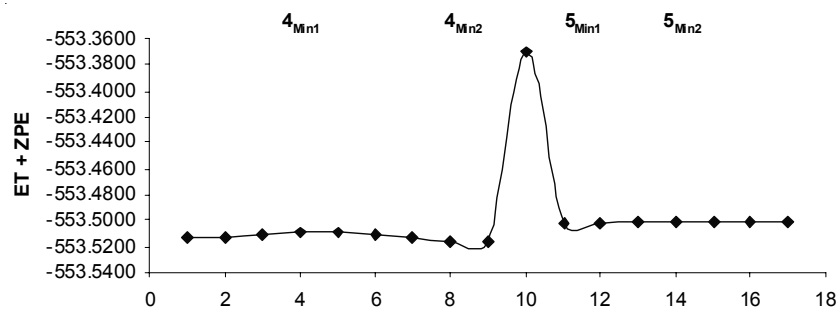

Fig. 9.   The least energetic pathway, for inter-conversions of five conformers of 2-hydroxy-1-phenyl-propenone oxime (**4**) and 3-nitroso-3-phenyl-propen-2-ol (**5**) (B3LYP/6-311G** level of theory) probed through scanning (one and/or two dimensional) and/or QST3 techniques)

requires the input of the optimized reactant and product as well as a propose transition state structures. Hence, the atoms are specified in the same order within the three structures (Figs. 1-5).

Different *ab initio* methods of calculations predict unanimously that the global minimum of oxime tautomer, **1**, is of the lowest energy compared to those of **2, 3, 4** and **5**. In turn, the global minimum of **3** is found to be more stable than that of **2**. Hence, the order of the stability of global minima encountered is: **1** > **3** > **2** > **4** > **5**.

Conclusion

Ab initio calculations portray a clear picture of 1-phenyl-1,2-propandione-1-oxime, **1**, tautomerizations to: 1-nitroso-1-phenyl-1-propen-2-ol (**2**), 1-nitroso-1-phenyl-2-propanone (**3**), 2-hydroxy-1-phenyl-propenone oxime (**4**) and 3-nitroso-3-phenyl-propen-2-ol (**5**). The order of the stability of global minima encountered is: **1** > **3** > **2** > **4** > **5**. Hydrogen bonding is observed in two conformers of **2**, one of which turns out to be the global minimum; one conformer of **4**, which happens to be the global minimum; one conformer of **1**, which dose not immerge as the global minimum; and no conformer of **3** and/or **5** indicating the higher significance of hydrogen bonding in tautomers **2** and/or **4**. Inter-conversion pathways of the five conformers of **1** are probed through scanning (one and/or two dimensional) and/or QST3 techniques. The same treatments are adopted for the eight conformers of **2**, the six conformers of **3**, the two conformers of **4** and the two conformers of **5**.

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