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Gas-Phase Structure and Rotational Barrier of Hydroxyphosphinecarbothialdehyde: A Computational Study

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ABSTRACT

The molecular structure of hydroxyphosphinecarbothialdehyde been studied in the gas phase. In addition, the interconversion of few isomeric tautomers of hydroxyphosphinecarbothialdehyde via intramolecular hydrogen transfer has been investigated by density functional calculations. The global isomeric structures, the transfer potential surfaces, rotational barrier, the harmonic frequency and transition states were calculated at the B3LYP/6-31++G(dp) // B3LYP/6-31G(d) levels of theory. Excluding the thiol forms with charge separating structures (CS1) and (CS2), the order of stability of these tautomers was 1b> 4b> 1a> 5b> 2b>> 3b, calculated at the single point level. Besides the hypervalent molecules 1b and 3b which was containing P=O bond character. The 1a, 2b and 5b are the thione forms, whereas 4b is the thiol form. The energy difference among the structures is no greater than 6.60 kcal mol^{-1}. The reaction pathway for the interconversion between tautomers was through the transition structures TS1 toTS7. TS3 was involved in the rate-determining step. Apart from the TS3, the ring strain was clearly affecting the activation barrier; in addition the calculations revealed that the bond lengths and the atomic charges have a direct role in the stability of the structures.

Keywords: Transition state, Activation barrier, Harmonic frequency and stability.

INTRODUCTION

The organophosphorus compounds have been potent inhibitors of cholinesterase, their action is non-competitive and not readily reversible, and furthermore many applications of organophosphorus compounds were investigated previously [1-3]. The structures of hydroxyphosphinecarbothialdehyde which was the phosphorus analogues of thioformohydroxamic acid was constructed by replacement of nitrogen atoms by phosphorus atoms. Hydroxamic acids like their thiohydroxamic acid counterparts play important roles in analytical and biological chemistry [4]. The structure and the deprotonation of the derivatives of these compounds have been the subject of several theoretical investigations [5-7]. Many hydroxamates exhibit metalloproteinase inhibition activity [8,9]. The existence of the phosphorus analogues of thiohydroxamic acids has not been proved experimentally and therefore no structural details are available, furthermore, no theoretical calculation has been carried out on this compound. Earlier theoretical calculations have been shown that the substitution of the central carbon atom with the silicon in formohydroxamic acid significantly influences the structure and acidity by comparison with parent molecule [10]. The aim of this work is to provide a consistent and reliable set of gas-phase structures for hydroxyphosphinecarbothialdehyde using high level theoretical calculations. Additional interests are the molecular geometries, activation barrier and how these properties change upon isosteric substitution of nitrogen atom in thioformohydroxamic acid molecule by phosphorus.

MATERIALS AND METHODS

The calculations were investigated the relative stabilities of the various tautomeric forms of hydroxyphosphinecarbothialdehyde, and then studied the reaction path leading from one to the other. The DFT calculations were performed with the B3LYP three parameter density functional, which includes Becke's gradient exchange correction [11] and the Lee–Yang–Parr correlation functional.[12,13] The geometries of all conformers, products and transition states were fully optimized at the B3LYP/6-31G(d) level of theory. This was followed by harmonic frequency calculations at this level; the optimized structures were confirmed to be real minima by frequency calculation (no imaginary frequency). The vibrational frequencies were scaled by a factor of 0.9614 [14]. The zero-point vibrational energy contribution is also considered. Single point calculations were then performed at the B3LYP/6-31++G(d,p) level for the geometries optimized at the B3LYP/6-31G(d) level. The SCF = Tight option was used in these calculations, performed using Gaussian 03 Revision C.02 [15].

RESULTS AND DISCUSSION

The optimized eight local minimum structures, including the thiol forms with charge separating species (CS1), (CS2) and seven corresponding transition structures TS of intramolecular hydrogen transfer are shown in Figure 1. The full optimized geometry of the structures and the barrier height in the processes are given in Table 1.

The calculations indicates that the main structures should be represented by three resonance structures, of which the later two are of major importance for the rotation barrier and charged isomer is suitable for the formation of metal complexes as in the scheme below.

Consequently the reaction path produced three isomeric tautomers of organophosphours compounds namely hydroxyphosphinecarbothialdehyde (I), (hydroxyphosphoranylidene)methanethiol (II) and (mercaptomethylene)phosphine (III) structures. The 1b structure showed three-member ring involving CSP atoms, the structure has the longest r(C-S) bond length 1.90Å and the lowest non-bonded distance between r(S---P) 2.08Å. CS1 and CS2 have the shortest r(C-P) bond length which is equal to 1.66 Å, in addition they have the highest sulfur charge +0.08 and +0.17 associated with CS1 and CS2 respectively. The seven transition structures (TS1 to TS7) was found on the potential energy surface of the reaction. TS3 is located on the reaction coordinate for 1b and 2b conversion; it is clear that it's the transition state of highest energy in the path and is involved in the rate-determining step. The other transition structures are located for proton transfer between pair of structures. Most of the optimized structures were found to be non-planar. The only planar structure was 4b with SCPO angle been the highest (180°), and thus in this structure the phosphorus adopted a pyramidal orientation.

The relative energies are listed in Table 2 and the schematic potential energy profile for the proton transfer is given in Figure 2. At the calculated level the 1b structure is calculated to be the most stable, and the energy values reported related to 1b in the hydroxyphosphinecarbothialdehyde. As expected the CS1 and CS2 have the highest energies which was 19.45 and 19.36 kcal mol^{-1} above the global minimum 1b respectively. The stability order for the local minimum structures are 4b>1a>5b>2b>3b.

The energy analysis indicated that the difference in energies among the structures is no greater than 6.60 kcal mol^{-1}. If the transformation of CS2 to 5b were to take place in one step, the only possible path would be the direct transfer of proton attached to sulfur to oxygen atom. It seems very difficult since the distance between the hydrogen and the oxygen is calculated to be 4.98 Å in the trans position and therefore, there is no sufficient kinetic energy to initiate such direct transfer. Thus interconversion between the CS2 and 5b form occur via a path (CS2$\rightarrow$TS6$\rightarrow$4b$\rightarrow$TS7$\rightarrow$5b) that has an overall activation barrier of 51.38 kcal mol^{-1}. This result is in excellent agreement with the activation barrier of thiohydroxamic acid which has been reported as 52.20 kcal mol^{-1} [16]. Excluding TS3, the difference in transition states energies are clearly related to the ring strain of the structure, therefore three-member ring TS4, TS6 and TS2 have higher energy thanTS5 and TS7. The TS3 has a unique structure since the oxygen atom lie above the SCP plane almost by right angle 92.98°.

The computed vibration frequencies are listed in Table 3. The computed infrared spectra of 2b and 4b tautomers are given in Figure 3. The calculated vibration frequencies are in conformity with the assignments of the experimental infrared spectra for related structures [16-18]. The computed vibrational frequencies for 4b structure showed a υ(SH) at 2561 cm^{-1} which in conformity with previously reported results [16]. The vibration stretching frequencies for (O-H), (C-H) and (P-O) are observed at 3629 and 3064 and 756 cm^{-1} respectively. On the other hand the 2b structure showed a very characteristic bands which are not observed for the thiol 4b structure. Thus the computed spectra had the υ(PH) and υ(S=O) at 2286 and 1020 cm^{-1} respectively. The DFT calculations showed that the νO-H of 2b is shifted to lower frequency in comparison with 4b form which has been attributed to intramolecular hydrogen bonding. The results for the other structures showed no different trend.

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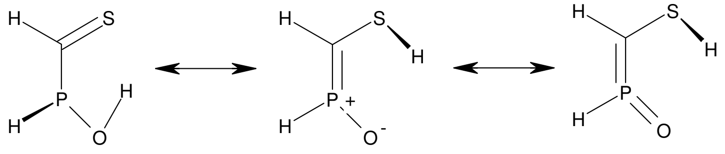

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Table 1: Optimized geometries of the structures (bond length in Angstroms).

System	C-S	C-P	P-O	S-H	r(S--P)	SCPO	ΔE_a
1a	1.64	1.83	1.64	-	3.07	10.2	
TS1	1.68	1.78	1.55	-	2.90	12.8	22.61
CS1	1.76	1.66	1.50	1.35	3.08	10.4	
TS2	1.82	1.71	1.49	-	3.18	20.6	40.22
1b	1.90	1.79	1.49	-	2.08	64.1	
TS3	1.69	1.87	1.59	-	2.95	75.6	80.17
2b	1.63	1.83	1.66	-	3.07	26.3	
TS4	1.64	1.80	1.60	-	3.02	158.7	63.79
3b	1.62	1.85	1.49	-	3.05	141.0	

TS5	1.66	1.87	1.50	-	2.83	154.0	39.91
CS2	1.77	1.66	1.45	1.36	2.95	172.1	
TS6	1.74	1.73	1.60	1.35	3.11	171.2	51.38
4b	1.76	1.68	1.68	1.35	3.10	180	
TS7	1.70	1.73	1.67	-	2.75	32.7	36.60
5b	1.63	1.83	1.68	-	3.06	21.1	

Table 2: The energies of the structures in (kcal mol^{-1}).

	ENERGY	Single energy	ZPE	Relative E
1a	-854.647307	-854.747197	0.040151	4.07
TS1	-854.6112721	-854.7111624	0.036136	26.68
CS1	-854.6220243	-854.7226941	0.038057	19.45
TS2	-854.5574993	-854.6585888	0.035200	59.67
1b	-854.6610503	-854.7536863	0.042513	0.00
TS3	-854.5270196	-854.625923	0.034134	80.17
2b	-854.6409908	-854.7417737	0.040139	7.48
TS4	-854.540366	-854.6401057	0.034926	71.27
3b	-854.6346042	-854.7299134	0.039602	14.92
TS5	-854.5669258	-854.666309	0.034256	54.83
CS2	-854.6239928	-854.7228383	0.038470	19.36
TS6	-854.5388451	-854.6409539	0.034272	70.74
4b	-854.6445617	-854.7491448	0.039542	2.85
TS7	-854.587249	-854.6908118	0.036640	39.45
5b	-854.642145	-854.7431635	0.040119	6.60

Table-3: Calculated vibrational frequencies in cm^{-1} for 2b and 4b structures.

2b	factorized	4b	factorized
98	94	90	87
186	179	186	179
301	289	209	201
417	401	301	289
598	575	337	324
771	741	710	683
807	776	774	744
873	839	786	756
940	904	956	919
1061	1020	1004	965
1105	1062	1093	1051
1283	1234	1284	1234
2378	2286	2664	2561
3074	2929	3187	3064
3728	3584	3775	3629

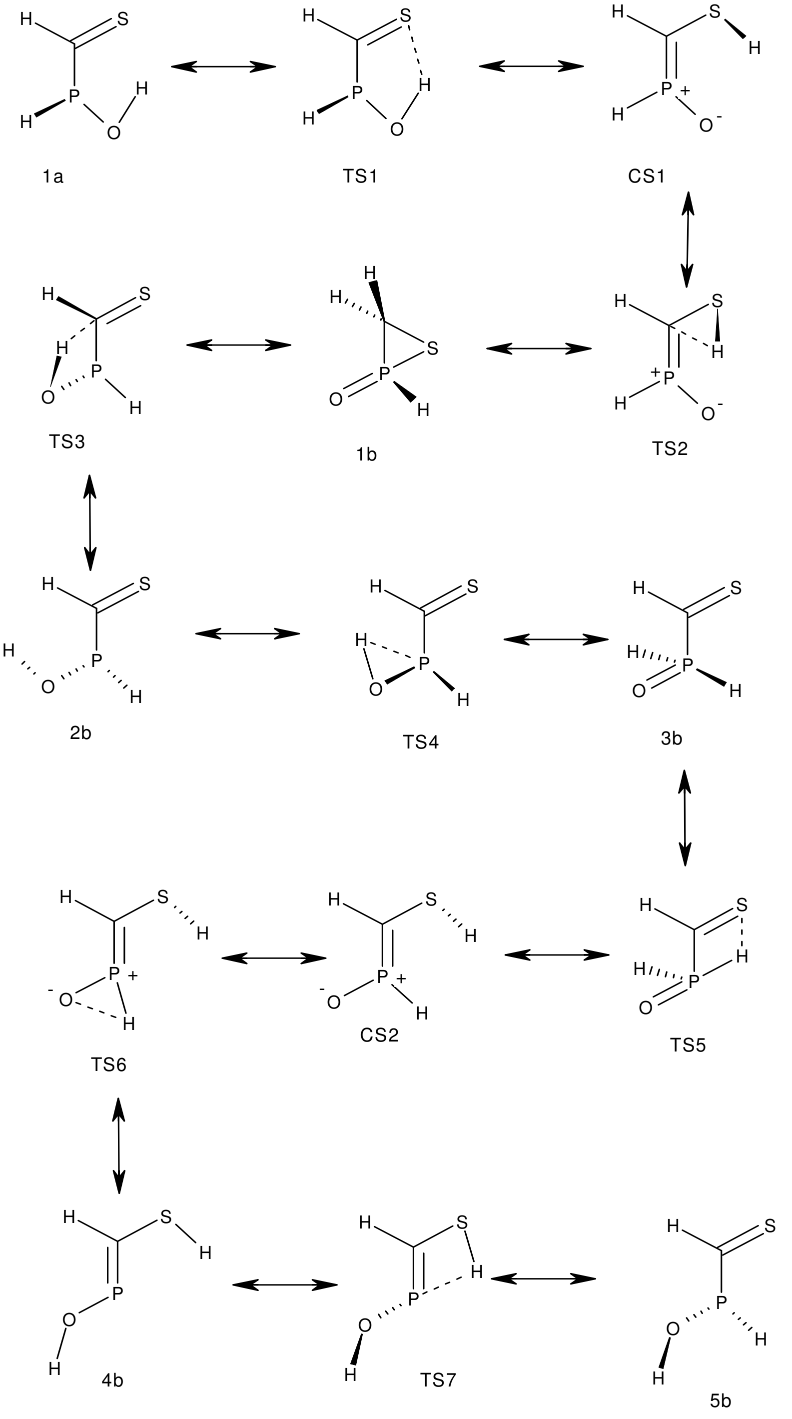

Fig.-1: The compound structures and the transition states interconnecting them.

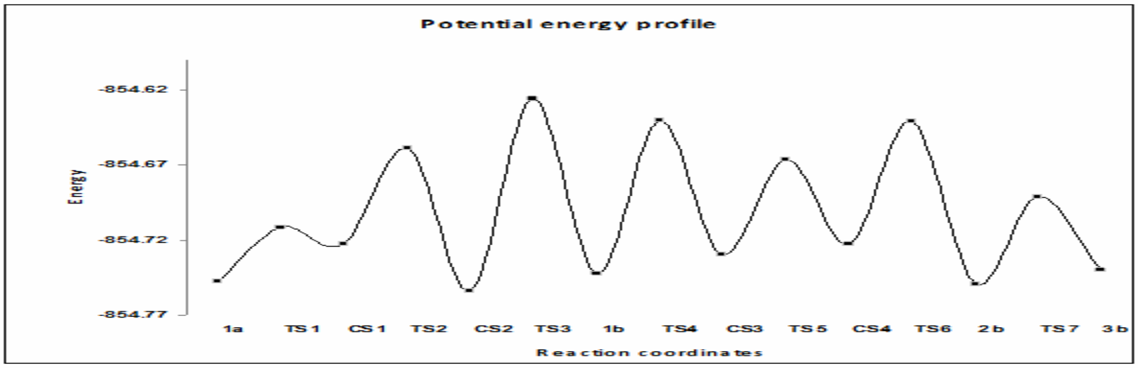

Fig.-2: Schematic potential energy profile for the proton transfer in the compound.

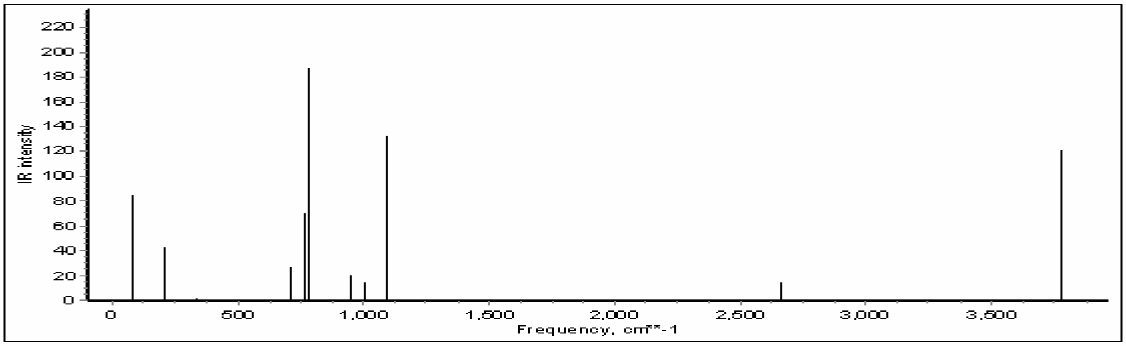

Fig.-3(a): The Computed infrared spectrum of the 4b structure.

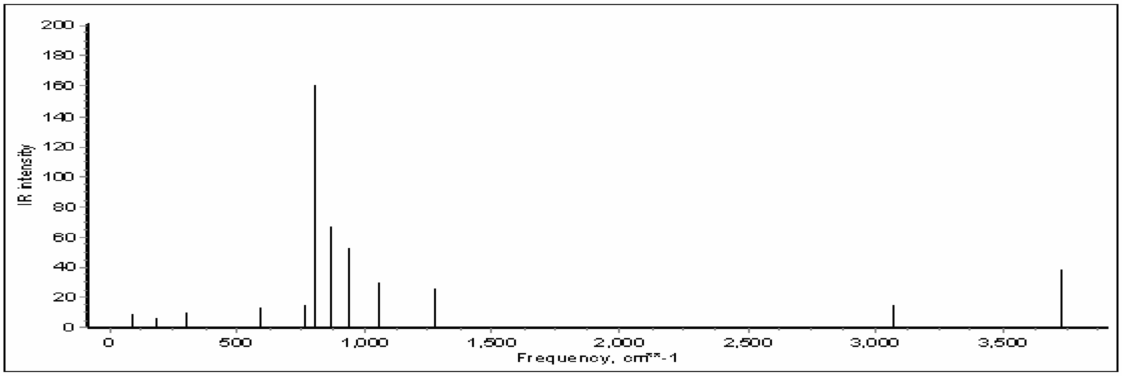

Fig.-3(b): The Computed infrared spectrum of the 2b structure.