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Comparision of Molecular Geometry Based On Ab Initio (HF) and DFT (B3LYP) and Thermodynamic Parameters of 2-Amino-4-Methoxy-6-Methyl Pyrimidine

Lalit Kumar[1] , Jyoti Chaudhary[2]
1. Meerut College, Meerut (U, P)
2. Shaheed Mangal Pandey Govt.Girls (P.G) College ,Meerut

Abstract: *Theoretical geometric parameters (bond lengths, bond angles and dihedral angle) were calculated using ab initio Hartree Fock (HF) and density functional B3LYP method with 6-31+G (d, p) and 6-31++G(d,p) basis set. Thermodynamic parameters such as total energy,zero-point energy, rotational constants dipole moment, thermal energy, specific heat and entropy of 2-amino-4-methoxy-6-methyl pyrimidine are calculated. The plots of thermodynamic parameters have been given in following paper.*
Keywords: *HF, DFT, 2,4,6-AMMP etc.*

I. Introduction

Recent spectroscopic studies of Pyrimidine and its derivatives have been motivated because of their biological and pharmaceutical importance. Pyrimidine nucleus is one of the most important heterocycles exhibiting remarkable pharmacological activities. Many pyrimidine derivatives have been developed as chemotherapeutic agents and are widely used. Pyrimidine also shows antifungal properties. Flucytosine is a fluorinated pyrimidine used as nucleosidal anti fungal agent for the treatment of serious systemic infections caused by susceptible strains of candida and Cryptococcus [1]. The pyrimidine when substituted with -OH, $-CH_3$ and NH_2 gives many biological important molecules like cytosine, thyemine etc [2-5]. The analysis of vibrational spectra of the molecules might be helpful in understanding of biological processes and in the analysis of relatively complex systems. Vibrational spectroscopy has been widely used as a standard tool for structural characterization of molecular systems by HF and DFT calculations. In this paper we apply HF and DFT levels of theory using 6-31+G(d,p) and 6-311++G(d,p) basis set to optimized geometry of the titled compound and a comparision made on different basis sets.

II. Experimental Details:

The pure sample of compound 2-amino-4-methoxy-6-methyl pyrimidine (2, 4, 6-AMMP) was obtained from Sigma–Aldrich Chemical Company (U.S.A.) and its purity was confirmed by elemental analysis and melting point determination. Infrared spectrum of the compound was recorded on Perkin-Elmer-Spectrophotometer in the region 400-4400 cm^{-1} in KBr pellets technique. Laser Raman spectrum of 2,4,6-AMMP was recorded in the region 200-2000 cm^{-1} on Spex-Rama Lab Spectrophotometer using 52 MG Argon-Krypton laser of wave length 488 nm. The thermodynamic parameters viz enthalpy function $[H^0-E_0{}^0]/T$, heat capacity $C_P{}^0$, free energy $[F^0-E_0{}^0]/T$ and entropy S^0 at different temperatures are calculating from rigid rotator-harmonic oscillator approximation.

III. Computational Details

HF and DFT calculations were performed by means of theGaussian'03 package of programs. The molecular structure of 2, 4, 6-AMMP in the ground state are optimized by HF and DFT/B3LYP with the 6-311++G(d,p) higher basis set. All the calculations are performed by using Gaussian 03 program package on the personal computer. Becke's three –parameters exchange functional (B3) in combination with the correlation functional of Lee, Yang and Parr (LYP) known as B3LYP. The optimized structural parameters were used in the vibrational frequency calculations at HF and DFT levels to characterize all stationary points as minima [6-7].

IV. Result And Discussion

4.1 Geometrical Parameters

The molecular structures of 2-amino-4-methoxy-6-methyl pyrimidine (2,4,6-AMMP) having Cs symmetry are shown in Fig. 1.1 . The optimized geometrical parameters (bond lengths and bond angles)

of 2,4,6-AMMP are calculated at HF/6-31+G(d,p), HF/6-311++G(d,p), B3LYP/6-31+G(d,p) and B3LYP/6-311++G(d, p) levels as shown in Table 1.1 and Table 1.2 respectively.

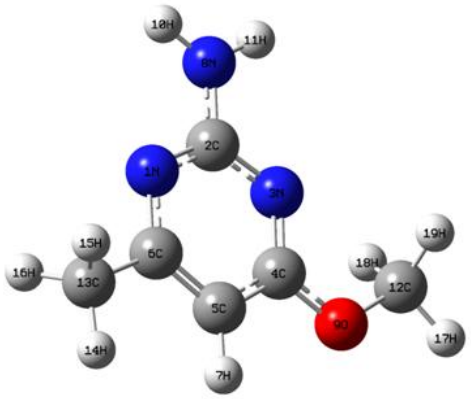

Fig. 1.1 Molecular structure of 2-amino-4-methoxy-6-methyl pyrimidine

Table 1.1: Optimized Bond Lengths of 2-amino-4-methoxy-6-methyl pyrimidine

BOND	Bond Lengths {Angstrom (Å)}			
	HF		DFT	
	HF/6-31+ G(d, p)	HF/6-311++G(d, p)	B3LYP/6 31+G(d, p)	B3LYP/6-311++G(d, p)
N1-C2	1.3172	1.3144	1.335	1.3303
N1-C6	1.3354	1.3345	1.341	1.3369
C2-N3	1.3364	1.335	1.3458	1.3419
C2-N8	1.3544	1.3569	1.3516	1.3486
N3-C4	1.3081	1.3058	1.3215	1.3164
C4-C5	1.4002	1.3993	1.3982	1.3941
C4-O9	1.3207	1.3186	1.3365	1.3327
C5-C6	1.3751	1.3729	1.3869	1.3819
C5-H7	1.0711	1.0708	1.0926	1.0905
C6-C13	1.5017	1.5014	1.4848	1.4816
N8-H10	0.9925	0.9924	1.0157	1.0142
N8-H11	0.9922	0.9921	1.0152	1.0136
O9-C12	1.415	1.4133	1.4145	1.4132
C12-H17	1.0795	1.0799	1.0991	1.0972
C12-H18	1.0812	1.0817	1.1039	1.1018
C12-H19	1.0813	1.0818	1.104	1.1018
C13-H14	1.0828	1.083	1.1008	1.0988
C13-H15	1.0845	1.0848	1.1035	1.1016
C13-H16	1.0844	1.0848	1.1035	1.1016

It is clear from the Table 1.1 that the bond lengths for C12-H18 and C12-H19 has the same bond length of 1.1018 Å at B3LYP/6-311++G(d,p) level and negligible difference of .0001 between bond lengths of C12-H18 and C12-H19 at the HF/6-311++G(d,p) level. The bond lengths for C13-H15 and C13-H16 has the same bond length of 1.0848 Å at the HF/6-311++G(d,p) level and 1.1016 at B3LYP/6-311++G(d,p) level. The bond angles for H14-C13-H15 and H14-C13-H15 are same i .e 109.2° at the HF/6-311++G(d,p) level and 109.18° at B3LYP/6-311++G(d,p) level as shown in the Table 1.2 . All the other bond lengths and bond angles are mentioned and compared in the Table 1.1 and 1.2.

Table 1.2: Optimized Bond Angles of 2-amino-4-methoxy-6-methyl pyrimidine

BOND	Bond angles (°)			
	HF		DFT	
	HF/6-31+G(d, p)	HF/6-311++G(d, p)	B3LYP /6-31+G(d,p)	B3LYP /6-311++G(d,p)
C2-N1-C6	116.6234	116.5628	116.454	116.468
N1-C2-N3	126.493	126.5812	126.57	126.486
N1-C2-N8	117.4046	117.4008	117.06	117.216
N3-C2-N8	116.0935	116.0069	116.368	116.392

C2-N3-C4	116.0163	115.997	115.576	115.704
N3-C4-C5	123.0149	122.9943	123.341	123.231
N3-C4-O9	119.531	119.5936	118.932	118.981
C5-C4-O9	117.4541	117.4121	117.726	117.788
C4-C5-C6	115.7042	115.7011	116.028	116.086
C4-C5-H7	120.8898	120.8833	121.083	121.029
C6-C5-H7	123.4057	123.4151	122.887	122.885
N1-C6-C5	122.1449	122.1593	122.032	122.025
N1-C6-C13	115.8711	115.9092	116.296	116.361
C5-C6-C13	121.9839	121.9315	121.671	121.615
C2-N8-H10	117.5214	116.968	118.605	118.629
C2-N8-H11	118.0337	117.4465	119.363	119.405
H10-N8-H11	118.8327	118.2563	121.56	121.769
C4-O9-C12	119.4453	119.5081	116.381	116.351
O9-C12-H17	105.2964	105.3908	105.672	105.668
O9-C12-H18	110.7327	110.8168	110.957	110.979
O9-C12-H19	110.7301	110.8147	110.961	110.982
H17-C12-H18	110.3606	110.2719	110.659	110.629
H17-C12-H19	110.3163	110.2223	110.637	110.612
H18-C12-H19	109.3551	109.2789	107.977	107.995
C6-C13-H14	111.7425	111.7331	111.977	111.996
C6-C13-H15	109.5407	109.4921	109.983	109.903
C6-C13-H16	109.5211	109.4713	109.979	109.901
H14-C13-H15	109.1963	109.2342	109.111	109.183
H14-C13-H16	109.2016	109.244	109.104	109.175
H15-C13-H16	107.543	107.5725	106.528	106.527

4.2. Thermodynamic functions

The total thermal energy, heat capacity, entropy along with their translational, rotational and vibrational contributions are calculated. The total thermal energy calculated by HF methods are overestimated as compared to B3LYP methods. The total dipole moment is also calculated by HF and B3LYP methods. Apart from the above theoretical thermodynamic parameters, some parameters with variation of temperature have also been calculated. To calculate the thermodynamic parameters one requires the principal moments of inertia, molecular weight, temperature and the vibrational fundamentals. Thermodynamic functions of 2-amino-4-methoxy-6-methyl pyrimidine have been calculated with the help of computer program at different temperatures between 200-1500 K using the experimental fundamental frequencies assuming rigid rotator-harmonic oscillator approximation [8]. The thermodynamic parameters viz enthalpy function $[H^0-E_0^0]/T$, heat capacity C_P^0, free energy $[F^0-E_0^0]/T$ and entropy S^0 at different temperatures are given in Tables 1.3. The plots of thermodynamic parameters have been given in Fig.1.2 and it was found that the thermodynamic functions rise more rapidly in the low temperature range and less rapidly in the high temperature range.

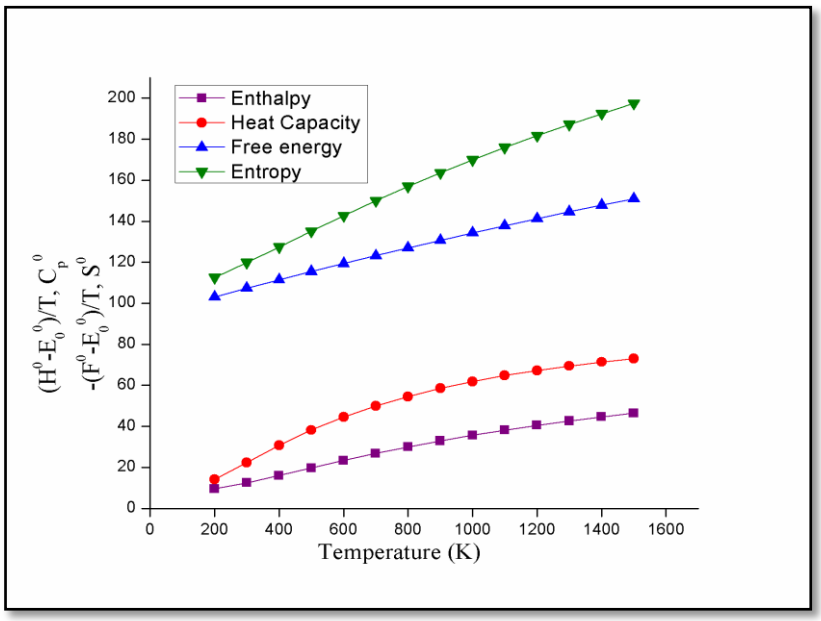

Fig. 1.2: Temperature V/s enthalpy, heat capacity, free energy and entropy of 2-amino-4-methoxy-6-methyl pyrimidine

At low temperatures only translational parts of motion gives its contribution but as temperature increases rotational and vibrational motions are excited [9]. Beyond a certain value of temperature (nearly at 1400 K) there is no further increase in molecular motion and therefore heat capacity becomes almost constant.

Table 1.3: Thermodynamic Functions of 2-amino-4-methoxy-6-methyl pyrimidine (in Cal. /Mol-K)

Temperature K	Enthalpy $(H^0-E_0^0)/T$	Heat Capacity C_p^0	Free energy $-(F^0-E_0^0)/T$	Entropy S^0
200	9.58	14.23	103.03	112.61
300	12.46	22.39	107.43	119.89
400	15.99	30.71	111.49	127.48
500	19.70	38.18	115.46	135.16
600	23.33	44.57	119.37	142.70
700	26.76	49.98	123.23	149.99
800	29.96	54.57	127.01	156.97
900	32.92	58.49	130.72	163.63
1000	35.65	61.87	134.33	169.97
1100	38.17	64.78	137.84	176.01
1200	40.49	67.30	141.27	181.76
1300	42.64	69.49	144.59	187.23
1400	44.63	71.41	147.83	192.45
1500	46.47	73.09	150.97	197.44

V. Conclusion

The structural parameters bond lengths and bond angles were determined and analysed both at HF and DFT levels of theory. Most of the bond lengths, bond angles and dihedral angles have same value in all four HF/6-31+G (d, p), HF/6-311++G (d,p), B3LYP/6-311++G(d,p) and B3LYP/6-311++G(d,p) basis sets. The thermodynamic parameters viz enthalpy function $[H^0-E_0^0]/T$, heat capacity C_P^0, free energy $[F^0-E_0^0]/T$and entropy S^0 at different temperatures are in good agreement with standard results.

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