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MOLECULAR GEOMETRY AND THERMODYNAMIC PARAMETERS OF 6-AMINO-1,3-DIPROPYL URACIL BY USING HARTREE FOCK AND DENSITY FUNCTIONAL THEORY

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ABSTRACT

KEYWORDS:

HF, DFT, 6-Amino-1,3-Dipropyl Uracil etc

Quantum mechanical calculations of energies, geometries and thermodynamic parameters of 6-Amino-1,3-Dipropyl Uracil were carried out by using ab initio HF theory with 6-31+G(d,p) and 6-311++G(d,p) basis sets and density functional theory (DFT/B3LYP) with 6-31+G(d,p) basis set. The optimized geometrical parameters such as bond length, bond angles etc obtained by HF and DFT calculations are in good agreement with each other. The thermodynamic parameters such as total thermal energy, Enthalpy heat capacity, entropy have also been computed in the temperature range 200-1500 K by using the standard expressions under the rigid rotator harmonic oscillator approximation.

1. INTRODUCTION

The aromatic compounds like pyrimidine, pyridine, uracil, cytosine and their derivatives are of great biological importance as they play an important role in the structure and properties of nucleic acids [1-10]. Pyrimidine compounds are used in the drug synthesis of antitumor, analgesic, antiarrhythmic, anticonvulsant, anti-malarial, anti-bacterial and anti-fungal activity[11-26]. DFT has big popularity as a cost effective general procedure for studying the physical properties of molecules. As an extension of the earlier works on the thermodynamic parameters of substituted uracils the present investigation is confined to the study of the heat capacity, enthalpy and entropy of 6-Amino-1,3-Dipropyl Uracil .There is no earlier work on the thermodynamic parameters of this molecule.

2. EXPERIMENTAL DETAILS:

The compound 6-amino-1,3-dipropyl uracil in the solid form was purchased from the Sigma–Aldrich Chemical Company (U.S.A.) and used as such to record thermodynamic parameters such as heat capacity, free energy enthalpy and entropy.

3 . COMPUTATIONAL DETAILS:

The entire calculations computed in the present work were performed at Hartee–Fock (HF) and B3LYP levels included in the Gaussian 03 [27] package program together with the 6−31+G(d,p) , 6−311++G(d,p) basis set functions of the density functional theory (DFT) utilizing gradient geometry optimization [28-30]. The optimized geometrical parameters and atomic charges of 6-amino-1,3-dipropyl uracil were calculated using HF and DFT with basis set 6−31+G(d,p) and 6−311++G(d,p). The thermodynamic parameters and electric dipole moment (μ), of the said compounds are also calculated by HF and DFT methods.

4. RESULT AND DISCUSSION:

4.1 GEOMETRICAL PARAMETERS:

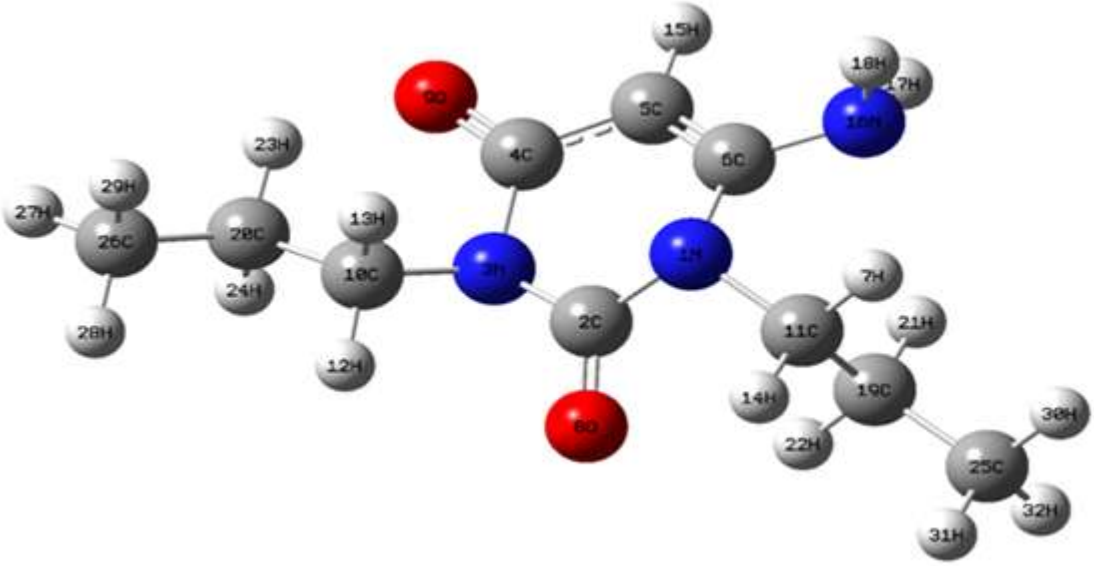

Figure 1: Molecular structure of 6-amino-1,3-dipropyl uracil

The molecular structures of 6-amino-1,3-dipropyl uracil (6-1-3ADPU) having *Cs* symmetry are shown in Figure 1 .The optimized geometrical parameters (bond lengths and bond angles) of (6-1-3ADPU) are calculated at HF/6-31+G(d,p) , HF/6-311++G(d,p) and B3LYP/6-31+G(d, p) levels as shown in Table 1 and Table 2.

Table 1: Optimized Bond Length of 6-amino-1,3-dipropyl uracil

BOND	BOND LENGTH {Angstrom (Å)}		
	HF/6-31+G(d, p)	HF/6-311++G(d,p)	B3LYP/6-31+G(d,p)
N1-C2	1.3901	1.3905	1.3985
N1-C6	1.3773	1.3765	1.3735
N1-C11	1.472	1.4716	1.4458
C2-N3	1.3674	1.3676	1.367
C2-O8	1.2021	1.1959	1.2296
N3-C4	1.3984	1.3985	1.4152
N3-C10	1.4719	1.4714	1.4467
C4-C5	1.4376	1.4378	1.4213
C4-O9	1.203	1.1969	1.2316
C5-C6	1.348	1.3452	1.3684
C5-H15	1.0711	1.0708	1.0916

C6-N16	1.3716	1.3739	1.3624
H7-C11	1.0824	1.0824	1.1099
C10-H12	1.0791	1.0793	1.1039
C10-H13	1.0787	1.0789	1.1041
C10-C20	1.5255	1.5256	1.5124
C11-H14	1.0768	1.077	1.1046
C11-C19	1.5266	1.5266	1.5138
N16-H17	0.9951	0.9949	1.0174
N16-H18	0.993	0.9931	1.018
C19-H21	1.0857	1.0859	1.1067
C19-H22	1.0853	1.0854	1.1058
C19-C25	1.528	1.5274	1.5109
C20-H23	1.0858	1.0859	1.1062
C20-H24	1.086	1.0862	1.1064
C20-C26	1.5279	1.5273	1.5109
C25-H30	1.0874	1.0877	1.1055
C25-H31	1.0862	1.0865	1.1043
C25-H32	1.0848	1.085	1.1017
C26-H27	1.0854	1.0856	1.1022
C26-H28	1.0868	1.0871	1.1047
C26-H29	1.0866	1.0869	1.1046

From the table 1 it is evident that the carbon–carbon bonds 6-amino-1,3-dipropyl uracil are not of the same length. The bonds C4–C5 and C5–C6, are about 1.42(Å) ,1.36 (Å) in length whereas the bonds C10–C20, C11–C19, C19-C25 and C20-C26 are about 1.51 (Å) in length by B3LYP/6-31+G(d,p). From the theoretical values, the most of the optimized bond lengths using B3LYP/6-31+G(d,p) are larger than the HF/6-311++G(d,p) .In this study, the bonds C2-O8 and C4-O9 approximately same in length i.e 1.23(Å). It is evident from table 2 value of C4-C5-C6 bond angle and C4-C5-H15 bond angle are same i.e 121.2417 at B3LYP/6-31+G(d,p) level and different at HF . All the other bond lengths and bond angles are mentioned and compared in the Table 1 and Table 2.

Table 2: Optimized Bond Angles of 6-amino-1,3-dipropyl uracil

BOND	**BOND ANGLE (°)**		
	HF/6-31+G(d, p)	**HF/6-311++G(d,p)**	**B3LYP/6-31+G(d, p)**
C2-N1-C6	120.8337	120.8326	121.7309
C2-N1-C11	116.0515	116.019	115.8701
C6-N1-C11	122.7891	122.7476	122.1551
N1-C2-N3	117.5916	117.4555	116.302
N1-C2-O8	120.3256	120.3818	120.6484
N3-C2-O8	122.0828	122.1624	123.0484
C2-N3-C4	124.1573	124.242	125.1785
C2-N3-C10	117.5418	117.4906	117.0591
C4-N3-C10	118.267	118.2062	117.6157
N3-C4-C5	115.3408	115.2357	114.8426
N3-C4-O9	120.2586	120.3596	119.2638

C5-C4-O9	124.3988	124.4024	125.8933
C4-C5-C6	120.8801	120.9082	121.2417
C4-C5-H15	117.5987	117.6269	121.2417
C6-C5-H15	121.5208	121.4644	121.1399
N1-C6-C5	121.1185	121.2161	120.5884
N1-C6-N16	117.0897	116.9989	116.5623
C5-C6-N16	121.7425	121.7375	122.8145
N3-C10-H12	107.3512	107.4072	107.5897
N3-C10-H13	106.5035	106.6021	106.0322
N3-C10-C20	112.5717	112.6785	112.0796
H12-C10-H13	109.2187	109.0178	110.4119
H12-C10-C20	110.6171	110.5968	110.4376
H13-C10-C20	110.4202	110.3762	110.178
N1-C11-H7	108.9673	109.04	109.6838
N1-C11-H14	106.4065	106.4708	105.292
N1-C11-C19	113.1544	113.2841	113.3295
H7-C11-H14	106.7218	106.5835	106.7523
H7-C11-C19	111.0769	110.9731	111.5633
H14-C11-C19	110.2127	110.1797	109.8322
C6-N16-H17	114.0069	113.5989	116.4641
C6-N16-H18	118.2924	117.5294	119.4397
H17-N16-H18	112.9738	112.5663	115.9492
C11-C19-H21	109.7535	109.6549	109.8606
C11-C19-H22	108.3581	108.3674	107.6256
C11-C19-C25	111.5691	111.6253	111.2642
H21-C19-H22	107.2718	107.2669	106.5976
H21-C19-C25	109.9989	110.0061	110.8357
H22-C19-C25	109.7789	109.8074	110.5004
C10-C20-H23	108.9418	108.9004	108.2585
C10-C20-H24	109.1396	109.0964	108.5165
C10-C20-C26	111.5185	111.6092	111.29
H23-C20-H24	107.623	107.5783	107.6049
H23-C20-C26	109.7825	109.802	110.5332
H24-C20-C26	109.7474	109.7609	110.5226
C19-C25-H30	111.4981	111.4589	111.5333
C19-C25-H31	111.2663	111.2328	111.168
C19-C25-H32	110.7389	110.7342	111.6654
H30-C25-H31	107.8723	107.8948	107.3308
H30-C25-H32	107.5684	107.6016	107.3726
H31-C25-H32	107.725	107.7516	107.5442
C20-C26-H27	110.8672	110.8551	111.7694
C20-C26-H28	111.2749	111.2571	111.144
C20-C26-H29	111.2246	111.1987	111.0977
H27-C26-H28	107.6861	107.7137	107.5429
H27-C26-H29	107.6903	107.714	107.5581
H28-C26-H29	107.935	107.9429	107.5258

4.2 THERMODYNAMIC PARAMETERS:

The thermodynamic parameters of compound 6-1-3ADPU have been computed at HF/6-311++G(d, p) and B3LYP/6-31+G(d, p) methods as given in Table 3. 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. The thermodynamic functions 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 of compound 6-1-3ADPU have been calculated at different temperatures between 200- 1500K , using (3n-6) fundamental frequencies and assuming rigid rotator harmonic oscillator approximation [31-32]. 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 4.

Table 3. The thermodynamic parameters of 6-amino-1,3-dipropyl uracil calculated at the HF/6-311++G(d,p) and B3LYP/6-31+G(d,p) methods.

PARAMETER	**HF/6-31+G(d, p)**	**HF/6-311++G(d, p)**	**B3LYP/6-311++G(d, p)**
Total Energy(a. u.)	-701.503059	-701.89127075	-702.35409869
Zero-Point Energy(kcal/mol)	183.71241	182.94503	167.46114
Rotational Constants(GHz)	0.90271	0.90145	0.92470
	0.39611	0.39728	0.39697
	0.29699	0.29768	0.30003
Dipole Moment (Debyes)	5.8318	5.8598	6.3238
ENERGY(THERMAL ENERGY) (kcal/mol)			
Total	193.209	192.449	177.666
Translational	0.889	0.889	0.889
Rotational	0.889	0.889	0.889
Vibrational	191.432	190.671	175.888
SPECIFIC HEAT C_V(cal/mol-Kelvin)			
Total	55.394	55.432	60.574
Translational	2.981	2.981	2.981
Rotational	2.981	2.981	2.981
Vibrational	49.433	49.470	54.612
ENTROPY(cal/mol-Kelvin)			
Total	124.899	124.985	129.774
Translational	41.946	41.946	41.946
Rotational	32.382	32.378	32.345
Vibrational	50.571	50.661	55.483

The plots of thermodynamic parameters have been given in Figure 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 which are in good agreement with the trend reported in literature [33-36] . Beyond a certain value of temperature (nearly at 1000 K) there is no further increase in molecular motion and therefore heat capacity becomes almost constant.

Table 4: Thermodynamic Functions of 6-amino-1,3-dipropyl uracil (in Cal. /Mol-K)

Temperature K	**Enthalpy** $(H^0\text{-}E_0^0)/T$	**Heat Capacity** C_p^0	**Free Energy** $-(F^0\text{-}E_0^0)/T$	**Entropy** S^0
200	10.11	16.69	107.05	117.15
300	14.23	28.49	111.88	126.10
400	19.32	40.59	116.65	135.97
500	24.70	51.64	121.54	146.24
600	30.01	61.31	126.52	156.53
700	35.10	69.69	131.53	166.63
800	39.89	76.94	136.53	176.42
900	44.36	83.21	141.49	185.85
1000	48.52	88.65	146.38	194.91
1100	52.39	93.36	151.19	203.58
1200	55.98	97.46	155.91	211.89
1300	59.31	101.03	160.52	219.83

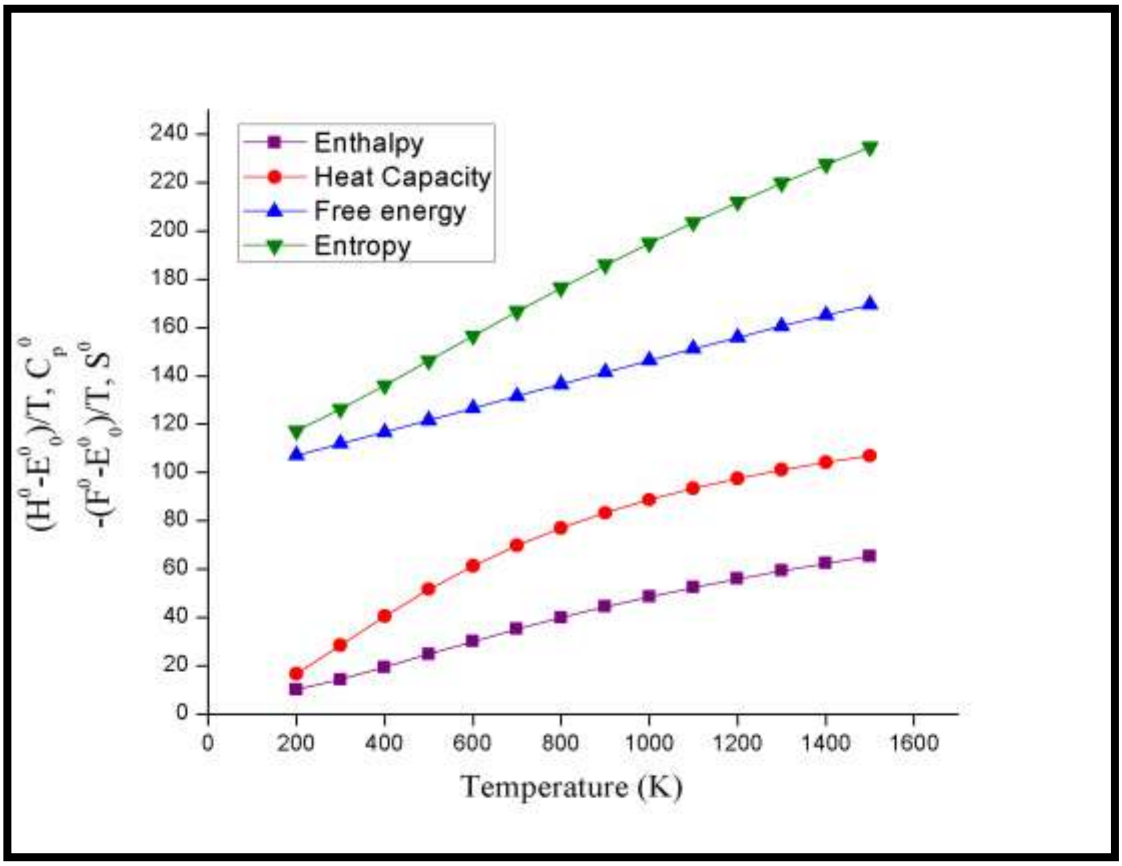

Figure 2. Variation of enthalpy, heat capacity, free energy and entropy with temperature for 6-amino-1,3-dipropyl uracil

5. CONCLUSION:

Thermodynamic parameters are important to understand the molecular structure and biological activity of the title molecule. The equilibrium geometries , and thermodynamic parameters of 6-amino-1,3-dipropyl uracil were determined and analysed both at HF and DFT levels of theory employing the 6- 311++G(d,p) basis set and 6-31+G(d,p) basis set respectively .

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