A Study of Structure and Thermo-dynamical Properties of Pyrimethamine Obtained by an Analytical Hessian Calculation

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Molecular modeling of the structure of Pyrimethamine molecule has been carried out in an attempt to understand its structure and thermo-dynamical properties using the Hessian matrix. Ab initio and DFT geometric optimizations were carried out at RHF/6-311++G** and B3Lyp/6-311++G** level of theory in the gas medium. The zero point vibrational energy (ZPVE), enthalpy (H), entropy (S) and relative free energy (G) have been calculated from the frequencies obtained by an analytical Hessian calculation. The polarizability tensor components, the average polarizability and the anisotropy have also been calculated. The theoretical calculation shows that B3LYP/6-311++G** values were higher than the RHF/6-311, a result we believe is due to the effect of electron correlation.

1. Introduction

Quantum mechanics (QM) seems to describe mathematically the correct behavior of electrons. In theory, QM can predict any property of an individual atom or molecule exactly. In practice, however, the QM equations have only been solved exactly for few electron systems. A number of methods ranging from semi-empirical to ab-initio (QM) approaches have been developed for approximating the solution for many electron systems. The former schemes usually need some parameters that are taken from or adjusted to experiments.

According to the Born-Oppenheimer (BO) approximation [1], the motion of electrons and nuclei can be separated due to their different masses. Thus, quantum mechanical methods (ab initio, density functional theory (DFT) and semi-empirical) [2, 3, 4, 5, 6] are based on solving the time-independent Schrödinger equation for electrons of a molecular system as a function of the nuclei positions.

Although semi-empirical calculations are much faster than their ab initio counterparts, if some parameters for semi-empirical simulations are not available, or some phenomena of a system are not yet known, one must rely only on ab initio calculations. A calculation is said to be “ab initio” (or from first principles) if it relies on the basic established laws of nature without additional assumptions or special methods. Ab initio calculations are based on the fundamental laws of quantum mechanics (masses and charges of electrons and atomic nuclei), the statistical thermodynamic and the values of physical constants (speed of light or Planck’s constant). The simplest type of ab initio electronic structure calculation is the well known Hartree-Fock (HF) scheme, which is based on a wave function given in the form of one Slater determinant. Though the results of such calculations using HF scheme are reliable, the major disadvantage is that they are computationally intensive. An alternative scheme is DFT, which is based on the electron density rather than on the wave functions, and commonly used to calculate the electronic structure of complex systems containing many atoms such as large molecules or solids.

In particular, ab initio methods are nowadays indispensable for a thorough understanding of properties and to understand the physics of molecular systems or materials at the atomic scale. Among these, Kohn-Sham density functional theory (DFT) in the local density approximation (LDA) or generalized gradient approximation (GGA) [7] has been the main tool used by theoreticians for modeling the structural and electronic properties of molecules. The basic idea of DFT is to replace the interacting many-electron problem with an effective single-particle problem. Therefore, the computational costs were relatively low as compared to the traditional methods which were based on the complicated many electrons wave functions, such as Hartree-Fock (HF) [8, 9] theory and its descendants. DFT allows calculating ground state properties of large systems.

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Remarkable results have been achieved for ground state properties of a huge number of systems ranging from atoms and molecules to solids and surfaces.

On the other hand, it turned out that the interaction between particles plays a very important role in physical properties. This indicates that the success of DFT is also accompanied by a number of serious problems. For instance, DFT underestimates the band gaps of semiconductors and insulators by some tens of percent due to the simplified treatment of electron-electron interaction. A much more serious problem of DFT arises when it is applied to calculate the electronic structures of some noble metals. Moreover, DFT is mathematically represented by a Hermitian Hamiltonian, so that the corresponding single particle states have infinite lifetime.

In order to overcome the above difficulties encountered by DFT, a number of attempts have been made for improving the DFT. An exact theory for a system of interacting electrons is based on solving its many-body Schrödinger equation. Unfortunately, the many-body Schrödinger equation cannot be solved exactly for most cases due to the nature of electrons. A better description for interacting electrons is to consider them as quasi-particles. The general notion was first introduced by L.D. Landau [10]. Landau's basic idea was that in a complicated system of strongly interacting particles, it may be still be possible to describe the properties of the system in terms of weakly interacting particles. A many body perturbation theory (MBPT) [11] treatment can deal with a weakly interacting system of particles, beginning with the non-interacting particles as the unperturbed state.

In this paper, we have optimized the structure of Pyrimethamine molecule [12] in an attempt to understand it structure, polarizability and thermo-dynamical properties as obtained from the Hessian matrix. Ab initio and DFT geometric optimizations were carried out at RHF/6-311++G** and B3LYB/6-311++G** level of theory in the gas medium. The zero point vibrational energy (ZPVE), enthalpy (H), entropy (S) and relative free energy (G) have been calculated from frequencies obtained by an analytical Hessian calculation.

2. Optimization Method

One of the most computationally demanding aspects of calculating free energy using electronic structure theory is the calculation of vibrational energy and entropy contributions. The computational expense is incurred by the calculation of the matrix of second energy-derivatives (i.e., the Hessian or force constant matrix) that yields harmonic vibrational frequencies upon diagonalization. The analytic computation of the Hessian matrix requires the evaluation of about 9 times as many atomic orbital integrals compared to an energy evaluation, as well as a partial integral transformation (to solve the coupled-perturbed Hartree–Fock equations) that requires significant amounts of memory and disk space. The numerical (finite-difference) computation of the Hessian requires a minimum of 3N + 1 energy and gradient evaluations (where N is the number of atoms), and usually 6N + 1 energy and gradient evaluations for acceptable accuracy. Thus, as the size of the system increases, the computation of the Hessian becomes very different. If only a single localized vibration is required, part of the potential-energy surface can be constructed by moving a selected atom or group of atoms and deriving the associated numerical force constant explicitly.

The Hessian matrix is the matrix of second derivatives of the energy with respect to the geometry. The most important Hessian is that which used in the Force calculation. Normal modes are expressed as Cartesian displacements; consequently the Hessian is based on Cartesian rather than internal coordinates.

In mathematics, the Hessian matrix (or simply the Hessian) is the square matrix of second-order partial derivatives of a function; that is, it describes the local curvature of a function of many variables. The Hessian matrix was developed in the 19th century by the German mathematician Ludwig Otto Hesse [13] and later named after him. Hesse himself had used the term "functional determinants".

Given the real-valued function

$$f\left(x_1, x_2, ..., x_n\right) \tag{1}$$

If all second partial derivatives of f exist, then the Hessian matrix of f is the matrix

$$H\left(f\right)_{ij}\left(x\right) = D_i D_j f\left(x\right) \tag{2}$$

Where, $x = (x_1, x_2, ..., x_n)$ and D_i is the differentiation operator with respect to the ith argument. The Hessian then becomes

$$H(f)=\begin{bmatrix} \frac{\partial^2 f}{\partial x_1^2} & \frac{\partial^2 f}{\partial x_1 \partial x_2} & \cdots & \frac{\partial^2 f}{\partial x_1 \partial x_n} \\ \frac{\partial^2 f}{\partial x_2 \partial x_1} & \frac{\partial^2 f}{\partial x_2^2} & \cdots & \frac{\partial^2 f}{\partial x_2 \partial x_n} \\ \vdots & \vdots & \ddots & \vdots \\ \frac{\partial^2 f}{\partial x_n \partial x_1} & \frac{\partial^2 f}{\partial x_n \partial x_2} & \cdots & \frac{\partial^2 f}{\partial x_n^2} \end{bmatrix} \quad (3)$$

Some mathematicians [14] define the Hessian as the determinant of the above matrix.

Hessian matrices are used in large-scale optimization problems within Newton-type methods because they are the coefficient of the quadratic term of a local Taylor expansion of a function. That is,

$$y = f(x+\Delta x) \approx f(x) + J(x)\Delta x + \frac{1}{2}\Delta x^T H(x)\Delta x \quad (4)$$

Where, J is the Jacobian matrix, a vector (the gradient) for scalar-valued functions. The full Hessian matrix can be difficult to compute in practice.

A full numerical Hessian computation and vibrational analysis is as follows. Consider a molecule, *A*, consisting of *N* atoms, each with nuclear charge Z_i, Cartesian coordinate $q_i(0)$, and mass m_i, $A\{Z_i, q_i(0)\ m_i\}$ i = 1, 2, 3, ……..3*N*. We assume that *A* is a stationary point so the energy gradients are zero.

$$g_i(0) = \left(\frac{\partial E}{\partial q_i}\right) q_i(0) = 0 \quad (5)$$

The matrix of energy second derivatives (the Hessian, *H*) can be computed numerically (in practice *H* is always symmetrized) as

$$H_{ii} = H_{jj} = \frac{1}{2}\left(H_{ii} + H_{jj}\right)$$

The simplest way to calculate second derivatives is to calculate first derivatives for a given geometry, then perturb the geometry, do a SCF calculation on the new geometry, and re-calculate the derivatives. The second derivatives are then calculated from the difference of the two first derivatives divided by the step size as shown by Hui Li et al. [15]

$$H_{ij} = \left[\frac{\partial^2 E}{\partial q_i \partial q_j}\right]_{q_i(0)} \approx \left(\frac{g_i(+j) - g_j(-j)}{2dl}\right) \quad (6)$$

$$\text{or} \approx \left(\frac{g_i(+j) - g_j(-j)_{(0)}}{dl}\right) \quad (7)$$

either by double or single displacement by an amount dl followed by a gradient evaluation:

$$g_i(\pm j) = \left(\frac{\partial E}{\partial q_i}\right) q_j = q_j \pm dl,\ j = 1,2,3,\ldots,3N \quad (8)$$

In order to calculate the vibrational frequencies, the Hessian matrix is first mass-weighted:

$$H_{i,j}^m = \frac{H_{i,j}}{\sqrt{M_i * M_j}} \quad (9)$$

The harmonic vibrational frequencies, $\{\upsilon_i\}$, of a molecule are obtained by

$$\nu_i = \left[\frac{\lambda_i^{1/2}}{2\pi}\right] \quad (10)$$

Where, $\{\lambda_i\}$, are the equivalues of the mass-weighted Hessian.

3. Computational Methodology

The molecular structure and geometry of Pyrimethamine were fully optimized with Windows version of Gaussian 03 [16] suit of ab initio quantum chemical program. Initially, geometry optimization was performed using the ab initio RHF method with 3-21G basis set and finally the calculations were carried out with the double polarized triple zeta split valence 6-311++G** basis set. The structure was refined further using Density Functional Theory, which is a cost effective method for inclusion of electron correlations with the three-parameter density functional generally known as Becke3LYP (B3LYP). This includes Becke's gradient exchange corrections [17], the Lee, Yang and Parr correlation functional [18] and the Vosko, Wilk and Nusair correlation functional [19] with a 6-311++G** basis set. As the first step, the geometry optimization was carried out and then the IR and Raman vibrational frequencies were calculated.

The optimized molecular structure was tested by computing the second derivatives using the Hessian matrix and checking that all the harmonic vibrational frequencies are found to be real at all levels of calculation.

4. Result and Discussion

4.1 Molecular structure

The geometry of a molecules or solid determines many of its physical and chemical properties. The ground state geometry of any system can be obtained by geometric optimization. In the Born-Oppenheimer (BO) approximation the total ground state energy of a system is a function of the coordinates of the nuclei. The minimum of this energy corresponds to the ground state geometry, whereas a first order saddle point on the BO surface gives the transition state geometry.

The geometric parameters of Pyrimethamine molecule are listed in Table 1, while the molecular structure is shown by Fig. 1. The calculated bond lengths at RHF/6-311++G** level are slightly (0.01Å to 0.04Å) smaller than the corresponding values obtained at the DFT/B3LYP/6-311++G** level. The bond angles vary from 0.1 to 2 degree at both levels of theories except for the angle A_{21}. Its RHF value is greater than its corresponding B3LYP value by approximately 4 degree. The six member carbon ring (Phenyl) and the other ring with two of the carbon atom replaced by Nitrogen atoms (pyrimidine) possibly gives added stability to the molecule. The Nitrogen atoms (N11, N12, N14 and N17) play a major role in the electron density configuration. Appreciable changes in bond angles are noted both at RHF/6-311++G** and B3LYP/6-311++G** levels, but no significant change in the bond length is noticed.

The RHF/6-311++G** and B3LYP/6-311++G** bond lengths and bond angles are approximately equal to the experimental values determined by Hellwege et al. [22], Roussy et al. [21] and Herzberg [22]. The B3LYP/6-311++G** values are in better accord to the experimental values than their corresponding RHF/6-311++G** values.

Table 1: Optimized geometrical parameters of Daraprim molecule obtained at RHF and B3LYP methods by employing 6- 311++G** basis sets. Bond Lengths are given in Armstrong (Å) and Bond Angles and Dihedral angles are in degrees (˚).

Geomet.	RHF/6-311++G**	B3LYP/6-311++G**	Experiment [19-21]
Parameters			
R(C1-C2)	1.4676	1.4419	1.399
R(C1-C6)	1.5191	1.5084	
R(C1-C7)	1.3529	1.3909	
R(C2-C3)	1.3312	1.3592	1.386
R(C3-C4)	1.4600	1.4411	1.402
R(C4-C5)	1.3161	1.3397	
R(C5-C6)	1.4999	1.4900	
R(C7-C8)	1.4836	1.4645	
R(C7-C10)	1.4947	1.4891	
R(C20-C21)	1.5302	1.5348	
R(C4-Cl13)	1.7454	1.7604	1.725
R(C5-H30)	1.0749	1.0834	
R(C2-H28)	1.0683	1.0794	
R(C3-H27)	1.0742	1.0832	
R(C6-H29)	1.0848	1.1032	1.082
R(C20-H22)	1.0873	1.0969	
R(C20-H23)	1.0814	1.0902	
R(C21-H24)	1.0858	1.0931	
R(C21-H25)	1.0813	1.0895	
R(C21-H26)	1.0855	1.0931	
R(C8-N11)	1.2712	1.3002	
R(C8-N20)	1.5198	1.5226	

R(C9-N11)	1.3892	1.3865	1.360
R(C9-N12)	1.2761	1.3006	
R(C9-N17)	1.3479	1.3611	
R(C10-N12)	1.3866	1.3870	
R(C10-N14)	1.2599	1.2937	
R(N14-H16)	1.0046	1.0221	1.036
R(N17-H18)	0.9919	1.0065	
R(N17-H19)	0.9928	1.0071	
A(C4-C5-H30)	120.989	121.0876	119.60
A(C1-C2-H28)	119.4443	119.4605	
A(C3-C2-H28)	117.7976	117.5702	
A(C2-C3-H27)	120.1191	120.0862	
A(C4-C3-H27)	118.1486	118.5468	
A(C6-C5-H30)	116.9048	117.6603	
A(C8-C20-H22)	108.2771	108.5762	109.46
A(C1-C6-H15)	108.0402	108.2218	
A(C1-C6-H29)	109.9126	109.6664	
A(C5-C6-H15)	108.4750	109.1419	
A(C5-C6-H29)	109.4080	111.3224	
A(C8-C20-H23)	109.7684	109.9217	
A(C21-C20-H22)	109.0559	108.7757	
A(C21-C20-H23)	109.4436	109.5586	
A(C20-C21-H24)	109.4153	109.8469	
A(C20-C21-H25)	111.3222	111.1172	
A(C20-C21-H26)	110.9702	110.9170	
A(C3-C4-Cl13)	116.9139	117.4104	119.80
A(C2-C1-C6)	116.0590	116.2501	
A(C2-C1-C7)	122.3605	122.0668	
A(C6-C1-C7)	121.5044	121.5384	
A(C1-C2-C3)	122.6049	122.7434	
A(C3-C4-C5)	120.888	120.8603	
A(C5-C4-Cl13)	122.1929	121.7226	
A(C4-C5-C6)	122.0977	121.2497	
A(C1-C6-C5)	116.5419	117.4778	
A(C1-C7-C8)	125.5280	124.5085	
A(C1-C7-C10)	123.0658	122.1469	
A(C8-C7-C10)	111.2219	113.2535	
A(C7-C8-C20)	122.8700	122.7951	
A(C8-C20-C21)	112.6834	112.8448	
A(C2-C3-C4)	121.7085	121.3239	
A(C7-C8-N11)	120.5857	121.5168	
A(N11-C8-C20)	116.2653	115.3545	
A(N11-C9,12)	126.3676	126.3414	
A(N11,9-N17)	113.0728	113.7140	
A(N12-C9,17)	120.5194	119.9025	
A(C7-C10-N12)	115.6151	117.2364	
A(C7-C10-N14)	121.8607	121.4397	
A(N12-C10-N14)	122.4825	121.2770	
A(C8-N11-C9)	117.5250	117.1495	
A(C9-N12-C10)	117.4445	117.8609	
A(C10-N14-H16)	109.0621	107.7203	

A(C9-N17-H18)	117.9875	117.8709	113.90
A(C9-N17-H19)	117.7085	117.880	
A(H18-N17-H19)	118.9561	119.0952	
A(H22-C20-H23)	107.4679	106.9812	109.01
A(H24-C21-H25)	108.7557	108.7960	
A(H24-C21-H26)	108.0855	108.0803	
A(H25-C21-H26)	108.2063	107.9960	
A(H15-C6-H29)	103.6641	99.4445	

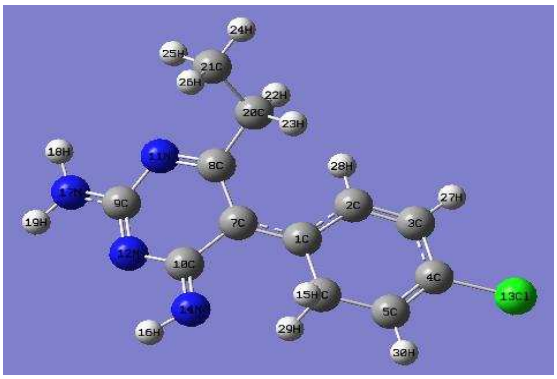

Fig.1. Pyrimethamine.

4.2 Energies

The zero point vibrational energy, the sum of electronic energies without zero point correction, with zero point correction, with thermal energy correction, with enthalpy correction, with free energy, and entropy for the molecule are listed in Table 2. The scaling factor for the zero point energy is 0.9877 for the 6-311++G** basis set [23]. The zero point correction is a correction of electronic energy to account for the effects of molecular vibrations which persist at 0K. It is the minimum energy due uncertainty principle.

From Table 2, the ZPVE is higher at the RHF/6-311++G** level as compared to the B3LYP/6-311++G** level of theory. This implies that the effect of electron correlation decreases the ZPVE, the sum of electronic energy without zero point correction, the sum of electronic energy with zero point correction, the sum of electronic energy with thermal energies, the sum of electronic energy with enthalpies, and the sum of electronic energy with thermal free energies as we go from the uncorrelated method to correlated method, whereas the entropy increases with the effect of electron correlation.

Table 2: Dipole moments and total electronic energies without and with zero point energy corrections, with thermal energy correction and with enthalpy correction of Pyrimethamine molecule obtained using RHF and B3LYP methods by employing 6-311++G** basis set. All energies are given in Kilocalories/Mol and the entropy is in cal/Mol/K.

	Methods/Basis Set	
	RHF/ 6-311++G**	**B3LYP/ 6-311++G****
ZPVE	159.16	148.79
E_{elec}	-714990.50	-718172.66
E_0	-714891.82	-718078.38
E	-714882.40	-718068.33
H	-714881.81	-718067.74
G	-714919.20	-718106.60
S	125.40	130.34

$$E_0 = E_{elec} + ZPVE,$$
$$E = E_0 + E_{vib} + E_{rot} + E_{trans},$$
$$H = E + RT, \qquad G = H - TS$$

ZPVE= zero point vibrational energy
E_{elec} = sum of Electronic Energy without Zero point correction, E_0 = sum Electronic Energy with Zero point correction, E = sum Electronic Energy with Thermal energies, H = sum Electronic Energy with enthalpies, G = Sum Electronic Energy with thermal free energies, S = entropy

4.3 Polarizability tensors, average polarizability and anisotropy

Polarizability is a property which depends on the second derivative of the energy with respect to the applied electric field. It gives information about the distribution of electrons in the molecule. The rotational excitation of a polyatomic molecule by electron collision is considered as caused by the polarization interaction as well as by the electrostatic interaction. Molecular polarizability plays a fundamental role in determining the

structural, orientational, dynamical and thermo-dynamical properties of a system [24]. The components α_{ii}(i=x, y, z) of the diagonalized α tensor and the associated average polarizability; $\alpha_{avec} =< \alpha >= \frac{1}{3}\left(\alpha_{ii} + \alpha_{ij} + \alpha_{kk}\right)$ and anisotropy $\Delta\alpha = \left\{\frac{1}{2}\left[\left(\alpha_{ii} - \alpha_{jj}\right)^2 + \left(\alpha_{ii} - \alpha_{kk}\right)^2 + \left(\alpha_{jj} - \alpha_{kk}\right)^2\right]\right\}^{\frac{1}{2}}$ are very important in polarizability studies as shown by Costa [25]. In 2006, Piquemal et al. [26] also showed that the ab initio polarization energy and the dipole moments of bifurcated water oligomers of various sizes, which could easily be reproduced if the anisotropic polarizability of water molecule is fairly described. Similar results were showed by Masia et al. for a different system [27-28].

The polarizability tensor components, the average polarizability and the anisotropy of Daraprim obtained at RHF/6-311++G** and B3LYP/6-311++G** level of theories are listed in Table 3. All the six polarizability tensor components of Pyrimethamine molecule α_{xx}, α_{xy}, α_{yy}, α_{xz} α_{yz} and α_{zz} components change significantly at both level of theory considered here. But they do not follow any regular pattern. The component α_{yz} is negative. From the table, we can see that the tensor α_{xx} is responsible for the greatest contribution both in the average polarizability and the anisotropy for the molecule at all levels of theory. We can also see that the inclusion of electron correlation affects the average polarizability, <α>, and anisotropy, Δα. We equally observe that the effect of inclusion of electron correlation increases <α> by 17.1 percent and Δα by 59 percent for Pyrimethamine.

Table 3: Polarizability tensors, average polarizability and anisotropy of Daraprim and Sulfadoxine using RHF and B3LYP methods by employing 6-311++G** basis set.

	Methods/Basis Set	
Tensor component	RHF/ 6-311++G**	B3LYP/ 6-311++G**
α_{xx}	266.054	334.059
α_{XY}	7.639	9.782
α_{YY}	165.501	188.045
α_{XZ}	5.719	9.684
α_{YZ}	-15.555	-17.344
α_{ZZ}	121.812	126.994
<α>	184.456	216.033
Δα	115.883	184.287

5. Conclusion

In this paper, we have studied the structure, polarizability, zero point vibrational energy (ZPVE), enthalpy (H), entropy (S), and the relative free energy (G). These have been calculated from frequencies obtained by an analytical Hessian calculation for Pyrimethamine molecule. The frequency calculations obtained at the B3LYP level are closer to the experimental value than those obtained at the RHF level due the effect of electron correlation. The polarizability tensor components, the average polarizability and the anisotropy are greater at the B3LYP level of theory. This implies that the inclusion of electron correlation increases the polarizability tensors, the average polarizability and the anisotropy. The average polarizability, <α>, increases by 17.1 percent, and the anisotropy, Δα, by 59 percent.

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