Linear and Non Linear Optical Effects of Pyrimethamine and Sulfadoxine: Ab-initio and Density Functional Study

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The molecular structures of pyrimethamine and sulfadoxine have been explored for non linear optical effects. The ab-initio Hartee Fock calculations and Density Functional Theory with B3LYP method have been carried out employing 6-311++G** basis set. The dipole moments (μ), polarizability (α), and first hyperpolarizability (β_{mol}) in gas phase and in solvated medium (water and ethanol) are calculated using the same level of theory. The variation of the C-N bond lengths suggests that there is an extended pi-electron delocalization over the pyrimidine moiety that is responsible for non linearity of these molecules. Equally, the large values of β_{mol} for these molecules suggest potential applications of these molecular systems in the development of non linear materials. The large β_{mol} values, which is a measure of the non linear optical activity of the molecular system, is associated with the intermolecular charge transfer resulting from an electron cloud movement through the pi-electron delocalization. Hence theoretical determination of β_{mol} is quite useful, both in the understanding of relationship between the molecular structure and non linear optical properties.

1. Introduction

Molecular materials with non linear optical (NLO) properties are currently attracting considerable attention because of their potentials applications in optoelectronics devices used in telecommunication, information storage, optical switching, signal processing, and terahertz wave generation [1,2,3,4]. Non linear optics is one of the few research frontiers where tremendous interest arises not only from the desire to understand new physical phenomena but also from the potential of technology applications [5].

Organic molecules with delocalized π-electrons showing large values of non linear optical parameters are gaining interest among researcher because of their potential applications in the field of optoelectronics, such as optical communication, optical computing, optical switching, and image processing [6,7,8,9,10]. The electro-optic effect arises in photorefractive materials (optoelectronic materials) in two forms; linear electro-optic (LEO) effect or Pockels effect and quadratic electro-optic (QEO) effect or Kerr effect. Organic molecules are good materials for nonlinear devices as they are chemically flexible and show a large and fast non linear optical response [11] as a result of which their optical and electronic properties can be studied. A number of organic and organometallic molecular systems have been studied for predicting nonlinearity [12]. Organic compounds with electron donating group on one side of the molecule and electron accepting group on other side have been studied by experimental and theoretical scientists for NLO properties [13]. Designs of these organic NLO active materials are based on the approach of charge transfer due to π-electron cloud movement from donor to acceptor groups on either side of these π-conjugated systems. This in turn affects the value of polarizability and hyper-polarizability [7]. It has been known from recent studies that molecular systems, based on electron donor and electron acceptor units connected through pi electron moieties, show many interesting non-linear optical characteristics and have higher value of second order NLO properties [14,15,16,17]. The types of pi-bridges studied so far for developing efficient NLO materials and molecules include donor-acceptor acetylenes [18], azo complexes [19], aromatic ring [14] and hetero-aromatic rings [20]. A good deal of work has been done for investigating nonlinear optical behavior of conjugated polymers consisting of six member and five-member aromatic units, such as benzene, pyridine, Thiophene, pyrrole, N,N- dimethyl-5-nitropyridin-2-amine, N,N-diethyl-5-nitropyridin-2-amine 5-nitro-2-phenylpyridine, and others [20,21]. Their derivatives are also considered to be promising materials for electronic and nonlinear

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optical technology. So far many studies have also been carried out to investigate the nonlinear behavior of two π-conjugated rings attached with a single bond such as biphenyls [20] and phenylpyridine [22]. However, pyrimethamine and Sulfadoxine can further be investigated as a bridge for the search of better NLO materials and for an understanding of the mechanism at atomic level. Theoretical calculations are quite useful both in understanding the relationship between molecular structures and nonlinear optical properties, and also provide guidelines to experimentalists for the design and synthesis of new organic NLO materials. A large number of semi-empirical and ab initio calculations have been reported on molecular hyperpolarizability (β), which is one of the key parameter in the investigation of second order NLO materials [23,24,25]. Experimental measurements and theoretical calculations on molecular hyper-polarizability have become one of the key factors in the determination of second-order NLO material design. Though, there is an effect of the basis set to determine the value of first molecular hyper-polarizability and electronic properties of the molecule. The effect is not very high but the electronic properties and the hyper-polarizability values have been reported to slightly increased on taking up higher basis sets like the 6-31G and 6-311++G** [18,26]. For this reason we have decided to carry out our computation using higher basis set. Equally, as documented in literature, accurate estimate of polarizability and hyper-polarizability need polarized and diffused basis sets as well as introduction of electron correlation contributions [27].

The aim of the present work is to predict NLO properties of molecules Pyrimethamine and sulfadoxine. The idea is to study the charge transfer effect from donor to acceptor through Pyrimidine moiety and determine theoretically the hyper-polarizability of these molecules. This is because the theoretical determination of hyper-polarizability is quite useful to understand both the relationship between their molecular structure and their NLO properties. In calculating the non linear behavior for the designed molecular systems, ab-initio and DFT calculations have been carried out with 6-311++G** basis set.

2. Computational Methodology

All calculations of polarizability and first static hyper-polarizability of pyrimethamine and Sulfadoxine molecules were performed using Gaussian 03W [28]. Initial geometry optimizations were performed using the ab-initio RHF method with 3-21G basis set. Subsequently, its results were utilized to 6-31G basis set and final calculations were carried out with double polarized triple zeta split valence 6-311++G** basis set. These structures were 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 [29], the Lee, Yang and Parr correlation functional [30] and the Vosko, Wilk and Nusair correlation functional [31] with a 6-311++G** basis set. As the first step, geometry optimizations were carried out and then IR and Raman frequencies were calculated using the Hessian, which is the matrix of second derivatives of the energy with respect to the geometry. We have chosen 6-311++G** basis set, which has been supplemented by including diffuse and polarization functions in order to ensure proper behavior of the polarizability and hyper-polarizabilities. This basis set is an adequate basis set and allows for physically correct polarization of the molecule in the presence of an electric field. Furthermore, accurate calculation of NLO properties requires the use of extended basis sets and a high level of theory [22], hence the used of B3LYP in our calculations.

The values of mean polarizability (α) of molecular systems and the isotropy (γ) reported in the present work were calculated by using the following equations

$$\alpha = \frac{1}{3}\left(\langle\alpha_{xx}\rangle + \langle\alpha_{yy}\rangle + \langle\alpha_{zz}\rangle +\right) \tag{1}$$

$$\gamma = \frac{1}{2}\left[\left(\langle\alpha_{xx}\rangle - \langle\alpha_{yy}\rangle\right)^2 + \left(\langle\alpha_{yy}\rangle - \langle\alpha_{zz}\rangle\right)^2 + \left(\langle\alpha_{zz}\rangle - \langle\alpha_{xx}\rangle\right)^2 + 6\left(\langle\alpha_{xy}\rangle^2 + \langle\alpha_{yz}\rangle^2 + \langle\alpha_{zx}\rangle^2\right)\right]^{\frac{1}{2}} \tag{2}$$

The total hyper-polarizability is defined as

$$\beta_{mole} = \frac{1}{3}\left(\beta_x^2 + \beta_y^2 + \beta_z^2\right)^{\frac{1}{2}} \quad (3)$$

The magnitude of β_{mole} is calculated from the computed components β using following equations

$$\beta_i = \frac{1}{3}\sum_{i,k}\left(\beta_{ikk} + \beta_{kik} + \beta_{kki}\right),$$

$$k = x, y, z; i = x, y, z \quad (4)$$

$$\beta_{mole} = \frac{1}{3}\left[\left(\beta_{xxx} + \beta_{xyy} + \beta_{xzz}\right)^2 + \left(\beta_{yyy} + \beta_{yxx} + \beta_{yzz}\right)^2 + \left(\beta_{zzz}^2 + \beta_{zxx} + \beta_{zyy}\right)^2\right]^{\frac{1}{2}} \quad (5)$$

3. Molecular Structure and Geometrical Properties

The molecular structure of Pyrimethamine is shown in Fig. 1 and that of Sulfadoxine is shown in Fig. 2. The geometric optimization of any system gives the ground state geometry of that system. The total ground state energy of a system is obtained as a function of the coordinates of the nuclei from Born-Oppenheimer (BO) approximation. The ground state geometry corresponds to the minimum total ground state energy whereas a first order saddle point on the BO surface gives the transition state geometry. Molecular geometries were fully optimized using Berny's optimization algorithm in Gaussian 03, as well as redundant internal coordinates.

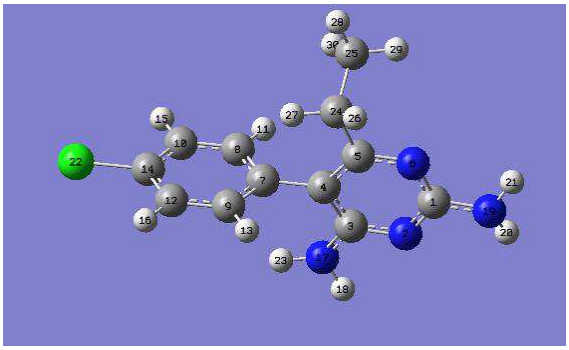

Fig.1: Optimized Structure of Pyrimethamine [32,33].

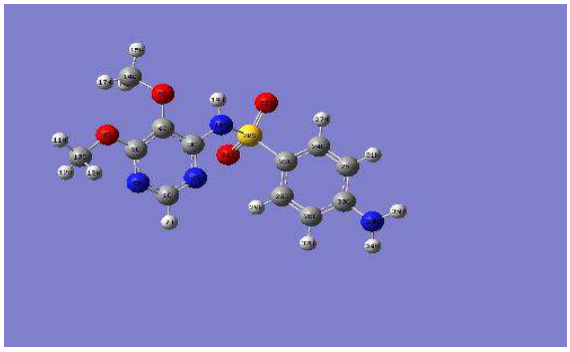

Fig.2: Optimized structure of Sulfadoxine [26,33].

3.1. Optimized geometrical properties of pyrimethamine

The geometrical parameters of a Pyrimethamine molecule in gas phase, water and ethanol are listed in Tables 1a and 1b. The calculated bond lengths at RHF/6-311++G** level are slightly smaller (ranging from 0.01Å to 0.04Å) than their corresponding values obtained at the B3LYP/6-311++G** level (Table 1a). It seems that inclusion of electrons correlation expand the molecules. Once dissolved (in water and ethanol), the bond lengths remain unaffected at RHF/6-311++G** level while at B3LYP/6-311++G** level, the bond lengths vary slightly except for the following N2-C3, C5-N6, C5-C4, C7-C8, C7-C9, C9-C12, C12-C14, C8-H11, C9-H13, C10-H15,C12-H16, C24-H27, C25-H28, C25-H29 and C25-H30, all of which remain unaffected. The bond lengths (Table 1a) at the RHF/6-311++G** and at the B3LYP/6-311++G** are approximately equal to the experimental results [34,35,36]. The B3LYP/6-311++G** results are in better accord with the experimental results and with the theoretical results given by [37]. For example in the Pyrimidine ring, the C5-N6 and C1-N6 bond lengths are exactly equal to those given by [37] and are 0.017Å and 0.013 Å smaller than the C-N experimental value, respectively, both in gas phase and in dissolved phase at the B3LYP/6-311++G** level. At the RHF/6-311++G** level, the C5-N6 and C1-N6 bond lengths are 0.029 Å and 0.041 Å smaller than the C-N experimental value, respectively, both in the gas phase, water and ethanol. From Table 1a, we observed that C-N bond lengths on the Pyrimidine ring vary slightly. This variation of the C-N bond lengths suggests that there is an extended pi-electron delocalization over the pyrimidine moiety.

The bond angles vary from 0.1 to 0.2 degree(s) in both RHF and DFT levels of theories with the 6-

311++G** basis set (Table 1b). The six member carbon ring (Phenyl) and the other ring with two of the carbon atoms replaced by Nitrogen atoms (pyrimidine) possibly give added stability to the molecule. The nitrogen atoms (N11, N12, N14 and N17) play a major role in the electron density configuration. Once dissolved (in water and ethanol) the bond angles remain unaffected at RHF/6-311++G** level of theory while at B3LYP/6-311++G** level of theory, the bond angles vary slightly as we move from gas phase to solution phase. Most of the bond angles increases as we move from gas medium to water and ethanol with the increase more significant in ethanol. The bond angles (Table 1b) at the RHF/6-311++G** and at the B3LYP/6-311++G** are approximately equal to the experimental results [34,35,36]. The RHF/6-311++G** results are in better accord with the experimental results.

Table 1a: Optimized geometrical parameters – Bond lengths of Pyrimethamine molecule in different mediums obtained by RHF and B3LYP methods employing 6- 311++G** basis sets and their corresponding experimental values in gas.

Geomet.	RHF/6-311++G**			B3LYP/6-311++G**			Exp't [34-36]
Parameters	Gas	Water	Ethanol	Gas	Water	Ethanol	
R(C1-N2)	1.3244	1.3244	1.3244	1.3395	1.3394	1.3394	1.360
R(C1-N6)	1.3185	1.3185	1.3185	1.3372	1.3372	1.3371	
R(C1- N19)	1.3582	1.3582	1.3582	1.3691	1.3693	1.3693	
R(N2-C3)	1.3187	1.3182	1.3187	1.3344	1.3344	1.3344	
R(C3-N17)	1.3547	1.3547	1.3547	1.3678	1.3679	1.3680	
R(C5-N6)	1.3305	1.3305	1.3305	1.3429	1.3429	1.3429	
R(C3-C4)	1.4131	1.4131	1.4131	1.4199	1.4198	1.4199	1.399
R(C4-C5)	1.3839	1.3839	1.3839	1.3974	1.3974	1.3974	1.386
R(C4-C7)	1.4967	1.4967	1.4967	1.4922	1.4921	1.4921	
R(C5-C24)	1.5101	1.5101	1.5101	1.5113	1.5112	1.5111	
R(C7-C8)	1.3911	1.3911	1.3911	1.4019	1.4019	1.4019	1.402
R(C7-C9)	1.3914	1.3914	1.3914	1.4020	1.4020	1.4020	1.402
R(C8-C10)	1.3853	1.3853	1.3853	1.3933	1.3932	1.3932	
R(C9-C12)	1.3854	1.3854	1.3854	1.3933	1.3933	1.3933	
R(C12-C14)	1.3812	1.3812	1.3812	1.3909	1.3909	1.3909	
R(C24-C25)	1.5329	1.5329	1.5329	1.5383	1.5382	1.5382	
R(C10-C14)	1.3813	1.3813	1.3813	1.3910	1.3911	1.3911	
R(C14-Cl22)	1.7450	1.7450	1.7450	1.7594	1.7593	1.7593	1.725
R(C8-H11)	1.0752	1.0752	1.0752	1.0843	1.0843	1.0843	1.082
R(C9-H13)	1.0756	1.0756	1.0756	1.0844	1.0844	1.0844	
R(C10-H15)	1.0737	1.0737	1.0737	1.0827	1.0827	1.0827	
R(C12-H16)	1.0737	1.0737	1.0737	1.0827	1.0827	1.0827	
R(C24-H26)	1.0849	1.0849	1.0849	1.0939	1.0940	1.0940	
R(C24-H27)	1.0821	1.0821	1.0821	1.0910	1.0910	1.0910	
R(C25-H28)	1.0858	1.0858	1.0858	1.0932	1.0932	1.0932	
R(C25-H29)	1.0836	1.0836	1.0836	1.0917	1.0917	1.0917	
R(C25-H30)	1.0863	1.0863	1.0863	1.0937	1.0937	1.0937	
R(N17-H18)	0.9929	0.9929	0.9929	1.0076	1.0077	1.0077	1.036
R(N17-H23)	0.9914	0.9914	0.9914	1.0064	1.0065	1.0065	

R(N19-H20)	0.9924	0.9924	0.9924	1.0065	1.0066	1.0066	
R(N19-H21)	0.9924	0.9924	0.9924	1.0066	1.0067	1.0067	

Bond Lengths (R) are given in Armstrong (Å) and atoms labeling according to Fig. 1.

Table 1b: Optimized geometrical parameters – Bond angles of Pyrimethamine molecule in different mediums obtained at RHF and B3LYP methods by employing 6- 311++G** basis sets and their corresponding experimental values in gas.

Geomet.	RHF/6-311++G**			B3LYP/6-311++G**			Exp't [34-36]
Parameters	Gas	Water	Ethanol	Gas	Water	Ethanol	
A(N2-C1-N6)	126.5661	126.5661	126.5661	126.5813	126.5887	126.5882	
A(N2-C1-N19)	116.4042	111.4042	116.4042	116.5302	116.5277	116.5253	
A(N6-C1-N19)	117.0147	117.0147	117.0147	116.8667	116.8614	116.8640	
A(N2-C3-N17)	116.0653	116.0653	116.0653	116.1734	116.1680	116.1686	
A(C1-N2-C3)	116.5644	116.5644	116.5644	116.3674	116.3618	116.3625	
A(C1-N6-C5)	116.8374	116.8374	116.8374	116.7324	116.7293	116.7302	
A(N2-C3-C4)	122.4486	122.4486	122.4486	122.4422	122.4458	122.4461	
A(C4-C3-N17)	121.4737	121.4737	121.4737	121.3714	121.3729	121.3721	
A(C3-C4-C5)	115.0879	115.0879	115.0879	115.5793	115.5766	115.5759	
A(C3-C4-C7)	120.7408	120.7408	120.7408	120.4696	120.4700	120.4766	
A(C5-C4-C7)	124.1710	124.1710	124.171	123.9511	123.9534	123.9475	
A(C4-C5-N6)	122.4880	122.4880	122.488	122.2910	122.2916	122.2910	
A(C4-C5-C24)	122.6870	122.6870	122.6870	122.6697	122.6674	122.6722	
A(C4-C7-C8)	121.0529	121.0529	121.0529	120.9668	120.9751	120.9811	
A(C4-C7-C9)	120.9544	120.9544	120.9544	121.0545	121.0507	121.0451	
A(C8-C7-C9)	117.9829	117.9829	117.9829	117.9685	117.9640	117.9639	
A(C7-C8-C10)	121.3749	121.3749	121.3749	121.3827	121.3856	121.385	
A(C7-C9-C12)	121.4024	121.4024	121.4024	121.4082	121.4102	121.4106	
A(C9-C12-C14)	119.1411	119.1411	119.1411	119.0947	119.0966	119.0967	119.80
A(C8-C10-C14)	119.1812	119.1812	119.1812	119.1240	119.1256	119.1266	
A(C10-C14-C12)	120.9153	120.9153	120.9153	121.0186	121.0148	121.0139	
A(C5-C24-C25)	111.9558	111.9558	111.9558	112.0507	112.0684	112.0646	
A(C10-C14-Cl22)	119.5466	119.5466	119.5466	119.4919	119.492	119.4934	
A(C12-C14-Cl22)	119.5380	119.5380	119.5380	119.4894	119.4924	119.4926	
A(C7-C8-H11)	119.4315	119.4315	119.4315	119.344	119.3386	119.3393	119.60
A(C10-C8-H11)	119.1936	119.1936	119.1936	119.273	119.2755	119.2754	
A(C7-C9-H13)	119.4153	119.4153	119.4153	119.3155	119.3184	119.3161	
A(C12-C9-H13)	119.1812	119.1812	119.1812	119.2758	119.2709	119.2728	
A(C8-C10-H15)	120.6316	120.6316	120.6316	120.7266	120.7265	120.7255	
A(C14-C10-H15)	120.1872	120.1872	120.1872	120.1492	120.1476	120.1476	
A(C9-C12-H16)	120.6491	120.6491	120.6491	120.7408	120.7385	120.7389	
A(C14-C12-H16)	120.2098	120.2098	120.2098	120.1644	120.1648	120.1644	
A(C5-C24-H27)	110.5948	110.5948	110.5948	110.4605	110.4617	110.4679	
A(C25-C24-H26)	109.3066	109.3066	109.3066	109.1122	109.1033	109.1035	109.46

A(C25-C24-H27)	109.8061	109.8061	109.8061	109.8103	109.8094	109.8121	
A(H26-C24-H27)	107.8799	107.8799	107.8799	107.7345	107.7305	107.7264	
A(C24-C25-H28)	110.1473	110.1473	110.1473	110.5216	110.5131	110.5133	
A(C24-C25-H29)	110.7270	110.7270	110.7270	110.4946	110.5022	110.5002	
A(C24-C25-H30)	111.1655	111.1655	111.1655	111.1290	111.1442	111.1429	
A(C3-N17-H18)	116.7362	116.7362	116.7362	116.5334	116.4973	116.4914	113.90
A(C3-N17-H23)	120.0663	120.0663	120.0663	119.5782	119.5473	119.5409	
A(C1-N19-H20)	117.1351	117.1351	117.1351	117.3233	117.3359	117.3108	
A(C1-N19-H21)	116.8222	116.8222	116.8222	116.8992	116.9110	116.8888	
A(H20-N19-H21)	118.0941	118.0941	118.0941	118.3329	118.3405	118.3083	
A(H18-N17-N23)	118.1127	118.1127	118.1127	117.9775	117.9435	117.9371	
A(H28-C25-H29)	108.4609	108.4609	108.4609	108.4215	108.4248	108.4265	109.01
A(H28-C25-H30)	107.9126	107.9126	107.9126	107.9423	107.9361	107.9357	
A(H29-C25-H30)	108.3325	108.3325	108.3325	108.2345	108.2224	108.2243	

Bond Angles (A) are in degrees (˚) and atoms labeling according to Fig.1.

3.2. Optimized geometric properties of sulfadoxine

The geometric parameters of Sulfadoxine molecule in gas phase, water and ethanol are listed in Table 2a. The calculated bond lengths at RHF/6-311++G** level are slightly smaller (ranging from 0.01Å to 0.04Å) than their corresponding values obtained at the B3LYP/6-311++G** level. In solution (water and ethanol) the bond lengths remain unaffected at the RHF/6-311++G** level of theory and at the B3LYP/6-311++G** level of theory. The RHF/6-311++G** and B3LYP/6-311++G** bond lengths are approximately equal to the experimental values [34,35,36]. The B3LYP/6-311++G** theoretical calculated values are in better agreement with experimental values than their corresponding RHF/6-311++G** theoretical calculated values. For example in the Pyrimidine ring, the C1-N2 bond length is 0.105 Å, which is smaller than the C-N experimental value at the B3LYP/6-311++G** level and at the RHF/6-311++G** level. It is 0.124 Å smaller than the C-N experimental value respectively both in the gas phase and solution in water and ethanol. The C1-N6 bond length is 0.097 Å smaller than the experimental value at the B3LYP/6-311++G** level and at the RHF/6-311++G** level, it is 0.114 Å smaller both in the gas phase and dissolved in water and ethanol. From Table 2a, we also observed that C-N bond lengths on the Pyrimidine ring vary slightly. This variation of the C-N bond lengths also suggests that there is an extended pi-electron delocalization over the pyrimidine moiety.

The bond angles vary from 0.1 to 0.2 degrees in both RHF and DFT levels of theories with the 6-311++G** basis set (Table 2b). The Phenyl group and the pyrimidine possibly give added stability to the molecule. The Nitrogen atoms (N4, N17, N18 and N32) and the oxygen atoms (O6, O7, O20 and O21) play a major role in the electron density configuration. In the water and ethanol dissolved state, the bond angles remain unaffected both at the RHF/6-311++G** level and at the B3LYP/6-311++G** level of theory as we move from gas phase to water and to ethanol. The bond angles (Table 2b) at the RHF/6-311++G** and at the B3LYP/6-311++G** are approximately equal to the experimental results [34,35,36].

Table 2a: Optimized geometrical parameters – Bond lengths of Sulfadoxine molecule in different medium obtained at RHF and B3LYP methods by employing 6- 311++G** basis sets and their corresponding experimental values.

Geomet.	RHF/6-311++G**			B3LYP/6-311++G*			Exp't [34-36]
Parameters	Medium			Medium			
	Gas	Water	Ethanol	Gas	Water	Ethanol	
R(C1-N2)	1.3074	1.3074	1.3074	1.3258	1.3258	1.3258	1.431
R(C1-N6)	1.3174	1.3174	1.3174	1.3336	1.3336	1.3336	
R(C5-N6)	1.3163	1.3163	1.3163	1.3312	1.3312	1.3312	
R(N2-C3)	1.3249	1.3249	1.3249	1.3395	1.3395	1.3395	
R(C3-N18)	1.3781	1.3781	1.3781	1.3845	1.3845	1.3845	1.391
R(C30-N33)	1.3809	1.3809	1.3809	1.3844	1.3844	1.3844	
R(C4-O9)	1.3544	1.3544	1.3544	1.3687	1.3687	1.3687	1.364
R(C5-O8)	1.3173	1.3173	1.3173	1.3445	1.3445	1.3445	
R(O8-C10)	1.4166	1.4166	1.4166	1.4385	1.4385	1.4385	1.364
R(O9-C14)	1.4151	1.4151	1.4151	1.4405	1.4405	1.4405	
R(C1-H7)	1.0755	1.0755	1.0755	1.0857	1.0857	1.0857	1.084
R(C10-H11)	1.0795	1.0795	1.0795	1.0882	1.0882	1.0882	
R(C10-H12)	1.0814	1.0814	1.0814	1.0908	1.0908	1.0908	
R(C10-H13)	1.0813	1.0813	1.0813	1.0906	1.0906	1.0906	
R(C14-H15)	1.0807	1.0807	1.0807	1.0889	1.0889	1.0889	
R(C14-H16)	1.0858	1.0858	1.0858	1.0942	1.0942	1.0942	
R(C14-H17)	1.0823	1.0823	1.0823	1.0902	1.0902	1.0902	
R(C24-H27)	1.0740	1.0740	1.0740	1.0827	1.0827	1.0827	
R(C25-H29)	1.0723	1.0723	1.0723	1.0814	1.0814	1.0814	
R(C26-H31)	1.0755	1.0755	1.0755	1.0848	1.0848	1.0848	
R(C28-H32)	1.0755	1.0755	1.0755	1.0848	1.0848	1.0848	
R(N18-S20)	1.6575	1.6575	1.6575	1.7142	1.7142	1.7142	1.764
R(S20-O21)	1.4192	1.4192	1.4192	1.4554	1.4554	1.4554	
R(S20-O22)	1.4263	1.4263	1.4263	1.4622	1.4622	1.4622	1.485
R(S20-C23)	1.7520	1.7520	1.7520	1.7774	1.7774	1.7774	1.799
R(C4-C5)	1.3906	1.3906	1.3906	1.4012	1.4012	1.4012	1.392
R(C3-C4)	1.3827	1.3827	1.3827	1.4015	1.4015	1.4015	
R(C23-C24)	1.3880	1.3880	1.3880	1.3955	1.3955	1.3955	
R(C23-C25)	1.3863	1.3863	1.3863	1.3947	1.3947	1.3947	
R(C24-C26)	1.3766	1.3766	1.3766	1.3856	1.3856	1.3856	
R(C25-C28)	1.3778	1.3778	1.3778	1.3855	1.3855	1.3855	
R(C26-C30)	1.3972	1.3972	1.3972	1.4068	1.4068	1.4068	
R(C28-C30)	1.3958	1.3958	1.3958	1.4064	1.4064	1.4064	
R(N33-H34)	0.9945	0.9945	0.9945	1.0080	1.0080	1.0080	1.036
R(N33-H35)	0.9945	0.9945	0.9945	1.0081	1.0081	1.0081	
R(N18-H19)	0.9970	0.9970	0.9970	1.0137	1.0137	1.0137	

Bond Lengths (R) are given in Armstrong (Å) and atoms labeling according to Fig. 2.

Table 2b: Optimized geometrical parameters – Bond angles of Sulfadoxine molecule in different medium obtained at RHF and B3LYP methods by employing 6- 311++G** basis sets and their corresponding experimental values.

Geomet.	RHF/6-311++G**			B3LYP/6-311++G*			Exp't [34-36]
Parameters	Medium			Medium			
	Gas	Water	Ethanol	Gas	Water	Ethanol	
A(C23-C24-H27)	119.9897	119.9897	119.9897	119.9464	119.9464	119.9464	119.88
A(C26-C24-H27)	119.9764	119.9764	119.9764	120.4453	120.4453	120.4453	
A(C23-C25-H29)	119.6635	119.6635	119.6635	119.6922	119.6922	119.6922	
A(C28-C25-H29)	120.4592	120.4593	120.4593	120.8456	120.8456	120.8456	
A(C24-C26-H31)	119.8620	119.8619	119.8619	119.7491	119.7491	119.7491	
A(C30-C26-H31)	119.8432	119.8433	119.8433	119.6797	119.6797	119.6797	119.88
A(C25-C28-H32)	119.7726	119.7726	119.7726	119.6487	119.6487	119.6487	
A(C30-C28-H32)	119.7614	119.7614	119.7614	119.6123	119.6123	119.6123	
A(C3-C4-C5)	115.6438	115.6438	115.6438	115.7975	115.7975	115.7975	
A(C24-C23-C25)	120.2142	120.2143	120.2143	120.7801	120.7801	120.7801	120.64
A(C23-C24-C26)	120.0275	120.0275	120.0275	119.5995	119.5995	119.5995	
A(C23-C25-C28)	119.8771	119.8771	119.8771	119.4618	119.4618	119.4618	
A(C24-C26-C30)	120.2932	120.2932	120.2932	120.5698	120.5698	120.5698	
A(C25-C28-C30)	120.4658	120.4659	120.4659	120.7389	120.7389	120.7389	
A(C26-C30-C28)	119.1203	119.1203	119.1203	118.8492	118.8492	118.8492	
A(C30-N33-H34)	116.2733	116.2733	116.2733	117.3144	117.3144	117.3144	114.92
A(C30-N33-H35)	116.3096	116.3096	116.3096	117.3334	117.3334	117.3334	
A(H34-N33-H35)	113.0062	113.0062	113.0062	113.8516	113.8516	113.8516	113.90
A(H11-C10-H12)	110.4143	110.4143	110.4143	110.6842	110.6842	110.6842	109.01
A(H11-C10-H13)	110.3132	110.3132	110.3132	110.5816	110.5816	110.5816	
A(H12-C10-H13)	109.3598	109.3598	109.3598	109.1566	109.1566	109.1566	
A(N2-C1-N6)	127.2026	127.2026	127.2026	127.1239	127.1239	127.1239	
A(N2-C3-N18)	118.8657	118.8657	118.8657	119.2549	119.2549	119.2549	
A(N2-C1-H7)	116.5600	116.5599	116.5599	116.5927	116.5927	116.5927	
A(N6-C1-H7)	116.2354	116.2354	116.2354	116.2811	116.2811	116.2811	
A(C1-N2-C3)	116.1156	116.1156	116.1156	116.0632	116.0632	116.0632	114.4
A(C1-N6-C5)	116.5139	116.5139	116.5139	116.4991	116.4991	116.4991	
A (N2-C3-C4)	122.4483	122.4483	122.4483	122.3333	122.3333	122.3333	
A(C4-C3-N18)	118.6516	118.6516	118.6516	118.367	118.367	118.367	
A(C4-C5-N6)	122.0483	122.0482	122.0482	122.132	122.132	122.132	
A(C26-C30-N33)	120.3781	120.3781	120.3781	120.5396	120.5396	120.5396	
A(C28-C30-N33)	120.4724	120.4724	120.4724	120.5756	120.5756	120.5756	
A(C3-C4-O9)	120.3587	120.3587	120.3587	118.6792	118.6792	118.6792	
A(C5-C4-O9)	123.8948	123.8947	123.8947	125.3600	125.3600	125.3600	124.5
A(C4-C5-O8)	117.8636	117.8637	117.8637	117.9257	117.9257	117.9257	
A(N6-C5-O8)	120.0855	120.0855	120.0855	119.9413	119.9413	119.9413	
A(C5-O8-C10)	119.2643	119.2644	119.2644	117.601	117.601	117.601	

A(C4-O9-C14)	116.3076	116.3076	116.3076	116.8665	116.8665	116.8665	
A(O8-C10-H11)	105.2619	105.2619	105.2619	104.9162	104.9162	104.9162	
A(O8-C10-H12)	110.7611	110.7611	110.7611	110.7865	110.7865	110.7865	
A(O8-C10-H13)	110.6802	110.6802	110.6802	110.6723	110.6723	110.6723	
A(O9-C14-H15)	106.4717	106.4717	106.4717	105.7057	105.7057	105.7057	
A(O9-C14-H16)	110.5699	110.5699	110.5699	110.31	110.31	110.31	
A(O9-C14-H17)	110.7178	110.7178	110.7178	110.7682	110.7682	110.7682	
A(H15-C14-H16)	109.5985	109.5985	109.5985	109.7083	109.7083	109.7083	
A(H15-C14-H17)	109.5906	109.5906	109.5906	110.1002	110.1002	110.1002	
A(H16-C14-H17)	109.8313	109.8313	109.8313	110.1588	110.1588	110.1588	
A(C3-N18-H19)	116.9503	116.9503	116.9503	116.0325	116.0325	116.0325	
A(C3-N18-S20)	127.4524	127.4525	127.4525	126.4137	126.4137	126.4137	
A(H19-N18-S20)	112.8406	112.8406	112.8406	111.7546	111.7546	111.7546	
A(N18-S20-O21)	109.3527	109.3527	109.3527	109.4269	109.4269	109.4269	
A(N18-S20-O22)	101.7625	101.7625	101.7625	101.4649	101.4649	101.4649	
A(N18-S20-C23)	106.7853	106.7853	106.7853	105.4541	105.4541	105.4541	
A(O21-S20-O22)	120.5877	120.5877	120.5877	121.4528	121.4528	121.4528	121.25
A(O21-S20-C23)	108.7410	108.7410	108.7410	109.0195	109.0195	109.0195	
A(O22-S20-C23)	108.7118	108.7118	108.7118	108.7657	108.7657	108.7657	106.5
A(S20-C23-C24)	119.5720	119.5720	119.5720	119.236	119.236	119.236	119.26
A(S20-C23-C25)	120.2006	120.2006	120.2006	119.9724	119.9724	119.9724	

Bond Angles (A) are in degrees (˚) and atoms labeling according to Fig. 2.

4. Atomic Charges, Polarizability and Hyper-polarizability

Atomic net charges are not quantum mechanical (QM) observables, and they cannot be determined directly with QM calculations or by experiments. Different methods exist for the estimation of atomic charges of the molecular system. Basically, the atomic charges are best derived by a least squares fit to the electrostatic potential (ESP), calculated in a large number of points around the molecule of interest [38].

The electrostatic potential derived charges using the CHELPG scheme of Breneman [39] at different atomic positions of Pyrimethamine and Sulfadoxine molecules at RHF/6-311++G** and B3LYP/6-311++G** levels of theories have been calculated. The Mulliken population analysis partitions the charges among the atoms of a molecule by dividing orbital overlap evenly between two atoms. Whereas, the electrostatic potential derived charges assign point charges to fit the computed electrostatic potential at a number of points on or near the Van der Waal surface. This sort of analysis is commonly used to create input charges for molecular mechanics calculation. Hence, it is appropriate to consider the charges calculated by CHELPG scheme of Breneman instead of Mulliken population analysis. Within a molecular system, atoms can be treated as a quantum mechanical system. On the basis of the topology of the electron density, the atomic charges in the molecule can be explained**.**

Polarizability is a property that 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. Polarizability plays an important role in the understanding of a large variety of physical phenomena [40,41,42]. The well-known experimental difficulties obtaining reliable results of polarizabilities justify the need of accurate theoretical results. In some cases, these results are the only source of information regarding polarizabilities. The polarizability tensor components, the average polarizability and the anisotropy in electrostatic units (esu) for Pyrimethamine and Sulfadoxine obtained at RHF/6-311++G** level and B3LYP/6-311++G** level of theories are listed in Tables 3 and 4, respectively. All the six polarizability tensor

components of Pyrimethamine and Sulfadoxine molecules α_{xx}, α_{xy}, α_{yy}, α_{xz} α_{yz} and α_{zz} components changes significantly at the RHF/6-311++G** level and B3LYP/6-311++G** level of theory considered here (although they do not follow any regular pattern).

In the case of Pyrimethamine, the polarizability tensor components do not show any change in going from gas phase to solution phase at the RHF/6-311++G** level but polarizability tensor components change slightly at the B3LYP/6-311++G** level. From Table 3, we can see that 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 $< \alpha >$ and the anisotropy γ in gas phase and in solution phase. We equally observe that the effect of inclusion of electron correlation increases $< \alpha >$ by 17.30 percent for the gas phase, 17.17 percent when dissolved in water and 17.31 percent in ethanol whereas γ increases by 45.50 percent for the gas phase, 45.56 percent when dissolved in water and 45.49 percent when in ethanol.

Table 3: Polarizability tensors, average polarizability and anisotropy (x 10^{-12} esu) of Pyrimethamine using RHF and B3LYP methods by employing 6-311++G** basis set.

Tensor	RHF/6-311++G**			B3LYP/6-311++G**		
Components	Gas	Water	Ethanol	Gas	Water	Ethanol
α_{xx}	39.429	39.429	39.429	49.508	49.359	49.513
α_{XY}	0.168	0.168	0.168	0.215	0.220	0.215
α_{YY}	24.527	24.527	24.527	27.868	28.252	27.870
α_{XZ}	0.848	0.848	0.848	1.435	1.409	1.440
α_{YZ}	-2.305	-2.305	-2.305	-2.570	-2.534	-2.563
α_{ZZ}	18.053	18.053	18.053	18.821	18.476	18.821
$<\alpha>$	27.336	27.336	27.336	32.065	32.029	32.068
γ	19.178	19.178	19.178	27.904	27.915	27.900

As observed in Pyrimethamine, the polarizability tensor components of Sulfadoxine do not show any change in going from gas phase to solution phase at the RHF/6-311++G** level but polarizability tensor components change slightly at the B3LYP/6-311++G** level. From Table 4, 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 $< \alpha >$ and the anisotropy γ in gas phase and in solution phase. We equally observed that the effect of inclusion of electron correlation increases $< \alpha >$ by 4.42 percent for the gas phase, 0.85 percent when dissolved in water or in ethanol whereas γ increases by 38.80 percent for the gas phase, 26.01 percent when dissolved in water or in ethanol.

Table 4: Polarizability tensors, average polarizability and anisotropy (x 10^{-12} esu) of Sulfadoxine using RHF and B3LYP methods by employing 6-311++G** basis set.

Tensor	RHF/6-311++G**			B3LYP/6-311++G**		
Components	Gas	Water	Ethanol	Gas	Water	Ethanol
α_{xx}	33.833	33.833	33.833	41.062	39.101	39.101
α_{XY}	-2.198	-2.198	-2.198	-2.314	-2.418	-2.418

α_{YY}	27.076	27.076	27.076	31.072	29.940	29.940
α_{XZ}	-1.034	-1.034	-1.034	-1.544	-1.217	-1.217
α_{YZ}	-2.122	-2.122	-2.122	-2.364	-2.189	-2.189
α_{ZZ}	21.517	21.517	21.517	23.215	23.067	23.067
$<\alpha>$	30.439	30.439	30.439	31.738	30.753	30.753
γ	12.056	12.056	12.056	16.733	15.225	15.225

The polarizability and hyperpolarizability of a molecule are presented as the output in the standard orientation in triangular and tetrahedral order, respectively. Hyper-polarizability is very sensitive to molecular structure and highly dependent on the choice of the basis set [43,44]. Tables 5 and 6 show the diagonal hyper-polarizabilities and the first molecular hyper-polarizability of Pyrimethamine and Sulfadoxine molecules. Since the values of the first molecular hyper-polarizability are given in atomic units, we have thus converted the values in electrostatic units.

In the case of Pyrimethamine, the component β_{xxx} of hyper-polarizability gives the highest contribution to the first molecular hyper-polarizability at the RHF/6-311++G** level in both gas phase and solution phase. At the B3LYP/6-311++G** level, the component β_{xxx} of the hyper-polarizability gives the highest contribution of the first molecular hyper-polarizability in gas phase and when dissolved in ethanol, whereas β_{zzz} component gives the highest contribution when dissolved in water. The first molecular hyper-polarizability is greater at the B3LYP/6-311++G** compared to the RHF/6-311++G**, both in gas phase and in solution phase.

In the case of Sulfadoxine, the component β_{zzz} of the hyper-polarizability gives the highest contribution to molecular hyper-polarizability at the RHF/6-311++G** level in both gas phase and solution phase. At the B3LYP/6-311++G** level, the component β_{yyy} of the hyper-polarizability gives the highest contribution of the first molecular hyper-polarizability when dissolved in water and ethanol and β_{zzz} component gives the highest contribution in gas phase. The first molecular hyper-polarizability is also greater at the B3LYP/6-311++G** compare to the RHF/6-311++G** both in gas phase and in solution phase.

Table 5: Components of diagonal hyper-polarizabilities and first molecular hyper-polarizabilities (x 10^{-33}esu) of Pyrimethamine using RHF and B3LYP methods by employing 6-311++G** basis set.

Components	RHF/6-311++G**			B3LYP/6-311++G**		
	Gas	Water	Ethanol	Gas	Water	Ethanol
β_{xxx}	2369.243	2369.181	2369.181	5439.796	1432.016	5347.286
β_{yyy}	-968.854	-968.811	-968.811	-709.433	-10234.486	698.980
β_{zzz}	417.727	417.840	417.840	-510.151	11323.963	-518.125
β_{molec}	2593.547	2593.493	2593.493	5509.531	15330.607	5417.610

Table 6: Components of diagonal hyper-polarizabilities and molecular first hyper-polarizability (x 10^{-33}esu) of Sulfadoxine using RHF and B3LYP methods by employing 6-311++G** basis set.

Components	RHF/6-311++G**			B3LYP/6-311++G**		
	Gas	Water	Ethanol	Gas	Water	Ethanol
β_{xxx}	-18845.976	-18845.976	-18845.976	-25100.063	2475.790	2475.790
β_{yyy}	-11599.634	-11599.634	-11599.634	-15575.985	-18058.020	-18058.020
β_{zzz}	-28028.844	-28028.844	-28028.844	-37368.636	-2209.536	-2209.536
β_{molec}	35711.881	35711.881	35711.811	47634.435	18360.383	18360.383

5. Conclusion

We observed that some charge transfer takes place in going from gas phase to solution medium at the B3LYP/6-311++G** level of theory. This charge transfer is more significant in the case of water than in the case of ethanol. The polarizability of these molecules changed slightly following their solution in different media, in comparison to gas phase, at the B3LYP/6-311++G** level of theory.

The high polarizability values of the molecules revealed that the electrostatic and dispersion contribution influence considerably the interaction of these molecules with other molecules. We also concluded that an appropriate treatment of the electron correlation is of fundamental importance in order to obtain accurate estimates for the electronic contributions to polarizabilities and hyper-polarizabilities.

The variation of the C-N bond lengths suggests an extended pi-electron delocalization over the pyrimidine moiety, which is responsible for the non linearity of these molecules.

Due to the large first hyper-polarizability of these molecules, we concluded that these molecules have the potential to produce second order optical effects much larger than those obtainable with inorganic materials which suggests potential for applications of these molecules in the development of non linear materials. Hence these molecules, which are Malaria drugs also, have application in electro optics devices, photorefractive materials, second harmonics generation, etc.

Due to the lack of existing experimental or theoretical results of the hyper-polarizability of these molecules, we are optimistic that our results will provide a benchmark study for these molecules, and serve as a reference for other studies.

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