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Structural and spectroscopic studies on dimerization and solvent-ligand complexes of Theobromine

Mustafa Tuğfan Bilkan *

Department of Physics, Faculty of Science, Çankırı Karatekin University, 18100 Çankırı, Turkey

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ABSTRACT

The solvent effects on structure and vibrational modes of Theobromine (TBR) were examined by using theoretical and experimental methods. Solvent-ligand complexes of TBR were handled in detail for Dimethylsulfoxide (DMSO) and Ethanol (EtOH) solvents. Density Functional Theory (DFT) was used for theoretical calculations. Polarized continuum model (PCM) was employed to characterize the solvent effects in implicit and explicit investigations. After the optimized molecular structures are determined in vacuum and solvent media, the wavenumbers and intensities of the vibrational frequencies were also computed in detail. Experimental FT-IR spectra of TBR in DMSO and EtOH solutions were recorded and compared with solid phase data. The results show that the structural and vibrational properties of TBR are affected by the solvent effect. Experimental and theoretical results show also that TBR may exist in dimer form in solid phase and it is bonded by hydrogen bonds with the solvent molecules in solutions.

1. Introduction

Theobromine (TBR) is a common known alkaloid and it is found in structures of cacao, tea, coffee etc. With a general description, TBR is expressed as methyl bonded xanthine (3,7-dimethylxanthine). It has investigated by scientists for many years because of its commercial and scientific importance [1–3]. TBR is also known with biological and pharmacological activities for living organisms [4,5].

The molecular structure of free TBR is shown in Fig. 1. In the literature, there are many studies on structural analyses of TBR and its complexes. Mikulski et al. have studied palladium and platinum chlorides complexes of TBR by experimental spectroscopic methods [6]. Cook et al. have investigated solid phase experimental infrared spectral and structural properties of TBR salts [7]. Ucun et al. made some ab initio calculations on molecular structures and vibrational frequencies of various xanthine derivatives by Hartree Fock and Density Functional Theories [8].

Although there are many published study about vibrational and structural properties of free TBR, to the best of our knowledge, there are no published studies on solvent effects, solvent-ligand complexes and dimer structures of TBR. Hence, in this study, we have investigated energies, optimized molecular structures and vibrational frequencies of theobromine dimers (TBR-TBR), theobromine-dimethylsulfoxide (TBR-DMSO) and theobromine-ethanol (TBR-EtOH) complexes by DFT/B3LYP method.

In our previous work, we have studied 2,2′-Dipyridylamine-Dichloromethane complexes experimentally and theoretically [9]. Solvent-ligand complexes and their interactions are important issues in experimental and computational chemistry. All interactions that occur in a living tissue, takes place in the liquid (solvent) medium. For this reason, there are growing interests on solute-solvent interactions by scientist for many years. There are two basic strategies in modelling solvent effect theoretically. These are implicit solvation technique and explicit solvation technique [10]. Explicit models rely on using too much of discrete solvent molecules [11] therefore this approach is so computationally demanding and costly. In implicit model, solvent medium is treated as continuous medium having the average properties of the real solvent, and surrounding the solute beginning at the van der Waals surface. Although the implicit model has a number of advantages, explicit approach often much better illustration the experimental results. In the first part of this study, solvent effects were investigated using Polarizable Continuum Model (PCM) [12]. This model has been used much in recent years because of the success in the calculation on solvent effects. In this model, solvent effects are examined as implicit. The solvents chosen are Ethanol (EtOH $\varepsilon = 24.85$) and Dimethylsulfoxide (DMSO $\varepsilon = 46.83$). In the second part, solvent effects were investigated as explicit. Therefore, all possible solvent-ligand complexes were drawn and examined in three dimensions. In addition to theoretical work, experimental FT-IR spectra of TBR were recorded in solid phase and solution phases. By analysing spectral data, solvent effects were also investigated experimentally. Since the experimental

* Corresponding author.
E-mail address: mtbilkan@gmail.com.

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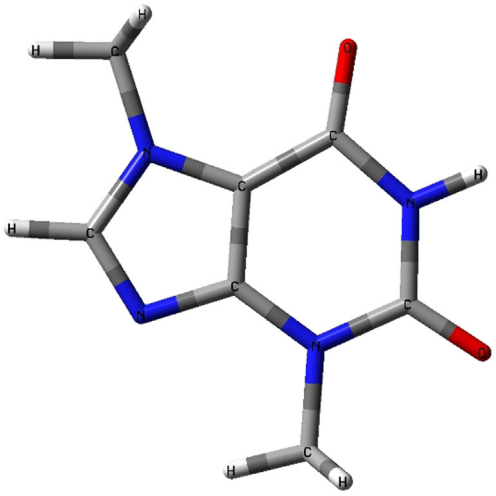

Fig. 1. Molecular structure of TBR.

solid phase FT-IR results show bound N—H vibration in structure of TBR and this case may refer to dimeric structure, dimer structure calculations have also carried out considering the possible dimeric forms of TBR by using same level of theory.

2. Computational method

The calculations of energies, optimized molecular structures and vibrational frequencies of TBR have been performed by using Gaussian03 program [13]. All calculations were made on personal computers. The calculated frequencies were scaled by a scale factor (0.9668) which taken from the literature [14] to correct the difference between the calculated and experimental vibrational frequencies. Firstly, the optimized molecular structures of TBR in vacuum and solvent media were performed using by 6-311++G(d,p) basis set. Secondly, based on the optimized structures, vibrational modes were calculated. The fundamental vibrational modes were characterized by their PED (potential energy distribution) obtained by using the VEDA4 program [15]. Interaction energies of all complex structure (TBR-TBR, TBR-EtOH and TBR-DMSO) were calculated by following formula;

$$\Delta E_{interaction} = E_{complex} - (E_{TBR} + E_X) \tag{2.1}$$

In here, E_X is the energy of any molecule that binds to the single TBR molecule. For example, dimer interaction energy of TBR was calculated by the following formula;

$$\Delta E_{interaction} = E_{dimer} - 2E_{monomer} \tag{2.2}$$

in this formula, $E_{monomer}$ is energy of single TBR molecule in gas phase. E_{dimer} is energy of dimer structure of TBR. The basis set superposition error (BSSE) was corrected with the Counterpoise method [16] for the energies. The method defined in the study of Bergero et al. was applied and then corrected energies were obtained according to Eq. (2.3);

$$E_{corr} = E + BSSE \tag{2.3}$$

On the other hand, when examining the solvent effects on TBR, only PCM implicit solvation model calculations were named as Model I. Both implicit and explicit solvation model calculations on TBR-DMSO and TBR-EtOH complexes were named Model II.

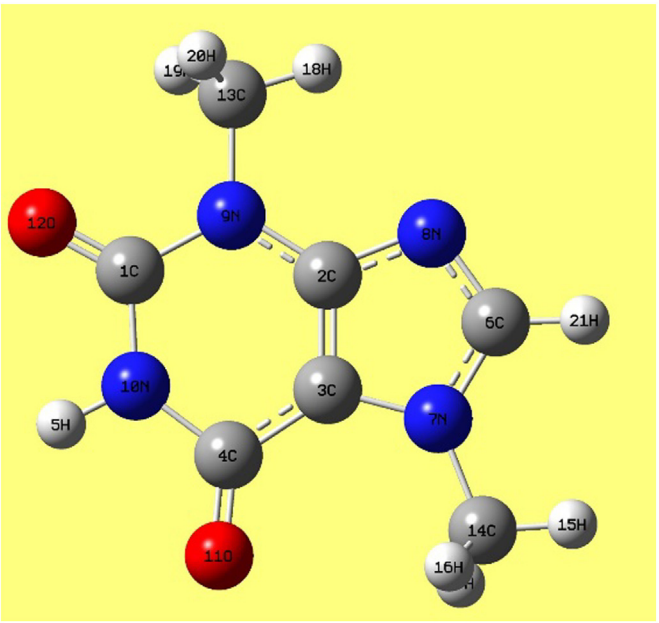

Fig. 2. Optimized molecular structure of TBR in vacuum medium.

3. Experimental procedure

Commercial samples of TBR, EtOH and DMSO were purchased from Aldrich and used without further purification. 1 mmol TBR (180 mg) was solved in 1 ml EtOH. At the same way, 1 mmol TBR (180 mg) was

Table 1
Selected geometric parameters of TBR in EtOH and DMSO media.

	Bond lengths	Vacuum	PCM		Ref[b]	Exp.[a]
			EtOH (protic)	DMSO (aprotic)		
1	1C-9N	1.393	1.385	1.385	1.391	1.377
3	1C-12O	1.215	1.223	1.223	1.220	1.231
4	2C-3C	1.383	1.386	1.386	1.384	1.364
5	2C-8N	1.371	1.370	1.370	1.359	1.363
7	3C-4C	1.434	1.429	1.429	1.435	1.426
8	3C-7N	1.403	1.403	1.403	1.386	1.388
9	4C-10N	1.411	1.407	1.407	1.408	1.397
10	4C-11O	1.220	1.226	1.226	1.225	1.225
11	10N-5H	1.012	1.013	1.013	1.012	0.856
12	6C-7N	1.343	1.339	1.339	1.356	1.343
13	6C-8N	1.292	1.296	1.296	1330	1.339
16	9N-13C	1.465	1.467	1.467	1.462	1.473
17	13C-18H	1.087	1.086	1.086	1.088	1.039
19	13C-20H	1.092	1.090	1.090	1.092	0.971
22	14C-17H	1.090	1.089	1.089	1.091	1.034
	Bond angles	Vacuum	PCM		Ref[b]	Exp.[a]
			EtOH (protic)	DMSO (aprotic)		
23	9N-1C-10N	115.34	115.79	115.79	115.40	116.37
24	9N-1C-12O	122.68	122.57	122.57	122.60	122.10
25	10N-1C-12O	121.99	121.64	121.64	122.00	121.53
26	3C-2C-8N	110.77	110.80	110.80	111.60	112.72
27	3C-2C-9N	122.86	122.89	122.89	122.10	122.40
29	2C-3C-4C	122.84	122.39	122.39	123.40	122.94
33	3C-4C-11O	128.58	128.74	128.74	128.30	128.63
35	7N-6C-8N	116.50	116.78	116.78	113.70	114.30
36	3C-7N-6C	103.93	103.87	103.87	105.70	105.62
40	1C-9N-2C	119.23	119.09	119.09	119.60	118.91
42	2C-9N-13C	122.04	122.11	122.11	122.20	121.76
43	1C-10N-4C	130.05	129.72	129.72	129.90	129.10
44	1C-10N-5H	114.16	114.43	114.43	114.00	116.67

[a] Data were taken from Ref [3].
[b] Data were taken from Ref [8].