The study of a new proton transfer compound; bis (2, 9-dimethyl-1, 10-phenanthrolinium) hydrogen (S, S) - tartrate nonahydrate by *ab initio* calculations

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Abstract

A new proton transfer compound of 2, 9-dimethyl-1, 10-phenanthroline and d-tartaric acid was synthesized and studied by using DFT and ab initio HF methods. The chemical formulas for the proton transfer ion pair is $(dmpH)_2^+ (d\text{-}tartH)_2^-.9H_2O$, where dmp = 2, 9-dimethyl-1, 10-phenantroline and $d\text{-}tartH_2$ = d-tartaric acid. In this crystal structure, d-hydrogen tartrate anions are joined together in a head-to-tail fashion via short hydrogen. A number of intermolecular O–H···O, N—H···O and C–H···O hydrogen bonding interactions, as well as π–π stacking, play important roles in this crystal structure. The geometrical parameters of $(dmpH)_2^+(d\text{-}tartH)_2^-$, $9H_2O$ ion pair have been optimazed with the B3LYP method of density functional theory (DFT) and ab initio Hartree-Fock (HF) methods for comparison. Theoretical calculations confirm a number of intermolecular O–H···O, N—H···O and C–H···O hydrogen bonding interactions, as well as π–π stacking, play important roles in this crystal structure.

Keywords: proton transfer; ion pair; crystal structure; tartaric acid; ab initio; B3LYP method.

1. Introduction

Crystal engineering, which was first used in 1955, [1] is ''the understanding of intermolecular interactions in the context of crystal packing and the utilization of such

1

understanding in the design of new solids with desired physical and chemical properties'' [2]. Its essence is the manipulation of intermolecular interactions by which molecular ordering of building blocks in the solid state may be controlled and materials with desired properties may be produced [3]. Among the different types of intermolecular forces, such as π–π [4] halogen-halogen [5], ionic interaction [6] all have been exploited in crystal engineering studies so far, hydrogen bonding and metal–ligand complexation are most extensively studied in crystal engineering as they are directional and significantly stronger than the other intermolecular interactions.

Hydrogen bonding, one of the better understood types of non-covalent interactions [7], is a powerful organizing force in designing solids for several reasons: it is directional, selective and its formation is reversible at room temperature [8].

Indeed, in many respects, hydrogen bonds can be compared with metal–ligand coordinate bonds: together with its directionality, the interaction between the protic hydrogen atom (arising from the donor, D–H) and the region of higher electronic density of the acceptor (:A) is similar to the metal-ligand interaction. Hydrogen bonds are extensively used for networking numerous organic and organometallic compounds [8]. The other non-covalent forces with an important role in self-assembly and molecular recognition processes are the aromatic–aromatic (π–π stacking) interactions [9]. They are weakly directional and weaker than the hydrogen bonds: calculations give about 10 kJ mol^{-1} [10] (for typical aromatic–aromatic interactions), in comparison with 15–40 kJ mol^{-1} (for moderate hydrogen bonds between neutral molecules). Ring stacking may enhance the stability of metal complexes both in solution and in solid-state.

The compound containing aromatic ligands can be assembled into various supramolecular architectures by means of π–π interactions of the aromatic rings. The numbers of the aromatic moieties, as well as their spatial arrangement are important factors in determining the dimensionality of the extended structure. For example, in the case of mononuclear monochelated complexes containing 2, 2'-bipyridine or 1, 10-phenanthroline, the aromatic–aromatic stacking usually gives pairs of interacting mononuclear complexes [11]. In this work we intended to report a new proton transfer compound is formed by D-tartaric acid and 2, 9-dimethyl-1, 10-phenanthroline fragments.

2. Computational approach

Density functional (DF) and Hartree-Fock (HF) calculations have been done with Gaussian98 program [12]. The DFT level calculations were performed with Beck's three parameter hybrid functional using the Lee–Yang–Parr correlation functional (B3LYP) [13]. For comparison of geometry parameters, optimization has been done with HF and DFT methods using 2 basis sets of 6-31G (d) and 6-311G (d). Natural bond orbital (NBO) analysis at the B3LYP level gives the natural electron population and the natural charge for each atom.

3. Results and discussion

3.1. Optimized structure of dmp and d-tart

The proton transfer ion pair compound was prepared by mixing aqueous and methanolic solutions containing equimolar quantities of tartaric acid and 2,9-dimethyl-1,10-phenantroline respectively at room temperature (Scheme 1). This proton transfer ion pair is stable under ambient conditions.
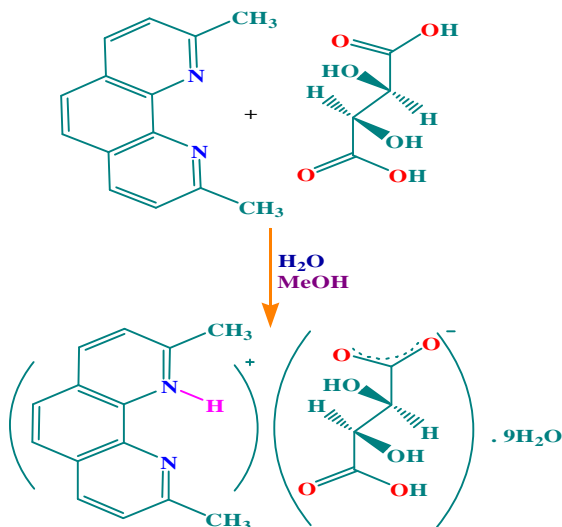
Scheme 1

Geometrical parameters of the optimized structure of the Optimized structure of dmp and d-tart (Fig. 1) obtained by HF and DFT quantum chemical calculations using different basis sets are reported in Table 1. These results have been compared to obtained experimental data in this work by X-ray crystallography method [14].
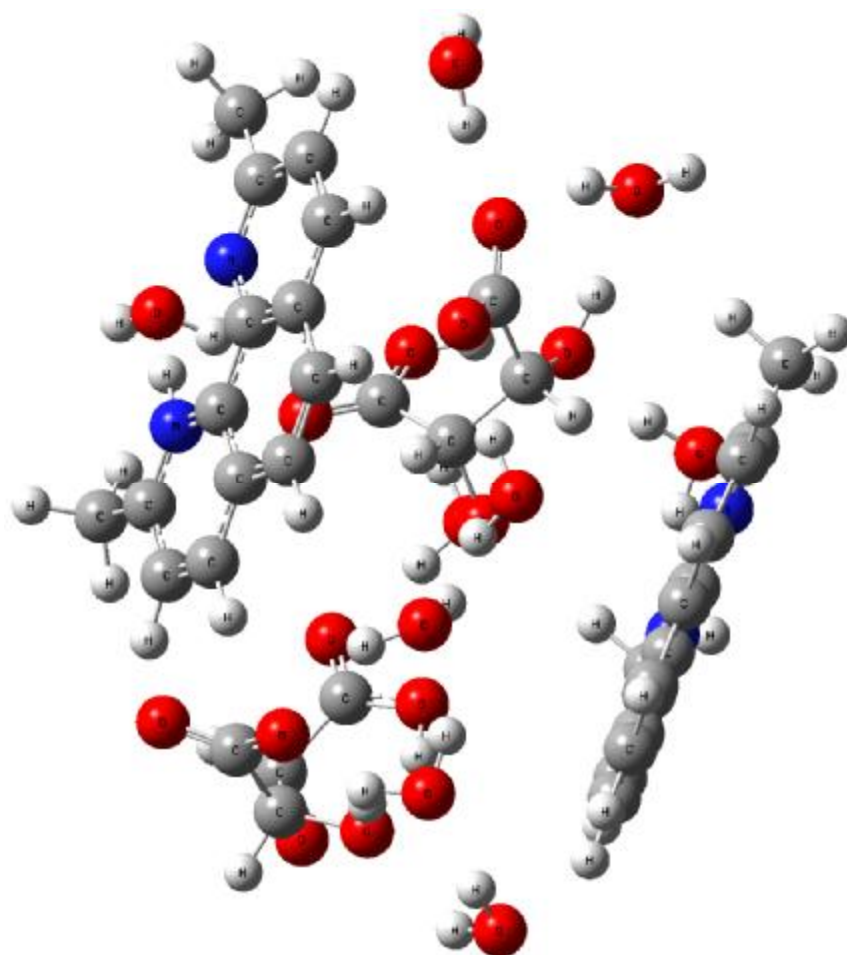
Fig 1. The geometry optimizations structure $(dmpH)_2^+ (tartH)_2^-.9H_2O$ obtained by DFT method.

Table 1: The optimized geometry parameters of the $(dmpH)_2{}^+ (tartH)_2{}^- 9H_2O$ (Fig. 5), dmp and tartaric acid (appear in [ ]) using HF and DFT methods with 6-31G(d,p) and 6-311G(p,d) basis sets with experimental data.

Copmputational methods		Geometrical parameters (Å, °)						
Methods	Basis set	C=N	C-N	C=O	C-O	O=C=O	δR	ΔR
HF	6-31G (d)	1.348	1.371	1.249	1.253	128.281	0.072	0.071
		[1.331]	[1.358]	[1.221]	[1.349]	[124.021]		
	6-311G (d)	1.346	1.370	1.247	1.251	127.879	0.069	
		[1.329]	[1.354]	[1.218]	[1.347]	[123.876]		
B3LYP	6-31G (d)	1.344	1.368	1.224	1.262	128.086	0.062	0.052
		[1.326]	[1.354]	[1.207]	[1.352]	[123.526]		
	6-311G (d)	1.343	1.365	1.242	1.265	127.572	0.042	
		[1.324]	[1.349]	[1.212]	[1.354]	[123.245]		
	[1]EXP	1.341	1.360	1.237	1.295	127.800		

[1] Experimental data has been obtained in this work by X-ray crystallography method and its paper was submitted to Journal of molecular structure.

The reliability of the optimized geometries is analyzed by calculating the differences between the experimental and theoretical values for the bond lengths, δ(R), (for each basis set) and, Δ(R), (for each level). By comparison, the predicted geometries using B3LYP/6-311G (d) method, (δ(R) = 0.042), are closer to the experimental bond distances than those obtained by the various levels. However, the HF method using all basis sets predicts the bond length of C=N in very good agreement with experimental data, overall the Δ(R) of HF and DFT methods show that the B3LYP method predicts the geometrical parameters better than HF method.

Also, the obtained results from computation show that the difference between bond lengths of O37–C33 and O36–C33 is more than that of O34–C30 and O35–C30 and also bond lengths of O52–C48 and O51–C48 is more than that of O50–C45 and O49–

C45. This can be explained by the acidic H atom which is still remaining on O36 and O51 atoms.

The optimized geometry in all methods confirms that the C=O bond length of tartaric acid in proton transfer form has been increased compared with the free tartaric acid. Also, this bond is shorter than C-O bond due to proton transfer. Therefore, this evidence shows that C=O is weakened upon proton transfer. The C-N and C=N bonds length in proton transfer form has been increased than free phenantroline. Based on the natural charges and electron configurations on the atoms of complex, free phenantroline and tartaric acid which have been calculated by natural bond orbital (NBO) analysis (Table 2), one can find out that, the natural charge of nitrogen atom has been decreased due to proton transfer. Also, the natural charge of oxygen atom in tartaric acid has been decreased due to proton transfer from tartaric acid and resonance. These results verify that in the proton transfer process, the oxygen atom of C-O bond acts as a donor, on the other hand the nitrogen atom as an acceptor for hydrogen atom.

The representation of HOMO and LUMO orbitals of phenantroline and tartaric acid in complex (Fig. 2), demonstrate higher MO distributions around oxygen atoms in HOMO and nitrogen atom in LUMO frontal orbitals which support the above mentioned evidences.
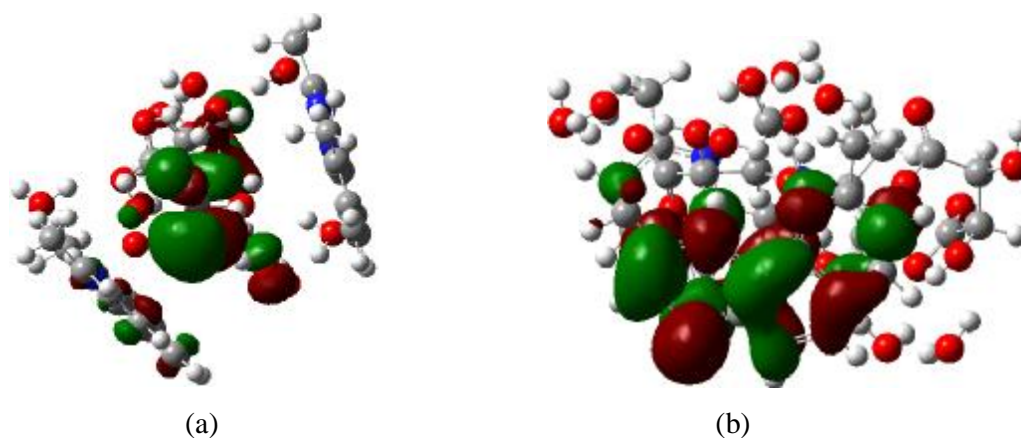

(a)   (b)

Fig 2. The 3D representation of HOMO (a) and LUMO (b) orbitals of $(dmpH)_2^+ (tartH)_2^- . 9H_2O$.

Table 2: The natural configurations and natural charges for the atoms of the $(dmpH)_2{}^+ (tartH)_2{}^- .9H_2O$ (Fig. 5which calculated using B3LYP/ 6-311G (d) method.

Atom	$(dmpH)_2{}^+ (tartH)_2{}^- 9H_2O$		dmpH		tartH	
	Configuration	Natural charge	Configuration	Natural charge	Configuration	Natural charge
N	[core]2s(1.35)2p(4.10)3p(0.01)3d(0.01)	-0.468	[core]2s(1.35)2p(4.06)3p(0.01)3d(0.01)	-0.469	-	-
N(N-H)	[core]2s(1.23)2p(4.23)3p(0.01)	-0.466	[core]2s(1.35)2p(4.06)3p(0.01)3d(0.01)	-0.469	-	-
C(=O)	[core]2s(0.76)2p(2.39)3s(0.01)3p(0.04)3d(0.01)	0.794	-	-	[core]2s(0.80)2p(2.33)3s(0.01)3p(0.03)3d(0.01)	0.820
O(=C)	[core]2s(1.72)2p(5.08)3d(0.01)	-0.815	-	-	[core]2s(1.70)2p(4.89)3d(0.01)	-0.613
C(⫶O)	[core]2s(0.80)2p(2.33)3s(0.01)3p(0.03)3d(0.01)	0.824	-	-	[core]2s(0.80)2p(2.33)3s(0.01)3p(0.03)3d(0.01)	0.820
O(⫶C)	[core]2s(1.70)2p(4.93)3d(0.01)	-0.638	-	-	[core]2s(1.69)2p(5.01)3d(0.01)	-0.709
C(N-C-CH3)	[core]2s(0.86)2p(2.82)3p(0.01)	0.304	[core]2s(0.83)2p(2.95)3p(0.02)	0.195	-	-
H	1s(0.51)	0.489	-	-	-	-
C(CH3)	[core]2s(1.11)2p(3.61)	-0.728	[core]2s(1.11)2p(3.59)	-0.706	-	-
O (O-H)	[core]2s(1.67)2p(5.03)3d(0.01)	-0.716			[core]2s(1.69)2p(5.01)3d(0.01)	-0.708

4. Conclusion

We have described a good proton donor-acceptor system that involves D-tartaric acid and 2, 9-dimethyl-1, 10-phenantroline. The structure of $(dmpH)_2^+ (tartH)_2^-$ $9H_2O$ contains cationic anionic fragments and water molecules. It is worth pointing out that there are two types of robust hydrogen bond synthon which link anionic fragments and water molecules. Also large linear water clusters and π–π stacking interaction between cationic fragments stabilizing crystal structure. The geometrical parameters of $(dmpH)_2^+ (tartH)_2^-$ $9H_2O$ compound, free phenantroline and tartaric acid have been optimized by using HF and DFT methods and two basis sets for comparison. The obtained results show that the B3LYP method predicts the geometrical parameters in good agreement with experimental data. Also, the natural bond orbital (NBO) analysis confirms the proton transfer process in formation of this complex.

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