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**Theoretical study of hydrogen bond effects on
Diphenylphosphorylazide**

S.Reihani¹, Z.Azizi², M.Khaleghian³, H.Passdar^{4*}, L.Pishkar⁵, R.Ahmadi⁶ and L.Saedi¹

1 Department of Chemistry, Islamic Azad University, Science and Research Campus, Tehran, Iran

2 Department of Chemistry, Islamic Azad University, Karaj Branch, Karaj, Iran

3 Department of Chemistry, Young Researcher Club, Varamin Pishva Branch, Tehran, Iran

4 Department of Chemistry, Islamic Azad University, North Tehran Branch, Tehran, Iran

5 Department of Biology, Islamic Azad University, Islamshahr Branch, Tehran, Iran

6 Department of Chemistry, Islamic Azad University, Shahr-e-Rey Branch, Tehran, Iran

ABSTRACT

The interaction of DPPA which is an important component in cellular membrane with molecules of water as media, cause some changes in geometry of DPPA .In this study we focused our attention on comparing this molecule with related hydrated complexes employing different basis sets at hartree-fock levels of theory. The theoretical NMR shielding tensor of some imported atoms were also reported.

Keywords: Hydrogen bond; DPPA; NMR shielding

* . Email:Hodapass@gmail.com

INTRODUCTION

Cells interact with their environment in a number of ways[1]. The boundary between any cell and its environment (through which substances must pass) is the plasma membrane, composed of phospholipids and protein molecules[2-6]. A phospholipid has both polar and non-polar regions. The fatty acid "tails" of the two phospholipid layers are oriented towards each other so that the hydrophilic "heads", which contain the phosphate portion, face out to the environment as well as into the cytoplasm of the cell's interior, where they form hydrogen bonds with surrounding water molecules. Because the individual phospholipid molecules are not bonded to each other, a membrane is flexible (or "fluid"), something which is pretty important to its functions[1-12].

COMPUTATIONAL METHODS

All calculations were carried out with the Gaussian 98 program package. Geometry of optimization of DPPA and hydrated DPPA were performed at hartree-fock (HF) and B3LYP levels of theory with STO-3G, 3-21G, 3-21G, 6-31G, 6-31G* basis sets. A frequency analysis was performed to look at how variation in the molecular structure occurs[13].

RESULTS AND DISCUSSION

In this study first we optimized DPPA with one water molecule and all geometer parameters were calculated then the second water molecule was added and such a procedure was repeated to add five molecules of water. The hydrogen bond length between two molecules was shown in table 1.

Table 1. Bond length of hydrogenic bonds

numb er of water	length bond(A)				
		STO-3G	3-21G	6-31G	6-31G*
n=1	r(O ₁ ...H ₄₅)	1.6295	-	1.7579	1.85994
n=2	r(O ₁ ...H ₅₁)	1.95405	2.00227	-	-
n=3	r(H ₃ ...O ₉)	1.72707	-	-	-
n=4	r(H ₂ ...O ₉)	1.54402	-	-	-
n=5	r(H ₂ ...O ₄)	1.75784	-	-	-

The bond and torsion angles of these complexes were also calculated which are shown in tables 2,3.

Table 2. Bond angles of different hydrated DPPA complexes

bond angle	(D)				
		STO-3G	3-21G	6-31G	6-31G*
n=1	<(O ₁ ...H ₄₅ ...O ₁)	148.62	-	145.383	153.525
n=2	<(O ₁ ...H ₅₁ ...C ₈)	163.435	165.85.66	-	-
n=3	<(H ₃ ...O ₉ ...C ₇)	119.996	-	-	-
n=4	<(H ₂ ...O ₅ ...P ₂)	113.998	-	-	-
n=5	<(H ₂ ...O ₄ ...P ₂)	127.014	-	-	-

Table 3. Torsion angles of different hydrated DPPA complexes

	torsion angle(D)	STO-3G	3-21G	6-31G	6-31G*
n=1	<(O ₁ ...H ₄₅ ...O ₁ ...P ₂)	2.96513	-	6.17713	16.1871
n=2	<(O ₁ ...H ₅₁ ...C ₈ ...C ₇)	4.60714	109.932	-	-
n=3	<(H ₃ ...O ₉ ...C ₇ ...C ₆)	49.8315	-	-	-
n=4	<(H ₂ ...O ₅ ...P ₂ ...O ₃)	30.1327	-	-	-
n=5	<(H ₂ ...O ₄ ...P ₂ ...O ₃)	24.5961	-	-	-

Calculations show that hydration of DPPA in water solvent causes the stabilization energies to be more negative than non-hydrated one. Calculations on DPPA have shown the lowest energy at HF/6-31G*. The stabilization energy of each hydrated DPPA complexes is reported in table 4.

Table 4. Comparison between calculated binding energies of DPPA-n=H₂O complexes in ab initio method (in kcalmol⁻¹)

Water	STO-3G	3-21G	6-31G	6-31G*
n=0	-1428775.88	-1438493.081	-1445796.6	-1446431.4
n=1	-1485943.32	-1489843.25	-1493489.56	-1494134.68
n=2	-1522861.76	-1541550.11	-	-
n=3	-1569924.67	-	-	-
n=4	-1616965.29	-	-	-
n=5	-1664004.36	-	-	-

Increasing water molecule in hydrated complexes of DPPA increases the energies. (Figure 1)

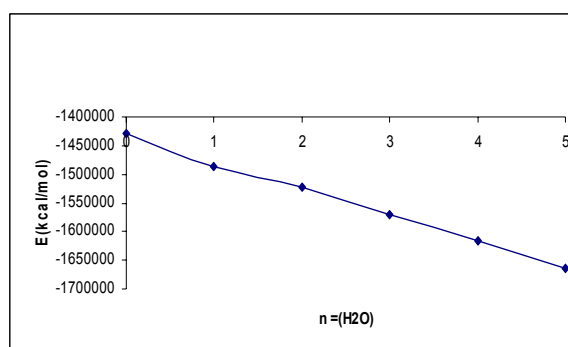


Fig.1. Comparison of calculated energies.

The P H...O could then be controllable and cooperative alternative for exploiting and directionality of hydrogen bonds in the hydrophobic environment. The large deshielding predicted for H is especially interesting since it has been implicated in a possible HB with P group of DPPA.

as expected, relaxation of this restriction permits the water molecule to swing around toward the P group (Fig 2,3).

The following diagrams show the variation in the molecular structure of DPPA respect to different number of molecules of water. The nomenclature DPPA are shown in figure 2 for better understanding.

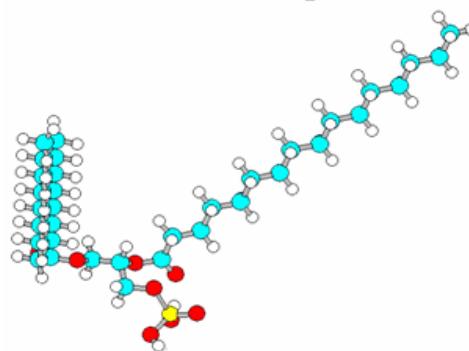


Fig. 2. Nomenclature DPPA.

Table 5. A principal values of the chemical shifts in hydrated DPPA

number of water	Shielding(ppm)							
	B3LYP/3-21G							
	S_{11}	S_{22}	S_{33}	S_{iso}	S_{aniso}	$?s$	S_{eff}	CSAa
n=0	421.645	325.757	489.056	412.219	251.259	115.255	475.914	115.469
n=1	286.467	231.585	251.551	256.534	77.984	-3.4754	48.1134	-3.4821
n=2	320.965	275.491	468.544	355.000	278.829	183.815	174.809	183.909

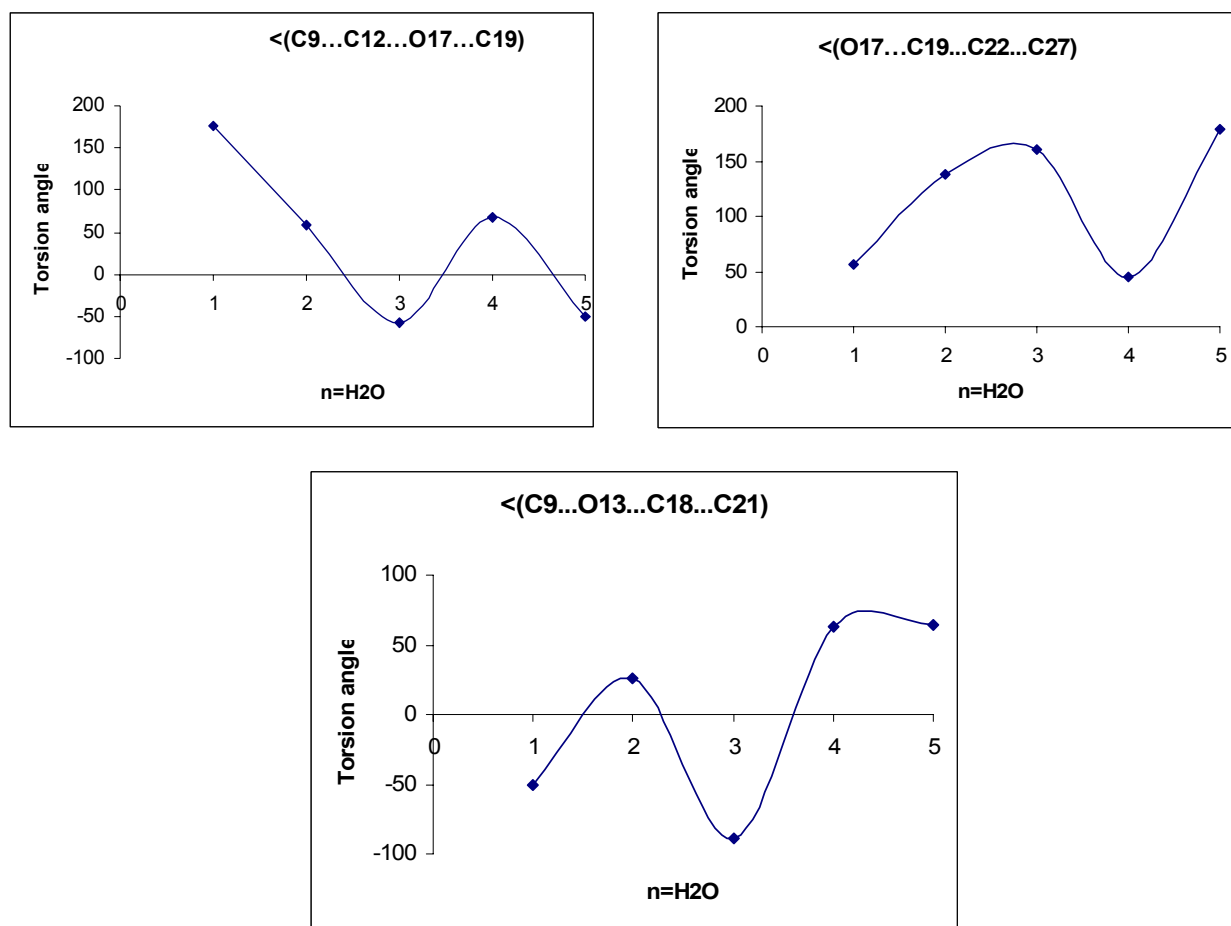
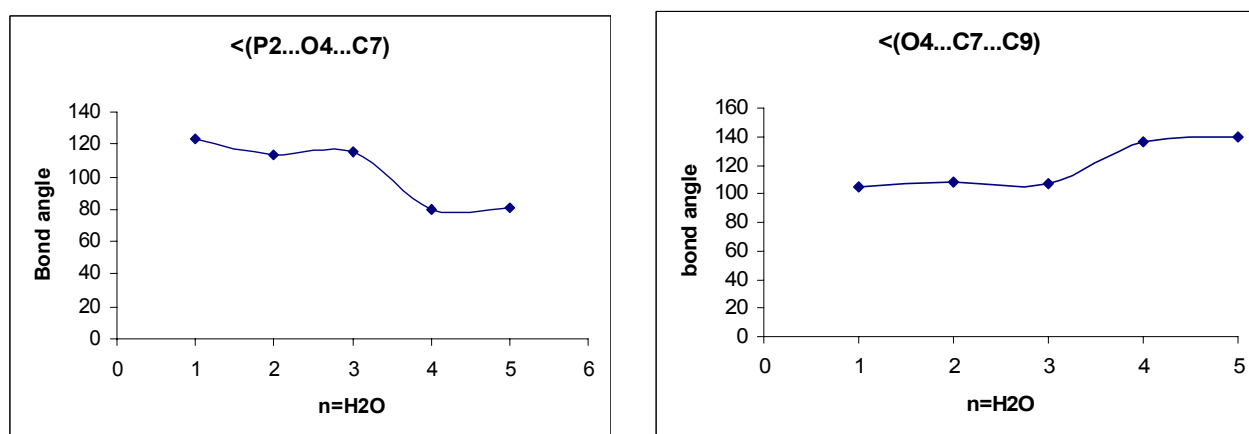


Fig.3. Variation of torsion angle of some atoms in DPPA



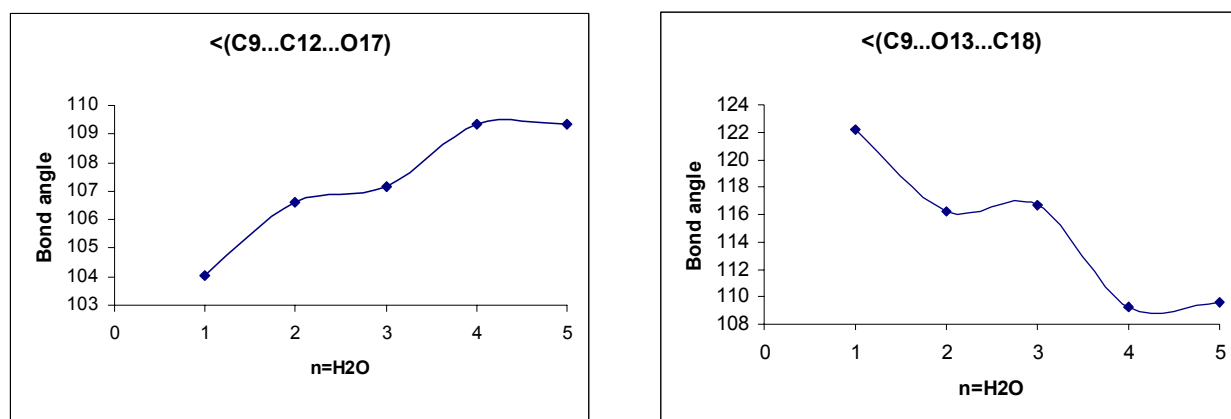


Fig.4. Variation of bond angle of some atoms in DPPA

CONCLUSIONS

The HF/STO_3G,3-21G,6-31G,6-31G* levels of theory of ab initio method have been employed to study of DPPA and hydrated DPPA complexes. The results show that optimization of DPPA at 3-21G* level yields molecular geometry which is in good agreement with real values.

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