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Studies of Hydrogen Bonding Effects on DiPalmitoyl Phosphatidyl Etanolamine (DPPE) by theoretical Methods

A.Nouri[2] and M.Monajjemi[1*]

1. Department of Chemistry, Science and Research Campus, Islamic Azad University, Tehran, Iran
2. Department of Chemistry, Shahriyar-Shahre Ghods Branch, , Islamic Azad University, Shahre Ghods, Iran

ABSTRACT

Hydrogen bonding of DPPE with water that surrounded of membrane, plays an important role in permeability of membrane that we were presented this matter with analysis of bond angles and torsion angles before and after of added water molecules.

Interaction with water molecules causes some changes in the geometry of DPPE which were explained by the contribution of zwitterionic form of DPPE molecule, also hydrated DPPE becomes stabilized. Comparison between theoretical and experimental values of geometry of DPPE molecule calculations at HF/3-21G level produce results in better agreement with the crystallography structure. The NMR shielding tensor of selected atoms in the hydrated complexes of DPPE were reported by ab initio level of theory.

Keywords: Hydrogen bonding; DPPE; Zwitterionic

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[*] . Corresponding author: E-mail: m_monajjemi@yahoo.com

INTRODUCTION

The structural backbone of a biological membrane is the lipid bilayer, which consists of a variety of phospholipids: phosphatidylcholines (PC), phopshatidylethanolamines (PE), phosphatidylglycerol (PG) and phosphatidylinositol (PI) among others [1,2]. Phospholipids are the basic structural components of biological membranes, which are essential in compartmenting the fluid biological phases of all organisms. They play an important role in membrane functions such as material transport, cell-cell recognition, and signal transduction [3-5]. Phospholipids are amphiphilic molecules with hydrophilic head groups of varying composition and two hydrocarbon tails. They assemble spontaneously to form bilayers with the hydrophobic tails pointed toward the center and the head groups exposed to the aqueous phase. The bilayer is a 40 Å thick lamella including the region in which the phosphates and several groups esterified to it (choline, ethanolamine, glycerol, inositol), are exposed to the water media (Figure 1) [1,2].

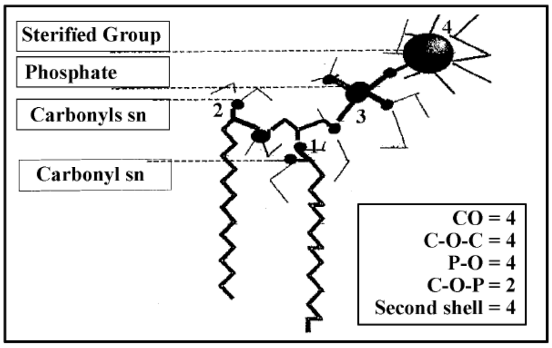


Fig.1. Organization of carbonyls, phosphates and esterified groups at the membrane surface with its hydration water molecules**.**
1**.** Carbonyl network at the membrane plane,
2. Carbonyl normal to the membrane plane,
3. Phosphate (P=O) groups,
4.Groups (choline, serine, inositol, glycerol) protruding into the water phase. The inset denotes the number of water molecules that may bind to different oxygen atoms.

Water is of crucial importance to life. It is even so important that most biomolecules would not work at all or even maintain their three-dimensional structure without the surrounding solvent. Water is the support where the cell structures lies. While the aim has been to resolve the structure of membranes and proteins, the aqueous environment plays a passive, and has a holder role.

Most biomolecular structures have also been found to be strongly influenced by their surrounding environment, usually water which constitutes about 70% of most cells. The water molecules close to surfaces like DNA, proteins or membranes are very tightly bound to the structures, and sometimes better characterized as being part of them rather than the bulk solvent [6].

The information obtained from investigation of experimental systems indicates water is mainly localized around the polar head groups of phospholipides. A total amount of 18 to 20 water molecules per lipid has been found, depending on the lipid species, distributed in the carbonyl, C-O-C and phosphates bonds [7]. Although it is known that water is located in the polar region, little is known about the organization and structure of water around the chemical groups of the polar heads, the distribution of the energy of interaction and the special organization of water dipoles around them, that may contribute to the dipole potential.

Thus, the modifications in the bilayer water interface by the presence of different types of phospholipids whose polar heads contain large dipoles, net charges and hydrogen bonding moieties, may be of significance for peptides and proteins to come into contact with the bilayer.

It is generally accepted that the distinctive properties of water can be ascribed to hydrogen bonding [8]. The fundamental dynamical process of the liquid is the making and breaking of hydrogen bonds. This dynamics, however, is far from being completely understood. Experiments such as infrared absorption and Raman scattering [9], depolarized light scattering [10], and inelastic neutron scattering [11]. Science these biological surfaces contain phospholipids, the interaction of water molecules with these lipids is of particular relevance to the biological function of the membrane surface [12].

Hydrogen bonds exist with a continuum of strengths. Nevertheless, it can be useful for practical reasons to introduce a classification, such as “weak”, “strong”, and possibly also “in between”. Jeffrey called hydrogen bonds moderate if they resemble those between water molecules or in carbohydrates (one could also call them “normal”), and are associated with energies in the range 4-15 kcalmol^{-1}. Hydrogen bonds with energies above and below this range are termed strong and weak, respectively. Some general properties of these categories are listed in Table 1. It must be stressed that there are no “natural” borderlines between these categories, and that there is no point in using this or any related system in too stringent a way. For a comment on the names of the categories, see footnote [13].

Table 1. Strong moderate and weak hydrogen bonds following the classification of Jeffrey[13]. The numerical data are guiding values only

	Strong	Moderate	Weak
Interaction type	strongly covalent	mostly electrostatic	electrostat./ disperse.
Bond lengths $[\overset{0}{A}]$			
H…A	1.2-1.5	1.5-2.2	>2.2
Lengthening of X-H $[\overset{0}{A}]$	0.08-0.25	0.02-0.08	<0.02
X-H versus H…A	X-H$\approx$H…A	X-H<H…A	X-H$\langle\langle$ H…A
X…A $[\overset{0}{A}]$	2.2-2.5	2.5-3.2	>3.2
directionality	strong	moderate	weak
bond angles[^{0}]	170-180	>130	>90
bond energy [kcalmol^{-1}]	15-40	4-15	<4
relat. IR shift $\Delta \bar{\nu}_{XH} [cm^{-1}]$	25%	10-25%	<10%
^{1}H downfield shift	14-22	<14	

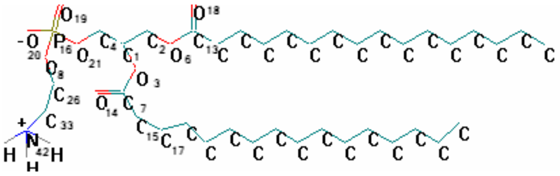
Hydrogen bonding is of central importance in many areas of chemistry, biochemistry, and biology [13-15]. Due to its versatility and applicability to molecular systems in all condensed phases, nuclear magnetic resonance (NMR) spectroscopy is commonly used for studying hydrogen-bonding phenomena. The hydrogen bonding effects on the isotropic chemical shift have been known, and understood in a qualitative manner for a long time [16-19]. In this work we made use of the ‘Gauge Including Atomic Orbitals’ (GIAO) method [20,21], which has recently become a widely used technique leading to gauge-independent results [22,23].

THEORETICAL METHODS

All quantum chemical calculations of geometry, energy, rotation, NMR measurements and solvent effects were carried out with the GAUSSIAN 98 program [24]. The *ab initio* method used is Hartree-Fock (HF).

HYDRATION OF DPPE MOLECULE

We have been optimized isolated molecule of DPPE with HF/ 3-21G, HF/ 6-31G, and HF/ 6-31G* level of theory in the gas phase. (**Fig.2** shows Atom labeling and dihedral angle notation for DPPE molecule).



$$\alpha_2(C_4\ O_{21}\ P_{16}\ O_8\ )$$
$$\alpha_3(O_{21}\ P_{16}\ O_8\ C_{26})$$
$$\alpha_5(O_8\ C_{26}\ C_{33}\ N_{42})$$

Figure 2. Atom labeling and dihedral angle notation for DPPE molecule.

For build a hydration shell around the optimized DPPE molecule, the first water molecule was added to the optimized DPPE molecule, and then monohydrated complex was reoptimized. It is obvious that in order to optimizations at higher levels of theory. After adding the first water molecule to the DPPE macromolecule, the produced hydrated complex has a lowest energy, in the same way such a procedure can be repeated until 5 water molecules are arranged around the DPPE molecule according to the Fig.3 Water molecules were distributed in the region of the polar head where phosphates and cholines are located. The energy values of DPPE-basis sets and DPPE-n H2O are listed in Fig.4.

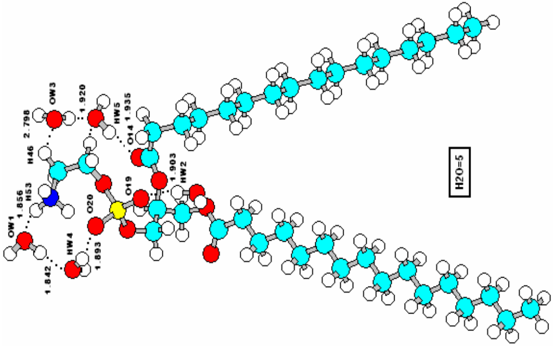


Figure3. Optimized structures of DPPE-5H2O with the HF/6-31G*.

NMR MEASURMENT

The nuclear magnetic shielding tensors, defined as the mixed second derivatives of energy molecular (E) with respect to the magnetic moment of the X-th nucleus ($\vec{m}_x$) and the external magnetic field ($\vec{B}$), represented by the equation below [25] (Greek superscripts denote the corresponding vector or tensor components):

$$\sigma_X^{\alpha\beta} = \frac{\partial^2 E}{\partial B^\alpha \partial m_X^\beta}$$

are primary importance. However, it has been long recognized that a calculation of the second-order magnetic response properties from the first principles, using a finite basis set, requires a gauge-independent algorithm[26-30].Number of computational techniques have been proposed to achieve the gauge-invariance. Within the so-called GIAO methodology (Gauge Independent Atomic Orbitals), based on the works of London and Ditchfield [25,31] the gauge-invariance is achieved using explicitly field-dependent basis functions [25-31].Application of the GIAO approach to molecular systems was significantly improved by an efficient implementation of the method for the *ab initio* SCF calculations, using techniques borrowed from analytic derivative methodologies[28,29].

The isotropic shielding values defined as

$$\sigma_{iso} = \frac{1}{3}\ (\sigma_{11}+\sigma_{22}+\sigma_{33})$$

(σ_{ii} being the principal tensor components) were used to calculate the isotropic chemical shifts (δ). The principal components of the calculated chemical shielding tensors are absolute shielding values.i.e.$\sigma = 0$ corresponds to shielding of the “bare” nucleus. The isotropic chemical shielding σ_{iso} can be converted to isotropic chemical shift δ_{iso} by $\delta_{iso}=\sigma_{iso}^{ref}-\sigma_{iso}^{molecule}$ where σ_{iso}^{ref} is the chemical shielding value of a reference substance (chosen have to be TMS for ^{1}H and^{13}C, CH3NO2 for^{15}N, H_3PO_4 for ^{31}P and H_2O for ^{17}O) that calculated at the same level.

RESULTS AND DISCUSSION

GEOMETRY OPTIMIZATION OF DPPE IN GAS PHASE

Zwiterionic DiPalmioylPhosphatidylEthanolamine molecule was chosen as starting structure for gas phase (Fig.2). Gas phase optimization of DPPE fragment at HF/3-21G level of theory resulted in dihedral values very close to those of PE crystal structure (see Table 2). With optimization, head group of DPPE leads to a different geometry, in which the molecule adopts a cyclic conformation.

Table 2. Comparison of some dihedral angles of DPPE between experimental and theoretical results

	Crystal structure	HF/3-21G	HF/6-31G	HF/6-31G*
$\alpha_2+\pi$	120	122.04	117.8	112.6
α_3	-71	-78.5	-79.3	-85.8
α_5	60	60.7	61	62.3

DPPE is found to be unstable in the gas phase when optimized at HF/3-21G, 6-31G and 6-31G* level and to convert into a natural structure by an intermolecular proton transfer from the ammonium group to one of the phosphate oxygenes (Fig.3), due to a very strong attraction between the (+) charged ammonium group and a (-) charged phosphate oxygen atom (O20). This strong attraction actually causes a proton transfer from ammonium nitrogen to the phosphate oxygen, thus it is made of converting the zwitterionic to a neutral molecule. The H^+ transfer was found, at all levels of theory investigated in this work.

GEOMETRY OPTIMIZATION IN THE DPPE-nH2O COMPLEXES

The characteristics of interactions of water molecules with the head group of phospholipids membrane are subject of special interest.

Theoretical studies on phospholipids-water cluster with ab initio method have not been reported yet. For comparison, we minimized the structure of DPPE molecule without water molecules.

Optimization of DPPE molecule with 3-21G, 6-31G and 6-31G* basis sets. The results of two levels of basis sets (3-21G and 6-31G) are not brought because of high volume of data. As it was expected, the most stable form was related to the 6-31G*. The results of calculations show that 5 water molecules are arranged around the DPPE head group that make to form hydrophilic part of DPPE molecule. The water molecule can bind to DPPE molecule along NH, CH and P-O-H sides as a proton acceptor and along P=O sides as a proton donor.

Hydration of DPPE molecule causes that the stabilization energies to be more negative than no-hydrated this compound (Fig.4). According to *ab initio* calculations insertion of water-DPPE complex to an intrinsically stable structure.

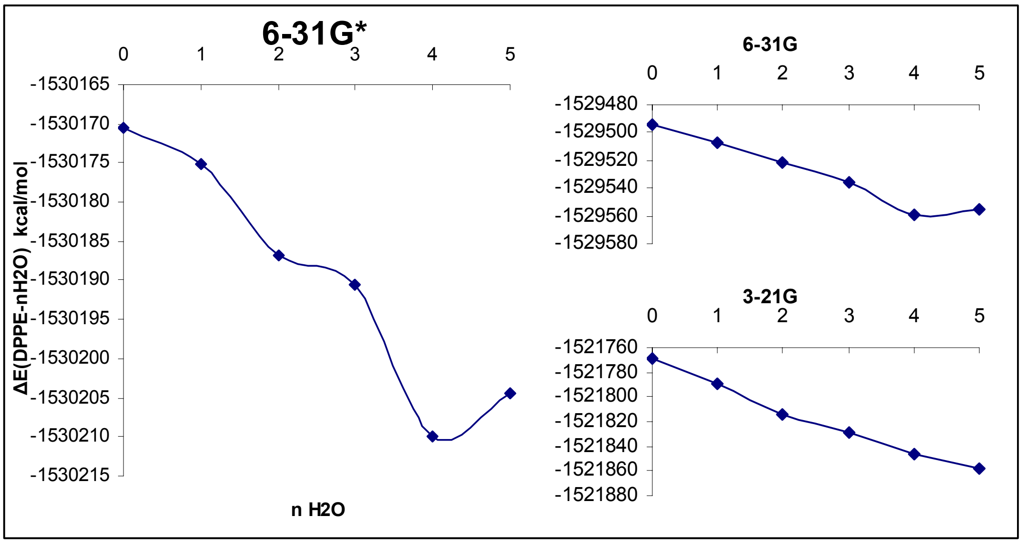


Figure 4: Comparison between calculated binding energies of DPPE-nH_2O complexes in four basis sets obtained from ab initio method (in kcal mol^{-1}) .

With adding one and two water molecules, we had natural structure but with adding from n=3 to n=5, DPPE molecule convert into a zwiterionic form that was our expected form and repeated in all of our methods and was important point which is reason was the highly interaction between O-H and N-H.

The O-H and N…H distances are 0.972 and 1.879 Å in the DPPE-1H2O and are 0.972 and 1.867Å in the DPPE-2H2O while the O…H and N-H distances become 1.49 and 1.086 Å in the DPPE-3H2O 1.725 and 1.031 Å in the DPPE-4H2O also 1.604 and 1.047 Å in the dppe-$5H_2O$ respectively.

The latter is a very short distance compared to the some of the vander waals radii [32] of hydrogen(1.2Å) and nitrogen(1.55Å) of 2.75Å .The bond analysis (Table 3) shows that this is more than a pure electrostatic interaction but much less than the covalent bonding between hydrogen and oxygen in the DPPE after proton transfer.

Table 3. The molecular geometries of DPPE in five orientations with water molecules at Hartree-Fock level of theory

number Of water	**basis sets (6-31G*)**					
	length bond(A^0)		**bond angle(D)**		**torsion angle(D)**	
dppe-water						
n=1	$R(O_{W1}\ldots H_{53})$	2.167	$\Theta(O_{W1}\ldots H_{53}—N_{42})$	55.49	$\Theta(O_{W1}\ldots H_{53}—N_{42}—C_{33})$	97.69
	$R(H_{W1}\ldots O_{21})$	2.134	$\Theta(H_{W1}\ldots O_{30}—P_{16})$	108.83	$\Theta(H_{W1}\ldots O_{30}—P_{16}—O_8)$	-48.23
dppe-water						
n=2	$R(O_{W1}\ldots H_{53})$	2.155	$\Theta(O_{W1}\ldots H_{53}—N_{42})$	155.67	$\Theta(O_{W1}\ldots H_{53}—N_{42}—C_{33})$	94.19
	$R(H_{W1}\ldots O_{21})$	2.137	$\Theta(H_{W1}\ldots O_{21}—P_{16})$	109.40	$\Theta(H_{W1}\ldots O_{21}—P_{16}—O_8)$	-48.06
	$R(H_{W2}\ldots O_{19})$	1.936	$\Theta(H_{W2}\ldots O_{19}—P_{16})$	142.95	$\Theta(H_{W2}\ldots O_{19}—P_{16}—O_{21}$	-108.31
	$R(O_{W2}\ldots H_{11})$	2.690	$\Theta(H_{W2}\ldots O_{11}—C_4)$	161.50	$\Theta(H_{W2}\ldots O_{11}—C_4—O_{21})$	-80.96
dppe-water						
n=3	$R(O_{W1}\ldots H_{53})$	1.895	$\Theta(O_{W1}\ldots H_{53}—N_{42})$	159.32	$\Theta(O_{W1}\ldots H_{53}—N_{42}—C_{33})$	95.77
	$R\ (H_{W1}\ldots O_{21})$	1.988	$\Theta(H_{W1}\ldots O_{21}—P_{16})$	107.74	$\Theta(H_{W1}\ldots O_{21}—P_{16}—O_8)$	-51.38
	$R(H_{W2}\ldots O_{19})$	1.885	$\Theta(H_{W2}\ldots O_{19}—P_{16})$	146.90	$\Theta(H_{W2}\ldots O_{19}—P_{16}—O_{21})$	-107.04
	$R(O_{W2}\ldots H_{11})$	2.728	$\Theta\ (O_{W2}\ldots H_{11}—C_4)$	163.93	$\Theta\ (O_{W2}\ldots H_{11}—C_4—O_{21})$	-76.18
	$R(O_{W3}\ldots H_{54})$	1.963	$\Theta(O_{W3}\ldots H_{54}—C_{33})$	168.12	$\Theta(O_{W3}\ldots H_{54}—C_{33}—N_{42})$	-44.17
dppe-water						
n=4	$R(O_{W1}\ldots H_{53})$	1.919	$\Theta(O_{W1}\ldots H_{53}—N_{42})$	147.76	$\Theta(O_{W1}\ldots H_{53}—N_{42}—C_{33})$	66.60
	$R\ (H_{W1}\ldots O_{21})$	1.872	$\Theta(H_{W1}\ldots O_{21}—P_{16})$	118.42	$\Theta(H_{W1}\ldots O_{21}—P_{16}—O_8)$	73.487
	$R(H_{W2}\ldots O_{19})$	1.917	$\Theta(H_{W2}\ldots O_{19}—P_{16})$	142.62	$\Theta(H_{W2}\ldots O_{19}—P_{16}—O_{21}$	-105.51
	$R(O_{W2}\ldots H_{11})$	2.086	$\Theta(O_{W2}\ldots H_{11}—C_4)$	170.25	$\Theta(O_{W2}\ldots H_{11}—C_4—O_{21})$	-58.94
	$R(O_{W3}\ldots H_{54})$	1.940	$\Theta(O_{W3}\ldots H_{54}—C_{33})$	146.41	$\Theta(O_{W3}\ldots H_{54}—C_{33}—N_{42})$	-79.01
	$R(H_{W4}\ldots O_{20})$	1.844	$\Theta(H_{W4}\ldots O_{20}—P_{16})$	133.25	$\Theta(H_{W4}\ldots O_{20}—P_{16}—O_8)$	40.95
	water-water					
	$R(O_{W2}\ldots H_{W4})$	1.884				
dppe-water						
n=5	$R(O_{W1}\ldots H_{53})$	1.856	$\Theta(O_{W1}\ldots H_{53}—N_{42})$	154.44	$\Theta(O_{W1}\ldots H_{53}—N_{42}—C_{33})$	90.01
	$R(H_{W2}\ldots O_{19})$	1.903	$\Theta(H_{W2}\ldots O_{19}—P_{16})$	139.70	$\Theta(H_{W2}\ldots O_{19}—P_{16}—O_{21})$	-92.06
	$R(O_{W2}\ldots H_{11})$	2.69	$\Theta(O_{W2}\ldots H_{11}—C_4)$	151.36	$\Theta(O_{W2}\ldots H_{11}—C_4—O_{21})$	-83.99
	$R(O_{W3}\ldots H_{46})$	2.798	$\Theta(O_{W3}\ldots H_{46}—C_{33})$	97.85	$\Theta(O_{W3}\ldots H_{46}—C_{33}—N_{42})$	-164.41
	$R(H_{W4}\ldots O_{20})$	1.893	$\Theta(H_{W4}\ldots O_{20}—P_{16})$	114.89	$\Theta(H_{W4}\ldots O_{20}—P_{16}—O_8)$	92.82
	$R(O_{W5}\ldots H_{38})$	-	$\Theta(O_{W5}\ldots H_{38}—C_{26})$	-	$\Theta(O_{W5}\ldots H_{38}—C_{26}—O_8)$	-146.94
	$R(H_{W5}\ldots O_{14})$	1.935	$\Theta(H_{W5}\ldots O_{14}—C_7)$	122.29	$\Theta(H_{W5}\ldots O_{14}—C_7—O_3)$	
	water-water					
	$R(H_{W1}\ldots O_{W4})$	1.842				
	$R(H_{W3}\ldots O_{W5})$	1.920				

The arrangement of water molecules is different in four basis sets that applied for optimization and every water molecule forms one or two hydrogen bond with DPPE molecule. With adding the water molecules, the hydrogen bond was forming between water molecules (see Fig.3 and Table 3).

Hydrogen bonds exist with a continuum of strengths (Table 2).

Based on the Y…H distance and value of the X-H…Y angle (>130) in Table 3 in the complex under study should be assigned as moderate.

EFFECT OF HYDROGEN BONDING ON THE CHEMICAL SHIELDING TENSORS OF SELECTED ATOMS

The calculations including intermolecular interactions give semi quantitative information on effects of Hydrogen Bonding (HB) on the principal values of chemical shift tensors. We were studied the influence of intermolecular interactions on chemical shielding tensors for ^{1}H, ^{15}N, ^{31}P,^{17}O some selected nucleus, in DPPE-nH2O(n=0-5).

The water molecule, according to the position which is located around the DPPE molecule has taken as the H-acceptor and H-donor, in the hydrogen bond discussed here. This may suggest that the intermolecular HB and the environmental interaction have a dramatic effect on the calculation of shielding tensors.

Hydrogen bond length effects on the chemical shielding tensor and orientation of nuclei.

It is noteworthy that the small variation in the position of atoms, eventually results in a considerable change in the lengths of the various intermolecular hydrogen bonds, which may probably effect the calculation of NMR shielding tensors.Based on the optimized structures, we calculated the shielding tensors for isolated and hydrated DPPE and corresponding data were list in Table 4 as well.For the compound studied, the most important intermolecular interaction arises from HB between adjacent molecules occluded. According to the results in Table 4 and Fig.5, the calculations predict significant intermolecular effects for all of the oxygen shift tensors considered here. For the protonated nitrogen, when we have proton transfer in nH2O=3 ($-NH_3^+$) σ_{iso} and σ_{aniso} show the largest intermolecular effect. The deshielding effects ranges from 272.69 to 266.57 ppm for σ_{iso} and ranges from 25.10 to 13.33 ppm for σ_{aniso}.

From the results presented above, the following qualitative observations follow that the largest HB effects are observed in the chemical shift components that are in O20, O21, O9 and O8 because these atoms have some HB interaction with water molecule and hydrogen atoms around, for the lowest HB effects are observed in the chemical shift components that are in H11 and H38 and the largest HB effects are observed in the chemical shift components when forth water molecule add.

Table 4. Effect of H-Bonding on Isotropic Chemical shift based on number of water molecule for selected atoms.

number of water	**σiso**	**σaniso**	**δiso**	**σiso**	**σaniso**	**δiso**
	H11			**O14**		
n=0	29.14	10.47	4.71	-72.39	633	419.3
n=1	28.4	9.97	5.46	-68.69	631.4	415.6
n=2	29.03	11.15	4.82	-64.8	624.8	411.7
n=3	29.14	10.47	4.71	-54.74	616.1	401.7
n=4	29.61	10.43	4.24	-59.73	619.9	406.7
n=5	29.22	10.15	4.64	-12.55	550.1	359.5
	H30			**O19**		
n=0	28.29	24.8	5.56	293.7	37.79	346.9
n=1	26.57	29.38	7.29	288.6	42.34	58.28
n=2	26.33	30.2	7.52	301.5	33.41	45.43
n=3	24.66	28.83	9.2	302.1	40.65	44.86
n=4	25.75	25.8	8.1	319.1	27.1	27.84
n=5	23.97	32.53	9.88	298.9	40.63	48.05
	H38			**O20**		
n=0	29.78	9.27	4.07	298.9	60.94	346.9
n=1	29.87	9.32	3.99	310.3	54.53	36.65
n=2	29.8	9.36	4.05	309.9	52.64	37
n=3	29.96	9.96	3.89	294.1	39.83	52.81
n=4	32.18	7.28	1.68	290	28.65	56.93
n=5	29.35	9.8	4.51	300.2	36.03	46.74
	H46			**O21**		
n=0	31.62	11.3	2.24	323.9	64.4	346.9
n=1	31.77	11.92	2.09	326.6	71.92	20.28
n=2	31.75	12.12	2.1	326.6	69.18	20.35
n=3	31.41	11.79	2.44	320	84.79	26.95
n=4	31.25	11.3	2.61	318.1	53.41	28.79
n=5	30.83	10.87	3.03	314.1	70.51	32.79
	H53			**P16**		
n=0	33.9	20.37	-0.03	489.4	147.6	-455.5
n=1	31.65	19.68	2.21	495.2	178.1	1.79
n=2	31.57	19.75	2.29	496.3	150.4	0.65
n=3	28.3	22.62	5.55	486.1	162.9	10.92
n=4	28.53	26.8	5.32	487.4	116.5	9.62
n=5	27.8	26.32	6.06	489.6	145.3	509.6

	N42	
σiso	**σaniso**	**δiso**
266.4	41.86	-429.1
272.4	25.56	-162.7
272.7	25.09	-435.4
266.6	13.32	-194.1
262.1	16.73	-424.8

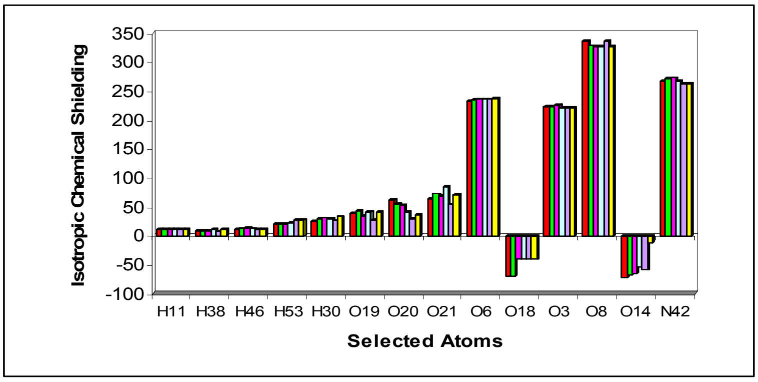


Figure 5. Effect of H-Bond on isotropic chemical shielding based on number of water molecule for selected atoms

5. HYDROGEN BONDING EFFECT ON PERMEABILITY OF MEMBRANE

Water is the support where the cell structures lies. In the structure of membranes and proteins, the aqueous environment plays a passive, holder role. The drying of cells below a given level promotes irreversible changes and death. In this work, we have chosen some bond angles and torsion angles at the head group of DPPE molecule that, fatty acid tails and part of the head group which is connected to the tails move with change these angles. Then we have studied them before and after deferent process of adding the water molecules.

As it is seen in the Fig.6, during the different processes of adding the water molecules, the angles have changed due to formation of hydrogen bonds between water molecules and active sites present in the head group of DPPE molecule. These changes cause movement of fatty acid tails and deviation of head group. These movements help permeability of molecules across the membrane. As a conclusion, formation of hydrogen bonds presents around polar head group of membrane phospholipids is one of the most important factors which helps permeability of membrane.

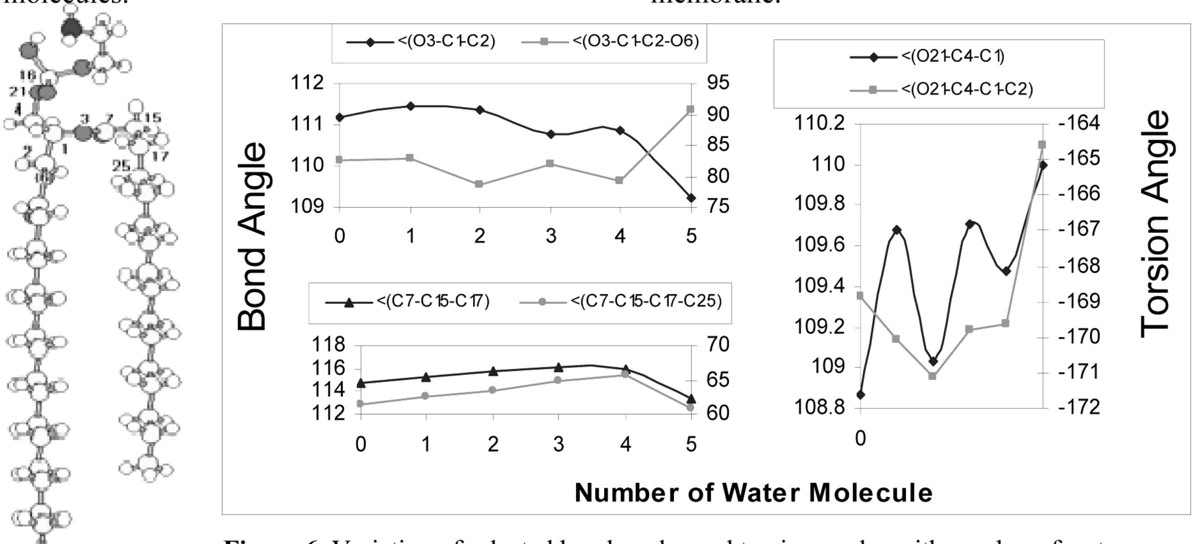


Figure 6. Variation of selected bond angles and torsion angles with number of water.

CONCLUSION

The HF/3-21G, 6-31G and 6-31G* levels of theory of ab initio method have been employed for DPPE and DPPE-water complex to study. Present results show that optimization of DPPE at the 3-21G level yields molecular geometries in good agreement with crystallography values. *Ab initio* calculations show that in the gas phase, the positive-charged ammonium of DPPE head group interacts with negative-charged phosphate oxygen atom and DPPE zwitterions convert into a neutral structure. Water is the most important solvent in nature. Because of its high dielectric constant and ability to form hydrogen bonds, the hydration effects can control many different molecular processes. In this work we have investigated the geometry of DPPE head group before and after of deferent process of adding water molecules. This investigation is important to understand more complicated process that occur for molecules in aqueous solutions. The presence of water in the membrane structure is crucial. Because Interaction with water molecules causes deformation of the intermolecular geometry of DPPE which it is crucial to maintaining its integrity and the permeability properties. Complex of DPPE-5 H_2O has been more stabilized than the other indicates compounds with this level of theory.

NMR calculations have been shown that in DPPE head group O19, O20 and O21 are most active site for the interaction of DPPE water molecules. These results determine the best site of hydrogen bonding of DPPE.

REFERENCES

1. S.H.White, M.C.Wiener, In Permeability and Stability of Lipid Bilayers. Disalvo,
2. Simon, Eds. CRC Press, Boca Raton, FL. (1995), 1.
3. E.A.Disalvo, de Gier, J., Chem. Phys. Lipids (1983), 32.
4. H. R.Petty, Molecular biology of membranes: structure and function, Plenum, New York. (1993).
   A.L.Lehninger, D. L.Nelson, & Cox, M. M. Principles of Biochemistry, Worth Publishers, New York. (1993).
   B.L. Silver, The physical chemistry of membranes: an introduction to the structure and dynamics of biological membranes, Solomon Press, NY.Jamaica. (1985).
   C.R. Cantor and P. R. Schimmel, Biophysical Chemistry .W. H. Freeman and Company, San Francisco. (1980).
5. G.L. Jendrasiak, Biochim. Biophys. Acta. (1974), 337, 79.
6. D. Eisenberg and W. Kauzmann, The Structure and Properties of Water (Oxford Univ. Press, New York, 1969); Correlations and Connectivity, Geometric Aspects of Physics, Chemistry and Biology, edited by H. E. Stanley and N. Ostrowsky (Kluwer Academic, Dordrecht, 1990); J. Teixeira, J. Phys. (France) IV 3, C1-(1993)162 .
7. G. E. Walrafen, in Water: A Comprehensive Treatise, edited by F. Franks (Plenum, New York, 1972), Vol. 1; G. E. Walrafen, J. Phys. Chem. (1990), 94, 2237; E. W. Castner, Y. J. Chang, Y. C. Chu, and G. E. Walrafen, ibid. (1995), 102, 653.
8. C. J. Montrose, J. A. Bucaro, J. Marshall-Coakley, and T. A. Litovitz, J. Chem. Phys. (1974), 60, 5025; W. Danniger and G. Zundel, J. Chem. Phys. (1981),74, 2769; O. Conde and J. Teixeira, Mol. Phys. (1984), 53, 951.
9. J. Teixeira, M. C. Bellissent-Funel, S. H. Chen, and A. J. Dianoux, Phys. Rev. (1985), A 31, 1913; S. H. Chen and J. Teixeira, Adv. Chem. Phys. (1986), 64 , 1.
10. G.L.Jendrasiak, and R.L.Smith., Chemistry and Physics of Lipids., (2004),131,183.
11. G. A. Jeffrey, An Introduction to Hydrogen Bonding, Oxford University Press, Oxford, (1997).
12. G.C. Pimental, A.L. McClellan, The Hydrogen Bond, Freeman, San Francisco, (1960).
13. W.C. Hamilton, J.A. Ibers, Hydrogen Bonding in Solids, Benjamin, New York,(1968).
14. Freure, and E. Verdurand., J. Am. Chem. Soc., (1998), 120, 13187.
15. J.Czernek, R. Fiala, and V.Sklenar., Journal of Magnetic Resonance, (2000), 145, 142.
16. S. Macholl, F.Börner, and G. Buntkowsky., Zeit. Phys. Chem., (2003), 217, 1473.
17. S. Hori, K.Yamauchi, S. Kuroki, and I. Ando., Int. J. Mol. Sci., (2002), 3, 907.
18. F. London., J. Phys. Radium., (1937), 8, 397.
19. H. F. Hameka., Molec. Phys, (1958), 1, 203.
20. R. Ditchfield., 1974, Molec. Phys., (1974), 27, 789.
21. K. Wolinski, J. F. Hinton, and P. Pulay., J. Am. chem. Soc.,(1990), 112, 8251.
22. Gaussian 98 Revision A.7, M.J. Frisch, G.W.Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R Cheeseman, V.G. Zakrzewski,J.A. Montgomery, Jr., R.E. Stratmann, J.C. Burant,`S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi , R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Raghavachari, J. Cioslowski, J. V. Ortiz, A.G. Baboul, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, J. A. Pople. Gaussian, Inc., Pittsburgh PA, 1998.
23. C. E. Dykstra, Quantum Chemistry & Molecular Spectroscopy, Prentice Hall, New Jersey, (1992), 336.
24. G. A. Webb, in: J. A. Tossell (Ed.), Nuclear Magnetic Shieldings and Molecular Structure, Kluwer Publishers, Netherlands, (1993), 1.
25. R. Ditchfield, Mol. Phys. (1974), 27, 789.
26. F. London, Phys. Radium (1937), 8, 397.
27. K.Wolinski, J. F. Hinton, and P. Pulay, J. Am. Chem. Soc. (1990), 112, 8251.
28. P. Pulay, J. F. Hinton, and K. Wolinski, in: J. A. Tossell (Ed.), Nuclear Magnetic Shieldings and Molecular Structure, Kluwer Publishers, Netherlands, (1993), 243.
29. J. R. Cheeseman, G. W. Trucks, T. A. Keith, and M. J. Frisch, J. Chem. Phys. (1996), 104 5497.
30. A, Bondi., J. Phys.Chem., (1964), 68, 441.