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Molecular computations on lipids: a numbering system for phospholipids and triglyceride

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Abstract

A standardized numbering system is elaborated upon for the efficient generation of input data for molecular computations on phospholipids and triglycerides. The advantages of such a comprehensive system in terms of the extraction of structural data and the increase in throughput allowing for the identification of the complete set of stable conformers are discussed.

Keywords: Phospholipids; Triglycerides; Numbering systems; Molecular computations

1. Preamble

Phospholipids are commonly found in the body, forming transporting vesicles, liposomes, micelles and lipid bilayers (Fig. 1). As a component of the cell membrane, their structures and flip–flop movement can possibly modulate the movement and local environment of different membrane proteins [1]. Lipids and phospholipids also associate with proteins to from lipoproteins [2]. As a body fluid, phospholipids are also very important to the function of many organs and are commonly found as cardiac sarcolemma plasmlogen, which, along with anionic phospholipids in the cardiac sarcolemma, are found to regulate trans-sarcolema sodium–calcium exchangers [3]. Another example is the phospholipids that act as pulmonary surfactants which line aveoli spaces to prevent the aveoli from collapse as a result of the surface tension of water on the aveoli [4]. The malfunction of some cerebrosides (phospholipids found in the brain) are also known to be linked to schizophrenia [5]. In addition, phospholipids are known to play a role in the formation of blood platelets [6]. In some cases, phospholipids also act as antioxidants, as they have radical scavenging properties when the fatty acids are unsaturated, inhibiting oxidation processes induced by peroxyl radicals [7]. Because of their dynamic and flexible nature,

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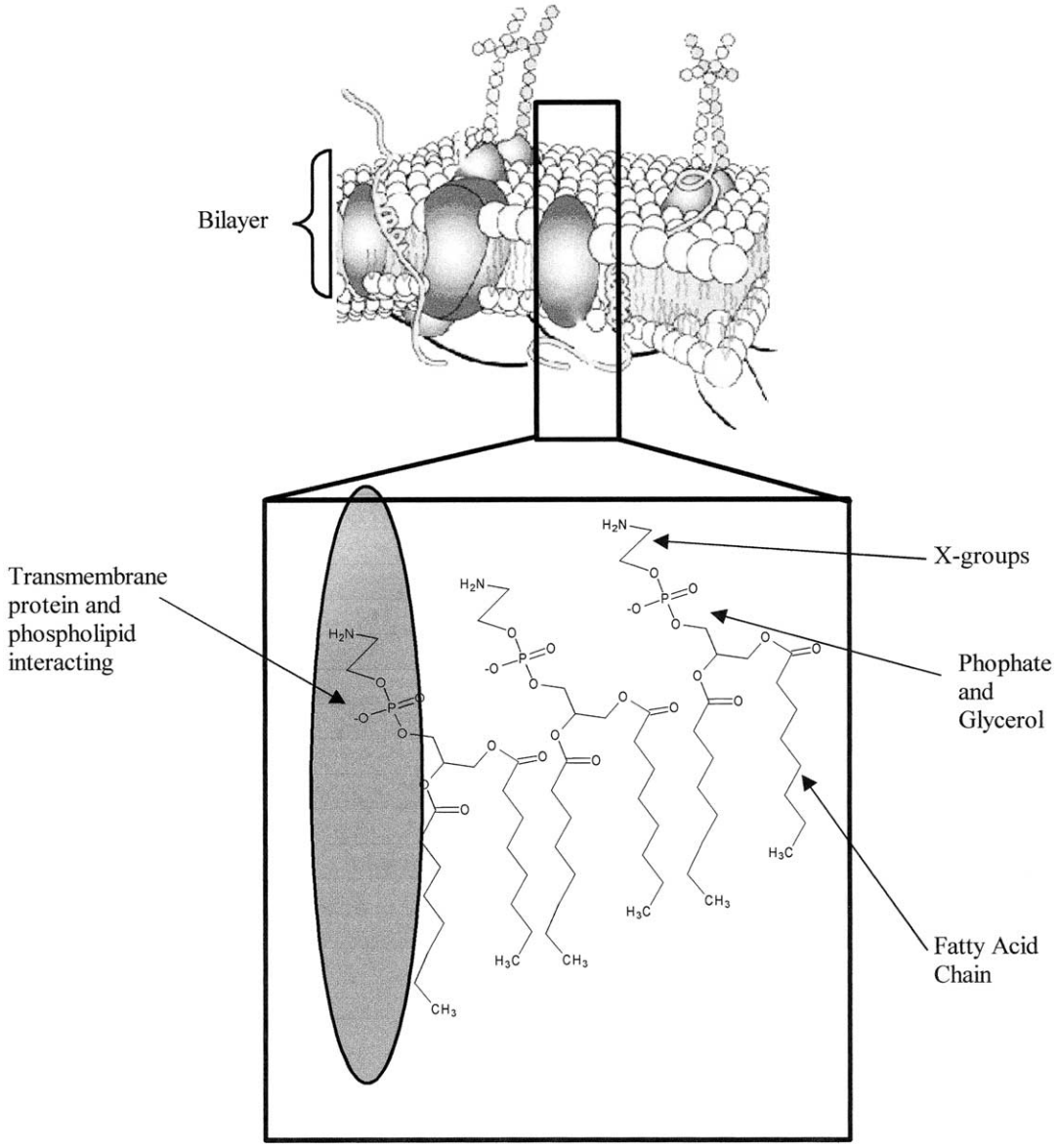


Fig. 1. Structure of a typical phospholipid bilayer.

phospholipids are also used in many industries, as industrial solvents due to the fact that they have both polar and non-polar nature. Recently, attempts have been made to manipulate their phospholipids and analogues into polymers and synthetic fibers [8]. Despite all this, relatively little is known about the conformational behaviour of lipids. They are relatively large molecules and an accurate theory to model and study them must eventually include all comprising units, or modules. It is hoped that through the standardization of the molecular definition of the relative spatial orientation of all constituent atomic nuclei forming these in lipids, that specific conformational trends may be recognized providing a more holistic understanding from reductionist bases.

Table 1
Different types of phospolipids

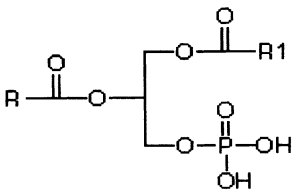
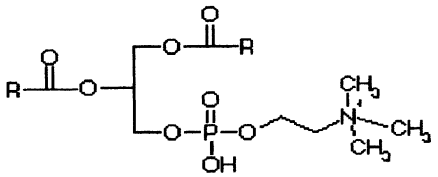
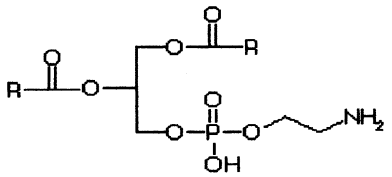
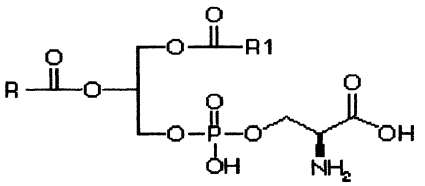
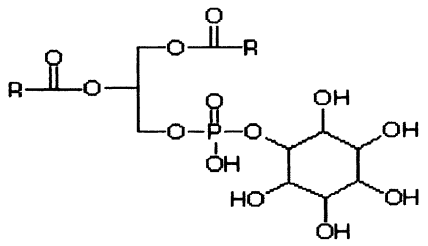
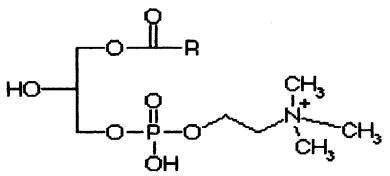
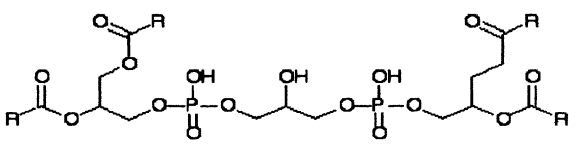
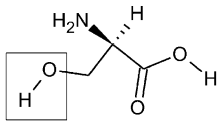
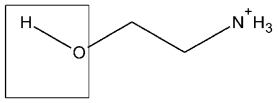
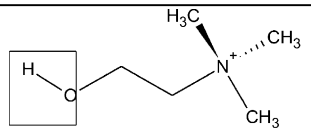
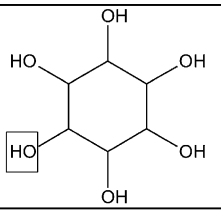
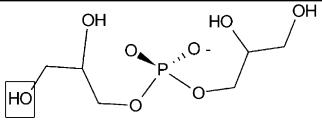
	Phosphatidyl acid
	Lecithin (phsophatidylcholine)
	Phsophatidylethanolamine
	Phosphatidylserine
	Phosphatidylinositol
	1-Lysolecithin
	Diphosphatidylglycerol (cardiolipin)

Table 2
X-groups commonly found attaching to the phosphate of phospholipids. Note that the OH in the box changes to a phosphorus atom when these groups becomes moieties on the phospholipid, therefore the OH groups inside the boxes are not included in the expression A_H

Structure	Name	Point of attachment $A_Q + A_H = A$
H	Hydrogen	$A_Q = 0$ $A_H = 1$ A =0+1=1
	Serine	$A_Q = 6$ $A_H = 6$ A = 6+6 =12
	Ethanolamine (Protonated)	$A_Q = 3$ $A_H = 7$ A =3+7=10
	Choline (Cationic)	$A_Q = 6$ $A_H = 13$ A = 6+13 = 19
	Inositol	$A_Q = 11$ $A_H = 11$ A = 11+11 = 22
	Diphosphatidylglycerol	$A_Q = 14$ $A_H = 13$ A = 14+13 =27

2. Introduction

2.1. Structural background

The structure of a phospholipid is highly variable (Table 1). However, it can be classified into five different structural subdivisions [9]. First is the glycerol group, second is the phosphate and the third is the X-groups—a structure with an OH functional group such as choline and ethanolamine (Table 2). The fourth and fifth subdivisions contain fatty acid chains (Table 3). In this table some of the fatty acids are unsatured and are in their *cis*-isomeric forms. These phospholipid structures can be subdivided into a number of modular substructure fragments (Fig. 2), where fragment I is the glycerol group and is the fundamental unit, which supports all of the other groups in the phospholipid. Fragment II is the phosphate group; these structures are commonly found in many biomolecules. Fragment III is the X-group. Table 2 represents a number of the many phospholipid X-groups, all of which contain an alcoholic functional group. Fragments IV and V are fatty acid chains, which are rarely found as isolated molecules as they are usually attached to a supporting group such as the glycerol module.

Theoretical modeling of such molecules is very useful in understanding the structure-activity relationship of phospholipids in the body. Therefore, it is suggested to establish a standardized numbering system, which must be modular and flexible enough to accommodate different modifications of substituents

on the phospholipid without disturbing the numeric definition of the molecular portions common to both the previous and subsequently modified systems. One must also be able to accurately and efficiently construct and identify the conformational identity of each model.

2.2. Cartesian versus internal coordinates

Traditionally, after an optimization is completed one must extract all relevant structural variables from the resultant data set, in terms of Cartesian coordinates, then make use of a visualization tool to tabulate the data, which may be time consuming. In contrast when a file is constructed using an internal coordinate system, all relevant bond lengths, bond angles and dihedral angles are expressed explicitly in the output. The latter method is used preferably, not only to make the analysis of the results more accurate and efficient but also to make easy comparison of the data when related molecules are examined and defined using this standardized numbering.

2.3. Advantages of a standardized numbering system

Defining a molecule using a standardized methodology provides many advantages. First, modules may be added or removed easily; second, the modules can be recognized in the input file quickly as a set of numbers, each with a unique numeric pattern. A standardized numbering system can also save time when analyzing the results from the resultant output. It is very easy to match the data of segments of a given molecule with the corresponding segment of another related molecule; provided their common structural units are defined in an identical fashion. Using this numbering system, the resultant internal coordinates of two differently substituted phospolipids can be lined up side by side and compared in terms of their bond lengths, bond angles and dihedral angles. In this way, this methodology provides the modeling and analysis of the molecules in an organized and logical order while optimizing the structures to their stable conformations. Also, this standardized methodology may facilitate the modeling of how molecules change in geometry as they are substituted; whereby an observed numerical perturbation *in silico* may be representative of a larger phenomenon *in vitro* or even *in vivo*.

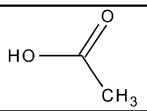
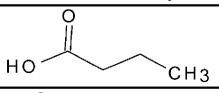
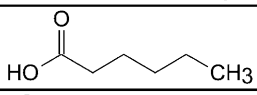
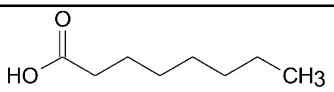
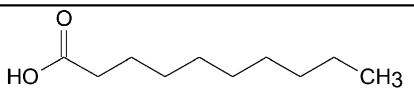
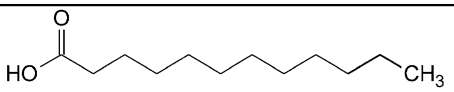
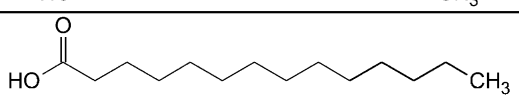
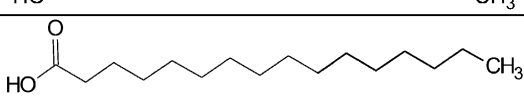
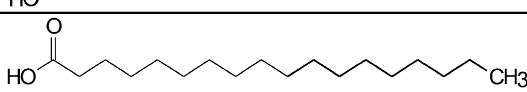
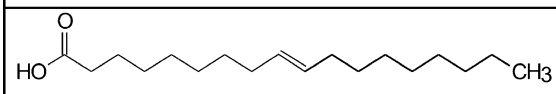
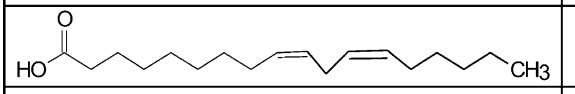
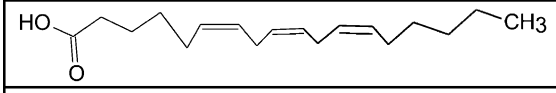
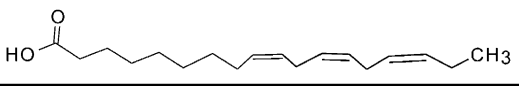
Furthermore, the standard may simplify the task of tracing and detecting changes in a molecule that has arisen during a specific iteration during optimizations, simplifying the identification of the source of errors. This also provides information as to the basis of the minimization of energy. With experience using such a standardized numbering system, one may also instantaneously numerically visualize this molecule in all of its 3N-6 dimensions. Numeric visualization can facilitate the investigation of the behaviour of phospholipids as they flip-flop across the perhaps helping explain mechanistically how small molecules diffuse through the cell membrane. Phospholipids often play the role of biological detergents and fluids such as pulmonary surfactants. It may therefore become easier to pinpoint the specific regions of the polar head group of the phospholipid that is interacting with water in the lungs. The methodology is flexible enough such that converting any phospholipids system to any of its analogues only requires a small numeric-perturbation in the input file.

Another great advantage is that the modules may be modeled separately in their entire conformational extents, in advance and assembled without redefining the relative spatial orientation of the constituent atomic nuclei for the entire assembled molecule. Once again the coupling of the modules may provide quantitive information itself as to the influence of each module upon all others, in the form of in silico numeric perturbations.

3. Method

Glycerol itself has 14 atoms and forms the backbone of all phospholipids. It supports the phosphate group of the polar head group and the fatty acid chains. It is reasonable, therefore, to start with this common central skeletal feature, which may have a number of well-defined geometric conformations. Consequently, it could be made to have the highest priority in the numbering system; as it is always comprised of 14 constituent atomic nuclei, it is therefore given the numbers 1 to 14. Number 1–5 will define the backbone structure, include the three carbons of the glycerol group and one hydrogen atom, on each of the terminal carbons. Next, the remaining hydrogens will carry the numbers 6–8.

Table 3
Different types of fatty acids

Structure	Name	$B_C (C_Q) + B_H (C_H) = B(C)$
	Acetic Acid	$B_Q (C_Q) = 2$ $B_H (C_H) = 3$ B (C) = 5
	Butyric Acid	$B_Q (C_Q) = 4$ $B_H (C_H) = 7$ B (C) = 11
	Caproic Acid	$B_Q (C_Q) = 6$ $B_H (C_H) = 11$ B (C) = 17
	Caprylic Acid	$B_Q (C_Q) = 8$ $B_H (C_H) = 15$ B (C) = 23
	Capric Acid	$B_Q (C_Q) = 10$ $B_{II} (C_{II}) = 19$ B (C) = 29
	Lauric Acid	$B_Q (C_Q) = 10$ $B_H (C_H) = 23$ B (C) = 35
	Myristic Acid	$B_Q (C_Q) = 14$ $B_H (C_H) = 27$ B (C) = 41
	Palmitic Acid	$B_Q (C_Q) = 16$ $B_H (C_H) = 31$ B (C) = 47
	Stearic Acid	$B_Q (C_Q) = 18$ $B_{II} (C_{II}) = 35$ B (C) = 53
	Oleic Acid	$B_Q (C_Q) = 18$ $B_H (C_H) = 33$ B (C) = 51
	Elaidic Acid	$B_Q (C_Q) = 18$ $B_H (C_H) = 33$ B (C) = 51
	Linolenic Acid	$B_Q (C_Q) = 18$ $B_H (C_H) = 31$ B (C) = 49
	Gamma linolenic Acid	$B_Q (C_Q) = 18$ $B_H (C_H) = 29$ B (C) = 47
	Alpha linolenic Acid	$B_Q (C_Q) = 18$ $B_H (C_H) = 29$ B (C) = 47

The oxygen atoms will be given the numbers 9–11 as these are used as the joining atoms between the central and radial parts of the phospholipids. The remaining hydroxyl protons are assigned the numbers 12–14. These hydrogens are numbered last so they can be easily replaced when the substituting groups are added on (Fig. 3) without disturbing any previously defined parts of modules of the molecular system.

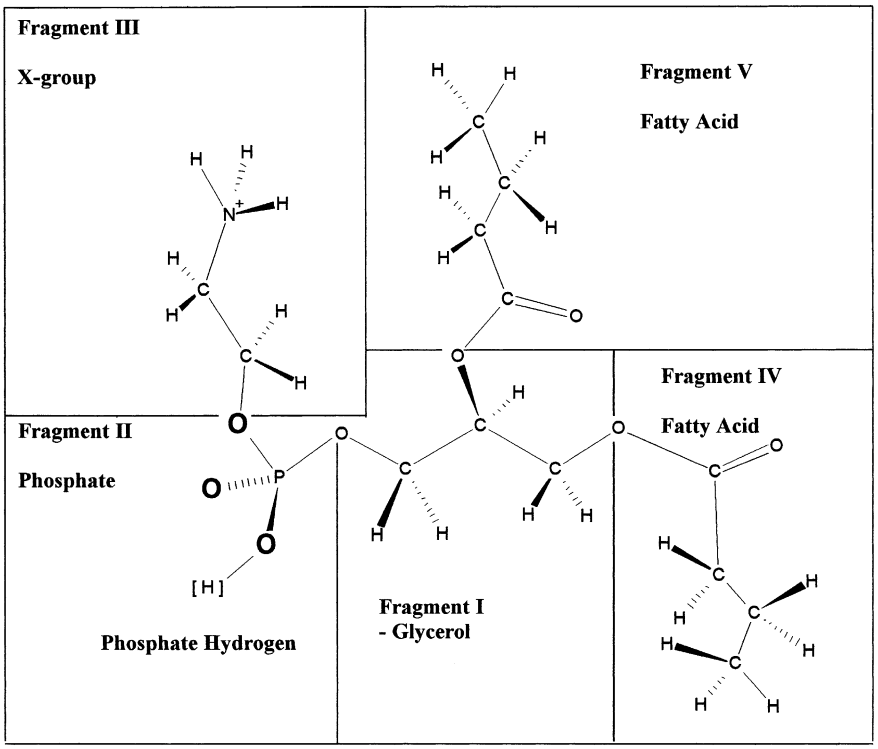


Fig. 2. Fragments of a typical phospholipid; the phosphate proton [H] may or may not be included.

A terminal group common to all phospholipids is the phosphate group. It is attached to one of the terminal glycerol OH groups via O_9 and to the alcoholic X-group together via the common O_{17}. By adding this phosphate, the terminal hydroxyl hydrogen H_{12} of glycerol can now easily be modified to a phosphorous atom (P_{12}). The remainder of the phosphate oxygen atoms will be given the numbers from 15 to 17 (Fig. 4). Note that the numbers 13 and 14 have previously been allocated to the two remaining backbone hydroxyl protons.

In the next step, the X-group will be numerically defined. The heavy (non-hydrogen) atoms of the X-group will be numerically defined first, followed by the hydrogen atoms. Since the backbone length will be variable, the numbering will be different in each case but will always start at 18. The numbering of the entire X-group will be $17 + 1 = 18$, $17 + 2 = 19$, $17 + 3 = 20$, …, $17 + A_Q$ where A_Q will be the number of non-hydrogen atoms within the X-group. Then, the hydrogen atoms of the X-group will be numbered next, where their total number will be represented by the variable A_H. Figs. 5, 6 and 7 show some examples of such numbering, where the X-group selected is protonated ethanolamine. The equation would be

Number of the last atom on the X-group

(Fragment III) $= 17 + A_Q + A_H$.

If $A = A_Q + A_H$, then the general equation is:

Number of the last atom on the X-group

(Fragment III) $= 17 + A$.

The acyl chain attached to C_4 is the next sub-structure to be numbered. To add this structure, H_{14} must first be changed into C_{14}. However, in this fatty acid chain system, C_{14} is not included in this module but is instead part of the glycerol one. The numbering of all of the heavy atoms starts from the carbonyl oxygen atom that is attached to the C_{14}. Thus, the number on this double-bonded oxygen atom will be $17 + A + 1 = 18 + A$. As this hydrocarbon chain is

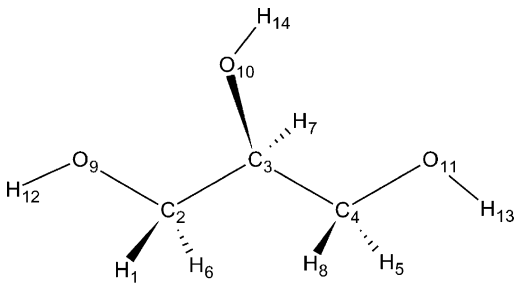


Fig. 3. Structure of glycerol (Fragment I); atoms are numbered from 1 to 14.

also highly variable from one phospholipid to another, the numbering will start at $18 + \mathrm{A} + 1 = 19 + A$ as the first carbon atom attached to the acyl C_{14}. Consequently, the numbering follows as $17 + A + 2$, $17 + A + 3, \ldots, 17 + A + B_{\mathrm{Q}}$, where B_{Q} will be the numerical value of all the heavy atoms within the carbon chain. The numbering of the hydrogen atoms on this chain will be next. The total number of the hydrogens can be represented by the variable B_{H}. Therefore, the equation is:

Number of the last atom on the acyl chain

$$\text{(Fragment IV)} = 17 + A + B_{\mathrm{Q}} + B_{\mathrm{H}},$$

if $B = B_{\mathrm{Q}} + B_{\mathrm{H}}$, then the general equation now becomes:

Number of the last atom on the first acyl chain

$$\text{(Fragment IV)} = 17 + A + B.$$

Fig. 6 exemplifies this method of numbering. Sometimes the central OH at C_3 is not esterfied by a fatty

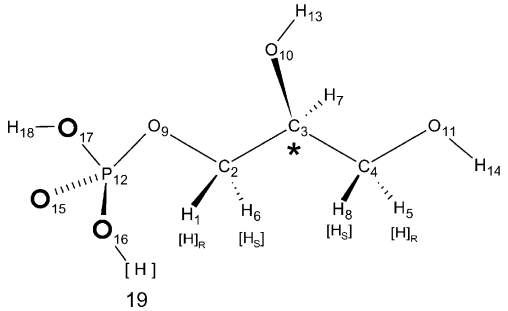


Fig. 4. Glycerol phosphate group (Fragments I and II). Note that the central carbon (C_3) denoted by * became a stereocentre.

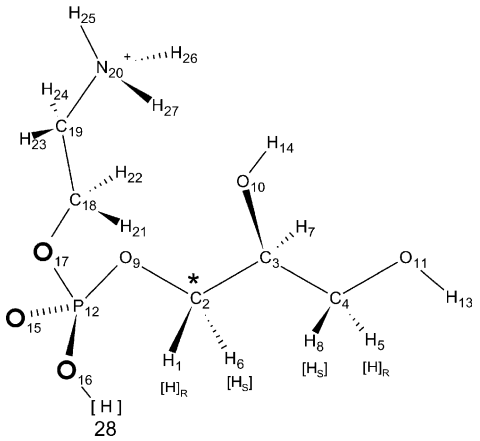


Fig. 5. Numbering of glycerol phosphate and a simple X-group (Fragments I, II, III). Note that [H], the proton of the phosphate OH has the highest number. Note that the central carbon (C_3) denoted by * became a stereocentre.

acid but more often than not it is; one must be able to easily construct either of these systems.

The final fatty acid chain is the one attached to C_3. H_{13} will become C_{13}. The first number on the chain will be the carbonyl oxygen atom attached to C_{13}, which is $17 + A + B + 1 = 18 + A + B$. Once again, the heavy on this fatty acid chain will be numbered next. As a result, the last heavy atom on this chain will have the number; $17 + A + B + C_{\mathrm{Q}}$, where C_{Q} represent the heavy atom on this carbon chain. The rest of the hydrogen atoms on the carbon chain will be given the numbers from $17 + A + B + C_{\mathrm{Q}} + 1$, to $17 + A + B + C_{\mathrm{Q}} + C_{\mathrm{H}}$, where C_{H} represents the total number of all the hydrogen atoms in this chain. In general, the equation can be summarized as:

Number of the last atom on the second acyl chain

$$\text{(Fragment V)} = 17 + A + B + C_{\mathrm{Q}} + C_{\mathrm{H}}$$

if $C = C_{\mathrm{Q}} + C_{\mathrm{H}}$ the equation becomes:

Number of the last atom on the second acyl chain

$$\text{(Fragment V)} = 17 + A + B + C.$$

Fig. 7 shows the numbering of two chains with a phosphate group and Table 4 shows the connectivity of the phospholipid example using internal coordinates.

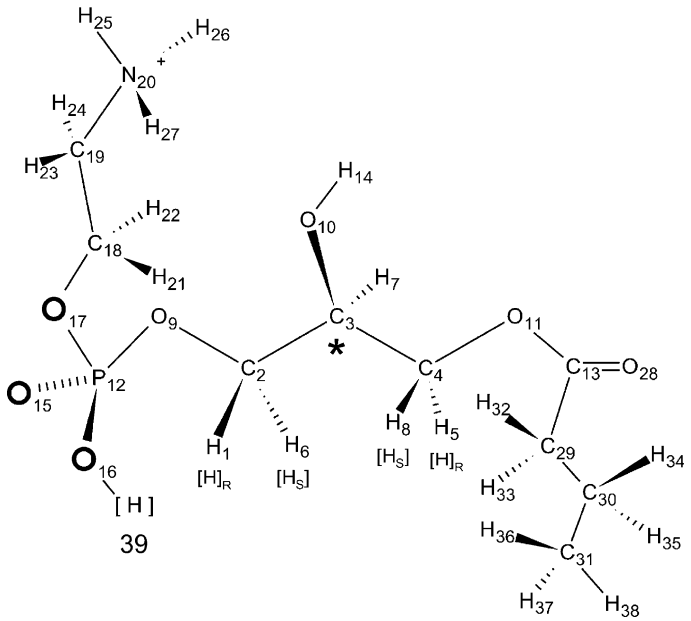


Fig. 6. The numbering of glycerol phosphate, X-groups and the hydrocarbon chain. Butyric acid used as fatty acid. (Fragments I, II, III, IV). Note that the central carbon (C_3) denoted by * became a stereocentre.

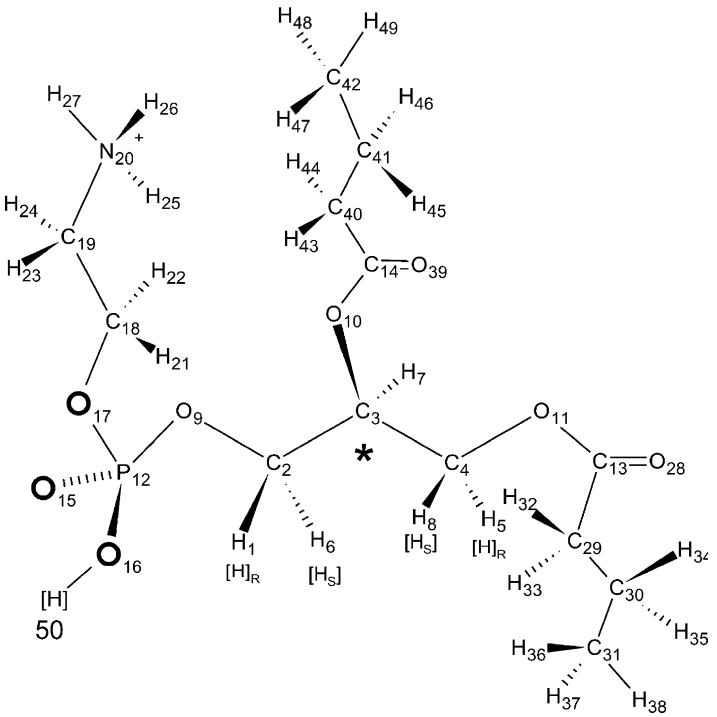


Fig. 7. Numbering of full phospholipids (Fragments I, II, III, IV, and V) Butyric acid used as fragment. Note that the central carbon (C_3) denoted by * became a stereocentre.

Table 4
Sample symbolic *z*-matrices of atom connectivity for various phospholipid size (bolded lines represent variable atoms that change as the result of the addition and the substitution of other fragments)

Glycerol (Fragment I)	Glycerol with phosphate (Fragments I + II)	Glycerol, phosphate, X-group (Fragments I–III)	Phospholipid first fatty acid included (Fragments I–IV)	Phospholipid first and second fatty acid included (Fragments I–V)	
0 1	0 1	+ 1 1	+ 1 1	+ 1 1	
H	H	H	H	H	1
C 1 R2	C 1 R2	C 1 R2	C 1 R2	C 1 R2	2
C 2 R3 1 A3	C 2 R3 1 A3	C 2 R3 1 A3	C 2 R3 1 A3	C 2 R3 1 A3	3
C 3 R4 2 A4 1 D4	C 3 R4 2 A4 1 D4	C 3 R4 2 A4 1 D4	C 3 R4 2 A4 A D4	C 3 R4 2 A4 A D4	4
H 4 R5 3 A5 2 D5	H 4 R5 3 A5 2 D5	H 4 R5 3 A5 2 D5	H 4 R5 3 A5 2 D5	H 4 R5 3 A5 2 D5	5
H 2 R6 3 A6 4 D6	H 2 R6 3 A6 4 D6	H 2 R6 3 A6 4 D6	H 2 R6 3 A6 4 D6	H 2 R6 3 A6 4 D6	6
H 3 R7 2 A7 1 D7	H 3 R7 2 A7 1 D7	H 3 R7 2 A7 1 D7	H 3 R7 2 A7 1 D7	H 3 R7 2 A7 1 D7	7
H 4 R8 3 A8 2 D8	H 4 R8 3 A8 2 D8	H 4 R8 3 A8 2 D8	H 4 R8 3 A8 2 D8	H 4 R8 3 A8 2 D8	8
O 2 R9 3 A9 4 D9	O 2 R9 3 A9 4 D9	O 2 R9 3 A9 4 D9	O 2 R9 3 A9 4 D9	O 2 R9 3 A9 4 D9	9
O 3 R10 2 A10 1 D10	O 3 R10 2 A10 1 D10	O 3 R10 2 A10 1 D10	O 3 R10 2 A10 1 D10	O 3 R10 2 A10 1 D10	10
O 4 R11 3 A11 2 D11	O 4 R11 3 A11 2 D11	O 4 R11 3 A11 2 D11	O 4 R11 3 A11 2 D11	O 4 R11 3 A11 2 D11	11
H 9 R12 2 A12 3 D12	**P 9 R12 2 A12 3 D12**	**P 9 R12 2 A12 3 D12**	**P 9 R12 2 A12 3 D12**	**P 9 R12 2 A12 3 D12**	12
H 10 R13 3 A13 2 D13	**H 10 R13 3 A13 2 D13**	**H 10 R13 3 A13 2 D13**	**H 10 R13 3 A13 2 D13**	**C 10 R13 3 A13 2 D13**	13
H 11 R14 4 A14 3 D14	**H 11 R14 4 A14 3 D14**	**H 11 R14 4 A14 3 D14**	**C 11 R14 4 A14 3 D14**	**C 11 R14 4 A14 3 D14**	14
	O 12 R15 9 A15 2 D15	O 12 R15 9 A15 2 D15	O 12 R15 9 A15 2 D15	O 12 R15 9 A15 2 D15	15
Phosphate	O 12 R16 9 A16 2 D16	O 12 R16 9 A16 2 D16	O 12 R16 9 A16 2 D16	O 12 R16 9 A16 2 D16	16
	O 12 R17 9 A17 2 D17	O 12 R17 9 A17 2 D17	O 12 R17 9 A17 2 D17	O 12 R17 9 A17 2 D17	17
	H 17 R18 12 A18 9 D18	**C 17 R18 12 A18 9 D18**	**C 17 R18 12 A18 9 D18**	**C 17 R18 12 A18 9 D18**	18
	H 16 R19 12 A19 9 D19	C 18 R19 17 A19 12 D19	C 18 R19 17 A19 12 D19	C 18 R19 17 A19 12 D19	19
		N 19 R20 18 A20 17 D20	N 19 R20 18 A20 17 D20	N 19 R20 18 A20 17 D20	20
		H 18 R21 17 A21 12 D21	H 18 R21 17 A21 12 D21	H 18 R21 17 A21 12 D21	21
		H 18 R22 17 A22 12 D22	H 18 R22 17 A22 12 D22	H 18 R22 17 A22 12 D22	22
-	X-group	H 19 R23 18 A23 17 D23	H 19 R23 18 A23 17 D23	H 19 R23 18 A23 17 D23	23
		H 19 R24 18 A24 17 D24	H 19 R24 18 A24 17 D24	H 19 R24 18 A24 17 D24	24
		H 20 R25 19 A25 18 D25	H 20 R25 19 A25 18 D25	H 20 R25 19 A25 18 D25	25
		H 20 R26 19 A26 18 D26	H 20 R26 19 A26 18 D26	H 20 R26 19 A26 18 D26	26
		H 20 R27 19 A27 18 D27	H 20 R27 19 A27 18 D27	H 20 R27 19 A27 18 D27	27
		H 16 R28 12 A28 19 D28	O 14 R28 11 A28 4 D28	O 14 R28 11 A28 4 D28	28
			C 14 R29 11 A29 4 D29	C 14 R29 11 A29 4 D29	29
			C 29 R30 14 A30 11 D30	C 29 R30 14 A30 11 D30	30
			C 30 R31 29 A31 14 D31	C 30 R31 29 A31 14 D31	31
			H 29 R32 14 A32 11 D32	H 29 R32 14 A32 11 D32	32
		Fatty acid	H 29 R33 14 A33 11 D33	H 29 R33 14 A33 11 D33	33
			H 30 R34 29 A34 14 D34	H 30 R34 29 A34 14 D34	34
			H 30 R35 29 A35 14 D35	H 30 R35 29 A35 14 D35	35
			H 31 R36 30 A36 29 D36	H 31 R36 30 A36 29 D36	36
			H 31 R37 30 A11 29 D37	H 31 R37 30 A11 29 D37	37
			H 31 R38 30 A38 29 D38	H 31 R38 30 A38 29 D38	38
			H 16 R39 12 A39 9 D39	O 13 R39 10 A39 3 D39	39
				C 13 R40 10 A40 3 D40	40
				C 40 R41 13 A41 10 D41	41
				C 41 R42 40 A42 13 D42	42
				H 40 R43 13 A43 10 D43	43
				H 40 R44 13 A44 10 D44	44
			Fatty acid	H 41 R45 40 A45 13 D45	45
				H 41 R46 40 A46 13 D46	46
				H 42 R47 41 A47 40 D47	47
				H 42 R48 41 A48 40 D48	48
				H 42 R49 41 A49 40 D49	49
				H 16 R50 12 A50 9 D50	50

Table 5
Geometrical variables for the various *z*-matrices of phospholipids shown Table 4

Glycerol (Fragment I)	Glycerol with phosphate (Fragments I + II)	Glycerol, phosphate, X-group (Fragments I–III)	Phospholipids, first fatty acid included (Fragments I–IV)	Phospholipids, first and second fatty acid included (Fragments I–V)
R2 = 1.1216	R2 = 1.126	R2 = 1.1281	R2 = 1.1283	R2 = 1.1252
R3 = 1.5315	R3 = 1.5329	R3 = 1.5317	R3 = 1.5328	R3 = 1.5352
R4 = 1.5296	R4 = 1.5356	R4 = 1.5316	R4 = 1.5284	R4 = 1.5335
R5 = 1.1221	R5 = 1.1219	R5 = 1.1226	R5 = 1.1211	R5 = 1.1203
R6 = 1.1224	R6 = 1.1262	R6 = 1.1243	R6 = 1.1246	R6 = 1.1253
R7 = 1.1258	R7 = 1.1257	R7 = 1.1267	R7 = 1.1265	R7 = 1.1285
R8 = 1.1214	R8 = 1.1225	R8 = 1.1212	R8 = 1.1208	R8 = 1.1205
R9 = 1.4106	R9 = 1.4068	R9 = 1.4136	R9 = 1.4131	R9 = 1.4091
R10 = 1.42	R10 = 1.4227	R10 = 1.4216	R10 = 1.4221	R10 = 1.4304
R11 = 1.419	R11 = 1.4126	R11 = 1.4171	R11 = 1.4311	R11 = 1.4332
R12 = 0.9668	**R12 = 1.7057**	**R12 = 1.6927**	**R12 = 1.6927**	R12 = 1.7089
R13 = 0.9662	**R13 = 0.9674**	**R13 = 0.9686**	**R13 = 0.9675**	R13 = 1.3797
R14 = 0.9638	**R14 = 0.967**	**R14 = 0.9652**	**R14 = 1.3815**	R14 = 1.3781
	R15 = 1.5521	R15 = 1.56	R15 = 1.5599	R15 = 1.5339
	R16 = 1.6807	**R16 = 1.6757**	R16 = 1.6757	R16 = 1.678
	R17 = 1.6792	R17 = 1.7129	R17 = 1.713	R17 = 1.7042
	R18 = 0.962	**R18 = 1.4015**	**R18 = 1.4014**	R18 = 1.4061
	R19 = 0.9631	R19 = 1.538	R19 = 1.5382	R19 = 1.5366
		R20 = 1.486	R20 = 1.4859	R20 = 1.4816
		R21 = 1.1262	R21 = 1.1262	R21 = 1.1299
		R22 = 1.1292	R22 = 1.1293	R22 = 1.1222
		R23 = 1.127	R23 = 1.127	R23 = 1.1287
		R24 = 1.1316	R24 = 1.1317	R24 = 1.1278
		R25 = 1.0221	R25 = 1.0222	**R25 = 1.0346**
		R26 = 1.0452	R26 = 1.0449	R26 = 1.0277
		R27 = 1.0219	R27 = 1.0219	R27 = 1.0269
		R28 = 0.9666	R28 = 1.2287	R28 = 1.2387
			R29 = 1.4938	R29 = 1.4879
			R30 = 1.5149	R30 = 1.5161
			R31 = 1.5064	R31 = 1.5065
			R32 = 1.1232	R32 = 1.1253
			R33 = 1.123	R33 = 1.1243
			R34 = 1.1223	R34 = 1.1221
			R35 = 1.1223	R35 = 1.1224
			R36 = 1.117	R36 = 1.117
			R37 = 1.1169	R37 = 1.1169
			R38 = 1.1171	R38 = 1.1175
			R39 = 0.9665	R39 = 1.2325
				R40 = 1.4934
				R41 = 1.5162
				R42 = 1.5069
				R43 = 1.1251
				R44 = 1.1223
				R45 = 1.1218
				R46 = 1.1228
				R47 = 1.117
				R48 = 1.1169
				R49 = 1.1172
				R50 = 0.9668

Table 5 (*continued*)

Glycerol (Fragment I)	Glycerol with phosphate (Fragments I + II)	Glycerol, phosphate, X-group (Fragments I–III)	Phospholipids, first fatty acid included (Fragments I–IV)	Phospholipids, first and second fatty acid included (Fragments I–V)
A3 = 110.0974	A3 = 109.1725	A3 = 109.9195	A3 = 109.8414	A3 = 111.1376
A4 = 110.4478	A4 = 110.9072	A4 = 109.9386	A4 = 109.268	A4 = 112.1617
A5 = 110.3795	A5 = 111.0577	A5 = 110.6167	A5 = 111.5957	A5 = 110.5231
A6 = 109.8647	A6 = 110.6528	A6 = 111.2454	A6 = 111.1582	A6 = 110.4884
A7 = 110.2977	A7 = 109.4897	A7 = 110.442	A7 = 110.4361	A7 = 109.4902
A8 = 110.2439	A8 = 110.6323	A8 = 110.1218	A8 = 111.12	A8 = 111.3046
A9 = 111.1015	A9 = 110.3678	A9 = 110.2706	A9 = 110.2921	A9 = 109.2875
A10 = 106.2381	A10 = 106.8801	A10 = 106.6297	A10 = 106.6623	A10 = 109.6952
A11 = 106.1371	A11 = 110.35	A11 = 105.3672	A11 = 105.3623	A11 = 104.8915
A12 = 106.9957	**A12 = 111.7365**	**A12 = 112.4255**	**A12 = 112.35**	**A12 = 113.684**
A13 = 106.6503	**A13 = 107.0443**	**A13 = 107.6328**	**A13 = 107.4828**	**A13 = 117.2627**
A14 = 106.8514	**A14 = 107.3144**	**A14 = 107.1963**	**A14 = 116.4654**	**A14 = 118.8617**
	A15 = 115.1375	A15 = 118.8107	A15 = 118.7567	A15 = 116.2749
	A16 = 103.8712	A16 = 109.4897	A16 = 109.174	A16 = 101.5556
	A17 = 102.1326	A17 = 102.3787	A17 = 102.4541	A17 = 95.025
	A18 = 104.2327	A18 = 113.8763	A18 = 113.8057	A18 = 116.0671
	A19 = 105.1155	A19 = 113.1627	A19 = 113.2176	A19 = 109.7724
		A20 = 113.5057	A20 = 113.577	A20 = 113.4188
		A21 = 111.7025	A21 = 111.6973	A21 = 105.8982
		A22 = 103.6839	A22 = 103.6782	A22 = 113.1914
		A23 = 108.7264	A23 = 108.6905	A23 = 109.2299
		A24 = 109.4808	A24 = 109.4409	A24 = 108.4871
		A25 = 110.4825	A25 = 110.4682	A25 = 111.103
		A26 = 108.5398	A26 = 108.5081	A26 = 109.9291
		A27 = 110.1548	A27 = 110.1837	A27 = 111.368
		A28 = 107.3796	A28 = 116.8871	A28 = 109.0617
			A29 = 112.2085	A29 = 121.4404
			A30 = 111.2038	A30 = 111.8053
			A31 = 110.8594	A31 = 110.8326
			A32 = 108.4512	A32 = 108.3245
			A33 = 108.4818	A33 = 108.957
			A34 = 109.4151	A34 = 109.3823
			A35 = 109.4035	A35 = 109.3674
			A36 = 110.8532	A36 = 110.9053
			A37 = 110.8574	A37 = 110.9152
			A38 = 109.9225	A38 = 109.8288
			A39 = 107.2186	A39 = 116.9821
				A40 = 112.6202
				A41 = 111.0045
				A42 = 110.6798
				A43 = 107.1833
				A44 = 109.8654
				A45 = 109.5367
				A46 = 109.4027
				A47 = 110.8377
				A48 = 110.8593
				A49 = 109.8775
				A50 = 106.6959

Table 5 (*continued*)

Glycerol (Fragment I)	Glycerol with phosphate (Fragments I + II)	Glycerol, phosphate, X-group (Fragments I–III)	Phospholipids, first fatty acid included (Fragments I–IV)	Phospholipids, first and second fatty acid included (Fragments I–V)
D4 = −60.1588	D4 = −53.7954	D4 = −63.8902	D4 = −66.5999	D4 = 26.8253
D5 = −59.1874	D5 = −6.3298	D5 = −54.5261	D5 = −61.2505	D5 = −179.811
D6 = 61.3828	D6 = 67.251	D6 = 58.3345	D6 = 55.4271	D6 = 148.3108
D7 = 61.3457	D7 = 68.3508	D7 = 57.6093	D7 = 54.9113	D7 = 149.334
D8 = 62.1282	D8 = 115.2874	D8 = 67.1209	D8 = 61.7809	D8 = −56.8221
D9 = −176.39	D9 = −168.746	D9 = −177.636	D9 = 179.5192	D9 = −88.8693
D10 = 179.5268	D10 = −173.729	D10 = 175.2217	D10 = 172.5609	D10 = −89.5396
D11 = **−178.533**	D11 = −129.247	**D11 = −173.41**	D11 = −178.943	D11 = 61.3632
D12 = −55.3082	**D12 = −99.5764**	**D12 = −92.835**	**D12 = −93.7806**	**D12 = −96.1656**
D13 = 175.5578	**D13 = 178.6422**	**D13 = 163.0249**	**D13 = 163.5726**	**D13 = −83.2318**
D14 = 175.6388	**D14 = 67.7852**	**D14 = −178.446**	**D14 = −169.178**	**D14 = 173.5444**
	D15 = −29.8477	D15 = −36.5255	D15 = −34.7588	D15 = −50.5988
	D16 = 100.7922	D16 = 100.9108	D16 = 102.5071	D16 = 78.688
	D17 = −153.691	D17 = −151.425	D17 = −149.719	D17 = −175.649
	D18 = 127.1654	**D18 = −156.821**	**D18 = −158.078**	**D18 = −76.1666**
	D19 = −69.5994	D19 = −66.268	D19 = −66.838	D19 = 115.6701
		D20 = −38.05	D20 = −37.4747	D20 = −62.6243
		D21 = 55.7906	D21 = 55.2686	D21 = −128.593
		D22 = 173.2979	D22 = 172.7539	D22 = −9.1516
		D23 = −159.578	D23 = −159.013	D23 = 57.8023
		D24 = 81.4758	D24 = 81.9385	D24 = 176.6851
		D25 = −50.936	D25 = −50.6133	D25 = −51.628
		D26 = 68.3443	D26 = 68.6355	D26 = 66.6063
		D27 = −172.363	D27 = −172.064	D27 = −171.324
		D28 = −30.827	D28 = −0.3377	D28 = 178.2039
			D29 = 179.6415	D29 = −2.0544
			D30 = −179.953	D30 = 174.0422
			D31 = 179.9618	D31 = 178.0883
			D32 = −58.2419	D32 = −64.6654
			D33 = 58.3206	D33 = 52.1424
			D34 = −58.4292	D34 = −60.4195
			D35 = 58.3732	D35 = 56.5049
			D36 = −60.1931	D36 = −60.7521
			D37 = 60.2132	D37 = 59.8156
			D38 = −179.987	D38 = 179.5414
			D39 = −29.4313	D39 = 2.9895
				D40 = 181.7598
				D41 = 141.2515
				D42 = 174.0639
				D43 = −98.3579
				D44 = 18.5726
				D45 = −64.73
				D46 = 52.6464
				D47 = −60.8242
				D48 = 59.6213
				D49 = 179.4392
				D50 = −114.629

Table 6
Sample symbolic internal coordinates of atom connectivity for 1,2,3-tributyl-s-glyceride (Note that hydrocarbon chains are the substituents on this molecule)

	Glycerol (Fragment I)	Fat first fatty acid included (Fragments I + II)	FAT first and second fatty acid included (Fragments I–III)	FAT first, second and third fatty acid included (Fragments I–IV)
Glycerol	0 1	0 1	0 1	0 1
	H	**H**	H	H
	C 1 R2	C 1 R2	C 1 R2	C 1 R2
	C 2 R3 1 A3	C 2 R3 1 A3	C 2 R3 1 A3	C 2 R3 1 A3
	C 3 R4 2 A4 1 D4	C 3 R4 2 A4 1 D4	C 3 R4 2 A4 1 D4	C 3 R4 2 A4 A D4
	H 4 R5 3 A5 2 D5	H 4 R5 3 A5 2 D5	H 4 R5 3 A5 2 D5	H 4 R5 3 A5 2 D5
	H 2 R6 3 A6 4 D6	H 2 R6 3 A6 4 D6	H 2 R6 3 A6 4 D6	H 2 R6 3 A6 4 D6
	H 3 R7 2 A7 1 D7	H 3 R7 2 A7 1 D7	H 3 R7 2 A7 1 D7	H 3 R7 2 A7 1 D7
	H 4 R8 3 A8 2 D8	H 4 R8 3 A8 2 D8	H 4 R8 3 A8 2 D8	H 4 R8 3 A8 2 D8
	O 2 R9 3 A9 4 D9	O 2 R9 3 A9 4 D9	O 2 R9 3 A9 4 D9	O 2 R9 3 A9 4 D9
	O 3 R10 2 A10 1 D10	O 3 R10 2 Al0 1 D10	O 3 R10 2 A10 1 D10	O 3 R10 2 A10 1 D10
	O 4 R11 3 A1 12 D11	O 4 R11 3 A11 2 D11	O 4 R11 3 A11 2 D11	O 4 R11 3 A11 2 D11
	H 9 R12 2 A12 3 D12	**C 9 R12 2 A12 3 D12**	**C 9 R12 2 A12 3 D12**	**C 9 R12 2 A12 3 D12**
	H 10 R13 3 A13 2 D13	**H 10 R13 3 A13 2 D13**	**H 10 R13 3 A13 2 D13**	**C 10 R13 3 A13 2 D13**
	H 11 R14 4 A14 3 D14	**H 11 R14 4 A14 3 D14**	**C 11 R14 4 A14 3 D14**	**C 11 R14 4 A14 3 D14**
	Fatty acid	O 12 R15 9 A15 2 D15	O 12 R15 9 A15 2 D15	O 12 R15 9 A15 2 D15
		C 12 R16 9 A16 2 D16	C 12 R16 9 A16 2 D16	C 12 R16 9 A16 2 D16
		C 16 R17 12 A17 9 D17	C 16 R17 12 A17 9 D17	C 16 R17 12 A17 9 D17
		C 17 R18 16 A18 12 D18	C 17 R18 16 A18 12 D18	C 17 R18 16 A18 12 D18
		H 16 R19 12 A19 9 D19	H 16 R19 12 A19 9 D19	H 16 R19 12 A19 9 D19
		H 16 R20 12 A20 9 D20	H 16 R20 12 A20 9 D20	H 16 R20 12 A20 9 D20
		H 17 R21 16 A21 12 D21	H 17 R21 16 A21 12 D21	H 17 R21 16 A21 12 D21
		H 17 R22 16 A22 12 D22	H 17 R22 16 A22 12 D22	H 17 R22 16 A22 12 D22
		H 18 R23 17 A23 16 D23	H 18 R23 17 A23 16 D23	H 18 R23 17 A23 16 D23
		H 18 R24 17 A24 16 D24	H 18 R24 17 A24 16 D24	H 18 R24 17 A24 16 D24
		H 18 R25 17 A25 16 D25	H 18 R25 17 A25 16 D25	H 18 R25 17 A25 16 D25
		Fatty acid	O 14 R26 11 A26 4 D26	O 14 R26 11 A26 4 D26
			C 14 R27 11 A29 4 D29	C 14 R27 11 A29 4 D29
			C 27 R28 14 A30 11 D30	C 27 R28 14 A30 11 D30
			C 28 R29 27 A31 14 D31	C 28 R29 27 A31 14 D31
			H 27 R30 14 A32 11 D32	H 27 R30 14 A32 11 D32
			H 27 R31 14 A33 11 D33	H 27 R31 14 A33 11 D33
			H 28 R32 27 A34 14 D34	H 28 R32 27 A34 14 D34
			H 28 R33 27 A35 14 D35	H 28 R33 27 A35 14 D35
			H 29 R34 28 A36 27 D36	H 29 R34 28 A36 27 D36
			H 29 R35 28 A11 27 D37	H 29 R35 28 A11 27 D37
			H 29 R36 28 A36 27 D36	H 29 R36 28 A36 27 D36
			Fatty acid	O 13 R37 10 A37 3 D37
				C 13 R38 10 A38 3 D38
				C 38 R39 13 A39 10 D39
				C 39 R40 38 A29 13 D40
				H 38 R41 13 A41 10 D41
				H 38 R42 13 A42 10 D42
				H 39 R43 38 A43 13 D43
				H 39 R44 38 A44 13 D44
				H 40 R45 39 A45 38 D45
				H 40 R46 39 A46 38 D46
				H 40 R47 39 A47 38 D47

Table 7
Variables of a triglyceride

Glycerol (Fragment I)	Fat first fatty acid included (Fragments I + II)	Fat first and second fatty acid included (Fragments I–III)	Fat first, second and third fatty acid included (Fragments I–IV)
R2 = 1.1216	R2 = 1.1205	R2 = 1.1204	R2 = 1.1221
R3 = 1.5315	R3 = 1.5325	R3 = 1.5334	R3 = 1.5302
R4 = 1.5296	R4 = 1.5306	R4 = 1.5288	R4 = 1.5306
R5 = 1.1221	R5 = 1.1223	R5 = 1.1203	R5 = l.1219
R6 = 1.1224	R6 = 1.1206	R6 = 1.1213	R6 = 1.1205
R7 = 1.1258	R7 = 1.1257	R7 = 1.1264	R7 = 1.1253
R8 = 1.1214	R8 = 1.1214	R8 = 1.1202	R8 = 1.1197
R9 = 1.4106	R9 = 1.4284	R9 = 1.4282	R9 = 1.4284
R10 = 1.42	R10 = 1.4194	R10 = 1.4198	R10 = 1.4354
R11 = 1.419	R11 = 1.4192	R11 = 1.4357	R11 = 1.4335
R12 = 0.9668	**R12 = 1.3774**	**R12 = 1.3778**	**R12 = 1.3762**
R13 = 0.9662	**R13 = 0.9669**	**R13 = 0.966**	**R13 = 1.3732**
R14 = 0.9638	**R14 = 0.9636**	**R14 = 1.3725**	**R14 = 1.3721**
	R15 = 1.2308	R15 = 1.2305	R15 = 1.2309
	R16 = 1.4949	R16 = 1.4948	R16 = 1.4954
	R17 = 1.5148	R17 = 1.5148	R17 = 1.5147
	R18 = 1.5061	R18 = 1.5061	R18 = 1.5061
	R19 = 1.1229	R19 = 1.1229	R19 = 1.1228
	R20 = 1.1236	R20 = 1.1235	R20 = 1.1234
	R21 = 1.1225	R21 = 1.1224	R21 = 1.1225
	R22 = 1.1222	R22 = 1.1222	R22 = 1.1222
	R23 = 1.117	R23 = 1.117	R23 = 1.117
	R24 = 1.117	R24 = 1.117	R24 = 1.117
	R25 = 1.1169	R25 = 1.1169	R25 = 1.1169
		R26 = 1.2309	R26 = 1.2312
		R27 = 1.4957	R27 = 1.496
		R28 = 1.514	R28 = 1.5147
		R29 = 1.5063	R29 = 1.5066
		R30 = 1.1229	R30 = 1.1218
		R31 = 1.1226	R31 = 1.1239
		R32 = 1.1223	R32 = 1.1229
		R33 = 1.1223	R33 = 1.1219
		R34 = 1.117	R34 = 1.1169
		R35 = 1.117	R35 = 1.117
		R36 = 1.1169	R36 = 1.1169
			R37 = 1.2307
			R38 = 1.4964
			R39 = 1.5146
			R40 = 1.5065
			R41 = 1.1239
			R42 = 1.1218
			R43 = 1.1219
			R44 = 1.1229
			R45 = 1.1169
			R46 = 1.1169
			R47 = 1.117
A3 = 110.0974	A3 = 110.8831	A3 = 111.1742	A3 = 109.142
A4 = 110.4478	A4 = 110.6974	A4 = 110.2722	A4 = 110.9223
A5 = 110.3795	A5 = 110.532	A5 = 111.7815	A5 = 110.1132
A6 = 109.8647	A6 = 109.6135	A6 = 109.6214	A6 = 110.7424

Table 7 (*continued*)

Glycerol (Fragment I)	Fat first fatty acid included (Fragments I + II)	Fat first and second fatty acid included (Fragments I–III)	Fat first, second and third fatty acid included (Fragments I–IV)
A7 = 110.2977	A7 = 110.1298	A7 = 110.0622	A7 = 110.6866
A8 = 110.2439	A8 = 109.4899	A8 = 110.8327	A8 = 111.8672
A9 = 111.1015	A9 = 105.914	A9 = 105.6611	A9 = 106.0801
A10 = 106.2381	A10 = 105.5937	A10 = 105.7309	A10 = 105.9291
A11 = 106.1371	A11 = 106.1792	A11 = 105.4591	A11 = 106.1598
A12 = 106.9957	**A12 = 117.5617**	**A12 = 117.5504**	**A12 = 117.5939**
A13 = 106.6503	**A13 = 106.2931**	**A13 = 106.3397**	**A13 = 117.8844**
A14 = 106.8514	**A14 = 106.8117**	**A14 = 116.5616**	**A14 = 116.5797**
	A15 = 111.6499	A15 = 111.6669	A15 = 111.8564
	A16 = 120.4212	A16 = 120.3534	A16 = 120.3786
	A17 = 111.4893	A17 = 111.4846	A17 = 111.5014
	A18 = 111.1289	A18 = 111.1301	A18 = 111.1598
	A19 = 109.1238	A19 = 109.0533	A19 = 109.0757
	A20 = 108.5296	A20 = 108.6015	A20 = 108.5406
	A21 = 109.2417	A21 = 109.2442	A21 = 109.2304
	A22 = 109.2872	A22 = 109.2763	A22 = 109.27
	A23 = 110.8344	A23 = 110.8325	A23 = 110.8349
	A24 = 110.8215	A24 = 110.8268	A24 = 110.8267
	A25 = 110.0297	A25 = 110.0259	A25 = 110.0358
		A26 = 117.8512	A26 = 118.0184
		A27 = 112.2647	A27 = 112.3912
		A28 = 111.3076	A28 = 111.1025
		A29 = 110.9926	A29 = 110.9567
		A30 = 108.3488	A30 = 109.7459
		A31 = 108.4598	A31 = 107.2226
		A32 = 109.3698	A32 = 109.2851
		A33 = 109.3481	A33 = 109.4675
		A34 = 110.803	A34 = 110.8037
		A35 = 110.8131	A35 = 110.7686
		A36 = 110.0289	A36 = 110.0437
			A37 = 118.3739
			A38 = 112.1131
			A39 = 111.1109
			A40 = 110.9469
			A41 = 107.1701
			A42 = 109.7047
			A43 = 109.4679
			A44 = 109.2902
			A45 = 110.0339
			A46 = 110.801
			A47 = 110.7749
D4 = −60.1588	D4 = 50.0202	D4 = 33.5711	D4 = −40.4434
D5 = −59.1874	D5 = −59.6731	D5 = −64.5566	D5 = −172.583
D6 = 61.3828	D6 = 171.6628	**D6 = 155.4752**	D6 = 81.8533
D7 = 61.3457	D7 = 171.1178	D7 = 154.7339	D7 = 82.8712
D8 = 62.1282	D8 = 61.5283	D8 = 58.696	D8 = −50.2572
D9 = −176.39	D9 = −68.8284	D9 = −85.361	D9 = −158.429
D10 = 179.5268	D10 = −70.6047	D10 = −86.7687	D10 = −157.321
D11 = −178.533	D11 = −178.502	D11 = 177.3589	D11 = 68.425
D12 = −55.3082	**D12 = −172.491**	**D12 = −173.858**	**D12 = −174.627**

Table 7 (*continued*)

Glycerol (Fragment I)	Fat first fatty acid included (Fragments I + II)	Fat first and second fatty acid included (Fragments I–III)	Fat first, second and third fatty acid included (Fragments I–IV)
D13 = 175.5578	**D13 = 171.6604**	**D13 = 175.5582**	**D13 = −152.01**
D14 = 175.6388	**D14 = −173.094**	**D14 = −177.047**	**D14 = 169.1387**
	D15 = −178.179	D15 = −179.617	D15 = −179.818
	D16 = 2.126	D16 = 0.5728	D16 = 0.3738
	D17 = −174.732	D17 = −175.643	D17 = −174.592
	D18 = −178.738	D18 = −179.025	D18 = −178.726
	D19 = −53.0396	D19 = −54.0308	D19 = −52.9545
	D20 = 64.0893	D20 = 63.1131	D20 = 64.2129
	D21 = −56.9809	D21 = −57.2687	D21 = −56.9511
	D22 = 59.5518	D22 = 59.2594	D22 = 59.5491
	D23 = −60.0065	D23 = −60.0304	D23 = −59.9758
	D24 = 60.2834	D24 = 60.2674	D24 = 60.3206
	D25 = −179.871	D25 = −179.885	D25 = −179.834
		D26 = −1.4399	D26 = 3.5768
		D27 = 178.6624	D27 = −175.987
		D28 = 179.6407	D28 = −144.064
		D29 = 179.8872	D29 = −174.235
		D30 = −58.6138	D30 = −21.4036
		D31 = 57.8167	D31 = 95.3267
		D32 = −58.4378	D32 = −52.6243
		D33 = 58.2292	D33 = 64.3993
		D34 = −60.1286	D34 = −59.3163
		D35 = 60.1401	D35 = 60.9258
		D36 = −179.989	D36 = −179.235
			D37 = −6.1713
			D38 = 173.5907
			D39 = 145.5699
			D40 = 174.2472
			D41 = −93.7769
			D42 = 22.9409
			D43 = −64.378
			D44 = 52.6389
			D45 = 179.2166
			D46 = 59.3154
			D47 = −60.9409

This model does not include the lone phosphate hydrogen. However, this hydrogen may or may not be included depending on the choice of whether the phosphate is neutral or anionic. To include this hydrogen, it can be added in the very last line of the internal coordinate definition and the equation becomes:

Number of the lone phosphate proton

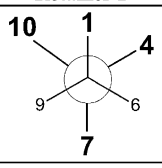
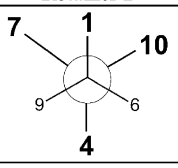
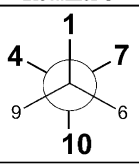
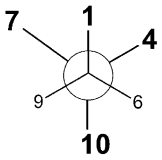
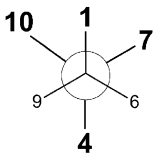
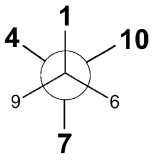
$$= 17 + A + B + C + 1 = 18 + A + B + C.$$

In closing it should be mentioned that the fatty acid chain length (i.e. B_Q and C_Q of Fragment IV and V, respectively) in phospholipids is predetermined only by the number of carbon atoms on the chain. However, B_H and C_H are predetermined not by the length of the chains but by the degree of saturation as seen in Table 3. This will be of particular importance when the mechanism of lipid peroxidation will be studied. The bolded atoms are the ones associated with the chiral center C_3.

3.1. Stereocenters

Stereocenters are also very important in the

Table 8
Possible rotamers the *S* and *R* conformer each can have

Dihedrals	Rotamer 1	Rotamer 2	Rotamer 3
S conformer			
$D_4(C_4)$	g+	a	g-
$D_7(H_7)$	a	g-	g+
$D_{10}(H_{10})$	g-	g+	a
R conformer			
$D_4(C_4)$	g+	a	g-
$D_7(H_7)$	g-	g+	a
$D_{10}(H_{10})$	a	g-	g+

numbering systems as it identifies the enantiomer being studied. In this work, only glycerol is devoid of stereocenters. All other examples herein have a stereocenter at C_3. They have all been constructed as the *S* enantiomer. In the standardized numbering system, there must be an efficient, accurate and easily reproducible method to define the enantiomeric state of any system at all stereocentre. The related dihedral angles around the stereocenters are D4, D7 and D10. Therefore, the *S* enantiomer defined by setting D4, D7 and D10 in a specific order. This can be achieved via the atomic 'ordering' of C_3 substituents as in Fig. 4. The dihedral section of Table 5 contains calculations of the *S* enantiomer of the phospholipid. Table 8 shows the different rotamers the *S* and *R* enantiomer each can have. The H atoms on the achiral carbons are also assigned *R* or *S*. This means that if an atom that is heavier than hydrogen but has a priority less than C_4 and O_{10}, the C_3 will become whichever conformation indicated on the H. For example, if a deuterium atom replaces the H_7 atom, then the C to which it is attached will have an *R* enantiomation. To make the system consistent, H_7 is always assigned the smaller number. This system of number designation will help in setting up and identifying, in the initial structural guesstimate, the *S* or *R* enantiomeric state.

5. Conclusions

In general, the molecule can be numbered as shown on Fig. 8 and the number can be separated into different modules, the glycerol module is assigned numbers 1– 14. The phosphate will take number 15–17. The X-group heavy atoms will take the numbers from 18 to $17 + A_Q$ and the number of hydrogens are included in A_H. Therefore its general equation will be $17 + A_Q + A_H(17 + A)$. The numbering for heavy atoms on the carbon chain which is attached to C_{14} will be represented by $17 + A_Q + A_H + B_Q$. However, the carbonyl carbon here is not included into this section of the numbering system. With the remainder of the hydrogen atoms on this chain, the general variables for the heavy and hydrogen atoms on this chain will be B_Q and B_H, making the equation $17 + A_Q + A_H + B_Q + B_H(17 + A + B)$. The fatty acid chain attached to C_{14} is numbered the same way as the previous chain. The general variables for all the heavy atoms and hydrogen atoms on this are C_Q and C_H, respectively. The equation will be $17 + A_Q + A_H + B_Q + B_H + C_Q + C_H(17 + A + B + C)$. If the phosphate hydrogen is added, the equation will be $18 + A_Q + A_H + B_Q + B_H + C_Q + C_H$. This model can also be used for other derivatives of phospholipids such as fats and oils. For mono, di or tri glycerides the

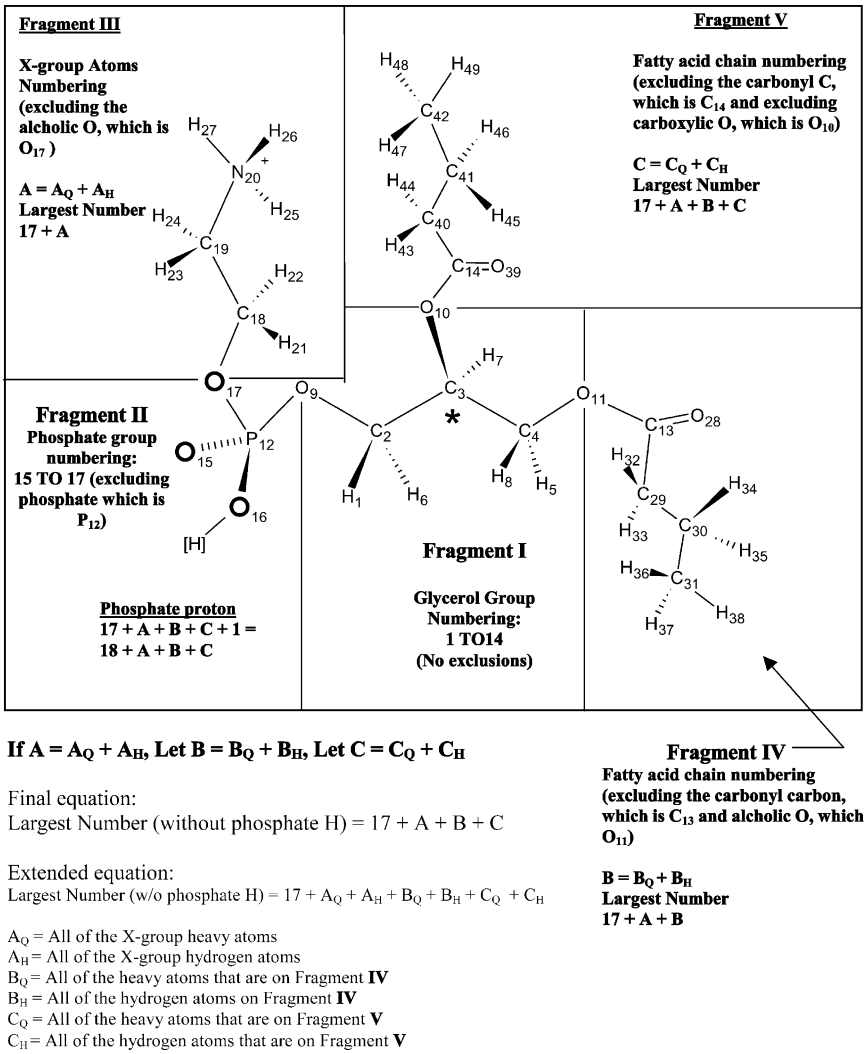


Fig. 8. Summary of atomic numbering in phospholipid. (Note H stands for hydrogen atoms, Q stands for non-hydrogen atoms like C, N, and O).

phosphate group and the X-group will become another hydrocarbon chain. They can be first numbered by the carbon chain, then by the O atom and then by the hydrogen atoms. When numbering a glyceride, it does not matter which chain is numbered first. However, an entire chain should be numbered before moving onto the next chain. For example, the internal coordinates for 1,2,3-tributyl-s-glyceride in Fig. 9 is shown in Table 6 and the variables are shown in Table 7. In general, this system can be used to classify and organize different molecules according to their sizes and substituents.

Although the explanation is somewhat lengthy and tedious, it follows a simple numeric and compartmentalized logic. All structural features are considered and under control of the researcher allowing for accurate construction of all enantiomers, isomers and geometric conformers efficiently, accurately and precisely. As with all numeric patterns and exercises, practical use and repetition bring about familiarity and proficiency. This methodology allows for extensive searches for and identification of geometric conformers to be automated and computational throughput and efficient and frugal resource (CPU) usage to be greatly improved.

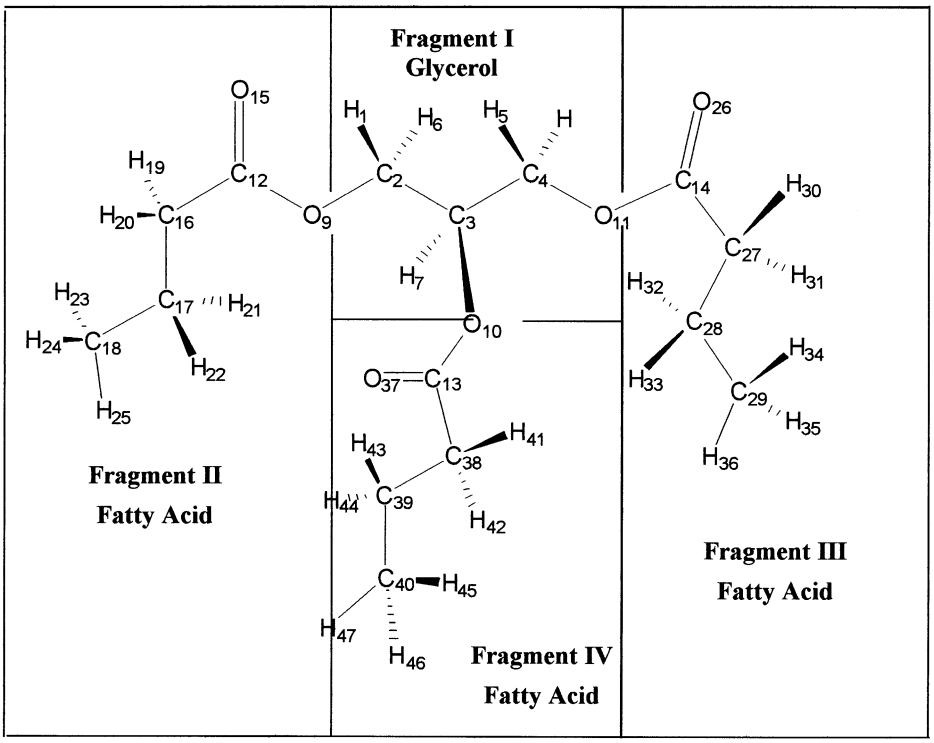


Fig. 9. Structure and numbering of other glycerol lipids (triglyceride in this case).

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