

Using the quantum chemistry for genesis of a nano biomembrane with a combination of the elements Be, Li, Se, Si, C and H

Abstract

Going beyond with imagination using quantum chemistry in calculations to obtain probable one new bio-inorganic molecule, to the Genesis of a biomembrane with a combination of the elements Be, Li, Se, Si, C and H. After calculation a bio-inorganic seed molecule from the previous combination, it led to the search for a molecule that could carry the structure of a membrane. From a simple molecular dynamics, through classical calculations, the structure of the molecule was stabilized. An advanced study of quantum chemistry using *ab initio*, HF (Hartree-Fock) method in various bases is applied and the expectation of the stabilization of the Genesis of this bio-inorganic was promising. The calculations made so far admit a seed molecule at this stage of the quantum calculations of the arrangement of the elements we have chosen, obtaining a highly reactive molecule with the shape polar-apolar-polar. The molecule obtained has a chemical structure $C_{13}H_{20}BeLi_2SeSi$ is plausible, correct and predicted by quantum chemistry through the RHF (Restricted Hartree-Fock) method in the TZV (Triple Zeta Valence) sets bases. The structure of the bio-inorganic seed molecule for a biomembrane genesis that challenges the current concepts of a protective mantle structure of a cell such as biomembrane to date is promising, challenging. Leaving to the biochemists their experimental synthesis.

Keywords: quantum chemistry, molecular dynamics, nucleosynthesis, molecular mechanics, elements, genesis, nano biomembrane, computational chemistry, nanomedicine, bio-inorganic seed molecule

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Abbreviations: LNB, low noise block; CBD, chronic beryllium disease; IARC, international agency for research on cancer; OSHA, occupational safety and health administration; PEL, permissible exposure limit; TWA, time-weighted average; NIOSH, national institute for occupational safety and health; REL, recommended exposure limit; IDLH, immediately dangerous to life and health; MP, møller-plesset; HF, hartree-fock; RHF, restricted hartree-fock; TZV, triple zeta valence.

Introduction

The initial idea was to construct a molecule that was stable, using the chemical elements Lithium, Beryllium, alkaline and alkaline earth metals, respectively, as electropositive and electronegative elements – Selenium and Silicon, semimetal and nonmetal, respectively. This molecule would be the basis of the structure of a crystal, whose structure was constructed only with the selected elements. The elements Li, Be, Se and Si were chosen due to their physicochemical properties, and their use in several areas of technology.¹⁻⁴ To construct such a molecule, which was called a seed molecule, quantum chemistry was used by *ab initio* methods.⁵⁻⁷ The equipment used was a cluster of the Biophysics laboratory built specifically for this task. It was simulated computationally via molecular dynamics, initially using Molecular Mechanics⁸⁻²⁴ and *ab initio* methods.⁵⁻⁷ The results were satisfactory. We found a probable seed molecule of the $BeLi_2SeSi$ structure predicted by quantum chemistry. Due to its geometry, it presents a probable formation of a crystal with the tetrahedral and hexahedral crystal structure.²³

The idea of a new molecule for a crystal has been upgraded. Why not build a molecule, in the form of a lyotropic liquid crystal that could be the basis of a new biomembrane? For this, the molecule should be amphiphilic, with polar head and apolar tail. Are basic requirement of the construction of a biomembrane.²⁵ Then it is necessary to add a hydrophobic tail, with atoms of carbon and hydrogen. Therefore, the molecule seed with a polar hydrophilic “head”. So would a new amphiphilic molecule. Several simulations were performed, always having as initial dynamics the use of Molecular Mechanics⁸⁻²⁴ for the initial molecular structure, moving to *ab initio* calculations of quantum chemistry. All attempts were thwarted. Quantum calculations of quantum chemistry did not accept the seed molecule as the polar head, even changing its binding structure. The silicon atom binds in double bond with the carbon chain and Selenium. It binds in double with beryllium and is simple with the two lithium atoms, thus making a stable molecular structure for Molecular Mechanics,⁸⁻²⁴ Mm^+ and BioCharm.²⁶ But in quantum calculations the seed molecule changed all its fundamental structure.¹ The linear structure of the tail with the polar head, in the form of a rope climbing hook, collapsed, bending toward the apolar tail.

In another simulation carried out the Selenium was connected in double bond to two atoms of Carbon added in double bond. As the +6 polarity of the selenium neutralized with the atoms two atoms of lithium, forming a wing. In the double bonded sequence is the Carbon with the Silicon and this in double bond with the Beryllium. A new structure for a probable lyotropic liquid crystal has now been formed. A polar tail with the seed molecule undone but retaining the five base

atoms of its fundamental structure.²⁵ The structure after Molecular Mechanics, Mm⁺ and BioCharmm,²⁶ the shape of the molecule obtained had a structure like a boomerang. After calculations *ab initio*, the polar tail was undone. The Beryllium atom did not remain in the structure of the molecule, releasing itself from it.

There is then a new idea. Why not separate the electropositive and electronegative elements in two polar heads? This would completely change the concepts known so far of a biomembrane with a lipid bilayer. The next challenging step of building a biomembrane that runs away from known concepts, with a single layer, with two polar heads and its non-polar backbone. Would it be a new way to have a biomembrane? A challenge for quantum chemistry. Then he concentrated the calculations on the probable structure of the molecule with polar ends separately then in pairs the atoms of Selenium with Beryllium and Silicon with the two bonds. Again the attempt failed, in quantum calculations. Beryllium was disconnected from the basic structure of the new molecule, polar-polar-polar polar structure. They have decided to further innovate the theory and “challenge” quantum chemistry. Add an aromatic ring to the polar head. The polar-polar-polar linear structure was now maintained, with a six-carbon cyclic chain. At a polar end, the Silicon is bonded to three atoms of the Hydrogen and is connected to a Carbon from the central chain. This one connected to the two atoms of the Lithium and the apolar central carbon chain. At the other polar end, the six-carbon cyclic chain attached in single bond to the carbonic chain. The cyclic chain with simple bonds, having at its center the Selenium with six bonds to the cyclic chain and a double with the Beryllium, thus forcing two more covalent bonds. Now with a +2 cationic head, the dynamics of the minimization energy with Mm⁺ and BioCharmm²⁶ calculations have maintained a stable structure of the molecule. A polar head similar to a “parabolic antenna”, with folded edges outward with the Hydrogen atoms. The expected, the obvious, Beryllium playing the role of the “LNB (Low Noise Block) receiver”. We then preceded to the *ab initio* calculations in several methods and bases, testing various possibilities with *ab initio* methods. The polar-apolar-polar (parabolic) molecule in *ab initio* calculation, by RHF^{25-6,27-32} in the TZV³³⁻³⁴ sets bases was shown to be stable by changing its covalent cyclic chain linkages, which was expected, Figure 2. The set of bases used was that of Ahlrichs and coworkers main utility are: the SV, SVP, TZV, TZVP keywords refer to the initial formations of the split valence and triple zeta basis sets from this group.^{33,34} Calculations continue to challenge concepts, experimenting. Going where imagination can lead us, getting results that challenge concepts.

Chemical properties of the compounds of beryllium, lithium, selenium and silicon

The Beryllium, Lithium, Selenium and Silicon elements were chosen due to their peculiar physicochemical properties and their wide use in industry, technology, life, health.

Beryllium

Beryllium is created through stellar nucleosynthesis and is a relatively rare element in the universe. It is a divalent element which occurs naturally only in combination with other elements in minerals. Notable gemstones which contain beryllium include beryl (aquamarine, emerald) and chrysoberyl. As a free element it is a steel-gray, strong, lightweight and brittle alkaline earth metal.² Beryllium improves many physical properties when added as an alloying

element to aluminium, copper (notably the alloy beryllium copper), iron and nickel. Tools made of beryllium copper alloys are strong and hard and do not create sparks when they strike a steel surface. In structural applications, the combination of high flexural rigidity, thermal stability, thermal conductivity and low density (1.85 times that of water) make beryllium metal a desirable aerospace material for aircraft components, missiles, spacecraft, and satellites. Because of its low density and atomic mass, beryllium is relatively transparent to X-rays and other forms of ionizing radiation; therefore, it is the most common window material for X-ray equipment and components of particle physics experiments.^{2,35}

Beryllium is a health and safety issue for workers. Exposure to beryllium in the workplace can lead to a sensitization immune response and can over time develop chronic beryllium disease (CBD).^{36,37} Approximately 35 micrograms of beryllium is found in the average human body, an amount not considered harmful. Beryllium is chemically similar to magnesium and therefore can displace it from enzymes, which causes them to malfunction.³⁸ Because Be²⁺ is a highly charged and small ion, it can easily get into many tissues and cells, where it specifically targets cell nuclei, inhibiting many enzymes, including those used for synthesizing DNA. Its toxicity is exacerbated by the fact that the body has no means to control beryllium levels, and once inside the body the beryllium cannot be removed.³⁹ c berylliosis is a pulmonary and systemic granulomatous disease caused by inhalation of dust or fumes contaminated with beryllium; either large amounts over a short time or small amounts over a long time can lead to this ailment. Symptoms of the disease can take up to five years to develop; about a third of patients with it die and the survivors are left disabled. The International Agency for Research on Cancer (IARC) lists beryllium and beryllium compounds as category I carcinogens.³⁸ In the US, the Occupational Safety and Health Administration (OSHA) has designated a permissible exposure limit (PEL) in the workplace with a time-weighted average (TWA) 0.002 mg/m³ and a constant exposure limit of 0.005 mg/m³ over 30 minutes, with a maximum peak limit of 0.025 mg/m³. The National Institute for Occupational Safety and Health (NIOSH) has set a recommended exposure limit (REL) of constant 0.0005 mg/m³. The IDLH (immediately dangerous to life and health) value is 4 mg/m³.⁴⁰

Lithium

Lithium like all alkali metals, lithium is highly reactive and flammable. Because of its high reactivity, lithium never occurs freely in nature, and instead, only appears in compounds, which are usually ionic. Lithium occurs in a number of pegmatitic minerals, but due to its solubility as an ion, is present in ocean water and is commonly obtained from brines and clays. Lithium and its compounds have several industrial applications, including heat-resistant glass and ceramics, lithium grease lubricants, flux additives for iron, steel and aluminum production, lithium batteries and lithium-ion batteries.² As lithium salts, are primarily used as psychiatric medication. This includes the treatment of major depressive disorder that does not improve following the use of other antidepressants, and bipolar disorder.⁴¹ In these disorders, it reduces the risk of suicide. Common side effects include increased urination, shakiness of the hands, and increased thirst. Serious side effects include hypothyroidism, diabetes insipidus, and lithium toxicity. Blood level monitoring is recommended to decrease the risk of potential toxicity. If levels become too high, diarrhea, vomiting, poor coordination, sleepiness, and ringing in the

ears may occur. If used during pregnancy, lithium can cause problems in the baby.⁴² In the nineteenth century, lithium was used in people who had gout, epilepsy, and cancer. Its use in the treatment of mental disorder began in 1948 by John Cade in Australia.⁴³ It is on the World Health Organization's List of Essential Medicines, the most effective and safe medicines needed in a health system.⁴⁴

Selenium

Selenium is found impurely in metal sulfide ores, copper where it partially replaces the sulfur. The chief commercial uses for selenium today are in glassmaking and in pigments. Selenium is a semiconductor and is used in photocells. Uses in electronics, once important, have been mostly supplanted by silicon semiconductor devices. Selenium continues to be used in a few types of DC power surge protectors and one type of fluorescent quantum dot.² Although it is toxic in large doses, selenium is an essential micronutrient for animals. In plants, it sometimes occurs in toxic amounts as forage, e.g. locoweed. Selenium is a component of the amino acids selenocysteine and selenomethionine. In humans, selenium is a trace element nutrient that functions as cofactor for glutathione peroxidases and certain forms of thioredoxin reductase.⁴⁵ Selenium-containing proteins are produced from inorganic selenium via the intermediacy of seleno-phosphate (PSeO_3^{3-}). Selenium is an essential micronutrient in mammals, but is also recognized as toxic in excess. Selenium exerts its biological functions through selenoproteins, which contain the amino acid selenocysteine. Twenty-five selenoproteins are encoded in the human genome.⁴⁶ Selenium also plays a role in the functioning of the thyroid gland. It participates as a cofactor for the three thyroid hormone deiodinases. These enzymes activate and then deactivate various thyroid hormones and their metabolites.⁴⁷ It may inhibit Hashimoto's disease, an auto-immune disease in which the body's own thyroid cells are attacked by the immune system. A reduction of 21% on TPO antibodies was reported with the dietary intake of 0.2 mg of selenium.⁴⁸ Selenium deficiency can occur in patients with severely compromised intestinal function, those undergoing total parenteral nutrition, and in those of advanced age (over 90).⁴⁹

Silicon

Silicon is the eighth most common element in the universe by mass, but very rarely occurs as the pure free element in nature. It is most widely distributed in dusts, sands, planetoids, and planets as various forms of silicon dioxide (silica) or silicates. Over 90% of the Earth's crust is composed of silicate minerals; making silicon the second most abundant element in the Earth's crust (about 28% by mass) after oxygen.¹¹ Elemental silicon also has a large impact on the modern world economy. Although most free silicon is used in the steel refining, aluminium-casting, and fine chemical industries (often to make fumed silica), the relatively small portion of very highly purified silicon that is used in semiconductor electronics (<10%) is perhaps even more critical. Because of wide use of silicon in integrated circuits, the basis of most computers, a great deal of modern technology depends on it.² Although silicon is readily available in the form of silicates, very few organisms use it directly. Diatoms, radiolaria and siliceous sponges use biogenic silica as a structural material for skeletons. In more advanced plants, the silica phytoliths (opal phytoliths) are rigid microscopic bodies occurring in the cell; some plants, for example rice, need silicon for their growth.⁵⁰⁻⁵² There is some evidence that silicon is important to nail, hair, bone and skin health in humans,⁵³ for example in studies that show that premenopausal women with higher dietary silicon

intake have higher bone density, and that silicon supplementation can increase bone volume and density in patients with osteoporosis.⁵⁴ Silicon is needed for synthesis of elastin and collagen, of which the aorta contains the greatest quantity in the human body⁵⁵ and has been considered an essential element.⁵⁶

Research methods and quantum mechanical techniques

Molecular dynamics

In short the goal of molecular mechanics is to predict the detailed structure and physical properties of molecules. Examples of physical properties that can be calculated include enthalpies of formation, entropies, dipole moments, and strain energies. Molecular mechanics calculates the energy of a molecule and then adjusts the energy through changes in bond lengths and angles to obtain the minimum energy structure.⁸⁻²⁴

$$E_{se} = E_{str} + E_{bend} + E_{str-bend} + E_{oop} + E_{tor} + E_{vdW} + E_{qq} \quad (1)$$

The steric energy, bond stretching, bending, stretch-bend, out of plane, and torsion interactions are called bonded interactions because the atoms involved must be directly bonded or bonded to a common atom. The van der Waals and electrostatic (qq) interactions are between non-bonded atoms.⁸⁻²⁴

Hartree-Fock

The Hartree-Fock self-consistent method^{5-6,27,32} is based on the one-electron approximation in which the motion of each electron in the effective field of all the other electrons is governed by a one-particle Schrödinger equation. The Hartree-Fock approximation takes into account of the correlation arising due to the electrons of the same spin; however, the motion of the electrons of the opposite spin remains uncorrelated in this approximation. The methods beyond self-consistent field methods, which treat the phenomenon associated with the many-electron system properly, are known as the electron correlation methods. One of the approaches to electron correlation is the Møller-Plesset (MP)^{5,6,57,58} perturbation theory in which the Hartree-Fock energy is improved by obtaining a perturbation expansion for the correlation energy.⁵ However, MP calculations are not variational and can produce an energy value below the true energy.⁶ The exchange-correlation energy is expressed, at least formally, as a functional of the resulting electron density distribution, and the electronic states are solved for self-consistently as in the Hartree-Fock approximation.²⁷⁻³⁰ A hybrid exchange-correlation functional is usually constructed as a linear combination of the Hartree-Fock exact exchange functional,

$$E_X^{HF} = -\frac{1}{2} \sum_{i,j} \iint \phi_i^*(r_1) \phi_j^*(r_1) \frac{1}{r_{12}} \psi_i(r_2) \psi_j(r_2) dr_1 dr_2 \quad (2)$$

and any number of exchange and correlation explicit density functional. The parameters determining the weight of each individual functional are typically specified by fitting the functional predictions to experimental or accurately calculated thermochemical data, although in the case of the "adiabatic connection functional" the weights can be set a priori.³² Terms like "Hartree-Fock" or "correlation energy" have specific meanings and are pervasive in the literature.⁵⁹ The vast literature associated with these methods suggests that the following is a plausible hierarchy:

$$HF \ll MP2 < CISD < CCSD < CCSD(T) < FCI \quad (3)$$

The extremes of ‘best’, FCI, and ‘worst’, HF, are irrefutable, but the intermediate methods are less clear and depend on the type of chemical problem being addressed.⁴ The use of HF in the case of FCI was due to the computational cost.

For calculations a cluster of six computer models was used: Prescott–256 Celeron © D processors,² featuring double the L1 cache (16 KB) and L2 cache (256 KB), Socket 478 clock speeds of 2.13GHz; Memory DDR2 PC4200 512MB; Hitachi HDS728080PLAT20 80GB and CD–R. The dynamic was held in Molecular Mechanics Force Field (Mm+), Equation (1), after the quantum computation was optimized via Mm+ and then by RHF^{5,6,27–32} in the TZV^{33,34} sets bases. The molecular dynamics at algorithm Polak–Ribiere,⁶⁰ conjugate gradient, at the termination condition: RMS gradient⁶¹ of 0.1kcal/A.mol or

405 maximum cycles in vacuum.^{6,41} The first principles calculations have been performed to study the equilibrium configuration of C₁₃H₂₀BeLi₂SeSi molecule using the Hyperchem 7.5 Evaluation,⁴¹ Mercury 3.8 a general molecular and electronic structure processing program,¹⁸ GaussView 5.0.8⁶⁴ an advanced semantic chemical editor, visualization, and analysis platform and GAMESS is a computational chemistry software program and stands for General Atomic and Molecular Electronic Structure System⁷ set of programs. The first principles approaches can be classified in the Restrict Hartree–Fock approach (Figure 1) (Figure 2).^{5,6,27–32}

The Figure 2 shows the final stable structure of the Bio–inorganic molecule obtained by an *ab initio* calculation with the method RHF^{5–6,27–32} TZV^{33–34} starting from the molecular structure of Figure 1 obtained through a molecular mechanical calculation, method Mm+ and BioCharmm.^{8–24,65–230}

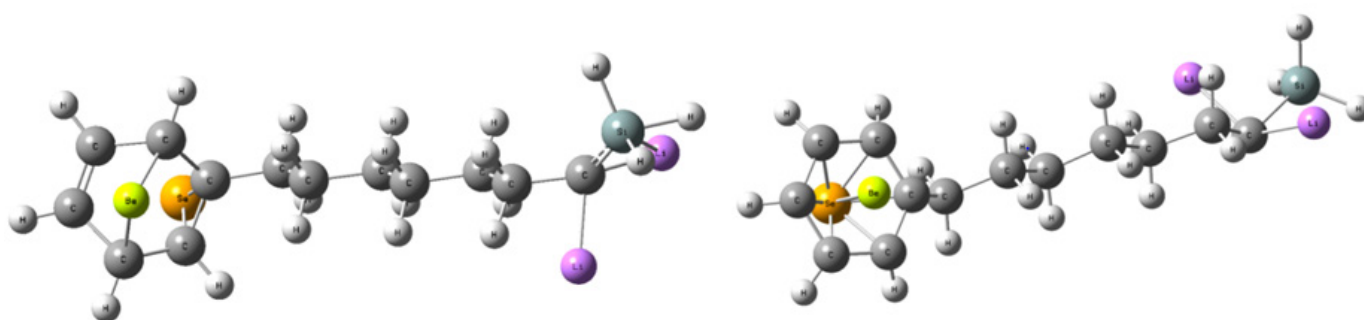


Figure 1 Above and to the left the representation of the molecular structure of C₁₃H₂₀BeLi₂SeSi seed obtained after dynamics with Molecular Mechanic. The geometry was optimized via BioCharmm and Mm^{8–24,26} obtained using computer programs HyperChem 7.5 Evaluation,²⁶ Above and to the right the representation of the molecular structure of C₁₃H₂₀BeLi₂SeSi, obtained through computer via *ab initio* calculation method RHF^{5,6,27–32} TZV^{33,34} sets bases obtained using computer programs GAMESS.⁷ Images obtained in the software Mercury 3.8.¹⁸ Represented in bluish gray color the atom of silicon, in the purple color lithium, in the lemon yellow color beryllium, in the orange the selenium, in dark gray color carbon and in light gray color hydrogen

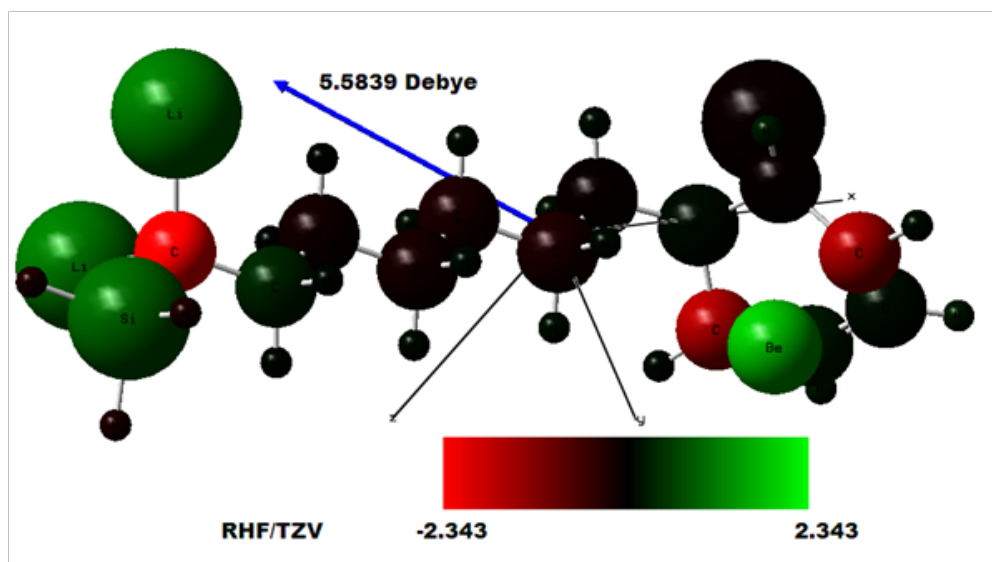


Figure 2 Molecule seed Bio–inorganic after dynamics with method *ab initio*. The molecule has a length of 15.799Å, obtained through computer via *ab initio* calculation method RHF^{5,6,27–32} TZV^{33,34} sets bases obtained using computer software GAMESS.⁷ Represented in green color the positive charge, passing through the absence of color – black – zero charge, for the positive charge red color. $A\Delta\delta = 4.686$ a.u. of elemental charge e ($e = \pm 1,607 \times 10^{-19}$ C). Images obtained in the software Gaussview, Version 5, 2009.⁶⁴

Results, discussions and conclusions

The molecular structure shown in Figure 2 of the bio-inorganic molecule $C_{13}H_{20}BeLi_2SeSi$, is represented in structure in the form of the van der Waals radius, with the charge distribution through it, whose charge variation is $\Delta\delta = 4.686$ au of elemental charge. In green color the intensity of positive charge displacement. In red color the negative charge displacement intensity. Variable, therefore, of $\delta^- = 2.343$ a.u. negative charge, passing through the absence of charge displacement, represented in the absence of black – for the green color of $\delta^+ = 2.343$ a.u. positive charge. The electric dipole moment obtained was 5.5839 Debye, perpendicular to the main axis of the molecule. By the distribution of charge through the bio-inorganic molecule it is clear that the molecule has a polar-apolar-polar structure, with neutral charge distributed on its main axis, the carbonic chain. A strong positive charge displacement (cation) at the polar ends of the molecule, in the two lithium and silicon atoms, bound to the carbon atom with strong negative (anion). Therefore, there is a displacement of electrons from the two lithium and silicon atoms towards the carbon attached to them. At the other end of the cyclic chain, attached to it is the totally neutral Selenium atom, while the beryllium is extremely charged with positive charge (cationic), represented in green color. While the two carbon atoms of the cyclic chain connected to Beryllium, with negatively charged (anionic), represented in red color. It happened, therefore, a displacement of electrons of the Beryllium atom towards the Carbons connected to it.

The calculations obtained by the RHF method, on the TZV sets basis, for the molecule $C_{13}H_{20}BeLi_2SeSi$ are plausible, correct and predicted by quantum chemistry. The structure of the Bio-inorganic seed molecule for a biomembrane genesis that defies the current concepts of a protective mantle structure of a cell such as biomembrane to date is promising, challenging. Leaving the biochemists their experimental synthesis. The quantum calculations must continue to obtain the structure of the bio-inorganic biomembrane.

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