

Molecular electrostatic potential of the main monoterpenoids compounds found in oil Lemon Tahiti - (*Citrus Latifolia Var Tahiti*)

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Abstract

The work is a study of the geometry of the molecules via molecular mechanics of the main monoterpenoids found in the oil of Lemon Tahiti. Lemon Tahiti is the result of grafting of Persia file on Rangpur lime and has no seeds. A computational study of the molecular geometry of the molecules through molecular mechanics of the main monoterpenoids compounds present in fruit oil is described in a computer simulation. The fruit has active terpenoids compounds: α -pinene, β -pinene, limonene and γ -terpinene. The studied monoterpenoids form two groups of distribution characteristics of fillers and similar electrical potentials between groups. Since α -pinene and limonene present, major and minor moment of electric dipoles, respectively.

Keywords

Citrus Latifolia, Citrus essential oil, Lemon Tahiti, Limonene, α -Pinene, β -Pinene, γ -Terpinene, Molecular Geometry, Molecular Mechanics.

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Introduction

Fruits Lemon Tahiti - *Citrus Latifolia var Tahiti*. Lemon Tahiti is the result of grafting of Persia file on Rangpur lime and has no seeds. The fruit has green bark, smooth or slightly rough, the most popular variety in the country, 90% of the plantations. The yield of juice is 50%, against 42% of real lemon (Sicilian) and is widely used in ice cream recipes and pastries. Well suited to the tropical climate, you need a lot of sun and humidity controlled to bear fruit juicy and adults, but it is very resistant to attack by disease, the most suitable for commercial cultivation and consumption "in natura". [1]

Fruit grow at home is a luxury and among the best-ranked small trees, citrus have secured place. Trees lemons, acid limes and oranges can be planted at hand, in the garden or in pots on sunny balconies. And within that list four species stand out for home planting: the Galician lemons, Tahiti, Cloves and Sicilian, which are easy to grow and occupy smaller spaces. Among these copies only the lemon is actually a lemon. Originally from Asia, the Sicilian is widely grown in the northern hemisphere, since it is not well suited to tropical climates. Here, the most frequently used, such as limes and Galician are actually acid limes, adaptable to the climate, which differ in taste and appearance of lemons,



Figure 1. Fruits Lemon Tahiti, *Citrus Latifolia*. [1]

but have better income and similar nutritional characteristics. Regardless of type, all have sour taste, originating in citric acid, and vitamin C, effective in combating colds and flu and still serve the cosmetics and chemical industry, lending its essence soaps, perfumes and cleaning products. [2]

The Tahiti lime is widely used in cooking, cleaning and preparing food (meat, pasta, cakes, confectionery) and preparing the delicious lemonade. Its fruits are ripe around 120 days after flowering and the seeds are rare or absent. In home medication the fruit is used as an aid in the treatment of colds and deficiency of vitamin C. [3]

0.1 Tree

Citrus latifolia, usually called Citrus Tahiti, is a vigorous tree, largely extended, measuring 4.5 to 6 m, almost without spines, dense green foliage. The leaves are of average sizes, large lancelets, petiole in the shape of wings. The young growths are purplish. *Citrus latifolia* has marvellous scented flowers. The skin of the fruit is sharp green in colour and becomes pale yellow when the fruit is ripe. It is fine, adhering to the pulp which is greenish pulp, very acidic, juicy and almost deprived of pectin. For storage, the fruits do not require any treatment. The fresh fruits could remain in good condition for 6 to 8 weeks under refrigeration. [4]

0.2 Scientific classification

Kingdom: *Plantae*
Division: *Magnoliophyta*
Class: *Magnoliopsida*
Order: *Sapindales*
Family: *Rutaceae*
Genus: *Citrus*
Species: *Citrus latifolia*
Binomial name: *Citrus Latifolia* Var *Tahiti*
[6]



Figure 2. Fruit from Tahiti Limon sliced - *Citrus Latifolia*. [5]

0.3 *Citrus Latifolia* Tanaka

Synonyms: *Citrus aurantiifolia* (Christm.) Swingle) var. *latifolia* Yu. Tanaka, *Citrus aurantiifolia* (Christm. et Panz.) Swingle var. *tahiti hort.*

Chinese: Kuan ye lai mu.

English: Tahiti lime, Seedless lime, Persian lime, Bearss lime.

Finnish: Persian limetti.

French: Lime de Perse, Lime de Tahiti, Limettier de Tahiti.

German: Persische Limette, Tahitilimette, Tahiti-Limonelle, Tahiti-Limonellenbaum.

Italian : Limetta di Tahiti.

Japanese: Tahichi raimu.

Portuguese: Limeira Bearss, Limão Tahiti.

Spanish: Lima común da Persia, Limero de Tahiti.

Vietnamese: Chanb Ba Tú, Chanh không, Chanh Tahiti.

[7]

0.4 Terpenes

Terpenes are a large and diverse class of organic compounds, produced by a variety of plants, particularly conifers [8], though also by some insects such as termites or swallowtail butterflies, which emit terpenes from their osmeteria. They are often strong-smelling. They may protect the plants that produce them by deterring herbivores and by attracting predators and parasites of herbivores [9]. Many terpenes are aromatic hydrocarbons and thus may have had a protective function [10]. The difference between terpenes and terpenoids is that terpenes are hydrocarbons, whereas terpenoids contain additional functional groups.

They are the major components of resin, and of turpentine produced from resin. The name “terpene” is derived from the word “turpentine”. In addition to their roles as end-products in many organisms, terpenes are major biosynthetic building blocks within nearly every living creature. Steroids, for example, are derivatives of the triterpene squalene.

When terpenes are modified chemically, such as by oxidation or rearrangement of the carbon skeleton, the resulting compounds are generally referred to as terpenoids. Some authors will use the term terpene to include all terpenoids.



Figure 3. Resin of tree. Many terpenes are derived commercially from conifer resins, such as those made by this pine. [11, 12]

Terpenoids are also known as isoprenoids.

Terpenes and terpenoids are the primary constituents of the essential oils of many types of plants and flowers. Essential oils are used widely as fragrances in perfumery, and in medicine and alternative medicines such as aromatherapy. Synthetic variations and derivatives of natural terpenes and terpenoids also greatly expand the variety of aromas used in perfumery and flavors used in food additives. Vitamin A is a terpene.

Terpenes are released by trees more actively in warmer weather, acting as a natural form of cloud seeding. The clouds reflect sunlight, allowing the forest to regulate its temperature. [13]

The aroma and flavor of hops, highly desirable in some beers, comes from terpenes. Of the terpenes in hops myrcene, β -pinene, β -caryophyllene, and α -humulene are found in the largest quantities. [14, 11, 12]

0.4.1 Monoterpene

More than 85% of volatile oil found in monoterpeneoides Lemon Tahiti are: limonene (52.20%), γ -terpinene (17%), α -pinene (3.2%) and β -pinene (13.00%) [15]

Monoterpenes are a class of terpenes that consist of two isoprene units and have the molecular formula $C_{10}H_{16}$. Monoterpenes may be linear (acyclic) or contain rings. Biochemical modifications such as oxidation or rearrangement produce the related monoterpeneoids.

Acyclic monoterpenes

Biosynthetically, isopentenyl pyrophosphate and dimethylallyl pyrophosphate are combined to form geranyl pyrophosphate.

Elimination of the pyrophosphate group leads to the formation of acyclic monoterpenes such as ocimene and the myrcenes. Hydrolysis of the phosphate groups leads to the prototypical acyclic monoterpeneoid geraniol. Additional rearrangements and oxidations provide compounds such as citral, citronellal, citronellol, linalool, and many others. Many monoterpeneoids found in marine organisms are halogenated, such as halomon.

Monocyclic monoterpenes

In addition to linear attachments, the isoprene units can make connections to form rings. The most common ring size in monoterpenes is a six-membered ring. A classic example is the cyclization of geranyl pyrophosphate to form limonene. The terpinenes, phellandrenes, and terpinolene are formed similarly. Hydroxylation of any of these compounds followed by dehydration can lead to the aromatic p-cymene. Important terpenoids derived from monocyclic terpenes are menthol, thymol, carvacrol and many others.

Bicyclic monoterpenes

Geranyl pyrophosphate can also undergo two sequential cyclization reactions to form bicyclic monoterpenes, such as pinene which is the primary constituent of pine resin. Other bicyclic monoterpenes include carene, sabinene, camphene, and thujene. Camphor, borneol and eucalyptol are examples of bicyclic monoterpeneoids containing ketone, alcohol, and ether functional groups, respectively. [11, 12]

Role in climate

Monoterpenes are emitted by forests and form aerosols that can serve as cloud condensation nuclei (CCN). Such aerosols can increase the brightness of clouds and cool the climate. [16]

1. Fundamentals and Methods

1.1 Introduction to Molecular Mechanics

The “mechanical” molecular model was developed out of a need to describe molecular structures and properties in as practical a manner as possible. The range of applicability of molecular mechanics includes:

- Molecules containing thousands of atoms.

- Organics, oligonucleotides, peptides, and saccharides (metallo-organics and inorganics in some cases).
- Vacuum, implicit, or explicit solvent environments.
- Ground state only.
- Thermodynamic and kinetic (via molecular dynamics) properties.

The great computational speed of molecular mechanics allows for its use in procedures such as molecular dynamics, conformational energy searching, and docking. All the procedures require large numbers of energy evaluations. Molecular mechanics methods are based on the following principles:

- Nuclei and electrons are lumped into atom-like particles.
- Atom-like particles are spherical (radii obtained from measurements or theory) and have a net charge (obtained from theory).
- Interactions are based on springs and classical potentials.
- Interactions must be preassigned to specific sets of atoms.
- Interactions determine the spatial distribution of atom-like particles and their energies.

Note how these principles differ from those of quantum mechanics. [17, 18, 19, 20, 21]

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. [18, 19, 20, 21]

1.2 Steric Energy

A molecule can possess different kinds of energy such as bond and thermal energy. Molecular mechanics calculates the steric energy of a molecule—the energy due to the geometry or conformation of a molecule. Energy is minimized in nature, and the conformation of a molecule that is favored is the lowest energy conformation. Knowledge of the conformation of a molecule is important because the structure of a molecule often has a great effect on its reactivity. The effect of structure on reactivity is important for large molecules like proteins. Studies of the conformation of proteins are difficult and therefore interesting, because their size makes many different conformations possible.

Molecular mechanics assumes the steric energy of a molecule to arise from a few, specific interactions within a molecule. These interactions include the stretching or compressing of bonds beyond their equilibrium lengths and angles, torsional effects of twisting about single bonds, the Van der Waals attractions or repulsions of atoms that come close together, and the electrostatic interactions between partial charges in a molecule due to polar bonds. To quantify the contribution of each, these interactions can be modeled by a potential function that gives the energy of the interaction as a function of distance, angle, or charge^{1,2}. The total steric energy of a molecule can be written as a sum of the energies of the interactions:

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

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. [18, 19, 20, 21].

As mentioned above, the expression for the potential energy of a molecular system that is used most frequently for simple organic molecules and biological macromolecules is the following:

$$V(r) = \sum_{bonds} \frac{k_d}{2} (d - d_o)^2 + \sum_{angles} \frac{k_\theta}{2} (\theta - \theta_o)^2 + \sum_{dihedrals} \frac{k_\phi}{2} (1 + \cos(\phi - \phi_o)) + \sum_{impropers} \frac{k_\psi}{2} (\psi - \psi_o)^2 + \sum_{no-bonded\ pairs(i,j)} 4\epsilon_{ij} \left[\left(\frac{\sigma^{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma^{ij}}{r_{ij}} \right)^6 \right] + \sum_{no-bonded\ pairs(i,j)} \frac{q_i q_j}{\epsilon_D r^{ij}} \quad (2)$$

[22]

1.3 Geometry Optimization

The dynamic was held in Molecular Mechanics Force Field (Mm+), Equations (1) and (2), computed geometry optimization molecular at algorithm Polak-Ribiere [23], conjugate gradient, at the termination condition: RMS gradient [24] of 0,1 kcal/A.mol or 405 maximum cycles in vacuum. Molecular properties: electrostatic potential 3D mapped isosurface, mapped function range, minimum 0.065 at maximum 0.689, display range legend, from positive color red to negative color blue, total charge density contour value of 0.05, gourand shaded surface. [21]

2. Physico-chemical properties of the monoterpenoid

2.1 Limonene

Limonene is a colourless liquid hydrocarbon classified as a cyclic terpene. The more common d-isomer possesses a strong smell of oranges [25]. It is used in chemical synthesis as a precursor to carvone and as a renewables-based solvent in cleaning products.

Limonene takes its name from the lemon, as the rind of the lemon, like other citrus fruits, contains considerable amounts of this compound, which contributes to their odor. Limonene is a chiral molecule, and biological sources produce one enantiomer: the principal industrial source, citrus fruit, contains d-limonene ((+)-limonene), which is the (R)-enantiomer. Racemic limonene is known as dipentene [26]. d-Limonene is obtained commercially from citrus fruits through two primary methods: centrifugal separation or steam distillation.

CAS No. 138-86-3

Chemical Name: Limonene

Synonyms: 1-Methyl-4-(1-methylethenyl)-cyclohexene;

4-Isopropenyl-1-methylcyclohexene; p-Menth-1,8-diene;

Racemic: DL-limonene; Dipentene; D-Limonene;

(+)-Limonene; (+)-(4R)-Limonene; (+)-carvone;

(4R)-Limonene; Citrene

Odor: pleasant lemon-like

Molecular Formula: C₁₀H₁₆

Molar mass: 136.23404 g/mol

Density: 0.8411 g/cm³

Melting point: -74.35 °C (-101.83 °F; 198.80 K)

Boiling point: 176 °C (349 °F; 449 K)

Solubility in water: insoluble

Solubility: miscible in alcohol, benzene, chloroform, ether, CS₂, and oils, soluble in CCl₄

Stability: Stable. Flammable. Incompatible with strong oxidizing agents.

[27, 28, 29, 30]

2.2 α -Pinene

α -Pinene is an organic compound of the terpene class, one of two isomers of pinene. It is an alkene and it contains a reactive four-membered ring. It is found in the oils of many species of many coniferous trees, notably the pine. It is also found in the essential oil of rosemary (*Rosmarinus officinalis*) [31]. Both enantiomers are known in nature; (1S,5S)- or (-)- α -pinene is more common in European pines, whereas the (1R,5R)- or (+)- α -isomer is more common in North America. The racemic mixture is present in some oils such as eucalyptus oil and orange peel oil. [26]

CAS No. 67762-73-6; 7785-70-8; 80-56-8

Chemical Name: α -pinene

Synonyms: Alfa-Pinene; 2-Pinene; Acintene A; .alpha.-Pinene;

Pinene isomer; Pinene, Alpha;

4,6,6-trimethylbicyclo[3.1.1]hept-3-ene

2,6,6-Trimethylbicyclo[3.1.1]hept-2-ene

Appearance: Clear colorless liquid

Molecular Formula: C₁₀H₁₆

Molar mass: 136.23404 g/mol

Density: 0.858 g/mL (liquid at 20 °C)

Melting point: -64 °C (-83 °F; 209 K)

Boiling point: 155 °C (311 °F; 428 K)

Solubility in water: Very low

Solubility: miscible in acetic acid, ethanol and acetone

Stability: Main hazards, flammable.

[27, 28, 29, 32]

2.3 β -Pinene

Beta-Pinene (β -pinene) is a monoterpene, an organic compound found in plants. It is one of the two isomers of pinene, the other being α -pinene. It is colorless liquid soluble in alcohol, but not water. It has a woody-green pine-like smell.

This is one of the most abundant compounds released by forest trees [33]. If oxidized in air, the allylic products of the pinocarveol and myrtenol family prevail. [34]

CAS No. 127-91-3

Chemical Name: β -pinene

Synonyms: 2,2,6-Trimethylbicyclo(3.1.1)hept-2-ene;

6,6-dimethyl-2-methylene-bicyclo(3.1.1)heptan;

6,6-dimethyl-2-methylene-bicyclo[3.1.1]heptan;

6,6-dimethyl-2-methylenebicyclo[3.1.1]heptane;

beta-1-Pinene;1-beta-Pinene; Nopinene; Nopinene;

2(10)-Pinene; Pseudopinene

Appearance: Colourless liquid

Molecular Formula: C₁₀H₁₆

Molar mass: 136.23404 g/mol

Density: 0.872 g/cm³

Refractive index: 1.4782

Melting point: -61 °C

Boiling point: 167 °C

[27, 28, 29, 35]

2.4 γ -Terpinene

γ -Terpinene and δ -terpinene (also known as terpinolene) are natural and have been isolated from a variety of plant sources.

Terpinolene is a water-white to light amber colored liquid. Insoluble in water and less dense than water. Used to make plastics and resins.

Low cost fragrance material used in citrus, pinaceous and herbaceous types. [36]

CAS No. 138-86-3; 99-85-4

Chemical Name: γ -terpinene Synonyms: P-Mentha-1,4-Diene;

Terpinene, Gamma-;

1,4-Cyclohexadiene, 1-methyl-4-isopropyl-;

1-isopropyl-4-methyl-1,4-cyclohexadiene;

1-Isopropyl-4-methyl-cyclohexa-1,4-diene;
 1-methyl-4-(1-methylethyl)-1,4-cyclohexadiene;
 1-methyl-4-(1-methylethyl)-4-cyclohexadiene;
 1-Methyl-4-isopropyl-1,4-cyclohexadiene;
 Crithmene; Moslene

Appearance: clear, colorless to faintly yellow

Molecular Formula: C₁₀H₁₆

Molar mass: 136.23404 g/mol

Density: 0.85 g/cm³

Boiling point: 182 °C

Solubility in water: Soluble [37, 27, 28, 29]

Table 1. Molecular electrostatic potential of the Monoterpenoids.

	1	2	3	4
Red (δ^+)	0.319	0.318	0.320	0.320
Blue (δ^-)	0.126	0.128	0.136	0.135
$\Delta\delta$	0.193	0.190	0.184	0.185

(1) α -Pinene; (2) β -Pinene; (3) Limonene and (4) γ -Terpinene.

3. Discussions

The method of molecular dynamics was Mm+ Equations (1) and (2) using *HyperChem 7.5 Evaluation* software. [38]

Figures 1 shows a photo of the fruits of Lemon Tahiti. Figure 2 shows the fruits of Lemon Tahiti cut into slices. Figure 3 shows a picture of a pine tree that is excreting resin. Figures 4 to 7 represent the electrostatic potential and molecular structure of each compound monoterpene studied with their respective charges density, and molecular geometry of the main monoterpene of the fruit after a molecular dynamics Mm+ using *HyperChem 7.5 Evaluation* software. [38]

Figure 4 and 5 is α -pinene and β -pinene compounds, respectively. Figures 6 and 7 depict the compounds Limonene and γ -terpinene, respectively.

Table 1 shows the densities of the respective charges monoterpene: α -pinene, β -pinene, gamma-terpinene and Limonene. According to the densities of charges obtained in Mm + calculation are formed by two distinct groups terpenoids. Group 1, represented by compounds: α -pinene and β -pinene and Group 2, represented by Limonene compounds and γ -terpinene. The Group 1 has a dipole moment greater than the second group, and the α -pinene has the highest electric dipole moment, limonene and the lowest electric dipole moment.

The α -pinene has a lower boiling point and lower electric dipole moment, and slightly soluble in water.

The β -pinene has boiling point, electric dipole moment larger than α -pinene and insoluble in water.

The γ -terpinene has a higher boiling point and higher electric dipole moment than the Limonene, water-soluble.

Limonene has the lowest boiling point of the γ -terpinene, and the lowest electric dipole moment and is insoluble in water.

That have higher and lower boiling point, and γ -terpinene, α -pinene, respectively, are soluble in water and electric dipole moments with large differences.

4. Conclusions

The study of molecular structure and the electric potential of the main monoterpene found in the volatile oils from the fruit peel Lime Tahiti, which correspond more than 85% of terpenes in the fruit.

The studied monoterpene form two groups of distribution characteristics of fillers and similar electrical potentials between groups. Since α -pinene and limonene present, major and minor moment of electric dipoles, respectively.

Group 1, represented by compounds: α -pinene and β -pinene and Group 2, represented by limonene compounds and γ -terpinene. The Group 1 has a dipole moment greater than the second group.

5. Attachments

5.1 Monoterpene figures

Figura 4. α -Pinene

Figura 5. β -Pinene

Figura 6. Limonene

Figura 7. γ -Terpinene

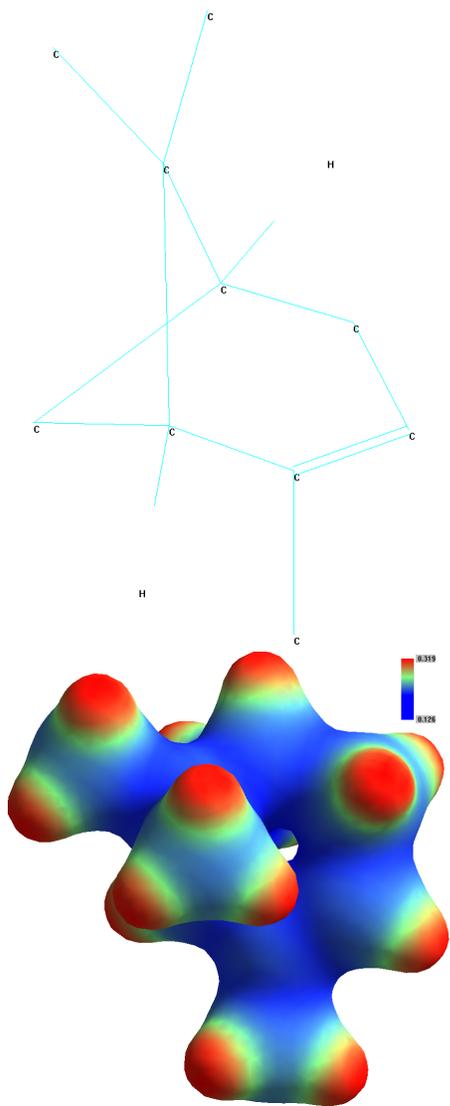


Figure 4. α -Pinene.

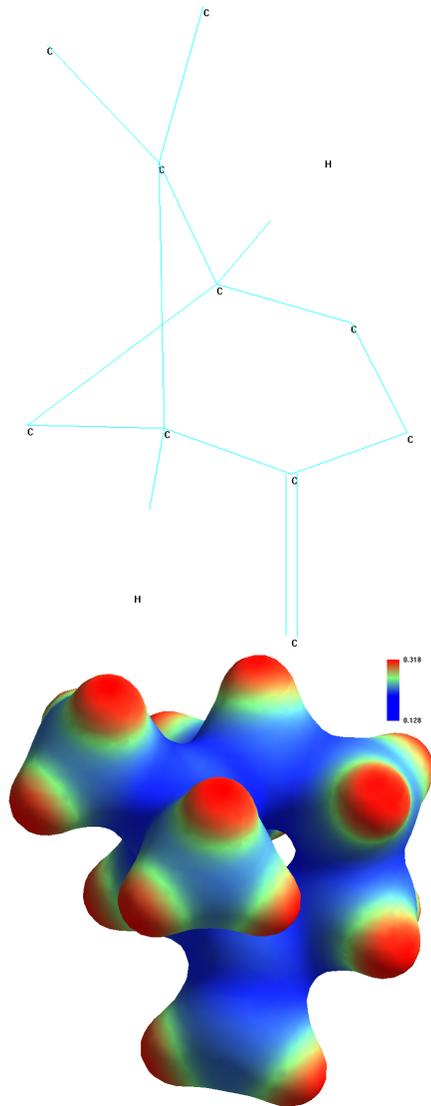


Figure 5. β -Pinene.

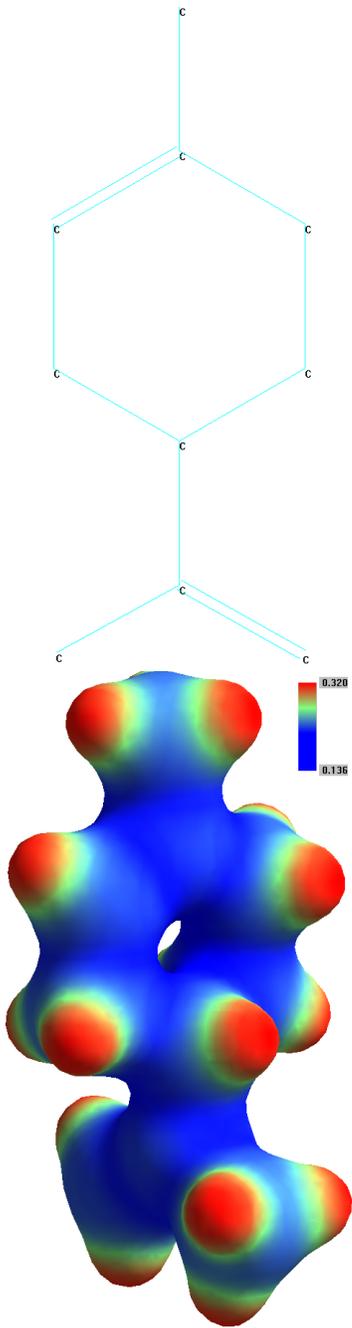


Figure 6. Limonene.

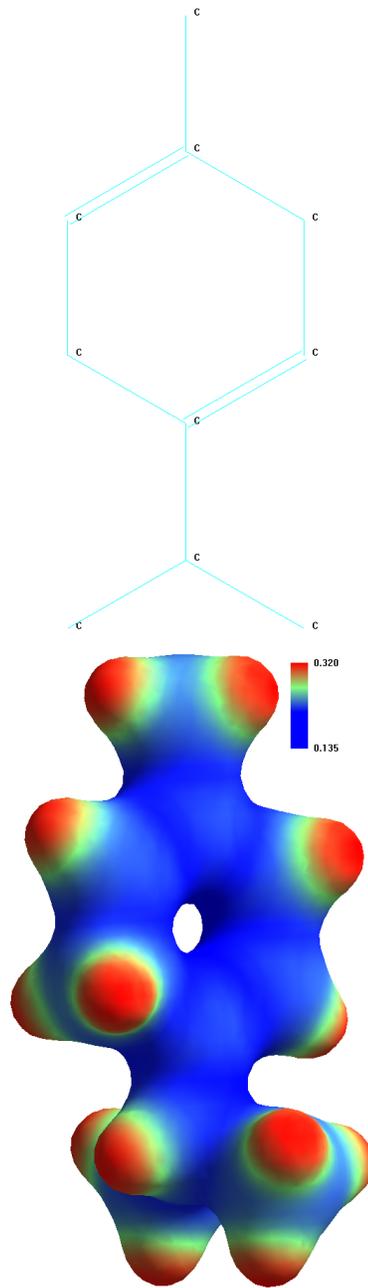


Figure 7. γ -Terpinene.

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