



Linoleic acid and its potassium and sodium salts: A combined experimental and theoretical study



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ABSTRACT

Linoleic acid (*cis*, *cis*-9,12-octadecadienoic acid) is the main polyunsaturated -omega 6- essential fatty acid. The conformational behaviour of linoleic acid (LA) in the gas phase was investigated by means of density functional theory (DFT). The structures of conformers of LA were fully optimized by using the B3LYP/6-311++G(d,p) method. The theory showed that the tttttt'CssCs'tt conformation of LA (conformer I) is the more stable than the other conformations.

Fourier Transform Infrared (FTIR) and micro-Raman spectra of pure LA in liquid form were recorded in the region 4000–450 and 3500–100 cm⁻¹, respectively. The DFT calculations on the molecular structure and vibrational spectra of the dimer form of most stable conformer of LA were also performed using the same method. The assignment of the vibrational modes was made based on calculated potential energy distributions (PEDs). The simulated spectra of dimer form of LA are in reasonably good agreement with the experimental spectra.

The sodium and potassium salts of LA were synthesized and characterized by FTIR and Raman spectroscopy, X-ray diffraction and DFT calculations. Several molecular and electronic properties of LA and its salts such as HOMO-LUMO energies, chemical hardness and electronegativity were also calculated and interpreted.

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1. Introduction

A rapidly growing literature describes the benefits of polyunsaturated fatty acids in alleviating cardiovascular disease, atherosclerosis, autoimmune disorder, diabetes, and other diseases. *Omega 6 Fatty acids* are a class of polyunsaturated fats which have been growing in prevalence in modern diets [1].

Linoleic acid, an omega-6 fatty acid (*cis*, *cis*-9,12-octadecadienoic acid) is considered essential fatty acid because it cannot be synthesized by human body. It is used in the biosynthesis of prostaglandins and cell membranes [2].

In all omega-6 fatty acids, the first double bond is located between the sixth and seventh carbon atom from the methyl end of the fatty acid. Linoleic acid (LA) has two *cis* double bonds with an 18-carbon chain (Scheme 1). It is present mostly in plant oils [3].

In the body, essential fatty acids serve multiple functions. It is important to elucidate the structural properties. Single crystal

study on linoleic acid, alpha-linoleic acid and arachidonic acid showed that polyunsaturated chains in crystals form highly ordered, and The closely packed molecules are stretched at a specific conformation [4].

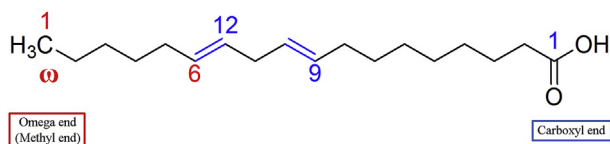
Rich [5] used quenched molecular dynamics simulations in vacuo and investigated conformational space of arachidonic (20:4) and related fatty acids: linoleic (18:2), oleic (18:1), arachidic (20:0), and stearic (18:0). Recent investigation using powder X-ray diffraction (XRD) indicated that there are three kinds of polymorphic phases in linoleic acid, low-temperature (LT, -20°), middle-temperature (MT, -40°) and high-temperature (HT, -60°) [6].

Vibrational spectroscopy has been used extensively for getting molecular structure information about biological compounds. FTIR spectroscopy has been applied to the determination of standard indices used in the classification of edible oils, such as the free fatty acids content [7–9].

Temperature-dependent FTIR spectra of linoleic acid were measured over a temperature range of -80 to -30 °C to explore solid-state phase transition of linoleic acid [10]. In a recent study,

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Scheme 1. Chemical structure of linoleic acid (LA).

Raman spectroscopy was used for the screening the oxidation process of linoleic acid [11].

Although these studies are helpful in elucidating the conformational space of LA, they did not analyse the vibrational properties of LA, in detail. On the other hand, up till now no vibrational study has been reported on the dimer form of LA. The present study describes a thorough conformational analysis of linoleic acid (LA) using density functional theory (DFT). A total of three energy minima were identified and characterized by means of B3LYP/6-311++G(d,p) geometry optimization in the gas phase for LA.

We also synthesized sodium (Na) and potassium (K) salts [sodium linoleate and potassium linoleate] of LA. These salts are commonly called soap salts. Fatty acids are poorly soluble in water in their undissociated (acidic) form, whereas they are relatively hydrophilic as potassium or sodium salts. Some potassium salts of fatty acids are also used as multi-purpose food additives. Therefore, the studies presented here also aiming to understanding of structural, electronic and vibrational properties for Na and K salts of LA.

The experimental FTIR and Raman spectra of liquid LA, Na and K salts of linoleic acid (solid form) were recorded. Density functional theory (DFT) calculations have been used to predict the theoretical spectra and to assist reliable assignments of the experimental frequencies.

2. Materials and methods

2.1. Experimental

Linoleic acid (Sigma-Aldrich, >99% purity) was purchased and to avoid oxidation stored at -20°C . All chemical compound used here were grade and used without further purification.

Linoleic acid (7.0 mmol) was dissolved in absolute ethanol (10 mL) and was reacted with 1 M sodium hydroxide or potassium hydroxide stock solution (7.0 mL). The mixture was refluxed for 60 min. The precipitate was filtered and washed with ethanol (70%). Sodium [sodium linoleate ($\text{C}_{18}\text{H}_{31}\text{NaO}_2$) and potassium [potassium linoleate ($\text{C}_{18}\text{H}_{31}\text{KO}_2$)] salts of linoleic acid were dried at 35°C in a vacuum oven for one day.

2.2. Vibrational spectra

ATR-FTIR spectra of LA and its salts were recorded using Perkin Elmer Spectrum 100 FTIR spectrometer at a spectral resolution of 4 cm^{-1} over 32 scans in the range of $4000\text{--}650\text{ cm}^{-1}$. FTIR spectra ($4000\text{--}450\text{ cm}^{-1}$) were also recorded from KBr pellets of salts.

Micro-Raman spectra were collected on a LabRAM (Horiba-Jobin-Yvon) spectrometer using a 632.8 nm excitation line from a He-Ne laser. A $100\times$ objective (Olympus, France) was used for focusing and collecting scattered Raman light. The laser power was approximately 10 mW on the sample surface.

2.3. XRD patterns of salts

The powder X-ray diffractometer (XRD, Rigaku D-Max B horizontal diffractometer) was used in order to record the diffraction

patterns ($10^{\circ} \leq 2\theta \leq 60^{\circ}$) solid form of sodium and potassium salts of LA at room temperature employing $\text{CuK}\alpha$ (1.5405 \AA) radiation.

2.4. Calculation

All the calculations were performed using Gaussian 09 Revision A.02 program [12] running on a unix system (Ubuntu 14.04.4 LTS) and GaussView 5.0.8. was used for visualization of the structure and simulated vibrational spectra.

The initial structure [4] of linoleic acid was obtained from Cambridge Structure Database (CSD LINOLA, NBS515621) and conformational analysis were carried out by using the density functional theory DFT(B3LYP) method. The level of theory used was Becke's three-parameter exchange functional [13] in combination with the correlation functional of Lee, Yang, and Parr [14] and the 6-311++G(d,p) basis set.

The relaxed potential energy scans were performed for rotation around the C9-C10-C11-C12 and C10-C11-C12-C13 dihedral angles (Fig. 1), starting from the initial optimized geometry of LA. The relaxed potential energy scan was also performed for rotation around the C1-C2-O25-H52 dihedral angle, starting from the lowest energy minimum of LA in the first PES. Conformational searches were performed by varying the respective dihedrals in steps of 10° from -180° to 180° . Then all energy minima were re-optimized again at the DFT/B3LYP/6-311 ++ G(d,p) and the three lowest-energy conformers are predicted in gas phase.

Geometry optimizations were followed by harmonic vibrational frequency calculations. We verified that all the vibrational frequencies of each equilibrium structure were real (no imaginary vibrational frequencies).

The harmonic vibrational frequencies were scaled by 0.96 (above 1800 cm^{-1}) and 0.98 (under 1800 cm^{-1}). The vibrational normal modes were analysed by carrying out the Potential Energy Distribution (PED) calculations using VEDA (Vibrational Energy Distribution Analysis) program [15]. This program reads the input data (molecular geometry in cartesian coordinates, force constant matrix and frequencies) from the output file of Gaussian program. In this program, the theoretical normal modes are represented by internal coordinates to generate symmetry coordinates. The initial coordinates (stretching and bending) is replaced by the set of internal coordinates, which was defined following the recommendations of Pulay et al. [16] and PED is recalculated. The average max. potential energy (EPM) value obtained for LA in this study was equal to 71.67%. Vibrational assignments were made on the basis of PED and with the help of GaussView graphical animation.

Calculation of LA in the dimer form was also carried out to improve the assignment of the bands in the liquid state experimental spectrum. The optimum geometries and harmonic vibrational wavenumbers of Na and K salts of LA were calculated using same method.

The calculated Raman activities by GAUSSIAN-09 program were subsequently converted to relative Raman intensities with Gauss-Sum program [17] according to the following equation [18]:

$$I_i = \frac{f(\nu - \nu_i)^4 S_i}{\nu_i \left[1 - \exp\left(-\frac{h\nu_i}{kT}\right) \right]} \quad (1)$$

where ν_0 is the exciting frequency (in this study we have used $15,822.78\text{ cm}^{-1}$), ν_i is the calculated vibrational frequency (cm^{-1}) of the i th normal mode, S_i is the Raman scattering activity of the i th normal mode. h ; c and k are fundamental constants, and f is normalization factor (10^{-12}) for all peak intensities. For the plots of simulated Raman spectra, Lorentzian band shapes were used with a bandwidth (FWHM) of 10 cm^{-1} .

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