Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 145 (2015) 340–352

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Molecular structure, vibrational, electronic and thermal properties of 4-vinylcyclohexene by quantum chemical calculations

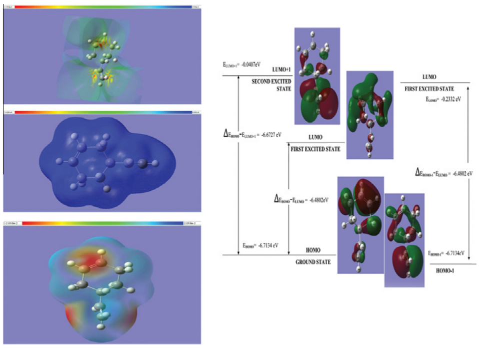
P.B. Nagabalasubramanian [a,*], S. Periandy [b], Mehmet Karabacak [c], M. Govindarajan [d]

[a] *Department of Physics, Arignar Anna Govt. Arts & Science College, Karaikal, Puducherry, India*
[b] *Department of Physics, Tagore Arts College, Puducherry, India*
[c] *Department of Mechatronics Engineering, H.F.T. Technology Faculty, Celal Bayar University, Turgutlu, Manisa, Turkey*
[d] *Department of Physics, Avvaiyar Govt. College for Women, Karaikal, Puducherry, India*

HIGHLIGHTS

- Spectroscopic features of 4-VCH were examined my FT-IR and FT-Raman.
- Frontier molecular orbital, global reactivity descriptors and electronic transitions were analyzed.
- Stability, charge delocalization were analyzed using NBO theory.
- Comparison of atomic charges by Mulliken and NBO analyses were predicted.
- Electrostatic potential, total density and molecular electrostatic potential were investigated.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 5 September 2014
Received in revised form 27 February 2015
Accepted 2 March 2015
Available online 9 March 2015

Keywords:
4-Vinylcyclohexene
Vibrational analysis
DFT
NLO and NBO
HOMO–LUMO

ABSTRACT

The solid phase FT-IR and FT-Raman spectra of 4-vinylcyclohexene (abbreviated as 4-VCH) have been recorded in the region 4000–100 cm^{-1}. The optimized molecular geometry and vibrational frequencies of the fundamental modes of 4-VCH have been precisely assigned and analyzed with the aid of structure optimizations and normal coordinate force field calculations based on density functional theory (DFT) method at 6-311++G(d,p) level basis set. The theoretical frequencies were properly scaled and compared with experimentally obtained FT-IR and FT-Raman spectra. Also, the effect due the substitution of vinyl group on the ring vibrational frequencies was analyzed and a detailed interpretation of the vibrational spectra of this compound has been made on the basis of the calculated total energy distribution (TED). The time dependent DFT (TD-DFT) method was employed to predict its electronic properties, such as electronic transitions by UV–Visible analysis, HOMO and LUMO energies, molecular electrostatic potential (MEP) and various global reactivity and selectivity descriptors (chemical hardness, chemical potential, softness, electrophilicity index). Stability of the molecule arising from hyper conjugative interaction, charge delocalization has been analyzed using natural bond orbital (NBO) analysis. Atomic charges obtained by Mulliken population analysis and NBO analysis are compared. Thermodynamic properties (heat capacity, entropy and enthalpy) of the title compound at different temperatures are also calculated.

---

[*] Corresponding author. Tel.: +91 9443875224.
E-mail address: ekrubha@yahoo.com (P.B. Nagabalasubramanian).

http://dx.doi.org/10.1016/j.saa.2015.03.043
1386-1425/

Introduction

In the case of 4-VCH, vinyl double bonds were reported to take part in the polymerization reaction, as the endocyclic double bond shows little ring strain and large steric hindrance. In the literature [1], half-chair conformation for cyclohexene was proposed on the basis of its measurements of the heats of bromination of cyclic olefins. Later in literature [2], the energy for different conformations was investigated and predicted that the most stable conformation was indeed the half-chair form (C_2 symmetry). Subsequently other theoretical calculations on the conformation of cyclohexene were published [3–5]. The half-chair conformation of cyclohexene was indicated by infrared and Raman spectra [6]. There are earlier literatures in Raman spectrum of 4,5-dichlorocyclohexene [7,8], X-ray diffraction studies of pentachlorocyclohexene [9,10] and electron diffraction results for 3,4,5,6-tetra-chlorocyclohexene [11]. A half-chair conformation is also present in cyclohexene oxide [12,13]. The FT-IR and FT-Raman vibrational analysis of 4-VCH [14] and the electronic spectra of 1-VCH [15] were studied.

The earlier literatures indicates that neither quantum chemical calculations nor the electronic properties and thermal properties of 4-vinylcyclohexene have been reported up to now in the detailed manner. Since there has been no exhaustive determination of the molecular structure of 4-VCH, this investigation was deemed necessary. The scantiness observed in the literature encouraged to do this theoretical and experimental vibrational spectroscopic research to provide a correct assignment of the fundamental bands in experimental FT-IR and FT-Raman spectra on the basis of the calculated TED. The present study intends to give a complete description of the molecular geometry, molecular vibrations, electronic properties (UV–Vis, FMO, MEP, NBO, atomic charges and global reactivity descriptors) and thermodynamic properties. A correlation graph was drawn between standard heat capacities (C), standard entropies (S), and standard enthalpy changes (H) with various temperatures.

Experimental details

The compound under investigation namely 4-VCHwas purchased from Aldrich Chemicals, USA which is of spectroscopic grade and hence used for recording the spectra as such without any further purification. The FT-IR spectra of the title compound were recorded in Brunker IFS 66V Spectrometer in the range of 3600–10 cm^{-1}. The spectral resolution is ±2 cm^{-1}. The FT-Raman spectra of compound was also recorded in the same instrument with FRA 106 Raman module equipped with Nd:YAG laser source operating at 1.064 μm line width with 200 mW power. The spectra were recorded with scanning speed of 30 cm^{-1} min^{-1} of spectral width 2 cm^{-1}. The frequencies of all sharp bands are accurate to ±1 cm^{-1}.

Computational methods

The primary task for the computational work is to determine the optimized geometry of the compound. The molecular structure optimization of the title compound and corresponding vibrational harmonic frequencies are calculated using DFT with hybrid Beckee-3-Lee-Yag-Parr(B3LYP) combined with 6-311++G(d,p) basis set using GAUSSIAN09package program without any constraint on the geometry. The stability of the optimized geometries is confirmed by wavenumber calculations, which gave positive values for all the obtained wavenumbers. TED calculations are carried out by VEDA4 program [16] which show the relative contributions of the redundant internal coordinates to each normal vibrational mode of the molecule and thus enable us numerically to describe the character of each mode. The optimized geometrical parameters, true rotational constants, fundamental vibrational frequencies, IR and Raman intensities, atomic charges, dipole moment, and other thermodynamical parameters were calculated using the Gaussian09 package [17]. By combining the results of the GAUSSVIEW [18] program with symmetry considerations, vibrational frequency assignments were made with a high degree of accuracy. To make best fit with the experimental frequencies, theoretical frequencies greater than 1700 cm^{-1} were scaled with 0.958 [19] and less than 1700 cm^{-1} were scaled with 0.9614 [19].

UV–Visible study was performed using TD-DFT [20–23] with B3LYP/6-311++G(d,p) basis set, based on the optimized structure in solvent (ethanol, DMSO and water) and gas phase to predict the electronic properties viz., HOMO–LUMO energies, dipole moment, absorption wavelengths, and oscillator strengths etc. The molecular electrostatic potential surface (MEPs) of the present molecule is illustrated and evaluated.

The global reactivity descriptors like chemical potential, electronegativity, chemical hardness, softness and electrophilicity index can be calculated using DFT. The electronic chemical potential, describing the escaping tendency of electron from a stable system can be calculated as $\mu = -(\mathrm{IP} + \mathrm{EA})/2$. Electronegativity ($\chi$) is described as negative of the electronic chemical potential. Chemical hardness which demonstrates the resistance to alteration in electron distribution is given by $\eta = (\mathrm{IP} - \mathrm{EA})/2$, and is well correlated with the stability and reactivity of the chemical system. The inverse of the hardness is expressed as the global softness $\zeta = (1/\eta)$. The global electrophilicity index (ψ), introduced is calculated in terms of chemical potential and the hardness as $\psi = \mu^2/2\eta$ and assess the lowering of energy due to maximal electron flow between donor and acceptor. Here the ionization potential(IP) and electron affinity (EA) are defined as the difference in ground state energy between the cationic and neutral system and difference in ground state energy between neutral and anionic system i.e., $\mathrm{IP} = E(\mathrm{N}-1) - E(\mathrm{N}) = -E_{\mathrm{HOMO}}$ and $\mathrm{EA} = E(\mathrm{N}) - E(\mathrm{N}+1) = -E_{\mathrm{LUMO}}$.

The changes in the heat capacity, entropy, and enthalpy of the title molecule were investigated for the different temperatures (from 100 K to 700 K) from the vibrational frequencies.

Results and discussion

Geometrical structure

The molecular structure along with numbering of atoms of 4-VCH is obtained from Gaussian09 program and is as shown in Fig. 1. The global minimum energy obtained by DFT structure optimization using 6-311++G(d,p) basis set for the title molecule as −312.12754 a.u. The most optimized structural parameters (bond length, bond angle and dihedral angle) calculated by the same method are compared with the microwave and electron diffraction experimental data and represented in Table 1 in accordance with the atom numbering scheme given in Fig. 1. The moment of inertia of the molecule varies as $I_A > I_B > I_C$ and the rotational constants as 4.25340, 1.37225 and 1.12508 GHz respectively indicates that the molecule is an asymmetric top molecule.

In this paper, the bond length and bond angles obtained theoretically were compared with the molecular structure of cyclohexene [24] in the vapor phase where electron diffraction method was utilized. In the above stated literature [24], geometrical parameters were obtained by least-squares analysis of the reduced molecular intensity pattern. In this paper, the bond lengths of C1=C6 & C15=C18 (vinyl) are 1.507 Å and 1.332 Å, respectively which were 1.335 Å and 1.350 Å [15] in the earlier literature shows that the presence of vinyl group elongates the double bond in the