

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/274725988>

Spectroscopic (FT-IR/FT-Raman) and computational (HF/DFT) investigation and HOMO/LUMO/MEP analysis on 1,1-difluoro-2-vinyl-cyclopropane

ARTICLE *in* SPECTROCHIMICA ACTA PART A MOLECULAR AND BIOMOLECULAR SPECTROSCOPY · MARCH 2015

Impact Factor: 2.35 · DOI: 10.1016/j.saa.2015.03.084 · Source: PubMed

READS

46

4 AUTHORS, INCLUDING:



S. Ramalingam

A.V.C. College (Autonomous)

71 PUBLICATIONS 383 CITATIONS

SEE PROFILE



Sengeny Periandy

Independent Researcher

82 PUBLICATIONS 683 CITATIONS

SEE PROFILE



Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

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

Spectroscopic (FT-IR/FT-Raman) and computational (HF/DFT) investigation and HOMO/LUMO/MEP analysis on 1,1-difluoro-2-vinyl-cyclopropane

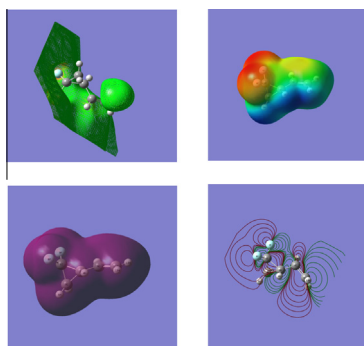
P. Senthil Raj^{a,*}, D. Shoba^b, S. Ramalingam^c, S. Periandy^d^aPRIST University, Vallam, Thanjavur, India^bPeriyar Maniammai University, Thanjavur, India^cDepartment of Physics, A.V.C. College, Mayiladuthurai, Tamilnadu, India^dDepartment of Physics, Tagore Arts College, Puducherry, India

HIGHLIGHTS

- FT-IR/FT-Raman spectra of 1,1-difluoro-2-vinyl-cyclopropane were recorded.
- The chemical shift was found and it is favor for its change of chemical property.
- The vibrational properties of the molecule have been studied.
- The electronic properties were studied using frontier molecular orbital analysis.
- The thermodynamical parameters have been studied for different temperature.

GRAPHICAL ABSTRACT

1,1-Difluoro-2-vinyl-cyclopropane is used as intermediates in the synthesis of complex molecules because of their ready reactivity. Cyclopropane analogues are proved to show varied biological applications such as anti-HIV, anticancer, antibacterial, antifungal, antiviral, antitumor, COX-II inhibitor properties. Due to their diverse applications in synthetic, agricultural, and medicinal chemistry as well as in material science a thorough analysis of the physical and chemical properties of 1,1-difluoro-2-vinyl-cyclopropane is made.



ARTICLE INFO

Article history:

Received 14 June 2014

Received in revised form 7 March 2015

Accepted 10 March 2015

Available online 31 March 2015

Keywords:

1,1-Difluoro-2-vinyl-cyclopropane

GIAO

Chemical shifts

Frontier molecular orbitals and molecular electrostatic potential

ABSTRACT

All the computational calculations were made in the ground state using the HF and DFT (B3LYP) methods with 6-31++G (d,p) and 6-311++G (d,p) basis sets. Making use of the recorded data, the complete vibrational assignments were made and analysis of the observed fundamental bands of molecule was carried out. The shifting of the frequencies in the vibrational pattern of the title molecule due to the substitutions; $-\text{CH}=\text{CH}_2$ and F were deeply investigated by the vibrational analysis. Moreover, ^{13}C NMR and ^1H NMR chemical shifts were calculated by using the gauge independent atomic orbital (GIAO) method with HF/B3LYP methods with 6-311++G (d,p). A study on the electronic properties, such as HOMO and LUMO energies, were performed by time-dependent DFT (TD-DFT) approach. Mulliken charges of the 1DF2VCP were also calculated and interpreted. The thermodynamic properties (heat capacity, entropy, and enthalpy) of the title compound at different temperatures were calculated in gas phase.

© 2015 Elsevier B.V. All rights reserved.

* Corresponding author. Tel.: +91 9843425541.

E-mail address: senstarphy@gmail.com (P. Senthil Raj).

Introduction

In recent times cyclopropane and its derivatives have gained importance for their biological and pharmaceutical applications [1]. Cyclopropane derivatives are interesting molecules for theoretical studies due to their relatively small size and similarity to biological species. Also this three membered ring compound exhibits notable antimicrobial activities [2]. Cyclopropane ring systems are omnipresent in nature and are present in a large number of natural products, insecticides, and pharmaceutical drug candidates. Cyclopropanes are handy intermediates in the synthesis of complex molecules because of their ready reactivity. Cyclopropane analogues are proved to show varied biological applications such as anti-HIV, anticancer, antibacterial, antifungal, antiviral, antitumor, COX-II inhibitor properties. However, due to their diverse applications in synthetic, agricultural, and medicinal chemistry as well as in material science many works have been already published on the synthesis and application of multi-substituted cyclopropanes [3].

However, the work with HF and DFT methods for this molecule has not been reported so far. In this work, a detailed study on the molecular geometry, vibrational frequencies, ^{13}C NMR and ^1H NMR chemical shifts, HOMO–LUMO, Mulliken atomic charge and thermodynamic studies and the performance of the computational methods for HF and DFT (B3LYP) are carried out. Here fluorine atom was chosen as the most suitable substituent for our purposes due to the high polarity of C–F bonds and the hydrophobicity of fluoropolymers.

Experimental details

The spectra of the compound under investigation namely 1DF2VCP was purchased from spectral library of Sigma Aldrich chemicals, U.S.A. The FT-IR spectrum of the compound is recorded in Bruker IFS 66V spectrometer in the range of $4000\text{--}100\text{ cm}^{-1}$. The spectral resolution is $\pm 2\text{ cm}^{-1}$. The FT-Raman spectrum of same compound is also recorded in the same instrument with FRA 106 Raman module equipped with Nd:YAG laser source operating at $1.064\text{ }\mu\text{m}$ line widths with 200 mW power. The spectra are recorded in the range of $4000\text{--}100\text{ cm}^{-1}$ with scanning speed of $30\text{ cm}^{-1}\text{ min}^{-1}$ of spectral width 2 cm^{-1} . The frequencies of all sharp bands are accurate to $\pm 1\text{ cm}^{-1}$.

Computational methods

The molecular parameters of 1DF2VCP in the ground state are computed by performing both HF and DFT (B3LYP) with 6-31++G (d,p) and 6-311++G (d,p) basis sets. In DFT methods, Becke's three parameter exact exchange-functional (B3) [11] combined with gradient-corrected correlational functional of Lee, Yang and Parr (LYP) [4–5] was chosen for their best predicting results for molecular geometry and vibrational modes for moderately larger molecule [6–7]. The minimum energy of geometrical structure is obtained by using same level of theory. All the computations have been done by adding polarization function 'p' and diffuse function 'd' on heavy atoms [8–11], in addition to triple split valence basis set (6-311++G (d,p)), for better treatment of polar bonds of Fluorine atom and vinyl group.

For NMR calculations, the title molecule was firstly optimized at 6-311++G (d,p) level. After optimization, ^1H and ^{13}C NMR chemical shifts were calculated using the GIAO method in chloroform at DFT method with 6-311++G (d,p) basis set [12]. TD-B3LYP was used to obtain absorption wavelengths λ_{max} and excitation energy, dipole moment and frontier molecular orbital energies. HF/DFT calculations for 1DF2VCP were performed using GAUSSIAN 09W program

package on Pentium IV processor personal computer. The assignment of the wavenumbers is done by animation option of GaussView 3.0 [13], a graphical interface of GAUSSIAN program.

Results and discussion

Molecular geometry

The title compound, 1,1-difluoro-2-vinyl-cyclopropane (1DF2VCP), is an aliphatic cyclopropane in which the substituents are fluorine (F) and a vinyl group ($-\text{CH}=\text{CH}_2$). The optimized structure of title compound is shown in Fig. 1. The comparative optimized structural parameters; bond lengths and bond angles are presented in Table 1. In 1997, Zhou and Liu [14] studied the vibrational spectra of trimethylcyclopropane, a similar compound to the title compound, and found that the bond length of the carbon atoms present in the cyclopropane ring was of the order $1.452\text{ }\text{\AA}$, but here in the title compound we observe the bond length of carbon atoms in the cyclopropane ring to be $1.472\text{ }\text{\AA}$, $1.461\text{ }\text{\AA}$ and $1.547\text{ }\text{\AA}$. This increase in the value of the bond length may be attributed to the heavy substitution of fluorine and vinyl to the cyclopropane ring. The ring structure of cyclopropane appears little distorted and angles are slightly out of perfect triangle structure by the substitutions of the F atom and $-\text{CH}=\text{CH}_2$ group in the place of H atoms. In comparison with the experimental values, it is observed that most of the calculated bond length values are in just about in agreement with the experimental values. This may be due to the fact that the calculations are performed for the isolated molecules (gaseous phase) while the experimental spectra are recorded in solid phase. In spite of the differences between the calculated and the experimental parameters the calculated geometrical parameters can be represented after good approximation, as they are the bases for the calculating other parameters, such as vibrational frequencies and thermodynamics properties. The breakdown of symmetry of the cyclopropane ring is obvious from the elongation of bond length C2–C3 ($1.548\text{ }\text{\AA}$) from the remaining bond lengths C1–C2 ($1.473\text{ }\text{\AA}$) and C1–C3 ($1.471\text{ }\text{\AA}$) since the replacements, fluorine atom and vinyl group, are with different masses. The order of the optimized bond lengths of the five C–C bonds of the ring lie as $\text{C9–C11} < \text{C1–C3} < \text{C1–C2} < \text{C2–C9} < \text{C2–C3}$. The C–F bond length ($1.332\text{ }\text{\AA}$) indicates a considerable increase in the bond length when F atom substituted in place of H atom. The calculated values for C–F bond length change from $1.326\text{ }\text{\AA}$ to $1.362\text{ }\text{\AA}$. Substitution with the halogen atom leads to some changes of the bond angles in the aliphatic compound. The C2–C9–H11 angle at the position of the vinyl substituent are higher (cal. 123.9°) than the fluorine substituent

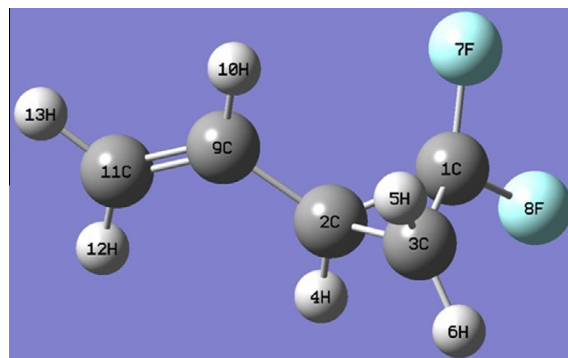


Fig. 1. The optimized structure of 1,1-difluoro-2-vinyl-cyclopropane.

Table 1

Optimized geometrical parameters for 1,1-difluoro-2-vinyl-cyclopropane computed at HF and B3LYP methods using 6-31++G (d,p) and 6-311++G (d,p) basis sets.

Geometrical Parameters	HF		B3LYP	
	6-31++G (d,p)	6-311++G (d,p)	6-31++G (d,p)	6-311++G (d,p)
<i>Bond length (Å)</i>				
C1–C2	1.472	1.473	1.489	1.487
C1–C3	1.461	1.462	1.472	1.469
C1–F7	1.333	1.327	1.362	1.359
C1–F8	1.333	1.327	1.363	1.359
C2–C3	1.547	1.548	1.569	1.567
C2–C9	1.484	1.483	1.480	1.477
C2–H4	1.077	1.076	1.087	1.085
C3–H5	1.075	1.074	1.086	1.083
C3–H6	1.076	1.075	1.085	1.083
C9–C11	1.322	1.320	1.337	1.332
C9–H10	1.078	1.078	1.089	1.087
C11–H13	1.077	1.077	1.085	1.086
C11–H12	1.075	1.075	1.087	1.083
<i>Bond Angle (°)</i>				
A(C2–C1–F7)	119.087	119.058	119.711	119.692
A(C2–C1–F8)	119.836	119.841	119.013	119.022
A(C3–C1–F7)	119.665	119.668	119.458	119.48
A(C3–C1–F8)	119.481	119.475	119.642	119.699
A(F7,C1–F8)	109.121	109.124	109.126	109.067
A(C1–C2–H4)	114.662	114.605	114.49	114.39
A(C1–C2–C9)	121.284	121.22	121.562	121.474
A(C3–C2–H4)	114.828	114.792	114.473	114.385
A(C3–C2–C9)	120.142	120.079	120.248	120.186
A(H4–C2–C9)	115.733	115.871	115.933	116.145
A(C1–C3–H5)	118.146	118.089	117.516	117.458
A(C1–C3–H6)	117.403	117.337	118.269	118.197
A(C2–C3–H5)	117.394	117.367	116.889	116.847
A(C2–C3–H6)	117.127	117.095	117.173	117.128
A(H5,C3–H6)	116.034	116.149	116.143	116.275
A(C2–C9–10)	116.474	116.436	116.28	116.222
A(C2–C9–11)	123.941	123.944	124.071	124.136
A(H10–C9–11)	119.585	119.62	119.649	119.643
A(C9–C11–12)	121.105	121.116	121.832	121.842
A(C9–C11–13)	121.948	121.933	121.238	121.238
A(C2–C11–13)	116.947	116.951	116.929	116.92

C3–C1–F7 and C3–C1–F8 (cal. 119.66° and 119.48°). The optimized bond angle of the compound is lie in order as C1–C2–C9 > C3–C1–F8 > C2–C1–F7.

Vibrational assignments

The title molecule consists of 13 atoms, which undergoes 33 normal modes of vibrations. Of the 33 normal modes of vibrations, 24 modes of vibrations are in-plane and remaining 9 are out-of-plane. In agreement with C1 symmetry all the 33 fundamental vibrations are active in both Raman scattering and IR absorption. The harmonic-vibrational frequencies calculated for (1DF2VCP) at HF and B3LYP levels using the triple split valence basis set along with the diffuse and polarization functions, 6-31++G (d,p)/6-311++G (d,p) and observed FT-IR and FT-Raman frequencies for various modes of vibrations have been presented in Table 2. The comparative IR and Raman spectra of experimental and calculated (HF/B3LYP) are given in Figs. 2 and 3.

Comparison of frequencies calculated at HF and B3LYP with the experimental values reveals the over estimation of the calculated vibrational modes due to the neglect of anharmonicity in real system. Inclusion of electron correlation in the density functional theory to certain extends makes the frequency values smaller in the comparison with the HF frequency data. Observed and unscaled calculated frequencies are presented in Table 3 (Supp), a comparative graph is shown in Fig. 4 (Supp). To rationalize the

calculated values with the experimental values, scaling factors are introduced. The scaled values are presented in Table 2. The scaled calculated frequencies minimize the root-mean square difference between calculated and experimental frequencies for bands with definite identifications. The descriptions concerning the assignment have also been indicated in Table 2.

The calculated frequencies were scaled by 0.903 for HF/6-31++G (d,p) and 0.904 for HF/6-311++G (d,p) [10]. For B3LYP with 6-31++G (d,p) set was scaled with 0.959, B3LYP/6-311++G (d,p) basis set was scaled with 0.957 [15].

Vibrational intensity analysis

Computed vibrational spectral IR intensities and Raman activities of the title molecule for corresponding wave numbers by HF [16] and DFT [17] methods with B3LYP [18] with 6-31++G (d,p) and 6-311++G (d,p) basis sets have been collected in Tables 4 and 5 (Supp). Comparison of IR intensities and Raman activities calculated theoretically with experimental values exposes the variation of IR intensities and Raman activities. In the case of IR intensities, the values of HF are found to be higher than B3LYP at both levels whereas in the case of Raman activities the effect is reversed. The comparative graph of IR intensities is presented in Fig. 5.

C–F vibrations

In the fluorine compounds, very intense absorption of C–F mode occurs in the region 1100–1350 cm^{−1} [12,19]. Infrared spectra of mono- and di-substituted fluorine derivatives have been studied by Narasimham et al. [20] and those of tri- and tetra-fluorobenzene by Ferguson et al. [21] and frequency have been assigned at 1250 cm^{−1} to C–F stretching mode of vibration. In analogy to these assignments, infrared frequency observed at 1235 cm^{−1}, is assigned as C–F stretching frequency for 1-fluoro-2,4-dinitrobenzene [22], corresponding Raman frequency for the same mode is 1246 cm^{−1}. For 2,3-difluoro phenol, Sundaraganesan et al. [23] assigned the strong bands at 1331 and 1279 cm^{−1} in FT-IR spectrum due to C–F stretching mode, and their counterpart in Raman spectrum is at 1332 and 1280 cm^{−1}. Mehmet Karabacak et al. assigned the strong bands at 1254 and 1222 cm^{−1} in the FT-IR spectrum due to the C–F stretching mode and their counterpart in the Raman spectrum at 1274 and 1245 cm^{−1}. The theoretically computed scaled value of 1271 and 1240 cm^{−1} at B3LYP/6-311++G (d,p) showed good agreement with experimental results for 5-fluoro salicylic acid [24]. In the present work wave numbers at 1290 cm^{−1} and 1210 cm^{−1} in FT-IR and FT-Raman are assigned to C–F stretching vibration for 1DF2VCP. C–F stretching modes were computed at 1261–1175 cm^{−1} showed in well correlation with the experimental values. Sundaraganesan et al. [25] observed strong band at 759 cm^{−1} in FT-IR and very strong band at 750 cm^{−1} in FT-Raman and assigned it to C–F in-plane bending mode for 2-amino-4,5-difluorobenzoic acid molecule. The C–F out-of-plane bending mode was identified, at 590 cm^{−1} as a weak band in FT-IR and 592 cm^{−1} in FT-Raman [25]. For 2-fluorophenylboronic acid molecule, Erdogdu et al. [26] observed one band at 520 cm^{−1} both in the FT-IR and in the FT-Raman spectra. The C–F out-of-plane bending modes of the bands are supported in literature [27–30]. In the present work we predicted at 710 cm^{−1} for C–F in-plane bending modes and 570 cm^{−1} for C–F out-of-plane bending modes.

C–H vibration

The title compound shows the presence of the C–H stretching vibration in the 3000–3100 cm^{−1} range which is the characteristic region for ready identification of C–H stretching vibration [31,32]. In this region, the bands are not affected appreciably by the nature of the substituents. The title compound (1DF2VCP) has 3 hydrogen atom attached to cyclopropane. For aliphatic hydrocarbons, with exception of small ring compounds, the C–H stretching vibrations

Table 2
Observed and calculated [scaled] vibrational frequencies (cm⁻¹) at HF and DFT (B3LYP) with 631++G (d,p) and 6-311++G (d,p) basis sets of 1,1-difluoro-2-vinyl-cyclopropane.

S. No.	Experimental		HF		B3LYP		Vibrational assignments
	FT-IR	FT-Raman	6-31++G (d,p)	6-311++G (d,p)	6-31++G (d,p)	6-311++G (d,p)	
1	3100w	3100vs	3073	3056	3114	3092	ν _{asym} (C–H)
2	3030w	3030vs	3070	3048	3110	3082	ν _{asym} (C–H)
3		2990s	3005	2984	3031	3006	ν(C–H)
4	2980w		2991	2971	3024	3002	ν(C–H)
5		2940vw	2989	2970	3023	2998	ν(C–H)
6	2930vw	2930vw	2982	2967	3010	2990	ν(C–H)
7	1650s	1650m	1677	1666	1641	1627	ν(C=C)
8		1520vw	1506	1501	1439	1428	ν(C–C)
9	1420m	1420m	1424	1417	1396	1387	ρ(H–C–H)
10	1380vs	1380w	1389	1383	1350	1342	ν(C–C)
11	1310s	1310vs	1327	1323	1280	1274	ν(C–C)
12	1290vs		1294	1290	1266	1262	ν(C–F)
13	1210vs	1210vw	1254	1249	1188	1175	ν(C–F)
14	1120vw		1120	1113	1083	1079	δ(C–H)
15		1090vs	1110	1105	1064	1059	δ(C–H)
16	1080w		1079	1074	1043	1036	δ(C–H)
17	1030vs	1030w	1055	1046	1003	997	δ(C–H)
18	1010s		1013	1013	974	974	δ(C–H)
19	990vs	990w	988	985	961	956	δ(C–H)
20	980vs	980vs	982	976	915	914	γ(C–H)
21	920vs	920vs	957	954	910	907	γ(C–H)
22	900vs	900vs	909	906	874	869	γ(C–H)
23	810m	810vs	810	807	792	788	γ(C–H)
24	710vs	710vs	707	707	686	684	γ(C–F)
25		680vw	677	678	658	659	γ(C–H)
26	570w	570m	555	555	531	532	γ(C–F)
27	490m	490vs	496	499	492	493	(C–C) skeletal
28		430m	453	457	438	442	ω(C–F)
29	370s	370s	375	375	364	366	δ(C–C)
30	330vw		329	329	317	317	δ(C–C)
31		180m	181	181	180	179	δ(C–C)
32	170vs	170s	179	179	173	173	γ(C–C)
33	80m		75	77	65	68	γ(C–C)

vs; very strong, s; strong, m; medium, w; weak, vw; very weak. ν; stretching, δ; in plane bending, γ; out of plane bending, ρ; scissoring, ω; wagging, τ; twisting, Γ; torsion.

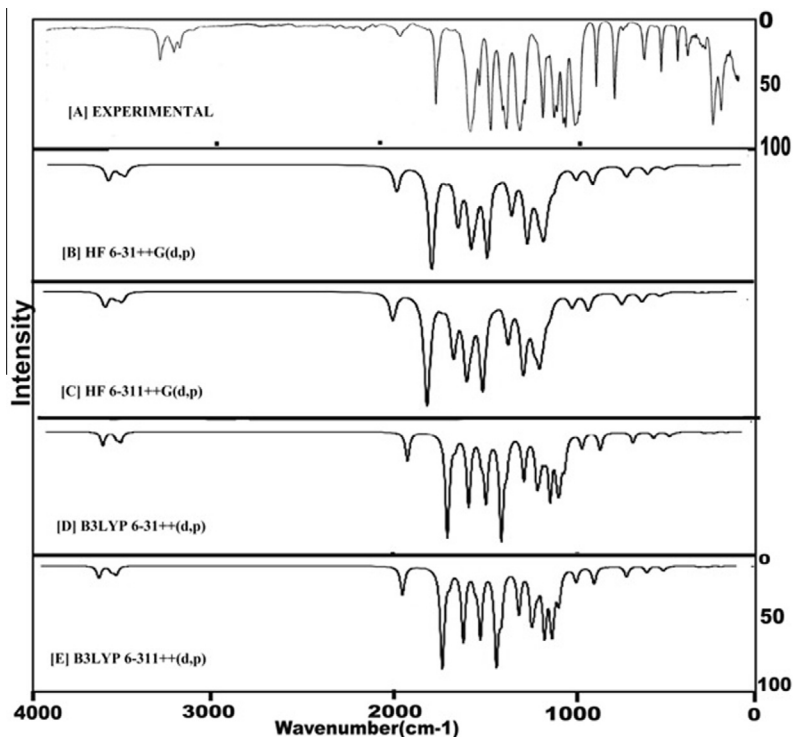


Fig. 2. Experimental [A] and calculated [B], [C], [D], and [E] FTIR spectra of 1,1-difluoro-2-vinyl-cyclopropane.

occur in the region 2975–2840 cm⁻¹ [33–35]. For cyclopropanes C–H absorption occur near 3050 cm⁻¹ and may easily be disguised from the nearby CH₂ absorption at about 2930 cm⁻¹ [36]. In our

present work the band at 3091 cm⁻¹ and 3081 cm⁻¹ calculated at B3LYP6-311++G (d,p) basis set are assigned to C–H asymmetric stretching vibration. Experimentally observed FT-IR and FT

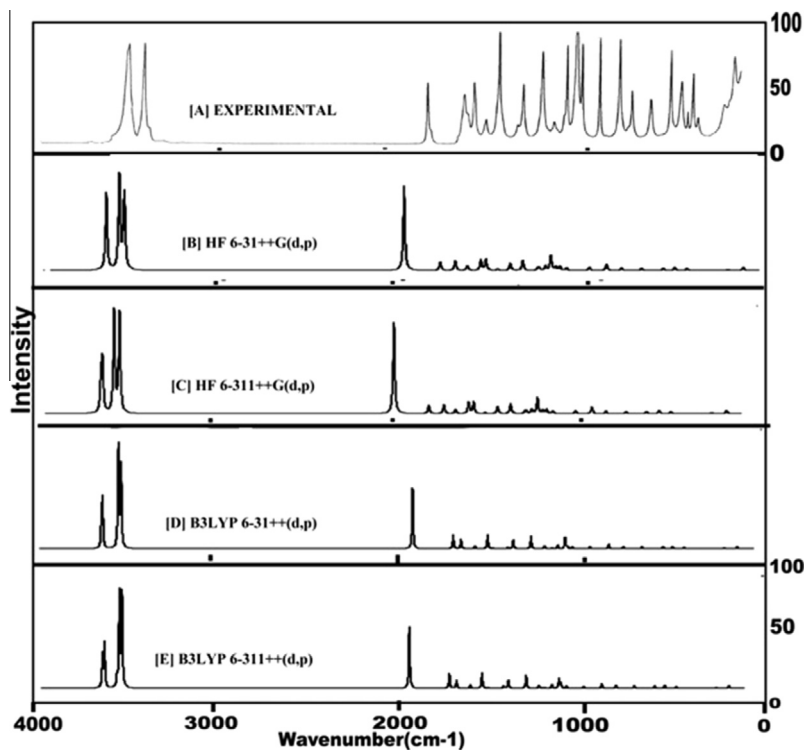


Fig. 3. Experimental [A] and calculated [B], [C], [D], and [E] FT-Raman spectra of 1,1-difluoro-2-vinyl-cyclopropane.

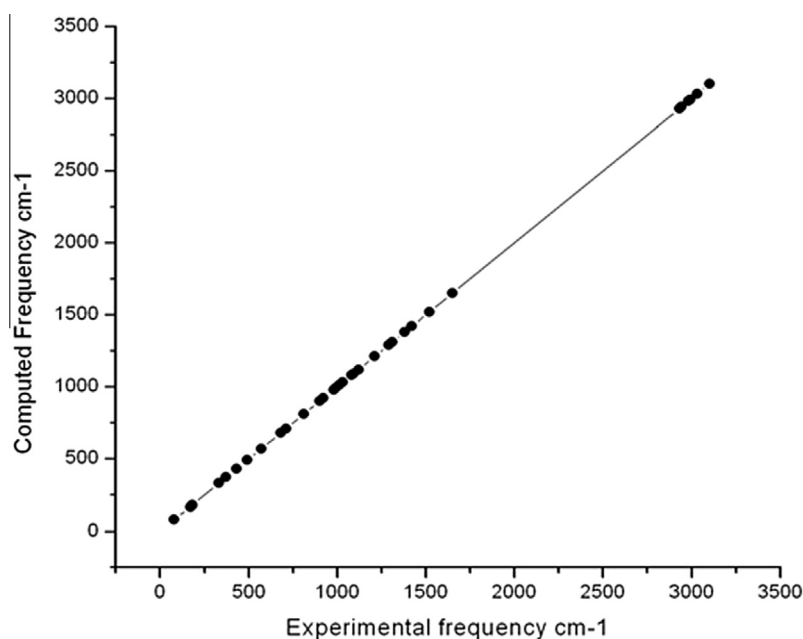


Fig. 5. Comparative graph between experimental and calculated frequency of 1DF2VCP.

Raman wave numbers coincides with the calculated wave numbers. The modes from 3 to 6 (2990 cm^{-1} , 2980 cm^{-1} , 2940 cm^{-1} and 2930 cm^{-1}) are assigned to C–H symmetric stretching vibration. The deformation vibration of C–H may be either perpendicular to or in the same plane as that containing C=C the absorption bands due to the out of plane vibrations occurs mainly at $1000\text{--}800\text{ cm}^{-1}$ and have strong to medium intensities. These bands are important in the characterization of alkenes [37–39]. For vinyl groups —CH=CH_2 the strong absorption [40] in the regions

$995\text{--}980\text{ cm}^{-1}$ and $915\text{--}905\text{ cm}^{-1}$ are due to C–H deformation vibrations. For title compound the C–H deformation vibrations are assigned to the mode no. 14–23 in Table 2.

C=C and C–C vibration

Non conjugated alkenes have a weak C=C stretching absorption band in the range $1680\text{--}1620\text{ cm}^{-1}$. This band is absent for symmetrical molecules. Therefore it is not surprising to find that olefins, which have terminal double bonds, have the most intense

absorptions. Vinyl, vinylidene and cis disubstituted olefin tend to absorb at lower end of the range given below 1665 cm^{-1} , whereas trans-disubstituted, tri and tetra substitute olefins absorb at the higher wave number. In our present work 1650 cm^{-1} is assigned to C=C vibration, which is found to be in good agreement with the C=C stretching vibrations observed in trimethylcyclopropane [14]. Further 1520 cm^{-1} , 1380 cm^{-1} and 1310 cm^{-1} were assigned to C–C vibrations. Cyclopropane derivatives have a band of variable intensity a $540\text{--}500\text{ cm}^{-1}$ [41,42]. An exception is that of vinyl cyclopropane which has a strong absorption at 455 cm^{-1} and other unsaturated cyclopropanes also have a medium-intensity absorption in this region. For (1DF2VCP) 490 cm^{-1} is assigned to C–C skeletal vibrations.

Electronic properties

UV spectrum and frontier molecular orbital analysis

Ultraviolet spectra analysis of (1DF2VCP) has been investigated in DMSO, chloroform and gas phase by theoretical calculation. On the basis of fully optimized ground-state structure, TD-DFT/B3LYP/6-311++G (d,p) calculations have been used to determine the low-lying excited states of (1DF2VCP). The theoretical electronic excitation energies, oscillator strengths and absorption wavelength are also listed in Table 7. Calculations of the molecular orbital geometry show that the absorption maxima of this molecule correspond to the electron transition between frontier orbitals such as translation from HOMO to LUMO. As can be seen from Table 7, the calculated absorption maxima values have been found to be 197.29, 195.44 and 183.96 nm for gas phase, 197.63, 195.63 and 184.05 nm for DMSO and 197.29, 195.44 and 183.96 nm for chloroform at DFT/B3LYP/6-311++G (d,p) method. It is seen from Table 7, calculations performed at DMSO and chloroform are close to each other when compared with gas phase. Also the absorption maxima values of gas phase are larger than that of the organic solvents. Calculated energy values are listed in Table 8 and the frontier molecular orbitals are shown in Fig. 10.

Electrostatic potential, total electron density and molecular electrostatic potential

In the present study, the electrostatic potential (ESP), total electron density (ED) and molecular electrostatic potential (MEP) of (1DF2VCP) are illustrated in Fig. 11. The MEP which is a plot of electrostatic potential mapped onto the constant electron density surface. The MEP is a useful property to study reactivity given that an approaching electrophilic will be attracted to negative regions (where the electron distribution effect is dominant). In the majority of the MEP, the maximum negative region which is preferred site for electrophilic attack indicated as red color, the maximum positive region which is preferred site for nucleophilic attack as blue color. The importance of MEP lies in the fact that it

simultaneously displays molecular size, shape as well as positive, negative and neutral electrostatic potential regions in terms of color grading Fig. 11 and is very useful in research of molecular structure with its physiochemical property relationship [43–46]. The different values of the electrostatic potential at the MEP surface are represented by different colors; red, blue and green, which represent the regions of most negative, most positive and zero electrostatic potential, respectively. The color code of these maps is in the range between -3.182 a.u. (deepest red) to 3.182 a.u. (deepest blue) in compound, where blue indicates the strongest attraction and red indicates the strongest repulsion.

Regions of negative $V(r)$ are usually associated with the lone pair of electronegative atoms. As can be seen from the MEP map of the title molecule, while regions having the positive potential are over the hydrogen atoms, the regions having the negative potential are over the electronegative fluorine atoms. From these results, it can be said that the H atoms indicate the strongest attraction and F atom indicates the strongest repulsion.

Thermodynamic properties

The values of some thermodynamic parameters (such as zero point vibrational energy, thermal energy, specific heat capacity, rotational constants, entropy, etc.) of (1DF2VCP), at 298.15 K in ground state are listed in Table 11. The variation in Zero-Point Vibrational Energies (ZPVEs) seems to be significant. The ZPVE is much lower by the DFT/B3LYP method than by the HF method. The biggest value of ZPVE of (1DF2VCP), are $278,302$ and $276,709\text{ J mol}^{-1}$ obtained at HF/6-31+G (d,p)/6-311++G (d,p) whereas the smallest values are $258,252$ and $257,244\text{ J mol}^{-1}$ obtained at B3LYP/6-31+G (d,p)/6-311++G (d,p). Dipole moment reflects the molecular charge distribution and is given as a vector in three dimensions. Therefore, it can be used as descriptor to depict the charge movement across the molecule. Direction of the dipole moment vector in a molecule depends on the centers of positive and negative charges. Dipole moments are strictly determined for neutral molecules. For charged systems its value depends on the choice of origin and molecular orientation. As a result of HF and DFT (B3LYP) calculations the smallest dipole moment was observed for B3LYP/6-311G++ (d,p) whereas the highest one was observed for HF/6-311++G (d,p) in each molecule.

On the basis of vibrational analysis, the statically thermodynamic functions heat capacity (C), entropy (S), and enthalpy (H) for the title molecule were obtained from the theoretical Harmonic frequencies and listed in Table 10. From the Table 10, it can be observed that these thermodynamic functions are increasing with temperature ranging from 100 to 600 K due to the fact that the molecular vibrational intensities increase with temperature [47]. The correlation equations between heat capacity, entropy, enthalpy changes and temperatures were fitted by Quadratic formulas and the corresponding fitting factors (R^2) for these thermodynamic properties are 0.9999 . The corresponding fitting equations are as follows and the correlation graphics of that show in Figs. 6–8 (Supp)

$$C_{p,m}^0 = 1.4726 + 0.082957T - 2.10571 \times 10^{-5}T^2 \quad (R^2 = 0.99904) \\ (\text{SD} = 0.48677)$$

$$S_m^0 = 49.9508 + 0.10945T - 3.26357 \times 10^{-5}T^2 \quad (R^2 = 0.99993) \\ (\text{SD} = 0.1702)$$

$$\Delta H_m^0 = 60.6922 + 0.0252T + 3.61571 \times 10^{-5}T^2 \quad (R^2 = 0.99998) \\ (\text{SD} = 0.02381)$$

All the thermodynamic data supply helpful information for the further study on the (1DF2VCP) they can be used to compute the other

Table 6

Experimental and calculated ^1H and ^{13}C NMR chemical shifts (ppm) of 1,1-difluoro-2-vinyl-cyclopropane.

Atom position	Experimental ^a	B3LYP 6-311++G (d,p)
C(1)	125.9	118.99
C(2)	–	37.26
C(3)	–	20.96
H(4)	2.3	2.11
H(5)	1.8	1.16
H(6)	–	0.80
C(9)	135.2	149.06
H(10)	6.0	6.02
C(11)	134.3	124.58
H(12)	5.00	5.35
H(13)	5.5	5.55

^a Durham E-Theses.

Table 7

Theoretical electronic absorption spectra of 1,1-difluoro-2-vinyl-cyclopropane using TD-DFT/B3LYP/6-311++G (d,p) method in DMSO, chloroform and gas phase.

DMSO			Chloroform			Gas			Assignment
λ (nm)	E (eV)	f	λ (nm)	E (eV)	f	λ (nm)	E (eV)	f	
197.63	6.273	0.2863	198.23	6.254	0.2733	197.29	6.284	0.2553	$\pi-\pi^*$
195.63	6.337	0.1018	196.16	6.320	0.1151	195.44	6.348	0.1138	$\pi-\pi^*$
184.05	6.736	0.0041	185.41	6.687	0.0051	183.96	6.739	0.0039	$\pi-\pi^*$

Table 8

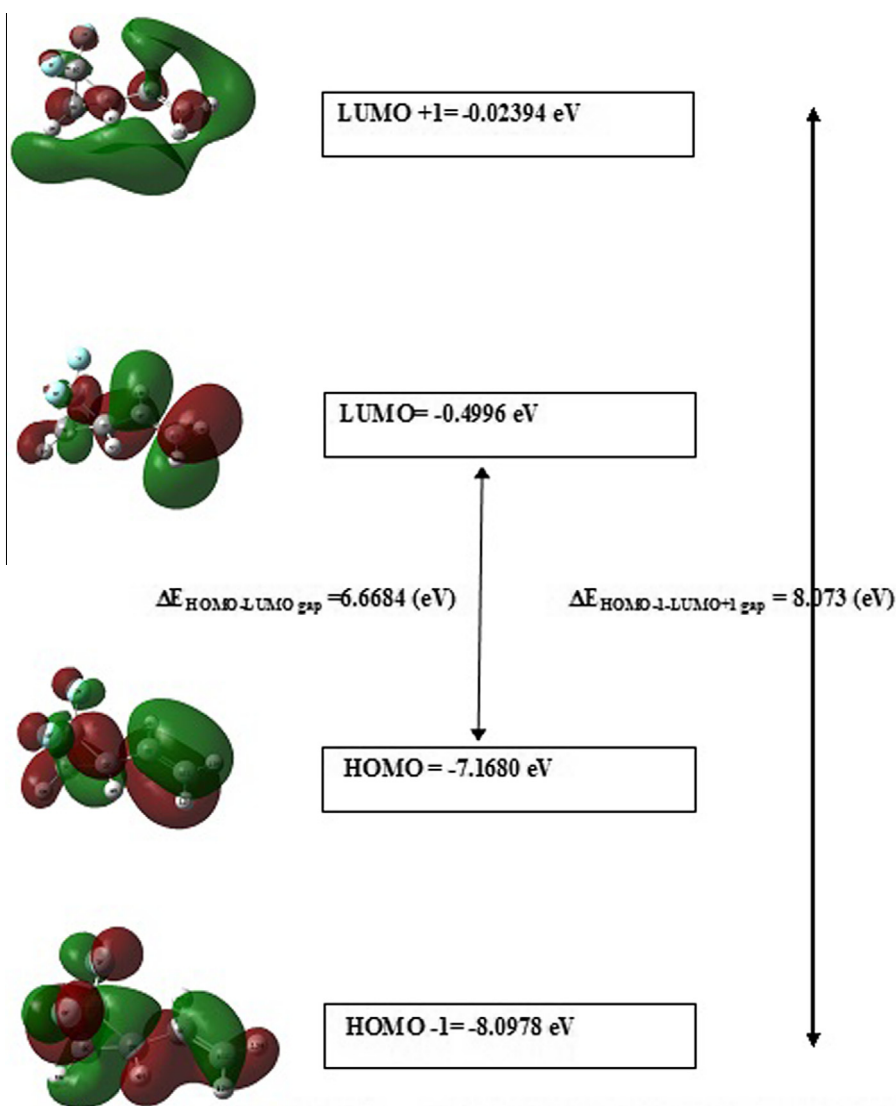
Calculated energies values of 1,1-difluoro-2-vinyl-cyclopropane in solvent (DMSO and chloroform) and gas phase.

TD-DFT/B3LYP/6-311++G (d,p)	DMSO	Chloroform	Gas
E_{total} (Hartree)	−393.6479	−393.6473	−393.6475
E_{HOMO} (eV)	−7.1682	−7.173	−7.1680
E_{LUMO} (eV)	−0.5001	−0.5126	−0.4996
$\Delta E_{\text{HOMO-LUMOgap}}$ (eV)	6.6681	6.6604	6.6684
$E_{\text{HOMO-1}}$ (eV)	−8.0981	−8.1030	−8.0978
$E_{\text{LUMO+1}}$ (eV)	−0.02476	−0.0495	−0.02394
$\Delta E_{\text{HOMO-1-LUMO+1gap}}$ (eV)	8.0733	8.0535	8.073
Chemical hardness η (eV)	3.33402	3.3302	3.3342
Electronegativity χ (eV)	−3.834	−3.842	−3.833
Chemical Softness ξ (eV)	0.1499	0.1501	0.1499
Electrophilicity index ω (eV)	1.187	1.070	1.187
Dipole moment (Debye)	2.8139	2.6699	2.8139

thermodynamic energies according to relationships of thermodynamic functions and estimate directions of chemical reactions.

Mullikan atomic charges

The Mullikan charge is directly related to the vibrational properties of the molecule, and quantifies how the electronic structure changes under atomic displacement; it is therefore related directly to the chemical bonds present in the molecule. It affects dipole moment, polarizability, electronic structure and more properties of molecular systems. The computation of the reactive atomic charges plays an important role in the application of quantum mechanical calculations for the molecular system. The Mullikan atomic charges of 1DF2VCP was computed by DFT/B3LYP method

**Fig. 10.** Frontier molecular orbitals (HOMO-LUMO) of 1DF2VCP.

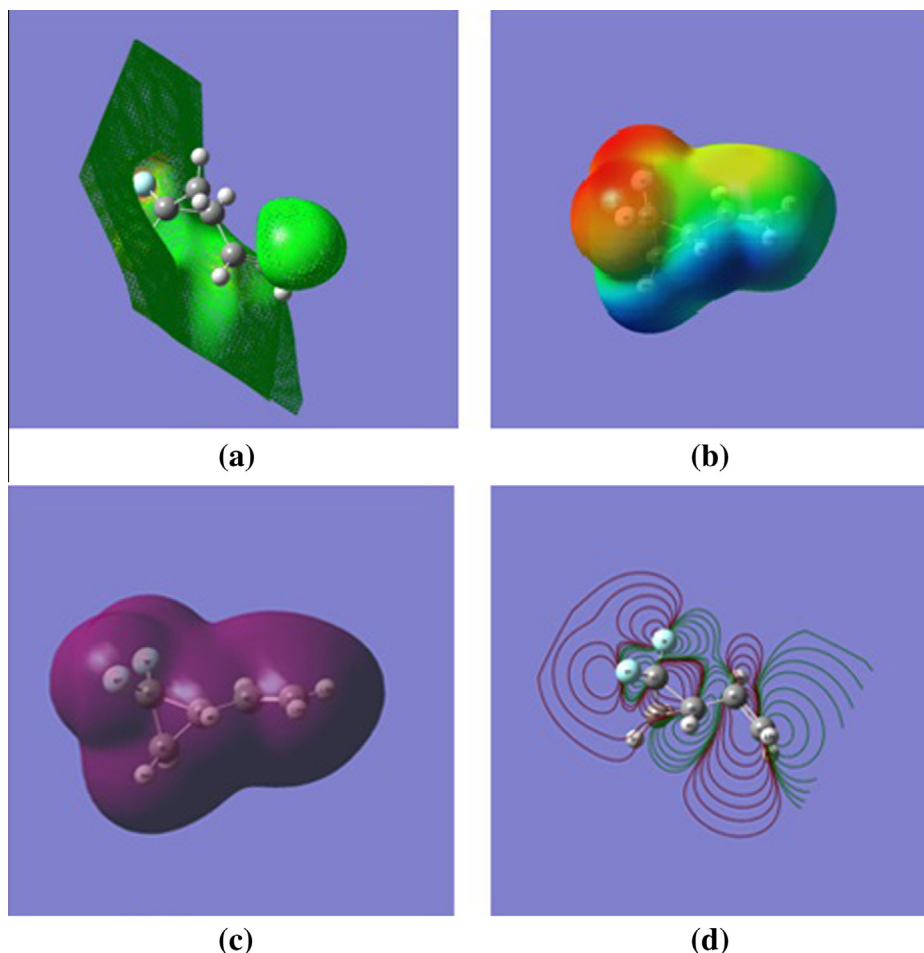


Fig. 11. (a) Electrostatic potential map (ESP), (b) molecular electrostatic potential (MEP) (c) electron density (ED), and (d) contour map, and for calculated at B3LYP/6-311++/G (d,p).

Table 9

Mulliken atomic charges of 1,1-difluoro-2-vinyl-cyclopropane using HF 6-311G++ (d,p) and B3LYP/6-311G++ (d,p) basis set.

Atoms	HF 6-311G++ (d,p)	B3LYP/6-311G++ (d,p)
C(1)	0.4944	−0.1824
C(2)	0.2455	0.1297
C(3)	−0.3210	−0.3213
H(4)	0.2017	0.2484
H(5)	0.1556	0.1680
H(6)	0.1532	0.1817
F(7)	−0.3868	−0.1072
F(8)	−0.3877	−0.1043
C(9)	−0.3821	0.0254
H(10)	0.1332	0.1855
C(11)	−0.1246	−0.4654
H(12)	0.1216	0.1109
H(13)	0.0968	0.1309

Table 10

Thermodynamic properties at different temperatures at the B3LYP/6-311++G (d,p) level of 1,1-difluoro-2-vinyl-cyclopropane.

T (K)	C (cal mol ^{−1} K ^{−1})	S (cal mol ^{−1} K ^{−1})	ΔH (k cal mol ^{−1})
100	9.782	60.488	61.314
200	16.751	70.722	62.631
300	24.515	79.781	64.693
400	31.679	88.415	67.513
500	37.474	96.577	70.982

NMR spectral analysis

The theoretical ¹H and ¹³C NMR chemical shifts of C and H have been compared with the experimental data [48] as shown in Table 6. Chemical shifts are reported in ppm relative to TMS for ¹H and ¹³C NMR spectra. The atom statues were numbered according to Fig. 1. Firstly, full geometry optimization of the 1DF2VCP was performed at the gradient corrected density functional level of theory using the hybrid B3LYP method based on Becke's three parameters functional of DFT. Then, gauge-including atomic orbital (GIAO) ¹H and ¹³C chemical shift calculations of the compound was made by the same method using 6-311++G (d,p) basis set. Cyclopropane carbon give signals in overlapped areas of the spectrum with chemical shift values from 100 to 150 ppm. In our present investigation, the experimental chemical shift values of

with 6-311++G (d,p) basis set shown in Table 9. The Mulliken charge distribution structure of 1DF2VCP is shown in Fig. 9 (Supp). The results show that substitution of the fluorine atoms leads to a redistribution of electron density. However, cyclopropane of molecules exhibits a different charge with each other. For example, the charge of C1, C3 and C11 atoms are negative whereas C2 and C9 having positive charge in cyclopropane and vinyl group. H4 having more positive value than other hydrogen atoms.

Table 11

The calculated thermo dynamical parameters of 1,1-difluoro-2-vinyl-cyclopropane molecule in ground state at 298.15 K.

Basic set	HF 6-31++G (d,p)	HF 6-311++G (d,p)	B3LYP 6-31++G (d,p)	B3LYP 6-311++G (d,p)
SCF energy (a.u.)	–391.6702258	–391.7542554	–393.792024	–393.8842231
Zero point vib. energy (J mol ^{–1})	278301.9	276709.0	258252.3	257244.3
Rotational constants (GHz)	5.16887	5.19254	5.01878	5.04653
	1.71118	1.71535	1.67649	1.68412
	1.61723	1.62204	1.58201	1.58928
Specific heat (C _v) (cal mol ^{–1} K ^{–1})	22.801	22.859	24.849	24.869
Entropy (S) (cal mol ^{–1} K ^{–1})	80.069	80.057	81.629	81.599
Dipole moment (Debye)	2.5533	2.6268	2.3556	2.3890
Enthalpy (K cal mol ^{–1})	70.530	70.153	66.006	65.763

Cyclopropane carbons are in the range 125.9–135.2 ppm. On the basis of ¹³C NMR spectra, in which the ring carbons C1 attached to the F atom have smaller chemical shift than the other carbon atoms in the vinyl group (CH₂=CH). The chemical shift values of C2 and C3 are smaller than the C1 because of the substitution of fluorine group and the vinyl group. The computed chemical shift values of 149.06 and 124.58 ppm (B3LYP) for vinyl group carbon atoms (C9 and C11) are in good agreement with the measured values (135.2 and 134.3 ppm). The chemical shifts obtained and calculated for the ¹H atoms of cyclopropane are quite low. Because, hydrogen atom attached nearby electron-withdrawing atom or group can decrease the shielding. The hydrogen atoms attached with the cyclopropane ring showed a chemical shift of 2.11, 1.16, and 0.80 ppm, these values showed good agreement with the ¹H chemical shift observed by Abraham et al. [49] in fluoro-cyclopropane. All hydrogen atoms of vinyl groups chemical shift values are 6.02, 5.35, 5.55 ppm due to the shielding effect. Table 6 depicts that the calculated chemical shifts are in agreement with the experimental findings.

Conclusion

Based on the HF and DFT/B3LYP methods with 6-31G++ (d,p) and 6-311G++ (d,p) levels, a complete vibrational properties of 1DF2VCP have been investigated. The breakdown in symmetry of the cyclopropane ring was observed and attributed to the difference in mass of the substituents. The influence of carbon-fluorine bond and vinyl group to the vibrational frequencies of the title compound were discussed in detail. The qualitative agreement between the calculated and observed frequencies confirms the minimum standard deviation between the theoretical and experimental wave number. The electrical and optical properties of 1DF2VCP are deeply investigated using frontier molecular orbital. The electrostatic potential map (ESP), molecular electrostatic potential (MEP) and electron density (ED) were performed and from which the change in chemical properties were discussed. Furthermore, the thermodynamic and electronic absorption properties of the compounds have been calculated. Theoretical molecular orbital coefficients analysis suggests that electronic transitions are assigned π – π^* type. The correlation between the statistical thermodynamics and temperature are also obtained. It was seen that the heat capacities, entropies and enthalpies increase with the increasing temperature owing to the intensities of the molecular vibrations increase with increase in temperature. The magnetic properties of the title compound were observed and the chemical shift were compared with the experimental data and found to be in good agreement for both ¹³C and ¹H. Mullikan atomic charges of the compound were computed and the redistribution of electron density was studied.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.saa.2015.03.084>.

References

- [1] Kumar et al., Int. J. Pharm. Pharm. Sci. 5 (1) (2013) 467–472.
- [2] M.P. Toraskar, V.J. Kadam, V.M. Kulkarni, Synthesis and antimicrobial activity of functional analogues of fluconazole, Int. J. Pharm. Pharma. Sci. 2 (2) (2010) 132–133.
- [3] W. Cao, H. Zhang, J. Chen, H. Deng, M. Shao, L. Lei, J. Qian, Y. Zhu, A facile preparation of trans-1,2-cyclopropanes containing p-trifluoromethylphenyl group and its application to the construction of pyrazole and cyclopropane ring fused pyridazinone derivatives, Tetrahedron 64 (2008) 6670–6674.
- [4] J.P. Perdew, K. Burke, Y. Wang, Phys. Rev. B 54 (1996) 16533.
- [5] J.P. Perdew, J.A. Chevary, S.H. Vosko, K.A. Jackson, M.R. Pederson, D.J. Singh, C. Fiolhais, Phys. Rev. B 48 (1993) 4979(E).
- [6] Yannick Carissan, Wim. Klopper, J. Mol. Struct. (Theochem.) 940 (2010) 115–118.
- [7] M.H. Jamroz, J.Cz. Dobrowolski, J. Mol. Struct. 565–566 (2001) 475–480.
- [8] T. Clark, J. Chandrasekhar, G.W. Spitznagel, P.V.R. Schleyer, J. Computat. Chem. (1983) 294–304.
- [9] M.J. Frisch, J.A. Pople, J.S. Binkley, J. Chem. Phys. 80 (1984) 3265.
- [10] D.C. Young, Computational Chemistry: A Practical guide for applying Techniques to Real world Problems (Electronic), John Wiley and Sons Inc., New York, 2001.
- [11] M. Karabacak, D. Karagoz, M. Kurt, Spectrochim. Acta 72 (2009) 1076–1083.
- [12] L.J. Bellamy, The Infrared Spectra of Complex Molecules, Wiley, New York, 1959.
- [13] R. Dennington, T. Keith, J. Millam, K. Eppinnett, W.L. Howell, R. Gilliland, GaussView, Version 3.07, Semichem Inc., Shawnee Mission, KS, 2003.
- [14] X. Zhou, R. Liu, Spectrochim. Acta A 53 (1997) 259–269.
- [15] N. Sundaraganesan, S. Illakiamani, H. Saleem, P.M. Wojciechowski, D. Michalska, Spectrochim. Acta A 61 (2005) 2995.
- [16] C. Moller, M.S. Plesset, Phys. Rev. 46 (1934) 618.
- [17] P. Hohenberg, W. Khon, Phys. Rev. B 136 (1964) 864.
- [18] A.D. Becke, J. Chem. Phys. 98 (1993) 5648.
- [19] C.N.R. Rao, Chemical Applications of Infrared Spectroscopy, Academic Press, New York, 1959.
- [20] N.A. Narasimham, M.Z. El-Saban, J. Rud-Nielson, J. Chem. Phys. (USA) 24 (1956) 420.
- [21] E.E. Ferguson et al., J. Chem. Phys. (USA) 21 (1953) 1464.
- [22] A.K. Ansari, P.K. Verma, Spectrochim. Acta 35 (1979) 35.
- [23] N. Sundaraganesan, B. Anand, C. Meganathan, B.D. Joshua, Spectrochim. Acta 68 (2007) 561–566.
- [24] M. Karabacak, E. Kose, M. Kurt, J. Raman Spectrosc. 41 (2010) 1085–1097.
- [25] N. Sundaraganesan, S. Ilakiamani, B.D. Joshua, Spectrochim. Acta 67 (2007) 287–297.
- [26] Y. Erdogan, M.T. Gulluoglu, M. Kurt, J. Raman Spectrosc. 40 (2009) 1615–1623.
- [27] V. Krishnakumar, V. Balachandran, Spectrochim. Acta 61 (2005) 1001–1006.
- [28] K. Wolinski, J.F. Hinton, P. Pulay, J. Am. Chem. Soc. 112 (1990) 8251.
- [29] S.H. Brewer, A.M. Allen, S.E. Lappi, T.L. Chase, K.A. Briggman, C.B. Gorman, S. Franzen, Langmuir 20 (2004) 5512.
- [30] M. Silverstein, G. Clayton Basseler, C. Morill, Spectrometric Identification of Organic Compounds, Wiley, New York, 2001.
- [31] G. Varsanyi, Assignments of Vibrational Spectra of Seven Hundred Benzene Derivatives, Adam Hilger 1–2 (1974).
- [32] H.J. Bernstein, Spectrochim. Acta 18 (1962) 161.
- [33] D.C. McKean et al., Spectrochim. Acta 1037 (1973) 29A.
- [34] M.T. Forel et al., J. Opt. Soc. Amer. 50 (1960) 1228.
- [35] C.J. Wurrey, A.B. Nease, Vib. Spectra Struct. 7 (1978) 1.

- [37] W.J. Potts, R.A. Nyquist, *Spectrochim. Acta* 15 (1959) 679.
- [38] E.M. Popov, G.I. Kajan, *Opt. Spectrosc.* 12 (1962) 102.
- [39] E.M. Popov et al., *Opt. Spectrosc.* 12 (1962) 17.
- [40] J. Overened, J.R. Scherer, *J. Chem. Soc. Perkin Trans.* (1974) 1569.
- [41] K.H. Ree, F.A. Miller, *Spectrochim. Acta* 27A (1971) 1.
- [42] N.C. Craig et al., *Spectrochim. Acta* 28A (1972) 1175.
- [43] J.S. Murray, K. Sen, *Molecular Electrostatic Potentials, Concepts and Applications*, Elsevier, Amsterdam, 1996.
- [44] E. Scrocco, J. Tomasi, in: P. Lowdin (Ed.), *Advances in Quantum Chemistry*, Academic Press, New York, 1978, p. 402.
- [45] F.J. Luque, M. Orozco, P.K. Bhadane, S.R. Gadre, *J. Phys. Chem.* 97 (1993) 9380–9384.
- [46] J. Sponer, P. Hobza, *Int. J. Quant. Chem.* 57 (1996) 959–970.
- [47] R. Zhang, B. Dub, G. Sun, Y. Sun, *Spectrochim. Acta A* 75 (2010) 1115–1124.
- [48] W. James Feast, Miquel Gimeno, Alan M. Kenwright, *Macromolecules* 39 (2006) 12.
- [49] R.J. Abraham, P. Leonard, C.F. Tormena, *Magn. Reson. Chem.* 50 (2012) 305–313.