

Vibrational Spectra (FT-IR, FT-Raman), NBO and HOMO, LUMO Studies of 2-Thiophene Carboxylic Acid Based On Density Functional Method.

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Abstract : The molecular structure and vibrational spectra of 2-thiophene carboxylic acid (TCA) is calculated with the help of B3LYP density functional theory (DFT) using 6-31G** as basis set. The solid phase FTIR and FT-Raman spectra of TCA have been recorded in the range 4000 - 400 and 3500-50 cm⁻¹ respectively. On the basis of B3LYP calculations, the normal coordinate analysis is performed to assign the vibrational fundamental frequencies according to potential energy distribution (PED). The over estimations of the calculated wave numbers are corrected by the aid of scaled quantum mechanical force field methodology (SQMFF). The computational frequencies are in good agreement with the observed results. The stability of the molecule is analyzed using NBO analysis. The calculated HOMO and LUMO energies show that charge transfer that charge transfer occurs within the molecule.

Keywords – TCA, FTIR, FT-Raman, DFT, NBO.

I. Introduction

Thiophene is one of the simplest aromatic molecules with a five - membered heterocyclic sulphur-containing ring. Thiophene obeys the $4n+2\pi$ electron rule and is considered to be aromatic. The aromaticity in thiophene is attributed to the delocalization of π electrons forming an aromatic sextet in which four electrons are contributed by carbon atoms and a pair of electrons by the sulphur atom in the ring. Thiophene is uniquely a electron rich heterocycle and has the highest resonance stabilization energy among the five membered heterocycles. Thiophenes are part of many organic compounds [1] having vast applications in the field of electronics and optoelectronics, medicine and materials [2-6]. The remarkable pharmacological efficiency of the compounds containing a thiophene ring in their structure are known for their antidepressant, anticonvulsant, anthelmintic (nematodes), antispasmodic, antihistaminic, anesthetic, antipruritic, antitussive, analgesic action [7]. Thiophene and its derivatives exhibit diverse biological properties such as nemotocidal [8], insecticidal [9], antibacterial [10], antifungal [11], antiviral [12] and antioxidant activity [13].

Quantum chemical computational methods have proved to be an essential tool for interpreting the vibrational spectra [14-16]. DFT calculations are known to provide excellent vibrational wavenumbers of organic compounds, if the calculated wavenumbers are scaled to compensate for the treatment of electron correlation, for basis set deficiencies and for anharmonic effects [17-19]. The present work reports a complete vibrational analysis of 2-thiophene carboxylic acid (TCA) by combining the experimental IR and Raman spectral data and theoretical information using scaled quantum chemical (SQM) technique based on Pulay's density functional theory (DFT). The redistribution of electron density (ED) in various bonding and antibonding orbitals and their stabilization energies $E(2)$ have also been calculated by natural bond orbital (NBO) analysis to give clear evidence of stabilization originating from the hyper conjugation of various intra-molecular interactions. The studies of HOMO, LUMO analysis have been used to elucidate information regarding charge transfer within the molecule.

II. Experimental Details

The title compound TCA was purchased from Sigma –Aldrich chemical Company (USA) with a stated purity of 99% and used as such without any further purification. The FTIR spectra of 2-thiophene carboxylic acid was recorded in the region 4000-400 cm⁻¹ on JASCO -6300 spectrometer with samples in the KBr. The FT-Raman spectrum of TCA was obtained in the range 3500-50 cm⁻¹ using Bruker RFS 100/s FT-Raman spectrophotometer with a 1064nm Nd:YAG laser source of 150mW power. The spectral resolution is 2cm⁻¹.

III. Computational Methods

The molecular geometry optimization, energy and Vibrational frequency calculations have been performed for TCA using Gaussian'03W program package [20] at the Becke3-Lee-Yang-Parr (B3LYP) level with standard 6-31G** basis set. The Cartesian representation of the theoretical force constants has been

computed at the fully optimized geometry. Multiple scaling of the force field has been performed by SQM procedure [21, 22] using selective scaling in the internal coordinate representation. Normal coordinate analysis has been performed to obtain full description of the molecular motion pertaining to the normal modes with MOLVIB program version 7.0 written by Sundius [23, 24]. For plots of simulated IR spectra, pure Lorentzian band shapes were used with a bandwidth (FWHM) of 10cm⁻¹. The Raman activity (S_i) calculated by Gaussian 03W program have been suitably adjusted by the scaling procedure with MOLVIB and subsequently converted to relative Raman intensity (I_i) using the following relationship derived from the basis theory of Raman Scattering.[25 , 26]

$$I_i = \frac{f(v_o - v_i)^4 S_i}{v_i \left[1 - \exp\left(\frac{-hc v_i}{kT}\right) \right]} \quad (1)$$

where v_o is the exciting frequency (in cm⁻¹ units), v_i is the vibrational wave number of the ith mode, h, c, k are universal constants, and f is the suitably chosen common scaling factor for all the peak intensities. The simulated IR and Raman spectra have been plotted using with Lorentzian shapes with full width at half maximum (FWHM) of 10 cm⁻¹. Natural bond orbital (NBO) [27] analysis were performed using NBO 3.1 program as implemented in the Gaussian 03 W package at the DFT/B3LYP/6-31G** level of theory.

IV. Results And Discussion

4.1 Molecular Geometry

The optimized molecular structure along with the numbering of atoms of TCA is as shown in Fig 1. Parameters corresponding to optimized geometry of the title compound are given in Table 1.

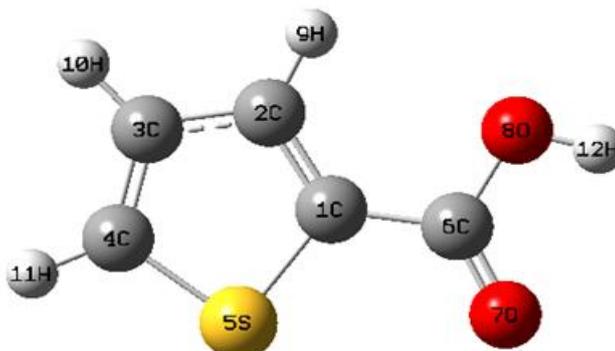


Fig.1. Molecular structure of TCA with numbering of atoms

TABLE 1-Optimized geometrical parameters of TCA obtained by B3LYP/6-31G** density functional calculations

Bond Length / Å		Bond Angle / °	
C1-C2	1.38	C2-C1- S5	111.52
C1-S5	1.74	C2-C1-C6	129.34
C1-C6	1.47	S5-C1-C6	119.14
C2-C3	1.42	C1-C2-C3	112.72
C2-H9	1.08	C1-C2-H9	122.52
C3-C4	1.37	C3-C2-H9	124.76
C3-H10	1.08	C2-C3-C4	112.36
C4-S5	1.08	C2-C3-H10	124.10
C4-H11	1.08	C4-C3-H10	123.54
C6-O7	1.22	C3-C4-C5	112.42
C6-O8	1.36	C3-C4-C5	112.42
O8-H12	0.97	C3-C4-H11	127.77
		C5-C4-H11	119.81
		C1-S5-C4	90.98
		C1-C6-O7	125.01
		C1-C6-O8	112.30
		O7-C6-O8	122.69
		C6-O8-H12	105.59

4.2 Vibrational spectra

The vibrational spectral assignments have been carried out with the help of normal coordinate analysis. Non-redundant set of local symmetry coordinates constructed by suitable linear combinations of internal coordinates chosen according to the recommendations of Pulay et al.[21] are given in Table 2. The computed wave numbers are selectively scaled according to the SQM procedure suggested by Rauhut and Pulay [22]. The detailed vibrational assignments of fundamental modes of TCA along with the observed and calculated wavenumbers, IR intensities, Raman activities and normal mode description (characterized by PED) are reported in Table 3. For a visual comparison, the observed and simulated FTIR and FT-Raman spectra are presented in Figs. 2 and 3 respectively.

TABLE 2- Definition of local symmetry coordinates in B3LYP/6-31G level for TCA**

L.No	Symmetry Coordinates ^a	Description ^b
1	$S_1 = r_{2,1}$	$\nu C2C1$
2	$S_2 = r_{3,2}$	$\nu C3C2$
3	$S_3 = r_{4,3}$	$\nu C4C3$
4	$S_4 = r_{1,6}$	$\nu C1C6$
5	$S_5 = r_{5,4}$	$\nu C4S5$
6	$S_6 = r_{1,5}$	$\nu C1 S5$
7	$S_7 = r_{6,7}$	$\nu C6O7$
8	$S_8 = r_{6,8}$	$\nu C6O8$
9	$S_9 = r_{8,12}$	$\nu O8H12$
10	$S_{10} = r_{4,11}$	$\nu C4H11$
11	$S_{11} = r_{3,10}$	$\nu C3H10$
12	$S_{12} = r_{2,9}$	$\nu C2H9$
13	$S_{13} = \beta_{1,2,9} - \beta_{3,2,9}$	$\beta C2H9$
14	$S_{14} = \beta_{2,3,10} - \beta_{4,3,10}$	$\beta C3H10$
15	$S_{15} = \beta_{3,4,11} - \beta_{5,4,11}$	$\beta C4H11$
16	$S_{16} = \beta_{5,1,6} - \beta_{2,1,6}$	$\beta C1C6$
17	$S_{17} = \beta_{7,6,1} - \beta_{8,6,1}$	$\beta C6C2$
18	$S_{18} = \beta_{4,5,2} + a(\beta_{5,1,2} + \beta_{3,4,5}) + b(\beta_{1,2,3} + \beta_{2,3,4})$	bring 1
19	$S_{19} = (a-b)(\beta_{5,1,2} - \beta_{2,3,4}) + (1-a)(\beta_{1,2,3} - \beta_{3,4,5})$	bring 2
20	$S_{20} = 2\beta_{8,6,7} - \beta_{7,6,1} - \beta_{8,6,1}$	βCOO
21	$S_{21} = \beta_{12,8,6}$	βCOH
22	$S_{22} = \gamma_{11,4,3,5}$	$\gamma C4H11$
23	$S_{23} = \gamma_{9,2,3,1}$	$\gamma C2H9$
24	$S_{24} = \gamma_{10,3,4,2}$	$\gamma C3H10$
25	$S_{25} = \gamma_{6,1,2,5}$	$\gamma C1C6$
26	$S_{26} = \gamma_{1,6,8,7}$	γCOO
27	$S_{27} = b(\gamma_{4,5,1,2} + \gamma_{3,4,5,1}) + a(\gamma_{5,1,2,3} + \gamma_{2,3,4,5}) + \gamma_{1,2,3,4}$	τ ring 1
28	$S_{28} = (a-b)(\gamma_{3,4,5,1} + \gamma_{1,2,3,4}) + (1-a)(\gamma_{4,5,1,2} + \gamma_{5,1,2,3})$	τ ring 2
29	$S_{29} = \tau_{12,8,6,2} + \tau_{12,8,6,7}$	τOH
30	$S_{30} = \tau_{8,6,1,2} + \tau_{8,6,1,5} + \tau_{7,6,1,5} + \tau_{7,6,1,2}$	τCC

For numbering of atoms refer Fig 1.

^aDefinitions are made in terms of the valence coordinates:

r_{ij} is the bond length between atoms i and j ; β_{ijk} is the valence angle between i,j,k where j is the central atom; γ_{ijkl} is the out-of-plane angle between the $i-j$ bond and the plane defined by the j,k,l atoms; τ_{ijkl} is the torsion (dihedral) angle between the plane defined by i,j,k and j,k,l atoms

^b(ν)stretching:(β)in-plane-bending:(γ)out-of-plane-bending (τ)torsion.

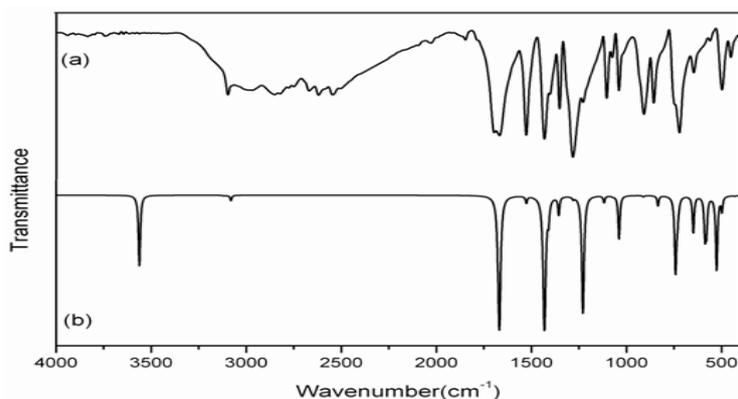


Fig.2 FT-IR spectra of TCA (a) observed (b) simulated

4.2.1 COOH Vibrations

Vibrational analysis of carboxylic acid is made on the basis of carbonyl group and hydroxyl group. The free hydroxyl group absorbs strongly in the region $3700\text{--}3584\text{ cm}^{-1}$, whereas the existence of intermolecular hydrogen bond formation can lower the O-H stretching frequency in the range $3500\text{--}3200\text{ cm}^{-1}$ [28, 29]. In the experimental IR of TCA, the bands due to the OH stretching are superimposed upon the CH stretching bands and cannot be distinguished from overtones and combinations, making the vibrational spectra more complicated [30]. However, this band is predicted at 3562 cm^{-1} by DFT/B3LYP/6-31G** and is assigned to a weak band at 3562 cm^{-1} in the FTIR spectra of the title molecule. The characteristic absorption bands of C=O stretching vibrations of acids are normally strong in intensity and found in the region $1800\text{--}1690\text{ cm}^{-1}$ [31]. The position of the C=O stretching band depends on the bond strength, which in turn depends on the inductive, conjugative, steric effects, the size of the ring to which it is attached and on the lone pair of electrons on oxygen. The intensity of carbonyl group can increase because of conjugation or formation of hydrogen bonds. In TCA the conjugation of C=O with C=C bond results in the lowered value of carbonyl stretching wavenumber. The very strong band observed at 1669 cm^{-1} in the FT IR spectrum is assigned to the C=O stretching vibration for TCA. The corresponding theoretically computed value at 1669 cm^{-1} is in good agreement with the experimental result [32]. Two other characteristic carboxylic group vibrations are C-O stretching and in-plane C-OH bending. The C-O stretching and in-plane C-OH bending are expected in the wide range of $1450\text{--}1150\text{ cm}^{-1}$ depending on whether the acid is monomeric or dimeric [33]. For TCA the bands observed at 1432 , 1232 and 1229 cm^{-1} have contributions from the C-O stretching and in-plane C-OH bending modes. According to PED results both these vibrations are described as mixed modes as shown in Table 3. In TCA a medium strong band at 742 cm^{-1} (FT-Raman) corresponds to γ C-COOH out of plane bending vibration. This assignment is in agreement with Subash chandrabose et al. and Chaitantya [34, 35]. As the τCO_2 modes are expected in the region $150\text{--}50\text{ cm}^{-1}$ [36] for TCA, the computed band at 70 cm^{-1} is assigned to this mode; for the same vibration, the FT Raman spectral measurements show a weak band at 70 cm^{-1} .

4.2.2 C-H Vibrations

Hetero aromatics such as furans, Pyrroles and thiophenes show C-H stretching bands in the region $3100\text{--}3000\text{ cm}^{-1}$ [37]. In the present study the aromatic C-H stretch computed in the range $3117\text{--}3080\text{ cm}^{-1}$ by B3LYP method shows good agreement with the recorded FTIR and FT-Raman bands in the range $3113\text{--}3083\text{ cm}^{-1}$. All the aromatic C-H bands are found to be weak, and this is due to a decrease in dipole moment caused by reduction of negative charge on the carbon atom [38]. In aromatic compounds the C-H in-plane bending wavenumbers appear in the range $1000\text{--}1300\text{ cm}^{-1}$ and C-H out-of plane bending in the range $750\text{--}1000\text{ cm}^{-1}$ [31, 39]. According to Socrates [39] the frequencies of thiophene appear in the region $1283\text{--}909\text{ cm}^{-1}$ for C-H in-plane bending and $832\text{--}710\text{ cm}^{-1}$ for C-H out-of-plane bending vibrations. For the title compound the bands at 1283 , 1105 , 1041 cm^{-1} in FT-IR and at 1114 cm^{-1} in FT-Raman are ascribed to C-H in plane bending modes. The C-H out-of-plane bending vibrations are assigned to the medium bands observed at 910 , 858 cm^{-1} in FTIR and to a weak band at 862 cm^{-1} in FT-Raman. The position and the number of C-H in-plane vibration modes depend on the orientation and the number of isolated ring hydrogen atoms, whereas the position of the C-H out-of-plane deformation bands depend on the number of free hydrogen atoms adjacent to one another [37]. The theoretically computed frequencies for both in-plane and out-of plane deformation vibrations by B3LYP/6-31G** show excellent agreement with experimental spectrum as well as literature data.

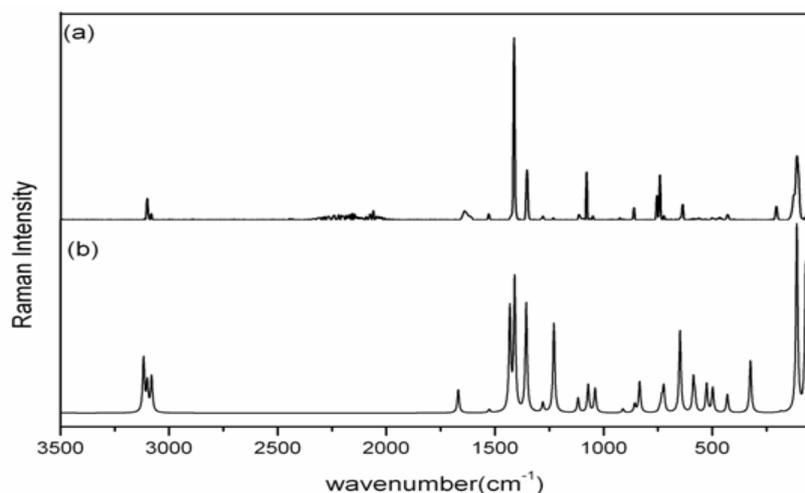


Fig.3. FT-Raman spectra of TCA (a) observed (b) simulated

4.2.3 Ring Vibration

The aromatic ring stretching vibrations occur generally in the region 1600-1350 cm^{-1} . The position and the intensity of the ring stretching bands of aromatic five membered ring hetero cycles are more sensitive than the corresponding bands of benzene to changes in the substituents so that wide frequency variation can occur, exceptionally in thiophene which involves the movement of the heavy sulphur heteroatom [37]. For 2 substituted thiophenes these bands are observed at 1514-1532, 1430-1454 and 1347-1367 cm^{-1} from the wavenumber ranges given by C. N. R. Rao [37] for the four bands in the region. In the present work the wavenumbers observed in the FT IR spectrum at 1528 and 1352 are assigned to C-C stretching vibrations. The same vibrations in the FT- Raman are at 1530, 1413 and 1354 cm^{-1} . The scaled vibrations by B3LYP calculation predicted at 1526, 1410 and 1356 cm^{-1} shows good agreement with the recorded spectral data. Coats [40] observed C-S stretching modes between 710 and 687 cm^{-1} and Kwiatkowski et al. [41] reported C-S stretching vibration at 839 and 608 cm^{-1} . In the present study the stretching of the C-S bond in the thiophene ring is identified at 852, 649 cm^{-1} theoretically (B3LYP), but only one peak is observed at 647/637 in the experimental FT IR/FT Raman spectrum. Small changes in the wavenumber observed for these modes are due to the change in force constants/reduced mass ratio resulting mainly from the extent of mixing between ring and substituent group.

TABLE 3- Assignments of fundamental vibrations of TCA by normal coordinate analysis based on SQM force field calculations using B3LYP/6-31G**

Observed wavenumbers		Calculated Wave numbers(cm^{-1}) Using B3LYP / 6-31G* force field	A_i IR ^a	I_i R ^b	Characterisation of normal modes with PED(%) ^c
IR	Raman				
3562w	-	3562	83.9	149.7	ν OH(100)
-	3113	3117	0.6	165.5	ν CH(98)
3097w	3102ms	3100	0.3	88.7	ν CH(98)
	3083w	3080	4.9	106.1	ν CH(98)
1669s		1669	299.3	64.1	ν C=O (48), ν C-O(37)
1528s	1530w	1526	6.3	1.9	ν CC(45), β ring 2(36), β CH(15).
1432s	-	1432	304.1	56	ν C-O(35), β COH(19), ν C-C _{ar} (18),
-	1413vs	1410	19.1	70	ν CC(52), β CH(37)
1352m	1354m	1356	17.6	54.1	ν CC(74), β CO(14)
1283vs	-	1280	2.4	4.2	β CH(39), ν CC(22), β CO(14)
1229m	1232w	1229	202.5	37.7	β COH(57), ν C=O(22), ν C-O(22)
1105m	1114m	1118	6.3	5.3	ν CC(39), β CH(27), β CO(19)
-	1080m	1071	0.6	9.5	ν CC (40), β CO(30), ν CS (10)
1041m	-	1039	45.4	7.9	β CH(23), ν CS (23), ν CC _{ar} (19)
910m	-	911	1.2	1	γ CH (75), τ ring 1(13)
858m	862w	858	0.1	2.1	γ CH (86)
-	-	852	9.4	7.2	ν CS (70), β ring 1(10)
-	742m	742	94.3	0.8	γ C-COO(69), γ CH (15)
-	-	732	20.7	2.5	γ CH (95)
723s	-	723	3.8	4.8	β ring 2(65), ν C=C _{ar} (22), ν CS (32)
647w	637m	649	37.5	13.4	ν CS (26), β ring 1(65)
	587w	587	39.7	4.7	τ ring 1 (50), τ OH(32).
562w	-	579	34.3	1.7	τ ring 1 (46), τ ring 1 (23), τ OH(23).
-	-	526	90.4	3.4	δ COO(51), τ ring 2(28)
498m	-	498	13.7	2.7	τ ring 2(64), τ ring 1(22)
-	431w	431	3.4	2.6	ν CS (31), β COO(20), β CC(19), β ring 1(14)
-	-	324	12.1	3	β COO(30), β ring 1(21), ν CC _{ar} (15), ν CS (13)
-	-	183	1.9	0	β COO(59), β CC(33)
-	111m	111	2.1	1.8	γ CC 78), τ ring 1(11),
-	70w	70	0	0.6	τ CO ₂ (60), γ CC (30),

(ν)stretching:(β)in-plane-bending:(γ)out-of-plane-bending:(δ)scissoring:(τ)torsion.

^aCalculated IR intensity(K mol^{-1}).

^bRaman activity($\text{A}^4 \text{amu}^{-1}$).

^cPED values greater than 10% are given

5 NBO Analyses

Natural bond analysis provides an efficient method for studying intra and intermolecular bonding and interaction among bonds, and also provides a convenient basis for investigating charge transfer or conjugative interactions in molecular systems. NBO method gives useful information about interactions in both filled and

virtual orbital spaces which could enhance the analysis of intra and intermolecular interactions [42]. This is carried out by considering all possible interactions between filled donor and empty acceptor NBOs and estimating their energy importance by second order perturbation theory. For each donor (i) and acceptor NBO (j) the stabilization energy E (2) associated with electron delocalization between donor and acceptor is estimated as

$$E(2)=\Delta E_{ij}=q^i F(i,j)/(E_j-E_i)$$

Where q^i is the orbital occupancy, E_j and E_i are diagonal elements and $F(i,j)$ is the off-diagonal NBO Fock matrix element. The larger the $E(2)$ value the more intensive is the interaction between electron donors and electron acceptors, i.e. more donating tendency from electron donors to electron acceptors and greater the extent of conjugation of the whole system. The results of second order perturbation theory analysis of Fock matrix at B3LYP/6-31G** level of theory are collected in Table 4. The intramolecular interaction are formed by the orbital overlap between bonding π (C1-C2) and antibonding π^* (C6-O7) orbital which results in intramolecular charge transfer (ICT) causing stabilization of the system. These interactions are observed as increase in electron density in (C6-O7) antibonding orbital which weakens the respective bond. The most important interaction energies related to resonance in the molecule are electron donation from the lone pair of the ring hetero sulphur atom n2 (S5) to the antibonding acceptors π^* (C1-C2) and π^* (C3-C4) (stabilization energy of 20.93 and 23.45KJ/mol), which measures the π delocalization within the thiophene ring. The magnitude of charge transfer from the lone pairs of n1(O8) to the antibonding C6-O7 σ orbitals amount to a stabilization of 7.09 Kcal/mol, while to the antibonding π orbits it is of the order of 45.5 Kcal/mol. The interaction ($n \rightarrow \sigma^*$) between the oxygen lone pair (O7) and the antibonding σ^* of C1-C6 and C6-O8 is seen to give more stabilization of 18.62 and 33.87 Kcal/mol respectively. In the case of OH bond, σ (O8-H12) conjugation with σ^* (C1-C6) and σ^* (C6-O7) leads to less stabilization energy of 5.09 and 1.02 Kcal/mol which shows that σ (O-H) bonds do not have the stability to cause any change in the thiophene ring.

The atomic charges of TCA calculated by NBO analysis using the B3LYP/6-31G** is show in Fig.2. From the listed atomic charge values, O8 and O7 oxygen atoms have a very large negative charge and behave as electron acceptors. The very high positive charge on charge atom C6 atom is due to the partial polar nature of the C=O group.

TABLE 4-Second order perturbation theory analysis of Fock matrix in NBO basis for TCA

Donor (i)	ED (i) (e)	Acceptor (j)	ED (j) (e)	E (2) ^a (KJmol ⁻¹)	E(j)-i) ^b (a.u)	F(i,j) ^c (a.u)
σ (C ₁ -C ₂)	1.9816	σ^* (C ₁ -C ₆)	0.0662	2.87	1.17	0.05
		σ^* (C ₂ -C ₃)	0.0130	2.14	1.26	0.05
		σ^* (C ₆ -O ₇)	0.0197	1.94	1.33	0.05
π (C ₁ -C ₂)	1.8095	π^* (C ₃ -C ₄)	0.2994	14.91	0.29	0.06
		π^* (C ₆ -O ₇)	0.2767	22.99	0.28	0.07
σ (C ₁ -S ₅)	1.9747	σ^* (C ₆ -O ₈)	0.1017	3.03	1.01	0.05
σ (C ₁ -C ₆)	1.9805	σ^* (C ₁ -C ₂)	0.0716	3.85	1.29	0.06
		σ^* (O ₈ -H ₁₂)	0.0134	2.75	1.13	0.05
		σ^* (C ₁ -C ₂)	0.2036	2.32	1.26	0.05
σ (C ₂ -C ₃)	1.9783	σ^* (C ₁ -C ₆)	0.0662	4.63	1.12	0.07
		σ^* (C ₃ -C ₄)	0.0156	2.05	1.26	0.05
		σ^* (C ₂ -C ₃)	0.0130	2.15	1.26	0.05
σ (C ₃ -C ₄)	1.9868	π^* (C ₁ -C ₂)	0.3411	17.48	0.29	0.07
π (C ₃ -C ₄)	1.8350	π^* (C ₁ -C ₂)	0.3411	17.48	0.29	0.07
σ (C ₄ -S ₅)	1.9810	σ^* (C ₁ -C ₆)	0.0662	3.22	1.11	0.54
σ (C ₆ -O ₇)	1.9973	σ^* (C ₁ -C ₂)	0.0204	1.15	1.66	0.04
π (C ₆ -O ₇)	1.9831	π^* (C ₁ -C ₂)	0.3411	4.56	0.39	0.04
σ (C ₆ -O ₈)	1.9943	σ^* (C ₁ -S ₅)	0.0258	2.39	1.14	0.05
σ (O ₈ -H ₁₂)	1.9862	σ^* (C ₁ -C ₆)	0.0662	5.09	1.18	0.07
		σ^* (C ₆ -O ₇)	0.0197	1.02	1.34	0.03
n1(S ₅)	1.9847	σ^* (C ₁ -C ₂)	0.2036	2.25	1.23	0.05
		σ^* (C ₃ -C ₄)	0.0156	2.14	1.23	0.05
n2(S ₅)	1.6039	π^* (C ₁ -C ₂)	0.3411	20.93	0.26	0.07
		π^* (C ₃ -C ₄)	0.2994	23.45	0.26	0.07
n1(O ₇)	1.9760	σ^* (C ₁ -C ₆)	0.0662	2.98	1.13	0.05
		σ^* (C ₆ -O ₈)	0.1017	1.31	1.03	0.03
n2(O ₇)	1.9760	σ^* (C ₁ -C ₆)	0.0662	18.62	0.7	0.10
		σ^* (C ₆ -O ₈)	0.1017	33.87	0.61	0.13
n1(O ₈)	1.9763	σ^* (C ₆ -O ₇)	0.0197	7.09	1.21	0.08
n2(O ₈)	1.8284	σ^* (C ₆ -O ₇)	0.0197	45.56	0.34	0.11

^a E(2) means energy of hyper conjugative interactions.

^b Energy difference between donor and acceptor I and j NBO orbitals.

^c F(i,j) is the Fock matrix element between i and j NBO orbital

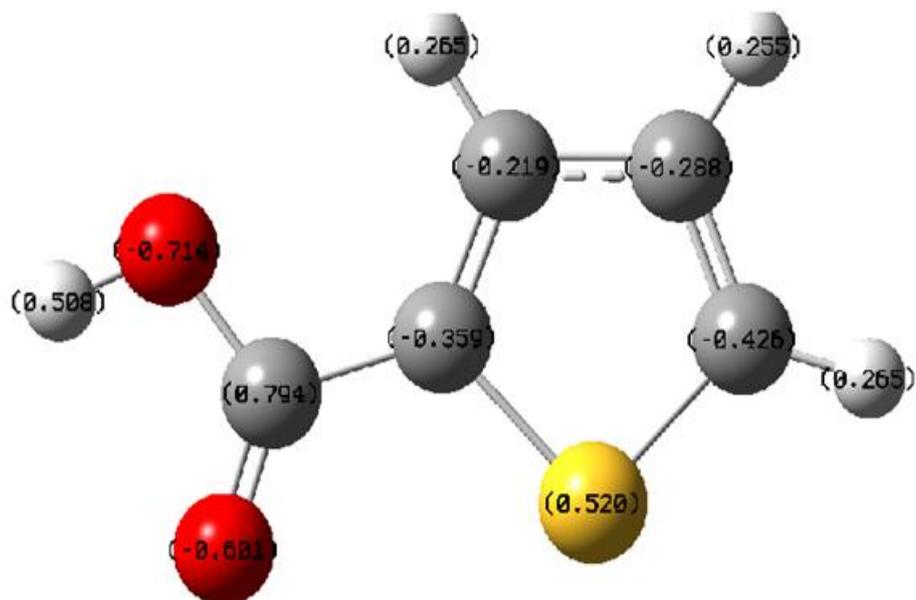


Fig. 4. Atomic charges of TCA by NBO analysis using B3LYP/6-31G**

6 HOMO, LUMO analysis

Both the highest occupied molecular orbital (HOMO) and the lowest unoccupied orbital (LUMO) are the main orbital that take part in chemical stability[43]. Molecular orbitals can provide insight into the nature of reactivity and some of the structural and physical properties of molecules. The HOMO represents the ability to donate an electron, while LUMO as an electron acceptor represents the ability to obtain an electron. The electronic transition absorption corresponds to the transition from ground to the first excited state and is mainly described by one electron excitation from the highest occupied molecular orbital to the lowest unoccupied molecular orbital [44, 45]. The HOMO of π nature, are well localized within the ring. By contrast, LUMO of π^* nature is delocalized over the entire part of the molecule. Consequently HOMO \rightarrow LUMO transition implies an energy transfer from the aromatic heterocyclic ring. The energy gap between HOMO and LUMO has been used to prove the bioactivity from intramolecular charge transfer [45]. The energy gap measures the kinetic stability of the molecules. A molecule with a small frontier orbital gap is more polarizable and it implies high chemical reactivity and low kinetic stability.

The HOMO and LUMO energy calculated by B3LYP /6-31G** method as shown below:

HOMO energy = -0.25059 a. u.

LUMO energy = -0.05697a. u.

HOMO – LUMO energy gap=0.1932 a. u.

The calculated self- consistent field (SCF) energy of TCA is -741.58657a. u. The HOMO and LUMO energy gap explains the eventual charge transfer interactions taking place within the molecule. The HOMO and LUMO plots of TCA are shown in Fig. 4.

6 Thermodynamic properties

Several thermodynamic parameters were calculated by using DFT with 6-31G** basis set are given in Table 5. Scale factors are recommended [46]for an accurate prediction in determining the zero-point vibrational energy(ZPVE) for DFT calculation

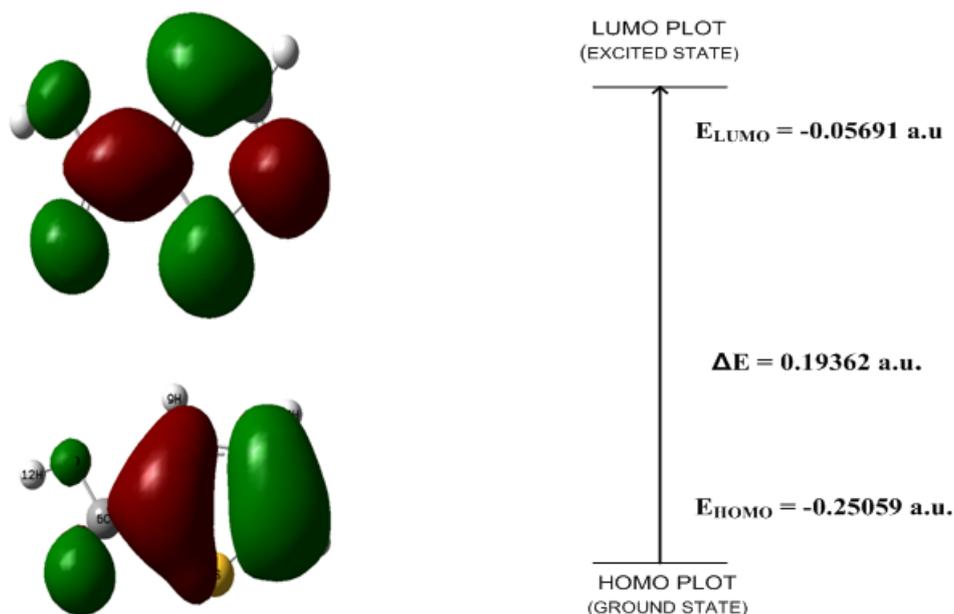


Fig. 4. HOMO and LUMO plot of TCA

V. Conclusions

The FT-IR and FT-Raman Spectra have been recorded and the detailed vibrational assignments' are presented for TCA. The equilibrium geometries, harmonic vibrational frequencies, IR and Raman spectra, NBO analysis, HOMO and LUMO analysis and thermodynamic properties of the title compound are determined and analyzed by B3LYP /6-31G** level of theory . The assignments of wave numbers of the title compound are quite comparable and unambiguous. NBO results reflect the charge transfer in the molecule due to the oxygen lone pairs in the thiophene ring and the carboxylic group. The lowering of HOMO and LUMO gap clearly explains the charge transfer interactions taking place within the molecule.

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TABLE 5 - The calculated thermodynamic parameters of TCA by B3LYP/6-31G** method

Parameters	B3LYP/6-31G**
SCF energy (Hartrees)	-741.536303
Total energy (thermal), Etotal (Kcal mol ⁻¹)	55.813
Heat capacity at const. volume, C _v (cal mol ⁻¹ K ⁻¹)	25.184
Entropy, S (cal mol ⁻¹ K ⁻¹)	83.358
Vibrational energy, Evib (Kcal mol ⁻¹)	54.035
Zero -point vibrational energy (Kcal mol ⁻¹)	51.521
Rotational constants (GHz)	
A	3.711
B	1.414
C	1.024
Dipole moment (Debye)	
μ _x	1.408
μ _y	1.712
μ _z	0.000
μ _{total}	2.216

References

- [1]. J. L. Reddinger, J. R. Reynolds, *Advances in Polymer Science*, 145, 1999, 57122 – 57135
- [2]. D. T. McQuade, A. E. Pullen, T.M. Swager, *Chemical Reviews*, 100, 2000, 2537- 2574.
- [3]. I. C. Choong, W. Lew, D. Lee, P. Pham, M.T. Burdett, J. W. Laam, C. Wiesmann, T. N. Luong, B. Fahr, W.L. DeLano, R. S. McDowell, D. A. Allen, D. Erlanson, E.M. Gordon ,T. O'Brien T, *J. Med Chem*, 45, 2002 5005 -5022.
- [4]. K. Dore, S. Dubus, H.A Ho, I. Levesque, M. Brunette, G. Corbeil, M. Boissinot, G.Boivin, M. G.Bergeron, D. Boudreau, M. Leclerc , *Journal of the American Chemical Society*, 126, 2004, 4240 -4244
- [5]. D. K. James, J.M. Tour J M , *Topics in Current Chemistry*, 257, 2005, 33 – 62.
- [6]. P. Si, Q. Chi, Z. Li, J. Ulstrup ,P.J. Moller , J. Mortensen J, *Journal of the American Chemical Society*, 129, 2007, 3888- 3896.

- [7]. Merck Index, 13th Edition, Merck & Co, Inc, Whitehouse Station, New Jersey, 2001.
- [8]. J. Bakker, F. J. Gommers, I. Nieuwenhuis, H. Wynberg, *Journal of Biological Chemistry*, 254, 1979, 1841-1844.
- [9]. S. Iyengar, J.T Arnason, B. J. R. Philogene, P. Morand, N. H. Werstiuk, G. Timmins, *Pesticide Biochemistry and Physiology*, 29, 1987, 1-9.
- [10]. H. Matsuura, G.Saxena, S.W. Farmer, R.E.W. Hancock, G.H Towers, *Planta Medica*, 62, 1996, 256 - 259.
- [11]. G.F.Q. Chan, G. H. N. Towers, J.C. Mitchell, *Phytochemistry*, 14 , 1975, 2295-2296.
- [12]. J.B. Hudson, E.A. Graham, N. Miki, G. H. N. Towers, L.L. Hudson, R. Rossi, A. Carpita, D. Neri, *Chemosphere*, 19 , 1989, 1329 – 1343.
- [13]. J. Malmstrom, M. Jonsson, I. A. Cotgreave, L. Hammarstrom, M.Sjodin, L. Engmann , *Journal of the American Chemical Society*, 123, 2001, 3434 – 3440.
- [14]. B. A. Hess Jr, J.L. Schaad, P. Carsky, R. Zahradnik, *Chemical Reviews*, 86, 1986, 709-730.
- [15]. Pulay P, Zhou X, Fogarasin G, in: R Fransto (Ed), NATO AS Series, vol. C. 406, Kluwer, Dordrecht, 1993, pp 99.
- [16]. D. N. Shin, J. W. Hahn, K.H. Jung, T. K. Ha, *Journal of Raman Spectroscopy*, 29(4), 1998, 245-249.
- [17]. N. C. Handy, C. W. Murray, R. D. Amos , *The Journal of Physical Chemistry*, 97, 1993, 4392-4396.
- [18]. P. J. Stephens, F. J. Delvin, C. F. Chavalowski ,M. J. Frisch , *The Journal of Physical Chemistry*, 98 ,1994, 11623-11627.
- [19]. F. J. Delvin, J. W. Finley, P. J. Stephens, M. J. Frisch, *The Journal of Physical Chemistry*, 99, 1995, 16883 - 16902.
- [20]. M. J. Frisch M J et al., Gaussian, Inc , Wallingford CT, 2004.
- [21]. P. Pulay, G. Forgarasi, G Pongor, J. E. Boggs, A. Vargh, *Journal of the American Chemical Society*, 105, 1983, 7037-7047.
- [22]. G. Rahut, P. Pulay, *The Journal of Physical Chemistry* , 99, 1995, 3093-3100.
- [23]. T. Sundius, *Journal of Molecular Structure: THEOCHEM* ,218, 1990, 321 -326.
- [24]. T. Sundius, *Vibrational Spectroscopy*, 29, 2002, 89-95.
- [25]. G. Keresztury, S. Holly, J. Varga, G. Besenyei, A. Wang, J. R. Doring, *Spectrochimica Acta A* 49 , 1993, 2007 – 2017.
- [26]. G. Keresztury, J. M. Chalmers, Griffith P R (Eds), *Raman Spectroscopy:theory in Handbook of Vibrational Spectroscopy*,vol 1,John Wiley &sons Ltd New York,2002.
- [27]. E. D. Glendenning, A. E. Reed, J. E Carpenter, F. Weinhold NBO 3.1, TCI,University of Wisconsin, Madison, 1998 .
- [28]. B. Smith, *Infrared Spectral Interpretation, A Systematic Approach*, CRC Press, Washington, DC, 1999
- [29]. R. M. Silverstein, F. X. Webster, *Spectrometric Identification of Organic Compounds*, sixth ed, John Wiley & Sons Inc, New York, 2003.
- [30]. V. Krishna Kumar, S. Muthunatesan, *Spectrochimica Acta Part A*, 65, 2006, 818 - 825.
- [31]. M. Silverstein, G. Clayton Basseler, C. Morill, *Spectrometric Identification of Organic Compounds*, sixth ed, John Wiley & Sons Inc, New York, 1981
- [32]. Stuart, *Infrared Spectroscopy: Fundamentals and Applications*, Wiley India Ed, 2010.
- [33]. P. Koczon, W. Lewandowski, A. P. Mazurek A P, *Vibrational Spectroscopy*, 20 , 1999, 143 - 149.
- [34]. S. Subashchandrabose, H. Saleem, Y. Erdogdu, O. Dereli, V. Thanikachalam, J. Jayabharathi, *Spectrochimica Acta Part A*, 86, 2012, 231 -241.
- [35]. K. Chaitanya, *Spectrochimica Acta Part A*, 86, 2012, 159 -173.
- [36]. Roeges, *A Guide to Complete Interpretation of Infrared Spectra of Organic Structures*, Wiley, New York, 1994
- [37]. C. N. R. Rao, *Chemical Application of Infrared Spectroscopy* , Academic Press, New York, 1981.
- [38]. N. Sundaraganesan, H. Saleem, S. Mohan, *Spectrochimica Acta Part A*, 59, 2003, 2511- 2517.
- [39]. Socrates, *Infrared and Raman Characteristic Group Frequencies, Tables and Charts*, Wiley, New York, 1974.
- [40]. J. Coates, *Interpretation of Infrared Spectra of Organic Structures* , John Wiley, New York, 2000
- [41]. J. S. Kwiatkowski, J. Leszczynski, I. Teca, *Journal of molecular structure*, 436-437, 1997, 451- 480.
- [42]. A.E. Reed, L. A. Curtiss, F. Weinhold, *Chemical Reviews*, 88 (1988) 899.
- [43]. S. Gunasekaran, R. A. Balaji, S. Kumaresan, G. Anand, S. Srinivasan, *Canadian Journal of Analytical Sciences and Spectroscopy*, 53 , 2008, 149 - 160.
- [44]. Y. Atalay, D. Avci, A. Basoglu , *Structural Chemistry*, 19 , 2008, 239 -249.
- [45]. M. Kurt, P. C. Babu, N. Sundaraganesan, M. Cinar, M. Karabacak , *Spectrochimica Acta Part A* 79, 2011, 1162 - 1170.
- [46]. M. Arivazhgan, S. Jeyavijan, *Spectrochimica Acta Part A*, 79, 2011, 376 -383.