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Experimental and Theoretical Characterization of Thiocoumarin by NLO single crystal in DFT Calculations

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Abstract

Experimental and theoretical electron densities in thiocoumarin have been analyzed based on the X-ray diffraction data at 90 K. These compound pack in the crystal lattice with weak C-H...O and C-H... π interactions, and variations in charge density properties and derived local energy densities have been investigated in the regions of intermolecular interactions. Theoretical charge density calculations on crystals using the B3LYP/6-311++G(d,p) method show remarkable agreement with the derived properties and energy densities from the experiment. The intermolecular interactions follow an exponential dependence of electron density and energy densities at the bond critical points. The Laplacian follows a “Morse-like” dependence on the length of the interaction line. Based on the set of criteria defined using the theory of “atoms in molecules”, it has become possible to distinguish between a hydrogen bond (C-H...O) and a van der Waals interaction (C-H... π). This has resulted in the identification of a “region of overlap” in terms of electron densities, energy densities, and mutual penetration of the hydrogen and acceptor atoms with respect to the interaction length. This approach suggests a possible tool to distinguish between the two types of interactions. High field indicates that this molecule exhibit considerable electrical conductivity in atomic charges. The ESP map is found to be positive throughout the backbone of the molecule. The negative charges have a tendency to drift from left to right. Thermodynamic parameters like heat capacities ($C_{p,m}^{\circ}$), entropies (S_m°) and enthalpies changes (H_m°) are used for various electrical field. Theoretical FT-IR and FT-Raman spectra of the title molecule have been constructed which show good agreement with recorded spectra.

Key words: TCN, XRD, HOMO – LUMO, MEP.

Introduction

Coumarins constitutes large group of phenolic compounds found in medicinal plants that share a common chemical structure of *2H*-thiochromen-2-one. They are produced as secondary plant metabolites, coumarin are mono- or deoxygenated on the heteroaromatic ring. Such as Umbelliferae, Apiaceae and Rutaceae coumarins accumulate in free form or as glycosides. In addition 2-hydroxycinnamic acid glycosides are enzymatically hydrolyzed and then lactonized into coumarins. Most of them have important biological effects including antioxidant, anti-inflammatory, anticoagulant, anti allergic, antiviral, anticancer and enzyme inhibitor activities although many are not suitable for therapeutic use because of their toxicity. Coumarin has been use in synthetic chemistry, medicinal chemistry, and photochemistry. Coumarin and its derivatives have contributed immensely to the area of solid-state photochemistry [1]. Some substituted coumarin derivatives find application in the dye and dye –sensitized solar cell industry and also in the area of LASER dyes based on the compound showing dependent variation in the static dipole moment. Coumarin has used to probe ultrafast solvation effects. Coumarin and its sulfur derivatives possess well-defined dipole moments and it exhibit second harmonic generation effects since they crystallize in noncentrosymmetric space groups. We have studied the geometry and molecular packing patterns of coumarin and their derivatives in order to evaluate the features of non covalent interactions. We have earlier reported the charge density distribution in *2H*-chromene-thione (thiocoumarin) and have evaluated the topological properties using the “atoms in molecules” approach. X-ray diffraction data at 90 K on the compound have been subjected to multipole atom refinements followed by the “atoms in molecules” approach to derive bond critical points [2-4]. The theoretical charge densities including the periodicity for the crystal have been calculated using the HF/DFT approach based on the experimentally derived structural model. C-H····O interactions in crystal engineering have been shown to influence packing model, and in a recent review weak hydrogen bonding is yet unclear. But the packing features of C-

H $\cdots\pi$ interactions, which bring out the features of such weak van der Waals interactions. Charge density measurement has characterized the nature of C-H $\cdots\pi$ interactions in terms of electron densities, bond critical points, and Laplacians. In this article, we looked into the characterization of C-H $\cdots$ O and C-H $\cdots\pi$ interactions. Koch and Popelier's criteria, for the first time we have classified C-H $\cdots$ O interactions into two categories (hydrogen bonded and weak van der Waals interaction) and C-H $\cdots\pi$ interactions as weak van der Waals interactions. The literature survey reveals that to the best of our knowledge, no ab initio HF and DFT method of the vibrational analysis of TCN have been reported so far. Therefore, the present investigation is undertaken to study the vibrational spectra of this molecule completely and to identify the various normal modes with greater wavenumber accuracy. Ab initio HF and density functional theory (DFT) calculations have been performed to support our wavenumber assignments. The HOMO and LUMO analysis have been used to elucidate information regarding charge transfer within the molecule. The thermodynamic parameters like heat capacities, entropies and enthalpies changes at constant pressure within the electrical field. But isoelectronic molecular electrostatic potential surfaces (MEPSs) and electron density surfaces were calculated using 6-311++G(d,p) basis set. Structures resulting from the plot of electron density surface mapped with electrostatic potential surface depict the shape, size, charge density distribution and the site of chemical reactivity of a molecule.

Experimental Section

All chemicals were purchased from Sigma–Aldrich or Fluka Chemical Company with a stated purity of greater than 99% and it was used as such without further purification. The FT-IR spectra were recorded in the region of 400–4000 cm^{-1} on Perkin-Elmer Spektrum 100 BX, FT-IR spectrophotometer. The FT-Raman spectrum is recorded in the wavenumber region 3500–100 cm^{-1} on a NEXUS 670 spectrophotometer equipped with Raman module accessory operating at 1.5W power with Nd:YAG laser of wavelength 1064 nm is used as an excitation source. The high-resolution single-

crystal X-ray diffraction data were collected on a Bruker AXS SMART APEX CCD diffractometer using Mo K α radiation (50 kV, 40 mA). To achieve the final temperature the ramp rate set to 40 K/hr. And the temperature was maintained at 90.0(2) K by using the Oxford Cryo Systems. Data were collected with different scan times of (20-60 s for thiocoumarin) to cover the full-sphere reciprocal space different 2θ settings of the detector (-25° , -50° , and -75°) and φ settings (0° , 90° , 180° , and 270°) of the goniometer. The scanning angle ω was set to 0.3° for each 606 frames. The crystal-to-detector distance was kept at 6.03 cms. This strategy provides high resolution, large redundancy, and better completeness in data sets, which are the key factors for multipole refinement model. The structures were resolved by direct methods using SHELXS97 and refined in the spherical atom approximation (based on F^2) by using SHELXL97 as included in a complete package WinGX. The molecular diagrams were generated using ORTEP.

Synthesis methods

A solution of 2.0g (18mmol) of freshly distilled thiophenol 3.27g (19mmol) of triethyl orthopropiolate and 1.60g (15mmol) of pivalic acid in 10mL of *p*-cymene was heated at reflux for 26 h. The reaction mixture was cooled to room temperature and then column chromatographed (hexane/Et₂O) on silica gel to give 2.79g (75%yield) of pale-yellow liquid (2-mercapto cinnamate). 2-mercapto cinnamate(1.00g,5.4mmol) dissolved in 10mL of 95% Et OH was added 0.75g (13.4mmol) KOH. The reaction mixture was heated at reflux for 2h, then cooled to 25°C , and acidified with 5% aqueous phase was extracted with ether (3x20mL), and the combined organic fractions were washed with H₂O (20mL) and brine (20mL), dried (Na₂SO₄), and evaporated. An 87% yield (0.85g) of crystalline was obtained.

The 2-mercaptocinnamic acid (50 mg, 0.27mmol) was stirred with 7mL of polyphosphoric acid at 100-105 °C for 35 min. The reaction mixture was poured on ice, the aqueous phase was extracted with ether (4x25mL), and the combined, dried (Na₂SO₄) organic phase was evaporated. Preparative thin- layer chromatography (CHCl₃/CH₃OH) of the residue afforded 25mg (57% yields) of crystalline (Table 1). Suitable crystals with reasonable sizes were mounted in a Lindeman capillary and allowed to stabilize at final temperature for one hour. The unit-cell parameters were determined repeatedly until the estimated standard deviations in cell dimensions did not vary beyond acceptable limits.

Preparation of thiocoumarin from mercaptocinnamic acid and polyphosphoric acid

Computational methods

HF/DFT calculations for TCN are performed using GAUSSIAN 09W [5] program package without any constraint on the geometry. The molecular structure of the title compound in the ground state is computed both *ab-initio*-HF and DFT (B3LYP) with 6–311++G (d, p) basis set. The minimum energy of geometrical structure obtained by using same basis set of HF and DFT methods. All the computations have been done by adding polarization function d and diffuse function on heavy atoms and polarization function p and diffuse function on hydrogen atoms, in addition to triple split valence basis set (6–311++G (d, p), for better treatment of polar bonds.

Prediction of Raman intensities

The prediction of Raman intensities are carried out by following the procedure outlined below: The Raman activities (S_i) calculated by the GAUSSIAN 09W program and adjusted during the scaling procedure with MOLVIB are converted by relative Raman Intensities (I_i) using the following relationship derived from the basic theory of Raman scattering [6-8].

$$I_i = \frac{f(v_o - v_i)^4 S_i}{v_i [1 - \exp(-hcv_i / kT)]}$$

where ν_0 is the exciting frequency (in cm^{-1} units), ν_i is the vibrational wave number of the i^{th} normal mode, h , c and k are the universal constants and f is a suitably chosen common normalization factor for all peak intensities.

Results and discussion

Molecular geometry

The molecular structure of the TCN belongs to C_s point group symmetry. The optimized monomer and dimer molecular structure of title molecule is obtained from GAUSSIAN 09W and GAUSSVIEW programs are shown in Fig. 1. The compound contains S and O connected with hetero aromatic ring. The structure optimization zero point vibrational energy of the title compound in HF and B3LYP/6-311++G (d, p) are -5572.0698 and -5577.9193 Hartrees, respectively. Experimental details of the unit cell parameter and multipole refinement parameter including the residual densities over the asymmetric unit are listed in Table 1. Fig 2 gives the ORTEP diagrams of the title compound, showing the thermal ellipsoids at 50% probability level along with atoms. The final atomic coordinates, thermal parameters, bond lengths, and angles of the compound are provided as Supporting Information. The bond structures satisfy Hirshfeld's rigid bond test [9]. The largest differences of mean-square displacement amplitudes $\Delta_{A,B}$ for thiocoumarin it is $8 \times 10^{-4} \text{ \AA}^2$ for the S1-C1 bond. The experimental topological parameters of the covalent bonds within the molecule for the compound along with the values obtained from periodic theoretical calculations are given in Table 2. It is note that the values obtained from experiment and theoretical calculations are in good agreement. So the maximum difference being 0.06, and 0.08 $\text{\AA}$ for the C6-C5 and C8-S1 bonds, respectively, in the location of the bond critical points. The electron density and Laplacian values at the bond critical points are in good agreement, demonstrating that both experimental and theoretical methodologies provide comparative measures of topological and charge density properties. The C=O bond length and the associated bond critical points differ in each case, which is a consequence of the nature of

intermolecular interaction originating from the O-atom. Thiocoumarin has also three C-H...O interactions at this O-atom. Fig 3 traces the bond paths (experimental) between O-atoms and H-atoms with the (3, -1) bond critical points along with representative bond path between C-H and the C π for each compound. Laplacian maps from experimental analysis showing the distribution in the region of the bond paths along C-H...O and C-H....C π are given in Fig 4. The multipole population parameters ($P_{lm\pm}$ and P_V) along with k and k' from experimental and theoretical refinements are provided Information's. This study is to characterize intermolecular interactions involving C-H...O and C-H.... π in each structure and evaluate them based on Koch and Popelier's criteria. The C-H.... π interactions considered for this study are limited to the aromatic carbon atom regions of the compound. The details of all the parameters characterizing and interactions are given in Table 3. The inclusion of C-H.... π interactions (van der Waals in nature) in our evaluation of the eight criteria arises from the fact that it provides an immediate comparison with a weak hydrogen bond such as C-H...O. Indeed C-H...O interactions define the possible limit of the hydrogen bond as can be seen in the evaluation of the eight criteria as follows. Thus these two interactions allow for the definition of a "region of overlap" between the hydrogen bond and a van der Waals interaction. The evaluation of integrated properties over the basin of the H-atoms involves the interactions forms the basis of these criteria. It determines the charge, dipolar polarization, potential energy, and volume of H-atoms involved in the C-H.....O and C-H..... π interactions considering the crystal (experimental and theoretical) and the isolated molecule. The theoretical values have been calculated for isolated molecules using both HF and DFT methods. Since the theoretical calculation in the crystal is evaluated using only DFT, the integration properties appear most reliable with respect to the DFT calculation for isolated molecule. The Table 3 has the value for the C-H.....O hydrogen bonds and from the C-H..... π van der Waals interactions. For example, the difference in charge on the H-atom increases from a value of 0.0376 e for C-H..... π to a value of 0.0825 e for C-H.....O hydrogen bond in the structure of

thiocoumarin. The intermediate values are taken by those H-atoms, which display both C-H $\cdots\pi$ and C-H $\cdots$ O character. Comparable electron losses were found in case of formation of a dihydrogen bond and also a set of C-H $\cdots$ O bonds containing van der Waals complexes, indicating that in general smaller electron loss reflects weak interaction. The differences in the potential energy (*PE*) in all cases depict the expected trend destabilizing the H-atom upon crystal. So calculations of nuclear *PE* values, and the kinetic energy output from the calculation on isolated molecules is subtracted from the corresponding estimate of the total energy. It shows that the increase in the *PE* for C-H $\cdots$ O hydrogen bond is larger compared to that in the C-H $\cdots\pi$ regime (for thiocoumarin, 0.0363 au -0.0126 au). The energy changes are between C-H $\cdots$ O hydrogen bond and C-H $\cdots\pi$ interaction. A measure of the extent and direction of dipolar polarization of the atomic electron density is given by the magnitude of the moment, and this value decreases by 0.0755 au for the C-H $\cdots$ O bond and 0.0290 au for a C-H $\cdots\pi$ interaction in thiocoumarin. The final criterion, decrease of H-atom's volume, is quite significant to bring in the difference in bond strength between the two interactions. The volume shrinks by 7.78 au for C-H $\cdots$ O as compared to 2.90 au for C-H $\cdots\pi$ interaction for thiocoumarin, respectively. All these criteria show similar trends and allow the types of interactions on quantitative steps are in Table [3].

Fig. 1: Optimized monomer and dimer molecular structure of Thiocoumarin.

Fig. 2: ORTEP diagram with labels for atoms of Tthiocoumarin at 90 K with 50% ellipsoid probability (non H-atoms).

Fig 3: Bond path character in thiocoumarin showing the critical point locations along the C-H $\cdots$ O and C-H $\cdots$ C π interactions shown in red.

Table1

Crystal data and structure refinement for Thiocoumarin.

Empirical formula	C ₉ H ₆ OS
Formula weight (g.mol ⁻¹)	162.2
Crystal size/mm	0.40×0.21×0.18
Crystal system	Monoclinic
Space group	<i>Pc</i>
Unit cell dimensions	
a (Å)	3.8056(3)
b (Å)	8.4552(7)
c (Å)	11.3651(10)
α (°)	90
β (°)	95.629(4)
γ (°)	90
V (Å ³)	363.93(5)
Z	2
μ (mm ⁻¹)	0.369
D _c /g cm ⁻³	1.48
(sinθ /λ) _{max} /Å ⁻¹	1.08
Reflections collected	6373
R(<i>F</i>); R _w (<i>F</i>)	0.0158; 0.0145
<i>S</i>	1.41
Nobs/Npar	20.14
Largest difference in peak and hole (eÅ ⁻³)	-0.203; 0.324

Table 2

Intramolecular Bond Critical Points for the Compounds and Bond Ellipticity $\epsilon = (\lambda_1/\lambda_2 - 1)^a$

Bond (A-B)	atom	ρ_b	$\nabla^2 \rho_b$	R_{ij}	$d_1(A-Cp)$	$d_2(Cp-B)$	λ_1	λ_2	λ_3	ϵ
S(1)-C(1)	S(1)	1.359(38)	-2.076(45)	1.7736	0.9107	0.8628	-8.45	-6.72	13.09	0.26
	C(1)	1.293	-4.894	1.7715	0.9633	0.8082	-7.34	-6.19	8.64	0.19
S(1)-C(8)	S(1)	1.336(43)	-1.219(51)	1.7472	0.8771	0.8700	-8.24	-6.44	13.47	0.28
	C(8)	1.401	-6.132	1.7456	0.8596	0.7860	-7.99	-6.82	8.68	0.17
O(1)-C(1)	O(1)	2.979(16)	-23.635(83)	1.2229	0.7993	0.4236	-25.93	-24.50	26.79	0.06
	C(1)	2.769	24.862	1.2241	0.7859	0.4381	-23.54	-22.24	20.92	0.06
C(1)-C(2)	C(1)	2.008(13)	-15.771(27)	1.4504	0.7208	0.7296	-14.94	-12.04	11.21	0.24
	C(2)	1.894	-14.336	1.4508	0.7666	0.6842	-13.46	-11.69	10.82	0.15
C(2)-C(3)	C(2)	2.401(15)	-22.244(31)	1.3578	0.6674	0.6904	-18.03	-14.09	9.88	0.28
	C(3)	2.224	-20.458	1.3558	0.6899	0.6659	-16.82	-13.35	9.71	0.26
C(9)-C(3)	C(9)	1.987(14)	-14.111(30)	1.4429	0.6981	0.7447	-14.52	-11.47	11.88	0.27
	C(3)	1.901	-15.085	1.4415	0.7188	0.7227	-13.86	-11.85	10.63	0.17
C(9)-C(4)	C(9)	2.184(14)	-17.383(31)	1.4110	0.7054	0.7056	-15.46	-13.42	11.50	0.15
	C(4)	2.005	-16.725	1.4103	0.7199	0.6904	-14.95	-12.13	10.36	0.23
C(5)-C(4)	C(5)	2.217(18)	-18.958(36)	1.3853	0.6747	0.7106	-17.03	-13.23	11.30	0.29
	C(4)	2.130	-18.644	1.3837	0.6816	0.7020	-16.01	-12.80	10.17	0.25
C(6)-C(5)	C(6)	2.241(17)	-18.632(39)	1.4015	0.6364	0.7651	-15.60	-13.54	10.51	0.15
	C(5)	2.091	-17.860	1.4019	0.6936	0.7084	-15.40	-12.94	10.48	0.19
C(6)-C(7)	C(6)	2.288(14)	-19.371(33)	1.3894	0.6759	0.7136	-16.49	-13.51	10.64	0.22
	C(7)	2.111	-17.845	1.3892	0.6812	0.7080	-15.49	-12.74	10.38	0.22
C(8)-C(7)	C(8)	2.308(13)	-20.965(31)	1.3998	0.7317	0.6681	-18.05	-13.71	10.79	0.32
	C(7)	2.090	-17.497	1.3984	0.7282	0.6702	-15.31	-12.61	10.42	0.21
C(8)-C(9)	C(8)	2.109(14)	-16.831(30)	1.4059	0.6632	0.7427	-15.38	-12.73	11.28	0.21
	C(9)	2.037	-16.982	1.4058	0.7175	0.6883	-14.96	-12.39	10.37	0.21

^a The values from periodic calculation using B3LYP/6-311++G method are given in Red colour.

Table 3:

Atomic Net Charges (q), Atomic Potential Energy (PE), Atomic Dipolar Polarization (M), and Atomic Volume (V) of the H-Atoms in the Crystal and in the Isolated Molecule and Their Corresponding Differences (in au).

Atomic Net Charges (q)									
Interactions	atom	q (crystal)		q (isolated)		Δq (crystal - isolated)			
		expt.(E)	theo.(T)	HF	DFT	E-HF	E-DFT	T-HF	T-DFT
O(1)...H(3)	H(3)	0.0991	0.0980	-0.0164	-0.0155	0.1155	0.0836	0.1144	0.0825
O(1)...H(4)	H(4)	0.2872	0.1092	-0.0334	0.0058	0.3206	0.2814	0.1426	0.1034
O(1)...H(6)	H(6)	0.3029	0.0809	-0.0250	0.0126	0.3279	0.29.3	0.1059	0.0683
C(4)...H(7)	H(7)	0.2810	0.0561	-0.0193	0.0185	0.3003	0.2625	0.0754	0.0376
Atomic Potential Energy (PE)									
Interactions	atom	q (crystal)		q (isolated)		Δq (crystal - isolated)			
		expt.(E)	theo.(T)	HF	DFT	E-HF	E-DFT	T-HF	T-DFT
O(1)...H(3)	H(3)	-1.2408	-1.2098	-1.2865	-1.2461	0.0457	0.0053	0.0767	0.0363
O(1)...H(4)	H(4)	-1.0306	-1.2061	-1.2960	-1.2498	0.2654	0.2192	0.0899	0.0437
O(1)...H(6)	H(6)	-0.9684	-1.2293	-1.2887	-1.2454	0.3203	0.2770	0.0594	0.1610
C(4)...H(7)	H(7)	-0.9787	-1.2526	-1.2837	-1.2400	0.3050	0.2613	0.0311	-0.0126
Atomic Dipolar Polarization (M)									
Interactions	atom	q (crystal)		q (isolated)		Δq (crystal - isolated)			
		expt.(E)	theo.(T)	HF	DFT	E-HF	E-DFT	T-HF	T-DFT
O(1)...H(3)	H(3)	0.1033	0.0953	0.0986	0.1253	0.0047	-0.0220	-0.0033	-0.0300
O(1)...H(4)	H(4)	0.0478	0.0505	0.0978	0.1260	-0.0500	-0.0782	-0.0473	-0.0755
O(1)...H(6)	H(6)	0.1021	0.0743	0.0969	0.1230	0.0052	-0.0209	-0.0226	-0.0487
C(4)...H(7)	H(7)	0.1561	0.0943	0.0971	0.1233	0.0590	0.0328	-0.0028	-0.0290
Atomic Volume (V)									
Interactions	atom	q (crystal)		q (isolated)		Δq (crystal - isolated)			
		expt.(E)	theo.(T)	HF	DFT	E-HF	E-DFT	T-HF	T-DFT
O(1)...H(3)	H(3)	34.45	41.27	47.44	47.96	-12.99	-13.51	-6.17	-6.69
O(1)...H(4)	H(4)	27.97	40.90	48.53	48.68	-20.56	-20.71	-7.63	-7.78
O(1)...H(6)	H(6)	34.80	43.28	48.54	48.52	-13.74	-13.72	-5.26	-5.24
C(4)...H(7)	H(7)	38.90	45.16	47.94	48.06	-9.04	-9.16	-2.78	-2.90

4.2. Vibrational assignments

The TCN consists of 17 atoms, and belongs to Cs symmetry. Hence the numbers of normal modes of vibrations for TCN are 45. The bands that belong to the in-plane modes are represented as A' while the out-of-plane modes as A'' Thus the 45 normal modes of vibrations are distributed as Vib = 31A'+14A''. The internal and symmetric co-ordinates of TCN are shown in Tables S1-S2,

respectively. The harmonic-vibrational frequencies calculated for TCN at HF and DFT-B3LYP levels using the triple split valence basis set along with the diffuse and polarization functions, 6-311++G (d, p), observed FT-IR and FT-Raman frequencies for various modes of vibrations are presented in Table S3. Although basis set are marginally sensitive as observed in the HF and DFT values using 6-311++G (d, p), reduction in the computed harmonic vibrational frequencies are noted. Without affecting the basic level of calculations, it is customary to scale down the calculated harmonic frequencies in order to get an agreement with the experimental values. The scaled calculated frequencies minimize the root-mean square difference between calculated and experimental frequencies for bands with definite identifications. The IR and Raman spectra of experimental and are given in the Figures.S1-S2., respectively.

C–H vibrations

The aromatic organic compounds structure shows the presence of asymmetric C–H stretching vibrations in the region $3100\text{--}3000\text{cm}^{-1}$ [10], which is the characteristics region for recognition on C–H stretching vibrations. In the title molecule, bands have been observed at 3090, 2172 and 2842,2821, 2801, 2157cm^{-1} assigned to C–H stretching vibrations in FT-IR and FT-Raman spectra, respectively. The C–H in-plane and out of- plane bending vibrations normally take place as a number of intensity sharp bends in the region of $1300\text{--}1000$ and $1000\text{--}750\text{cm}^{-1}$, respectively. The bands for C–H in plane bending vibrations are identified at 1499, 1472, 1456,1442,1421,1392 and 1455 cm^{-1} in FT-IR and FT-Raman spectra, respectively and the C–H out-of-plane bending vibrations are found at 721 and $958,788,604,582,570\text{cm}^{-1}$. Theoretical Positive field and negative field for C–H in-plane and C–H out-of-plane bending vibrations by B3LYP/ 6-311++G (d, p) method showed excellent agreement with recorded spectrum.

C- C vibrations

Generally the C-C stretching vibrations in aromatic compounds are seen in the region of 1430–1650 cm^{-1} . The presence of conjugate substituent such as C-C causes a heavy doublet formation around the region 1625–1575 cm^{-1} [11]. The six ring carbon atoms undergo coupled vibrations, which are known as skeletal vibrations give a maximum of four bands in the region 1660–1420 cm^{-1} . As predicted in the earlier references [12], the prominent peaks are due to strong C-C stretching 1999, 1971, 1852, 1720, 1709, 1672, 1656 cm^{-1} and 1952, 1914, 1342 cm^{-1} in FT-IR and Raman, respectively are due to C–C vibrations for the title compound. The C–C in-plane and out-of-plane bending modes of TCN are in Table S3.

C–S vibrations

The C–S stretching bands are usually observed in the range 670–930 cm^{-1} with a moderate intensity. In general, the assignment of band due to the C–S stretching vibration in different compounds is difficult in the infrared since the band is of variable intensity and may be found over the wide region 1035–245 cm^{-1} , whereas, in general, C–S stretching vibrations in IR spectra which are normally easy to identify [12]. The C-S group is less polar than carbonyl links and has a considerably weaker band. In consequence, the band is not intense, and it falls at lower frequencies, where it is much more susceptible to coupling effects. Identification is therefore difficult and uncertain. The absorption of C–S group with other substituents usually appears in between 1250–1020 cm^{-1} . Consideration of these factors leads to assign the IR band at 1366, 1347 cm^{-1} in TCN to C-S stretching vibration. Besides the stretching vibrations, the sulfur atom gives rise to bending vibrations with the neighbouring atoms. The respective peaks for in-plane and out-of-plane bending vibrations C–S group are listed in Table S3. All the C–S vibrational bands of TCN are in line with the literature values and nearly in agreement with the computed values by B3LYP/6-311++G(d,p).

C=O vibrations

The interaction of carbonyl group with other groups present in the system did not produce such a drastic and characteristic change in the frequency of C- O stretch as did by interaction of C-S stretch. The carbon-oxygen double bond is formed by $p\pi-p\pi$ between carbon and oxygen. Because of the different electron negativities of carbon and oxygen atoms, the bonding electrons are not equally distributed between the two atoms. The lone pair of electrons on oxygen also determines the nature of the carbonyl group. The position of the C-O stretching vibration is very sensitive to various factors such as the physical state, electronic effects by substituent, ring strains. Normally carbonyl group vibrations occur in the region $1850-1600\text{cm}^{-1}$ [12]. In this study, the C-O stretching vibrations of TCN are observed at 2148 cm^{-1} in FTIR spectrum and these modes are confirmed by their PED values. The in-plane and out-of-plane bending vibrations of C-O group have also been identified and presented in Table S3 for the title molecule.

5. Prediction of first hyperpolarizability

The first hyperpolarizability (β_0) of this novel molecular system and the related properties (β_0, α_0) of TCN are calculated using the B3LYP/6-311++G(d,p) basis set, based on the finite field approach. From the applied electric field, the energy of a system is a function of the electric field. So the first hyperpolarizability is a third-rank tensor that can be described by a $3 \times 3 \times 3$ matrix. The 27 components of the 3D matrix can be reduced to 10 components due to the Kleinman symmetry [12]. It can be given in the lower tetrahedral. The components of β are defined as the coefficients in the Taylor series expansion of the energy in the external electric field. When the external electric field is weak and homogenous, this expansion becomes:

$$E = E_0 - \mu_\alpha F_\alpha - 1/2\alpha_{\alpha\beta} F_\alpha F_\beta - 1/6\beta_{\alpha\beta\gamma} F_\alpha F_\beta F_\gamma + \dots$$

Where E_0 is the energy of the unperturbed molecules, F_α the field at the origin and μ_α , $\alpha_{\alpha\beta}$ and $\beta_{\alpha\beta\gamma}$ are the components of dipole moment, polarizability and the first hyperpolarizabilities,

respectively. The total static dipole moment μ , the mean polarizability α_0 and the mean first hyperpolarizability β_0 , using the x, y, z components they are defined as follows:

$$\begin{aligned}\mu &= (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2} \\ \alpha_0 &= (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3 \\ \alpha &= 2^{-1/2} [(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6\alpha_{xx}^2]^{1/2} \\ \beta_0 &= (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2} \\ \beta_{\text{vec}} &= 3/5[(\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2}]\end{aligned}$$

where

$$\begin{aligned}\beta_x &= \beta_{xxx} + \beta_{xyy} + \beta_{xzz} \\ \beta_y &= \beta_{yyy} + \beta_{yxx} + \beta_{yzz} \\ \beta_z &= \beta_{zzz} + \beta_{zxx} + \beta_{zyy}\end{aligned}$$

The β_0 components of GAUSSIAN 09W output are reported in atomic units and therefore the calculated values are converted into e.s.u. units ($1 \text{ a.u.} = 8.3693 \times 10^{-33} \text{ e.s.u.}$). The calculated value of hyperpolarizability and polarizability of TCN are tabulated in Table S4. From this conclusion that the title molecules are an attractive object for future studies of NLO properties.

6. HOMO–LUMO energy gap and related molecular properties

The properties of the frontier molecular orbitals(FMOs) are very useful for physicists and chemists. The electron densities of these FMOs were used for predicting the most reactive position in π -electron systems and also explained several types of reactions in conjugated systems [13]. Moreover, eigen values of the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) and their energy gap reflect the chemical reactivity of the molecule. Recently the energy gap between HOMO and LUMO has been used to prove the bioactivity from intramolecular charge transfer (ICT) [13]. The HOMO–LUMO energy gap for the studied compound is calculated by B3LYP/6–311G(d,p). The HOMO and LUMO pictures are shown in Figure S4. It is found that the HOMO level is mainly localized on the benzene ring π -system and extended to the C1-C2, C5-S6,

O11-C1, C9-C8 and C10-C5 bonds. The LUMO is located mainly on the O group of the heterocycles. The EHOMO and ELUMO are calculated to be -0.24549a.u and -0.08935a.u respectively. The HOMO–LUMO energy gap (ΔE) represents the lowest energy electronic transition. In the studied compound, the HOMO–LUMO energy gap of the studied compound is 0.15614a.u. (Figures S4) . In this investigation, the more relevant electronic potential (IP), electron affinities (EA), chemical potential (μ) it is the negative of electro negativity (χ), hardness (η), softness (S) and the electrophilic index(ω) were calculated. The ionization potential is calculated as the energy difference between the energy of the molecule derived from electron-transfer (radical cation) and the respective neutral molecule; $IP = E_{cation} - E_n$. The EA was computed as the energy difference between the neutral molecule and the anion molecule: $EA = E_n - E_{anion}$ [16].The HOMO and LUMO energy was also used to estimate the IP and EA in the framework of Koopmans' theorem:

$$IP = -\epsilon_{HOMO} \text{ and } EA = -\epsilon_{LUMO}$$

Within the framework of the density functional theory (DFT), one of the global quantities is chemical potential (μ), which is measures the escaping tendency of an electronic cloud, and equals the slope of the Energy versus N(number of electrons) curve at external potential $v(r)$:

$$\mu = (\partial E / \partial N)_{V(r)}$$

Finite difference approximation to Chemical Potential gives,

$$\chi = -\mu = -(\partial E / \partial N)_{V(r)}$$

The theoretical definition of chemical hardness has been provided by the density functional theory as the second derivative of electronic energy with respect to the number of electrons N, for a constant external potential $v(r)$:

$$\eta = \frac{1}{2}(\partial^2 E / \partial N^2)_{V(r)} = \frac{1}{2}(\partial \mu / \partial N)_{V(r)}$$

Finite difference approximation to Chemical hardness gives,

$$\eta = (I - A)/2$$

For Insulator and semiconductor, hardness is half of the energy gap ($\epsilon_{\text{HOMO}} - \epsilon_{\text{LUMO}}$), and the softness is given as [14] :

$$S = 1/2\eta = (\partial^2 E / \partial N^2)_{V(r)} = (\partial E / \partial N)_{V(r)}$$

Electrophilicity index is a measure of energy lowering due to maximal electron flow between donor and acceptor. Electrophilicity index (ω) is defined as,

$$\omega = \mu^2 / 2 \eta$$

B3LYP functional used in this study has a high efficient to calculate the electronic properties for the organic studied molecules, such as ionization potentials (IP), electron affinities (EA), electro negativity (χ), absolute hardness (η), absolute softness (S), electrophilic index (ω). The behavior of electro negativity, softness and electrophilic index for the studied molecules shows the magnitude large than these for the original ring, adding the radicals give the molecule more softness. The calculated value of electrophilicity index describes the biological activity of TCN. All the calculated values of hardness, potential, softness and electrophilicity index are shown in Table S5.

7. Multipole Model and Deformation Densities

The final refinement, of the Hirshfeld rigid bond test was applied to the covalent bonds involving non-hydrogen atoms. The values of maximum differences of mean-square displacement amplitudes are found to be $9(2) \times 10^{-4} \text{ \AA}^2$ at C8-C9 respectively, which are below the standard limit of $10^{-3} \text{ \AA}^2$. The residual electron densities calculated (with $I > 3 \sigma(I)$) over the molecular planes are almost minimum and maximum densities are in the range of -0.223 to $0.130 \text{ e \AA}^{-3}$. The residuals are very similar to the reported values. The static deformation electron density maps obtained from experimental and theoretical analyses of the crystal shown in Figure S5 The electron lone pairs of O atom, except the atoms affected by disorder, are clearly visible in the deformation electron density maps. The deformation electron density maps associated with the other part of the molecule were also shown to

have high accurate bonding features. The statistical analysis was performed on the static deformation electron density grids obtained from the experimental and theoretical multipole modeling. The correlation between the experimental and theoretical deformation electron densities $\Delta \rho$ is 90% and 87%. The diffraction data of the crystal are of slightly better quality in terms of resolution and R-factors, which is in accordance with the higher correlation [15].

8. Electrostatic Potentials

Analysis of deformation electrostatic potential (ESP) derived from the deformation electron densities on the molecular surfaces was performed to highlight the effect of crystalline environment and also to point out the differences and the similarities between the two polymorphic forms. The construction of a three-dimensional ESP map plotted over the molecular surfaces from experimental charge densities clearly brings out the differences of electrostatic nature of the three forms (Figures.S6-S8). The electropositive and electronegative surfaces are well separated in the forms. It displays a larger electronegative surface in ESP mapping. This is due to the conformational difference at the C-O side chain and additionally due to the involvement of the π electrons of three bonded atoms C1-C2-H12 in C-H... π type of contacts and the presence of π ... π contacts. The electronegative surface is mainly seen around the oxygen atoms, which are involved in C-H...O type of intermolecular contacts. However, the atom O11 shown to have less prominent electronegative surface compared to other S atom in the structures. This is because the atom O11 is not involved in any intermolecular contacts, whereas the corresponding atom in the S is seen to interact remotely with the neighbour molecule (Figure S9). The corresponding maps from the theoretical analysis revealed similar features. The ESP maps clearly emphasize the preferred binding sites to form the networks of interactions and also highlight the difference in nature of interactions [16].

9. THERMODYNAMIC PROPERTIES

Based on the vibrational analysis at B3LYP/6-311++G(d,p) level and statistical thermodynamics, the standard thermodynamic functions; heat capacities ($C_{p,m}^0$), entropies (S_m^0) and enthalpies changes (H_m^0) are obtained at constant pressure for zero (monomer and dimer) and applied electric field in Table S6. As seen from Table S6, the standard thermodynamic functions increase with increasing temperature, due to the intensities of molecular vibration increase; it is observed that the entropy increases but the enthalpy and heat capacity remain constant. According to Boyle's law for gases, a molecule is compressed at constant temperature its volume decreases [17-18]. Due to decreasing volume, the number of possible sites that occupied by particles of the molecule may be restricted. Thus, the entropy tends to decrease with increasing pressure at constant temperature. This investigation will be helpful for the further studies of the title molecule. The correlation graph for zero (monomer and dimer) applied EFs are shown in Figure S10 and the corresponding fitting equations are as follows:

For 0.00 VÅ⁻¹

$$S_m^0 = 210.23396 + 0.71772T - 0.00238 \times 10^{-5} T^2 \quad (R^2 = 0.99884)$$

$$C_{p,m}^0 = 9.94698 + 0.48974T + 3.33885 \times 10^{-5} T^2 \quad (R^2 = 0.99886)$$

$$H_m^0 = -2.8146 + 1.31434T - 2.62041 \times 10^{-5} T^2 \quad (R^2 = 0.9994)$$

For 0.01 VÅ⁻¹

$$S_m^0 = 227.93312 + 0.41634T + 8.49829 \times 10^{-5} T^2 \quad (R^2 = 0.99906)$$

$$C_{p,m}^0 = 1.81101 - 6.67441T - 0.06719 \times 10^{-4} T^2 \quad (R^2 = 0.99988)$$

$$H_m^0 = 3.68006 + 1.71434T + 2.01163 \times 10^{-4} T^2 \quad (R^2 = 0.99942)$$

For 0.02 VÅ⁻¹

$$S_m^0 = 228.93312 + 0.23581T + 7.55761 \times 10^{-5} T^2 \quad (R^2 = 0.99928)$$

$$C_{p,m}^0 = 1.61301 + 0.4950T - 2.1175 \times 10^{-4} T^2 \quad (R^2 = 0.9988)$$

$$H_m^0 = -3.80606 - 1.1436T + 2.09860 \times 10^{-4} T^2 \quad (R^2 = 0.99947)$$

For Dimer

$$S_m^0 = 311.40643 + 1.13227T - 3.22688 \times 10^{-4} T^2 \quad (R^2 = 0.99981)$$

$$C_{p,m}^0 = 6.48149 + 5.36266T - 0.0397 \times 10^{-4} T^2 \quad (R^2 = 0.99866)$$

$$H_m^0 = -5.87053 + 2.49217T - 0.0397 \times 10^{-4} T^2 \quad (R^2 = 0.99960)$$

10. ATOMIC CHARGES

Atomic charges for molecule can be derived in multiple ways with a high level of convergence to the same values and only then, knowing the remaining uncertainty, are suited for molecular simulations. Mulliken charges arise from the mulliken population analysis [19] and provide a means of estimating partial atomic charges from calculations carried out by the methods of computational chemistry. Generally, Mulliken population analysis (MPA) and Natural Population analysis (NPA) methods are used to calculate the atomic charges of atoms in molecules. The difference of MPA charges distribution for zero and various applied EFs ($\pm 0.02 \text{ V \AA}^{-1}$) are listed in Table S7. The MPA charges of all C-atoms for zero field vary from 2.0632 a.u to -1.0486 a.u. When the applied field increases, the charge value decreases for C-atoms. The variations in MPA charge are small due to be systematic and almost uniform. Additionally, the magnitudes of the hydrogen atomic charges were noted to be only positive values, indicating the charge transfer from hydrogen to carbon atom.

The results show that:

- All the hydrogen atoms in the molecules lost electrons.
- The sulphur atoms in the molecules lost electrons.
- Carbon atomic charges were found to be both positive values except C4.
- Charge migration to heavy atoms can be related to molecular interactions.
- Oxygen atoms accept electrons while the atomic charges were found to be negative.

11. Potential energy surface scan

The potential surface scans of theoretical approximations were performed for title molecule is shown in Figure S11. The bond angle $C_1-S_6-O_{11}$ for TCN is also the relevant coordinate for conformational flexibility within the molecule. During the calculations all the geometrical parameters were simultaneously relaxed during the calculations while the $C_1-S_6-O_{11}$ angle was varied in steps of 10° , 20° , 30° ,, 70° . The barrier of this rotation mildly increases shows that the sulfonyl group cannot be hindered by halogen atom present in the position (due to intramolecular bonding). The large energy barrier indicates that the rotation of C=O group is very much restricted.

Conclusion

Experimental and theoretical charge density calculation are belonging to the thiocoumarin suggests that there exists a well-defined “region of overlap” between hydrogen bond and van der Waals interaction. But the experimental results are closer to that at a critical distance (donor)-H $\cdots$ A (acceptor) interaction is switched from “hydrogen bond” to “van der Waals” type. Theoretically it is sufficient to describe both qualitative and quantitative measures to evaluate the nature of C-H $\cdots$ O and C-H $\cdots$ π interactions. HOMO - LUMO energy gap explains the eventual charge transfer interaction taking place within the molecule. The summation of total electrostatic interaction energy values of the monomer suggests electrostatic interaction. The plotting of 3 dimensional deformation electrostatic potential maps over the molecular surfaces elucidates the nature of interactions. The result describes the variation in electrostatic and transport properties for zero and various external applied field. The variation in MPA charges are small due to the application of EFs: however, in most cases it is found to be systematic and almost uniform. The results clearly show the superiority of MPA scheme. This study may be useful to design new molecules with more electrical conductivity. A complete vibrational analysis of TCN have been investigated by FT-IR and FT-Raman spectroscopies and are based on *ab initio* and DFT calculation at the HF/6-311++G(d,p) and B3LYP/6-311++G(d,p) levels and their frequencies are compared. In particular, the results of DFT-B3LYP method indicates better fit to experimental values. The optimized geometrical parameters calculated at B3LYP method are slightly larger than calculated HF level. The predicted first hyperpolarizability reveals that the title molecule is an attractive object for future studies of non-linear optical properties. The results of the TED calculation are also useful for understanding the delocalisation of electrons involved in this compound.

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Figures

Figure 1

Optimized monomer and dimer molecular structure of Thiocoumarin.

Figure 2

ORTEP diagram with labels for atoms of Tthiocoumarin at 90 K with 50% ellipsoid probability (non H-atoms).

Figure 3

Bond path character in thiocoumarin showing the critical point locations along the C-H...O and C-H...C π interactions shown in red.