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Quantum Chemical Vibrational Study, Molecular Properties and HOMO-LUMO Energies of 2-Chlorophenylisothiocyanate via Density Functional Theory

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Abstract:

Density functional theory calculations with B3LYP/ CEP-121G basis sets was used to determine ground state molecular geometries (bond lengths and bond angles), harmonic vibrational frequencies and infrared intensities for 2-chlorophenylisothiocyanate (CPIC) molecule . The assignments of the vibrational spectra have been carried out. The total energies, thermodynamic data, electronic states, energy gaps, ionization potentials, electron affinities, chemical potential, global hardness, softness, global electrophilicity, dipole moment and dipole polarizability and were calculated . The calculated HOMO and LUMO energies show that charge transfer occurs within the molecule. The effects of Cl and NCS on the geometry of benzene and its normal modes of vibrations have also been studied. Finally the calculations results were applied to simulate infrared of the title compound which shows good agreement with observed spectra.

Key words: DFT, Ionization potential, electron affinity, energy gap, and IR spectrum.

1. INTRODUCTION

The derivatives of phenyl isothiocyanate are of spectroscopic interest due to the role of NCS and its substituents play in the vibrational structures and spectra .It seems that there have been a fewer studies on the vibrational spectroscopy of the derivatives. The derivative CPIC is a colorless liquid with molecular formula C_7H_4CINS. It is of irritating odor and readily volatilized with steam and soluble in alcohol and ether, insoluble in water. In the infrared assignments of five mono substituted benzene, namely nitrobenzenes, phenyl isocyanate, phenyl isothiocyanate, thionyl aniline and anisole, Stephenson et al [1]. Treated them all, following Whiffen [2] as belonging to C_{2V} symmetry. Quantum chemical computational methods have been proved to be an essential tool for interpreting and predicting the vibrational spectra [3,4]. A significant advancement in this area was made by DFT having its own advantages [5-8]. Hence, in the present study, the optimized geometries, vibrational spectra and molecular structure for this molecule have been investigated. The effects of chlorine atom and –NCS group on the geometry and different normal modes of the benzene molecule have been analyzed. The vibrational frequencies of the title compound are assigned to their corresponding normal mode vibration using band intensities.

2. COMPUTATIONAL DETAILS

The entire calculations conducted in the present work were performed at B3LYP levels included in the Gaussian 03W package [9] program together with the CEP-121G basis set function of the density functional theory (DFT) utilizing gradient geometry optimization[10]. All the geometries were then optimized using CEP-121G by density functional theory (DFT) [11] employing the Becke's three-parameter hybrid functional [12] combined with Lee-Yang-Parr correlation [13] functional (B3LYP) method. The hybrid functional B3LYP had been shown to be highly successful for calculation the electronic properties such as ionization potentials, electronic states and energy gaps [14],[15].

The DFT partitions the electronic energy as E = ET+EV+EJ+EXC, where ET, EV, and EJ are the electronic kinetic energy, the electron nuclear attraction and the electron-electron repulsion terms respectively. The optimized structural parameters were used in the vibrational frequency calculations at the DFT levels to characterize all stationary points as minima. Then vibrationally averaged nuclear positions of CPIC are used for harmonic vibrational frequency calculations resulting in IR frequencies with intensities. The DFT hybrid B3LYP functional also tends to overestimate the fundamental modes in comparison to the other DFT methods; therefore, scaling factors have to be used to obtain considerably better agreement with experimental data. Finally, calculated normal mode vibrational frequencies, provide thermodynamic properties by way of statistical mechanics. By combining the results of the Gauss. View program [16] with symmetry considerations, vibrational frequency assignments were made with high degree of accuracy. There is always some ambiguity in defining internal coordination. However, the defined coordinate form complete set and matches quite well with the motions observed using the Gauss. View program. To achieve a close agreement between observed and calculated frequencies, the least square fit refinement algorithm was used. HOMO-LUMO energy gaps have been computed and other related molecular properties are calculated. In this investigation, the more relevant ionization potential (IP), electron affinities (EA), hardness (η), electric dipole polarizability (α), softness (S), electrophilic index (ω) and chemical potential (K) (it is the negative of electronegativity (χ)), were calculated . The HOMO and LUMO energy was used to estimate the IP and EA in the frame work of Koopmans' theorem:

IP = -EHOMO and EA= -ELUMO. The hardness corresponds to the gap between the HOMO and LUMO orbital energies. The larger the HOMO-LUMO energy gap the harder the molecule. The global hardness, $\eta = 1/2(\mathrm{ELUMO} - \mathrm{EHOMO})$. The hardness has been associated with the stability of chemical system [17]. Here, α is a second-rank tensor property called the dipole polarizability and mean polarizability $< \alpha >$ is evaluated using the relation [18], $<a >= 1/3\ (a_{xx} + a_{yy} + a_{zz})$. The electron affinity can be used in combination with ionization energy to give electronic chemical potential, K=1/2(EHOMO+ELUMO), The global electrophilicity index, $\omega = K^2/2\eta$ is also calculated and softness $S= 1/2\eta$ [19]. Density functional theory has also been used to calculate the dipole moment μ and anisotropy of polarizability ($\Delta\alpha$), they are defined respectively by [20],[21] :

$$\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2} ,$$

$$\Delta\alpha = \sqrt{2}[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{xx})^2 + 6\alpha_{xx}^2]^{1/2}$$

The molecule is belong to C_1 point group symmetry according to our quantum chemical computational method. Experimentally , the liquid phase FT-IR spectra of CPIC has been recorded in the region (4000- 400 cm^{-1}) at room temperature[22].

3. RESULTS AND DISCUSSION

3.1. Molecular geometry:

Geometry optimization is one of the most important steps in the theoretical calculations. The molecular structure of CPIC having C1 point group. The optimized structure parameters of molecules calculated by DFT-B3LYP levels with the CEP-121G basis set are listed in the table1 in accordance with the atom numbering scheme given in figure1. The calculated optimized geometrical parameters obtained in this study for the title compound are compared with the experimental[23, 24] values and presented in table 1 . From the theoretical values, we can find that most of the optimized bond length are slightly larger than the experimental values, due to the theoretical calculations belong to isolated molecules in gaseous phase and the experimental results belong to molecules in solid state[17] .

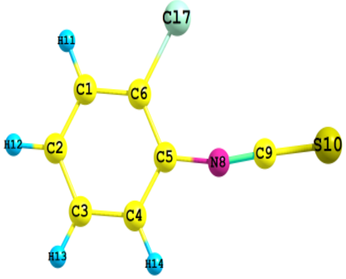

Fig.-Optimized geometrical structure and atomic labeling of CPIC.

3.2. Energies and Some important variables

Table 2 shows the values of the total energy and electronic states for the analyzed structures and the energy gap of the studied molecule. The frontier orbital (HOMO and LUMO) of the chemical species are very important in defining its reactivity[25]. B3LYP functional used in this study has a high efficient to calculate the electronic properties for the organic studied molecule, such as ionization potentials **(IP),** electron affinities **(EA),** chemical potential **(K),** absolute hardness **(η),** absolute softness **(S),** electrophilic index **(ω)** and anisotropy of polarizability ($\Delta\alpha$) **.** The properties are computed by the way that is based on the differences between the HOMO and the LUMO energies of the neutral molecule and is known as orbital-vertical (Koopmans' theorem). The strength of an acceptor is measured by its electron affinity (EA) which the energy released when adding one electron to LUMO. An acceptor must have a high EA, adding the Cl to the phenylisothiocyanate molecule leads to increasing the ability of the electron affinity for the molecule. The Koopmans' theorem is a crude but useful and fast approach [26,27]. The larger the

HOMO-LUMO orbital energy gap, the harder the molecule. The hardness has been associated with the stability of the chemical system[25].

3.3. Molecular polarizability

One of the objectives of the present investigation is to study the effect of the basis sets B3LYP/ CEP-121G levels on molecular polarizability of molecule using the Gaussian03W program. In this study, the computation of the molecular polarizability <a> was reported. The calculated dipole moment and polarizability by DFT method are summarized in Table 3.

3.4. Thermodynamic properties

On the basis of vibrational analysis at B3LYP/CEP-121G level, several thermodynamic parameters are calculated and are presented in Table 4 . ΔS°, ΔU°, ΔH°, ΔA° and ΔG° properties have been calculated.

3.5. Vibrational assignments

3.5.1. C-H Vibrations

The title compound belong to C_1 symmetry, consists of 14 atoms and its 36 normal modes according to 3N-6. The detailed vibrational assignments of fundamental modes of CPIC along with observed and calculated frequencies, infrared intensities, and normal mode description are reported in table 5. CPIC gives rise to the four C-H stretching corresponding to C_1-H_{11}, C_2-H_{12}, C_3-H_{13}, C_4-H_{14} and eight C-H bending vibrations, since CPIC is distributed aromatic system therefore, the four C-H moieties are adjacent to one another. The C-H stretching frequency in phenyl [28] is normal lies between 3100 and 3000 cm^{-1}. In this region, the bands are not affected appreciably by the nature of substituents. Hence, in our present study, the FT-IR bands observed at 3036, 3016 and 2995 cm^{-1} are assigned to

C-H stretching vibrations. The C-H in plane ring bending vibrations are usually expected to occur in the region 1400-1200 cm^{-1} and these vibrations are very useful for characterization purpose[29]. Hence, in our present investigation, the FT-IR bands observed at 1435 and 1133 cm^{-1} are assigned as C-H in plane ring vibrations. The frequencies of the C-H out of plane ring bending vibrations which occur in the region 1000-700 cm^{-1}, are mainly determined by the number of adjacent hydrogen atoms on the ring and not very much affected by the nature of substitutions [30] normally. The stretching, in plane and out of plane bending vibrations of CH group are found to be within the characteristic region and literature [31]. The theoretically computed frequencies are found to be in a good agreement with experimental frequencies and presented in table 5.

3.5.2. C-C Vibrations

C-C vibrations—The ring C-C and C=C stretching vibrations [32], known as semi-circular stretching usually occur in the regions 1380-1280 cm^{-1} and 1625-1430 cm^{-1} respectively. The C-C stretching vibrations of CPIC are observed at 1301 and 1155 cm^{-1} in the FT-IR spectrum. In accordance with above literature data in our present study, the bands for C=C stretching vibrations are observed at 1622 , 1501 and 1488 cm^{-1} in FT-IR spectrum. These observed frequencies show that the substitutions in the region to some extent about the ring mode of vibrations. The comparison of the theoretically computed values is found to be in a good agreement with the theoretical values obtained by CEP-121G (table 5).

3.5.3. C-N Vibrations

C-N vibrations—To identify the C-N stretching frequency is a rather difficult task from other vibrations. Silverstein *et al* [33] assigned C-N stretching absorption in the region 1382-1266 cm^{-1}. In benzotrizole, the C-N stretching bands are found to be present at 1307 and 1382 cm^{-1} .Shanmugam *et al* [34] have reported the C-N stretching frequency observed at 1368 cm^{-1}. C-N in plane bending vibrations are found to be at 454 cm^{-1} during computation by B3LYP/CEP-121G, while the experimentally assigned value is 430 cm^{-1} (table 5).

3.5.4. C-Cl Vibrations

C-Cl vibrations—the C-Cl stretching vibrations [35], generally ,give strong band in the region 765-505 cm^{-1} .The vibrational coupling [36] with other groups may result in the absorption to as high as in 840 cm^{-1}. Most of the aromatic chloro compounds have aband of strong assignment made for Cl atom and NCS to medium in the region 385-265 cm^{-1} due to C-Cl in plane bending vibrations [36] .Accordingly , the IR band identified at 232 cm^{-1} has been assigned in the C-Cl in plane bending mode (table 5).

3.5.5. -N=C=S Vibrations

-N=C=S vibrations— There are six vibrations for NCS moiety; in phenyl isothiocyanate molecule asymmetric stretching, symmetric stretching, in plane bending, in plane wagging, out of plane bending and out of plane wagging in vibrations. Similarly, in our title molecule also for NCS moiety, one can expect the above said vibrations. Hence in our present study, the FT-IR bands observed at 2112 and 950 cm^{-1} are assigned to asymmetric and symmetric stretching vibrations respectively. The vibrations by B3LYP/CEP-121G are found in a good agreement with the experimentally recorded spectra . The FT-IR observed at 508 cm^{-1} is assigned to in plane bending . The theoretically computed values show good agreement with experimental observation (table 5).

4. CONCLUSION

The normal mode frequencies and corresponding vibrational assignments of the CPIC are examined theoretically using the Gaussian 03 package. The optimized geometry parameters calculated at B3LYP/CEP121G are slightly shorter as well as longer than experimental values coincide well compared with experimental data. The harmonic vibrational frequencies infrared intensities and IR spectrum of CPIC have been determined and analyzed at DFT/B3LYP/CEP-121G level of theory. The close agreement obtained between calculated frequencies and observed calculations are also supporting the group present in the molecule.

Table 1 : Optimized geometrical parameters of 2-chlorophenylisothiocyanate, bond length(Å), Interaxial angles(°)

parameter	Calculated	Experimental [25,26]
Bond length(Å)		
R(1-2)	1.414	1.394
R(1-6)	1.407	1.389
R(1-11)	1.085	1.084
R(2-3)	1.415	1.399
R(2-12)	1.087	1.076
R(3-4)	1.408	1.414
R(3-13)	1.087	1.084
R(4-5)	1.422	1.396
R(4-14)	1.086	-
R(5-6)	1.425	1.388
R(7-6)	1.821	-
R(5-8)	1.387	1.394
R(8-9)	1.204	1.201
R(9-10)	1.648	-
Bond angles(°)		
A(2-1-6)	119.6	119.29
A(2-1-11)	121.0	121.04
A(1-2-3)	120.1	121.68
A(1-2-12)	119.5	120.44
A(6-1-11)	119.4	119.67
A(1-6-5)	121.1	122.86
A(3-2-12)	120.4	116.70
A(2-3-4)	120.3	116.18
A(2-3-13)	120.2	118.67
A(4-3-13)	119.5	121.38
A(3-4-5)	120.4	120.44
A(3-4-14)	121.2	-
A(5-4-14)	118.4	-
A(4-5-6)	118.6	-
A(4-5-8)	119.6	117.03
A(6-5-8)	121.8	121.28
A(5-8-9)	167.0	-
A(8-9-10)	177.2	175.1

Table 2: Total energy, Electronic states, Energy gap and related molecular properties for CPIC calculated by DFT with B3LYP system and CEP-121G basis set .

Property	Value
E_{HOMO} eV	-6.648
E_{LUMO} eV	-1.847
Energy gap eV	4.8003
Ionization Potential (IP) in eV	6.648
Electron affinity(EA) in eV	1.847
Global Hardness (η) in eV	2.4001
Softness (S) in 1/eV	0.2083
Chemical potential (K) in eV	-4.247
Global Electrophilicity (ω) in eV	3.757
Electronegativity (χ) in eV	4.247
Total energy (E) in a.u	-76.7935
Dipole moment(μ) in Debye	4.98
Anisotropy of polarizability ($\Delta\alpha$)	758.937

Table 3: calculated components of α_i (i = xx,yy,zz) an average of the dipole polarizability $< \alpha >$ in atomic units for CPIC

Parameter by CEP-121G basis set	α_{xx}	α_{yy}	α_{zz}	$< \alpha >$
Value	212.80	107.52	44.49	121.603

Table 4 : Thermodynamic properties of CPIC calculated by DFT with B3LYP system and CEP-121G basis set .

Thermodynamic property	Value
ΔU° (kcal/mole)	62.470
ΔH° (kcal/mole)	63.062
ΔS° (cal/mole K)	96.940
ΔG°(kcal/mole)	34. 249

Table 5 : vibrational assignments of fundamental observed and calculated frequencies for 2-chlorophenylisothiocyanate using B3LYP/CEP-121G level [wave number cm^{-1} ; IR intensities(km $mole^{-1}$)]

FT-IR Obs. Frequencies[22]	FT-IR Cal. Frequencies	FT-IR intensities	Assignments
-	3200	13.318	ν_{ss}CH
3036 (s)	3193	12.957	ν_{ass}CH
3016 (ms)	3179	3.179	ν_{ass}CH
2995 (ms)	3164	1.707	ν_{ass}CH
2112 (vs)	2177	1666.86	ν_{ass} NCS
1622 (s)	1610	23.76	νCC

1501 (vs)	1584	1.858	νCC , δCH
1488 (vs)	1491	60.37	νCC, δCH , νC_5N_8
1435 (s)	1455	19.1717	δCH
-	1321	0.3020	νCC , δCH
1301 (vw)	1292	5.150	νC_5N_8 , δCH, νCC
-	1261	0.1906	νCN, νCC
1155 (vw)	1193	0.0535	δCH
1133 (w)	1140	1.0217	δCH
-	1060	24.791	δCH
-	1034	22.307	νCC, Ring breath
950 (ms)	1013	0.3237	δCH, ν_{ss} NCS
941 (s)	980	3.510	δCH
928 (vw)	904	34.662	Ring breath
-	895	2.283	ωCH
815 (vw)	794	91.736	ωCH
-	708	0.0026	ωCCl, Ring ωCCC
728 (vs)	700	37.688	ωCH, δCCC, νCCl
-	653	24.361	ωCH, Ring elongation
-	545	0.168	Ring ωCCC
508 (ms)	494	16.0056	NCS ipb
430	454	5.0005	δCN, ωCCC
-	439	4.319	δCCC, νCCl, NCS ipb
-	419	1.370	ωCN , NCS opb
400 (vw)	397	4.660	δ NCS
-	315	1.975	$\delta C_1C_6C_5$,Ring elongation
-	276	0.383	NCS opb
-	232	1.182	δCCC, δCCl
-	163	0.195	ωCCl, ω Ring
-	63	0.1417	C_9-S_{10},C_3-C_4,C_1-C_6 opb
-	28	0.3259	CNC ipb
S- strong ; m- medium ;w- weak ;vw- very weak ; vs- very strong ; ν- stretching; δ-in plane bending ; ω- out of plane bending ; obp- out of plane bending ; ibp- in plane bending ; ipw- in plane wagging ; opw- out of plane wagging			

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