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Vibrational Spectroscopy

Elixir Vib. Spec. 44 (2012) 7536-7545

Vibrational spectroscopic investigation using HF and DFT analysis on the structure of 2, 6-dichloro benzyl chloride

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ARTICLE INFO	ABSTRACT
Article history:	In this work, the vibrational
Received: 6 October 2011;	spectroscopy in the range 400
Received in revised form:	6-dichlorobenzyl chloride. Th
16 March 2012;	intensity of the vibrational ba
Accepted: 26 March 2012;	normal coordinate force field
	basis set. The complete vibrat

Keywords

FTIR, FT Raman, 2, 6-dichlorobenzyl chloride, Homo-lumo.

spectral analysis is carried out using FTIR and FT Raman 0-4000cm⁻¹ and 50-3500 cm⁻¹, respectively, for the molecule 2he molecular structure, fundamental vibrational frequencies and ands are interpreted with the aid of structure optimizations and d calculations based on HF and DFT methods with 3-21 + G The complete vibrational assignment for different normal modes of the molecule is done. Mulliken population analysis, charge distributions, thermodynamic properties and HOMO-LUMO are also discussed. With the help of specific scaling procedure, an excellent agreement between observed and calculated frequencies has been made.

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Introduction

2,6-Dichlorobenzyl chloride (DCBC) or a chlorinated toluene is a dichloro substituted benzyl chloride at 2 and 6 positions. It is a clear to yellowish liquid with chlorine like odour. Generally in the dye industry benzyl chloride is used as an intermediate in the manufacture of triphenyl methane dyes. Organic compounds including benzyl alcohol, benzyl cyanide and other benzyl compounds used in the end applications of perfumery, many flavored products dyes, pharmaceuticals, synthetic resins, photographic chemicals, warfare compounds, penicillin's, quaternary ammonium compounds, plasticizer and esters, it is used in fuel as a gum inhibitor chlorinated toluene. It is used as an intermediate in the production of a number of products, including agricultural chemicals, dyes and pigments and pharmaceuticals. Due to greater pharmaceutical and industrial importance, DCBC has been taken for this present study.

Α detailed quantum chemical study will aid in understanding the vibrational modes of this DCBC. So, in this present work, the vibrational wave numbers, geometrical parameters, modes of vibrations, rotational constants, atomic charges, HOMO - LUMO and other thermodynamical parameters of DCBC were investigated using HF/3-21+G and DFT/3-21+G methods. Scaling was employed in the predicted frequencies for the accuracy.

Experimental details

The DCBC was purchased from M/S Aldrich Chemicals, U.S.A. which is of Spectroscopic grade and hence used for recording the Spectra as such without any further purification. The FT-IR Spectrum of the compound was recorded in Perkin-Elmer 180 spectrometer in the range of 4000-400cm⁻¹. The spectral resolution is $\pm 2 \text{ cm}^{-1}$. The FT-Raman Spectrum of the compound was also recorded in the range50-3500 cm⁻¹ in same instrument with FRA 106 Raman module equipped with Nd: YAG laser source operating at 1.064µm line width with 200mW power. The spectrum was recorded with scanning speed of 30cm⁻¹ min⁻¹ of spectral width 2cm⁻¹. The frequencies of all sharp bands are accurate to $\pm 1 \text{ cm}^{-1}$.

Computational methods

The molecular structure optimization of the title compound and corresponding vibrational harmonic frequencies were calculated using HF and B3LYP combined

3-21+G basis set using GAUSSIAN 09W program package without any constraint on the geometry [1]. Geometries have been first optimized with full relaxation on the potential energy surfaces at HF/3-21+G and DFT/3-21+G basis sets. The optimized geometrical parameters, true rotational constants, fundamental vibrational frequencies, IR intensity, Raman activity and depolarization ratio were calculated using GAUSSIAN 09W package. The atomic charges, dipole moment and other thermodynamical parameters were also calculated theoretically using the GAUSSIAN 09W package.

By combining the results of GAUSSVIEW [2] program with symmetry considerations along with the available related molecules, vibrational frequency assignments were made with a high degree of accuracy. However, the defined coordinate from complete set and matches quite well with the motions observed using GAUSSVIEW program.

Results and Discussion

Molecular geometry

The molecular structure along with numbering of atoms ofDCBC is shown in Fig.1. The maximum number of potentially active observable fundamentals of a non-linear molecule which contains N atoms is equal to (3N-6) apart from three translational and three rotational degrees of freedom [3].

Since this is an asymmetric top molecule having rotational symmetry number one, and do not possess any rotational, reflection or inversion symmetry, the molecule is considered under Cs point group symmetry. The definition of internal coordinates and local symmetry coordinates of DCBC is given in Tables 1 and 2, respectively.



Fig.1 The optimized geometrical structure along with numbering of atoms of DCBC

The most optimized structural parameters (bond length, bond angle and dihedral angle) by HF, DFT with 3-21+G basis set were shown in Table3.

From the experimental values of literature [4], the C-C single bond length is 1.5037Å, C- H single bond length is 1.0853Å and C-Cl bond length is 1.827Å for benzyl chloride. The C-Cl bond length (Cl atom of -CH₂ Cl group) is 1.821Å in the earlier work done by Durig et.al [5] and the bond distance is more consistent with the results from the electron diffraction study [6]. From the literature [7], the C-C bond length varies between the value 1.3752 and 1.3866Å, while the C-H bond length varies from 1.0705 to 1.0719Å. From the literature [8], C-C Single bond length is 1.4009Å, H-C Single bond length is 1.0875Å and C-Cl bond length is 1.8405Å for benzyl chloride. Taking account of the effect of conjugation, the calculated values of DCBC is in reasonable agreement with the above mentioned experimental data. The HF/3-21+G bond lengths are slightly exaggerated electron correlation effect. So, compared with the experimental values, DFT/3-21 + G bond lengths are best.



Fig.2 Observed FT-IR Spectra of DCBC Vibrational assignments

DCBC molecule has 15 atoms with 39 normal modes of vibrations. This molecule defines a symmetry plane, i.e., the molecule belongs to the Cs point group symmetry, which divides entire modes of vibration into two categories: Planar A' and Non-Planar A''. For N-atomic molecule, 2N-3 of its vibrations are planar and N-3 are non-planar [9]. Thus, with respect to the reflection of the symmetry plane, 27 of these modes should be planar (A') and 12 should be non-planar (A''). In agreement with Cs symmetry, all the 39 fundamental vibrations are active in both Raman Scattering and infrared absorption. The A' vibrations are totally symmetric and gives rise to polarized Raman lines whereas A'' vibrations are antisymmetric and gives rise to depolarized Raman lines.

The detailed vibrational analysis of fundamental modes with FT-IR and FT-Raman experimental frequencies using HF/3-21 + G and DFT/3-21 +G basis sets, IR intensity, Raman activity, depolarization ratio, reduced mass and force constant ofDCBC were reported in Tables 4 and 5, respectively. The experimental FT-Infrared and FT-Raman spectra in solid phase were shown in Figs. 2 and 3, respectively.



Fig.3 Observed FT Raman Spectra of DCBC



Fig4. Comparison of Atomic Charges at HF/ 3-21+G and DFT/3-21+G

It made a reliable one to one correspondence between the experimental fundamentals and any of the frequencies calculated by the HF/3-21+G and DFT/3-21+G methods. In order to improve the calculated values, it is necessary to scale down the harmonic frequencies. The vibrational frequencies calculated at DFT/3-21+G was scaled by 0.97 for wave numbers less than 1700 cm^{-1} and 0.98 for higher wave number. The scaled values used in HF/3-21+G were 0.91 for wave numbers less than 1700 cm^{-1} and 0.92 for higher wave numbers.



Fig 5 Comparison of Mulliken charges at HF/ 3-21+G and DFT/3-21+G

C-H vibrations

In the aromatic compounds, the C-H stretching vibrations normally occur at 3100-3000cm⁻¹ [10]. These vibrations are not found to be affected due to the nature and position of the substituent. Most of the aromatic compounds have nearly four infrared peaks in the region 3080-3010cm⁻¹ due to ring C-H Stretching bonds [11, 12]. In this work, the FT-IR band at 3142, 3078, 3059cm⁻¹ and Raman band at 3145,3081 cm⁻¹are assigned to stretching vibrations.

The C-H in-plane bending vibrations usually occur useful for characterization purposes [13]. It is noted from literature [14] that strong band around 1200cm⁻¹ appears due to valence oscillations in benzene and substituted benzene. The peaks

appear at 1283,1229,1217 cm⁻¹ due to the effect of C-H-inplane-bending vibrations.

The strong peaks below 900cm⁻¹, i.e., around 784, 766, 754cm⁻¹ clearly indicate its aromativitiy. Substitution patterns on the ring can be judged from the out-of-plane bending of the ring C-H bonds in the region 900-675cm⁻¹ and these bands are highly informative [15]. In the present work the peaks at 1104,1084 in FT-Raman and 1092, 1070 cm⁻¹ in FTIR confirms the C-H outof-plane bending vibrations which agrees with the literature [15.16].

CH₂ and C-CH₂ vibrations

For the assignments of CH₂ group frequencies, basically six fundamentals can be associated to each CH₂ group namely CH₂ symmetric stretch; CH₂ asymmetric stretch; CH₂ scissoring and CH₂ rocking which belongs to in-plane vibrations and two outof-plane vibrations, Viz., CH2 wagging and CH2 twisting modes, which are expected to be depolarized [17]. The asymmetric CH_2 stretching vibrations are generally observed above 3000cm⁻¹ while the symmetric stretch will appear between 3000 and 2900cm⁻¹ [18-20]. In the molecule DCBC, the asymmetric and symmetric stretching vibrations were observed in 3028 and 2991 in IR and 2989 cm⁻¹ in Raman, respectively. For n-alkyl benzenes, the assignment of the fourth skeletal C-C Stretching mode at about 1464cm⁻¹ is quite problematic, since this band is frequently masked by the more intense bands at 1446-1465 cm⁻¹ arising from the CH₂ Scissoring vibrations [21, 22]. For α chlorotoluene, the CH₂ scissoring mode has been assigned to the strong intensity IR bands at about 1460 cm⁻¹ [23]. Thus a Similar band at 1472cm⁻¹ in FT-Raman has been assigned to the CH₂ scissoring vibration. The band at 900 in IR and 909cm⁻¹ was assigned to CH₂ rocking in-plane bending vibration [24]. The CH_2 wagging and twisting out-of-plane bending vibrations at 1269 and 328 cm⁻¹ are exactly coincides with the reported value of the earlier work [24].

C-C and C-C-C vibrations

Generally the C=C Stretching vibrations in aromatic compounds form the band in the region of 1430-1650cm⁻¹ [15, 25]. According to Socrates [26], the presence of conjugate substituent such as C=C Causes a heavy doublet formation around the region 1625-1575cm⁻¹. The six ring carbon atoms undergo coupled vibrations called skeletal vibrations and give a maximum of four bands in the region 1660-1420cm⁻¹ [27]. As predicted in the earlier references, in this title compound also the prominent peaks at 1682, 1581, 1553, 1505, 1446, 1438 and 1312cm⁻¹ are due to strong C-C stretching vibrations.

C-Cl vibrations

The presence of halogen on alkyl substituted aromatic ring can be detected indirectly from its electronic impact on the inplane C-H bending vibrations [28]. The C-Cl stretching vibrations give generally strong bands in the region 730-580 cm⁻ [29]. In this title compound, the peaks at 784, 766, 754 cm^{-1} in IR and 785,771 in Raman are due to CH₂-Cl, C-Cl and C-Cl vibrations and it may also imply that the dichlorinated compound in the alkyl substituted aromatic ring. The peaks at 678, 615, 606 cm⁻¹ in IR and 671, 611 in Raman and 507, 487, 403cm⁻¹ are due to in-plane and out-of-plane vibrations, respectively.

Mulliken population analysis

The total atomic charges of DCBC obtained by Mulliken population analysis with HF and DFT methods with 3-21+G basis set were plotted in Fig.4. From the result, it is clear that the substitution of CH₂Cl atoms in the aromatic ring leads to a redistribution of electron density. The σ -electron withdrawing character of the chlorine atom in DCBC is demonstrated by the decrease of electron density on C7 atom. The atomic charges in the CH₂ group are almost identical. The atomic charge obtained from HF/3-21+G shows that C_1 atom is more basic due to more negative charges.

Charge distributions

APT Charges at various atomic sites of DCBC computed at the HF and DFT methods with 3-21+G basis set are ploted in fig.5. The pattern of the charges is similar at both the levels. HOMO & LUMO analysis

Many organic molecules that containing conjugated π electrons are characterized hyperpolarizabilities and were analyzed by means of vibrational spectroscopy [30, 31]. In most cases, even in the absence of inversion symmetry, the strongest bands in the Raman spectrum are weak in the IR spectrum and vice versa. But the intra-molecular charge transfer from the donor to acceptor group through a single - double bond conjugated path can induce large variations of both the molecular dipole moment and the molecular polarizability, making IR and Raman activity strong at the same time. The experimental spectroscopic behavior described above is well accounted for by abinitio calculations in π conjugated system that predict exceptionally large FT-Raman and FT-IR intensities for the same normal modes [31].



Fig 6 Atomic orbital (a) HOMO and (b) LUMO compositions of the frontier molecular orbital for DCBC

As observed in our title molecule the bands observed in FT-IR and FT-Raman Spectra show that the relative intensities in IR and Raman spectra are comparable resulting from the electron cloud movement through π conjugated frame work from electron donor to electron acceptor groups. The analysis of the wave function indicates that the electron absorption corresponds to the transit from the ground to the first excited state and is mainly described by one electron excitation from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). The LUMO, of π nature (*ie.* benzene ring) is molecular delocalized over chloro ethyl and one of the two chlorine atoms, consequently the HOMO \rightarrow LUMO transition implies an electron density transfer to benzene ring of π conjugated system from chloro ethyl and one of the two chlorine atoms. Moreover, these three orbitals significantly overlap in the different positions of the benzene ring. The atomic orbital compositions of the frontier molecular orbital are sketched in Figs.6(a) and 6(b).

The HOMO – LUMO energy gap of DCBC calculated at the DFT/3-21+ G level as shown below, reveals that the energy gap reflects the chemical activity of the molecule.

LUMO as an electron acceptor represents the ability to obtain an electron, HOMO represents the ability to donoate an electron.

HOMO energy	=	-0.357917 a.u.
LUMO energy	=	-0.065457 a.u.
HOMO – LUMO energy gap	=	0.29246 a.u.
		a

The calculated self – consistent field (SCF) energy of DCBC is -1638.3552a.u.; Moreover, the lower value in the HOMO and LUMO energy gap explains the eventual charge transfer interactions taking place within the molecule.

Thermodynamical properties

Zero point vibrational energy, Rotational constants, Rotational temperatures, energy, entropy and Molar capacity at constant volume for DCBC have been calculated and presented in Table 6. The variations in the Zero point vibrational energies are seem to be insignificant. The changes in the total entropy of DCBC at room temperature at different methods are only marginal. The values of rotational constants and rotational temperatures have direct proportionate relationship. That is, as the rotational temperature increases, there will be an increase in rotational constant value.

Conclusion

Attempts have been made in the present study for the proper frequency assignments for the title compound DCBC from the FT-IR and FT-Raman spectra. The equilibrium geometries, harmonic frequencies IR intensity, Raman activity. depolarization ratio, reduced mass and force constant of the title compound were determined and analyzed both at HF and DFT levels of theory utilizing 3-21+G basis set. Comparison between the calculated vibrational frequencies and the experimental values indicates that both the methods can predict the FT-IR and FT-Raman spectra of the title compound well. Scaling factors results are in good agreement with the experimental ones. In particular the results of DFT/3-21+G method indicate better fit to experimental ones than ab initio HF upon evaluation of vibrational frequencies. The influence of CH_2 group and the electron withdrawing nature of Cl atom in the compound selected were also discussed. The discrepancy noted between the observed and the calculated frequencies may be due to the fact that the calculation have been actually done on a single molecule contrary to the experimental values recorded in the presence of intermolecular interactions. Therefore, the assignments made at higher level of theories with only reasonable deviations from the experimental values seem to be consistent.

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Table-1	
Definition of internal Co-ordinates of DCB	2

Number	Symbol	Туре	Definition ^a
Stretching	5		
1-7	ri	C-C	C_1 - C_2 , C_2 - C_3 , C_3 - C_4 ,
			$C_4-C_5, C_6-C_1, C_1-C_7$
8-10	Ri	C-H	C_3 - H_{12} , C_4 - H_{13} , C_5 - H_{14}
11-13	Q_i	C-Cl	C_2 - Cl_{11} , C_6 - Cl_{15} , C_7 - Cl_{10}
14-15	Ri	C-H (ethyl)	C_7-H_8, C_7-H_9
Bending			
16-21	α _i	Ring	C_1 - C_2 - C_3 , C_2 - C_3 - C_4 ,
			$C_3-C_4-C_5, C_4-C_5-C_6$
			$C_5-C_6-C_1, C_6-C_1-C_2$
22-27	βi	CCH	H1 ₂ -C ₃ -C ₂ , H1 ₂ -C ₃ -C ₄
			H ₁₃ -C ₄ -C ₃ , H ₁₃ -C ₄ -C ₅
			$H_{14}-C_5-C_4, H_{14}-C_5-C_6$
28-29	γ_i	CCC	$C_7-C_1-C_2, C_7-C_1-C_6$
30-33	δ _i	CCC1	$Cl_{11}-C_2-C_1, Cl_{11}-C_2-C_3$
			$Cl_{15}-C_{6}-C_{5}, Cl_{15}-C_{6}-C_{1}$
34-35	βi	CCH (ethyl)	$C_1 - C_7 - H_8, C_1 - C_7 - H_9$
36	θ_i	НСН	H ₈ -C ₇ -H ₉
37	δ_i	CCC1	$C_1 - C_7 - Cl_{10}$
Out -of-p	lane bendin	g	
38-40	ω _i	C-H	$H_{-12}-C_3-C_2-C_4$
	-		$H_{13}-C_4-C_3-C_5$
			$H_{14}-C_5-C_4-C_6$
41-42	π_{i}	C-Cl	$Cl_{11}-C_2-C_3-C_1$
	•		$Cl1_{5}-C_{6}-C_{5}-C_{1}$
43	Ψ_i	CC	$C_7 - C_1 - C_2 - C_6$
44	Π_{i}	C-Cl	Cl ₁₀ -C ₇ -H ₈ -H ₉
Torsion			
45-50	τ_{i}	τ Ring	C1-C2-C3-C4, C2-C3-C4-C5 C3-C4-C5-C6, C4-C5-C6-C1 C5-C6-C1-C2, C6-C1-C2-C3
51	$ au_{i}$	$\tau C-CH_2$	$C_1 - C_7 - H_8 - H_9$

	Table-2 D	efinition of local symmetry Co-ordinates forDCBC
No (i)	Symbol ^a	Definition ^b
1-7	C-C	r ₁ r ₂ r ₃ r ₄ r ₅ r ₆ r ₇
8-10	C-H	R_8, R_9, R_{10}
11-13	C-Cl	Q11, Q12, Q13
14	CH ₂ ss	$(R_{14} + R_{15}) / \sqrt{2}$
15	CH ₂ ass	$(R_{14} + R_{15}) / \sqrt{2}$
16	R trigd	$(\alpha_{16} - \alpha_{17} + \alpha_{18} - \alpha_{19} + \alpha_{20} - \alpha_{21})/\sqrt{6}$
17	R Symd	$(\alpha_{16} - \alpha_{17} + 2 \alpha_{18} - \alpha_{19} - \alpha_{20} + 2 \alpha_{21})/\sqrt{12}$
18	R asymd	$(\alpha_{16} - \alpha_{17} + \alpha_{19} - \alpha_{20}) / \sqrt{2}$
19-21	bCH	$(\beta_{22} - \beta_{23})/\sqrt{2}(\beta_{24} - \beta_{25})/\sqrt{2}(\beta_{26} - \beta_{27})/\sqrt{2}$
22	bCC	$(\gamma_{28} - \gamma_{29})/\sqrt{2}$
23-24	bCC1	$(\delta_{30} - \delta_{31})/\sqrt{2}, (\delta_{32} - \delta_{33})/\sqrt{2}$
25	CH ₂ twist	$(\beta_{34} + \beta_{35}) / \sqrt{2}$
26	CH ₂ rock	$(\beta_{34} - \beta_{35}) / \sqrt{2}$
27	CH ₂ Sciss	$(2\theta_i - \beta_{34} - \beta_{35})/\sqrt{6}$
28	bCC1	$(\delta_{36} - \delta_{37})$
29-31	ωCH	$\omega_{38}, \omega_{39}, \omega_{40}$
23-33	ωCCl	π_{41}, π_{42}
34	ωCC	π_{43}
35	ωCCl	π_{44}
36	tRtrig	$(\tau_{45}-\tau_{46}+\tau_{47}-\tau_{48}+\tau_{49}-\tau_{50})/\sqrt{6}$
37	tSym	$(\tau_{45} - \tau_{47} + \tau_{48} - \tau_{50})/\sqrt{2}$
38	tasym	$(-\tau_{45}+2\tau_{46}-\tau_{47}-\tau_{48}+2\tau_{49}-\tau_{50})/\sqrt{12}$
39	CH ₂ wag	τ ₅₁

^aThese symbols are used for description of normal modes. ^bThe internal coordinates used here are defined in Table 3.

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	Table – 3	
mized geometrical pa	rameters (l	oond length, bond
hedra <u>l angle) of DCB</u>	<u>C HF/3-21 -</u>	+ G and DF $1/3-21$
C1-C2	HF/3-21+G	$\frac{DF1 / 3-21 + G}{1.4028}$
C1-C6	1.3866	1.4108
C1-C7	1.491	1.5201
C2-C3	1.3752	1.3962
C2-CI11 C3-C4	1.8151	1.8306
C3-H12	1.0705	1.0831
C4-C5	1.3836	1.3963
C4-H13	1.0719	1.0841
C5-H14	1.3752	1.3844
C6-C115	1.8151	1.8414
C7-H8	1.0715	1.0889
C7-H9	1.0715	1.0888
C/-CIIU Bond Angles (%)	1.9036	1.8835
C2-C1-C6	116.0212	114.5472
C2-C1-C7	121.9848	131.1547
C6-C1-C7	121.9904	114.2981
C1-C2-C3 C1-C2-C111	122.8773	122.3793
C3-C2-Cl11	116.9324	113.4489
C2-C3-C4	119.1855	120.5082
C2-C3-H12	119.7961	118.7833
C4-C3-H12	121.0183	120.5082
C3-C4-H13	120.0738	120.308
C5-C4-H13	120.0725	120.3316
C4-C5-C6	119.1865	118.4873
C4-C5-H14	121.0165	121.5117
C0-C3-H14 C2-C1-C7	122 8757	120.001
C2-C1-C7	120.1917	119.0779
C4-C5-H14	116.9325	109.8795
C6-C5-H14	11.131	109.8673
C2-C1-C7	113.1301	120.0051
C4-C5-H14	111.572	103.829
C6-C5-H14	104.4425	103.7903
Dihedralangle (°)		
C6-C1-C2-C3	-0.0031	-0.0587
C7-C1-C2-C11	-179.9354	179.9198
C7-C1-C2-Cl11	0.6125	-0.0446
C2-C1-C6-C5	0.0089	0.0494
C2-C1-C6-C115	-179.9307	-179.9379
C7-C1-C6-C15	-0.6078	-1/9.9801
С2-С1-С7-Н8	153.6968	119.8315
С2-С1-С7-Н9	25.5826	-120.4108
C2-C1-C7-C110	-90.3596	-0.3217
C6-C1-C7-H8 C6-C1-C7-H9	-25.5858	-060.1329
C6-C1-C7-C110	90.3577	179.7138
C1-C2-C3-C4	-0.0234	0.0303
C1-C2-C3-H12	-179.9855	-179.9808
CLII-C2-C3-C4 C11 C2 C3 H12	-179.9639	-179.9502
C1-C2-C3-C4-C5	0.0445	0.013
C2-C3-C4-H13	-179.941	-179.9985
H12-C3-C4-C5	-179.9939	-179.9756
H12-C3-C4-H13	0.0206	0.0129
C3-C4-C5-C6 C3-C4-C5-H14	-0.0391 179 9818	-0.0228 179 9759
H13-C4-C5-C6	179.9464	179.9887
H13-C4-C5-Cl15	-0.0326	-0.0126
C4-C5-C6-C1	0.0121	-0.01
U4-U5-U6-U115 H14-C5-C6-C1	1/9.9535 170.001/	1/9.9//6 179.9913
H14-C5-C6-C115	-0.0671	-0.0211

Opti dih angle, + G

For numbering of atoms refer Fig.1

Table – 5 Experimental and Calculated DFT/3-21+G level vibrational frequencies (cm⁻¹), IR intensity (kM mol⁻¹) Raman activity (A⁴ amu⁻¹), Raman depolarization ratios and reduced masses (amu), force constant (mdyne A⁻¹) of DCBC

	G	Exper	imental	Calcul	ated	m	D		D 1 1		¥7'1 .' 1
S1.	Symmetry	Freq	uency	freque	ncy	IR	Raman	Depolarization	Reduced	Force	Vibrational
	species	FT-IR	Raman	Unscaled	Scaled	intensity	activity	Tatio	mass	constant	Assignments
1	A	3142	3145	3233	3141	1.2828	203.1899	0.5589	1.0962	6.725	γСН
2	A [']	(w) 3078	3081 (s)	3227	3073	0.1043	65.0850	0.8517	1.0906	6.6903	γСН
3	A	(III) 3059 (vm)	-	3207	3052	3.1227	72.6276	0.7879	1.0871	6.5859	γСН
4	A	3028 (vw)	-	3187	3022	0.2820	40.8586	0.8749	1.1091	6.6356	$\gamma_{ass}CH_2$
5	A'	2991 (vm)	2989 (m)	3128	2985	2.8170	105.5047	0.5212	1.0551	6.0841	$\gamma_{ss}CH_2$
6	A'	1682 (vw)	-	1614	1677	15.2803	24.9996	0.7690	5.6941	8.7362	γCC
7	A	1581 (m)	1578 (s)	1578	1576	47.6089	14.4291	0.8724	4.6465	6.8146	$\gamma C\text{-}CH_2$
8	A	1553 (s)	1552 (w)	1512	1548	17.9686	6.1237	0.7871	1.2824	1.7270	γCC
9	A'	1505 (vw)	-	1478	1499	43.3194	3.6796	0.8438	1.6235	2.0895	γCC
10	A'	-	1472 (vw)	1452	1468	25.8796	1.1620	0.7941	2.3748	2.9505	δCH_2
11	A	-	1446 (w)	1369	1441	0.0447	6.5474	0.8748	2.7804	3.0685	γCC
12	A	1438 (vs)	-	1364	1432	28.4763	5.7725	0.7379	1.2792	1.4026	γCC
13	A	-	1312 (vw)	1293	1308	1.6606	19.3407	0.6720	5.0315	4.9553	γCC
14	A [']	-	1283 (s)	1261	1279	1.6404	1.8770	0.8749	1.3924	1.3055	bCH
15	A ["]	1269 (s)	- ``	1254	1263	10.2098	5.7820	0.6493	1.4333	1.3288	βCH_2
16	A	-	1229 (s)	1204	1224	3.3576	11.2591	0.5610	2.0423	1.7441	bCH
17	A	1217 (m)	-	1180	1214	35.8406	1.3815	0.6106	2.2330	1.8345	bCH
18	A ["]	-	1104 (m)	1102	1100	3.0328	28.6458	0.5244	3.0020	2.1490	ωCH
19	Α"	1092 (s)	1084 (s)	1093	1088	15.0938	8.4571	0.792	7.9037	5.5624	ωCH
20	A"	1070 (vw)	-	1034	1065	2.6459	0.1343	0.8749	1.4274	0.8992	ωCH
21	A	975 (m)	-	978	971	0.0033	0.3557	0.8750	1.5272	0.8606	bCC
22	A	900 (s)	909 (vw)	897	895	8.2260	2.5339	0.8750	1.5170	0.7195	ρCH_2
23	A	-	837 (w)	845	832	26.8997	0.0498	0.8570	5.7860	2.4364	Rtrigd
24	A	825 (m)	-	799	821	68.3050	0.0333	0.8737	1.1774	0.4428	Rasymd
25	A	820 (m)	-	756	816	59.2722	4.7008	0.6289	8.6900	2.9294	Rsymd
26 27	A A	784 (vs) 766 (vs)	785 (vw) 771 (s)	675	781 762	42.9336 0.0007	8.8254 0.7841	0.6806 0.8749	7.1388 3.8975	2.1874 1.0454	γCCI γCCI
28	A	754 (vs)	-	603	751	0.1160	13.2422	0.5393	6.5450	1.4042	γCCl
29	A	678 (vs)	671 (vs)	571	674	0.4985	0.0056	0.8365	2.6853	0.5174	βCCl
30	A	615 (w)	611 (m)	460	612	13.9095	15.7022	0.6333	10.1772	1.2697	BCCI
31	A	606 (vw)	-	396	601	4.9954	6.3466	10.6118	7.3031	0.6759	βCCI
32	A	507 (m)	-	362	502	4.0694	9.7922	0.5642	12.2604	0.9445	ωCCl
33	A	-	487 (m)	283	482	7.3390	1.4256	0.8750	3.8834	0.1828	ωCCl
34	A	-	403 (s)	232	399	0.8670	5.7703	0.8526	15.7927	0.4987	ωCCl
35	A	-	392 (vs)	218	386	0.0037	1.0810	0.8750	4.4185	0.1238	ωCC
36	A	-	328 (m)	214	322	0.1669	1.9571	0.6999	24.1369	0.6492	τCH_2
37	A	-	225 (vs)	174	219	1.1731	1.9810	0.8660	20.1783	0.3592	t Rtrig
38	A	-	217 (s)	138	213	5.3764	0.3266	0.8747	3.4007	0.0382	t Rsym
39	А	-	152 (vs)	34	147	0.1566	1.1227	0.8/49	8.5564	0.0058	t Kasym

; ms,

Abbreviations: SS, Symmetric Stretching; ass, anti symmetric stretching; b, in-plane-bending; ω , out-of-plane bending; t, torsion; R, Ring; δ , scissoring; ρ , rocking; β , wagging; τ , twisting; Vs, very strong; S, strong; ms, medium strong; m, medium; W, weak, vw, very weak.

Table – 4
Experimental and Calculated HF/3-21+G level vibrational frequencies (cm ⁻¹), IR intensity (kMmol ⁻¹) Raman activity (A ⁴ amu ⁻¹),
Raman depolarization ratios and reduced mass (amu), force constant (mdyne A^{-1}) of DCBC

		Experi	imental	Calcul	ated						
S1.	Symmetry	Freq	uency	freque	ncy	IR	Raman	Depolarization	Reduced	Force	Vibrational
51.	species	FT-IR	FT-	Unscaled	Scaled	intensity	activity	ratio	mass	constant	Assignments
	• '	2142	Raman	2422	2140	2 0 0 0 5	20,4000	0.0750	1 1 1 20	7 (000	CIL
1	А	3142 (W)	5145 (ww)	3433	3142	2.0805	30.4000	0.8750	1.1129	7.0809	γCH
2	A	3078	3081 (s)	3403	3073	1.7803	176.0422	0.5585	1.0971	7.4837	γСН
2	۸'	(m)		2206	2055	0.0777	57 55(2)	0.9750	1.0020	7 4007	CII
3	А	5059 (vm)	-	3390	3055	0.0777	57.5505	0.8750	1.0929	1.4237	γCH
4	A'	3028	-	3373	3024	2.5261	70.8784	0.7828	1.0892	7.2990	$\gamma_{ass} CH_2$
5	A [']	(VW) 2991	2989	3347	2986	1.6871	64.0890	0.5252	1.0565	6.9735	$\gamma_{ss}CH_2$
6	A [']	(Vm) 1682	(m) -	1758	1677	24.1680	58.4402	0.7345	5.6376	10.2696	γCC
7	A	(VW) 1581	1578 (s)	1724	1576	45.8111	8.2905	0.8750	5.4141	9.4812	γC - CH_2
8	A	(m) 1553	1552 (w)	1650	1549	15.8135	6.8865	0.8683	1.1017	1.7678	γCC
9	A	(s) 1505	-	1617	1501	57.4084	1.1255	0.8750	1.8612	2.8668	γCC
10	A	(vw) -	1472	1597	1467	5.1652	5.9093	0.8405	2.7393	4.1180	δCH_2
11	Δ.	_	(vw) 1446 (w)	1412	1441	3 9829	2 5634	0.8750	1 /178	1 6655	vCC
12	Ă	1438	-	1406	1432	53.6193	31.8331	0.6879	1.2330	1.4371	γCC
		(vs)		1100	1.02	0010170	0110001	0.0077	112000	1110/1	100
13	A	-	1312 (vw)	1339	1308	10.4596	36.8387	0.5775	2.8438	3.0035	γCC
14	Ă	-	1283 (s)	1306	1279	0.1508	4.0018	0.8750	1.1587	1.1649	bCH
15	A"	1269	-	1288	1263	19.7671	24.8563	0.8750	2.9409	2.8740	βCH_2
		(s)									
16	A	-	1229 (s)	1288	1223	0.9433	3.9462	0.6080	2.8204	2.7453	bCH
17	A	1217 (m)	-	1221	1212	10.2167	3.2920	0.8750	2.2357	1.9645	bCH
18	A	-	1104 (m)	1204		27.5414	12.6600	0.8049	7.6603	6.5381	ωСН
19	A	1092 (s)	1084 (s)	1172	1009	0.3256	32.3911	0.5274	2.7829	2.2532	ωСН
20	A	1070 (vw)	-	1126	1085	0.2715	3.2335	0.5527	1.9144	1.4300	ωCH
21	A	975 (m)	-	1124	1066	0.0086	0.4968	0.8750	1.4532	1.0825	bCC
22	A	900 (s)	909 (vw)	988	972	23.6347	2.8986	0.8750	1.5447	0.8892	ρCH_2
23	A	-	837 (w)	926	894	68.5345	0.8575	0.8390	1.3368	0.6752	Rtrigd
24	A	825 (m) 820 (m)	-	903	821	10.8557	5.7641	0.8/21	4.1080	1.9734	Rasyma
25	A	820 (III) 784	- 785 (ww)	810 715	814 706	71.9390	0.5562	0.8730	3 8800	2.0281	wCC1
20	Α	(vs)	705 (VW)	/15	770	/2.210/	57.5505	0.0234	5.0007	1.1701	peer
27	A'	766 (vs)	771 (s)	689	761	0.0000	0.6981	0.8750	4.4938	1.2564	γCCl
28	A'	754 (vs)	-	662	749	17.8802	14.0467	0.8502	6.6741	1.7243	γCCl
29	A'	678 (vs)	671 (vs)	581	672	16.8413	26.4594	0.5583	4.3160	0.8580	βCCl
30	A	615 (w)	611 (m)	530	609	1.6857	2.0860	0.8750	3.8301	0.6331	BCC1
31	Ă	606	-	428	601	8.5218	6.6822	0.8750	5.6301	0.6082	BCC1
20	• "	(vw)		410	500	11 2211	21 2001	0.5295	11 4000	1 1210	r
32 32	A ^"	507 (m)	-	410	502 492	11.2211	21.2801	0.5386	11.4206 8 1125	1.1312	OCCI
33 34	A ^"	-	407 (m)	33U 320	482 307	0.0000	4.4929	0.8750	0.4433 3 7270	0.0111	wCC1
54 35	Α Δ"	-	405 (S) 302 (ve)	228 228	388	2.0014	0.2313	0.8750	5.1519 1 3811	0.2321	
36	Δ"	-	372(vs) 378 (m)	230	300	2 3/7/	1 2/17	0.8750	4.3011	0.1457	wee τCH-
37	А. А.	-	225 (m)	154	224	1.0900	2.9852	0.0433	16 7542	0.2343	t Rting
38	A"	-	217(s)	80	211	1.4309	2.8550	0.8742	11.8610	0.0453	t R Svm
39	Ä	-	152 (vs)	56	145	0.7660	2.9442	0.8750	16.1755	0.0294	t Rasym

Table – 6

Theoretically Computed Zero point vibrational energy (Kcalmol⁻¹), rotational constants (GHZ) rotational temperature (Kelvin) thermal energy (Kcalmol⁻¹) molar capacity at constant volume (calmol⁻¹ k⁻¹) and entropy (calmol k⁻¹)

entropy (calmo	DI K ⁻)	
Parameter	HF	DFT
i aranicici	3-21 + G	3-21 + G
Zero point vibrational energy	68.9953	64.5133
Rotational constants		
	0.9548	1.0304
	0.7591	0.6843
	0.4585	0.4123
Rotational temperatures		
	0.4558	0.0494
	0.0364	0.0328
	0.0220	0.0197
Energy		
Total	74.335	70.162
Translational	0.889	0.889
Rotational	0.889	0.889
Vibrational	72.558	68.385
Entropy		
Total	94.917	97.029
Translational	41.693	41.693
Rotational	31.248	31.381
Vibrational	21.976	23.955
Molar capacity at constant volume		
Total	30.336	32.284
Translational	2.981	2.981
Rotational	2.981	2.981
Vibrational	24.375	26.322