Synthesis, spectroscopic investigation and computational studies of 2-formyl-4-(phenyldiazenyl)phenyl methyl carbonate and 4-((4-chlorophenyl)diazenyl)-2-formylphenyl methyl carbonate

A. Arokiasamy^a, G. Manikandan^{b*}, V. Thanikachalam^a,
K. Gokula Krishnan^a

^aDepartment of Chemistry, Annamalai University, Annamalainagar–608 002, TamilNadu, India.

^bChemistry Section (FEAT), Annamalai University, Annamalainagar–608 002, TamilNadu, India.

* Corresponding Author E-mail: phdmani@gmail.com

Keywords: Diazenyl carbonates; vibrational assignments; FT–IR; FT–Raman; NMR spectra

ABSTRACT. Two new compounds namely 2-formyl-4-(phenyldiazenyl)phenyl methyl carbonate (FPMC) and 4-((4-chlorophenyl) diazenyl)-2-formylphenyl methyl carbonate (CFPMC) have been synthesized and have characterized using FT-IR, FT-Raman, ¹H and ¹³C NMR techniques. Computational optimization studies have been carried out using Hatree–Fock (HF) and Density Functional Theory (DFT–B3LYP) methods with 6–31+G(d, p) basis set of *Gaussian 09W* software. The stable configuration of the title compounds were achieved theoretically by potential energy surface scan analysis. The complete vibrational assignments were performed on the basis of total energy distribution (TED) and natural bonding orbital (NBO) have been studied. Various parameters such as E_{HOMO}, E_{LUMO}, total energy, dipole moment, polarizability, first order hyperpolarizability, zero–point vibrational energy as well as thermal properties were analyzed and reported for the title compounds.

1. INTRODUCTION

Azobenzenes and organic carbonate derivatives play a vital role in our modern life along with rapidly increasing applications in e.g. plastic materials, fuel additives and scientific laboratories [1–7] (e.g., solvents and synthetic blocks). Besides, organic carbonates are versatile compounds used as solvents or reagents in the chemical industry and as electrolytes in lithium batteries and fuel additives [8]. They are also frequently encountered as endower molecules in pharmaceuticals and agrochemicals. They are important precursors in biological/medicinal fields [9] and are useful synthetic intermediates [10].

Synthesis of linear carbonates mainly makes use phosgene and its derivatives [11–14] as the starting material, while cyclic carbonates are synthesized from propylene oxide. As an alternative approach, substituted chloroformates [15–17] are the most frequently used reagents for the preparation of organic carbonates. This reagent has gained much attention recently, because of easy handling, non–toxic nature as well as good reactivity which have led to a successful synthesis of azo organic carbonates. Literature survey reveals that DFT calculations and experimental studies on FPMC and CFPMC compounds have not been reported. Therefore, the present work deals with FT–IR, FT–Raman and NMR spectroscopic investigations of FPMC and CFPMC, utilizing HF and B3LYP methods with 6–31+G(d, p) as basis set. NBO analysis by B3LYP method revealed clear evidences of stabilization which originate from the hyper conjugation of various intramolecular interactions. The HOMO and LUMO analyses have been used to elucidate the information regarding charge transfer within the molecule.

2. EXPERIMENTAL

Synthesis of FPMC and CFPMC

In the first step, 2-hydroxy-5-(phenyldiazenyl)benzaldehyde (HPDB) and 5-((4-chlorophenyl)diazenyl)-2-hydroxybenzaldehyde (CPDB) have been synthesized according to the procedure as mentioned in literature [18] and the second step reaction, the reaction between HPDB and methyl chloroformate were carried out in different solvents in order to study about the feasibility of the reaction. Optimization of reaction conditions is shown in **Table 1** and DCM/K₂CO₃ yielded the product quantitatively (**Entry 4**). A typical experimental procedure for the synthesis of the title compounds is as follows: the stirring solution containing HPDB (0.59 g) and dichloromethane (5 mL), potassium carbonate (0.51 g, 3.75 mmol), after 15 min stirring methyl chloroformate (0.3 mL, 3.75 mmol) was added drop wise to the reaction mixture for a period of 15 min. It was stirred at an ambient temperature for 6 hours and the progress of the reaction was monitored by thin layer chromatography. Upon completion of reaction, the reaction mixture was diluted with water (20 mL) and extracted with dichloromethane (2×20 mL). The combined organic layer was washed with water (2×20 mL) and brine solution (20 mL) and dried over anhydrous sodium sulphate (2.5 g), filtered and concentrated under reduced pressure. The crude product was then recrystallised from ethanol to get the pure FPMC [19]. A similar procedure was adopted for the synthesis of CFPMC. The synthetic routes of azo carbonates are outlined in **Scheme 1**.

Table 1. Optimization of reaction conditions.

Entry No.	Solvents	Base	Reaction time [h]		Yield [%]	
			FPMC	CFPMC	FPMC	CFPMC
1	Dimethylformamide	K ₂ CO ₃	18	14	30	40
2	Tetrahydrofuran	K ₂ CO ₃	18	14	30	40
3	Acetonitrile	K ₂ CO ₃	12	8	50	50
4	Dichloromethane	K ₂ CO ₃	6	4	70	75

Scheme 1. Synthesis of compounds FPMC and CFPMC.

Spectral measurements

The melting points were measured in open capillary and are uncorrected. FT-IR spectra were recorded on a Thermo Nicolet iS5 FT-IR spectrometer in the range of 500 to 4000 cm⁻¹ by ATR at Annamalai University, Annamalai Nagar, India. FT-IR spectra of these compounds were recorded at room temperature with number of scans equals 16. FT-Raman spectra were recorded on a Bruker: RFS 27 spectrometer. The spectral measurements were carried out at SAIF, Indian Institute of Technology (IIT), Chennai (Tamil Nadu, India). The spectral features are reported in wave number (cm⁻¹). ¹H NMR spectra were recorded on a Bruker 400 MHz spectrometer and ¹³C NMR spectra were recorded on a Bruker 100 MHz spectrometer at Annamalai University,

Annamalai Nagar, India. Chemical shift values are reported in parts per million (ppm) from tetramethylsilane (TMS) as internal standard.

Computational details

The entire set of calculations have been performed at HF and DFT–B3LYP methods with 6–31+G(d, p) basis set using *Gaussian 09W* program package [20]. Gradient corrected density functional theory (DFT) has been used with the three parameter hybrid functional (B3) for the exchange part and the Lee–Yang–Parr (LYP) correlation function [21,22]. The optimized geometry was determined by minimizing the energy with respect to all geometry parameters without imposing molecular symmetry constraints. The optimized structural parameters were used for the calculation of vibration frequency, electronic properties and isotropic chemical shift calculations. The validity of the optimized geometry was confirmed by frequency calculations, which gave real values for all the obtained frequencies. The frequency values computed at these levels contain known systematic errors. Therefore, we have used the scaling factor values of 0.9608 for B3LYP and 0.8929 for HF methods [23]. Finally, the calculated normal mode vibrational frequencies provide thermodynamic properties through the principle of statistical mechanics. By combining the results of *GaussView 5.0* program with symmetry considerations, vibrational frequency assignments were made with high degree of accuracy.

3. RESULTS AND DISCUSSION

Potential energy surface scan analysis

The conformational analysis of FPMC and CFPMC were carried out through the potential surface scan with B3LYP/6–31+G(d, p) level of theoretical approximation for determining the most stable geometry. The preliminary search of low energy structures were performed for the dihedral angles of FPMC and CFPMC is C3–C4–N12–N13 and C3–C4–N11–N12, respectively which are also relevant coordinate for conformational flexibility within the molecule. During the calculation, all the geometrical parameters have been simultaneously relaxed with the above dihedral angles which are varied in steps of 10 ° from 0 ° to 360 ° during the scan. The potential energy barrier obtained by the rotation of FPMC and CFPMC with the dihedral angle is shown in **Fig. 1**.

Figure 1. Potential energy surface scan of FPMC (left side) and CFPMC (right side).

From **Fig. 1**, the FPMC has attained minimum energy (-989.23 a.u) at 0.46 ° and 360.46 ° and the CFPMC has attained minimum energy (-1448.82 a.u) at -0.61 ° and 359.61 ° in the rotation. From the result of potential energy surface scan analysis, the CFPMC showed minimum energy which has more stability than that of FPMC besides the optimized geometrical structures of FPMC and CFPMC are shown in **Figs. 2** and **9**.

Molecular geometry

The molecular structural parameters like bond lengths, bond angles and dihedral angles for compounds FPMC and CFPMC have been calculated using HF and B3LYP methods with /6–

31+G(d, p). The calculated structural parameters have been compared with the crystal structure of azo compounds available in the literature [18,24]. The calculated structural parameters of FPMC and CFPMC are depicted in **Tables 8** and **9**, respectively.

Figure 2. Optimized structure of FPMC.

It is observed from the **Figs. 2** and **9** that the basic azo dye unit in FPMC and CFPMC are planar and aromatic in nature due to the continuous delocalization of electrons in the benzene ring system. However, the computed C–H and C–C bond lengths of benzene ring were found to be in good agreement within 0.01–0.02 Å compared to the corresponding literature values [24]. From the **Tables 8** and **9**, the variations in FPMC, CFPMC and the corresponding literature value bond lengths of C4–C5 (1.403/1.402/1.396 Å), C14–C15/C13–C14 (1.397/1.397/1.374 Å), C17–C31/C16–C30 (1.480/1.480/1.419 Å), C17–C21/C16–C20 (1.41/1.41/1.44 Å) and C16–C19/C15–C18 (1.39/1.39/1.36 Å) are ascribable due to substituent effect, electronegativity and lone pair of electrons present in the molecule. Besides, from the above results compared to the C–C bond lengths of benzene (1) ring was found to be significantly small within 0.01–0.02 Å for CFPMC than that of FPMC due to chlorine atom in C1 carbon of CFPMC and the C–C bond lengths of with carbonate attached benzene ring is increases in both compounds (C16–C19/C15–C18) due to carbonate group attachment. The bond length values of C4–N12/C4–N11 (1.42/1.42/1.43 Å), N13–C14/N12–C13 (1.42/1.42/1.43 Å) are found to coincide with related compounds [18].

The compounds FPMC and CFPMC are formed an intramolecular hydrogen bond (C–H...O) with the bond angles of C19–C21–O23 (116.5°), C18–C20–O22 (116.43°) from that of C17–C21–O23 (122.6°), C16–C20–O22 (122.68°) in the benzene (2) ring respectively. The decrease in bond angle due to the electronegativity of ligand atom (O23/O22) is more than that of the central atom (C21/C20) of FPMC and CFPMC, respectively. In addition, a significant difference present in the benzene (1) ring of FPMC and CFPMC between the bond angles of C2–C1–H7 (119.9°), C2–C1–Cl33 (119.3°) and C6–C1–H7 (120.1°) C6–C1–Cl33 (119.6°) are respectively due to presence of chlorine atom in the C1 carbon of CFPMC. The dihedral angle of between the two benzene rings are C4–N12–N13–C14 (179.90°) and C4–N11–N12–C13 (179.88°). Besides the C17–C21–O23–C24, C16–C20–O22–C23, C19–C21–O23–C24 and C18–C20–O22–C23 planes are inclined by 69.0°, 68.40°, -117.7° and -117.81° in the skeleton from the molecular plane of the both compounds, respectively. The structural parameters obtained from computed methods are in good agreement with the literature values [18].

Vibrational analysis

The compounds FPMC and CFPMC have 33 atoms which belong to C1 symmetry and possess 93 normal modes of vibrations. All the 93 modes of vibrations are distributed as 34 stretching, 29 in–planes, 25 torsion and 5 out–of–plane vibrations in the infrared spectra of FPMC and CFPMC. The experimental and calculated scaled frequencies as well as the TED of FPMC are listed in **Table 10** (CFPMC –**Table 11**). The calculated frequencies of the investigated molecules are found to be very close to the corresponding literature values. The mean percentage deviations of the calculated frequencies from the experimental ones are about 1.0–2.0 %. The experimental FT–IR and FT–Raman spectra with the corresponding theoretically simulated ones for FPMC are shown in **Figs.3** and **4** (CFPMC – **Figs. 10** and **11**).

C=O vibrations of FPMC and CFPMC

The C=O stretching vibrational band can be easily identified from the FT-IR and FT-Raman spectra, because of the degree of conjugation, strength and polarizations. The carbonyl stretching vibrations are expected in the region between $1715 - 1680\text{ cm}^{-1}$ [18,24,25]. In our case, two C=O stretching bands were observed in both experimental FT-IR and FT-Raman spectra. In FT-IR spectra, C=O stretching bands were observed at $1768/1767\text{ cm}^{-1}$ for carbonate and at $1689/1695\text{ cm}^{-1}$ for aldehyde. In FT-Raman spectra, C=O stretching bands were observed at $1768/1768\text{ cm}^{-1}$ for carbonate and at $1688/1693\text{ cm}^{-1}$ for aldehyde of FPMC and CFPMC, respectively. From the B3LYP/6-31+G(d, p) calculation, two C=O stretching bands were observed, one at $1789/1783\text{ cm}^{-1}$ (mode no. 81/82) for aldehyde and another at $1714/1707\text{ cm}^{-1}$ for carbonate (mode no. 80/81) of FPMC and CFPMC, respectively which are correlated with the experimental FT-IR and FT-Raman values. These wave number shifts from the expected range is due to the substitution of carbonate in the para position of azo group.

Figure 3. a) Experimental FT-IR spectrum of FPMC. b) Theoretical FT-IR spectrum of FPMC.

Figure 4. a) Experimental FT-Raman spectrum of FPMC. b) Theoretical FT-Raman spectrum of FPMC.

C-C and C=C vibrations of FPMC and CFPMC

The six ring carbon atoms undergo coupled vibrations, known as semicircular stretching which usually occurs in the region $1400-1625\text{ cm}^{-1}$ [26]. The actual positions of these modes are determined not so much by the nature of the substituent but by the form of substitution around the ring [27]. In the experimental FT-IR spectra, C-C vibration bands are observed with variable intensities at $1607, 1595, 1578$ and 1315 cm^{-1} for FPMC whereas for CFPMC, notable spectrum intensities were observed at $1606, 1587$ and 1280 cm^{-1} . FT-Raman bands were observed at $1652, 1597, 1564$ and 1314 cm^{-1} for FPMC whereas in CFPMC, the bands appeared at around $1603, 1585$ and 1303 cm^{-1} . The theoretically computed frequencies in B3LYP/6-31+G(d, p) method are predicted at $1596, 1588, 1573$ and 1318 cm^{-1} (mode nos. 79, 78, 77 and 65) for FPMC similarly in CFPMC at $1589, 1575$ and 1296 cm^{-1} (mode nos. 80, 79, and 66). Most of the theoretical modes of vibrations are close to the experimental frequencies of FPMC and CFPMC.

C–H vibrations of FPMC and CFPMC

The C–H stretching vibrations in aromatic ring characteristically appear above 3000 cm^{-1} [25] and are typically exhibited as a multiplicity of weak to moderate bands [28]. From B3LYP/6–31+G(d, p) method, twelve (mode nos. 82–93) and eleven (mode nos. 83–93) C–H stretching vibrations occurred in FPMC and CFPMC, respectively. The C–H stretching frequency of both benzene rings having seven modes which are mode nos. 86 to 93 at the region of $3073\text{--}3118\text{ cm}^{-1}$ for FPMC and mode nos. 87 to 93 at the region of $3068\text{--}3105\text{ cm}^{-1}$ for CFPMC. The remaining four modes [mode nos. 82–85 and 83–86] are C–H asymmetric vibrations of carbonate methyl group. The aromatic C–H in-plane bending vibrations at 1424 , 1292 , 1237 , 1143 , 1089 and 1005 cm^{-1} (mode nos. 64, 63, 57, 53 and 50) and at 1458 , 1265 , 1232 , 1085 cm^{-1} (mode nos. 75, 65, 54, 55) for FPMC and CFPMC, respectively.

In experimental FT–IR spectra, the strong bands occur in the region $3438\text{--}3027$ and $3521\text{--}3051\text{ cm}^{-1}$ for FPMC and CFPMC, respectively which have been assigned as C–H asymmetric stretching vibrations of aromatic benzene rings. The C–H in-plane bending harmonic vibrations occurred at around 1280 , 1257 , 1140 , 1067 and 1024 cm^{-1} in FPMC spectrum whereas at 1455 , 1234 , 1095 and 1024 cm^{-1} in CFPMC spectrum. In experimental FT–Raman spectra, bands are observed at 1259 , 1233 , 1140 , 1062 and 1000 cm^{-1} in FPMC and at 1451 , 1261 , 1228 1094 cm^{-1} in CFPMC which are showed good agreement with medium and strong FT–IR and FT–Raman bands.

Methyl group vibrations

The asymmetric stretching vibrations of CH_3 are expected to appear at about 2980 cm^{-1} and symmetric stretching vibrations around 2870 cm^{-1} [24]. In computed FT–IR spectrum of FPMC, C–H stretching vibrations of CH_3 were observed at 3070 , 3047 and 2964 cm^{-1} (mode nos. 85–83) and in the experimental FT–IR spectra of FPMC and CFPMC, at 3057 , 3034 and 2951 cm^{-1} (mode nos. 86–84) and at 2962 , 2924 and 2877 cm^{-1} respectively. Furthermore in experimental FT–Raman spectrum of FPMC, C–H stretching vibrations of CH_3 were noted at around 2965 , 2880 and 2851 cm^{-1} and in CFPMC spectrum, the peaks appeared at around 3047 , 3016 and 2959 cm^{-1} respectively. The C–H in-plane bending vibrations were observed at 1424 , 1416 and 1416 cm^{-1} (mode no. 69), at 1418 , 1416 and 1416 cm^{-1} (mode no. 71) in theoretical, experimental FT–IR and FT–Raman spectra, respectively for FPMC and CFPMC, respectively. All these assignments are found to be in good agreement with literature values.

In addition, the stretching frequency of N12–N13 are observed at 1499 , 1479 and 1489 cm^{-1} (mode no: 75) in theoretical, experimental FT–IR and FT–Raman spectra of FPMC, respectively and at 1486 , 1479 and 1486 cm^{-1} (mode no. 76) in theoretical, experimental FT–IR and FT–Raman spectra of CFPMC, respectively. The correlations between the experimental and theoretical wave numbers of compounds FPMC and CFPMC are good for ring vibrations.

Mulliken population analysis

Mulliken population analysis provides the atomic charge density or an orbital density on individual atom. The charge distributions over the atoms suggest the formation of donor and acceptor pairs involving the charge transfer in the molecule [28,29].

Figure 5. Comparison of Mulliken charge distribution of FPMC and CFPMC.

The net Mulliken atomic charge distribution comparison of FPMC and CFPMC are shown in Fig. 5. The Mulliken atomic charges of CFPMC for C1, C3, C5, C18, H7, H8, H9 and H10 are found to be increased while the C2, C4, C13, C14, C15 and C16 charges decreased as compared to FPMC due to chlorine atom attached in C1. In compounds FPMC and CFPMC, the magnitude of carbon atom attached at nitrogen atoms have attained highest negative charge and behaved as electron acceptors (C4), and the large accumulation of positive charge were found to be on carbon atoms (C16/C15 and C17/C16) than the other atoms. The Mulliken atomic charge values are listed in Table 2.

Table 2. Mulliken atomic charges of FPMC and CFPMC.

FPMC Atoms	Charges		CFPMC Atoms	Charges	
	HF	B3LYP		HF	B3LYP
1C	-0.072	0.022	1C	0.124	0.2007
2C	-0.3822	-0.3173	2C	-0.35	-0.335
3C	0.27	0.5086	3C	0.282	0.5639
4C	-1.0117	-0.9936	4C	-1.436	-1.403
5C	0.6326	0.3382	5C	0.853	0.562
6C	-0.3279	-0.2536	6C	-0.544	-0.497
7H	0.1742	0.1304	7H	0.194	0.1503
8H	0.1744	0.1329	8H	0.198	0.1533
9H	0.1909	0.1472	9H	0.182	0.1405
10H	0.175	0.1337	10H	0.196	0.1507
11H	0.1753	0.1325	11N	0.053	0.0335
12N	0.051	0.0381	12N	0.006	-0.014
13N	-0.0043	-0.0253	13C	-0.96	-1.131
14C	-0.9642	-1.1515	14C	-0.27	-0.135
15C	-0.284	-0.1542	15C	0.482	0.657
16C	0.524	0.6969	16C	0.799	0.8538
17C	0.8078	0.8757	17H	0.191	0.143
18H	0.1913	0.143	18C	0.373	0.1676
19C	0.3247	0.1458	19H	0.207	0.158
20H	0.2073	0.1583	20C	-0.886	-0.793
21C	-0.8809	-0.7979	21H	0.197	0.1513
22H	0.1956	0.1503	22O	-0.507	-0.383
23O	-0.5076	-0.3836	23C	0.908	0.6389
24C	0.91	0.6399	24O	-0.546	-0.452
25O	-0.548	-0.4532	25O	-0.431	-0.304
26O	-0.4312	-0.3033	26C	-0.078	-0.191
27C	-0.0776	-0.1909	27H	0.137	0.1502
28H	0.1364	0.1499	28H	0.15	0.1662
29H	0.1497	0.1657	29H	0.153	0.1741
30H	0.1521	0.1737	30C	0.383	0.3991
31C	0.3791	0.3895	31O	-0.453	-0.359
32O	-0.4546	-0.3606	32H	0.125	0.113
33H	0.1245	0.1124	33Cl	0.269	0.2697

NBO analysis

NBO analysis was performed using the *Gaussian 09W* package at the B3LYP/6–31+G(d, p) level. This analysis was carried out in order to understand the various second–order interactions between the filled orbitals of one subsystem and vacant orbitals of another subsystem, which is a measure of the intermolecular delocalization or hyper conjugation. The second order Fock matrix was carried out to evaluate the donor–acceptor interactions in the NBO basis [30]. For each donor (i) and acceptor (j), the stabilization energy $E^{(2)}$ associated with the delocalization is estimated as:

$$E^{(2)} = \Delta E_{ij} = q_i \frac{F(i,j)^2}{\varepsilon_j - \varepsilon_i}$$

Where q_i is the donor orbital occupancy, ε_i and ε_j are diagonal elements and $F(i,j)$ is the off diagonal NBO Fock matrix element. The NBO analysis is proved to be an effective tool for the chemical interpretation of hyper conjugative interaction and electron density transfer from the filled lone pair electrons [31]. A larger $E^{(2)}$ value indicates a more intense interaction between electron donors and electron acceptors which leads to a greater extent of conjugation in the system. The intramolecular hyperconjugative interactions are formed by the orbital overlap between $\pi(\text{C–C})$ and $\pi^*(\text{C–C})$ bond orbitals which results intramolecular charge transfer (ICT) causing stabilization of the system. These interactions are observed as an increase in electron density (ED) in C–C anti-bonding orbital that weakens the respective bonds.

In FPMC, the strong intra-molecular hyperconjugative interaction of π electrons from C1–C6, C2–C3 and C4–C5 bonds to the $\pi^*(\text{C1–C6})$ bond of the benzene (1) ring which increases the ED (0.319 eV) leading to stabilization of 20.43 kcal/mol. Furthermore the π -electron delocalization is maximum around the C14–C15, C16–C18 and C17–C21 of the benzene (2) ring which increases the ED (0.414 eV) leading to stabilization of 24.14 kcal/mol. This enhanced $\pi^*(\text{C17–C21})$ NBO further conjugates with $\pi^*(\text{C16–C19})$ resulting to a stabilization of 241.09 kcal/mol. Similarly in CFPMC, the stabilization energy of benzene (1) ring is 20.79 and 24.11 kcal/mol for benzene (2) ring which increases the ED (0.2776 eV) leading to stabilization of 241.41 kcal/mol. From the above data, the stabilization energy of benzene (1) ring is slightly increases (0.36 kcal/mol) and ED values of benzene (2) ring decreases due to chloride substitution in para position of azo group in benzene (1) ring of CFPMC.

In FPMC, the interaction energy between the filled bond orbital $\pi(\text{C–C})$ and the empty anti-bond orbital $\pi^*(\text{N–N})$ of benzene (1) and benzene (2) rings are 21.03 and 19.52 kcal/mol, respectively, as shown in **Table 3**. Besides these kinds of electron transaction occurs in CFPMC which are 20.77 and 20.03 kcal/mol for benzene (1) and benzene (2) rings respectively as shown in **Table 12**. From the above comparison confirms CFPMC having strong delocalization than FPMC. Furthermore the NBO studies of both compounds confirm the lone pair electrons of the azo group is involved in delocalization since lone pairs lie in the molecular plane which is orthogonal to the π system. The azo group being co-planar with the benzene (1) ring increases the conjugation between them which supports electron delocalization from benzene (1) ring to the azo group which is revealed by the high value of the interaction of $\pi^* \rightarrow \pi^*$ energy which is equal to 133.63 kcal/mol for CFPMC but in FPMC $\pi^* \rightarrow \pi^*$ interaction is absent. These intra-molecular charge transfer ($n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$ and $\pi^* \rightarrow \pi^*$) can induce large non linearity to the molecule.

The most important interaction energy in both compounds, related to the resonance in the molecule is electron donation from lone pair oxygen (LP(1 or 2) O23 and LP(1 or 2) O32) to the antibonding acceptor $\pi^*(\text{C–C})$ of the benzene (2) ring. In FPMC, electron donation from LP(1) O23 to $\pi^*(\text{C24–O25})$ is equivalent to 12.4 kcal/mol but there is no electron donation from LP(1) O23 to $\pi^*(\text{C17–C21})$ which confirm electron delocalization or extension is not present in between the oxygen (O23) of the carbonate group and benzene (2) ring (C21). Beside LP(2) O32 to $\pi^*(\text{C17–C31})$ does not occur therefore electron delocalization or extension is not forming in between the oxygen (O32) of the aldehyde group and benzene (2) ring (C17). Similarly the CFPMC also does not showing electron delocalization or extension in between LP(1) O22 and $\pi^*(\text{C16–C20})$ or LP(2) O32 to $\pi^*(\text{C16–C30})$. Therefore in both compounds delocalization is present in between the two

benzene rings via azo group and the delocalization or extension of benzene ring to carbonate or aldehyde group have been not showed.

Table 3. Second order perturbation theory analysis of Fock matrix in NBO basis for FPMC.

Type	Donor (i)	ED (i)(e)	Acceptor (j)	ED (j)(e)	^a E ⁽²⁾ [kcal/mol]	^b E(j)–E(i) a.u	^c F(i,j) a.u.
π – π^*	C1–C6	1.653	C4–C5	0.374	21.4	0.28	0.069
π – π^*	C2–C3	1.674	C1–C6	0.319	20.43	0.28	0.068
π – π^*		1.674	C4–C5	0.374	19.01	0.28	0.066
π – π^*	C4–C5	1.612	C1–C6	0.319	18.51	0.28	0.065
π – π^*		1.612	C2–C3	0.285	18.88	0.28	0.067
π – π^*		1.612	N12–N13	0.210	21.03	0.23	0.064
π – π^*	N12–N13	1.913	C4–C5	0.374	9.95	0.4	0.061
π – π^*		1.913	C14–C15	0.351	10.49	0.39	0.061
π – π^*	C14–C15	1.612	N12–N13	0.210	19.52	0.24	0.064
π – π^*		1.612	C16–C19	0.279	20.28	0.28	0.07
π – π^*		1.612	C17–C21	0.414	17.89	0.27	0.063
π – π^*	C16–C19	1.654	C14–C15	0.351	17.33	0.28	0.062
π – π^*		1.654	C17–C21	0.414	24.14	0.27	0.074
π – π^*	C17–C21	1.602	C14–C15	0.351	22.19	0.29	0.072
π – π^*		1.602	C16–C19	0.279	15.73	0.29	0.062
π – π^*		1.602	C31–O32	0.114	17.91	0.27	0.068
σ – σ^*	O26–C27	1.987	O23–C24	0.114	3.93	1.16	0.062
LP (1)	N12	1.951	C3–C4	0.033	8.56	0.97	0.081
LP (1)	N13	1.950	C14–C16	0.033	8.84	0.96	0.082
LP (1)	O23	1.925	C24–O26	0.106	6.52	0.92	0.07
LP (2)	O23	1.828	C24–O25	0.158	12.4	0.66	0.081
LP (2)	O25	1.814	O23–C24	0.114	33.64	0.6	0.129
LP (2)		1.814	C24–O26	0.106	31.14	0.62	0.127
LP (1)	O26	1.956	C24–O25	0.158	7.44	0.9	0.075
LP (2)	O26	1.813	C24–O25	0.166	14.96	0.64	0.088
LP (2)	O32	1.881	C17–C31	0.059	19.4	0.71	0.106
LP (2)		1.881	C31–H33	0.061	21.39	0.67	0.108
π^* – π^*	N12–N13	0.037	C4–C5	0.374	25	0.05	0.059
π^* – π^*		0.037	C14–C15	0.351	29.05	0.04	0.058
π^* – π^*	C17–C21	0.414	C16–C19	0.279	241.09	0.01	0.082
π^* – π^*		0.414	O23–C24	0.114	1.71	0.34	0.042
π^* – σ^*	C24–O25	0.166	C21–O23	0.034	7.28	0.02	0.033
π^* – σ^*		0.166	C24–O25	0.158	1104.14	0.02	0.306

^a Energy of hyper conjugative interaction (stabilization energy), ^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 orbitals.

HOMO–LUMO analysis

The HOMO and LUMO are important quantum chemical parameters to determine the molecular interaction with other species and to characterize the chemical reactivity, global hardness, softness and kinetic stability of the molecule *etc.* [32]. The energy gap between HOMO and LUMO orbitals of compounds FPMC and CFPMC are in decreasing order: CFPMC > FPMC and are given in **Table 4**.

Table 4. Calculated HOMO–LUMO energies of FPMC and CFPMC.

Energy	FPMC		CFPMC	
	HF [eV]	B3LYP [eV]	HF [eV]	B3LYP [eV]
E_{HOMO}	-8.132	-8.22	-8.137	-8.226
E_{LUMO}	-5.796	-5.865	-5.721	-5.794
ΔE_1	2.336	2.355	2.416	2.432
$E_{\text{HOMO}-1}$	-8.911	-8.71	-8.627	-8.464
$E_{\text{LUMO}+1}$	-5.302	-5.342	-5.281	-5.326
ΔE_2	3.609	3.368	3.346	3.139

The 3D plots of HOMO and LUMO of compounds FPMC and CFPMC calculated using HF and B3LYP/6–31+G(d, p) methods are shown in **Fig. 6** and **Fig. 12.**, respectively. According to **Fig. 6**, the HOMO orbital is localized over the nitrogen and carbon atoms of C3, C4, C14 and C15 while the LUMO is characterized by a charge distribution over entire molecule except –O–CH₃ part of carbonate. Moreover a small difference in the HOMO and LUMO energy gap (2.355 eV for FPMC and 2.432 eV for CFPMC) explains the eventual charge transfer interactions occurring within the molecule.

Figure 6. HOMO–LUMO plot of FPMC using HF (left side) and B3LYP (right side) methods.

Using HOMO and LUMO orbital energies, the ionization potential (I), electron affinity (A), electronegativity (χ), hardness (η) and softness (σ) can be expressed as:

$$\begin{aligned}
 I &= -E_{\text{HOMO}}; & A &= -E_{\text{LUMO}} \\
 \eta &= (I_p - A)/2; & \chi &= (I + A)/2 \\
 \sigma &= 1/\eta & \text{and} & \omega = \eta^2/2\mu
 \end{aligned}$$

Which are given by Koopman's theorem [33]. The conversion factors for α , β , μ and HOMO, LUMO energies in atomic and cgs units: 1 atomic unit (a.u.) = 0.1482×10^{-24} electrostatic unit (esu) for polarizability; 1 a.u. = 8.639418×10^{-33} esu for first hyperpolarizability; 1 a.u. = 0.50367×10^{-39} esu for second hyperpolarizability; 1 a.u. = 27.2116 eV (electron volt) for HOMO and LUMO energies.

NMR spectral analysis

The ^1H and ^{13}C chemical shift calculations [34] of FPMC have been carried out by HF and B3LYPs method with 6–31+G(d, p) basis set and compared with the experimental values and are presented in **Fig. 7** and **Table 5** (CFPMC – **Fig. 13** and **Table 13**).

Figure 7. a) ^1H and b) ^{13}C NMR spectra of FPMC in CDCl_3 .

In ^1H NMR, one signal observed in up field region at 3.99 ppm (s) with three protons integral corresponds to H28, H29 and H30 atoms, respectively. In the downfield region the signals at 10.26 (s), 8.45(s) and 8.29 (d) ppm correspond to H33, H18, and H22 atoms, respectively. The chemical shift values are found to be in good agreement with the computed values such as 8.49,

8.39, 8.39, 8.97, 8.56, 9.27, 4.08, 4.62 and 4.43 ppm with B3LYP/6–31+G(d, p) level for H7, H8, H9, H10, H11, H20, H28, H29 and H30 atoms, respectively. The root mean square values for hydrogen chemical shifts are found to be 0.980 for B3LYP/6–31+G (d, p) basis set.

In the present investigation, ^{13}C NMR spectral signals for aliphatic and aromatic carbons of the FPMC are observed at 44.5, 117.8, 113.8, 99.0, 137.9, 120.2, 113.9, 135.9, 127.1, 106.4, 114.7, 110.1 and 139.3 ppm, respectively. The shielded signal at 56.1 ppm is assigned to the carbonate methyl carbon (C27). The deshielded signals for carbonyl carbon of aldehyde and carbonate carbons appeared at 188.2 and 153.5 ppm, for CFPMC signals appeared at 188.24, 163.99 ppm, respectively. The signal at 150.5, 152.3 and 152.9 ppm are assigned to C4, C14 and C21 which are more deshielded than other ring carbons due to N12–N13 and O23–C24–O25–O26 bonds. The RMS values for carbon chemical shifts are found to be 0.983 from B3LYP method using 6–31+G (d, p). From the RMS values of ^1H and ^{13}C chemical shifts the experimental and theoretical values are very close and also close to the literature value [35].

Table 5. Experimental and calculated ^1H and ^{13}C chemical shift (ppm) values FPMC.

Atom	HF	B3LYP	Expt.	Atom	HF	B3LYP	Expt
H7	7.41	7.89	7.55	C1	132.64	132.37	129.12
H8	7.31	7.76	7.53	C2	127.83	128.53	129.25
H9	7.98	8.57	7.94	C3	115.27	114.16	123.17
H10	7.93	8.7	7.96	C4	149.09	151.81	152.98
H11	7.49	7.95	7.53	C5	134.21	134.66	123.17
H18	8.22	9.16	8.45	C6	128.76	128.62	129.25
H20	8.26	8.92	8.22	C14	145.75	149.96	152.29
H22	6.97	7.53	7.48	C15	142.01	141.42	131.81
H28	2.62	3.08	3.99	C16	125.02	121.29	123.76
H29	3.20	3.5	3.99	C17	126.56	129.35	128.5
H30	2.99	3.43	3.99	C19	121.47	124.83	125.46
H33	10.02	9.72	10.27	C21	152.62	153.16	153.36
				C24	144.3	149.06	150.47
				C27	50.90	61.29	56.09
				C31	185.72	188.13	188.25

Molecular electrostatic potential

To predict the reactive sites for electrophilic and nucleophilic attack for the compounds FPMC and CFPMC, the MEP have been calculated at B3LYP/6–31+G (d, p) method. Each molecule is encompassed by a characteristic three dimensional surface corresponding to contour of 0.002 a.u. isodensity surface. As seen in the **Fig. 8** and **Fig. 14**., the potential region of the map is in between the range of -1.152 to 1.152 and -1.403 to 1.403 for FPMC and CFPMC, respectively. Furthermore, the reactive sites of compounds FPMC and CFPMC are in favor of electrophilic attack. The negative region is mainly localized on the oxygen atom of the carbonate (O25/O24).

Figure 8. a) Electron density surface mapped with ESP of FPMC (left side). b) ESP mapped with total density of FPMC (right side).

NLO Properties

The first order hyperpolarizabilities (β_0) and related properties (μ , α_{total} , α_0) of the compounds FPMC and CFPMC have been calculated using B3LYP method with 6-31+G(d, p) basis set. Molecules having higher values of dipole moment, molecular polarizability and first hyperpolarizability show more active NLO properties [36-38]. The total dipole moment, mean polarizability, anisotropy of polarizability and mean first order hyperpolarizability, using the x, y, z components are defined as

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

$$\alpha_0 = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3 \quad (2)$$

$$\alpha_{total} = 2^{-1/2} [(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6(\alpha_{xx}^2 + \alpha_{yy}^2 + \alpha_{zz}^2)]^{1/2} \quad (3)$$

$$\beta_x = (\beta_{xxx} + \beta_{xyy} + \beta_{xzz}) \quad (4)$$

$$\beta_y = (\beta_{yyy} + \beta_{xxy} + \beta_{yzz}) \quad (5)$$

$$\beta_z = (\beta_{zzz} + \beta_{xxz} + \beta_{yyz}) \quad (6)$$

$$\beta_0 = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2} \quad (7)$$

The first hyperpolarizability (β) and the components of hyperpolarizability β_x , β_y and β_z of FPMC and CFPMC along with related properties (μ_D , α_{total} and α_0) are listed in **Table 6**.

Besides, efficient second order NLO properties are usually related to compounds that present intramolecular charge transfer (ICT). These ICT processes are usually of one dimensional character, being associated to appreciable dipole moment changes, between the ground and the first excited state, currently identified as the "charge transfer state" [39,40] related to the electron transfer between these states. Typical compounds (FPMC and CFPMC) showing these types of properties are p conjugated molecules with a D-p-A structure, where D and A are respectively electron donor and acceptor groups and p is a para conjugated system.

Table 6. Calculated dipole moment (μ_D), polarizability (α_0) and first hyperpolarizability (β_{total}) of FPMC and CFPMC.

Parameters	FPMC		CFPMC	
	HF	B3LYP	HF	B3LYP
α_{xx}	-135.95	-129.53	-181.91	-171.48
α_{yy}	-110.56	-112.09	-121.09	-122.59
α_{zz}	-121.9	-120.75	-132.95	-131.86
α_{total}	3.51×10^{-23}	3.33×10^{-23}	4.74×10^{-23}	4.45×10^{-23}
α_0	-122.8	-120.78	-145.31	-141.98
μ_x	-5.98	-5.67	-3.8	-3.78
μ_y	-0.04	-0.09	-0.33	-0.29
μ_z	2.85	2.8	2.5	2.53
μ_D	6.63	6.33	4.56	4.55
β_{xxx}	-269.23	-263.83	-126.89	-138.38
β_{xxy}	-8.41	-0.86	-25.89	-13.85
β_{xyy}	-8.94	-9.58	-14.41	-15.54
β_{yyy}	-3.9	-6.78	-5.17	-7.58
β_{xxz}	114	111.34	120.33	120.03
β_{xyz}	-4.01	-4.01	-5.33	1.64
β_{yyz}	-0.4	0.7	-0.76	1.24
β_{zzz}	64.97	59.97	59.09	53.7
β_{yzz}	0.88	1.77	2.67	4.43
β_{zzz}	17.78	15.79	23.63	20.56
β_{total}	2.17×10^{-30}	2.15×10^{-30}	1.45×10^{-30}	1.51×10^{-30}

This push-pull characteristic generally lead to high $\langle\beta\rangle$ value, which can be further, maximized through an adequate substitution of D and A groups. The parameters δ_D and δ_A are used to characterize the effectiveness of donor and acceptor groups. Here, δ_D is the stands for the energy

difference between the calculated HOMO (highest occupied molecular orbital) of the donor-substituted HPDB (2-hydroxy-5-(phenyldiazenyl)benzaldehyde) as a model compound and that of HPDB and δ_A is the stands for the energy difference between the calculated LUMO of the acceptor-substituted HPDB as a model compound and that of HPDB ie $\delta_A = E(\text{LUMO})_A - E(\text{LUMO})_P$ where $E(\text{LUMO})_A$ the represents lowest unoccupied orbital energy of the A acceptor substituted HPDB. The strength of donor-acceptor pairs is characterized by $\delta_{DA} = \delta_D - \delta_A$. From the literature, around the interval of δ_{DA} is 1.2 to 1.5 eV almost in the quinoid form having weak first-order (β) and second-order (γ) NLO susceptibilities [41]. From our calculated results, we find that the δ_{DA} value of FPMC is 1.46 eV and CFPMC is 0.077 eV. The δ_{DA} value of CFPMC is decreased than FPMC due to the presence of chlorine atom in the para position of CFPMC.

Thermodynamic function analysis

The total energy of a molecule is the sum of translational, rotational, vibrational and electronic energies. The statistical thermochemical analysis of FPMC and CFPMC were carried out at room temperature 298.15 K at 1 atm. pressure. The temperature dependence of thermodynamic properties of heat capacity at constant pressure (C_p), entropy (S) and zero-point vibrational energy for FPMC and CFPMC were also determined by HF and B3LYP levels with 6-31+G(d, p) basis set and the values of compounds FPMC and CFPMC are listed in **Table 7**.

Table 7. Calculated thermodynamic parameters of FPMC and CFPMC.

Parameters	FPMC		CFPMC	
	HF	B3LYP	HF	B3LYP
SCF energy [a.u.]	-983.157	-989.033	-1442.271	-1448.824
Total energies [kcal/mol]	177.577	166.226	171.983	160.933
Zero point energy [kcal/mol]	166.688	154.652	160.355	148.587
Rotational constants [GHz]				
X	1.041	1.042	1.0148	1.013
Y	0.109	0.106	0.0735	0.072
Z	0.104	0.102	0.0716	0.07
Entropy [cal/mol.K]	140.173	144.422	146.929	151.347
Heat capacity [cal/mol.K]	63.512	68.401	67.279	72.24

The FPMC and CFPMC having minimum total energy -989.23 and -1448.82 a.u, respectively by B3LYP compared with HF method. The scale factors [33] have been used for accurate determination of thermodynamic properties.

4. CONCLUSION

Novel compounds 2-formyl-4-(phenyldiazenyl)phenyl methyl carbonate (FPMC) and 4-((4-chlorophenyl)diazenyl)-2-formylphenyl methyl carbonates (CFPMC) have been synthesized and characterized by spectroscopic methods. The harmonic vibrational frequencies and thermodynamic properties of FPMC and CFPMC were determined and analyzed by both HF and B3LYP methods with standard basis set 6-31+G(d, p). The complete vibrational band assignments have been made for FPMC and CFPMC using FT-IR and FT-Raman spectra. The optimized geometrical parameters and the vibrational frequencies of the fundamental modes of compounds FPMC and CFPMC were performed and the vibrational modes are assigned on the basis of TED. The scaled vibrational frequencies were found in good agreement with the experimental values. The NBO analysis and thermodynamic parameters confirmed the ability of the methodology applied for the interpretation of the vibrational spectra of the title compounds in the solid phase. From the dipole moment, polarizability and hyperpolarizability data indicate that the compounds FPMC and CFPMC possess less NLO behavior due to pull-push character of molecules. The difference in HOMO and LUMO energies of compounds FPMC and CFPMC support the charge transfer takes place within the molecule.

Supplementary Information

Figure 9. Optimized structure of CFPMC. **Figure 10.** a) Experimental FT-IR spectrum of CFPMC. b) Theoretical FT-IR spectrum of CFPMC. **Figure 11.** a) Experimental FT-Raman spectrum of CFPMC. b) Theoretical FT-Raman spectrum of CFPMC.

Figure 12. HOMO–LUMO plot of CFPMC using HF (left side) and B3LYP (right side) methods.

Figure 13. a) ^1H and b) ^{13}C NMR spectra of CFPMC in CDCl_3 .

Figure 14. a) Electron density surface mapped with ESP of CFPMC (left side). b) ESP mapped with total density of CFPMC (right side).

Table 8. Selected structural parameters of FPMC.

Bond lengths [Å]	HF	B3LYP	Expt. (Ref [18])	Bond angles [°]	HF	B3LYP	Expt. (Ref [18])	Dihedral angles [°]	HF	B3LYP	Expt. (Ref [18])
C1–C2	1.392	1.403	1.393	C2–C1–C6	120	120	117.7	C6–C1–C2–C3	0	0	-0.9
C2–C6	1.385	1.397	1.398	C2–C1–H7	119.9	119.9	120.9	C6–C1–C2–H8	180	180	
C1–H7	1.075	1.086	1.503	C6–C1–H7	120.1	120.1	121.4	H7–C1–C2–C3	-180	-180	-180
C2–C3	1.382	1.391	1.378	C1–C2–C3	120.5	120.5	121	H7–C1–C2–H8	0	0	
C2–H8	1.075	1.086	0.93	C1–C2–H8	119.9	119.8	120.2	C2–C1–C6–C5	0	0	0.3
C3–C4	1.394	1.407	1.39	C3–C2–H8	119.7	119.7	118.8	C2–C1–C6–H11	-180	-180	
C3–H9	1.073	1.084	0.96	C2–C3–C4	119.4	119.5	121.4	H7–C1–C6–C5	180	180	180
C4–C5	1.386	1.403	1.402	C2–C3–H9	120.8	121.3	121.6	H7–C1–C6–H11	0	0	
C4–N12	1.421	1.418	1.428	C4–C3–H9	119.9	119.3	117.3	C1–C2–C6–C4	0	0	0.6
C5–C6	1.388	1.395	1.376	C3–C4–C5	120.3	120	118.7	C1–C2–C3–H9	180	180	
C5–H10	1.075	1.086	0.92	C3–C4–N12	124.3	124.7	126.1	H8–C2–C3–C4	-180	-180	
C6–H11	1.075	1.086	0.96	C5–C4–N12	115.4	115.3	115.2	H8–C2–C3–H9	0	0	
N12–N13	1.218	1.258	1.259	C4–C5–C6	120.1	120.1	119.7	C2–C3–C4–C5	0	0	-1
N13–C14	1.42	1.418	1.425	C4–C5–H10	118.9	118.5	119.2	C2–C3–C4–N12	180	180	179
C14–C15	1.383	1.397	1.381	C6–C5–H10	121	121.4	121	H9–C3–C4–C5	-180	-180	
C14–C16	1.392	1.407	1.412	C1–C6–C5	119.8	119.8	121.9	H9–C3–C4–N12	0	0	
C15–C17	1.392	1.402	1.396	C1–C6–H11	120.3	120.2	118.6	C3–C4–C5–C6	0	0	0.8
C15–H18	1.076	1.087	0.92	C5–C6–H11	119.9	120	119.5	C3–C4–C5–H10	180	180	
C16–C19	1.382	1.39	1.37	C4–N12–N13	116.1	115.5	114.6	N12–C4–C5–C6	-180	-180	-179
C16–H20	1.073	1.084	0.93	N12–N13–C14	115.7	114.9	113.5	N12–C4–C5–H10	0	0	
C17–C21	1.393	1.41	1.415	N13–C14–C15	115.9	115.8	117.1	C3–C4–N12–N13	0.4	0.5	177
C17–C31	1.484	1.48	1.459	N13–C14–C16	124.8	125	124.6	C5–C4–N12–N13	-179.7	-179.6	-3.7
C19–C21	1.384	1.397	1.392	C15–C14–C16	119.3	119.1	118.3	C4–C5–C6–C1	0	0	0.1
C19–H22	1.074	1.085	0.97	C14–C15–C17	121.6	121.8	122	C4–C5–C6–H11	180	-180	
C21–O23	1.366	1.382	1.34	C14–C15–H18	118.5	118.4	120.4	H10–C5–C6–C1	-180	-180	
O23–C24	1.335	1.366		C17–C15–H18	119.9	119.8	117.6	H10–C5–C6–H11	0	0	
C24–O25	1.18	1.201		C14–C16–C19	119.9	119.9	120.8	C4–N12–N13–C14	-180	179.9	179
C24–O26	1.311	1.34		C14–C16–H20	119.8	119.2	120.8	N12–N13–C14–C15	-179.4	-179.6	176
O26–C27	1.423	1.444		C19–C16–H20	120.3	120.9	118.4	N12–N13–C14–C16	1	0.9	-4
C27–28H	1.079	1.089		C15–C17–C21	118.2	118	118.6	N13–C14–C15–C17	179.8	179.7	-180
C27–29H	1.08	1.092		C15–C17–C31	117.7	117.4	120.1	N13–C14–C15–H18	-0.3	-0.4	
C27–30H	1.08	1.092		C21–C17–C31	124.1	124.6	121.3	C16–C14–C15–C17	-0.7	-0.8	-0.2
C31–32O	1.191	1.218	1.219	C16–C19–C21	120.4	120.5	120.7	C16–C14–C15–H18	179.3	179.1	
C31–33H	1.094	1.111	0.97	C16–C19–H22	120.9	121.1	120.1	N13–C14–C16–C19	179.8	179.9	-179
				C21–C19–H22	118.7	118.4	119.1	N13–C14–C16–H20	0.1	0.1	
				C17–C21–C19	120.6	120.6	119.6	C15–C14–C16–C19	0.3	0.4	1.1

				C17-C21-O23	122.2	122.6	122.7	C15-C14-C16-H20	-179.4	-179.4	
				C19-C21-O23	117	116.5	117.7	C14-C15-C17-C21	0.3	0.1	-0.7
				C21-O23-C24	123.4	122.7	106	C14-C15-C17-C31	-179.7	179.3	179
				O23-C24-O25	121.4	121.4		H18-C15-C17-C21	-179.7	-179.7	
				O23-C24-O26	112.3	111.5		H18-C15-C17-C31	0.3	-0.5	
				O25-C24-O26	126.3	127		C14-C16-C19-C21	0.6	0.5	-1.1
				C24-O26-C27	116.5	114.9		C14-C16-C19-H22	-179	-179.3	
				O26-C27-H28	105.4	105.2		H20-C16-C19-C21	-179.8	-179.6	
				O26-C27-H29	110.2	110.2		H20-C16-C19-H22	0.6	0.6	
				O26-C27-H30	109.8	109.8		C15-C17-C21-C19	0.6	0.8	0.7
				H28-C27-H29	110.7	110.9		C15-C17-C21-O23	174.7	174.3	-179
				H28-C27-H30	110.7	110.9		C31-C17-C21-C19	-179.4	-178.3	-179
				H29-C27-H30	110	109.9		C31-C17-C21-O23	-5.3	-4.9	1
				C17-C31-O32	125.8	126.2	122.7	C15-C17-C31-O32	171.4	174.6	177
				C17-C31-H33	114	113.5	114.1	C15-C17-C31-H33	-8.1	-5.3	
				O32-C31-H33	120.3	120.3	122.2	C21-C17-C31-O32	-8.6	-6.3	-3.5
								C21-C17-C31-H33	171.9	173.9	
								C16-C19-C21-C17	-1	-1.2	0.2
								C16-C19-C21-O23	-175.4	-175	180
								H22-C19-C21-C17	178.6	178.6	
								H22-C19-C21-O23	4.2	4.8	
								C17-C21-O23-C24	74.6	69	
								C19-C21-O23-C24	-111	-117.4	
								C21-O23-C24-O25	-175	-171.7	
								C21-O23-C24-O26	7.8	12	
								O23-C24-O26-C27	-176.4	-177.1	
								O25-C24-O26-C27	6.6	6.9	
								C24-O26-C27-H28	179.7	-179.3	
								C24-O26-C27-H29	-60.8	-59.8	
								C24-O26-C27-H30	60.4	61.4	

Table 9. Selected structural parameters of CFPMC.

Bond lengths (Å)	HF	B3LYP	Expt. (Ref [18])	Bond angles (°)	HF	B3LYP	Expt. (Ref [18])	Dihedral angles (°)	HF	B3LYP	Expt. (Ref [18])
C1–C2	1.389	1.401	1.393	C2–C1–C6	121.2	121.3	117.7	C6–C1–C2–C3	0	0	-0.9
C1–C6	1.381	1.395	1.398	C2–C1–Cl33	119.3	119.3	120.9	C6–C1–C2–H7	180	180	
C1–Cl33	1.74	1.754	1.503	C6–C1–Cl33	119.6	119.6	121.4	Cl33–C1–C2–C3	180	180	-180
C2–C3	1.381	1.39	1.378	C1–C2–C3	119.6	119.5	121	Cl33–C1–C2–H7	0	0	
C2–H7	1.074	1.085	0.93	C1–C2–H7	119.9	119.8	120.2	C2–C1–C6–C5	0	0	0.3
C3–C4	1.393	1.407	1.39	C3–C2–H7	120.5	120.7	118.8	C2–C1–C6–H10	180	180	
C3–H8	1.072	1.084	0.96	C2–C3–C4	119.8	120	121.4	Cl33–C1–C6–C5	180	180	179.6
C4–C5	1.385	1.402	1.402	C2–C3–H8	120.2	120.7	121.6	Cl33–C1–C6–H10	0	0	
C4–N11	1.42	1.416	1.428	C4–C3–H8	120	119.4	117.3	C1–C2–C3–C4	0	0	0.6
C5–C6	1.387	1.394	1.376	C3–C4–C5	120	119.7	118.7	C1–C2–C3–H8	180	180	
C5–H9	1.075	1.085	0.92	C3–C4–N11	124.4	124.8	126.1	H7–C2–C3–C4	180	180	
C6–H10	1.073	1.084	0.96	C5–C4–N11	115.6	115.5	115.2	H7–C2–C3–H8	0	0	
N11–N12	1.218	1.259	1.259	C4–C5–C6	120.5	120.6	119.7	C2–C3–C4–C5	0	0	-1
N12–C13	1.419	1.417	1.425	C4–C5–H9	119.1	118.7	119.2	C2–C3–C4–N11	180	180	178.6
C13–C14	1.383	1.397	1.381	C6–C5–H9	120.4	120.7	121	H8–C3–C4–C5	180	180	
C13–C15	1.392	1.407	1.412	C1–C6–C5	119	118.9	121.9	H8–C3–C4–N11	0	0.1	
C14–C16	1.392	1.402	1.396	C1–C6–H10	120.3	120.2	118.6	C3–C4–C5–C6	0	0	0.8
C14–H17	1.076	1.087	0.92	C5–C6–H10	120.7	120.9	119.5	C3–C4–C5–H9	180	180	
C15–C18	1.382	1.39	1.37	C4–N11–N12	116	115.4	114.6	N11–C4–C5–C6	180	180	-179
C15–H19	1.073	1.084	0.93	N11–N12–C13	115.8	115	113.5	N11–C4–C5–H9	0	0.1	
C16–C20	1.393	1.411	1.415	N12–C13–C14	115.9	115.8	117.1	C3–C4–N11–N12	0.4	0.6	176.8
C16–C30	1.484	1.48	1.459	N12–C13–C15	124.8	125	124.6	C5–C4–N11–N12	180	179	-3.7
C18–C20	1.385	1.397	1.392	C14–C13–C15	119.3	119.2	118.3	C4–C5–C6–C1	0	0	0.1
C18–H21	1.074	1.085	0.97	C13–C14–C16	121.6	121.8	122	C4–C5–C6–H10	180	180	
C20–O22	1.365	1.381	1.34	C13–C14–H17	118.6	118.5	120.4	H9–C5–C6–C1	180	180	
O22–C23	1.336	1.367		C16–C14–H17	119.9	119.8	117.6	H9–C5–C6–H10	0	0	
C23–O24	1.18	1.201		C13–C15–C18	119.9	119.9	120.8	C4–N11–N12–C13	180	180	179.4
C23–O25	1.311	1.339		C13–C15–H19	119.8	119.3	120.8	N11–N12–C13–C14	180	179	175.8
O25–C26	1.423	1.444		C18–C15–H19	120.3	120.8	118.4	N11–N12–C13–C15	1	0.2	-4
C26–H27	1.079	1.089		C14–C16–C20	118.2	118	118.6	N12–C13–C14–C16	180	180	-180
C26–H28	1.08	1.092		C14–C16–C30	117.7	117.4	120.1	N12–C13–C14–H17	0.3	0.6	
C26–H29	1.08	1.092		C20–C16–C30	124.1	124.6	121.3	C15–C13–C14–C16	0.7	0.7	-0.2

C30-O31	1.19	1.218	1.219	C15-C18-C20	120.4	120.5	120.7	C15-C13-C14-H17	179	179	
C30-H32	1.094	1.111	0.97	C15-C18-H21	120.9	121.1	120.1	N12-C13-C15-C18	180	180	-179
				C20-C18-H21	118.7	118.4	119.1	N12-C13-C15-H19	0.1	0.1	
				C16-C20-C18	120.6	120.6	119.6	C14-C13-C15-C18	0.3	0.5	1.1
				C16-C20-O22	122.2	122.7	122.7	C14-C13-C15-H19	179	179	
				C18-C20-O22	116.9	116.4	117.7	C13-C14-C16-C20	0.3	0	-0.7
				C20-O22-C23	123.5	122.8	106	C13-C14-C16-C30	180	179	179.2
				O22-C23-O24	121.3	121.4		H17-C14-C16-C20	180	180	
				O22-C23-O25	112.3	111.5		H17-C14-C16-C30	0.3	0.7	
				O24-C23-O25	126.4	127.1		C13-C15-C18-C20	0.6	0.5	-1.1
				C23-O25-C26	116.5	114.9		C13-C15-C18-H21	179	179	
				O25-C26-H27	105.4	105.2		H19-C15-C18-C20	180	180	
				O25-C26-H28	110.2	110.2		H19-C15-C18-H21	0.6	0.5	
				O25-C26-H29	109.8	109.8		C14-C16-C20-C18	0.6	1	0.7
				H27-C26-H28	110.7	110.9		C14-C16-C20-O22	175	175	-179
				H27-C26-H29	110.7	110.9		C30-C16-C20-C18	179	178	-179
				H28-C26-H29	110	109.9		C30-C16-C20-O22	5.3	4.5	1
				C16-C30-O31	125.7	126.2	122.7	C14-C16-C30-O31	171	175	176.5
				C16-C30-H32	114	113.6	114.1	C14-C16-C30-H32	8	5.1	
				O31-C30-H32	120.3	120.3	122.2	C20-C16-C30-O31	8.6	6.2	-3.5
								C20-C16-C30-H32	172	174	
								C15-C18-C20-C16	1	1.2	0.2
								C15-C18-C20-O22	175	175	179.9
								H21-C18-C20-C16	179	179	
								H21-C18-C20-O22	4.2	4.7	
								C16-C20-O22-C23	75	68.4	
								C18-C20-O22-C23	111	117.81	
								C20-O22-C23-O24	175	172	
								C20-O22-C23-O25	7.9	12	
								O22-C23-O25-C26	176	177	
								O24-C23-O25-C26	6.6	6.9	
								C23-O25-C26-H27	180	179	
								C23-O25-C26-H28	61	60	
								C23-O25-C26-H29	60	61	

Table 10. Experimental and calculated vibrational spectra values of FPMC with proposed assignments.

Mode No	Observed frequency [cm^{-1}]		Calculated Frequency [cm^{-1}]		Intensity		Red. masses	Force constants	Vibrational Assignments with TED $\geq 10\%$
	FT-IR	Raman	Un Scaled	Scaled	IR	Raman			
1			19	18	1.77	3.7	4	0	$\tau\text{N13N12C4C3}$ (41) + $\tau\text{C15C14N13N12}$ (49)
2			28	27	1.91	2.71	5.86	0	$\tau\text{C16C19C17C21}$ (17) + $\tau\text{C4N12N13C14}$ (21) + $\Gamma\text{O23C17C19C21}$ (10) + $\Gamma\text{N13C14C16C15}$ (18)
3			48	46	2.81	2.95	4.81	0.01	$\tau\text{C17C21O23C24}$ (45)
4			63	61	3.81	1.46	5.45	0.01	$\beta\text{C4N12N13}$ (16) + $\beta\text{C16C14N13}$ (13) + $\beta\text{C14N13N12}$ (16) + $\tau\text{C17C21O23C24}$ (15)
5			75	72	2.22	1.59	5.38	0.02	$\beta\text{C21}\Gamma\text{23C24}$ (14) + $\tau\text{C21O23C24O26}$ (15) + $\tau\text{C4N12N13C14}$ (20) + $\Gamma\text{O23C17C19C21}$ (10) + $\Gamma\text{N12C3C5C4}$ (13)
6		79	86	83	3.55	0.83	4.82	0.02	$\tau\text{C21O23C24O26}$ (37)
7			102	98	6.48	1.73	7.19	0.04	$\tau\text{C15C17C31O32}$ (18) + $\tau\text{C3C4N12N13}$ (14) + $\tau\text{C21O23C24O26}$ (10)
8			113	109	3.15	0.96	4.32	0.03	$\beta\text{C21O23C24}$ (10) + $\tau\text{C3C4N12N13}$ (10) + $\tau\text{C16C14N23N12}$ (13) + $\tau\text{C27O26C24O23}$ (17)
9			129	124	1.63	0.3	1.25	0.01	$\tau\text{H28C27O26C24}$ (20) + $\tau\text{H29C27O26C24}$ (23) + $\tau\text{H30C27O26C24}$ (19)
10			183	177	7.92	0.46	5.13	0.1	$\tau\text{C15C17C31O32}$ (18)
11			187	180	3.63	0.32	5.45	0.11	$\tau\text{H28C27O26C24}$ (12) + $\beta\text{C15C17C31}$ (16) + $\tau\text{C27O26C24O23}$ (28)
12			193	186	8.46	0.93	5.12	0.11	$\beta\text{C4N12N13}$ (10) + $\beta\text{C16C14N13}$ (12) + $\beta\text{C5C4N12}$ (13)
13			207	200	6.62	0.12	7.11	0.18	$\beta\text{C15C17C31}$ (29) + $\tau\text{C27O26C24O23}$ (10)
14			260	251	3.27	0.28	3.38	0.13	$\Gamma\text{C31C15C21C17}$ (28)
15			271	262	4.66	5.45	6.19	0.27	$\beta\text{C5C4N12}$ (14) + $\beta\text{C24O26C27}$ (12) + $\tau\text{C3C2C4C5}$ (29)
16			284	274	3	2.64	5.52	0.26	$\tau\text{C3C2C4C5}$ (29)
17			306	295	8.03	3.31	4.74	0.26	$\beta\text{C24O26C27}$ (36)
18			361	348	10.78	0.76	8.52	0.66	νO23C21 (10) + $\beta\text{O25C24O26}$ (10) + $\beta\text{C17C21C19}$ (15)
19			389	375	8.93	2.64	5.28	0.47	$\tau\text{C14C16C21C19}$ (31) + $\Gamma\text{N13C14C16C15}$ (11)
20			419	403	9.9	0.01	2.94	0.3	$\tau\text{H10C5C6C1}$ (11) + $\tau\text{C2C1C6C5}$ (12) + $\tau\text{C3C2C1C6}$ (36) + $\tau\text{C4C5C6C1}$ (28)
21			419	404	11.58	1.59	7.56	0.78	$\beta\text{C17C31O32}$ (14) + $\beta\text{C19C21O23}$ (45) + $\tau\text{C1C6C4C5}$ (56) + $\tau\text{C1C6C2C3}$ (24)

22			457	441	7.1	2.83	3.55	0.44	τ C14C16C21C19 (15) + τ C16C19C17C21 (21) + τ C17C15C21C19 (12) + τ C31C15C21C17 (11)
23			480	463	6.55	17.1	8.3	1.13	ν C17C31 (11)
24			513	495	3.8	0.11	3.29	0.51	τ C1C6C2C3 (13) + Γ N12C3C5C4 (29)
25			540	521	11.03	0.76	6.36	1.09	β C4N12N13 (14) + β C16C19C21 (10) + β C16C14N13 (18) + β C5C4N12 (15) + β C14N13N12 (11)
26		547	573	553	10.28	12.6	7.82	1.51	β C2C1C6 (15)
27			594	573	12.38	3.59	4.3	0.89	τ C4N12N13C14 (11) + Γ C31C15C21C17 (11) + Γ N13C14C16C15 (19)
28			627	605	1.16	16.1	6.51	1.51	β C4C5C6 (36) + β C2C3C4 (43)
29		616	647	624	6.65	1.51	4.37	1.08	β O23C24O26 (15) + β C21O23C24 (10) + τ C14C16C21C19 (10)
30	660	641	679	655	5.14	7.59	7.2	1.95	ν C17C21(10) + β O25C24O26 (16) + β C17C21C19 (13)
31	677		694	670	19.17	0.08	2.01	0.57	τ H7C1C6C5 (20) + τ H9C3C4C5 (15) + τ H10C5C6C1 (16) + C1C6C2C3 (21) + τ C3C2C4C5 (15)
32	694	691	721	696	12.41	1.32	6.24	1.91	β C17C31O32 (19) + β C2C1C6 (15)
33		714	739	713	15.58	2.88	6.75	2.17	Γ 25 Γ 23 Γ 26C24 (55)
34			754	728	5.27	6.79	5.04	1.69	Γ 25 Γ 23 Γ 26C24 (22)
35	743	752	782	755	18.28	8.42	1.98	0.71	τ C7C1C6C5 (15) + τ C8C2C1C6 (14) + τ H11C6C1C2 (15) + Γ O12C3C5C4 (14)
36	772	762	786	758	17.74	20.7	4.19	1.53	ν C17C21 (16)
37			822	793	4.11	21.4	5.62	2.24	β C16C19C21 (12)
38	823	827	855	825	0.06	0.29	1.25	0.54	τ H8C2C1C6 (25) + τ H8C2C1C6 (25)+ τ H10C5C6C1 (25) + τ H11C6C1C2 (25)
39	842	853	871	841	14.79	2.92	1.59	0.71	τ H20C16C19C21 (32) + τ H22C19C21C17 (36) + Γ O23C17C19C21 (12)
40		870	911	879	9.67	5.19	6.28	3.07	ν C3C4 (14) + β C14N13N12 (14)
41		892	925	893	12.12	0.94	1.44	0.73	τ H18C15C17C21(74)
42	905	906	945	912	22.64	6.11	6.02	3.17	ν O26C24 (14) + ν O26C27 (13) + β O23C24O26 (10)
43			948	915	7.76	0.09	1.42	0.75	τ H7C1C6C5 (31) + τ H8C2C1C6 (17) + τ H10C5C6C1 (33)
44	935	932	975	941	11.77	11.5	4.49	2.52	ν C14C16 (14) + β C16C19C21 (14)
45			992	957	0.14	0.13	1.36	0.79	τ H8C2C1C6 (18) + τ H8C2C1C6 (22) + τ H10C5C6C1 (15) + τ H11C6C1C2 (30)

46			996	961	1.54	0.42	1.35	0.79	$\tau\text{H20C16C19C21 (49) + } \tau\text{H22C19C21C17 (35)}$
47	964	965	1006	971	0.38	1.12	1.29	0.77	$\tau\text{H7C1C6C5 (22) + } \tau\text{H8C2C1C6 (24) + } \tau\text{H8C2C1C6 (11) + } \tau\text{H11C6C1C2 (12) + } \tau\text{C1C6C2C3 (18)}$
48	971		1013	978	5.02	192	6.05	3.66	$v\text{C3C4(10) + } \beta\text{C4C5C6 (20) + } \beta\text{C2C1C6 (20) + } \beta\text{C2C3C4 (19)}$
49			1023	987	2.67	2.01	1.8	1.11	$\tau\text{H33C31C17C15 (75) + } \tau\text{C15C17C31O32 (10)}$
50	1024	1000	1041	1005	9.32	24.4	2.06	1.31	$\beta\text{H9C3C4 (10) + } v\text{C1C6 (25) + } v\text{C1C2 (31)}$
51	1049	1046	1077	1039	14.14	35.5	8.74	5.98	$v\text{O23C24 (19) + } v\text{O26C27(57)}$
52			1101	1062	9.06	22.3	1.48	1.06	$\beta\text{H7C1C2 (11) + } \beta\text{H9C3C4 (12) + } \beta\text{H10C5C6 (15) + } v\text{C2C3 (14) + } v\text{C5C6 (19)}$
53	1067	1062	1128	1089	29.29	911	1.56	1.17	$\beta\text{H20C16C19 (32)}$
54	1084	1091	1166	1125	16.4	1534	1.61	1.29	$\beta\text{H18C15C17 (15) + } \beta\text{H22C19C16 (16)}$
55			1178	1137	12.92	149	1.3	1.06	$\beta\text{H28C27H30 (11) + } \beta\text{H28C27H29 (10) + } \tau\text{H28C27O26C24 (27) + } \tau\text{H29C27O26C24 (12) + } \tau\text{H30C27O26C24 (12)}$
56			1179	1138	16	107	1.29	1.06	$\beta\text{H9C3C4 (12) + } \tau\text{H28C27O26C24 (11)}$
57	1140	1140	1184	1143	1.21	14.3	1.11	0.92	$\beta\text{H7C1C2 (38) + } \beta\text{H7C1C2(10) + } \beta\text{H11C6C1 (26)}$
58	1185		1214	1172	4.81	15.1	1.51	1.31	$\beta\text{H29C27H30 (19) + } \tau\text{H29C27O26C24 (29) + } \tau\text{H30C27O26C24 (29)}$
59	1204	1182	1225	1182	15.32	2277	3.16	2.8	$\beta\text{H7C1C2 (10) + } v\text{N12C4 (22) + } v\text{C17C31 (11)}$
60	1237	1205	1238	1195	100	133	6.39	5.77	$v\text{O26C24 (21) + } v\text{O23C24 (32) + } v\text{O23C21 (20)}$
61			1255	1211	38.42	55.4	4.13	3.83	$\beta\text{H18C15C17 (12) + } v\text{O26C24 (14)}$
62			1270	1226	34.97	246	6.37	6.05	$v\text{O26C24 (10) + } v\text{N13C14 (12) + } v\text{O2321 (20)}$
63	1257	1233	1282	1237	15.48	91	1.55	1.5	$\beta\text{H18C15C17 (21) + } \beta\text{H20C16C19 (12) + } \beta\text{H22C19C16 (28)}$
64	1280	1259	1339	1292	5.13	274	1.46	1.54	$\beta\text{H8C2C3 (14) + } \beta\text{H9C3C4 (21) + } \beta\text{H10C5C6 (25) + } \beta\text{H11C6C1 (14)}$
65	1315	1314	1366	1318	13.08	55.7	6.32	6.95	$v\text{C2C3 (16) + } v\text{C1C6 (14) + } v\text{C5C6 (10) + } v\text{C1C2(10) + } v\text{C4C5 (12) + } v\text{C3C4 (11)}$
66			1369	1321	13.55	23.4	9.8	10.82	$v\text{C16C19 (13) + } v\text{C14C15 (16) + } v\text{C14C16 (10) + } v\text{C17C21 (19)}$
67	1402	1354	1416	1366	18.34	157	1.8	2.13	$\beta\text{H33C31O32 (41) + } v\text{C15C17 (12)}$
68		1380	1456	1405	10.29	154	2.11	2.64	$\beta\text{H33C31O32 (41) + } v\text{C16C19 (12) + } v\text{C15C17 (18)}$

v – Stretching, β – in-plane bending, τ – torsional vibrations, Γ – out of plane bending.

Table 11. Experimental and calculated vibrational spectra values of CFPMC with proposed assignment.

Mode no	Observed frequency (cm ⁻¹)		Calculated frequency (cm ⁻¹)		Intensity		Red. Masses	Force constants	Vibrational Assignments with TED ≥ 10%
	IR	Raman	Un scaled	Scaled	IR	Raman			
1			19.31	19	0.33	3.5	4.05	0.0	τN12N11C4C3 (39) + τC14C13N12N11 (50)
2			23.4	22	0.57	1.23	8.15	0.0	τC18C15C13C14 (12) + τC13N12N11C4 (29) + ΓC15C14N12C13 (19) + ΓN11C3C5C4 (11)
3			41.72	40	0.59	1.46	6.93	0.0	βN12N11C4 (16) + βC14C13N12 (12) + βC13N12N11 (17) + τC23O22C20C16 (25)
4			51.63	50	0.99	1.13	6.91	0.0	τC23O22C20C16 (12)
5			64.17	62	1.79	3.1	5.03	0.0	τC23O22C20C16 (31) + τC26O25C23O22 (13)
6		70	81.26	78	0.56	1.08	5.35	0.0	τC25C23C22C20 (54)
7		97	95.63	92	0.91	0.66	7.03	0.0	βC23O22C20 (19)
8			108.76	104	3.59	1.07	4.89	0.0	τO31C30C16C14 (17) + τC26O25C23O22 (21)
9			129.55	124	0.36	0.33	1.23	0.0	τH27C26O25C23 (17) + τH28C26O25C23 (22) + τH29C26O25C23 (19)
10			163.22	157	0.74	0.82	9.23	0.1	βC14C13N12 (11) + βN11C4C5 (11)
11		162	177.73	171	3.28	0.27	8.11	0.2	τN12N11C4C3 (12) + τC2C1C6C5 (17) + τC13N12N11C4 (14) + ΓC133C2C6C1 (24)
12			185.65	178	4.98	0.34	6.72	0.1	βC30C16C14 (23) + τO31C30C16C14 (12)
13			188.31	181	3.38	0.31	4.44	0.1	τH27C26O25C23 (10) + τC18C15C13C14 (15) + τC26O25C23O22 (23)
14		189	193.74	186	3.18	0.46	5.89	0.1	τO31C30C16C14 (11) + τC26O25C23O22 (19)
15		236	247.01	237	4.96	2.82	9.05	0.3	βC30C16C14 (17) + βC133C1C6 (16)
16			262.92	253	0.57	0.7	3.21	0.1	βC26Γ25C23 (11) + ΓC30C14C20C16 (32)
17			298.36	287	9.59	4.11	4.66	0.2	βC26O25C23 (45)
18		295	314.35	302	8.45	2.23	7.01	0.4	βC133C1C6 (43)
19			347.87	334	0.89	3.75	6.80	0.5	ΓC133C2C6C1 (15) + ΓC15C14N12C13 (14) + ΓN11C3C5C4 (13)
20		349	364.14	350	16.43	1.36	7.79	0.6	βO24C23O25 (12)
21		371	398.5	383	9.07	1.06	5.05	0.5	τC2C1C6C5 (11) + τC20C18C15C13 (19) + τC13N12N11C4 (11)
22			412.48	396	13.05	1.59	11.09	1.1	νC133C1 (28) + βC2C1C6 (11)
23			421.64	405	13.1	1.16	6.74	0.7	βO31C30C16 (13) + βO22C20C18 (39)
24			427.1	410	1.71	0.15	3.37	0.4	τC3C2C1C6 (19) + τC4C5C6C1 (41)

25		459	458.38	440	5.19	2.29	3.53	0.4	$\tau\text{H17C14C16C20}$ (13) + $\tau\text{C16C14C13C15}$ (25) + OC30C14C20C16 (14)
26		482	511.1	491	5.59	35.03	7.21	1.1	$\tau\text{H9C5C6C1}$ (14) + $\Gamma\text{F33C1C2C6}$ (23) + $\Gamma\text{N11C3C5C4}$ (19)
27		498	516.68	496	7.81	2.15	2.99	0.5	$\tau\text{H7C2C1C6}$ (10) + $\Gamma\text{C13C2C6C1}$ (14) + $\Gamma\text{N11C3C5C4}$ (23)
28			542.82	522	7.7	5.48	6.23	1.1	$\beta\text{N12N11C4}$ (11) + $\beta\text{C14C13N12}$ (16) + $\beta\text{N11C4C5}$ (13) + $\beta\text{C13N12N11}$ (14)
29			589.1	566	15.7	0.84	4.22	0.9	$\Gamma\text{C30C14C20C16}$ (11) + $\Gamma\text{C15C14N12C13}$ (18)
30			623.8	599	1.89	1.49	7.09	1.6	νC133C1 (14) + $\beta\text{C15C13C14}$ (17)
31		608	641.87	617	0.79	16.13	7.25	1.8	βC4C5C6 (19) + βC3C2C1 (14) + βC1C6C5 (30)
32			647.78	622	5.95	1.23	4.57	1.1	$\beta\text{O25C23O22}$ (12)
33			688.97	662	5.77	5.2	7.19	2.0	$\beta\text{C18C15C13}$ (18)
34	693	694	716.6	689	1.95	1.63	4.12	1.2	$\tau\text{C3C2C1C6}$ (26) + $\tau\text{C2C1C6C5}$ (17) + $\tau\text{C4C5C6C1}$ (20)
35	711		737.09	708	12.34	2.74	5.81	1.9	$\beta\text{O31C30C16}$ (10) + $\Gamma\text{O24O22O25C23}$ (14)
36	746		741.23	712	42.52	4.62	8.67	2.8	$\Gamma\text{O24O22O25C23}$ (53)
37			756.5	727	9.89	9.64	5.16	1.7	$\Gamma\text{O24O22O25C23}$ (14)
38	766	756	786.83	756	23.64	25.45	5.67	2.1	$\beta\text{C18C15C13}$ (13)
39	772		824.12	792	5.02	26.57	5.71	2.3	$\tau\text{H7C2C1C6}$ (20) + $\tau\text{H8C3C4C5}$ (30) + $\tau\text{H9C5C6C1}$ (19) + $\tau\text{H10C6C1C2}$ (31)
40	834		835.43	803	0.05	0.12	1.25	0.5	$\tau\text{H7C2C1C6}$ (28) + $\tau\text{H8C3C4C5}$ (22) + $\tau\text{H9C5C6C1}$ (22) + $\tau\text{H10C6C1C2}$ (28)
41	843	822	853.68	820	36.73	0.17	1.56	0.7	$\tau\text{H7C2C1C6}$ (20) + $\tau\text{H9C5C6C1}$ (14) + $\tau\text{H10C6C1C2}$ (18) + $\Gamma\text{N11C3C5C4}$ (13)
42			871.7	838	31.16	3.9	1.60	0.7	$\tau\text{H19C15C18C20}$ (34) + $\tau\text{H21C18C20C16}$ (35) + $\Gamma\text{O22C16C18C20}$ (10)
43			910.69	875	2.36	5.39	6.34	3.1	βC2C1C6 (16) + $\beta\text{C13N12N11}$ (11)
44			926.49	890	19.03	1.43	1.45	0.7	$\tau\text{H17C14C16C20}$ (64) + $\tau\text{C16C14C13C15}$ (11)
45	911	904	944.88	908	67.55	6.87	6.08	3.2	νO25C23 (14) + νO25C26 (14) + $\beta\text{O25C23O22}$ (11)
46	935	935	972.24	934	0.52	0.68	1.32	0.7	$\tau\text{H9C5C6C1}$ (41) + $\tau\text{H10C6C1C2}$ (30)
47			975.27	937	11.16	11.68	4.46	2.5	νC14C13 (10) + νC15C13 (24)
48			988.42	950	0.01	0.05	1.34	0.8	$\tau\text{H7C2C1C6}$ (29) + $\tau\text{H8C3C4C5}$ (420)
49	963	964	996	957	0.35	0.46	1.35	0.8	$\tau\text{H19C15C18C20}$ (39) + $\tau\text{H21C18C20C16}$ (28) + $\tau\text{C20C18C15C13}$ (20)

50		978	1023	983	39.99	52.28	3.11	1.9	$\beta C3C2C1$ (37) + $\beta C1C6C5$ (21) + $\beta C2C1C6$ (20)
51			1023	983	1.9	3.87	1.81	1.1	$\tau H32C30C16C14$ (72)
52	1009	1010	1076	1034	19.13	40.67	8.75	6.0	$vO22C23$ (21) + $vO25C26$ (58)
53	1053	1050	1101	1058	123.8	243.59	3.36	2.4	$vC1C6$ (23) + $vC2C1$ (26) + $vC13C1$ (21)
54			1124	1080	30.94	395.65	1.37	1.0	$vC6C5$ (12) + $\beta H8C3C1$ (16) + $\beta H9C5C6$ (13) + $\beta H10C6C1$ (10)
55	1095	1094	1129	1085	78.78	810.79	1.46	1.1	$\beta H19C15C18$ (27)
56			1166	1121	28.71	2277.6	1.58	1.3	$\beta H9C5C6$ (11) + $\beta H17C14C16$ (13) + $\beta H21C18C20$ (12)
57			1178	1132	9.93	80.61	1.28	1.0	$\beta H27C26H29$ (11) + $\beta H28C26H27$ (11) + $\tau H27C26O25C23$ (31) + $\tau H28C26O25C23$ (14) + $\tau H29C26O25C23$ (13)
58			1178	1132	37.81	236.07	1.31	1.1	$\beta H8C3C1$ (12) + $\beta H9C5C6$ (10) + $\tau H27C26O25C23$ (10)
59	1141	1142	1214	1167	1.45	19.62	1.50	1.3	$\beta H29C26H28$ (18) + $\tau H28C26O25C23$ (29) + $\tau H29C26O25C23$ (30)
60			1227	1179	21.48	3214.4	3.36	3.0	$vN11C4$ (22) + $vC30C16$ (13)
61	1154	1182	1237	1188	1088	139.03	6.66	6.0	$vO25C23$ (22) + $vO22C23$ (32) + $vO22C20$ (18)
62			1256	1206	124.8	18.66	3.92	3.6	$vO25C23$ (13) + $\beta H17C14C16$ (13)
63			1271	1221	140.3	212.35	6.25	5.9	$vC20C18$ (11) + $vO25C23$ (10) + $vN12C13$ (11) + $vO22C20$ (21)
64	1234	1228	1282	1232	20.06	118.91	1.58	1.5	$\beta H17C14C16$ (22) + $\beta H19C15C18$ (12) + $\beta H21C18C20$ (26)
65		1261	1316	1265	0.44	111.91	1.36	1.4	$\beta H7C2C1$ (23) + $\beta H8C3C1$ (17) + $\beta H9C5C6$ (20) + $\beta H10C6C1$ (22)
66	1280	1303	1349	1296	11.27	283.28	8.27	8.9	$vC3C2$ (13) + $vC2C1$ (25) + $vC4C5$ (29)
67			1370	1316	25.81	27.26	10.04	11.1	$vC18C15$ (19) + $vC14C13$ (25) + $vC20C18$ (17) + $vC16C14$ (10)
68			1416	1361	32.83	226.52	1.80	2.1	$vC16C14$ (11) + $\beta H32C30O32$ (45)
69			1438	1382	9.78	714.25	3.28	4.0	$vC3C2$ (20) + $vC6C5$ (25) + $\beta H10C6C1$ (12)
70	1399	1399	1456	1399	10.35	202.2	2.11	2.6	$vC18C15$ (12) + $vC16C14$ (18) + $\beta H32C30O32$ (40)
71	1416	1416	1476	1418	38.35	3.29	1.18	1.5	$\beta H27C26H29$ (31) + $\beta H28C26H27$ (43) + $\beta H29C26H28$ (11)
72			1489	1431	8.33	10.88	1.05	1.4	$\beta H27C26H29$ (36) + $\beta H28C26H27$ (34) + $\tau H27C26O25C23$ (19)
73			1501	1442	4.81	502.36	1.12	1.5	$\beta H27C26H29$ (10) + $\beta H29C26H28$ (59) + $\tau H29C26O25C23$ (12)

74	1442		1504	1445	10.07	3845.3	2.28	3.0	$\nu\text{N12N11 (11)} + \beta\text{H8C3C1 (11)}$
75	1455	1451	1518	1458	125.1	7.77	2.58	3.5	$\beta\text{H7C2C1 (10)} + \beta\text{H21C18C20 (12)}$
76	1479	1486	1547	1486	16.25	8475.4	6.81	9.6	$\nu\text{N12N11 (57)}$
77	1532		1606	1543	30.82	8.26	7.21	11.0	$\nu\text{C15C13 (24)} + \beta\text{C16C14C13 (10)}$
78	1576		1618	1554	8.66	47.73	7.73	11.9	$\nu\text{C1C6 (23)} + \nu\text{C4C5 (21)}$
79	1587	1585	1639	1575	119	315.82	6.25	9.9	$\nu\text{C3C2 (27)} + \nu\text{C6C5 (12)} + \nu\text{C4C5 (14)}$
80	1606	1603	1654	1589	119.5	588.92	6.63	10.7	$\nu\text{C18C15 (13)} + \nu\text{C14C13 (16)} + \nu\text{C20C18 (19)} + \nu\text{C16C14 (20)}$
81	1695	1693	1777	1707	426.5	146.06	10.14	18.9	$\nu\text{O31C30 (87)}$
82	1767	1768	1855	1783	827.9	15.18	12.04	24.4	$\nu\text{O24C23 (85)}$
83	2768	2869	2924	2809	86.91	107.79	1.08	5.5	$\nu\text{C30H32 (100)}$
84	2917	2959	3072	2951	38.69	145.55	1.03	5.7	$\nu\text{C26H27 (23)} + \nu\text{C26H28 (40)} + \nu\text{C26H29 (38)}$
85	2958	3016	3158	3034	10.31	60.95	1.11	6.5	$\nu\text{C26H28 (51)} + \nu\text{C26H29 (49)}$
86	3010	3047	3182	3057	9.13	48.02	1.11	6.6	$\nu\text{C26H27 (77)} + \nu\text{C26H28 (10)} + \nu\text{C26H29 (13)}$
87	3051	3069	3193	3068	0.96	35.32	1.09	6.5	$\nu\text{C14H17 (99)}$
88			3208	3082	1.48	40.78	1.09	6.6	$\nu\text{C5H9 (79)} + \nu\text{C6H10 (19)}$
89			3212	3086	2.75	130.39	1.09	6.6	$\nu\text{C15H19 (10)} + \nu\text{C18H21 (90)}$
90			3214	3088	1.44	109.24	1.09	6.6	$\nu\text{C2H7 (84)} + \nu\text{C3H8 (14)}$
91	3096	3099	3225	3098	3.38	163.18	1.10	6.7	$\nu\text{C5H9 (19)} + \nu\text{C6H10 (80)}$
92	3366		3231	3105	2.52	88.47	1.09	6.7	$\nu\text{C2H7 (14)} + \nu\text{C3H8 (4)}$
93	3521		3232	3105	3.31	56.61	1.09	6.7	$\nu\text{C15H19 (89)} + \nu\text{C18H21 (10)}$

ν – stretching, β – inplane bending, τ – torsional vibrations, Γ – out of plane bending.

Table 12. Second order perturbation theory analysis of Fock matrix in NBO basis of CFPMC.

Type	Donor (i)	ED (i)(e)	Acceptor (j)	ED (j)(e)	^a E ⁽²⁾ kcal/mol	^b E(j)–E(i) a.u	^c F(i,j) a.u.
$\pi-\pi^*$	C1 – C6	1.6681	C2 – C 3	0.2788	17.06	0.3	0.065
$\pi-\pi^*$		1.6681	C4 – C5	0.3754	19.6	0.29	0.069
$\pi-\pi^*$	C2 – C3	1.6788	C1 – C6	0.3814	20.79	0.27	0.067
$\sigma-\sigma^*$	C3 – C4	1.9787	C4 – C5	0.0206	3.14	1.26	0.056
$\pi-\pi^*$	C4 – C5	1.6092	C1 - C6	0.3814	20.79	0.26	0.066
$\pi-\pi^*$		1.6092	C2 - C3	0.2788	19.42	0.28	0.068
$\pi-\pi^*$		1.6092	N11 – N12	0.2147	20.77	0.23	0.065
$\sigma-\sigma^*$	C4 – N11	1.9808	N12 – C13	0.0286	4.14	1.2	0.063
$\sigma-\sigma^*$	C5 – C6	1.9724	C1 –Cl33	0.0294	4.76	0.85	0.057
$\pi-\pi^*$	N11 – N12	1.9119	C4 – C5	0.3754	10.17	0.39	0.061
$\pi-\pi^*$		1.9119	C13 – C14	0.3527	10.41	0.39	0.061
$\pi-\pi^*$	C13 – C14	1.6114	N11 – N12	0.2147	20.03	0.24	0.064
$\pi-\pi^*$		1.6114	C15 – C18	0.2776	20.22	0.28	0.07
$\pi-\pi^*$		1.6114	C16 – C20	0.4123	17.79	0.27	0.063
$\pi-\pi^*$	C15 – C18	1.655	C13 – C14	0.3527	17.3	0.28	0.062
$\pi-\pi^*$		1.655	C16 – C20	0.4123	24.11	0.27	0.074
$\pi-\pi^*$	C16 – C20	1.6006	C13 – C14	0.3527	22.37	0.29	0.072
$\pi-\pi^*$	C16 – C20	1.6006	C15 – C18	0.2776	15.66	0.29	0.062
$\pi-\pi^*$	C16 – C20	1.6006	C30 – O31	0.1129	17.84	0.28	0.068
$\sigma-\sigma^*$	C16 – C30	1.9822	C18 – C20	0.0230	2.44	1.22	0.049
$\sigma-\sigma^*$	C18 – C20	1.9787	C16 – C30	0.0595	3.09	1.16	0.054
$\sigma-\pi^*$	C20 – O22	1.988	C23 – O24	0.1710	2.02	1.21	0.046
$\sigma-\sigma^*$	O22 – C23	1.9803	O25 – C26	0.0114	2.27	1.16	0.046
$\sigma-\sigma^*$	C23 – O24	1.9937	C23 – O24	0.1527	1.01	1.1	0.031
$\pi-\pi^*$		1.9925	C20 – O22	0.0341	1.45	1.04	0.035
$\sigma-\sigma^*$	O25 – C26	1.9865	O22 – C23	0.1145	3.93	1.16	0.062
$\pi-\pi^*$	C30 – O31	1.9785	C16 – C20	0.4123	4.6	0.39	0.042
LP (1)	N11	1.9506	C3 – C4	0.0330	8.65	0.96	0.082
LP (1)	N12	1.9502	C13 – C15	0.0334	8.81	0.96	0.082
LP (2)	O22	1.8272	C23 – O24	0.1527	11.72	0.67	0.08
LP (2)	O24	1.8135	O22 – C23	0.1145	33.78	0.59	0.129
LP (2)		1.8135	C23 – O25	0.1063	31.13	0.62	0.127
LP (2)	O25	1.8125	C23 – O24	0.1710	15.82	0.62	0.089
LP (2)	O31	1.8803	C16 – C30	0.0595	19.44	0.71	0.106
LP (2)	O31	1.8803	C30 – H32	0.0611	21.39	0.67	0.108
LP (3)	Cl33	1.9213	C1 – C6	0.3814	12.81	0.32	0.062
$\pi^*-\pi^*$	C1 – C6	0.3814	C2 – C3	0.2788	133.63	0.02	0.078
$\pi^*-\pi^*$	C1 – C6	0.3814	C4 – C5	0.3754	218.23	0.02	0.083
$\pi^*-\pi^*$	N11 – N12	0.2147	C13 – C14	0.3527	28.24	0.04	0.058
$\pi^*-\pi^*$	C16 – C20	0.4123	C15 – C18	0.2776	241.41	0.01	0.082
$\pi^*-\sigma^*$	C23 – O24	0.171	C23 – O24	0.1527	461.97	0.04	0.306

^a Energy of hyper conjugative interaction (stabilization energy), ^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 orbitals

Table 13. Experimental and calculated ^1H and ^{13}C chemical shift (ppm) values of CFPMC.

Atom	HF	B3LYP	Expt.	Atom	HF	B3LYP	Expt
H7	6.794	8.06	7.469	C1	142	147.36	137
H8	7.613	8.75	7.526	C2	128.4	128.96	124.05
H9	7.759	8.67	7.505	C3	116.3	115	118.71
H10	7.003	8.24	7.491	C4	147.8	149.75	162.42
H17	8.306	9.06	8.441	C5	134.5	135.06	129.73
H19	8.041	9.03	8.198	C6	129	128.86	129.38
H21	6.596	7.84	7.904	C13	145.4	149.54	150.73
H27	1.908	3.74	3.997	C14	142.2	141.68	129.58
H28	2.354	4.3	3.997	C15	125.1	121.46	120.34
H29	2.275	4.12	3.997	C16	126.6	129.29	129.45
H32	8.897	10.8	10.27	C18	121.5	124.81	123.99
				C20	153	153.9	163.99
				23C	144.2	149.03	145.78
				26C	50.94	61.417	55.63
				30C	185.6	188.03	188.24

REFERENCES

- [1] S.C. Catino, E. Farris, Concise encyclopedia of chemical technology, John Wiley and Sons, New York, 1985.
- [2] K. Venkataraman, The Chemistry of synthetic dyes, Academic Press, New York and London, 1970 (Chapter VI).
- [3] R. Egli, A.P. Peter, Colour chemistry: the design and synthesis of organic dyes and Pigments, Ed., H.S. Freeman, Elsevier, London, 1991 (Chapter VII).
- [4] J.P. Parrish et al. Perspectives on alkyl carbonates in organic synthesis, Tetrahedron. 56 (2000) 8207–8237.
- [5] E. Balaraman et al. Efficient hydrogenation of organic carbonates, carbamates and formates indicates alternative routes to methanol based on CO_2 and CO, Nature Chemistry. 3 (2011) 609–614.
- [6] B. Schaffner et al. Organic carbonates as solvents in synthesis and catalysis, Chem. Rev. 110 (2010) 4554–4581.
- [7] H. Zhang et al. Organic carbonates from natural Sources, Chem. Rev. 114 (2014) 883–898.
- [8] T. Sakakura, K. Kohno, The synthesis of organic carbonates from carbon dioxide, Chem. Commun. (2009) 1312–1330.
- [9] C. Ghiron et al. The stereoselective synthesis of 4-formyltrinem a key Intermediate for novel triamines, Tetrahedron Lett. 38 (1997) 3569–3570.
- [10] A.A.G. Shaikh, S. Sivaram, Organic carbonates, Chem. Rev. 96 (1996) 951–976.
- [11] G. Grynkiewicz et al. The synthesis of mixed carbonates from alcohols, dialkyl azodicarboxylate and tris(dimethylamino)-phosphine, Tetrahedron. 31 (1975) 1411–1414.
- [12] R.M. Burk, M.B. Roof, A safe and efficient method for conversion of 1,2- and 1,3-Diols to cyclic carbonates utilizing triphosgene, Tetrahedron Lett. 34 (1993) 395–398.

-
- [13] G. Bertolini et al. A new simple one-pot regioselective preparation of mixed diesters of carbonic Acid, *J. Org. Chem.* 63 (1998) 6031–6034.
- [14] P. Majer, R.S. Randad, A safe and efficient method for preparation of N,"-unsymmetrically disubstituted ureas utilizing triphosgene, *J. Org. Chem.*, 59 (1994)1937–1938.
- [15] P.G.M. Wuts, T.W. Greene, *Green's protective groups in organic synthesis*, 4th ed., Wiley, New Jersey, 2007.
- [16] J.S. Yadav et al. Zinc promoted simple and convenient synthesis of carbamates : An easy access for amino group protection, *Tetrahedron Lett.* 39 (1998) 3259–3262.
- [17] D. Mormeneo et al. A practical synthesis of carbamates using an in-situ generated polymer-supported chloroformate, *Tetrahedron Lett.* 45 (2004) 6831–6864.
- [18] M. Odabasoglu et al. Some polyhydroxy azo–azomethine derivatives of salicylaldehyde: Synthesis, characterization, spectroscopic, molecular structure and antimicrobial activity studies, *J. Mol. Struct.* 840 (2007) 71–89.
- [19] R. Sivakumar et al. Bioorganic synthesis, spectral and antimicrobial evaluation of some novel 1-methyl-3-alkyl-2,6-diphenylpiperidin-4-one oxime carbonates, *Bioorg. Med. Chem. Lett.* 23 (2013) 3195–3199.
- [20] J.A. Montgomery et al. Gaussian 03, Revision C.02, Gaussian, Inc., Wallingford, CT, 2004.
- [21] C. Lee et al. Development of the colle-salvetti correlation-energy formula into a functional of the electron density, *Phys. Rev. B*, 37 (1988) 785–789.
- [22] A.D. Becke, Density functional thermochemistry. III. The role of exact exchange, *J Chem Phys.* 98 (1993) 5648–5652.
- [23] A. Frish et al. GaussView user manual, Gaussian Inc., Pittsburg, pA, 2000.
- [24] C. Albayrak et al. (E)-2-Methyl-4-(phenyldiazenyl)phenol, *Acta. Cryst. E*, 63 (2007) o3662–o3663.
- [25] M.A. Palafox, Scaling factors for the prediction of vibrational spectra. II. The aniline molecule and several derivatives, *Int. J. Quantum Chem.* 77 (2000) 661–684.
- [26] B.H. Stuart, *Infrared Spectroscopy: Fundamentals and Applications*, John Wiley and Sons. Chichester, U.K, 2004.
- [27] T. Uno et al. Machida, Resonance Raman spectra of p-hydroxyazobenzene and its ring-deuterated derivatives, *Spectrochim. Acta*, 32 (1976) 1319–1322.
- [28] R.S. Mulliken, Electronic population analysis on LCAOMO molecular wave functions I, *J. Chem. Phys.* 23 (1955) 1833–1840.
- [29] R.S. Mulliken, Electronic population analysis on LCAOMO molecular wave Functions. II. Overlap populations, bond orders and covalent bond energies, *J. Chem. Phys.* 23 (1955) 1841–1846.
- [30] C.J. Cramer, *Essentials of computational chemistry: Theories and models*, 2nd ed., N.J. Hoboken, Wiley, 2004.
- [31] M. Snehalatha et al. Spectroscopic analysis and DFT calculations of a food additive carmoisine, *Spectrochim. Acta Part A*, 72 (2009) 654–662.
- [32] I. Fleming, *Frontier orbitals and organic chemical Reactions*, Wiley-Blackwell, New York, 1976.
- [33] T.C. Koopmans, By assigning wave functions and eigen values for the individual electrons of an atom, *Physica (Amsterdam)*. 1 (1934) 104-113.
- [34] H.P. Ebrahimi et al. Gauge invariant atomic orbital-density functional theory prediction of accurate gas phase ¹H and ¹³C NMR Chemical Shifts, *Concepts in magnetic resonance Part A*, 38 (2011) 269–279.
- [35] A. Manimekalai, R. Balachander, Theoretical investigation of the conformation and hydrogen bonding ability of 5-arylazosalicylaldoximes, *J. Mol. Struct.* 1027 (2012) 175–185.
- [36] J. Gerratt, Force constants and dipole moment derivatives of molecules from Perturbed Hartree–Fock calculations, *J. Chem. Phys.* 49 (1968) 1719-1729.

-
- [37] P. Pulay, Second and third derivatives of variational energy expressions: Application to multiconfigurational self consistent field wave functions, *J. Chem. Phys.* 78 (1983) 5043-5051.
- [38] C.E. Dykstra, P.G. Jasien, Derivative Hartree-Fock theory to all orders, *Chem. Phys. Lett.* 109 (1984) 388-393.
- [39] M.D.R. Kanis et al. Design and construction of molecular assemblies with large second-order optical nonlinearities quantum chemical aspects, *Chem. Rev.* 94 (1994) 195-242.
- [40] J.L. Oudar, Optical nonlinearities of conjugated molecules stilbene derivatives and highly polar aromatic compounds, *J. Chem. Phys.* 67 (1977) 446-457.
- [41] Y. Sheng, Y. Jiang, Polarizability and hyperpolarizability of push-pull quinoid molecules Simulation of donor-acceptor pairs, *J. Chem. Soc. Faraday Trans.* 94 (1998) 1829-1833.