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RESEARCH ARTICLE

STUDIES ON STRUCTURES, VIBRATIONAL FREQUENCIES AND FIRST-ORDER HYPERPOLARIZABILITY OF O-CHLOROBENZOYL CHLORIDE BASED ON DENSITY FUNCTIONAL THEORY CALCULATIONS

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ABSTRACT

The FT-IR and FT-Raman spectra of O-chlorobenzoyl chloride (OCBC) were recorded in the regions 4000-400 cm^{-1} and 3500-100 cm^{-1} . The fundamental vibrational frequencies and intensity of vibrational bands were evaluated using density functional theory (DFT) and standard B3LYP/6-311+G** basis set combination. The vibrational spectra were interpreted, with the aid of normal coordinate analysis based on a scaled quantum mechanical (SQM) force field. The infrared and Raman spectra were also predicted from the calculated intensities. Comparison of simulated spectra with the experimental spectra provides important information about the ability of the computational method to describe the vibrational modes. Unambiguous vibrational assignment of all the fundamentals was made using the total energy distribution (TED). Further, density functional theory (DFT) combined with quantum chemical calculations to determine the first-order hyperpolarizability.

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INTRODUCTION

Benzoyl Chloride belongs to acyl halides. OCBC, is a halogenated aromatic monocarboxylic acid indicated for use as a pharmaceutical intermediate. It is also used in the synthesis of benzophenone and its derivatives used in manufacturing pesticides, pharmaceuticals, perfume fixative, polymerization catalyst, benzoylating agents and dyestuffs. So the vibrational studies of these molecules would be helpful in understanding the various types of bonding and normal modes of vibration involved in this system.

Quantum chemical computational methods have proved to be an essential tool for interpreting and predicting the vibrational spectra (Hess et al., 1986 and Pulay et al., 1993). A significant advancement in this area was made by combining semi empirical quantum mechanical method; ab initio quantum mechanical method and density functional theory (DFT), each method having its own advantage (Hehre et al., 1986; Shin et al., 1998; Ziegler, 1991 and Blom et al., 1976). In scaled quantum mechanical (SQM) approach, the systematic errors of the computed harmonic force field are corrected by a few scale factors which are found to be well transferable between chemically related molecules (Pulay et al., 1993; De Mare et al., 1994 and Yamakita et al., 1995) and were recommended for general use.

In the present investigation, the vibrational analysis of OCBC using the SQM force field method based on DFT calculation was presented. The infrared and Raman spectra of the title compound were also simulated utilizing the computed dipole derivatives for IR and polarisability derivatives for Raman activities. Further, we adopted density functional theory (DFT) combined with quantum chemical calculations to determine the first-order hyperpolarizability.

MATERIALS AND METHODS

Spectroscopically pure OCBC was obtained from Lancaster chemical company, U.K. and used as such for the spectral measurements. The room temperature Fourier transform infrared spectra of OCBC was recorded in the 4000-400 cm^{-1} region at a resolution of $\pm 1 \text{ cm}^{-1}$, using BRUKER IFS-66V vacuum Fourier transform spectrometer, equipped with an MCT detector, a KBr beam splitter and globar source. The FT-Raman spectrum was recorded on the same instrument with FRA-106 Raman accessories in the region 3500-100 cm^{-1} . Nd:YAG laser operating at 200 mW power with 1064 nm excitation was used as source.

Computational details

In order to find the most optimized molecular geometry, the energy and vibrational frequency calculations were carried out for OCBC with GAUSSIAN 98W software package (Frisch et al., 2002) using the B3LYP functional (Becke et al., 1993 and Lee et al., 1998) standard 6-311+G**

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(large) basis sets. The Cartesian representation of the theoretical force constants have been computed at optimized geometry by assuming C_s point group symmetry. Scaling of the force field was performed according to the SQM procedure (Pulay et al., 1983 and Rauhut et al., 1995) using selective scaling in the natural internal coordinate representation (Fogarasi et al., 1985 and 1992). Transformation of the force field and subsequent normal coordinate analysis including the least square refinement of the scale factors, calculation of the total energy distribution (TED) and the prediction of IR and Raman intensities were done on a PC with the MOLVIB program (version 7.0-G77) (Sundius, 1990 and 2002). For the plots of simulated IR and Raman spectra, pure Lorentzian band shapes were used with a bandwidth of 10 cm^{-1} .

The symmetry of the molecule was also helpful in making vibrational assignments. By combining the results of the GAUSSVIEW program (Frisch et al., 2000) with symmetry considerations, vibrational frequency assignments were made with a high degree of confidence. The defined local symmetry coordinates form complete set and matches quite well with the motions observed using the GAUSSVIEW program.

Prediction of Raman intensities

The Raman activities (S_i) calculated with the GAUSSIAN 98W program and adjusted during the scaling procedure with MOLVIB were subsequently converted to relative Raman intensities (I_i) using the following relationship derived from the basic theory of Raman scattering (Polavarapu, 1990; Keresztury et al., 1993 and 2002).

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

Where v_o is the exciting frequency (in cm^{-1}), v_i is the vibrational wavenumber of the i^{th} normal mode; h , c and k are fundamental constants, and f is a suitably chosen common normalization factor for all peak intensities.

Essentials of nonlinear optics related to β

The nonlinear response of an isolated molecule in an electric field $E_i(\omega)$ can be represented as a Taylor expansion of the total dipole moment μ_i induced by the field:

$$\mu_i = \mu_0 + \alpha_{ij} E_j + \beta_{ijk} E_i E_j + \dots$$

Where α is linear polarizability, μ_0 the permanent dipole moment and β_{ijk} are the first-order hyperpolarizability tensor components.

The components of first-order hyperpolarizability can be determined using the relation

$$\beta_i = \beta_{iii} + \frac{1}{3} \sum_{i \neq j} (\beta_{jji} + \beta_{jjj} + \beta_{jji})$$

Using the x , y and z components the magnitude of the total static dipole moment (μ), isotropic polarizability (α_0), first-order hyperpolarizability (β_{total}) tensor, can be calculated by the following equations:

$$\mu_1^0 = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2}$$

$$\beta_{\text{tot}} = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2}$$

The complete equation for calculating the first-order hyperpolarizability from GAUSSIAN 98W output is given as follows (Frisch et al., 2002):

$$\beta_{\text{tot}} = [(\beta_{xxx} + \beta_{yy} + \beta_{zz})^2 + (\beta_{yy} + \beta_{yz} + \beta_{yx})^2 + (\beta_{zz} + \beta_{zx} + \beta_{zy})^2]$$

The β components of GAUSSIAN 98W output are reported in atomic units, the calculated values have to be converted into electrostatic units ($1 \text{ a.u.} = 8.3693 \times 10^{-33} \text{ esu}$).

Before calculating the hyperpolarizability for the investigated compound, the optimization has been carried out in the UHF (unrestricted open-shell Hartree-Fock) level. Molecular geometries were fully optimized by Berny's optimization algorithm using redundant internal coordinates. All optimized structures were confirmed to be minimum energy conformations. An optimization is complete when it has converged. i.e., when it has reached a minimum on the potential energy surface, thereby predicting the equilibrium structures of the molecules. This criterion is very important in geometry optimization. The inclusion of d polarization and double zeta function in the split valence basis set is expected to produce a marked improvement in the calculated geometry (Becke, 1993). At the optimized structure, no imaginary frequency modes were obtained proving that a true minimum on the potential energy surface was found. The electric dipole moment and dispersion free first-order hyperpolarizability were calculated using finite field method. The finite field method offers a straight forward approach to the calculation of hyperpolarizabilities (Cohen et al., 1964). All the calculations were carried out at the DFT level using the three-parameter hybrid density functional B3LYP and a 3-21 G (d, p) basis set.

RESULTS

Molecular geometry

The optimized molecular structure of OCBC was shown in Fig.1. The global minimum energy obtained by the DFT structure optimization was presented in Table 1. The optimized geometrical parameters obtained by the large basis set calculation were presented in Table 2.

Detailed description of vibrational modes can be given by means of normal coordinate analysis (NCA). For this purpose, the full set of 48 standard internal coordinates containing 12 redundancies were defined as given in Table 3. From these, a non-redundant set of local symmetry coordinates were constructed by suitable linear combinations of internal coordinates in Table 4. The theoretically calculated DFT force fields were transformed in this later set of vibrational coordinates and used in all subsequent calculations.

Table 1. Total energies of OCBC, calculated at DFT (B3LYP)/6-31G* and (B3LYP)/6-311+G level**

Method	Energies (Hartrees)
6-31G*	-1264.54843900
6-311+G**	-1264.76957264

Analysis of vibrational spectra

The 36 normal modes of OCBC are distributed among the symmetry species as $\Gamma_{3N-6} = 25 A'$ (in-plane) + 11 A'' (out-of-plane), and in agreement with C_s symmetry. All the vibrations were active both in Raman scattering and infrared absorption. In the Raman spectrum the in-plane vibrations (A') give rise to polarized bands while the out-of-plane ones (A'') to depolarized band.

The detailed vibrational assignments of fundamental modes of OCBC along with calculated IR, Raman intensities and normal mode descriptions (characterized by TED) were

$$RMS = \sqrt{\frac{1}{n-1} \sum_i^n (u_i^{calc} - u_i^{exp})^2}$$

Table 2. Optimized geometrical parameters of OCBC obtained by B3LYP/ 6-311+G density functional calculations**

Bond length	Value(Å)	Bond angle	Value(Å)	Dihedral angle	Value(Å)
C2-C1	1.41414	C3-C2-C1	120.3423	C4-C3-C2-C1	0.98560
C3-C2	1.39565	C4-C3-C2	120.34093	C5-C4-C3-C2	-0.65574
C4-C3	1.39287	C5-C4-C3	120.12402	C6-C5-C4-C3	-0.29085
C5-C4	1.39512	C6-C5-C4	119.62347	C7-C1-C6-C5	177.02637
C6-C5	1.38942	C7-C1-C6	120.69086	O8-C7-C1-C6	-155.47786
C7-C1	1.48656	O8-C7-C1	127.66669	C19-C7-C1-C6	24.83177
O8-C7	1.18951	C19-C7-C1	114.17689	C110-C2-C1-C6	-178.44100
C19-C7	1.84426	C110-C2-C1	122.98120	H11-C3-C2-C1	-179.02943
C110-C2	1.74763	H11-C3-C2	118.93682	H12-C4-C3-C2	179.56864
H11-C3	1.08446	H12-C4-C3	119.43315	H13-C5-C4-C3	179.97229
H12-C4	1.08623	H13-C5-C4	120.56340	H14-C6-C5-C4	-179.71471
H13-C5	1.08540	H14-C6-C5	119.93207		
H14-C6	1.08284				

*for numbering of atom refer Fig. 1

Table 3. Definition of internal coordinates of OCBC

No(i)	symbol	Type	Definition
Stretching			
1-4	r _i	C-H(aro)	C3-H11,C4-H12,C5-H13,C6-H14
5	R _i	C-Cl(aro)	C2-Cl10
6	R _i	C-Cl (sub)	C7-C19
7	p _i	C-O(sub)	C7-O8
8-13	P _i	C-C(ring)	C1-C2,C2-C3,C3-C4,C4-C5,C5-C6,C6-C1
14	P _i	C-C(sub)	C7-C1
Bending			
15-22	θ _i	C-C-H	C2-C3-H11,C4-C3-H11, C3-C4-H12,C5-C4-H12,C4-C5-H13, C6-C5-H13,C5-C6-H14,C1-C6-H14
23	β _i	C-C-Cl	C1-C7-Cl9
24-25	β _i	C-C-Cl	C1-C2-Cl10,C3-C2-Cl10
26	γ _i	C-C-O	C1-C7-O8
27-28	α _i	C-C-C	C6-C1-C7,C2-C1-C7
29-34	α _i	C-C-C(ring)	C1-C2-C3,C2-C3-C4,C3-C4-C5, C4-C5-C6,C5-C6-C1,C6-C1-C2
Out-of-plane			
35-38	ω _i	C-H	H11-C3-C2-C4,H12-C4-C3-C5, H13-C5-C4-C6,H14-C6-C5-C1
39	ω _i	C-Cl	C110-C2-C1-C3
40	ω _i	C-C	C7-C1-C2-C6
41	ω _i	C-Cl	C1-C7-O8-Cl9
Torsion			
42-47	τ _i	τring	C1-C2-C3-C4,C2-C3-C4-C5, C3-C4-C5-C6,C4-C5-C6-C1, C5-C6-C1-C2,C6-C1-C2-C3
48	τ _i	τC-Cl	C2(C6)-C1-C7-O8(Cl9)

*for numbering of atom refer Fig. 1

reported in Table 5. For visual comparison, the observed and simulated FT-IR and FT-Raman spectra of OCBC are produced in a common frequency scales in Fig. 2 & Fig. 3. Root mean square (RMS) values of frequencies were obtained in the study using the following expression,

DISCUSSION

The RMS error of the observed and calculated frequencies (unscaled / B3LYP/6-311+G**) of OCBC was found to be 109 cm⁻¹. This is quite obvious; since the frequencies calculated on the basis of quantum mechanical force fields usually differ appreciably from observed

frequencies. This is partly due to the neglect of anharmonicity and partly due to the approximate nature of the quantum mechanical methods. In order to reduce the

present study the C–H vibrations of the title compounds are observed at 3097, 3074, 3026 cm^{-1} in the FT-IR spectrum and 3082 in FT-Raman for OCBC.

Table 4. Definition of local symmetry coordinates and the value corresponding scale factors used to correct the force fields for OCBC

No.(i)	Symbol ^a	Definition ^b	Scale factors used in calculation
1-4	C-H	r_1, r_2, r_3, r_4	0.920
5	C-Cl(aro)	R5	0.927
6	C-Cl(sub)	R6	0.927
7	C-O	p7	0.918
8-13	C-C	P8, P9, P10, P11, P12, P13	0.902
14	C-C(sub)	P14	0.902
15-18	C-C-H	$(\theta_{15}-\theta_{16})/\sqrt{2}, (\theta_{17}-\theta_{18})/\sqrt{2},$ $(\theta_{19}-\theta_{20})/\sqrt{2}, (\theta_{21}-\theta_{22})/\sqrt{2}$	0.942
19	C-C-Cl	β_{23}	0.947
20	C-C-Cl	$(\beta_{24}-\beta_{25})/\sqrt{2}$	0.947
21	C-C-O	γ_{26}	0.979
22	C-C-C	$(\alpha_{27}-\alpha_{28})/\sqrt{2}$	0.986
23	bring	$(\alpha_{29}-\alpha_{30}+\alpha_{31}-\alpha_{32}+\alpha_{33}-\alpha_{34})/\sqrt{6}$	0.986
24	bring	$(2\alpha_{29}-\alpha_{30}-\alpha_{31}+2\alpha_{32}-\alpha_{33}-\alpha_{34})/\sqrt{12}$	0.986
25	bring	$(\alpha_{30}-\alpha_{31}+\alpha_{33}-\alpha_{34})/2$	0.986
26	C-H	$\omega_{35}, \omega_{36}, \omega_{37}, \omega_{38}$	0.963
27-30	C-Cl	ω_{39}	0.965
31	C-C	ω_{40}	0.935
32	C-Cl	ω_{41}	0.963
33	tring	$(\tau_{42}-\tau_{43}+\tau_{44}-\tau_{45}+\tau_{46}-\tau_{47})/\sqrt{6}$	0.935
34	tring	$(\tau_{42}-\tau_{44}+\tau_{45}-\tau_{47})/2$	0.935
35	tring	$(-\tau_{42}+2\tau_{43}-\tau_{44}-\tau_{45}+2\tau_{46}-\tau_{47})/\sqrt{12}$	0.935
36	τ C-Cl	$\tau_{48}/4$	0.945

^a These symbols are used for description of the normal modes by TED in Table 5.

^b The internal coordinates used here are defined in Table 3.

overall deviation between the unscaled and observed fundamental frequencies, scale factors were applied in the normal coordinate analysis and the subsequent least square fit refinement algorithm resulted into a very close agreement between the observed fundamentals and the scaled frequencies. Refinement of the scaling factors applied in this study achieved a weighted mean deviation of 9 cm^{-1} between the experimental and scaled frequencies of the title compound.

C-C vibrations:

The bands between 1650–1480 cm^{-1} are assigned to C–C stretching modes (Sathyanarayana, 2004). In the present study, the carbon stretching vibrations of the title compound have been observed at 1638, 1588, 1568 cm^{-1} in the FT-IR and 1592, 1574 cm^{-1} in FT-Raman spectrum and are presented in Table 5. These assignments are in good agreement with literature (George Socrates, 2001 and Krishna kumar et al., 2003).

C-H vibrations:

Aromatic compounds commonly exhibit multiple weak bands in the region 3100–3000 cm^{-1} due to aromatic C–H stretching vibrations. The bands due to C–H in-plane ring bending vibration interacting with C–C stretching vibration are observed as a number of m-w intensity sharp bands in the region 1300–1000 cm^{-1} . C–H out-of-plane bending vibrations are strongly coupled vibrations and occur in the region 900–667 cm^{-1} (Mohan, 2001). Accordingly, in the

C-Cl vibrations:

C–Cl vibrations are found in the region below 1000 cm^{-1} . The C–Cl stretching frequency is generally observed in the region 800–600 cm^{-1} depending on the configuration and conformation of the compound (Lakshmaiah et al., 1989 and George et al., 1985). Based on this, the FT-IR bands at 766, 726, 707, 668, 642 cm^{-1} and FT-Raman bands at 664, 647 cm^{-1} have been assigned to C–Cl stretching in OCBC.

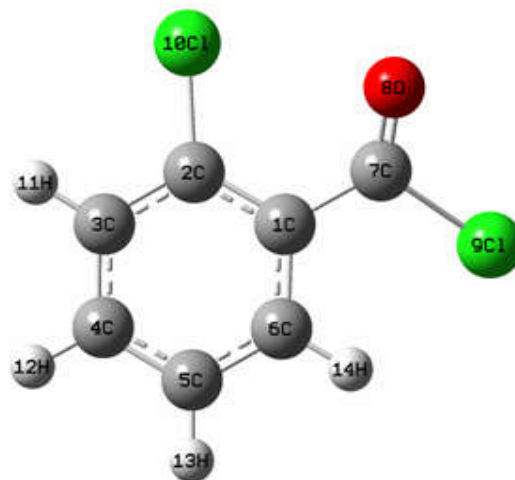


Fig. 1. The optimized molecular structure of OCBC

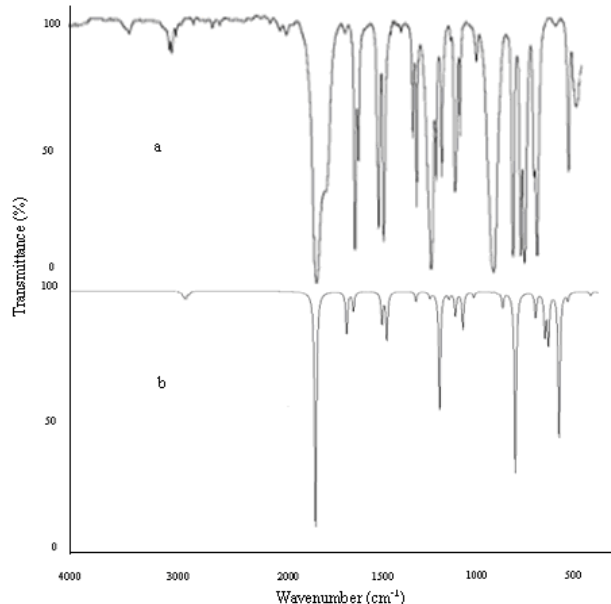


Fig. 2 FT-IR spectra of OCBC
(a) Observed (b) Calculated with B3LYP/6-311+G**

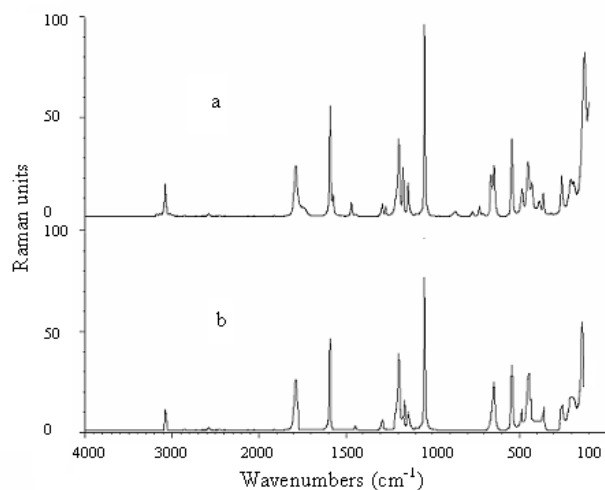


Fig. 3 FT-Raman spectra of OCBC
(a) Observed (b) Calculated with B3LYP/6-311+G**

C-O vibrations:

The carbonyl stretching frequency is very sensitive to the factors that disturb the nature of the carbonyl group and its precise frequency is characteristic of the type of the carbonyl compound being studied. Particularly detailed correlations have been made for the carbonyl bond stretching frequency. The carbonyl stretching frequency has been most extensively studied by infrared spectroscopy. This multiply bonded group is highly polar ($>C^{\delta+}=O^{\delta-}$) and therefore gives rise to an intense infrared absorption band. The carbon-oxygen double bond is formed by the p_{π} - p_{π} bonding between carbon and oxygen. Because of the different electronegativities of carbon and oxygen atoms, the bonding electrons are not equally distributed between the two atoms. The following two resonance forms contribute to the bonding of the carbonyl group $>C=O \leftrightarrow C^+-O^-$. The lone pair of electrons on oxygen also determines the nature of the carbonyl group. The position of the C=O stretching vibration

is very sensitive to various factors such as the physical state, electronic effects by substituents, ring strains, etc. (Sathyanarayana et al., 2004). Consideration of these factors provides further information about the environment of the C=O group. The carbonyl stretching generally occurs as a strong absorption in the region from 1730 to 1645 cm^{-1} . This portion of the infrared spectrum is most useful because the position of the carbonyl absorption is quite sensitive to substitution effects and the geometry of the molecule. Accordingly, in the present investigation, the peaks identified at 1790 and 1786 cm^{-1} have been assigned to C=O stretching vibrations for OCBC.

Ring vibrations:

Many ring modes are affected by the substitution in the aromatic ring. In the present study, the bands absorbed at 1192, 1166, 1138, 1067, 1043, 957, 866 cm^{-1} and 486, 440 cm^{-1} have been designated to ring in-plane and out-of-plane bending modes, respectively.

Hyperpolarizability calculations

The first-order hyperpolarizability (β_{ijk}) of the novel molecular system of OCBC is calculated using 3-21 G (d,p) basis set based on finite field approach. Hyperpolarizability is a third rank tensor that can be described by a $3 \times 3 \times 3$ matrix. It strongly depends on the method and basis set used. The 27 components of 3D matrix can be reduced to 10 components due to Kleinman symmetry (Kleinman, 1962). The calculated first-order hyperpolarizability (β_{total}) of OCBC is 1.289537×10^{-30} esu, which is nearly seven times that of urea (0.1947×10^{-30} esu). The calculated dipole moment (μ) and first-order hyperpolarizability (β) are shown in Table 6. The theoretical calculation seems to be more helpful in determination of particular components of β tensor than in establishing the real values of β . Domination of particular components indicates on a substantial delocalization of charges in those directions. It is noticed that in β_{xxx} (which is the principal dipole moment axis and it is parallel to the charge transfer axis) direction, the biggest values of hyperpolarizability are noticed and subsequently delocalization of electron cloud is more in that direction. The higher dipole moment values are associated, in general, with even larger projection of β_{total} quantities. The electric dipoles may enhance, oppose or at least bring the dipoles out of the required net alignment necessary for NLO properties such as β_{total} values. The connection between the electric dipole moments of an organic molecule having donor-acceptor substituent and first hyperpolarizability is widely recognized in the literature (Prasad et al., 1991). The maximum β was due to the behavior of non-zero μ value. One of the conclusions obtained from this work is that non-zero μ value may enable the finding of a non-zero β value. Of course Hartree-Fock calculations depend on the mathematical method and basis set used for a polyatomic molecule.

Conclusion

In this work, the SQM force field method based on DFT calculations at the B3LYP/6-311+G** level have been carried out to analyze the vibrational frequencies of OCBC. Refinement of the scaling factors applied in this study achieved a weighted RMS deviation of 9 cm^{-1} between the experimental and scaled frequencies. This close agreement established between the experimental and scaled frequencies obtained using large basis set (6-311+G**) calculations has proved to be more reliable and accurate than the calculations using lower basis sets. The first-order hyperpolarizability

Table 5. Detailed assignments of fundamental vibrations of OCBC by normal mode analysis based on SQM force field calculation.

No.	Symmetry species Cs	Observed frequency (cm ⁻¹)		Calculated frequency (cm ⁻¹) with B3LYP/6-311+G ^{**} force field				TED (%) among type of internal coordinates ^c
		Infrared	Raman	Unscaled	Scaled	IR ^a A _i	Raman ^b I _i	
1	A'	3113 w		3162	3117	0.133	67.02	CH(99)
2	A'	3097 w	3082 s	3254	3095	0.103	91.11	CH(99)
3	A'	3074 vw		3213	3070	0.345	22.70	CH(99)
4	A'	3026 vw		3194	3028	0.307	81.88	CH(99)
5	A'	1942 w		2145	1947	0.732	76.02	CO(47),gClO(18),CC(12),tCCl(7),bCCl(5)
6	A'	1786 vs	1790 s	1992	1791	0.127	63.50	CO(68),bCH(18),bring(12)
7	A'	1638 s		1936	1641	0.937	23.18	CC(68),bCH(16),bring(11)
8	A''	1588 w	1592 vs	1803	1601	0.796	1.599	CC(50), bCH(44)
9	A'	1568 s	1574 s	1773	1572	0.39	16.26	CC(52), bCH(35),bCC(8)
10	A''	1463 s		1623	1467	0.654	3.34	CC(89)
11	A'	1439 s		1672	1442	0.486	16.42	bCH(66),CC(19),bCC(8)
12	A''	1348 w		1536	1352	0.373	14.98	CC(56),bring(26),bCH(12)
13	A'	1287 vs		1514	1292	0.324	17.87	bCH(86),CC(13)
14	A''	1267 s		1472	1271	0.207	6.41	CC(41),bCH(38),CCl(9),bCC(8)
15	A''	1192 s	1196 s	1388	1196	0.028	5.19	bring(47),CC(23),CCl(17),bCH(10)
16	A'	1166 s	1171 s	1377	1169	0.082	7.43	bring(77),bCH(19)
17	A'	1138 s	1142 s	1342	1142	0.723	4.28	tring(83),gCH(16)
18	A'	1067 s		1317	1069	0.558	8.39	tring(81),gCH(11),gCC(5)
19	A'	1043 s	1047 s	1243	1046	0.744	1.14	tring(70),CO(6),gCC(6),gCH(6)
20	A''	957 vs		1047	959	0.155	6.99	bring(21),CC(21),bCO(14),gClO(14),gCH(7),CCl(6)
21	A''	866 s		1038	870	0.996	6.11	gCH(50),gCC(24),tring(11),bCO(6),bCCl(5)
22	A''	766 s		921	768	0.06	0.86	gCCl(26),gCC(24),bring(12),bCO(9),gCH(7),tring(7)
23	A'	726 s		942	729	0.03	3.54	gCCl(31),gCC(19),bring(10),gCH(9),tring(9),gClO(6)
24	A'	707 s		901	711	0.351	11.43	gCCl(36),gClO(27),bring(9),bCC(6)
25	A'	668 s	664 s	872	671	0.147	0.62	bCCl(23),CO(18),gClO(18),bCO(13),tring(6),gCH(5)
26	A''	642 s	647 w	832	647	0.86	1.16	bCCl(20),tring(11),CC(11),gCC(10),gClO(8),bCC(8)
27	A'		545 s	743	548	0.79	5.65	tring(38),gCCl(25),gCH(9),CO(7),tCCl(6)
28	A'		486 s	646	491	0.68	6.44	tring(43),tCCl(23),gCC(16),CO(7)
29	A''	460 s	451 s	620	464	0.291	0.18	tCCl(38),CCl(16),gClO(11),bring(10),gCH(10)
30	A''	440 s		598	445	0.143	0.12	bCCl(28),tring(16),CO(13),bCC(10),gClO(7)
31	A'		431 s	586	436	0.876	4.78	tCCl(18),CO(16),bCCl(12),bCO(12),bring(12),CC(10)
32	A'		363 w	547	367	0.10	1.36	bCCl(42),CO(12),gCC(10),gCCl(9),tring(7)
33	A'		260 s	428	266	0.103	2.43	CO(34),gCC(24),gCCl(14),tring(13)
34	A'		247 s	412	253	0.141	0.53	CO(47),bCCl(18),bCC(14),gClO(10)
35	A'		173 w	363	177	0.129	3.03	tring(33),CCl(21),CO(15),gCC(12),tCCl(11)
36	A'		141 w	244	145	0.35	0.28	tCCl(40),CO(37),CCl(16)

Abbreviations used: b, bending; g, wagging; t, torsion; s, strong; vs, very strong; w, weak; vw, very weak;

^a Relative absorption intensities normalized with highest peak absorption

^b Relative Raman intensities calculated by Eq.1 and normalized to 100.

^c For the notations used see Table 4.

Table 6. The dipole moment (μ) and first-order hyperpolarizability (β) of OCBC derived from DFT calculations

β_{xxx}	24.6798306
β_{xxy}	4.1106034
β_{xyy}	2.7371947
β_{yyy}	-3.5868028
β_{zxx}	-118.5181275
β_{syz}	-0.7739399
β_{zyy}	1.3003588
β_{xzz}	-12.4290667
β_{yzz}	5.030306
β_{zzz}	-36.030306
β_{total}	1.289537
μ_x	2.1196756
μ_y	0.0228399
μ_z	0.570441
μ	2.195211

Dipole moment (μ) in Debye, hyperpolarizability $\beta(-2\omega;\omega,\omega)$ 10^{-30} esu.

(β_{ijk}) of the novel molecular system of OCBC is calculated using 3-21 G (d,p) basis set based on finite field approach. The calculated first-order hyperpolarizability (β_{total}) of OCBC is 1.289537×10^{-30} esu, which is nearly seven times that of urea (0.1947×10^{-30} esu).

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REFERENCES

- Becke, A.D.1993. Density-functional thermochemistry. III. The role of exact exchange. *J.Chem. Phys.* 98: 5648-5652.
- Blom, C.E., and Altona, C. 1976. Application of self-consistent-field *ab initio* calculations to organic molecules. *Mol. Phys.* 31:1377-1391.

- Cohen, H.D., and Miroslav Synek 1964. Accurate Analytical Self-Consistent Field Functions for Atoms. VI. The Ground States of Mo⁺ and Mo. *Phys. Rev.* 133: 1263-1266.
- De Mare, G.R., Panchenko, Y.N., and Bock, C.W. 1994. An MP2/6-31G*/MP2/6-31G* vibrational analysis of s-trans and s-cis-acryloyl fluoride, CH₂=CH-CF=O. *J. Phys. Chem.* 98: 1416-1420.
- Fogarasi, G., and Pulay, P. 1985. In: Durig, J.R., Editor, *Vibrational Spectra and Structure* vol. 14, Elsevier, Amsterdam, p. 125.
- Fogarasi, G., Xhov, X., Taylor P.W., and Pulay, P. 1992. Geometry optimization in redundant internal coordinates. *J. Am. Chem. Soc.* 114: 8191-8201.
- Frisch, M.J., Trucks, G.W., Schlegel, H.B., Scuseria, G.E., Robb, M.A., Cheesman, J.R., Zakrzewski, V.G., Montgomery Jr., J.A., Stratmann, R.E., Burant, J.C., Dapprich, S., Millam, J.M., Daniels, A.D., Kudin, K.N., Strain, M.C., Farkas, O., Tomasi, J., Barone, V., Cossi, M., Cammi, R., Mennucci, B., Pomelli, C., Adamo, C., Clifford, S., Ochterski, J., Petersson, G.A., Ayala, P.Y., Cui, Q., Morokuma, K., Roga, N., Salvador, N., Dannenberg, J.J., Malick, D.K., Rabuck, A.D., Rahavachari, K., Foresman, J.B., Cioslowski, J., Ortiz, J.V., Baboul, A.G., Stefanov, B.B., Liu, G., Liashenko, A., Piskorz, P., Komaromi, I., Gomperts, R., Martin, R.L., Fox, D.J., Keith, T., Al-Laham, M.A., Peng, C.Y., Nanayakkara, A., Challa-Combe, M., Gill, P.M.W., Johnson, B., Chen, W., Wong, M.W., Andres, J.L., Gonzalez, C., Head-Gordon, M., Replogle, E.S., and Pople, J.A. 2002. Gaussian 98, Revision A 11.4, Gaussian Inc., Pittsburgh, PA.
- Frisch, A., Nielson, A.B., and Holder, A.J. 2000. Gaussview Users Manual, Gaussian Inc., Pittsburgh, PA.
- George Socrates. 2001. *Infrared and Raman Characteristic Group Frequencies - Tables and Charts* (third ed.), John Wiley & Sons, Chichester.
- George, W.O., Goodfield, J.E., and Maddams, W.F. 1985. Conformations of chlorinated hydrocarbons. A vibrational spectroscopic study of 2-chlorobutane, 2,4-dichloropentane and 2,4,6-trichloroheptane. *Spectrochim. Acta A.* 41: 1243-1250.
- Hehre, W. J., Random, L., Schleyer, P.V.R., and Pople, J.A. 1986. *Ab Initio Molecular Orbital Theory*, Wiley, New York. P.548.
- Hess Jr., B.A., Schaad, J., Carsky, P., and Zahradnik, R. 1986. *Ab initio Vibrational Spectra and Their Use in the Identification of Unusual Molecules*. *Chem. Rev.* 86: 709-730.
- Keresztury, G., Holly, S., Varga, J., Besenyi, G., Wang, A.V., and Durig, J.R. 1993. Vibrational spectra of monothiocarbamates-II. IR and Raman spectra, vibrational assignment, conformational analysis and ab initio calculations of S-methyl-N,N-dimethylthiocarbamate. *Spectrochim. Acta A.* 49: 2007 - 2017.
- Keresztury, G. 2002. in: Chalmers, J.M., and Griffiths, P.R.(Eds). 2002. *Handbook of Vibrational Spectroscopy* vol.1, John Wiley & Sons Ltd. p.71.
- Kleinman, D.A. 1962. Nonlinear Dielectric Polarization in Optical Media. *Phys. Rev.* 126,1977-1979.
- Krishna kumar, V., and John Xavier, R. 2003. Normal coordinates analysis of vibrational spectra of 2-methylindoline and 5-hydroxyindane. *Indian J. Pure Appl. Phys.* 41: 95-99.
- Lakshmaiah, B., and Ramana Rao, G. 1989. Vibrational analysis of substituted anisoles. I-Vibrational spectra and normal coordinate analysis of some fluoro and chloro compounds. *J. Raman Spectrosc.* 20: 439-448.
- Lee, C., Yang, W., and Parr, R.G. 1998. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B.* 37: 785-789.
- Mohan, J. 2001. *Organic Spectroscopy-Principles and Applications*, second ed., Narosa Publishing House, New Delhi.
- Polavarapu, P.L. 1990. *Ab initio Raman and Raman optical activity spectra*. *J. Phys. Chem.* 94: 8106-8112.
- Prasad, P.N., and Williams, D.J. 1991. *Introduction to Nonlinear Optical Effects in Molecules and Polymers*, Wiley, New York.
- Pulay, P., Fogarasi, G., Pongor, G., Boggs, J.E., and Vargha, A. 1983. Combination of theoretical ab initio and experimental information to obtain reliable harmonic force constants. Scaled quantum mechanical (QM) force fields for glyoxal, acrolein, butadiene, formaldehyde, and ethylene. *J. Am. Chem. Soc.* 105: 7037-7047.
- Pulay, P., Zhou, X., and Fogarasi, G. 1993. in: Fransto, R. (Ed.), *NATO AS Series*, Kluwer, Dordrecht, Vol.C, 406: p.99.
- Rauhut, G., and Pulay, P. 1995. Transferable Scaling Factors for Density Functional Derived Vibrational Force Fields. *J. Phys. Chem.* 99: 3093-3100.
- Sathyanarayana, D.N. 2004. *Vibrational Spectroscopy—Theory and Applications*, second ed., New Age International (P) Limited Publishers, New Delhi.
- Shin, D.N., Hahn, J.W., Jung, K.H., and Ha, T.K. 1998. Study of the *cis* and *trans* conformers of 2-halophenols using coherent anti-Stokes Raman spectroscopic and quantum chemical methods. *J. Raman Spectrosc.* 29: 245-249.
- Sundius, T. 1990. Molvib - A flexible program for force field calculations. *J. Mol. Struct.* 218: 321-326.
- Sundius, T. 2002. Scaling of ab initio force fields by MOLVIB. *Vib. Spectrosc.* 29: 89-95.
- Sundius, T. 2002. MOLVIB (v.7.0), Calculation of harmonic force fields and vibrational modes of molecules, QCPE Program No. 807.
- Yamakita, Y., and Tasuni, M. 1995. Vibrational analyses of p-benzoquinodimethane and p-benzoquinone based on ab initio Hartree-Fock and second-order Moller-Plesset calculations. *J. Phys. Chem.* 99: 8524- 8534.
- Ziegler, T. 1991. Approximate density functional theory as a practical tool in molecular energetics and dynamics. *Chem. Rev.* 91: 651-667.
