

Experimental and theoretical determination of structural and vibrational properties of pentachlorophenol and pentachlorothiophenol

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ARTICLE INFO

Article history:

Received 26 July 2018

Received in revised form

11 September 2018

Accepted 8 October 2018

Available online 9 October 2018

Keywords:

Pentachlorophenol

Pentachlorothiophenol

Vibrational spectra

Bifurcated hydrogen bond

DFT

ABSTRACT

Fourier Transform Raman (3500–100 cm⁻¹) and Fourier Transform Infrared (4000–400 cm⁻¹) spectra were measured for Pentachlorophenol (PCP). Barrier to internal rotation, optimized geometry parameters, harmonic vibrational frequencies, along with Raman and infrared intensities were computed, for PCP and Pentachlorothiophenol (PCTP), using DFT and employing B3LYP functional with 6–311++G (d,p) basis set. Scaling was used for a better fit between the experimental and predicted frequencies. They agreed with rms error 8.4 and 7.6 cm⁻¹ for PCP and PCTP, respectively. A zero order normal coordinate analysis was made for PCP-OD, which is an isotopomer of PCP, by transferring the optimized force constants from PCP. This resulted in calculated frequencies that agreed with corresponding experimental frequencies with rms error 12.1 cm⁻¹. The vibrational assignments were made with the help of potential energy distribution (PED), eigenvectors, and frequency shifts expected on the basis of PED in PCP, and increased mass of deuterium and sulphur atoms. Geometry optimization was made for dimers of PCP and PCTP in order to lend theoretical support for the existence of bifurcated hydrogen bond in PCP and rule out such possibility for PCTP, at the same level of theory as used for the monomers.

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1. Introduction

Pentachlorophenol (PCP) is one of the nineteen possible congeners of substituted chlorophenols. It is known that PCP is hazardous to human health and ecosystem [1], as it is toxic and carcinogenic. In spite of this it found increasing applications in agriculture and pharmaceutical industries [2–7]. Hence PCP was extensively investigated with regard to nature of hydrogen bonding [8,9], phase transitions [9], vibrational spectra [10–14], and crystal structure [9,15]. It was one of the compounds investigated theoretically to understand the relationship between molecular structure and properties in a series of chlorophenols [16]. However vibrational spectroscopic investigations, reported by earlier investigators, in this regard have several deficiencies, unacceptable theoretical results, and hence not reliable (details are given in

section 5.4 on vibrational assignments). For example, Green et al. [10] and Faniran [11] disagree even on the tentative assignment of several fundamentals of PCP proposed by them on the basis of qualitative considerations; Czarnik-Matusewicz et al. [13], employing quantum chemical calculations, identified seven C–C stretching vibrations in PCP, instead of six, where as Pawlukoic et al. [14] assigned seven out-of-plane (CCL) wagging modes, instead of five; more over authors of these publications [13,14] preferred to avoid inclusion of numerical values of potential energy distribution (PED), which is the most important result of any normal coordinate treatment, without which it is impossible to draw meaningful conclusions. Further, from a survey of literature on PCP, we found that, computed Raman spectrum is not available; there is no theoretical attempt to substantiate the existence of bifurcated hydrogen bond inferred by Sakurai [15] from an analysis of nuclear quadrupole resonance and X-ray spectra.

Hence we thought that it is worthwhile to revisit experimental and theoretical investigation of PCP to address the above shortcomings. To this end, we propose to

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- 1) record FT-Raman and FTIR spectra of PCP, and
- 2) carry out DFT calculations on the molecule in order to: obtain torsional potential for rotation around the C–O bond in the ground state and identify the most stable rotational conformer; optimize the equilibrium geometry for the most stable rotational isomer and its dimer; and predict harmonic vibrational fundamentals and their IR and Raman intensities using scaling.

The situation with regard to PCP-OD is no different from that of PCP. In the case of PCTP, except for a report of vibrational frequencies by Green et al. [10], no other work seems to be reported. It is well-known that to assist with the assignment of vibrational frequencies of a given molecule, the spectra of its deuterated analogues, wherever possible, were abundantly used. Such is not the case with related molecules such as PCP and PCTP, wherein the only difference between the two molecules stems from the presence of sulphur atom in PCTP in place of oxygen atom in PCP (note that oxygen and sulphur belong to group 6A of the periodic table). The required information is embedded in PED for PCP, which can be employed advantageously for correct assignment of related fundamentals of PCTP, along with its PED and eigen vectors. The process will be made clear in section 5.4 dealing with vibrational assignments. Hence we felt the need to undertake

- (i) the normal coordinate analysis of PCP-OD. Optimized force constants from PCP will be used for this purpose.
- (ii) the DFT calculations on pentachlorothiophenol (PCTP), for its barrier, geometry, dimer, vibrational frequencies, and IR and Raman intensities.

2. Spectral measurements

Pure sample of solid PCP was purchased from Tokyo Kasei Kogyo Co. Ltd, Japan. It was used, as such for spectral measurements.

Fourier transform Raman spectrum of PCP was measured with RFS 100 FT-Raman spectrometer, equipped with Ge diode detection system in the 3500–100 cm^{-1} Stokes region. Nd-YAG laser operating at 200mw power provided the exciting radiation at 1064 nm. The spectrum was a result of co-addition of 256 scans.

Fourier transform IR spectrum of the sample was recorded, in the spectral range 4000–400 cm^{-1} , using Nicolet-740 single beam spectrometer equipped with liquid nitrogen-cooled deuterated triglycine sulphate (DTGS) detector, by diluting the sample in KBr pellet. The spectrum was a result of co-addition of 32 scans. All the spectra (Raman, IR) were recorded at room temperature.

3. Computational considerations

Ab initio quantum chemical computations were carried out, applying the density functional theory (DFT) with Beck's three parameter hybrid exchange functional B3 [17], using Lee-Yang-Parr correlation functional [18] employing enlarged basis set 6-311++G (d,p), by means of the Gaussian 09/DFT program package [19]. The valence triple basis set i.e. 6-311++G (d,p) was augmented by 'd' polarization functions on heavy atoms (carbon, oxygen, chlorine) and 'p' polarization functions on hydrogen atom for better description of polar bonds of molecules [20,21]. It should be noted that usage of 'p' polarization functions on hydrogen atoms was necessitated to reproduce out-of-plane vibrations involving hydrogen atoms with fair degree of accuracy.

C–O is the only bond around which rotation is permitted in PCP. Hence to find rotational conformer of lowest energy, torsional potential energy was computed as a function of angle of rotation around the C–O bond in steps of 10° between 0° and 360°. This

yielded two-fold potential barrier of PCP with minimum energy at 0°. The lowest energy conformer was subjected to rigorous preliminary geometry optimization with simultaneous relaxation of all structural parameters. This process led to planar structure, which almost remained unchanged in the final optimization, yielding planar structure of C_s symmetry. On repeating the above process for PCTP around C–S bond we obtained two fold potential barrier with minimum energy again at rotation angle 0°. Geometry optimization gave planar structure of C_s symmetry in this case also. PCP consists of 13 atoms. Hence it has 33 vibrational fundamentals. In C_s symmetry they are distributed as 23 in-plane vibrations of a' -species and 10 out of plane vibrations of a'' -species, according to the formulae $2N-3$ and $N-3$, respectively, where N is the number of atoms in the molecule. All the vibrations of C_s symmetry are active in both infrared absorption and Raman scattering.

C_s planar structure was used as equilibrium reference geometry. Vibrational Cartesian force constants, harmonic vibrational wavenumbers, the dipole moment along with its derivatives, and the thermodynamic properties were computed first for PCP and PCTP. In all further calculations, the reference geometry and corresponding force constants were taken as initial data. The force constants were transformed using MOLVIB 7.0 program [22,23] into a non-redundant set of 33 natural internal coordinates (i.e. local symmetry coordinates), obtained from 46 redundant internal coordinates, according to the recommendations of Fogarasi et al. [24]. Note that the difference between PCP and PCTP is that in place of oxygen atom in PCP, sulphur atom is present in PCTP. In order to ensure a better fit of observed and calculated frequencies, the force constants were scaled using empirical scaling factors employing multiple scaling method of Fogarasi and Pulay [25] and Arenas et al. [26] with least square refinement of the scale factors, wherein the calculated normal frequencies of PCP or PCTP were fitted to their experimentally ascribed vibrational fundamentals. We would like to mention here that several of the experimental frequencies of PCP required for scaling were taken from Faniran [11] and those below 300 cm^{-1} were taken from inelastic neutron scattering measurements reported by Pawlukojs et al. [14]. The scaled general valence force field, obtained as above for PCP, was applied for the normal coordinate analysis of PCP-OD using MOLVIB 7.0 program [22,23]. In order to characterize the normal modes we computed potential energy distribution (PED), and relative IR absorption intensities [27], relative Raman scattering intensities [28,29], in addition to obtaining fundamental frequencies and corresponding eigenvectors. To understand the nature of intermolecular hydrogen bond in PCP and PCTP, their dimers were subjected to geometry optimization. IR and Raman spectra were simulated for PCP using a pure Lorentzian band shape with full width at half maximum (FWHM) of 10 cm^{-1} , in order to compare them with corresponding experimental spectra recorded by us.

4. Results

The two-fold potential barriers obtained for PCP and PCTP as explained in section 3 are shown graphically in Fig. 1. Optimized geometry obtained by solving self-consistent field equations iteratively, for PCP and PCTP, is shown in Fig. 2. The same geometry for dimers is shown in Fig. 3. These figures contain numbering of atoms also. The optimized structure parameters consisting of bond lengths, bond angles and dihedral angles of PCP and PCTP are presented in Table 1 along with their corresponding experimental values [15,30] in their most stable conformation. We have also entered structure parameters computed by earlier investigators [13] in this table. This table also contains calculated structure parameters of dimers of PCP and PCTP. Experimental IR and Raman frequencies, corresponding unscaled and scaled frequencies,

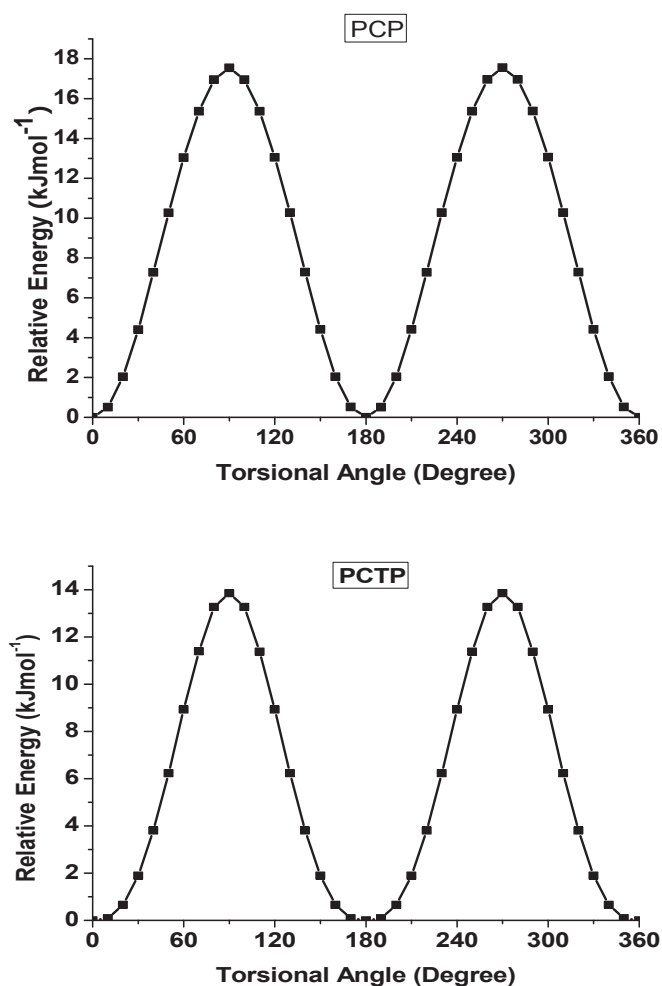


Fig. 1. Relative torsional potential energy as a function of rotational angle of PCP and PCTP computed at the DFT/B3LYP level using 6-311++G (d,p) basis set.

calculated IR and Raman intensities, potential energy distribution (PED) and vibrational assignments of PCP, PCP-OD, and PCTP are collected in Tables 2–4, respectively. Wilson's notation [31] is used to label different modes having their origin in the aromatic nucleus. A visual comparison of experimental and simulated FTIR and FT-Raman spectra of PCP is made in Figs. 4 and 5, respectively.

5. Discussion

5.1. Barrier to internal rotation

Fig. 1, is generated by taking relative energies of various rotamers, with respect to the rotational isomer of lowest energy on the ordinate and angle of rotation on the abscissa. From this figure we see that there are two barriers to internal rotation for PCP and PCTP each, one situated between 0° to 180° and the other is between 180° to 360° , proving the existence of two-fold barrier in one complete rotation. The height of the barrier hindering internal rotation, around C–O bond in PCP and C–S bond in PCTP is obtained as the difference between the energies of the point of lowest energy and the point of highest energy known as transition state [32], in Fig. 1. They occur at rotational angle of 0° and 90° , respectively, in both PCP and PCTP. The respective energy differences are $17.55 \text{ kJ mol}^{-1}$ ($4.20 \text{ kcal mol}^{-1}$) and $13.86 \text{ kJ mol}^{-1}$ ($3.31 \text{ kcal mol}^{-1}$) for PCP and PCTP. This is the same as 1466 cm^{-1}

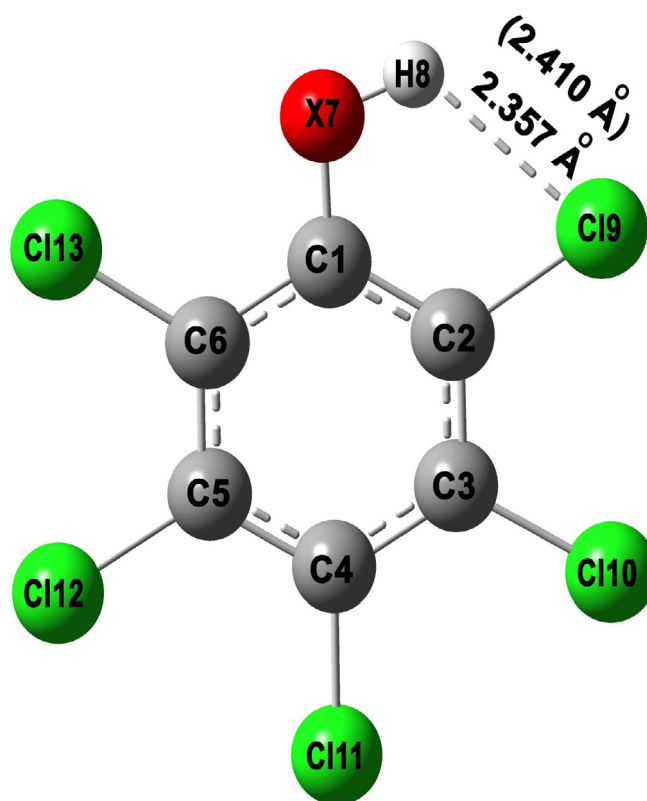


Fig. 2. Optimized molecular structure of PCP and PCTP monomer showing intra-molecular hydrogen bond with numbering of atoms ($E_{\text{PCP}} = -2605.6425$ Hartree and $E_{\text{PCTP}} = -2928.6058$ Hartree) (X: O for PCP; S for PCTP. Value in braces is for PCTP).

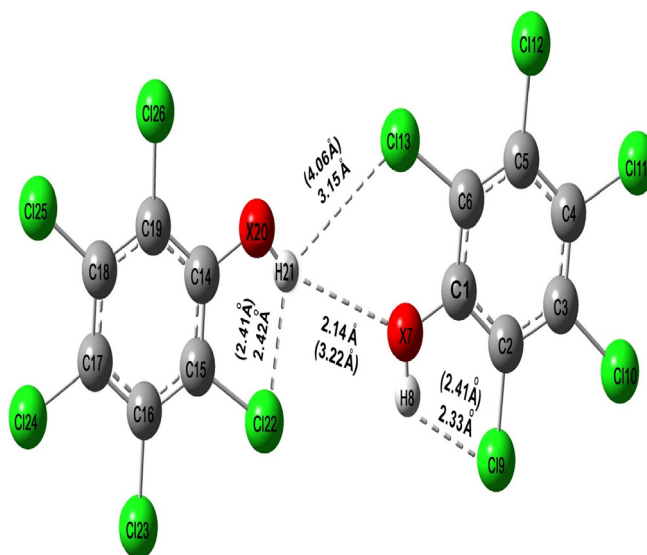


Fig. 3. Optimized molecular structure of PCP and PCTP dimers showing bifurcated and intra-molecular hydrogen bonds with numbering of atoms (dimer $E_{\text{PCP}} = -5211.2900$ Hartree & $E_{\text{PCTP}} = -5857.2151$ Hartree) (X: O for PCP dimer; S for PCTP dimer. Values in braces are for PCTP).

and 1159 cm^{-1} for PCP and PCTP, respectively. The value calculated for PCP compares very well with its counterpart reported by Faniran [11] at $1318 \pm 9 \text{ cm}^{-1}$. According to Larsen and Nicolaisen [33] the barrier height in phenol is 1213 cm^{-1} . It is to be noted that the computed barrier for PCP disagrees by a considerable amount

Table 1

Experimental and DFT/B3LYP/6-311++G (d,p) optimized geometric parameters of pentachlorophenol (PCP), pentachlorothiophenol (PCTP) and their dimers.

Geometric parameter	PCP			Experimental ^a	PCTP		
	Calculated value				Monomer	Dimer	Experimental ^b
	Monomer		Dimer				
	This work	Ref. [13]	This work				
Bond lengths (in Å)							
C1–C2	1.399	1.400	1.398	1.373	1.405	1.405	1.396
C2–C3	1.396	1.369	1.398	1.368	1.400	1.400	1.394
C3–C4	1.400	1.400	1.403	1.365	1.400	1.399	1.402
C4–C5	1.403	1.400	1.401	1.365	1.401	1.401	1.396
C5–C6	1.398	1.397	1.396	1.438	1.397	1.397	1.394
C6–C1	1.401	1.401	1.398	1.371	1.405	1.404	1.402
C1–O7	1.346	1.344	1.354	1.329	–	–	–
C1–S7	–	–	–	–	1.775	1.778	1.726
C2–Cl9	1.748	1.749	1.735	1.704	1.747	1.746	1.728
C3–Cl10	1.735	1.736	1.733	1.707	1.736	1.735	1.728
C4–Cl11	1.737	1.738	1.736	1.734	1.735	1.735	1.726
C5–Cl12	1.734	1.735	1.733	1.673	1.735	1.735	1.728
C6–Cl13	1.734	1.735	1.747	1.683	1.742	1.741	1.728
O7–H8	0.967	0.968	0.969	0.968	–	–	–
S7–H8	–	–	–	–	1.346	1.347	*
Bond angle (in °)							
C1–C2–C3	121.21	121.30	121.01	121.60	121.09	121.08	120.90
C2–C3–C4	119.58	119.60	119.56	119.40	120.12	120.07	119.60
C3–C4–C5	119.61	119.60	119.69	121.70	119.54	119.57	119.50
C4–C5–C6	120.34	120.40	120.23	118.40	119.80	119.88	120.90
C5–C6–C1	120.27	120.40	120.21	119.20	121.56	121.36	119.60
C6–C1–C2	118.96	*	119.24	119.70	117.86	118.01	119.50
C1–C2–Cl9	117.26	*	117.36	119.10	120.21	120.36	120.90
C3–C2–Cl9	121.52	*	121.59	120.30	118.68	118.55	120.50
C2–C3–Cl10	119.79	*	119.78	121.10	120.17	120.07	119.90
C4–C3–Cl10	120.62	*	120.64	119.50	119.70	119.84	119.60
C3–C4–Cl11	120.08	*	120.06	120.30	120.26	120.28	120.00
C5–C4–Cl11	120.29	*	120.23	117.90	120.18	120.13	120.50
C4–C5–Cl12	120.03	*	120.16	122.60	120.04	120.02	119.50
C6–C5–Cl12	119.61	*	119.59	118.90	120.14	120.08	119.60
C5–C6–Cl13	121.71	*	121.61	120.30	119.80	119.50	120.5
C1–C6–Cl13	118.00	*	118.17	120.50	118.62	119.13	*
C6–C1–O7	118.34	*	118.62	120.40	–	–	–
C2–C1–O7	122.68	*	122.12	119.80	–	–	–
C6–C1–S7	–	–	–	–	117.42	117.60	*
C2–C1–S7	–	–	–	–	124.71	124.37	*
C1–O7–H8	109.27	109.00	108.95	*	–	–	–
C1–S7–H8	–	–	–	–	95.43	95.90	*
Dihedral angle (in °)							
C1–C2–C3–C4	0.00	*	0.015	*	0.00	0.086	*
C2–C3–C4–C5	0.00	*	0.044	*	0.00	0.026	*
C3–C4–C5–C6	0.00	*	0.029	*	0.00	0.066	*
C4–C5–C6–C1	0.00	*	0.046	*	0.00	0.006	*
C5–C6–C1–C2	0.00	*	0.105	*	0.00	0.116	*
O7–C1–C2–Cl9	0.00	*	0.104	*	–	–	–
S7–C1–C2–Cl9	–	–	–	–	0.00	0.343	*
C1–C2–C3–Cl10	–180.00	*	–179.99	*	180.00	179.79	*
C2–C3–C4–Cl11	180.00	*	179.93	*	180.00	179.80	*
C3–C4–C5–Cl12	180.00	*	179.88	*	180.00	179.70	*
C4–C5–C6–Cl13	180.00	*	179.78	*	180.00	179.89	*
C5–C6–C1–O7	180.00	*	179.88	*	–	–	–
C6–C1–O7–H8	–180.00	*	–179.71	*	–	–	–
C2–C1–O7–H8	0.00	*	0.059	*	–	–	–
C5–C6–C1–S7	–	–	–	–	180.00	179.97	*
C6–C1–S7–H8	–	–	–	–	180.00	178.72	*
C2–C1–S7–H8	–	–	–	–	0.00	1.38	*
Intermolecular H-bond lengths(in Å) and angles(in °) of dimer							
(i) PCP							
O20–H21...O7			2.140	2.970			
O7...O20			2.923	2.970			
O20–H21...Cl13			3.150	3.280			
C1–O7...O20			2.923	*			
O7...Cl22			3.648	3.280			
C1–O7			1.350	1.330			
O20–H21...O7			135.59	*			
O20–H21...Cl13			129.89	*			
C1–O7...O20			122.12	125.00			
(ii) PCTP							
S20–H21...S7			3.229	*			

(continued on next page)

Table 1 (continued)

Geometric parameter	PCP			PCTP		
	Calculated value			Experimental ^a		
	Monomer		Dimer	Monomer		Dimer
	This work	Ref. [13]	This work			Experimental ^b
S7...S20		4.294				*
S20–H21...C13		4.068				*
C1–S7...S20		4.294				*
S7...C122		4.450				*
C1–S7		1.778				*
S20–H21...S7		135.61				*
S20–H21...C113		97.60				*
C1–S7...S20		124.37				*

*: Not available; -: Not relevant.

^a : From Ref. [15].

^b : From Ref. [30].

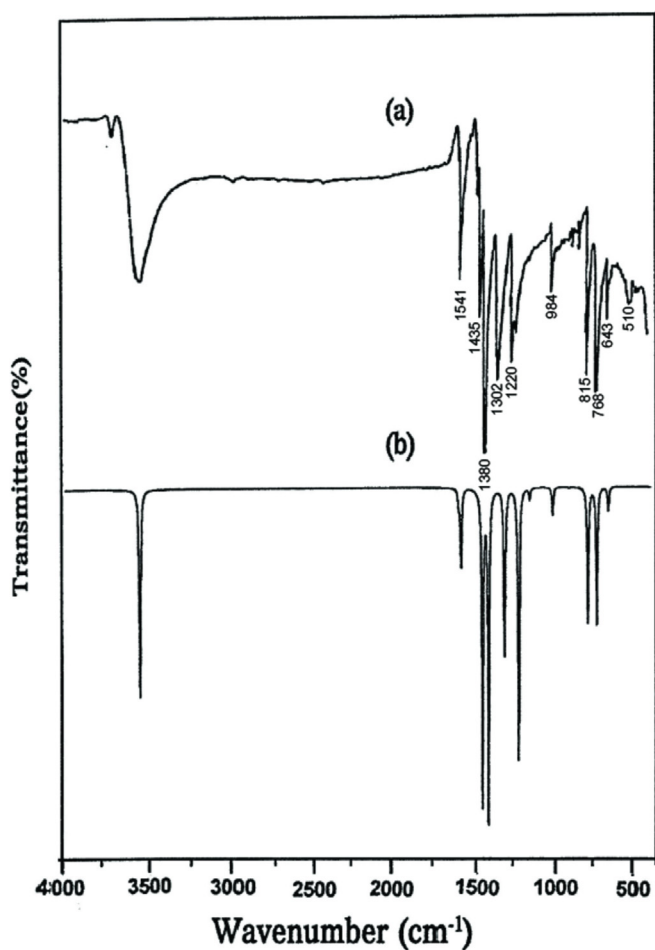


Fig. 4. FTIR Spectrum of Pentachlorophenol (a) Experimental and (b) simulated with DFT/B3LYP/6-311++G (d,p) basis set.

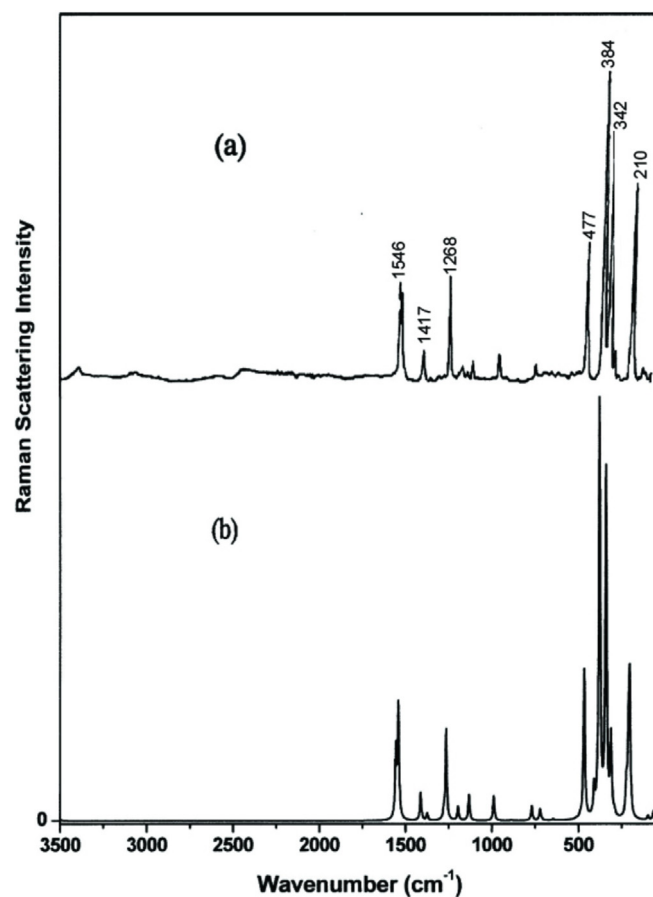


Fig. 5. FT-Raman Spectrum of Pentachlorophenol (a) Experimental and (b) Simulated with DFT/B3LYP/6-311++G (d,p) basis set.

from that put forward by Green et al. [10], at 2190 cm^{-1} , which is substantiated by Siguenza et al. [12] by employing a cosine potential function containing four terms to compute the barrier height. However, it is very important to note the suggestion of earlier workers that, if the torsional mode of the hydroxyl group mixes substantially with other fundamentals, then its torsional potential is no longer a cosine function of the hydroxyl torsional angle [33–37]. It is interesting to note that a barrier of 267 cm^{-1} is reported for thiophenol [33], which is nowhere near the value of

PCTP obtained in this work. It is to be noted here that the introduction of electronegative substituents in ortho or meta positions considerably increases the internal rotation barrier [32]. Further, the lower value of internal rotational barrier in PCTP when compared to that of PCP implies a lower conjugative interaction of the SH moiety with the aromatic ring than that of the OH moiety. It is known that experimental barrier heights depend on structure parameters and corresponding torsional frequency [11], whereas the main source of error in the B3LYP method comes from a systematic underestimation of the classical barrier height [38]. It may not be out of place to draw a parallel between the origin of the

barrier in phenol and PCP (or PCTP). The barrier in phenol arises due to conjugation between π -electrons of the benzene nucleus and lone pair on oxygen atom according to Campagnero and Wood [39], imparting partial double bond character to the C–O bond. This is also true for barrier in PCP (or PCTP).

5.2. Equilibrium molecular geometry

5.2.1. Monomer and intra-molecular hydrogen bonding

In Table 1 of reference 13 the authors reported values of five \angle CCC bond angles and one \angle COH bond angle only. They did not present any data for ten angles involving chlorine atoms, two angles formed by C–O bond with the ring, and \angle C6C1C2 angle, even though corresponding experimental data is available [15]. Further dihedral angles were not computed. We addressed this deficiency through our calculations presented here.

We have seen in section 3 that PCP (or PCTP) prefers planar configuration of C_s symmetry. This is due to conjugation between π -electrons of the benzene ring and lone pair on oxygen atom (sulphur for PCTP) of hydroxyl moiety. A glance at Table 1 reveals that the structure parameters comprising of bond distances and bond angles, for PCP and PCTP agree exceedingly well with nuclear quadrupole resonance and X-ray investigation results for PCP [15] and X-ray diffraction results for PCTP [30]. For example, according to computations for PCP, the average value of C–C bond length is 1.399 Å; the average value of C–Cl bond distance is 1.738 Å; and O–H bond distance is 0.967 Å. They agree extremely well with their corresponding experimental values 1.380 Å; 1.700 Å; and 0.968 Å. Significantly higher experimental value of C5–C6 bond length 1.438 Å, when compared to other C–C bond distances and its calculated value 1.398 Å has been attributed to intermolecular hydrogen bonding [13,15].

Three bond angles around C1 carbon atom are expected to be affected by the presence of oxygen atom in PCP. These are \angle C6C1C2, \angle C6C1O7, and \angle C2C1O7 having computed values 118.96°, 118.34°, and 122.68°, respectively. They agree reasonably well with the corresponding nuclear quadrupole resonance and X-ray diffraction results of PCP [15] at 119.70°, 120.40°, and 119.80°. Similar conclusions can be drawn in respect of PCTP by referring to the results in Table 1.

The distance between the lone hydrogen atom and its nearest chlorine atom (Cl9) is 2.357 Å and 2.410 Å in PCP and PCTP (see Fig. 2), as per our calculations, respectively. From this it can be inferred that there is a weak intra-molecular hydrogen bond in these molecules.

5.2.2. Dimer and inter-molecular hydrogen bonding

It is to be stated here that dimer of PCP (or PCTP) was treated as a supra molecule consisting of two stable monomers in their lowest energy conformation with experimental values for inter-molecular hydrogen bond. The resulting configuration was subjected to rigorous geometry optimization with simultaneous relaxation of all structural parameters as in the case of monomer. This process led to structure of C_1 symmetry for both PCP and PCTP dimers. Consequently the two monomer units of the dimer do not share the same molecular plane. As the monomer and dimer are treated at the same level of theory, comparative results are expected to be reliable.

The minimum energy of PCP-dimer is -5211.2900 Hartree, whereas the corresponding value for PCTP-dimer is -5857.2151 Hartree. For formation of dimer these energies should be less than twice the minimum energy of corresponding monomers. We find that the difference between the energy of PCP-dimer and twice the energy of its monomer is -0.005086 Hartree or -13.35 kJ mol $^{-1}$. The corresponding quantity for PCTP-dimer is -0.003583 Hartree

or -9.41 kJ mol $^{-1}$. Hence formation of dimer is favored in both PCP and PCTP.

In dimers of PCP and PCTP structural configuration around atoms involved in inter-molecular hydrogen bond is of special interest (see Fig. 3). The relevant bond distances and bond angles, both observed and calculated are available in Table 1. In the case of PCP-dimer hydrogen atom of hydroxyl moiety of one molecule (H21) is involved in hydrogen bonding with O7 and Cl13 of the other molecule of the dimer. This is called the bifurcated hydrogen bond. Experimental values of H21 ... $\cdot\cdot$ Cl13 and H21 ... $\cdot\cdot$ O7 hydrogen bond lengths are 3.28 Å and 2.97 Å [15] respectively. Corresponding calculated values are 3.150 Å and 2.140 Å. It can be seen that the agreement between the observed and computed values of H21 ... $\cdot\cdot$ Cl13 hydrogen bond distance is excellent, whereas that for H21 ... $\cdot\cdot$ O7 bond length is not that good. Hence it can be concluded that the calculations presented here qualitatively account for the existence of bifurcated hydrogen bond in PCP. However, the results can be improved by including dispersion correction [40] in DFT, which is not taken into account by B3LYP functional.

In the case of PCTP the distance between H21 and Cl13 atom is 4.068 Å, which is clearly outside the range of hydrogen bond formation. Hence there is no hydrogen bond between H21 and Cl13 in dimer of PCTP. However there is a weak hydrogen bond between H21 and S7 in PCTP dimer, as the corresponding distance is 3.229 Å, which favors hydrogen bond formation. Thus it can be concluded that bifurcated hydrogen bond exists in PCP-dimer, whereas simple weak hydrogen bond is present in PCTP-dimer.

5.3. Scaled force constants

We have defined 33 natural internal coordinates for each of the molecules PCP and PCTP. They belong to 23 in-plane coordinates of a' -species and 10 out-of-plane coordinates of a'' -species. The interaction between coordinates of a' - and a'' -species is symmetry-forbidden. Hence there should be $23 \times 10 = 230$ force constants having zero value for PCP and PCTP, each. As the force constant matrix is symmetric, the number of general valence force constants is given by $n(n+1)/2$, where n is the number of natural internal coordinates or basis coordinates. Hence the total number of force constants for PCP or PCTP is 561 (i.e. $33 \times 34/2$). As 230 of them are zero due to symmetry reasons, the expected number of non-zero force constants is 331 (i.e. $561 - 230$). Out of these 276 (i.e. $23 \times 24/2$) constants belong to in-plane force constants of a' -species and 55 (i.e. $10 \times 11/2$) constants belong to out-of-plane force constants of a'' -species. In fact DFT calculations generated a force field, which perfectly conforms to the foregone conclusions (i.e. 276 in-plane force constants, 55 out-of-plane force constants and 230 symmetry-forbidden force constants). Within a given species, a very small number of interaction constants have significant values; some have relatively small values; yet some others have negligibly small and zero values. To demonstrate this statement, let us consider the stretch-stretch interaction constants between C1–C2 bond of the aromatic nucleus and other stretching coordinates of PCP (see Fig. 2). Neighboring stretching coordinates to C1–C2 bond are, two ortho carbon-carbon bonds (C2–C3 and C1–C6), C–O bond, and C2–Cl9 bond. The interaction constants associated with these bonds involving C1–C2 bond, as per DFT calculations are, 0.710, 0.740, 0.512 and 0.429 respectively, which are significant due to geometric proximity. The exception to proximity rule is C–C, C–C meta interaction constants in PCP, whose values are -0.497 (C3–C4) and -0.492 (C5–C6). These values are significant. It is note-worthy that such exception is also found for meta interaction constants (i.e. C–C, C–C) of the aromatic nucleus in the case of substituted benzenes [e.g Refs. [41,42] obtained by solving inverse

vibrational problem using Wilson's GF matrix method [43]. Other stretch-stretch interaction constants involving C1–C2 bond have values in the range -0.02 to -0.113 . The O–H stretch interaction constant with C4–C11 stretch deserves special mention. Because its value is zero, as the coordinates involved are in geometrically remote parts of the molecule.

5.4. Vibrational assignments

The rms error between observed and scaled frequencies, for PCP and PCTP is 8.4 cm^{-1} and 7.6 cm^{-1} , respectively. Corresponding error for PCP-OD, is 12.1 cm^{-1} . Experimental IR and Raman fundamentals agree fairly well with their theoretical counterparts see Table 2, Figs. 4 and 5 for PCP; see Table 3 for PCP-OD; and see Table 4 for PCTP. Further, vibrations of PCP-OD and PCTP show expected decrease on the basis of PED for PCP and increased mass of deuterium and sulphur. Hence, the vibrational assignments can be made, on the basis of these calculations for PCP, PCP-OD and PCTP.

Before proceeding further with a discussion of vibrational assignments it is essential to understand the deficiencies and unacceptable nature of assignments made by earlier investigators [10,11,13 and 14]. They are:

- (i) Proposed assignments by Green et al. and Faniran: The vibrational assignments of PCP proposed by Green et al. [10] and Faniran [11] are essentially empirical as they are made on the basis of qualitative considerations, and hence tentative. Further, they do not agree even on the tentative assignment of several fundamentals. The most serious of them is $\tau(\text{OH})$, which was assigned to the band at 409 cm^{-1} by Green et al., whereas Faniran identified it at 318 cm^{-1} . The other disagreements on this account are: Faniran [11] assigned the bands at 650 (ν_{15}), 435 (ν_{17}), 321 (ν_{20}), 410 (ν_{26}) and 308 (ν_{29}) cm^{-1} in PCP to $\alpha(\text{CCC})$, x-sensitive mode, $\beta(\text{CCI})$, $\phi(\text{CC})$, and $\gamma(\text{CCI})$, respectively. The absorptions corresponding to ν_{15} , ν_{17} , ν_{20} , ν_{26} and ν_{29} above were identified by Green et al. [10] near 645 , 438 , 332 , 409 and 307 cm^{-1} , respectively, and proposed that their origin was in the vibrations ν_{16} i. e. $\phi(\text{CC})$, ($\nu_{10} + \nu_{11}$), ν_{27} i. e. $\nu(\text{CCI})$, $\gamma(\text{OH})$, i. e. $\tau(\text{OH})$, and ν_{28} (Faniran labeled it ν_{29}) i. e. $\beta(\text{CCI})$. The band at 318 cm^{-1} was not observed by Green et al. [10]. It is important to distinguish between the designation of modes ν_1, ν_2, \dots used by Faniran [11] and Green et al. [10]. Faniran assumed C_s symmetry for PCP and designated all the 33 vibrations of the molecule, whereas Green et al. presumed C_{2v} symmetry and confined to designate 30 vibrations that have their origin in the aromatic nucleus of the molecule. Hence ν_n of Faniran need not be the same as ν_n of Green et al. For example ν_1 for Faniran designates $\nu(\text{OH})$, while it denotes $\nu(\text{CC})$ for Green et al.
- (ii) Investigations by Czarnik-Matusiewicz et al.: The attempts made by Czarnik-Matusiewicz et al. [13] to quantify vibrational assignments, and hence resolve the disagreement between Faniran and Green et al., regarding the assignments of PCP and its OD isotopomer (PCP-OD), with density functional theory (DFT) using B3LYP functional employing 6-311G (d,p) basis set is necessarily incomplete for the following reasons.
 - (a) The authors listed 25 vibrational frequencies only in Tables 2 and 3 of reference 13, for each of the molecules PCP and PCP-OD, respectively, whereas each one of them should have 33 vibrational frequencies.
 - (b) In the assignment column of Tables 2 and 3 of reference 13, numerical values corresponding to potential energy

distribution (PED) are missing, for the reasons best known to the authors. In the absence of such values it is impossible to understand the extent of mixing of vibrational frequencies in terms of PED. This defeats the very purpose of normal coordinate analysis reported by the authors, using DFT.

- (c) Having done normal coordinate analysis the authors are expected to identify each one of the thirty vibrations that have their origin in the benzene nucleus, with an independent label (e.g. Wilson's notation for benzene modes [31]). Instead they used symbols $\nu_R, \delta_R, \gamma_R, \nu(\text{C–Cl})$ etc to designate the fundamentals. When the authors say $\nu(\text{C–Cl})$ it is not clear to which of the five C–Cl stretching vibrations of PCP or PCP-OD they are referring to. This information is embedded in the eigenvectors, which should be gleaned out using proper phase relations. The authors did not do anything in this regard. Thus the results presented by them in Tables 2 and 3 of reference 13, can at best be approximate. Further, in Table 2 of reference 13, the authors, on the basis of their DFT vibrational analysis of PCP, listed 8 vibrations that draw their PED from C–C stretching vibrations (represented by ν_R by the authors) of the ring. There is no problem in recognizing five bands at $1561, 1548, 1417, 1382$ and 1302 cm^{-1} with C–C stretching vibrations of the ring, in spite of the fact that in-plane bending mode of OH moiety (represented by $\delta(\text{OH})$ by the authors) makes a PED contribution to the lowest four of them, as this is not the region for $\delta(\text{OH})$ to exist. The fundamental at 1281 cm^{-1} , which is reported as a mixed mode of C–C stretching of the ring and C–O stretching, can be associated with $\nu(\text{C–O})$ vibration. Now, we are in an awkward situation to choose one of the two pure ν_R vibrations at 1136 and 986 cm^{-1} for the remaining lone C–C stretching vibration, as there are only 6 C–C stretching fundamentals of the ring. We find no way to do that. Nor we can accept both of them as $\nu(\text{C–C})$ stretching vibrations, precipitating an absurdity, as it is tantamount to accepting the existence of 7 C–C bonds in the aromatic ring. Further, the band at 702 cm^{-1} , with its calculated counterpart near 696 cm^{-1} , is ascribed to $[\delta(\text{R}) + \gamma(\text{OH})]$. It may be noted that $\delta(\text{R})$ is an in-plane vibration of a' symmetry, whereas $\gamma(\text{OH})$ is an out-of-plane vibration of a'' symmetry. Such mixing is symmetry-forbidden. This is yet another unacceptable result. Hence the results presented in reference 13, cannot be taken seriously.
- (d) The authors did not report the computed infrared spectrum in reference 13. They were content by stating that the computed infrared spectrum did not agree quantitatively with the experimental spectrum and the agreement was only qualitative. The reason is the authors scaled the frequencies (with a single scale factor 0.990 for PCP and 0.988 for PCP-OD) instead of force constants. It is important to note that scaling the force constants affects the resultant normal modes and hence the calculated intensities, which remain unaffected if only the frequencies are scaled [44].
- (iii) Studies conducted by Pawlukoic et al.: The investigations of Czarnik - Matusiewicz et al. [13] were followed by inelastic neutron scattering (INS) studies on the low frequency vibrations of pentachlorophenol (PCP) by Pawlukoic et al. [14]. One of the goals of the authors was to supplement the work reported by Czarnik - Matusiewicz et al. [13] below 300 cm^{-1} , as details of vibrational analysis of fundamentals in this

Table 2
Observed frequencies, DFT/B3LYP/6-311++G (d,p) computed frequencies along with intensities and vibrational assignment of PCP.

Mode ^a	Obs. freq. (cm ⁻¹)			Cal. freq. (cm ⁻¹)		Intensity ^b		Vibrational assignment ^c
	IR	Raman	INS ^d	Unscaled	Scaled	IR (I _i)	Raman (A _i)	
(i) Vibrations of the aromatic nucleus								
(a) In-plane vibrations(a'-species)								
$\nu(\text{C}-\text{C})$ 8a	1553 w	1559 w	–	1557	1556	3.70	39.55	64 (8a)+11 (6b)+7 (15)+7 [$\beta(\text{COH})$]+5 (9b)
$\nu(\text{C}-\text{C})$ 8b	1541vs	1546 w	–	1542	1542	28.23	64.29	67 (8b)+12 (6a)+7 (9a)+7 (13)
$\nu(\text{C}-\text{C})$ 14	1280 ^e ms	1281 ^e ms	–	1280	1279	50.94	2.49	68 (14)+22 [$\beta(\text{COH})$]
$\nu(\text{C}-\text{C})$ 19a	1412 s 1435 ms	1417 vw	–	1412	1413	99.72	13.50	51 (19a)+28 (13)+11 (18a)+6 (20a)
$\nu(\text{C}-\text{C})$ 19b	1380 vs	–	–	1376	1374	100	1.90	53 (19b)+13 (9a)+11 (20b)+10 [$\beta(\text{COH})$]+6 (15)+5 (13)
$\nu(\text{C}-\text{Cl})$ 2	–	384 vs	386	380	379	0.11	28.35	62 (2)+23 (1)+14 (12)
$\nu(\text{C}-\text{Cl})$ 7a	459 w	–	442	470	468	0.41	13.93	42 (7a)+33 (6a)+12 (1)+8 (13)
$\nu(\text{C}-\text{Cl})$ 7b	882 ^e ms	881 ^e ms	893	884	887	0.36	0.18	62 (7b)+32 (6b)
$\nu(\text{C}-\text{Cl})$ 20a	768 vs	773 vw	783	769	770	42.59	2.78	61 (20a)+15 (6a)+10 (18a)+7 (19a)+6 (13)
$\nu(\text{C}-\text{Cl})$ 20b	716 ^e ms	–	723	711	713	41.65	0.19	61 (20b)+22 (15)+12 (18a)
$\beta(\text{CCl})$ 3	643 s	–	632	639	647	7.74	0.22	73 (3)+15 (15)+9 (2)
$\beta(\text{CCl})$ 9a	–	210 ms	–	204	210	0.05	1.31	88 (9a)+7 (19b)
$\beta(\text{CCl})$ 9b	–	229 ^e w	–	224	224	0.006	0.94	97 (9b)
$\beta(\text{CCl})$ 18a	–	218 ^e ms	220	212	213	0.02	0.96	88 (18a)+7 (19b)
$\beta(\text{CCl})$ 18b	–	–	201	209	205	0.01	2.89	91 (18b)+6 (14)
$\nu(\text{C}-\text{C})$ 1	–	1268 w	–	1268	1265	6.09	36.88	55 (1)+24 (2)+10 (13)+8 (18a)
$\beta(\text{CCC})$ 6a	–	342 vs	349	314	342	1.38	10.09	32 (6a)+25 (7a)+18 (9b)+15 (15)+9 (8a)
$\beta(\text{CCC})$ 6b	322 ^e vw	321 ^e w	–	343	312	1.60	3.76	47 (6b)+17 (7b)+16 (15)+15 (9a)
$\beta(\text{CCC})$ 12	–	1134 vw	–	1129	1132	5.21	8.79	43 (12)+35 (7a)+14 (1)+6 (13)
$\nu(\text{C}-\text{O})$ 13	984 s	985 vw	–	985	989	8.46	6.77	40 (20a)+31 (6a)+17 (13)+10 (1)
$\beta(\text{CO})$ 15	–	355 ^e w	–	344	343	1.00	10.18	28 (2)+26 (6b)+19 (3)+15 (15)+11 (1)
(b) Out-of plane vibrations(a''-species)								
$\tau(\text{CCCC})$ 4	709 ^e s	708 ^e vw	–	705	722	0.92	1.93	58 (5)+29 (4)+13 (17a)
$\tau(\text{CCCC})$ 16a	470 w	476 ms	–	477	491	0.84	0.22	62 (17a)+38 (16a)
$\tau(\text{CCCC})$ 16b	510 ms	–	–	520	513	0.03	0.09	51 (16b)+49 (17a)
$\pi(\text{CCl})$ 11	181 ^e w	–	–	152	160	0.06	0.001	78 (11)+21 (4)
$\pi(\text{CCl})$ 17a	–	–	67	59	61	0.006	0.003	90 (16a)+8 (17a)
$\pi(\text{CCl})$ 17b	–	–	91	64	66	0.006	0.02	88 (4)+5 (17b)
$\pi(\text{CCl})$ 10a	–	310 vw	–	274	293	0.56	0.21	97 (10a)
$\pi(\text{CCl})$ 10b	318 ^e w	319 ^e vw	316	304	317	0.20	0.47	72 (10b)+26 (16b)
$\pi(\text{CO})$ 5	–	–	108	93	98	0.007	0.032	71 (4)+20 (17a)+8 (5)
(ii) Vibrations of OH moiety								
(a) In-plane vibrations(a'-species)								
$\nu(\text{OH})$	3520 ^e s	–	–	3520	3520	66.00	100	100 [$\nu(\text{OH})$]
$\beta(\text{OH})$	1192 ms	1193 vw	–	1194	1195	85.85	5.22	65 (14)+26 [$\beta(\text{OH})$]
(b) Out-of plane vibrations(a''-species)								
$\tau(\text{OH})$	409 ^f	–	–	356	410	50.98	2.11	90 [$\tau(\text{OH})$]+6 (17a)

–: Not observed.

vs: very strong; s: strong; ms: medium strong; w: weak; vw: very weak; sh: shoulder.

^a Mode in Wilson's notation [31]. ν : stretching; β : in-plane bending; π : out-of-plane bending; τ : torsion.

^b Relative infrared and Raman intensities are normalized to 100.

^c Number before the parenthesis is % PED and number in the parenthesis is vibrational mode. PED less than 5% is not shown.

^d From Ref. [14] (INS: inelastic neutron scattering).

^e From Ref. [11].

^f From Ref. [10].

region, using DFT, were not presented in Tables 2 and 3 of reference 13. To this end the authors performed DFT calculations at the B3LYP/6-31G** level. But a glance at Table 1 of reference 14 reveals unacceptable results of serious nature. These are:

- In Table 1 of reference 14, the authors identified five CCl out-of-plane bending vibrations that do not mix with any other vibration of PCP. In addition they ascribed two fundamentals mixing with $\gamma(\text{CO})$, to $\gamma(\text{CCl})$ modes, at 91 and 108 cm⁻¹. This makes the total number of $\gamma(\text{CCl})$ vibrations seven in PCP. This is obviously impossible as there should be just five $\gamma(\text{CCl})$ vibrations corresponding to five C–Cl bonds of the molecule.
- According to the authors there are six deformations denoted by Rdef by them. This is true as there are three in-plane bendings and three torsions of the ring (note

that the authors did not make any distinction between them). So far the matter is very plane. It becomes complex when we recognize that there are two vibrations, with their calculated values at 172 and 298 cm⁻¹ in Table 1 of reference 14, attributed to $\gamma(\text{CCl})$ + $\gamma(\text{CO})$ and $\gamma(\text{CO})$ + Rdef, respectively, by the authors. If the former is ascribed to $\gamma(\text{CO})$, then the latter has to be due to Rdef. This makes the total number of ring deformations seven, which is not acceptable. If the latter is assigned to $\gamma(\text{CO})$, then the former has to be due to $\gamma(\text{CCl})$. This takes the total number of $\gamma(\text{CCl})$ vibrations to eight (note that in item (i) above we identified seven $\gamma(\text{CCl})$ vibrations), which is clearly unacceptable.

- The band at 316 cm⁻¹ was attributed to $\delta(\text{CCl})$ + $\gamma(\text{OH})$. Note that $\delta(\text{CCl})$ is an in-plane vibration of a'-species and $\gamma(\text{OH})$ is an out-of-plane vibration of a''-species in C_s symmetry. Such mixing is symmetry-forbidden.

Table 3

Observed frequencies, calculated frequencies using scaled force field for PCP and vibrational assignment of PCP-OD.

Mode ^a	Obs. freq. (cm ⁻¹)		Cal. freq. (cm ⁻¹)	Vibrational assignment ^b
	IR ^c	INS ^d		
(i) Vibrations of the aromatic nucleus				
(a) In-plane vibrations(a'-species)				
$\nu(\text{C}-\text{C})$ 8a	1555	—	1548	67 (8a)+13 (6a)+8 (13)+8 (9a)
$\nu(\text{C}-\text{C})$ 8b	1537	—	1532	70 (8b)+11 (6b)+7 (15)
$\nu(\text{C}-\text{C})$ 14	1247	—	1244	93 (14)
$\nu(\text{C}-\text{C})$ 19a	1410	—	1407	49 (19a)+32 (13)+11 (18a)+6 (20a)
$\nu(\text{C}-\text{C})$ 19b	1374	—	1363	60 (19b)+14 (20b)+14 (9a)+8 (15)
$\nu(\text{C}-\text{Cl})$ 2	—	389	379	62 (2)+24 (1)+14 (12)
$\nu(\text{C}-\text{Cl})$ 7a	—	442	462	42 (7a)+33 (12)+12 (1)+7 (13)
$\nu(\text{C}-\text{Cl})$ 7b	—	880	886	60 (7b)+30 (6b)+6 (14)
$\nu(\text{C}-\text{Cl})$ 20a	764 ^e	—	768	61 (20a)+15 (6a)+11 (18a)+7 (19a)+6 (13)
$\nu(\text{C}-\text{Cl})$ 20b	692 ^e	685	692	69 (20b)+10 (15)+9 [$\beta(\text{OD})$]+8 (18a)
$\beta(\text{CCl})$ 3	637	632	636	74 (3)+19 (15)
$\beta(\text{CCl})$ 9a	—	203	205	91 (9a)+6 (19b)
$\beta(\text{CCl})$ 9b	—	220	224	97 (9b)
$\beta(\text{CCl})$ 18a	—	220	213	88 (18a)+7 (14)
$\beta(\text{CCl})$ 18b	—	203	210	88 (18b)+7 (14)
$\nu(\text{C}-\text{C})$ 1	1270	—	1266	53 (1)+25 (2)+10 (13)+8 (3)
$\beta(\text{CCC})$ 6a	—	347	341	49 (6a)+37 (7a)+11 (1)
$\beta(\text{CCC})$ 6b	—	315	306	34 (6b)+28 (15)+21 (9a)+10 (7b)+5 (14)
$\beta(\text{CCC})$ 12	1136	—	1135	43 (12)+35 (7a)+14 (1)+7 (13)
$\nu(\text{C}-\text{O})$ 13	990	—	995	32 (2)+24 (6a)+17 (13)+15 [$\beta(\text{OD})$]+9 (1)
$\beta(\text{CO})$ 15	—	347	335	23 (6b)+23 (3)+23 (7b)+21 (15)+8 (19a)
(b) Out-of plane vibrations(a''-species)				
$\tau(\text{CCCC})$ 4	717	731	743	53 (5)+32 (4)+14 (17a)
$\tau(\text{CCCC})$ 16a	—	503	513	63 (17b)+37 (16a)
$\tau(\text{CCCC})$ 16b	585	586	559	50 (16b)+50 (17a)
$\pi(\text{CCl})$ 11	—	—	160	81 (11)+16 (4)
$\pi(\text{CCl})$ 17a	—	68	60	89 (16a)+6 (17a)
$\pi(\text{CCl})$ 17b	—	92	66	88 (16b)+6 (17b)
$\pi(\text{CCl})$ 10a	—	315	330	62 (10a)+20 (4)+14 [$\tau(\text{OD})$]
$\pi(\text{CCl})$ 10b	—	292	304	60 (10b)+33 [$\tau(\text{OD})$]+7 (4)
$\pi(\text{CO})$ 5	—	108	96	69 (4)+23 (17b)+7 (5)
(ii) Vibrations of OD moiety				
(a) In-plane vibrations(a'-species)				
$\nu(\text{OD})$	2600 ^e	—	2562	100 [$\nu(\text{OD})$]
$\beta(\text{OD})$	968	—	966	52 [$\beta(\text{OD})$]+21 (20a)+11 (12)+9 (14)
(b) Out-of plane vibrations(a''-species)				
$\tau(\text{OD})$	298 ^e	—	285	64 (10a)+36 [$\tau(\text{OD})$]

^a -: As in Table 2.^b Same as c in Table 2.^c From Ref. [13].^d From Ref. [14].^e From Ref. [10].

(d) There are several typographical errors in the sense that the values quoted in the text do not agree with those in the Table 1 of reference 14. In the case of PCP, INS values in Table 1 at 91; 139; 349 and 525 cm⁻¹ are mentioned in the text as 92; 138; 350 and 526 cm⁻¹, respectively. Further, the modes $\nu(\text{CCl})$ and $\delta(\text{CCl})$ in the table are mentioned as $\delta(\text{CCl})$ and $\nu(\text{CCl})$, respectively, in the text.

(e) Numerical values of potential energy distribution (PED) are not included in the table. This is the most important result of any normal coordinate treatment, without which no meaningful conclusions can be drawn.

Hence the results reported by these authors should be viewed with suspicion.

The PED presented in Tables 2–4 are self-explanatory. Hence we confined the discussion of vibrational assignments mostly to PCP only.

5.4.1. C–C stretching vibrations

Modes 8a and 8b are expected in the range 1500–1600 cm⁻¹ in PCP, PCP-OD and PCTP, as in the case of substituted benzenes. The

higher frequency has about 64–75% C–C stretching character in the three molecules investigated here. It is to be noted that this fundamental mixes with $\angle\text{CCC}$ in-plane bending mode 6b in PCP, whereas such mixing comes from mode 6a in PCP-OD and PCTP. Further, the PED contribution to this mode, from CCl in-plane bending vibration 9b in PCP, and fundamental 9a [i.e., $\beta(\text{CCl})$] in PCP-OD and PCTP is also note-worthy. This mode derives an additional PED contribution from CO in-plane bending vibration 15 in PCP, whereas this is replaced by CO stretching mode 13 in PCP-OD. The PED contribution from $\beta(\text{COH})$ and fundamental 15 to this mode in PCP has special significance. It indicates that the corresponding frequency in PCTP should occur at lower frequency, when compared to PCP, thus providing additional support for assignment made for PCTP (In fact they are located at 1553 and 1524 cm⁻¹, respectively, in PCP and PCTP). The lower frequency in the three molecules is a C–C stretching vibration to the extent of 67–73%. It mixes with mode 6a in PCP, whereas it is replaced by mode 6b in PCP-OD and PCTP. Mixing of this vibrations with $\nu(\text{CO})$ i. e, mode 13 in PCP, tells that it should decrease in going from PCP to PCTP. This is found true as it goes down from 1541 cm⁻¹ in PCP to 1523 cm⁻¹ in

Table 4
Observed frequencies^a, DFT/B3LYP/6-311++G (d,p) computed frequencies along with intensities and vibrational assignment of PCTP.

Mode ^b	Obs. freq. (cm ⁻¹)		Cal. freq. (cm ⁻¹)		Intensity ^c		Vibrational assignment ^d
	IR	Raman	Unscaled	Scaled	IR (I _i)	Raman (A _j)	
(i) Vibrations of the aromatic nucleus							
(a) In-plane vibrations(a'-species)							
$\nu(\text{C}-\text{C})$ 8a	1524 w	1522 vs	1545	1527	2.43	91.88	75 (8a)+12 (6a)+10 (9a)
$\nu(\text{C}-\text{C})$ 8b	1523 w	1522 ms	1528	1512	0.13	27.92	73 (8b)+12 (6b)+7 (15)
$\nu(\text{C}-\text{C})$ 14	1231 ms	1233 s	1260	1243	5.19	2.88	94 (14)
$\nu(\text{C}-\text{C})$ 19a	1341 vs	1342 vw	1346	1334	100	0.49	63 (19a)+22 (18a)+12 (20b)
$\nu(\text{C}-\text{C})$ 19b	1341 vs	1342 vw	1351	1342	95	0.03	61 (19b)+15 (13)+14 (15)+ 8 (9b)
$\nu(\text{C}-\text{Cl})$ 2	371 vw	376 vs	364	369	0.17	29.50	51 (2)+36 (1)+13 (7a)
$\nu(\text{C}-\text{Cl})$ 13	371 vw	376 vs	384	390	0.01	0.10	57 (13)+29 (12)+13 (7a)
$\nu(\text{C}-\text{Cl})$ 7b	876 ms	875 vw	864	880	0.64	0.63	59 (7b)+33 (6b)
$\nu(\text{C}-\text{Cl})$ 20a	680 s	680 vw	667	680	35.82	0.66	64 (20a)+17 (18a)+12 (7a)
$\nu(\text{C}-\text{Cl})$ 20b	686 s	–	676	689	29.50	0.44	63 (20b)+16 (18b)+15 (7a)
$\beta(\text{CCl})$ 3	–	610 vw	612	607	1.05	0.27	78 (3)+20 (9b)
$\beta(\text{CCl})$ 15	211 w	–	219	216	0.02	0.44	88 (15)+8 (19a)
$\beta(\text{CCl})$ 9a	220 ms	–	225	222	0.10	1.52	84 (9a)+10 (9b)
$\beta(\text{CCl})$ 18a	220 ms	–	232	229	0.10	1.04	89 (18a)+6 (9b)
$\beta(\text{CCl})$ 18b	211 w	–	213	213	8.77	0.30	65 (18b)+22 (9b)+10 (14)
$\nu(\text{C}-\text{C})$ 1	1215 w	–	1201	1204	0.02	53.16	58 (1)+33 (2)+8 (7a)
$\beta(\text{CCC})$ 6a	–	323 s	319	321	0.07	4.74	57 (6a)+23 (2)+11 (7a)+5 (14)
$\beta(\text{CCC})$ 6b	–	323 s	321	324	0.008	4.88	58 (6b)+31 (7b)
$\beta(\text{CCC})$ 12	1101 w	–	1087	1098	0.79	0.15	61 (12)+34 (13)
$\nu(\text{C}-\text{S})$ 7a	876 ms	875 vw	868	881	1.05	1.14	42 (13)+34 (6a)+18 (7a)
$\beta(\text{CS})$ 9b	243 w	246 vw	252	252	0.73	0.37	60 (15)+36 (9b)
(b) Out-of plane vibrations(a''-species)							
$\tau(\text{CCCC})$ 4	–	680 vw	663	682	0.007	0.002	51 (4)+42 (5)+7 (17b)
$\tau(\text{CCCC})$ 16a	–	610 vw	593	614	0.006	0.07	57 (17a)+33 (16a)+10 (17b)
$\tau(\text{CCCC})$ 16b	–	610 vw	581	604	0.09	0.11	53 (11)+34 (16b)+13 (17b)
$\pi(\text{CCl})$ 5	–	107 w	89	90	0.10	0.06	75 (4)+18 (5)
$\pi(\text{CCl})$ 11	–	81 w, sh	65	65	0.04	0.02	90 (16a)+8 (11)
$\pi(\text{CCl})$ 17a	–	81 w, sh	62	62	0.06	0.07	93 (16b)+5 (17a)
$\pi(\text{CCl})$ 10a	–	349 w	337	348	0.01	0.70	98 (10a)
$\pi(\text{CCl})$ 10b	–	349 w	325	339	0.08	0.33	71 (10b)+28 (17b)
$\pi(\text{CS})$ 17b	–	–	162	168	0.29	0.008	77 (11)+19 (17b)
(ii) Vibrations of SH							
(a) In-plane vibrations(a'-species)							
$\nu(\text{SH})$	2587 ms	2576 w	2682	2589	3.10	100	100 [$\nu(\text{SH})$]
$\beta(\text{SH})$	954 ms	948 w	967	954	7.31	7.89	80 [$\beta(\text{SH})$]+8 (20b)+5 (19a)
(b) Out-of plane vibrations(a''-species)							
$\tau(\text{SH})$	211 w	–	220	213	0.50	0.02	88 [$\tau(\text{SH})$]+7 (11)

a; b; c; d; -: Same as f; a; b; c; -, in Table 2, respectively.

vs; s; ms; w; vw; sh; same as in Table 2.

PCTP. Other modes mixing with this vibration can be seen from Tables 2–4. We find that mode 8a is greater in frequency than vibration 8b in PCP and PCP-OD, whereas they are almost equal in PCTP.

Vibrations 19a and 19b are expected in the spectral region 1300–1400 cm⁻¹ in this set of molecules. The higher frequency exhibits C–C stretching nature to the extent of 49–63%. The remaining PED comes from $\nu(\text{CO})$ i. e, mode 13, $\beta(\text{CCl})$ i. e, vibration 18a, and $\nu(\text{CCl})$ i. e, fundamental 20a in PCP and its isotopomer PCP-OD, whereas the contributing fundamentals, apart from C–C stretching in PCTP, are $\beta(\text{CCl})$ 18a and $\nu(\text{CCl})$ 20b. The PED contribution 28% from $\nu(\text{CO})$ 13, in PCP, signifies that in PCTP it should occur at lower frequency, when compared to that in PCP. This is found true as it decreases from 1421 cm⁻¹ in PCP, to 1341 cm⁻¹ in PCTP. The lower frequency is a C–C stretching vibration having C–C stretching nature that varies from 53 to 61% in the three molecules. PED contribution to this vibration from $\beta(\text{COH})$ and $\nu(\text{CO})$ 13 in PCP again indicates that it should decrease to lower frequency in PCTP. In fact it decreases by 39 cm⁻¹ from its value 1380 cm⁻¹ in PCP and appears around 1341 cm⁻¹ in PCTP. Other modes participating in this vibration can be seen from Tables 2–4. Thus we can conclude that the frequency of mode 19a is greater in magnitude than the vibration 19b in the three molecules.

Mode 14 in which alternate carbon bonds of the ring, either increase or decrease, appears at 1281 cm⁻¹ in PCP, with 68% C–C stretching character. It mixes with $\beta(\text{COH})$ to the extent of 22%. This mixing is responsible for it to decrease to 1247 cm⁻¹ in PCP-OD, and to 1231 cm⁻¹ in PCTP. It is almost pure getting 93–94% PED from respective vibration in PCP-OD and PCTP.

5.4.2. Ring vibrations

Vibrations 1, 6a, 6b, and 12 are called ring vibrations in benzene and substituted benzenes. They are sensitive to the nature of substituents on the aromatic nucleus. Hence they are also known as substituent sensitive modes. We have used symmetry coordinates defined in terms of primitive internal coordinates for 6a, 6b, and 12. Hence it is expected that, for a mode say 6a, in the eigen vector matrix the corresponding element should have a large value in comparison with the elements of other two modes. This is found to be true in the case of mode 12 with corresponding eigen vector element taking the values 0.848, -0.848 and -0.909 in PCP, PCP-OD and PCTP, respectively, with the value of other two elements ranging from -0.05 to 0.075. Further, the frequency of mode 12, which is at 1134 cm⁻¹ in PCP, decreases to 1101 cm⁻¹ in PCTP due to mixing of this vibration in PCP with mode 13 i.e., $\nu(\text{CO})$.

Modes 6a and 6b are identified with the help of phase

relations ++; and + - in these molecules, respectively. The main PED contribution comes from the corresponding \angle CCC bending vibration to these fundamentals. The decrease of mode 6b from 342 cm^{-1} in PCP to 323 cm^{-1} in PCTP is in accordance with its mixing with mode 15 i.e., $\beta(\text{CO})$, in PCP.

In mode 1 all the C–C bonds, either increase or decrease in length simultaneously. It is totally symmetric and separated by a large extent from C–H stretching vibrations in benzene. Hence it is a pure C–C stretching vibration in benzene. As these restrictions are removed in the present set of molecules, mode 1 can mix with several of the bending modes and also with the lower frequencies of the substituent stretching modes. As a result a pure mode cannot be expected corresponding to mode 1 of benzene. The assignment of this fundamental frequency around 1215 cm^{-1} in PCTP is straight forward as it gets 58% of its PED from mode 1. It mixes with $\nu(\text{CCl})$ i.e., mode 2 and $\nu(\text{CS})$ i. e, mode 7a. The bands having almost similar character occur near 1268 and 1270 cm^{-1} in PCP and PCP-OD, respectively, wherein the PED from vibration 7a in PCTP is replaced by corresponding fundamental 13 in PCP and PCP-OD. Hence they can be attributed to mode 1 with high degree of confidence in these molecules. Further, the decrease of this vibration by 53 cm^{-1} in going from PCP to PCTP is also in line with its mixing with $\nu(\text{CO})$ i. e, mode 13 in PCP.

5.4.3. Vibrations associated with C–Cl bonds

There are 15 vibrations that have their origin in the five bonds of, each of the three molecules, under investigation. These are five C–Cl stretchings, designated 2, 7a, 7b, 20a, and 20b; five C–Cl in-plane bends denoted 3, 9a, 9b, 18a, and 18b; and five C–Cl out-of-plane bends identified 11, 17a, 17b, 10a, and 10b in PCP and PCP-OD. In PCTP the above designations remain unaltered except that the modes 7a, 9b, and 17b are replaced by vibrations 13, 15, and 5, respectively. All of them fall below 1000 cm^{-1} . As this is a complicated region of the vibrational spectrum, majority of them cannot be pure. This makes their assignment more difficult. To circumvent this problem and identify each one of them with a specific mode we used the following phase relations among the corresponding elements of eigen vector matrix.

+1	+1	+1	+1	+1	for modes 2, 3 and 11
-1	-1	2	-1	-1	for modes 7a, 9b and 17b
-2	2	0	-2	2	for modes 7b, 9a and 17a
+1	-1	2	-1	+1	for modes 20a, 18b and 10b
-2	-2	0	+2	+2	for modes 20b, 18a and 10a

For PCP and PCP-OD. Corresponding phase relations for 13, 15 and 5, in PCTP are: +1 -1 +1 -1 +1. As already stated these appear in place of 7a, 9b, and 17b of PCP, respectively. The + ve and -ve signs indicate increase and decrease, respectively. These statements are approximately true in the case of substituted benzenes under investigation due to lowering of symmetry. However it may still be possible that many of the vibrations may be determined to a large extent by one particular phase relation. In that case it can be correlated with the benzene mode, which is best approximated by that phase relation. Patel et al [45] used this criterion for the assignment of substituent sensitive modes in dihalogenated benzenes. In this way the absorptions near 384 , 459 , 881 , 768 , 718 , 643 , 210 , 229 , 218 , 201 , 310 , 318 , and 181 cm^{-1} are ascribed to the modes 2, 7a, 7b, 20a, 20b, 3, 9a, 9b, 18a, 18b, 10a, 10b, and 11, respectively, in PCP, as $\nu(\text{CCl})$ vibrations get 42–62% PED; $\beta(\text{CCl})$ modes obtain 73–97% PED; and three of the five $\pi(\text{CCl})$ fundamentals, namely 10a, 10b, and 11, draw 72–97% PED, from the corresponding modes. The only frequencies which contain some C–Cl out-of-plane bending character and at the same time cannot be considered as C–X in-plane bend (X is Cl or O), \angle CCC in-plane bend, ring torsion,

C–O out-of-plane bend, or COH in-plane bend or its torsion in PCP comes around 67 and 91 cm^{-1} . They are identified as modes 17a and 17b, respectively. Mixing of all the above 15 vibrations with other fundamentals can be understood from Table 2. It is important to note that Faniran [11] attributed the vibrations around $1135(\nu_{10})$, $879(\nu_{12})$, $775(\nu_{13})$, $718(\nu_{14})$, and $465(\nu_{16})$ to the five $\nu(\text{C–Cl})$ modes, whereas those near $345(\nu_{19})$, $323(\nu_{20})$, $229(\nu_{21})$, $218(\nu_{22})$, and $212(\nu_{23})$ to the five $\beta(\text{CCl})$ vibrations, while the absorptions at $309(\nu_{29})$, $181(\nu_{30})$, $131(\nu_{31})$, $107(\nu_{32})$, and $78(\nu_{33})$ to the five $\pi(\text{CCl})$ fundamentals. It can be seen that, majority of these assignments differ from the present assignments made on the basis of DFT normal coordinate analysis. This underlines the need for a rigorous theoretical analysis of vibrational frequencies for their accurate assignments. Following the same procedure vibrational assignment of corresponding modes in PCP-OD and PCTP was made. The nature of these vibrations in terms of mixing of PED can be read from Tables 3 and 4, respectively.

5.4.4. Vibrations of CXY moiety (X = O, Y = H for PCP; X = O, Y = D for PCP-OD; X = S, Y = H for PCTP)

There are six vibrations associated with CXY moiety. These are: $\nu(\text{CX})$, $\beta(\text{CX})$, $\pi(\text{CX})$, $\nu(\text{XY})$, $\beta(\text{CXY})$, and $\tau(\text{XY})$. When Y is D, it is directly present in the last three vibrations. Due to its increased mass in comparison with hydrogen atom in PCP, these vibrations decrease in magnitude drastically in PCP-OD. When X is S, it is present directly in the above six vibrations of PCTP. Due to its increased mass in comparison with oxygen atom, the six vibrations mentioned above show marked decrease in the magnitude of their frequencies in comparison with their corresponding modes in PCP. These are obvious inferences. The subtle inferences that arise due to PED in PCP have been discussed earlier (for example see section 5.4.1 dealing with C–C stretching vibrations). A glance at Tables 2–4 reveals the truth of these statements.

The bands at 3520 , 2607 , and 2587 cm^{-1} are due to $\nu(\text{OH})$, $\nu(\text{OD})$, and $\nu(\text{SH})$ in PCP, PCP-OD and PCTP, respectively. They are pure as each one of them gets 100% PED from the corresponding vibration. The band at 1192 cm^{-1} attributable to $\beta(\text{COH})$ in PCP, decreases to 968 cm^{-1} as $\beta(\text{COD})$, in PCP-OD, whereas the corresponding band assignable to $\beta(\text{CSH})$ in PCTP is at a further low value 954 cm^{-1} . The vibrations $\tau(\text{OH})$, $\tau(\text{OD})$, and $\tau(\text{SH})$, in PCP, PCP-OD and PCTP, respectively are at 410 , 298 , and 211 cm^{-1} . As expected by Green et al. [10], its mixing with other vibrations is negligibly small in PCP. This is also true of $\tau(\text{SH})$ in PCTP. In contrast, in PCP-OD, $\tau(\text{OD})$ has predominant contribution of 60% PED from $\pi(\text{CCl})$ 17b and almost half of this (i.e., 33%) from $\tau(\text{OD})$. In PCTP C–(SH) bond acquires a partial double bond character due to the delocalization of charge between lone-pair on sulphur and π -charge on the aromatic nucleus. Hence ν C–(SH) frequency is expected to be higher than that of $\nu(\text{C–S})$ single bond and lower than that of $\nu(\text{C=S})$. The ranges for $\nu(\text{C–S})$ and $\nu(\text{C=S})$ are 600 – 630 cm^{-1} and 1130 – 1160 cm^{-1} , respectively [58]. DFT calculations made here identified the ν C–(SH) near 876 cm^{-1} , with perfect agreement with the above expectation in PCTP. The assignment of C–O stretching vibration in PCP deserves special mention as it does not align with expectations. In alcohols it should appear in the range 1020 – 1050 cm^{-1} according to Varsanyi [46], whereas Faniran [11] expects it around 1281 cm^{-1} (ν_7) in agreement with its assignment in phenol and its pentahalo derivatives. DFT calculations presented here negate both these expectations and predict it at 984 cm^{-1} . This low value of its frequency can be traced to its mixing with lower frequencies $\nu(\text{CCl})$ 20a to the extent of 40% and $\beta(\text{CCl})$ 6a to the extent of 31%. It is to be noted that the band at 1281 cm^{-1} has been assigned to mode 14 in section 5.4.1.

The assignment of ring torsions in the three molecules under investigation can be understood by referring to PED Tables 2–4.

6. Conclusion

From the above investigations the following main points of importance can be inferred.

- (i) Both PCP and PCTP possess a two-fold potential barrier that hinders internal rotation around the C–O bond in PCP and C–S bond in PCTP. Both the molecules are planar with C_s point group symmetry, attaining lowest energy at 0° rotational angle around C–O bond in PCP and C–S bond in PCTP. This theoretical result is in excellent agreement with experimental findings.
- (ii) Theoretically determined structure parameters agree very well with their experimental counterparts for both PCP and PCTP.
- (iii) Unambiguous vibrational assignments are made for PCP, PCP-OD and PCTP, using PED, eigenvectors, and expected lowering of frequencies based on PED for PCP, in going from PCP to PCP-OD and PCTP, for the first time. Symmetry forbidden mixing of PED is not observed in the three molecules investigated, which correctly contradicts the findings of earlier workers.
- (iv) There is a good agreement between the experimental and calculated frequencies for the three molecules. Experimental IR and Raman spectra agree fairly well with their computed spectra for PCP.
- (v) DFT calculations made for dimers of PCP and PCTP substantiate the existence of bifurcated hydrogen bond in PCP and rule out such possibility in the case of PCTP.

Acknowledgements

The authors sincerely acknowledge the University Grants Commission, New Delhi, India (No. F.530/24/DRS-II/2015 (SAP)) for having granted financial support for this investigation. The authors are also thankful to Sophisticated Analytical Instrumentation Facility (SAIF), IIT Madras, Chennai, India for providing spectral measurements. First two authors are grateful to the management of S R Engineering college (Autonomous), Warangal, India, for permitting them to undertake this research work.

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