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COMPARATIVE HYDROGEN BOND STUDIES OF o-CHLOROPHENOL + CYCLIC/ACYCLIC ETHER COMPLEXES BY EXPRIMENTAL AND DFT METHODS

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ABSTRACT

The Fourier transform infrared (FTIR) spectra of binary mixture of o-chlorophenol (OCP) with diphenyl ether (DPE), t-butyl methyl ether (TBME), tetrahydrofuran (THF) and 1,4 dioxane (DN) have been recorded over the entire composition range at room temperature in the regions 4000-400 cm^{-1}. The study indicated bonding interaction between the components of liquid mixtures. These spectra have been investigated in terms of various fundamental modes of vibration. The molecular structures of the binary complexes have been investigated by density functional theory (DFT) using B3LYP functional and 6-31 G (d) basis sets. Computed values have been analyzed and their characterization was made with the help of Gauss View visualization program utilizing the data obtained from Gaussian 03 W calculation. The results of the calculations are compared with the experimentally determined data.

Key words: o-Chlorophenol, Ether, Fourier transform infrared (FTIR), Density functional theory (DFT), Binary complexes.

INTRODUCTION

In recent years, experimental results have been frequently supported with theoretical calculations, which have proved quite helpful in explaining the comparative relativities and many other properties of the organic molecules/complexes.

The most frequently spectroscopic methods for organic chemists are ultra-violet, infra-red, nuclear magnetic resonance and mass-spectrometry. Infra-red (I.R.) measurement through liquid mixtures provide an excellent tool to investigate inter and intramolecular interactions between like and unlike molecules. It is also useful tool for calculations on larger and runs calculations very quickly. The density functional theory (DFT) methods have

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become powerful tools for the investigation of molecular structure and vibrational spectra. Supplemented by visualization program, the assignments can accurately be made. The calculations using DFT with LYP (Lee, Yang and Parr) as correlation functional have been performed for hydrogen, ethers and their complexes. The DFT method[1] that includes correlation in an alternative way has affording opportunities of performing vibrational analysis moderately large organic molecules. In the frame work of DFT approach, different exchange and correlation and functions are routinely used. Among these, the B3LYP combination[2,3] is the most used, since it proved its ability in reproducing various molecular properties, including vibrational spectra. In the present study, the DFT calculation is applied to interpret the vibrational spectra and structure of o-chlorophenol + cyclic/acyclic ether complexes. These DFT computations have recently become at efficient tool in the prediction of molecular structure, vibrational frequencies and IR activities of compounds[4,5].

Hydrogen bonding is of central importance in the molecular sciences for both; practical and theoretical reasons[6-8]. It represents the strongest force governing the influence of solvent on molecular structure and reactivity and a quantitative accounting for hydrogen bonding interactions is a prerequisite for the proper understanding of chemical activity in solution. Hydrogen bonding has held particular interest in recent years due to the central role, it plays with regard to molecular recognition in both; biological and artificial systems[9].

Hydrogen bonded systems are very interesting because hydrogen bond plays vital role in chemical, physical and biological processes. The choice of OCP has been based on its limited association through hydrogen bond in pure state. The *Cis* isomer in OCP presents an intra-molecular hydrogen bonding of the type O — H ---- Cl. This fact determines inability of formation of hydrogen bonding with another molecule of the same kind. The IR spectrum of OCP shows O — H ---- O bonding between the *cis* and *trans* isomers with only 10% of the latter, approximately. Thus, the addition of the components causes the rupture of inter-molecular and intra-molecular hydrogen bonding in OCP and which may be followed by the association of unlike molecules through new type of specific interaction[10].

EXPERIMENTAL

All chemicals were used of A.R. grade (SRL) with purity > 90% and used as such. Binary mixtures of OCP with DPE, TBME, THF and DN were prepared by mixing a known mass of each liquid in airtight stoppered glass bottle with precision 0.01 mg and care was taken to avoid evaporation and contamination during the mixing process. The uncertainty in the mole fraction is ± 0.0001. The measurements were recorded on a digital balance (SHIMADZU AUX 220) to an accuracy of $\pm 1 \times 10^{-4}$ g. Different compositions of mixtures

(0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, and 0.9) were obtained by adding the second component to the standard sample and weighing the added amount.

FTIR spectra were recorded on a FTIR spectrometer (Model : SHIMADZU 8400S PC) by using KBr pellet in the region 400-4000 cm^{-1} with 4.0 cm^{-1} resolution. The transmission values were read in steps of 5%. The spectrometer possesses out to aligned energy optimization and dynamically aligned interferometer. It is fitted with KBr beam splitter, a DLATGS detector. A base line correction was made for the spectra recorded. In order to investigate variation in hydrogen bond interactions between constituent molecules of binary liquid mixtures of o-chlorophenol with cyclic and acyclic ethers, FTIR of the liquid mixtures were recorded at room temperature and atmospheric pressure.

Computational

Geometry optimization and vibrational frequencies of titled compounds were calculated at the DFT levels with B3LYP (Becke-Lee-Yang-Parr three parameters) hybrid functional with correlation function such as one proposed by Lee, Yang and Parr[11] B3LYP is most promising in providing reasonable acceptable vibrational wave numbers for organic molecules. Standard 6-311G (d,p) basis set have been used in the both methods in order to see the effect of correlation. Gaussian 03 software packages[12] have been utilized to accomplish all the calculations.

RESULTS AND DISCUSSION

The FTIR frequencies of the binary mixtures of OCP with ethers over the entire range of compositions at room temperature and atmospheric pressure are listed in Tables 1. Scaled frequencies and hydrogen bonding (O --- H) of optimized systems at B3LYP level using 6-31G (d, p) basis set are shown in Table 2.

Table 1: IR stretching frequencies of –OH (cm^{-1}) in x_1 OCP and (1-x_1) ethers systems

x_1	OCP+DN	OCP+THF	OCP+DPE	OCP+TBME
0	-	-	-	-
0.1	3278.76 (w)	3230.87 (w)	3525.63 (w)	3440.8 (w)
0.2	3280.69 (m)	3246.31 (vw)	3525.63 (w)	3421.5 (w)
0.3	3278.76 (m)	3221.23 (m)	3523.70 (m)	3438.8 (w)
0.4	3419.56 (m)	3259.81 (w)	3523.70 (m)	3425.3 (w)

Cont…

x_1	OCP+DN	OCP+THF	OCP+DPE	OCP+TBME
0.5	3284.55 (w)	3219.30 (m)	3523.70 (w)	3219.0 (vw)
0.6	3298.05 (m)	3221.23 (m)	3523.70 (s)	3224.8 (vw)
0.7	3315.41 (m)	3225.09 (vw)	3521.78 (s)	3222.8 (vw)
0.8	3521.78 (w)	3427.62 (vw)	3519.85 (s)	3438.8 (w)
0.9	3521.78 (w)	3446.90 (vw)	3519.85 (s)	3446.6 (vw)
1.0	3621 (s) broad	3621 (s) broad	3621 (s) broad	3621 (s) broad

s- Strong, m- medium, w- weak, vw- very weak

Table 2: Optimized systems at B3LYP level using 6-31G (d, p) basis set

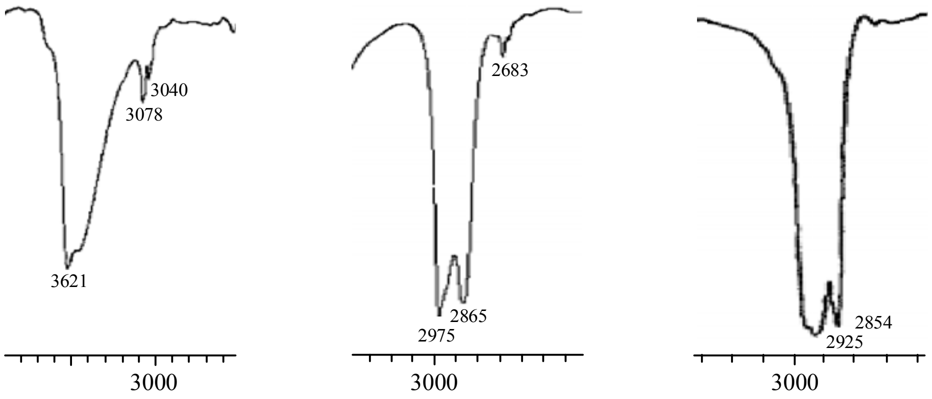
S. No.	System	-OH stretching frequency cm^{-1} (Scaled)	O-H (Å)
1	Trans OCP	3526.90	---
2	Cis OCP	3476.33	---
3	Trans OCP + DN	3752.39	5.3045
4	Trans OCP + THF	3213.63	1.7476
5	Trans OCP + DPE	3384.56	1.8941
6	Trans OCP + TBME	3224.14	1.7698
7	Cis OCP + DN	3469.58	4.4540
8	Cis OCP + THF	3236.75	1.8313
9	Cis OCP + DPE	3404.88	2.0113
10	Cis OCP + TBME	3249.61	1.8538

Fig. 1 represents the FTIR spectra of pure compounds and Fig. 2-5 shows IR frequencies spectra of -OH (cm^{-1}) for OCP + ether systems.

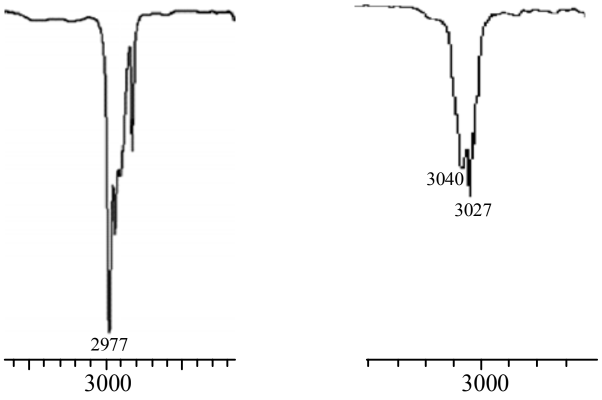
O-H stretching vibrations

The non-hydrogen-bonded hydroxyl group of phenols absorbs strongly in the 3584-3700 cm^{-1} region. The sharp free hydroxyl bands are observed in the vapour phase and in very dilute solution in non-polar solvent[13]. Intermolecular hydrogen bonding increases as the concentration of solution increases and additional bands appears at lower frequencies at 3200-3550 cm^{-1}. In our investigation, magnitude of IR frequencies is more for the binary mixtures OCP + DPE at all compositions as compared to the other binary systems. It is observed from Table 1 that there are not many variations in magnitude for the system OCP + DPE. but absorption of IR radiation increases from $x_1 \approx 0.1$-0.5 and remain same in the range $x_1 \approx 0.6$ - 0.9 (Fig 5).

Intermolecular hydrogen bonding in O-H--O leads to significant shifts to low field although formally the electron density is increased through an interaction with the free electron pair of the accepter atom. However, the electric dipole field of the hydrogen bonding and the peak appears to affect deshielding. A decrease in concentration in a nonpolar solvent disrupts such hydrogen bonding and the peak appears at high field. Rapid exchangeability of the -OH peak of O-H--O is usually observed as a singlet. An –OH in OCP + THF mixtures splits into doublet whereas in the OCP + TBME system, it is complicated with multiplates.



(a) o-Chlorophenol **(b) Tetrahydrofuran** **(c) 1,4-Dioxan**



(d) Tert. butyl methyl ether **(e) Diphenyl ether**

Fig. 1: Neat FTIR spectra

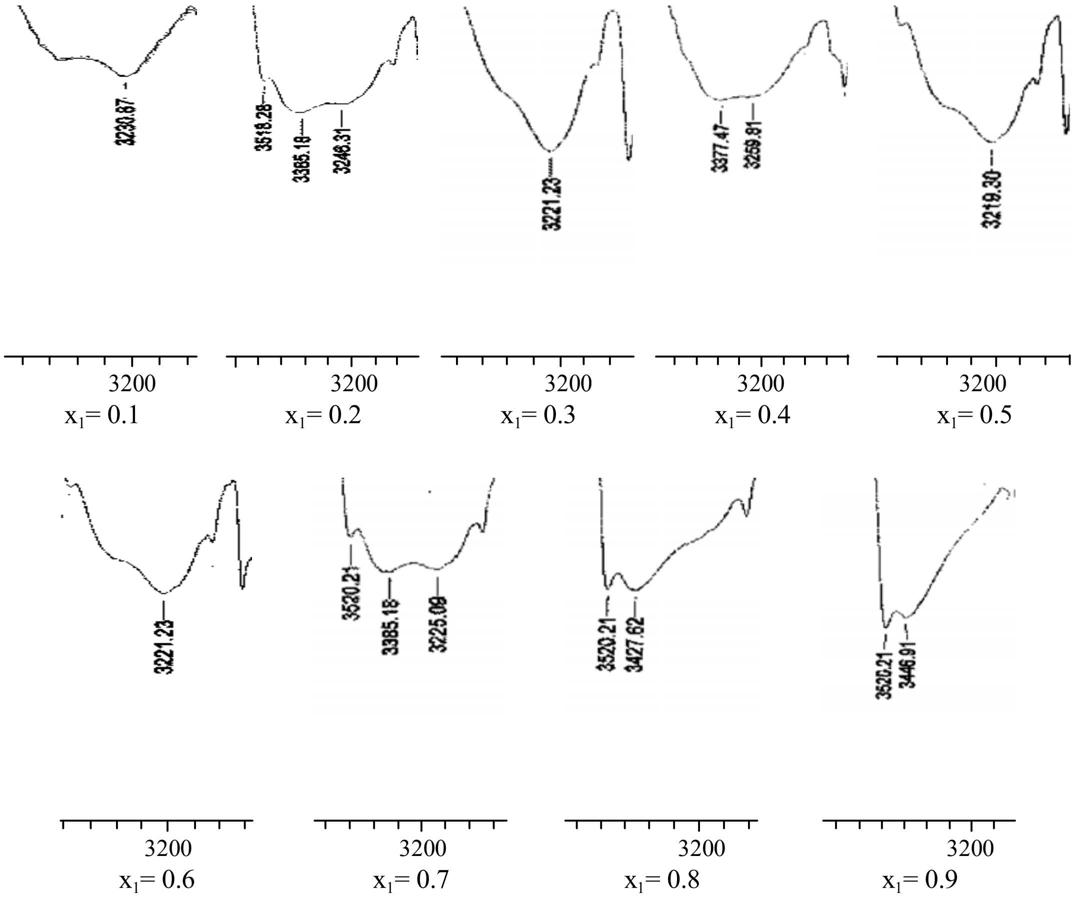
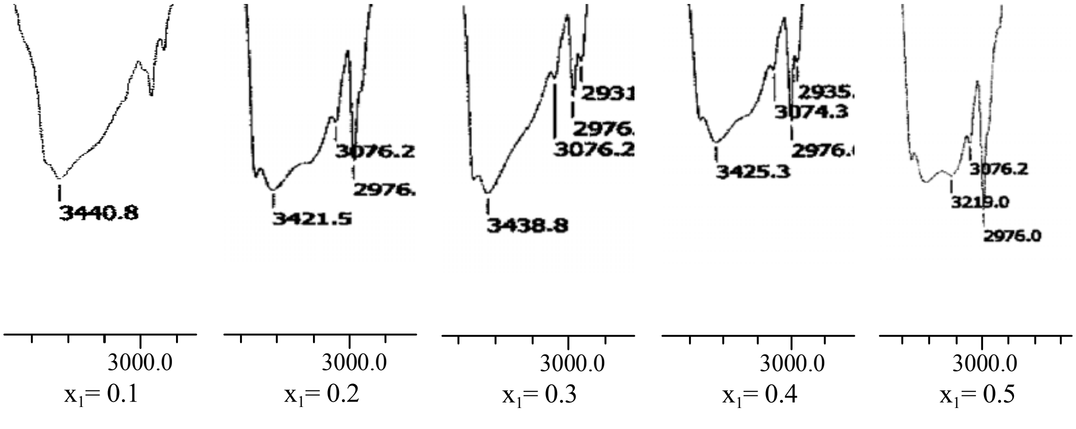


Fig. 2: IR stretching frequencies spectra of -OH (cm^{-1}) for OCP + THF system



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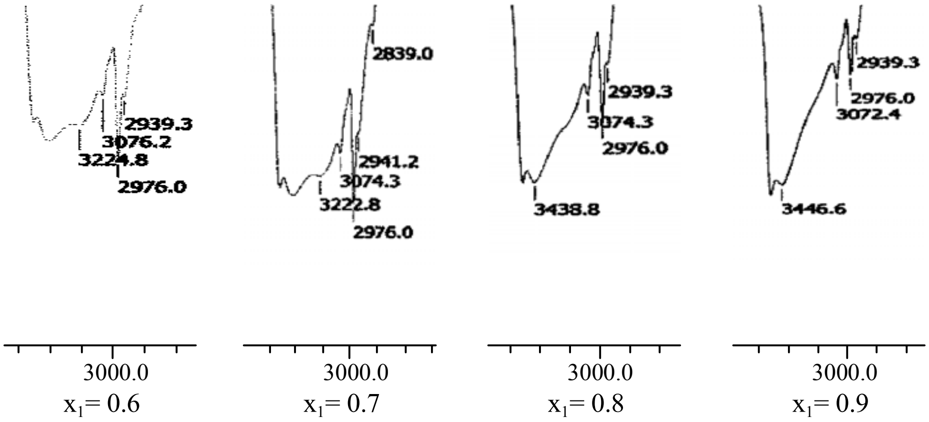


Fig. 3: IR stretching frequencies spectra of -OH (cm^{-1}) for OCP + TBME system

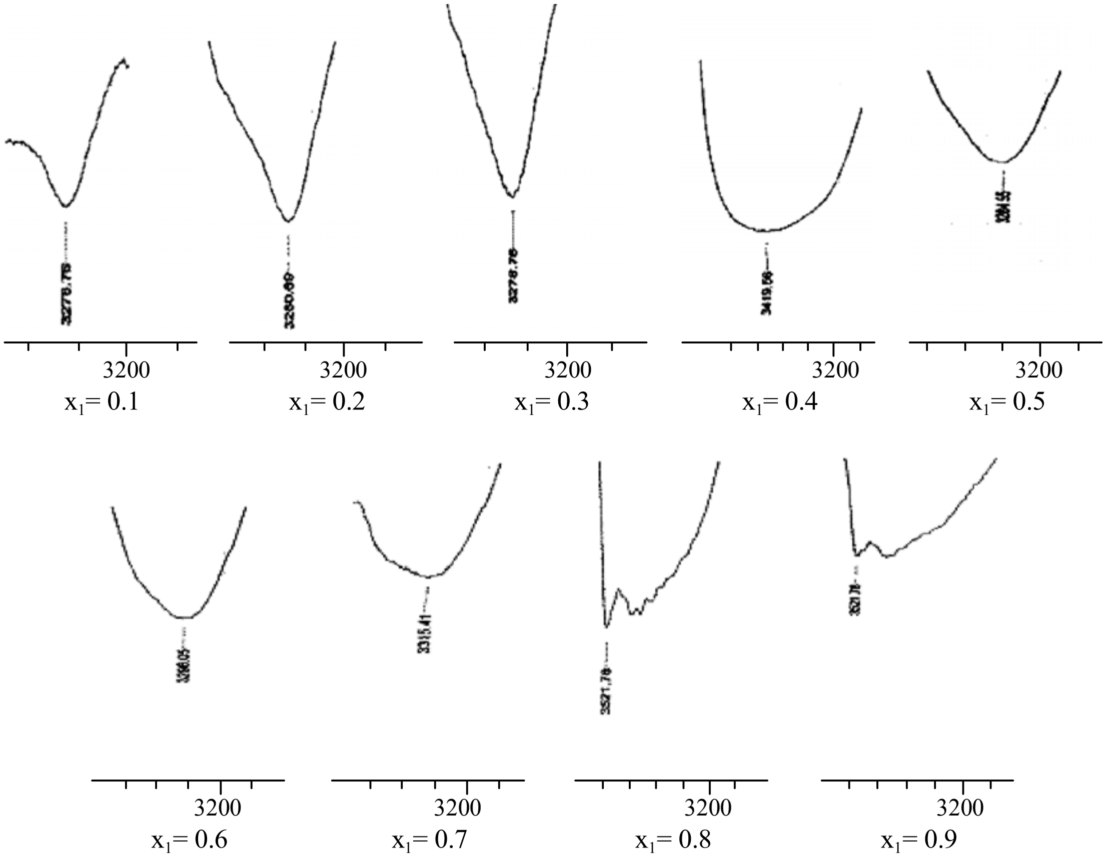


Fig. 4: IR stretching frequencies spectra of -OH (cm^{-1}) for OCP + DN system

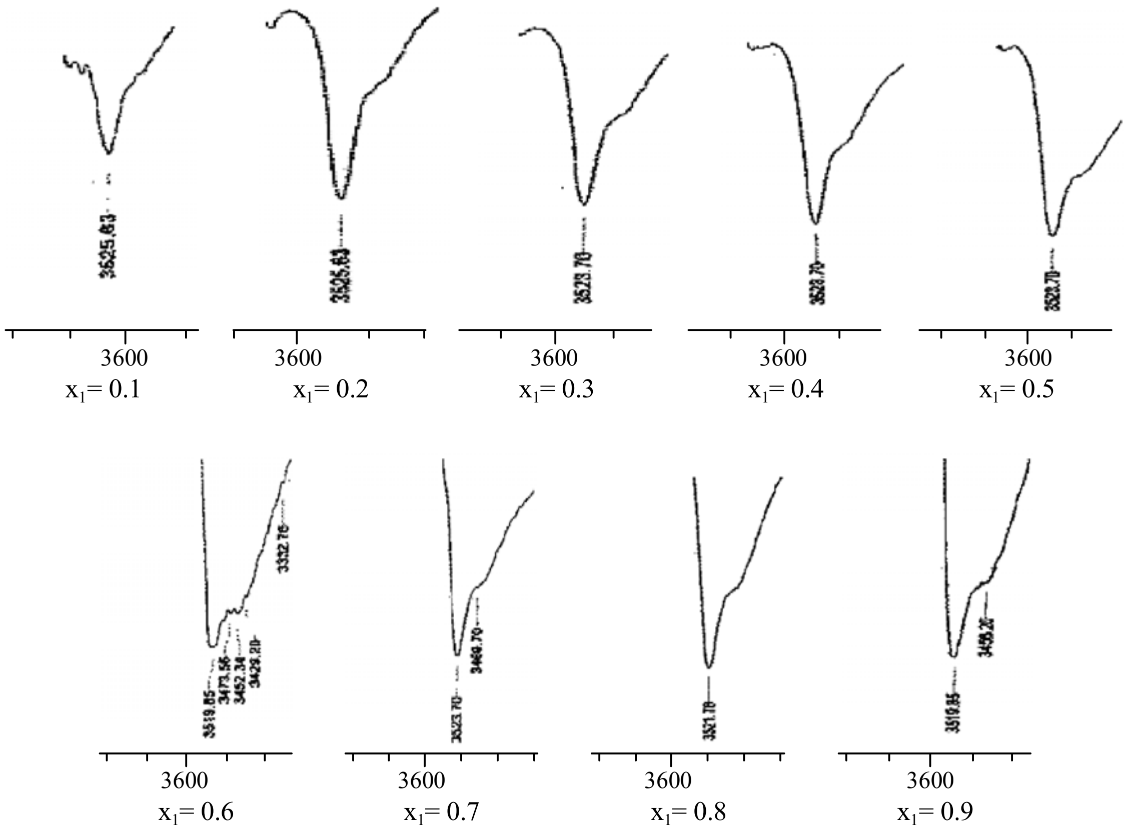
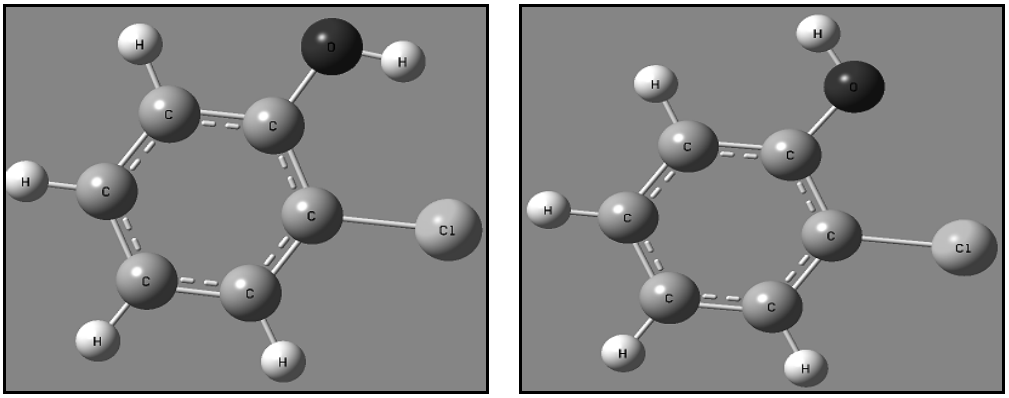


Fig. 5: IR stretching frequencies spectra of -OH (cm^{-1}) for OCP + DPE system



(a) Cis OCP (b) Trans OCP

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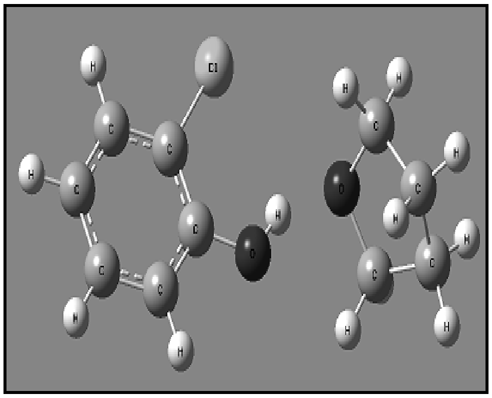
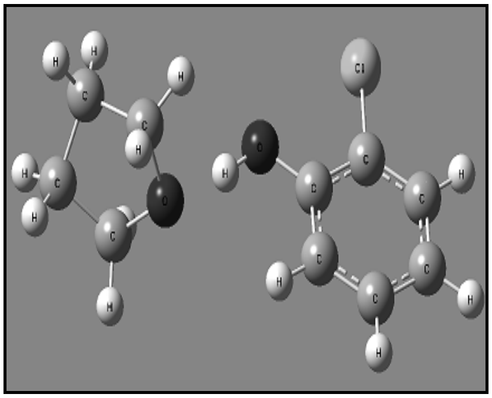
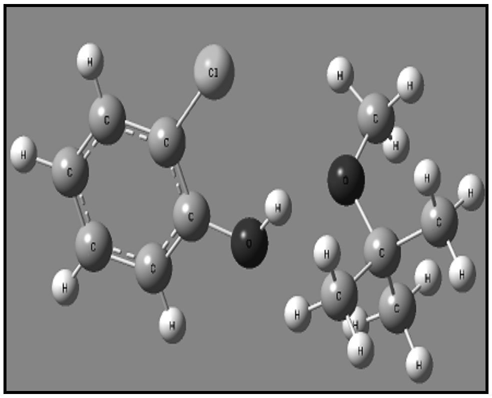


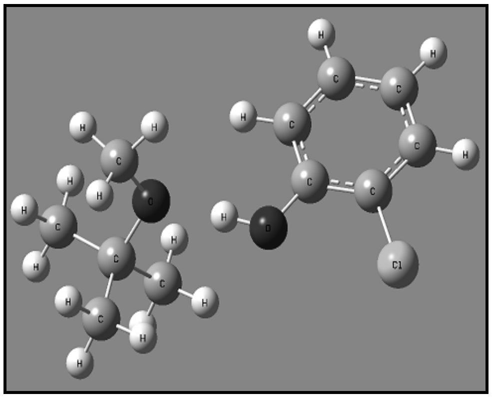
(c) Trans OCP+THF



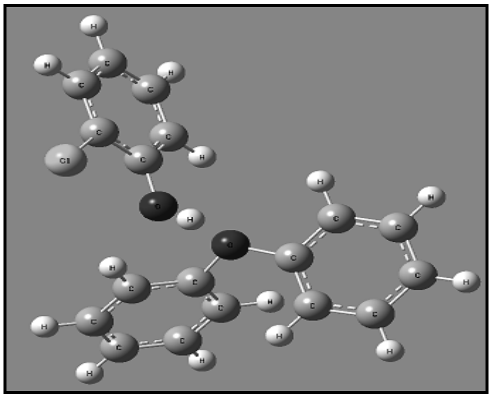
(d) Cis OCP+THF



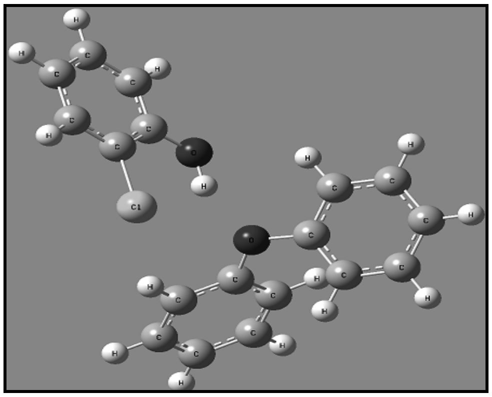
(e) Cis OCP+TBME



(f) Trans OCP+TBME



(g) Trans OCP+DPE



(h) Cis OCP+ DPE

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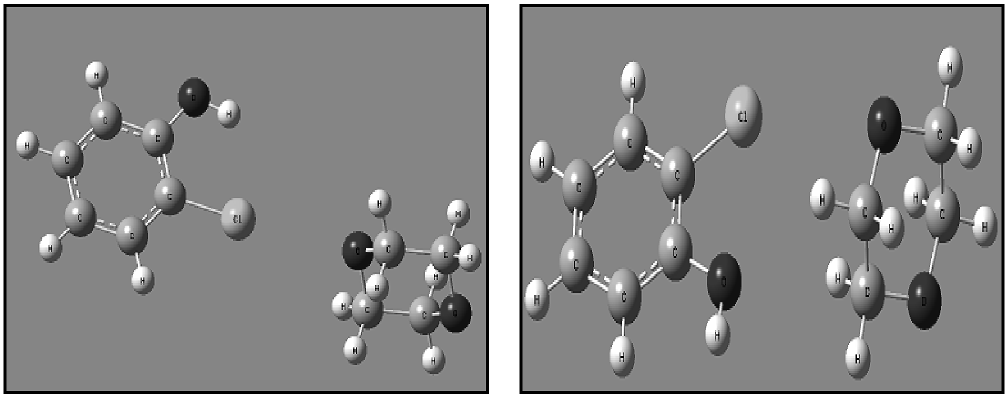

(i) Trans OCP+DN (j) Cis OCP+DN

Fig. 6: Optimized geometries by DFT method at B3/6-3LYP1G (d, p) level

The position and breadth of an –OH absorption band depend on the concentration of the solution. The more concentrated solution, the more likely it is for the –OH containing molecules to form intermolecular hydrogen bonds. It is easier to stretch an O-H bond, if it is hydrogen bonded, because the hydrogen is attracted to the oxygen of a neighboring molecule.

Hydrogen bonded OH group have broader absorption bands while that of non-hydrogen-bonded OH groups are sharper.

The OCP results in O-H stretching, and these vibrations are sensitive to hydrogen bonding. O-H bending modes are not independent on vibrational modes because they couple with the vibrations of adjacent groups[13]. The O-H stretching frequency of OCP is 3621 cm^{-1}, which decreases with ethers because of intermolecular hydrogen bonding between them. The decrease in –OH stretching frequency is not same at all concentrations of OCP + ether systems. The binaries OCP + THF and OCP + TBME show large decrease in the –OH stretching frequencies, because phenolic –OH of OCP form strong intermolecular hydrogen bonding and –OH is more stretched and frequency decreases but in other binary systems OCP + DPE, the decrease is less as compared to others, due to weak intermolecular H-bonding because of bulkier alkyl group present in ethers.

Spectrum of some OCP + ethers show two absorption bands -OH. The sharp band is due to free –OH while weak band is due to hydrogen bonded –OH.

The interesting behavior of intramolecular hydrogen bonds both from the practical and theoretical points of view has received increased attention in recent years[14-22]. This can be attributed to the fact that the value of hydrogen bond energy is only a few kilocalories per mole and can readily perturb by any change in its environment. This is especially important in studies of weakly bound complexes of ethers and OCP.

The difference between the observed and scaled frequency values of most of the fundamentals in many cases is very small. Any discrepancy noted between the observed and the calculated frequencies may be due to the fact that the calculations have been actually done on a single molecule/complex between two molecules in the gaseous state contrary to the experimental values recorded in the presence of intermolecular interactions. Therefore, the assignments made at higher levels of theory with only reasonable deviations from the experimental values seem to be correct.

From Table 2, maximum hydrogen bond distance noted for *Cis*/Trans OCP+DN, showed weak intermolecular hydrogen bond formation and minimum distance (i.e. strongest hydrogen bond among complexes) for *Cis* /*Trans* OCP + THF, and *Trans* OCP + TBME systems.

REFERENCES

1. R. G. Parr and W. Yang, Density Functional Theory of Atoms and Molecules, Oxford, New York (1989).
2. A. D. Becke, J. Chem. Phys., **98**, 5648 (1993).
3. C. Lee, W. Yang and R. G. Parr, Phys. Rev., **B37**, 785 (1998).
4. J. Binoy, C. James, J. I. Hubert and V. S. Jaykumar, J. Mol. Struct., **32**, 784 (2006).
5. C. James, Raj A. Amal, R. Raghunathan, V. S. Jaykumar and J. I. Hubert, J. Raman Spectrosc., **37**, 1381 (2006).
6. G. C. Pimemental and A. L. McClellan, The Hydrogen Bond, W. H. Freeman, San Francisco (1990).
7. M. D. Josesten and L. Schaad, Hydrogen Bonding, Marcel Dekker, New York (1974).
8. S. N. Vinogradav and R. H. Linnell, Hydrogen Bonding, Van Nostand Reinhold, New York (1971).
9. P. S. Kalsi, Spectroscopy of Organic Compounds, New Age International Publishers, New Delhi (2008).
10. R. Kumar, R. Mahesh, B. Shanmugapriyan and V. Kannappan, Indian J. Pure and Appl. Phys., **50**, 633 (2012).

11. M. J. Frisch, G. W. Trucks, H. B. Schlegel and G. E. Scuseria, Gaussian 03, Revision C 02, Inc., Wallingford CT (2004).
12. J. A. Pople, H. B. Schlegel, R. D. Krishnan, J. Defrees, J. S. Binkley, M. J. Frish, R. A. Whiteside, R. H. Haut and W. J. Hahre, Int. J. Quantum Chem. Quantum Chem. Symp., **15**, 269 (1981).
13. R. M. Silverstein and F. X. Webster, Spectrometric Identification of Organic Compounds 6th Ed., New York (2006).
14. H. Nazir, M. Yildiz, H. Yilmaz, M. N. Tahir and D. Ulku, J. Mol. Struct., **524**, 241 (2000).
15. M. Cuma, S. Scheiner and T. Kar, J. Am. Chem. Soc., **120**, 1049 (1998).
16. A. Filarowski, T. Glowiak and A. Koll, J. Mol. Struct., 484, 75 (1999).
17. H. Raissi, E. Moshfeghi, A. F. Jalbout, M. S. Hosseini and M. Fazli, Int. J. Quant. Chem., **107**, 1835 (2007).
18. M. Cuma, S. Scheiner and T. Kar, J. Mol. Struct., 467, 37 (1999).
19. G. Chung, O. Kwon and Y. Kwon, J. Phys. Chem., **A 102**, 2381 (1998).
20. M. Fores and S. Scheiner, Chem. Phys., **246**, 65 (1999).
21. C. Cheng, S. F. Shyu and F. S. Hsu, Int. J. Quant. Chem., **74**, 395 (1999).
22. V. Barone, P. Palma and N. Sanna Phys. Lett., **381**, 45 (2003).

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