

Chapter 2

Characterization of dimers of 2-substituted-benzo[d][1,3]oxazin-4-ones

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2.1 Introduction

The study of inter molecular interaction is a frontier topic because of its prolific role in a wide variety of chemical and biological phenomena (Karger *et al.*, 1999). This intermolecular interaction plays important roles in the biological activities possessed by medicinally important compounds. One such interaction, the hydrogen bonding, gives rise to the hydrogen bonded molecular assemblies is the major building blocks of supramolecules. The hydrogen bond represents one of the modern frontiers of scientific venture because of its role in the structure stabilizing, or even structure-directing role. The hydrogen bonded structures are studied in various disciplines of science including self-organized and biologically relevant molecules. The hydrogen bond is a unique phenomenon in structural chemistry and biology (Desiraju & Steiner, 2001). In spite of various studies, the role of hydrogen bond in structure stabilizing is yet not fully explored. Here, a brief review of hydrogen bond is presented to understand its arrangement and importance.

2.1.1 Definition of hydrogen bond

The term “Hydrogen bond” was brought into the mainstream by Pauling (1939). Pauling's definition of a hydrogen bond is that ‘*Under certain conditions, an atom of hydrogen is attracted by rather strong forces to two atoms instead*’. It is clear from this definition that the strength of the hydrogen bond depends upon the relative electro negativity of the donor and acceptor atoms (Pauling, 1939).

In 1960, Pimentel and McClellan further refined the definition of hydrogen bond like this- “*A hydrogen bond is said to exist when (1) there is evidence of a bond, and (2)*

there is evidence that this bond specifically involves a hydrogen atom already bonded to another atom” (Pimente & McClellan, 1960). It is indeed surprising that most authors felt the need for a universal definition of ‘hydrogen bond’. However IUPAC defines it as follows: The hydrogen bond is an attractive interaction between a hydrogen atom from a molecule or a molecular fragment X–H in which X is more electronegative than H, and an atom or a group of atoms in the same or a different molecule, in which there is evidence of bond formation (Arunan *et al.*, 2011).

2.1.2 Type of hydrogen bond

The O-H and N-H groups are considered as the most general proton donor groups that form strong hydrogen bonds. Similarly, the most conventional proton acceptors are the O-atom and the N-atom. The C-H group acts as a proton donor even though the polarity of C-H group is apparently less than that of O-H and N-H groups (Bonchev & Cremaschi, 1974). The capacity of *n* electronic clouds of -OC- bonds and aromatic rings to act as hydrogen bond acceptors was recognized (Levitt & Perutz, 1988).

Although the strength of a hydrogen bond is not as big as a covalent bond, it is able to control a molecular ensemble due to its directionality and cooperative effects. Jeffrey and Saenger (1991) (Jeffrey & Saenger, 1991) has classified hydrogen bond as “strong” and “weak”. According to Desiraju, hydrogen bonds that are able to control crystal and supramolecular structure effectively are stronger e.g. O-H-O=C, N-H-O=C and O-H-O-H, while weak hydrogen bond has variable influence on crystal structure and packing (Desiraju & Steiner, 2001). The type of interactions mentioned elaborately involves *conventional* hydrogen bonds such as O-H...O and N-H...O, that are in contact, where the acceptor and donor atoms are electronegative. Fascinatingly, researchers at present emphasizes on another sort of hydrogen bonds where the donor is an atom with low or moderate electronegativity, and which possess strength weaker than that observed in *conventional* hydrogen bonds (Desiraju & Steiner, 1999).

Many of the evidences of these *weak* hydrogen bonds can be found in biomolecules, organic molecules, organometallic compounds and inclusion complexes; and many were characterized with the aid of several diffraction methods. Particular cases of such interactions are the C-H...O and the C-H...N hydrogen bonds, where the acceptor

atom can be oxygen or nitrogen, and the donor is the carbon atom. The role of such interaction on the structural stabilization in molecular systems is still unclear and also a debatable issue. Yet, the number of such studies exploring the importance of this interaction is increasing with time.

2.1.3 C-H-O interaction

In 1937, C-H...O interaction was first hinted by Samuel Glasstone. He established the concept of C-H...O interactions in mixtures of acetone with different halogenated derivatives of hydrocarbons. Though C-H...O hydrogen bond is well-established in structural chemistry and physical organic chemistry but existence of a C-H...O interaction itself is still debated amongst the authors. Over the past decade the concept of supramolecular chemistry was envisaged as an 'emergent phenomena'. (Stoddart, 2009). The fact remains that most of the studies are limited to the systems in which hydrogen is attached to some hetero-atom. The importance of newer motifs for molecular assemblies framed with much weaker hydrogen bonded systems like C-H...O=C H-bond hitherto remained largely unexplored. Sutor (Sutor, 1963) and Ramachandran (Ramachandran *et al.*, 1963) believed that these interactions contribute significantly to crystal stability and Sutor proposed the existence of this type of hydrogen bond in the early 1960s. Today many crystallographers and structural chemists accept that these interactions are of significance. A landmark study was done by Taylor and Kennard in 1982 (Taylor & Kennard, 1982), providing conclusive evidence about the existence of C-H...O hydrogen bonds in crystals. Subsequently, G. R. Desiraju asserts in his published text as- 'It certainly is'. (Desiraju, 1991; Desiraju, 2002) Since then, several articles were published on this type of hydrogen bonded system; but the subsistence of such H-bonds in solution state still remained in the probing stage of - 'may be' because of the inherent feeble nature compared to other H-bonds.

Although C-H...O interactions are much weaker than the conventional O-H...O bonds, it is now well established that it plays an important role in a wide variety of chemical and biochemical phenomena. The energy of C-H...O hydrogen bonds rarely exceeds 8 kJ mol⁻¹ while it significantly contributes in crystal packing and

supramolecular design (Desiraju, 1996; Steiner 1997). Interestingly, in past decade, literatures have suggested that C-H-O hydrogen bonds are also key interacting bonds in the structure and activity of biological systems. The occurrence of C-H-O hydrogen bonds was also reported in the active sites of enzymes such as serine hydrolases (Derewenda *et al.*, 1994) and kinase inhibitors (Talyor & Kennard, 1982). Despite the intrinsic weakness in strength, these types of bonds are being recognized to have certain roles in many aspects of chemistry and biology (Harumi & yukihiro, 2005). Formation of aryl -CH---O hydrogen bond in certain kind of Kinase inhibition studies is established in crystal structure of protein complex of pyrazol-3-quinazolin-4-ylamine (Pierce *et al.*, 2005).

Additionally, theoretical methods also used to estimate the binding energies of these non-conventional hydrogen bonds. Theoretical studies proved that this is a very important stabilizing force in some systems (Louit *et al.*, 2002; Ruiz *et al.*, 2004; Graza *et al.*, 2005; Navarrete-lopez *et al.*, 2007). Previous authors estimated the strength (2.1 kcal/mol) of the C-H interaction, with the C=O group in four conformers of the *N,N*-dimethylformamide dimer in approximately 2.1 kcal/mol (Vargas *et al.*, 2000). They have also reported that by using a linear correlation between C-H...O bond energies and gas-phase proton affinities, the ΔH for the C-H...O=C hydrogen bond in around 3.0 kcal/mol, about 2.3 kcal/mol less than the N-H...O=C hydrogen bond strength. This fact reveals that the C-H...O=C hydrogen bonds involved in proteins are strong enough to play an important role in the stabilization of secondary and ternary structure of these systems (Ramírez *et al.*, 2008). Although most of the experimental results reported refer to the crystalline state, what remains yet to be known or established are the small molecular assemblies with C-H---O bonds which can exist in protic solvents as well. Though it is reported that cooperative interactions of the weak forces enhances the stability of the molecular assembly (Prins *et al.*, 2001). It is a general chemical intuition that this zipper effect should be insufficient to stabilize the system particularly in water or methanol solution.

2.2 Materials and methods

The curve fitting for the studies were done using ORIGIN 6.1, owned by Department of Physics, North Bengal University. Quantum mechanical calculations were carried out on a Desk Top PC with an intel Pentium IV Core 2 Duo processor. The semi empirical program package MOPAC 2000 (Fujitsu) program, in Chem 3D Ultra 8.0 Graphic interface under CambridgeSoft software Chem Office 3D Ultra 8.0 Graphic interface under CsmbridgeSoft software Chem Office Ultra 2004 was used for visualization. For each compound, computations were carried out with the PM3 method. The semi-empirical (MOPAC) method for the quantum mechanical calculations was. The molecular structures obtained in this were used in a configurational interaction calculation to compute dipole moments, bond orders, and electronic transition energy.

The other spectroscopic methods were written in the Chapter-1.

2.3 Results and Discussion

2.3.1 UV-spectrometric study:

The absorption spectra of the 2-substituted-bezo[d][1,3]oxazin-4-one were observed in the range of 250-400 nm in various solvents, the corresponding λ_{\max} with molar extinction coefficients are tabulated in the in the Table 2.1. A typical UV-spectral graph in different concentrations is shown in the Figure 2.1 the peaks with higher intensity in the range of wave lengths 250 nm to 270 nm were for π - π^* transitions and the peaks of lower intensity in the range of 270 nm to 340 nm were due to n- π^* transitions. It is apparent from the graph that with increasing concentrations there was a shift of λ_{\max} values to higher wave length which is more prominent in the 250 nm to 270 nm range but not so prominent in the peaks at 270 nm to 340 nm range which originated due to forbidden n- π^* transition. Another interesting point is that the spectra have an explicit isosbestic point 340 nm. The occurrence of the isosbestic point signifies that the substance under study is converted to another that has very close molar absorption

Table 2.1- UV-spectrometric study of the compound 1a, 1b, 1c and 1d.

Compound(s)	Solvent(s)	Lambda max (nm) (λ_{max})	Molar Extinction coefficients
1a	Water + 35% methanol	232	20443
		265	11182
		307	6955
	n-octanol	215	20505.5
		239.5	20406.5
		290.5	16700.2
		317	11598
1b	Water +35% methanol	237.5	18282
		267.5	11776
		306.5	7406
	n-octanol	217.5	34012
		243.5	26603.5
		293.5	28723
		320	21527.5
1c	Water +35% methanol	239	18328
		279	11180
	n-octanol	222	31256
1d	Water + 35% ethanol	252	27374.5
	n-octanol	236	21362
1a = 2-phenylbenzo[d][1,3]oxazin-4-one, 1b = 2-(4-methoxyphenyl)benzo[d][1,3]oxazin-4-one , 1c = 2-(4-chlorophenyl)benzo[d][1,3]oxazin-4-one, 1d = 2-methyl-4H-benzo[d][1,3]oxazin-4-one			

of UV radiations and are in equilibrium. This converted product should be a dimer as we have also seen in the DART method of Mass spectra one peak corresponded to $2M^+$.

The UV-spectral property was also studied in water, chloroform and toluene, wherein all the spectra indicated involvement of carbonyl in the dimer formation. The stock solution of all derivatives of 1×10^{-4} was prepared in different solvents (methanol, toluene, chloroform and water) and each solution was diluted with same solvents up to concentrations 1×10^{-5} . However, in case of dilution with water, the stock solution was prepared in methanol.

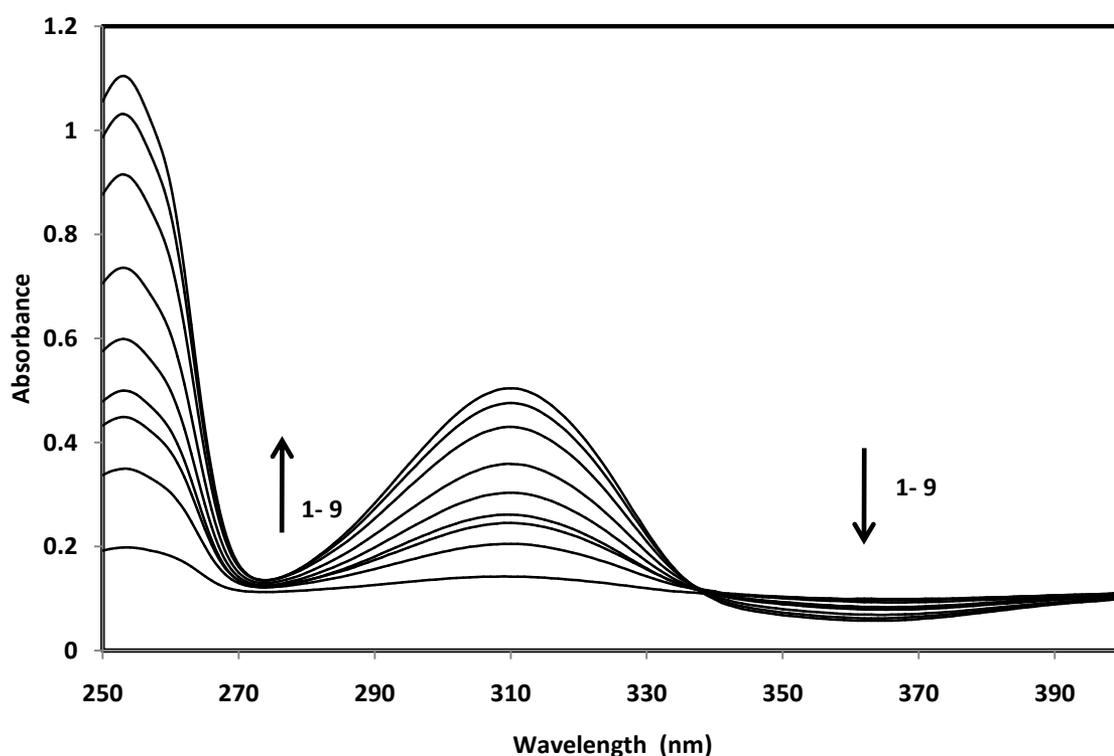


Figure 2.1: UV-spectra of compound 2-methyl-4H-bezo[d][1,3]oxazin-4-one at different molar conc. in methanol (1) 1×10^{-5} (2) 2×10^{-5} (3) 3×10^{-5} (4) 4×10^{-5} (5) 5×10^{-5} (6) 6×10^{-5} (7) 7×10^{-5} (8) 8×10^{-5} (9) 1×10^{-4} .

2.3.2 Determination of the Dimerization Constant

To analyze the association feature of these compounds, we have used a simple association model in which associate constant will indicate about their association strength. The average extinction coefficients in the wavelength within 250-350 nm were plotted by various concentrations within range of 10^{-4} to 10^{-5} molar.

The dimerization constant was determined using following equations where M is monomer, [M] is molar concentrations of monomer, D is dimer, [D] is molar concentration of dimer and P is observed property (average molar extinction coefficient, OD)

$$K = \frac{[D]}{[M]^2} \quad (1)$$

$$C = [M] + 2[D] \quad (2)$$

$$\frac{C - M}{2} = K[M]^2$$

$$C - M = 2K[M]^2$$

$$2K[M]^2 + M - C = 0$$

$$M = \frac{-1 \pm \sqrt{1 + 8KC}}{4K}$$

$$D = \frac{4KC + 1 - \sqrt{1 + 8KC}}{2a}$$

$$P = [M]P_M + [D]P_D \quad (3)$$

$$P = \alpha P_\alpha + \beta P_\beta \quad (4)$$

The observed optical density OD_{obs} can be formulated by the solution of equations (1) to (3) which is given by

$$OD_{\text{obs}} = OD_{[M]} \cdot \frac{-1 + \sqrt{1 + 8K_a C}}{4K_a} + OD_{[D]} \cdot \frac{1 + 4K_a C - \sqrt{1 + 8K_a C}}{8K_a}$$

C is the monomer concentration and [M] and [D] are calculated in terms of C because it is measurable.

The curve fitting for the studies were done using ORIGIN 6.1. The “best-fit” curve was fitted by a minimum sum of squares method to the plot of average properties against concentration C to obtain the dimerization constant (K_a) value in different solvents. Average extinction coefficients case equation (4) gave better curve-fit results. Some curve fit data along with the predicted cum observed values are presented. The dimerization constants are determined within the dilution range 10^{-5} to 10^{-4} molar in UV spectroscopic method.

UV spectra of 2-methyl-4H-bezo[d][1,3]oxazin-4-one and 2-methyl-4H-bezo[d][1,3]oxazin-4-one showing average absorbance of calculated vs. observed in different concentration in different solvents and their curve fitted graph. Some of the data used in curve fittings and the nature of the fit is shown in following Figure 2.2 and 2.3 respectively.

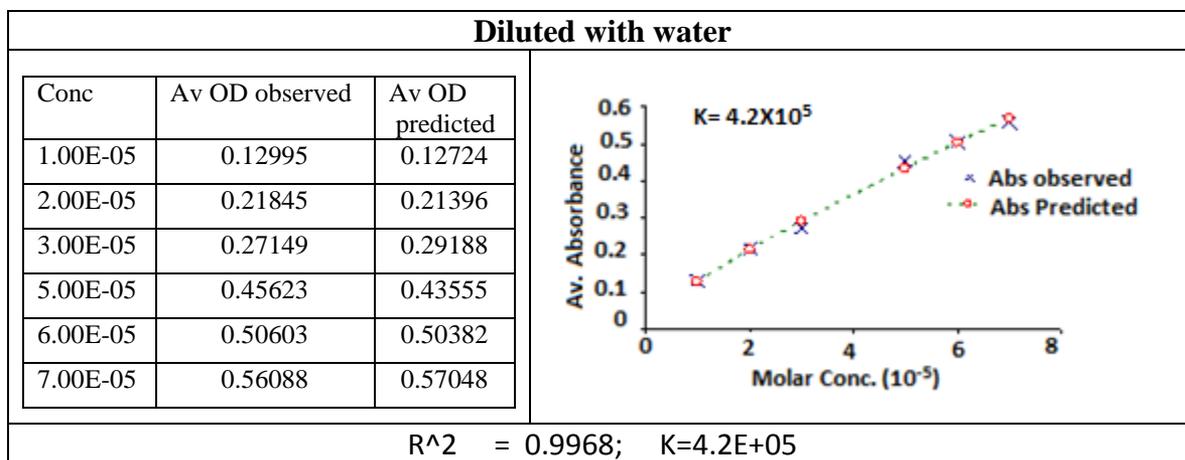


Figure 2.2 (a): UV spectra of 2-phenyl-4H-bezo[d][1,3]oxazin-4-one showing average absorbance of calculated vs. observed in different concentration in water and their curve fitted graph

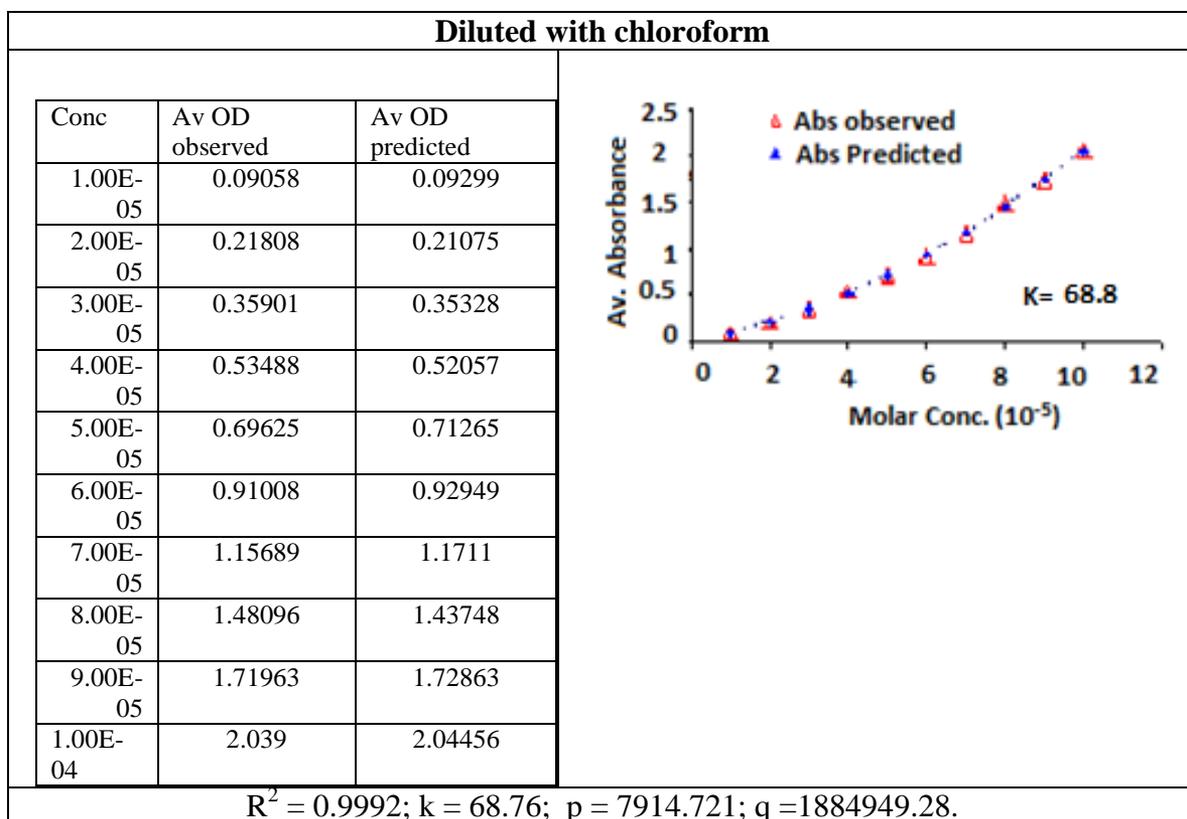


Figure 2.2 (b): UV spectra of 2-phenyl-4H-bezo[d][1,3]oxazin-4-one showing average absorbance of calculated vs. observed in different concentration in chloroform and their curve fitted graph.

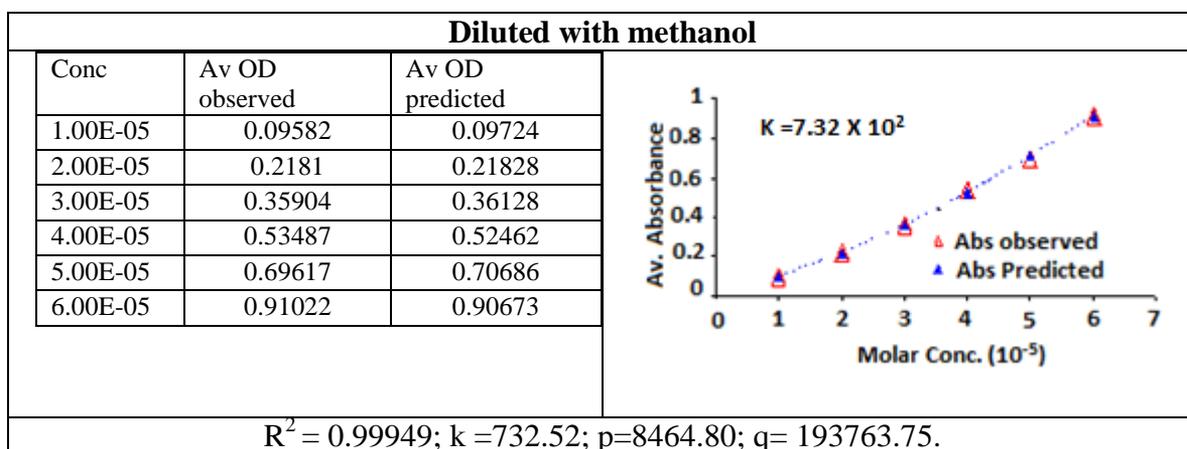


Figure 2.2 (c): UV spectra of 2-phenyl-4H-bezo[d][1,3]oxazin-4-one showing average absorbance of calculated vs. observed in different concentration in methanol and their curve fitted graph.

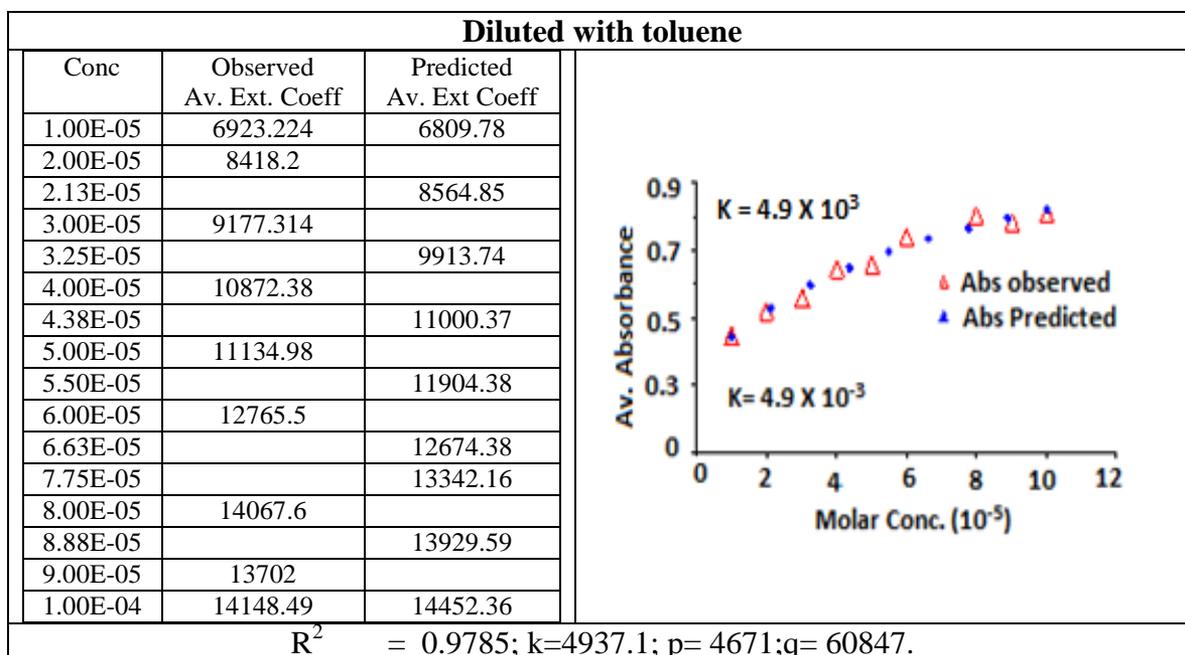


Figure 2.2 (d) : UV spectra of 2-phenyl-4H-bezo[d][1,3]oxazin-4-one showing average absorbance of calculated vs. observed in different concentration in toluene and their curve fitted graph.

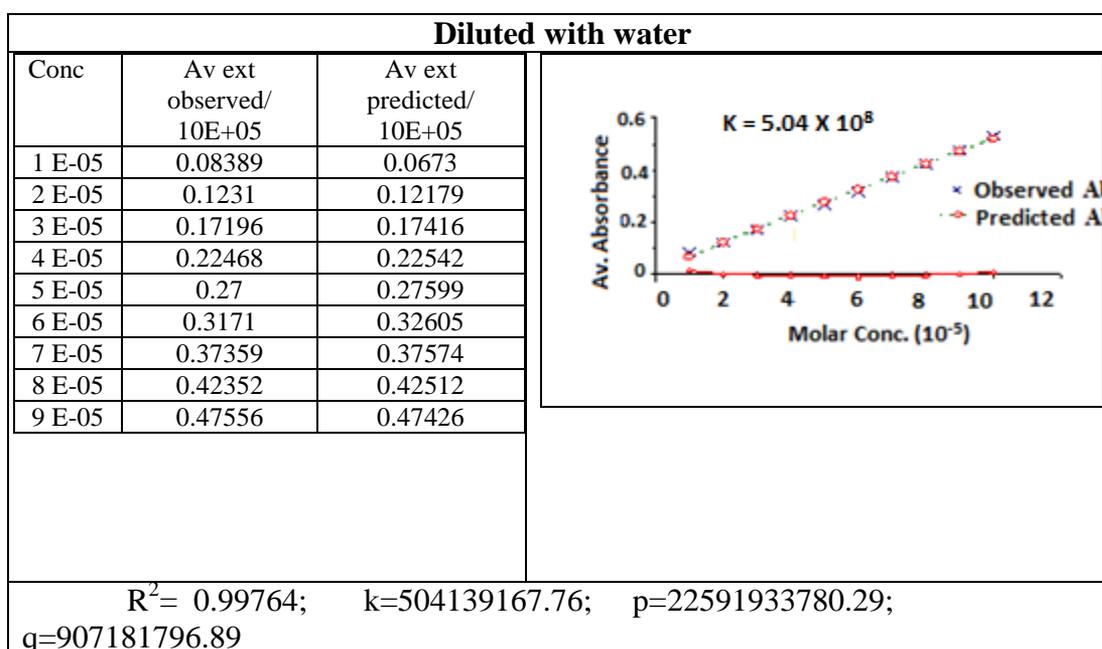


Figure 2.3 (a) : UV spectra of 2-methyl-4H-bezo[d][1,3]oxazin-4-one showing average absorbance of calculated vs. observed in different concentration in water and their curve fitted graph.

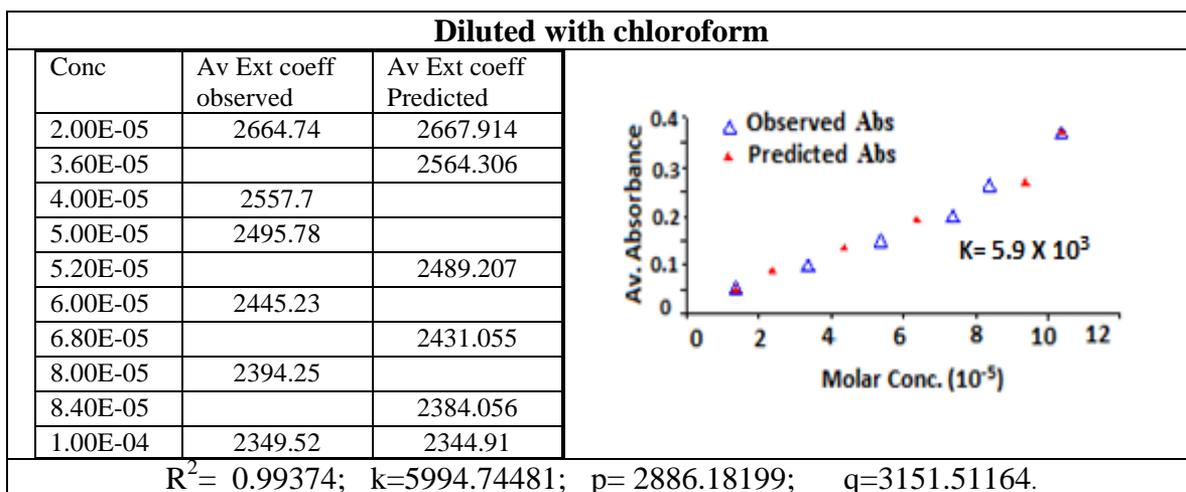


Figure 2.3 (b): UV spectra of 2-methyl-4H-bezo[d][1,3]oxazin-4-one showing average absorbance of calculated vs. observed in different concentration in chloroform and their curve fitted graph.

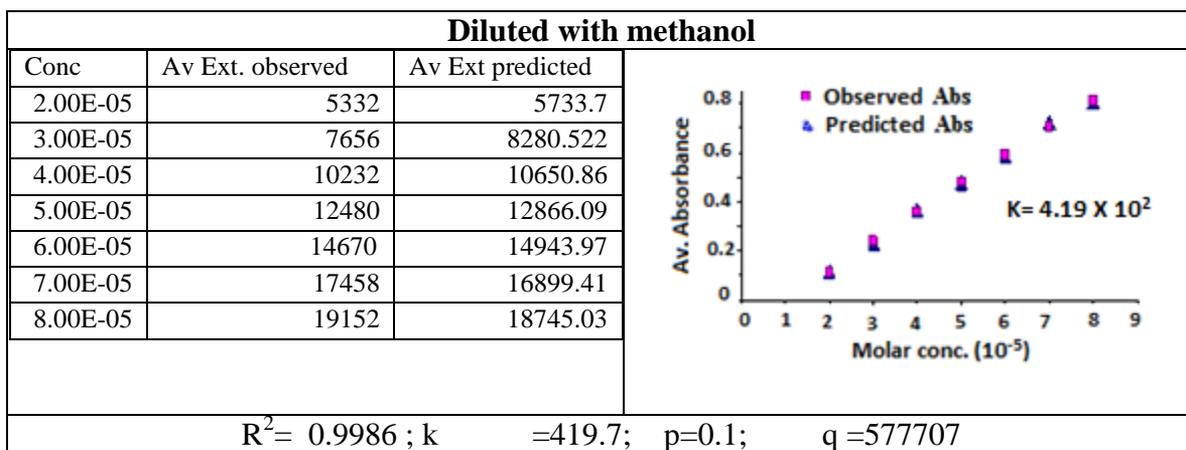


Figure 2.3 (c): UV spectra of 2-methyl-4H-bezo[d][1,3]oxazin-4-one showing average absorbance of calculated vs. observed in different concentration in methanol and their curve fitted graph.

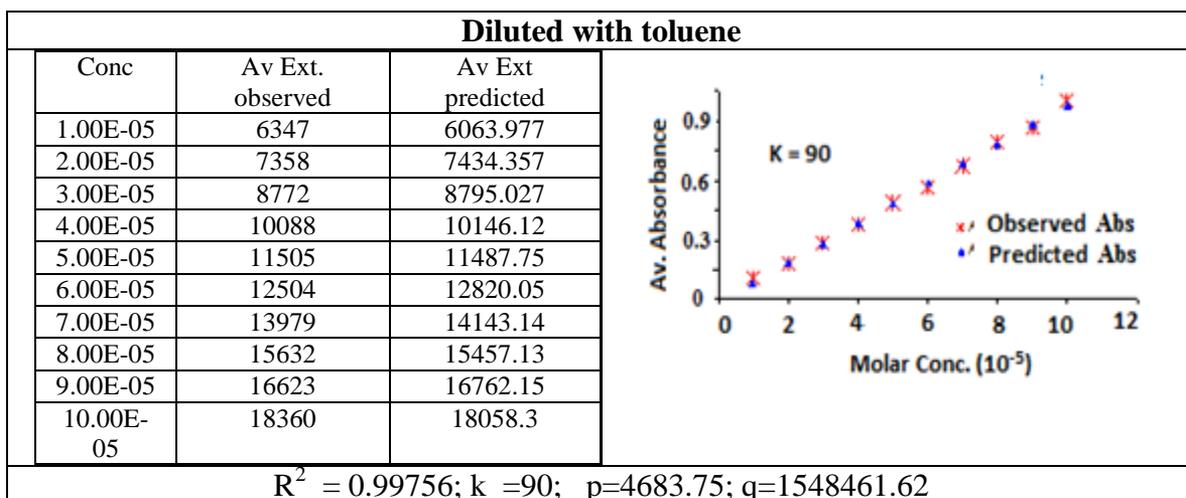


Figure 2.3(d) : UV spectra of 2-methyl-4H-benzo[d][1,3]oxazin-4-one showing average absorbance of calculated vs. observed in different concentration in toluene and their curve fitted graph.

Different workers have used to determine dimerization constants, assuming the only existence of dimers and monomers of the compounds in solution, the formation of the dimer is expressed by the equations $K_a = [D]/[M]^2$ (eqn-1) and $C = [M] + 2[D]$ (eqn-2) (Matsumoto *et al.*, 2003) and observed property (P) as in equation-(3); when P is expressed in mole-fraction equation-(3) is used for the determination of dimerization constant in Self-Association model (Martin, 1996).

The approximation used in mole fraction calculation in eqn (3), is the use of C with the consideration that the dimer concentration is very low and the average extinction coefficient is calculated in terms of monomer concentration, it should not impair significantly the value of dimerization constant since the existence of isosbestic point signifies comparable molar ODs for both the monomer and dimer and as a consequence the average value would not be dominated preferentially by monomer or dimer.

Table 2.2. Dimerization constants of compounds 1a, 1b, 1c and 1d in different solvents.

Compound	Methanol	Chloroform	Water	Toluene
2-phenyl-4H-bezo[d][1,3]oxazin-4-one (R=phenyl)	7.3E+02	6.8E+01	4.2E+05	4.9E+03
1b (R=p-Me-phenyl)	7.1E+05	1.0E+04	1.4E+09	-----
1c (R=p-Cl-phenyl)	1.8E+03	3.0E+03	1E+07	-----
2-methyl-4H-bezo[d][1,3]oxazin-4-one (R=methyl)	4.2E+02	5.9E+03	5.0E+08	9E+01

The changes observed in the association constants in different solvents (Table-2.2) can be attributed to the ability of the solvent to engage in hydrogen bonding which can compete with self-association and to differential solution of the different dipoles of the associated and unassociated species. It is observed that the value of dimerization constant is lesser in protic polarisable solvents like methanol and chloroform (0.1M to 1E-05M range). But in polar protic solvent water the dimerization constants are comparatively much higher. As water is the least polarizable among the solvents studied we can say that solvent polarizability has significant role in dissolving the monomer. The self-association of daunorubicin (anthracycline antibiotic) in aqueous solution was examined using visible absorption (Martin, 1980). Similarly, they have also interpreted Spectral changes in the concentration range 10^{-6} to 1.5×10^{-3} M in terms of a monomer-dimer equilibrium for daunorubicin and data were analyzed using a nonlinear curve-fitting technique.

2.3.3 Analysis of NMR Spectra

NMR spectroscopy is an important tool to study the weak interaction such as C-H-O in solution state. On the basis of the importance of NMR, we initiated NMR spectroscopic characterization. The spectra were taken in $CDCl_3$. The proton and carbon peaks in NMR spectra are assigned unequivocally by proton homonuclear and proton

carbon heteronuclear correlation spectra. After proper assignment of all the peaks the effect of dilution on the peak positions was investigated; it is revealed that in CDCl_3 all the proton peaks shifts regularly to higher δ -values with dilution. The changes in chemical shift values of all the protons with dilution for 2-methyl-4H-bezo[d][1,3]oxazin-4-one is depicted in Figure 2.4.

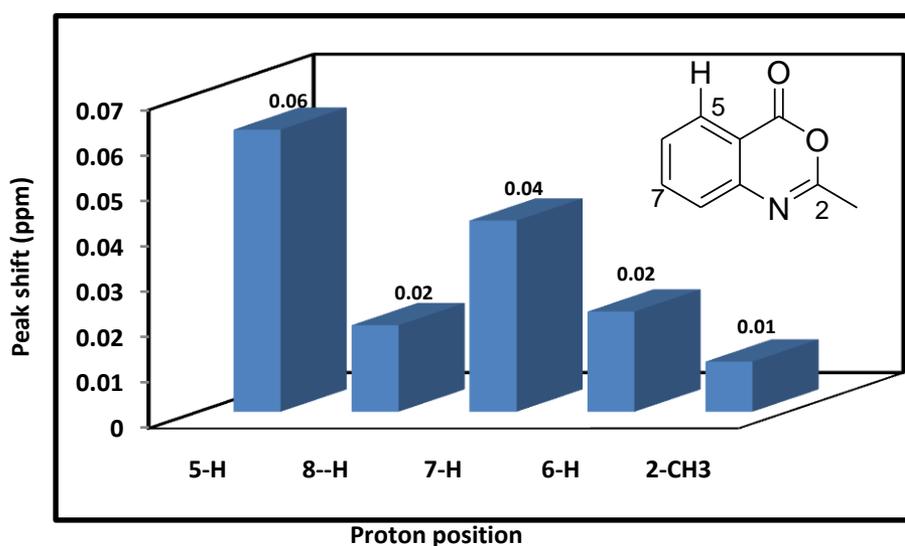


Figure 2.4: Change of proton chemical shift within the dilution range

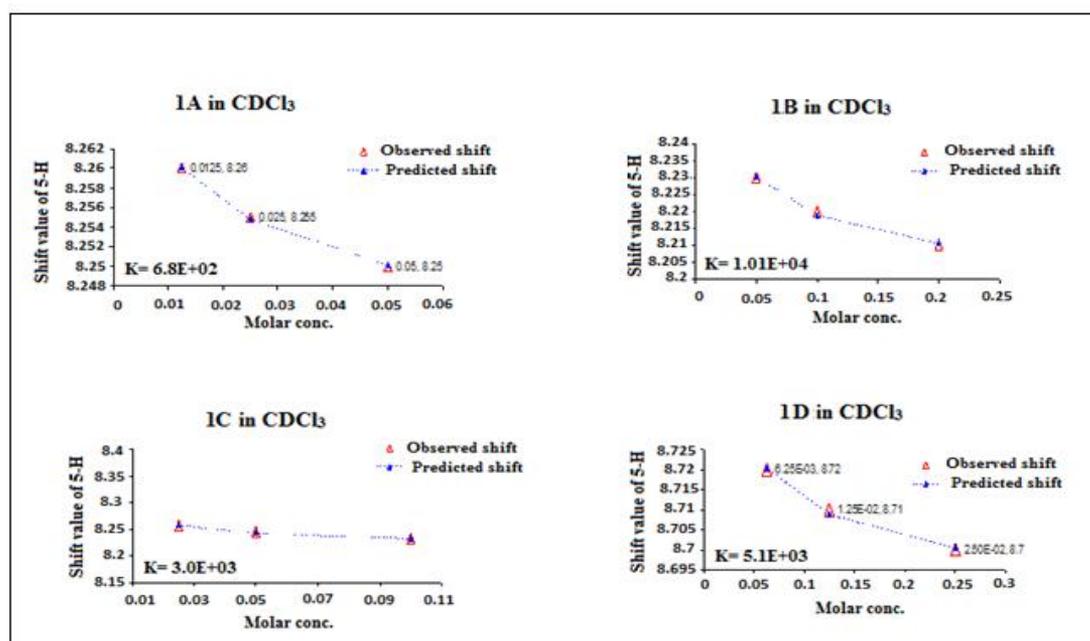


Figure 2.5: Shift of peaks at 5-H in different concentrations in 1a-1d.

Using similar equations used for the calculation of dimerization constants in UV-spectra, here we also found good fit. Curves which corresponded to the values in chloroform in UV-method. Some curve fit tables are shown in Figure 2.5.

Previous author has reported the presence of unusual N-H-O hydrogen bond in benzoxazine dimer by using solid state NMR (Schnell *et al.*, 1998; Goward *et al.*, 2001). Thilagavathy *et al.* (2009) recently reported that 2-phenylbenzo[d][1,3]oxazin-4-one is stabilized by weak intermolecular C-H...O interaction and pi-pi stacking held responsible for stabilization of the crystal packing (Thilagavathy *et al.*, 2009). So far, various studies reported the presence of weak interaction having C-H...O H-bond in solid state but in liquid it is still unanswered and need more investigation or study. Interestingly, the occurrence of C-H...O hydrogen bonds in liquids has aroused much interest recently (Jedlovszky & Turi, 1997; Yuhnevich & Tarakanova, , 1998; Gil *et al.*, 1995; Ribeiro-Claro *et al.*, 1997; Karger *et al.*, 1999; Marques *et al.*, 2001). Moreover, various authors focused on the exploring the presence of weak hydrogen bonds in dimer in solid state (Brown *et al.*, 2001; Brown & Spiess, 2001; Aliev & Kenneth, 2004). In this study we have tried to detect and explore the role of C-H...O hydrogen bond in dimer of the said moiety in solution state. Generally two of the criteria supposed to suggest presence of C-H...O hydrogen bond in compound if, the deshielding of H in HX observes in NMR and a shift toward lower field in the spectra. It is also reported that proton donating ability of a C-H bond can only be observed by ¹H NMR (Dingley & Grzesiek, 1998; Pecul 2000).

After careful observation we found that proton at the ortho position i.e. H5 shows slightly high values of peak shift of 0.06, while proton at para position i.e H-7 shows peak shifts of 0.04 to the carbonyl. It was reported that downfield shift is ca 1-2 ppm in case when interaction occurs with proton acceptors in sterically favourable conditions and it becomes insignificant in case of weak interaction. The same pattern of slight peak shift was also observed in case of 4-methoxybenzaldehyde (Karger *et al.*, 1999; Marques *et al.*, 2001). Therefore, the higher value of the peak shifts may be because they are deshielded due to the pull of electron from carbonyl oxygen, due to salvation of monomer in CDCl₃. So, here we are in a position to satisfy both criteria (above mentioned) to claim

the presence of hydrogen bond. As well as, at this point we may safely say that monomer is found to be better solvated than monomer

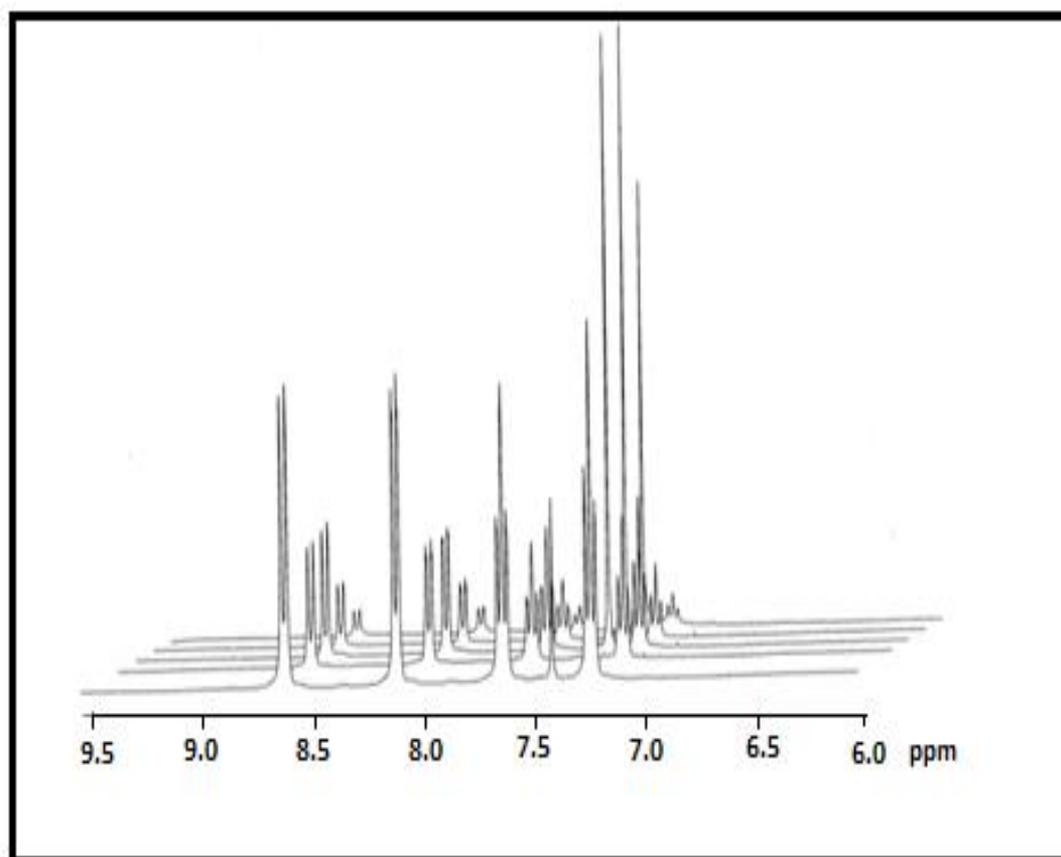


Figure 2.6: Stacked ^1H -NMR of 2-methyl-4H-benzo[d][1,3]oxazin-4-one in CDCl_3 in different dilutions.

This spectrum also revealed that major solvation effect is observed on the carbonyl group, as seen from the NMR shift pattern of the H-5 and H-7 protons. This pattern was observed most prominent in compound 2-methyl-4H-benzo[d][1,3]oxazin-4-one which do not bear any substituted aryl group. The shift in proton peaks at different position easily seen in the stacking plot of NMR spectra of 2-methyl-4H-benzo[d][1,3]oxazin-4-one in different dilution ranges. In the other compounds 1a, 1b and 1c), the effect was masked to a certain extent for 2-aryl derivatives due to pi- electron polarization of the aromatic ring.

2.3.4 Vibrational spectral analysis

In vibrational spectral analysis we have used both the IR and Raman-spectral analysis. The analysis was supplemented by DFT as well as lower level PM3 method wherever necessary. The vibrational ranges are split into carbonyl range and aromatic proton range.

2.3.4.1 The C=O region

Evidence of the presence of C-H---O=C hydrogen bonds in the solution phase was gathered from the observed changes in the $\nu_{\text{C=O}}$ region of the vibrational spectra with dilution. The vibrational spectral analysis of the compound 2-phenyl-4H-benzo[d][1,3]oxazin-4-one (in KBr) is reported by us; the absorption peaks at 1783 cm^{-1} (DFT) 1763 cm^{-1} (IR) and the 1757 cm^{-1} (Raman) was assigned to the $\nu_{\text{C=O}}$ stretching mode, the C(=O)-O asymmetric stretching band at 1258 cm^{-1} in IR and 1259 cm^{-1} in Raman and the C=N stretching band at 1692 cm^{-1} in IR were also almost unequivocally assigned. The observed deviation from the calculated and observed value of the C=O stretching bands only suggested possible existence of H-bonding. A priori IR studies by Marques *et al* (2001) have shown the existence of C-H---O=C hydrogen bond in 4-ethoxybenzaldehyde where 1700 cm^{-1} and 1690 cm^{-1} bands were assigned to as stretching band for free HC=O and for H-bonded HC=O respectively; the increase in intensity of the free carbonyl stretching with the increase of dilution in carbon tetrachloride was reported. Similar observation was also reported by Ribeiro-Claro *et al* (1997) and Matsumoto *et al* (2003) in which the carbonyl absorption band at the higher frequency was assigned to the free carbonyl and the relative intensity of this peak increases with dilution in non hydrogen bonding solvents.

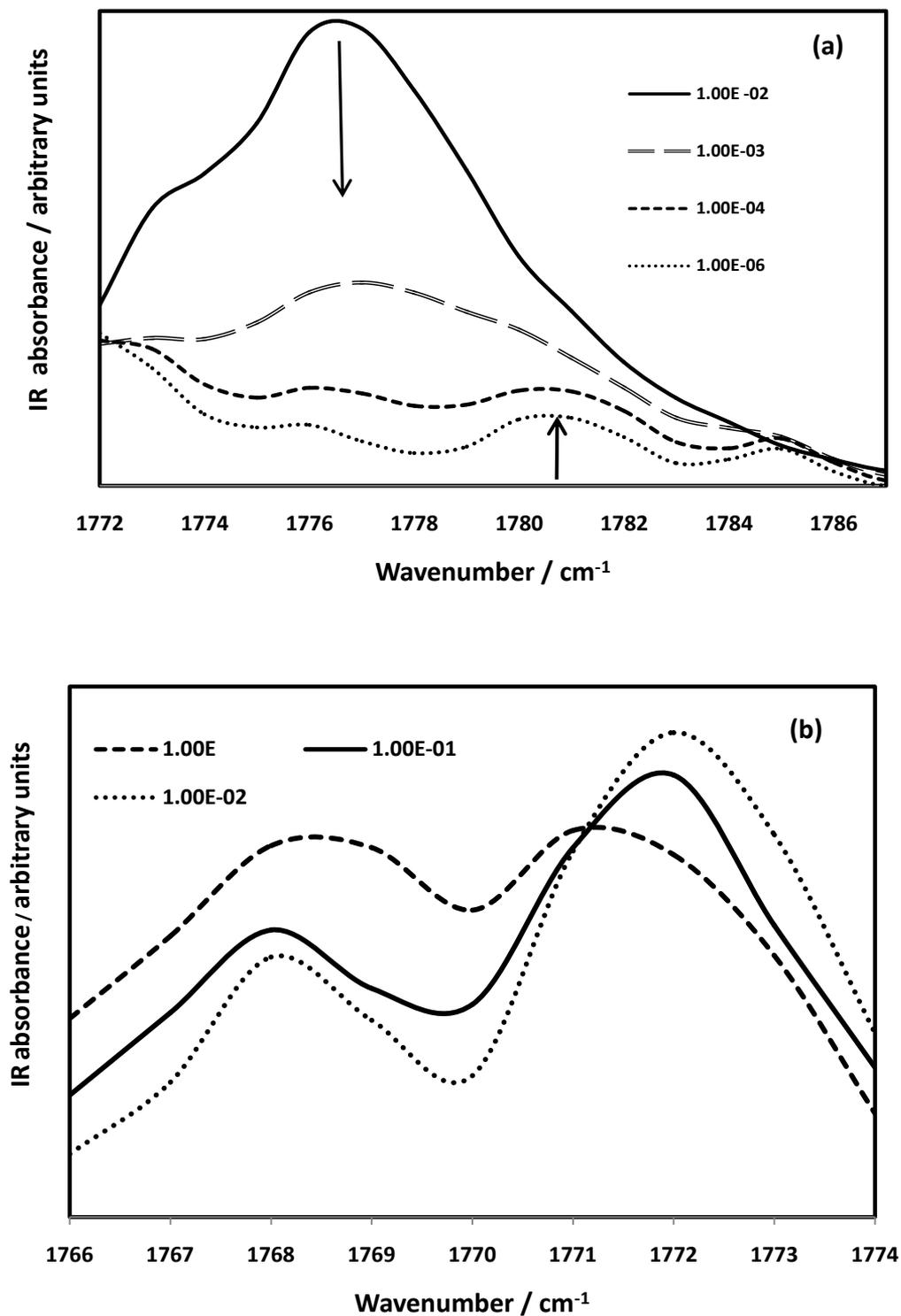


Figure 2.7: IR-spectra of compound 2-phenyl-4H-benzo[d][1,3]oxazin-4-one in (a) hexane and (b) CCl₄ in the region of C=O stretching modes at different concentration.

The FTIR spectra of the compound 2-phenyl-4H-benzo[d][1,3]oxazin-4-one in a non donor solvent hexane at different concentration in the region of the C=O stretching modes is shown in Figure 2.7a. The higher wave number component (1781cm^{-1} , more close to the DFT-calculated value with respect to that observed in KBr) corresponds to the free C=O group and the lower wave number component (1776cm^{-1} , close to the observed value in KBr) to the hydrogen-bonded C=O group. The relative intensity of the peak near 1781cm^{-1} increased with dilution which signifies that the compound exists as mostly C=O---H-C bonded dimer in KBr. In CCl_4 (Figure 2.7b) a similar change in the intensity is observed for the free C=O at 1772cm^{-1} and hydrogen bonded C=O at 1768cm^{-1} . The sample dilution leads to an increase in the free (monomer) $\nu_{\text{C=O}}$ band intensity relative to the bonded (dimer) $\nu_{\text{C=O}}$ band.

In the compound 2-methyl-4H-benzo[d][1,3]oxazin-4-one, an intense band for the carbonyl was found to be visible at 1757cm^{-1} (KBr), while the same compound diluted in hexane displayed the band at 1774.4cm^{-1} (Figure 2.8). In H-bonding solvent chloroform the intensity of the C=O band was greatly reduced and bifurcated into two bands at 1749.3cm^{-1} and 1751.2cm^{-1} ; the intensity of the band at 1751.2cm^{-1} increased with progressive dilution (Figure 2.9). These observations can be related to the presence of two C-H---O interactions. The C=N stretching band for the compound 2-methyl-4H-benzo[d][1,3]oxazin-4-one appeared at 1649cm^{-1} , 1653cm^{-1} , and 1684cm^{-1} in nujol, dilute solution in hexane and chloroform respectively. Thus, the H-bonded and free carbonyl absorption bands are visible in solvents of different polarizability and new bands appeared in chloroform solution which can form new H-bond with the carbonyl. It can be safely noted that two molecules can approach each other as DA-AD pair only if the C5-H proton participate in the H-bonding in the dimer.

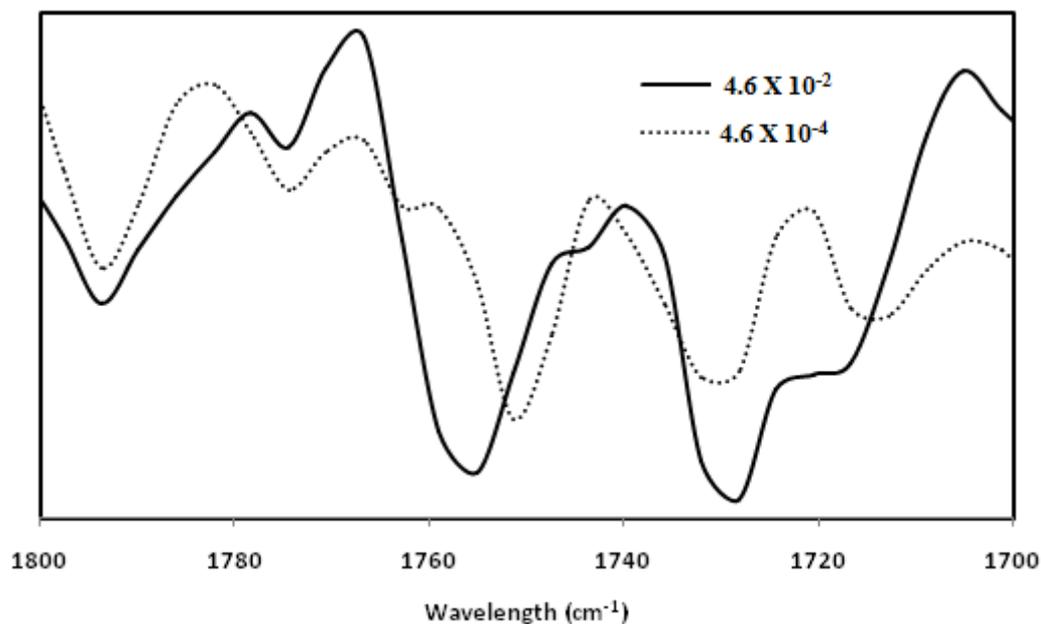


Figure 2.8: The expanded band of Raman spectra of 2-methyl-4H-benzo[d][1,3]oxazin-4-one in CHCl_3 .

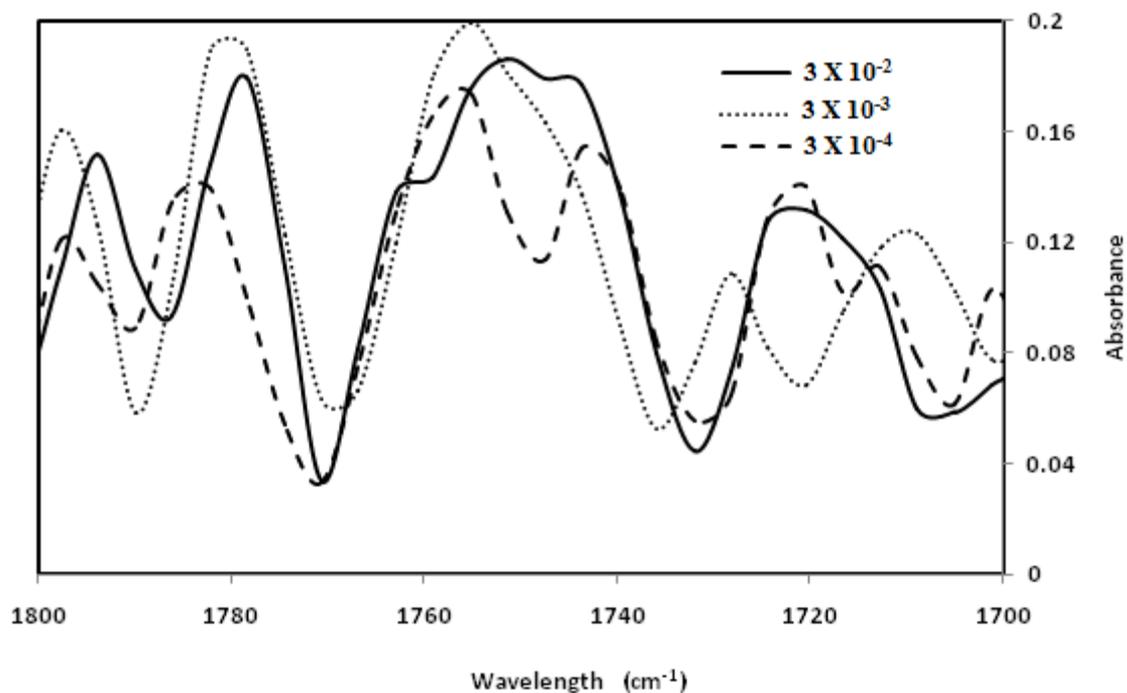


Figure 2.9: The expanded band of IR spectra of 2-methyl-4H-benzo[d][1,3]oxazin-4-one in hexane.

2.3.4.2 C-H stretching region

The C-H stretching occurs above 3000 cm^{-1} and is typically exhibited as a multiplicity of weak to moderate bands, compared with the aliphatic C-H stretch. In solid KBr the bands observed at 3040 , 3050 and 3060 cm^{-1} in the IR spectrum were assigned as $\nu\text{C-H}$ modes of the benzene ring. In the Raman spectrum two bands are observed at 3022 and 3070 cm^{-1} . Proper assignment of this bands are reported by us in a priori work (Ambujakshan *et al.*, 2008) for the compound 2-phenyl-4H-benzo[d][1,3]oxazin-4-one. In solution the spectra being more sharp a complex pattern of more bands were observed. In order to make the matter simple we like to confine our discussion with the compound 2-methyl-4H-benzo[d][1,3]oxazin-4-one where the aromatic hydrogen is least in number. Still the spectra are complex as shown in Figure. 2.10 and 2.11.

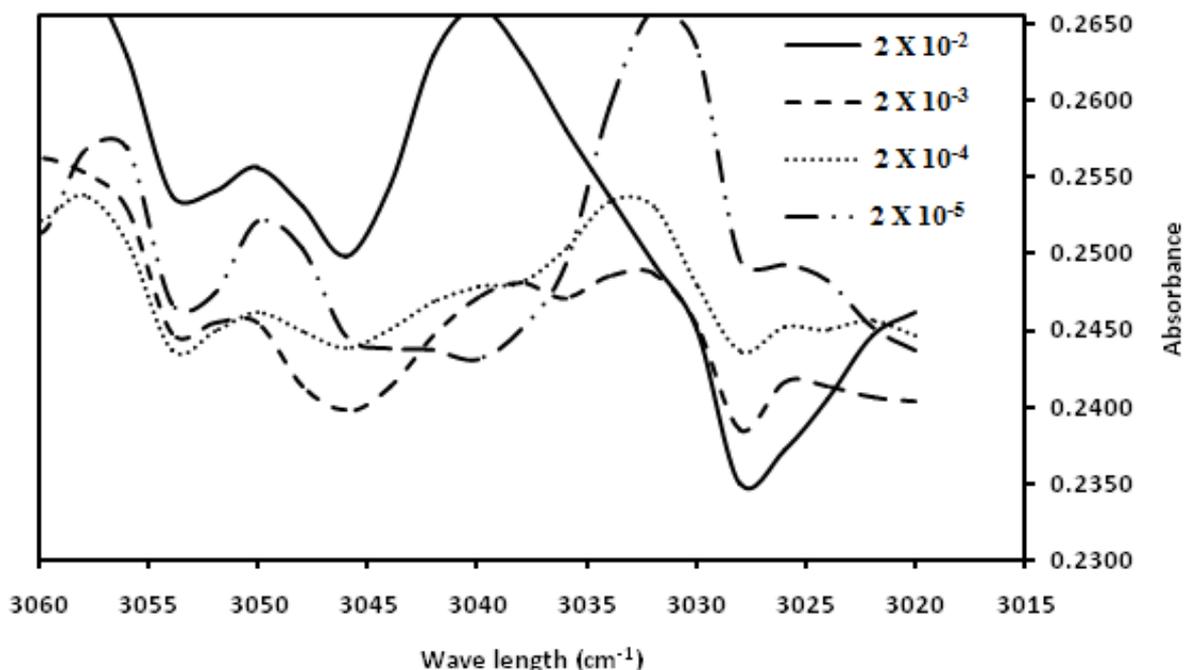


Figure 2.10: IR spectra of 2-methyl-4H-benzo[d][1,3]oxazin-4-one in CCl₄.

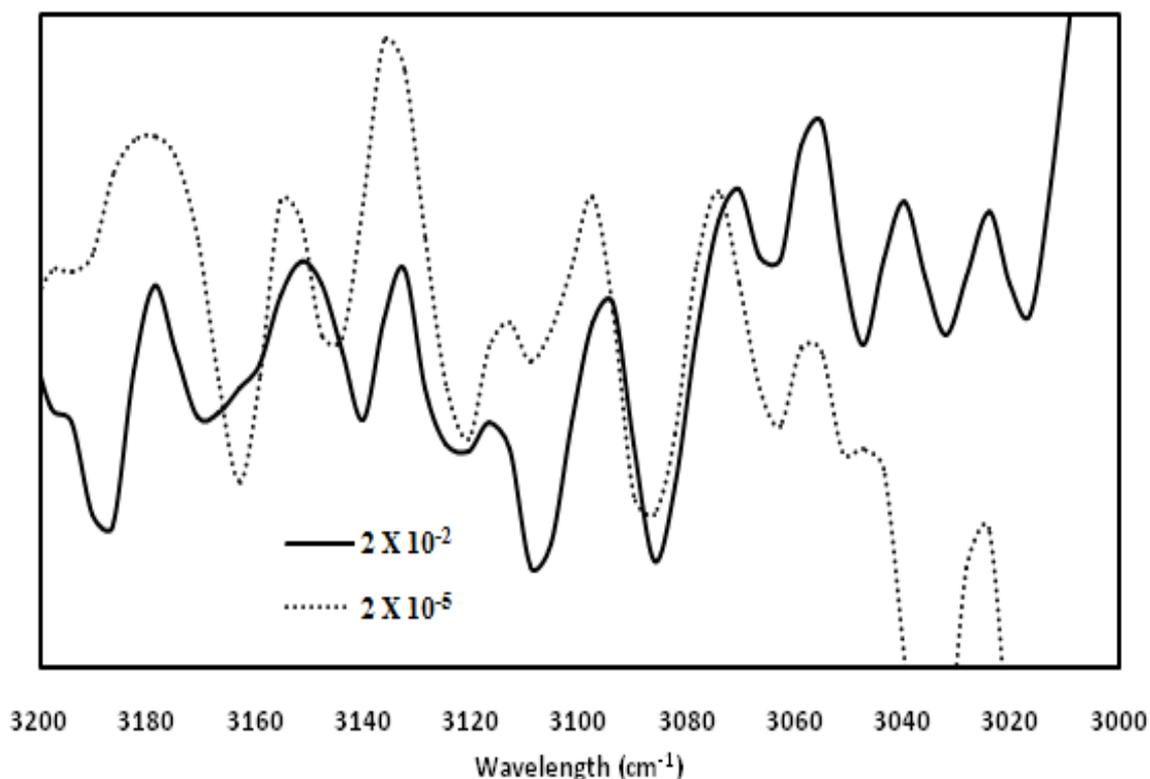


Figure 2.11: Raman spectra of 2-methyl-4H-benzo[d][1,3]oxazin-4-one in THF.

In these above figures we tried to keep the spectral range in comparable intensity so that the relative changes in frequency as well as intensity become easily visible. Now we computed the vibration frequencies for both the monomer and H-bonded dimers. The calculated frequencies with their respective intensity for the C-H bond stretching range are plotted in a radial plot (Figure- 2.12). The band shift is associated with intensity; however we used the monomer frequency in radial axes.

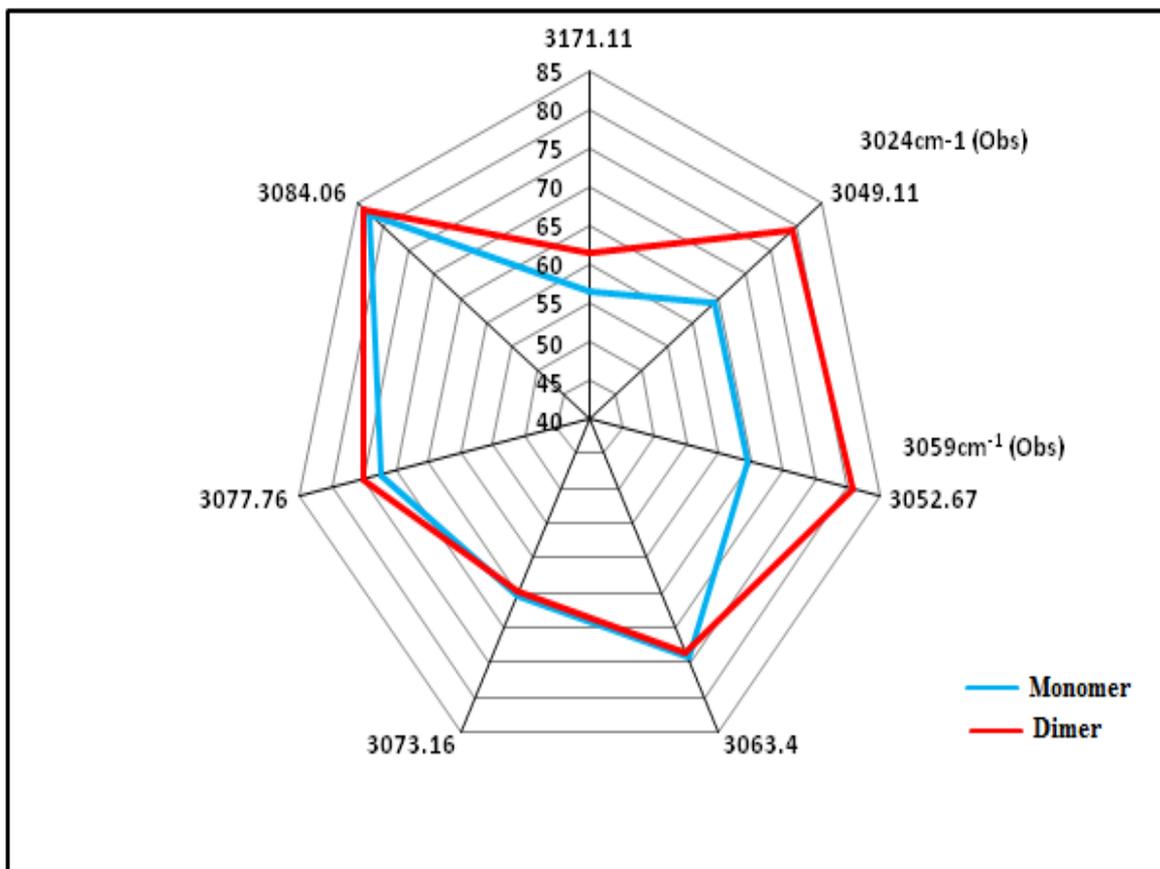


Figure 2.12: Radial plot for frequency in cm^{-1} vs intensity of 2-methyl-4H-benzo[d][1,3]oxazin-4-one.

Moreover, from this radial plot it is imperative that change in intensity as well as band shift of two specified peaks must be there in our observed spectra if our proposition is correct (Figure 2.12). Thus, from the experimental IR- spectra we have chosen the most concentrated solution where dimer concentration should be higher and the most dilute solution where the monomer concentration should be higher. Now the calculated frequencies corresponded with the observed frequencies for the stated solution since intensity is arbitrary. Thus we got a plot as shown in Figure.2.13.

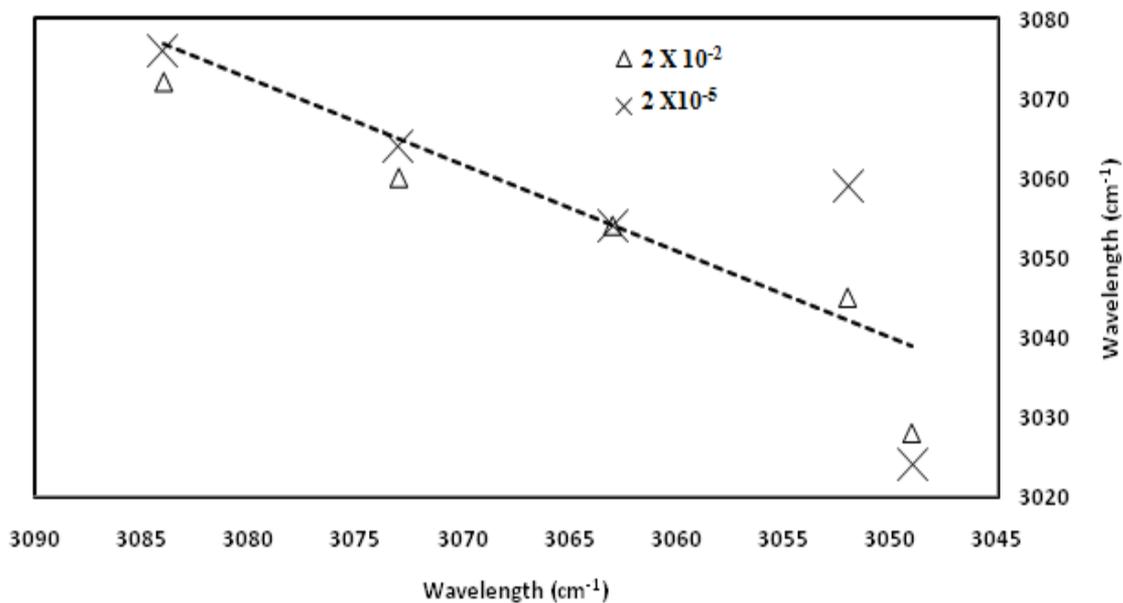


Figure 2.13: IR absorption bands of calculated monomer vs. observed in Dilute sol.(X) and in Conc. Sol. (Δ) 2-methyl-4H-benzo[d][1,3]oxazin-4-one.

The graph clearly suggested that two points have deviated from the trend line and this deviation is greater for the concentrated solution compared to that in the dilute solution. Thus the spectral analyses unequivocally prove the existence of monomer dimer equilibrium in the solution state and the dimer is H-bonded dimer.