

Analysis of C-H.....F and O-H.....N Intermolecular Interactions Involving Fluorine in A New Mixed Composite Material 5- Fluoro salicylaldehyde – Aniline

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Abstract: We synthesized a new composite material containing 5-Fluoro salicylaldehyde with Aniline in CCl₄ medium. A detailed packing analysis has been undertaken to delineate the role of C-H....F interactions amid other hetroatom interactions. The composite material have been characterized by elemental analyses, Spectroscopic studies (IR, multinuclear NMR) and Physico-chemical behavioural studies. The complex structure is calculated by the spectral analyses as non-centro symmetric, bent, complex in nature, containing five interacting nuclei A BB' MM' system. The composite material was stabilized by a variety of hydrogen bonding interactions (i.e) O-H.....N and C-H.....F. Furthermore, packing analyses reveal that C-H.....F interactions can manifest even in the presence of a large number of hetroatom interactions. To reinforce the ideas investigated and to reveal the validity of the proposed models, experimental results are discussed with the outputs through the Software MATLAB7.0.

Keywords: Intermolecular interactions, second sphere interactions, 5FS-A composite material

1. Introduction

Synthesis of organic materials in liquid state is a fascinating area of current research. The design of such liquids follows the well laid principles based on inter molecular interactions and establishes the relationships between the structures of a molecular liquid and its properties. The term composite material and co-ordination bonds are now well- established in the understanding of such organic liquids. The co-ordination bonds between the molecular centers and organic moieties are important in the design of hybrid compound while hydrogen bonds hold the prime position in the molecular recognition in many organic liquids.

Fluorinated organic compounds have been known for their fascinating properties as fluorine can impart significant effect on their properties such as increased chemical stability, solubility, dipole-dipole and hydrogen bonding interactions. As a result, they have number of applications. (I), about 20-25% of drugs in pharmaceuticals contain at least one fluorine atom in their molecules. (II), fluorine substitution is commonly used in medicinal chemistry to improve the metabolic stability, bio availability and protein ligand interactions. The role of non- covalent C-H.....F interactions immediately warrants consideration, but their role in chemical stabilization has elicited immense importance and debate.

Earlier view about organic fluorine is that it hardly involves in the hydrogen bonding and does not contribute to the molecular packing . But Shimoni and Glusker¹, however, pointed out that although C-H.....F-C interactions are weak as compared to the C-H.....O-H interactions, their contribution in determining the modes of molecular packing in fluorinated complexes cannot be overlooked. Recent

investigations have also augmented this point of view. It was observed that when two fragments involved in the interactions are neutral, C-H....F interactions behave as weak hydrogen bonds. The relavant work was done by Graber D et. al² in 2008.

A careful choice of the materials become essential as we are trying to evaluate molecular events. This article reports the role of weak C-H.....F, O-H.....N interactions in 5-FS –A in CCl₄ medium. The selection of 5-FS has a purpose- Fluorine may ensure an entirely different interaction pattern in the new complex.

As a result of intermolecular H-bond formation, the proton donating group 5-FS increases its electron donating power , and the proton accepting group aniline increases its electron accepting power. It is worth mentioning that estimating intermolecular H-bond energy is not an easy due to the possible implications of internal reorganization of bonds or steric effects. Recent decades have been increased interest in this problem. Various approaches have been introduced to handle the issue. Here a few of these are reported. Same study were made by Desiraju G R et. al³. 1989 and Ramachandra Raja C et.al⁴ in 2012.

A halogen substituent is electron releasing, fluorine releases electrons into the ring by resonance and increases its electron density but electron- withdrawing because of its high electro negativity. Higher electro negativity of fluorine decreases the electron density of the ring by inductive effect dominates the resonance effect ,and the net result is that the ring ended in electron- deficient. Ramachandra Raja C et.al⁵ in 2013 and Singh A.et al⁶ in 2009 pointed out the same relative work.

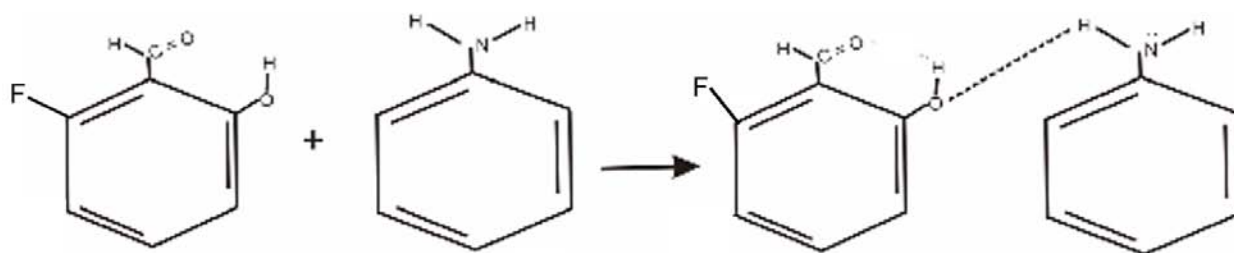
2. Experimental

2.1 Materials and measurements

Analytical grade reagents were used without any further purification. Infrared spectrum of the title complex liquid mixture was recorded using PERKIN ELMER Spectrum RX FT-IR system. ¹H-NMR spectrum of title complex liquid mixture was run in the solvent CDCl₃ by using BRUKER AC 400F(400MHZ) Spectrometer. The chemical shift values were expressed as δ value (ppm) down field from (CDCl₃ as an internal standard)/TMS. The sound speed was measured using a single crystal Ultrasonic Interferometer, with an operating frequency of 2 MHZ. The viscosity was measured using an Oswald's Viscometer, calibrated with double distilled water. The density was measured by a 10ml specific gravity bottle calibrated with double distilled water and acetone. Refractive indices were measured with an Abbe refractometer (Erma, A302A) and the values were obtained for Na-D light with an error less than ± 0.0002 units.

2.2 Synthesis of 5-FS with aniline in CCl₄ solvent

Materials having moderate to high solubility in the temperature range ambient to room temperature 303K at atmospheric pressure, form the complexes when their samples were carefully mixed. In the present systems, the various concentrations of the ternary liquid mixtures were prepared in terms of mole fractions out of which the mole fractions of the first component 5-FS are varied from 0.01 to 0.05m/l and the second component aniline were varied from 0.066, 0.0132, 0.0199, 0.265, 0.332 m/l. The required solute concentrations of the above title mixture in 5ml CCl₄ was prepared. The formation of the complex was noticed by its pale color and also the absence of precipitation of solid.



3.3 Spectroscopic characterization

FT-IR spectra of newly synthesized composite material has been recorded in the region of (400-4000 cm⁻¹). The IR spectral bands in the range near 3400, 2900-2695, 2000-1650, 1580 two bands 1180-1360, 1300-1000, 900-675cm⁻¹ were assigned to γ(N-H) of aniline. γs(C-H), γ(C=O), γ(C-N), γ(C-H) in plane and out of plane bending respectively in the new material. These peaks are characteristic for the formation of new composite material. 5-Fluorosalicylaldehyde attached to aniline through hydrogen bonding.

In the case of new material, the band at 3364 cm⁻¹ was assigned to γs(N-H). The band 1871, 1845, 1733, 1621 were assigned to γs(C-F), γ(C=O) vibrations, the weak

Spectral data for the selected product are as follows

IR- Found (cm⁻¹) 3364γ(NH), 2925, 2851 γs(C-H), 1871γ(C-F), 1733 γ(C=O), 1580 γ(N-H) bending, 1353, 1170(aniline), 1320 γs(C-N), 1251, 1202, 1140, 1030 γ(C-H) in plane bending, 962, 908, 872, 783 γ(C-H) out of plane bending.

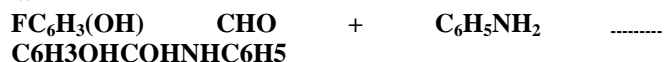
IR- Calculated (cm⁻¹) γ(N-H) 3400, γs(C-H) (2900-2695), γ(C-F) 1869, γ(N-H) bending 1580, aniline 1360, 1180, γ(C-H) in plane bending (1300-1000), γ(C-H) out of plane bending (900-675).

¹H-NMR (500 MHz)CDCl₃ δ 1.57(6H), 1.27(4H), 6.99(3H), 7.13(5H), 7.33(3,4H), 7.47(8H), 4.01(9H), 4.50(7H), 8.59(2H) (S, 2H, CH₂), (m, 2H, CH₂), (S, 10H, ArH, NH₂), (CH₂, C4H, 2H 1H CHS).

3. Results and Discussion

3.1 Synthesis

The composite material was synthesized by reaction of 5-FS with aniline in 1:1 molar ratio in the CCl₄ medium. The composite material has been characterized by spectroscopic studies (IR and ¹H-NMR) and acoustical studies.



Schematic representation of chemical reaction

3.2 Structure of the Composite material

combination and overtone bands which is characteristic of the substitution pattern of the ring. The stretching frequency of the carbonyl group in the new material increases, when more fluorine is added in the carbon attached to the carbonyl. The normal value of carbonyl absorption is 1700 cm⁻¹ γ(C-F) but it reaches its maximum in the new material at 1871⁻¹ because of the inductive effect of the fluorine atoms (see William Kemp⁷ in 1971).

In salicylaldehyde the carbonyl absorption is at 1656.01 cm⁻¹ due to intramolecular hydrogen bonding. In 5-FS it is at 1622 cm⁻¹ due to the intramolecular hydrogen bonding. The decrease in stretching frequency of C=O band may be attributed to the formation of the complex. With the addition of aniline a new band appears at 1733 cm⁻¹ and the intensity of the original band slowly decreases. The new low

frequency band of 5-FS and aniline mixture observed at 1733 cm^{-1} may be ascribed to the 1:1 complexes formed between the proton acceptor and the proton donor, due to the presence of intermolecular hydrogen bonding (see Banwell C.N⁸ in 1972). The bands at 1580, 1456, 1385, 1320 cm^{-1} were assigned to γ (N-H) bending, γ (O-H) bending and γ s (C-N) vibrations of the new compound . The two bands at 1353, 1170 cm^{-1} are due to the strong vibrations of aniline. The bands at 1251, 1202, 1140 , 1030 cm^{-1} are the in plane bending C-H vibrations of the new compound. The bands at 962, 908, 872, 783, 691, 673 cm^{-1} were assigned to out of plane bending vibrations of the C-H bands. The peak assignments have been made in consultation with literature values.

Table 1: Observed IR Frequencies (cm^{-1}) and band assignments for 5FS-A at room temperature

Frequencies	Assignments Observed IR frequencies
3364	N-H Stretching vibration (intermolecular)
2925,2851	C-H Stretching vibration of aldehyde group
2046,1943,1845,1621	Overtone combination regions of substitution of the ring
1871	Shift due to Fluorine stretching frequency
1733	C=O stretching due to intermolecular hydrogen bonding
1580	N-H bending
1456,1385	O-H bending
1353,1170	Aniline stretching frequency
1320	C-N stretching
1251, 1202,1140,1030	C-H in plane bending
962, 908,872,783,691,673	C-H out of plane bending

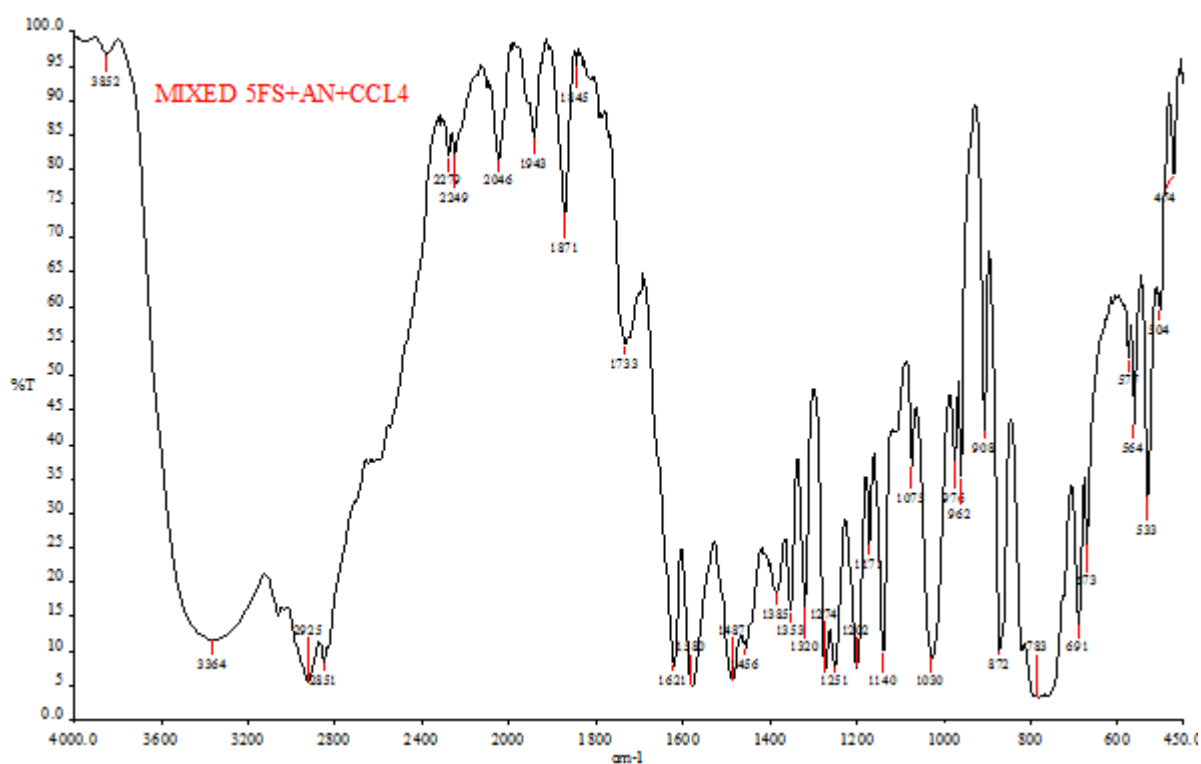


Figure 1: FT-IR Spectrum of 5-Fluoro salicylaldehyde- Aniline composite material

The ^1H -NMR spectra of the title composite material were recorded in CDCl_3 . Aromatic rings with a highly electronegative substituent, such as Fluorine exhibit complex second order spectra. The figure shows the spectrum of the new material which might be referred to as system containing five interacting nuclei ABB'MM' system, where two protons α to fluorine are M and M' the three most distant protons are A BB'. Singlet at 8.594 ppm was assigned to aldehydic proton H_2 and multiplets at 7.479 ppm, 7.334 ppm, 7.135ppm, 7.020ppm were assigned to protons H8, H3,4 H5 and H3 of mono-substituted benzene ring.

Multiplets at 1.578 ppm and 1.277 ppm were assigned to H6 and H4 protons of the fluorine. Multiplet at 4.0 ppm and 4.50 ppm were assigned to protons H9, H7 of amino exchangeable with 5-FS. Similar peak at 13.040 ppm has been reported due to long deshielding and the formation of the intermolecular hydrogen bonding of the new compound 5-FS-A. The signals observed in the NMR spectra are in good agreement with reported values in the literature (see Jag Mohan⁹ in 2003).

5-Fluoro salicylaldehyde with aniline.....IdamalarSelvi,

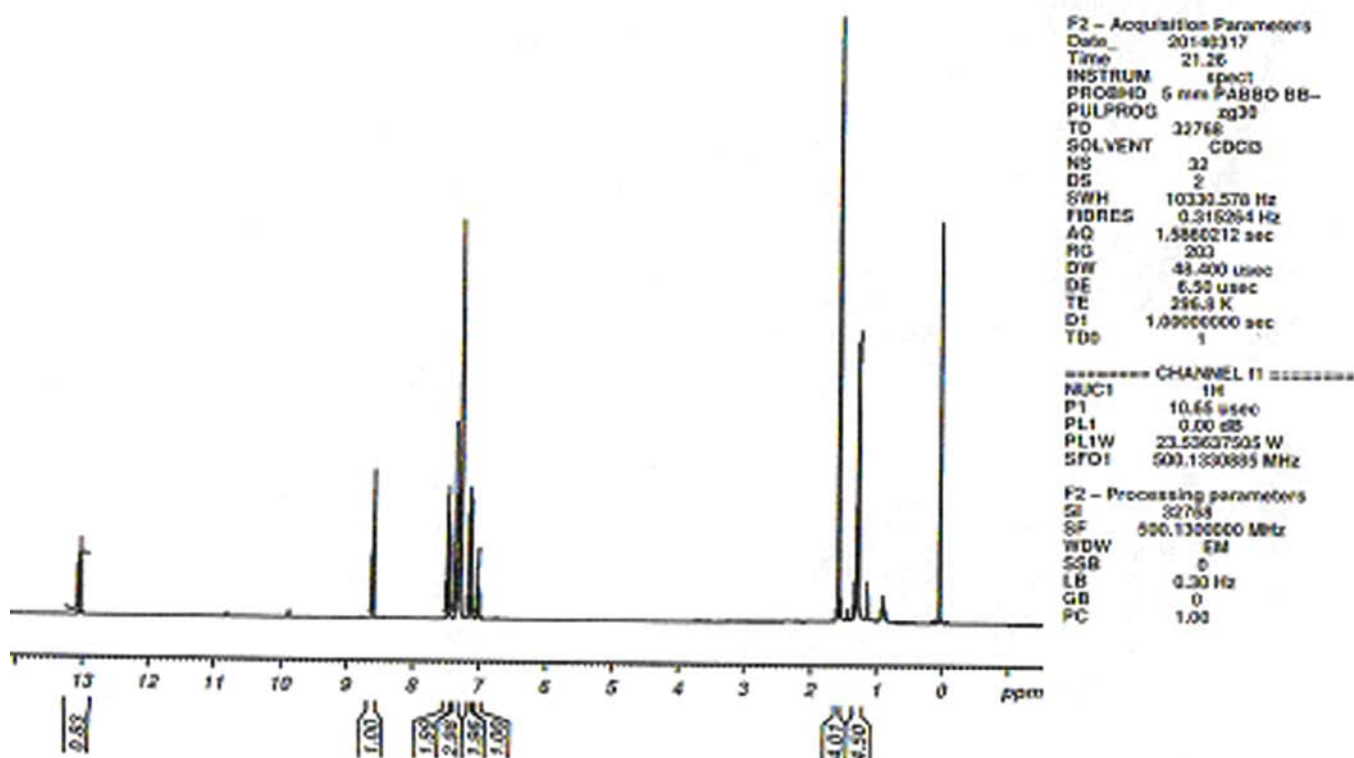


Figure 2: ¹H-NMR Spectrum of 5-Fluoro salicylaldehyde- Aniline composite material

Ultrasonic studies has been increasingly used in organic synthesis in the last three decades .It has been demonstrated as an alternative energy source for organic reactions ordinarily accomplished by heating. Ultrasonic velocities of liquid mixtures containing polar and non- polar groups were of considerable importance in the formation of new compounds through intermolecular interaction between component molecules. There were higher variations in some intermediate concentration range given by Namato's¹⁰ relation (0.02m/l to 0.04 m/l 5FS+ 0.0132, 0.0199, 0.265m/l aniline in 5ml CCl₄) suggesting the existence of strong tendency of association between component molecules as a result of hydrogen bonding .The molecular association between the title mixtures have been investigated by measuring sound speed, viscosity, refractive index, densities and thermo acoustical parameters at 303k with different mole fractions in CCl₄ solutions were evaluated.

The variation of sound speed in a solution depends upon the increase or decrease of intermolecular free length (L_f) after mixing the compounds. Based on the sound propagation proposed by Eyring and Kincaid¹¹, sound speed should increase, if the intermolecular free length decreases and vice-versa. This fact noticed in the present system. A reduction in adiabatic compressibility is an indication that component molecules are held close to each other. The internal pressure of the new material in the present study increases with the increasing concentration of 5-FS can be attributed as there is definite interaction presents between the unlike components of the mixture. Similar results were reported by Rama Chandra Raja C et. al¹² in 2013 and R.A.Patil et. al¹³ in 2013. The experimental values and the thermo-acoustic parameters were listed in Table 2&3.

Table 2: Mole fractions of 5-FS (X_1), mole fractions of Aniline (X_2), Values of Density (ρ), viscosity (η), velocity(c) and Refractive index (D)

X_1	X_2	C ms ⁻¹	ρ kgm ⁻³	$\eta \times 10^{-3}$ Nsm ²	D
0.04	0.0265	1476	1.5929	0.001493	1.4774
0.08	0.0531	1227	1.5970	0.007110	1.4778
0.12	0.0797	1117	1.6180	0.02022	1.4796
0.16	0.1063	812	1.6250	0.02215	1.4830
0.20	0.1329	734	1.6410	0.02461	1.4821

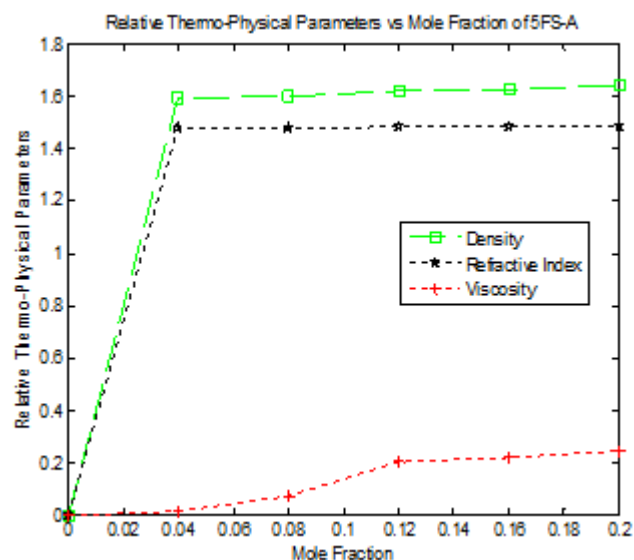


Figure 3: The MATLAB output of Thermo- Physical parameters vs Mole fractions of 5FS –Aniline mixture

The viscosity increases as the molar concentration of the solute mixture increases upto 100 mole % and mixture

further increase of the mole fraction of the solute mixture it still increases, it shows the strong formation of the new material. The similar results were reported by V.K.Syal et al¹⁴ in 2003. The density, viscosity and refractive index shows a increasing tendency due to the strong formation of the hydrogen bonding and the molecular association of the new material. The applicability of the more common mixing rules were studied. Same study was made by G.P Duebey et al¹⁵ in 2005. Rao's constant was found to be an additive relation that it can be calculated as a sum of increments from the atoms /atom groups in the molecule and from the chemical bonds under consideration. From the present study it is observed that Rao's constant varies non- linearly with the concentration. Estimation of salvation of organic liquid mixtures have been made by salvation number. Using Passynsky equation (Passynsky, 1943) the solvent molecules participating in the salvation were effectively incompressible due to strong localized electric fields. In the present study the salvation number has decreases with increase of concentration indicates that the number of solvated molecules "S" per monomer unit is high for lower concentration. As the concentration increases the number of monomer units increases and hence the value of "S" decreases.

Table 3: Mole fraction of 5FS (X_1), mole fraction of aniline (X_2), Values of adiabatic compressibility (β), internal pressure (π), free length (L_f), Rao's constant(R), Salvation number (S) of 5FS with aniline in CCl_4 .

X_1	X_2	$\beta \times 10^3$ ($N^{-1} m^2$)	$L_f \times 10^{-10} m$	$\pi \times 10^6$ (Mm^{-2})	R	$S \times 10^{-10}$
0.04	0.0265	6.9753	46.350	2.4375	4327.58	5.9501
0.08	0.0531	6.9574	47.036	2.7220	3588.28	2.9181
0.12	0.0797	6.8671	47.459	2.9241	3224.17	1.7568
0.16	0.1063	6.8376	48.073	3.4763	2333.67	1.2712
0.20	0.1329	6.7709	48.591	3.7334	2088.97	0.9337

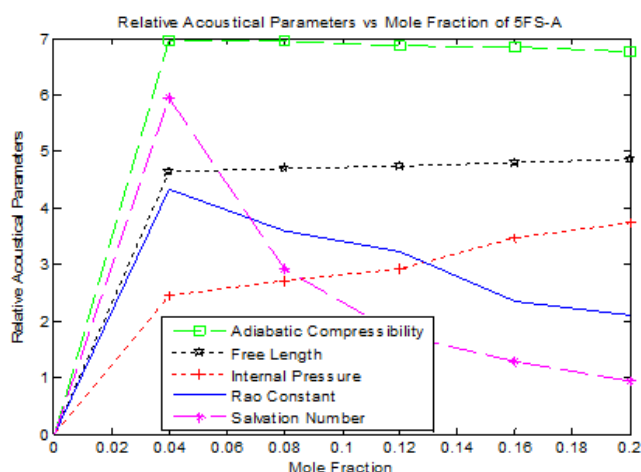


Figure 4: The MATLAB output of Acoustical Parameters vs Mole

Fractions of 5FS – Aniline mixture

4. Conclusions

The potential of weak second sphere interactions (C-H...F and C-H...O) in the binding of 5-Fluoro salicylaldehyde–aniline has been explored by forming and characterizing the

new composite material. As laid down as an objective at the outset to evaluate C-H...F interactions amid the presence of NH_2 group has shown that C-H...F interactions can indeed manifest in the new complex. Thus, it is important to consider the cooperative interplay of weak second sphere interaction of the kind C-H...F even in molecular system in which molecules are endowed with halogen substitution. Such consideration may facilitate the composite material of this kind of molecular system in which weak second sphere co-ordination has a marked influence even in the presence of strong O-H...N and N-H...O interactions.

The scope and generality of Ultrasonic process is illustrated with respect to various aromatic aldehydes. Aromatic aldehydes substituted with either electron- donating or electron – withdrawing groups have undergone smooth reaction and gave the corresponding reaction 5- Fluoro salicylaldehyde – Aniline in moderate to excellent yields. In general, it was found that the compounds having fluoro substitution along with salicylaldehyde and aniline systems exhibited good formation of composite material through hydrogen bonding.

5. Acknowledgements

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