Structural and vibrational study of molecular interaction in a ternary liquid mixture of benzylamine, ethanol and benzene

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Abstract
The structural study of the non-covalent interactions in the ternary mixture of benzylamine (BA), ethanol and benzene has been attempted through Density Functional Theory (DFT) calculation. The optimized structure of monomers (BA, ethanol and benzene), BA dimer and their complexes (BA-benzene, BA-ethanol, BA-ethanol-benzene) and their interaction energies are used to describe the intermolecular interaction. In addition to conventional H-bonding, the stability of the system is found to depend on several other interactions such as CH/π, NH/π, OH/π interactions. The Fourier Transform InfraRed (FTIR) spectroscopy technique is also used to study the molecular interaction. An interpretation of the IR stretching bands based on the interaction is also provided. The variation in IR band position and intensity of spectra with change in concentration of the mixture shows that different kinds of interactions are present in the mixture. The strength of these interactions varies with concentration. At lower concentration of benzylamine, weak OH/π interaction between benzene and ethanol takes place, while at other mole fractions, N-H-----O, O-H------N or NH/π interaction are present between the molecules.

Keywords Conventional and non-conventional H-bonding · DFT · Non-covalent interaction · FTIR

Introduction
The widespread use of amine [1] and the presence of the amine group in many compounds of biological interest make it an interesting functional group. Benzylamine is used in pharmaceutical industries in the preparation of several drugs. It is also used to manufacture explosives and as propellant in rockets and missiles [2]. There are several studies done on the binary liquid mixture comprising primary amine, secondary amine, tertiary amine and cyclic amine with aromatic hydrocarbon, alcohol, non-ionic solvents and cyclic ether [3–7].

In view of the importance of BA mixture with other organic compounds and to engineer the properties of such mixtures, the knowledge of intermolecular interactions is a must. Also, the intermolecular interactions predominantly control the molecular mechanism of the substance and its understanding helps in the improvement of properties of the system [8]. In the present investigation, the molecular interaction study of BA with aromatic substance in the polar environment is undertaken via theoretical quantum chemical calculation and experimental FTIR spectroscopy.

The quantum chemical calculations help to understand the molecular geometry and the electronic properties at atomic level. They can directly provide the intrinsic strength and geometrical preferences of interactions as found in small model systems. These calculations can also determine the relative importance of the fundamental forces that make up the interactions like electrostatic, induction, dispersion, and exchange-repulsion forces and tell about the nature of the interaction [9–11].

In conjugation with theoretical calculations, vibrational spectroscopy also has the potential to yield valuable structural and conformational information of organic compounds. The analysis of vibrational frequencies shift, change in spectral band shape and intensity upon changing environment also provides the information about intermolecular interactions. The absorption peak is usually sharper in the IR spectrum and so, it is exceptionally sensitive to change in bond strength and even a small change of 0.02 % can be easily detected by it [12, 13]. The sensitivity of IR
Spectroscopy towards a small change has made it a good tool to investigate the structure and molecular interaction in the last several decades [14–17].

In the liquid medium, vibrational relaxation band and rotational motion band mixing makes the analysis of the IR band complicated. For analysing the spectra with overlapping bands, the curve fitting method [18–21] is used. The concept of deconvolution assumes that a spectrum of single band is broadened in a liquid mixture due to molecular interaction.

In the present work, the structures of monomers (benzylamine (BA), ethanol and benzene), BA dimers and their complexes (BA-benzene, BA-ethanol, BA-ethanol-benzene) have been optimized using density functional theory with B3LYP functional. The geometry optimization gives the bond parameters and dipole moment which are good sources of information related to non-bonded interactions. DFT with ω B97X-D functional has been used to calculate interaction energy because it includes the dispersive interaction. All the computations were done with DFT with a basis set of 6–311++G**(d,p). The vibrational analysis of the mixture by FTIR (Fourier Transformed InfraRed Spectroscopy) is used to get the detailed description of structural modification and intermolecular interaction on mixing the liquids.

**Experimental and methods**

**Experimental**

The chemicals, benzene and benzylamine were purchased from SRL India and ethanol was purchased from MERCK. All chemicals had a minimum assay of 99.9 % and used without further purification. The mixture of different mole fractions was prepared by mass. The weighing was done using a digital balance of accuracy ± 1 mg. The mole fraction of the second compound, i.e. ethanol was kept fixed at 0.4 while the mole fraction of the other two (x1 of benzylamine and x3 of benzene) varied from 0.0 to 0.6 to have the mixtures of various mole fractions.

The FTIR (Fourier Transformed InfraRed) spectra of pure components and their mixtures at different concentration were recorded in transmission mode. Samples were scanned using “Spectrum Two™ FTIR spectrophotometer (PerkinElmer)” equipped with deuterated triglycine sulphate (DTGS) detector and potassium bromide (KBr) as a beam splitter. The instrument was connected to Spectrum 10 EST™ software and spectra were scanned at wavenumbers of 4000–400 cm⁻¹, at a resolution of 2 cm⁻¹ and room temperature 293 K.

**Decomposition of spectra**

The decomposition of overlapped band was performed by using a fitting algorithm implemented in Origin 2018. The number of Gaussian peaks were varied from one to ten. The individual components of the spectra were determined by an iterative curve-fitting procedure that assumed Gaussian band envelopes for the components. In this procedure, the peak position, the intensity and the width were taken as the fitting parameter. Experimentally measured transmittance is converted into absorbance and then peak fitting was performed.

**Computational**

The possible interactions between like and unlike molecules were investigated by quantum chemical calculations. The study of the dimer of benzylamine (BA) and the complex of BA, ethanol and benzene were optimized in the gas phase and their interaction energies were calculated. The common practice of running a high-level single point energy calculation on the geometry computed by the use of a cheaper method is as effective as performing all calculations at a higher level of theory [22]. The calculations were performed at the DFT/6-311++G(d,p) level using the GAMESS program [23] at the web-based interface facility www.chemcompute.org [24]. The geometry is optimized by B3LYP functional while single point energy on optimized geometry was calculated with ω b97X-D functional. The ω B97X-D functional includes empirical atom-atom dispersion corrections and is significantly superior for non-bonded interactions. It yields satisfactory accuracy for thermochemistry, kinetics and non-covalent interactions [25]. The interaction energies were determined by using the “Supermolecular” method [26].

**Results and discussion**

**Theoretical: geometries and noncovalent interactions**

Figure 1a–f are the optimized geometries of molecules, BA dimer and their complexes. The optimized geometries of benzene and ethanol were taken from Hema at al. [27]. They help in establishing relationships among molecular structure and intermolecular interactions. The single point energy, interaction energy and dipole moment of monomers and dimers are summarised in Table 1.

The interaction between structural subunits modifies the bond length, bond angle and leads to some preferred geometry which is the most fundamental source to understand the intermolecular interaction. The possible interaction between
molecules based on structural changes and interaction energies are discussed as:

Benzylamine (BA) (Fig. 1a) is a polar molecule (Table 1) and can interact with any other polar as well as non-polar molecules. BA molecules have a π-ring (π-plane) which interacts with H-donor molecules. Since such interaction is a plane-to-point kind of interaction, there could be more than one possible conformation geometries.

BA dimer has two configurations (Fig. 1b, c). In one configuration, NH₂ group of BA molecule interacts via H-bonding (Fig. 1b) and in other, the N-H bond of one molecule takes a perpendicular position above the plane of π-ring of another molecule (Fig. 1c). The interaction energy of BA dimer in these configurations is −7.795 and −7.117 Kcal/mol respectively. In H-bonded configuration, the bond length r(C-N) of the doner BA molecule gets increased by 0.005 Å while r(N-H) of the acceptor gets increased by 0.004 Å. On the other hand, in plane-to-point kind of interaction, the interaction distance between the N-H bond and π-ring of two BA molecules are 2.903 Å and 3.066 Å. This is slightly higher than the Hπ/π interaction distance of 2.365 Å [27]. The N-H bond perpendicular to the π-ring gets elongated because of the interaction between two BA molecules. Hussain et al. [7] also reported that BA dimer is stabilized by NH/π and N-H------O type of molecular interactions.

BA and ethanol both are polar molecules and can form H-bond. As N------H-O hydrogen bond is stronger than O---H-N hydrogen bond, it is expected that when BA-ethanol complex is formed (Fig. 1d), they will interact via N------H-O

|       | Energy (au) | ΔE (au) | ΔE (Kcal/mol) | Dipole moment (D) |
|-------|-------------|---------|---------------|-------------------|
| Benzylamine | −326.8871912961 | 1.296 | | |
| Ethanol  | −155.0421486608 | 1.774 | | |
| Benzene  | −232.2233040759 | 0.000 | | |
| BA-BA (I) | −653.7868039628 | −0.012421 | −7.795 | 1.948 |
| BA-BA (II) | −653.7857246619 | −0.011342 | −7.117 | 0.585 |
| BA-B    | −559.1183893867 | −0.007894 | −4.954 | 1.404 |
| BA-Eth  | −481.9413852910 | −0.012045 | −7.559 | 2.665 |
| BA-Eth-B| −714.1744453674 | −0.021801 | −13.681 | 2.665 |

Fig. 1 Structure of (a) BA, (b) BA dimer (I), (c) BA dimer (II), (d) BA-ethanol complex, (e) BA-benzene complex and (f) BA-ethanol-benzene complex (distances in Å)
bond (Zaitseva et al. [28] reported that aliphatic amines dissolved in methanol form O-H…-N type H-bonding). It seems that the π-ring of BA provides better stability to the O-H bond of ethanol. Therefore, it takes a geometry perpendicular to π-ring at 2.930 Å. The CH₂ group of BA provides flexibility to the N-H bond and so it interacts with ethanol via O----H-N hydrogen bond. Its interaction energy and interaction length is found to be -4.461 Kcal/mol and 2.220 Å respectively. On clustering of BA and ethanol, the increase in bond length r(O-H) of ethanol indicates the OH/π kind of interaction between BA and ethanol, while increased r(N-H) and decreased r(C-N) of BA shows the presence of N-H-----O type H-bonding interaction between them.

The interaction between benzene and BA (Fig. 1e), results in geometry such that, the N-H bond of BA takes position perpendicular to π-ring of benzene at a distance of 3.056 Å. This indicates the presence of NH/π interaction between them. Also, the dispersive forces between the π-π ring of benzene and BA cause the interaction of two π-rings in such a way that the two π-rings, one of benzene and other of BA, takes T-shape similar to benzene dimer (T-shape structure [27]) and the bond length r(C-H) of benzene gets decreased by 0.001 Å. This indicates the presence of CH/π interaction as defined by Hobza and Havlas [29]. He studied the C–H/π interaction, the interaction between a C-H donor and a π-face of an aromatic moiety and characterized it by a shortening of the C–H bond length. So, the BA-benzene cluster is stabilized by two interactions, NH/π interaction and CH/π interaction with interaction energy -4.954 Kcal/mol.

In BA-ethanol-benzene complex (Fig. 1f), the stabilization takes place by different kind of interaction between different moiety such as NH/π interaction between BA-benzene, O-H…-N hydrogen bonding between BA-ethanol complex etc. The interaction energy of this complex is -13.36 Kcal/mol.

So, in all, we can say that the various intermolecular interactions in different systems are (1) between BA dimer: NH/π and N-H-----O, (2) between benzene and BA: NH/π and CH/π and (3) between ethanol and BA: Hπ/π and H-bonding. The space between benzene and benzylamine molecule is the largest.

**FTIR spectral analysis**

FT-IR spectroscopy is a suitable technique to investigate the intermolecular interaction. The interactions between the different molecules lead to the formation of the new vibrational degree of freedom which appears at shifted frequencies. So, the vibrational frequency shifts, changes of shape and intensity of IR absorption peaks resulting from some characteristic functional groups can be attributed to the existence of intermolecular interaction [30, 31].

**Band assignment**

The spectrum is evaluated by assigning vibrational peaks to different functional groups. In Table 2, the spectral peak and vibrational bands of pure components taken from the literature [32–35] are presented.

The experimental FTIR spectra of the mixture at different concentrations and of pure components (Fig. S1 in supplementary file) are a complex spectrum. So, the discussion of different frequency range depending upon the major vibrational bands is as follows:

**O-H and N-H stretching vibration range: 3550–3100 cm⁻¹**

The measurement of the X-H stretching frequencies can be a preferred tool to investigate H-bond in X-H-----Y system. According to Arunan et al. [36], the greater the lengthening of the X-H bond in the X-H-----Y system, the stronger and shorter is the H-----Y hydrogen bond and vice versa. H-----Y hydrogen bond length also depends on the bond angle.

Both N-H and O-H stretching vibration lies in the spectral range 3550–3100 cm⁻¹ (Fig. 2). The O-H stretching vibration in ethanol shows a peak at 3309 cm⁻¹ with transmittance

| Benzylamine | Ethanol | Benzene |
|-------------|---------|---------|
| w(cm⁻¹) | Band | w(cm⁻¹) | Band | w(cm⁻¹) | Band |
| 3290, 3373 | NH₂ stretching (primary amine) | 3230 - 3550 | OH stretching | 3099, 3068 | CH stretching |
| 3027-3106 | CH (sp) stretching | 2961 | CH (sp) stretching | 3032 | CH stretching |
| 2368-2920 | CH (sp)₂ stretching | 2927 | CH (sp)₂ stretching | 1506, 1614, 1465 | CC stretching |
| 1605 | NH₂ bending | 1102, 1055 | CO stretching | 1086, 1035 | In plane CH bending |
| 1496, 1605 | C=C stretching (aromatic) | 907 | In plane C=C bending | 738 | oop CH bending |
| 1454 | CH₂ bending | 1026 | CN stretching | 1026 | CN stretching |
| 698, 739 | Oop (out of plane) |
The N-H stretching vibration in benzylamine shows two peaks at 3371 cm$^{-1}$ and 3285 cm$^{-1}$ corresponding to symmetric and asymmetric (higher frequency) vibration. Benzene does not show any peak in this region.

For $x_1=0.0$, the peak is at 3325 cm$^{-1}$ with increased transmittance to 90.57%. There is a shift of 16 cm$^{-1}$ towards a higher wavenumber. When benzene and ethanol are mixed, the H-bonding between ethanol molecules rupture and the OH/π interaction between benzene and ethanol takes place. The shift in O-H stretching vibration wavenumber towards higher wavenumber shows that the O-H bond length of H-bonded ethanol (such as ethanol dimer) gets decreased on interacting with benzene via OH/π interaction. This indicates that the strength of OH/π interaction is weak compared to conventional H-bonding of ethanol. Previous, theoretical interaction energies also show that the OH/π interaction is weaker than H-bonding [27]. It is a well-established fact that the formation of hydrogen bonding lowers the frequency of OH stretching vibration and so, a broader band appears at a lower frequency as compared to the free OH group. This gives a sharp band in the frequency range of 3650–3590 cm$^{-1}$ [37]. The intensity of O-H stretching vibration gets decreased at 0.0 mole fraction. This is because as compared to pure ethanol, a smaller number of ethanol molecules are present to absorb the radiation corresponding to O-H stretching vibration in the mixture.

After 0.0, i.e. when BA is introduced in the mixture, the spectra become complex because O-H and N-H absorb in the same frequency range, but the N-H band is sharper and of

![FTIR spectra (3550–3100 cm$^{-1}$ wavelength range) of benzylamine, ethanol, benzene and their mixture at different concentration](image)

### Table 3 FTIR spectra peak(s) details of wavenumber range 3550–3100 cm$^{-1}$

| System | Peak (3550–3000 cm$^{-1}$) |
|--------|-----------------------------|
|        | $\tilde{v}$ (cm$^{-1}$) | $T$ (%) | $\tilde{v}$ (cm$^{-1}$) | $T$ (%) | $\tilde{v}$ (cm$^{-1}$) | $T$ (%) |
| BA     | 3371           | 94.53   | 3285           | 95.61   | –                 | –       |
| Ethanol| 3309           | 75.97   | –              | –       | –                 | –       |
| Benzene| –              | –       | –              | –       | –                 | –       |
| 0.6    | 3360           | 89.77   | 3286           | 88.96   | 3177             | 89.94   |
| 0.5    | 3361           | 92.06   | 3285           | 90.80   | 3173             | 91.89   |
| 0.4    | 3360           | 90.32   | 3287           | 89.90   | 3178             | 91.35   |
| 0.3    | 3361           | 90.17   | 3292           | 89.99   | 3180             | 91.70   |
| 0.2    | 3361           | 90.82   | 3300           | 90.87   | –                 | –       |
| 0.1    | 3363           | 90.64   | 3300           | 90.70   | –                 | –       |
| 0.0    | 3325           | 90.57   | –              | –       | –                 | –       |
lower intensity. The change in shape and shift in wavenumber takes place with increasing concentration of BA. Table 3 shows that the respective peak position of N-H symmetric, N-H asymmetric and O-H stretching vibrations gets shifted. At $x_1 = 0.6$, the main peak of N-H stretching vibration gets red shifted. This indicates that the N-H bond length gets increased resulting in an overall decrease in NH stretching vibration frequency.

The O-H stretching band is important to study the H-bonding, but it gets extensively overlapped with N-H stretching bands in ethanol-BA mixture. The accurate number of peaks and their position in the overlapped band helps us to study the contribution of H-bonding. The peak fitted spectra at $x_1 = 0.6$ (Fig. 3) show that the peak in the 3500–3100 cm$^{-1}$ is made of five components. One is due to O-H stretching (3361 cm$^{-1}$), the second and third due to N-H symmetric and asymmetric stretching (3361 cm$^{-1}$ and 3288 cm$^{-1}$) and as the hydrogen bonding creates an additional relaxation channel, so the other two will be due to the interaction present in the mixture between different components such as OH/π and N-H----O interactions. Also, on mixing ethanol and BA, N-H stretching frequency gets red-shifted (Rajpurohit et al. [38] show that N-H----O bonding shows a red-shift in amino group frequency) while O-H stretching frequency gets blue shifted. This indicates that the strength of the interaction in the BA-eth mixture is weaker than that of pure ethanol but stronger than the interaction in pure BA. On analysing the components of the peak fitted spectrum, it is seen that on mixing ethanol and BA, the O-H stretching frequency gets more affected compared to N-H vibration frequency. This indicates that in BA-ethanol mixture O-H----N hydrogen bonding dominates over the N-H----O hydrogen bonding (similar to aliphatic amine and alcohol mixture as reported by Zaitseva et al. [28]). Theoretical results also predict the N-H----O type hydrogen bonding in the BA-ethanol complex.

But with mole fraction, the intensity and wavenumber both do not follow a particular pattern because in a mixture the extent of interaction of each molecule with the other is different. The concentration of the mixture and relative strength of interactions are the key factor to decide the IR spectra of the mixture.

C-H stretching vibration: 3100–2900 cm$^{-1}$

The C-H stretching vibrations of ethanol, BA and benzene fall in the wavenumber range 3100–2900 cm$^{-1}$ (Fig. 4). For benzene, the peak is at 3036 cm$^{-1}$. BA shows two C-H stretching vibration bands at 3026 and 2912 cm$^{-1}$ due to the aromatic C-H and CH$_2$ groups. Ethanol also shows two C-H stretching bands at 2973 and 2929 cm$^{-1}$ due to CH$_2$ and CH$_3$ group (Table 4).

In aromatic C-H stretching vibration, the stabilization of π-π interaction in the polar environment (Meyer et al. [8] also reported the strong π-π interaction in the polar environment).
solvent) leads to the shortening of C-H bond length and increases the aromatic C-H vibration frequency. This kind of vibrational frequency increase is also observed for ethanol-benzene system at 0.0 mole fraction and BA-ethanol at 0.6 mole fraction. The increased polarity of solvent reduces the transition dipole moment of C-H vibration [39]. This will cause a fall in the intensity of aromatic C-H vibration with increasing $x_1$. The C-H stretching vibration frequency of ethanol gets decreased when it gets mixed with benzene ($x_1 = 0.0$), indicating that the C-H bond length in the mixture gets decreased compared to H-bonded ethanol. The increased redshift with mole fraction (Table 4) indicates the weakening of the C-H bond of ethanol.

On expanding the wavelength range $3010–3045$ cm$^{-1}$, the aromatic C-H stretching vibration is found to be the combination of two aromatic C-H vibrations, one of benzene and other of BA. At lower mole fractions, it is mainly due to benzene, while at higher, it is due to BA. At mid mole fraction, such as 0.3, the peak fitting of the band shows that the C-H vibration is due to benzene, BA, and the interaction between them (Fig. 5).

**Aromatic C-C stretching and NH$_2$ bending vibration:**

1700–1550 cm$^{-1}$

In this wavelength range, two bands at 1604 cm$^{-1}$ and 1585 cm$^{-1}$ corresponding to NH$_2$ bending and aromatic C-C stretching of BA (Fig. 6) are obtained. On increasing the mole fraction, there is almost negligible shift in band position but there is decrease in transmittance.

| Table 4 FTIR spectra peak(s) details of wavenumber range 3100–2900 cm$^{-1}$ |

| System | Peak (3100–2900 cm$^{-1}$) |
|--------|-----------------------------|
|        | $\tilde{\nu}$ (cm$^{-1}$) | $T$ (%) | $\tilde{\nu}$ (cm$^{-1}$) | $T$ (%) | $\tilde{\nu}$ (cm$^{-1}$) | $T$ (%) |
| BA     | 3026                        | 88.54   | –                        | –       | 2912                        | 93.41   |
| ethanol| –                           | –       | 2973                      | 71.37   | 2925                        | 85.79   |
| Benzene| 3036                        | 80.08   | –                        | –       | –                           | –       |
| 0.6    | 3028                        | 88.82   | 2968                      | 83.85   | 2918                        | 87.28   |
| 0.5    | 3029                        | 91.45   | 2968                      | 85.79   | 2922                        | 88.75   |
| 0.4    | 3034                        | 89.10   | 2970                      | 84.0    | 2922                        | 89.45   |
| 0.3    | 3034                        | 88.70   | 2970                      | 84.55   | 2921                        | 90.54   |
| 0.2    | 3036                        | 87.96   | 2971                      | 85.25   | 2921                        | 91.39   |
| 0.1    | 3036                        | 86.94   | 2972                      | 85.33   | 2924                        | 92.01   |
| 0.0    | 3037                        | 87.34   | 2973                      | 87.52   | –                           | –       |
Aromatic C-C stretching vibration of benzene: 1465–1490 cm$^{-1}$

The aromatic C-C vibration of benzene shows a peak at 1478 cm$^{-1}$ with a transmittance of 80.26% (Fig. 7). It also shows a small shift towards higher wavenumber with increasing mole fraction (Table 5). The absorption intensity of IR spectra depends on molecular dipole moment [40, 41]. The increased intensity of aromatic C-C stretching at 0.0 mole fraction also shows the increase in molecular dipole moment in a polar (ethanol) environment. But with further increase in mole fraction, the decrease in intensity is due to decrease
in benzene concentration. The strong π-π interaction leads to stabilization of π-ring which leads to a blue shift in absorption frequency. A similar observation of blue shift of aromatic C-C stretching frequency is reported by Li et al. [42] for pyridine+ water complex.

C-N stretching vibration of BA and C-O stretching vibration of ethanol: 1070–1020 cm\(^{-1}\)

The information about the strength and type of intermolecular interaction can be obtained by the stretching frequency of the bonds that are directly involved in it and also due to the nearest neighbouring bonds. So, the stretching frequency of C-N and C-O can be a good source to study the intermolecular interaction in the chosen mixture.

The position of the C-O stretching frequency of ethanol is 1046 cm\(^{-1}\) (Fig. 8). In the mixture, the wavenumber of C-O stretching gets increased because in all interactions involving ethanol, the C-O bond length gets decreased. With increasing mole fraction (from 0.0 to 0.2), the variation in the interaction strength causes a shift towards higher wavenumber. However, for the mole fraction above 0.2, the nature of the interaction is the same, so almost no shift is observed. The transmittance is the same for all mole fractions because the mole fraction of ethanol is fixed.

The C-N stretching vibrational band appears at 1025 cm\(^{-1}\) with a transmittance of 85.32%. The C-N stretching vibration disappears at a lower mole fraction (lower than 0.5).

Some of the FTIR results are in excellent agreement with theoretical results but few could be explained either experimentally (FTIR) or theoretically. For example, some weak interactions like CH/π interaction can be better explained theoretically rather than FTIR spectra because in the bulk mixture, it is difficult to detect the weak interaction due to the presence of other dominating forces. Both FTIR and theoretical results support the presence of HP/π interaction between ethanol and benzene and N-H-----O type H-bonding between ethanol and BA. The OH/π interaction is found to be weaker than conventional H-bonding in both studies. Theoretically, it is observed that on complex formation, there is variation in the bond length, e.g. contraction of C-O bond length of ethanol, lengthening of N-H bond of BA etc. The FTIR results also explain the aromatic C-C and C-H stretching vibration frequency shift.

### Table 5 FTIR spectra peak(s) details of wavenumber range 1490–1465 cm\(^{-1}\)

| System | \(\tilde{\nu}\) (cm\(^{-1}\)) | T (%) |
|--------|-----------------|------|
| BA     | –               | –    |
| Ethanol| –               | –    |
| Benzene| 1478            | 80.26|
| 0.6    | 1479            | 94.23|
| 0.4    | 1480            | 84.74|
| 0.3    | 1479            | 82.21|
| 0.2    | 1479            | 76.73|
| 0.1    | 1479            | 75.65|
| 0.0    | 1479            | 70.40|
Conclusion

In the present investigation, the presence of various types of interaction between benzylamine (BA), ethanol and benzene is established using DFT investigation of the geometrical parameter and energies. The optimized structure of the BA dimer shows that BA is self-associated through conventional H-bonding and NH/π interaction. The BA-B structure is a delicate balance of NH/π and CH/π interaction and in BA-ethanol complex N-H-----O hydrogen bonding and OH/π interactions are present. FTIR technique is used to study the structural changes and intermolecular interactions. A blue shift in O-H stretching frequency indicates the presence of OH/π interactions between benzene and ethanol. N-H stretching frequency shows a red-shift due to NH/π and N-H-----O bonding interaction. Aromatic C-C and C-H stretching frequency shift in the polar environment indicates that the strength of π-π interaction gets enhanced in the polar environment. Both, theoretical and experimental results show that in the BA-ethanol-benzene mixture, different kinds of interactions are present. The strength of these interactions varies with concentration. At lower concentration ($x_1=0.0$), weak OH/π interactions between benzene and ethanol take place while at other mole fraction, N-H-----O, O-H-----N, NH/π interaction are present.

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Author contribution

The original ideas, image and data analysis, presentation of the finding, and writing was done by Hema. Dr. Tara Bhatt has supervised the work and helped in literature consultation, and editing of the paper. Pratibha Arya, Dr. Charu Ch. Dhondiyal, Himani Tiwari and Dr. Kamal Devlal helped in the interpretation of the study and writing.

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Data availability

Supplementary file.

Code availability

The open-source code programmes available for free download at the following address are used for present work.

GAMMES: https://www.msg.chem.iastate.edu/gamess/
Avogadro: https://avogadro.cc/
ChemCraft: https://www.chemcraftprog.com/

Declarations

Conflict of interest

The authors declare no competing interests.
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