Conformational and dielectric analysis of hydrogen bonded polar binary mixtures of methyl benzoate with aniline

M Chitra, B Subramanyam & V R K Murthy

Department of Physics, Indian Institute of Technology, Madras 600 036

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The dielectric properties of the hydrogen bonded binary system of non-associated polar liquid methyl benzoate (ester) and polar liquid aniline (primary amine) have been studied on both pure and equimolar binary mixtures of methyl benzoate and aniline in dilute solutions of benzene. AM1 semi-empirical calculations are performed on various conformers of the hydrogen bonded complex. The minimum energy conformer is then selected and ab initio geometry optimization is performed with 6-31g(d) basis set. Self-consistent reaction field calculations have been performed on the resultant geometry to include solvent effects. The calculated dipole moment is compared with the experimental value.

1 Introduction

The molecular structure of methyl benzoate (A) and its binary complex with aniline (B) form complex through hydrogen bonding, which designates intermolecular interactions that can result from very different kinds of physical interactions. The precise definition of hydrogen bond continues to be elusive\(^1\). Linear hydrogen bonding is in general stable\(^2\). The circular hydrogen bonding is also found to be stable in many cases such as formamide-methanol complex and acetone-methanol complex\(^3\). Geometry optimization programs are designed to find the minimum energy structure for the most stable configuration. Unfortunately, there is no way to locate the global minimum automatically by geometry optimization molecular orbital programs\(^4\). In the present study, different possible linear and ring-like conformers of A + B were explored using AM1 semi-empirical calculations and the most stable conformer was selected and ab initio geometry optimization and self-consistent reaction field calculations were performed on the resultant molecular structure. The calculated dipole moment values are then compared with those obtained from experiments. The importance of hydrogen bonding between C=O and N-H group lies in the study of biological macromolecules such as protein structures, nucleic acids and polypeptide chains and are called salt bridges in proteins\(^5\).

Dielectric dispersion studies of polar liquids and their binary mixtures are carried out with a view to determine the electric dipole moment and relaxation time. The presence of hydrogen bond brings a considerable change in the relaxation time and dipole moment of the binary system, with respect to the corresponding values in the pure components\(^6\). In the determination of dipole moment, the dipole-dipole interactions are minimized by dilution in a non-polar solvent\(^7\). Equimolar binary mixture of methyl benzoate and aniline was used to ensure 1:1 availability of species A and B. Dielectric permittivity and loss factor were measured as a function of frequency and concentration.

Geometry optimization was performed using ab initio calculation in the 6-31g(d) basis set for the monomers of methyl benzoate and aniline. The resultant geometry of the monomers were used for the input of different A + B combinations as shown in Fig 1. Four linear hydrogen bonded structures and two ring-like structures of A + B are explored with AM1 semi-empirical calculations. From the results, minimum energy geometry was selected for ab-initio geometry optimization in 6-31g(d) basis set with the HF theory level, followed by a SCRF calculation using Onsager model reaction field. The final calculated dipole moment values are compared with the experimental values. The calculations were performed using Gaussian 94W software\(^8\).
2 Experimental Details

All Chemicals were analar grade with purity greater than 99% and benzene was used as the non-polar solvent. Equimolar binary mixture of methyl benzoate and aniline was prepared and dielectric permittivity measurements were carried out for the following frequencies viz. 300 KHz using a Toshniwal RL09 type dipole meter whose working is based on the heterodyne beat method, 5.59 GHz (J-band) and 9.75 GHz (X-band) using the flat movable plunger technique and 71 GHz (E-band) using the free space propagation technique. The least square fit for the reflected power profile, with 80 or more experimental data points, is obtained by optimizing the values of the attenuation constant, propagation constant and saturation power output. The value of the dielectric constant determined at 300 KHz is taken as the static value \( \varepsilon_s \). The high frequency dielectric permittivity was determined using the relationship \( \varepsilon_r = n^2 \) where \( n \) is the refractive index. The refractive index was measured with a Carl-Zeiss Abbe Refractometer with a sodium vapor lamp as the light source. All experiments were conducted at the room temperature (27°C).

2.1 Determination of Parameters

![Diagram of molecular structure](image-url)  
Fig. 1 — Methyl benzoate + aniline (structure I): Ring-like structure with double N-H...O attack.  
- \( r(OH) = 1.452 \text{ Å}, \angle\text{NHO} = 130.1^\circ \)  
- \( r(OH) = 1.337 \text{ Å}, \angle\text{NHO} = 134.8^\circ \)  
- Angle between the two benzene planes = 93.4°

![Graphs](image-url)  
Fig. 2 — Plots of \( \varepsilon_s, \varepsilon', \varepsilon'' \) and \( \varepsilon_r \) versus the weight fraction of solute (a, b, c and d respectively) for the binary mixture methyl benzoate + aniline at 5.59 GHz.
The parameters $a_{\alpha}, a', a''$, and $a_{\alpha}$ are respectively the slopes obtained from the linear plots of $\varepsilon_{\alpha}$, $\varepsilon'$, $\varepsilon''$, and $\varepsilon_{\alpha}$ versus the weight fraction of solute (binary mixture) diluted in benzene. The linear plots obtained for the binary mixture of methyl benzoate and aniline at 5.59 GHz (J band) are shown in Figs 2(a-d). From the Cole-Cole plots of $a''$ versus $a'$ [Figs 3(a-c)], the average relaxation time of the binary system is determined ($\tau$). The dipole moment of the solute molecule has been determined using the Guggenheim’s method.

$$\mu' = 27kT/4\pi N (\varepsilon_{\alpha} + 2) (n_{1}^2 + 2). (\Delta/C)_{\alpha}$$

where $\Delta = (\varepsilon_{\alpha}) - n_{2}^2 - (\varepsilon_{\alpha} - n_{1}^2); 1$ - solvent, 12 - solution, $C$ - concentration of the solute in moles/cc. The error in the estimation of $\mu$ is $\pm 2\%$.

The interaction energy or the hydrogen bonding energy is calculated using the procedure:

$$\Delta E = \Delta T - \Delta T_{0}$$

where $\Delta T$ is the total energy of the complex, $\Delta T_{0}$ is the sum of total energies of the monomers and $\Delta E$ is the H-bond energy expressed in kcal mol$^{-1}$.

The Kirkwood-Frohlich relation for the determination of the $g$-factor, extended to the solution, can be written as:

$$g = 9kTC (2\varepsilon + \varepsilon_{\alpha} + 2) / 4\pi N \mu^{2} X_{1} (\varepsilon_{\alpha} + 2)^2 (2\varepsilon + 1)$$

where

$C = V(\varepsilon - 1)/(\varepsilon + 3); V = \text{molar volume of mixture}; V_{1} = \text{molar volume of solvent and solute respectively}; X_{1}$ and $X_{2} = \text{mole fraction of the solvent and solute respectively}; \varepsilon = \text{square of the refractive index of the polar solute}; \varepsilon_{\alpha} = \text{dielectric permittivity of the mixture}; \varepsilon_{1} = \text{dielectric permittivity of the non-polar solvent}; k = \text{Boltzman Constant}; N = \text{avagadro number};$ and $T = \text{temperature in Kelvin}.$

The $g$ factor can be calculated. This value gives the information whether the dipoles dispersed in the solvent medium remain parallel ($g > 1$) or they remain anti-parallel ($g < 1$) with respect to each other.

![Fig. 3 - Cole-Cole plots for (a) aniline, (b) methyl benzoate and (c) methyl benzoate + aniline](image)

3 Results and Discussion

The structures I and II are hydrogen bonded ring like structures with double N-H...O attacks (Fig. 1) and N-H...O + C-H...N attack (Fig. 4) respectively. The structures III and IV are linear hydrogen bonded conformers with their two benzene rings in plane, on the same side of the hydrogen bond as represented in Fig. 5 and on the opposite side of the hydrogen bond as represented in Fig. 6 respectively. The remaining conformers are formed by rotation of aniline molecule about N-H axis through 90° into the plane of the paper.
(structure V) and out of the plane of the paper (structure VI) as represented in Fig. 7.

Table 1 — AM1 optimization results of various structures

<table>
<thead>
<tr>
<th>Structure</th>
<th>AM1 Heats of formation (in kcal/mol)</th>
<th>Dipole moment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Full structure Hydrogen bond</td>
<td></td>
</tr>
<tr>
<td>Structure I</td>
<td>-44.2784 -4.3002</td>
<td>1.8882 D</td>
</tr>
<tr>
<td>Structure II</td>
<td>-44.6099 -4.6287</td>
<td>3.9516 D</td>
</tr>
<tr>
<td>Structure III</td>
<td>-44.5071 -4.5289</td>
<td>3.6456 D</td>
</tr>
<tr>
<td>Structure IV</td>
<td>-44.4734 -4.4952</td>
<td>3.6648 D</td>
</tr>
<tr>
<td>Structure V</td>
<td>-44.4421 -4.4639</td>
<td>3.0336 D</td>
</tr>
<tr>
<td>Structure VI</td>
<td>-44.5066 -4.5284</td>
<td>3.6386 D</td>
</tr>
</tbody>
</table>

The AM1 heat of formation of methyl benzoate is found to be -61.3524 kcal/mol and that of aniline is found to be 21.3742 kcal/mol. The AM1 results of all the binary complex structures are tabulated in Table 1. From Table 1, it is seen that the AM1 optimized output of structure II yields the structure of lowest energy. The AM1 output of the structure II is no more a ring like structure after the geometry

Fig. 4 — Methyl benzoate + aniline (structure II): Ring-like structure with N-H...O and C-H...N attack

\[ r(\text{OH}) = 1.689 \, \text{Å} \angle \text{NHO} = 161.2^\circ \]

\[ r(\text{NH}) = 1.743 \, \text{Å} \angle \text{CHN} = 116.8^\circ \]

Angle between the two benzene planes = 35°

Fig. 5 — Methyl benzoate + aniline (structure III)

Linear structure with two benzene rings in-plane on the same side of the HB

\[ r(\text{OH}) = 2.202 \, \text{Å} \angle \text{NHO} = 178.4^\circ \]

\[ \angle \text{COH} = 178.9^\circ \]

The AM1 heat of formation of methyl benzoate is found to be -61.3524 kcal/mol and that of aniline is found to be 21.3742 kcal/mol. The AM1 results of all the binary complex structures are tabulated in Table 1. From Table 1, it is seen that the AM1 optimized output of structure II yields the structure of lowest energy. The AM1 output of the structure II is no more a ring like structure after the geometry

Fig. 6 — Methyl benzoate + aniline (structure IV): Linear structure with two benzene rings in plane on the opposite side of the HB

\[ r(\text{OH}) = 1.966 \, \text{Å} \angle \text{NHO} = 177.9^\circ \]

\[ \angle \text{COH} = 178.9^\circ \]

Fig. 7 — Methyl benzoate + aniline (structures V and VI): Aniline molecule is rotated 90° into the plane of the paper about N-H axis for Structure V and out of the plane of paper for Structure VI
optimization process, but has converged to a structure similar to structure VI. This structure II was the chosen starting structure for ab initio geometry optimization in 6-31g(d) basis set and optimization was carried out. A final SCRF calculation was performed on the ab initio gas phase optimized structure using Onsager’s field model with 6-31+g(d) basis set.

![Image](image.png)

**Fig. 8** — Final ab initio optimized output of the HB complex

\[ \tau(\text{OH}) = 2.218 \text{Å}, \angle \text{NHO} = 164.2^\circ \]

\[ \angle \text{COH} = 178.9^\circ \]

Angle between the two benzene planes = 100°

The dielectric data of the pure and equimolar binary mixtures in dilute solutions of benzene are tabulated in Table 2. The calculated dipole moments, relaxation time and g-factor are tabulated in Table 3. The experimental dipole moment values of the monomers agree well with the reported standard values\(^1\). The relaxation time of aniline is 9.1 ps and relaxes with 9.8 ps in its complex form with methyl benzoate. There is no large increase in the relaxation time because aniline exists in associated form in its pure state. When diluted in benzene, degree of association will decrease but still may exist in HB clusters of 2 or 3. This is also shown by the g-factor (g < 1) which says that there is anti-parallel alignment of the dipoles of solute molecules in the benzene solution. The experimental dipole moment values are found to be lower than the calculated dipole moment values. This may be due to the fact that benzene may get polarized in the presence of polar molecules (solute). The induced polarization in benzene is in the opposite direction and effectively decreases the dipole moment value.

**4 Conclusion**

The ab initio optimized final geometry is given in Fig. 8. Ring-like hydrogen bonded starting geometries (structures I and II) resulted in structures similar to structure VI and are less favourable than linear hydrogen bonded structures. The interaction energy of the binary complex is found to be 6.2332
The experimental dipole moment values are found to be slightly lower than the calculated values. This may be due to the fact that benzene is not strictly non-polar in the presence of polar solutes.

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References