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STUDY OF INTERMOLECULAR INTERACTIONS IN ANILINE-CHLOROFORM SOLUTIONS

Annotation

In this work, when analyzing the vibrational bands of aniline in chloroform solutions using experiment (Raman spectroscopy) and calculations, a partial red shift was observed in the N-H stretching vibration band and a blue shift in the remaining bands. AIM, NCI and RDG analyses were performed to determine non-covalent interactions in molecular systems, and accordingly, it was confirmed that a partial red shift was formed due to the presence of weak H-bonds through the N-H group in aniline-chloroform complexes. It was determined that mainly Van der Waals bonds were formed through the C-H group, and therefore blue shifts were observed. Also, molecular electrostatic potentials surface (MEPS) and frontier molecular orbitals (FMO) analyses were performed for the complexes to characterize chemical bonds in molecular systems and determine the zones where electrons are located.

Key words: aniline, Raman, H-bonding, DFT calculation, topological analyses.

ИЗУЧЕНИЕ МЕЖМОЛЕКУЛЯРНЫХ ВЗАИМОДЕЙСТВИЙ В РАСТВОРАХ АНИЛИН-ХЛОРОФОРМ

Аннотация

В данной работе при анализе колебательных полос анилина в растворах хлороформа с использованием эксперимента (рамановская спектроскопия) и расчетов наблюдалось частичное красное смещение в полосе валентных колебаний N-H и синее смещение в остальных полосах. Были проведены анализы AIM, NCI и RDG для определения нековалентных взаимодействий в молекулярных системах, и соответственно было подтверждено, что частичное красное смещение образовалось из-за наличия слабых водородных связей через группу N-H в комплексах анилин-хлороформ. Было определено, что в основном связи Ван-дер-Ваальса образовались через группу C-H, и поэтому наблюдались синие смещение. Также были проведены анализы поверхности молекулярных электростатических потенциалов (MEPS), анализ граничных молекулярных орбиталей (FMO) для комплексов для характеристики химических связей в молекулярных системах и определения зон, где находятся электроны.

Ключевые слова: анилин, Раман, водородные связи, расчет DFT, топологический анализ.

ANILIN-XLOROFORM ERITMALARIDA MOLEKULARARO TA’SIRLARNI O‘RGANISH

Annotatsiya

Ushbu ishda tajriba (Raman spektroskopiyasi) va hisoblashlar yordamida anilinning chloroform eritmalaridagi tebranish polosalalari tahlil qilinganda N-H valent tebranish polosasida qisman qizil va qolganpolosalarida ko‘k siljish kuzatildi. Molekulyar sistemalardagi nokovalent o‘zaro ta'sirlarni, aniqlash uchun AIM, NCI va RDG analizlari o‘tkazildi, shunga ko‘ra anilin-chloform komplekslarida N-H guruhi orqali kuchsiz H-bog‘lanishlar mavjudligi tufayli qisman qizil siljish hosil bo‘lishi tasdiqlandi. C-H guruhi orqali esa asosan Van der Waals bog‘lanishlar hosil bo‘lishi va shu tufayli ko‘k siljishlar kuzatilishi aniqlandi. Shuningdek keltirilgan komplekslar uchun **m**olecular electrostatic potentials surface (MEPS), chegara molekulyar orbitallari (FMO) analizlari o‘tkazildi.

Kalit so‘zlar: anilin, Raman, H-bog’lanish, DFT hisoblash, topologik analizlar.

Introduction. The study of intermolecular interactions and their effect on solutions is of practical importance [1-3]. In addition to hydrogen bonding, it is also important to study weak van der Waals, NH-π, OH-π, CH-π and cation-π interactions [4]. Hydrogen bonding through NH vibrations is important in chemistry, biology and materials science. Aniline is a simple amine representative of aromatic ring substances and is a good module for studying hydrogen bonding using NH vibrations and spectroscopic methods [5-6]. Also, this substance is of interest to many researchers because it is one of the substances widely used in materials science, industry and production. The structure of aniline has been studied using three different semi-empirical, ab-

initio and DFT methods [7]. In [8-10], the eigen vibrational frequencies of aniline have been studied using NIR-FT Raman spectra. Among other non-covalent bonds, there is also a sticking bond, which is said to be important in the formation of aggregations in aromatic substances.

In this work, the vibrations of aniline in chloroform solution were analyzed using Raman spectroscopy. Using calculations, interactions in aniline-chloroform complexes, molecular electrostatic potential surface (MEPS) surface, frontier molecular orbital (FMO) analysis, atoms in molecules (AIM), quantum chemical parameters such as reduced density gradient (RDG) and non-covalent interaction (NCI) analysis were performed.

Methods. Raman spectra of aniline and its chloroform solutions were recorded at room temperature on a Renishaw Invia Raman spectrometer with a diffraction grating with a period of 1200 lines/mm. A laser with a wavelength of 532 nm and a power of 50 mW was used as the excitation light source. A standard Renishaw CCD Camera detector was used to record the scattered light. Quantum-chemical calculations were performed using the density functional theory (DFT) method in the Gaussian 09W program [11]. B3LYP/6-311++G(d.p) was used for the partial complement. The geometric structure of the molecule was described by MEPS and VMD tools [12]. The topological parameters of AIM and RDG were calculated by the Multiwfn 3.8 bin (Win 64) program [13].

Results and Discussion

Vibrational analysis

Figure 1 shows the Raman spectra of pure aniline and its chloroform solution. The solutions are given in mole fraction (m. f.). The maximum of the N-H vibration band involved in hydrogen bonding corresponds to 3359 cm^{-1}, and at 0.9 m. f. this maximum (3357 cm^{-1}) shifted by 2 cm^{-1}. However, when the concentration was reduced to 0.7 m. f. and experiments were conducted, a blue-shift to a higher frequency occurred at 3364 cm^{-1}. This indicates that this aniline is bound to chloroform through N-H through weak H-bonding or van der Waals interaction. In the C-H and CC+NHN vibration bands, a blue-shift to a higher frequency occurred by 2 cm^{-1} with a decrease in the concentration of aniline.

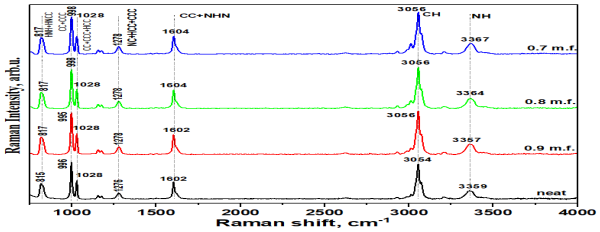
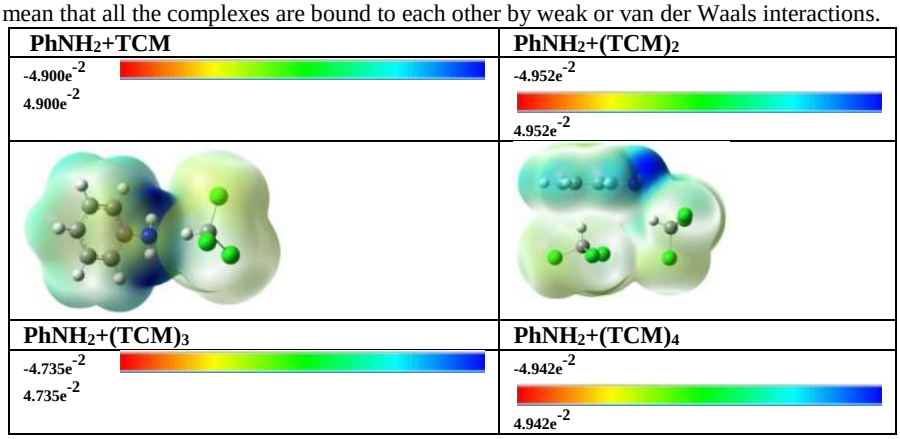


Figure 1. Raman spectra of aniline-chloroform complexes (m.f.=mole fraction).

Similarly, the maximum of the NC+HCC+CCC vibration system corresponds to pure aniline at 1276 cm^{-1} and a blue shift of up to 2 cm^{-1} (1278 cm^{-1}) was observed at a concentration of 0.7 m. f. As the concentration decreased, the CC+CCC+HCC (1028) bands did not change, and the CC+CCC (996) and HNH+HNCC (817) bands showed a blue shift of 2 cm^{-1}. This suggests that the aniline-chloroform interaction is weak or due to van der Waals interactions, with blue shift or no shift at all. Quantum-chemical calculations were performed to confirm these results.

Molecular electrostatic potential surface (MEPS) analysis

Molecular electrostatic potential surface analysis plays an important role in visualizing charge distribution and studying charge-dependent parameters, electrophilic, nucleophilic reactions, and noncovalent interactions. Electrostatic potential is also used to identify reactive parts of a molecule. According to the MEPS color code for aniline ($PhNH_2$)+chloroform $(TCM)_n$ (n=1-4) shown in Figure 2, the electrostatic potential increases from red to violet [14]. According to the figure, the MEPS electrostatic potentials for $PhNH_2$+TCM, $PhNH_2$+$(TCM)_2$, $PhNH_2$+$(TCM)_3$ and $PhNH_2$+$(TCM)_4$ are given in the range of $-4.900e^{-2}$~$4.900e^{-2}$ eV, $-4.952e^{-2}$~$4.952e^{-2}$ eV, $-4.735e^{-2}$~$4.735e^{-2}$ eV and $-4.942e^{-2}$~$4.942e^{-2}$ eV, respectively. It can be seen from the figure that the energy value decreases as the number of TCM molecules increases, and it increases again in $PhNH_2$+$(TCM)_4$. This is because in complexes with up to three TCMs, the TCM molecules are only bonded through N-H, while in complexes with four TCMs, the TCM molecules are close to the ring on both sides. Also, according to the figure, no red and yellow areas were observed, and all were green and blue areas, which mean that all the complexes are bound to each other by weak or van der Waals interactions.



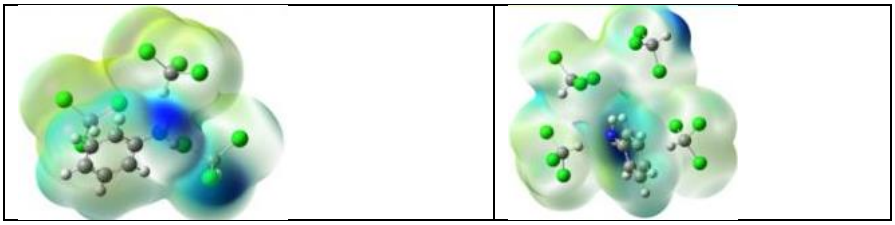


Figure 2. MEP diagram of $PhNH_2$+$(TCM)_m$ (m=1-4) complexes

Frontier molecular orbital (FMO) analysis

The electronic properties and reactivity of molecules can be explained by examining the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). The HOMO is important for electron-donating or nucleophilic reactions, and a molecule with a high energy HOMO is a good electron donor and can easily participate in oxidation or nucleophilic reactions. The LUMO represents the next orbital that electrons can occupy, which is an electron-occupied or empty molecular orbital. Molecules with a low LUMO energy are generally good electron acceptors and can participate in electrophilic reactions [15]. The energy difference between HOMO-LUMO is an important characteristic of molecular reactivity. A smaller HOMO-LUMO energy difference (ΔE) means that the molecule is easily excited and more reactive. Figure 3 shows the HOMO-LUMO visualization and the bond energy (ΔE). Table 1 lists the parameters determined by the dipole moment, ΔE, in $PhNH_2$+$(TCM)_n$ (n=1-4) complexes. According to Table 1, the dipole moment of $PhNH_2$+$(TCM)_3$ is larger than the others. As the TCM number increases, ΔE also increases, reaching the maximum value for $PhNH_2$+$(TCM)_2$ and then decreasing. The global hardness is 2.488555 eV ($PhNH_2$+TCM), 2.500935 eV ($PhNH_2$+$(TCM)_2$), 2.250735 eV ($PhNH_2$+$(TCM)_3$) and 2.397805 eV ($PhNH_2$+$(TCM)_4$), and is the largest for PhNH2+$(TCM)_2$. The ionization potential and electrophilicity are the largest for the $PhNH_2$+$(TCM)_2$ complex in the same order.

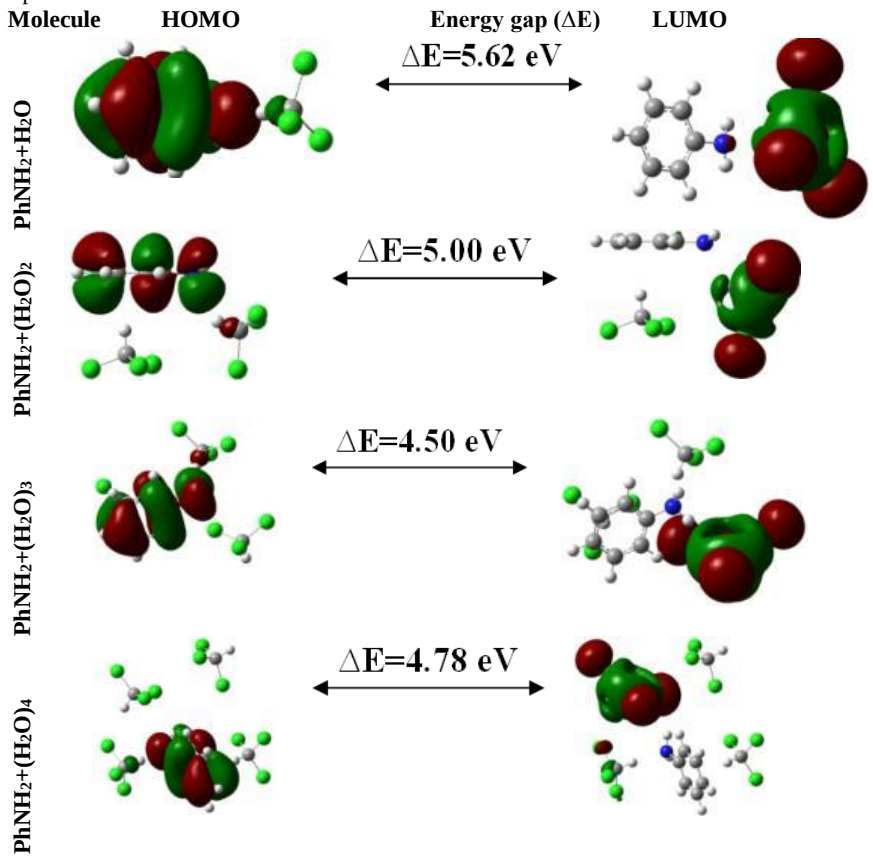


Figure.3. FMO diagrams of $PhNH_2$+(TCM)n (n=1-4) complexes

Table 1. Thermodynamical and chemical parameters of title complexes.

Parameters	$PhNH_2$+TCM	$PhNH_2$+$(TCM)_2$	$PhNH_2$+$(TCM)_3$	$PhNH_2$+$(TCM)_4$
Dipole moment (Debye)	2.805420	3.459178	3.823264	1.201417
E_{HOMO} (eV)	-6.24458	-6.40458	-6.31207	-6.45138
E_{LUMO} (eV)	-1.26747	-1.40271	-1.8106	-1.65577
$\Delta E=E_{LUMO}-E_{HOMO}$	4.97711	5.00187	4.50147	4.79561
Global hardness $\eta=\Delta E/2$	2.488555	2.500935	2.250735	2.397805
Chemical potential $\mu=(E_{LUMO}+E_{HOMO})/2$	-3.75603	-3.90365	-4.06134	-4.05358
Global electrophilic index $\omega=\mu^2/2\eta$	2.834521	3.046549	3.664235	3.426357
$IE=-E_{HOMO}$	6.24458	6.40458	6.31207	6.45138
EA= - E_{LUMO}	1.26747	1.40271	1.8106	1.65577

Atoms in molecules (AIM) analysis

AIM is used to determine non-covalent interactions in molecular systems, in particular intra- and intermolecular hydrogen bonds. The formation of critical points (CPs) in the electron density due to the bond path between two interacting atoms means that

the gradient of its electron density disappears at these points [16]. Figure 4 shows the electron density $\rho(r)$, the electron density Laplacian $\nabla^2\rho(r)$, the energy density H(r), and the Lagrangian kinetic energy density G(r) and potential energy density V(r) for $PhNH_2$+$(TCM)_n$ (n=1-4) complexes in BCPs (Table 2).

Table 2. Topological parameters of $PhNH_2$+$(TCM)_n$ (n=1-4) complexes

Complex	H-bonds	Bond length *r, Å*	Density of all electrons $\rho(r)$	Lagrangian kinetic energy *G(r)*	Potential energy density *V(r)*	Energy density *H(r)*	Laplacian of electron density $\nabla^2\rho(r)$	Hydrogen bond energy E_{HB}, kcal/mol
$PhNH_2$+TCM	2(H)…17(N)	2.2508	0.01772	0.01086	-0.00944	0.00141	0.04907	5.92
$PhNH_2$+$(TCM)_2$	2(H)…22(N)	2.3966	0.01363	0.00823	-0.00700	0.00123	0.03784	4.39
$PhNH_2$+$(TCM)_3$	27(N)…7(H)	2.3612	0.01435	0.00860	-0.00733	0.00126	0.03945	4.60
$PhNH_2$+$(TCM)_4$	7(H)…32(N)	2.2441	0.01794	0.01096	-0.00956	0.00140	0.04947	6.00

According to Table 2, the electron density Laplacian ($\nabla^2\rho(r)$) for the $PhNH_2$+$(TCM)_n$ (n=1-4) complexes takes positive values in the range of 0.03784-0.04907 au. Similarly, the energy densities (H(r)) indicate the presence of weak H-bonds at all points.

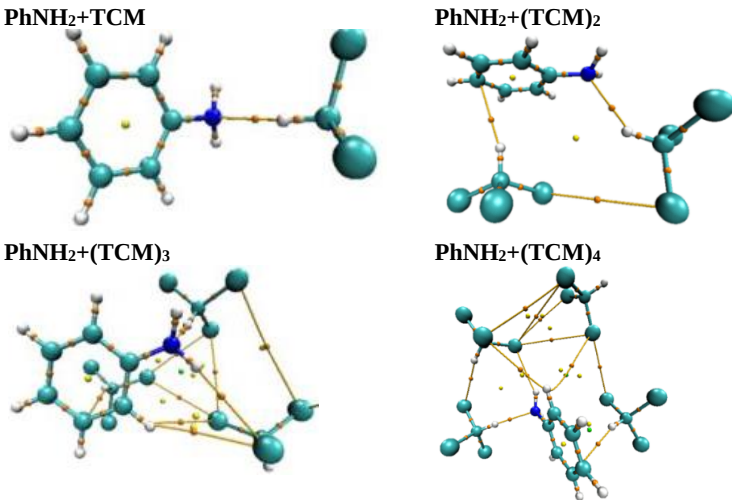


Figure 4. The molecular diagrams of $PhNH_2$+$(TCM)_n$ (n=1-4) complexes

The formula EHB=-V(r)/2 was used to calculate the hydrogen bond energy. At critical points H_{BCPs}<0, the hydrogen bond has a covalent nature, while H_{BCPs}>0 has an electrostatic nature. According to the table, all bonds are weak hydrogen bonds and are characteristic of the electrostatic effect. If we look at the bond lengths, all of them have a length of 2.1 Å and more, which confirms the presence of weak mutual H-bonding in all complexes, and such bonds can also be called Van der Waals interactions.

Reduced density gradient (RDG) and non-covalent interaction (NCI) analyses

RDG and NCI analyses are used to characterize weak intermolecular interactions. The NCI index is used to characterize intermolecular interactions and assess the nature of weak interactions. RDG is a fundamental dimensionless quantity consisting of the density and its first derivative, and is expressed by formula (1):

$$RDG(r) = \frac{1}{2(3\pi^2)^{1/3}} \frac{|\nabla\rho(r)|}{\rho(r)^{4/3}} \quad (1)$$

Determining the electron density $sign(\lambda_2)\rho$ relative to the RDG provides information about the nature of intermolecular interactions and the magnitude of these interactions. In molecular systems, blue indicates mutual attraction, while red indicates repulsion. $sign(\lambda_2)\rho$<0 indicates repulsion between bonded atoms, while $sign(\lambda_2)\rho$ >0 indicates repulsion between non-bonded atoms.

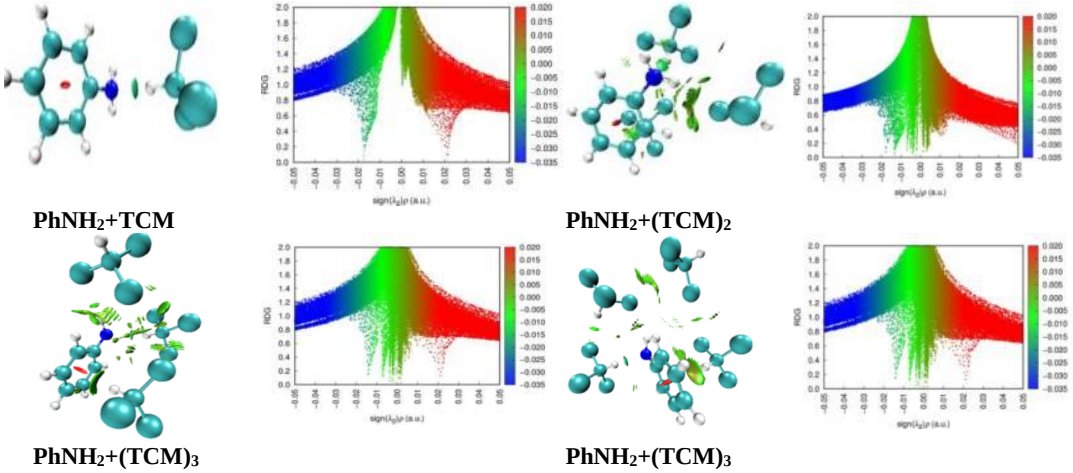


Figure 5. NCI and RDG analyses for $PhNH_2$+$(TCM)_n$ (n=1-4) complexes

The RDG scattering plot of the complexes is shown on the right side of Figure 5. According to the figure, red color represents strong repulsive forces (steric or cyclic effect), blue color represents H-bonding, and green color represents the presence of Van der Waals interactions. According to the results, the red marks between the $PhNH_2$ rings indicate the presence of cyclic effect (Figure 5 a). It can also be seen from the RDG scattering plot on the right side of Figure 5 a) that the scattering mainly occurs in the range of $sign(\lambda_2)\rho$, and the value of -0.01-0.00 represents Van der Waals interactions. According to the left part of Figure 5, all complexes have Van der Waals interactions of the Cl-H$\cdots$N type between the NH_2 group of $PhNH_2$ and the atoms in the Cl-H group of TCM, which corresponds to the range of $sign(\lambda_2)\rho$ in the RDG scattering plot of -0.02-0.01. Accordingly, a blue shift of $PhNH_2$ was observed. In general, Van der Waals interactions play a dominant role in these complexes.

Conclusion. In this work, vibrational bands were studied using vibrational spectroscopy (Raman) to study the interactions of aniline and its compounds with chloroform. In this case, a partial red shift and a mainly blue shift were observed in the vibrational bands in aniline solutions. It was predicted that the cause of such shifts was the formation of mainly Van der Waals bonds between aniline and the solvent. This was confirmed when MEPS, FMO, AIM, NCI and RDG analyses were performed to determine the non-covalent interactions.

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