



Interaction between Picric Acid and 5-aminoquinoline: A Theoretical Study

Nupur Pandey¹, Mohan Singh Mehata*²  and Sanjay Pant¹

¹Photophysics Laboratory, Department of Physics, Centre of Advanced Study, DSB Campus, Kumaun University, Nainital 263002, India

²Laser Spectroscopy Laboratory, Department of Applied Physics, Delhi Technological University, Delhi 110042, India

*Corresponding author: msmehata@gmail.com

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Abstract. In the present work, density functional theory and time-dependent density functional theory were employed to investigate the hydrogen-bonded charge transfer complex of 5-aminoquinoline (5AQ) and picric acid (PA) at B3LYP/6-31G(d,p) level in the gas phase as well as CHCl_3 . The geometrical parameters, optimization energies, interaction energies, frontier molecular orbitals (FMOs), and ground-state dipole moment were considered, which supported the stability of the complex. Hence, the theoretical study of the 5AQ-PA complex provides valuable information about its molecular structure, possible interaction sites and electronically excited states.

Keywords. 5AQ; DFT/TD-DFT; Hydrogen bonding; Charge transfer complex

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1. Introduction

The association of the donor and the acceptor moiety via weak hydrogen bonding ($\text{N}-\text{H}^+\cdots\text{O}$) results in the formation of charge transfer (CT) complex, which was first proposed and discussed by Mulliken and Person [7].

CT complexes have been widely explored owing to their widespread applications in different fields, such as sensors, organic semiconductors, organic solar cells, medicinal chemistry, drug-receptor, antibacterial/antimicrobial studies, DNA binding, and second-order nonlinear optical activity [5, 6, 10].

A new absorption band is observed in the absorption spectrum of the complex, which neither assigns to the donor nor the acceptor. This new absorption peak assures the charge transfer from the *highest occupied molecular orbital* (HOMO) of the donor to the *lowest unoccupied molecular orbital* (LUMO) of the acceptor species. The complexation among the donor and the acceptor species gets affected by the functional group carrying sulfur, oxygen, or nitrogen atoms [1, 6].

Over the last few years, various organic donor-acceptor-based CT complexes have been explored using spectroscopic and theoretical techniques, including *density functional theory* (DFT) and *time-dependent density functional theory* (TD-DFT) and provided valuable information about the molecular structures, interaction sites and excited states [1, 4].

Numerous photophysical and photochemical studies on aminoquinolines have been carried out in the past few years as these molecules exhibit a wide spectrum of biological and chemical activities [9]. Aminoquinoline derivatives have a significant role in supramolecular chemistry, electron transfer/charge transfer processes, and sensing applications [8].

In the present study, the H-bonded charge-transfer complex of 5-aminoquinoline (5AQ) and (PA) in the gas phase and chloroform (CHCl_3) has been explored using DFT and TD-DFT.

2. Computational Method

The 5-aminoquinoline (5AQ), picric acid (PA), and their possible complex were optimized using the density functional theory (DFT) by employing the B3LYP level using 6-31G(d,p) basis set with the Gaussian-9 program's package [3]. Gauss-view 5.0 was used to draw the molecular structures. The geometrical parameters, optimization energies, zero-point energy corrections, interaction energies, and thermodynamic parameters were calculated from the optimized molecular structures and used to predict the stability of the complex. The polarizable continuum model (IEF-PCM) has been considered in the case of solvent.

3. Results and Discussion

Figure 1 displays the optimized molecular structures of the donor (5AQ), acceptor (PA), and the formed complex (5AQ-PA) in the gas phase. The most stable configuration of the formed complex favors the alignment of OH of PA towards the 5AQ's ring nitrogen atom. It can be seen that the complexation occurs mainly due to the proton transfer hydrogen bonding (H-bonding). The formation of H-bond has led to major changes in bond lengths, particularly for those near the H-bonding interactions sites in the complex.

In proton transfer, H-bonded complex O14-H15-N34, the increase in the length of OH bond from 1.672 Å to 1.819 Å and 1.801 Å was observed on switching from the gas phase to CHCl_3 , while the length of N-H bond decreased from 1.054 Å to 1.038 Å and 1.036 Å. Table 1 displays the H-bonded parameters of the 5AQ-PA complex. The variations can also be observed in the bond lengths of the 5AQ part of the complex nearby the H-bond center. Considering the PA moiety of the complex, the bond length C(1)-C(6) increased from 1.420 to 1.458, C(1)-C(2) from 1.426 Å to 1.458 Å while C(1)-O(14) reduced from 1.315 Å to 1.25 Å compared with free PA in the gas phase. It is worth mentioning that similar results have been obtained in CHCl_3 .

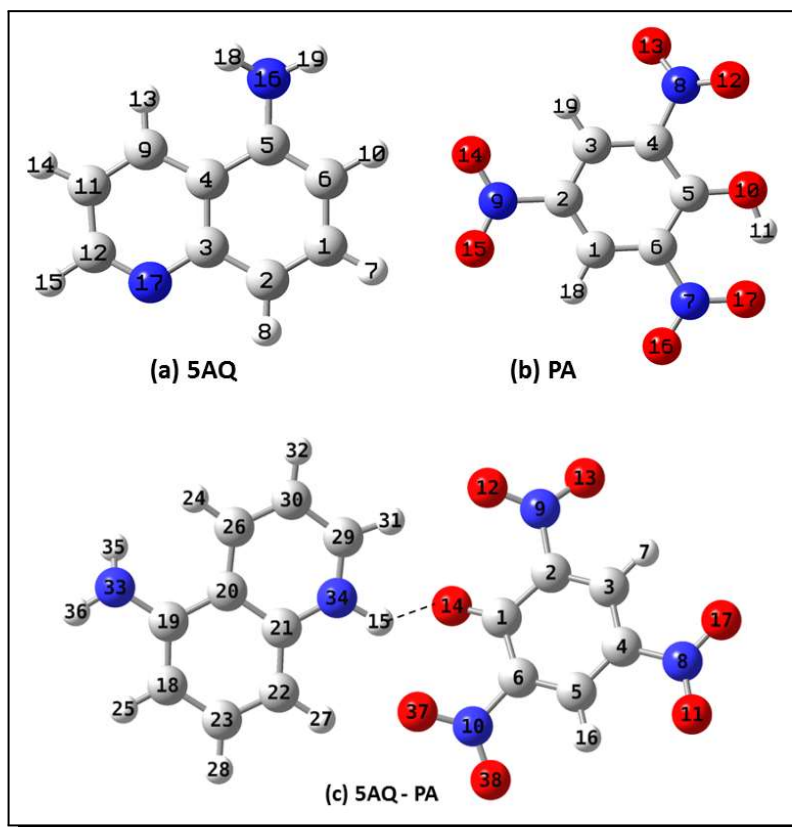


Figure 1. Optimized molecular structures of (a) 5AQ, (b) PA and (c) 5AQ–PA in the gas-phase with atomic numbering and H- bonds

Notable changes were seen in the optimized bond angles of 5AQ moiety near the H-bonding interaction region. Thus changes observed in the optimized bond lengths and bond angles endorse the presence of H-bonding as well as CT in the formed complex.

Table 1. Hydrogen bonding parameters of 5AQ–PA complex in the gas phase and CHCl_3

Medium	Distance (Å)			Angle (°)
	O14–H15	N34–H15	O14–N34	O14–H15–N34
Gas	1.668	1.054	2.561	139.210
CHCl_3	1.794	1.039	2.655	137.500

The interaction energy (ΔE) is an important parameter that defines the stability of the complex and can be calculated using eq. (1):

$$\Delta E = E_{\text{complex}} - (E_{\text{donor}} + E_{\text{acceptor}}). \quad (1)$$

The optimization energy (E_{total}), zero-point vibrational energy (E_0), corrected optimization energy ($E_{\text{corr.}}$), interaction energy (ΔE), and ground-state dipole moment of the complex are surmised in Table 2.

Table 2. Values of total optimization energy (E_{total}), interaction energy (ΔE), zero-point vibrational energy (E_0), corrected optimization energy (E_{corr}), and ground-state dipole moment (μ_g) of the complex using the B3LYP/631-G(d,p) method

Parameter	Gas	CHCl ₃
E_{total} (kcal mol ⁻¹)	-864885.551	-864898.375
E_0 (kcal mol ⁻¹)	167.231	167.169
E_{corr} (kcal mol ⁻¹)	-864703.925	-864716.897
ΔE (kcal mol ⁻¹)	-12.262	-29.807
μ_g (Debye)	18.092	22.113

The interaction energy for 5AQ-PA recorded -12.262 , and -29.807 kcal mol⁻¹ in the gas phase and CHCl₃, respectively, confirming a stable complex formation.

The theoretically obtained dipole moment for 5AQ ranged between 3.4 D – 4.5 D in the gas phase and the chosen solvent, whereas it ranged from 1.5 D – 2.5 D for PA. Therefore, there is a huge difference between the dipole moment of the complex (5AQ-PA) compared with free 5AQ and PA, confirming electron density migration from 5AQ towards PA. The computed dipole moment of the complex showed higher values for CHCl₃ (22.11 D) than the gas phase (18.09 D).

The frontier molecular orbital diagram is a powerful tool in explaining the chemical reactivity and kinetic stability of the molecule [2]. Figure 2 represents the occupied orbital (HOMO) and virtual orbital (LUMO) of complex in the gas phase.

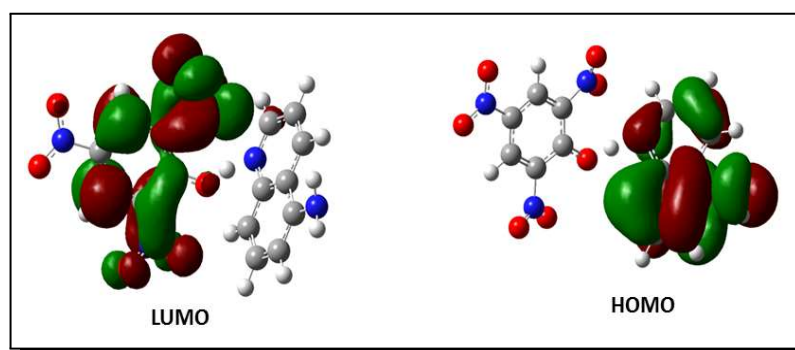


Figure 2. HOMO and LUMO of the complex in CHCl₃

The HOMO is mainly distributed over the 5AQ moiety, whereas LUMO is distributed over the PA moiety of the formed complex. The energy gap between the HOMO energy of the donor and the LUMO energy of the acceptor is comparatively small. In the present system, this energy gap is 2.13 eV, 1.86 eV in the gas phase and CHCl₃, which supports the possibility of CT from 5AQ towards PA.

The theoretically computed absorption spectrum of 5AQ, PA, and their complex in CHCl₃ is shown in Figure 3. In CHCl₃, the first three absorption bands along with the oscillator strength (f) were estimated at 431 nm ($f = 0.0770$), 398 nm ($f = 0.1498$), and 394 nm ($f = 0.003$), which corresponds to $S_0 \rightarrow S_1$, $S_0 \rightarrow S_2$, and $S_0 \rightarrow S_3$ transitions, respectively. The new band was detected in the visible region where neither the donor nor the acceptor absorbed. This new band originates possibly from the overlapping of LUMO of the acceptor with HOMO of the donor.

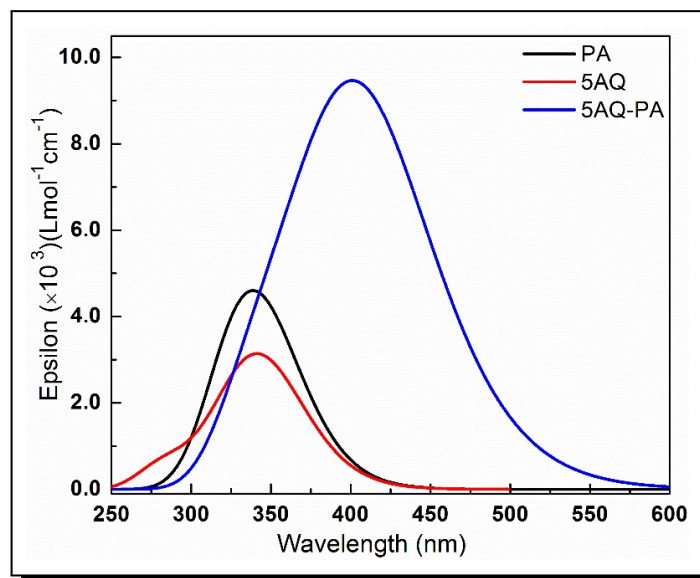


Figure 3. Estimated absorption spectra of 5AQ, PA, and their complex in CHCl_3 using IEFPCM/TD-DFT/B3LYP/631-G(d,p) method

4. Conclusion

The H-bonded CT complex of 5AQ (donor) with PA (π -acceptor) was studied based on the density functional theory (DFT) and time-dependent density functional theory (TD-DFT) at B3LYP level using 6-31G(d,p) basis set. The interaction energy of the studied complex was calculated in the gas phase and CHCl_3 , supporting the formation of a stable complex. A new absorption band was noticed in the absorption spectrum where neither the donor nor the acceptor absorbed. Thus the theoretical study of the considered complex provides valuable information about its molecular structure, possible interaction sites and electronically excited states.

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Competing Interests

The authors declare that they have no competing interests.

Authors' Contributions

All the authors contributed significantly in writing this article. The authors read and approved the final manuscript.

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