

Interaction site and proton transfer equilibrium in the 4-aminoantipyrene-pentachlorophenol hydrogen-bonded adduct

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The hydrogen-bonding interaction site between 4-aminoantipyrene (4AAP) and pentachlorophenol (PCP) was investigated in the crystalline form using FT-IR and in solution using FT-IR, UV-Vis and ^1H , ^{13}C NMR spectroscopies.

Keywords: 4-aminoantipyrene, pentachlorophenol, hydrogen bonding

Because of its importance for humans and the environment,¹⁻³ PCP is an interesting compound in which to study hydrogen bonding. Relatively little information has been reported about the hydrogen bonding interaction between PCP and polybasic amines. Consequently the aim of the current work is to study the H-bonding of PCP through its complexation with 4AAP containing two basic groups $-\text{C}=\text{O}$ and NH_2 . 4AAP has numerous biological, chemical and pharmacological applications and it has been used in complexing metals.¹⁴⁻¹⁹ Here we investigate the preparation of the H-bonded complex between PCP and 4AAP in the crystalline form and the location of the hydrogen bonding interaction site in the solid state. Another aim is to study such interactions in solution and to determine the hydrogen bonding, proton transfer equilibrium constant K_{PT} between PCP and 4AAP in some basic solvents. The solid complex between PCP and 4AAP was prepared by precipitation from an equimolar solution of the components in acetonitrile. The composition of the complex was confirmed by elemental analysis of the 1:1 complex. The FT-IR spectra of the solid complex were recorded on a Perkin-Elmer Paragon 1000 spectrophotometer with a resolution power 4 cm^{-1} in KBr pellets. The ^1H and ^{13}C NMR spectra were measured on 0.2M solution of the d-DMSO and CH_3OD at room temperature using a Bruker 300MHz spectrometer. The UV-Vis spectra were measured on a Shimadzu 160A spectrophotometer employing 1 cm matched silica cells in the wavelength range 200–800 nm. The centre of gravity of the protonic vibration was estimated using the equation²¹

$$v_{\text{cg}} = \frac{\sum Av}{\sum A} \text{ cm}^{-1}$$

where A is the absorbance and v is the frequency. The proton transfer equilibrium constant K_{PT} of the 4AAP-PCP complex was estimated applying the minimum-maximum absorbances method.²⁰⁻²³

The FT-IR spectrum of the complex showed two sharp regions, the low frequency absorption region is intense with numerous Evan holes producing a continuum^{24,25} and extends from 1700 to 500 cm^{-1} with v_{cg} equal to 1231 cm^{-1} ; it represents the vibration ($\text{O}-\text{H}\dots\text{O}$). The higher frequency region contains two broad bands at 2981 and 2567 cm^{-1} representing asymmetric and symmetric stretching vibrations of NH_2 group involved in intermolecular hydrogen bonding with the phenolate oxygen. For the deuterated complex, $\nu(\text{O}-\text{D}\dots\text{O})$ covered the range $500-1600\text{ cm}^{-1}$ and is characterized by weak intensities. The v_{cg} of this continuum lies at 1166 cm^{-1} and the isotopic ratio $\nu(\text{OH})/\nu(\text{OD})$ is about 1.05 suggesting a strong OHO hydrogen bonding bridge. The FT-IR spectra in the carbonyl range is presented for 4AAP and its complex with PCP where the amide carbonyl group at 1679 cm^{-1} is completely absent in the complex asserting that the interaction site is the carbonyl group. The electronic spectra of a 10^{-4} M solution of a 1:1 4AAP-PCP complex in acetonitrile and methanol showed an absorption band at 395 nm due to the $\Pi-\Pi^*$ transition. This band is used to study the 1:1 proton transfer equilibrium between PCP and 4AAP in methanol and acetonitrile.

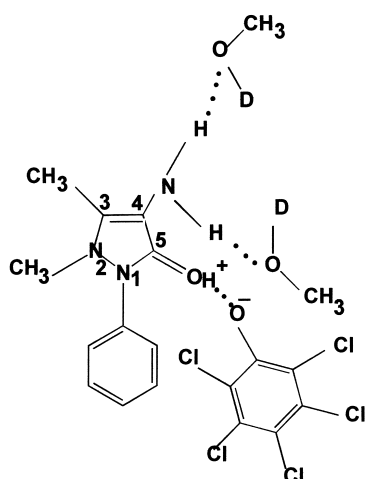
Table 1 Calculations of $K_{(\text{PT})}$ by using minimum-maximum absorbances method

CH_3OH							
A_{mix}	A_{min}	$A_{\text{mix}}-A_{\text{min}}$	A_{max}	$A_{\text{max}}-A_{\text{mix}}$	Conc (M)	$(A_{\text{mix}}-A_{\text{min}})/\text{conc}$	K_{PT}
0.146	0.058	0.088	1.163	1.017	0.0039	22.56	22.18
0.236	0.058	0.178	1.163	0.927	0.0078	22.82	24.61
0.362	0.058	0.304	1.163	0.801	0.0117	25.98	32.43
0.469	0.058	0.411	1.163	0.694	0.0156	26.34	37.95
0.543	0.058	0.485	1.163	0.62	0.0195	24.87	40.11
0.631	0.058	0.573	1.163	0.532	0.0234	24.48	40.02
0.739	0.058	0.681	1.163	0.424	0.0273	24.94	58.83
0.812	0.058	0.754	1.163	0.351	0.0312	24.16	68.83
$K_{(\text{PT})}$ average =40.6							
CH_3CN							
0.156	0.071	0.085	0.82	0.664	0.0078	10.89	16.4
0.204	0.071	0.133	0.82	0.616	0.01	13.3	21.59
0.266	0.071	0.195	0.82	0.554	0.0124	15.72	28.37
0.368	0.071	0.297	0.82	0.452	0.0156	19.03	42.12
0.434	0.071	0.363	0.82	0.386	0.0179	20.27	52.51
0.456	0.071	0.385	0.82	0.364	0.02	19.25	52.88
0.608	0.071	0.537	0.82	0.212	0.0234	22.94	108.208
0.7	0.071	0.629	0.82	0.12	0.0312	20.16	168
$K_{(\text{PT})}$ average=61.26							

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The proton transfer equilibrium data are gathered in Table 1. Clearly the value of the 1:1 proton transfer equilibrium constant K_{PT} is low compared to other systems that are reported in the literature^{26,27} which could be interpreted in terms of higher steric hindrance of the formed complex together with the lower value of the acidity constant of PCP (≈ 5.5)

The ¹H NMR spectra of 0.2M 4AAP and 4AAP-PCP complex were obtained in CH₃OD. For 4AAP, the two protons of the amino group appeared at 4.8 ppm. In the spectrum of the complex a signal at 4.89 ppm is attributed to eight protons, two protons from the amino group and six protons from two molecules of CH₃OD hydrogen-bonded with the two amino group protons (short-range solvation effect). These results confirmed that the interaction site is the carbonyl group in CH₃OD and the proposed structure is shown as structure (I).



Structure 1 Proton transfer complex between 4AAP and PCP in deuterated methanol

The situation is completely different in d-DMSO, a signal was observed at 6.12 ppm which integrated as three protons and presumably arises from NH₃⁺, confirming that the interaction site is the amino group in d-DMSO solution. In the ¹³C NMR spectra of the 4AAP and the 4AAP-PCP complex in CH₃OD,

one observes the carbonyl carbon signal at 165 ppm for 4AAP which shifts to 116 ppm upon complexation with PCP. These results strongly confirmed that the hydrogen bonding directs towards the carbonyl group, consistent with the ¹H NMR data. It seems that the formation of the proton transfer complex, structure I, accelerates the inductive process from the two methyl groups and the neighboring nitrogen atoms, producing shielding of C₅. Hence its chemical shift moves to a lower value 116.5 ppm. The situation is different in DMSO where the chemical shift of the carbonyl carbon signal is not affected in both 4AAP and the complex, confirming that the hydrogen bonding directs towards the amino group. This result is strongly consistent with the ¹H NMR data in d-DMSO.

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