Scientific paper

The Infrared Spectra of 2-Pyridone···Ammonia and 2-Hydroxypyridine···Ammonia Hydrogen-Bonded Complexes Interpreted by DFT Calculations and AIM Charge Densities

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Abstract

The optimized geometries and infrared spectra of the 2-pyridone···ammonia and 2-hydroxypyridine···ammonia hydrogen-bonded complexes were examined using the B3LYP/6-311++G(d,p) level of theory. By taking into account the tautomerism in the 2-pyridone and 2-hydroxypyridine molecules, the ammonia functions as donor and acceptor of proton in each hydrogen-bonded complex. Thereby, some classic aspects of hydrogen bonds can be observed, such as the red-shift (bathochromic) effects in the N–H(ammonia), N–H(2-pyridone), and O–H(2-hydroxypyridine) bonds. In this insight, a theoretical investigation of these frequencies was performed not only by the B3LYP/6-311++G(d,p) calculations, but also by means of charge density integrations ruled by protocol of the theory of atoms in molecules (AIM), by which some molecular operators were computed, such as the electronic density centers (ρ) and Laplacian fields ($\nabla^2\rho$).

Keywords: Tautomerism; 2-hydroxypyridine; 2-pyridone; B3LYP; AIM.

1. Introduction

Tautomerism is one of the most important phenomena in organic chemistry.[1] By considering the equilibrium between 2-pyridone (P) and 2-hydroxypyridine (HP), it is clear that this tautomerism is ruled by a proton transfer between nitrogen and oxygen.[2–6] According to theoretical simulations reported by Maes *et al.*[7] it was shown that the interactions of P and HP with ammonia (A) can be a representation of tautomerism phenomenon. In related works, calculations of density functional theory (DFT)[8] and Møller–Plesset perturbation of second order (MP2)[9] have given good results for equilibrium geometry and rotational constants of the P···(NH_3) and HP···(NH_3) complexes.[10–11] As prediction, Maes *et al.*[7] developed a detailed description of the infrared harmonic spectrum of the P···(NH_3) and HP···(NH_3) complexes. Because the ammonia has a function of acceptor and donor of proton, this molecule is responsible by the vibrational red-shifts (bathochromic effect) on the N–H (2-pyridone) and O–H (2-hydroxypyridine) bonds after the formation of the hydrogen-bonded complex. In Figure 1, by analyzing the formation of the N(A···H) hydrogen bonds in both P···(NH_3) and HP···(NH_3) complexes, their red-shift effects are caused through the charge transfer from nitrogen *n* lone electron pair of the ammonia to the hydrogen atoms of the N–H and O–H bonds.

However, other hydrogen bonds also are formed, such as the interaction of the carbonyl group (P) and the

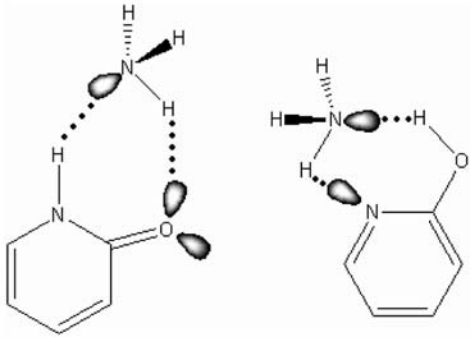

Figure 1. Illustration of the P···(NH_3) and HP···(NH_3) hydrogen-bonded complexes.

hydrogen atom of the ammonia, (O···H)P in the P···(NH_3) complex, as well as the contact of the nitrogen (HP) with the hydrogen atom of the ammonia, (N···H)HP in the HP···(NH_3) complex. Consequently, a charge transfer from the *n* lone electron pairs of both oxygen and nitrogen to the hydrogen of the ammonia must be also considered. Thereby, it is expected that the red-shift effect also can be observed in the N–H bonds of the ammonia. Thus, the objective of this work is dedicated to a theoretical study of the chemical nature of the red-shifts on the N–H(P), O–H(HP), and N–H(A) bonds in both P···(NH_3) and HP···(NH_3) complexes.

Theoretically, the red-shift phenomenon in hydrogen-bonded complexes is widely reported in literature,[12–14] although besides the DFT and/or MP2 calculations routinely applied, some other methodologies have been employed successfully to study vibrational modes of hydrogen-bonded complexes, such as for example the generalized atomic polar tensor (GAPT)[15] and topological calculations embodied in the theory of atoms in molecules (AIM).[16] In this context, we admit that AIM calculations are an efficient tool to quantify the charge density on P···(NH_3) and HP···(NH_3) complexes and thereby, a suitable explanation about their red-shifts can be discussed. From AIM theory, the topology of the charge density of the P···(NH_3) and HP···(NH_3) complexes can be evaluated through the calculations of the electronic density (ρ) and Laplacian ($\nabla^2\rho$).[17] These parameters are computed through the location of bond critical points (BCP), which are located within each chemical bond of the hydrogen-bonded complex.[18–20] Indeed, a recent theoretical study developed by Jia *et al.*[21] has shown the importance of the AIM calculations and its topological parameters to characterize hydrogen-bonded complexes, in particular the P(NH_3) and HP(NH_3) systems.

2. Computational Methods

The optimized geometries of the P···(NH_3) and HP···(NH_3) complexes were obtained by applying the B3LYP/6-311++G(d,p) theoretical level, where all calculations were executed using the GAUSSIAN 98W software.[22] The AIM calculations were performed through the GAUSSIAN 98W and AIM 2000 1.0 program.[23]

3. Results and Discussion

3. 1. Geometry of the P···(NH_3) and HP···(NH_3) Complexes

From B3LYP/6-311++G(d,p) calculations, the optimized geometries of the P···(NH_3) and HP···(NH_3) complexes, as well as of the P, HP and NH_3 isolated species were obtained. By analyzing these, it was concluded that they correspond to a deep minimum of the energy surface because neither imaginary frequency has been observed for each one of these systems. In Table 1, however, are listed the values of the selected structural parameters of these complexes.

Table 1. Main structural parameters of the P···(NH_3) and HP···(NH_3) hydrogen–bonded complexes using the B3LYP/6–311 ++G(d,p) calculations.

Parameters	**Hydrogen–bonded complexes**	
	P···(NH_3)	**HP···(NH_3)**
δR(N–H)P	0.020	–
δR(O–H)HP	–	0.030
δR(NA–H)	0.008	0.005
R(NA···H)	1.954	1.783
R(O···H)P	2.213	–
R(N···H)HP	–	2.400

[*] All values are given in ångstroms, Å;
[*] δ indicates structural deviations on complexes in comparison with the isolated species.

Although the ammonia behaves as donor and acceptor of proton, the R(NA···H) hydrogen bond distances indicate a tendency of the ammonia to exert a function of hydrogen acceptor. Although the values of 1.954 Å and 1.783 Å are related to the R(NA···H) shortest distances, some important deformations in the molecular structure of the P···(NH_3) and HP···(NH_3) complexes were verified, such as the changes on (N–H)P and (O–H)HP bonds. Indeed, in comparison with the δR(NA–H) increments of 0.008 Å and 0.005 Å, the δR(N–H)P and δR(O–H)HP values of 0.020 Å and 0.030 Å are the most relevant changes on the P(NH_3) and HP(NH_3) complexes.

3. 2. Infrared Stretch Modes of the P···(NH_3) and HP···(NH_3) Complexes

After analysis of the vibrational harmonic spectrum of the P···(NH_3) and HP···(NH_3) complexes at the B3LYP/6-311++G(d,p) level of theory, the results of their main stretch frequencies (ν) and absorption intensities (I) are listed in Table 2. Corroborating with the structural parameters significant red-shifts on the (N–H)P and (O–H)HP bonds were observed, whose displacements are $-360.7\ cm^{-1}$ and $-602.2\ cm^{-1}$, respectively. On the other hand, moderate red-shifts on NA–H bonds of ammonia have been computed, whose downward values are $-64.5\ cm^{-1}$ and $-36\ cm^{-1}$.

In terms of intermolecular stretching frequencies, it can be observed that the values of $175.2\ cm^{-1}$ and $203.7\ cm^{-1}$ indicate that the (NA···H) hydrogen bonds are the strongest, whereas (O···H)P and (N···H)HP are the weaker ones because their stretching modes are $110.7\ cm^{-1}$ and $102\ cm^{-1}$, respectively. Indeed, we can perceive that strong and weak intermolecular stretching frequencies are correlated with large and small red-shifts. However, another adequate evaluation of the hydrogen bond strength

Table 2. Main vibrational harmonic modes of the P···(NH_3) and HP···(NH_3) hydrogen bonded–complexes using the B3LYP/6–311 ++G(d,p) calculations.

Parameters	**Hydrogen–bonded complexes**	
	P···(NH_3)	**HP···(NH_3)**
$\delta\nu$(N–H)P	–360.7	–
I(N–H)P,c/ I(N–H)P,i	14.0	–
δk(N–H)P	–1.51	–
$\delta\nu$(O–H)HP	–	–602.2
I(O–H)HP,c/ I(O–H)HP,i	–	9.9
δk(O–H)P	–	–2.53
$\delta\nu$(NA–H)	–64.5	–36
I(NA–H),c/ I(NA–H),i	49	39.9
δk(NA–H)	–0.18	–0.11
ν(NA···H)	175.2	203.7
I(NA···H)	3.9	17.6
k(NA···H)	0.080	0.114
ν(O···H)P	110.7	–
I(O···H)P	27.1	–
k(O···H)P	0.030	–
ν(N···H)HP	–	102
I(N···H)HP	–	19.3
k(N···H)HP	–	0.020

* Values of and I are given in cm^{-1} and km mol^{-1} respectively;

* Values of the force constant (k) and its variations (δk) are given in mDyne $Å^{-1}$;

* The intensity rations (I(O–H)HP,c/I(O–H)HP,i and I(NA–H),c/I(NA–H),i) were calculated by taking into account the absorbance of the P···(NH_3) and HP···(NH_3) complexes (c) in comparison with the isolated (i) species

* δ indicates vibrational variations on complexes in comparison with the isolated species.

must be related to its harmonic force constants (k), wherein for the P···(NH_3) and HP···(NH_3) complexes; the Table 2 also list the values of the variation of the force constants (δk) of the (N–H)P, (O–H)HP, and (NA–H) bonds. By examining the graph illustrated in Figure 2 and the linear coefficient of 0.99, a direct relationship between the red-shifts ($\delta\nu$) and the correspondent variation on their force constants (δk) was obtained. Certainly, this is an indication that larger and smaller red-shifts are well correlated with stronger and weaker bonds of proton donors.

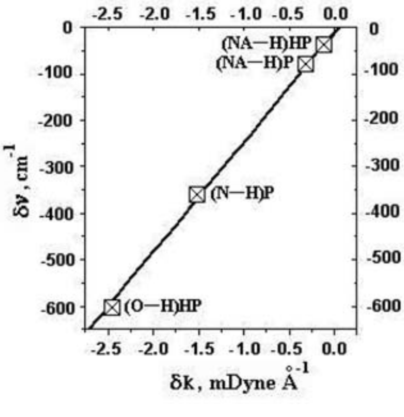

Figure 2. Relationship between the $\delta\nu$ red-shifts and δk force constants of the (N–H), (O–H)HP, and (NA–H) bonds of the P···(NH_3) and HP···(NH_3) hydrogen-bonded complexes using the B3LYP/6-311++G(d,p) calculations. $\delta\nu = 235.3\ \delta k - 11.6$, $r^2 = 0.99$.

3. 3. Contribution of AIM Densities for an Interpretation of the Stretching Modes of the P···(NH_3) and HP···(NH_3) Complexes

By the molecular charge density, however, we expect that topological calculations derived from AIM theory can explain the strength of the (N–H)P, (O–H)HP, and (NA–H) bonds. According to the AIM protocol elaborated by Bader,[16–17] high and low centers of electronic density can be interpreted through the corresponding negative and positive Laplacian fields, which are described by the kinetic (K) and potential (U) operators, respectively. In practice, concentration and depletion of charge density seems to be useful to interpret the red-shift effects presented in this work. Thus, the Table 3 presents the result of the AIM calculations, where values of electronic density (ρ) and Laplacian ($\nabla^2\rho$) were collected for the for the P(NH_3) and HP(NH_3) complexes.

Table 3. AIM topological parameters for the P···(NH_3) and HP···(NH_3) hydrogen–bonded complexes.

Parameters	**Hydrogen–bonded complexes**	
	P···(NH_3)	**HP···(NH_3)**
$\delta\rho$(N–H)P	–0.020	–
$\delta\nabla^2$(N–H)P	–1.671	–
$\delta\rho$(O–H)P	–	–0.037
$\delta\nabla^2$(O–H)P	–	–2.220
$\delta\rho$(NA–H)	–0.006	–0.004
$\delta\nabla^2$(NA–H)	–1.550	–1.557
ρ(NA···H)	0.030	0.043
$\nabla^2\rho$ (NA···H)	0.085	0.098
ρ(O···H)P	0.016	–
$\nabla^2\rho$ (O···H)P	0.052	–
ρ(N···H)HP	–	0.013
$\nabla^2\rho$ (N···H)HP	–	0.042

* Values of ρ and $\nabla^2\rho$ are given in electronic units (e.u.);

* Values of $\nabla^2\rho$ for the N–H and O–H bonds are –1.683 e.u. and –2.52 e.u., respectively;

* δ indicates charge density variations on complexes in comparison with the isolated species.

Regarding the P···(NH_3) and HP···(NH_3) complexes, their (NA···H), (O···H), and (N···H) hydrogen bonds have positive values of $\nabla^2\rho$ and low amounts of ρ. Only for comparison, the electronic density values of the hydrogen bonds on the P···(NH_3) and HP···(NH_3) complexes are in the range of 0.013–0.043 e.u., whereas the electronic density in van der Waals interaction varies in 10^{-3} e.u.[24] As has been established in recent studies of intermolecular systems[25–28] that stronger hydrogen bonds provoke notable electronic changes on the P···(NH_3) and HP···(NH_3)

complexes, such changes can be interpreted by analyzing the variations of the charge density. In this context, the linear coefficient of 0.95 provides a direct relationship between the variations of the force constants (δk) and electronic densities ($\delta\rho$) in the (N–H)P, (O–H)HP, and (NA–H) bonds, as can be seen in Figure 3. From this picture, we can observe that changes in the electronic distribution considerably affect the infrared spectrum of the $P\cdots(NH_3)$ and $HP\cdots(NH_3)$ complexes. Note that greater δk values indicate a great variation of electronic density ($\delta\rho$), mainly on the (N–H)P and (O–H)HP bonds. Not surprisingly, but this corroborates with the analysis of the red-shift ($\delta\nu$) effects, as well as modifications on bond lengths. Thus, a satisfactory concordance between vibrational parameters and topological parameters were obtained in this work, indicating that the AIM calculations can corroborate or else predict successfully the infrared spectrum of hydrogen-bonded complexes.

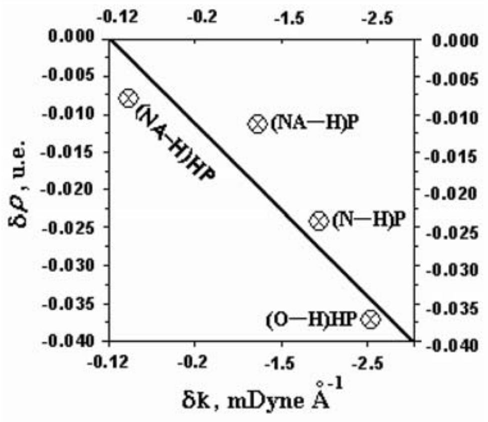

Figure 3. Relationship between the variation on the δk force constants and $\delta\rho$ electronic densities of the (N–H), (O–H)HP, and (NA–H) bonds of the $P\cdots(NH_3)$ and $HP\cdots(NH_3)$ hydrogen bonded complexes using B3LYP/6-311++G(d,p) calculations. $\delta k = -0.013\ \delta\rho + 0.015$, $r^2 = -0.95$.

4. Conclusions

The red-shift effects on 2-pyridone···ammonia and 2-hydroxypyridine···ammonia complexes were studied through the B3LYP/6-311++G(d,p) calculations as well as by analysis of charge density obtained from theory of atoms in molecules. It was verified that the red-shifts on (N–H)P, (O–H)HP, and (NA–H) bonds are ruled by variation on their charge densities upon the formation of the hydrogen-bonded complex. The larger red-shifts are associated with great variations of electronic density, although the AIM results have shown that the bond strength of the proton donors are directly affected by their topological conditions, wherein the greatest increments of the force constants were explained by drastic variations of electronic density.

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Povzetek

Optimizirane geometrije in infrardeči spektri kompleksov 2-piridonamoniak in 2-hidroksipiridin···amoniak, povezanih z vodikovimi vezmi, smo preučevali s pomočjo teorije B3LYP/6-311++G(d,p). Z upoštevanjem tavtomerije med 2-piridonom in 2-hidroksipiridinom se izkaže, da amoniak deluje kot donor in akceptor protonov v vsakem izmed kompleksov, ki so povezani z vodikovimi vezmi. Zatorej lahko pri vezeh N–H(amoniak), N–H(2-piridon) in O–H(2-hidroksipiridin) opazimo klasične značilnosti vodikovih vezi, kot je npr. rdeči premik (batokromni učinek). Skladno s tem, smo izvedli teoretično raziskavo frekvec ne le z B3LYP/6-311++G(d,p) izračuni, marveč tudi s pomočjo integriranja gostote nabojev, ki jo ponuja teorija atomov v molekulah (AIM), s pomočjo katere lahko izračunamo nekatere molekulske operatorje, kot npr. centre elektronske gostote (ρ) in Laplaceova polja ($\nabla^2\rho$).

SUPPORTING INFORMATION

Cartesian coordinates of the optimized geometries of the P(NH_3) and HP(NH_3) hydrogen-bonded complexes, as well as of the P, HP and NH_3 isolated species. All these geometries were determined using B3LYP/6-311++G(d,p) calculations.

P(NH_3)				HP(NH_3)			
C	–2.287729	0.315649	0.000331	C	2.285053	–0.497287	0.000230
C	–0.712123	–1.476401	–0.000227	C	0.911682	1.451723	–0.000154
C	–2.017833	–1.080971	0.000148	C	2.182900	0.899098	0.000260
H	–3.318549	0.655204	0.000641	H	3.257518	–0.977539	0.000368
H	–0.408027	–2.516095	–0.000383	H	0.779795	2.530200	–0.000390
H	–2.813153	–1.812675	0.000300	H	3.060331	1.533171	0.000542
N	0.294648	–0.564872	–0.000457	N	–0.218643	0.727693	–0.000349
H	1.280598	–0.868957	–0.000539	O	–1.217906	–1.350555	–0.000036
O	1.088624	1.580825	–0.000294	C	–0.107770	–0.603710	–0.000220
C	0.111651	0.826402	–0.000249	H	–3.876816	0.609942	0.823059
H	3.792714	–0.774918	–0.817091	C	1.135256	–1.264165	–0.000099
H	2.952586	0.387386	–0.001688	H	1.159665	–2.346192	–0.000306
C	–1.276708	1.233834	0.000164	H	–2.571622	1.203132	0.000341
H	–1.467279	2.299104	0.000354	H	–2.027879	–0.768831	–0.001465
N	3.216369	–0.600153	0.000476	N	–3.295586	0.485519	–0.000002
H	3.791453	–0.771558	0.819627	H	–3.880876	0.614123	–0.819513

P				HP				NH_3			
C	1.112079	1.202251	0.000011	C	1.197344	1.152636	0.000004	N	0.000000	0.000000	0.109104
C	1.061733	–1.186489	0.000029	C	1.002436	–1.227330	0.000012	H	0.000000	0.946888	–0.254576
C	1.802864	–0.045136	–0.000006	C	1.814983	–0.102386	–0.000001	H	–0.820029	–0.473444	–0.254576
H	1.687418	2.122275	0.000064	H	1.793233	2.058446	0.000013	H	0.820029	–0.473444	–0.254576
H	1.495017	–2.178621	0.000097	H	1.431367	–2.224705	0.000017				
H	2.882320	–0.094496	0.000028	H	2.892894	–0.202056	–0.000007				
N	–0.300682	–1.124282	–0.000014	N	–0.337180	–1.168447	–0.000010				
H	–0.848851	–1.974795	0.000024	O	–2.255167	0.083539	0.000005				
O	–2.287302	0.002879	0.000095	C	–0.902117	0.031156	–0.000033				
C	–1.064754	0.061928	–0.000197	C	–0.185149	1.234476	0.000001				
C	–0.250006	1.262317	0.000002	H	–0.712410	2.179390	0.000025				
H	–0.784208	2.203354	0.000089	H	–2.568471	–0.831564	0.000083				