Hydrogen Bonding in Excited States of Pyridine & Pyrazine

Ch V RAMA RAO, CHACKO JACOB & A K CHANDRA*

Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560 012

Hydrogen bonding in the excited n-π^* and π-π^* states of pyridine and pyrazine has been examined by calculating electric field at different points in space from the CNDO charges. Results reveal that the hydrogen bond which is formed in the ground state is broken upon excitation to the n-π^* state in pyridine while a weak hydrogen bonding is possible in the n-π^* state of pyrazine.

Not much work seems to have been done on hydrogen bonding in the excited electronic states. Hydrogen bonding in the excited electronic state may be divided into two categories. In the first category the proton donor is excited to its lowest electronic state, which then forms hydrogen bond with the proton acceptor. Suzuki and Baba[1] examined the proton donating ability of anthrols and found that it was greater in the π-π^* state than that in the ground state of anthrol.

In the second category, the proton acceptor is excited to either n-π^* or π-π^* state which then forms hydrogen bond with the ground state proton donor molecule. Hydrogen bonding usually causes significant changes in the electronic transitions of a proton acceptor. The first effect observed was the blue shift of the $n \rightarrow \pi^*$ band[2], indicating that the hydrogen bond was stronger in the ground state than in the excited state. The second effect observed was the blue or red shift of the $\pi \rightarrow \pi^*$ band. Most of the reported theoretical studies on the $\pi \rightarrow \pi^*$ band have used the π-electron theory. Principal papers are those by Julg and Bonnet[3], Besnainon et al[4]. and Ponomarev et al[5]. In all these papers, the presence of a hydrogen bond is accounted for by suitably modifying the σ-core parameters. Bratoz[6], who reviewed various earlier theories, concluded that the charge-transfer model was more successful in explaining the $\pi \rightarrow \pi^*$ electron transition shifts than the simple electrostatic model. But this model is highly parameterised and the σ-electron migration is taken into account in a very approximate way. Therefore, no physical insight into this problem is achieved. The main problem is to know the detailed electron distributions in the excited state.

In this paper, we have dealt with the excited states of the proton acceptor bases, viz. pyridine and pyrazine, whose hydrogen bonding abilities have been examined by considering their detailed charge distributions. Weak hydrogen bonding is indicated in the n-π^* excited state of pyrazine by a study of the solvent effects on absorption and emission spectra[7] while pyridine does not form a hydrogen bond in its lowest singlet or triplet n-π^* state. More recently, CNDO[8] and *ab initio*[9] studies have been made on the hydrogen bonding equilibrium of the formaldehyde-water sys-

tem in the excited state of formaldehyde, but the agreement between these two approaches is lacking.

In order to gain physical insight into the mechanism of hydrogen bonding in the excited state, we have estimated the charge distributions in the excited states of the base molecules and then computed the electrostatic field around the proton acceptor atom to examine if the electric field around the base is congenial for hydrogen bonding. The theoretical index, proposed in a previous paper[10] to discuss hydrogen bonding in the ground state, has been presently examined in the excited state. For the calculation of the electric field around the base molecules, we have employed the semi-empirical theories based on Slater-type atomic orbitals, as these lead to evaluation of the molecular force integrals by the standard method.

Theory

The excited states of pyridine and pyrazine have been treated according to the original parameterization of the CNDO/2 method, where the ground state is treated in a closed shell approximation, while the excited state is treated according to the unrestricted open shell method. In this treatment, the $\alpha\alpha$ component of the lowest triplet state is considered and at this level of approximation, there is no separation between the singlet and triplet states because the relevant integrals are ignored in the CNDO theory[11]. We have therefore, not considered any distinction between the singlet and triplet excited states. The key feature of the open shell method[12] is that it optimises the molecular orbitals for the excited state electron configurations.

The hydrogen bonding interaction can be characterised by the distances r_a and r_b as shown in Fig. 1. The potential (V) of the proton is such that the force exerted on the proton in the Z-direction is given by

$$F_{H,Z} = - \frac{d_V}{dH_Z} = F_{H,Z}^{AH} - F_{H,Z}^{B} \qquad ...(1)$$

where

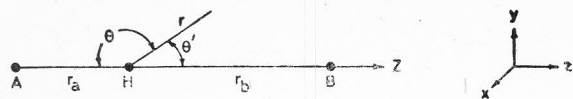$$F_{H,Z}^{B} = \frac{Z_B}{r_b^2} - \int \rho_B(r) \frac{\cos \theta'}{r^2} dr \qquad ...(2)$$

Fig. 1—Coordinate system A-H..B for hydrogen bonding interaction

and $F_{H,z}^{AH}$ is similarly defined. ρ_{AH} and ρ_B are the charge densities in the acid (AH) and the base molecule(B). Z_A and Z_B are the nuclear charges on the atoms A and B resepctively that are directly linked to the H-atom. Such a classical approach is valid in quantum mechanics too, according to the Hellmann-Feynman theorem if the wave mechanical charge distributions are employed in the calculation of the integrals in Eqs (1) and (2).

For a given acid (AH) and different bases (B), $F_{HZ,B}^{AH}$ may be assumed constant in the first approximation while $F_{H,z}$ varies. When we refer to the relative strengths of bases, the species which creates the greater attractive field at the proton for any value of r_b will be the stronger of the two bases. We have observed a correlation between the base strength and the electric field created at the proton due to the charge density centered in the base molecule[10]. The charge density ρ_B has been obtained using the CNDO/2 wave-functions. It is not necessary to consider the two inner electrons in the carbon and nitrogen atoms as they effectively screen two units of the nuclear charge. According to the CNDO wave-functions, ρ_B on any atom in the proton acceptor molecule is made up of densities contributed by $2s$, $2p_\sigma$ and $2p_\pi$-orbitals. We have shown in a previous paper[10] that the fields created by the orbital densities decrease for any atom in the order $p_\sigma > s > p_\pi$. This suggests that the magnitude of the electric field created at finite distance from the proton acceptor atom depends not only on its total density but also on the nature of the atomic orbitals that are primarily occupied.

Parameters

The CNDO method relies upon a proper selection of certain empirical parameters. For calculations on pyridine and pyrazine the CNDO/2 parameters have been used for the ground and excited states.

These molecules are planar in the ground state, hence for calculations, we have employed the observed ground state geometries of these molecules. Therefore the electronic charge distributions of the excited states corresponding to the ground state geometry refer to the vertical transitions. According to the Franck-Condon principle, the maximum of the absorption band is determined by the ground state geometry because there is no time for nuclear rearrangement during the transition. The emission band, however, extends to longer wavelength than the corresponding absorption. This gives rise to lower value of the transition energy when using the excited state geometry.

Results and Discussion

In Table 1 are presented the charge densities of the valence electrons on various atoms in the ground. n-π^* and π-π^* states of pyridine and pyrazine. The results show that in both pyridine and pyrazine, the density on the nitrogen atom increases in the π-π^* state. In the n-π^* state, the pyridine nitrogen has less electron density than in the ground state, while pyrazine has greater density than in its ground state. The density difference from the ground state is, however, very small in both the molecules in their n-π^* state. This is because in the n-π^* state, an electron is removed from the σ-frame of the molecule to the vacant π-orbitals which are delocalised over all the carbon and nitrogen atoms. So the net change in total density is small. Part of the increased π-density is seen as an increase in the nitrogen electron density. However, the net effect of this excitation ($n \rightarrow \pi^*$) is to leave the nitrogen atom in pyridine very slightly negatively charged in the excited state because of an electron deficiency in the σ-system. On this basis, pyridine should be a poor proton acceptor molecule for hydrogen bond formation.

The effect of the $n \rightarrow \pi^*$ transition in pyrazine is to remove an electron from a σ-orbital which is delocalised over both the nitrogen atoms. As a result, when both nitrogen atoms lose electron density, they still remain highly negatively charged (—0.183 a.u.) in the n-π^* excited state.

Employing, the CNDO wavefunctions, the electric field $F_{H'Z}^{B}$ has been estimated as a function of r_b from the heteroatom and in different positions around the ring using Eq. (2) and then forming the vector sum of the forces contributed by all the atoms of the ring. The calculations reveal that the electric field

Table 1—Valence Electron Densities on Various Atoms in Pyridine and Pyrazine

Atoms	Ground state	$n \rightarrow \pi^*$ excited state	$\pi \rightarrow \pi^*$ excited state
		Pyridine molecule	
N	5.1423	5.0584	5.4653
C_1	3.8995	3.9062	3.7564
C_2	4.0313	4.0088	3.8405
C_3	3.9584	4.2645	4.3032
C_4	4.0313	4.0088	3.8405
C_5	3.8995	3.9062	3.7564
H_1	1.0194	0.9779	1.0194
H_2	1.0194	0.9779	1.0194
H_3	0.9969	0.9775	0.9969
H_4	1.0050	0.9365	1.0050
H_5	0.9969	0.9775	0.9969
		Pyrazine molecule	
N_1	5.1079	5.1832	5.4456
C_1	3.9342	3.9284	3.7653
C_2	3.9342	3.9284	3.7653
N_2	5.1079	5.1832	5.4456
C_3	3.9342	3.9284	3.7653
C_4	3.9342	3.9284	3.7653
H_1	1.0118	0.9800	1.0118
H_2	1.0118	0.9800	1.0118
H_3	1.0118	0.9800	1.0118
H_4	1.0118	0.9800	1.0118

Table 2—Variation of $F_{H,Z}^B$ with r_b from Nitrogen Atom of Pyridine in the Direction of Lone Pair and One of the Nitrogen Atoms of Pyrazine also in the Direction of Lone Pair

r_b (Å)	$F_{H,Z}^B$ ground state	$F_{H,Z}^B$ (a.u) $n \to \pi^*$ state	$F_{H,Z}^B$ (a.u) $\pi \to \pi^*$ state
	Pyridine molecule		
1.0	0.13549	0.20369	0.08913
1.2	0.01407	0.06255	—0.02007
1.4	—0.01345	0.01994	—0.03875
1.6	—0.01594	0.00726	—0.03494
1.8	—0.01309	0.00347	—0.02759
2.0	—0.00995	0.00227	—0.02119
2.2	—0.00749	0.00181	—0.01633
2.4	—0.00571	0.00157	—0.01275
2.6	—0.00443	0.00141	—0.01011
2.8	—0.00349	0.00127	—0.00814
	Pyrazine molecule		
1.0	0.14074	0.16412	0.09333
1.2	0.01786	0.03356	—0.01689
1.4	—0.01067	—0.00105	—0.03632
1.6	—0.01385	—0.00815	—0.03304
1.8	—0.01149	—0.00812	—0.02607
2.0	—0.00869	—0.00668	—0.01994
2.2	—0.00648	—0.00526	—0.01529
2.4	—0.00487	—0.00412	—0.01188
2.6	—0.00373	—0.00326	—0.00935
2.8	—0.00291	—0.00261	—0.00748

is least repulsive in the plane of the ring and the minima occur in the direction of the lone pair of the nitrogen atoms of the bases.

The variations of the electric field $F_{H,Z}^B$ as a function of r_b from the nitrogen atom in the direction of its lone pair in the plane of the molecule (Fig. 1) for both pyridine and pyrazine are shown in Table 2. The calculations reveal that the electric field is positive from the pyridine N-atom in all directions in the n-π^* state, while it is attractive in the plane of the molecule in the π-π^* state. This suggests that the hydrogen bond which is formed in the ground state of pyridine is broken upon excitation to n-π^* state.

In the case of pyrazine, although the net charge densities on the N-atoms are higher than in the ground state, the magnitude of the electric field in the n-π^* state is smaller than in the ground state. Since the electric field around one of the N-atoms in pyrazine is still attractive, the possibility of weak hydrogen bonding in the n-π^* state cannot be ruled out according to this analysis. The *ab initio* treatment of pyrazine-HF by Del Bene[13] reveals that this dimer remains bound in the excited n-π^* state. Krishna and Goodman[7] also observed the excited state bonding of pyrazine in hydrogen bonding solvents. These two observations lend support to our analysis based on the proposed theoretical index for hydrogen bonding abilities. The data in Table 2 further reveal that in the π-π^* state, both pyridine and pyrazine should form stronger hydrogen bonds than in their ground state. No report is available so far to check these observations.

References

1 Suzuki H & Baba H, *J chem Phys*, **38** (1963) 349.
2 Kasha M, Discuss *Faraday Soc*, **9** (1950) 14; McConnell H, *J. chem Phys*, **20** (1952) 700.
3 Julg A & Bonnet M, *Theoret Chim Acta*, **1** (1962) 6.
4 Besnainon S, Prat R & Bratoz S, *J chim Phys*, **61** (1964) 222.
5 Ponomarov, O A, Morozora J 'P & Danitora V, *Vodorodnaia, Svjaz*, edited by N D Sokolov and V M Tschulanovskii (Nauka, Moscow) 1954, 236.
6 Bratoz S, *Adv Quant Chem*, **3** (1967) 209.
7 Krishna V G & Goodman L, *J chem Phys*, **33** (1960) 381.
8 de Jeu W, *Chem Phys Lett*, **7** (1970) 153.
9 Del Bene J E, *Chem Phys Lett*, **23** (1973) 287.
10 Rama Rao Ch V, Jacob Chacko & Chandra A K, *J chem Soc Faraday Trans I*, (1982) 78, 3025.
11 Pople J A & Segal G A, *J chem Phys*, **44** (1966) 3289.
12 Kroto H W & Santry D P, *J chem Phys*, **47** (1967) 2736.
13 Del Bene J E, *J Am chem Soc*, **97** (1975) 5330.