Studying the Theoretical Aspect of 2-(Methylamino)Pyridine by DFT and Other Calculations

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ABSTRACT

We have tried to study organic drug 2-(Methylamino) Pyridine (2MAP) by Theoretical point of view. The calculated ground and excited state potential, charge density, bond length and dipole moment evince that 2MAP is conducive to ESIPT.

Keywords : 2-(Methylamino) Pyridine, ESIPT, Artificial Neural Network
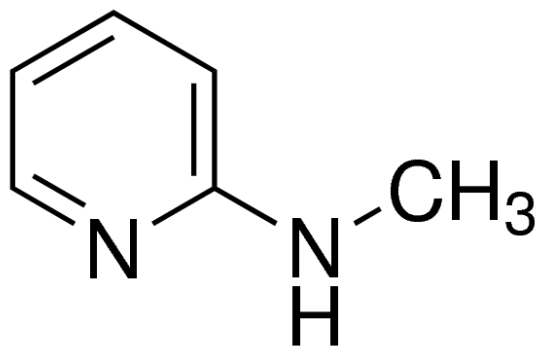
I. INTRODUCTION

The study of Excited state intermolecular and intramolecular proton transfer (ESIPT) is not very new and its being observed now for a long time [1–11]. In an excited state, an organic molecule can undergo structural changes and can possesses a different structural geometry due to significant charge redistribution [12].

2-(Methylamino)Pyridine (2MAP) [Scheme-I] is potentially a good reagent for Intermolecular Proton Transfer. The two amino tautomers with nearly isoenergetic conformation around the C–N(HCH3) bond for 2MAP change into N-2(1H)-pyridinylidenemethanamine as the methyl-imino tautomers by intramolecular hydrogen-atom (or proton) transfer. By introducing an electron withdrawing group, both a structural change and a change in either the basicity or acidity of the groups could occur in the excited state in order to facilitate ESIPT in 2-(Methylamino)Pyridine (2MAP). Our work also helped to establish the mechanistic details of ESIPT in 2MAP by using steady-state absorption and emission spectroscopy.

The gas phase ground state geometries of HNA and NHNA were fully optimized with and without symmetry constraints using both a time-dependent density functional theory method using the Becke3LYP hybrid functional [13] and Hartree–Fock theory employing the 6-31G and 6-311G basis sets [14], as implemented in the Gaussian 03 package. Configuration interaction with singles (CIS) was done in order to optimize the first excited singlet state (SI) [15]. Vertical excitations were carefully analyzed by inspecting the corresponding Kohn–Sham orbital contours. Time-dependent density functional theory (TDDFT) calculations were performed on the gas phase optimized geometry of the ground state (S_0)[16] in order to obtain the excitation energies and oscillator strengths in the gas phase.

II. Experimental

2MAP was purchased from the Aldrich chemical company and was recrystallized before use
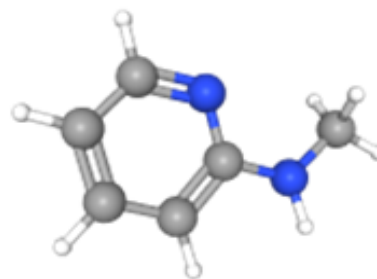
Scheme-I

In the ground state, the Z form is highly unstable, and that the absence of the Z form might be due to a high energy barrier.

Scheme-II

III. RELATED WORK

The optimized minima of the potential energy surface and the stable ground states of 2MAP are similar to the structures given in Scheme-1. In 2MAP, the O–H bond length was 1.005 Å, and the O– H bond length for the excited state was 1.003 Å, which is comparable to hydrogen bonding distance. The theoretically computed change in the dipole moment from the ground to the excited state was large (Dl ~ 1.9D) for 2MAP.

2MAP can show a zwitterionic form (S*– Z*) (Z-form)only in the excited state and not in the ground state. However, we observed that the energy difference between the N (Normal form) and Z forms of 2MAP was not significantly high, since the Z form could be opti- mized independently. For 2MAP (Scheme-II), the enthalpy and free energy differences at 298.2 K are tabulated in Table 1. From Table 1, it is seen that the N form is more stable than the Z form (DG298.15 = 5.556 kcal mol—1 and DG298.15 = 9.57 kcal mol—1 at the B3LYP/6-311G (d, p) and RHF/6311G theory levels respectively). We also observed that the addition of water close to the photolabile proton lowered the ground state energy difference to DG298.15 = 4.51 kcal mol—1. From a thermodynamic point of view, this decrease indicates that the zwitterionic form could exist in the ground state; however, only the N form was populated in solution, indicating that there was a GSIPT.

The negative charge density of the acceptor atom H, and the donor atom, (O–H group), of 2MAP is 0.236 au and 0.305 au, respectively, whereas the electron withdrawing group on 2MAP increases the negative charge on the acceptor atom (—0.732 au), and decreases the negative charge on the donor atom (- 0.292 au). These features indicate that intramolecular proton transfer is favorable for 2MAP.

Table 1. Difference in the enthalpy (DH) and the free energy (DG) at 298.15 K between the normal form and the zwitterionic (ESIPT) form of 2MAP.

Level of theory	DH298.15	(kcal/mol)	DG298.15	(kcal/mol)
RHF/6-311G	9.06	9.57		
DFT/B3LYP/6-311G (d, p)	5.12	5.56		

IV. CONCLUSION

This part of theoretical calculation through computer simulation technique of 2MAP shows that this molecule is a strong contender to show ESIPT mainly in its excited state.

V. REFERENCES

[1].   A. Weller, Naturewissenschaften 42 (1955) 175.
[2].   A. Weller, Discuss. Faraday Soc. 27 (1959) 28.
[3].   K.M. Solntsev, E.N. Sullivan, L.M. Tolbart, S. Ashkenazi, P. Leiderman, D. Huppert, J. Am. Chem. Soc. 126 (2004) 12701.

[4]. H. Ushiyama, K. Takatsuka, Angew. Chem. Int. Ed. 44 (2005) 1237.

[5]. J.L. Perez-Lustres, F. Rodriguez-Prieto, M. Mosquera, T.A. Senyushkina, N.P. Ernsting, S.A. Kovalenko, J. Am. Chem. Soc. 129 (2007) 5408.

[6]. M.H. Van Benthem, G.D. Gillispie, J. Phys. Chem. 88 (1984) 2954.

[7]. K.P. Ghiggino, A.D. Scully, H.I. Leaver, J. Phys. Chem. 90 (1986) 5089.

[8]. E. M Kosower, D. Huppert, Annu. Rev. Phys. Chem. 37 (1986) 127.

[9]. J. Goodman, L.E. Brus, J. Am. Chem. Soc. 100 (1978) 7472.

[10]. J.L. Herek, S. Pederson, L. Banares, A.H. Zewail, J. Chem. Phys. 97 (1992) 9046.

[11]. K.Y. Law, J. Shoham, J. Phys. Chem. 99 (1995) 12103.

[12]. J.A. Reese, T.V. Nguyen, T.M. Korter, D.W. Pratt, J. Am. Chem. Soc. 126 (2004) 11387.

[13]. A.D. Becke, J. Chem. Phys. 98 (1993) 5648.

[14]. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A.Montgomery, Jr., T. Vreven, K.N.Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V.Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A.Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R.Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O.Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J. A. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P.Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M.Challacombe, P.M.W. Gill, B.G. Johnson, W. Chen, M.W. Wong, C. Gonzalez and J.A. Pople, GAUSSIAN 03 (Revision C.02), Gaussian, Inc., Wallingford, CT, 2004.

[15]. J. B Foresman, M. Head-Gordon, J.A. Pople, M.J. Frisch, J. Phys. Chem. 96 (1992) 135.

[16]. R.E. Stratmann, G.E. Scuseria, M.J. Frisch, J. Chem. Phys. 109 (1998) 8218.