



Computational study of the intramolecular proton transfer reactions of dipicolinic acid (pyridine-2,6-dicarboxylic acid) and its dimers

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ABSTRACT

The intramolecular proton transfer (IPT) reaction and dimerization processes of dipicolinic acid (DPA) have been investigated using density functional theory (DFT) at the B3LYP/6-31G++(d) basis set level. The influence of the solvent on the zwitterion-to-neutral transition of DPA was examined using the continuum model (CPCM) with different dielectric constants ($\epsilon = 4.9$, CHCl_3 ; $\epsilon = 7.42$, THF; $\epsilon = 32.63$, CH_3OH ; $\epsilon = 78.39$, H_2O). The intramolecular proton transfer reaction occurs more readily in the gas phase than solution. Results also show that the stability of DPA dimers in the gas phase is directly affected by the hydrogen bond angle and electrostatic potential (ESP) value in the dimer structure.

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1. Introduction

Since intramolecular proton transfer (IPT) is one of the most important reactions in many chemical and biological processes, numerous experimental and theoretical studies have been carried out to increase knowledge of the mechanisms of IPT [1–14].

Dipicolinic acid (DPA, pyridine-2,6-dicarboxylic acid, $\text{C}_5\text{H}_3\text{N}(\text{COOH})_2$) was first identified in 1936 as a viscous matter in Natto, a Japanese food made with steamed soybeans and fermented with *Bacillus Natto* [15]. It was not until 1953 that DPA was first recognized to be a by-product of bacterial spore germination [16,17]. Since then, DPA has been investigated as a potential indicator of bacterial spore formation and germination using a wide range of detection techniques [18–20]. It can protect bacterial spores because of its strong ability to absorb UV light, hence up to 50% of the solids excreted by spores are compounds of DPA. It is well-known to be a molecule with high chelation. Experiments performed on wet paste and dry crystal forms of DPA and CaDPA have shown interesting effects on their fluorescence intensities [21]. Other experimental and theoretical investigations of DPA and its derivatives have been relatively sparse [22–30]. The X-ray structure of DPA shows that the molecules are arranged as one-dimensional supramolecular structure and stabilized in the solid state through a strong symmetric double hydrogen bond [31–33].

The recent study by Massaro and Blaisten-Barojas reports that DPA has six predicted neutral isomers in the gas phase. N (see Fig. 1) is the global minimum structure taking into account that its total electronic energy plus the zero point energy is the lowest of the six predicted structures [34]. Another structure which can exhibit N is the zwitterionic form (Z), in which the nitrogen atom and one of COOH groups become NH^+ and COO^- , respectively [35]. The zwitterionic forms of DPA may be conveniently studied in solution with the suitable pH value [36] and in the presence of an appropriate amine [37–48] or their self-assembled systems [49–61]. Therefore, DPA is a good model compound for *intra*- and *intermolecular* proton transfer studies. The carboxyl protons are involved in the *intra*- and *inter*-molecular hydrogen bonds (the pyridine's nitrogen atom and the carboxyl's oxygen lone pairs can be hydrogen bond acceptors). In this paper, we report the investigation of the IPT reaction between the N and Z structures (see Fig. 1) of DPA. In order to follow the atoms of DPA, they have been numbered in a consistent scheme. By following the Isin's method [6] in this work, we carried out calculations using Becke's Three Parameter Hybrid Functional together with the correlation functional of Lee, Yang, and Parr (B3LYP) methods [62,63] for DPA in the gas phase, chloroform, THF, methanol and water in order to evaluate the effect of the solvent on IPT. Also, computations on DPA dimers with two different structures were performed in the gas phase at the B3LYP/6-31G(d) level. Based on a search of the literature, this is the first computational study of the IPT reaction between two structures of DPA and the hydrogen bonding between their dimers. Therefore, we hope that our study provides an enhanced interpretation of DPA as well as its derivatives.

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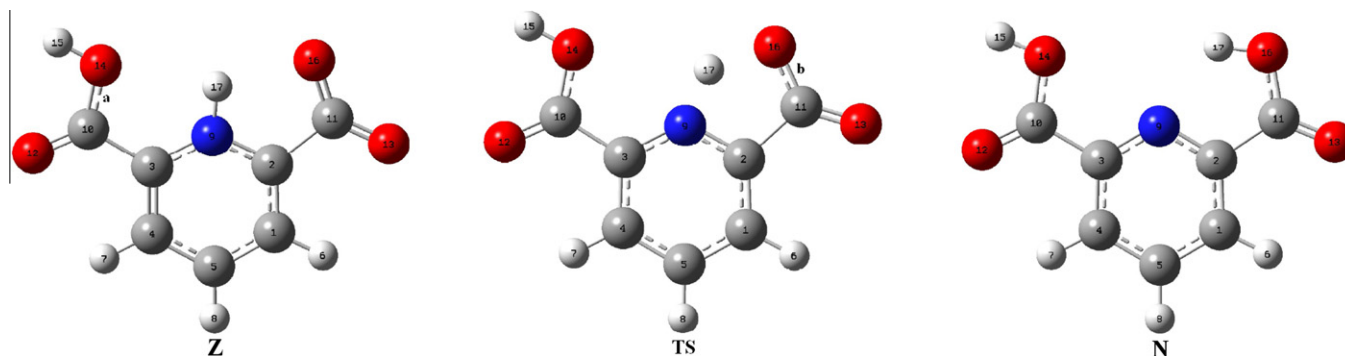


Fig. 1. Optimized molecular structures of N, Z and the transition state (TS). Carbon atoms are colored in gray, oxygen atoms in red, nitrogen atoms in blue, and hydrogen atoms in white. (a) The $C_{10}O_{14}$ bonds are single, in the gas phase (in all forms). (b) The $C_{11}O_{16}$ bond is double, in the gas phase (in TS form).

2. Computational details

The stationary structures (N and Z) in the IPT reaction of DPA and (NN and ZZ) in the dimerization of DPA were optimized using density functional theory (DFT) at the most popular B3LYP method [62,64] and a double- ζ basis set with an extra d polarization function and diffuse functions on all atoms (6-31G++(d)). The vibrational frequencies were obtained at the same level to characterize the local minimum and the transition states (corresponding to a single negative eigenvalue of the Hessian). The non-specific solvent effects of the solvent medium were studied by means of the conductor-polarizable continuum model (CPCM) [65]. The CPCM has been used for energy calculations with a different dielectric constants ($\epsilon = 4.9$, $CHCl_3$; $\epsilon = 7.42$, THF; $\epsilon = 32.63$, CH_3OH ; $\epsilon = 78.39$, H_2O) in the IPT reactions of DPA. The basis set superposition error (BSSE) associated with the hydrogen bond energy in the dimerization of DPA was computed via the counterpoise method using the individual bases as fragments [66]. Also the molecular electrostatic potential (ESP) were calculated for DPA dimers. All the calculations were performed with the Gaussian 09 W package [67].

3. Results and discussion

The B3LYP/6-31G++(d) optimized geometries for N, Z and TS (the transition state) are shown in Fig. 1, and selected structural parameters are listed in Table 1.

The IPT reaction $Z \rightarrow TS \rightarrow N$ was considered. The transfer of a hydrogen atom from the N_9 to the O_{16} atom is accompanied by a rearrangement of the six-membered ring, and substantial changes are observed in the carbon–oxygen, nitrogen–hydrogen and oxygen–hydrogen bonds. The distance between H_{17} and O_{16} decreases upon the IPT. The N_9-H_{17} and $O_{16}-H_{17}$ distances for TS are 1.170 Å and 1.438 Å in the gas phase. Compared to initial content of those, it can be concluded that the N_9-H_{17} bond is broken and an $O_{16}-H_{17}$ bond is formed during the IPT process in DPA. During proton transfer $Z \rightarrow TS \rightarrow N$, the C_2-C_{11} and $C_{11}-O_{13}$ distances decrease, the C_3-C_4 and $C_{11}-O_{16}$ distances increase, the C_1-H_6 , C_4-H_7 , C_5-H_8 and $O_{14}-H_{15}$ distances remain unchanged, the C_1-C_2 distance first decreases and then increases in all phases. The $C_{10}O_{14}$ distance and the $C_2N_9H_{17}$ angle decrease on $Z \rightarrow N$ transfer, while the angles $C_1C_2N_9$, $C_3C_{10}O_{14}$ and $C_2C_{11}O_{13}$ increase. The angles $C_4C_3N_9$, $C_4C_3C_{10}$, $C_2N_9C_3$, $O_{12}C_{10}O_{14}$, $O_{13}C_{11}O_{16}$ and

Table 1
Selected bond lengths, bond and dihedral angles derived from B3LYP/6-31G++(d) geometric optimization of DPA in the gas and solution phases.

Parameters ^a	Gas phase			Chloroform ($\epsilon = 4.9$)			THF ($\epsilon = 7.42$)			Methanol ($\epsilon = 32.63$)			Water ($\epsilon = 78.39$)		
	N	TS	Z	N	TS	Z	N	TS	Z	N	TS	Z	N	TS	Z
<i>Distance</i>															
C_1C_2	1.399	1.392	1.398	1.398	1.390	1.395	1.398	1.389	1.394	1.398	1.389	1.394	1.398	1.389	1.394
C_3C_4	1.400	1.393	1.386	1.400	1.395	1.386	1.400	1.395	1.386	1.401	1.396	1.386	1.401	1.396	1.386
C_2C_{11}	1.512	1.552	1.562	1.507	1.536	1.547	1.507	1.535	1.546	1.506	1.533	1.543	1.506	1.533	1.543
$C_{10}O_{14}$	1.347	1.345	1.347	1.343	1.341	1.342	1.343	1.341	1.341	1.342	1.340	1.340	1.342	1.340	1.340
$C_{11}O_{16}$	1.342	1.283	1.256	1.341	1.294	1.258	1.341	1.295	1.258	1.341	1.296	1.258	1.341	1.297	1.258
N_9H_{17}	2.023	1.170	1.043	2.011	1.225	1.031	2.008	1.231	1.030	2.005	1.240	1.029	2.005	1.242	1.028
$O_{16}H_{17}$	0.984	1.438	1.940	0.985	1.341	2.072	0.986	1.331	2.087	0.986	1.319	2.107	0.986	1.316	2.110
$C_{11}O_{13}$	1.211	1.227	1.238	1.215	1.229	1.246	1.216	1.230	1.248	1.216	1.230	1.249	1.217	1.230	1.249
<i>Bond angle</i>															
$N_9C_2C_{11}$	115.69	108.00	113.12	115.19	107.44	114.50	115.12	107.38	114.64	115.03	107.32	114.83	115.01	107.32	114.86
$C_2C_{11}O_{16}$	114.16	108.27	111.01	114.37	108.51	112.96	114.39	108.56	113.20	114.41	108.62	113.54	114.42	108.63	113.60
$O_{13}C_{11}O_{16}$	122.97	132.72	134.58	122.04	129.88	131.66	121.94	129.58	131.29	121.78	129.14	130.78	121.76	129.07	130.68
$C_{10}O_{14}H_{15}$	106.78	108.10	108.69	107.69	108.65	109.50	107.79	108.70	109.59	107.93	108.78	109.71	107.95	108.79	109.74
$C_1C_2N_9$	123.39	120.83	118.76	123.52	121.59	118.61	123.53	121.65	118.60	123.55	121.76	118.59	123.56	121.78	118.59
$C_4C_3N_9$	122.65	119.09	118.69	122.58	119.37	118.84	122.57	119.39	118.88	122.56	119.43	118.91	122.55	119.44	118.92
$C_4C_3C_{10}$	118.72	121.14	121.75	118.95	121.56	122.12	118.98	121.28	122.14	119.03	121.30	122.18	119.04	121.31	122.19
$C_2N_9C_3$	118.35	122.99	124.33	118.28	122.30	124.24	118.27	122.25	124.22	118.26	122.15	124.18	118.26	122.13	124.18
$C_3C_{10}O_{14}$	113.40	112.09	111.56	113.44	112.29	111.56	113.44	112.31	111.53	113.44	112.33	111.52	113.44	112.34	111.52
$O_{12}C_{10}O_{14}$	123.32	124.64	124.94	123.39	124.66	125.31	123.40	124.65	125.38	123.41	124.64	125.44	123.41	124.64	125.45
$C_2C_{11}O_{13}$	122.86	119.01	114.41	123.58	121.61	115.38	123.67	121.86	115.50	123.80	122.24	115.68	123.82	122.30	115.71
$C_2N_9H_{17}$	–	98.37	110.12	–	96.27	113.19	–	96.07	113.51	–	95.80	113.95	–	95.76	114.02

^a Distances in Å; angles in degrees. For numbering of atoms, see Fig. 1.

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