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1*H*–pyrazole–3–carboxylic acid: Experimental and computational study

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ABSTRACT

The FT–IR and UV–Vis spectra for 1*H*–pyrazole–3–carboxylic acid (H_2pc) were recorded in methanol solvent. The optimized molecular structure, vibrational frequencies and NMR chemical shifts of the title molecule in methanol solvent and gas phase were obtained by using DFT/B3LYP and DFT/HSEh1PBE methods with 6–311++G(d,p) basis set. TD–DFT calculations in methanol solvent and gas phase were used to investigate UV–Vis absorption wavelengths. Furthermore, the NLO parameters and FMO energies of the molecule were calculated by using B3LYP and HSEh1PBE methods with 6–311++G(d,p) basis set. In order to investigate intermolecular hydrogen bonds and π–π interactions, NBO study was fulfilled by the same levels. To sum up, the fact that the title compound used frequently in coordination chemistry field has encouraged us to do experimental and theoretical characterizations of H_2pc

1. Introduction

Heterocycles are widely found in many natural products and play a vital role in metabolism because of their constructional units, such as vitamins, hormones and antibiotics besides the pharmaceuticals, agrochemicals and dyes [1]. Heterocyclic carboxylic acids like pyridinecarboxylic acid [2–4], imidazolecarboxylic acid [5–8] and pyrazolecarboxylic acid [9–12] are extraordinarily significant and unique class of compounds and have various ligands with multi-dentate modes [13].

Pyrazoles are well known instance of aromatic heterocycles including two nitrogen atoms [14]. They form a substantial heterocyclic family covering a natural products which show chemical, biological and pharmacological properties [15,16]. Pyrazole derivatives represent one of the most active classes of compounds and in recent years some drugs have been improved from pyrazole derivatives such as celecoxib, rimonabant, sildenafil and fomepizole [15,17]. Various derivatives of the pyrazole carboxylic acid can establish diverse types of complexes and can be easily deprotonated owing to pyrazole N atoms and carboxyl O atoms, and it is helpful to synthesize new complexes [18–21]. Pyrazolecarboxylic acid has more sophisticated coordination ability than pyridinecarboxylic acid since the pyrazole nitrogens in pyrazolecarboxylic acids can coordinate to create mono– or multi–dentate bonds, but also form intermolecular hydrogen bonds for assembling high dimensional networks [19].

1*H*–pyrazole–3–carboxylic acid (H_2pc) is a multifunctional ligand involving both pyrazole nitrogen and carboxylate oxygen atoms. To date, FT–IR and NMR spectroscopic studies were carried out with the synthesis of this ligand. However, it is important to create the basis for future studies, due to the lack of detailed spectroscopic characterization studies particularly electronic properties on this ligand and its potential to be used in the coordination chemistry. In this study, the molecular spectroscopic properties were investigated by FT–IR and UV–Vis spectroscopy. Moreover, TD/DFT computations in methanol solvent and gas phase have been also performed on structural, spectroscopic, electronic and non-linear optical properties.

2. Computational details

The calculations of H_2pc were fulfilled by using the Gaussian 09, Rev. D01 program [22] and the output files were visualized by GaussView 5 software [23]. The molecular structure and vibrational frequencies of H_2pc in methanol solvent and gas phase were calculated through B3LYP [24,25] and HSEh1PBE [26–30] functional methods at 6–311++G(d,p) basis set. Furthermore, the assignments of vibrational modes were presented with PED% contributions (potential energy distribution) by using VEDA program [31]. GIAO ^{1}H and ^{13}C chemical shifts of H_2pc in methanol

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solvent and gas phase were calculated through performing B3LYP and HSEh1PBE methods at 6–311++G(d,p) basis set. Electronic transition were obtained by using TD–DFT level [32] at 6–311++G(d,p) basis set with CPCM model [33] in methanol solvent and gas phase. Major contributions to electronic transition were determined via SWizard program [34]. The frontier molecular energies were calculated at same level. The nonlinear optical parameters in methanol solvent and gas phase were computed at same levels. NBO (Natural Bond Orbital) [35] study has been applied to investigate intermolecular hydrogen bonds and π–π interactions in H_2pc. Lastly, the molecular electrostatic potential (MEP) and electrostatic potential (ESP) surfaces were analyzed by using the same levels.

3. Results and discussion

3.1. Geometric optimization

The ground state geometry optimization for 1*H*–pyrazole–3–carboxylic acid (H_2pc) in methanol solvent and gas phase has been applied by using B3LYP and HSEh1PBE methods with 6–311++G(d,p) basis set. Obtained structural parameters are compared with previously presented XRD results for a similar structure [36] and given in Table 1. According to the obtained results, it can be said that there is no important difference between the computed and experimental [36] geometric parameters in both methods and solvents for H_2pc. Optimized molecular structure obtained by B3LYP method in methanol solvent is present in Fig. 1. The N4–N8 bond length was observed as 1.330 Å [36]. The corresponding bond length in methanol solvent and gas phase was calculated at 1.333 and 1.337 Å by using B3LYP level. Similarly, this bond in methanol solvent and gas phase was obtained at 1.322 Å and 1.326 Å by using HSEh1PBE level. The C1–N8 bond length was reported as 1.344 Å [36], this bond distance in methanol solvent and gas phase was obtained at 1.339 Å and 1.335 Å for B3LYP level, 1.333 Å and 1.330 Å for HSEh1PBE level. The C3–N4 bond length was observed at 1.351 Å [36]. This bond length in methanol solvent and gas phase was calculated at 1.359 Å and 1.362 Å for B3LYP level, 1.353 Å and 1.356 Å for HSEh1PBE level. The C9–O10 and C9–O11 bond lengths were reported as 1.224 Å and 1.296 Å. In our

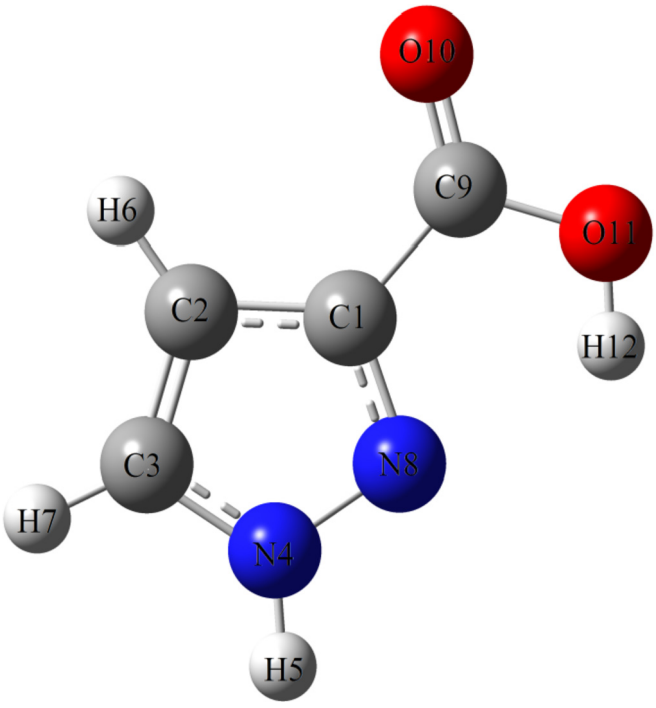

Fig. 1. The optimized molecular structure of H_2pc at B3LYP/6–311++G(d,p) level in methanol solvent.

Table 1
Selected experimental and calculated bond length and bond angles for H_2pc.

Parameters	B3LYP		HSEh1PBE		Experimental [36]
	Methanol	Gas phase	Methanol	Gas phase	
Bond lengths (Å)					
C1–C2	1.412	1.413	1.407	1.407	1.394 (17)
C2–C3	1.379	1.377	1.376	1.374	1.376 (16)
C3–N4	1.359	1.362	1.353	1.356	1.351 (16)
N4–N8	1.333	1.337	1.322	1.326	1.330 (14)
N8–C1	1.339	1.335	1.333	1.330	1.344 (16)
C1–C9	1.476	1.486	1.472	1.481	1.470 (16)
C9–O10	1.211	1.202	1.207	1.200	1.224 (16)
C9–O11	1.349	1.351	1.338	1.341	1.296 (17)
O11–H12	0.973	0.971	0.971	0.970	0.820
N4–H5	1.011	1.008	1.009	1.007	0.840 (2)
C2–H6	1.077	1.076	1.078	1.077	0.930
bond angles (°)					
C1–C2–C3	104.3	104.4	104.0	104.2	104.3 (10)
C2–C3–N4	106.5	106.5	106.5	106.4	107.0 (10)
C3–N4–N8	113.0	112.8	113.2	113.0	112.5 (10)
N4–N8–C1	104.6	104.7	104.7	104.7	104.6 (10)
N8–C1–C2	111.6	111.6	111.6	111.6	111.6 (11)
N8–C1–C9	119.3	120.0	118.9	119.7	120.0 (11)
C2–C1–C9	129.2	128.4	129.5	128.7	128.4 (11)
C1–C9–O10	124.2	123.4	124.1	123.3	121.0 (12)
C1–C9–O11	115.2	114.7	114.8	114.4	113.7 (11)
O10–C9–O11	120.6	122.0	121.0	122.3	125.3 (12)
C9–O11–H12	109.1	108.8	108.6	108.3	109.5
N8–N4–H5	119.7	119.3	119.7	119.3	117.8 (16)
H5–N4–C3	127.3	127.9	127.1	127.7	129.7 (16)
C3–C2–H6	127.7	128.3	127.9	128.5	127.9
H6–C2–C1	128.0	127.3	128.1	127.4	127.9