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Theoretical studies on the effect of substituent in the proton transfer reaction of 4-substituted pyrazoles

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ABSTRACT

Density functional theory (B3LYP and CAM-B3LYP) and MP2 methods have been employed to study of proton transfer in annular tautomerism and double proton transfer reaction of a series of pyrazoles substituted at the 4 position (**NH_2**, **OH**, **CH_3**, **F**, **H**, **Cl**, **CN**, **NO_2**, **CHO**, **NO**). It was found that activation energy for monomers of pyrazole derivatives via tautomerism process is in the range of 47.8–55.5 kcal/mol. In addition the pyrazole with electron releasing groups have lower activation energy than electron withdrawing ones. Moreover it was found that formation of dimers favored, and corrected interaction energies were found in the range of 11.4–12.0, 10.0–10.6 and 12.2–12.8 kcal/mol using CAM-B3LYP, B3LYP and MP2 methods, using 6-311++G(d,p) basis function, respectively. The double proton transfer reaction was studied for dimers and the obtained results showed that corrected activation energies vary in the range of 13.0–15.0 and 11.4–12.6 kcal/mol at DFT and MP2 levels of theory, respectively. A good correlation between B3LYP and CAM-B3LYP results for prediction of hydrogen bond strength was observed.

1. Introduction

Pyrazole and its derivatives represent one of the most active classes of compounds having a wide spectrum of biological activities. During the past years, considerable evidence has been accumulated to demonstrate the efficacy of pyrazole derivatives including antibacterial [1,2], antifungal [3–5], herbicidal [6], acaricide [7], insecticidal [4,8], and other biological activities [9,10]. Up till now, a great variety of these kinds of compounds have been synthesized, among which some commercial pesticides have been developed [11–13]. Moreover pyrazole derivatives have adjacent nitrogen atoms that could incorporate more than one reactive metal atom in close proximity, thus facilitating potentially unique chemical reactivity and physical properties. Pyrazole-based chelating ligands have attracted significant attention since their first introduction in 1966 [14]. Currently, the representatives of this family that hold the most interest are poly pyrazolylborates (scorpionates) poly pyrazolylmethanes 2,3,4 and 2,6-bis(pyrazolyl)pyridines [15–18]. Many homo or hetero metallic complexes of pyrazole derivatives containing short metal_metal distances have found wide applications in material science [19] bioinorganic chemistry [20], and homogeneous catalysis [21].

Among all the non-bonded interactions, hydrogen bonding has proved to be the most useful and reliable because of its strength and directional properties [22–27]. Many natural building blocks, such as amino acids, nucleic acids and carbohydrates, have groups that form hydrogen bonds. Hydrogen-bonding interactions in DNA/RNA systems have recently inspired the use of such motifs to stabilize a range of synthetic structures, and it has led to the formation of various ensembles [28,29]. These compounds may be successfully used in energetic formulations as oxidizers, plasticizers, and elastomeric binders [30]. Because of its structure, pyrazole and its derivatives can be act as appropriate building block. Sun et al. studied eight pyrazole–imidazole dimers using DFT method and conclude that they can be formed by two modes, the single H-bond mode and the double H-bond mode [31]. Elguero and co-workers have investigate 3,5-disubstituted pyrazoles using ^{13}C and/or ^{15}N-CP/MAS solid-state NMR spectroscopy and X-ray crystallography, showing that they form a variety of hydrogen-bonded cyclic dimers, trimers, and tetramers [32–34]. Moreover Castaneda et al. studied vibrational spectra and structure of hydrogen bonded complexes formed by pyrazole and 3,5-dimethylpyrazole (DMP) and examined complexation with some proton donating compounds [35]. The double proton transfer reactions between some substituted pyrazoles and guanidine molecule were studied by Schweiger and co-workers [and showed that the minimum energy path is more relevant for a plateau reaction than a straight linear path [36]. In addition Limbach and co-workers studied structure

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of solid pyrazole-4-carboxylic acid and found that the compound forms quasi-linear ribbons in which the molecules are linked by cyclic hydrogen bonds between pyrazole and carboxylic acid groups with disordered hydrogen-bonded protons [37].

Recently, Ochsenfeld et al. have presented an elegant study about the insertion of pyrazole units in a peptide which associates intermolecularly, giving rise to nanorosette-type structures in water [38]. In another work Garcia and co-workers studied tautomeric behavior and aggregation of a series of 3(5)-phenyl pyrazoles in the solid and solution phase [39].

In continuum with our research program to study of effect of substituent in the strength of hydrogen bonding and proton transfer reactions [40–43] herein we report results of our calculations on aggregation of 4-substituted pyrazoles in the gas phase and study of proton transfer reaction in monomer and dimers of pyrazole derivatives.

2. Computational details

DFT and MP2 calculations were performed using GAUSSIAN 09 package [44]. Density functional theory was used with Becke3–Lee–Yang–Parr (B3–LYP) exchange–correlation 6-311++G(d,p) basis set [45,46]. According to recent reports hybrid functionals can provide better description for the systems with hydrogen bonds [47,48]. Vibrational frequencies were calculated to verify the nature of the stationary points found on the potential energy surface. The hydrogen bonding energy of the studied dimers was corrected both with basis set superposition error (BSSE) and zero-point vibrational energies (ZPVE) [49]. In our calculation particular emphasizes delivered on the 6-311++G(d,p) basis set because this basis set is of triple $-\xi$ quality [50,51] for valence electrons with diffuse functions, which are useful in calculations for anions and structures with lone-pair electrons [52,53]. A comparison of results of different basis sets reflects that most crucial achievement of H-bond energy comes with this basis set. This observation reasonably complies with other reports [54].

3. Results and discussion

The structures and numbering of dimers of pyrazole derivatives that considered in the present study shown in Fig. 1. For the nitroso and carbaldehyde groups that may be exist in two forms, we consider the most stable isomer.

3.1. Monomers

Due to the small size of pyrazole and its rigidity, it has been used as a model study for the evaluation of the accuracy of different computational methods so its geometry has been extensively studied by different structural determination methods. These include microwave, electron diffraction and X-ray methods [55–60]. The optimized interatomic distances of pyrazole derivatives calculated at MP2/6-311++G(d,p) level are listed in Table 1. A close look at the Table 1 reveals the geometrical parameters of the pyrazole cycle calculated by DFT method are in excellent agrees with the experimental data. In the case of unsubstituted pyrazole, the difference between the interatomic distances experimentally measured by microwave [55], and the calculated ones at DFT level may reach to only 0.004 Å. In addition comparing the theoretical values with experimental data obtained from X-ray results [58] indicates that all optimized bond lengths are slightly larger than their experimental counterparts. Since the theoretical calculations are performed for an isolated molecule in the gas phase and the experimental results are obtained for a molecule in the solid state therefore, they are subjected to intermolecular forces, such as van der Waals interactions and crystal packing forces.

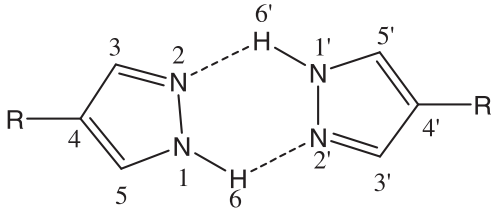

Fig. 1. Structure of pyrazole dimers which have been considered in this work.

The comparison of predicted bond lengths calculated at MP2 method with experimental data obtained for parent pyrazole ring show difference up to 0.017 Å.

From Table 1 it follows that on going from electron releasing groups to electron-withdrawing ones, a significant elongation of the N1–N2 bond and a shortening of the N2–C3 and N1–C5 bond obtained, while the C4– C5 and C3–C4 bonds are not considerably altered.

Moreover we investigated 1H, 2H tautomerism in the pyrazole derivatives and in Fig. 2 the optimized structures with activation energies and important geometrical parameters of transition states have been presented. The obtained results show that activation energies for proton transfer reaction varies in the range of 47.8–55.5 kcal/mol. Analyzing of the results reveals proton migration is easier in pyrazoles with electron donating groups. For example the activation energy of the process in the 4-amino and 4-nitro pyrazole was found to be 47.9 and 54.4 kcal/mol, respectively. In addition we found a good correlation between substituent constants (σ_p) and activation energy of proton transfer reaction. In fact activation energy easily obtained as: $E_a = 4.802\sigma_p + 50.06$ with $cc = 0.915$ (see Fig. 3).

In addition a close look at the Fig. 2 reveals proton distance from pyrazole ring varies in the range of 1.240–1.250 Å. Here with

Table 1
Calculated geometrical parameters of pyrazole monomers using DFT and MP2/6-311++G(d,p) method.

	N1–N2	N2–C3	C3–C4	C4–C5	N1–C5	N1–H6	N2N1H6
MP2							
NH_2	1.339	1.351	1.411	1.394	1.366	1.009	118.8
OH	1.339	1.352	1.408	1.390	1.365	1.009	118.6
CH_3	1.343	1.348	1.413	1.392	1.363	1.010	118.7
F	1.341	1.350	1.402	1.386	1.363	1.009	118.5
H	1.343	1.348	1.410	1.389	1.362	1.010	118.6
Cl	1.342	1.347	1.407	1.389	1.362	1.010	118.6
CN	1.343	1.342	1.416	1.394	1.357	1.011	118.6
NO_2	1.345	1.344	1.407	1.387	1.356	1.011	118.4
CHO	1.347	1.344	1.416	1.395	1.354	1.011	118.4
NO	1.352	1.340	1.419	1.394	1.352	1.011	118.3
DFT							
NH_2	1.338	1.332	1.417	1.383	1.368	1.006	119.2
OH	1.340	1.333	1.413	1.379	1.364	1.007	119.0
CH_3	1.346	1.330	1.418	1.381	1.360	1.01	119.1
F	1.344	1.331	1.405	1.376	1.361	1.007	118.9
H	1.348	1.330	1.414	1.380	1.358	1.007	119.0
Cl	1.346	1.329	1.411	1.379	1.358	1.007	119.0
CN	1.351	1.322	1.423	1.388	1.349	1.008	118.7
NO_2	1.357	1.322	1.413	1.383	1.345	1.008	118.7
CHO	1.357	1.324	1422	1.390	1.345	1.008	118.7
NO	1.364	1.319	1.427	1.391	1.342	1.008	118.6
EXP[a]	1.349	1.331	1.416	1.372	1.359	0.998	118.4
EXP[b]	1.344	1.323	1.369	1.361	1.335	0.87	–

[a] Microwave Ref. [52].
[b] X-ray Ref. [55].