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A systematic investigation of cooperativity between two types of hydrogen bonding in the nonlinear clusters of an aromatic molecule: Pyrazole

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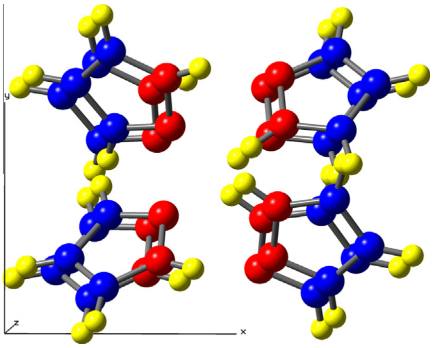
HIGHLIGHTS

- HBs of pyrazole can be considered as interesting ones in the recent studies of cooperativity between different HBs.
- Changes of different properties of clusters against crystal size were investigated by diagrams fitted to $ln(1-\frac{a}{n})$.
- Charge transfer in the crystalline pyrazole and gas phase value of C_Q of N(2) were assessed from calculated data.

GRAPHICAL ABSTRACT



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ABSTRACT

Crystalline pyrazole consists of nonlinear chains of an aromatic molecule. It includes two independent molecules which in turn causes two different types of hydrogen bonds (HBs). These two types of HBs with slight differences in their N—H···N geometries can be considered as interesting ones in the recent studies of cooperativity between different HBs. These HBs are investigated in several pyrazole clusters by electronic structure calculations. Parameters such as structure, binding energy, charge transfer, chemical shielding and electric field gradient (EFG) parameters calculated at the second order Moller–Plesset perturbation (MP2) and density functional (DF) levels of theory. Both the basis set superposition error (BSSE) and zero point vibrational energy (ZPVE) corrections on the cooperativity enhancement were considered. Changes of different properties of clusters against crystal size were investigated by proposed diagrams fitted to a logarithmic function which renders their extrema in the crystal limit. In each cluster, pyrazole molecules for which their parameters are more affected by cooperativity enhancement were explored employing these fitted diagrams. Most calculated energetic and spectroscopic parameters were in good linear correlations with both the structural parameters and charge transfer along HB ($q_{n(N2)\to\sigma^*(N1-H1)}$). These correlations in the cases of nuclear magnetic resonance (NMR) and nuclear quadrupolar resonance (NQR) parameters, were explained in the terms of natural charges of bonding (σ(N1—H1)) and antibonding (σ^*(N1—H1)) orbitals. Organizing calculated data for mental clusters with similar molecules and HB types produced better regression values in all linear correlations. According to the experimental C_Q of N(2) in solid state and zero charge transfer in the gas phase, the value of charge transfer in the crystalline pyrazole and gas phase value of C_Q of N(2) were assessed, respectively. Diagrams of the structural parameters against either crystal size or HB cooperativity propose that experimental structure in the case of both hydrogen and heavy nuclei positions is in doubt and should be revisited.

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Introduction

The vital role of hydrogen bonding (HB) in most biological systems, from the molecular level up to the bulk one is clear from the extensive investigations about HB in these systems [1]. The HB is so important that recently a IUPAC commission has offered a technical report to define it: "The hydrogen bond is an attractive interaction between a group X—H and an atom or group of atoms Y in the same or different molecule(s), where there is evidence of bond formation" [2]. Most properties of hydrogen bonded moieties, X—H and Y, such as structural parameters, binding energy and charge distribution can be affected by HB formation. Since HB is on average the strongest form of noncovalent bonds, its formation causes changes of structural parameters to a very large extent, especially in its position [3–8]. Its formation and accompanying binding energy overcome most other factors in the structural studies of these moieties. They determine nucleic acid base pairing, the folding of polypeptides, crystal structures and polymorphism of hydrogen bonded species. Thus, HB studies offer a wealth of information which is very important in exploring its effects.

One such effect is cooperativity of hydrogen bonds. It is employed in the molecular identification studies in the gas, liquid and solid states [9–11]. For example Hoepfer et al. employed HB cooperativity effects to discuss the layered structure of crystalline guanidine [11]. Other properties, influenced by large charge redistributions between HB moieties, are the nuclear magnetic resonance (NMR) and nuclear quadrupole resonance (NQR) parameters. Ordinarily, these parameters of non-hydrogen bonded liquids and solids do not differ much with their gas phase values. But, in hydrogen bonded systems, they are so affected by this charge transfer in the liquids and solids that they are not comparable with gas phase data. Moreover, cooperativity between connected HBs is a special characteristic of this sort of bonding and it is described as nonadditive enhancement of the strength of an HB over cooperation of its constituent moieties in other HBs [12,13]. Since introduction of the concept of hydrogen bonding, frequent occurrence of its cooperativity in these systems has been subject to extensive spectroscopic, thermodynamic, theoretical and computational studies [12]. Following the cooperativity studies between different schemes of noncovalent bonds, such as between a hydrogen bond and a hydric bond, most studies are nowadays concerning the cooperativity between different types of HBs.

These sorts of HB cooperativity are most prominent in both the occurrence and strength points of view [14–16]. For example Cong et al. found higher cooperativity energy for heteroclusters ($H_3N{:}(HNC{:})_n$) in comparison to the homoclusters ($HNC{:}(HNC{:})_n$) [15]. Another important scheme of HB clusters which is observed in many processes, consists of aromatic molecules [12]. The aromatic effect can moderate charge redistribution within HB constituents and modulated HB cooperativity by distributing produced charge over all atoms of this ring. Since major parts of theoretical studies on HB and its cooperativity include linear clusters, it seems interesting to investigate them in nonlinear clusters composed of aromatic molecules. These clusters such as pyrazole better resemble what is happening in nature.

Pyrazole was subject of a wide range of experimental and theoretical studies because of both of its importance and special structure [17–72]. Some of these studies directly focus on the HB phenomenon [28–33,66] and many others employ its effects to conduct their discussion part [21–26,45,51,57–65]. N-unsubstituted pyrazoles which include the important N—H···N type of HB, are biologically very relevant and have received very much attention in the study of its drug and natural product derivatives [73–76]. The HB network in the crystalline pyrazole seems to be an excellent example for a cooperativity study because it satisfies all conditions mentioned above. It includes cooperativity of a catemer in solid state with aromatic molecules and two very closely related HB types [17–20].

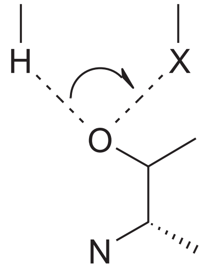
In this paper, this delicate HB cooperativity is investigated employing a variety of computed energetic and spectroscopic parameters. They are structural, energetic, charge transfer, chemical shielding and electric field gradient (EFG) parameters. The EFGs are obtained from some spectroscopy experiments such as NMR, NQR and microwave, where nuclear quadrupole coupling constant is related to the EFG. Relations between structural parameters and the number of hydrogen bonded molecules illustrate the effects of these parameters on the HB cooperativity and vice versa. For example, in the cooperativity study between HBs and halogen bonds, Voth et al. stated that directions of halogen bonds are perpendicular to the hydrogen bonds that include carbonyl oxygen (Scheme 1) [77]. They also stated that halogen bonds are energetically independent of HBs [77]. Binding energy analysis which provides explicit values for HB's energy and cooperativity, was used to categorize different HBs as strong and weak ones.

Stabilization energy, $E(2)$, obtained from natural bonding orbital (NBO) analysis is evidence of the attractive interaction along HB and is used to characterize its strength [78]. The NBO analysis also provides values of transferred charge between HB moieties which in turn reflect charge redistribution over its formation. Chemical shielding and EFG parameters are very sensitive to the charge redistribution and they will be both the best observable and best measurable outcomes of this phenomenon. Larger changes of all of the mentioned parameters over formation of second, third and next HBs in comparison to formation of first one, are evidences of its cooperativity.

In this brief study, it will be tried to investigate structural and energetic properties of HB in pyrazole by means of structural binding energy, charge transfer, chemical shielding and EFG parameters calculated at the second order Moller–Plesset perturbation (MP2) and density functional (DF) levels of theory. To this end, real crystal structures of pyrazole will be employed as starting point. Moreover mental clusters will be used in data analyses.

Computational details

All calculations employed two different clusters of pyrazole, hereafter called cat1 and cat2 (Fig. 1) [19]. This crystal structure was used because it was the only one that was based on neutron diffraction (ND) study. Such methods render accurate positions for hydrogen nuclei. Each of the clusters starts with an independent molecule of the crystalline pyrazole. They were used beside each other because their starting molecules are different. In cat1 it is almost perpendicular to the next molecule, while in cat2 it is coplanar with the next molecule. Along the geometry optimization, constraints were applied on the intermolecular dihedral angles in order to keep molecules in the catemer orientation of crystalline pyrazole. All of these dihedral angles include nitrogen nuclei of



Scheme 1. The directions of halogen bonds are perpendicular to the hydrogen bonds that include carbonyl oxygen.