

**GEOMETRIC RELAXATION OF ZEOLITIC IMIDAZOLATE FRAMEWORKS:  
COMPARISON OF STRUCTURES BASED ON CRYSTALLINE POROUS PROPERTIES  
OBTAINED BY DIFFERENT FORCE FIELDS**

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**Abstract.** Crystalline porous materials have various industrial applications; in that sense Zeolites Imidazolate Frameworks (ZIF) are a subclass of organometallic structures which may be technologically feasible for storage of chemicals, chemical detector, chemical stripper, including separations based membrane [1]. Identification of materials suitable for a given application can be done by screening of an enumerated database of materials. Such screening requires high performance automated tools that analyze and calculate the topological and geometrical parameters to describe the pores. The structure descriptors can be used to compare, select, and classify a group of materials. The project objective is to develop and apply such tools to characterize pore geometries in materials such as zeolites and Metal Organic Frameworks (MOF) to identify materials with adsorption properties relevant to a number of gas storage and separation applications.

A molecular simulation study is reported for ZIF. The effects of the force fields with standard and extended parameters are systematically examined and compared with experimental data. Among three force fields (UFF [2], CHARMM [3], and DREIDING [4]), DREIDING has the best agreement with experiment. Other important aspect of the structural analysis of these materials is the investigation of the geometrical parameters describing pores. Our methods are based on the Voronoi decomposition according the algorithm implemented with free software, Zeo ++ [5], the resulting is analyzed to obtain the diameter of the largest included sphere and the largest free sphere, which are two geometrical parameters that are frequently used to describe pore geometry. Accessibility Surface Area is also determined with Monte Carlo Sampling and reported in this work.

**Key words:** ZIF, MOF.

**Introduction.** The study of adsorbent materials has assumed importance in recent years, Zeolites imidazolate Frameworks (ZIF) (fig. 1) are a subclass of organometallic structures (MOF) which may be technologically feasible for storage of chemicals, chemical detector, chemical stripper, including separations based membrane. Structurally they have isomorphism similar to zeolites, the ZIF adopts crystalline architectures, where typically ions play the role of oxygen, which are combined with molecules of imidazole (IM). Just over 100 different structures ZIFs have been reported and compared with more than 190 known zeolites but only a fraction of them have been considered for development in the industry and its applications.

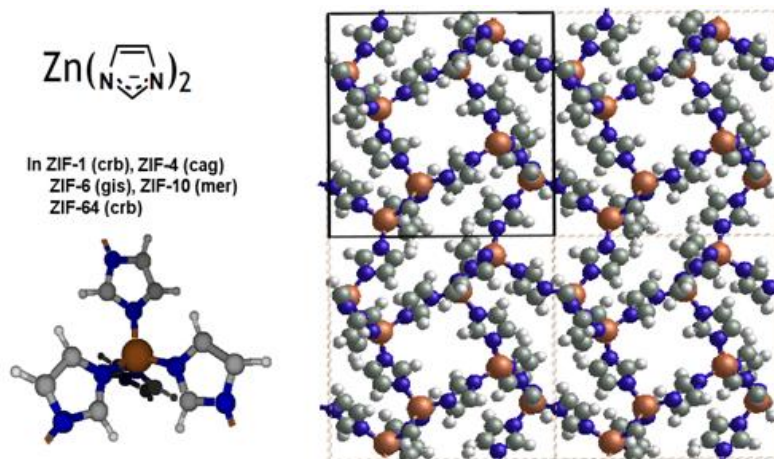


Figure 1 – ZIF structure

To know about of relevant material properties and select the most viable for theoretical or experimental research, we can develop numerical models, which start from the force fields. Force fields are not always have appropriate parameters for all atoms especially for metals such as zinc and this practically hinder the molecular modeling studies of ZIF. To facilitate this task, there are three options, the first is to use a non-bonding method, the second option is to use semibonded model, and the last option is the bonded model, it treats the connections between zinc and their ligands covalently and helps to preserve the tetrahedral configuration of coordination, besides taking into account the distribution of atomic charges and Van der Waals parameters.

In this work three force fields were used to present a comparison of porous descriptors based on Voronoi decomposition; UFF [2], CHARMM [3] and Dreiding [4] to obtain the structure relaxation from hypothetical or data available at the Center Cambridge Crystallographic Data (CCDC) structures.

**Methodology.** We begin choosing a set of experimental structures of ZIFs: ZIF-23, ZIF- 1, ZIF-90, ZIF- 4, ZIF-64, ZIF- 6, ZIF- 8, ZIF-62, ZIF -72, ZIF-77, ZIF-7 and ZIF-10, which can take different forms according to the number of links between Zn (IM)<sub>2</sub>. Include molecules imidazole may contain other functional groups, for example, methyl (in ZIF-8), benzene

(in ZIF-7 and 62), nitro (in ZIF-77), aldehyde (in ZIF-90) and chlorine (in ZIF-72). ZIFs structures have unit cells in a range of volume of  $1205.66 \text{ \AA}^3$ - $14210.80 \text{ \AA}^3$ , and the number of atoms per cell varies from 108-544. Experimental crystal structures of porous materials can contain additional solvents these species have been removed from the beginning. Since ZIFs have the same topology of zeolites, this makes them possess a high diversity. From the International Zeolite Association (IZA) database IZA we have been constructed different ZIFs computationally applying TOBUNPOROUS, where basically the chains of Si-O-Si chains are replaced by Zn-Im-Zn.

To describe the interaction between atoms pairs of all molecules studied in this work the following expression for the potential energy was used:

$$E(r_{ij}) = E_{bond} + E_{angle} + E_{dih} + E_{nb}. \quad (1)$$

The first term helps to represent the bond energy, the second describes the bending bond, the third represents the dihedral angles energy, and the last term is used to describe the interactions of atoms non bonded to take account Coulomb and Van der Walls interactions. Simultaneously we assume that the imidazole is physically rigid, so we focus only on the parameters of zinc, the functional groups and hydrogens. To detect the atoms forming the rigid rings of imidazole, the Smallest Set of Smallest Ring algorithm (SSSR) was consider.

GULP program was used to calculate the energy (1) of each structure in each force field, the primitive cells were minimized with a geometry optimization at constant pressure, the atomic coordinates were relaxed using the options "opt" and "comp". Moreover, an important parameter is the number of coordination, which was also taken account, according to Addicoat et al [6] in relation to the extended UFF they propose. Once obtained the structures of relaxation is needed geometrical comparison of the conformations obtained with classical and quantum methods, but for our study, we have also based on comparison of other important topological parameters, such as the largest included sphere ( $D_i$ ), the largest free sphere ( $d_f$ ), the Volume and of the Accesible Surface Area (ASA). These latter characteristics are obtained by analysis to represent the void of the porous material through the computer network Voronoi. In this study, the algorithm is implemented with free software, Zeo ++ [5]. The program determinates the accessibility of each Voronoi node, ASA is calculated by integration of Monte Carlo, where points are sampled on spheres centered on each atom fraction of viable points.

**Results.** We obtain the bond lengths Zn-N and angles N-Zn-N for relaxed structures, the distribution for this data are showed in the histograms of the Figure 2. In the experimental structures the average distances Zn-N is  $1.98 \text{ \AA}$ , and only Dreiding force field maintains this behavior, on the other hand, UFF, CHARMM and DFT the produce longer distances, theirs averages are  $2.04 \text{ \AA}$ ,  $2.03 \text{ \AA}$  and  $2.03 \text{ \AA}$  a respectively, for this reason the histogram for distances Zn-N obtained from Dreiding data has a positive kurtosis. The valence angles N-Zn-N are reproduced with the same tendency for all methods, with the higher frequency is close to  $109.5^\circ$ .

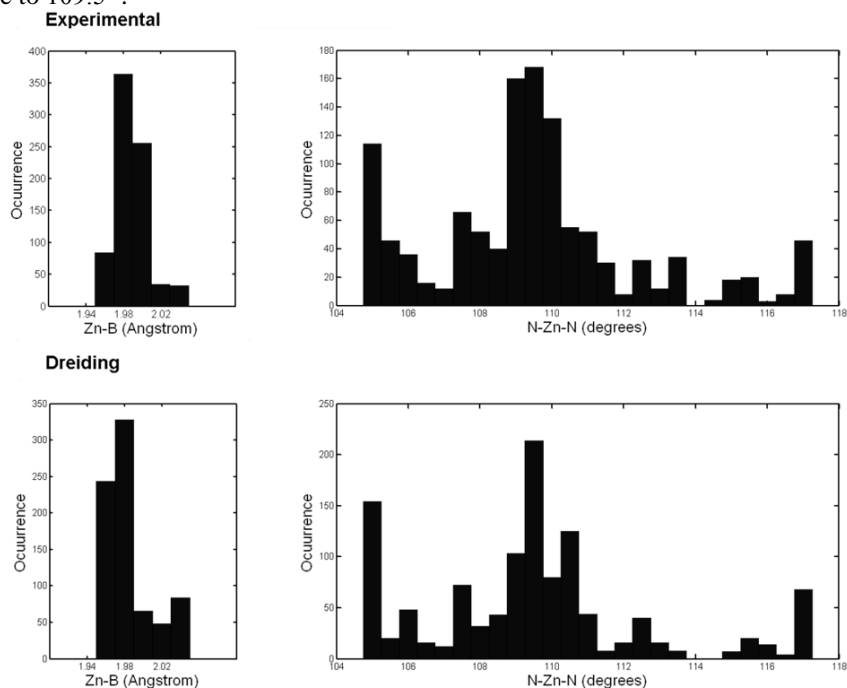


Figure 2 – Histogram of distances for the Zn-N bonds and valence angles N-Zn-N

To decide which force field is better to approach the geometry to the experimental structures, the relative errors for the radius of the largest included sphere, the radius of the largest free sphere, and de accessible surface area was calculated. The mean square error for the variables,  $D_i$ ,  $d_f$ , and the volume of the cell, were lower for Dreiding, not so for the ASA variable, since in this case UFF with modified parameters is lower with only a difference of 10 % respect to Dreiding. That is the order of approach to  $D_i$ ,  $d_f$  and the volume compared to the experimental data is maintained in the order Dreiding <UFF <CHARMM, while for the ASA the order of approach is UFF<Dreiding <CHARMM.

Figure 3 graphically show the comparison of each of the variables obtained with the three force fields respect to the experimental values, in general these methodologies reproduced with few errors the experimental data. Additionally the parameter for Zn was used according to the extended UFF.

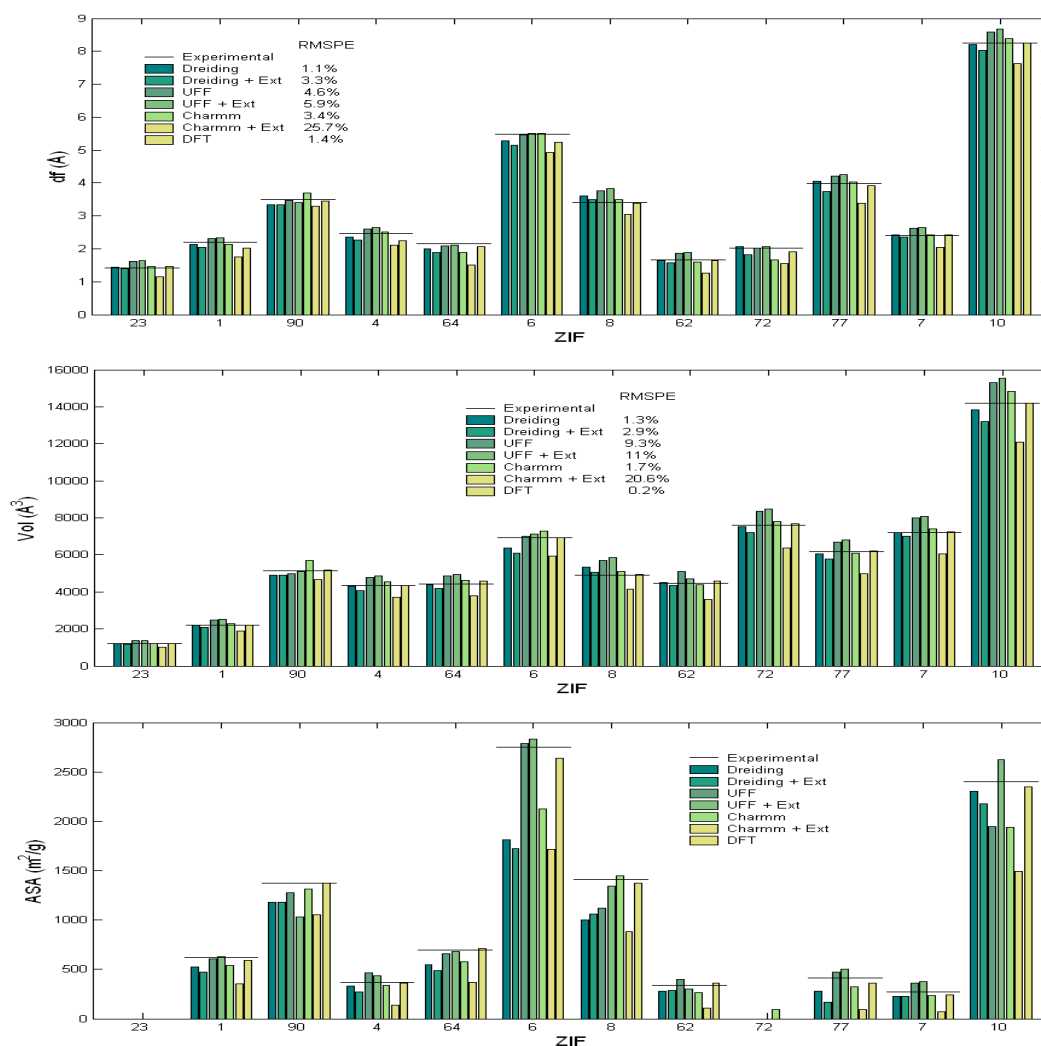


Figure 3 – Comparing data: the largest included sphere ( $D_i$ ), the largest free sphere ( $d_f$ ), the Volume and of the Accessible Surface Area (ASA) obtained from experimental, DFT, Dreiding, UFF and CHARMM data. (+ Ext) indicates that extension of parameters were used

**Conclusion.** The relaxation structures were analyzed for a set of ZIFs by three force fields to be closer to the experimental results with structures obtained with Dreiding. Furthermore, according to the comparison made with the experimental structures from variables largest included sphere, largest free sphere and accessible surface area calculated analysis Voronoi, we can mention that the Dreiding force field has a better approach to the experimental data as well as the results obtained by the DFT theory. The extended UFF parameters help in some cases to reduce relative errors of each of the geometric and topological variables.

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