

Molecular Dynamics Study of Ferrocene in Low and Room Temperatures

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Abstract : Ferrocene ($\text{Fe}(\text{C}_5\text{H}_5)_2$, i.e., di-cyclopentadienyle iron (FeCp_2) or Fc) is a unique example of 'wrong but seminal' in chemistry history. It has significant applications in a number of areas such as homogeneous catalysis, polymer chemistry, molecular sensing, and nonlinear optical materials. However, the 'molecular carousel' has been a 'notoriously difficult example' and subject to long debate for its conformation and properties. Ferrocene is a dynamic molecule. As a result, understanding of the dynamical properties of ferrocene is very important to understand the conformational properties of Fc. In the present study, molecular dynamic (MD) simulations are performed. In the simulation, we use 5 geometrical parameters to define the overall conformation of Fc and all the rest is a thermal noise. The five parameters are defined as: three parameters d ---the distance between two Cp planes, α and δ to define the relative positions of the Cp planes, in which α is the angle of the Cp tilt and δ the angle the two Cp plane rotation like a carousel. Two parameters to position the Fe atom between two Cps, i.e., d_1 for Fe-Cp1 and d_2 for Fe-Cp2 distances. Our preliminary MD simulation discovered the five parameters behave differently. Distances of Fe to the Cp planes show that they are independent, practically identical without correlation. The relative position of two Cp rings, α , indicates that the two Cp planes are most likely not in a parallel position, rather, they tilt in a small angle $\alpha \neq 0^\circ$. The mean plane dihedral angle $\delta \neq 0^\circ$. Moreover, δ is neither 0° nor 36° , indicating under those conditions, Fc is neither in a perfect eclipsed structure nor a perfect staggered structure. The simulations show that when the temperature is above 80K, the conformers are virtually in free rotations, A very interesting result from the MD simulation is the five C-Fe bond distances from the same Cp ring. They are surprisingly not identical but in three groups of 2, 2 and 1. We describe the pentagon formed by five carbon atoms as 'turtle swimming' for the motion of the Cp rings of Fc as shown in their dynamical animation video. The Fe- C(1) and Fe-C(2) which are identical as 'the turtle back legs', Fe-C(3) and Fe-C(4) which are also identical as turtle front paws', and Fe-C(5) ---'the turtle head'. Such as 'turtle swimming' analog may be able to explain the single substituted derivatives of Fc. Again, the mean Fe-C distance obtained from MD simulation is larger than the quantum mechanically calculated Fe-C distances for eclipsed and staggered Fc, with larger deviation with respect to the eclipsed Fc than the staggered Fc. The same trend is obtained for the five Fe-C-H angles from same Cp ring of Fc. The simulated mean IR spectrum at 7K shows split spectral peaks at approximately 470 cm^{-1} and 488 cm^{-1} , in excellent agreement with quantum mechanically calculated gas phase IR spectrum for eclipsed Fc. As the temperature increases over 80K, the clearly splitting IR spectrum become a very board single peak. Preliminary MD results will be presented.

Keywords : ferrocene conformation, molecular dynamics simulation, conformer orientation, eclipsed and staggered ferrocene

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