Chapter 2

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Abstract

Conditions for simulations using the PM3 and AM1 methods were established in this chapter. The simulations allow determining the reaction conditions of different materials, so through the application of methods PM3 and AM1 were determined Gibbs free energy. In addition the main signals of vibrational and sites for nucleophilic and electrophilic attacks of different structures simulated.

Keywords: FTIR, Electrostatic Potential, Structural Parameters

2.1 Geometry Optimization

It is necessary to carry out the geometry optimization or energy minimization of the system being examined. After it has been sketched, since sketching often creates the structure in a high energy configuration and starting a simulation from such an unoptimized structure can lead to erroneous simulations and results. In this work three aspects were considered to selection of geometry optimization method and algorithm: system size, convergence level and force field used. In this study the semi-empirical methods were used for describing the potential energy function of the system. Next a minimization algorithm is chosen to find the potential energy minimum corresponding to the lower-energy

structure. Iterations number and convergence level lead optimal structure. The optimizing process of structures used in this work was started using the PM3 and AM1 methods, because it generates a lower-energy structure even when the initial structure is far away from the minimum structure. The Polak-Ribiere algorithm was used for mapping the energy barriers of the conformational transitions. For each structure, 1350 iterations, a level convergence of 0.001 kcal/mol/Å and a line search of 0.1 were carried out [1].

2.2 Structural Parameters

The optimized structural parameters were used in the vibrational wavenumber calculation with PM3 and AM1 method to characterize all stationary points as minima. The structural parameters were calculated select the Constrain bond and length options of Build menu for two method of analysis.

2.3 FTIR

The infrared spectrum is commonly obtained by passing infrared electromagnetic radiation through a sample that possesses a permanent or induced dipole moment and determining what fraction of the incident radiation is absorbed at a particular energy [2]. The energy of each peak in an absorption spectrum corresponds to the frequency of the vibration of a molecule part, thus allowing qualitative identification of certain bond types in the sample.

The FTIR was obtained by first selecting menu Compute, vibrational, rotational option, once completed this analysis, using the option vibrational spectrum of FTIR spectrum pattern is obtained for two methods of analysis.

2.4 Electrostatic Potential

After obtaining a free energy of Gibbs or optimization geometry using PM3 and AM1 methods, we can plot two-dimensional contour diagrams of the electrostatic potential surrounding a molecule, the total electronic density, the spin density, one or more molecular orbitals, and the electron densities of individual orbitals.

HyperChem software displays the electrostatic potential as a contour plot

when you select the appropriate option in the Contour Plot dialog box. Choose the values for the starting contour and the contour increment so that you can observe the minimum (typically about –0.5 for polar organic molecules) and so that the zero potential line appears.

A menu plot molecular graph, the electrostatic potential property is selected and then the 3D representation mapped isosurface for both methods of analysis. Atomic charges indicate where large negative values (sites for electrophilic attack) are likely to occur. However, the largest negative value of the electrostatic potential is not necessarily adjacent to the atom with the largest negative charge [3].

2.5 Orbitals Molecular

The interaction between charges favors reaction between sites (on the two species) that have extreme charge values: the most positive charge interacts with the most negative. This ionic reaction generally involves strongly polar reactants. The second term favors interactions where the HOMO and the LUMO can overlap most favorably. This generally occurs for less polar reactants and is important when the two have similar energies, so that the denominator is small [3].

The HOMO–LUMO analysis has been carried out to explain the charge transfer within the molecule. The chemical hardness (g) and chemical potential (l) have been calculated using the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). This analysis has been performed using PM3 and AM1 method level in order to elucidate the intermolecular hydrogen bonding, intermolecular charge transfer (ICT), rehybridization, and delocalization of electron density [4].

2.6 Conclusions

Conditions for simulations using the PM3 and AM1 methods were established in this chapter. Geometry optimization was determined to obtain the Gibbs free energy and determinate the spontaneity of the reaction. The structural parameters are calculated to indicate whether the molecules is linear or not, by the length and angle bond. With FTIR analyses the characteristic signals were calculated. Finally, the analysis of molecular orbital and electrostatic potentials were obtained to assigned where the attractions will be

stronger to form bonds.

References

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