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Computational Approach to Investigation of Template/Monomer Complex in Imprinted Polymers; Dinitrobenzene Sensor

S. Riahi[1,2,*], *S. Eynollahi*[2], *M.R. Ganjali*[2,3] *and P. Norouzi*[2,3]

[1] Institute of Petroleum Engineering, Faculty of Engineering, University of Tehran, Tehran, Iran
[2] Center of Excellence in Electrochemistry, Faculty of Chemistry, University of Tehran, P. O. Box 14155-6455, Tehran, Iran
[3] Endocrinology & Metabolism Research Center, Tehran University of Medical Sciences, Tehran, Iran
[*]E-mail: riahisv@khayam.ut.ac.ir

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In this research a computational approach was applied to screening the mechanism of imprinting polymers. Semi-empirical PM3 and HF/6-31G methods were carried out for molecules optimization and calculation of intra molecular interaction. MAA (Methacrylic acid), the most commonly used functional monomer was chosen as functional monomer and EGDMA (Etylen glycol dimetacrilic acid) was chosen as cross linker for Dinitrobenzene (DNB) imprinting polymer. It was found that 1:4 ratios of template: functional monomers were the most stable conformation.

Keywords: Computational approach, Imprinted polymer, Chemometrics, Interaction energy, HF

1. INTRODUCTION

Molecular imprinting is a new technique that produces synthetic receptors that preferentially bind with a particular molecule (template). The principle of molecular imprinting is based on co-polymerization of functional monomers and cross-linkers in the presence of template (1-2). In this way, complementary groups situate behind them. The polymers are synthesized using this method are called “artificial receptors”. These receptors show high selectivity towards template molecules. Also, these receptors are used in solid phase extraction (SPE), electrochemistry, drug delivery and high liquid chromatography (HPLC) because of its high selectivity (3-6). For evaluation of the selectivity of MIP, absorption of a molecule that is similar to the template molecule in structure, called pseudo template is measured. In this work, Dinitrobenzene was selected as template and TNT as pseudo template.

The affinity and selectivity of imprinting polymer basically depend on the parameters which are determined by the strength and type of intermolecular interactions. Therefore the knowledge of the type and orientations of involved functional monomers is crucial for imprinting polymers.

Molecular simulation techniques play important roles in understanding and imagination of molecular level manners. These methods are powerful in calculating intra molecular energy and atomic charges in different phases. Molecular simulation softwares are able to depict a three dimensional picture from molecules that help us understand and imagine molecule configurations. Compared with experimental methods, computational approaches have advantages such as: low costs, less time consuming, safe for the human body (many solvents are cancerogen) and safe for the environment - no exposed chemicals. These methods maybe successfully applied in rational design and solvent prediction in imprinting polymer. There are several ways to compute and evaluate interaction energy between functional monomers and templates. In recent MIP researches, functional monomers and solvents were initially selected and then experimental were performed. In most cases computational methods such as DFT and HF methods were used (13-21). In grate molecules because of ab initio methods are time consuming, MD (molecular dynamics), MM (molecular mechanics) and semi empirical methods were used (21-28). In macro molecules simulation, only MM, MDNVT methods (mole, volume, temperature) and MDNPT (mole, volume, pressure, temperature) were used (29-31). In all these approaches, the main goal is to find the interaction energy between monomer(s) and template. This energy is the measure of monomer-template stability.

Since only ab initio methods are reliable in the description of hydrogen bonding systems, we used HF/6-31G method in the calculation of interaction energy between DNB and MAA.

In imprinting polymers, the commonly template/monomer ratio are 1/n (n≤), thus we have designed different configuration of template/monomers complexes for each ratio. Depend on binding energy, high binding energy corresponding to high stability. The most stable configuration consider as real station.

2. COMPUTATIONAL DETAILS

In recent years the DFT method was applied in different branches of chemistry [7-31]. The experimental results were reported in Ref. [32]. Molecular structures of DNB, MAA and TNT were created with the HYPERCHEM software. The optimized molecular geometries were obtained through AM1 semi-empirical calculations and the Eigenvector Following method included in HYPERCHEM. Conformational analysis was carried out to localize the global minimum of each molecule. Frequency calculations were performed to confirm the nature of the stationary points. Vibrational frequencies were unscaled. Then, these optimized molecular geometries have been optimized using HF/6-31G methods in Gaussian 98. The optimized configuration of DNB, MAA are shown in Figure 1 and geometrical parameters are shown in tables 1 and 2.

Table 1. Significant computed geometrical parameters for DNB before and after complex formation

DNB dihedrals	Before interacting MAA	After interacting MAA	DNB dihedrals	Before interacting MAA	After interacting MAA
D(6,1,2,3)	0.0	-0.376	D(1,2,9,11)	180.0	148.209
D(6,1,2,9)	180.0	178.768	D(3,2,9,10)	180.0	147.997
D(13,1,2,3)	180.0	-179.355	D(2,3,4,5)	0.0	0.020
D(2,1,6,5)	0.0	-0.1333	D(2,3,4,15)	180.0	179.807
D(2,1,6,7)	180.0	-179.934	D(14,3,4,5)	180.0	-179.144
D(13,1,6,5)	180.0	178.849	D(3,4,5,6)	0.0	-0.525
D(1,2,3,4)	0.0	0.434	D(3,4,5,16)	180.0	179.882
D(1,2,3,14)	180.0	179.591	D(15,4,5,6)	180.0	179.687
D(9,2,3,4)	180.0	-178.711	D(1,2,9,10)	0.0	-31.153
D(4,5,6,1)	0.0	0.582	D(1,6,7,8)	0.0	-34.230
D(4,5,6,7)	180.0	-179.616	D(1,6,7,12)	180.0	147.715
D(16,5,6,1)	180.0	-179.830	D(5,6,7,8)	180.0	145.967

DNB dihedrals	Before interacting MAA	After interacting MAA	DNB dihedrals	Before interacting MAA	After interacting MAA
R(1,2)	1.398	1.398	R(4,15)	1.096	1.096
R(1,6)	1.398	1.396	R(5,6)	1.400	1.399
R(1,13)	1.105	1.106	R(5,16)	1.100	1.102
R(2,3)	1.400	1.400	R(6,7)	1.505	1.499
R(2,9)	1.505	1.495	R(7,8)	1.212	1.215
R(3,4)	1.389	1.389	R(7,12)	1.213	1.213
R(3,14)	1.100	1.102	R(9,10)	1.212	1.216
R(4,5)	1.389	1.389	R(9,11)	1.213	1.214

DNB dihedrals	Before interacting MAA	After interacting MAA	DNB dihedrals	Before interacting MAA	After interacting MAA
A(2,1,6)	119.605	119.296	A(4,5,16)	119.509	119.617
A(2,1,13)	120.196	120.529	A(6,5,16)	120.731	120.769
A(6,1,13)	120.197	120.166	A(1,6,5)	120.136	120.424
A(1,2,3)	120.138	120.390	A(1,6,7)	120.019	119.814
A(1,2,9)	120.019	119.892	A(5,6,7)	119.844	119.760
A(3,2,9)	119.842	119.711	A(6,7,8)	119.189	119.036
A(2,3,4)	119.758	119.605	A(6,7,12)	118.916	119.538
A(2,3,14)	120.730	120.703	A(8,7,12)	121.893	121.395
A(4,3,14)	119.512	119.686	A(2,9,10)	119.189	119.291
A(3,4,5)	120.602	120.668	A(2,9,11)	118.917	119.695
A(3,4,15)	119.697	119.686	A(10,9,11)	121.892	121.010
A(5,4,15)	119.699	119.645	A(4,5,6)	119.759	119.611

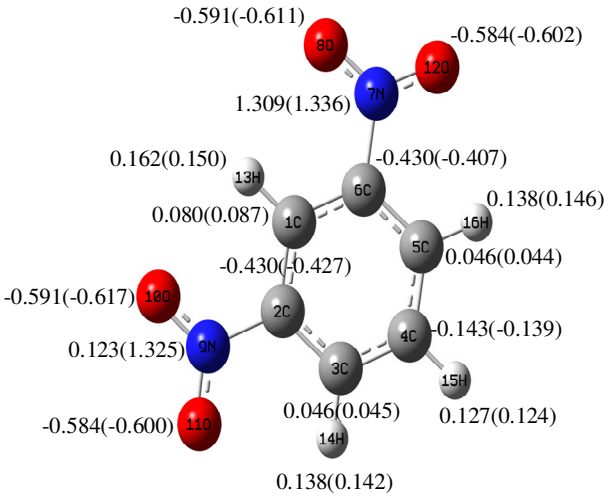

Figure 1. The optimized structure and the atomic charges of DNB before and after complexation

Table 2. Significant computed geometrical parameters for MAA before and after complex formation

EGDMA dihedrals	Before interacting DNB	After interacting DNB	EGDMA angels	Before interacting DNB	After interacting DNB
D(3,1,2,4)	179.696	179.711	A(2,1,3)	122.861	122.843
D(3,1,2,8)	0.459	0.336	A(2,1,7)	120.812	120.844
D(7,1,2,4)	-0.205	-0.167	A(3,1,7)	116.326	116.312
D(2,1,3,9)	121.155	121.144	A(1,2,4)	121.795	121.882
D(2,1,3,10)	-120.294	-120.296	A(1,2,8)	120.779	120.721
D(7,1,3,9)	-58.938	-58.972	A(4,2,8)	117.420	117.393
D(1,2,4,5)	-4.955	0.830	A(1,3,9)	110.356	110.334
D(1,2,4,6)	178.995	-175.102	A(1,3,10)	110.235	110.249
D(8,2,4,5)	174.306	-179.775	A(1,3,11)	113.291	113.291
D(2,4,6,12)	-164.827	-165.421	A(9,3,10)	107.464	107.475
D(2,4,6,13)	-31.775	-30.526	A(9,3,11)	107.654	107.645
D(5,4,6,12)	18.797	18.319	A(10,3,11)	107.620	107.626
			A(2,4,5)	125.343	125.053
EGDMA bond lengs	**Before interacting DNB**	**After interacting DNB**	A(5,4,6)	117.224	117.124
R(1,2)	1.336	1.337	A(5,4,6)	117.224	117.124
R(1,3)	1.478	1.478	A(4,6,12)	115.251	115.845
R(1,7)	1.099	1.099	A(4,6,13)	114.271	114.752
R(2,4)	1.479	1.479	A(12,6,13)	112.798	113.223
R(2,8)	1.098	1.098			
R(3,9)	1.098	1.098			
R(3,10)	1.098	1.098			
R(3,11)	1.098	1.098			
R(4,5)	1.225	1.229			
R(4,6)	1.421	1.414			
R(6,12)	0.995	0.998			
R(6,13)	0.994	0.994			

According to Mulliken charges and common chemical properties, possible configurations of 1/n DNB/MAA complex molecular systems were designed and optimized using PM3 semi-empirical method and interaction energies (ΔE) were calculated from following equation:

$$\Delta E = E\text{ (template–monomer complex)} - [E\text{ (template)} + nE\text{ (monomer)}]$$

"n" refers to the number of monomers in the template-monomer complex. For a given complex, the higher values of ΔE indicate high binding energy and the most stable conformation.

The most stable conformation was selected as its ratio conformation. Then, the interaction energies were calculated with HF/6-31G using Gaussian 98.

Interaction energies are reported in Table 3. According this table, it was found that the 1/4 template-monomer ratios, the most stable in DNB imprinting polymer.

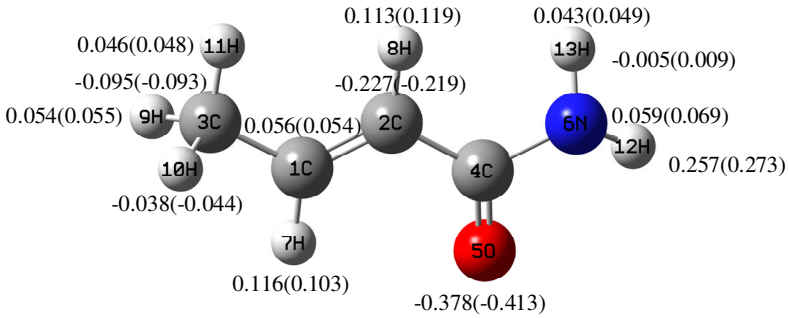

Figure 2. The optimized structure and atomic charges of MAA before and after complexation

Table 3. Interaction energies for 1/2 to 1/5 template-monomer ratios

Number of functional monomers	Interaction energy
1	-1.83
2	-3.5
3	-5.8
4	-12
5	-6.3

3. IMPRINTED POLYMER DESIGN FOR DNB

The optimized structure of the complex of DNB and MAA are shown in Figure 3. The equilibrium geometries of the complex subsystem were determined and confirmed by subsequent calculations of the vibrational frequencies. The geometrical optimizations were performed using the HF method and the significant computed geometrical parameters are available in Table 1. This table contains some significant geometrical values including: bond lengths, bond angles and dihedral angles.

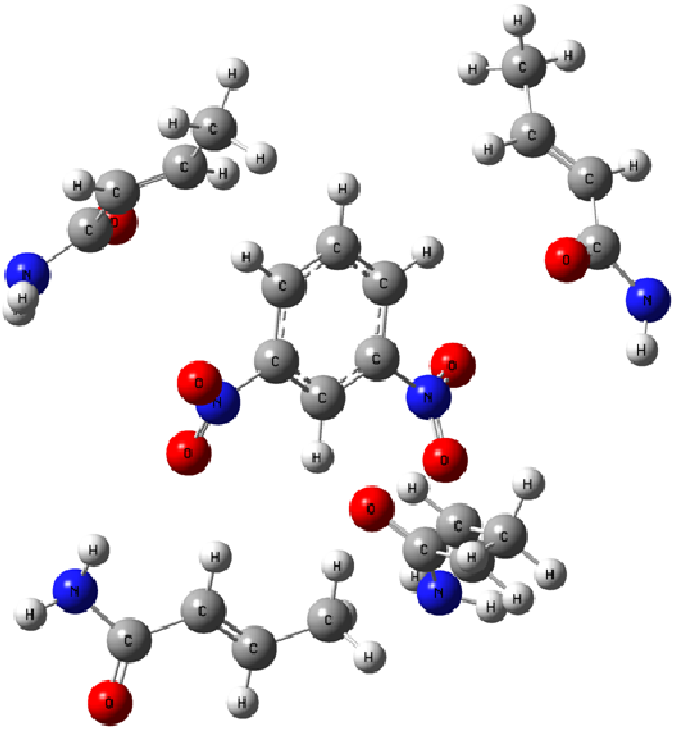

Figure 3. The optimized structures of the complex of MAA and DNB

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4. ANALYSIS OF MULLIKEN CHARGES

Results for charges in the following cases (Figures 1,2) were studied to illustrate the mechanism of template absorption in the polymer cavity:

1) Charges of polymers in the unoccupied polymer
2) Charges of polymers in the occupied polymer with template
3) Charges of polymers in the occupied polymer with pseudo template
4) Charges of the template and pseudo template in free stations, and to replace those in the polymer cavity

Overall, in order to illustrate the cross linker role in imprinting, the most stable arrangement of template with MMA that is similar to the cross linker was designed and interaction energies were calculated. In this complex the role of MMA is a functional monomer.

Charge distributions of polymers have three categories: polymer, polymer-template and polymer-pseudo-template, which essentially show no considerable difference between one another. In the other words, charge distribution in the above three categories are approximately equal. In the case of DNB and TNT, they are both very different in charge distribution in the free molecule and in the molecule that replaces the polymer cavity. The outer atom charges are adopted in a manner that electrostatic attractions are maximized. From this we conclude that if a great molecule is replaced or

induced in solution, there are many different charge distributions on its surface. Small molecules could be replaced behind it and adopted towards the grate molecule and the total systems are stablest compare with two single atoms and adsorption occurs.

5. CONCLUSIONS

In this research it was found that 1/4 template monomer ratio is the most configuration. Interaction energies between polymer-template is (-12. 6) KCal/Mol, and that between the polymer-pseudo-template is (-8.7) KCal/Mol. These results indicate the selectivity of the polymer towards DNB and TNT. These results were also obtained in the experimental setting but at a lower degree. Failure of this depends on several reasons such as; high similarity between two molecules, similarity in type and position of functional groups in two molecules, disability in simulation of solution matrices etc.

Nevertheless the designing of this polymer has some advancement over other automatic polymerization software such as; inducing the cross linker, variability in density of polymers depending on experimental solution temperature and concentration, cavity design on the polymer, and last but not least it illustrates some molecular manners and mechanisms such as adsorption.

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