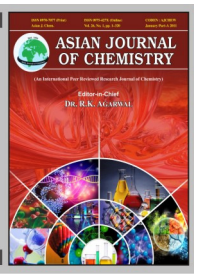
Asian Journal of Chemistry; Vol. 26, No. 1 (2014), 161-163

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2014.15363



Computer Simulation Study on the Effect of Recognized Characteristics of Cotinine Imprinted Polymer with Different Functional Monomers

HUI-MIN BI[1,*], JUN-PING HU[1], YAN LIU[1], XING-QUAN CHAI[1], LI-XIONG TONG[1] and CHUN-HUA DONG[1,2]

[1]Handan Key Laboratory of Organic Small Molecule Materials, Handan College, Handan 056002, Hebei Province, P.R. China
[2]Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, P.R. China

*Corresponding author: E-mail: binbi99@163.com

Received: 26 February 2013; *Accepted*: 20 May 2013; *Published online*: 26 December 2013; AJC-14494

The geometry optimization, energy and binding energy (ΔE) of imprinted molecule with functional monomer was studied by Gaussian 03. The template molecule is cotinine and methacrylic acid, 2-(trifluoromethyl)propenoic acid and acrylamide as functional monomer, respectively. The order of the binding energy of cotinine with the above monomers was discussed and the lowest binding energy is found with 2-(trifluoromethyl)propenoic acid. It is helpful to interpret experiment phenomena and found functional monomer selectivity.

Keywords: Cotinine, Molecularly imprinted polymer, Functional monomer, Computer simulation.

INTRODUCTION

The molecular recognition plays an important role in biological activity in nature and most biological separation techniques depends on the role of molecular recognition. The molecular imprinting technique has developed rapidly[1-3]. It has been used in many fields widely, such as chromatography, simulation of antibody or receptor, simulation of biosensors and enzyme and synthesis of catalyst. Molecular imprinting technique is a method to synthesize molecularly imprinted polymer (MIP) and the molecularly imprinted polymer has the function to identification for the target molecule (it is called template molecule). Molecularly imprinted polymer has got a lots of interest because of its versatility and amazing stereospecific recognition.

The study on the recognition performance of different functional monomers on the molecularly imprinted polymer has important significance for improving the affinity and selectivity of a molecularly imprinted polymer[4-6]. The computational chemistry methods were introduced for the study of the synthesis of molecularly imprinted polymer recently, It can reduce the number of experimental synthesis conditions greatly and reduce unnecessary consumption of reagents and labor and it has a guiding role in improving the efficiency to research and development of molecularly imprinted polymer. The results of quantum chemical calculations have more instructive because of its higher accuracy.

Cotinine is the major metabolite of nicotine[7-10]. It satisfies the conditions to be an ideal biological markers, such as high selectivity and long retention time and it can be measured in all humoral matrix (including plasma, saliva, urine). Therefore, the detection choice of the cotinine in humoral in quantitative assessment of flue gas exposure in active and passive smoking crowd. It is very important to establish accurate detection of these biomarkers analysis method.

The computer simulation was studied by Gaussian 03, The template molecule is cotinine (COT) and methacrylic acid (MAA), 2-(trifluoromethyl) propenoic acid (TFMAA) and acrylamide (AM) as functional monomer, respectively. The order of the binding energy of cotinine with the above monomers was discussed and the highest binding energy is TFMAA. It is helpful to interpret experiment phenomena and found functional monomer selectivity.

EXPERIMENTAL

The geometries of all compounds were optimized using the PM3 method. Harmonic vibrational frequencies calculated at the same level were used for characterization of stationary points as a minimum. All quantum calculations were performed with the Gaussian 03 program. Hydrogen bonding is the main consideration to form the molecularly imprinted polymer in the pre-assembled system. the binding energy reflected the interaction between cotinine and different monomer, it was calculated according to the following formula:

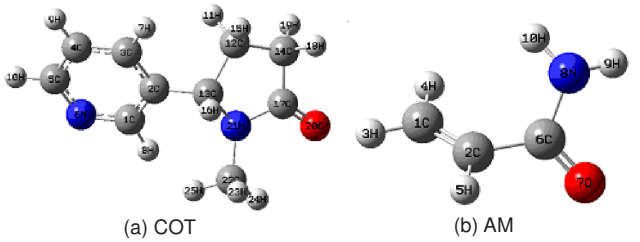
$$\Delta E = E(MIP) - \Delta E(\text{Each components of the MIP})$$

The E is the single energy of components. In order to select the functional monomer, all the possible complexes formed the monomer and template molecules were calculated

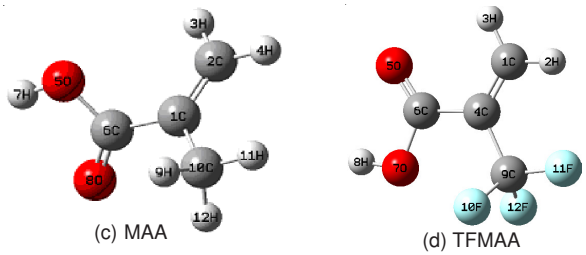
in the study and the comparison of the strength of the interaction between the template molecule and the functional monomer.

RESULTS AND DISCUSSION

Stability configurations of template molecule and functional monomer: The geometry parameters of template molecule and functional monomer are shown in Fig. 1.



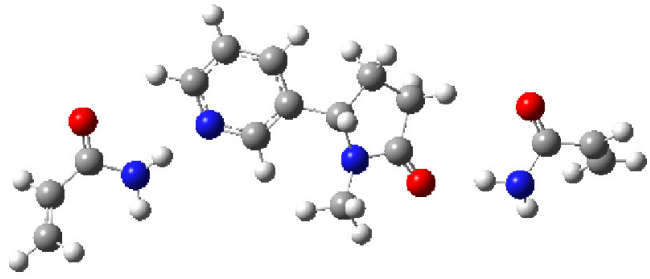
(a) COT (b) AM



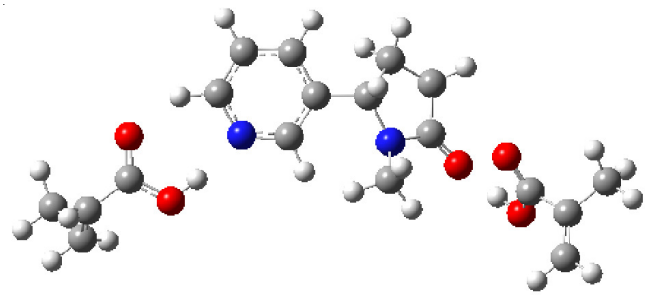
(c) MAA (d) TFMAA

Fig. 1. Conformation of COT, MAA, TFMAA and AM

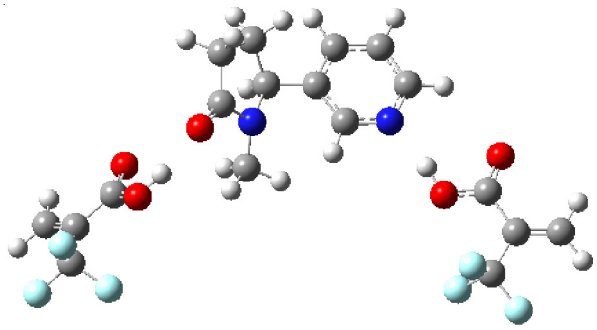
Stability configurations of molecularly imprinted polymer: The molecularly imprinted polymer of cotinine and different functional monomer were build and the principle is the lowest of binding energy. The geometry parameters are shown in Fig. 2.



(a) COT+2AM



(b) COT+2MAA



(c) COT+2TFMAA

Fig. 2. Complex formed between COT with functional monomer

Binding energy between template molecule and different functional monomer: The energies of the template molecule, different functional monomer , the precomplex and their binding energies (ΔE) were listed in Table-1.

TABLE-1
ENERGIES (E) OF THE TEMPLATE MOLECULE, FUNCTIONAL MONOMERS AND THE PRECOMPLEX AND THEIR BINDING ENERGIES (ΔE)

Conformation	E (au)	ΔE (au)	ΔE (KJ mol^{-1})
COT	0.178536	–	–
AM	0.039142	–	–
MAA	-0.038284	–	–
TFMAA	-0.292660	–	–
Complex (a)	0.250964	-0.005856	15.38138307
Complex (b)	0.092362	-0.009606	-25.23114169
Complex (c)	-0.420033	-0.013249	-34.79985387

Complex (a): COT + 2AM, Complex (b): COT + 2MAA, Complex(c): COT + 2TFMAA.

The list of the possible mode of action of molecularly imprinted polymer pre-polymerization process may occur in between the template molecule and functional monomer. The lower of ΔE, the more stable of complexes that were pre-polymerization by the template molecule and functional monomer. The functional monomer imprinting effect is stronger. So the order of the ΔE of the complexes simulated by different functional monomers with a template molecule could screening functional monomer effective and selecting the functional monomer whose imprint is better. It could reduced the time and consumption of the experimental greatly.

It can be concluded that ΔE Complex(c) < ΔE Complex(b) < ΔE Complex(a), it can be speculated that the best molecular recognition ability is by the molecularly imprinted polymer of cotinine and TFMAA, the MAA is better and the AM is the worst.

There are three F atoms in the TFMAA and their electron-withdrawing ability is stronger than the three hydrogen atoms' on the MAA, so the stability of the hydrogen bonds between TFMAA and COT is more than the hydrogen bonds between MAA and COT.

The hydrogen bonds between AM and COT are N-H···O and the hydrogen bonds between TFMAA (MAA) and COT are O-H···O, the stability of the hydrogen bonds between AM and COT is the worst than the hydrogen bonds between TFMAA (MAA) and COT, because of the electronegativity of O atom is more than the electronegativity of N atom.

Conclusion

The template molecule is cotinine (COT) and methacrylic acid (MAA), 2-(trifluoromethyl) propenoic acid (TFMAA) and acrylamide (AM) as functional monomer, respectively. The molecularly imprinted polymers are simulated between COT and different functional monomer, the binding energies (ΔE) were calculated and be compared, the lowest binding energy is TFMAA. It can be speculated that the best molecular recognition ability is by the molecularly imprinted polymer of cotinine and TFMAA. It is helpful to interpret experiment phenomena and found functional monomer selectivity.

ACKNOWLEDGEMENTS

This project was supported by the Science and Technology Projects of Hebei Province (Contract No. 10273939).

REFERENCES

1. A. Hakan, D. Nizam and O.S. Nefise, *Asian J. Chem*., **18**, 1710 (2006).
2. H.M. Jiang, S.F. Zhang and Q. Shi, *Asian J. Chem*., **23**, 3783 (2011).
3. I. Chianella, M. Lotierzo, S.A. Piletsky, I.E. Tothill, B. Chen, K. Karim and A.P.F. Turner, *Anal. Chem*., **74**, 1288 (2002).
4. E. Dinç and D. Baleanu, *Asian J. Chem*., **23**, 2377 (2011).
5. X.B. Wu, J. Xue, L.L. Zhang, N. Sun and D.J. Liu, *Asian J. Chem*., **24**, 3829 (2012).
6. W.G. Dong, M. Yan, M.L. Zhang, Z. Liu and Y.M. Li, *Anal. Chin. Acta*, **542**, 186 (2005).
7. J. Yang, Y. Hu, J.B. Cai, X.L. Zhu and Q.D. Su, *Anal. Bioanal. Chem*., **384**, 761 (2006).
8. D. Yildiz, *Toxicon*, **43**, 619 (2004).
9. J.O. Ebbert, L.C. Dale, L.M. Nirelli, D.R. Schroeder, T.P. Moyer and R.D. Hurt, *Addict. Behav.*, **29**, 349 (2004).
10. J. Yang, X.L. Zhu, J.B. Cai, Q.D. Su, Y. Gao and L. Zhang, *Chin. Chem. Lett*., **16**, 1503 (2005).