A New Synthesis of the Schiff Base Derived from 2, 3, 4-Trihydroxybenzaldehyde and 4-Aminobenzoic Acid via Airflow Grinding Technology

Lisha Zhao, Shuangqing Liu, Yanhua Cai*, Junyang Chen
Chongqing Key Laboratory of Environmental Materials & Remediation Technologies, Chongqing University of Arts and Sciences, Yongchuan-402160, P.R. China
E-mail: mci651@163.com

Abstract: Exploring a new reaction system is necessary to widen the application of supersonic speed airflow grinding technology in chemical filed. In this work, the supersonic speed airflow grinding instrument was firstly improved via adding the microwave technology. And then the improved instrument was used to try to synthesize a Schiff base derived from 2, 3, 4-trihydroxybenzaldehyde and 4-aminobenzoic acid, and the molecular structure of synthesized Schiff base was characterized by $^1$H nuclear magnetic resonance and fourier transform infrared spectrometer. Finally the geometric structure of synthesized Schiff base was optimized by DMol3 density functional theory. The relevant results showed that the airflow grinding technology was a feasible method to synthesize the Schiff base, and HOMO and LUMO of optimized Schiff base were -0.197684 eV and -0.096761 eV, respectively. Additionally, the theoretical calculation further showed that, with increasing of temperature, the entropy, heat capacity and enthalpy of Schiff base increased, but the free energy decreased.

1. Introduction

Usually, Schiff bases are synthesized via some typical methods including liquid reaction [1], grinding [2], ball mill [3], etc. However, these methods still have some inherent defects, for instances, the liquid method need to speed a very long time in completing the entire reaction; it is very difficult to realize industrial production through grinding technology; and ball mill has large energy consumption. Thus, developing a new synthesis route is very important to avoid shortages of the current methods and broaden Schiff base’s application. Supersonic speed airflow grinding technology as a traditional crushing method have been applied in food processing, mineral superfine, Chinese medicinal materials deep-processing, etc. Recently, in order to widen the application of supersonic speed airflow grinding technology and make full use of the huge energy during the process of grinding, Peng and her colleagues employed this supersonic speed airflow grinding technology to develop the chemical reaction route, and carbonate, Schiff bases, isopropylidene malonate derivative and manganese-based metal-organic frameworks had been successfully prepared [4-8]. For instance, the ultra-fine calcium carbonate with 0.5 μm was successfully prepared using this method, and the reaction was completed within only 60 min [4]. Compared to the other preparation route, this technology exhibited the higher conversion, shorter reaction time, mild conditions and simple operation [2, 4], furthermore, the reaction process is solvent-free, showing the feature of green chemistry. However, up to now, the number of compounds obtained using this technology is very limited, hence, developing more reaction systems via this
technology is very necessary to promote supersonic speed airflow grinding technology to extend to large-scale production.

In this work, the supersonic speed airflow grinding technology was further used to synthesis another Schiff base derived from 2, 3, 4-trihydroxybenzaldehyde and 4-aminobenzoic acid (TBAA), and the molecular structure of synthesized Schiff base was determined by $^1$H nuclear magnetic resonance ($^1$H NMR) and fourier transform infrared spectrometer (FT-IR). Meantime, the optimization of geometric structure of Schiff base was carried out by DMoI3 and the relevant performances were obtained.

2. Experimental section

2.1. Reagents and equipment

The chemical reagents including 2, 3, 4-trihydroxybenzaldehyde and 4-aminobenzoic acid were purchased from Chengdu Kelong Chemical Reagents Company of China. The supersonic speed airflow grinding device was improved through adding the microwave technology in our lab to activate the reactant and further increase the delivery of energy (See Figure.1).

![Figure 1: The improved supersonic speed airflow grinding device](image)

2.2. Synthesis of TBAA

The synthetic route of TBAA is shown in Figure 2. The reaction molar ratio of 2, 3, 4-trihydroxybenzaldehyde and 4-aminobenzoic acid is 1:1, and the 2, 3, 4-trihydroxybenzaldehyde and 4-aminobenzoic acid were thoroughly mixed, and this mixture was introduced into the improved supersonic speed airflow grinding device, after reacting for some time, the procudt was collected. And the detailed operational process is similar to our previous works [9].

![Figure 2: Synthetic route of TBAA](image)

2.3. Characterization of TBAA

The $^1$H NMR and FT-IR were used to demonstrate the structure of synthesized TBAA. And the DMSO was chose to be as deuterium reagent for $^1$H NMR measurement. The FT-IR measurement used KBr pellet method to prepare the testing sample, and the testing wavenumber was 400 cm$^{-1}$ to 4000 cm$^{-1}$. The DMoI3 modules of MS software performed the theoretical optimization of TBAA molecular geometric structures, and the calculation parameters were medium quality and using symmetry.

3. Results and discussion

3.1. Molecular structure of TBAA
The characterized data of TBAA including $^1$H nuclear magnetic resonance ($^1$H NMR) and fourier transform infrared spectrometer (FT-IR) are follows: $^1$H NMR δ: 8.83 (s, 1H, CH=N), 10.35 (s, 3H, Ar-OH), 12.74 (s, 1H, COOH), 6.99～7.99 (m, 6H, Ar); FT-IR υ: 3419.8 cm$^{-1}$, 1681.1 cm$^{-1}$, 1635.5 cm$^{-1}$, 1601.6 cm$^{-1}$, 1518.7 cm$^{-1}$, 1441.9 cm$^{-1}$, 1370.9 cm$^{-1}$, 1290.4 cm$^{-1}$, 1173.8 cm$^{-1}$, 1080.6 cm$^{-1}$, 847.5 cm$^{-1}$, 771.9 cm$^{-1}$. For $^1$H NMR, the single peak at δH=12.74 and 10.35 belong to the Ar-COOH and Ar-OH proton resonance peak, respectively. The single proton resonance peak of CH=N is at δH=8.83, and the multiple proton resonance peaks at δH=6.99～7.99 are attributed to the proton resonance of Ar. For FT-IR, the absorption peak at 3419.8 cm$^{-1}$ is stretching vibrations of O-H; the peak at 1681.1 cm$^{-1}$ is thought to be the stretching vibration absorption of C=O, and the peaks at 1601.6 cm$^{-1}$, 1518.7 cm$^{-1}$ and 1441.9 cm$^{-1}$ belong to the C-C characteristic absorption of benzene; the peak at 1173.8 cm$^{-1}$ is due to the stretching vibration of C-O, and the 847.5 cm$^{-1}$ and 771.9 cm$^{-1}$ are C-H vibration of hydrogen aromatics. Through the analysis of $^1$H NMR and FT-IR, the TBAA has been successfully synthesized by the supersonic speed airflow grinding technology.

3.2. Theoretical calculation for TBAA

Theoretical calculation can obtain many important structure performances [10]. Figure.3 shows the theoretical optimization result for TBAA’s geometry structure, meantime, the HOMO and LUMO are obtained. As shown in Fig.3, both the HOMO and LUMO focus on the benzene and imine, and the HOMO and LUMO are -0.197684 eV and -0.096761 eV, respectively.

Additionally, the effect of temperature on the TBAA’s thermodynamic parameters such as entropy, heat capacity, enthalpy and free energy is displayed in Fig.4. As far as the synthesized TBAA is concerned, it is clear that, with increasing of temperature, the entropy, heat capacity and enthalpy increase, whereas the free energy exhibits the opposite change trend, that is to say, an increase of temperature leads to the decrease in the free energy. It is obvious that these thermodynamic properties intrinsically depend on the TBAA itself. More in-depth experiments will be performed to verify these theoretical calculation results in a future study.
4. Conclusion
The Schiff base derived from 2, 3, 4-trihydroxybenzaldehyde and 4-aminobenzoic acid was synthesized by the supersonic speed airflow grinding technology, which confirmed that the supersonic speed airflow grinding technology was an effective way to perform the chemical reaction; and the $^1$H NMR and FT-IR further determined the structure of the synthesized Schiff base TBAA. The DMol3 optimized the geometric structure of TBAA, and the frontier orbital energy was obtained. Additionally, in contrast with the free energy, the entropy, heat capacity and enthalpy increased with increasing of temperature.

Acknowledgements
This work was supported by Foundation of Chongqing Municipal Science and Technology Commission (cstc2017shmsA20021 and cstc2019jcyj-msxmX0876), Scientific and Technological Research Program of Chongqing Municipal Education Commission (project number KJQN201801319), and Foundation of Yongchuan District (project number Ycstc, 2018cc0801).

References
[1] Cevasco, G., Thea, S. (1999) Mechanism of alkaline hydrolysis of some HO-π-COO Aracyl derivatives [J], The Journal of Organic Chemistry, 64: 5422-5426.
[2] Cai, Y.H., Peng, R.F., Ma, D.M, Chu, S.J., Zuo J. (2007) Studies on solid-state synthesis of a Schiff base derived from p-hydroxybenzaldehyde and p-aminobenzoic acid at supersonic speed airflow and low-heating temperature. Modern Chemical Industry, 27(11): 43-46. (In Chinese)
[3] Kauppa, G., Schmeyers, J., Naimi-Jamala, M.R., Zoob, H., Renb, H. (2002) Reactive milling with the Simoloyer®: environmentally benign quantitative reactions without solvents and wastes. Chemical Engineering Science, 57(5): 763-765.
[4] Cai, Y.H., Peng, R.F., Chu, S.J. (2008) Preparation of Ultra-fine Calcium Carbonate by a Solvent-free Reaction using Supersonic Airflow and Low Temperatures. South African Journal of Chemistry-Suid- Afrikaanse Tydskrif vir Chemie, 61: 112-114.
[5] Cai, Y.H., Ma, D.M., Peng, R.F., Jin, B., Chu, S.J., Zuo, J. (2007) Research on preparation of ultra-fine bar ium carbonate by supersonic airstream comm inution method. Inorganic Chemicals Industry, 39(11): 19-20. (In Chinese)
[6] Yuan, B.Q., Peng, R.F., Jin, B., Li, H.B., Chu, S.J. (2009) Solvent-free condensation reactions of aromatic aldehydes and isopropylidene malonate under supersonic speed airflow. China Powder Science and Technology, 15(6): 52-55. (In Chinese)
[7] Cai, Y.H., Peng, R.F., Chu, S.J., Yin, J.B. (2010) Synthesis of Schiff bases derived from p-aminobenzoic acid by novel solvent-free reaction using improved jet milling. Asian Journal of Chemistry, 22(8): 5835-5840.
[8] Cheng, Z., Peng, R.F., Jin, B., Wang, H.L., Chu, S.J., Zuo, J., Lu, B. (2018) Low temperature solid phase synthesis of manganese-based metal-organic frameworks by high-speed air flow method. Fine Chemicals, 35(5): 796-800. (In Chinese)

[9] Cai, Y.H., Luo, W. (2014) Preparation of Schiff base derived from 3, 4-dimethoxybenzaldehyde and p-aminobenzoic acid by supersonic speed gas impacting method. Journal of Chemistry, Volume 2014, Article ID 218376, 5 pages.

[10] Cai, Y.H. (2013) Synthesis and theoretical calculation of suberoyl chloride. Journal of Chongqing University of Arts and Sciences, 32(5): 70-72.