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Synthesis and Properties of Schiff Bases with Nitro Group by Gas Flow Crushing

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The synthesis of Schiff bases with nitro group had been achieved by low-temperature solid-state reaction using improved gas flow crushing. The structure of the synthesized compound had been characterized by FT-IR, ^{1}H NMR. The optimized geometric structure and frontier molecular orbital energy of Schiff bases with nitro was carried out by theoretical calculations using the semiempirical method PM3. The results of thermal stability of Schiff bases with nitro indicated that thermal decomposition of Schiff base was multi-step decomposition reaction and decomposition temperature significantly increased with increasing of heating rate and decomposition rate was the fastest in the second stage at all heating rate. Upon all heating rate, the onset decomposition temperature was above 160 ºC.

Key Words: Schiff base, Gas flow crushing, Thermal stability, Geometric structure.

INTRODUCTION

The research of low-temperature solid-state reaction has gained considerable momentum owing to energy problems and environmental pollution. In previous paper, we had reported that the solid-state reaction using gas flow crushing was an important technology of green chemistry and the new technology has particular advantages: mild conditions, simple operation, high yields *etc*. Schiff base is very important organic compound. In recent years, Schiff base and its derivatives have been widely used in synthesis of intermediates[1,2], biological actions[3,4], polymers[5,6] *etc*. and obtained a lot of progress. For example, Nahid *et al*[6]. reported that Schiff base derived from salicylaldehyde and 1,3-diaminopropane was subjected to polycondensation reaction with formaldehyde and piperazine in basic medium. The resin was found to form polychelates readily with Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) metal ions. All the synthesized metal-polychelates showed excellent antibacterial activities against the selected bacteria. In this paper, we synthesized Schiff bases with nitro using improved gas flow crushing. The optimized geometric structure and thermal properties of Schiff bases with nitro group were investaged.

EXPERIMENTAL

All materials used in this study were of analytical grade (AR). *p*-Nitrobenzaldehyde and *o*-nitrobenzaldehyde were purchased from Chengdu Kelong Chemical Reagents Company (Sichuan Province, China). The *p*-aminobenzoic acid was purchased from Beijing Chemical Reagents Company (Beijing, China).

The reaction equipment is improved gas flow crushing which has described in our previous paper[7].

Synthesis of Schiff bases with nitro: Schiff base was prepared as follows: *p*-aminobenzoic acid and nitrobenzaldehyde, in a 1:1 molar ratio, were mixed and the specific reaction process has described in our previous paper[8]. The product was collected and dried in a vacuum at 90 ºC (Fig. 1).

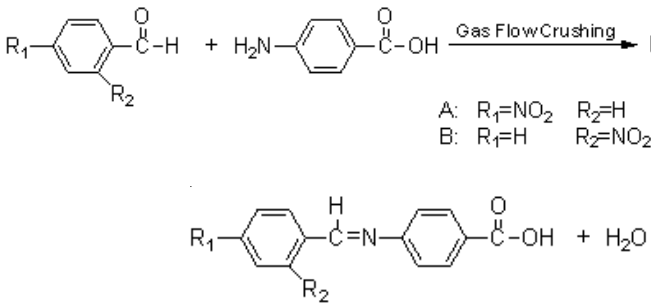


Fig. 1. Synthesis of Schiff bases with nitro

Schiff bases with nitro tests (attribute): The infrared spectra was measured on Nicolet 380 FT-IR spectrometer, in the range 4000-400 cm^{-1}. The ^{1}H nuclear magnetic resonance was recorded on Brucker AVANCE 300 spectrometers the solvent was dimethyl sulphoxide (DMSO). TGA thermal analyzer was performed using a simultaneous thermal analysis Q500 (TA instrument USA) with a heating ramp of 2.5, 5.0, 10, 20 ºC/min under nitrogen flow (60 mL/min) from room temperature to 500 ºC.

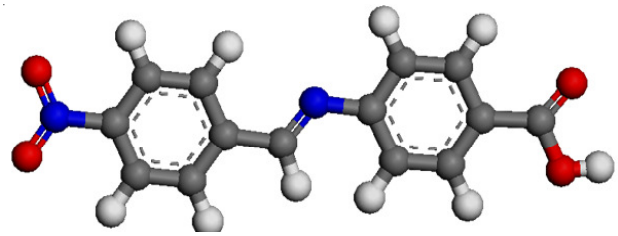
RESULTS AND DISCUSSION

Structures of compounds

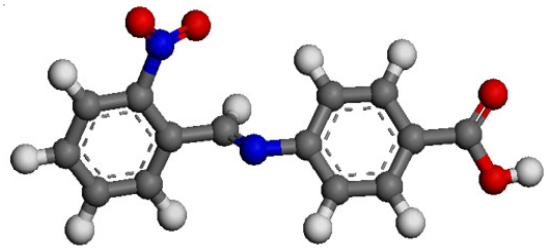
Schiff base derived from *p*-nitrobenzaldehyde and *p*-aminobenzoic acid (compound A): IR (KBr, ν_{max}, cm^{-1}): 3425.5, 1681.2, 1629.8, 1601, 1589.5, 1572.2, 1515.8, 1424.8, 1343.2, 856.8, 775.4; ^{1}H NMR (DMSO, 300 MHz, ppm) δ: 8.82 (s, 1H, CH=N), 12.78 (s, 1H, COOH), 7.38-8.39 (m, 8H, Ar).

Schiff base derived from *o*-nitrobenzaldehyde and *p*-aminobenzoic acid (compound B): IR (KBr, ν_{max}, cm^{-1}): 3450.5, 1669.7, 1631.7, 1598.8, 1573.4, 1517.7, 1427.2, 1349.3, 860.6, 772.1; ^{1}H NMR (DMSO, 300 MHz, ppm) δ: 8.87 (s, 1H, CH=N), 12.62 (s, 1H, COOH), 7.33-8.18 (m, 8H, Ar).

Geometry optimization of Schiff bases with nitro group: In order to investigate the structure of Schiff bases with nitro group, the optimized geometric structure of Schiff bases with nitro group was carried out by the theoretical calculation and the calculations were performed with the program VAMP using the semiempirical method PM3. The optimized geometry structure of Schiff bases with nitro including compound A and B is shown in Fig. 2 and the HOMO and LUMO of compound A and B are shown in Fig. 3 and the values of the HOMO and LUMO of compound A and B are -9.827 eV, -1.813 eV and -9.733 eV, -1.187 eV, respectively. The difference of the frontier molecular orbital energy between compound A and B may result from the position of nitro, which also may indicate different properties between compound A and B.

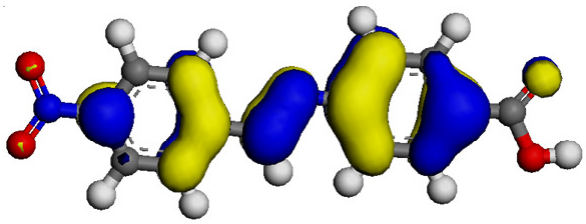


(a)

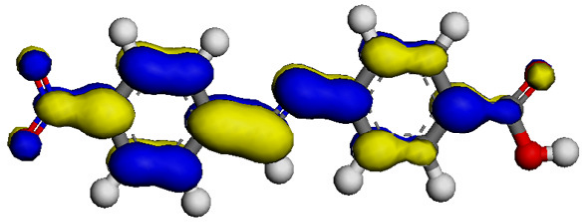


(b)

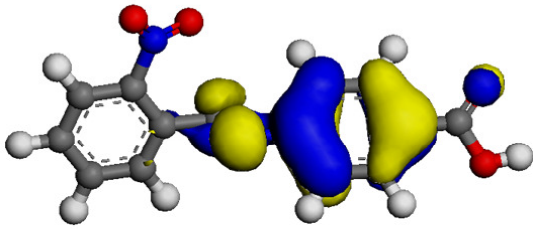
Fig. 2. Optimized geometric structure of Schiff bases with nitro



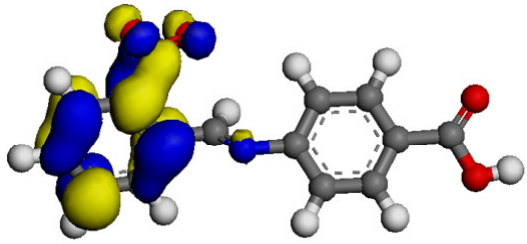
(a) HOMO



(a) LUMO



(b) HOMO



(b) LUMO

Fig. 3. HOMO and LUMO of Schiff bases with nitro

Thermal stability of Schiff bases with nitro group: Thermal stability of Schiff bases with nitro group is very important for wide application of Schiff bases with nitro group, thus, we investigate the thermal stability of Schiff base derived from *o*-nitrobenzaldehyde and *p*-aminobenzoic acid. Fig. 4 shows the TGA curves of Schiff base derived from *o*-nitrobenzaldehyde and *p*-aminobenzoic acid with a heating rate of 2.5, 5, 10, 20 ºC/min under nitrogen flow from room temperature to 500 ºC. As seen in Fig. 4, there existed four break points on TGA curves, which indicate that the thermal decomposition of Schiff base derived from *o*-nitrobenzaldehyde and *p*-aminobenzoic acid is multi-step decomposition reaction and that the decomposition rate of Schiff base derived from *o*-nitrobenzaldehyde and *p*-aminobenzoic acid decomposes is the fastest in the second stage at all heating rates. Meantime, decomposition temperature significantly increased with increasing of heating rate, the reason is that rapid heating rate make decomposition of Schiff bases with nitro group not achieve at set temperature, at the same time, the temperature has get into the following set temperature, resulting in decomposition achieving at higher temperature. Upon all heating rate, the onset decomposition temperature is above 160 ºC, which indicates that Schiff base derived from *o*-nitrobenzaldehyde and *p*-aminobenzoic acid shows good thermal stability under 160 ºC.

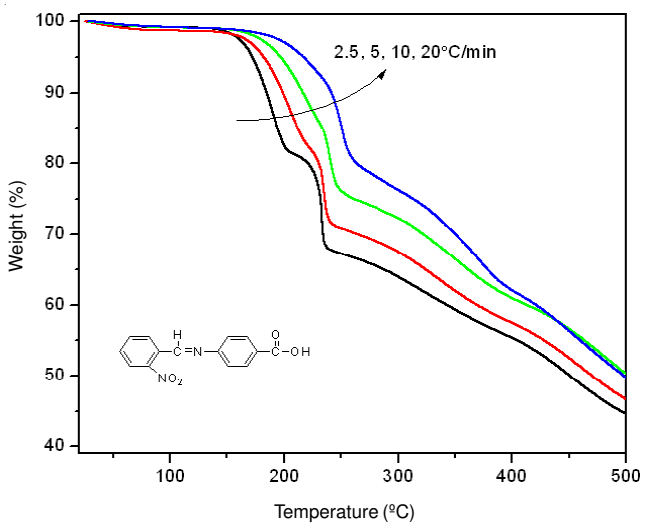


Fig. 4

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