

Optimization of the Process Parameters for the Synthesis of High Purity 4,6-Dinitrobenzofuroxan (4,6-DNBF)

Jin-Shuh Li,^{*,[a]} Fu-Jen Chen,^[b] Hsiu-Wen Yang,^[c] and Kai-Tai Lu^[a]

Abstract: 4,6-Dinitrobenzofuroxan (4,6-DNBF) is explosive and can also be used as an important intermediate in the synthesis of other explosives. It can be prepared by nitrating benzofuroxan (BF) with mixed nitric/sulfuric acid. However, little is known about its optimal synthesis parameters in the preparation process. In this study, Taguchi's experimental design method was used to improve the yield of 4,6-DNBF. A L_9 (3^4) orthogonal array with four control factors and three levels of each control factor was used to design nine experimental conditions. The experimental data were transformed into a signal-to-noise (S/N) ratio to analyze and evaluate the experimental conditions of the optimal parameter combination for the maximum yield of 4,6-DNBF. The verification results indicated that the optimal

synthesis parameters were as follows: nitration temperature was 40 °C, mass ratio of BF to H_2SO_4 was 1:15, volume ratio of HNO_3 to H_2SO_4 was 1:2.0 and reaction time was 4 hours, and then the maximum crude yield and the maximum yield after purification could reach 73.2% and 49.0%, respectively. Furthermore, the synthesized 4,6-DNBF was identified by scanning electron microscopy (SEM), nuclear magnetic resonance spectrometer (NMR), Fourier transform infrared spectrometer (FTIR), elemental analyzer (EA), ultraviolet-visible spectrometer (UV-Vis) and thermogravimetry-differential scanning calorimetry (TG-DSC), and its sensitivity was determined using BAM fallhammer, BAM friction tester, and electrostatic spark sensitivity tester.

Keywords: 4,6-DNBF · Maximum yield · Optimal synthesis parameters · Taguchi design method

1 Introduction

Primary explosives are used to initiate main (secondary) explosives, propellants, and pyrotechnics, and are usually contained in detonators or ignition caps. Traditional primary explosives are often heavy metal salts, especially salts of lead, such as lead azide (LA) and lead styphnate (LS), which can cause environmental pollution problems, particularly in shooting ranges. Therefore, a number of heterocyclic compounds are being developed to replace lead-containing primary explosives [1]. 4,6-Dinitrobenzofuroxan (4,6-DNBF) possesses explosive properties and can be used as a primary explosive and a primer mixture. 4,6-DNBF is not particularly sensitive, but it is acidic and easily reacts with alkali metal carbonates to form δ Meisenheimer complex salts [2–3]. Therefore, it can also be used as an important intermediate in the synthesis of other energetic materials, such as potassium salt of 4,6-DNBF (KDNBF), which is being used in cap compositions [4–6]. Potassium is generally considered an innocuous and much safer alternative to lead. Therefore, KDNBF has been used as a suitable green primary explosive alternative to LA and LS [7].

4,6-DNBF was first prepared in 1892. The structure of the furoxan ring has not been known for a long time. Until the 1960s, the furoxans were assumed to be o-dinitroso compounds. The structure of benzofuroxan was later discovered and confirmed by X-ray diffraction [8–9]. 4,6-DNBF can be prepared by nitrating benzofuroxan (BF) with mixed

nitric/sulfuric acid or by reacting picryl chloride (PicCl) with sodium azide and heating the resulting picryl azide (PicAz) in an inert solvent [10]. These two methods are easy to implement and the separation of product from the reaction medium is straightforward. One of the problems associated with the preparation of 4,6-DNBF by the nitration of BF is that the crude yield and the yield after purification are only about 63% and 44%, respectively. In addition, Spear et al. [11] have reported that less than 1% of 5,6-DNBF isomer is present in the nitrated product. Another method for preparing 4,6-DNBF by reacting PicCl with sodium azide also has a major drawback in that the intermediate PicAz must be isolated and then heated under reflux in xylene to obtain 4,6-DNBF, but PicAz is a powerful explosive more sensi-

[a] J.-S. Li, K.-T. Lu

Department of Chemical and Materials Engineering, Chung Cheng Institute of Technology, National Defense University, 33551, Taoyuan, Taiwan, ROC
Tel.: +886-3-3891716
Fax: +886-3-3892494
*e-mail: lijinsuh@gmail.com

[b] F.-J. Chen

Master Program of Chemical Engineering, Chung Cheng Institute of Technology, National Defense University, 33551, Taoyuan, Taiwan, ROC

[c] H.-W. Yang

System Manufacturing Center, National Chung Shan Institute of Science and Technology, 23742, New Taipei, Taiwan, ROC

tive than tetryl [12]. The yield after purification can reach 80%. Although the synthesis of 4,6-DNBF from PicCl gives a significantly higher yield, the cost of PicCl is more than 2.5 times that of BF. Furthermore, BF is commercially available, but PicCl is a regulated explosive material. From the above comparison, it can be found that the preparation of 4,6-DNBF by the nitration of BF may be a better choice. However, it is indeed a challenge to further improve the yield of 4,6-DNBF in the preparation process.

This study mainly explored the optimal synthesis parameters to improve the yield of 4,6-DNBF. It is synthesized by nitration of BF with mixed nitric/sulfuric acid. Taguchi's experimental design method was used to design the experimental conditions. Four control factors were selected, including nitration temperature, a mass ratio of BF to H_2SO_4 , a volume ratio of HNO_3 to H_2SO_4 and reaction time, each at three levels. These four factors were assigned to an $L_9(3^4)$ orthogonal array containing nine experimental conditions. The experimental data were used to analyze and evaluate the experimental conditions with optimal parameters combination for the maximum yield of 4,6-DNBF. Furthermore, the synthesized 4,6-DNBF was identified by means of scanning electron microscopy (SEM), nuclear magnetic resonance spectrometer (NMR), Fourier transform infrared spectrometer (FTIR), elemental analyzer (EA), ultraviolet-visible spectrometer (UV-Vis) and thermogravimetry-differential scanning calorimetry (TG-DSC), and its sensitivity was determined using BAM fallhammer, BAM friction tester, and electrostatic spark sensitivity tester.

2 Experimental

2.1 Materials

Benzofuroxan (BF, 98%) was reagent grade and purchased from Sigma-Aldrich. Fuming nitric acid (HNO_3 , 98%) and fuming sulfuric acid (H_2SO_4 , 20% free SO_3 basis) were reagent grade and purchased from Merck. Deionized water was used in washing and filtering processes. Ethanol ($\text{C}_2\text{H}_5\text{OH}$, 99.9%) was purchased from Sigma-Aldrich and used as a solvent in the cooling recrystallization process.

2.2 Design of Experimental Conditions

Taguchi method is one of the most widely used design methods [13,14], which is making use of an orthogonal array from the experimental design to study more variables in a minimal number of experiments. An $L_9(3^4)$ orthogonal array with four control factors and three levels had been referred to in the literature [15,16], which was used to design the experimental conditions in this study. Four control factors were selected, including nitration temperature, a mass ratio of BF to H_2SO_4 , a volume ratio of HNO_3 to H_2SO_4 and reaction time, each at three levels, as shown in Table 1. The

Table 1. The control factors and levels of the Taguchi experiments.

Control factor	Level		
	1	2	3
A. Nitration temperature ($^{\circ}\text{C}$)	30	35	40
B. Mass ratio of BF to H_2SO_4	1:10	1:15	1:20
C. Volume ratio of HNO_3 to H_2SO_4	1:1.5	1:2.0	1:2.5
D. Reaction time (hours)	2	3	4

above four factors were assigned to the $L_9(3^4)$ orthogonal array containing nine experimental formulas as shown in Table 2.

2.3 Apparatus and Procedures for Synthesis of 4,6-DNBF

4,6-DNBF was prepared by nitrating benzofuroxan (BF) with mixed nitric/sulfuric acid. Firstly, 5.0 grams of BF and the required amount (50, 75 or 100 grams) of H_2SO_4 were brought together in a double-jacketed glass vessel of about 250 ml capacity, which was stirred and maintained at less than 5°C by a circulating water bath with an accuracy of $\pm 0.3^{\circ}\text{C}$. In addition, 30 ml of mixed acid solution with the required volume ratio of HNO_3 to H_2SO_4 (1:1.5, 1:2.0 or 1:2.5) was prepared by adding H_2SO_4 to HNO_3 in another double-jacketed glass vessel of about 50 ml capacity, which was stirred and maintained at less than 25°C by a circulating water bath. Afterward, the mixed acid solution was slowly dropped into the double-jacketed glass vessel with BF solution. During the addition process, the temperature of the solution was maintained at less than 5°C . After the addition, the mixed solution was warmed to a set temperature (30, 35 or 40°C) and continuously stirred for a set time (2, 3 or 4 h). Finally, the mixed solution was poured into a 750 ml beaker containing 500 ml of ice water and stirred with a magnetic stirrer for 3 min. The precipitate of 4,6-DNBF was collected by filtering and washed with de-

Table 2. The $L_9(3^4)$ orthogonal array of the Taguchi experiments.

Exp. No.	Nitration temperature ($^{\circ}\text{C}$)	Mass ratio of BF to H_2SO_4	Volume ratio of HNO_3 to H_2SO_4	Reaction time (hours)
A1	30	1:10	1:1.5	2
A2	30	1:15	1:2.0	3
A3	30	1:20	1:2.5	4
A4	35	1:10	1:2.0	4
A5	35	1:15	1:2.5	2
A6	35	1:20	1:1.5	3
A7	40	1:10	1:2.5	3
A8	40	1:15	1:1.5	4
A9	40	1:20	1:2.0	2

ionized water several times, and then dried at 50 °C for 12 hours in a vacuum oven. Furthermore, the recrystallization process was carried out using ethanol as a solvent to further purify 4,6-DNBF. The schematic diagram of the experimental procedure is shown in Figure 1.

The synthesized 4,6-DNBF was identified by means of scanning electron microscopy (SEM, Hitachi S-3000H), nuclear magnetic resonance spectrometer (NMR, Bruker AVIII 500 MHz), Fourier transform infrared spectrometer (FTIR, PerkinElmer Spectrum 100), elemental analyzer (EA, Elementar vario EL cube), ultraviolet-visible spectrometer (UV-Vis, ChromTech CT-8600) and thermogravimetry-differential scanning calorimetry (TG-DSC, Netzsch STA 449 F3). SEM was used to observe the morphology and size of the synthesized product. ^1H -NMR, ^{13}C -NMR, and ^{15}N -NMR were used to determine the types and amount of hydrogen, carbon and nitrogen atoms present in the molecule, respectively, and confirm the structure of the synthesized product. Dimethyl sulfoxide- d_6 (DMSO- d_6) was used as the solvent in NMR experiments because of its good solubilizing ability for 4,6-DNBF. FTIR was used to analyze the functional group of the synthesized product in the 3500–500 cm^{-1} region with a spectral resolution of 4 cm^{-1} . EA was used to determine carbon (C), hydrogen (H), nitrogen (N) and oxygen (O) contents of the synthesized product and confirm the desired product. UV-Vis was used to measure the absorption spectrum of the synthesized product at 25 °C. Simultaneous TG-DSC measurements were carried out in an argon atmosphere at a heating rate of 10 °C min^{-1} using the sample weight in the range of 0.5–1.0 mg to study the thermal properties of the synthesized product.

2.4 Sensitivity Test

The impact sensitivity of the synthesized 4,6-DNBF powder was determined by the BAM fallhammer (Reichel & Partner GmbH). The test sample was placed in a sample cell consisting of two co-axial steel cylinders, which was already in the locating ring on the intermediate anvil. The upper steel cylinder was set to be 1 mm above the lower cylinder and was held in that position by means of an O ring. When the sample cell was properly positioned, the drop-weight was released and the impact result was observed. In addition, the Bruceton method [17] was used to evaluate the impact sensitivity, which was based on a statistical analysis by determining the drop height (H_{50}) at which there was a 50% probability of obtaining an ignition. Each sample was tested utilizing a 2.0 kg drop-weight for 30 times to obtain a H_{50} . The impact energy (E_{50}) was calculated using the formula $E_{50}(\text{Joule}) = mgH_{50}$, where m is drop-weight mass [kg], g is the acceleration due to gravity [ms^{-2}], and H_{50} is drop height [m].

The friction sensitivity of the synthesized 4,6-DNBF powder was determined by the BAM friction tester (Reichel & Partner GmbH). The test sample was placed between two ceramic pieces of controlled friction coefficient. A weight was applied to the upper ceramic unit and the lower ceramic unit was scrapped under it. The friction sensitivity is defined as the smallest load at which an audible or visible decomposition reaction is obtained from at least one out of six trials. The measurement range of the friction load was from 0.5 to 360 N.

The electrostatic spark sensitivity of the synthesized 4,6-DNBF powder was determined by the small-scale electrostatic spark sensitivity tester (OZM Research X SPARK 10). The measurement of the electrostatic spark sensitivity was based on the principle of capacitive discharge driven

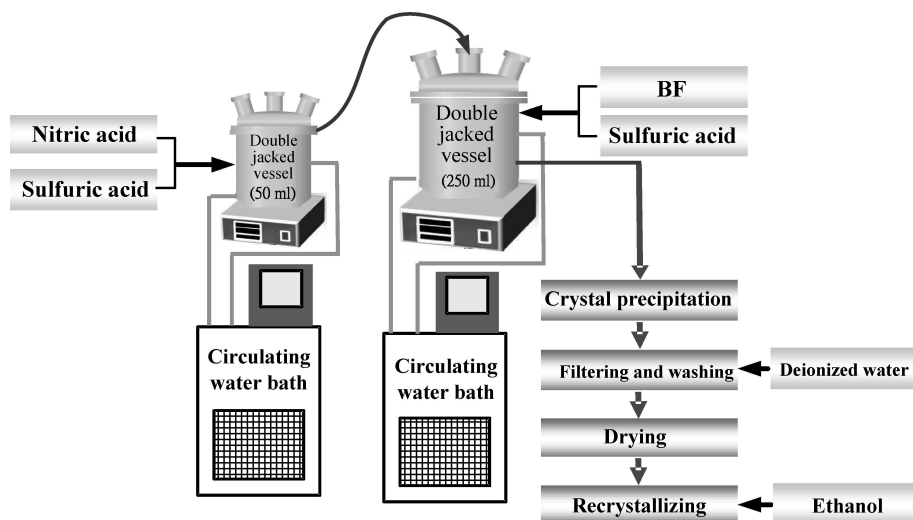


Figure 1. Schematic diagram of the experimental procedure.

Table 3. Experimental results of Taguchi's orthogonal array for yield of 4,6-DNBF.

Exp. No.	A1	A2	A3	A4	A5	A6	A7	A8	A9
Crude amount (g)	5.87	5.97	5.89	5.91	6.25	5.87	6.06	5.87	6.14
Crude yield (%)	70.6	71.8	70.9	71.1	75.2	70.6	72.9	70.6	73.9
Amount after purification (g)	3.52	3.72	3.52	3.76	3.47	3.43	3.58	3.71	3.71
Yield after purification (%)	42.3	44.8	42.4	45.2	41.8	41.3	43.1	44.6	44.6

Table 4. Range and contribution rank of each factor for yield of 4,6-DNBF (unit: %).

Level	Control factors			
	A (Nitration temperature)	B (Mass ratio of BF to H ₂ SO ₄)	C (Volume ratio of HNO ₃ to H ₂ SO ₄)	D (Reaction time)
1	43.17	43.53	42.73	42.90
2	42.77	43.73	44.87	43.07
3	44.10	42.77	42.43	44.07
Range	1.33	0.96	2.44	1.17
Rank	2	4	1	3

through the granular bed of the test sample. The selected capacitor was charged by the built-in high voltage power supply and electric discharge of the desired energy was generated. The discharge was carried by the leading cable to the spark gap, where the spark was formed and affected the test sample which was placed in between the two electrodes. If the test sample had flash, spark, burn, odor or noise other than instrument noise, it should be tested at the next lower level until 20 consecutive failures were reported. The discharge energy was calculated using the formula $E(\text{Joule}) = 1/2 CV^2$, where C is capacitance [μF], and V is voltage [kV]. The measured discharge energy ranged from 25 μJ to 25 J and the sample weight used was about 10 mg.

3 Results and Discussion

3.1 Analysis and Verification of Taguchi Experiments

A series of synthesis experiments of 4,6-DNBF with different operating parameters such as nitration temperature, a mass ratio of BF to H₂SO₄, a volume ratio of HNO₃ to H₂SO₄ and reaction time were carried out, and then the effects of operating parameters on the yield of 4,6-DNBF were examined. The experimental results of L₉ (3⁴) orthogonal array are listed in Table 3. The obtained experimental results were transformed into a signal-to-noise (S/N) ratio using Taguchi method. The S/N ratio was used as the measure of the effect of noise factors on the target characteristics [18]. The yield of 4,6-DNBF was chosen as the quality characteristic in this study. The analysis of yield used larger-the-better type, the larger value represented higher yield, as well

as better quality characteristics. The range and contribution rank of each factor for the yield of 4,6-DNBF are shown in Table 4. In the table, the target values of different levels on each factor are the arithmetic average of target values corresponding to each level. The range is the difference between maximum and minimum of the target values on each factor and the rank represents the order of effect of each factor on the quality characteristic [18]. Figure 2 shows the trend of parameter influence for four factors. In the figure, levels A3, B2, C2, and D3 have the largest value of yield for the factors nitration temperature, a mass ratio of BF to H₂SO₄, a volume ratio of HNO₃ to H₂SO₄ and reaction time, respectively.

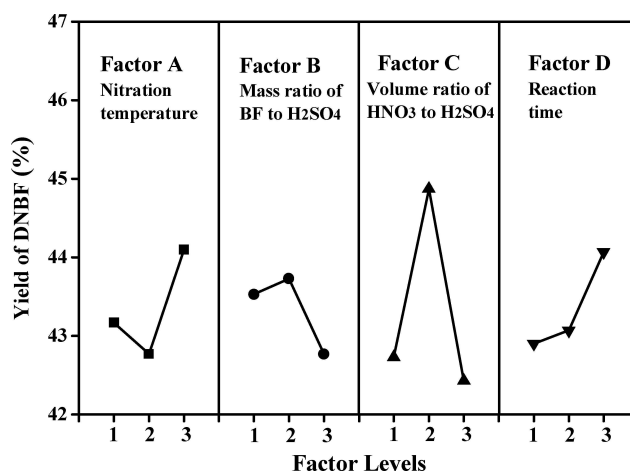
**Figure 2.** The trend of parameter influence for four factors on yield of 4,6-DNBF.

Table 5. Results of confirmation experiments.

Optimal parameter combinations	Exp. No.	Crude amount (g)	Crude yield (%)	Amount after purification (g)	Yield after purification (%)
A3B2C2D3	1	6.04	72.7	4.04	48.7
	2	6.23	75.0	4.14	49.9
	3	5.98	72.0	4.01	48.3
	Average	6.08	73.2	4.06	49.0
	value				

From the above analysis, the maximum value of yield may be found on the condition that nitration temperature is 40 °C, a mass ratio of BF to H₂SO₄ is 1:15, a volume ratio of HNO₃ to H₂SO₄ is 1:2.0 and reaction time is 4 hours. It is also observed that the order of effect of each factor on this quality characteristic is the volume ratio of HNO₃ to H₂SO₄ > nitration temperature > reaction time > mass ratio of BF to H₂SO₄. The volume ratio of HNO₃ to H₂SO₄ (factor C) has the greatest influence.

Additional confirmation experiments were performed to verify the effectiveness of the optimal parameters identified with the Taguchi method. The optimal design factor was the A3B2 C2D3 parameter combination for a yield of 4,6-DNBF.

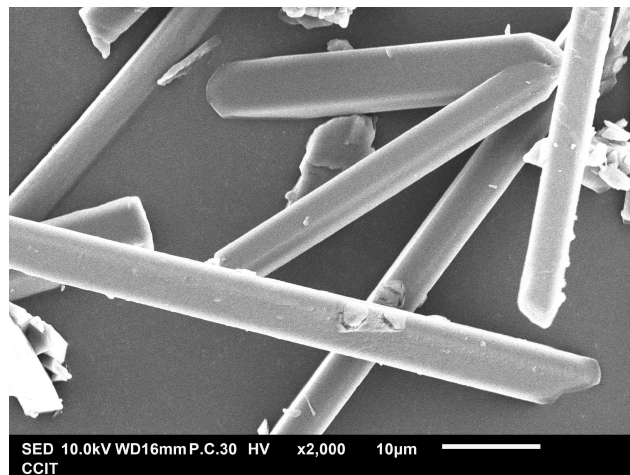
Table 5 gives the results of the confirmation experiment. This experiment was run three times under the same test condition and the averaged value was obtained. The experimental result indicates that the A3B2C2D3 parameter combination produces a larger yield of 4,6-DNBF than the other combinations tested. Taguchi method is successful in predicting this optimal parameter combination in order to obtain the maximum yield. In this way, the maximum crude yield and the maximum yield after purification of 4,6-DNBF can reach 73.2% and 49.0%, respectively.

3.2 Identification of Synthesized Products

The morphology and size of the synthesized product crystals were observed by SEM. Figure 3 shows the SEM image of synthesized 4,6-DNBF powder under the operating condition of the optimal parameter combination (A3B2 C2D3). As can be seen from Figure 3, the synthesized 4,6-DNBF powder has a needle-like morphology.

3.2.1 ¹H-NMR, ¹³C-NMR and ¹⁵N-NMR Spectrum

The structure of the synthesized product was confirmed by NMR. Figures 4–6 show the ¹H-NMR, ¹³C-NMR and ¹⁵N-NMR spectra of synthesized 4,6-DNBF in DMSO-d₆. ¹H-NMR spectrum shows two signals at 8.9 (H5) and 9.2 (H7) ppm, which correspond to the hydrogen atoms in the benzene ring. The other two signals at 2.5 and 3.5 ppm are attributed to

**Figure 3.** The synthesized 4,6-DNBF powder under the operating condition of A3B2C2D3 parameter combination.

DMSO-d₆ solvent and H₂O, respectively. ¹³C-NMR spectrum shows six signals at 116.7 (C8), 120.9 (C7), 126.6 (C5), 136.5 (C4), 144.7 (C6) and 145.0 (C9) ppm in the region of 116–145 ppm, which correspond to the carbon atoms in the benzene ring. The other signals in the region of 39–40 ppm are attributed to DMSO-d₆ solvent. In addition, ¹⁵N-NMR spectrum shows four signals at 359.5 (N1), 361.8 (N10), 363.8 (N11) and 375.5 (N3) ppm, which correspond to the nitrogen atoms in the molecule. The above NMR analysis can be used to confirm that the synthesized product is 4,6-DNBF. Terrier et al. [19] have also reported the same results in their study.

3.2.2 FTIR Spectrum

The functional group of the synthesized product was analyzed by FTIR. Figure 7 shows the FTIR spectrum of synthesized 4,6-DNBF powder. The aromatic C=C stretching is observed at 1450, 1521, 1556 and 1600 cm⁻¹, indicating the presence of a benzene ring structure. In addition, Ar–H stretching is found at 3079 cm⁻¹, Ar–NO₂ symmetric and asymmetric stretchings are respectively found at 1328 and 1534 cm⁻¹, and –ONO stretching is found at 1566 and 1628 cm⁻¹. These analysis results are similar to the report of

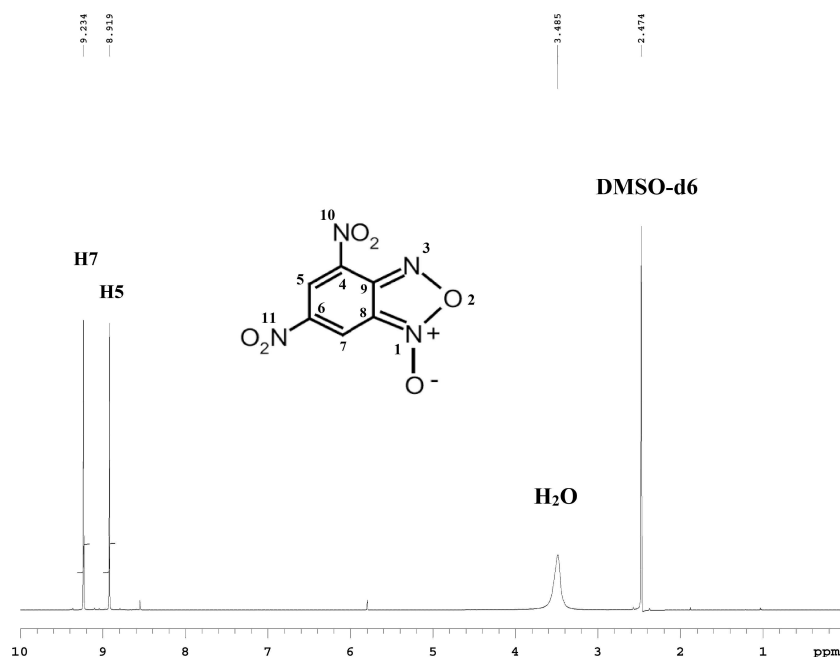


Figure 4. ^1H -NMR spectrum of synthesized 4,6-DNBF in DMSO-d_6 .

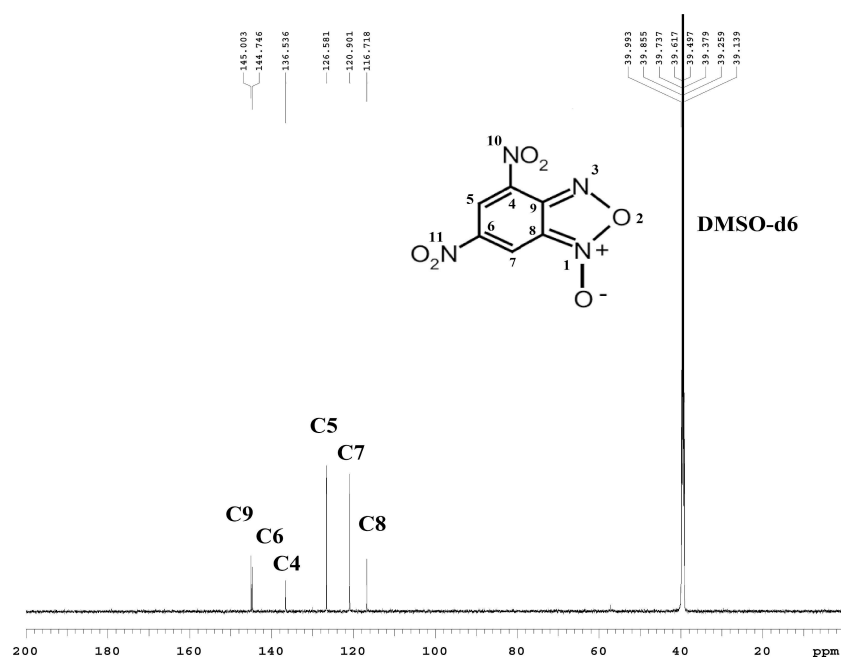


Figure 5. ^{13}C -NMR spectrum of synthesized 4,6-DNBF in DMSO-d_6 .

Sarlauskas et al. [20]. Therefore, the FTIR spectrum can further verify that the synthesized product is 4,6-DNBF.

3.2.3 EA Analysis

The elemental composition of the synthesized product was analyzed by EA. The experiment was run three times and the average value of each element content was calculated as shown in Table 6. The analysis result shows that the synthesized 4,6-DNBF contains 31.87% carbon, 1.04% hydro-

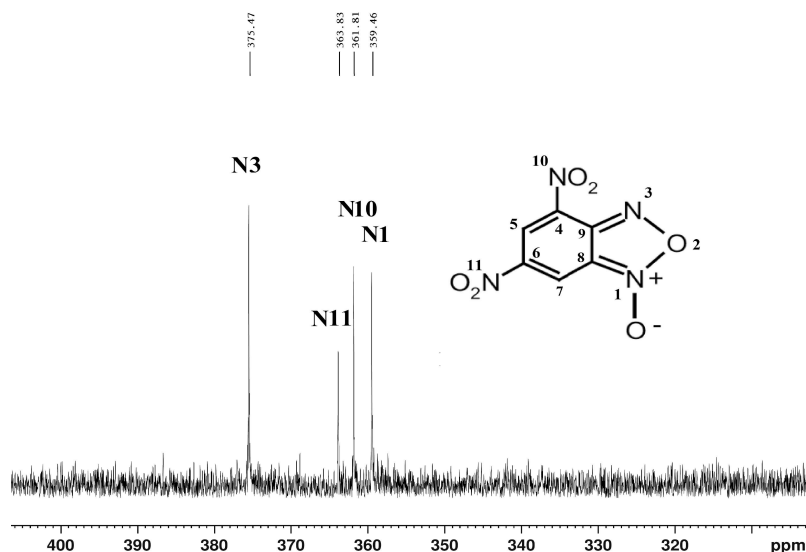


Figure 6. ^{15}N -NMR spectrum of synthesized 4,6-DNBF in DMSO-d_6 .

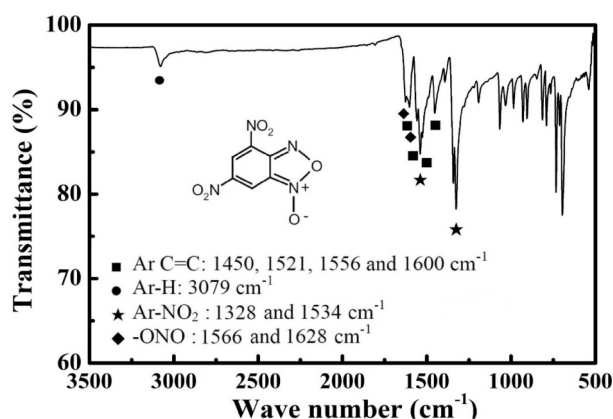


Figure 7. FTIR spectrum of synthesized 4,6-DNBF powder.

gen, 24.43% nitrogen and 42.66% oxygen, which are very close to the theoretical values of 4,6-DNBF composition. Among them, the hydrogen and oxygen contents are slightly higher in the synthesized product, possibly due to the presence of moisture from the atmosphere.

3.2.4 UV-Vis Spectrum

The absorption spectrum of the synthesized product was measured by UV-Vis. Figure 8 shows the UV-Vis spectrum of synthesized 4,6-DNBF in acetonitrile. As can be seen from Figure 8, it is characterized by a maximum absorbance at 418 nm ($\lambda_{\text{max}} = 418 \text{ nm}$) in the 300–600 nm region. Asghar [21] has also reported the same experimental result.

3.2.5 TG-DSC Thermogram

The thermal properties of the synthesized product were studied by simultaneous TG-DSC analysis. Figure 9 shows the TG-DSC curves of synthesized 4,6-DNBF powder. It is found that the DSC curve exhibits an endothermic peak at around 172°C , while the TG curve indicates no weight change at this temperature. Therefore, this peak can be concluded due to the melting behavior of 4,6-DNBF. It is consistent with the melting temperature of 4,6-DNBF. In addition, the DSC curve also shows a weak exothermic peak at around 204°C and an endothermic peak at around 246°C after the melting point, these two peaks can be reasonably attributed to the decomposition of 4,6-DNBF and the gas-

Table 6. Elemental analysis of synthesized 4,6-DNBF.

Element	Molecular formula $\text{C}_6\text{H}_2\text{N}_4\text{O}_6$ (Molecular weight 226.1 g/mol)				Theoretical value
	Test 1	Test 2	Test 3	Average value	
C (wt.%)	31.82	31.90	31.89	31.87	31.87
H (wt.%)	1.10	1.03	0.98	1.04	0.89
N (wt.%)	24.33	24.46	24.51	24.43	24.78
O (wt.%)	42.75	42.61	42.62	42.66	42.46

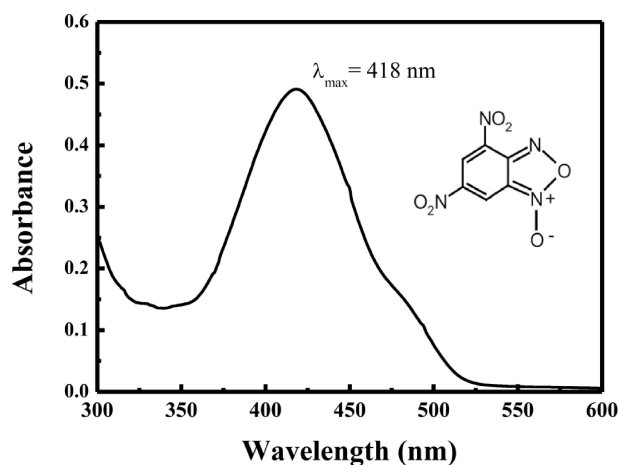


Figure 8. UV-Vis spectrum of synthesized 4,6-DNBF in acetonitrile.

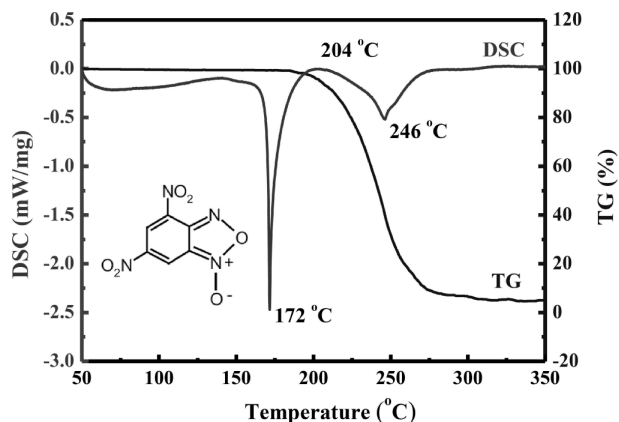


Figure 9. TG-DSC curves of synthesized 4,6-DNBF powder.

ification of decomposition products, respectively, because the TG curve shows continuous weight loss in these two stages.

3.3 Measurement of Sensitivity

The impact sensitivity, friction sensitivity and electrostatic spark sensitivity of the synthesized 4,6-DNBF powder were determined by BAM fallhammer, BAM friction tester, and electrostatic spark sensitivity tester, respectively. Each experiment was run three times and the average value was calculated as shown in Table 7. The impact sensitivity (E_{50}), friction sensitivity and electrostatic spark sensitivity are 3.33 J, 110 N and 1.17 J, respectively. It is found that the 4,6-DNBF powder exhibits the sensitivity characteristics of sensitive secondary explosives such as RDX, tetryl, and PETN. It can be induced to detonate by the strong shock from detonating lead azide, but the power output appears to be less than RDX.

Table 7. Sensitivity test results of 4,6-DNBF.

Exp. No.	Impact sensitivity H_{50} (cm)	E_{50} (J)	Friction sensitivity (N)	Electrostatic spark sensitivity (J)
1	17	3.33	108	1.00
2	16	3.14	112	1.25
3	18	3.53	112	1.25
Average value	17	3.33	110	1.17

4 Conclusion

This study successfully used the Taguchi's experimental design method to obtain the experimental condition of optimal parameter combination to further improve the yield of 4,6-DNBF. The optimal synthesis parameters were as follows: nitration temperature was 40 °C, mass ratio of BF to H_2SO_4 was 1:15, volume ratio of HNO_3 to H_2SO_4 was 1:2.0 and reaction time was 4 hours, and then the maximum crude yield and the maximum yield after purification could reach 73.2% and 49.0%, respectively. In addition, the synthesized 4,6-DNBF powder had high purity, which had been confirmed by NMR, FTIR, EA, UV-Vis and TG-DSC analyses. The impact sensitivity, friction sensitivity and electrostatic spark sensitivity of the synthesized 4,6-DNBF powder are 3.33 J, 110 N and 1.17 J, respectively. Its sensitivity characteristics are similar to sensitive secondary explosives such as RDX, tetryl, and PETN, but the power output appears to be less than RDX.

Acknowledgements

This research was financially supported by the System Manufacturing Center, National Chung Shan Institute of Science and Technology, R.O.C. under grant number of YR08112P092PE-CS.

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Manuscript received: December 12, 2019

Revised manuscript received: January 16, 2020

Version of record online: March 18, 2020