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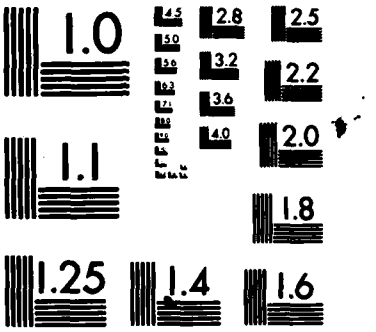

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AD-A171 389

Improved Synthesis of 7-Amino-4,6-Dinitrobenzofuroxan (ADNBF)

by
W. P. Norris
Research Department

MAY 1986

NAVAL WEAPONS CENTER
CHINA LAKE, CA 93555-6001

Naval Weapons Center

FOREWORD

A simple high-yield synthesis for 7-amino-4,6-dinitrobenzofuroxan (ADNBF) has been developed. ADNBF is an insensitive, high-density, high explosive with calculated explosive power slightly greater than 1,3,5-triamino-2,4,6-trinitrobenzene (TATB). Improved synthesis makes ADNBF available for scale-up and application to weapon systems requiring insensitive high-energy material.

The work was performed with exploratory development funding, Program Element Number 62633N, Project Number RS33337, Task Number R33337, and Work Unit Number 132120. This report has been reviewed for technical accuracy by R. A. Hollins and R. A. Henry.

Approved by
R. L. DERR, Head
Research Department
9 May 1986

Under authority of
K. A. DICKERSON
Capt., USN
Commander

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An improved synthesis of insensitive, high-density, high-explosive, 7-amino-4,6-dinitrobenzofuroxan (ADNBF) is reported. Treatment of 2,3,4,6-tetranitroaniline with sodium azide in acetic acid leads to an isolated 96% yield of high-purity ADNBF. 2,3,4,6-Tetranitroaniline is readily prepared from inexpensive m-nitroaniline by direct nitration.

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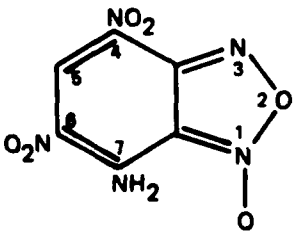
CONTENTS

INTRODUCTION

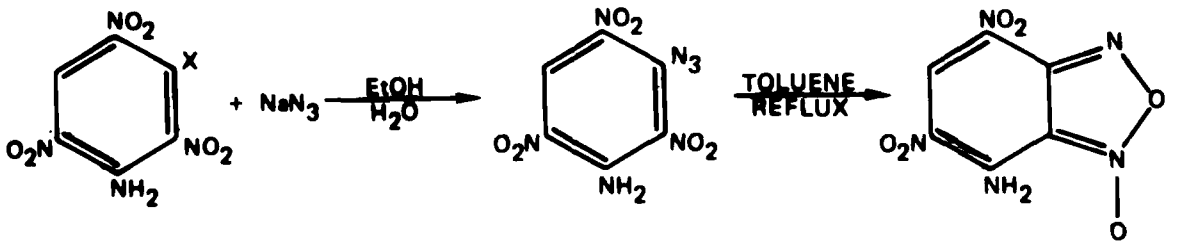
This report describes an improved synthesis for 7-amino-4,6-dinitrobenzofuroxan (ADNBF), an insensitive, high-density, high explosive (Reference 1). The intermediate, 3-azido-2,4,6-trinitroaniline, is isolated and described. The infrared spectra and thermal analysis (Figures 1 through 6) are at the end of the report.



ADNBF

PREVIOUS SYNTHETIC METHODS

7-Amino-4,6-dinitrobenzofuroxan was first prepared by Hobin by the route shown below with a combined yield of 63% (Reference 2). The author did not know whether the amino group was in the 7- or the 5-position. (For structure proof, see Reference 1.)

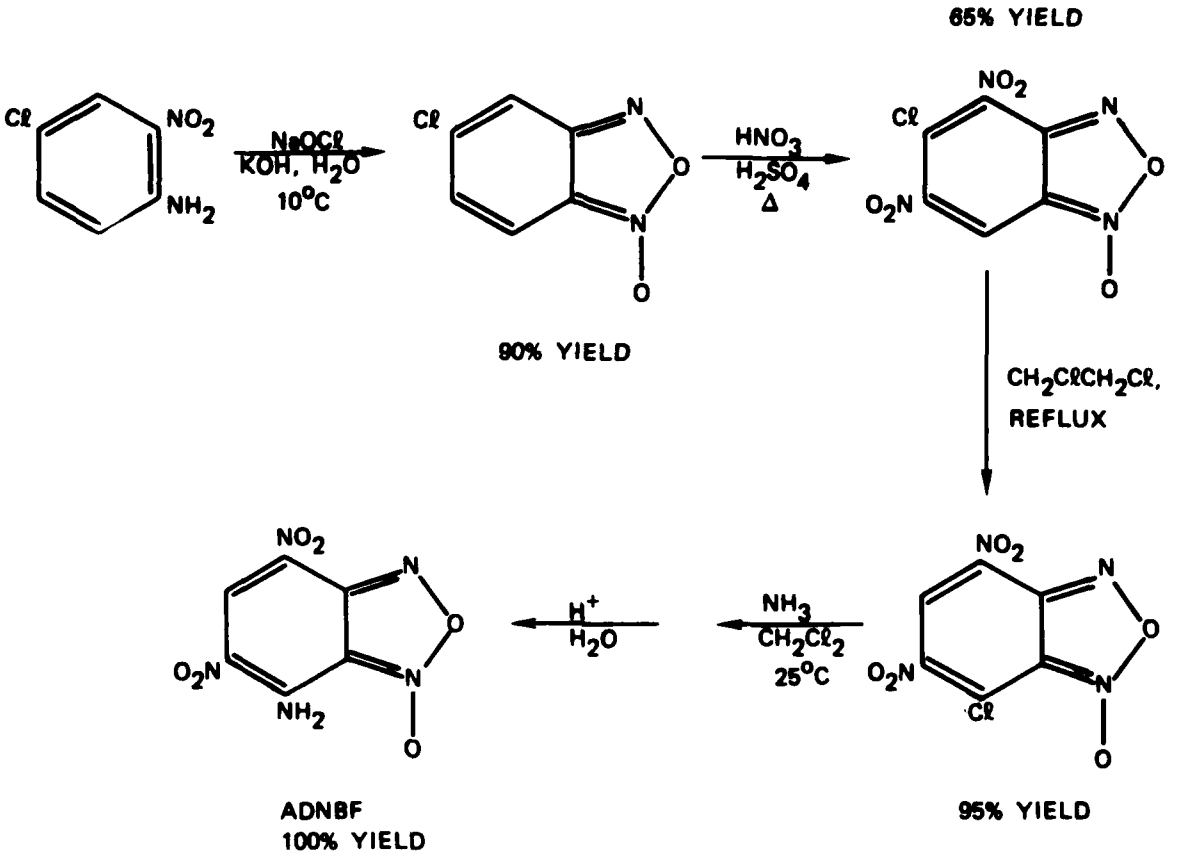


X = Br, NO_2

75% YIELD

ADNBF
84% YIELD

Another procedure for preparing ADNBF is the multistep synthesis shown (Reference 1). It has a combined yield of 56%.



NEW IMPROVED SYNTHESIS OF ADNBF

This procedure starts with 2,3,4,6-tetranitroaniline (Reference 3) and sodium azide, as in the first mentioned procedure, but importantly, the reaction solvent is acetic acid (Reference 4).*

There are several advantages:

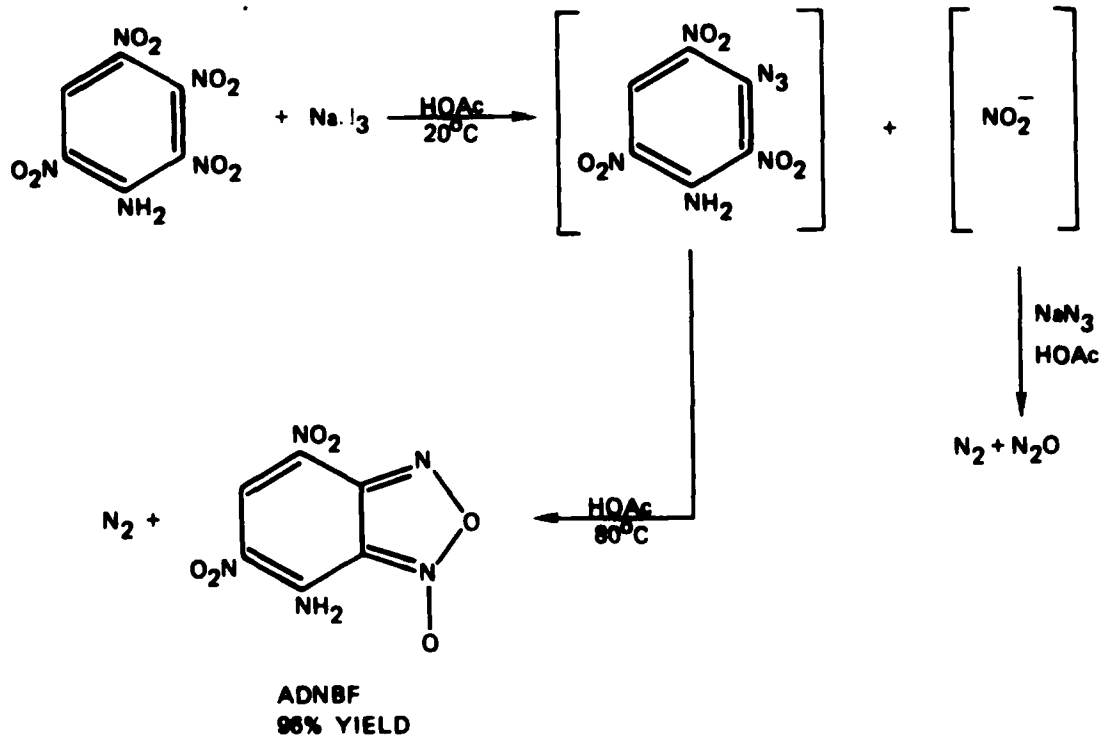
1. The method becomes a "one-pot" synthesis since intermediate 3-azido-2,4,6-trinitroaniline is not isolated but thermolyzed directly in acetic acid to ADNBF.

* Acetic acid has been used as a solvent for sodium azide in its reaction with picryl chloride to give picryl azide.

2. Nitrite ion, from azide displacement of 3-NO_2, is immediately converted, by sodium azide in acetic acid, to N_2 and N_2O (Reference 5). This prevents nitrite from competing with azide for unreacted tetranitroaniline. Reaction of nitrite with tetranitroaniline would generate a contaminating by-product, 3-hydroxy-2,4,6-trinitroaniline, and lower the yield of ADNBF. It is necessary to use two equivalents of azide per mole of tetranitroaniline to both displace nitrite with azide and to destroy the displaced nitrite ion.

3. The displacement of nitrite by azide and the subsequent thermolysis step must be virtually quantitative reactions since high purity ADNBF, in 96% yield, is obtained by simply filtering the cooled reaction mixture. The slight solubility of ADNBF in the acetic acid reaction solvent and in the wash water used following filtration could account for the 4% loss.

This is a highly efficient ADNBF synthesis.



ADNBF
96% YIELD

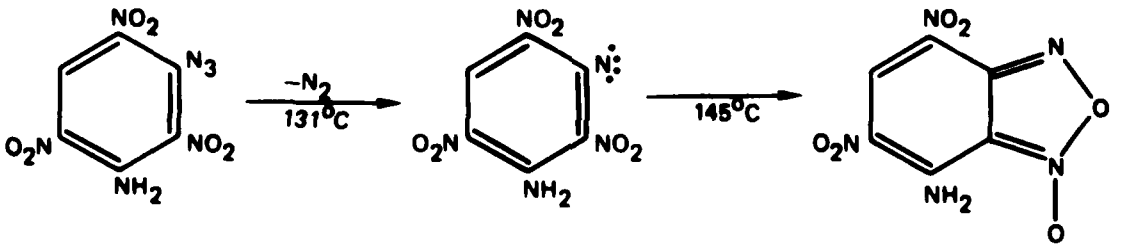
3-AZIDO-2,4,6-TRINITROANILINE

By keeping the reaction temperature at 20°C, 3-azido-2,4,6-trinitroaniline, the intermediate that is normally not isolated, can be obtained in high purity by filtration from the reaction mixture. 3-Azido-2,4,6-trinitroaniline, a known compound (Reference 2), has not been well-characterized. An infrared spectrum (Figure 2), thermal analysis (Figure 5), and an elemental analysis are reported here.

The thermal analysis trace (Figure 5) shows two exothermic events, peaks at 131 and 145°C, followed eventually by the decomposition trace of ADNBF with an additional small exotherm at 260°C.

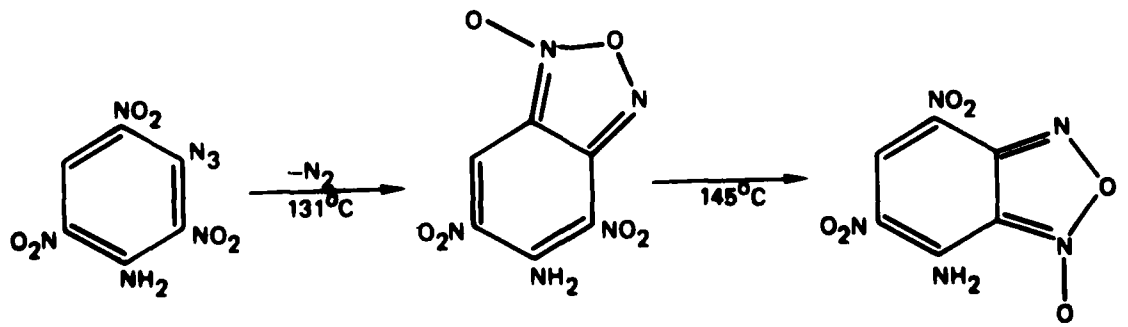
The trace could suggest formation of an intermediate at 131°C, followed by formation of ADNBF at 145°C.

One possibility is the formation of a nitrene intermediate followed by ADNBF formation. Nitrenes are generally so reactive that such prolonged separate existence seems most unlikely.



ADNBF

Another possibility is the initial formation of kinetically favored 5-amino-4,6-dinitrobenzofuroxan followed by isomerization to thermodynamically favored ADNBF. There are examples in the literature of



ADNBF

formation of kinetically favored reaction products which later convert to thermodynamically favored isomers (Reference 6).

Following the thermolysis of 3-azido-2,4,6-trinitroaniline in CD_3CN, ^1H NMR shows only δ 9.03, H-5 for 3-azido-2,4,6-trinitroaniline and δ 9.05, H-5 for ADNBF. There is no NMR evidence for an intermediate.

Still another possibility is the initial formation in the solid thermal analysis sample of ADNBF of a meta-stable crystal form (131°C) followed by exothermic conversion to the stable crystal form of ADNBF (145°C).

There is no supporting evidence for any of the three suggested possibilities. It may be one of these or yet another. However, the exothermic decomposition pattern at the end is identical with that of ADNBF (Figure 6).

INFRARED SPECTRA

Samples were prepared by dispersing the compounds in KBr powder and pressing, under vacuum, into discs. The spectra were recorded on a Perkin Elmer 137 Sodium Chloride Spectrophotometer. Figure 1 (2,3,4,6-tetranitroaniline) shows NH_2, 3360, 3240; CH, 3020 cm^{-1}. Figure 2 (3-azido-2,4,6-trinitroaniline) shows NH_2, 3410, 3310; CH, 3070; N_3, 2170 cm^{-1}. Figure 3 (ADNBF) shows NH_2, 3350, 3240; CH, 3030 cm^{-1}.

THERMAL ANALYSIS

Approximately 1 mg samples of the compounds were examined on a DuPont 1090 Differential Scanning Calorimeter. The heating rate was 10°C/min. Figure 4 (2,3,4,6-tetranitroaniline) shows melting starting at 215°C. Thermal decomposition ensues immediately after 225°C. Figure 5 was discussed previously. 7-Amino-4,6-dinitrobenzofuroxan begins thermal decomposition at 269°C (Figure 6). The little peak at 274°C may be due to isomerization to 5-amino-4,6-dinitrobenzofuroxan (Reference 1).

EXPERIMENTAL SECTION

IMPROVED PREPARATION OF ADNBF

With stirring, 4.87 g (0.0738 mol) of NaN_3 (99%) were added all at once to 10.00 g (0.0366 mol) of 2,3,4,6-tetranitroaniline (Reference 3) suspended in 100 mL HOAc at 25°C. The reaction vessel was immersed in a 25°C water bath. Gas evolution was vigorous and the temperature in the reaction vessel rose to 40°C in 4 minutes. The temperature dropped to 30°C after another 6 minutes and gas evolution had slowed considerably. Yellow solid was suspended in the reaction solvent. The reaction mixture was then heated, and at about 67°C, the suspended solids all dissolved to give a light-orange-colored solution. Heating was continued and at 80°C (about 4 minutes later) solids began separating. Gas evolution was moderate. After 1 hour at 80°C, gas evolution had ceased. Reaction mixture was allowed to stand at 25°C for 6 hours. Solids were filtered from the reaction mixture, washed with 200 mL H_2O (25°C) on filter funnel, dried, and weighed to give 8.48 g (96.1% yield) of ADNBF.

Analysis calculated for $C_6H_3N_5O_6$: C 29.89; H, 1.25; N, 29.05. Found: C, 29.66; H, 1.28; N, 28.60. Elemental analysis of the product agrees quite well with theoretical values, although N is a little low.

PREPARATION OF 3-AZIDO-2,4,6-TRINITROANILINE

One gram (0.00366 mol) of 2,3,4,6-tetranitroaniline was suspended in 10 mL HOAc and cooled to 18°C, and 0.482 g (0.00735 mol) of NaN_3 (99%) was added while the mixture was being stirred. Gas evolution commenced immediately. The reaction temperature was maintained at 20°C ± 2° for 4 hours using a cooling bath. Solids were filtered from the reaction mixture, washed on the filter with 100 mL H_2O (25°C), and dried to give 0.717 g (73% yield) of 3-azido-2,4,6-trinitroaniline. Figure 2 shows the infrared spectrum and Figure 5 shows the thermal analysis.

Analysis calculated for $C_6H_3N_7O_6$: C, 26.77; H, 1.12; N, 36.43. Found: C, 27.10; H, 1.32; N, 35.55. Elemental analysis was excellent for C and H and somewhat low for N. The azide group might lose N_2 even at room temperature which may account for the low value of N.

PREPARATION OF 2,3,4,6-TETRANITROANILINE*

First, 150 mL of 90% HNO_3 were added dropwise, with stirring, to 250 mL of 30% oleum keeping the temperature below 50°C by use of a cooling bath.

---

*Adapted from a procedure in Reference 3.

Next, in another reaction vessel, 85.0 g (0.615 mol) of m-nitroaniline was added, with stirring, to 750 mL of concentrated H_2SO_4; then heat to 60°C. To this reaction mixture, 50 mL of the previously prepared HNO_3-oleum solution was added rapidly, with stirring. The temperature raised quickly to about 75°C. When the temperature starts to drop, add the remainder of the HNO_3-oleum solution dropwise, keeping the temperature at 75°C ±5° by rate of addition of HNO_3-oleum and by use of a cooling bath. After completion of addition of HNO_3-oleum, the temperature was allowed to cool to 60°C; then the reaction mixture was poured, with stirring, onto about 6 L of ice cubes. Filtration, followed by washing on the filter with 2 L of ice water and drying gave 106 g (63% yield) of 2,3,4,6-tetranitroaniline.

Recrystallization of 27.5 g from 275 mL of CH_3CN gave 23.3 g; mp 223°C (decomposition).

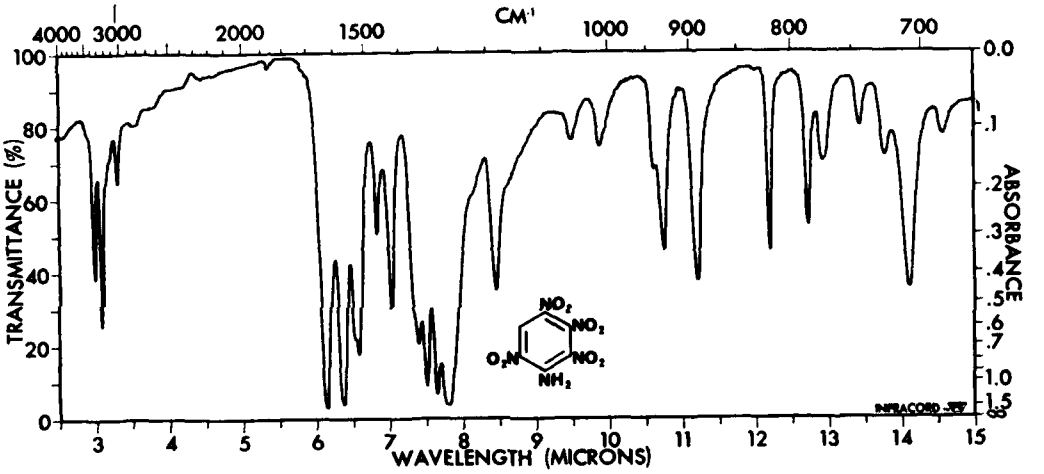


FIGURE 1. Infrared Spectrum of 2,3,4,6-Tetranitroaniline.

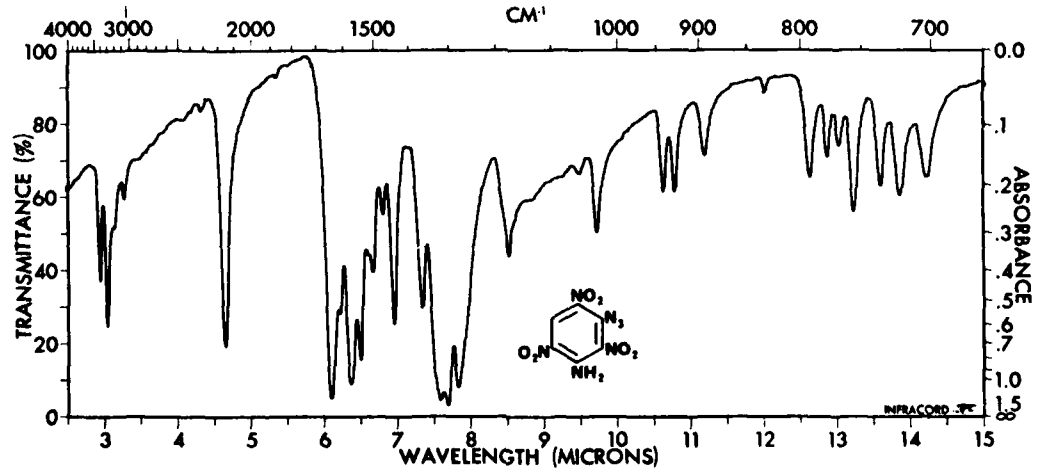


FIGURE 2. Infrared Spectrum of 3-Azido-2,4,6-trinitroaniline.

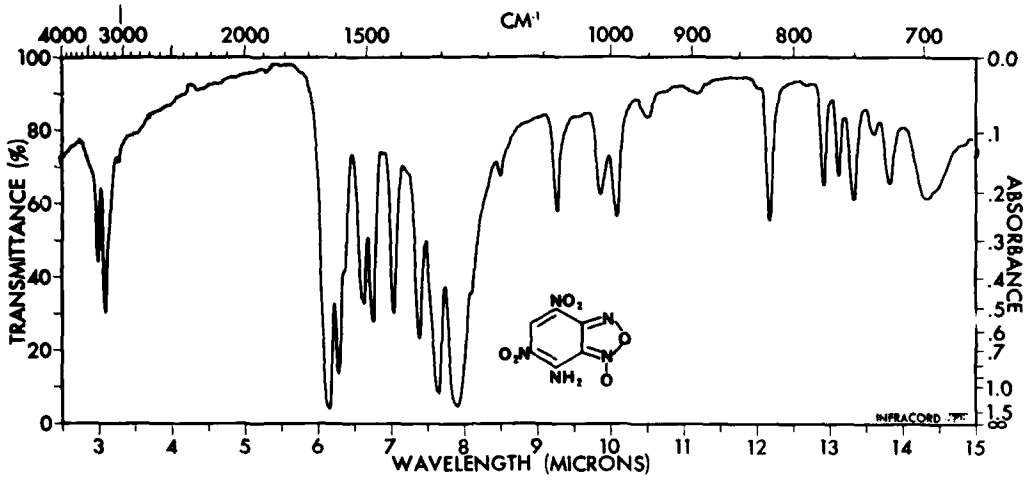


FIGURE 3. Infrared Spectrum of ADNBF.

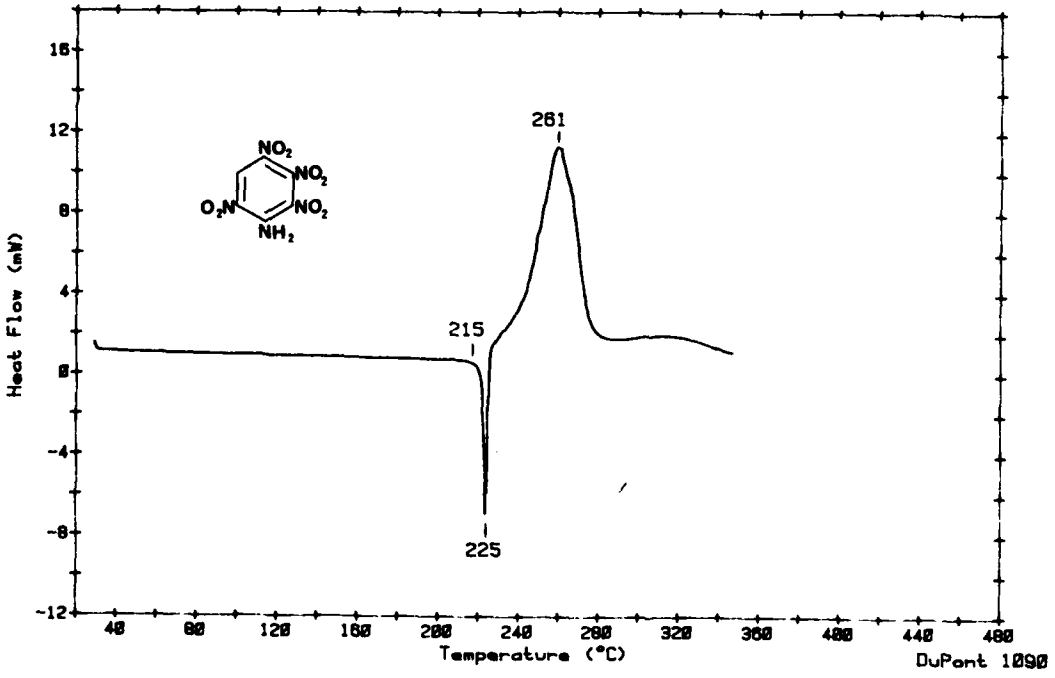


FIGURE 4. Thermal Analysis of 2,3,4,6-Tetranitroaniline.

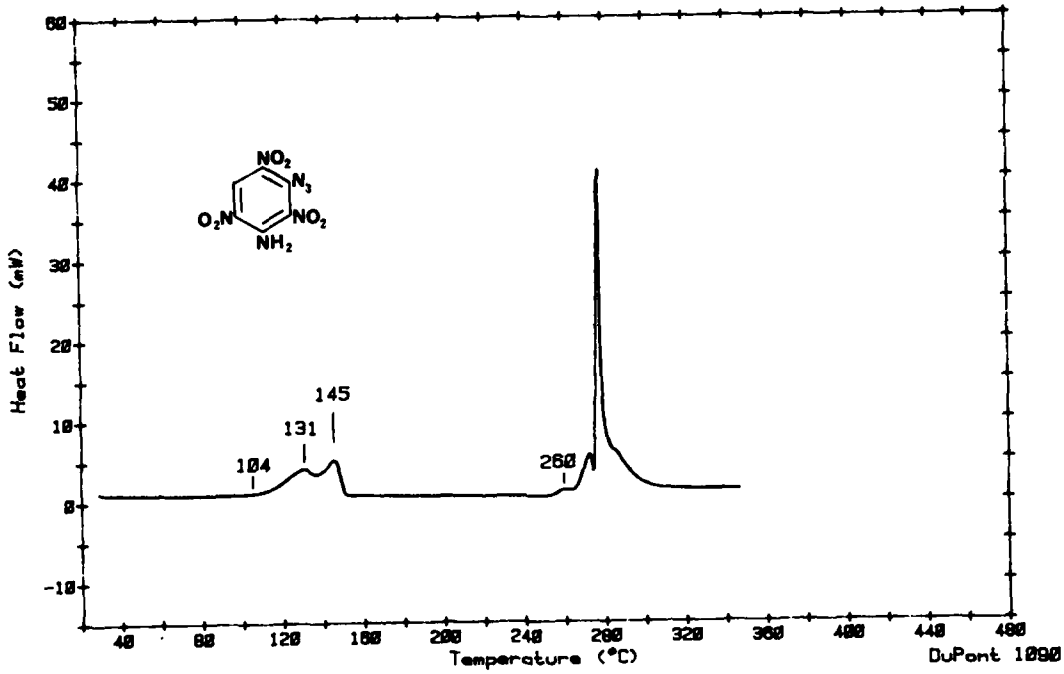


FIGURE 5. Thermal Analysis of 3-Azido-2,4,6-trinitroaniline.

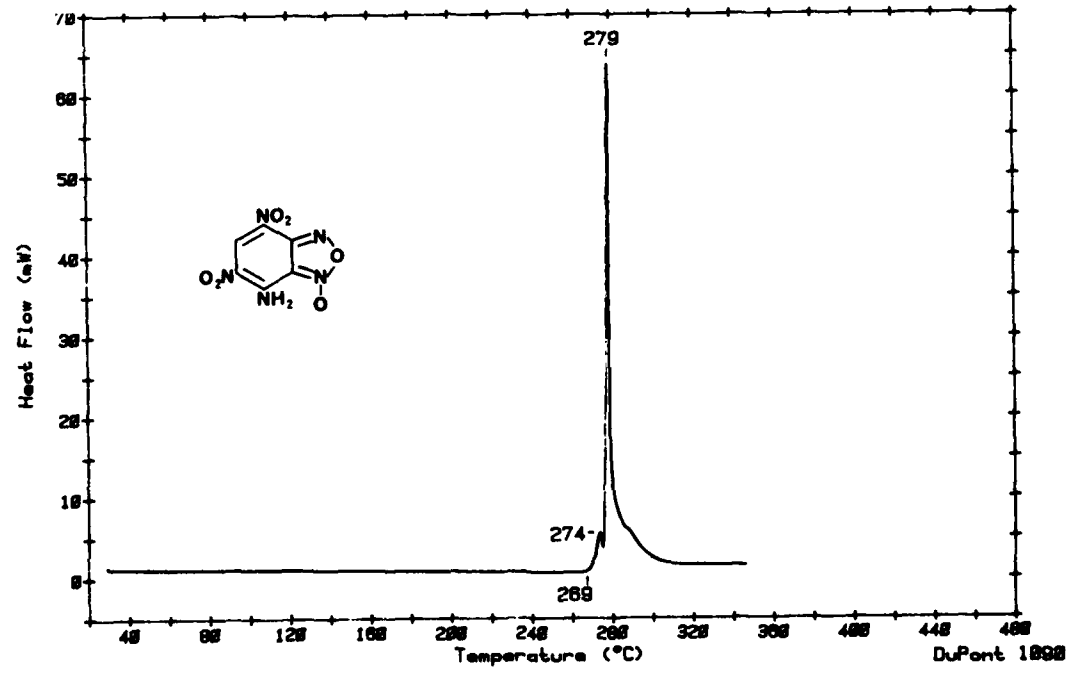


FIGURE 6. Thermal Analysis of ADNBF.

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