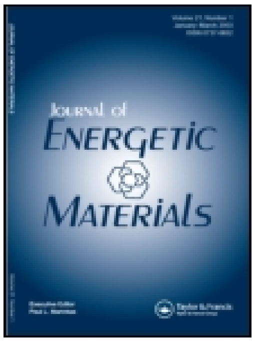

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Thermal Decomposition of Dinitro-chloro-azido Benzenes: A Comparison of Theoretical and Experimental Results

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*1,2-Dichloro benzene (***I***) and 1,2,3-trichloro benzene (***II***) were nitrated under appropriate strong conditions. Nitrated mixtures were reacted with* NaN_3 *in polar solvents. As a result of the nucleophilic substitution, mixtures of nitro-chloro-azido benzene were prepared. After fractional crystallization, two crystalline substances were obtained from the mixtures. These crystalline substances were characterized by infrared (IR),* ^{1}*H-NMR spectroscopy, mass spectroscopy, and elemental analysis. It was understood that the substance obtained from compound* **I** *was 2-chloro-4,6-dinitro azido benzene (***III***). The crystals of compound* **III** *were suitable for single-crystal X-ray diffraction (XRD). The molecular structure of this substance was determined by the mentioned method, XRD. It was revealed that the crystalline substance obtained from compound* **II** *was most probably 1,5-dinitro-2,4-diazido-3-chloro benzene (***IV***). In addition, compounds* **III** *and* **IV** *were investigated by thermogravimetry (TG) and differential scanning calorimetry (DSC). Compound* **III** *turned into 4-nitro-6-chloro phenoxazine (***V***) at about 120°C with an exothermic reaction. Compound* **IV** *completely decomposed at about 150°C with an exothermic reaction similar to that of explosive materials. In addition, theoretical formation enthalpies of compounds* **III** *and* **IV** *were calculated with Gaussian 09, CBS-4 M algorithm. The enthalpies of thermal reactions observed in the TG curves were calculated using the theoretical formation enthalpies. Finally, the theoretical results were compared with the experimental findings obtained from DSC.*

Keywords azido-nitro compounds; DSC; heat of formation; TG; theoretical calculation

Introduction

The azido group converts to N_2 so easily that azido-substituted compounds behave like explosive materials [1,2]. However, due to the mesomeric tendency of the azido

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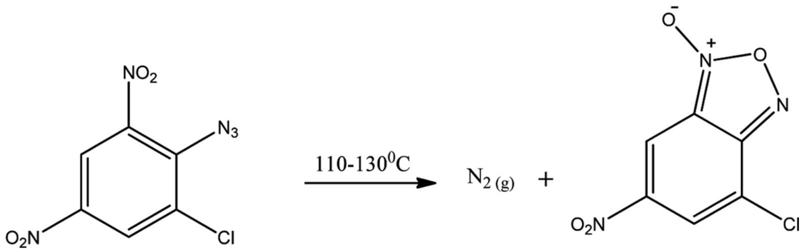


Figure 1. Thermal conversion of the NO_2 and N_3 groups of compound **III** to furoxan.

group, it activates the aromatic ring and if it is added to conventional aromatic explosives, it will decrease the stress of the nitro group in the ring [3,4]. On the other hand, the azido group increases the amount of gas produced during the explosion reaction and usually increases the enthalpy of the explosion [5]. If the azido group is located side by side with a nitro group, the compound will not decompose suddenly as in conventional explosives. Instead, compounds lose one N_2 between 100–130°C. After such a loss, the formation of a phenoxazine has been reported in the literature [6–8]; see Fig. 1.

The formation of phenoxazine is exothermic and the phenoxazines formed are stable [7]. There are two recommended methods for preparing aromatic azido compounds in the literature. The first method is diazotization of aromatic primer amines and the second method is the nucleophilic substitution reaction of the azide ion and the halogen group of the nitrated aromatic ring [6,9].

In this study, compounds **I** and **II** were nitrated with a fuming HNO_3/H_2SO_4 mixture at 110°C. The obtained mixtures were reacted with NaN_3 in MeOH/Me_2CO/H_2O in accordance with the proposed synthesis methods in the literature. After the reaction, the nitro-azido-chloro benzene mixtures were obtained. These mixtures were investigated by high-performance liquid chromatography (HPLC) to determine the number of components. However, purification by the column was not successful. Two components were observed to crystallize in MeOH. Therefore, crystallization was performed in MeOH/MeCN (V:V 90:10) solution. The dimensions of the crystals obtained from compound **I** were a few millimeters and they were impure. Therefore, recrystallization was performed in the same solvent. The crystals obtained from compound **II** were plate-shaped and they were of the same type as the crystals obtained from compound **II**. Both substances were found to be pure by HPLC and were further characterized by infrared (IR), ^{1}H-NMR spectroscopy, mass spectroscopy, and elemental analysis. These crystals belong to 2-chloro-4,6-dinitro azido benzene and 1,5-dinitro-2,4-diazido-3-chloro benzene. However, the crystals of compound **IV** were not suitable for single-crystal X-ray diffraction (XRD) analysis, so its molecular structure could only be estimated from mass spectrometry (MS) and elemental analysis (Fig. 2).

The crystalline substances obtained were investigated by thermogravimetry (TG). Different thermal behaviors were observed for both of them. Conversion of compound **III** to 4-nitro-6-chloro phenoxazine (**V**) at about 120°C with an exothermic reaction was detected. However, 1,5-dinitro-2,4-diazido-3-chloro benzene (**IV**) thermally decomposed like conventional explosives with a 90% mass loss at a higher temperature. Both exothermic peaks were symmetric because they were Gaussian-type peaks. Energies of the reactions were determined by differential scanning

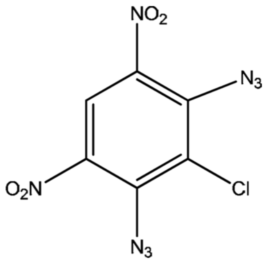


Figure 2. Estimated structure of the compound obtained as a result of nitration and nucleophilic substitution of compound **II**.

calorimetry (DSC). At the same time, the theoretical formation enthalpies of compounds **III** and **IV** were determined with certain algorithms in Gaussian 09 software [10]. The theoretical formation enthalpy of compounds **III** and **V** was measured and the enthalpy of reaction was calculated according to Hess's law. The calculated enthalpy of reaction was compared with the experimental findings [11]. Because compound **IV** decomposed like conventional explosives, the oxygen balance (Ω) was investigated for its decomposition [12]. Finally, the theoretical reaction enthalpy was compared with the experimental data.

Experimental Section

General

In this study, thermogravimetric analyses were performed on a Shimadzu DTG-60H (Ankara, Turkey). In the thermogravimetric analysis process, the temperature was varied between 30 and 600°C. These analyses were performed at a 10°C/min rate and under N_2 atmosphere with Pt pans. A Shimadzu Infinity model Fourier transform infrared spectrometer with three attenuated total reflectance attachments was employed for the characterization of synthesized azido benzene derivatives. Mass spectra were obtained by a Shimadzu 2010 plus equipped with a direct inlet (DI) unit and an electron impact ionizer. The DI temperature was changed between 35 and 110°C and ionization was achieved with 70 electron volt (eV) electrons. During the ionization interval between 5 and 10 minutes, 10 points were selected to read m/z values. For elemental analysis, a JEOL JSM-6400 scanning electron microscope (Ankara, Turkey) was used and energy-dispersive X-ray analysis was performed with 10 selected points minimum. In addition, C, H, N elemental analyses were performed on an Elemantar Vario Micro Cube instrument (Kırıkkale, Turkey). ^{1}H-NMR spectra were recorded on a Bruker Ultrashield 300 MHz NMR spectrometer (Ankara, Turkey). The solvent was $CDCl_3$.

Nitration of 1,2-Dichloro Benzene

The methods proposed in the literature [13] were used for the nitration reactions.

About 5.0 g of 1,2-dichloro benzene and 20 mL of fuming HNO_3 were dissolved in 20 mL H_2SO_4. The temperature was increased to 120°C in a sand bath and was kept constant for about 2 h. After cooling to room temperature, this solution was poured into 200-mL of ice water. The solid substance was filtered and dried in air.

To determine the number of components, the substance was analyzed by HPLC. A 55% MeCN, 45% H_2O mobile phase was used.

Nitration of 1,2,3-Trichloro Benzene

This compound was nitrated in the same way as the nitration of 1,2-dichloro benzene. The only difference was that the temperature was increased up to 125°C. All three nitrated products could be seen in the chromatograms.

Synthesis of Nitro-chloro-azido Benzenes from Nitro-chloro Benzenes (Nucleophilic Substitution)

About 2 g of the resulting mixture was dissolved in 20 mL of $MeOH/Me_2CO$ (V:V 50:50) at 50°C. A solution of 2 g NaN_3 in 20 mL $MeOH/Me_2CO/H_2O$ (V:V:V 30:30:40) was added dropwise while stirring according to the literature [5]. After stirring for 2 h, this solution was poured into 250-mL of ice water. The solid substance was filtered and dried in air. The solid substance was analyzed with HPLC. A 55% MeCN, 45% H_2O mobile phase was used. Among the three components in the mixture resulting from 1,2-dichloro benzene, one was the starting compound and the other two were nitro-chloro-azido benzenes. On the other hand, there were three nitro-chloro-azido benzene components in the mixture prepared from 1,2,3-trichloro benzene.

Separation by Crystallization

The obtained mixture of nitro-chloro-azido benzene from 1,2-dichloro benzene was first recrystallized in MeOH. Two different crystals were detected using a microscope. In order to improve purity, it was recrystallized in MeCN but it was observed that the substance was even more soluble in MeCN. Therefore, one more recrystallization was performed in MeCN:MeOH (V:V 10:90) mixture. After 6 h, the solution was filtered. Crystals of dimensions 0.3 × 2–3 mm that were homogeneous and of equilateral quadrangle shape were obtained. The purity of these crystals was checked by HPLC and they were taken for spectroscopic characterization. Their molecular structure was determined by XRD.

IR data for 2-chloro-4,6-dinitro azido benzene (cm^{-1}) are as follows: 3098 ($\nu_{\text{C-H(Ar)}}$), 2119(ν_{N3}), 1593($\nu_{C=C(Ar)}$), 1566, 1517, 1448, 1336($\nu_{N=O}$), 1273, 1170, 1157, 1122, 1022, 935, 896, 881, 854, 844, 777($\delta_{\text{C-H(Ar)}}$), 759, 732, 702. m/z: 243 (molecular peak), 215, 138, 111, 88 (base peak), 74.

The results of elemental analysis of 2-chloro-4,6-dinitro azido benzene are as follows: Expected (%): C, 29.57; N, 38.75; Cl 14.56; O, 26.29; Found (%): C, 32.06 ± 2.24; N, 26.52 ± 1.14; Cl 14.42 ± 0.50; O, 27.43 ± 1.21.

Important ^{1}H-NMR data for 2-chloro-4,6-dinitro azido benzene are as follows: (δ, ppm, in $CDCl_3$): 8.15 (d), 8.79 (d) $J = 1.2$ Hz; 0.2 g of compound **III** was kept at in oven at 130°C for 1 h.

Important IR data for the obtained solid (cm^{-1}) are as follows: ν_{Ar}: 3087, $\nu_{C=C\ (Ar)}$: 1624, $\nu_{N=O}$: 1331, $\delta_{\text{C-H(Ar)}}$: 753.

As can be seen, the stretching vibration of N_3 at about 2120 cm^{-1} was replaced by stretching vibration of phenoxazine's C=N on *o*-quinoid at about 2120 cm^{-1}.

A similar application was made for obtained mixture from 1,2,3-trichloro benzene. This substance was recrystallized in MeOH; 0.5 g of 1,2-3-trichloro benzene was dissolved in 15 mL MeOH by heating. Then, this solution was kept in a deep freeze at −20°C for 1 h. The plate-shaped crystals were filtered and dried in air. The obtained crystals were homogeneous. The purity of these crystals was checked by HPLC and it was determined that they contained very little impurities. The molecular structure and exact location of the azido group was not exactly determined because suitable crystals could not be selected for XRD, so they were only estimated. If the azido and nitro groups were placed side by side on the aromatic ring, nitrogen gas should be released between 100 and 120°C. Therefore, it was assumed that azido and nitro groups were not in a side-by-side placement on the aromatic ring.

The results of elemental analysis of dinitro-diazido-chloro benzene, $C_6HClN_8O_4$, were as follows: Expected (%): C, 25.3; N, 39.37; Cl, 12.46; O, 22.49; Found (%): C, 25.74 ± 1.62; N, 29.52 ± 1.14; Cl, 12.42 ± 0.50; O, 23.43 ± 1.21.

IR data for dinitro-diazido-chloro benzene (cm^{-1}) were as follows: 3094 ($\nu_{C\text{-}H(Ar)}$), 2125(ν_{N3}), 1573($\nu_{C=C(Ring)}$), 1525, 1504, 1431, 1320($\nu_{N=O}$), 1290($\nu_{C\text{-}N}$), 1269, 1153, 983, 906, 891, 777 ($\delta_{C\text{-}H(Ar)}$), 742, 704. m/z: 284 (molecular peak), 256, 228, 168 (base peak), 138, 121,110, 88, 87.

Important ^{1}H-NMR data for dinitro-diazido-chloro benzene were as follows: (δ, ppm, in $CDCl_3$): 8.82 (s).

X-ray Crystal Structure Analysis of 4,6-Dinitro-2-Chloro Azido Benzene

Single crystals of 4,6-dinitro-2-chloro azido benzene (**III**) were analyzed on an Oxford Diffraction Xcalibur single-crystal X-ray diffractometer with a sapphire CCD detector (Darmstadt, Germany) [14].

The diffraction measurements were performed at room temperature using MoK_α radiation ($\lambda = 0.71073$ Å) and ω-2θ scan mode. Unit cell dimensions were determined and refined by using the angular settings of 25 automatically centered reflections in the $2.563 \leq \theta \leq 27.673$ range. The empirical absorption corrections were applied by the semi-empirical method via CrysAlis CCD software [14].

The structure of compound **III** was revealed by direct methods using SHELXS97 of WinGX package [15,16].

Theoretical Calculations

All theoretical calculations were carried out using Gaussian G09 W (revision B.01) [10].

The structure and frequency calculations were performed with Becke's B3 parameter hybrid functional by using the LYP correlation functional (B3LYP) [17]. For all H, C, N, and O atoms, a correlation consistent polarized double-zeta basis set was used (cc-pVDZ) [18].

The enthalpies (H) and free energies (G) were calculated using the complete basis set (CBS) method of Ochterski and coworkers in order to obtain very accurate energies [19]. The CBS models use the known asymptotic convergence of a pair natural orbital expressions to extrapolate from calculations using a finite basis set to the estimated CBS limit. CBS-4 begins with an HF/3-21G(d) geometry optimization; the zero point energy is computed at the same level. It then uses a large basis set self consistent field calculation as a base energy and an MP2/6-31 + G calculation with a

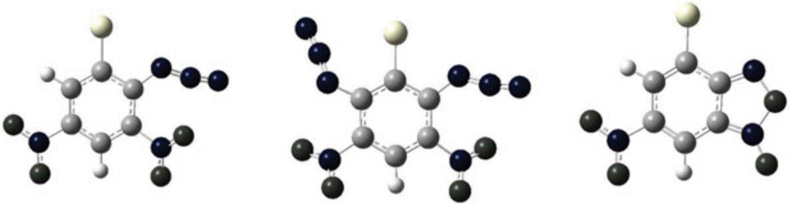


Figure 3. Optimized molecular structures of **III** (left), **IV** (center), and **V** (right). (color figure available online.)

CBS extrapolation to correct the energy through second-order iteration. A MP4(SDQ)/6-31 + (d, p) calculation was used to approximate higher order contributions. In this study, we applied the modified CBS-4 M method (M refers to the use of minimal population localization), which is a reparameterized version of the original CBS-4 method and includes some additional empirical corrections [19,20].

Computational Aspects

The molecular structures of compounds **III**, **IV**, and **V** were fully optimized without symmetry constraints at the B3LYP/cc-pVDZ level of theory to C_1 symmetry in all cases (Fig. 3).

The enthalpies of the gas-phase species M were computed according to the atomization energy method (Eq. (1); Tables 1–3) [21–23]. In Eq. (1), $\Delta_f H°(g,M)$ stands for the gas-phase enthalpy of formation of the molecule, M, under investigation; $H(M)$ represents the CBS-4 M calculated enthalpy of the molecule M (H_{298} in Table 1); $\Sigma_{atoms}H°$ denotes the CBS-4 M calculated enthalpies for the individual atoms (see bottom of Table 1); and $\Sigma_{atoms}\Delta_f H°$ stands for the experimentally reported literature values for the enthalpies of formation for the corresponding atoms ($\Delta_f H°_{298}$ in Table 2).

$$\Delta_f H^0_{(g,M)} = H_{(M)} - \Sigma H^0 + \Sigma \Delta_f H^0. \tag{1}$$

Table 1 CBS-4 M results

Compound	p.g.[a]	NIMAG[b]	$-H^{298}$/a.u.[c]	$-G^{298}$/a.u.[d]
III	C_1	0	1,262.959078	1,263.014613
IV	C_1	0	1,426.336818	1,426.399783
V	C_1	0	1,153.594792	1,153.643692
H		0	0.500991	0.514005
C		0	37.786156	37.803062
N		0	54.522462	54.539858
O		0	74.991202	75.008515

[a] Point group.
[b] Number of imaginary frequencies.
[c] CBS-4 M calculated enthalpy.
[d] CBS-4 M calculated free energy.

Table 2 Literature values for atomic $\Delta H_{f^{\circ}298}$ (kcal mol^{-1})

Atoms	Curtiss et al. [21]	NIST [25]
H	52.6	52.1
C	170.2	171.3
N	113.5	113.0
O	60.0	59.6

Table 3 Enthalpies of the gas-phase species M

M	$\Delta_f H^{\circ}_{(g,M)}$ (kcal mol^{-1})	$\Delta_f H^{\circ}_{(g,M)}$ (kJ mol^{-1})
III	90.3	377.7
IV	182.0	760.8
V	64.6	270.1

Table 4 Enthalpies of sublimation (ΔH_{sub}) [24]

M	T_m (K)	ΔH_{sub} (kJ mol^{-1})
III	337	63.3
IV	331	62.2
V	350	65.8

The enthalpies of sublimation for all species **III**, **IV**, and **V** were estimated according to Trouton's rule (Eq. (2), Table 4) [24] with observed melting points from TG curves of 64, 58, and 77°C, respectively. The validity of Trouton's rule reflects the fact that the entropy of vaporization is approximately constant for many compounds and that $\Delta H_{sub.} \approx \Delta H_{vap.} + \Delta H_{fusion}$, with $\Delta H_{vap} >> \Delta H_{fusion}$ so that $\Delta H_{sub} \approx \Delta H_{vap}$.

$$\Delta H_{sub.} = 188\,\mathrm{T_m}\,\mathrm{J\,mol^{-1}} \tag{2}$$

The calculated molar enthalpies of formation for compounds **III**, **IV**, and **V** are summarized in Table 5.

Table 5 Enthalpies of formation ($\Delta_f H^{\circ}$) of the compounds

M	$\Delta_f H^{\circ}_{(s,M)}$ (kJ mol^{-1})
III	314.3
IV	698.6
V	204.3

The gaseous-phase heats of formation of $NO_{(g)}$ and $C_2H_{4(g)}$, decomposition products of compound **IV**, are given in the literature as +90.28 and +52.47 kJ mol^{-1}, respectively [25].

Results and Discussion

The ORTEP drawings of 4,6-dinitro-2-chloro azido benzene (**III**) are given in Fig. 4. XRD data and structure refinement for compound **III** are given in Table 6, and the selected bond angles and bond lengths obtained from the X-ray diffraction studies are given in Table 7. TG curves of compounds **III** and **IV** are given in Figs. 5a and 5b. Average thermoanalytical data are given in Table 8.

In the elemental analysis findings, it can be seen that the amount of nitrogen found was lower than expected. This was because the neighboring nitro and azide groups decomposed to yield N_2 at about 110°C. In this study, elemental analysis studies were performed with a conventional elemental analysis instrument and repeated with an electron microscope. C, H, and N elements were analyzed by conventional elemental analysis. C, N, O, and Cl were determined using the electron microscope. During sample preparation for the electron microscope, the samples were covered with carbon; this caused the amount of C found to be higher than expected. Therefore, only Cl and O values from the electron microscope findings were considered. Unfortunately, with both methods, the amount of nitrogen found was lower than expected. However, other elemental findings were quite close to the expected values. Nevertheless, the MS results and the determined structure of compound **III** proved the accuracy of the proposed structures.

The base peak of compound **III** was at m/z = 215, and peaks at 243 and 185 were also observed, as well as isotope peaks at m/z = 245, 216, 217, and 187.

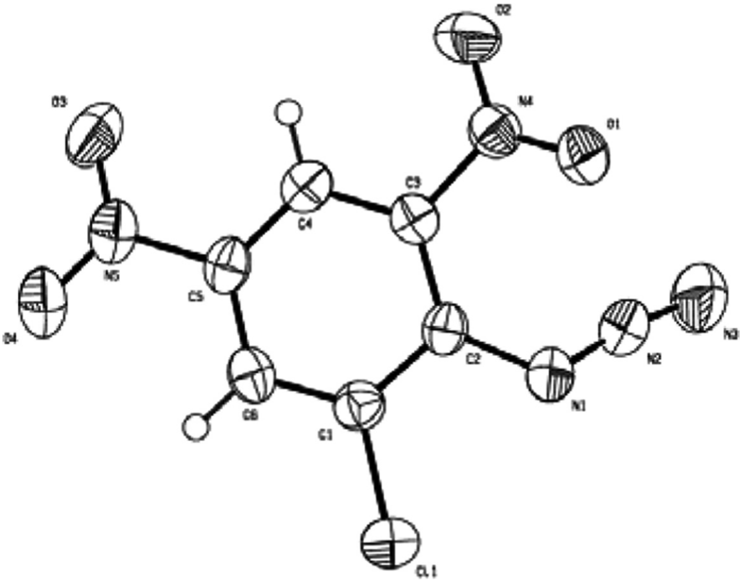


Figure 4. ORTEP drawing of compound **III**.

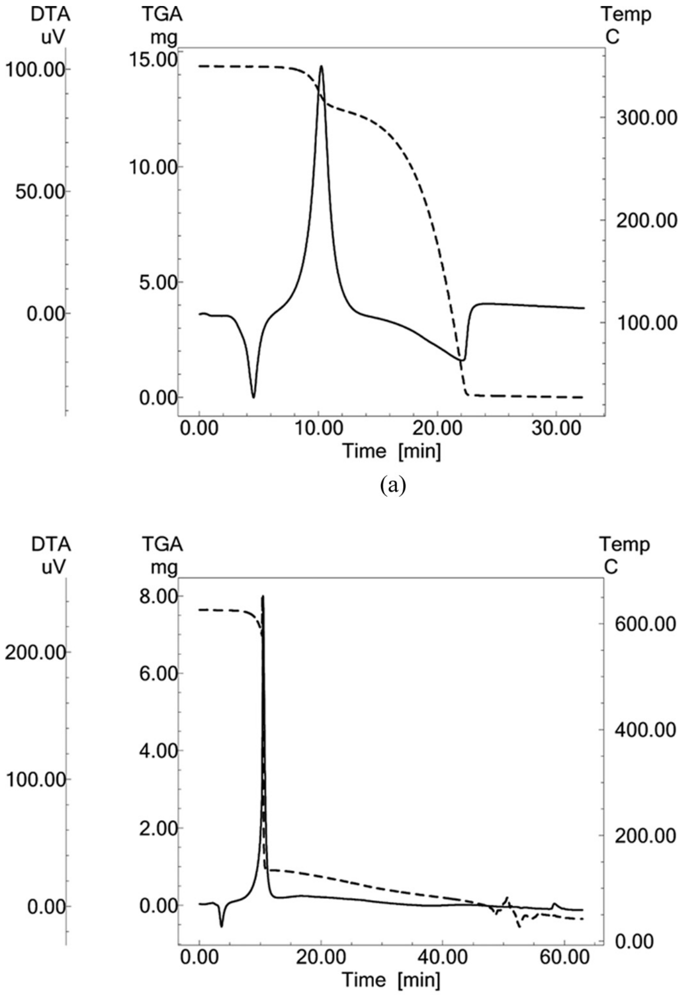
Table 6 Data and structure refinement for compound **III**

Empirical formula	$C_6H_2ClN_5O_4$
Formula weight	243.58
T (K)	293(2) K
Crystal size (mm)	0.40 × 0.36 × 0.16 mm
Crystal system	Orthorhombic
Space group	*P*bca
a (Å)	10.6968(5)
b (Å)	11.8243(6)
c (Å)	14.4515(7)
Alpha (α)	90.00
Beta (β)	90.00
Gamma (γ)	90.00
V (Å^3)	1,827.86(15)
Z	8
Calc. density (g cm^{-3})	1.770
μ (mm^{-1})	0.427
F(000)	976
$T_{\mathrm{min}} - T_{\mathrm{max}}$	0.8477–0.9348
Theta range (°)	2.93–26.37
Index ranges	$-12 \leq h \leq 13$, $-14 \leq k \leq 9$, $-18 \leq l \leq 17$
Reflections collected	4,827
Reflections unique	4,827/1,862
R_1, wR_2	0.0394/0.0801
R_1, wR_2 (all)	0.0570/0.0878
Data/parameters	1,862/145
Goodness of fit of F^2	1.074
Largest difference peak/hole (e Å^{-3})	0.342/−0.384

Although 243 was the expected molecular mass, the peak at 243 was not the base peak. However, this can be accounted for by the loss of N_2. If the molecule loses one N_2, the molecular mass will decrease to 215 and it would appear as the base peak. In addition, with the loss of one NO, the molecular mass decreased to 185,

Table 7 Selected bond lengths (Å) and angles (°) of compound **III**

N1 N2 1.245(3)	N2 N1 C2 118.58(19)
N2 N3 1.116(3)	N3 N2 N1 170.0(3)
N4 O2 1.215(2)	O2 N4 O1 123.90(19)
N4 O1 1.222(2)	O2 N4 C3 118.00(19)
N5 O3 1.216(3)	O1 N4 C3 118.01(18)
N5 O4 1.225(2)	O3 N5 O4 123.9(2)
C1 Cl1 1.724(2)	O3 N5 C5 118.3(2)
C3 N4 1.471(3)	O4 N5 C5 117.7(2)
C5 N5 1.464(3)	C6 C1 Cl1 118.78(17)
C2 N1 1.400(3)	C2 C1 Cl1 119.10(16)



(a)

(b)

Figure 5. a. TG-DTA curve of 4,6-dinitro-2-chloro-azido benzene; b. TG-DTA curve of 1,5-dinitro-2,4-diazido-3-chloro benzene.

Table 8 Average thermoanalytical data of compounds **III** and **IV**

Compound	Melting point (°C)	Temperature range (°C)	Mass loss Expected (%)	Mass loss Experimental (%)
4,6-Dinitro-2-chloro-azido benzene (**III**)	64	104–146	11.50	11.87 ± 0.24
1,5-Dinitro-2,4-diazido-3-chloro benzene (**IV**)	79	112–154	—	90.22 ± 0.72

which appeared as the other noted peak in the spectrum. The peaks at 245, 217, and 187, which can be clearly seen in the MS spectrum, were caused by the relative abundance of ^{37}Cl. Similarly, the base peak of compound **IV** at m/z = 168 and molecular peak at m/z = 284 were noticeable. In this molecule, two azido-nitro neighbors and m/z values, 256 and 228, related to the first and the second loss of nitrogen, can be easily seen in the spectrum. Finally, due to the loss of NO, the mass value should be 168, which appeared as the base peak. Therefore, it can be concluded that the mass spectra were in accordance with the proposed structures of both compounds.

The position of the only hydrogen in 1,5-dinitro-2,4-diazido-3-chloro benzene structure could not be confirmed. ^{1}H-NMR signals, FTIR spectra, and results of elemental analysis did not show the exact position of this lone hydrogen. However, the mass spectra clearly indicate that two nitro and two azido groups were neighbors. Considering that the starting material was 1,2,3-trichloro benzene, all of the evidence supports that the product was 1,5-dinitro-2,4-diazido-3-chloro benzene. Moreover, in the mass spectrum of 2-chloro-4,6-dinitro azido benzene, the base peak was observed at 88. This should belong to the formed nitrile azide $O_2N\text{-}N_3$ [26,27].

As can be seen from Table 8 and Fig. 5a, 4,6-dinitro-2-chloro-azido benzene lost one N_2 at 120°C and was converted to 4-chloro-6-nitro furoxan. In this reaction, the expected mass loss was 11.50%, which was very close to the experimental finding. The peak of this exothermic reaction was almost a perfectly Gaussian-type peak. Because the starting material and the reaction products were known, the theoretical formation enthalpy can be calculated according to Hess's law:

$$\Delta H^0_{\text{Reaction}} = \Sigma\Delta H^0_{\text{f(products)}} - \Sigma\Delta H^0_{\text{f(reactants)}}$$

For the reaction given in Fig. 1, there were two products: one was 4-chloro-6-nitro-fenoxazine and the other was N_2. $\Delta H^0_{\text{f}} = 0$ for N_2 so calculation of $\Delta H^0_{\text{Reaction}}$ is pretty straightforward. It should also be noted that the amount of work performed by the release of one mole of N_2 must be added to the DSC measurement. The theoretical and experimental results related to DSC are provided in Table 9. Note that the experimental results were in good agreement with the theory.

In the structure of 4,6-dinitro-2-chloro azido benzene, an azido and a nitro group were located side by side. As a result of the reaction between these neighboring groups, a stable furoxan was formed.

On the other hand, in 1,5-dinitro-2,4-diazido-3-chloro benzene, two azido and two nitro groups were neighbors. When these groups react to yield two nitrogens, the aromaticity deteriorates, which makes it impossible to achieve the quinoid

Table 9 Experimental and theoretical data of thermal reaction

Compound	Theoretical data of ΔH° (kJ/mol)	Experimental data of ΔH° measured by DSC (kJ/mol)
4,6-Dinitro-2-chloro-azido benzene	−110.01	−101.12 ± 2.43
1,5-Dinitro-2,4-diazido-3-chloro benzene	−324.36	−324.55 ± 4.35

structure given in Fig. 1. The compound formed was hardly stable and it decomposed very easily; see Fig. 5b. The thermal decomposition was exothermic when the mass loss was about 90%, resembling explosives (as can be seen in Fig. 5b). In such a case, the oxygen balance (Ω) entries in the literature [12] can be used to estimate the explosion products.

The decomposition reaction of compound **IV** is as follows:

$$C_6HN_8O_4Cl \rightarrow 1/2\,H_2O_{(g)} + 7/2\,CO_{(g)} + 5/2\,C_{(k)} + 4\,N_{2(g)} + 1/2\,Cl_{2(g)}$$

For this reaction, ΔH^0 values of the products were provided in the literature [25].

If we take $\Delta H^0 = -241.80$ kJ/mol for H_2O and $\Delta H^0 = -110.53$ kJ/mol for CO, the theoretical ΔH^0 is calculated as 98.60 kJ/mol for compound **IV**. Then,

$$\Delta H^0_{\text{reaction}} = [0.5(-241.80) + 3.5(-110.53)] - [698.60].$$

The measured value by DSC under constant pressure was 324.55 kJ/mol, which was much lower than the calculated value. However, it should be noted that as the molecule tore apart, it is quite probable that the oxygen atom formed NO gas with the remaining nitrogen atom. In addition, the most probable action of the only hydrogen atom in the aromatic ring was to form ethylene. If the reaction is written in this manner, it becomes the reaction shown in Fig. 6.

When the theoretical measurements were performed according to the above total reaction, the result was very close to the experimental finding:

$$\Delta H^0_{\text{reaction}} = [4(90.28) + 0.25(52.47)] - [698.60] = -324.36\,\text{kJ/mol}.$$

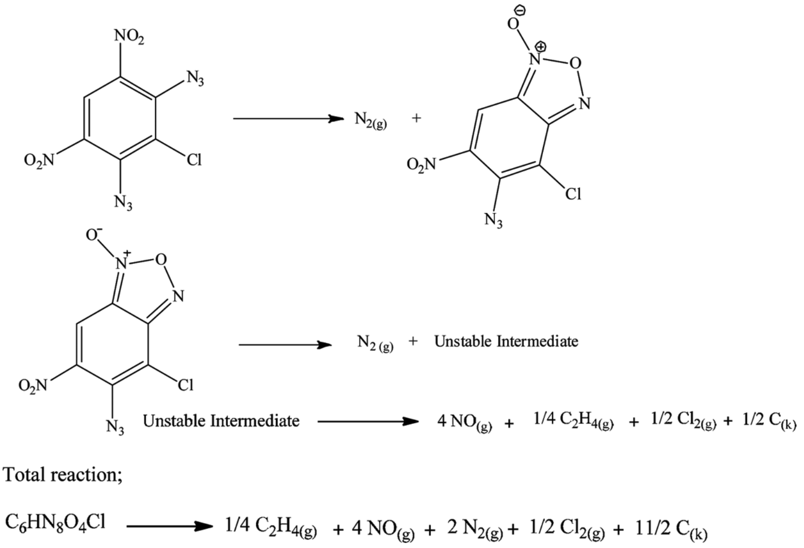


Figure 6. Probable intermediate reaction and products of thermal decomposition of compound IV.

Work was done against external pressure, which must be added to the DSC result. In this case, the work done by 6.5 moles of gas must be added to the average value 318.60 kJ/mol. If we take the temperature of the reaction as 130°C and room temperature as 30°C, the work done for an approximate temperature differential of $\Delta T = 110°\mathrm{C}$ is as follows:

$$W = -nRT = -6.5 \times 8.314 \times 110 = 5.95\,\mathrm{kJ/reaction}.$$

Therefore, the experimental enthalpy of the reaction was 324.55 kJ/mol.

At this point, the success of the theoretical program should be noted. The CBS-4 M algorithm, which was used in this study, has been found to be very accurate for energetic materials. In addition, oxygen balance (Ω) is a series of rules for explosions that has been long accepted, but this study made it clear that the molecular structure and geometry should also be taken into consideration for the theoretical explosion equations. It is important to note the importance of thermal analysis methods for analytical chemistry. Both TG and DSC methods played major roles in structural determination in this study.

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