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Some new energetic benzaldoximes

Synthesis, structure and a comparison of theoretic and experimental results of thermal decomposition

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Abstract 5-Nitro-2-hydroxy benzaldoxime (**I**), 3-nitro-4-hydroxy benzaldoxime (**II**), 3,5-dinitro-2-hydroxy benzaldoxime (**III**), and 3,5-dinitro-4-hydroxy benzaldoxime (**IV**) were prepared from their respective nitrated aldehydes. Prepared oximes were characterized by IR spectroscopy, elemental analysis, and mass spectrometry. Suitable crystals of compounds **II** and **III** were obtained and molecular structures were determined by means of the single crystal XRD method. All benzaldoximes were investigated by TG. At temperatures above 140 °C, it was observed that compounds **II** and **IV** lost one H_2O and was converted to the respective benzonitriles. Only thermal analysis peaks of 3,5-dinitro-4-hydroxy benzonitrile (**V**) were found proper for both experimental and theoretic calculations; whereas, compounds **I** and **III** were converted to phenoxazines by Beckmann rearrangement along with dehydration. Beckmann product of compound **III** is referred as compound **VI** and its tautomer as compound **VII**. Similarly only 3,5-dinitro phenoxazine **(VIII)** was investigated experimentally and theoretically since its thermal analysis peaks were proper for the purpose. DFT-based structure optimizations and frequency analyses were performed at the B3LYP/cc-pVDZ level of theory. The enthalpies of formation for compounds **III**–**VIII** were calculated by means of the complete basis set (CBS-4M) method of Petersson and coworkers to obtain accurate energies. The enthalpies of decomposition for compounds **III** and **IV** were obtained from calculated enthalpies of formation according to Hess' law and were compared with the experimental values which were available from DSC analyses and were found to be in good agreement with the theoretic values.

Keywords Oxime · CBS-4M · TG · DSC · Thermal decomposition

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Introduction

Oximes, which are products of condensation of carbonyl compounds and hydroxyl amine, have been in the literature for nearly 100 years [1]. Owing to their role in Beckmann rearrangement reaction, oximes are frequently used in the industrial field. For this reason, a part of the literature related to oximes focus on cyclohexanone [2–12]. In addition, the oximes having appropriate geometric structure, behave as strong ligands. In the literature, there are many studies about complexes of oximes, especially transition metal complexes with 2-pfyridine carbaldehyde and other oximes [13–20]. Some complexes of oximes are inhibitors of nerve gas so there are a number of studies about the inhibition effect of oximes in the literature [21–23]. However, there are only a few studies about thermal decomposition of oxime complexes and a small number of studies about synthesis of paracetamol from

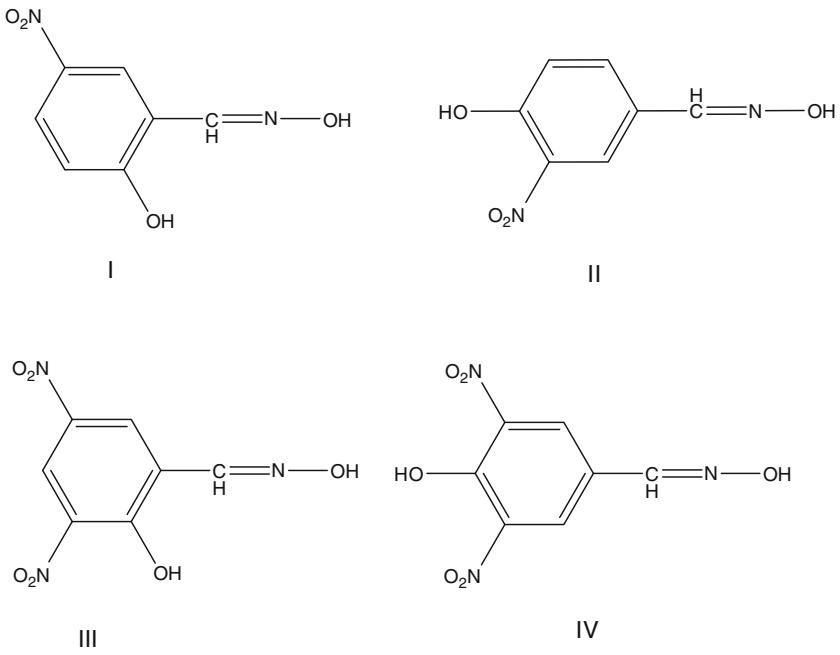


Fig. 1 Prepared nitro hydroxy benzaldoximes

2-hydroxy acetophenone oxime via Beckmann rearrangement [24, 25].

In this study, 5-nitro-2-hydroxy benzaldehyde, 3-nitro-4-hydroxy benzaldehyde, 3,5-dinitro-4-hydroxy benzaldehyde, and 3,5-dinitro-2-hydroxy benzaldehyde were synthesized using corresponding nitrated forms of 2-hydroxy benzaldehyde and 4-hydroxy benzaldehyde. These aldehydes were converted to nitro hydroxy benzaldoximes by condensation reaction with NH_2-OH in EtOH medium (Fig. 1).

This study had been planned to examine the behavior of oximes as energetic materials. All prepared compounds were characterized by IR, Elemental Analysis, and direct inlet MS. Afterward thermal behavior of nitro hydroxy benzaldoximes were investigated by TG.

In addition, the theoretic values were calculated. First, geometric optimizations of all molecules were done with the help of Gaussian 09 software. Then, the standard enthalpies of formation of these molecules were calculated theoretically with CBC-4M algorithm. CBC-4M algorithm was chosen because of its success in the calculation of formation enthalpies [26]. After calculation of the enthalpy of formations, enthalpy of reaction was calculated by Hess's Law [27].

$$\Delta H^{\circ}_{\text{Reaction}} = \sum \Delta H^{\circ}_{\text{Products}} - \sum \Delta H^{\circ}_{\text{Reactants}}$$

The nature of the observed exothermic peaks in the TG curves at approximately 200 °C were close to Gaussian peaks so the heat of reactions were determined by DSC and compared with experimental results and theoretic findings.

Experimental

General: In this study, Shimadzu Infinity model FTIR-Spectrometer with three reflectional ATR attachment was used for IR spectra. Elemental analyses were performed on Elemantar Vario Micro Cube instrument. Mass Spectra were obtained using Shimadzu, 2010 plus with DI unit and electron impact ionizer. DI temperature was varied in between 40 and 140 °C and the ionization was achieved with 70 eV electrons. Thermogravimetric analyses were performed using Shimadzu DTG-60H. In thermogravimetric analyses, temperature was varied between 30 and 600 °C. They were performed at 10 °C min^{-1} temperature raise rate, under N_2 atmosphere and in Pt pans. Calibration of the instrument was done with metallic In, Pb, or Zn. Used chemicals were Merck or Fluka brands and purification was not needed.

Nitration of 2-hydroxy benzaldehyde

Reaction was performed in two steps according to the literature [28]. 10 mL 2-hydroxy benzaldehyde and 10 mL HNO_3 (63 %) were dissolved in 50 mL of CH_3COOH and the mixture was stirred for half an hour in ice-water bath at 0–5 °C. After that, the reaction vessel was kept at room temperature and the solution became warmer because of the exothermic nitration reaction. Before starting to boil, this solution was poured into a 250 mL of ice-water mixture. Mixture of 3-nitro-2-hydroxy benzaldehyde and 5-nitro-2-hydroxy benzaldehyde were the precipitates which were then filtered and air dried. Yield of this reaction is found to be 90 %.

Separation of 3-nitro-2-hydroxy benzaldehyde and 5-nitro-2-hydroxy benzaldehyde

10 grams of the dried mixture was weighed, put into 125 mL NaOH (8 %) solution, stirred, and heated under hydrothermal conditions. This dark red solution was allowed to stand for a day and the crystalline precipitate was filtered. This crystalline substance was sodium salt of 3-nitro-2-hydroxy benzaldehyde. Obtained crystalline substance was dissolved in 100 mL of 4M HCl; the separated yellow organic substance was filtered and air dried. The remaining part was the solution of sodium salt of 5-nitro-2-hydroxy benzaldehyde and this part was added to 100 mL of 4M HCl; the separated yellow organic substance was filtered and air dried.

Melting point of 3-nitro-2-hydroxy benzaldehyde is 109 °C and the reaction yield is calculated as 65 %.

Important IR Data of 3-nitro-2-hydroxy benzaldehyde (cm^{-1}) are the following:

$\nu_{O-H} = 2804 \quad \nu_{C=O} = 1653 \quad \nu_{C=C} = 1631$

$\nu_{N=O} = 1334 \quad \nu_{C-H(Ar)} = 3091-3068$

$\nu_{C-H(Ald)} = 2887 \quad \delta_{C-H(Ar)} = 751$

The results of elemental analysis of 3-nitro-2-hydroxy benzaldehyde are as follows:

Expected C% = 50.31, $H = 3.01$, $N = 8.37$

Found C% = 49.80, $H = 3.36$, $N = 8.12$

Melting point of 5-nitro-2-hydroxy benzaldehyde is 127 °C and the reaction yield is found as 72 %.

Important IR Data of 5-nitro-2-hydroxy benzaldehyde (cm^{-1}) are the following:

$\nu_{O-H} = 2812 \quad \nu_{C=O} = 1654 \quad \nu_{C=C} = 1625$

$\nu_{N=O} = 1331 \quad \nu_{C-H(Ar)} = 3068-3047$

$\nu_{C-H(Ald)} = 2887 \quad \delta_{C-H(Ar)} = 748$

The results of elemental analysis of 5-nitro-2-hydroxy benzaldehyde are as follows:

Expected C% = 50.31, $H = 3.01$, $N = 8.37$

Found C% = 50.17, $H = 3.41$, $N = 7.86$

Synthesis of 3,5-dinitro-2-hydroxy benzaldehyde

10 grams of pulverized mixture of 3-nitro-2-hydroxy benzaldehyde and 5-nitro-2-hydroxy benzaldehyde was weighed and dissolved in 100 mL of H_2SO_4 (98 %) between 0 and 10 °C. After that, 20 mL of HNO_3 (99.5 %) was added to this solution slowly. The temperature was kept in between 10 and 30 °C. After the addition of HNO_3, the solution was stirred for about 1 h and poured into 500 mL ice-water mixture. Six hours later, 3,5-dinitro-2-hydroxy benzaldehyde was separated by filtering and was air dried.

For 3,5-dinitro-2-hydroxy benzaldehyde, MP: 56 °C, yield 90.95 %

IR data of 3,5-dinitro-2-hydroxy benzaldehyde/cm^{-1}

$\nu_{O-H} = 2774 \quad \nu_{C=O} = 1672 \quad \nu_{C=C} = 1629-1606$

$\nu_{N=O} = 1320 \quad \nu_{C-H(Ar)} = 3102-3072$

$\nu_{C-H(Ald)} = 2889 \quad \delta_{C-H(Ar)} = 756$

The results of elemental analysis of 3,5-dinitro-2-hydroxy benzaldehyde:

Expected C% = 39.64, $H = 1.90$, $N = 13.20$

Found C% = 39.72, $H = 2.19$, $N = 12.94$

Synthesis of 3-nitro-4-hydroxy benzaldehyde

It was synthesized according to the method described in the literature [29]. 5 g of 4-hydroxy benzaldehyde was dissolved in 25 mL of CH_3COOH at hydrothermal conditions and the solution was heated. 10 mL of HNO_3 (63 %) was added to this solution and the mixture was stirred while keeping the temperature below 110 °C. Then, the solution was poured into 250 mL ice-water mixture, filtered, and dried in the oven at 60 °C.

For 3-nitro-4-hydroxy benzaldehyde, MP: 142 °C, Yield 82 %

IR Data of 3-nitro-4-hydroxy benzaldehyde (cm^{-1})

$\nu_{O-H} = 3228 \quad \nu_{C=O} = 1683 \quad \nu_{C=C} = 1610$

$\nu_{N=O} = 1329 \quad \nu_{C-H(Ar)} = 3092-3063$

$\nu_{C-H(Ald)} = 2871 \quad \delta_{C-H(Ar)} = 740$

The results of elemental analysis of 3-nitro-4-hydroxy benzaldehyde:

Expected C% = 50.31, $H = 3.01$, $N = 8.37$

Found C% = 50.14, $H = 3.22$, $N = 7.91$

Synthesis of 3,5-dinitro-4-hydroxy benzaldehyde

5 grams of 3-nitro-4-hydroxy benzaldehyde was put into the solution of 20 mL of H_2SO_4 and 20 mL of fuming HNO_3 and the mixture was stirred for 1 h at 0 °C and for 6 h between 20 and 50 °C afterward. This solution was poured into 500 mL ice-water mixture, the precipitated yellow substance was filtered and dried in the oven at 60 °C.

For 3,5-dinitro-4-hydroxy benzaldehyde, MP: 142 °C, yield 82 %

IR data of 3,5-dinitro-4-hydroxy benzaldehyde (cm^{-1})

$\nu_{O-H} = 3150 \quad \nu_{C=O} = 1695 \quad \nu_{C=C(Ar)} = 1616$

$\nu_{N=O} = 1321 \quad \nu_{C-H(Ar)} = 3070-3042 \quad \delta_{C-H} = 763$

The results of elemental analysis of 3,5-dinitro-4-hydroxy benzaldehyde:

Expected C% = 39.64, $H = 1.90$, $N = 13.20$
Found C% = 40.07, $H = 2.28$, $N = 12.67$

Synthesis of oximes

All oximes were synthesized following the same procedure. The aldehyde component was dissolved in 50 mL of MeOH. An equivalent mole of $NH_2OH.HCl$ with the aldehyde component was dissolved in 20 mL of MeOH: H_2O (1:1) mixture and this solution is added to the aldehyde solution. After that, 5 mL MeOH solution of equivalent moles of Et_3N was added to this solution. The final solution was heated until boiling. After 24 h, the crystalline precipitate was filtered and air dried. It was recrystallized in MeOH. Data of the analyses for obtained oximes are as follows.

5-Nitro-2-hydroxy benzaldoxime

IR data of 5-nitro-2-hydroxy benzaldoxime/cm^{-1}
$\nu_{O-H(oxime)} = 3288$ $\nu_{C=N} = 1621$ $\nu_{C=C(Ar)} = 1575$
$\nu_{N=O} = 1331$ $\nu_{O-H(Phenol)} = 2762-2802$
$\nu_{C-H(Ar)} = 3097-3066$ $\delta_{C-H(Ar)} = 750$
MS data: $m/z = 182$

The results of elemental analysis of 5-nitro-2-hydroxy benzaldoxime:
Expected C% = 46.16, $H = 3.32$, $N = 15.37$
Found C% = 45.97, $H = 3.21$, $N = 15.18$

c3-Nitro-4-hydroxy benzaldoxime

IR data of 3-nitro-4-hydroxy benzaldoxime/cm^{-1}
$\nu_{O-H(oxime)} = 3286$ $\nu_{C=N} = 1624$ $\nu_{C=C(Ar)} = 1601$
$\nu_{O-H(Phenol)} = 3142$ $\nu_{C-H(Ar)} = 3092-3059$
$\delta_{C-H(Ar)} = 763$ $\nu_{N=O} = 1323$
MS data: $m/z = 182, 134, 109, 86, 63$

The results of elemental analysis of 3-nitro-4-hydroxy benzaldoxime:
Expected C% = 46.16, $H = 3.32$, $N = 15.37$
Found C% = 45.85, $H = 3.44$, $N = 14.92$

c33,5-Dinitro-2-hydroxy benzaldoxime

IR data of 3,5-dinitro-2-hydroxy benzaldoxime/cm^{-1}
$\nu_{O-H(oxime)} = 2285$ $\nu_{C=N} = 1629$ $\nu_{N=O} = 1324$
$\nu_{O-H(Phenol)}$ = unidentified
$\nu_{C-H(Ar)} = 3098-3078$ $\delta_{C-H(Ar)} = 749$
MS data: $m/z = 227$(molecular peak)

The results of elemental analysis of 3,5-dinitro-2-hydroxy benzaldoxime:
Expected C% = 37.02, $H = 2.22$, $N = 18.49$
Found C% = 36.86, $H = 2.17$, $N = 18.31$

3,5-Dinitro-4-hydroxy benzaldoxime

IR data of 3,5-dinitro-4-hydroxy benzaldoxime/cm^{-1}
$\nu_{O-H(oxime)} = 3215$ $\nu_{C=N} = 1631$
$\nu_{N=O} = 1340$ $\nu_{O-H(Phenol)} = 2787$
$\nu_{C-H(Ar)} = 3124-3062$ $\delta_{C-H(Ar)} = 773$
MS data: $m/z = 227$(molecular peak),
211(thermal peak), 209, 165, 119, 91, 62

The results of elemental analysis of 3,5-dinitro-4-hydroxy benzaldoxime:
Expected C% = 37.02, $H = 2.22$, $N = 18.49$
Found C% = 36.58, $H = 2.37$, $N = 19.13$

X-ray crystal structure analysis of 3-nitro-4-hydroxy benzaldoxime and 3,5-dinitro-2-hydroxy benzaldoxime

The diffraction measurements of 3-nitro-4-hydroxy benzaldoxime were done at room temperature on an oxford diffraction xcalibur (TM) Single crystal x-ray diffractometer with sapphire CCD detector using MoK_α radiation ($\lambda = 0.71073$ Å) and ω-2θ scan mode. Unit cell dimensions were determined and refined using the angular settings of 25 automatically centered reflections in $2.93 \leq \theta \leq 26.37$ range. The empirical absorption corrections were applied by the semi-empirical method via CrysAlis CCD software [30].

The X-ray diffraction intensity data of 3,5-dinitro-2-hydroxy benzaldoxime were collected at 100 K using an Enraf–Nonius CAD 4 diffractometer [31] working with MoKα radiation and on $\omega/2\theta$ scan mode. The cell parameters were determined from least squares of 16 centered reflections in the range of $3.07 \leq \theta \leq 28.31$. Three standard reflections for every 120 min were periodically measured during data collection and they showed no significant intensity variation.

Both models were obtained from the results of the cell refinement and the data reductions were carried out by means of the solution software SHELXL97 [32]. The structures of each compound were revealed by direct methods by means of SHELXS97 in the WinGX package [33].

Note that the displacement ellipsoids were drawn for the probability level of 50 % in the PLATON drawings.

Theoretical calculations

All theoretical calculations were carried out by means of Gaussian G09W (revision B.01) software package [26].

The structure and frequency calculations were performed by Becke's B3 parameter hybrid functional by means of the LYP correlation functional (B3LYP) [34]. For all H, C, N, and O atoms, a correlation-consistent polarized double-zeta basis set was used (cc-pVDZ) [35].

The enthalpies (H) and free energies (G) were calculated by the complete basis set (CBS) method of Petersson and coworkers to obtain accurate energies. The CBS models use the known asymptotic convergence of 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 SCF calculation as a base energy level and a MP2/6-31+G calculation with a CBS extrapolation to correct the energy through second order. A MP4(SDQ)/6-31+(d,p) calculation is used to approximate higher order contributions. In this study, we applied the modified CBS-4M

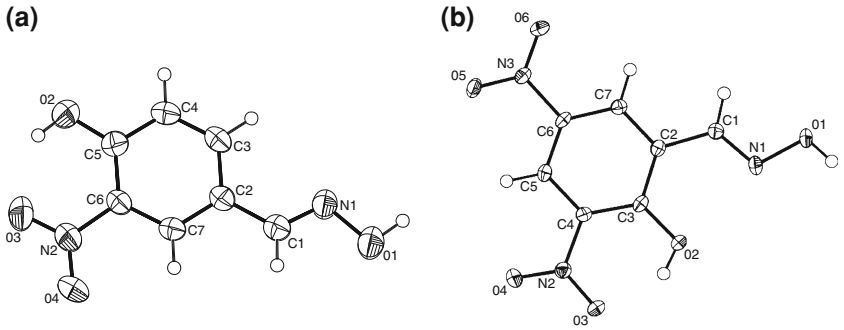


Fig. 2 The ORTEP drawings of 3-nitro-4-hydroxy benzaldoxime and 3,5-dinitro-2-hydroxy benzaldoxime

Table 1 Data and structure refinement for compounds **II** and **III**

Compound	**II**	**III**
Empirical formula	$C_7H_6N_2O_4$	$C_7H_5N_3O_6$
Formula mass/g mol^{-1}	182.14	227.14
T/K	293(2)	100(2)
Crystal size/mm	0.50 × 0.32 × 0.04 mm	0.45 × 0.29 × 0.19
Crystal system	Triclinic	Monoclinic
Space group	P^{-1}	$P2_1/c$
a/Å	7.0936(7)	6.6837(3)
b/Å	7.2149(7)	9.5550(4)
c/Å	8.0660(5)	13.4563(6)
Alpha	106.821(7)	90.00
Beta	100.963(7)	100.008(2)
Gamma	91.116(8)	90.00
V/Å^3	386.72(6)	846.28(6)
Z	2	4
Calc. density/g cm^{-3}	1.564	1.783
μ/mm^{-1}	0.131	0.159
F (000)	188	464
T_{min}–T_{max}	0.9374–0.9948	0.9646–0.970
Θ range/°	2.93–26.37	2.63–28.36
Index ranges	$-8 \le h \le 8$, $-9 \le k \le 8$, $-10 \le l \le 7$	$-7 \le h \le 8$, $-10 \le k \le 12$, $-17 \le l \le 17$
Reflections collected	7290	7681
Reflections unique	2457/1536	2108/1676
R_1, wR_2 (2ó)	0.0477/0.1010	0.0504/0.1068
R_1, wR_2 (all)	0.0817/0.1154	0.0372/0.0960
Data/parameters	1536/124	2108/147
GOOF of F^2	1.085	1.036
Largest difference peak hole/e Å^{-3}	0.221/−0.175	0.393/−0.264

method (M referring to the use of minimal population localization), which is a reparametrized version of the original CBS-4 Method and also includes some additional empirical corrections [36, 37].

Table 2 Selected bond lengths (Å) and angles (°) of compounds **II** and **III**

Compound **II**	
C(1)–N(1)	1.266(3)
C(5)–O(2)	1.344(3)
C(6)–N(2)	1.448(3)
N(1)–O(1)	1.411(2)
N(2)–O(4)	1.213(2)
N(2)–O(3)	1.229(2)
O(4)–N(2)–O(3)	122.08(19)
O(4)–N(2)–C(6)	119.35(19)
O(3)–N(2)–C(6)	118.6(2)
N(1)–O(1)–H(1A)	103.5(18)
Compound **III**	
O(1)–N(1)	1.3957(16)
O(3)–N(2)	1.2384(15)
O(5)–N(3)	1.2266(16)
O(6)–N(3)	1.2279(16)
O(4)–N(2)	1.2153(16)
O(2)–C(3)	1.3302(16)
N(1)–C(1)	1.2749(18)
N(2)–C(4)	1.4544(18)
N(3)–C(6)	1.4611(17)
C(1)–N(1)–O(1)	111.11(12)
O(1)–N(2)–O(3)	122.26(12)
O(4)–N(2)–C(4)	119.19(12)
O(3)–N(2)–C(4)	118.54(12)
O(5)–N(3)–O(6)	123.84(12)
O(5)–N(3)–C(6)	118.25(12)
O(6)–N(3)–C(6)	117.90(12)

Results and discussion

The ORTEP drawings of 3-nitro-4-hydroxy benzaldoxime and 3,5-dinitro-2-hydroxy benzaldoxime are given in Fig. 2a, b, respectively. XRD Data and structure refinement for compound **II** and **III** are given in Table 1, the selected bond angles and bond lengths obtained from the X-ray diffraction studies are given in Table 2, and the possible inter and intra H bonds and angles for **II** and **III** are given in Table 3. TG curves of compounds **I, II, III,** and **IV** are given in Fig. 3a–d, respectively. Average thermoanalytical data are given in Table 4.

As seen from Table 4, 3,5-dinitro-2-hydroxy benzaldoxime (**III**) remains as a solid up to 190 °C. Although it should be the otherwise due to the intermolecular hydrogen bonding, 3,5-dinitro-2-hydroxy benzaldoxime (**III**) remains as a solid up to a higher temperature than 3,5-dinitro-4-hydroxy benzaldoxime (**IV**). One melting peak can be seen in the thermogram of 3,5-dinitro-4-hydroxy benzaldoxime (**IV**) at around 180 °C. This peak is followed by an 8 % mass loss. Then, it turns into a stable compound which decomposes between 160 and 190 °C with an exothermic reaction. Therefore, 3,5-dinitro-4-hydroxy benzaldoxime (**IV**) was kept between 175 and 178 °C in a temperature-controlled oven. After this treatment, a new band was observed between 2123 and 2228 cm^{-1} in the IR spectra of the obtained stable compound. It probably corresponds to breaking away a water molecule from CH=N–OH because 8 % mass loss points that way (Fig. 4).

The C≡N vibration was observed in the IR spectrum of the aforementioned stable compound. But, $\nu_{O-H(oxime)}$ stretching band of oximes at 3280–3300 cm^{-1} has not been observed for the newly formed dinitro-hydroxy benzonitrile. In addition, a molecular peak was observed ($m/z = 209$) in the direct inlet mass spectra. Other important peaks were $m/z = 228$, 150, 88, and 62. $m/z = 227$, 211, 165, 119, and 91 peaks appeared more clearly with

Table 3 Possible inter and intra H bonds and angles for **II** and **III**

Donor–H–Acceptor	D–H	H–A	D–A	D–H–A
Compound **II**				
O(1)–H(1A)–N(1) #1	0.915(17)	1.99(2)	2.846(2)	155(2)
O(2)–H(2A)–O(3)	0.827(17)	1.92(2)	2.619(2)	141(3)
O(2)–H(2A)–O(3) #2	0.827(17)	2.34(2)	3.027(2)	140(2)
Compound **III**				
O(1)–H(1)–O(2)	0.84	2.15	2.8781(15)	145
O(1)–H(1)–N(1)	0.84	2.18	2.8682(16)	139
O(2)–H(6)–O(3)	0.84	1.85	2.5736(16)	143
O(2)–H(6)–N(2)	0.84	2.45	2.8974(16)	114
O(2)–H(6)–O(5)	0.84	2.57	3.1031(15)	123
O(2)–H(6)–O(6)	0.84	2.39	2.9742(15)	127

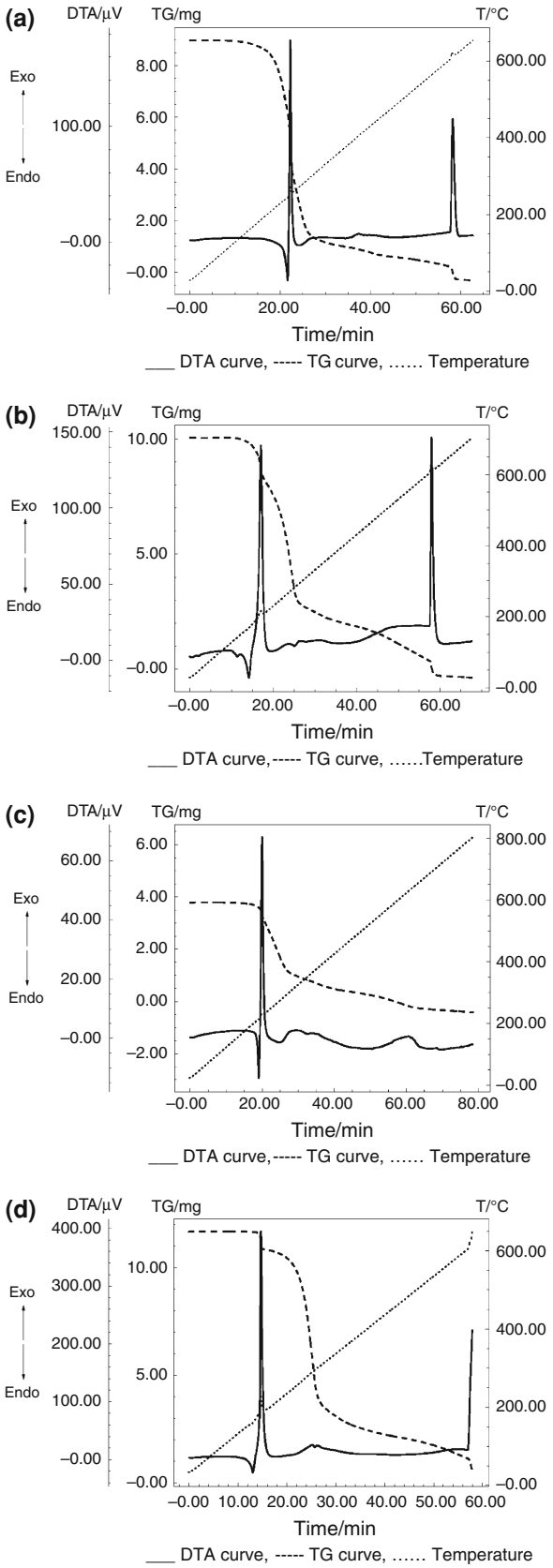


Fig. 3 **a** TG curve of compound **I**; **b** TG curve of compound **II**; **c** TG curve of compound III; **d** TG curve of compound **IV**

increasing DI temperature. $m/z = 209$ and 211 are common peaks for compounds **IV** and **V**. $m/z = 228$ peak is of only compound IV. $m/z = 228$, 227, and 211 peaks are due to molecule IV not undergoing thermal reaction. All the other m/z values can be explained easily with the help of the thermal analysis results.

3,5-Dinitro-4-hydroxy benzonitrile which is formed at 160 °C decomposes at 255 °C with an exothermic reaction as expected.

3,5-Dinitro-2-hydroxy benzaldoxime (**III**) remains as a solid up to 190 °C. Between 191 and 195 °C, an endothermic peak was observed, but in this thermal reaction there was no mass loss. So, this was the most probable melting. After that, an exothermic peak was observed. In this exothermic reaction, an 8 percent mass loss was observed. This exothermic peak was followed by another exothermic thermal reaction between 230 and 280 °C. This compound was kept for 4 h in a temperature-controlled oven between 160 and 190 °C. The IR signal around 2100–2200 cm^{-1} ceased to exist after the treatment. In addition, higher number of wave than 3200 cm^{-1} was not observed. However, thermal peak was observed at DI-MS spectrum around $m/z = 209$. At that time, according to literature, Beckmann rearrangement must be observed. After Beckmann rearrangement, most probably product was dinitro phenoxazine [38].

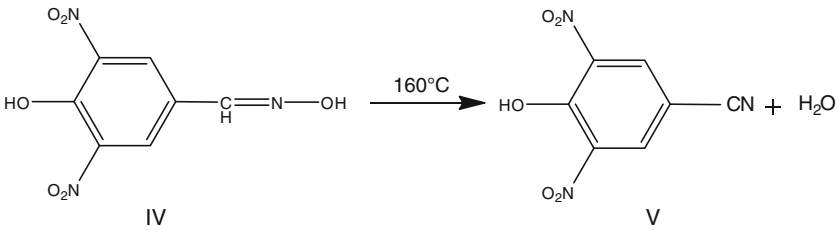
As shown in the Fig. 5, compound **III** was converted to dinitro phenoxazine with three intermediate reactions.

After the formation of dinitro phenoxazine, it decomposed thermally with an exothermic reaction. Therefore, thermal study was conducted by means of computerized TG. Temperature was increased at 10 °C min^{-1} rate up to 180 °C and was kept constant for half an hour. Then, it was increased to 190 °C by means of a rate of 2 °C min^{-1} and was kept constant for another half an hour. After that, the rate of temperature rise was always 10 °C min^{-1}. A continuous and sharp exothermic peak was observed at 280 °C. Most probably, this exothermic reaction was the decomposition of dinitro phenoxazine.

In fact, the melting points of many p-substituted organic compounds are higher than their o-substituted counterparts. However, in contrary to the general case, melting point of 3,5-dinitro-2-hydroxy benzaldoxime is higher than 3,5-dinitro-4-hydroxy benzaldoxime. The melting range of 3,5-dinitro-2-hydroxy benzaldoxime is between 193 and 195 °C and it is between 163 and 166 °C for 3,5-dinitro-4-hydroxy benzaldoxime. After melting, both of these compounds turned into new substances. The oxime group of 3,5-dinitro-4-hydroxy benzaldoxime (**IV**) is turned into a $-C\equiv N$ group by departing of an H_2O molecule. 3,5-dinitro-2-hydroxy benzaldoxime shaped up as dinitro phenoxazine via Beckmann rearrangement. The most important difference between compound **III** and **IV** is the strong

Table 4 The thermoanalytical data of investigated benzaldoximes

Compound	Melting point/ °C	First thermal reaction (H_2O elimination)			Second thermal reaction	
		Temperature range/ °C	Calculated mass loss %	Found mass loss %	Temperature range/ °C	Found mass loss %
I	240	240–280 DTA peak 265 Exotherm	9.89	86	–	–
II	165	198–224 DTA peak 213 Exotherm	9.89	10.46 ± 0.84	246–295	58.96 ± 1.89
III	191	195–230 DTA peak 208 Exotherm	7.92	8.21 ± 0.46	276–324	65.23 ± 2.96
IV	161	175–224 DTA peak 182 Exotherm	7.92	7.48 ± 0.27	255–304	66.38 ± 3.58



IV V

Fig. 4 Dehydration reaction of compound **IV**

intermolecular hydrogen bonding of compound III. There are some studies in literature about strong hydrogen bonding in 2-hydroxy schiff bases [39]. And, in some cases, even the phenolic proton of dinitro compounds passing through the iminic nitrogen, iminic structure converts to amine [40, 41] (Fig. 6).

There is a similar situation between compounds **I** and **II**. Compound **I** degrades at a higher temperature than 5-nitro-2-hydroxy benzaldoxime (260 °C) and probably goes through Beckmann rearrangement. However, the loss of water is not clearly observable in the TG curves. 3-nitro-4-hydroxy benzaldoxime (**II**) behaves like 3,5-dinitro-4-hydroxy benzaldoxime. This compound loses one H_2O at about 160 °C. At this step, formation of benzonitrile is observable by IR. The only significant difference between 3-nitro-4-hydroxy benzonitrile and 3,5-dinitro-4-hydroxy benzonitrile is in the decomposition reactions of these two. 3-nitro-4-hydroxy benzonitrile decomposed with a weak endothermic reaction, whereas the other decomposed with an exothermic reaction.

As mentioned in the introduction, heats of thermal reactions of compound **III** and compound **IV** between 160 and 220 °C were estimated theoretically with the help of Gaussian 09 software and were determined experimentally by DSC. All these data are given in Table 5. The theoretic findings and the experimental data are in good agreement with each other.

The kinetics of the three reactions is fast enough to calculate the enthalpies.

First reaction (Beckmann rearrangement);

$$\Delta H^{\circ}_{\text{intermediate reaction1}} = -376.479 - (-192.481) = -183.999 \text{ kJ mol}^{-1}$$

Second reaction (prototropic form exchange):

$$\Delta H^{\circ}_{\text{intermediate reaction2}} = -248.408 - (-376.479) = 128.071 \text{ kJ mol}^{-1}$$

Third reaction:

$$\Delta H^{\circ}_{\text{intermediate reaction3}} = [(-102.727) + (-240{,}605)] - (-248.408) = -94.924 \text{ kJ mol}^{-1}$$

Enthalpy of total reaction:

$$\Delta H^{\circ}_{\text{reaction}} = (-183.99) + (128.07) + (-94.92) = -150.85 \text{ kJ mol}^{-1}$$

Experimental data was -142.31 ± 5.36 kJ mol^{-1}. Similarly, for reaction given in Fig. 3,

$$\Delta H^{\circ}_{\text{reaction}} = [(-68.71) + (-240.61)] - (-141.07) = -168.248 \text{ kJ mol}^{-1}$$

Fig. 5 Possible intermediates following Beckmann rearrangement reaction

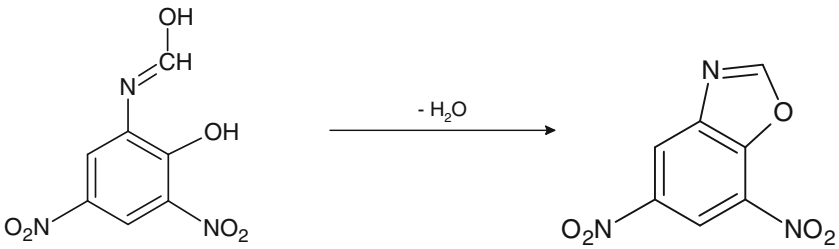
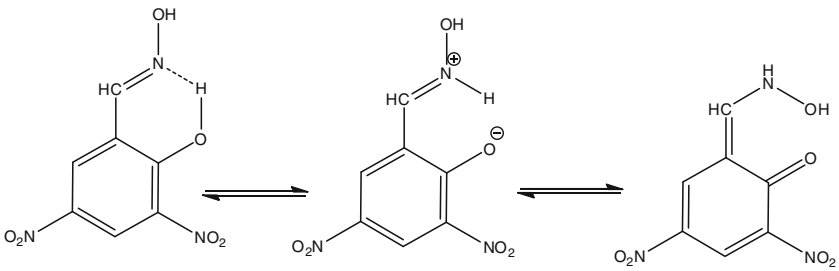


Fig. 6 Tautomeric forms and resonance structures of compound **III**



For the same reaction, experimental data were -144.89 ± 9.90 kJ mol^{-1}.

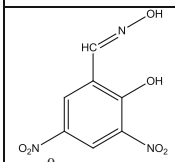
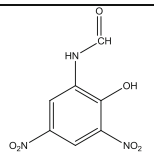
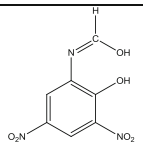
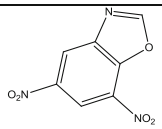
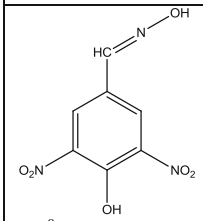
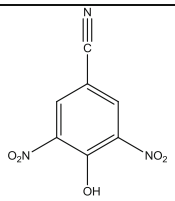
In one of the studies about the formation of benzonitrile in the literature, product analysis was performed by GC. In this study, waste products were determined except benzonitrile. Yield of formation of benzonitrile was 80–85 % [42]. Most probably, owing to the same reason, there is a significant difference between the theoretic and experimental data of compound **IV**.

Computational aspects

The molecular structures of compounds **III**–**VIII** were fully optimized without symmetry constraints at B3LYP/cc-pVDZ level of theory to C_1 symmetry in all cases (Fig. 7). The frequencies were calculated at the same level of theory and compared with the experimental values (Table 6).

The enthalpies of the gas-phase species M were computed according to the atomization energy method (Eq. 1) (Tables 7, 8, 9) [43–45]. 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-4M-calculated enthalpy of the molecule M (H_{298} in Table 7), $\Sigma_{atoms} H°$ denotes the CBS-4M-calculated enthalpies for the individual atoms (see bottom of Table 7), and $\Sigma_{atoms} \Delta_f H°$ stands for the experimentally reported literature values for

Table 5 Comparison of experimental and theoretic data of compound **III** and compound **IV**

Reactant and enthalpy of formation / kJmol^{-1}	Estimated intermediate compound and theoretical enthalpy of formation/ kJmol^{-1}		Final compound and theoretical enthalpy of formation/ kJmol^{-1}	Reactions theoretical enthalpy of formation/ kJ mol^{-1}	Measured enthalpy of reaction at DSC/ kJ mol^{-1}
 $\Delta H^0 = 192.481$	 $\Delta H^0 = -376.479$	 $\Delta H^0 = -316.558$	 $\Delta H^0 = -102.727$	–146.81	–142.31 ± 5.36
 $\Delta H^0 = -141.074$			 $\Delta H^0 = -68.71$ $\Delta H^0 = -240.605$	–168.24	–144.66 ± 2.40

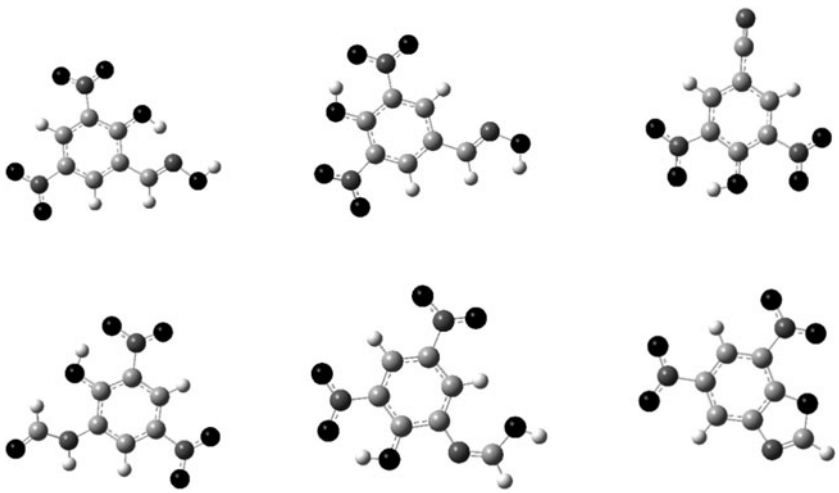


Fig. 7 Optimized molecular structures of **III** (*top left*), **IV** (*top center*), **V** (*top right*), **VI** (*bottom left*), **VII** (*bottom center*) and **VIII** (*bottom right*)

Table 6 Comparison of the calculated (B3LYP/cc-pVDZ) and experimentally observed vibrational frequencies of compounds **I**, **II** and **III**

Assignment	**III**		**IV**		**V**		**VIII**	
	Calculated frequencies/ cm^{-1}	Observed IR frequencies/ cm^{-1}	Calculated frequencies/ cm^{-1}	Observed IR frequencies/ cm^{-1}	Calculated frequencies/ cm^{-1}	Observed IR frequencies/ cm^{-1}	Calculated frequencies/ cm^{-1}	Observed IR frequencies/ cm^{-1}
νC–H(Ar)	3224	3158	3219	3125	3236	3163	3250	3086
νC–H (Aldehydic)	3130	2870	3035	2901	–	–	–	–
νC–H (Phenoxazinic)	–	–	–	–	–	–	3276	2877
νC–C (Ar)	1656	1570	1601	1543	1602	1610	1644	1608
νNO_2	1383	1333	1388	1359	1388	1344	1385	1343
νOH (Phenolic)	3197	3265	3237	3216	3228	3290	–	–
νOH (Oxime)	3764	3238	3548	3460	–	–	–	–
νC=N	1702	1630	1675	1633	–	–	1576	1631
νC≡N	–	–	–	–	2348	2223	–	–

Table 7 CBS-4M Results

Compound	p.g.[a]	NIMAG[b]	$-H^{298}$/a.u.[c]	$-G^{298}$/a.u.[d]
III	C_1	0	884.001225	884.057159
IV	C_1	0	883.985558	884.042014
V	C_1	0	807.692661	807.744725
VI	C_1	0	884.070201	884.125708
VII	C_1	0	884.047341	884.102597
VIII	C_1	0	807.707429	807.757262
H			0.500991	0.514005
C			37.786156	37.803062
N			54.522462	54.539858
O			74.991202	75.008515

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

the enthalpies of formation for the corresponding atoms ($\Delta_f H°_{298}$ in Table 8).

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

The enthalpies of sublimation for all species **III**–**VIII** were estimated according to Trouton's rule (Eq. 2, Table 9) [46] with observed melting points from the TG curves, 191, 136, 288, 208, 208, and 256 °C. The validity of Trouton's law reflects the fact that the entropy of vaporization is approximately constant for many compounds and that $\Delta H_{\text{sub.}} \approx \Delta H_{\text{vap.}} + \Delta H_{\text{fusion}}$, with $\Delta H_{\text{vap}} >> \Delta H_{\text{fusion}}$ so that $\Delta H_{\text{sub.}} \approx \Delta H_{\text{vap.}}$.

Table 8 Literature values for atomic $\Delta H°_f{}^{298}$/kcal mol^{-1}

	Ref. [43]	NIST [46]
H	52.6	52.1
C	170.2	171.3
N	113.5	113.0
O	60.0	59.6

$$H_{\text{sub.}} = 188\, T_m \text{ J mol}^{-1} \quad (2)$$

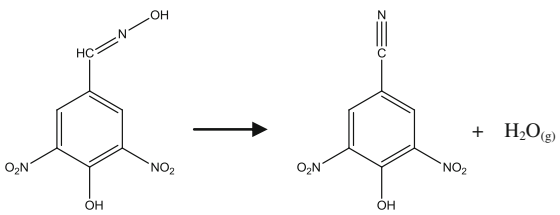
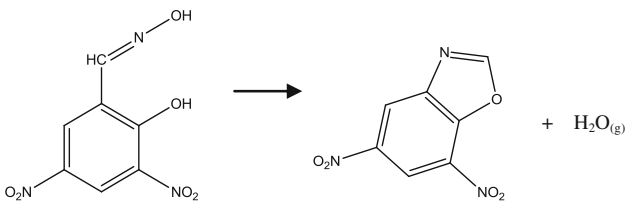
The calculated molar enthalpies of formation for the compounds **I**–**VI** are summarized in Table 9.

The calculated and experimental enthalpies of decomposition have been compared. Compounds **III** and **IV** are transformed to **VIII** and **V**, respectively, in Table 10, including the elimination of water.

Table 9 Enthalpies of the gas-phase species M, enthalpies of sublimation (ΔH_{sub}) and enthalpies of formation ($\Delta_f H°$) of the compounds

M	$\Delta_f H°$(g,M)/kJ mol^{-1}	ΔH_{sub}/kJ mol^{-1}	$\Delta_f H°$(s,M)/kJ mol^{-1}
III	−113.1	87.2 (464 K)	−192.5
IV	−64.2	76.9 (409 K)	−141.1
V	36.8	105.5 (561 K)	−68.7
VI	−286.0	90.4 (481 K)	−376.5
VII	−226.1	90.4 (481 K)	−316.5
VIII	−2.0	100.8 (529 K)	−102.7

Table 10 Comparison of the calculated and experimental enthalpies of decomposition for compounds **III** and **IV**

	ΔH/kJ mol^{-1} (CBS-4M)	ΔH/kJ mol^{-1} (exp.)
	−168.25 (exothermic)	−144.66 ± 2.40 (exothermic)
	−146.81 (exothermic)	−142.34 ± 5.40 (exothermic)

Conclusions

The thermal decomposition of compounds **III** and **IV** have been studied theoretically and experimentally. **III** was seen to lose water more easily with respect to **III** and consecutively transform into benzonitrile. This confirmed the stability of **III** and its transformation into phenoxazine via the Beckmann rearrangement. The formation enthalpies and decomposition reaction enthalpies were calculated by means of the CBS-4M theoretic program for both situations. Theoretic and experimental results were in harmony.

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