Full Paper

Experimental and Computational Studies on the Thermal Degradation of Nitroazidobenzenes

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Abstract: In this combined experimental and theoretical study the thermal degradation of 2-nitroazidobenzene (**I**), 2,4-dinitroazidobenzene (**II**) and 2,4,6-trinitroazidobenzene (**III**) to yield benzofuroxan (**IV**), 4-nitrobenzofuroxan (**V**), and 4,6-dinitrobenzofuroxan (**VI**) were investigated by thermoanalytical (TG, DSC) and computational methods. In contrast, furoxan formation was not observed for 4-nitroazidobenzene (**VII**) under heating due to the *para* position of the nitro group in the benzene ring. All compounds were characterized by elemental analysis, vibrational (IR) spectroscopy and mass spectrometry. The crystal structure of compound **III** was determined by single-crystal X-ray diffraction. DFT-based structure optimizations and frequency analyses were performed at the B3LYP/cc-pVDZ level of theory. The structural parameters of the fully optimized compound **III** showed very good agreement with the single-crystal X-ray data. The enthalpies of formation for compounds **I**, **II**, **III**, **IV**, **V**, and **VI** were calculated using the complete basis set (CBS-4M) method of Petersson and co-workers in order to obtain accurate energies. The enthalpies of degradation for compounds **I**, **II**, and **III** were obtained from calculated enthalpies of formation according to the Hess Law and were compared with the experimental values, which were available from DSC analysis and were found to be in very good agreement.
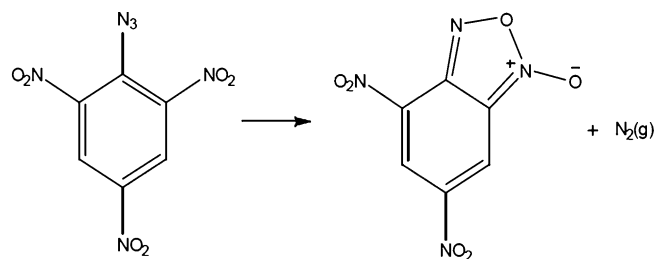
Keywords: Benzofuroxan · CBS-4M · Density functional calculations · Nitroazidobenzene · Thermal analysis

1 Introduction

It is well known that azide ions show nucleophilic substitution reactions in aromatic ring systems [1–6]. Especially nitro-substituted halobenzenes tend to form nitroazidobenzenes by nucleophilic substitution of the halogen with an azide unit in polar organic solvents (e.g. DMSO, DMF) and volatile solvents (e.g. aceton, methanol). Nitroazidobenzenes can also be obtained by diazotization of nitroanilines and hydrazines.

It has been reported in literature that nitroazidobenzenes, which are stable at room temperature, decompose to form nitrobenzofuroxan derivatives at 100–130 °C (Scheme 1) [7]. In the series of the nitroazidobenzene derivatives, **I**, **II**, **III**, and **VII** only the thermal decomposition of compound **III** has been investigated experimentally [7]. Among the decomposition products only the crystal structure of 4,6-dinitrobenzofuroxan (**VI**) has been determined in 1972 [8] and recently re-determined in 2004 by single-crystal X-ray diffraction [9]. A literature survey reveals that the thermal decomposition of nitroazidobenzene derivatives under investigation in this study has so far not been studied theoretically. Only the electronic energy of 2,4,6-tri-nitroazidobenzene (**III**) has been calculated and reported to be $E^{B3LYP} = -1009.285757$ a.u. [10a,b].

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Scheme 1. Transformation of TNAB to 4,6-DNBF.

The goal of this combined experimental and theoretical study was to perform detailed thermal analyses on thermal degradation of some nitroazidobenzene derivatives with thermoanalytical techniques and to develop computational methods to understand the thermal degradation behavior. The computed enthalpies of decomposition were compared with the experimental values to check the accuracy of employed methods. The effects of the substitution pattern and the number of the nitro groups in the aromatic ring on the decomposition pathway were also discussed.

2 Results and Discussion

2.1 Thermal Behavior

The TG-DTA curves of **I**, **II**, and **III** are shown in Figure 1. Each species yields benzofuroxan derivatives by elimination of nitrogen at 110–130 °C. The decomposition product of **III**, 4,6-dinitrobenzofuroxan **VI**, decomposes to gaseous products with a second exotherm at higher temperature due to the nitro groups, whereas **V** and **VII** behave as an organic compound and evaporate without an exotherm. In contrast, benzofuroxan formation was not observed for compound **VII** due to the *para* position of nitro group with respect to the azide unit. In the TG-DTA curve of compound **VII** (Figure 2) weight loss for nitrogen elimination does not occur, the compound decomposes to gaseous products with a weak exotherm. The heats of exotherms
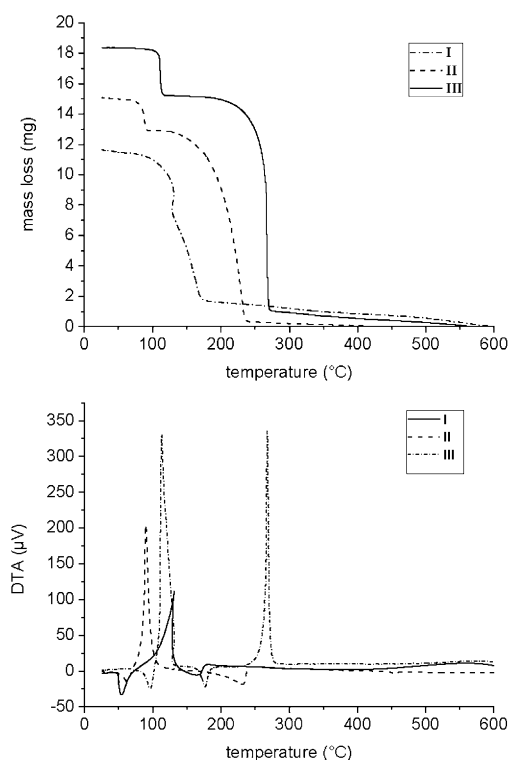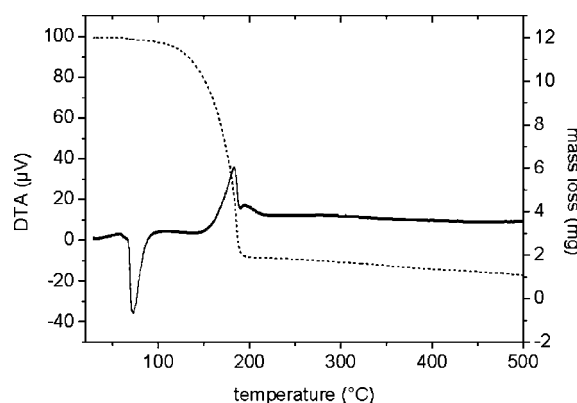
Figure 2. TG-DTA curve of compound VII.
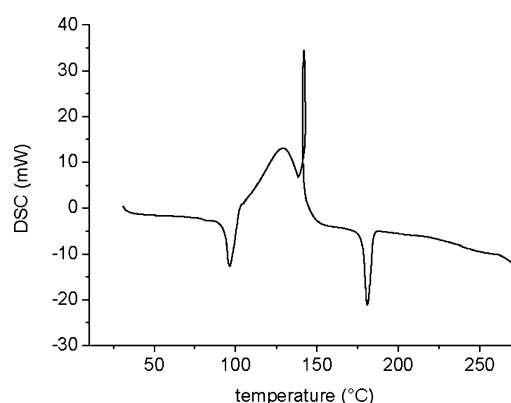
Figure 3. DSC curve of compound III (exo up, endo down).

for compounds **I**, **II**, and **III** were measured by DSC (DSC curve of **III** is given in Figure 3). The enthalpy of decomposition can be obtained experimentally according to the below equation. The constant pressure molar heat capacity for diatomic nitrogen is approximately $C_p = 7/2$ R (29.10 J mol^{-1}K^{-1}) and is given as $C_p = 28.58 + 3.77 \times 10^{-3}T - 0.5 \times 10^{-5}T^2$ J mol^{-1}K^{-1} in literature [11]. Since C_p involves both increase in internal energy and work done against outer pressure, Equation (1) can be expressed as $\Delta H =$ heat measured by DSC $+ C_p \cdot \Delta T$. Between temperatures of 30 °C and 120 °C $C_p \cdot \Delta T$ is equal to 2.62 kJ mol^{-1}. All thermoanalytical results for the investigated compounds are summarized in Table 1.

$$\Delta H_{reac.} = \text{Heat measured by DSC (kJ mol}^{-1})$$
$$+ \text{energy required to heat N}_2 \, \Delta T \text{ (kJ mol}^{-1})$$
$$+ \text{work term for N}_2 \text{ (kJ mol}^{-1})$$

2.2 X-ray Structure

Single crystals of 2,4,6-trinitroazidobenzene (**III**) suitable for X-ray diffraction were obtained by recrystallization from methanol. The structure was solved by direct methods using SHELXS97 implemented in the WinGX package [12].

Figure 1. (a) TG curves (b) DTA curves of compound I, II, and III.

Table 1. Thermoanalytical results.

	I. Thermal reaction: Formation of benzofuroxan derivatives with elimination of nitrogen				II. Thermal reaction: Degradation	
	Temp. range/°C	Exp. mass loss/%	Obs. mass loss/%	Heat measured by DSC + $C_p \cdot \Delta T$/kJmol^{-1}	Temp. range/°C	Mass loss/%
2-NAB (**I**)	77–155	17.0	27.1	−113.3 (±0.5)	135–184	–
2,4-DNAB (**II**)	54–118	13.4	12.8	−90.9 (±2.8)	202–257	78.3
2,4,6-TNAB (**III**)	88–126	11.0	13.5	−125.1 (±6.2)	236–284	79.6

The molecular structure of compound **III** in the crystalline state is depicted in Figure 4 with selected bond lengths (pm) and angles (°). Crystallographic data are reported in Table 2.

2.3 Computational Aspects

The molecular structures of compounds **I**, **II**, **III**, **IV**, **V**, and **VI** were fully optimized without symmetry constraints at B3LYP/cc-pVDZ level of theory to C_1 symmetry in all cases (Figure 5). The frequencies were also calculated at the same level of theory. As shown by Politzer and others, the DFT method has proven to be an efficient and reliable tool in the prediction of the molecular structures and energetics of nitrobenzene derivatives [13a, b].

The enthalpies of the gas-phase species M were computed according to the atomization energy method (Equation (1)) (Table 3 and Table 4) [14–16]. In Equation (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 3), $\Sigma_{atoms}H°$ denotes the CBS-4 M calculated enthalpies for the individual atoms (see bottom of Table 3) (1 a.u. = 2623.7 kJ mol^{-1}), and $\Sigma_{atoms}\Delta_f H°$ stands for the experimentally reported literature values for the enthalpies of formation

Table 2. Data and structure refinement for compound **III**.

	III
Empirical formula	$C_6H_2N_6O_6$
Formula weight	254.14
T/K	293(2)
Crystal size /mm	0.24 × 0.20 × 0.08
Crystal system	orthorhombic
Space group	*Pbca*
a/pm	1033.09(7)
b/pm	1253.40(10)
c/pm	1469.50(10)
β/°	90
V/pm^3	1.902×10^9 (2)
Z	8
ρ/kg m^{-3}	1774
μ/mm^{-1}	0.161
F(000)	1024
θ range/°	2.77–26.37
Index ranges	$-12 \leq h \leq 12$
	$-11 \leq k \leq 15$
	$-17 \leq l \leq 18$
Reflections collected	7290
Reflections unique	1945 (R(int) = 0.0296)
R_1, wR_2 (2σ)	0.0480/0.0923
R_1, wR_2 (all)	0.0954/0.1110
Data/restraints/parameters	1945/0/163
GOOF of F^2	1.055
Largest difference peak/hole /10^{-3} pm^3)	0.305/−0.217
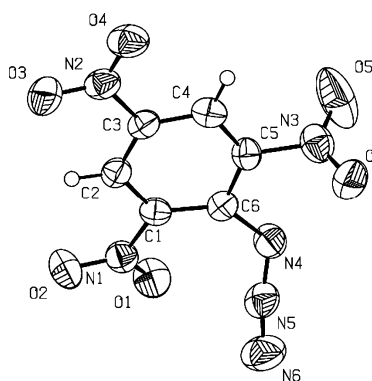
Figure 4. Molecular structure of **III** as ORTEP presentation at the 50 % level; selected bond lengths/pm and angles/° of **III**: C(1)–N(1) 146.7(3), C(3)–N(2) 146.7(3), C(5)–N(3) 147.1(3), C(6)–N(4) 139.4(3), N(3)–O(5) 119.8(3), N(3)–O(6) 120.1(3), N(4)–N(5) 125.0(3), N(5)–N(6) 111.5(3), C(2)–C(1)–N(1) 116.0(2), C(6)–C(5)–N(3) 117.6(2), N(4)–C(6)–C(5) 114.2(2), O(5)–N(3)–O(6) 125.0(3), O(5)–N(3)–C(5) 117.2(3), N(5)–N(4)–C(6) 119.3(2), N(6)–N(5)–N(4) 170.0(3).
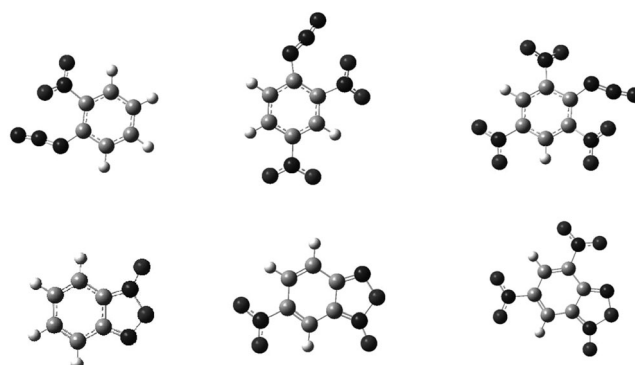
Figure 5. Optimized molecular structures of **I** (top left), **II** (top center), **III** (top right), **IV** (bottom left), **V** (bottom center), and **VI** (bottom right).

Table 3. CBS-4M results.

	p.g.[a]	NIMAG[b]	$-H_{298}$[c]/a.u.	$-G_{298}$[d]/a.u.
I	C_1	0	599.518684	599.564683
II	C_1	0	803.809930	803.862396
III	C_1	0	1008.088011	1008.146837
IV	C_1	0	490.151227	490.190365
V	C_1	0	694.444920	694.490552
VI	C_1	0	898.727422	898.779401
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-4 M calculated enthalpy. d) CBS-4 M calculated Gibbs free energy.

Table 4. Enthalpies of gas phase species M.

M	$\Delta_f H°(g,M)$/kcal mol^{-1}	$\Delta_f H°(g,M)$/kJ mol^{-1}
I	98.2	410.7
II	98.1	410.2
III	106.3	444.3
IV	74.5	311.4
V	72.9	304.6
VI	78.2	327.0

($\Delta_f H°_{298}$) for the corresponding atoms H, C, N, O to be 217.98, 716.68, 472.68, and 249.18 kJ mol^{-1}, respectively [17].

$$\Delta_f H^0(g,M) = H(M) - \Sigma_{atoms} H° + \Sigma_{atoms} \Delta_f H° \qquad (1)$$

The enthalpies of sublimation for all species **I**, **II**, **III**, **IV**, **V**, and **VI** were estimated to be 61.3, 61.7, 68.3, 64.6, 64.5, and 83.8 kJ mol^{-1}, respectively, according to Trouton's rule (Equation (2)) [18] with observed melting points from TG curves of 52.9 °C, 55.0 °C, 90.3 °C, 70.4 °C, 70.0 °C, and 172.7 °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

$\Delta H_{vap.} \gg \Delta H_{fusion}$ so that $\Delta H_{sub.} \approx \Delta H_{vap.}$

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

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

The calculated and experimental enthalpies of decomposition of compounds **I**, **II**, and **III** to **IV**, **V**, and **VI**, respectively, with elimination of nitrogen are compared in Table 6.

Table 5. Enthalpies of formation ($\Delta_f H°$) of the compounds.

	$\Delta_f H°(s,M)$/kJ mol^{-1}
I	349.4
II	348.5
III	376.0
IV	246.8
V	240.1
VI	243.2

Table 6. Comparison between the calculated and the experimental enthalpies of decomposition of compounds **I**, **II**, and **III**.

	$\triangle H$/kJ mol^{-1} (CBS-4 M)	$\triangle H$/kJ mol^{-1} (exp.)
2-NAB→BF + N$_2$(g)	−102.6	−111.3 ($\pm$0.5)
2,4-DNAB→4-NBF + N$_2$(g)	−108.4	−90.9 ($\pm$2.8)
TNAB→4,6-DNBF + N$_2$(g)	−132.8	$\cong$125.1($\pm$6.2)

3 Experimental and Theoretical Methods

General: TGA-DTA and DSC curves were obtained with a Shimadzu TG-60H and a DSC-60 instrument, with a heating rate of 10 K min^{-1} in a nitrogen atmosphere in platinum pans. DSC measurements were calibrated by standard pure indium at a heating rate of 10 K min^{-1}. For statistical reasons, all DSC experiments were repeated up to five times. Infrared spectra were recorded with a Shimadzu Infinity model FTIR-Spectrometer with ATR attachment. Elemental analyses were performed with a Elementar Vario Micro Cube instrument. Mass spectra were obtained with a Shimadzu 2010 plus instrument with ionization of solid samples by direct electron impact (DEI) in a DI unit.

Structure Characterization: A single crystal of compound **III** was analyzed with an Oxford Diffraction Xcalibur (TM) Single Crystal X-ray Diffractometer with a sapphire CCD detector using Mo-K_α radiation ($\lambda = 71.073$ pm) operating in the $\omega/2\theta$ scan mode. The unit-cell dimensions were determined and refined by using the angular settings of 25 automatically centered reflections in $2.77 \leq \theta \leq 26.37$ range. The empirical absorption corrections were applied by the semi-empirical method via the CrysAlis CCD software [19]. Models were obtained from the results of the cell refinement and the data reductions were carried out using the solution software SHELXL97 [20]. The structure of compound **III** was solved by direct methods using the SHELXS97 software implemented in the WinGX package [12].

Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository number CCDC-860838 (**III**) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

All theoretical calculations were carried out using the Gaussian G09W (revision B.01) program package [21].

The structure and frequency calculations were performed with Becke's B3 parameter hybrid functional by using the LYP correlation functional (B3LYP) [22]. For all H, C, N, and O atoms, a correlation consistent polarized double-zeta basis set was used (cc-pVDZ) [23].

The enthalpies (*H*) and Gibbs free energies (*G*) were calculated using the complete basis set (CBS) method of Petersson and co-workers in order to obtain very 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 uses a large basis set SCF calculation as a base energy, and an MP2/6-31+G calculation with a CBS extrapolation to correct the energy through second order. An MP4(SDQ)/6-31+(d,p) calculation is used to approximate higher order contributions. In this study, we applied the modified CBS-4M 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 [24a,b]. For a reference concerning the suitability and reliability of the applied CBS-4 M method see for example ref. [25].

4 Synthesis of Compounds

2-Nitroazidobenzene (I): The compound was obtained by following the procedure described in Ref. [3]. 2-Nitroaniline (8 g, 0.05 mol) was dissolved by heating in concentrated sulfuric acid (80 mL,) and water (20 mL). The solution was cooled to −5 °C in a salt-ice bath and NaNO$_2$ (3.45 g, 0.05 mol) in water (20 mL) was added dropwise. After 1 h of stirring at 0 °C, NaN$_3$ (3.25 g, 0.05 mol) in water (20 mL) was added dropwise. **Caution!** HN$_3$ may form, which is highly toxic and volatile. Appropriate safety precautions should be taken. The precipitated yellow crystals were filtered off and washed with water and dried in air. The filtrate was recrystallized from methanol. Yield: 82%; m.p. 53 °C. Elemental analysis for C$_6$H$_4$N$_4$O$_2$ (164.12): calcd. C 43.9, H 2.5, N 34.1%; found: C 43.7, H 2.5, N 29.4%. IR: $\tilde{v} =$ 3103 (vC−H$_{Ar}$), 1601 (vC−C$_{Ar}$), 2116 (vN$_3^-$), 1341 (vNO$_2$), 729 (δC−H$_{Ar}$) cm^{-1}. **MS** (DEI): *m/z*: 136, 76 (DI temp. 62 °C).

2,4-Dinitroazidobenzene (II): The compound was obtained by following the procedure given in Ref. [2]. 2,4-Dinitrophenylhydrazin (10 g, 0.05 mol) was dissolved in H$_2$SO$_4$ (10%, 80 mL) and cooled to −5 °C in a salt-ice bath. To this solution, NaNO$_2$ (3.45 g, 0.05 mol) in water (20 mL) was added dropwise. After 1 h of stirring at 0 °C, NaN$_3$ (3.25 g, 0.05 mol) in water (20 mL) was added dropwise. **Caution!** HN$_3$ may form, which is highly toxic and volatile. Appropriate safety precautions should be taken. The precipitated yellow solid was filtered off and washed with water and dried in a vacuum (85–133 kPa). Yield: 68%; m.p. 55 °C. Elemental analysis for C$_6$H$_3$N$_5$O$_4$ (209.12): calcd. C 34.5, H 1.4, N 33.5%; found: C 34.1, H 1.7, N 28.4%. IR: $\tilde{v} =$ 3127 (vC−H$_{Ar}$), 1601 (vC−C$_{Ar}$), 2120 (vN$_3^-$), 1340 (vNO$_2$), 719 (δC−H$_{Ar}$) cm^{-1}. **MS** (DEI): *m/z*: 181, 75 (DI temp. 68 °C).

2,4,6-Trinitroazidobenzene (III): The compound was obtained by following the procedure in Ref. [3]. 2-Nitroazidobenzene (5 g, 0.03 mol) was added to a well-stirred mixture of fuming HNO$_3$ (10 mL) and concentrated H$_2$SO$_4$ (10 mL) which was cooled to 0 °C. After 1 h of stirring at 0 °C, the reaction mixture was carefully poured onto ice, the yellow solid was filtered off and washed with water. The filtrate was recrystallized from methanol. Yield: 62%; m.p. 90 °C. Elemental analysis for C$_6$H$_2$N$_6$O$_6$ (254.12): calcd. C 28.4, H 0.8, N 33.1%; found: C 27.9, H 0.8, N 28.9%. IR: $\tilde{v} =$ 3096 (vC−H$_{Ar}$), 1601 (vC−C$_{Ar}$), 2133 (vN$_3^-$), 1339 (vNO$_2$), 711 (δC−H$_{Ar}$) cm^{-1}. **MS** (DEI): *m/z*: 254, 226, 196, 74 (DI temp. 77 °C).

4-Nitroazidobenzene (VII): The compound was synthesized from 4-nitroaniline (8 g, 0.05 mol) by following the same procedure as described for 2-nitroazidobenzene (**II**) [3]. Yield: 82%; m.p. 72 °C. Elemental analysis for C$_6$H$_4$N$_4$O$_2$ (164.12): calcd. C 43.9, H 2.5, N 34.1%; found: C 44.3, H 2.4, N 26.2%. IR: $\tilde{v} =$ 3105 (vC−H$_{Ar}$), 1604 (vC−C$_{Ar}$), 2119 (vN$_3^-$), 1338 (vNO$_2$), 747 (δC−H$_{Ar}$) cm^{-1}. **MS** (DEI): *m/z*: 164, 136, 76, 51 (DI temp. 72 °C).

5 Conclusions

From this combined experimental and theoretical study the following conclusions can be drawn:

(i)   The thermal degradation of compounds **I**, **II**, **III**, and **VII** was investigated by thermoanalytical techniques using TG-DTA and DSC. While compounds **I**, **II**, and **III** decompose to benzofuroxan derivatives with strong exotherms, compound **VII** decomposes to gaseous products with a weak exotherm.

(ii) The enthalpies of decomposition of compounds **I**, **II**, and **III** to form **IV**, **V**, and **VI**, were measured by DCS to be −113.3 (±0.5), −90.9 (±2.8) and −125.1 (± 6.2) kJ mol^{-1}, respectively.

(iii) The crystal structure of compound **III** was determined by single-crystal X-ray diffraction.

(iv) The molecular structures and frequencies of compounds **I**, **II**, **III** and their decomposition products **IV**, **V**, and **VI**, respectively, were calculated at B3LYP/cc-pVDZ level of theory. The calculated frequencies of all species are in good accord with observed IR spectra. The structural parameters of the fully optimized compound **III** showed very good agreement with the single-crystal X-ray data which gives credence to the reliability of the computed molecular structures for the other compounds under investigation in this study.

(v)   The enthalpies of formation for compounds **I–VI** were calculated using the complete basis set (CBS-4M)

method of Petersson and co-workers in order to obtain accurate energies.

(vi) The calculated enthalpies of decomposition for compounds **I**, **II**, and **III** were compared with the experimental values, which were available from DSC analysis. The good agreement between the experimentally observed enthalpies of decomposition and the CBS-4M calculated values also gives credence to the accuracy of the applied CBS-4M method.

Acknowledgments

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