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Thermochemistry of organic azides revisited

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Dedicated to Prof. Ch. Rüchardt on the Occasion of His 85th Birthday

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1. Introduction

Organic azides have a broad field of application as propellants, plasticizers and pharmacy products [1]. Thermochemical data for azides are in disarray [2]. Most of enthalpies of formation and enthalpies of sublimation/vaporization available in the literature are of technical quality or reported without any sample purity information. Nowadays, the modern quantum-chemical methods allow for performing the enthalpy data evaluation, provided that sufficient amount of the experimental data with the benchmark quality are available for the methods attestation. This paper extends our previous experimental study of a series of organic azides [3]. A complex thermochemical studies (including transpiration, combustion calorimetry and DSC) on highly pure samples of 4-nitro-phenyl azide, 1-octyl azide and 1 decyl-azide. These new data are expected to help for validation of the high-level quantumchemical calculations.

ABSTRACT

Highly pure samples of 4-nitro-phenyl azide, 1-octyl azide and 1 decyl-azide were prepared for thermochemical studies. Vapour pressures over the solid and the liquid sample of 4-nitro-phenyl azide have been determined by the transpiration method. The molar enthalpies of vaporization/sublimation for this compound were derived from the temperature dependencies of vapour pressures. The molar enthalpy of fusion of 4-nitro-phenyl azide was measured by DSC. The measured data set for 4-nitro-phenyl azide was successfully checked for internal consistency. Molar enthalpies of vaporization of 1-octyl azide and 1 decyl-azide were measured by transpiration. The molar enthalpies of formation of the liquid 1-octyl azide and 1 decyl-azides were derived from the combustion calorimetry. New experimental results for these organic azides have been used to derive their molar enthalpies of formation in the gas state and for comparison with results from quantum-chemical method G4.

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2. Experimental

2.1. Materials

Samples of 4-nitro-phenyl azide, 1-octyl azide and 1 decylazide were prepared and purified at the University of Málaga, according to the literature procedures with some modifications.

2.1.1. 4-Nitro-phenyl azide

In a round bottom flask equipped with a magnetic stirrer, a sample of 4-nitroaniline (1 g, 7.25 mmol) was dissolved in 5 mL of HCl and 5 mL of water. 10 mL of cold aqueous solution of sodium nitrite (0.5 g, 7.25 mmol) was dropped into the flask under stirring at 273 K. Then, 12 mL of aqueous solution of sodium azide (0.47 g 7.25 mmol) was dropped into the flask and the reaction was allowed to continue for 30 min. The precipitate was extracted with chloroform and washed with water. The organic layer was dried over anhydrous sodium sulphate, and the solvent was evaporated in vacuo to get 4-nitro-phenyl azide, yield 90% (1.07 g) [4], ¹H NMR (400 MHz, CDCl₃): δ 8.18 (d, *J* = 9.2 Hz, 2H), 7.09 (d, *J* = 9.2 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 146.8, 144.5, 125.5, 119.3.



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2.1.2. 1-Octyl azide

NaN₃ (2.53 g, 38.86 mmol) was added to a solution of 1bromooctane (5 g, 25.91 mmol) in dimethylformamide (10 mL). The reaction mixture was stirred at room temperature for 4 h. Water (100 mL) was added to the reaction mixture and the aqueous layer was extracted with ethyl acetate (3×50 mL). The combined organic phase was washed with 100 mL brine (26% of NaCl in MilliQ Water, pH 6.8), dried over anhydrous Na₂SO₄ and evaporated at reduced pressure to give azide (3.5 g, 87%) as a colourless oil. ¹H NMR (400 MHz, CDCl₃): δ 3.25 (t, *J*=6.9 Hz, 2H), 1.60 (quin, *J*=6.7 Hz, 2H), 1.28 (br s, 10H), 0.80 (t, *J*=6.4 Hz, 3H).

2.1.3. 1-Decyl azide

NaN₃ (5.25 g, 80 mmol) and 1-bromo-decane (7.08 g, 32 mmol) were dissolved in acetone: H₂O (10:1), and left stirred for 3 days under reflux at 65 °C. The extraction procedure of the azide was carried out with diethyl ether (3×50 mL) and dichloromethane (2×50 mL). To ensure the total extraction and absence of H₂O, the organic phase was washed with brine (26% of NaCl in MilliQ Water, pH 6.8), dried over anhydrous Na₂SO₄ and evaporated in vacuum. A further purification process was carried out by silica chromatography in a porous disc filter funnel, where the pure 1 decyl azide was obtained by a flow of hexane (400 mL), whereas the traces of starting 1-bromo-decane were trapped in the silica. ¹H NMR (400 MHz, CDCl₃) δ 3.25 (t, *J* = 7.0 Hz, 2H), 1.67–1.52 (m, 2H), 1.43–1.18 (m, 14H), 0.88 (t, *J* = 6.9 Hz, 3H).

The solid sample of 4-nitrophenyl azide was purified by recrystallization from ethanol and then by fractional sublimation in vacuum. The liquid samples of 1-octyl azide and 1 decyl azide were purified by a repeated fractional distillation at reduced pressure. Purities of samples were determined by a Hewlett Packard gas chromatograph 5890 Series II equipped with a flame ionization detector. We used a 25 m capillary column HP-5 with inside diameter of 0.32 mm and a film thickness of 0.25 mm. The standard temperature program of the GC was T= 333 K for 180 s followed by a heating rate of 0.167 K s⁻¹ to T= 523 K. No impurities (greater than mass fraction 0.001) for both samples could be detected in the samples used for the thermochemical measurements.

Provenance and purity of the compounds prepared for thermochemical studies in this work are given in Table 1.

Cautions should be taken during the manipulation and storage of azides. These compounds must be handled in a powerful fume hood. They should be handled only on a small scale with appropriate safety precautions (face shields, leather gloves and protective clothing).

2.2. Vapour pressure measurements

Vapour pressures of organic azides were determined using the method of transpiration [5,6] in a saturated nitrogen stream. About 0.5 g of the sample was mixed with small glass beads and placed in a thermostated U-shaped saturator. A well defined nitrogen stream was passed through the saturator at a constant temperature (\pm 0.1 K), and the transported material was collected in a cold trap.

Table 1

Provenance and purity of the synthesis materials.

The amount of condensed sample of 1-octyl azide and 1 decylazide was determined by GC analysis using an external standard $(n-C_8H_{18} \text{ and } n-C_{11}H_{24})$. The amount of condensed sample of 4nitro-phenyl azide was determined by weighing of the trap $(\pm 0.0001 \text{ g})$. The absolute vapour pressure p_i at each temperature T_i was calculated from the amount of the product collected within a definite period of time. Assuming validity of the Dalton's law applied to the nitrogen stream saturated with the substance i, values of p_i were calculated with equation:

$$p_{i} = \frac{m_{i} \times R \times T_{a}}{V \times M_{i}}; V = V_{N2} + V_{i}; V_{N2} \gg V_{i}$$

$$\tag{1}$$

where $R = 8.314472 \text{ JK}^{-1} \text{ mol}^{-1}$; m_i is the mass of the transported compound, M_i is the molar mass of the compound, and V_i ; its volume contribution to the gaseous phase. V_{N2} is the volume of the carrier gas and T_a is the temperature of the soap bubble meter used for measurement of the gas flow. The volume of the carrier gas V_{N2} was determined from the flow rate and the time measurement. Experimental results are given in Tables 2 and 3.

2.3. Combustion calorimetry

The molar enthalpies of combustion of 1-octyl azide and 1 decyl-azide were measured with an isoperibolic calorimeter with a static bomb and a stirred water bath. The sample was placed (under an inert atmosphere in a glove-box) in a polythene ampoule and burned in oxygen at 3.04 MPa pressure. The detailed procedure has been described previously [7]. The combustion products were examined for carbon monoxide (Dräger tube) and unburned carbon but neither was detected. The energy equivalent of the calorimeter ε_{calor} was determined with a standard reference sample of benzoic acid (sample SRM 39j, NIST). For the reduction of the data to standard conditions, conventional procedures [8] were used. Auxiliary data are collected in Table 4. Correction for nitric acid formation was based on titration with 0.1 mol dm⁻³ NaOH (aq). The residual water concentration in the liquid samples was determined by Karl Fischer titration before starting experiments and appropriate corrections have been made for combustion results.

2.4. Phase transitions in the solid state. DSC-measurements

The thermal behaviour of 4-nitro-phenyl azide including melting temperature and enthalpy of fusion was determined with a PerkinElmer DSC-2. The fusion temperature and enthalpies were determined as the peak onset temperature and by using a straight baseline for integration, respectively. The temperature and heat flow rate scale of the DSC was calibrated by measuring high-purity indium. The thermal behaviour of the specimen was investigated during heating the sample at a cooling rate of 10 K min⁻¹. The DSC measurements were repeated in triplicate and values agreed within the experimental uncertainties $u(\Delta_{cr}^{er}H_m) = 0.2$ kJ mol⁻¹ for the enthalpy of fusion and u(T) = 0.5 K for the melting temperature.

4-Nitro-phenyl azide	1-Octyl azide	1-Decyl azide
1516-60-5	7438-05-3	62103-13-3
Synthesis in this work	Synthesis in this work	Synthesis in this work
Fractional sublimation	Fractional distillation	Fractional distillation
0.999 ^a	0.999	0.999
	306.42 ppm	266.02 ppm
	4-Nitro-phenyl azide 1516-60-5 Synthesis in this work Fractional sublimation 0.999 ^a	4-Nitro-phenyl azide1-Octyl azide1516-60-57438-05-3Synthesis in this workSynthesis in this workFractional sublimationFractional distillation0.999a0.999306.42 ppm

^a The same result was measured by DSC.

Table 2

T

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V C

Results from measurements of the vapour pressure p of azides using the transpiration method. Cas_flow

"d

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(K)	(mg)	(dm^3)	(dm^3/h)	(Pa)	(%)	$\Delta_{l} n_{m} 0$
()	(8)	()	(()	()	$\Delta_{\rm cr}^{\rm o} H_{\rm m}$
						(kJ mol ⁻¹)
4-Nitro-	phenyl az	zide; $\Delta^{\mathrm{g}}_{\mathrm{cr}}H_{\mathrm{m}}$ (2	298.15 K) = 93	$.0 \pm 0.6$ kJ m	ol^{-1}	
$\ln(\frac{p}{2})^{321}$.63 _ 99935	$\frac{42}{23.3} \ln \left(\frac{T}{23.3} \right)$	<u>,K</u>)			
313.3	× κ·(<i>I</i> , <i>I</i>	202.0	450	1 20	0.02	02.64
2174	21.1	502.9	4.50	1.20	0.92	92.04
217.4	9.4	20.4	4.50	1.69	0.70	92.34
222.5	9 10 4	26.6	4.50	5.58	0.04	92.4
220.J	10.4	20.0	4.50	0.02	0.56	92.20
224.0	12.6	17.0	4.50	0.25	0.50	92.22
2281	13.0	17.9	4.50	11.52	0.54	92.15
330.0	10.5	15.0	4.50	19.55	0.55	92.00
A_Nitro_	nhenvl 17	$\Lambda^{g}H$ (7)	-4.50	$0 \pm 0.6 k \text{Im}$	0.55	52.02
4-141110-	224.80 08	$\Delta_1 m_m (2)$	(TK)	0 ± 0.0 KJ III	01	
$\ln(\frac{p}{Pa}) =$	$\frac{524.89}{R} - \frac{98}{R}$	$\frac{383.24}{(T,K)} - \frac{80.2}{R} \ln(1)$	$\left(\frac{1,\kappa}{298.15}\right)$			
345.1	13.7	7.4	4.50	28.47	0.52	70.71
350.2	18.0	6.5	4.50	42.36	0.51	70.30
355.2	14.8	3.8	4.50	58.58	0.51	69.90
360.2	17.7	3.2	4.50	82.79	0.51	69.50
365.3	19.2	2.6	4.50	113.38	0.50	69.09
370.5	25.5	2.6	4.50	150.41	0.50	68.68
1-Octyl	azide; Δ_1^g	H _m (298.15 K	$) = 58.9 \pm 0.3$ l	kJ mol−1		
ln(<u>p)330</u>	.24 _ 89107.	$.94 - 101.5 \ln(-$	<u>T,K</u>			
276.2	$R = R \times (T, T)$	K) R(29	98.15 <i>)</i>	6.25	0.50	61.07
270.2	1.65	4.28	3.02	6.25	0.58	61.07
279.8	1.92	3.42	3.02	9.04	0.56	60.71
282.5	1.88	2.56	3.02	11.72	0.54	60.44
285.8	2.15	2.21	3.02	15.48	0.53	60.1
289.4	2.02	1.51	3.02	21.19	0.52	59.74
292.2	2.25	1.29	1.01	27.51	0.52	59.45
293.2	2.04	1.11	3.02	29.11	0.52	59.35
296.2	2.13	0.905	3.02	37.07	0.51	59.04
300.2	1.91	0.628	1.11	48.08	0.51	58.64
302.1	2.04	0.553	1.01	58.05	0.51	58.45
303.1	3.12	0.755	3.02	65.04	0.51	58.34
307	1.96	0.369	1.11	83.45	0.51	57.94
310	3.48	0.503	3.02	108.88	0.50	57.64
313.9	2.39	0.277	1.11	135.49	0.50	57.24
317.9	6.02	0.503	3.02	188.01	0.50	56.84
320.9	3.96	0.259	1.11	240.59	0.50	56.54
321.8	3.82	0.252	1.01	238.5	0.50	56.44
323.9	4.57	0.277	1.11	259.2	0.50	56.24
323.9	4.29	0.252	1.01	268.35	0.50	56.24
325.8	10.36	0.503	3.02	323.7	0.50	56.04
325.8	10.36	0.503	3.02	323.61	0.50	56.04
325.8	5.02	0.252	1.01	313.49	0.50	56.04
1-Decyl	azıde; Δ_l°	$^{\circ}H_{\rm m}$ (298.15 K	$() = 67.8 \pm 0.4$	kJ mol ⁻¹		
$ln\left(\frac{p}{Pa}\right)\frac{357}{k}$	$\frac{.51}{R \times (T)} = \frac{103213}{R \times (T)}$	$\frac{2.11}{K} - \frac{118.2}{R} \ln \left(\frac{1}{2} + \frac{1}{2} \ln \left(\frac{1}{2} + \frac$	$\frac{T,K}{298.15}$			
299.1	1.44	4.481	4.80	4.31	0.07	67.69
304	1.39	2.801	4.80	6.66	0.07	67.1
309	1.49	1.953	3.66	10.17	0.06	66.5
314	1.3	1,159	3.66	14.89	-0.3	65.91
318.9	1.48	0.915	3.66	21.52	-0.83	65.33
324	2.12	0.854	3.66	33.05	0.04	64.72
329	2.83	0 793	3.66	47 44	013	64.13
333.9	3.73	0 732	3.66	67.69	1.05	63.55
339	629	0.915	3.66	914	-2.49	62.94
3441	2.26	0 2 2 5	104	134.7	4 17	62.34
511.1	2.20	0,223	1.54	1.5 1.7	1.17	02.31

Saturation temperature (u(T) = 0.1 K).

b Mass of transferred sample condensed at T = 243 K.

^c Volume of nitrogen $(u(V) = 0.005 \text{ dm}^3)$ used to transfer m(u(m) = 0.0001 g) of the sample.

^d Vapour pressure at temperature T, calculated from the m and the residual vapour pressure at T = 243 K.

2.5. Computational details

Standard ab initio molecular orbital calculations for azides were performed with the Gaussian 09 series of programs [9]. Energies of compounds under study were calculated using G4 level [10]. Details on this method have been given in our previous paper [11]. Calculated enthalpies of azides are based on the electronic energy calculations obtained by the compound method using standard procedures of statistical thermodynamics [12].

3. Results and discussion

3.1. Vapour pressure and sublimation/vaporization enthalpies

Temperature dependence of vapour pressures measured for azides were fitted with the following equation [12]:

$$R \times \ln p_{i} = a + \frac{b}{T} + \Delta_{1}^{g} C_{p} \times \ln\left(\frac{T}{T_{0}}\right)$$
⁽²⁾

where *a* and *b* are adjustable parameters and $\Delta_{i}^{g}C_{p}$ is the difference of the molar heat capacities of the gaseous and the liquid phase respectively. T_0 appearing in Eq. (2) is an arbitrarily chosen reference temperature (which has been chosen to be 298.15 K). Consequently, vaporization (or sublimation) enthalpy at temperature T was indirectly derived from the temperature dependence of vapour pressures using Eq. (3):

$$\Delta_{l}^{g}H_{m}(T) = -b + \Delta_{l}^{g}C_{p} \times T$$
(3)

Eqs. (2) and (3) are also valid for the study of the solid sample. For this case the enthalpy of sublimation is derived from Eq. (3) by using the appropriate values of $\Delta_{cr}^{g}C_{p}$. Values of $\Delta_{cr}^{g}C_{p}$ and $\Delta_{l}^{g}C_{p}$ have been calculated according to the procedure developed by Chickos et al. [13] based on isobaric molar heat capacities C_p^l and C_p^{cr} . The C_p^{l} values were estimated by group-contribution method [14]. The experimental value $C_p^{cr} = 164.1 \text{ JK}^{-1} \text{ mol}^{-1}$ measured by DSC [4] was used for 4-nitro-phenyl azide. Experimental results for azides and parameters *a* and *b* are listed in Table 2.

The compilation of sublimation/vaporization enthalpy measurements on azides from this work and from the literature is presented in Table 3. Only few experimental studies of azides relevant to this study were found in the literature [15,16]. We treated experimental literature data using $\Delta_{l}^{g}C_{p}$ -values listed in Table 3 and calculated $\Delta_{cr}^{g}H_{m}$ (298.15 K) or $\Delta_{l}^{g}H_{m}$ (298.15 K) for the sake of comparison with our results. It has turned out that the enthalpy of sublimation of 4-nitro-phenyl azide $81 \pm 3 \text{ kJ mol}^{-1}$ admittedly used until today in the literature was roughly assessed by analogy with the enthalpy of sublimation of 1,3-dinitrobenzene [4]. Thus, any reasonable explanation of $10 \text{ kJ} \text{ mol}^{-1}$ difference with our experimental value (see Table 3) was hardly required. In this work, vapour pressures for 4-nitro-phenyl azide were measured over the solid as well as over liquid sample. The enthalpy of vaporization $\Delta_{l}^{g}H_{m}$ (298.15 K) = 74.5 ± 1.1 kJ mol⁻¹ for 4-nitro-phenyl azide measured in this work by transpiration was significantly different from the value $\Delta_1^g H_m$ (298.15 K) = 116.9 \pm 0.7 k mol⁻¹ measured with the same method earlier [15]. It makes oneself conspicuous that the latter value is even larger than available enthalpies of sublimation of 4-nitro-phenyl azide (see Table 3). Consequently, the transpiration result from [15] seems to be in error.

The molar enthalpy of vaporization of 1-alkyl azides were measured earlier by very simple static device [16]. Using Eqs. (2) and (3) we adjusted vaporization enthalpies from this work [16] to the reference temperature for comparison with our new results: 1octyl azide $\Delta_1^g H_m$ (298.15 K)=62.1 kJ mol⁻¹ and of 1 decyl azide $\Delta_1^{g} H_{m}$ (298.15 K) = 73.4 kJ mol⁻¹ (see Table 3). These literature results are significantly higher in comparison to our more reliable results from transpiration method (see Table 3). In our previous work [3] we reported that the family of 1-alkyl-azides fit very well in the linear correlation. The dependence of vaporization enthalpy

Table 3	
Compilation of data on enthalpies of vaporization $\Delta_l^g H_m$	(298.15 K) of azides.

Compounds	T-range (K)	$C_p^1(\Delta_{cr}^g C_p)C_p^{cr}(\Delta_l^g C_p) (J mol^{-1} K^{-1})$	$\Delta^{ m g}_{ m cr} H_{ m m} ext{ or } \Delta^{ m g}_{ m l} H_{ m m}$ at $T_{ m av}$ (kJ mol $^{-1}$)	$\Delta^{ m g}_{ m cr} H_{ m m}$ or $\Delta^{ m g}_{ m l} H_{ m m}$ at 298.15 K	Ref
4-Nitro-phenyl azide (cr)		164.0		81.0 ± 3.0	[4]
	313.3-338.1	(-25.3)	92.4	93.0 ± 0.6	This work
4-Nitro-phenyl azide (liq)	363-393	267.7	110.5	116.9 ± 0.7	[15]
	345.1-370.5	(-80.2)	69.7	$\textbf{74.5} \pm \textbf{1.1}$	This work
1-Octyl azide (l)	350-420	349.5	53.3	62.1	[16]
		(-101.5)		58.5 ^a	This work
	276.2-325.8		58.4	58.9 ± 0.3	This work
1-Decyl azide (l)	373-480	413.3	58.2	73.4	[16]
		(-118.8)		67.9 ^a	This work
	299.1-344.1		65.1	67.8 ± 0.4	This work

^a Calculated using Eq. (4).

on the number of C-atoms $N_{\rm C}$ was calculated solely using the literature data. Having measured two representatives of this series in this work, we have refined this correlation with the new data:

We would recommend to use Eq. (4) for thermochemical calculations of 1-alkyl azides of general formula CH₃-(CH₂)_n-N₃.

3.2. Enthalpies of formation from the combustion calorimetry

Results of combustion experiments on 1-octyl azide and 1 decyl-azide are summarized in Tables 4-6. Values of the standard specific energy of combustion, $\Delta_{c}u^{\circ}$, the standard molar enthalpy of combustion, $\Delta_c H_m^{\circ}$, and the standard molar enthalpy of formation in the liquid state $\Delta_{f} H_{m}^{\circ}$ (l) was based on the reactions:

$$C_8H_{17}N_3 + 12.25O_2 = 8CO_2 + 8.5H_2O + 1.5N_2 (5)$$
(5)

$$C_{10}H_{21}N_3 + 15.25O_2 = 10CO_2 + 10.5H_2O + 1.5N_2 (6)$$
(6)

Values of the molar enthalpy of formation, $\Delta_{\rm f} H_{\rm m}^{\circ}$ (l) of 1-alkyl azides were calculated from the enthalpy balance for Reactions (5) and (6) according to the Hess's Law using molar enthalpies of formation of $H_2O(1)$ and $CO_2(g)$ as assigned by CODATA [17]. The uncertainties of the standard molar energy and enthalpy of combustion correspond to expanded uncertainties of the mean (0.95 level of confidence) and include the contribution from the calibration with benzoic acid and from the values of the auxiliary quantities used. Enthalpy of combustion and the $\Delta_{\rm f} H_{\rm m}^{\circ}$ (1)=96.7 \pm 3.0 kJ mol⁻¹ of 1-octyl azide was earlier published in the U.S. Naval Powder Factory report [18]. Our new $\Delta_{\rm f} H_{\rm m}^{'}$ (1)-value is of 17 kJ mol⁻¹ less positive. Study of scarce details in this report has not revealed any explanation. Analysis of the experimental data for 1-alkyl-azide (alkyl = pentyl, hexyl, heptyl and octyl) reported by Murrin et al. [18] have revealed the general inconsistency of the enthalpies for this series. For example the enthalpies of formation $\Delta_{\rm f} H_{\rm m}^{\circ}$ (l) = 151 kJ mol⁻¹ were identical for 1-pentyl azide and 1hexyl azide. Such an anomalous behaviour has never been observed for any homologous family [23], because $\Delta_{\rm f} H_{\rm m}^{\circ}$ (1)values of 1-pentyl azide and 1-hexyl azide are expected to be different by at least -28.85 kJ mol⁻¹ (contribution for CH₂ group) [23]. In contrast, our new enthalpies of formation of 1-octyl azide $\Delta_{\rm f} H_{\rm m}^{\circ}$ (l) = 80.6 ± 2.2 kJ mol⁻¹ and 1 decyl-azide $\Delta_{\rm f} H_{\rm m}^{\circ}$ (l) = 29.0 \pm 3.0 kJ mol⁻¹ (see Table 7) differ by 51.6 kJ mol⁻¹. These differences meet expectation for contributions from two CH₂ groups (within the combined experimental uncertainties) and prove consistency of our new values.

Energy of combustion of 4-nitro-phenyl azide was earlier determined using an isoperibol static bomb combustion calorimeter [4]. The purity of the sample used and the quality of experimental results reported in this work were apparently on the high level. The molar enthalpy of formation $\Delta_{\rm f} H_{\rm m}^{\circ}$ (cr)=308.7 $\pm 4.3 \text{ kJ} \text{ mol}^{-1}$ (see Table 7) of 4-nitro-phenyl azide [4] was accepted in this work for the further thermochemical calculation.

3.3. Enthalpy of fusion of 4-nitro-phenyl azide

As per the rule, prior to the vapour pressure measurements, the crystalline samples have to be studied by DSC. Information about possible phase transitions in the sample under study helps choosing of the temperature range for investigation and guide vapour pressure measurements within the range where the compound of interest exists in only a certain crystalline modification. The melting temperature, purity (0.999 mass fraction), and enthalpy of fusion of 4-nitro-phenyl azide were measured in the present work by DSC. No phase transitions other than melting of 4-nitro-phenyl azide have been detected. The onset, peak and end temperatures of the DSC run were as follows: 341.4 K, 342.5 K and 344.4 K. For comparison, the melting point of 345 K was reported in Ref. [4], but it is not quite clear which method was used for this measurement. In any case, the end temperature of the melting peak in our work was in agreement with those from [4]. Moreover, the purity of our sample of 0.999 mass fraction, was confirmed by the GC method. The experimental

Formula, density ρ (T = 293 K), massic heat capacity c_p (T = 298.15 K), and expansion coefficients $(\delta V/\delta T)_{\rm p}$ of the materials used in the present study.

Compounds	Formula ^a	ho (g cm ⁻³)	$C_{\rm p} \ (J {\rm K}^{-1} {\rm g}^{-1})$	$\begin{array}{c} 10^{-6} \times (\delta V / \delta T)_p{}^b \\ (dm^3 K^{-1}) \end{array}$
1-Octyl azide	C ₈ H ₁₇ N ₃	0.84 ^c	2.25 ^d	1.0
1-Decyl azide	C ₁₀ H ₂₁ N ₃	0.87 ^c	2.26 ^d	1.0
Polyethylene ^e	CH _{1.93}	0.92 [7]	2.53 [7]	0.1
Cotton ^f	CH _{1.774} O _{0.887}	1.50 [7]	1.67 [7]	0.1

^a The relative atomic masses used for the elements C, H, N and O were calculated as the mean of the bounds of the interval of the standard atomic weights recommended by the IUPAC commission in 2011 [27] for each of these elements. ^b Estimated [8].

^c Measured with a calibrated pycnometer with uncertainties u(T) = 0.1 K and u $(\rho) = 0.01 \,\mathrm{g}\,\mathrm{cm}^{-3}$.

Calculated by group-contribution method [13].

Table 4

Energy of combustion $\Delta_c u^{\circ}$ (polyethylene) = -46357.3 J g⁻¹; $u(\Delta_c u^{\circ})$ = 3.6 J g⁻¹.

^f Energy of combustion $\Delta_c u^{\circ}$ (cotton) = -16945.2 J g⁻¹; $u(\Delta_c u^{\circ})$ = 4.2 J g⁻¹.

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C_{2}	Result	ts for	combustion	experiments	at T	= 298.15 K ($(p^{\circ} = 0)$).1 MPa) of	the	1-octv	/l azid
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m(substance)/g	0.323745	0.323617	0.389136	0.176607	0.268154
<i>m</i> ′(cotton)/g	0.001169	0.001107	0.001221	0.001423	0.001178
m" (polyethene)/g	0.279711	0.342548	0.280926	0.392715	0.338976
$\Delta T_{\rm c}/{\rm K}$	1.66819	1.86402	1.83278	1.6596	1.71677
$(\varepsilon_{calor}) \times (-\Delta T_c)/J$	-24817.5	-27730.8	-27266	-24689.7	-25540.2
$(\varepsilon_{\rm cont}) \times (-\Delta T_{\rm c})/J$	-27.07	-31.07	-30.29	-27.15	-28.13
$\Delta U_{\rm decomp}$ HNO ₃ /J	69.88	76.45	74.06	51.96	62.71
$\Delta U_{\rm corr}/J$	6.75	7.8	7.54	7.09	7.25
$-m' imes \Delta_c u'/J$	19.81	18.76	20.69	24.11	19.96
$-m'' imes \Delta_c u''/J$	12966.65	15879.6	13022.97	18205.21	15714.01
$\Delta_{\rm c} u^{\circ}({ m liq})/({ m Jg^{-1}})$	-36391.3	-36398.7	-36416.7	-36399.6	-36413.3
$-\Delta_{\rm c} u^{\circ}({ m liq})/({ m Jg^{-1}})$			36403.7		
$u(\Delta_{ m c} u^\circ)/{ m J}{ m g}^{-1}$			4.8 ^b		

^a The definition of the symbols assigned according to Ref [8] is as follows: *m* (substance) and *m'* (cotton) are, respectively, the mass of compound burnt and the mass of fuse (cotton) used in each experiment, masses were corrected for buoyancy; *V*(bomb) = 0.2511 dm³ is the internal volume of the calorimetric bomb; $p^i(gas) = 3.00$ MPa is the initial oxygen pressure in the bomb; $m^i(H_2O) = 10.00$ g is the mass of water added to the bomb for dissolution of combustion gases; $\varepsilon_{calor} = (14876.9 \pm 1.0)$ JK⁻¹ is the energy equivalent of the calorimeter; $\Delta T_c = T^f - T^i + \Delta T_{corr}$ is the corrected temperature rise from initial temperature T^i to final temperature T^f , with the correction ΔT_{corr} for heat exchange during the experiment; ε_{cont} is the energy equivalents of the bomb contents in their initial $\varepsilon_{i cont}^i$ and final states ε_{cont}^f , the contribution for the bomb content is calculated with (ε_{cont}) × ($-\Delta T_c$) = ($\varepsilon_{i cont}^i$) × ($T^i - 298.15$) + ($\varepsilon_{i cont}^f$) × ($298.15 - T^f + \Delta T_{corr}^f$). ΔU_{decomp} HNO₃ is the energy correction for the nitric acid formation. ΔU_{corr} is the correction to standard states.

^b Uncertainties in this table are expressed as the standard deviation of the mean.

molar enthalpy of fusion $\Delta_{cr}^{1}H_{m} = 21.3 \pm 0.5 \text{ kJ mol}^{-1}$ measured in this work is significantly higher than $\Delta_{cr}^{1}H_{m} = 17.1 \pm 0.3 \text{ kJ mol}^{-1}$ at 345 K measured by DSC in [4]. The reason for this disagreement is difficult to identify because of absence of the necessary details in [4]. Probably it could be insufficient peak integration in the earlier DSC software. Generally, the experimental molar enthalpy of fusion $\Delta_{cr}^{1}H_{m}$ is referred to the melting temperature T_{fus} . The measured enthalpy of fusion have to be adjusted to the reference temperature T = 298.15 K. The adjustment was calculated from the equation [19]:

$$\begin{aligned} \{\Delta_{cr}^{1}H_{m}(T_{fus}/K) - \Delta_{cr}^{1}H_{m}(298.15K)\}/(Jmol^{-1}) \\ &= \{(0.75 + 0.15C_{p}^{cr})[(T_{fus}/K) - 298K]\} \\ &- \{(10.58 + 0.26C_{p}^{1})[(T_{fus}/K) - 298.15K]\} \end{aligned}$$
(7)

With this adjustment (the uncertainty of the correlation was not taken into account), the molar enthalpies of fusion, $\Delta_{cr}^1 H_m$ (298.15 K) = 18.9 ± 0.5 kJ mol⁻¹, was calculated and used to establish consistency of the thermochemical data set for 4-nitro-phenyl azide as it described below.

3.4. Consistency test of the vaporization, sublimation and fusion enthalpies of 4-nitro-phenyl azide

Since a significant discrepancy between available fusions enthalpies of 4-nitro-phenyl azide have been observed, the additional argument to support the reliability of our new result is required. A valuable test of consistency of the experimental data on the phase change sequence sublimation–melting–vaporization provides a simple calculation according to Eq. (8):

$$\Delta_{\rm cr}^{\rm I} H_{\rm m}(298.15\rm{K}) = \Delta_{\rm cr}^{\rm g} H_{\rm m}(298.15\rm{K}) - \Delta_{\rm 1}^{\rm g} H_{\rm m}(298.15\rm{K})$$
(8)

Indeed, in this work the sample of 4-nitro-phenyl azide was deliberately investigated by the transpiration method in both ranges, above and below the $T_{\rm fus}$ = 341.4 K. The value of $\Delta_{\rm cr}^{\rm g} H_{\rm m}$ (298.15 K) = 93.0 ± 0.6 kJ mol⁻¹ was obtained in this work over the solid sample in the temperature range 313.3–338.2 K and the vaporization enthalpy for 4-nitro-phenyl azide $\Delta_{\rm l}^{\rm g} H_{\rm m}$ (298.15 K) = 74.5 ± 1.1 kJ mol⁻¹ from measurements over the liquid sample in the temperature range 345.1–370.5 K. The molar enthalpy of fusion calculated according to Eq. (7) as the difference: $\Delta_{\rm cr}^{\rm l} H_{\rm m}$ (298.15 K) = $\Delta_{\rm cr}^{\rm g} H_{\rm m} - \Delta_{\rm l}^{\rm g} H_{\rm m} = 18.5 \pm 1.3$ kJ mol⁻¹ was in good agreement with (298.15 K) = 18.9 ± 0.5 kJ mol⁻¹, directly measured in this work by DSC and adjusted to T = 298.15 K. Thus, our new results for sublimation, fusion and vaporization enthalpies for 4-nitro-phenyl azide have been proven to be consistent.

3.5. Gas phase enthalpies of formation of azides

Experimental values of sublimation and vaporization enthalpies of azides from Tables 2 and 3 can now be used together with

Table 6

Results for combustion experiments at $T = 298.15 \text{ K} (p^\circ = 0.1 \text{ MPa})$ of the 1-decyl azide.^a

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m (substance)/g	0.192052	0.263736	0.219859	0.290458	0.356894
m' (cotton)/g	0.001314	0.001404	0.001232	0.000995	0.001177
m" (polyethene)/g	0.321215	0.312549	0.342801	0.292872	0.297984
$\Delta T_{\rm c}/{\rm K}$	1.50253	1.6596	1.64137	1.66665	1.85263
$(\varepsilon_{calor}) \times (-\Delta T_c)/J$	-22237.1	-24561.7	-24291.9	-24666	-27418.6
$(\varepsilon_{\rm cont}) \times (-\Delta T_{\rm c})/J$	-24.17	-27.04	-26.77	-27.17	-30.64
$\Delta U_{ m decomp}$ HNO ₃ /J	54.35	59.73	57.93	63.91	68.09
$\Delta U_{\rm corr}/J$	6.11	6.79	6.78	6.75	7.62
$-m' imes \Delta_{c} u'/J$	22.27	23.79	20.88	16.86	19.94
$-m'' \times \Delta_{\rm c} {\rm u}''/{ m J}$	14890.66	14488.93	15891.33	13576.76	13813.73
$\Delta_{ m c} u^{\circ}(m liq)/(m Jg^{-1})$	-37947.7	-37952.6	-37941.2	-37970.8	-37937.9
$-\Delta_{\rm c} u^{\circ}({ m liq})/({ m J}{ m g}^{-1})$			37950.0 ^b		
$u(\Delta_{ m c} u^\circ)/{ m Jg^{-1}}$			5.8 ^c		

^a The definition of the symbols assigned is identical to those in Table 5.

 $^{\rm b}\,$ The energy equivalent of the calorimeter ϵ_{calor} = (14799.8 \pm 1.0) J K $^{-1}$

^c Uncertainties in this table are expressed as the standard deviation of the mean.

F

Table 7

Thermochemical data at $T = 298.15 \text{ K} (p^\circ = 0.1 \text{ MPa})$ for azides (in kJ mol⁻¹).^a

Compounds	$\Delta_{\rm c} H_{\rm m}^{'}({ m liq} \ { m or} \ { m cr})$	$\Delta_{\mathrm{f}} H^{^{\circ}}_{\mathrm{m}}(\mathrm{liq} \ \mathrm{or} \ \mathrm{cr})$	$\Delta_{\mathrm{cr}} H_{\mathrm{m}}^{\circ}$ or $\Delta_{1} H_{\mathrm{m}}^{\circ}$	$\Delta_{\rm f} H_{\rm m}^{^{\circ}}$ (g) Exp.	$\Delta_{\rm f} H_{\rm m}^{^{\circ}}$ (g)
4-Nitro-phenyl azide (cr)	$-3241.4 \pm 4.2 \ \textbf{[4]}$	308.7 ± 4.3 [4]	$\begin{array}{l} 93.0 \pm 0.6 \\ 74.5 \pm 1.1^{b} \end{array}$	401.7 ± 4.3	396.6 ± 4.0^{c}
1-Octyl azide (liq) 1-Decyl azide (liq)	$\begin{array}{r} -5658.2 \pm 2.0 \\ -6965.3 \pm 2.6 \end{array}$	$\begin{array}{c} 80.6\pm2.2\\ 29.0\pm3.0\end{array}$	$\begin{array}{l} 58.9 \pm 0.3 \\ 67.8 \pm 0.4 \end{array}$	$\begin{array}{c} 139.5\pm2.2\\ 96.8\pm3.0\end{array}$	$\begin{array}{c} 137.7 \pm 4.0 \\ 94.8 \pm 4.0 \end{array}$

^a Uncertainties correspond to expanded uncertainties of the mean (0.95 level of confidence).

^b Enthalpy of vaporization from Table 3.

^c The original G4 value 384.6 kJ mol⁻¹ obtained from the atomisation procedure was corrected according to the empirical correlation from [25] (see text).

the results from combustion experiments (see Tables 5 and 6) for further calculation of the gas standard enthalpies of formation, $\Delta_f H_m^{\circ}(g)$ at 298.15 K. The resulting experimental values of $\Delta_f H_m^{\circ}(g)$ for 4-nitro-phenyl azide and 1-alkyl azides are given in Table 7 (column 5) and they could be now compared with the theoretical results from quantum chemical calculations.

We have calculated using the G4 method total energies E_0 at T = 0 K and enthalpies H_{298} at T = 298.15 K (see Table 8). In this work we used the atomization procedure (AT) for calculation the alkyl azides. These values are given in Table 7 (column 6). Enthalpy of formation for 4-nitro-phenyl azide was calculated according to the procedure developed for nitro-compounds and described in our previous paper [25]. The linear correlation between experimental and G4 calculated enthalpies of formation $\Delta_{\rm f} H_{\rm m}^{\circ}$ (exp)/in kJ mol⁻¹ = 1.0083 $\Delta_{\rm f} H_{\rm m}^{\circ}$ (G4) + 8.8 with (r = 0.9993). With this linear correlation and the G4 value 384.6 kJ mol⁻¹ obtained from the procedure the atomization current result $1.0083 \times 384.6 + 8.8 = 396.6 \text{ kJ mol}^{-1}$ was calculated. The latter value is in a good agreement with $\Delta_{\rm f} H_{\rm m}^{\circ}$ (G4)=393.9 kJ mol⁻¹ derived in [2] by using different isodesmic reactions. Results calculated by using G4 for 4-nitro-phenyl azide and 1-alkyl azides are in very close agreement with the experiment within the combined uncertainties. Thus, the composite G4 method can be further recommended for calculations of the azide family. At the same time, such are good agreement could serve as an evidence of consistency of thermochemical results measured in this work by different techniques.

3.6. Pairwise interactions of substituents in nitro-phenyl azides

Mutual interactions of substituents on the benzene ring belong to the basics of organic chemistry. Energetics of interplay of electron-donating and electron-accepting substituents in the *ortho-*, *meta-* and *para-*position on the ring determine the mechanism of a chemical reaction. Having established a set of G4 enthalpies H_{298} for nitro-phenyl azide isomers (see Table 8) we are able now to calculate effects of mutual interactions of nitrogroup with the azide-group on the benzene ring in the *ortho-*, *meta-* and *para-*position.

In our recent work [20,21] we suggested to derive the interactions on the benzene ring directly from enthalpies H_{298} .

Table 8

G4 total energies at 0 K, enthalpies at 298.15 K and standard enthalpy of formation $\Delta_f H_m^{\prime}(g)$ at 298.15 K of the nitro-phenyl azides and parent compounds.

Compounds	E ₀	H ₂₉₈	$\Delta_{\rm f} H_{\rm m}^{\circ} { m G4}$
	(Hartree)	(Hartree)	(kJ mol ⁻¹)
2-Nitro-phenyl azide 3-Nitro-phenyl azide 4-Nitro-phenyl azide Phenyl azide	-600.090788 -600.100265 -600.101321 -395.644363	-600.080359 -600.089780 -600.090835 -395636364	396.7 399.7 424.4
Nitro-benzene	-436.551642	-436.543854	-
Benzene	-232.093987	-232.088586	

For this purpose the well balanced distribution reaction:

$$\begin{aligned} & \text{Phenylazide} + \text{nitro} - \text{benzene} \\ & = x - \text{nitro} - \text{phenylazide} + \text{benzene} \end{aligned} \tag{9}$$

was applied. Enthalpies H_{298} of all reaction participants were calculated in this work by G4 method (Table 9). Enthalpy of this distribution reaction, $\Delta_r H_m^\circ$, was calculated according to the Hess's Law. The value of $\Delta_r H_m^\circ$ for the distribution Reaction (9) expresses energetic of the mutual interaction of substituents on the benzene ring depending on their *ortho-*, *meta-* or *para-*position. A significant advantage of the quantum-chemical calculations towards benzene derivatives is that this method allows estimation of substituent effects directly from enthalpies H_{298} skipping the common step of the calculation of $\Delta_f H_m^\circ$ (g) for the Reaction (9) participants by any theoretical or empirical method [20,21].

Substituent effects in nitro-phenyl azide isomers defined by $\Delta_r H_m^{\circ}$ of Reaction (9) are listed in Table 9. It is apparent that all three isomers are significantly destabilized. Destabilizations of the *meta*- and *para*-isomers are approximately on the same level of about 2–4 kJ mol⁻¹. The nitro- and azide-groups for *meta*- and *para*-isomers are in plane with the benzene ring (Fig. 1). In contrast, the nitro-group is out of plain in 2-nitro-phenyl azide and this steric interaction caused the profound destabilization of the *ortho*-isomer of 29.6 kJ mol⁻¹ (see Table 9).

It is interesting to compare the size of substituent effects in nitro-phenyl azides with those in similar benzene derivatives nitro-benzonitriles, where reliable experimental data are available [22]. Using archival experimental enthalpies of formation for gaseous benzene and its cyano and nitro derivatives [23–26], we calculated values of $\Delta_r H_m^{\circ}$ according to the reaction:

$$Benzonitrile + nitro - benzene = x-nitro - benzonitrile + benzene$$
(10)

Results for interactions of the nitro- and cyano-groups are given in Table 9 and we can conclude that the *meta*- and *para*-nitro-

Table 9

Compounds

Mutual interactions of substituents, $\Delta_r H_m^\circ$, on the benzene ring for nitro-phenyl azides and the analogous nitro-benzonitriles as calculated by G4 (at 298.15 K, in kJ mol⁻¹).

 $\Delta_{\rm r} H_{\rm m}^{\circ}$

2-Nitro-phenyl azide	29.6 ^a
3-Nitro-phenyl azide	4.9ª
4-Nitro-phenyl azide	2.1ª
2-Nitro-benzonitrile	19.5 ± 3.9^{b}
3-Nitro-benzonitrile	$10.6\pm4.0^{\rm b}$
4-Nitro-benzonitrile	14.4 ± 4.4^b

^a Calculated using the G4 energies from Table 7 for the reaction: phenyl azide + nitro-benzene = x-nitro-phenyl azide + benzene.

^b Calculated using the experimental data [22–26] for the reaction: benzonitrile + nitro-benzene = *x*-nitro-benzonitrile + benzene.



Fig. 1. Optimized with the G4 structures of the nitro-phenyl azides.

benzonitrile are also destabilized by 10.6 ± 4.0 and 14.4 ± 4.4 kJ mol⁻¹ respectively. This level of destabilization is stronger than those for nitro-phenyl azides. Cyano is a quite small in comparison to the azide group. Consequently, the destabilization due to both steric and electronic interactions in *ortho*-nitro-benzonitrile of 19.5 ± 3.9 kJ mol⁻¹ as expected lower in comparison to 2-nitrophenyl azide. Thus, the mutual substituent effects for nitro-phenyl azide derived in this work seem to be reasonable in size.

4. Conclusion

Complex of thermochemical studies leading to the molar enthalpy of formation of three organic azides was accomplished. The G4 theoretical gaseous enthalpies of formation of the title compounds were in agreement with the experiment within the combined uncertainties. The composite G4 method combined with the atomization procedure was shown to be suitable for calculation of enthalpies of formation of the azide family.

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