Electronic Supplementary Material (ESI) for RSC Advances. This journal is © The Royal Society of Chemistry 2021

### RSC Advances 2021 · ISSN SUPPORTING INFORMATION

<u>DOI:</u> <u>Title:</u> <u>Author(s):</u>

# Contents

Spectral data	S4
<sup>1</sup> H NMR (500.1 MHz, [D <sub>6</sub> ]acetone) spectrum of compound <b>4</b>	S4
$^{13}$ C NMR (125.8 MHz, [D <sub>6</sub> ]acetone) spectrum of compound 4	S5
Fragment of ${}^{1}H - {}^{13}C$ HSQC (500.1/125.8 MHz, [D <sub>6</sub> ]acetone) spectrum of compound 4	<b>S6</b>
Fragment of ${}^{1}\text{H} - {}^{13}\text{C}$ HMBC (500.1/125.8 MHz, [D <sub>6</sub> ]acetone) spectrum of compound 4	S7
<sup>14</sup> N NMR (36.1 MHz, $[D_6]$ acetone) spectrum of compound <b>4</b>	S8
<sup>15</sup> N NMR ([INVGATED], 50.7 MHz, [D <sub>6</sub> ]DMSO) spectrum of compound <b>4</b>	<b>S9</b>
<sup>1</sup> H NMR (600.1 MHz, $[D_6]$ acetone) spectrum of compound <b>5</b>	S10
$^{13}$ C NMR (150.9 MHz, [D <sub>6</sub> ]acetone) spectrum of compound <b>5</b>	S11
<sup>14</sup> N NMR (43.4 MHz, $[D_6]$ acetone) spectrum of compound <b>5</b>	S12
<sup>15</sup> N NMR ([INVGATED], 60.8 MHz, [D <sub>6</sub> ]acetone) spectrum of compound <b>5</b>	<b>S1</b> .
<sup>1</sup> H NMR (600.1 MHz, $[D_6]$ DMSO) spectrum of compound <b>6</b>	S14
$^{13}$ C NMR (150.9 MHz, [D <sub>6</sub> ]DMSO) spectrum of compound <b>6</b>	S15
Fragment of ${}^{1}\text{H} - {}^{13}\text{C}$ HSQC (600.1/150.9 MHz, [D <sub>6</sub> ]DMSO) spectrum of compound <b>6</b>	S16
Fragment of ${}^{1}\text{H} - {}^{13}\text{C}$ HMBC (600.1/150.9 MHz, [D <sub>6</sub> ]DMSO) spectrum of compound <b>6</b>	S17
<sup>14</sup> N NMR (43.4 MHz, $[D_6]$ DMSO) spectrum of compound <b>6</b>	S18
<sup>15</sup> N NMR ([INVGATED], 60.8 MHz, $[D_6]$ DMSO) spectrum of compound <b>6</b>	S19
<sup>1</sup> H NMR (600.1 MHz, $[D_6]DMSO$ ) spectrum of compound <b>11</b>	S20
<sup>1</sup> H NMR (500.1 MHz, $[D_6]$ acetone) spectrum of compound <b>11</b>	S21
$^{13}$ C NMR (150.9 MHz, [D <sub>6</sub> ]DMSO) spectrum of compound <b>11</b>	S22
$^{13}$ C NMR (125.8 MHz, [D <sub>6</sub> ]acetone) spectrum of compound <b>11</b>	S23
$^{13}$ C NMR ([GATED], 150.9 MHz, [D <sub>6</sub> ]DMSO) spectrum of compound <b>11</b>	S24
Fragment of ${}^{1}\text{H} - {}^{13}\text{C}$ HSQC (500.1/125.8 MHz, [D <sub>6</sub> ]acetone) spectrum of compound <b>11</b>	S25
Fragment of ${}^{1}\text{H} - {}^{13}\text{C}$ HMBC (500.1/125.8 MHz, [D <sub>6</sub> ]acetone)) spectrum of compound <b>11</b>	S26
<sup>14</sup> N NMR (36.1 MHz, $[D_6]$ acetone) spectrum of compound <b>11</b>	S27
<sup>15</sup> N NMR ([INVGATED], 60.8 MHz, $[D_6]$ DMSO) spectrum of compound <b>11</b>	S28
<sup>1</sup> H NMR (500.1 MHz, [D <sub>6</sub> ]DMSO) spectrum of compound <b>7</b>	S29
$^{13}$ C NMR (125.8 MHz, [D <sub>6</sub> ]DMSO) spectrum of compound <b>7</b>	S30
<sup>13</sup> C NMR ([GATED], 125.8 MHz, [D <sub>6</sub> ]DMSO) spectrum of compound <b>7</b>	S31
Fragment of ${}^{1}\text{H} - {}^{13}\text{C}$ HSQC (500.1/125.8 MHz, [D <sub>6</sub> ]DMSO) spectrum of compound 7	S32
Fragment of ${}^{1}\text{H} - {}^{13}\text{C}$ HMBC (500.1/125.8 MHz, [D <sub>6</sub> ]DMSO) spectrum of compound <b>7</b>	S33
<sup>14</sup> N NMR (36.1 MHz, $[D_6]$ DMSO) spectrum of compound 7	S34
<sup>15</sup> N NMR ([INVGATED], 50.7 MHz, [D <sub>6</sub> ]DMSO) spectrum of compound <b>7</b>	835
X-ray crystal structure determination	S36
Thermal analysis	S40
Calorimetric measurements	S42

Calculation of the standard enthalpies of combustion and formation of compounds 4–7 Combustion performance References





Fragment of <sup>1</sup>H -<sup>13</sup>C HSQC (500.1/125.8 MHz, [D<sub>6</sub>]acetone) spectrum of compound 4



Fragment of  $^{1}H - ^{13}C$  HMBC (500.1/125.8 MHz, [D<sub>6</sub>]acetone) spectrum of compound 4





# <sup>15</sup>N NMR ([INVGATED], 50.7 MHz, [D<sub>6</sub>]DMSO) spectrum of compound 4







<sup>13</sup>C NMR (150.9 MHz, [D<sub>6</sub>]acetone) spectrum of compound 5







## <sup>1</sup>H NMR (600.1 MHz, [D<sub>6</sub>]DMSO) spectrum of compound 6





# Fragment of <sup>1</sup>H -<sup>13</sup>C HSQC (600.1/150.9 MHz, [D<sub>6</sub>]DMSO) spectrum of compound 6

![](_page_15_Figure_1.jpeg)

# Fragment of <sup>1</sup>H -<sup>13</sup>C HMBC (600.1/150.9 MHz, [D<sub>6</sub>]DMSO) spectrum of compound 6

![](_page_16_Figure_1.jpeg)

![](_page_17_Figure_1.jpeg)

![](_page_18_Figure_1.jpeg)

![](_page_19_Figure_0.jpeg)

S20

<sup>1</sup>H NMR (500.1 MHz, [D<sub>6</sub>]acetone) spectrum of compound 11

![](_page_20_Figure_1.jpeg)

![](_page_21_Figure_0.jpeg)

## <sup>13</sup>C NMR (125.8 MHz, [D<sub>6</sub>]acetone) spectrum of compound 11

![](_page_22_Figure_1.jpeg)

## <sup>13</sup>C NMR ([GATED], 150.9 MHz, [D<sub>6</sub>]DMSO) spectrum of compound 11

![](_page_23_Figure_1.jpeg)

![](_page_24_Figure_0.jpeg)

#### S25

![](_page_25_Figure_0.jpeg)

![](_page_26_Figure_1.jpeg)

# <sup>15</sup>N NMR ([INVGATED], 60.8 MHz, [D<sub>6</sub>]DMSO) spectrum of compound 11

![](_page_27_Figure_1.jpeg)

# <sup>1</sup>H NMR (500.1 MHz, [D<sub>6</sub>]DMSO) spectrum of compound 7

![](_page_28_Figure_1.jpeg)

![](_page_29_Figure_0.jpeg)

![](_page_30_Figure_0.jpeg)

Fragment of  ${}^{1}H - {}^{13}C$  HSQC (500.1/125.8 MHz, [D<sub>6</sub>]DMSO) spectrum of compound 7

![](_page_31_Figure_1.jpeg)

## Fragment of <sup>1</sup>H -<sup>13</sup>C HMBC (500.1/125.8 MHz, [D<sub>6</sub>]DMSO) spectrum of compound 7

![](_page_32_Figure_1.jpeg)

## $^{14}N$ NMR (36.1 MHz, [D<sub>6</sub>]DMSO) spectrum of compound 7

![](_page_33_Figure_1.jpeg)

## <sup>15</sup>N NMR ([INVGATED], 50.7 MHz, [D<sub>6</sub>]DMSO) spectrum of compound 7

![](_page_34_Figure_1.jpeg)

\*\*

#### X-ray crystal structure determination

Single crystal X-ray diffraction data were collected on a Bruker APEX DUO diffractometer ( $\lambda$ (MoK $\alpha$ ) = 0.71072 Å, graphite monochromator,  $\omega$ -scans). A semiempirical absorption correction was applied with the SADABS program<sup>[1]</sup> using intensity data of the equivalent reflections. Structures were solved with a dual-space method with SHELXT program<sup>[2]</sup> and refined on  $F^2$  in anisotropic approximation with SHELXL program.<sup>[2]</sup> Hydrogen atoms of the amino groups in aminofurazan **4** were found from difference Fourier synthesis and refined in isotropic approximation. All other hydrogen atoms were placed in calculated positions and refined in a riding model with isotropic displacement parameters  $U_{iso}$ (H) equal 1.2 $U_{eq}$ (C). Detailed crystallographic information is provided in Table TS1. Full crystallographic data have been deposited with the Cambridge Crystallographic Data Center. Copies of the data can be obtained free of charge via https://www.ccdc.cam.ac.uk/structures/.

X-ray powder diffraction studies were performed on a Bruker AXS D8 Advance Vario diffractometer for compound **4** (primary monochromator, CuK $\alpha_1$ ,  $\lambda = 1.54056$  Å, transmission mode) and on a Bruker AXS D8 diffractometer for compounds **5** and **6** (CuK $\alpha$ ,  $\lambda = 1.534$  Å, reflection mode), both equipped with a LynxEye position sensitive detector. Data collection was performed at ambient temperature with a step size of 0.02° and 1 s per step exposure for the 2 $\theta$  range of 4–60°. Unit cell parameters were refined with a constrained Rietweld method using atomic coordinates and equivalent isotropic displacement parameters taken from low-temperature single-crystal experiments. In all cases, no phase transition was observed. Final unit cell data are provided in Table TS2, and fits are shown in Figures S1–S3.

Table TS1.	Crystallographic	data for crystals	of compounds 4-6.
------------	------------------	-------------------	-------------------

compound	4	5	6
CCDC	2067440	2067439	2067441
empirical formula	$C_4H_3N_9O_4$	C <sub>4</sub> HN <sub>9</sub> O <sub>6</sub>	$C_8H_2N_{18}O_8$
Т, К		120	L
crystal system	orthorhombic	monoclinic	orthorhombic
space group	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	<i>P</i> 2 <sub>1</sub>	Pbcn
Z / Z'	4 / 1	2 / 1	4 / 0.5
a, Å	4.8786(8)	6.2831(10)	17.283(8)
b, Å	7.9416(13)	6.0046(10)	7.552(2)
c, Å	22.587(4)	13.003(2)	13.411(6)
β, °		91.560(3)	
V, Å <sup>3</sup>	875.1(2)	490.38(14)	1750.3(12)
d <sub>calc</sub> , g·cm <sup>−3</sup>	1.830	1.836	1.815
μ (MuKα), mm <sup>-1</sup>	1.62	1.7	1.61
2θ <sub>max</sub> , °	60	60	60
refIns. collected/unique	11090 / 2555	8776 / 2859	19761 / 2574
refins. with I > $2\sigma(I)$	1987	2016	1843
R <sub>1</sub>	0.0415	0.0511	0.0393
wR <sub>2</sub>	0.0875	0.1175	0.0942
GOF on F <sup>2</sup>	1.029	0.987	1.022
$\rho_{max/}\rho_{min},e^{\cdot} {\mathring{A}}^{-3}$	0.244/-0.245	0.274/-0.264	0.358/-0.220

Table TS2. Unit cell pa	arameters and densities	s for compounds 4-6	determined by powder
diffraction at room temp	perature (~298 K).	·	

Compound	4	5	6
Space group	P212121	<i>P</i> 2 <sub>1</sub>	Pbcn
Z / Z'	4 / 1	2 / 1	4 / 0.5
a, Å	4.9395(2)	6.3224(2)	17.5863(7)
b, Å	7.9224(5)	6.0655(2)	7.5609(4)
c, Å	22.9376(13)	13.0743(4)	13.5315(6)
β, °		90.9396(15)	
V, Å <sup>3</sup>	897.62(9)	501.31(3)	1799.25(14)
d, g·cm <sup>−1</sup>	1.784	1.796	1.765

![](_page_37_Figure_0.jpeg)

Figure S1. Constrained Rietweld refinement of PXRD data for aminofurazan 4 (Rwp = 3.3).

![](_page_37_Figure_2.jpeg)

Figure S2. Constrained Rietweld refinement of PXRD data for nitrofurazan 5 (Rwp = 4.9).

![](_page_38_Figure_0.jpeg)

Figure S3. Constrained Rietweld refinement of PXRD data for azofurazan 6 (Rwp = 5.1).

### Thermal analysis

### 1. 3-Amino-4-[(3-nitro-1*H*-1,2,4-triazol-1-yl)-*NNO*-azoxy]furazan (4):

Sample of compound 4 melts at 200 °C with decomposition.

![](_page_39_Figure_3.jpeg)

### 2. 3-Nitro-4-[(3-nitro-1*H*-1,2,4-triazol-1-yl)-*NNO*-azoxy]furazan (5):

Sample of compound **5** melts at 117 °C with subsequent decomposition at 228 °C (the extrapolated onset of exothermic peak).

![](_page_39_Figure_6.jpeg)

# 3. 3,3'-(*E*)-Diazen-1,2-diylbis{4-[(3-nitro-1*H*-1,2,4-triazol-1-yl)-*NNO*-azoxy]furazan} (6):

Sample of compound 6 reveals the complex DSC signal with an extrapolated onset of 184 °C.

![](_page_40_Figure_2.jpeg)

![](_page_40_Figure_3.jpeg)

## 4. *N,N'*-Dinitro-*N,N'*-bis{4-[(3-nitro-1*H*-1,2,4-triazol-1-yl)-*NNO*-azoxy]-furazanyl}methanediamine (7):

Sample of compound 5 decomposes after 147 °C.

![](_page_40_Figure_6.jpeg)

![](_page_40_Figure_7.jpeg)

#### **Calorimetric measurements**

The main method for determining the enthalpy of formation of energetic compounds is combustion calorimetry. The measurements were performed on a precision automatic combustion calorimeter with an isothermal shell (designed by the Laboratory of Thermodynamics of High-Energy Systems of the Federal Research Center of Chemical Physics named after N. N. Semenov of the Russian Academy of Sciences for the combustion of energetic compounds).<sup>[3]</sup>

Basic design features of the calorimeter used in this study: 1) small heat equivalent (~500 cal·degree<sup>-1</sup>) with a large volume of bomb (200 cm<sup>3</sup>); 2) simple installation bomb calorimeter – just remove the cap shell and the calorimetric vessel, drop the bomb and close the cover; 3) continuously thermostatic shell; 4) permanently fixed to the sheath liquid hermetic calorimeter vessel is in the form of a glass with double walls (calorimeter constant volume of fluid that delivers constant heat equivalent); 5) low measurement error. The calorimeter allows you to measure the thermal effect of the combustion reaction of substances with an extended uncertainty of 0.01-0.02%. Calibration of the calorimeter was carried out with the reference benzoic acid of the K-1 brand produced by the D. I. Mendeleev Institute of Metrology. The combustion energy of benzoic acid under standard conditions was  $6322.6\pm1.2$  cal·g<sup>-1</sup>. The absence of a systematic error in calorimetric measurements was controlled by burning secondary reference substances-succinic and hippuric acids, whose combustion energies on this calorimeter were 3020.3±0.6 cal·g<sup>-1</sup> (0.02%) and 5631.4±3.4 cal·g<sup>-1</sup> (0.06%), respectively. Samples of the studied substances **4–7** were burned in a platinum crucible. Pressed tablets of substances were weighed on Bunge microanalytic scales with an error of  $2 \cdot 10^{-6}$  g. The suspended sample of the substance was placed in a calorimetric bomb and filled with oxygen. The initial oxygen pressure during the combustion of all substances is about 30 atm (3 MPa). Before the experiment, 1 mL of distilled water was injected into the bomb to create a saturated vapor pressure and dissolve the nitrogen oxides formed during the combustion process.

The samples were ignited with a cotton thread, which in turn was ignited by incandescent platinum wire (diameter 0.3 mm) with a dosed pulse of current supplied from a special device. The combustion energy of cotton yarn was measured in a series of seven experiments and amounted to 3968.9 ±1.6 cal·g<sup>-1</sup>. When determining the combustion energy, corrections for the thermal effects of nitric acid formation, heat exchange of a calorimetric vessel with an isothermal shell, and the combustion energy of the auxiliary substance and cotton thread were taken into account. A detailed procedure for preparing samples and conducting an incineration experiment was described earlier.<sup>[4]</sup> The combustion energies ( $-\Delta U'_{B}$ , cal·g<sup>-1</sup>) under calorimetric bomb conditions for the studied compounds **4–7** are given in Table TS3.

S42

Compound 4								
Ν	<i>m</i> , g	$\Delta T$ ,	Q,	q <sub>a</sub> ,	q <sub>i</sub> ,	q <sub>N</sub> ,	$q_{\rm cot}$ ,	<i>–U</i> ′ <sub>В</sub> ,
		°C	cal	cal	cal	cal	cal	cal·g⁻¹
1	0.072759	2.18375	1173.96	968.43	7.27	1.86	8.18	2585.5
2	0.075734	2.30987	1241.76	1027.58	7.24	1.96	9.10	2586.4
3	0.070916	2.24653	1207.71	1006.78	7.28	1.82	8.22	2589.1
4	0.073417	2.28122	1226.36	1018.40	7.24	1.88	8.92	2586.9
5	0.074246	2.25315	1211.27	1000.98	7.29	1.90	9.01	2587.2
					$-\Delta U'_{\rm B} = 2$	2587.0 ± 1	.5 cal·g <sup>−1</sup>	
			Com	pound <b>5</b>				
N	<i>m</i> , g	$\Delta T$ ,	Q,	q <sub>a</sub> ,	q <sub>i</sub> ,	q <sub>N</sub> ,	$q_{\rm cot}$ ,	<i>–U</i> ′ <sub>В</sub> ,
		°C	cal	cal	cal	cal	cal	cal·g⁻¹
1	0.074342	2.06544	1110.36	935.17	7.33	3.38	7.66	2109.4
2	0.069135	2.01226	1081.77	917.33	7.24	3.11	8.15	2111.0
3	0.068085	1.97863	1063.69	901.19	7.27	3.04	8.36	2112.5
4	0.069632	1.99820	1074.21	908.64	7.28	3.11	8.41	2107.8
5	0.069061	1.97681	1062.71	898.19	7.27	3.11	8.40	2110.4
					-Δl	<i>J</i> ′ <sub>B</sub> = 2110	.2 ± 2.0 c	al⋅g <sup>−1</sup>
			Com	pound <b>6</b>				
N	<i>m</i> , g	$\Delta T$ ,	Q,	q <sub>a</sub> ,	q <sub>i</sub> ,	q <sub>N</sub> ,	$q_{\rm cot}$ ,	$-U'_{B},$
		°C	cal	cal	cal	cal	cal	cal·g⁻¹
1	0.082358	2.32427	1249.50	1026.56	7.32	2.55	8.51	2483.8
2	0.071262	2.15510	1158.56	963.65	7.29	2.21	8.67	2480.1
3	0.070806	2.17045	1166.81	972.58	7.30	2.18	8.76	2485.6
4	0.089324	2.12530	1142.54	952.29	7.28	2.12	8.79	2481.9
5	0.068503	2.12850	1144.26	956.09	7.29	2.10	8.87	2480.3
						$-\Delta U'_{\rm B} =$	= 2482.3 ±	2.7 cal·g <sup>-1</sup>
			Com	pound <b>7</b>				
Ν	<i>m</i> , g	$\Delta T$ ,	Q,	q <sub>a</sub> ,	<i>q</i> i,	q <sub>N</sub> ,	$q_{\rm cot}$ ,	- <i>U</i> ' <sub>B</sub> ,
		°C	cal	cal	cal	cal	cal	cal·g <sup>−1</sup>
1	0.064274	2.01164	1081.44	916.68	7.24	2.21	8.11	2290.2
2	0.067711	2.02464	1088.43	915.87	7.32	2.35	7.58	2293.7
3	0.069246	2.01084	1080.98	904.71	7.21	2.42	8.02	2289.8
4	0.062342	1.98584	1067.57	907.40	7.24	2.14	8.21	2287.1
				•		$-\Delta U'_{B}$	= 2290.2 :	± 3.5 cal·g <sup>-1</sup>

Table TS3. Combustion energies of compounds 4-7.

N – the ordinal number of the experiment;

m – weight of the sample of the compound in vacuum, g;

 $\Delta T$  – corrected temperature rise in the calorimeter, degrees;

Q- the amount of heat measured in the experiment, cal;

 $q_{\rm a}$  – heat of the combustion of the auxiliary substance benzoic acid, cal;

 $q_i$  – ignition energy, cal;

 $q_{\rm N}$  – correction for the formation of nitric acid, cal;

 $q_{\rm cot}$  – heat generation from combustion of the cotton thread, cal;

 $\Delta U'_{\rm B}$  – combustion energy of a substance in the bomb, cal·g<sup>-1</sup>.

#### Calculation of the standard enthalpies of combustion and formation of compounds 4–7

The energies of combustion as measured by bomb calorimetry for the studied compounds **4–7** are given in Table TS3. Reactions of combustion of compounds **4–7** proceed in accordance with the stoichiometry presented by equations (I)–(IV), respectively:

$C_4H_3N_9O_{4(cr)} + 2.75O_{2(g)} = 4CO_{2(g)} + 1.5H_2O_{(l)} + 4.5N_{2(g)}$	( I)
$C_4HN_9O_{6(cr)}$ + $3O_{2(g)}$ = $4CO_{2(g)}$ + $0.5H_2O_{(l)}$ + $4.5N_{2(g)}$	(II)
$C_8H_2N_{18}O_{8(cr)} + 4.5O_{2(g)} = 8CO_{2(g)} + H_2O_{(l)} + 9N_{2(g)}$	(111)
$C_9H_4N_{20}O_{12(cr)} + 4O_{2(g)} = 9CO_{2(g)} + 2H_2O_{(I)} + 10N_{2(g)}$	(IV)
where the subscripts cr. g. and I correspond to the crystalline.	aaseous.

where the subscripts cr, g, and I correspond to the crystalline, gaseous, and liquid states, respectively.

The enthalpies of formation of compounds **4–7** were calculated based on the enthalpies of combustion using equations (V)–(VIII), respectively:

$$\Delta H_{f}^{i}[C_{4}H_{3}N_{9}O_{4}]_{(cr)} = 4\Delta H_{f}^{i}[CO_{2}]_{(g)} + 1.5\Delta H_{f}^{i}[H_{2}O]_{(l)} + 4.5\Delta H_{f}^{i}[N_{2}]_{(g)} - \Delta H_{c}^{i} \quad (V)$$

$$\Delta H_{f}^{i}[C_{4}HN_{9}O_{6}]_{(cr)} = 4\Delta H_{f}^{i}[CO_{2}]_{(g)} + 0.5\Delta H_{f}^{i}[H_{2}O]_{(l)} + 4.5\Delta H_{f}^{i}[N_{2}]_{(g)} - \Delta H_{c}^{i} \quad (VI)$$

$$\Delta H_{f}^{i}[C_{8}H_{2}N_{18}O_{8}]_{(cr)} = 8\Delta H_{f}^{i}[CO_{2}]_{(g)} + \Delta H_{f}^{i}[H_{2}O]_{(l)} + 9\Delta H_{f}^{i}[N_{2}]_{(g)} - \Delta H_{c}^{i} \quad (VII)$$

$$\Delta H_{f}^{i}[C_{9}H_{4}N_{20}O_{12}]_{(cr)} = 9\Delta H_{f}^{i}[CO_{2}]_{(g)} + 2\Delta H_{f}^{i}[H_{2}O]_{(l)} + 19\Delta H_{f}^{i}[N_{2}]_{(g)} - \Delta H_{c}^{i} \quad (VII),$$
where  $\Delta H_{c}^{i} -$  the standard enthalpy of combustion of the corresponding compound, kcal·mol<sup>-1</sup>,  
and  $\Delta H_{f}^{i} -$  the standard enthalpy of its formation, kcal·mol<sup>-1</sup>.

When calculating the standard enthalpies of formation of the studied compounds, we used the reference values of the enthalpies of formation of combustion products:

 $\Delta H_{f}^{\circ}[CO_{2}]_{(g)} = -94.051 \pm 0.031 \text{ kcal} \cdot \text{mol}^{-1} \text{ and}$  $\Delta H_{f}^{\circ}[H_{2}O]_{(l)} = -68.315 \pm 0.009 \text{ kcal} \cdot \text{mol}^{-1}.^{[5]}$ 

compounds 4–7.

Table TS4 compiles the obtained thermochemical characteristics of the studied compounds.

Table TS4. Standard thermochemical characteristics for

Compound	–Δ <i>U</i> <sub>B</sub> ′, cal·g <sup>−1[a]</sup>	–ΔHঁ <sub>c</sub> , kcal·mol <sup>−1[b]</sup>	ΔH <sup>°</sup> <sub>f</sub> , kcal·mol <sup>-1[c]</sup>
4	2587.0 ± 1.5	$619.4 \pm 0.4$	$140.7 \pm 0.4$
5	2110.2 ± 2.0	566.5 ± 0.5	156.1 ± 0.5
6	2482.3 ± 2.7	1177.7 ± 1.3	356.9 ± 1.3
7	2290.2 ± 3.5	1326.3 ± 2.0	343.2 ± 2.0

[a] Energy of combustion of under bomb conditions. [b] Standard enthalpy of

combustion. [c] Standard enthalpy of formation.

### **Combustion performance**

### Energetic properties of compounds 4-7 as components of solid composite propellants

**Table TS5.** The main energetic characteristics of binary formulations containing the organic energetic filler + the active binder (18 vol.%, 14.5–15.5 w.%) + aluminum (AI) or ammonium perchlorate (AP).

Organic	w.% of	AP, %	AI, %	binder, %	Density,	Temperature	<i>I</i> <sub>sp</sub> , s
energetic	organic				g·cm⁻°	in the	
mer	filler					compustion	
4	84.55	0	0	15.45	1.736	3080	240.6
	81.71	0	3	15.29	1.754	3155	245.8
	78.85	0	6	15.15	1.772	3020	245.2
	10.00			10110		0020	2.0.2
	74 65	10	0	15 35	1 750	3190	244 0
	64.8	20	0	15.2	1 765	3260	246.6
	54 95	30	0	15.05	1.780	3300	248.2
	45.06	40	0	14 94	1 795	3280	248.5
	40.00	-10	0	14.04	1.7 00	0200	240.0
5	84 75	0	0	15 25	1 761	3680	259 7
Ŭ	81.03	0	3	15.20	1.701	3787	261.2
	79.07	0	6	14.03	1.776	3895	262.5
	76.21	0	Q Q	14.30	1.730	3965	262.0
	73.35	0	12	14.75	1.014	3970	262.5
	75.55	0	12	14.05	1.052	3970	202.5
	74.87	10	0	15 13	1 772	3580	257.5
	64.07	20	0	15.13	1.772	3500	257.5
	55.07	20	0	14.02	1.704	3400	254.7
	00.07 45.17	30	0	14.95	1.797	3400	201.2
	40.17	40	0	14.03	1.009	3300	240.0
6	94.47	0	0	15.52	1 729	2542	252.2
U	04.47	0	0	15.33	1.720	3545	252.5
	70.04	0	5	15.30	1.740	3030	250.1
	70.01	0	0	15.19	1.704	3420	250.6
	75.95	0	9	15.05	1.702	3234	240.2
	74.6	10	0	15 1	1 7 4 0	2520	252.2
	74.0	10	0	15.4	1.743	3520	253.2
	64.72	20	0	15.28	1.758	3480	253.3
	54.87	30	0	15.13	1.774	3430	252.5
	45.02	40	0	14.98	1.790	3350	250.2
	04.55	0	0		4 700	0500	050.0
1	84.55	0	0	15.45	1.730	3580	256.8
	81.71	0	3	15.29	1.754	3680	259.4
	78.85	0	6	15.15	1.772	3760	261.2
	75.99	0	9	15.01	1.790	3780	261.7
	/3.18	0	12	14.82	1.809	3730	256.1
	74.05	10	0	45.05	4 750	2500	050.0
	/4.65	10	0	15.35	1.750	3530	256.2
	04.78 54.04	20	0	15.22	1.705	3470	254.9
	54.91	30	0	15.09	1.780	3400	252.0
	45.04	40	U	14.96	1.795	3310	249.0
CL 20	06.0	0		40.0	1 0 4 4	2450	255 7
GL-20	00.2	0		13.8	1.944	3430	∠00.1
	<u>ک</u> ر ک	0	3	13.7	1.959	3060	257.3
	80.4	0	6	13.6	1.973	3670	∠58.5

	77.5	0	9	13.5	1.988	3780	259.5
	74.6	0	12	13.4	2.003	3870	260.2
	71.7	0	15	13.3	2.018	3930	260.5
	68.8	0	18	13.2	2.033	3945	259.5
	76.12	10	0	13.88	1.935	3410	254.2
	66.05	20	0	13.95	1.926	3350	251.9
	55.98	30	0	14.02	1.916	3280	248.5
	45.91	40	0	14.09	1.907	3200	243.5
RDX	84.75	0	0	15.25	1.761	3180	251.1
	81.9	0	3	15.1	1.778	3280	254.6
	79.05	0	6	14.95	1.796	3390	257.5
	76.2	0	9	14.8	1.814	3500	259.6
	73.35	0	12	14.65	1.832	3590	260.9
	70.5	0	15	14.5	1.851	3660	261.7
	67.65	0	18	14.35	1.870	3670	261.7
	74.88	10	0	15.12	1.772	3220	251.9
	64.97	20	0	15.03	1.784	3200	252.1
	55.06	30	0	14.94	1.796	3230	251.3
	45.15	40	0	14.85	1.809	3180	248.8
НМХ	85.35	0	0	14.65	1.832	3175	251.0
	82.5	0	3	14.5	1.848	3285	254.6
	79.62	0	6	14.38	1.865	3390	257.4
	76.74	0	9	14.26	1.882	3500	259.5
	73.86	0	12	14.14	1.899	3590	260.8
	71	0	15	14	1.916	3660	261.6
	68.14	0	18	13.86	1.934	3670	261.7
	75.4	10	0	14.6	1.836	3220	251.9
	65.42	20	0	14.58	1.840	3240	252.2
	55.44	30	0	14.56	1.844	3230	251.3
	45.46	40	0	14.54	1.848	3180	248.7

[1] L. Krause, R. Herbst-Irmer, G. M. Sheldrick and D. Stalke, *J. Appl. Crystallogr.*, 2015, 48, 3–10.
[2] G. M. Sheldrick, *Acta Crystallogr. A*, 2015, 71, 3–8.

[4] T. S. Kon'kova, Yu. N. Matyushin, E. A. Miroshnichenko and A. B. Vorob'ev, *Russ. Chem. Bull.*, 2009, **58**, 2020–2027.

[5] J. D. Cox, D. D. Wagman and V. A. Medvedev Eds., CODATA key values for thermodynamics. *Final Report of the CODATA Task Group on Key Values for Thermodynamics*, New York, Washington, Philadelphia, London, 1989.

<sup>[3]</sup> Ya. O. Inozemtsev, A. B. Vorob'ev, A. V. Inozemtsev and Yu. N. Matyushin, *Combustion and Explosion (Gorenie i vzryv)*, 2014, **7**, 260–270.