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SUPPORTING INFORMATION

Azasydnone – Novel green building block for designing of high energetic compounds

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General Experimental

IR spectra were recorded on a BrukerALPHA instrument in KBr pellets. ^{1}H, ^{13}C, and ^{14}N spectra were acquired on a Bruker AM-300 instrument (300.13, 75.47 and 21.69 MHz, respectively) in DMSO-d_6 at 299 K. The chemical shifts of ^{1}H and ^{13}C nuclei were reported relative to TMS, for ^{14}N – relative to $MeNO_2$, high-filed chemical shifts are given with a minus sign. High-resolution mass spectra with electrospray ionization were recorded on a Bruker MicroOTOF II instrument. Elemental analysis was performed on a PerkinElmer 2400 Series II instrument. The reaction progress and purity of the obtained compounds were controlled by TLC on Merck Silicagel 60 F_{254} plates. Visualization of spots on TLC plate was accomplished with UV light (254 nm). Density was determined by helium gas pycnometer AccuPyc II 1340 at 298 K.

Enthalpy of formation values were determined with high-precision combustion bomb calorimeter developed in Semenov Institute of Chemical physics.[1,2] Impact and friction sensitivities were measured with BAM-type apparatus in a series of experiments according to STANAG procedures.[3,4] Detonation parameters were calculated with Smirnov[5] and Kamlet-Jacobs equations.[6] Thermal stability of the compounds was monitored using DSC 204 HP (Netzsch) apparatus. Samples 0.5-2 mg mass were placed in closed Al pans with laser-cut pinholes and heated at constant rate of 5 K min^{-1} rates under nitrogen flow (100 ml min^{-1}). Environmental pressure was increased to 2 MPa for selected materials to reveal the decomposition rather than evaporation.[7]

Materials Most of the reagents and starting materials were purchased from commercial sources and used without additional purification. The starting 3,5-dinitroaniline (**1c**),[8] 1-(4-nitrophenyl)-1*H*-1,2,3,4-tetrazole (**4a**)[9], 1-(3-nitrophenyl)-1*H*-1,2,3,4-tetrazole (4**b**),[10] 4-nitroazidobenzene **5a**[11] and 3-nitroazidobenzene **5b**[12] were obtained published procedures.

Caution! Although we have encountered no difficulties during preparation and handling of these compounds, they are potentially explosive energetic materials. Manipulations must be carried out by using appropriate standard safety precautions (earthed equipment, Kevlar® gloves, Kevlar® sleeves, face shield, leather coat, and ear plugs).

General procedure for synthesis of hydrazones 2a–d.[13] A suspension of appropriate amine **1a-d** (0.02 mol) in hydrochloric acid (19%, 30 ml) was stirred at 0–5 °C and treated by dropwise addition of a solution $NaNO_2$ (1.86 g, 0.027 mol) in H_2O (6 ml). The mixture was stirred for 40 min, gave a solution of the diazonium salt.

A slurry of NaOH (0.80 g, 0.02 mol), CH_2BrNO_2 (2.8 g, 0.02 mol) and KOAc (4 g) in a mixture of H_2O (2 ml) and EtOH (5 ml) at 0–5°C was treated by dropwise addition a solution of the above diazonium salt and stirred for 40 min. The precipitate that formed was filtered off, washed with water and dried. Obtained hydrazones **2a-d** were used for the next step without further purification.

1-Nitro-*N′*-(4-nitrophenyl)formohydrazonoyl bromide (2a). Yield 3.36 g (60%).

1-Nitro-*N′*-(3-nitrophenyl)formohydrazonoyl bromide (2b). Yield 3.35 g (58%).

1-Nitro-*N′*-(3,5-dinitrophenyl)formohydrazonoyl bromide (2c). Yield 3.61 g (54%).

1-Nitro-*N′*-(2,4-dinitrophenyl)formohydrazonoyl bromide (2d). Yield 1.67 g (25%).

General procedure for synthesis of azasydnones 3a–d from hydrazones 2a–d.[14] A appropriate hydrazone **2a–d** (3.5 mmol) was added to a solution NH_4NO_3 (0.4 g, 5 mmol) in anhydrous MeCN (30 ml). The mixture was stirred for 24 h at 20°C and filtered off. The filtrate was concentrated *in vacuo* and the residue was dilute with $CHCl_3$ (100 ml). The resulting solution was filtered through a small layer of silica gel. The filtrate was concentrated *in vacuo*, gave propuct.

3-(4-Nitrophenyl)-1,2,3,4-oxatriazolium-5-olate (3a). Yield 0.65 g (89%), light-yellow needles, DSC mp 167 ºC (EtOH) (mp 168–169 ºC[14,15]). ^1H NMR (300.1 MHz, [D$_6$]DMSO): δ = 8.56 (d, 2H, J = 9.1 Hz), 8.39 (d, 2H, J = 9.1 Hz) ppm. ^{13}C NMR (75.5 MHz, [D$_6$]DMSO): δ = 165.09 (C-O), 150.18, 138.19, 125.70 (CH), 123.23 (CH) ppm. ^{14}N NMR (21.7 MHz, [D$_6$]DMSO): δ = –14.36 (NO_2), –75.37 (N^+) ppm. Found (%): C 40.30, H 1.79, N 26.94. $C_7H_4N_4O_4$. Calcd. (%): C 40.40, H 1.94, N 26.92.

3-(3-Nitrophenyl)-1,2,3,4-oxatriazolium-5-olate (3b): Yield 0.49 g (67%), light-brown crystals, DSC mp 111 ºC (EtOH:H_2O, 1:1). IR: ν = 3110 (w), 3092 (w), 1795 (vs), 1527 (s), 1352 (s), 1310 (m), 1192 (m), 990 (w), 825 (m), 739 (w) cm^{-1}. ^1H NMR (300.1 MHz, [D$_6$]DMSO): δ = 8.76 (s, 1 H, H^2), 8.66 (d, $^3J_{H,H}$ = 8.3 Hz, 1 H, H^4), 8.57 (d, $^3J_{H,H}$ = 8.2 Hz, 1 H, H^6), 8.07 (t, $^3J_{H,H}$ = 8.2 Hz, 1 H, H^5) ppm. ^{13}C NMR (75.5 MHz, [D$_6$]DMSO): δ = 165.07 (C-O), 148.34, 134.90, 132.23 (CH), 128.24 (CH), 127.73 (CH), 116.93 (CH) ppm. ^{14}N NMR (21.7 MHz, [D$_6$]DMSO): δ = –14.92 (NO_2), –74.75 (N^+) ppm. Found (%): C 40.34, H 1.86, N 26.84. $C_7H_4N_4O_4$. Calcd. (%): C 40.40, H 1.94, N 26.92.

3-(3,5-Dinitrophenyl)-1,2,3,4-oxatriazolium-5-olate (3c). Yield 0.36 g (41%), cream solid, DSC mp 153 ºC (EtOH). IR: ν = 3109 (m), 1807 (s), 1794 (s), 1544 (s), 1347 (s), 1313 (m), 1187 (m), 1078 (w), 909 (w), 733 (s) cm^{-1}. ^1H NMR (300.1 MHz, [D$_6$]DMSO): δ = 9.17 (s, 1H), 9.12 (s, 2H) ppm. ^{13}C NMR (75.5 MHz, [D$_6$]DMSO): δ = 164.84 (C-O), 148.80, 135.08, 123.00 (CH), 122.75 (CH) ppm. ^{14}N NMR (21.7 MHz, [D$_6$]DMSO): δ = –18.91 (NO$_2$), –77.43 (N$^+$) ppm. HRMS (ESI): *m/z* calcd. for $C_7H_3N_5NaO_6$ [M+Na]$^+$ 275.9976; found 275.9971. Found (%): C 33.21, H 0.97, N 27.60. $C_7H_3N_5O_6$. Calcd. (%): C 33.21, H 1.19, N 27.67.

3-(2,4-Dinitrophenyl)-1,2,3,4-oxatriazolium-5-olate (3d). Yield 0.13 g (15%), light-brown crystals, DSC mp 151 ºC (hexane–CH$_2$Cl$_2$, 1:1) (mp (decomp.) 125 ºC[15]). IR: ν = 3118 (w), 3096 (w), 1803 (vs), 1619 (w), 1557 (m), 1537 (s), 1342 (s), 1318 (m), 1184 (m), 1033 (w), 969 (w), 916 (w), 848 (w), 821 (w), 743 (m) cm^{-1}. ^{1}H NMR (300.1 MHz, [D$_6$]DMSO): δ = 9.12 (d, 1H, *J* = 2.1 Hz), 8.94 (dd, 1H, *J* = 8.7, 2.1 Hz), 8.54 (d, 1H, *J* = 8.7 Hz) ppm. ^{13}C NMR (75.5 MHz, [D$_6$]DMSO): δ = 164.77 (C-O), 150.65, 143.01, 130.45 (CH), 130.19, 129.97 (CH), 122.53 (CH) ppm. ^{14}N NMR (21.7 MHz, [D$_6$]DMSO): δ = –21.75 (NO$_2$), –84.56 (N$^+$) ppm. ^{15}N NMR (30.4 MHz, [D$_6$]DMSO): δ = 7.95 ($N^2_{\text{oxatriazoles}}$), –11.37 (NO$_2$), –14.71 (NO$_2$), –74.72 (N$^+$), –137.60 (N^4) ppm. Found (%): C 33.08, H 1.05, N 27.67. $C_7H_3N_5O_6$. Calcd. (%): C 33.21, H 1.19, N 27.67.

3,5-Dinitroazidobenzene (5c). At 0 °C and stirring, a solution of 3,5-dinitroaniline (0.18 g, 1 mmol) in hydrochloric acid (20%, 4 ml) was treated by a cool solution NaNO$_2$ (0.13 g, 2 mmol) in H$_2$O (2 ml). The mixture was stirred for 40 min at 0–5°C and treated by dropwise addition of a cool solution NaN$_3$ (0.13 g, 2 mmol) in H$_2$O (3 ml). After 2 h the precipitate that formed was filtered off, washed with water, and air-dried, gave 0.18 g (89%) crude **5c**. The solid was dilute hot CHCl$_3$ (5 ml), cooled and filtered. The filtrate was diluted with hexane (35 ml) the precipitate that formed was filtered off, washed with water, and air-dried. Yield of pure product **5c** was 0.15 g (80%), light-brown needles, mp 82–84 ºC. IR: ν = 3144 (w), 3090 (w), 2131 (s), 2095 (m), 1540 (vs), 1451 (w), 1347 (s), 1329 (s), 1304 (s), 1165 (w), 1074 (m), 920 (w), 888 (m), 814 (w), 729 (s), 702 (w), 645 (w) cm^{-1}. ^{1}H NMR (300.1 MHz, [D$_6$]DMSO): δ = 8.60 (s, 1H); 8.32 (s, 2H) ppm. ^{13}C NMR (75.5 MHz, [D$_6$]DMSO): δ = 148.72, 143.12, 120.04 (CH), 114.33 (CH) ppm. ^{14}N NMR (21.7 MHz, [D$_6$]DMSO): δ = –15.94 (NO$_2$), –142.46 (N$_3$). Found (%): C 34.57; H 1.42; N 33.29. $C_6H_3N_5O_4$. Calcd. (%): C 34.46; H 1.45; N 33.49.

X-ray analysis of the involved materials.

X-ray experiments for compounds **3a-c**, **4a,b** and **5a-c** were carried out using SMART APEX2 CCD diffractometer (λ(Mo-Kα)=0.71073 Å, graphite monochromator, ω-scans) at 100K. Collected data were processed by the SAINT and SADABS programs incorporated into the APEX2 program package.[16] The structures were solved by the direct methods and refined by the full-matrix least-squares procedure against F^2 in anisotropic approximation. The refinement was carried out with the SHELXTL program.[17] The details of data collection and crystal structures refinement are summarized in Table 1S for azasydnone derivatives and in

Table 2S for tetrazoles and azides along with CCDC numbers which contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

Table 1S. Crystallographic data for azasydnone derivatives **3a-c**.

	3a	**3b**	**3c**
formula	$C_7H_4N_4O_4$	$C_7H_4N_4O_4$	$C_7H_3N_5O_6$
fw	208.14	208.14	253.14
crystal system	Monoclinic	Monoclinic	Orthorhombic
space group	$P2_1/c$	$P2_1/n$	$Pca2_1$
a, Å	12.608(3)	5.3726(12)	9.893(3)
b, Å	5.6499(11)	17.510(4)	18.586(6)
c, Å	12.102(2)	8.6127(19)	9.943(3)
β, deg.	110.626(4)	93.895(5)	90
V, Å^3	806.8(3)	808.4(3)	1828.2(10)
Z	4	4	8
d_{cryst}, g·cm^{-3}	1.714	1.710	1.839
F(000)	424	424	1024
μ, mm^{-1}	0.144	0.144	0.164
θ range, deg.	3.4 – 30.0	2.3 – 28.0	1.1 – 28.3
reflections collected	13624	15218	26673
independent reflections / R_{int}	2354 / 0.0642	1943 / 0.0399	4496 / 0.1133
Completeness to theta θ, %	99.7	100	99.7
refined parameters	136	136	464
GOF (F^2)	1.015	1.048	1.043
reflections with $I>2\sigma(I)$	1631	1562	2655
$R_1(F)$ $(I>2\sigma(I))$[a]	0.0418	0.0350	0.0566
$wR_2(F^2)$ (all data)[b]	0.1062	0.0933	0.1275
Largest diff. peak/hole, e·Å^{-3}	0.304 / -0.224	0.263 / -0.196	0.203 / -0.180
CCDC number	1854060	1854061	1854062

[a] $R_1 = \sum|F_o - |F_c||/\sum(F_o)$; [b] $wR_2 = (\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]^{½}$

Table 2S. Crystallographic data for tetrazole (**4a,b**) and azido (**5a-c**) derivatives.

	4a	**4b**	**5a**	**5b**	**5c**
formula	$C_7H_5N_5O_2$	$C_7H_5N_5O_2$	$C_6H_4N_4O_2$	$C_6H_4N_4O_2$	$C_6H_3N_5O_4$
fw	191.16	191.16	164.13	164.13	209.13
crystal system	Monoclinic	Monoclinic	Orthorhombic	Triclinic	Orthorhombic
space group	$P2_1/c$	$P2_1/n$	$P2_12_12_1$	P-1	$Pna2_1$
a, Å	7.2094(8)	11.1512(5)	3.6798(4)	3.7040(2)	9.7268(6)
b, Å	7.7337(9)	17.2780(7)	10.3754(10)	10.7498(5)	8.3199(5)
c, Å	14.2011(16)	12.9735(5)	18.1767(18)	17.5309(9)	9.8210(6)
α, deg.	90	90	90	98.1710(10)	90
β, deg.	93.215(2)	106.2590(10)	90	94.5500(10)	90
γ, deg.	90	90	90	92.6580(10)	90
V, Å^3	790.54(16)	2399.6(2)	693.98(12)	687.59(6)	794.77(8)
Z	4	12	4	4	4
d_{cryst}, g·cm^{-3}	1.606	1.587	1.571	1.586	1.748
F(000)	392	1176	336	336	424
μ, mm^{-1}	0.125	0.123	0.124	0.125	0.150
θ range, deg.	2.8 – 30.2	2.0 – 29.0	2.3 – 30.2	2.1 – 31.1	3.2 – 29.2
reflections collected	22139	47363	13294	10802	7840
independent reflections/R_{int}	2339/ 0.0309	6343/0.0419	2066/0.0443	4436/0.0194	2149/0.0263
Completeness to theta θ, %	99.9	99.7	99.8	99.8	99.9
refined parameters	127	506	109	217	148
GOF (F^2)	1.049	1.158	1.052	1.030	1.042
reflections with $I>2\sigma(I)$	2022	5010	1861	3670	1984
$R_1(F)$ ($I>2\sigma(I)$)[a]	0.0382	0.0528	0.0333	0.0377	0.0280
$wR_2(F^2)$ (all data)[b]	0.1132	0.1187	0.0875	0.1080	0.0668
Largest diff. peak/hole,eÅ^{-3}	0.349/ -0.283	0.302/ -0.241	0.275/-0.180	0.455/-0.231	0.264/-0.173
CCDC number	1854063	1854064	1854065	1854066	1854067

[a] $R_1 = \sum|F_o - |F_c||/\sum(F_o)$; [b] $wR_2 = (\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2\ ]^{½}$

Coputational Part

The gas phase enthalpy of formation (ΔH_f^0) for compounds of this study was evaluated in the G3B3 approximation[18] using the so-called "the atomization reaction procedure".[19] The literature values of ΔH_f^0 for the elements in the standard state were used.[20] Geometry optimization of isolated molecules was carried out at the M052X/6-311G(df,pd) level of theory that was succesfully utilized in our recent studies on polynitro compounds.[21] The GAUSSIAN program was used for calculation.[22] The wave functions obtained from calculation of isolated molecules were analyzed in terms of R. Bader "AIM" topological theory[23] using the AIMALL program.[24]

Crystal packing analysis was carried out using two methods. The first one is based on combination of geometrical and energetic approaches, and was adopted in our recent studies on high energetic compounds.[22,25] It is based on analysis of close and shortened intermolecular contacts between central molecule and its closest environment in the crystal, and estimation of interaction energy between central molecule and each molecule from its closest environment (pair interaction energies or dimerization energies). Molecule is included in the closest environment if at least one atom…atom contact is shorter than sum of van-der-Waals radii[26] plus 0.5Å. All found intermolecular contacts are separated into three groups according to interatomic distances ($d_{1\text{-}2}$): 1) ordinary van-der-Waals contacts ($d_{1\text{-}2} > r_{vdw1} + r_{vdw2} + 0.05$Å), 2) shortened contacts ($r_{vdw1} + r_{vdw2} + 0.05\text{Å} > d_{1\text{-}2} > r_{vdw1} + r_{vdw2} - 0.1$Å), 3) close contacts ($d_{1\text{-}2} < r_{vdw1} + r_{vdw2} - 0.1$Å). Here, r_{vdw1} and r_{vdw2} are van-der-Waals radii of corresponding atoms. Only shortened and close contacts are given in Tables 5S-16S.

Interaction energy of a molecular pair (dimer) was estimated according to well-known general formula $E_{int} = E_{AB} - E_A - E_B$, where E_{AB} – energy of a dimer, and E_A, E_B – energies of isolated molecules from which this dimer consists of. In the case of one symmetrically independent molecule in the unit cell, $E_A = E_B$. For E_{int} estimation, the structures of a dimer and isolated molecules were taken from the X-ray data without further optimization. The BSSE correction was taken into account.

The second approach for crystal packing analysis was based on recently proposed Δ_{OED} (overlap of electron density) criterion.[27] It is assumed that upon crystal formation, molecules interact to each other by means of overlap of their electron densities. It means that volume of isolated molecule is larger than that of the molecule in a crystal. Similarly, density of an isolated molecule (d_{mol}) is lower than that in a crystal (d_{cryst}). The latter is the density of the crystal structure obtained from X-ray experiment. The value of d_{mol} can be estimated by analysis of the electron density of optimized isolated molecule in terms of the AIM theory. It is defined as a ratio of molecular mass per molecular volume (the latter is presented as the sum of atomic volumes)

$$d_{mol} = m_{mol}/V_{mol}\ ; \qquad m_{mol} = M_{mol}/N_A\ ; \qquad V_{mol} = \sum_i V_{at}^{(i)}$$

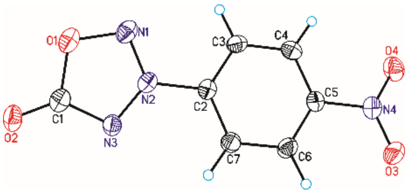
Here, M_{mol} and m_{mol} are molar and molecular masses, respectively, N_A is Avogadro number, V_{mol} and V_{at} are molecular and atomic volumes, respectively. It is convenient to present d_{mol} in g/cm^3 units. Evidently, the volume and density of any molecular fragment can be calculated in a similar way. For estimation of V_{mol}, isodensity surface of 0.0004 e/a_o^3 (a_o – Bohr radius) was utilized for integration procedure. So estimated molecular volume comprises about 99.8% of all electrons (nearly whole molecule), and charge leakage does not exceed 0.002 e/Å^3 that approximately corresponds to numerical error of integration of calculated electron density. It is evident, that difference between crystal and molecular density can be served as a measure of how pronounced is the overlap of molecular electron densities upon crystal structure formation. Therefore, the Δ_{OED} criterion defined as $\Delta_{OED} = d_{cryst} - d_{mol}$ would characterize tightness of crystal packing. Combined analysis of d_{mol} and Δ_{OED} values would clarify an origin of the observed crystal packing density. The results on d_{cryst}, Δ_{OED}, d_{mol} and V_{mol} (including characteristics of both whole molecules and their fragments) are summarized in Table 3S.

Table 3S. Molecular and crystal volumes (Å^3) and densities (g/cm^3) and Δ_{OED} criterium for compounds **3-5** from topological analysis of calculated electron densoty and X-ray data.

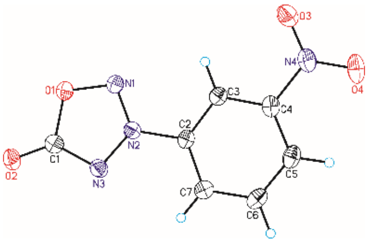
En-try	Property	Molecular unit	**3a**	**3b**	**3c**	**4a**	**4b**	**5a**	**5b**	**5c**
1	Volume (V_{mol})	azasydnone	91.94	91.97	91.87	–	–	–	–	–
2		terazole	–	–	–	87.20	87.35	–	–	–
3		N_3	–	–	–	–	–	56.27	56.34	56.22
4		Whole mol.	252.82	252.96	285.19	249.15	249.56	219.87	220.06	251.91
5	Density (d_{mol})	azasydnone	1.554	1.554	1.555	–	–	–	–	–
6		terazole	–	–	–	1.315	1.313	–	–	–
7		N_3	–	–	–	–	–	1.240	1.239	1.241
8		Whole mol.	1.367	1.366	1.474	1.274	1.272	1.240	1.239	1.379
9	d_{cryst}		1.714	1.710	1.839	1.606	1.587	1.571	1.586	1.748
10	Δ_{OED}		0.347	0.344	0.365	0.332	0.315	0.331	0.347	0.369

Molecular and crystal structure analysis

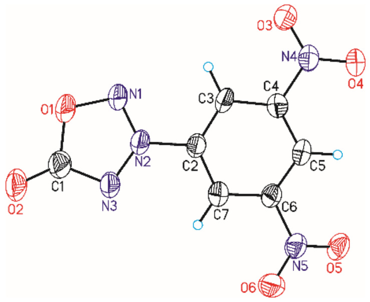
Eight compounds (**3a-c**, **4a,b**, **5a-c**) were investigated by the single crystal X-ray diffraction at 100K. Their molecular structures are depicted in Fig. 1S.



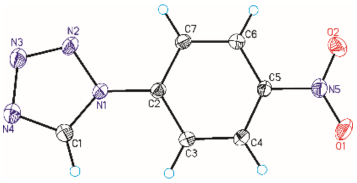
3a



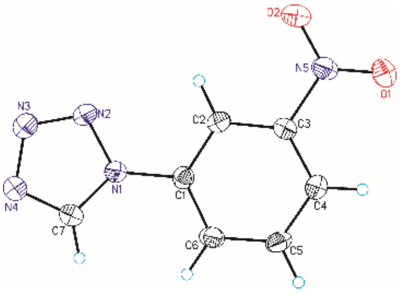
3b



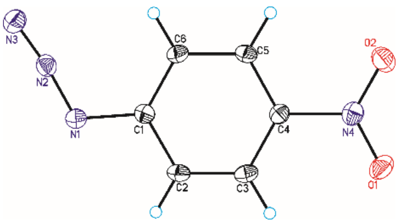
3c



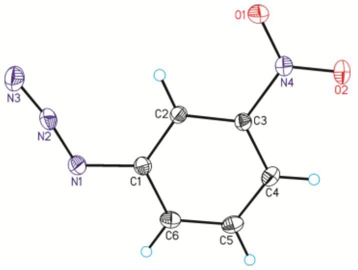
4a



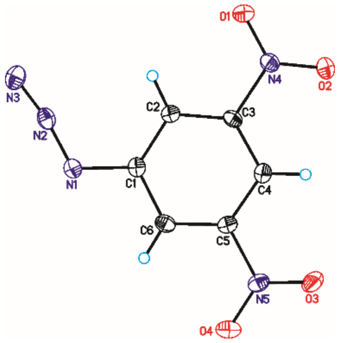
4b



5a



5b



5c

Figure 1S. General view of structurally charatrized azasydnones, tetrazoles and azides.

The structures of tetrazole **4a** (refcode NAGGOU)[28] and azide **5a** (refcode NIPHAZ)[29] were known earlier, however those experiments were carried out at room temperature. An asymmetric unit cell of compounds **3a**, **3b**, **4a**, **5a**, **5c** contains one molecule. Two symmetrically independent molecules are found in crystals of **3c** and **5b**, while for **4b**, three symmetrically independent molecules are observed. In crystals of **3c** and **4b**, one of symmetrically independent molecules is totally disordered over two positions. They are denoted as A', A" for compound **3c**, and A", B" for compound **4b**.

Crystal packing of compounds **3b,c**, **4b**, **5b,c** is presented in Figures 2S-6S (those for compounds **3a**, **4a**, **5a** can be found in the main text). The results on geometrical and energetic analysises of the crystal packing are given for compounds **3-5** in Tables 5S-16S. Results on all independent molecules are given in separate tables. In those cases when molecule is disordered, the system of close contacts and pair energies were calculated for all disordered parts separately. In such cases pair energy is calculated by averaging as follows:

(i) for interaction between two disordered molecules

$E_{\text{cont}}=E(\text{part1}\ldots\text{part1})\times p_1^2+E(\text{part1}\ldots\text{part2})\times p_1p_2+E(\text{part2}\ldots\text{part1})\times p_1p_2+E(\text{part2}\ldots\text{part2})\times p_2^2$;

(ii) for interaction between ordered molecule and disordered molecule

$E_{\text{cont}} = E(\text{ordered mol.}\ \ldots\ \text{part1})\times p_1 + E(\text{ordered mol.}\ \ldots\ \text{part2})\times p_2$.

Here p_1 and p_2 are occupancies of each part of the disorder ($p_1 + p_2 = 1$).

From the results it can be seen that in tetrazole derivatives, π…π stacking interactions provide sizable contribution into crystal packing stabilization. The tetrazole ring actively participates in those interactions. Role of stacking interactions in azasydnones is significantly less pronounced. In azides, stacking interactions take place also, however azido group is not involved in those interactions. In Table 4S we compared contributions of π…π stacking into total crystal structure stabilization by calculation of a number of pair interactions which are formed by π…π stacking and their energies.

Table 4S. Contribution of π…π stacking interactions into stabilization of crystal packing*.

	3a	**3b**	**3c**	**4a**	**4b**	**5a**	**5b**	**5c**
π…π stacking is observed for *n* molecular pairs	0	1	2	2	3.3	2	2	0
contribution to the total energy, %	0	18	18	24	35	25	24	0

* for those structures in which two or more (Z'>1) symmetrically independent molecules are observed, we averaged percentage contribution and *n* value over Z'.

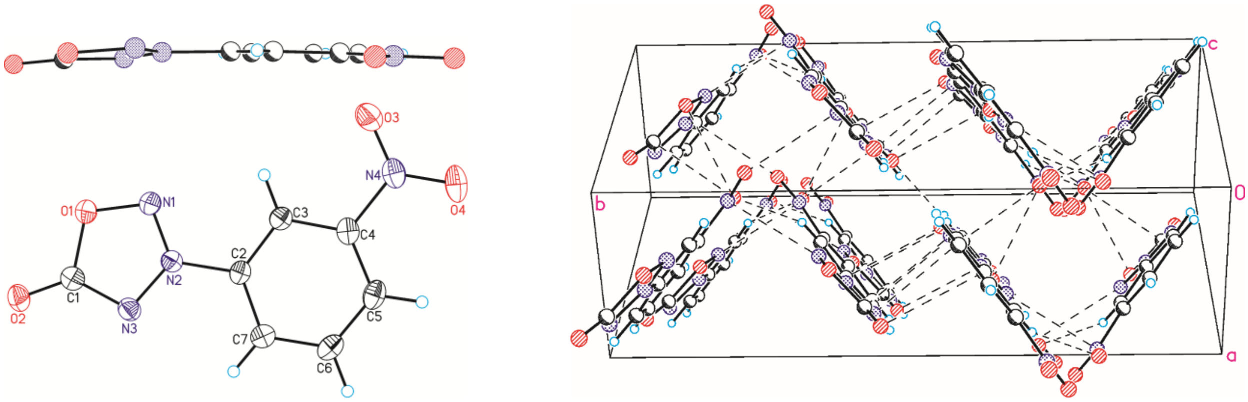


Figure 2S. Left: molecular structure of compound **3b** along with its lateral view to show planarity/unplanarity; right: crystal packing fragment: corrugated layers are built up via C-H…O and π…π stacking interactions. Interlayer interactions are provided by C-H…O and O…π contacts.

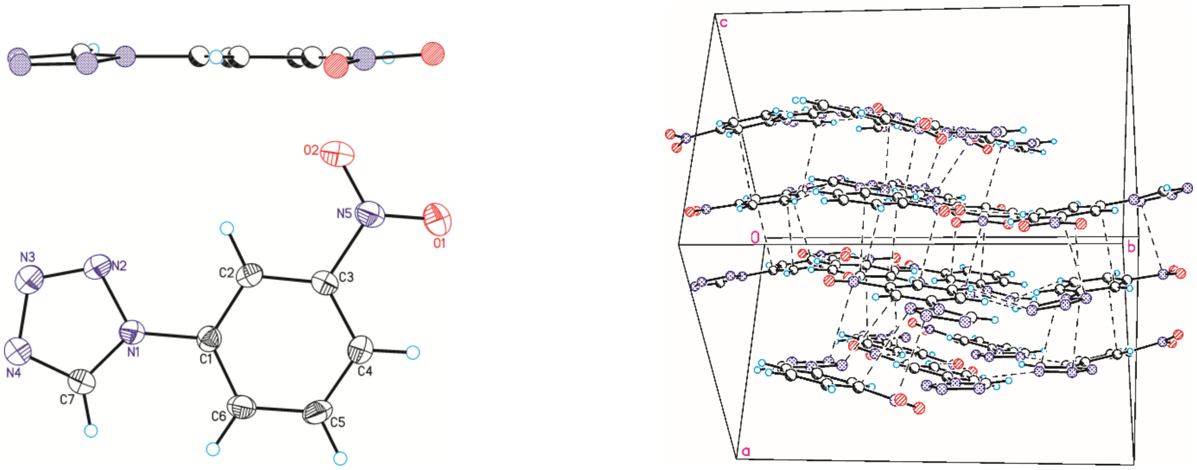


Figure 3S. Left: molecular structure of compound **4b** along with its lateral view to show planarity/unplanarity; right: Crystal packing fragment. H-bonded layers are connected by stacking interactions (vertical dashed lines)

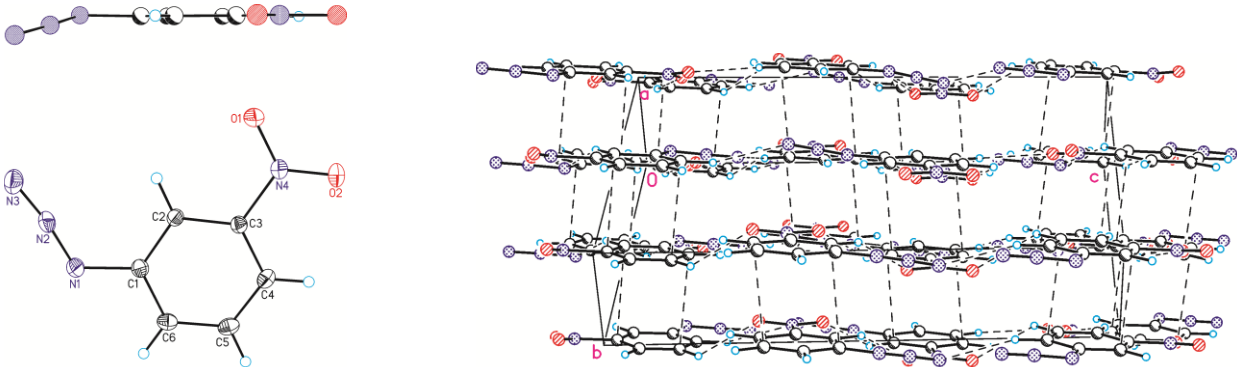


Figure 4S. Left: molecular structure of compound **5b** along with its lateral view to show planarity/unplanarity; right: Crystal packing fragment. H-bonded layers are connected by weak Ph…Ph stacking interactions (vertical dashed lines)

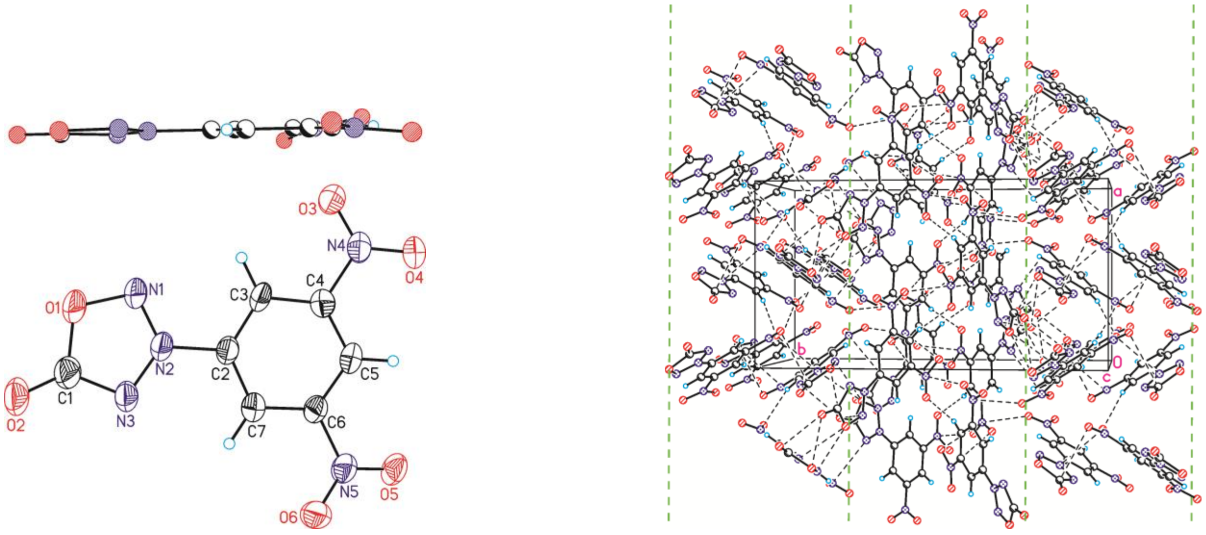


Figure 5S. Left: molecular structure of compound **3c** along with its lateral view to show planarity/unplanarity; right: Crystal packing fragment. Pojection on *ab* plane; layers perpendicular to the plane of figure are separated by green dashed lines; each layer consists of only one type of molecules (A or A'); interactions in the layer are provided by C-H…O H-bonds O…π and stacking interactions; layers are connected to each other by O…π interactions.

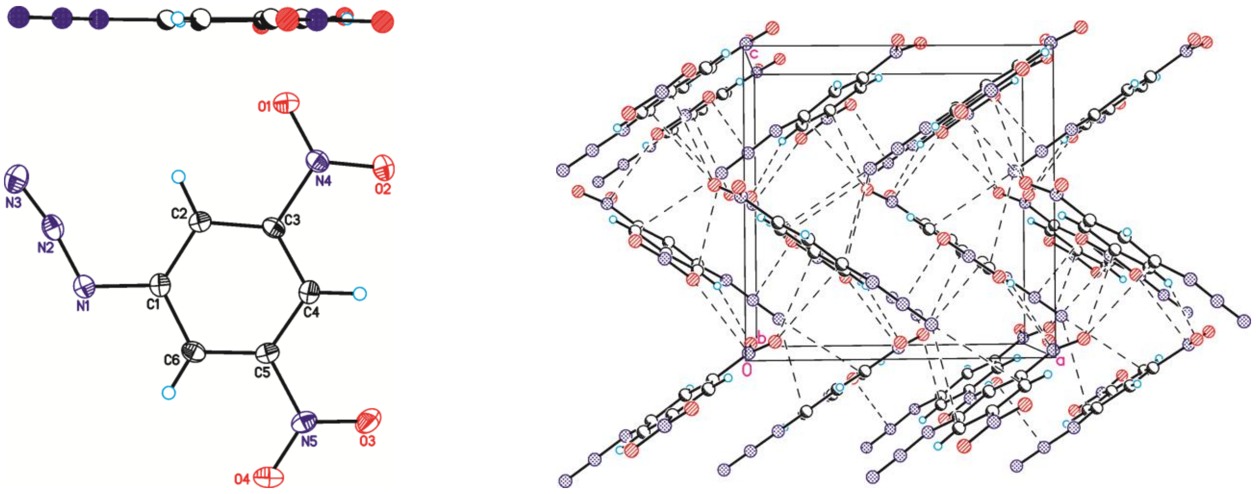


Figure 6S. Left: molecular structure of compound **5c** along with its lateral view to show planarity/unplanarity; right: Crystal packing fragment: corrugated layers are built up via C-H…O and O…π interactions. Interlayer interactions are provided by O…π and N…π contacts.

Table 5S. Pair intermolecular interaction energies (kcal/mol) and shortened contacts (Å) of molecule of compound **3a** with its closest environment in the crystal obtained at M052X/6-311G(df,pd) level of approximation.

Entry	Symmetry Code	Atomic pair		Distance	Type of interaction	Energy
1	x,-1+y,z	No close contacts			vdW	-3.0
2	x,1+y,z	No close contacts			vdW	-3.0
3	1-x,-1-y,2-z	No close contacts			vdW	-6.3
4	1-x,-y,2-z	O2	C7	3.249	C-H…O h-bond	-9.7
		O2	H7A	2.531		
		C7	O2	3.249		
		H7A	O2	2.531		
5	2-x,-2-y,2-z	O4	C4	3.323	C-H…O h-bond	-4.0
		O4	H4A	2.527		
		C4	O4	3.323		
		H4A	O4	2.527		
6	2-x,-1-y,2-z	No close contacts			vdW	-0.1
7	1-x,-1/2+y,1.5-z	N1	O2	2.984	O…π	-5.8
		N2	O2	2.899		
		C1	O1	3.124		
8	1-x,1/2+y,1.5-z	O1	C1	3.124	O…π	-5.8
		O2	N1	2.984		
		O2	N2	2.899		
9	2-x,-1/2+y,2.5-z	No close contacts			vdW	-2.5
10	2-x,1/2+y,2.5-z	No close contacts			vdW	-2.5
11	x,-1.5-y,-1/2+z	C3	O3	3.226	C-H…O h-bond	-1.5
		H3A	O3	2.430		
12	x,-1.5-y,1/2+z	O3	C3	3.226	C-H…O h-bond	-1.5
		O3	H3A	2.430		

Table 6S. Pair intermolecular interaction energies (kcal/mol) and shortened contacts (Å) of molecule of compound **3b** with its closest environment in the crystal obtained at M052X/6-311G(df,pd) level of approximation.

Entry	Symmetry Code	Atomic pair		Distance	Type of Interaction	Energy
1	-1+x,y,-1+z	H5A C5	O1 O1	2.589 3.666	C-H…O h-bond	-4.9
2	1+x,y,1+z	O1 O1	H5A C5	2.589 3.666	C-H…O h-bond	-4.9
3	-1+x,y,z	No close contacts			vdW	-0.2
4	1+x,y,z	No close contacts			vdW	-0.2
5	x,y,-1+z	O4 O4	O1 C1	2.998 2.858	O…π	-5.2
6	x,y,1+z	O1 C1	O4 O4	2.998 2.858	O…π	-5.2
7	-1-x,-y,-z	No close contacts			vdW	-0.2
8	-1-x,-y,1-z	O2 O2 C6 H6A	C6 H6A O2 O2	3.301 2.529 3.301 2.529	C-H…O h-bond	-12.3
9	-x,-y,1-z	O2 N3 C1 C2	C2 C1 N3 O2	3.197 3.112 3.112 3.197	π…π stacking	-9.8
10	-1/2+x,1/2-y,-1/2+z	O4 O4 N4	C3 H3A N1	3.201 2.313 2.990	C-H…O h-bond N…NO_2	-2.3
11	1/2+x,1/2-y,1/2+z	N1 C3 H3A	N4 O4 O4	2.990 3.201 2.313	C-H…O h-bond N…NO_2	-2.3
12	-1/2+x,1/2-y,1/2+z	C2	O3	3.128	O…π	-2.9
13	1/2+x,1/2-y,-1/2+z	O3	C2	3.128	O…π	-2.9

Table 7S. Pair intermolecular interaction energies (kcal/mol) and shortened contacts (Å) of molecule A of compound **3c** with its closest environment in the crystal obtained at M052X/6-311G(df,pd) level of approximation.*

Entry	Symmetry Code	Atomic pair		Distance	Type of Interaction	Energy	Molecular pair
1	x,y,-1+z	C5 H5A	O2 O2	3.118 2.447	C-H…O H-bond	-3.5	A…A
2	x,y,1+z	O2 O2	C5 H5A	3.118 2.447	C-H…O h-bond	-3.5	A…A
3	1-x,2-y,-1/2+z	N5 O5 O5 O5 O6	N3 N2 N3 C2 C1	3.050 3.024 3.156 3.062 3.197	π…π. stacking NO$_2$…sydnone	-5.4	A…A
4	1-x,2-y,1/2+z	N2 N3 N3 C1 C2	O5 N5 O5 O6 O5	3.024 3.050 3.156 3.197 3.062	π…π. stacking NO$_2$…sydnone	-5.4	A…A
5	-1/2+x,2-y,z	C3 C4 C5	O6 O6 O6	3.328 3.041 3.351	weak O…π	-2.1	A…A
6	1/2+x,2-y,z	O6 O6 O6	C3 C4 C5	3.328 3.041 3.351	weak O…π	-2.1	A…A
7	1/2-x,y,-1/2+z	N4 O3	N1 N1	3.287 3.008	weak N…NO$_2$	-2.0	A…A
8	1/2-x,y,1/2+z	N1 N1	N4 O3	3.287 3.008	weak N…NO$_2$	-2.0	A…A
9	1.5-x,y,-1/2+z	C2 C7	O2 O2	3.404 2.923	O…π	-6.1	A…A
10	1.5-x,y,1/2+z	O2 O2	C2 C7	3.404 2.923	O…π	-6.1	A…A
11A'	1-x,1-y,1/2+z	O3 O3 O3	C4' N4' O3'	3.002 2.822 3.004	O…π	-4.2	A…A'
11A"	**1-x,1-y,1/2+z**	**O3 O3 O3 O3 O3**	**N1" N2" N3" C1" C4"**	**3.043 2.847 3.106 3.317 3.286**	O…π	**-4.3**	**A…A"**
12A'	2-x,1-y,1/2+z	can not exist too close C1…O2 contact of 2.578Å					A…A'
12A"	**2-x,1-y,1/2+z**	**No close contacts**			**vdW**	**-1.6**	**A…A'**
13A'	-1/2+x,1-y,z	N4 O3 C3 C4 C5	N3' N3' O2' O2' O2'	2.976 3.122 3.277 3.102 3.256	N…π O…π	-7.5	A…A'
13A"	**-1/2+x,1-y,z**	**N4 C4**	**O3" O3"**	**2.970 3.162**	O…π	**-5.7**	**A…A"**
14A'	-1/2+x,1-y,1+z	O1 O1 O1	N2' C2' C3'	3.030 3.032 3.255	O…π	-2.8	A…A'
14A"	**-1/2+x,1-y,1+z**	**O1 O1**	**C2" C3"**	**3.096 3.126**	**weak O…π**	**-0.3**	**A…A"**

* Interatomic contacts that include minor part of the disorder (A") are given in bold.

Table 8S. Pair intermolecular interaction energies (kcal/mol) and shortened contacts (Å) of molecule A'(A") of compound **3c** with its closest environment in the crystal obtained at M052X/6-311G(df,pd) level of approximation.*

Entry	Symmetry code	Atomic pair		Distance	Type of interaction	Energy	Molecular pair
1'	1+x,y,z	No close contacts			vdW	-0.4	A'…A'
1'-"	**1+x,y,z**	**O1'** **N1'** **C7'** **H7'A**	**O1"** **O1"** **O2"** **O2"**	**3.086** **3.005** **3.361** **2.422**	**weak O…*π*** **C-H…O**	**-4.2**	**A'…A"**
1"-'	**1+x,y,z**	**No close contacts**			**vdW**	**-0.3**	**A"…A'**
1"	**1+x,y,z**	**Cannot exist, too close O6"…O2" contact of 2.276Å**					**A"…A"**
2'	-1+x,y,z	No close contact			vdW	-0.4	A'…A'
2'-"	**-1+x,y,z**	**No close contact**			**vdW**	**-0.3**	**A'…A"**
2"-'	**-1+x,y,z**	**O1"** **O1"** **O2"** **O2"**	**O1'** **N1'** **C7'** **H7'A**	**3.086** **3.005** **3.361** **2.422**	**weak O…*π*** **C-H…O**	**-4.2**	**A"…A'**
2"	**-1+x,y,z**	**Cannot exist, too close O6"…O2" contact of 2.276Å**					**A"…A"**
3'	2-x,1-y,-1/2+z	O5' O5' O5'	C2' C3' C7'	3.026 3.275 3.119	O…*π*	-4.1	A'…A'
3'-"	**2-x,1-y,-1/2+z**	**O5'** **O5'** **O5'** **O5'** **O5'**	**C2"** **C3"** **C4"** **C6"** **C7"**	**3.148** **3.153** **3.190** **3.217** **3.180**	**O…*π***	**-3.9**	**A'…A"**
3"-'	**2-x,1-y,-1/2+z**	**No close contacts**			**vdW**	**-1.8**	**A"…A'**
3"	**2-x,1-y,-1/2+z**	**No close contacts**			**vdW**	**-1.6**	**A"…A"**
4'	2-x,1-y,1/2+z	C2' C3' C7'	O5' O5' O5'	3.026 3.275 3.119	O…*π*	-4.1	A'…A'
4'-"	**2-x,1-y,1/2+z**	**No close contacts**			**vdW**	**-1.8**	**A'…A"**
4"-'	**2-x,1-y,1/2+z**	**C2"** **C3"** **C4"** **C5"** **C6"** **C7"**	**O5'** **O5'** **O5'** **O5'** **O5'** **O5'**	**3.148** **3.153** **3.190** **3.222** **3.217** **3.180**	**O…*π***	**-3.9**	**A"…A'**
4"	**2-x,1-y,1/2+z**	**No close contacts**			**vdW**	**-1.6**	**A"…A"**
5'	-1/2+x,1-y,z	H5'A O4' O4' O5'	O6' C6' N5' O6'	2.244 3.173 2.922 3.033	C-H…O NO_2…NO_2	-1.7	A'…A'
5'-"	**-1/2+x,1-y,z**	**Cannot exist, too close C5'…O6" contact of 2.841Å**					**A'…A"**
5"-'	**-1/2+x,1-y,z**	**O2"** **O2"**	**C5'** **C6'**	**3.152** **3.172**	**O…*π***	**-5.7**	**A"…A'**
5"	**-1/2+x,1-y,z**	**N3"** **N3"** **N3"**	**C6"** **N5"** **O5"**	**3.342** **2.967** **3.125**	**N…*π***	**-4.5**	**A"…A"**
6'	1/2+x,1-y,z	N5' O6' O6' O6'	O4' C5' H5'A O5'	2.922 3.156 2.244 3.033	C-H…O NO_2…NO_2	-1.7	A'…A'
6'-"	**1/2+x,1-y,z**	**C5'** **C6'**	**O2"** **O2"**	**3.152** **3.172**	**O…*π***	**-5.7**	**A'…A"**
6"-'	**1/2+x,1-y,z**	**Cannot exist, too close C5'…O6" contact of 2.841Å**					**A"…A'**

6"	**1/2+x,1-y,z**	**C6"** **N5"**	**N3"** **N3"**	**3.342** **2.967**	**N…π**	**-4.5**	**A"…A"**
7'	1.5-x,y,-1/2+z	C5' C6' O5' O5' O5'	O3' O3' N4' O3' O4'	3.058 3.145 2.997 2.979 2.960	π…π stacking between NO_2 and NO_2 and Ph	-3.6	A'…A'
7'-"	**1.5-x,y,-1/2+z**	**Cannot exist, too close O5'…C1" contact of 2.723Å**					**A'…A"**
7"-'	**1.5-x,y,-1/2+z**	**O2"** **O2"**	**N3'** **C1'**	**2.930** **3.370**	**O…π**	**-5.8**	**A"…A'**
7"	**1.5-x,y,-1/2+z**	**N5"** **O5"** **O5"**	**O1"** **O1"** **C1"**	**3.127** **2.862** **3.003**	**π…π stacking between NO_2 and sydnone**	**-4.6**	**A"…A"**
8'	1.5-x,y,1/2+z	N4' O3' O3' O3' O4'	O5' C5' C6' O5' O5'	2.997 3.058 3.145 2.979 2.960	π…π stacking between NO_2 and NO_2 and Ph	-3.6	A'…A'
8'-"	**1.5-x,y,1/2+z**	**N3'** **C1'**	**O2"** **O2"**	**2.930** **3.370**	**O…π**	**-5.8**	**A'…A"**
8"-'	**1.5-x,y,1/2+z**	**Cannot exist, too close O5'…C1" contact of 2.723Å**					**A"…A'**
8"	**1.5-x,y,1/2+z**	**O1"** **O1"** **C1"**	**N5"** **O5"** **O5"**	**3.127** **2.862** **3.003**	**π…π stacking between NO_2 and sydnone**	**-4.6**	**A"…A"**
9'	2.5-x,y,-1/2+z	Cannot exist, too close N1'…O2' contact of 2.572Å					A'…A'
9'-"	**2.5-x,y,-1/2+z**	**No**	**close**	**contacts**	**vdW**	**-3.7**	**A'…A"**
9"-'	**2.5-x,y,-1/2+z**	**C7"** **O6"** **O6"**	**C1'** **N1'** **N2'**	**3.314** **3.062** **2.990**	**π…π stacking**	**-5.1**	**A"…A'**
9"	**2.5-x,y,-1/2+z**	**O6"** **O6"** **O6"**	**C2"** **N4"** **O4"**	**3.015** **2.843** **2.875**	**NO_2…NO_2**	**-4.6**	**A"…A"**
10'	2.5-x,y,1/2+z	Cannot exist, too close N1'…O2' contact of 2.572Å					A'…A'
10'-"	**2.5-x,y,1/2+z**	**C1'** **N1'** **N2'**	**C7"** **O6"** **O6"**	**3.314** **3.062** **2.990**	**π…π stacking**	**-5.1**	**A'…A"**
10"-'	**2.5-x,y,1/2+z**	**No close contacts**			**vdW**	**-3.7**	**A"…A'**
10"	**2.5-x,y,1/2+z**	**C2"** **N4"** **O4"**	**O6"** **O6"** **O6"**	**3.015** **2.843** **2.875**	**NO_2…NO_2**	**-4.6**	**A"…A"**
11'	1-x,1-y,-1/2+z	C4' N4' O3'	O3 O3 O3	3.002 2.822 3.004	O…π	-4.2	A'…A
11"	**1-x,1-y,-1/2+z**	**N1"** **N2"** **N3"** **C1"** **C4"**	**O3** **O3** **O3** **O3** **O3**	**3.043** **2.847** **3.106** **3.317** **3.286**	**O…π**	**-4.3**	**A"…A**
12'	2-x,1-y,-1/2+z	Cannot exist, too close O2'…C1 contact of 2.578Å					A'…A
12"	**2-x,1-y,-1/2+z**	**No close contacts**			**vdW**	**-1.6**	**A"…A**
13'	1/2+x,1-y,z	O2' O2' O2' N3' N3'	C3 C4 C5 N4 O3	3.277 3.102 3.256 2.976 3.122	N…π O…π	-7.5	A'…A
13"	**1/2+x,1-y,z**	**O3"** **O3"**	**N4** **C4**	**2.970** **3.162**	**O…π**	**-5.7**	**A"…A**

14'	1/2+x,1-y,-1+z	N2'	O1	3.030	O…π	-2.8	A'…A
		C2'	O1	3.032			
		C3'	O1	3.255			
14"	**1/2+x,1-y,-1+z**	**C2"**	**O1**	**3.096**	**weak O…π**	**-0.3**	**A"…A**
		C3"	**O1**	**3.126**			

* Interatomic contacts that include minor part of the disorder (A") are given in bold.

Table 9S. Pair intermolecular interaction energies (kcal/mol) and shortened contacts (Å) of molecule of compound **4a** with its closest environment in the crystal obtained at M052X/6-311G(df,pd) level of approximation.

Entry	Symmetry Code	Atomic pair		Distance	Type of interaction	Energy
1	x,-1+y,z	N2	C4	3.376	H-bond	-6.6
		N2	H4	2.447		
		H7	O1	2.553		
		C7	O1	3.483		
2	x,1+y,z	O1	H7	2.553	H-bond	-6.6
		O1	C7	3.483		
		C4	N2	3.376		
		H4	N2	2.447		
3	-x,-1/2+y,1.5-z	N4	C1	3.239	H-bond	-4.4
		N4	H1	2.300		
4	-x,1/2+y,1.5-z	C1	N4	3.239	H-bond	-4.4
		H1	N4	2.300		
5	1-x,-1/2+y,1/2-z	No close contacts			vdW	-1.6
6	1-x,1/2+y,1/2-z	No close contacts			vdW	-1.6
7	-x,-y,1-z	N4	C5	3.374	π…π stacking	-4.4
		C1	C5	3.355		
		C1	C6	3.277		
		C2	C2	3.385		
		C5	N4	3.374		
		C5	C1	3.355		
		C6	C1	3.277		
8	1-x,-y,1-z	N2	N5	3.153	π…π stacking	-4.2
		N5	N2	3.153		
		C2	C6	3.300		
		C6	C2	3.300		
9	x,1/2-y,-1/2+z	No close contacts			vdW	-1.4
10	x,1/2-y,1/2+z	No close contacts			vdW	-1.4

Following three Tables (10S-12S) describe three independent molecules of compound **4b**. We denoted them as A, A' and A''. However, third independent molecule is totally disordered. Therefore A'' stands for the major part while B'' stands for the minor partis. Contacts that include minor part of the disorder are given in bold.

Table 10S. Pair intermolecular interaction energies (kcal/mol) and shortened contacts (Å) of molecule A of compound **4b** with its closest environment in the crystal obtained at M052X/6-311G(df,pd) level of approximation.

Entry	Symmetry code	Atomic pair		Distance	Type of interaction	Energy	Molecular pair
1	1-x,-y,1-z	No close contacts			vdW	-3.4	A…A
2	-1/2+x,1/2-y,-1/2+z	No close contacts			vdW	-3.0	A…A
3	1/2+x,1/2-y,1/2+z	No close contacts			vdW	-3.0	A…A
4	x,y,z	N2	C3'	3.296	π…π stacking	-4.4	A…A'
		N5	N2'	3.161			
		C1	C6'	3.376			
		C2	C1'	3.459			
		C3	N2'	3.259			
5	-x,-y,-z	N3	C7'	3.220	C-H…N h-bond	-5.5	A…A'
		N3	H7'	2.274			
6	1-x,-y,1-z	No close contacts			vdW	-5.4	A…A'
7	1/2-x,-1/2+y,1/2-z	O2	C5'	3.212	C-H…O h-bond	-3.6	A…A'
		O2	H5'	2.574			
8	1/2-x,1/2+y,1/2-z	C7	N4'	3.184	C-H…N	-4.2	A…A'
		H7	N4'	2.275			
9A''	x,y,z	C1	N4A	3.227	π…π stacking	-3.1	A…A''
		C4	C2A	3.455			
		C6	C7A	3.365			
9B''	**x,y,z**	**C5**	**C2B**	**3.553**	**π…π stacking**	**-3.6**	**A…B''**
		C6	**N5B**	**3.362**			
		C6	**C3B**	**3.534**			
10A''	-x,-y,1-z	N2	C3A	3.365	π…π stacking	-5.7	A…A''
		N3	N5A	3.100			
		N5	N4A	3.147			
		C2	N2A	3.262			
10B''	**-x,-y,1-z**	**N5**	**O1B**	**3.031**	**π…π stacking**	**-4.2**	**A…B''**
		C3	**O1B**	**3.226**			
		O2	**N5B**	**3.025**			
		N3	**C7B**	**3.237**			
11A''	-1/2+x,1/2-y,-1/2+z	No close contacts			vdW	-2.2	A…A''
11B''	**-1/2+x,1/2-y,-1/2+z**	**No close contacts**			**vdW**	**-0.3**	**A…B''**

Table 11S. Pair intermolecular interaction energies (kcal/mol) and shortened contacts (Å) of molecule A' of compound **4b** with its closest environment in the crystal obtained at M052X/6-311G(df,pd) level of approximation.

Entry	Symmetry code	Atomic pair		Distance	Type of interaction	Energy	Molecular pair
1'	-x,-y,-z	No close contacts			vdW	-3.8	A'…A'
2'	-x,-y,-z	No close contacts			vdW	-3.8	A'…A'
3'	-1/2+x,1/2-y,-1/2+z	No close contacts			vdW	-2.5	A'…A'
4'	1/2+x,1/2-y,1/2+z	No close contacts			vdW	-2.5	A'…A'
5'(4)	x,y,z	C3'	N2	3.296	π…π stacking	-4.4	A'…A
		N2'	N5	3.161			
		C6'	C1	3.376			
		C1'	C2	3.459			
		N2'	C3	3.259			
6'(5)	-x,-y,-z	C7'	N3	3.220	C-H…N	-5.5	A'…A
		H7'	N3	2.274			
7'(6)	1-x,-y,1-z	No close contacts			vdW	-5.4	A'…A
8'(7)	1/2-x,1/2+y,1/2-z	C5'	O2	3.212	weak C-H…O	-3.6	A'…A
		H5'	O2	2.574			
9'(8)	1/2-x,-1/2+y,1/2-z	N4'	C7	3.184	C-H…N	-4.2	A'…A
		N4'	H7	2.275			
10'A"	x,y,-1+z	C2'	C4A	3.394	π…π stacking	-2.5	A'…A"
		C2'	C5A	3.379			
		C3'	C5A	3.306			
10'B"	**x,y,-1+z**	**C7'**	**N2B**	**3.341**	**π…π stacking**	**-3.8**	**A'…B"**
		C3'	**C6B**	**3.432**			
11'A"	1-x,-y,1-z	N3'	C4A	3.183	π…π stacking	-5.0	A'…A"
		N4'	C4A	3.273			
		N4'	C5A	3.357			
11'B"	**1-x,-y,1-z**	**C6'**	**N3B**	**3.266**	**π…π stacking**	**-7.2**	**A'…B"**
		C6'	**N4B**	**3.283**			

Table 12S. Pair intermolecular interaction energies (kcal/mol) and shortened contacts (Å) of molecule A"(B") of compound **4b** with its closest environment in the crystal obtained at M052X/6-311G(df,pd) level of approximation.

Entry	Symmetry code	Atomic pair		Distance	Type of Interaction	Energy	Molecular pair
1"A"A"	1/2-x,-1/2+y,1.5-z	No close contacts			vdW	-4.5	A"…A" 3546
1"A"B"	**1/2-x,-1/2+y,1.5-z**	**O2A O2A**	**C5B H5B**	**3.235 2.585**	**C-H…O**	**-3.5**	**A"…B"**
1"B"A"	**1/2-x,-1/2+y,1.5-z**	**N4B N4B**	**C7A H7A**	**3.356 2.428**	**C-H…N**	**-4.3**	**B"…A"**
1"B"B"	**1/2-x,-1/2+y,1.5-z**	**Cannot exist, too close N4B…C4B contact of 2.911Å**					**B"…B"**
2"A"A"	1/2-x,1/2+y,1.5-z	No close contacts			vdW	-4.5	A"…A"
2"A"B"	**1/2-x,1/2+y,1.5-z**	**H7A C7A**	**N4B N4B**	**2.428 3.356**	**C-H…N**	**-4.3**	**A"…B"**
2"B"A"	**1/2-x,1/2+y,1.5-z**	**C5B H5B**	**O2A O2A**	**3.235 2.585**	**C-H…O**	**-3.5**	**B"…A"**
2"B"B"	**1/2-x,1/2+y,1.5-z**	**Cannot exist, too close N4B…C4B contact of 2.911Å**					**B"…B"**
3"A"A"	-x,-y,1-z	No close contacts			vdW	-0.2	A"…A"
3"A"B"	**-x,-y,1-z**	**C2A H2A N4A N4A**	**O1B O1B C7B H7B**	**3.435 2.490 3.277 2.409**	**C-H…O C-H…N**	**-5.2**	**A"…B"**
3"B"A"	**-x,-y,1-z**	**O1B O1B C7B H7B**	**C2A H2A N4A N4A**	**3.175 2.490 3.277 2.409**	**C-H…O C-H…N**	**-5.2**	**B"…A"**
3"B"B"	**-x,-y,1-z**	**O1B O1B O1B O1B C7B C2B H2B H7B**	**C2B H2B C7B H7B O1B O1B O1B O1B**	**3.373 2.434 3.230 2.329 3.230 3.373 2.434 2.329**	**C-H…O**	**-9.7**	**B"…B"**
4"A"A"	1-x,-y,2-z	O1A O1A C4A H4A	C4A H4A O1A O1A	3.310 2.546 3.310 2.546	C-H…O	-3.8	A"…A"
4"A"B"	**1-x,-y,2-z**	**C4A H4A**	**N3B N3B**	**3.219 2.440**	**C-H…N**	**-4.4**	**A"…B"**
4"B"A"	**1-x,-y,2-z**	**N3B N3B**	**C4A H4A**	**3.219 2.440**	**C-H…N**	**-4.4**	**B"…A"**
4"B"B"	**1-x,-y,2-z**	**no close contacts**			**vdW**	**-3.4**	**B"…B"**
5"A"A"	-1/2+x,1/2-y,-1/2+z	N3A N3A	C5A H5A	3.246 2.373	C-H…N	-2.0	A"…A"
5"A"B"	**-1/2+x,1/2-y,-1/2+z**	**no close contacts**			**vdW**	**-4.2**	**A"…B"**
5"B"A"	**-1/2+x,1/2-y,-1/2+z**	**O2B O2B**	**C5A H5A**	**3.059 2.177**	**C-H…O**	**-1.4**	**B"…A"**
5"B"B"	**-1/2+x,1/2-y,-1/2+z**	**no close contacts**			**vdW**	**-3.3**	**B"…B"**

6"A"A"	1/2+x,1/2-y,1/2+z	C5A	N3A	3.246	C-H…N	-2.0	A"…A"
		H5A	N3A	2.373			
6"A"B"	**1/2+x,1/2-y,1/2+z**	**C5A**	**O2B**	**3.059**	**C-H…O**	**-1.4**	**A"…B"**
		H5A	**O2B**	**2.177**			
6"B"A"	**1/2+x,1/2-y,1/2+z**	**no close contacts**			**vdW**	**-4.2**	**B"…A"**
6"B"B"	**1/2+x,1/2-y,1/2+z**	**no close contacts**			**vdW**	**-3.3**	**B"…B"**
7"A"(9)	x,y,z	N4A	C1	3.227	π…π stacking		A"…A
		C2A	C4	3.455			
		C7A	C6	3.365			
7"B"(9)	**x,y,z**	**C2B**	**C5**	**3.553**	**π…π stacking**		**B"…A**
		N5B	**C6**	**3.362**			
		C3B	**C6**	**3.534**			
8"A"(10)	-x,-y,1-z	N5A	N3	3.100	π…π stacking	-5.7	A"…A
		N2A	C2	3.262			
		N4A	N5	3.147			
		C3A	N2	3.365			
8"B"(10)	**-x,-y,1-z**	**O1B**	**N5**	**3.031**	**π…π stacking**	**-4.2**	**B"…A**
		O1B	**C3**	**3.226**			
		N5B	**O2**	**3.025**			
		C7B	**N3**	**3.237**			
9"A"(11)	1/2+x,1/2-y,1/2+z	no close contacts			vdW	-2.2	A"…A
9"B"(11)	**1/2+x,1/2-y,1/2+z**	**no close contacts**			**vdW**	**-0.3**	**B"…A**
10"A"(10')	x,y,1+z	C4A	C2'	3.394	π…π stacking	-2.5	A"…A'
		C5A	C2'	3.379			
		C5A	C3'	3.306			
10"B"(10')	**x,y,1+z**	**N2B**	**C7'**	**3.341**	**π…π stacking**	**-3.8**	**B"…A'**
		C6B	**C3'**	**3.432**			
10"A"(11')	1-x,-y,1-z	C4A	N3'	3.183	π…π stacking	-5.0	A"…A'
		C4A	N4'	3.273			
		C5A	N4'	3.357			
10"B"(11')	**1-x,-y,1-z**	**N3B**	**C6'**	**3.266**	**π…π stacking**	**-7.2**	**B"…A'**
		N4B	**C6'**	**3.283**			

Table 13S. Pair intermolecular interaction energies (kcal/mol) and shortened contacts (Å) of molecule of compound **5a** with its closest environment in the crystal obtained at M052X/6-311G(df,pd) level of approximation.

Entry	Symmetry Code	Atomic pair		Distance	Type of interaction	Energy
1	-1+x,y,z	C1	C2	3.426	π…π. stacking Ph…Ph	-4.2
		C1	C3	3.464		
		C5	C4	3.429		
		C6	C4	3.467		
		C6	C5	3.454		
2	1+x,y,z	C2	C1	3.426	π…π. stacking Ph…Ph	-4.2
		C3	C1	3.464		
		C4	C5	3.429		
		C4	C6	3.467		
		C5	C6	3.454		
3	1/2-x,-y,-1/2+z	no close contacts			vdW	-1.2
4	1/2-x,-y,1/2+z	no close contacts			vdW	-1.2
5	1.5-x,-y,-1/2+z	no close contacts			vdW	-1.5
6	1.5-x,-y,1/2+z	no close contacts			vdW	-1.5
7	1-x,-1/2+y,1/2-z	no close contacts			vdW	-3.5
8	1-x,1/2+y,1/2-z	no close contacts			vdW	-3.5
9	2-x,-1/2+y,1/2-z	O1	C5	3.196	C-H…O h-bond	-4.4
		O1	H5	2.617		
		C3	O2	3.505		
		H3	O2	2.504		
10	2-x,1/2+y,1/2-z	O2	C3	3.505	C-H…O h-bond	-4.4
		O2	H3	2.504		
		C5	O1	3.196		
		H5	O1	2.617		
11	-1/2+x,-1/2-y,1-z	N1	C2	3.478	C-H…N h-bond	-1.2
		N1	H2	2.570		
12	1/2+x,-1/2-y,1-z	C2	N1	3.478	C-H…N h-bond	-1.2
		H2	N1	2.570		
13	-1/2+x,1/2-y,1-z	no close contacts			vdW	-0.8
14	1/2+x,1/2-y,1-z	no close contacts			vdW	-0.8

Table 14S. Pair intermolecular interaction energies (kcal/mol) and shortened contacts (Å) of molecule A of compound **5b** with its closest environment in the crystal obtained at M052X/6-311G(df,pd) level of approximation.

Entry	Symmetry code	Atomic pair		Distance	Type of interaction	Energy	Molecular pair
1	-	C2	C1	3.381	π…π stacking Ph…Ph	-4.3	A…A
	-1+x,y,z	C2	C6	3.492			
		C3	C5	3.491			
		C4	C5	3.382			
2	1+x,y,z	C1	C2	3.381	π…π stacking Ph…Ph	-4.3	A…A
		C5	C3	3.491			
		C5	C4	3.382			
		C6	C2	3.492			
3	-x,2-y,1-z	O1	C2	3.473	C-H…O h-bond	-4.5	A…A
		O1	H2	2.589			
		C2	O1	3.473			
		H2	O1	2.589			
4	1-x,2-y,1-z	no close contacts			vdW	-5.6	A…A
5	1-x,3-y,1-z	no close contacts			vdW	-1.1	A…A
6	2-x,3-y,1-z	no close contacts			vdW	-2.1	A…A
7	-1+x,y,z	O2	C5'	3.215	C-H…O h-bond	-2.1	A…A'
		O2	H5'	2.521			
8	x,y,z	no close contacts			vdW	-1.6	A…A'
9	x,1+y,z	no close contacts			vdW	-0.2	A…A'
10	1+x,1+y,z	C5	N3'	3.494	C-H…N h-bond	-0.3	A…A'
		H5	N3'	2.655			
11	-x,2-y,1-z	no close contacts			vdW	-0.6	A…A'
12	1-x,2-y,-z	C5	O1'	3.375	C-H…O h-bond	-3.3	A…A'
		H5	O1'	2.602			
13	1-x,2-y,1-z	N3	N3'	3.013	Azid…Azid	-1.2	A…A'

Table 15S. Pair intermolecular interaction energies (kcal/mol) and shortened contacts (Å) of molecule A' of compound **5b** with its closest environment in the crystal obtained at M052X/6-311G(df,pd) level of approximation.

Entry	Symmetry code	Atomic pair		Distance	Type of interaction	Energy	Molecular pair
1	-1+x,y,z	C2'	C3'	3.371	π…π stacking Ph…Ph	-3.6	A'…A'
		C6'	C5'	3.379			
2	1+x,y,z	C3'	C2'	3.371	π…π stacking Ph…Ph	-3.6	A'…A'
		C5'	C6'	3.379			
3	-x,1-y,-z	N1'	C2'	3.435	C-H…N h-bond	-5.0	A'…A'
		N1'	H2'	2.541			
		C2'	N1'	3.435			
		H2'	N1'	2.541			
4	1-x,1-y,-z	no close contacts			vdW	-4.3	A'…A'
5	1-x,2-y,-z	no close contacts			vdW	-3.0	A'…A'
6	2-x,2-y,-z	O2'	C4'	3.354	C-H…O h bond	-5.2	A'…A'
		O2'	H4'	2.618			
		C4'	O2'	3.354			
		H4'	O2'	2.618			
7	1+x,y,z	C5'	O2	3.215	C-H…O h bond	-2.1	A'…A
		H5'	O2	2.521			
8	x,y,z	no close contacts			vdW	-1.6	A'…A
9	x,-1+y,z	no close contacts			vdW	-0.2	A'…A
10	-1+x,-1+y,z	N3'	C5	3.494	C-H…N h bond	-0.3	A'…A
		N3'	H5	2.655			
11	-x,2-y,1-z	no close contacts			vdW	-0.6	A'…A
12	1-x,2-y,-z	O1'	C5	3.375	C-H…O h bond	-3.3	A'…A
		O1'	H5	2.602			
13	1-x,2-y,1-z	N3'	N3	3.013	Azid…Azid	-1.2	A'…A

Table 16S. Pair intermolecular interaction energies (kcal/mol) and shortened contacts (Å) of molecule of compound **5c** with its closest environment in the crystal obtained at M052X/6-311G(df,pd) level of approximation.

Entry	Symmetry code	Atomic pair		Distance	Type of interaction	Energy
1	x,-1+y,z	no close contacts			vdW	-1.4
2	x,1+y,z	no close contacts			vdW	-1.4
3	1-x,1-y,-1/2+z	C1	O3	3.321	O…π	-2.9
		C2	O3	3.174		
		C3	O3	3.336		
4	1-x,1-y,1/2+z	O3	C1	3.321	O…π	-2.9
		O3	C2	3.174		
		O3	C3	3.336		
5	2-x,1-y,-1/2+z	N3	C2	3.347	N…π	-0.6
		N3	C3	3.256		
		N3	C4	3.446		
6	2-x,1-y,1/2+z	C2	N3	3.347	N…π	-0.6
		C3	N3	3.256		
		C4	N3	3.446		
7	-1/2+x,1/2-y,z	O1	N3	3.189	N…π	-4.6
		O2	N2	2.981		
		O2	N3	3.064		
8	1/2+x,1/2-y,z	N2	O2	2.981	N…π	-4.6
		N3	O1	3.189		
		N3	O2	3.064		
9	-1/2+x,1.5-y,z	O4	N1	3.041	O…π	-2.6
		O4	C1	3.218		
10	1/2+x,1.5-y,z	N1	O4	3.041	O…π	-2.6
		C1	O4	3.218		
11	1.5-x,-1/2+y,-1/2+z	O1	O4	3.062	O…π C-H…O h-bond	-4.5
		O1	N5	2.931		
		O1	C5	3.245		
		C2	O4	3.279		
		H2	O4	2.396		
12	1.5-x,1/2+y,1/2+z	O4	O1	3.062	O…π C-H…O h-bond	-4.5
		N5	O1	2.931		
		C5	O1	3.245		
		O4	C2	3.279		
		O4	H2	2.396		

Experimental determination of the enthalpy of formation.

For thermochemical experiments of each compound, several samples obtained and purified by different methods were used. The purity of the samples was at least 99.5% (HPLC).

The energies of combustion of several derivatives azasydnones **3a−d** and tetrazoles **4a,b** are measured by the method of a bombing calorimetry of burning and enthalpies of formation in a standard condition are calculated. Measurements are executed on a precision automatic calorimeter of burning with an isothermal cover (a design of laboratory of thermodynamics of high energetic systems ICP of the Russian Academy of Sciences), developed specially for burning of energetic materials[2]. The technique of preparation of samples and the burning experiment in the calorimetric bomb were described earlier.[30].

For Tables S17-S19, following designations are accepted:

m – mass of samples, g;

ΔT – the corrected temperature lifting for the calorimeter, conditional degree;

Q – the quantity of heat measured in an experience, cal;

q_a – a thermal emission from combustion of auxiliary substance (reference benzoic acid), cal;

q_i – the energy of an ignition measured by the special electronic device, cal;

q_N – the amendment on nitric acid formation, cal;

q_{cot} – a thermal emission from combustion of a cotton thread, cal;

$\Delta U'_B$ – energy of combustion of a sample in the conditions of the bomb, cal·g^{-1};

ΔH^o_c – a standard enthalpy of combustion of compound, kcal·mol^{-1};

ΔH^o_f – a standard enthalpy of formation of compound, kcal·mol^{-1}.

Table 17S. Energies of combustion of azasydnones **3a–d** and tetrazoles **4a,b**

3-(4-Nitrophenyl)-1,2,3,4-oxatriazolium-5-olate, $C_7H_4N_4O_4$ (**3a**)								
Sample 1 (crystallized from EtOH)								
N	m	ΔT	Q	q_a	q_i	q_N	q_{cot}	$-\Delta U'_B$
1	0.048912	2.18383	1174.01	968.21	5.84	1.31	8.81	3881.3
2	0.053236	2.23282	1200.34	977.59	5.83	1.45	8.67	3884.6
Sample 2 (crystallized from EtOH)								
1	0.053721	2.32958	1252.36	1026.55	5.93	1.17	9.95	3886.0
2	0.053091	2.36572	1271.72	1051.33	5.83	1.17	7.31	3882.9
	$-\Delta U'_B = 3884 \pm 4$ cal·g^{-1}							
3-(3-Nitrophenyl)-1,2,3,4-oxatriazolium-5-olate, $C_7H_4N_4O_4$ (**3b**)								
Sample 1 (crystallized from EtOH)								
N	m	ΔT	Q	q_a	q_i	q_N	q_{cot}	$-\Delta U'_B$
1	0.076974	2.51442	1351.73	1036.21	5.85	1.77	7.64	3900.8
2	0.077326	2.48683	1336.89	1019.92	5.86	1.77	8.16	3894.9
3	0.084926	2.52626	1358.09	1010.62	5.80	1.95	8.79	3896.7
	$-\Delta U'_B = 3898 \pm 6$ cal·g^{-1}							
	Sample 2 (crystallized from EtOH:H_2O=2:1)							
N	m	ΔT	Q	q_a	q_i	q_N	q_{cot}	$-\Delta U'_B$
1	0.089036	2.33470	1255.11	891.67	5.80	2.04	8.68	3896.4
2	0.091042	2.34283	1259.48	887.56	5.83	2.07	8.80	3901.7
3	0.094015	2.34815	1262.34	879.20	5.80	2.14	8.72	3898.1
4	0.091433	2.33139	1253.33	880.18	5.82	2.07	8.93	3901.0
5	0.048169	2.05339	1103.88	900.19	5.82	1.10	8.95	3899.2
	$-\Delta U'_B = 3899 \pm 3$ cal·g^{-1}							
3-(3,5-Dinitrophenyl)-1,2,3,4-oxatriazolium-5-olate, $C_7H_3N_5O_6$ (**3c**) (crystallized from EtOH)								
N	m	ΔT	Q	q_a	q_i	q_N	q_{cot}	$-\Delta U'_B$
1	0.076312	2.21883	1192.82	942.25	5.90	1.61	9.19	3064.7
2	0.080237	2.20748	1186.72	925.07	5.83	1.73	8.49	3060.9

3	0.075279	2.18780	1176.14	930.25	5,78	1.59	8.01	3062.1
4	0.082698	2.22419	1195.70	926.50	5.86	1.79	8.39	3061.3
5	0.078317	2.19121	1172.97	921.92	5.85	1.68	8.60	3063.4
	$-\Delta U'_B = 3063 \pm 2$ cal·g^{-1}							
3-(2,4-Dinitrophenyl)-1,2,3,4-oxatriazolium-5-olate, $C_7H_3N_5O_6$ (**3d**) (crystallized from hexane–CH_2Cl_2, 1:1)								
N	m	ΔT	Q	q_a	q_i	q_N	q_{cot}	$-\Delta U'_B$
1	0.081214	2.26877	1219.67	953.66	5.93	2.07	8.40	3074.2
2	0.042939	2.05074	1102.46	954.94	5.92	1.04	8.31	3079.9
3	0.035802	2.02881	1096.67	965.56	5.90	0.76	8.28	3077.2
4	0.075211	2.05039	1102.30	854.93	5.91	1.45	8.62	3076.1
5	0.096089	2.17839	1171.08	859.28	5.95	1.86	8.48	3075.4
6	0.073948	2.03766	1095.43	851.57	5.94	1.38	8.81	3079.6
	$-\Delta U'_B = 3077 \pm 2$ cal·g^{-1}							
1-(4-Nitrophenyl)-1*H*-1,2,3,4-tetrazole (**4a**)								
Sample 1 (crystallized from EtOH)								
N	m	ΔT	Q	q_a	q_i	q_N	q_{cot}	$-\Delta U'_B$
1	0.080963	2.35944	1268.41	865.96	5.87	2.00	9.43	4757.1
2	0.081216	2.36388	1270.80	867.75	5.94	2.04	9.06	4752.9
3	0.080593	2.36597	1271.92	872.60	5.91	2.00	8.56	4750.4
Sample 2 (crystallized from CH_3CN)								
N	m	ΔT	Q	q_a	q_i	q_N	q_{cot}	$-\Delta U'_B$
1	0.088743	2.51163	1350.23	911.44	5.97	2.35	9.20	4747.1
2	0.083911	2.41827	1300.04	884.01	5.94	2.21	9.20	4751.2
3	0.081318	2.40003	1290.23	886.83	5.91	2.14	8.71	4754.8
	$-\Delta U'_B = 4752.1 \pm 3.5$ cal·g^{-1}							
1-(3-Nitrophenyl)-1*H*-1,2,3,4-tetrazole (**4b**)								
Sample 1 (crystallized from EtOH)								
N	m	ΔT	Q	q_a	q_i	q_N	q_{cot}	$-\Delta U'_B$
1	0.086263	2.44969	1316.93	890.35	5.91	2.22	7.99	4758.2
2	0.084352	2.43730	1310.27	893.22	5.93	2.18	8.15	4751.4
3	0.088047	2.49242	1339.90	905.19	5.92	2.28	7.89	4754.5
Sample 2 (crystallized from $CH_3CN:H_2O$ = 1:3)								
N	m	ΔT	Q	q_a	q_i	q_N	q_{cot}	$-\Delta U'_B$
1	0.083368	2.54401	1367.63	953.22	5.92	2.35	9.57	4756.9
2	0.084071	2.45964	1322.28	905.52	5.89	2.37	8.88	4753.4
3	0.087142	2.48158	1334.07	902.34	5.84	2.46	8.70	4759.2
	$-\Delta U'_B = 4755.6 \pm 3.0$ cal·g^{-1}							

The measured energies of combustion compounds **3a-b** and **3c-d** and **4a-b** proceed according to following of reaction (equations 1, 2 and 3, respectively):

$$C_7H_4N_4O_{4(cr)} + 6O_{2(g)} \rightarrow 7CO_{2(g)} + 2H_2O_{(l)} + 2N_{2(g)} \quad (1),$$

$$C_7H_3N_5O_{6(cr)} + 4.75O_{2(g)} \rightarrow 7CO_{2(g)} + 1.5H_2O_{(l)} + 2.5N_{2(g)} \quad (2),$$

$$C_7H_5N_5O_{2(cr)} + 7.25O_{2(g)} \rightarrow 7CO_{2(g)} + 2.5H_2O_{(l)} + 2.5N_{2(g)} \quad (3)$$

where *cr*, *g* and *l* correspond to crystalline, gaseous and liquid conditions respectively. Enthalpies of formation for compounds of this study are calculated from enthalpies of combustion according to equations 4-6.

$$\Delta H^o_f[C_7H_4N_4O_4]_{(cr)} = 7\Delta H^o_f[CO_2]_{(g)} + 2\Delta H^o_f[H_2O]_{(l)} - \Delta H^o_c \qquad (4),$$

$$\Delta H^o_f[C_7H_3N_5O_6]_{(cr)} = 7\Delta H[CO_2]_{(g)} + 1.5\Delta H^o_f[H_2O]_{(l)} - \Delta H^o_c \qquad (5),$$

$$\Delta H^o_f[C_7H_5N_5O_2]_{(cr)} = 7\Delta H^o_f[CO_2]_{(g)} + 2.5\Delta H^o_f[H_2O]_{(l)} - \Delta H^o_c \qquad (6)$$

where ΔH^o_c – the standard enthalpy of combustion. The enthalpy of formation for the combustion products,[31] i.e., $\Delta H^o_f[CO_2]_{(g)} = -94.051 \pm 0.031$ kcal mol^{-1}, $\Delta H^o_f[H_2O]_{(l)} = -68.315 \pm 0.009$ kcal mol^{-1}. The results are presented in Table 18S.

Table 18S. Thermochemical characteristics of azasydnones **3a–d** and tetrazoles **4a,b**

Compound	$-\Delta U'_B$ cal·g^{-1}	$-\Delta H^o_c$ kcal·mol^{-1}	ΔH^o_f kcal·mol^{-1}
3-(4-Nitrophenyl)-1,2,3,4-oxatriazolium-5-olate, $C_7H_4N_4O_4$ (**3a**)	3884 ± 4	805.6 ± 0.6	10.6 ± 0.6
3-(3-Nitrophenyl)-1,2,3,4-oxatriazolium-5-olate, $C_7H_4N_4O_4$ (**3b**)	3899 ± 2	808.8 ± 0.4	13.8 ± 0.4
3-(3,5-Dinitrophenyl)-1,2,3,4-oxatriazolium-5-olate, $C_7H_3N_5O_6$ (**3c**)	3063 ± 2	771.0 ± 0.5	10.5 ± 0.5
3-(2,4-dinitrophenyl)-1,2,3,4-oxatriazolium-5-olate, $C_7H_3N_5O_6$ (**3d**)	3077 ± 3	775.5 ± 0.8	14.7 ± 0.8
1-(4-nitrophenyl)-1H-1,2,3,4-tetrazole, $C_7H_5N_5O_2$ (**4a**)	4752 ± 4	906.1± 0.7	76.9 ± 0.7
1-(3-nitrophenyl)-1H-1,2,3,4-tetrazole, $C_7H_5N_5O_2$ (**4b**)	4756 ± 3	906.8± 0.6	77.6 ± 0.6

Details of the gas-phase enthalpy of formation evaluation

Several methods are developed for assessment of the gas phase enthalpy of formation (ΔH_f^0), namely Gaussian-*n*, CBS (complete basis set) and W-n.[18a] Here the G3B3 approximation[18b] was used, since G4 underestimates the ΔH_f^0 for nitro compounds by ~ 10 kJ/mol on the average.[19a] The literature ($\Delta H^{298} - \Delta H^0$) values for elements in their standard states[19b] were used.[20] The total energy (E_0) and thermodynamic parameters, including zero point energy (ZPE) and ΔH_f^0, obtained for the structures optimized at the B3LYP/6-31G** level, are given in Table 19S.

Table 19S. Calculated total energy (E_0) and enthalpy of formation ($\Delta H_{f\ calc}^0$) of compounds **3a–d, 4a-b** and **5a–c**

Compond	E_0 (a.u.)	$\Delta H_{f\ calc}^0$ (kcal/mol)	$\Delta H_{f\ calc}^0$ (kJ/mol)
3a	−788.442840	+30.4	+127.19
3b	−788.442168	+30.8	+128.87
3c	−992.855909	+29.00	+121.34
3d	−992.846064	+35.2	+147.28
4a	−600.004290	+86.75	+362.96
4b	−600.003140	+87.47	+365.97
5a	−693.412443	+96.49	+403.71
5b	−693.411215	+97.26	+406.94
5c	−804.420422	+83.40	+348.95

Detonation performance of azasydnones. Table 20S lists the results of thermodynamic calculations using Smirnov[5] and Kamlet-Jacobs[6] empirical method. The necessary for computations values for structurally similar compounds were taken from literature, viz., NB,[32] 1,3-DNB, 1,4- DNB, TNB.[33]

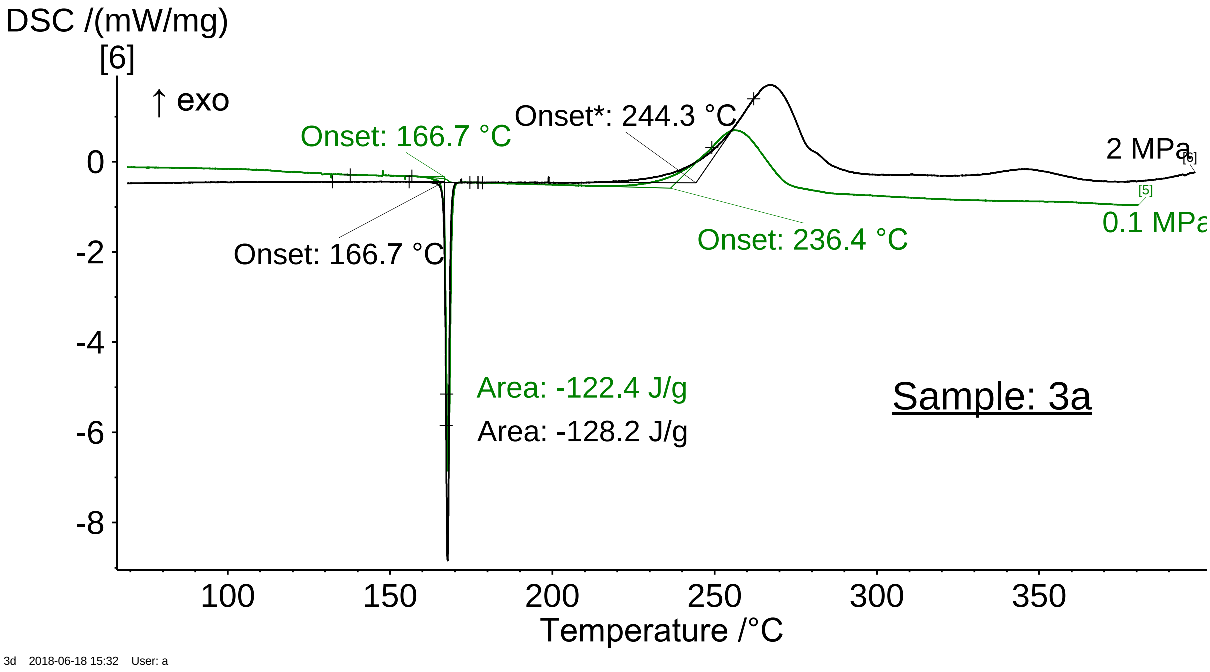
Table 20S. Calculation of detonation performance for azasydnones and related compounds: input data and results.

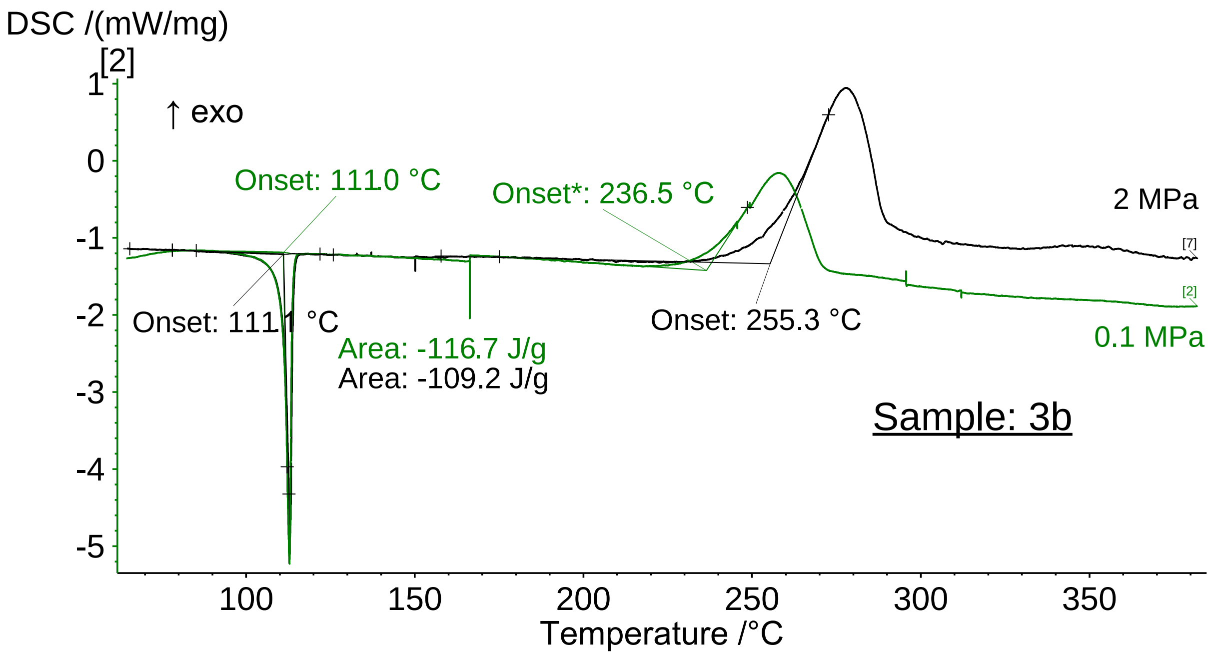
Code	Formula	$\rho_{\mathbf{x\text{-}ray}}^{298K}$, g/cm^3	ΔH_f^0, kJ/mol	D,[c] km/s	P_{CJ},[c] ГПа	D,[d] km/s	P_{CJ},[d] ГПа	Q,[d] cal/g
3a	$C_7H_4N_4O_4$	1.65[a]	57.7	6.44	17.4	6.76	22.1	827
3b	$C_7H_4N_4O_4$	1.66[a]	44.4	6.44	17.5	6.77	22.1	816
3c	$C_7H_3N_5O_6$	1.78[a]	43.9	7.36	23.9	7.50	27.2	997
3d	$C_7H_3N_5O_6$	1.72[a]	61.5	7.21	22.4	7.36	25.7	1000
4a	$C_7H_5N_5O_2$	1.55[a]	321.0	5.89	14.0	6.49	20.5	821
4b	$C_7H_5N_5O_2$	1.54[a]	325.1	5.87	13.9	6.47	20.3	825
5a	$C_6H_4N_4O_2$	1.52[a]	298.5[b]	5.97	14.2	6.56	20.5	900
5b	$C_6H_4N_4O_2$	1.53[a]	304.9[b]	6.01	14.5	6.61	20.9	909
5c	$C_6H_3N_5O_4$	1.69[a]	282[b]	7.13	21.7	7.42	26.6	1046
NB	$C_6H_5NO_2$	1.20	12.5	4.45	6.7	4.88	10.4	641
1,3-DNB	$C_6H_4N_2O_4$	1.58	–27.2	6.40	16.7	6.52	20.3	900
1,4-DNB	$C_6H_4N_2O_4$	1.63	–38.5	6.51	17.7	6.63	21.4	897
1,3,5-TNB	$C_6H_3N_3O_6$	1.69	–37.2	7.32	22.9	7.28	24.9	1091
TNT	$C_7H_5N_3O_6$	1.65	–62.8	7.00	20.6	7.02	23.3	1011

[a] Calculated by equipment:[21a,21e,34] $\rho_{\mathbf{x\text{-}ray}}^{298K} = \rho_{\mathbf{x\text{-}ray}}^{100K} - 0.034 \times \rho_{\mathbf{x\text{-}ray}}^{100K}$. [b] Calculated by G3B3. [c] Calculated by Kamlet's method. [d] Calculated by Smirnov's method.

Thermal stability for compounds of this study. For 1-(4-nitrophenyl)-1*H*-1,2,3,4-tetrazole (**4a**), literature melting points are in range of 191[35]–200 °C.[9] However, our results clearly show that this temperature corresponds to thermal decomposition rather than melting (Figure 5b). Contrary, 1-(3-nitrophenyl)-1*H*-1,2,3,4-tetrazole (**4b**) first melts (according to literature m. p. is 108–109 °C,[14] present study value 108 °C) and decomposes at 171°C. Note, that although the heat effect for **4a** and **4b** is essentially the similar (1360 and 1240 J g^{-1}, respectively), the rate of heat release is notably different.

p-Nitroazidobenzene (**5a**) melts at 70 °C (literature: 70,[11] 69.5–71[36] °C) with subsequent decomposition masked by significant evaporation. Under elevated pressure the decomposition onset of 164 °C was clearly observed. *m*-Nitroazidobenzene (**5b**) has a melting point of 52 °C (literature: m.p. 44–47,[12] 52,[37] 58–59[38] °C) with further decomposition at 165 °C registered under normal pressure. 3,5-Dinitroazidobenzene (**5c**) melts at 83 °C close to the literature values 80,[39] 85–86[40] °C and then decomposes (extrapolated onset is 175 °C) with 50% of mass loss.





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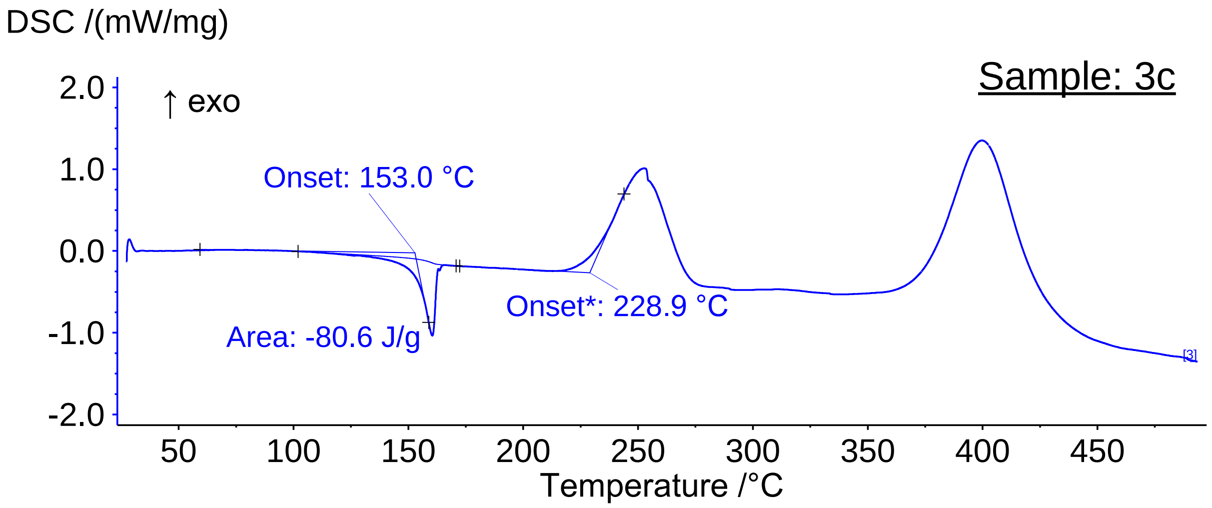

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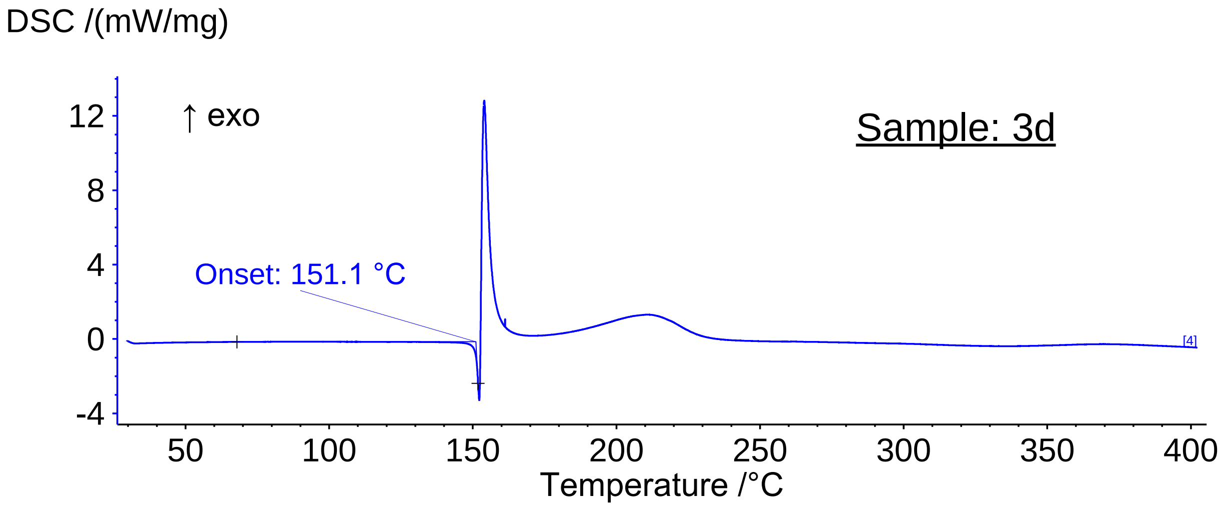

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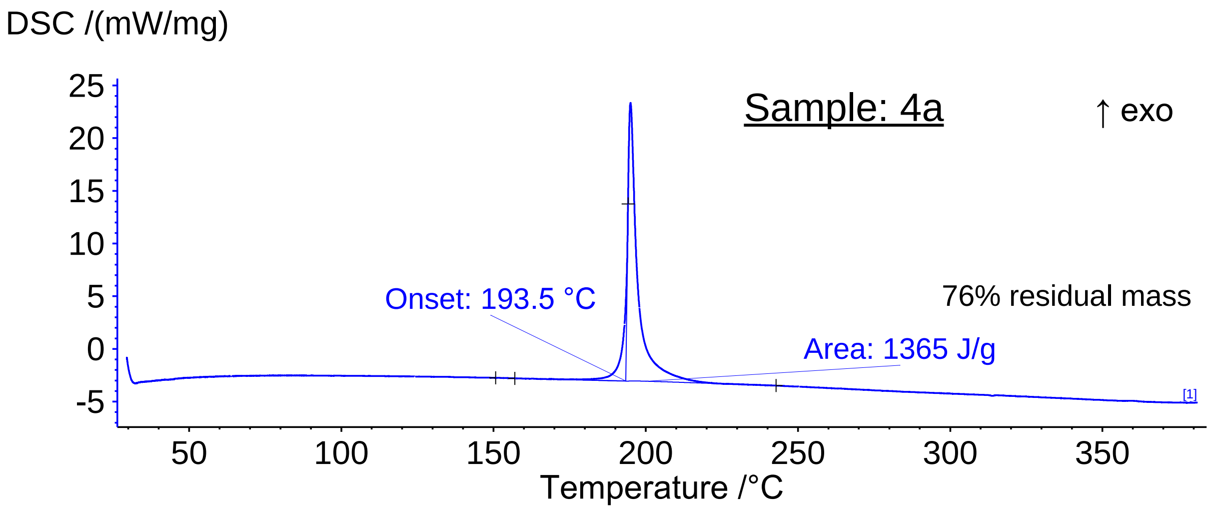

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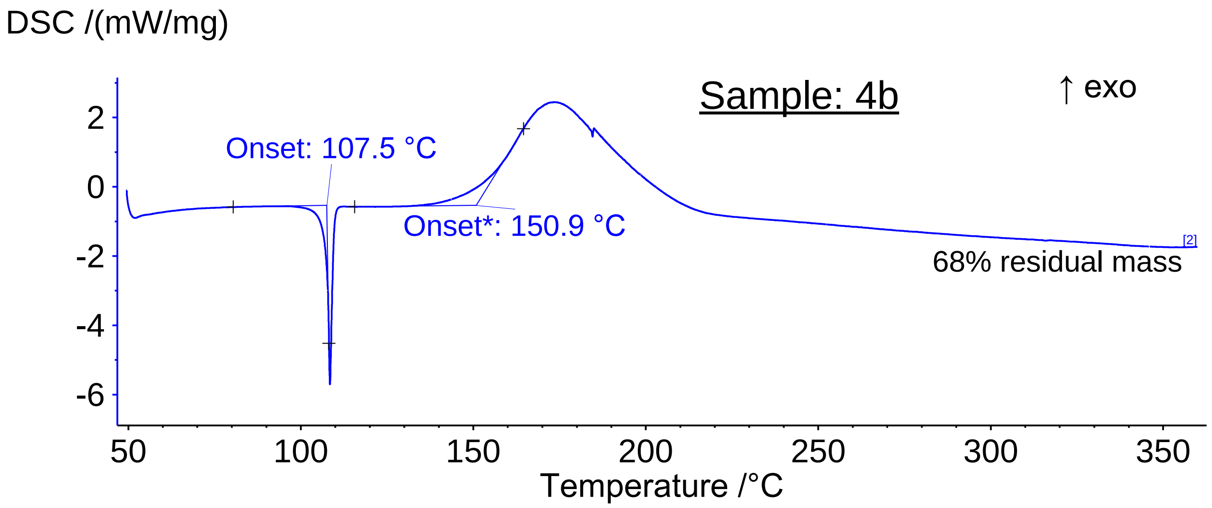

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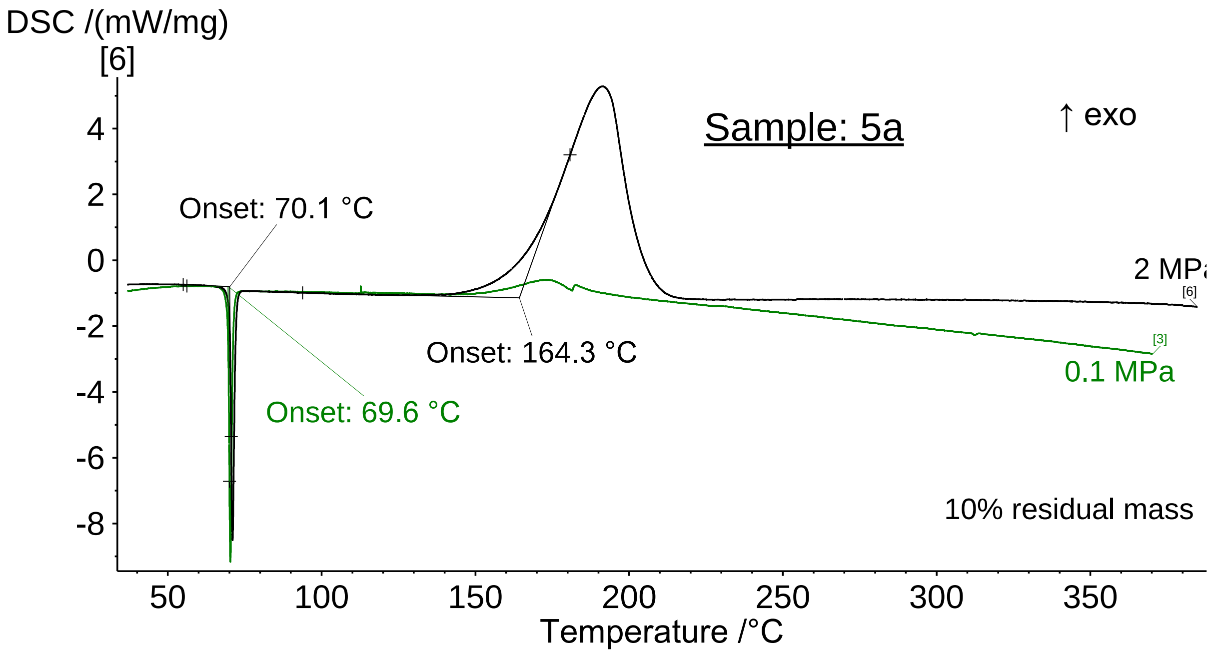

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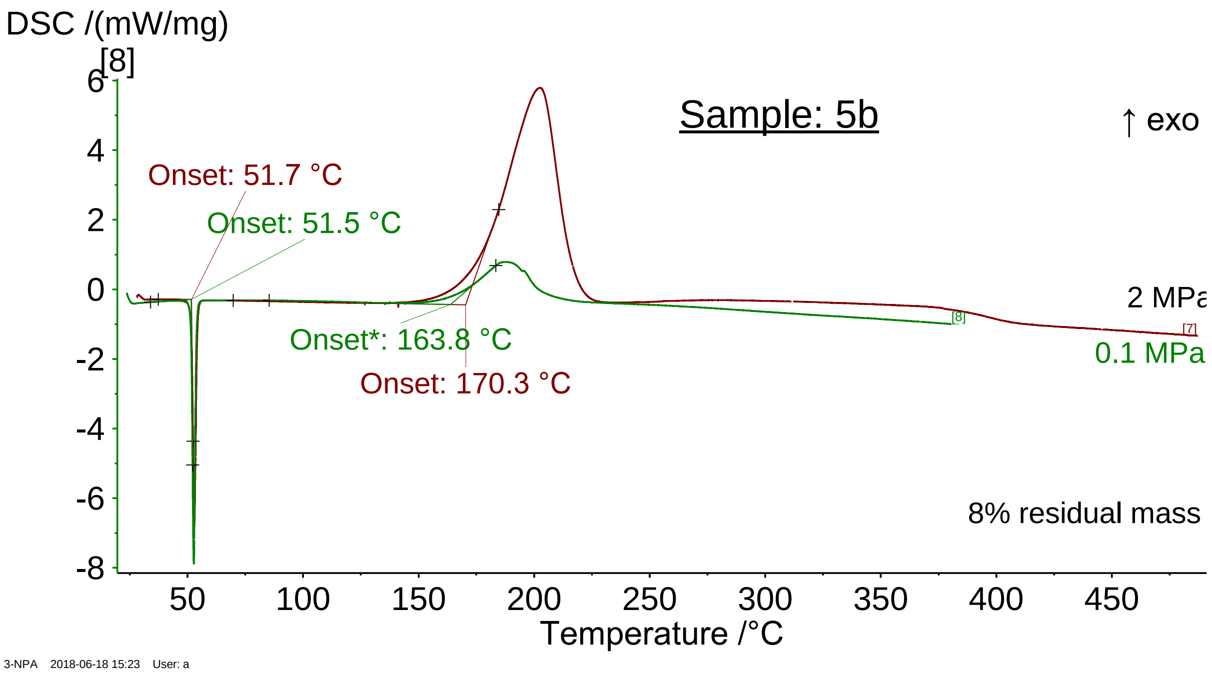

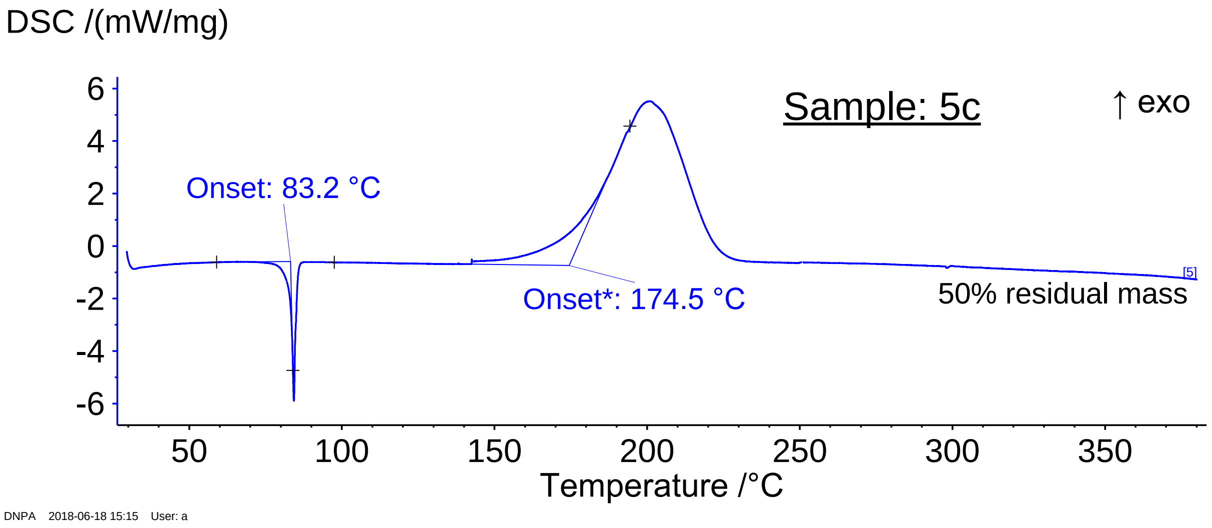

REFERENCES

1. V. I. Pepekin, Y. N. Matyushin and T. V. Gubina, *Russ. J. Phys. Chem. B*, 2011, **5**, 97–100.
2. Y. O. Inozemtsev, A. B. Vorob'ev, A. V. Inozemtcev and Yu. N. Matyushin, Calorimetry of energetic materials. *Combustion and Explosion* [*Goren. Vzryv*], 2014, **7**, 260–270.
3. STANAG 4489, *Explosives, Impact Sensitivity Tests*, NATO, Brussels, 1999.
4. STANAG 4487, *Explosives, Friction Sensitivity Tests*, NATO, Brussels, 2002.
5. C. L. Mader, *Numerical modeling of explosives and propellants*, CRC Press, Boca Raton, 3rd ed., 2008.
6. M. J. Kamlet and S. J. Jacobs, *J. Chem. Phys.*, 1968, **48**, 23–35.
7. N. V. Muravyev, K. A. Monogarov, A. A. Bragin, I. V. Fomenkov and A. N. Pivkina, *Thermochim. Acta*, 2016, **631**, 1–7.
8. A. Kh. Shakhnes, S. S. Vorob'ev and S. A. Shevelev, *Russ. Chem. Bull., Int. Ed.*, **2006**, *55*, № 5, 938-939.

9. M. Esmaeilpour, J. Javidi and S. Zahmatkesh, *Appl. Organomet. Chem.*, 2016, **30**, 897–904.
10. K. Nishiyama, M. Oba and A. Watanabe, *Tetrahedron*, 1987, **43**, 693–700.
11. T. Y. Liang and G. B. Schuster, *J. Am. Chem. Soc.*, 1987, **109**, 7803–7810.
12. J. T. B. Kueh, K. W. Choi and M. A. Brimble, *Org. Biomol. Chem.*, 2012, **10**, 5993.
13. A. I. Dynchenko, L. S. Pupko and P. S. Pelkis, *Zh. Org. Khim.*, 1974, **10**, 2229.
14. S. A. Shevelev, I. L. Dalinger, V. I. Gulevskaya, T. I. Cherkasova, V. M. Vinogradov, B. I. Ugrak and A. M. Starosotnikov, *Chem. Heterocycl. Comp*., **1999**, 35, 363-373.
15. M. N. Martynova, M. S. Pevzner, N. A. Smorygo and N. M. Serebryakova, *Chem. Heterocycl. Compd.*, 1981, **17**, 1238–1240.
16. *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA, **2009**.
17. G. M. Sheldrick, *Acta Crystallogr*. **2008**, *A64*, 112-122.
18. . (a) Quantum-chemistry prediction of thermochemical data, J. Cioslowsky (Ed.), New-York: Kluwer, 2001; (b) L. A. Curtiss, K. Raghavachari, P. C. Redfern, V. Rassolov and J. A. Pople, *J. Chem. Phys.* 1998, **109**, 7764-7776.
19. (a) O. V. Dorofeeva, I. N. Kolesnikova, I. I. Marochkin, O. N. Ryzhova, *Struct. Chem.*, 2011, **22**, 1303–1314. (b) L. A. Curtiss, K. Raghavachari, P. C. Redfern and J. A. Pople, *J. Chem. Phys.* 1997, **106**, 1063-1079
20. http://www.chem.msu.su/rus/handbook/ivtan/welcome.html
21. (a) I. L. Dalinger, A. Kh. Shakhnes, K. A. Monogarov, K. Yu. Suponitsky, A. B. Sheremetev, *Mendeleev Commun.*, 2015, **25**, 429; (b) A. B. Sheremetev, B. V. Lyalin, A. M. Kozeev, N. V. Palysaeva, M. I. Struchkova, K. Yu. Suponitsky, *RSC Adv.*, 2015, **5**, 37617; (c) A. O. Dmitrienko, V. A. Karnoukhova, A. A. Potemkin, M. I. Struchkova, I. A. Kryazhevskikh, K. Yu. Suponitsky, *Chem. Heterocycl. Compounds*, 2017, **53**, 532; (d) I. L. Dalinger, I. A. Vatsadze, T. K. Shkineva, A. V. Kormanov, M. I. Struchkova, K. Yu. Suponitsky, A. A. Bragin, K. A. Monogarov, V. P. Sinditskii, A. B. Sheremetev, *Chem. Asian J.*, 2015, **10**, 1987-1996.
22. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A.; Kudin, K. N., Jr.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03, Revision E.01*, Gaussian, Inc.: Wallingford, 2004.
23. Bader, R. F. W. *Atoms in Molecules. A Quantum Theory*, Clarendon Press, Oxford, 1990.
24. Keith, T. A. **2014**, *AIMAll, Version 14.11.23*. TK Gristmill Software, Overland Park KS, USA (http://aim.tkgristmill.com)
25. A. B. Sheremetev, N. S. Aleksandrova, N. V. Palysaeva, M. I. Struchkova, V. A. Tartakovsky, K. Yu. Suponitsky, *Chem. Eur. J.*, 2013, **19**, 12446.
26. R.S. Rowland, R. Taylor, *J. Phys. Chem.* **1996**, *100*, 7384-7391.
27. (a) I. L. Dalinger, A. V. Kormanov, K. Yu. Suponitsky, N. V. Muravyev, A. B. Sheremetev, *Chem. Asian J.*, **2018**, *13*, 1165-1172. (b) A. E. Frumkin, N. V. Yudin, K. Yu. Suponitsky, A. B. Sheremetev, *Mendeleev Commun.*, 2018, **28**, 135-137; (c) I. L. Dalinger, K. Yu. Suponitsky, T. K. Shkineva, D. B. Lempert, A. B. Sheremetev, *J. Mater. Chem. A*, 2018, **6**, ASAP Article, DOI: 10.1039/C8TA05179H.

28. N. Yilmaz, S. Oz, A. Atakol, I. Svoboda, B. Aydiner, M. A. Akay, O. Atakol, *J. Thermal Analysis and Calorimetry*, **2015**, *119*, 2321.
29. A. Mugnoli, C. Mariani, M. Simonetta, *Acta Crystallogr*., **1965**, *19*, 367.
30. T. S. Kon'kova, Yu. N. Matyushin, E. A. Miroshnichenko, A. B. Vorob'ev. *Russ. Chem. Bull.* 2009, **58**, 1-8.
31. J. D. Cox, D. D. Wagman and V. A. Medvedev, Eds., *CODATA key values for thermodynamics*, Hemisphere Pub. Corp., New York, 1989.
32. S. P. Verevkin, V. N. Emel'yanenko, V. Diky and O. V. Dorofeeva, *J. Chem. Thermodyn.*, 2014, **73**, 163–170.
33. M. A. Suntsova and O. V. Dorofeeva, *J. Chem. Eng. Data*, 2016, **61**, 313–329.
34. (a) Vatsadze, I. A.; Serushkina, O. V.; Dutov, M. D.; Shkineva, T. K.; Suponitsky, K. Yu.; Ugrak, B. I.; Dalinger, I. L. *Chem. Heterocycl. Compd.* **2015**, *51*, 695-703; (b) Sheremetev, A. B.; Aleksandrova, N. S.; Suponitsky, K. Y.; Antipin, M. Y.; Tartakovsky, V. A. *Mendeleev Commun.* **2010**, *20*, 249.
35. M. A. Karimi Zarchi and F. Nazem, *J. Iran. Chem. Soc.*, 2014, **11**, 91–99.
36. J. E. Leffler and R. D. Temple, *J. Am. Chem. Soc.*, 1967, **89**, 5235–5246.
37. K. Kutonova, M. Trusova, P. Postnikov, V. Filimonov and J. Parello, *Synthesis*, 2013, **45**, 2706–2710.
38. A. R. Hajipour and F. Mohammadsaleh, *Tetrahedron Lett.*, 2014, **55**, 6799–6802.
39. T. Severin, R. Schmitz, J. Loske and J. Hufnagel, *Chem. Ber.*, 1969, **102**, 4152–4156.
40. P. A. Grieco and J. P. Mason, *J. Chem. Eng. Data*, 1967, **12**, 623–624.