Highly Energetic Compounds

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Combination of 1,2,4-Oxadiazole and 1,2,5-Oxadiazole Moieties for the Generation of High-Performance Energetic Materials**

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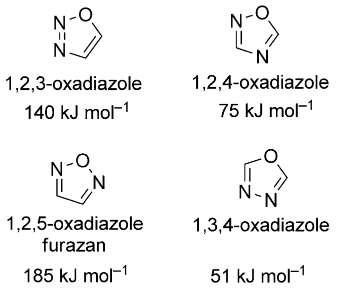
Abstract: *Salts generated from linked 1,2,4-oxadiazole/1,2,5-oxadiazole precursors exhibit good to excellent thermal stability, density, and, in some cases, energetic performance. The design of these compounds was based on the assumption that by the combination of varying oxadiazole rings, it would be possible to profit from the positive aspects of each of the components. All of the new compounds were fully characterized by elemental analysis, IR spectroscopy, ^{1}H, ^{13}C, and (in some cases) ^{15}N NMR spectroscopy, and thermal analysis (DSC). The structures of* ***2–3*** *and* ***5-1****$\cdot 5\,H_2O$ were confirmed by single-crystal X-ray analysis. Theoretical performance calculations were carried out by using Gaussian 03 (Revision D.01). Compound* ***2-3****, with its good density (1.85 $g\,cm^{-3}$), acceptable sensitivity (14 J, 160 N), and superior detonation pressure (37.4 GPa) and velocity (9046 $m\,s^{-1}$), exhibits performance properties superior to those of 1,3,5-trinitroperhydro-1,3,5-triazine (RDX).*

The synthesis and design of new high-energy-density materials (HEDMs) have attracted interest worldwide over the last decade.[1] Heterocyclic compounds play an important role owing to their higher heats of formation, density, thermal stability, oxygen balance, and environmental greenness.[2]

In attempts to meet the continuing need for improved energetic materials, oxadiazoles have attracted considerable attention.[3] There are four oxadiazole isomers: 1,2,4-oxadiazole, 1,2,5-oxadiazole, 1,3,4-oxadiazole, and 1,2,3-oxadiazole, which is unstable and reverts to the diazoketone tautomer.[4] 1,2,5-Oxadiazole (furazan) is highly energetic and has potential use in both propellant and explosive formulations.[3a–e] A large number of nitro-, amino-, and nitramine-functionalized monofurazan compounds,[5] macrocyclic furazans,[6] linked furazans,[7] and ring-fused furazans bridged by azo, oxy, and azoxy groups have been reported.[8] However, 1,2,4-oxadiazoles[3f–l] and 1,3,4-oxadiazoles[3n–q] have been studied only rarely as energetic materials.

The heats of formation of the parent oxadiazoles are shown in Scheme 1. 1,2,5-Oxadiazole (furazan) has the highest positive heat of formation, which explains in part why this isomer is often the best choice of the oxadizole family in the design of energetic materials. However, the furazan ring is, in fact, very sensitive. On the basis of the observation that the presence of fewer readily cleaved N−O bonds in the ring results in a highly thermally stable compound,[10] 1,2,4-oxadiazole and 1,3,4-oxadiazole should be more stable than furazan. At the same time, owing to the difference in their heats of formation, 1,2,4-oxadiazole and 1,3,4-oxadiazole have a slightly lower energy than furazan.



Scheme 1. Four isomers of oxadiazole with calculated gas-phase heats of formation (G2 atomization method).[9]

Efforts to develop new energetic compounds frequently encounter the difficulty of attempting to reconcile two seemingly contradictory objectives: to maximize detonation performance while minimizing sensitivity,[11] since factors that promote one of these objectives often conflict with the other. The goal is often to discover an optimum balance between them. An effective approach is the combination of a few of the same or different heterocyclic subunits in a molecule. For example, 5-nitro-2-hydroxytetrazole (Scheme 2) is an extremely sensitive compound;[12] however, following the introduction of a relatively insensitive triazole ring to form 5-(3-nitro-1,2,4-1*H*-triazol-5-yl)tetrazol-1-ol, sensitivity towards external stimuli is considerably reduced, but good performance is maintained.[13] Therefore, it appeared that the combination of furazan with 1,2,4-oxadiazole could be favorable for obtaining a high level of detonation performance while fulfilling the requirement of insensitivity.

Herein we report the synthesis and characterization of a series of highly energetic nitrogen- and oxygen-rich salts based on 3-nitroamino-4-(5-nitroamino-1,2,4-oxadiazol-3-yl)furazan, which comprises furazan and the 1,2,4-oxadiazole

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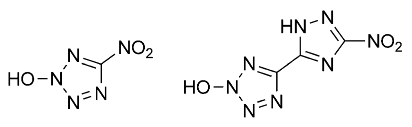
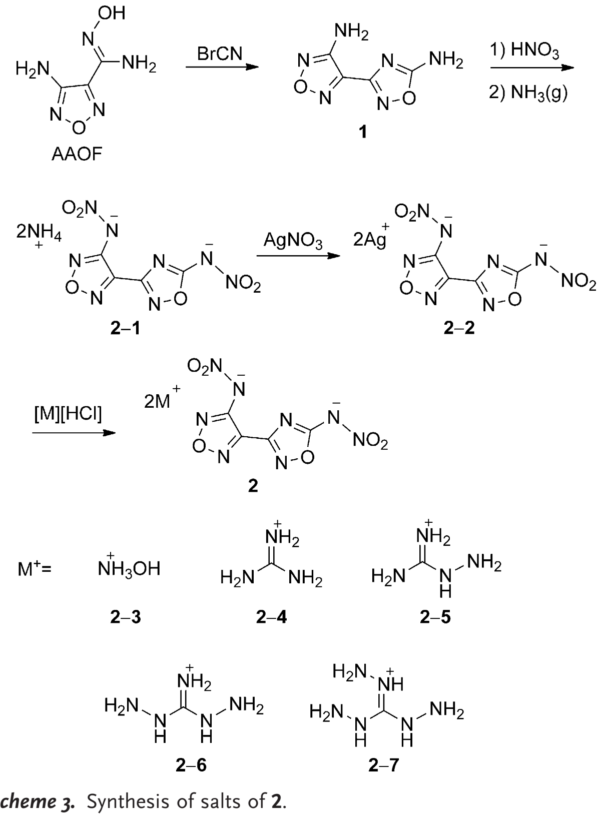


Scheme 2. 5-Nitro-2-hydroxytetrazole and 5-(3-nitro-1,2,4-1*H*-triazol-5-yl)tetrazol-1-ol.

ring. These compounds were characterized by infrared and multinuclear NMR spectroscopy, elemental analysis, and differential scanning calorimetry (DSC). The structures of **2–3** and **5–1**$\cdot 5\,H_2O$ were confirmed by X-ray crystallography. Calculated detonation properties and experimental sensitivity values confirmed the initial hypothesis that the union of different oxadiazole rings is indeed an effective method to combine the benefits of each of the fragments.[13]

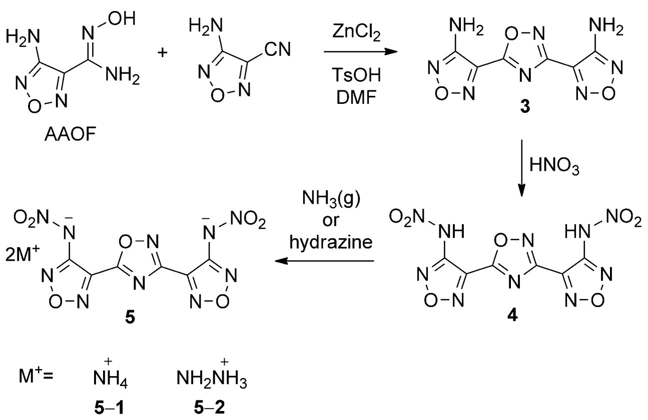
The synthetic pathway to the new energetic salts is shown in Scheme 3. 3-Amino-4-amidoximinofurazan (AAOF) was readily synthesized through the reaction of malononitrile, sodium nitrite, and hydroxylamine,[14a] and was then treated with cyanogen bromide in aqueous ethanol to give the diamino compound **1**.[14b] Compound **1** was nitrated with fuming nitric acid at −5 °C to form the dinitramino compound, which was extracted from the reaction mixture with diethyl ether.



Scheme 3. Synthesis of salts of **2**.

The solution in diethyl ether was then treated with an excess of gaseous ammonia to precipitate the yellow ammonium salt **2–1.** The corresponding silver salt, **2–2**, was obtained in high yield (97 %) by treating **2–1** with $AgNO_3$ (2 equiv) in H_2O. Salts **2–3**, **2–4**, **2–5**, **2–6**, and **2–7** (Scheme 3) were synthesized by metathesis reactions of **2–2** with hydroxylammonium, guanidinium, aminoguanidinium, diaminoguanidinium, and triaminoguanidinium chloride in aqueous solution.

In this study, compound **3** was synthesized on the basis of a patent describing the use of $ZnCl_2$ as the Lewis acid to promote the preparative reaction (Scheme 4).[15] Compound **4** was obtained by the treatment of **3** with excess fuming nitric acid, and was found to be stable as a solution in diethyl ether. The ethereal solution was treated directly with gaseous ammonia or hydrazine hydrate to form salt **5–1** or **5–2**.



Scheme 4. Synthesis of salts of **4**. DMF = *N*,*N*-dimethylformamide, Ts = *p*-toluenesulfonyl.

All new salts were characterized by IR, ^1H NMR, and ^{13}C NMR spectroscopy as well as elemental analysis. ^{15}N NMR spectra were recorded for **2–1**, **2–3**, and **5–1** in [D$_6$]DMSO (Figure 1). The ^{15}N NMR spectra of **2–1** and **2–3** had 9 signals each, and that of **5–1** had 11 signals. The N6 signals of the 1,2,4-oxadiazole, at $\delta = -173.9$ (**2–1**), −173.5 (**2–3**), and −136.2 ppm (**5–1**), were downfield from the other signals for ring nitrogen atoms because the N6 atom is adjacent to two carbon atoms. On the basis of normal chemical-shift values for ammonium and hydroxylammonium moieties, the resonance peaks at highest field were assigned to the NH_4^+ and NH_3^+OH groups.[16]

Crystals of **2–3** and **5–1**$\cdot 5\,H_2O$ suitable for single-crystal X-ray diffraction were obtained by dissolving the compounds in a minimum amount of water held at room temperature, followed by filtration of the crystals after the volume of water had been reduced (Figures 2 and 3; see the Supporting Information for the crystallographic data and refinement details). The N−O bond lengths are longer in the 1,2,4-oxadiazole [1.4083(15) (N4−O3) in **2–3** and 1.428(6) (N4−O1) in **5–1**] than in the 1,2,5-oxadiazole [1.3952(16)(N6−O4) and 1.3653(15) (N5−O4) in **2–3** and 1.397(2) (N1−O2) and 1.365(19) (N2−O2) in **5–1**]. Interestingly, the 1,2,4-oxadiazole and 1,2,5-oxadiazole rings in **2–3** (torsion angle N3-C2-C3-N5: 1.11°) are coplanar. However, in **5–1**, the 1,2,4-oxadiazole and 1,2,5-oxadiazole rings are not coplanar (torsion angle C1-C2-C3-O1: −10.4°).

The phase-transition temperature and thermal stability of the salts were determined by DSC measurements with

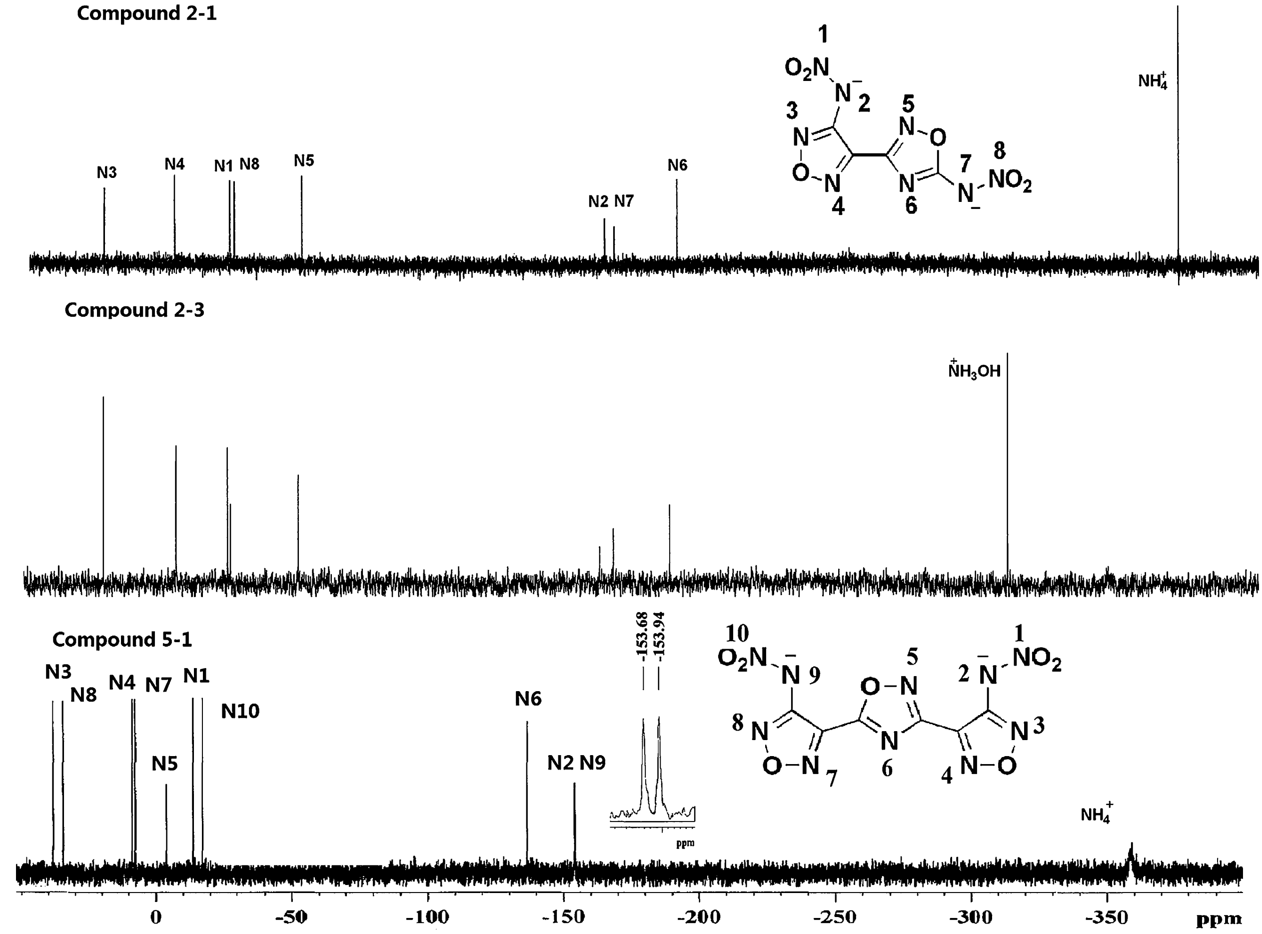


Figure 1. ^{15}N NMR spectra of compounds **2–1**, **2–3**, and **5–1** in [D$_6$]DMSO with respect to CH_3NO_2 as an external standard.

Table 1: Physical properties of the salts and comparison with TNT and RDX.

Compd	T_m[a] [°C]	T_d[b] [°C]	Ω[c] [%]	d[d] [g cm^{-3}]	$\Delta_f H_{lat}$[e] [kJ mol^{-1}]	$\Delta_f H$[f] [kJ mol^{-1}/(kJ g^{-1})]	D[g] [m s^{-1}]	P[h] [GPa]	IS[i] [J]	FS[j] [N]
2–1	–	218	−10.9	1.70	1335.1	154.9/(0.53)	8102	27.6	14	120
2–3	–	193	0	1.85	1325.3	250.8/(0.77)	9046	37.4	16	160
2–4	–	269	−25.5	1.71	1215.9	172.9/(0.44)	8147	25.0	26	240
2–5	179	208	−27.5	1.71	1180.9	425.1/(1.05)	8426	26.6	21	160
2–6	167	172	−29.3	1.74	1156.9	618.3/(1.42)	8764	29.3	15	120
2–7	142	210	−30.9	1.67	1110.0	894.3/(1.92)	8653	28.0	14	160
5–1	–	231	−22.2	1.71	1236.3	425.1/(1.18)	8271	27.9	16	120
5–2	–	234	−45.1	1.71	1196.5	752.1(1.93)	8603	30.1	19	240
TNT	–	295	−24.7	1.65	–	−67.0(−0.30)	6881	19.5	15	353
RDX	–	204	0	1.80	–	80.0/(0.36)	8762	35.0	7.4	120

[a] All new compounds were anhydrous, except **2–4**, which was a monohydrate. [b] Thermal-decomposition temperature (onset) under nitrogen (DSC, 5 °C min^{-1}). [c] Oxygen balance for $C_aH_bO_cN_d$: $1600(c-a-b/2)/MW$; MW = molecular weight. [d] Density was measured with a gas pycnometer (25 °C). [e] Calculated lattice energy of the salt. [f] Calculated heat of formation. [g] Detonation velocity. [h] Detonation pressure. [i] Impact sensitivity. [j] Friction sensitivity.

scanning at 5 °C min^{-1} (Table 1). All salts showed good thermal stability with decomposition temperatures ranging from 172 (**2–6**) to 269 °C (**2–4**). Salts **2–5**, **2–6**, and **2–7** melted between 142 and 179 °C and then decomposed. The decomposition temperature of all compounds, except **2–3** and **2–6**, was above 200 °C, which indicates their thermal stability.

Density is one of the most important factors in determining the performance of energetic compounds. The experimentally determined densities of all salts ranged from 1.67 to 1.85 g cm^{-3} and were thus comparable with those of currently used explosives (1.6–1.8 g cm^{-3}). Finally, we used the Gaussian 03 (Revision D.01)[18] suite of programs to determine the

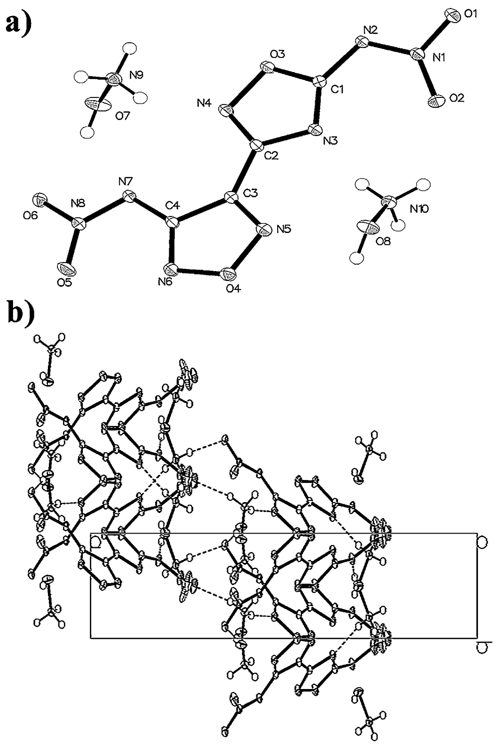


Figure 2. a) Thermal-ellipsoid plot (50%) and atom-labeling scheme for hydroxylammonium 3-nitroamino-4-(5-nitroamino-1,2,4-oxadiazol-3-yl)furazan (**2–3**). b) Ball-and-stick packing diagram of **2–3** viewed down the *c* axis. Dashed lines indicate strong hydrogen bonding.

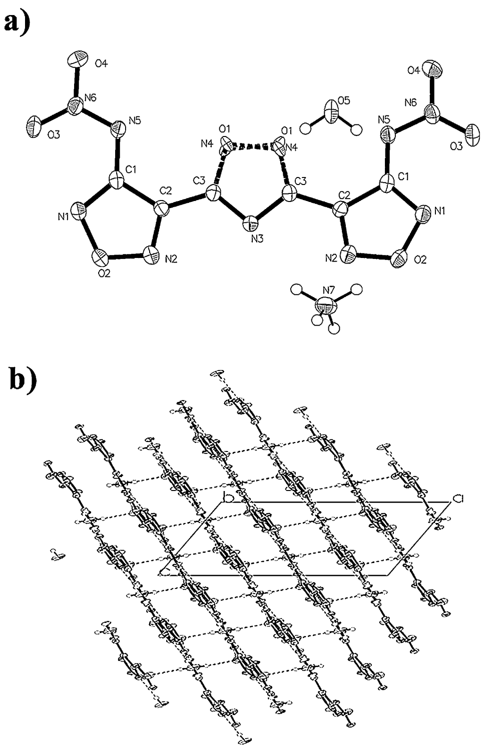


Figure 3. a) Thermal-ellipsoid plot (50%) and atom-labeling scheme for diammonium 3,5-bis(4-nitroamino-l,2,5-oxadiazol-3-yl)-l,2,4-oxadiazole, **5–1**$\cdot$5 H_2O. Four water molecules and one ammonium ion per unit cell are highly disordered and were treated by SQUEEZE.[17] b) Ball-and-stick packing diagram of **5–1**$\cdot$5 H_2O viewed down the *b* axis. Dashed lines indicate strong hydrogen bonding.

heats of formation of the cations and anions (see the Supporting Information). The standard enthalpies of formation ($\Delta_f H$) of all new salts were calculated by the use of Born–Haber energy cycles (see the Supporting Information).

On the basis of the experimental values for the densities of all salts, we calculated their detonation pressure (P) and velocity (vD) by using EXPLO5 v6.01. The calculated detonation velocities lay between 8102 and 9046 $\mathrm{m\,s^{-1}}$, and the calculated detonation pressures were between 25.0 and 37.4 GPa (Table 1). Several compounds, for example, **2–3**, **2–6**, **2–7**, and **5–2**, exhibited good detonation properties. In particular, the hydroxylammonium salt **2–3** displayed favorable performance values ($P = 37.4$ GPa, $vD = 9046\ \mathrm{m\,s^{-1}}$), which exceeded those of RDX.

Oxygen balance (OB) is the index of the deficiency or excess of oxygen in a compound required to convert carbon into carbon monoxide and all hydrogen into water. All compounds except **2–3** possessed a negative OB value in the range from -10.9 to -45.1%; these values are more negative than that of RDX. Notably, the OB value of compound **2–3** was zero.

For safety testing, the sensitivity of each of the salts towards impact and friction was measured. We determined the impact sensitivity (IS) by using standard BAM Fallhammer techniques.[19] All new salts are less impact sensitive (at 14–26 J) than RDX. The friction sensitivity (BAM friction tester) was greater than 120 N for **2–3**, **2–4**, **2–5**, **2–7**, and **5–1**, which makes these compounds less sensitive than RDX as well. The most promising compound for industrial scale-up and practical use is the hydroxylammonium salt **2–3**, which has a high density (1.85 $\mathrm{g\,cm^{-3}}$), acceptable sensitivity (16 J, 240 N), perfect oxygen balance (0), and good detonation pressure (37.4 GPa) and velocity (9046 $\mathrm{m\,s^{-1}}$). The combination of these high-performance properties suggests that this compound could be used a new secondary explosive or propellant ingredient.

In summary, salts based on 1,2,4-oxadiazole coupled with one or more 1,2,5-oxadiazole moieties were synthesized and fully characterized. All new salts exhibited reasonable physical properties, such as a relatively high density (1.67–1.85 $\mathrm{g\,cm^{-3}}$) and good thermal stability ($T_d = 172$–269 °C). Their detonation properties were evaluated by a combination of theoretical and experimental calculations. Their calculated detonation velocities (8102–9046 $\mathrm{m\,s^{-1}}$) and detonation pressures (24.2–37.4 GPa) were comparable to those of the energetic compounds TNT and RDX. The hydroxylammonium salt **2–3** had a high density (1.85 $\mathrm{g\,cm^{-3}}$) as well as a good detonation pressure (37.4 GPa) and velocity (9046 $\mathrm{m\,s^{-1}}$), which were superior to those of RDX and TNT. The simple preparation of this compound makes it attractive as a new HEDM.

Keywords: detonation properties · energetic materials · heterocycles · oxadiazoles · X-ray diffraction

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[19] a) http://www.bam.de. b) A 20 mg sample was subjected to a drop-hammer test with a 5 or 10 kg dropping weight. The impact sensitivity was characterized according to the UN recommendations (insensitive > 40 J; less sensitive ≥ 35 J; sensitive ≥ 4 J; very sensitive ≤ 3 J).

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