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1-Amino-1-hydroxyamino-2,2-dinitroethene: novel insights in chemistry of FOX-7

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CAUTION! All compounds are potentially explosive and should be handled with appropriate precautions.

***N*'-Hydroxy-2,2-dinitroacetimidamide potassium salt** (**4**). To a solution of compound **1** (3 g, 20 mmol) and KOH (1.3 g, 23 mmol) in water (15 ml), a solution of 50% aqueous hydroxylamine (7.3 g, 110 mmol) in methanol (30 ml) was added, and the mixture was refluxed for 3 h. After cooling to room temperature, the yellow solid was collected by filtration, washed with methanol (30 ml) and dried in air to give K-salt **4** (2.7 g, 67%). No further crystallization was needed, mp 109-110°C (decomp.). IR (KBr, ν/cm^{-1}): 3438, 3396, 3342, 3313, 2735, 1657, 1597, 1504, 1470, 1388, 1199, 1115, 934. ^{1}H NMR (300 MHz, DMSO-d$_6$) δ: 5.36 (s, 2H, NH$_2$), 9.13 (b.s., 1H, OH). ^{13}C NMR (DMSO-d$_6$) δ: 129.8 ($\underline{C}$-NO$_2$), 146.7 ($\underline{C}$=NOH). Found (%): C, 11.79; H, 1.46; N, 27.56. Calc. For $C_2H_3K_1N_4O_5$ (202.17) (%):C, 11.88; H, 1.50; N, 27.71.

1-Amino-1-hydroxyamino-2,2-dinitroethene (**2**). To a slurry of salt **4** (0.5 g, 2.5 mmol) in absolute diethyl ether (5 ml) was added 4*N* HCl in THF (0.62 ml). After stirring for 30 min, the precipitated KCl was filtered off. The solvent from the filtrate was removed by rotary evaporation, and the yellow solid formed was recrystallized from ether as fine yellow crystals (0.32 g, 78%). IR (KBr, ν/cm^{-1}): 3414, 1618, 1509, 1500, 1384, 1258, 1154, 1044. ^{1}H NMR (300 MHz, DMSO-d$_6$) δ: 8.87 (s, 1H, NH$_2$), 9.14 (s, 1H, NH$_2$), 11.1 (s., 1H, N$\underline{H}$OH), 12.62 (s., 1H, OH). ^{13}C NMR (DMSO-d$_6$) δ: 123.9 ($\underline{C}$-NO$_2$), 153.0 ($\underline{C}$-HNOH). ^{14}N NMR (DMSO-d$_6$) δ: -21.7 (NO$_2$). Found (%): C, 14.60; H, 2.49; N, 34.07. Calc. For $C_2H_4N_4O_5$ (164.08) (%):C, 14.64; H, 2.46; N, 34.15.

***N*'-Hydroxy-2,2-dinitroacetimidamide guanidinium salt**. Guanidine hydrochloride (0.26 g, 2.75 mmol) was added to a solution of sodium ethoxide (0.19 g, 2.75 mmol) in absolute ethanol (5 ml). After stirring for 1 h, the precipitated NaCl was filtered off. The filtrate was added to a solution of compound **2** (0.41 g, 2.5 mmol) in absolute ethanol (3 ml). After cooling to 5°C, the precipitate thus formed was collected by filtration, washed with ethanol and dried *in vacuo* overnight at room temperature to afford brown crystals (0.24 g, 43%), mp 90-91°C (dec.). IR (KBr, ν/cm^{-1}): 3440, 3206, 1662, 1570, 1499, 1419, 1357, 1246, 1132, 928. ^{1}H NMR (300 MHz, DMSO-d$_6$) δ: 5.45 (bs.), 6.80 (bs.). ^{13}C NMR (DMSO-d$_6$) δ: 129.8, 146.7, 158.1. Found (%): C, 16.23; H, 4.11; N, 43.88. Calc. For $C_3H_9N_7O_5$ (223.15) (%):C, 16.15; H, 4.07; N, 43.94.

Discussion

First of all we would like to comment on the results for NH_2-FOX. As stated in the main text, the structure available from Cambridge Structural Database (CSD) from ref. [S1] is incorrectly refined. Such planar conformation leads to unrealistic extremely short H…H contact of 1.72Å. Probably, the orientation of the nitro groups of NH_2-FOX also needs to be clarified. In Figure S1 we have shown two possible molecular conformations assuming no disorder and planar symmetry according to X-ray data. It appears that the energy of conformer with planar orientation of the amino groups in the NH-NH_2 fragment is 18.2 kcal/mol higher than that for the conformer with perpendicular orientation of NH and NH_2 fragments. It is evident that such unfavorable conformation cannot exist. From Table S2, it is also followed that molecular conformation is not correctly defined. Too big range of the energies of interaction of molecule with its neighbours is observed. Especially, high positive energy (Entries 3 and 4 in Table S3) of 6.5 kcal/mol can be due incorrectness of the structure determination. It should however be noted that this structure was correctly reinvestigated by Klapötke et al [S2]. Data on bond length distribution from that article is included in Table S1 for comparison with FOX and compounds **2** and **4**. However the CIF-file for NH_2-FOX from ref. S2 is not yet available in CSD. Based on above, we excluded this structure from further crystal packing analysis.

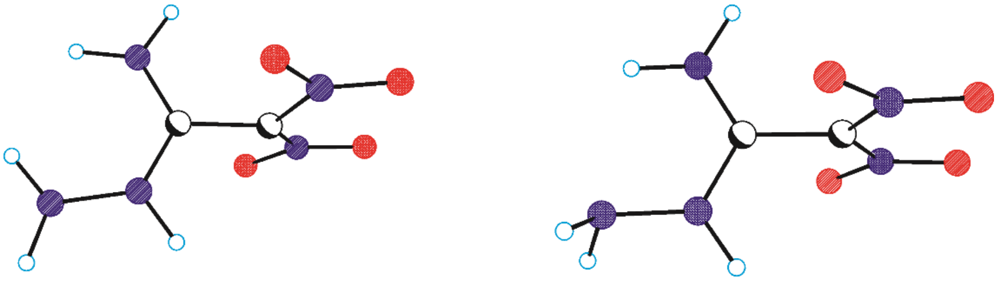

Figure S1. Planar and perpendicular conformers of NH_2-FOX as calculated by M052X/6-311G(pf,pd) level of theory

Table S1. Comparison of selected geometry characteristics of compound **2** with FOX-7, NH_2-FOX, and their potassium salts at 100K.

Compound	Bond Lengths, Å					Angle
	C1-C2	C1-N1	C1-N2	C2-N3	C2-N4	N1-C1-C2-N3
FOX-7	1.453	1.424	1.398	1.331	1.323	4.8
NH_2-FOX [a]	1.476	1.373	1.373	1.294	1.297	-89.8
Compound **2**, mol A[b]	1.457	1.418	1.382	1.303	1.322	6.1
Compound **2**, mol B[b]	1.439	1.435	1.365	1.313	1.325	1.6
K-Salt of FOX-7	1.497	1.378	1.361	1.351	1.274	-92.3
K-Salt **4**	1.475(3)	1.372(3)	1.385(3)	1.373(3)	1.284(3)	94.7(2)

[a] At 298K. [b] Compound **2** crystallizes with two symmetrically independent molecules A and B.

Crystal packing analysis

Table S2. Close intermolecular contacts (Å), types and energies of pair interactions (kcal/mol) obtained at M052X/6-311G(df,pd) level in the crystal structure of compound FOX-7.

Entry	Atomic pair		Symmetry code	Distance	Type of interaction	Energy
1	N3	O3	-1+x,y,z	3.005	H-bond	-0.3
	H2	O3		2.244		
2	O3	N3	1+x,y,z	3.005	H-bond	-0.3
	O3	H2		2.244		
3	No close contact		-x,-y,-z	-	vdW	-0.8
4	No close contact		-x,1-y,-z	-	vdW	-9.7
5	No close contact		1-x,-y,-z	-	vdW	-6.2
6	No close contact		1-x,1-y,-z	-	vdW	-10.3
7	N1	O4	1/2-x,-1/2+y,1/2-z	3.024	NO_2…NO_2	-8.1
	N2	O2		3.069		
8	O2	N2	1/2-x,1/2+y,1/2-z	3.069	NO_2…NO_2	-8.1
	O4	N1		3.024		
9	N3	O1	-1/2+x,1/2-y,-1/2+z	2.886	H-bond	-14.6
	H1	O1		2.014		
	H1	O4		2.311		
	N4	O4		2.986		
	H3	O4		2.024		
10	O1	N3	1/2+x,1/2-y,1/2+z	2.886	H-bond	-14.6
	O1	H1		2.014		
	O4	H1		2.311		
	O4	N4		2.986		
	O4	H3		2.024		
11	O1	O3	-1/2+x,1/2-y,1/2+z	3.000	H-bond	-3.8
	O1	N4		2.990		
	O1	H4		2.170		
	O2	N4		2.994		
	O2	H3		2.489		
12	O3	O1	1/2+x,1/2-y,-1/2+z	3.000	H-bond	-3.8
	N4	O1		2.990		
	H4	O1		2.170		
	N4	O2		2.994		
	H3	O2		2.489		

Table S3. Close intermolecular contacts (Å), types and energies of pair interactions (kcal/mol) obtained at M052X/6-311G(df,pd) level in the crystal structure of compound NH$_2$-FOX.

Entry	Atomic pair		Symmetry code	Distance	Type of interaction	Energy
1	No close contact		-1+x,y,z	-	vdW	-32.4
2	No close contact		1+x,y,z	-	vdW	-32.4
3	No close contact		x,-1+y,z	-	vdW	6.4
4	No close contact		x,1+y,z	-	vdW	6.4
5	No close contact		1/2-x,-y,-1/2+z	-	vdW	-8.7
6	No close contact		1/2-x,-y,1/2+z	-	vdW	-8.7
7	No close contact		1/2-x,1-y,-1/2+z	-	vdW	-8.7
8	No close contact		1/2-x,1-y,1/2+z	-	vdW	-8.7
9	N4	O2	-x,-1/2+y,1-z	3.025	H-bond	-28.9
	H3	O2	-x,-1/2+y,1-z	2.265		
	O3	N4	-x,-1/2+y,1-z	3.025		
	O3	H3	-x,-1/2+y,1-z	2.265		
10	O2	N4	-x,1/2+y,1-z	3.025	H-bond	-28.9
	O2	H3	-x,1/2+y,1-z	2.265		
	N4	O3	-x,1/2+y,1-z	3.025		
	H3	O3	-x,1/2+y,1-z	2.265		
11	N5	O2	1-x,-1/2+y,1-z	3.310	H-bond	-23.9
	H4	O2		2.484		
	N3	O2		3.245		
	H1	O2		2.430		
	O3	N5		3.310		
	O3	H4		2.484		
	O3	N3		3.245		
	O3	H1		2.430		
12	O2	N5	1-x,1/2+y,1-z	3.310	H-bond	-23.9
	O2	H4		2.484		
	O2	N3		3.245		
	O2	H1		2.430		
	N5	O3		3.310		
	H4	O3		2.484		
	N3	O3		3.245		
	H1	O3		2.430		
13	O1	N2	-1/2+x,1/2-y,1.5-z	2.969	NO$_2$…NO$_2$	-2.7
	O4	N1		2.969		
14	N1	O4	1/2+x,1/2-y,1.5-z	2.969	NO$_2$…NO$_2$	-2.7
	N2	O1		2.969		

Table S4. Close intermolecular contacts (Å), types and energies of pair interactions (kcal/mol) obtained at M052X/6-311G(df,pd) level in the crystal structure of compound **2**, molecule A.

Entry	Atomic pair		Symmetry code	Distance	Type of interaction	Mol. pair	Energy
1	O3 N2	O2 O2	x,-1+y,z	3.011 2.975	NO$_2$…NO$_2$	A…A	-0.2
2	O2 O2	O3 N2	x,1+y,z	3.011 2.975	NO$_2$…NO$_2$	A…A	-0.2
3	O5 H5	O4 O4	-1/2+x,-y,z	2.674 1.721	H-bond	A…A	-10.4
4	O4 O4	O5 H5	1/2+x,-y,z	2.674 1.721	H-bond	A…A	-10.4
5	N3 N3 H1 H1	O1 O4 O1 O4	-1/2+x,1-y,z	3.138 2.864 2.453 2.008	H-bond	A…A	-7.9
6	O1 O1 O4 O4	N3 H1 N3 H1	1/2+x,1-y,z	3.138 2.453 2.864 2.008	H-bond	A…A	-7.9
7	N4 H4	O5' O5'	x,-1+y,z	2.917 2.188	H-bond	A…A'	-4.5
8	O5 O5	N4' H4'	x,y,z	2.854 2.045	H-bond	A…A'	-3.9
9	O1 O1	N3' H2'	1-x,2-y,1/2+z	3.217 2.408	H-bond	A…A'	-4.2
10	O3	O3'	1/2+x,-y,z	3.081	NO$_2$…NO$_2$	A…A'	-1.5
11	O3 N2	N2' O3'	1/2+x,1-y,z	3.025 2.965	NO$_2$…NO$_2$	A…A'	-9.5
12	N3 C2	O2' O2'	1/2-x,-1+y,1/2+z	3.117 3.031	weak O…π	A…A'	-1.1
13	O2 O2 N3 H2	O1' N1' O2' O2'	1/2-x,y,1/2+z	2.914 2.977 3.020 2.209	H-bond NO$_2$…NO$_2$	A…A'	-0.3

Table S5. Close intermolecular contacts (Å), types and energies of pair interactions (kcal/mol) obtained at M052X/6-311G(df,pd) level in the crystal structure of compound **2**, molecule A'.

Entry	Atomic pair		Symmetry code	Distance	Type of interaction	Mol. pair	Energy
1'	O4' N2'	O1' O1'	x,-1+y,z	2.923 3.053	NO_2…NO_2	A'…A'	-0.2
2'	O1' O1'	O4' N2'	x,1+y,z	2.923 3.053	NO_2…NO_2	A'…A'	-0.2
3'	O4' O4'	O5' H5'	-1/2+x,1-y,z	2.714 1.772	H-bond	A'…A'	-11.8
4'	O5' H5'	O4' O4'	1/2+x,1-y,z	2.714 1.772	H-bond	A'…A'	-11.8
5'	O1' O1' O1' O4' O4'	O5' N3' H1' N3' H1'	-1/2+x,2-y,z	2.964 3.039 2.228 2.863 2.012	H-bond	A'…A'	-9.4
6'	O5' N3' H1' N3' H1'	O1' O1' O1' O4' O4'	1/2+x,2-y,z	2.964 3.039 2.228 2.863 2.012	H-bond	A'…A'	-9.4
7'	O5' O5'	N4 H4	x,1+y,z	2.917 2.188	H-bond	A'…A	-4.5
8'	N4' H4'	O5 O5	x,y,z	2.854 2.045	H-bond	A'…A	-3.9
9'	N3' H2'	O1 O1	1-x,2-y,-1/2+z	3.217 2.408	H-bond	A'…A	-4.2
10'	O3'	O3	-1/2+x,-y,z	3.081	NO_2…NO_2	A'…A	-1.5
11'	O3' N2'	N2 O3	-1/2+x,1-y,z	2.965 3.025	NO_2…NO_2	A'…A	-9.5
12'	O2' O2'	N3 C2	1/2-x,1+y,-1/2+z	3.117 3.031	weak O…π	A'…A	-1.1
13'	O1' O2' O2' N1'	O2 N3 H2 O2	1/2-x,y,-1/2+z	2.914 3.020 2.209 2.977	H-bond NO_2…NO_2	A'…A	-0.3

From the data on intermolecular close contacts and interaction energies (Tables S2,S4,S5) as well as visual representation of the crystal packing patterns in Fig. 3 (in the main text) it is followed that main difference in the crystal packing is formation of 2-D or 3-D H-bonded frameworks. It can be guessed that 3-D framework should be denser because strong intermolecular interactions are formed in all three dimentions. Such a conclusion is supported by higher density of compound **2** relative to FOX-7. However, from the same Tables it is also seen that the energies of van-der-Waals and NO_2…NO_2 interactions, which are supposed to be significantly weaker than hydrogen bonds, are, in fact, comparable to the latter or even bigger. Therefore, the main question to be answered is to figure out which one of two following types of intermolecular interactions lead to more tight crystal packing:

1) many atom…atom contacts with distances being slightly less or slightly more than sum of van-der-Waals distances

2) one or two strong hydrogen bonds

In our recent studies, it was observed that due to directionality of strong intermolecular interactions, such as hydrogen bonds, the density of crystal packing can decrease [S3]. Such an idea can be illustrated by example of water which solid phase density is lower than that in the liquid phase due to directionality of H-bonds.

In order to find an explanation of the results obtained in the present work, we used an approach proposed in our recent study [S4]. It is based on combined analysis of two characteristics, namely, density of an isolated molecule (d_{mol}) and overlapping of electron density criterion ($\Delta_{OED} = d_{cryst} - d_{mol}$). The d_{cryst} term is simply crystal density obtained from X-ray study. Molecular density, d_{mol}, can be estimated as the ratio of mass of molecule per its volume ($d_{mol} = m_{mol}/V_{mol}$). Using topological theory of "Atoms in Molecules" (AIM) [S5] one can estimate atomic volumes using set of wave functions obtained from quantum chemical calculation of isolated molecule [S6]. Atomic volume is estimated as a space surrounded by zero-flux surface. For outer atoms (which are not completely surrounded by their neighbors) we used isosurface of electron density at 0.0004 e/a_o^3 as implemented in AIMALL program package [S7] to restrict atomic volume. Then molecular volume is obtained as a sum of atomic volumes. Being defined as the difference between crystal and molecular density, the Δ_{OED} criterion serves as measure of tightness of crystal packing. The higher is the $d_{cryst} - d_{mol}$ difference the higher is the degree of overlapping of molecular electron densities and the more tight is the molecular arrangement upon crystal structure formation.

Using the combination of d_{mol} and Δ_{OED} values we can easily answer the main question on the reason of the difference in density of FOX-7 and its hydroxy derivative **2**. The values of molecular densities are equal to 1.431 g/cm^3 for FOX-7, and 1.487 g/cm^3 for OH-FOX. At the same time, the Δ_{OED} criterion is higher for FOX-7 compound being equal to 1.941-1.431=0.510 g/cm^3 while for compound **2** it is only 1.959-1.487=0.472 g/cm^3. These results clearly demonstrate that formation of dense crystal packing would benefit from the multiple van-der-Waals atom…atom contacts observed in the crystals of FOX-7 rather than from highly directional hydrogen bonds. However, OH-FOX molecule itself is more dense. Difference in molecular densities (1.487-1.431=0.056 g/cm^3) exceeds the difference in tightness of crystal packing (0.510-0.472=0.038 g/cm^3) that results in increased density of compound **2** relative to FOX-7.

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