

Article

Molecular and Crystal Structure of a New High Energy Density Material: Aminoguanidinium-styphnate, $[\text{H}_2\text{NNHC}(\text{NH}_2)_2]_2[\text{C}_6\text{HO}_2(\text{NO}_2)_3]$

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Abstract: The title compound $[\text{H}_2\text{NNHC}(\text{NH}_2)_2]_2[\text{C}_6\text{HO}_2(\text{NO}_2)_3]$ (**2**) was prepared in 85% yield by treatment of sodium styphnate with 2 equivalents of aminoguanidinium nitrate, followed by crystallization from aqueous solution. Compound **2** crystallizes in the triclinic space group $P\bar{1}$ with unit cell dimensions $a = 6.7224(3)$ Å, $b = 10.7473(4)$ Å, $c = 11.9604(5)$ Å, $\alpha = 113.212(4)^\circ$, $\beta = 90.579(3)^\circ$, $\gamma = 99.815(3)^\circ$, $V = 779.68(6)$ Å³, $Z = 2$. In the solid state structure of **2**, no water of crystallization is present. Bond angles within the aromatic ring of the styphnate anion indicate a significant distortion with larger angles (122.04(18)–125.96(18) Å) at the carbons bearing the nitro groups, and smaller ones (113.30(17) and 114.07(17) Å) at the C-O⁻ carbon atoms. The crystal structure of **2** consists of layers formed by an extensive network of N-H⁺⋯O hydrogen bonds between NH₂ groups of the aminoguanidinium cation and the negatively charged oxygens of the styphnate anion. The layers are again interconnected by N-H⁺⋯N hydrogen bonds between neighboring aminoguanidinium cations.

Keywords: high density energy materials; styphnates; aminoguanidinium styphnate; hydrogen bonds

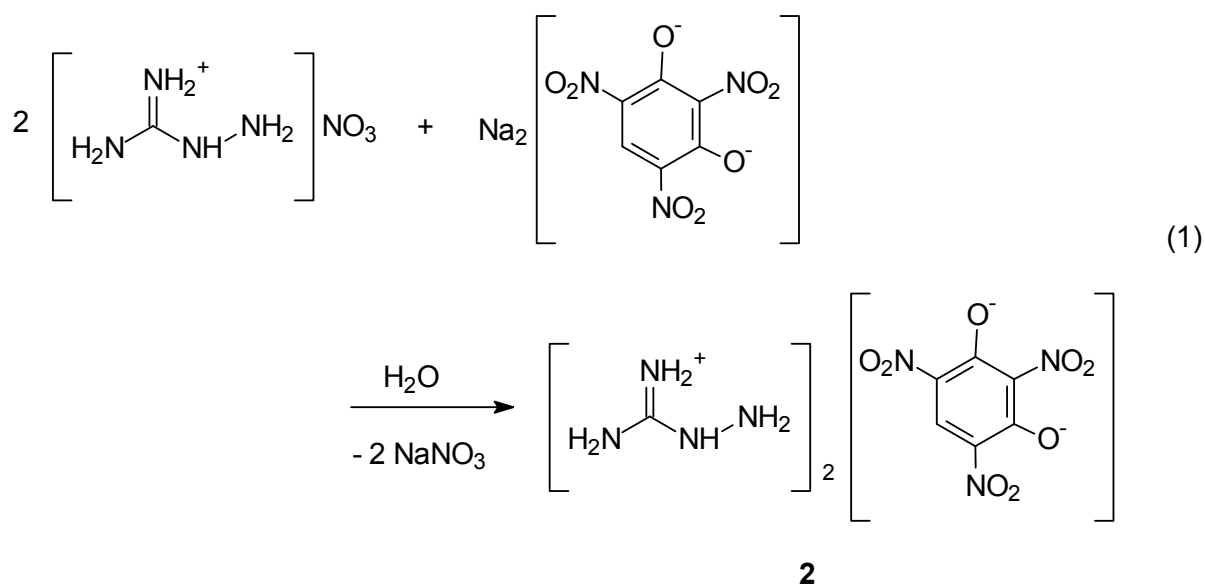
1. Introduction

High energy density materials (HEDM's) form an important class of explosive compounds. Several significant advantages such as high heats of combustion, high propulsive power, high specific impulse, as well as smokeless combustion make them highly useful as propellants, explosives, and pyrotechnics [1–6]. Besides picric acid and its salts [1,7], 2,4,6-trinitro-resorcinol (= styphnic acid, **1**) is one of the polynitrophenole derivatives having industrial importance. Styphnic acid was first reported by Merz and Zetter in 1879 [8]. Its synthesis involves treatment of resorcinol with sulfuric acid followed by nitration of the intermediate resorcinoldisulfonic acid. Salts of 2,4,6-trinitro-resorcinol are commonly named styphnates or trizitates. Several styphnates have found various applications in explosive devices. Particularly important are lead(II) styphnate and basic lead(II) styphnate which are being used in primers and military ammunition [9]. A major drawback of lead(II) styphnate and related styphnates is their high static sensitivity and especially the serious heavy metal pollution associated with their use. Thus a common theme in current HEDM research is the search for environmentally friendly initiators. Styphnates of alkali and alkaline earth metals have frequently been employed in the automobile industry, e.g. as ignitors for airbags [10,11], and their structural chemistry has been thoroughly investigated. We report here the synthesis and crystal structure of a new, metal-free styphnate, namely aminoguanidinium styphnate, $[H_2NNHC(NH_2)_2]_2[C_6HO_2(NO_2)_3]$ (**2**).

2. Results and Discussion

2.1. Synthesis and Characterization of $[H_2NNHC(NH_2)_2]_2[C_6HO_2(NO_2)_3]$ (**2**)

The preparation of the title compound aminoguanidinium styphnate, $[H_2NNHC(NH_2)_2]_2[C_6HO_2(NO_2)_3]$ (**2**) was achieved according to Equation (1) by treatment of sodium styphnate with 2 equivalents of aminoguanidinium nitrate in aqueous solution. The product was fully characterized by IR and NMR spectroscopy as well as elemental analysis.



2.2. Crystal Structure

Single crystals of **2** suitable for X-ray diffraction were obtained by recrystallization from hot water. It was observed that fast crystallization from concentrated solution afforded yellow-orange, needle-like crystals, whereas from diluted solutions more compact, block-like crystals were obtained. However, elemental analyses of the different crystalline forms revealed no difference in the analytical composition.. Figure 1 illustrates the habit of the crystals obtained from dilute aqueous solution.

Figure 1. Compact crystals of $[\text{H}_2\text{NNHC}(\text{NH}_2)_2]_2[\text{C}_6\text{HO}_2(\text{NO}_2)_3]$ (**2**) obtained by recrystallization from dilute aqueous solutions.

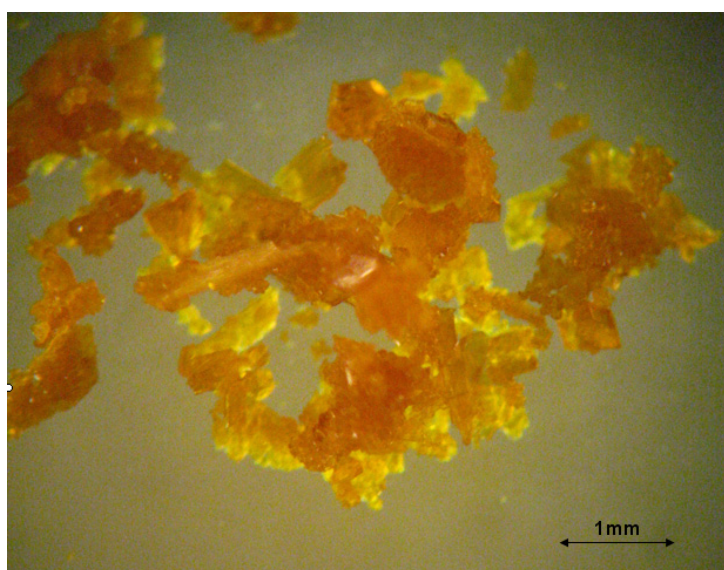
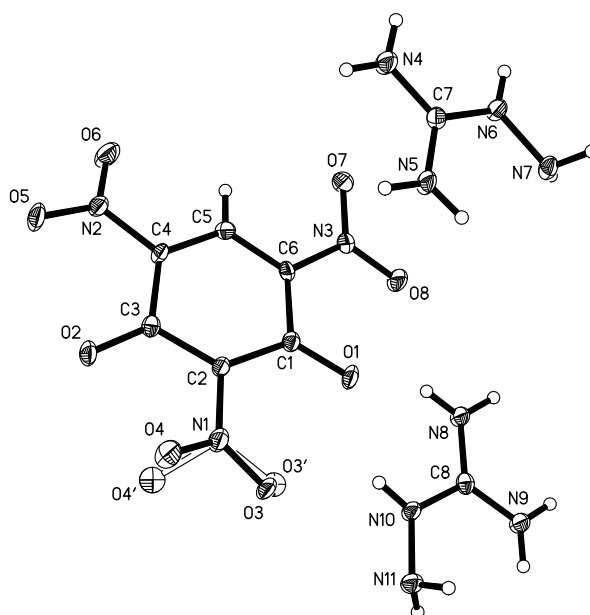


Figure 2. Structure of aminoguanidinium styphnate, $[\text{H}_2\text{NNHC}(\text{NH}_2)_2]_2[\text{C}_6\text{HO}_2(\text{NO}_2)_3]$ (**2**) in the crystal, showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level.



Compound **2** crystallizes in the triclinic space group $P\bar{1}$ with one styphnate anion and two aminoguanidinium cations. Crystal data and refinement parameters are summarized in Table 1. Figure 2 depicts the content of the unit cell, and selected bond lengths and angles are listed in Table 2. Surprisingly, although crystallized from aqueous solutions, the crystals of **2** contain no water of crystallization. As can be deduced from the data in Table 2, both the aminoguanidinium cation and the styphnate anion show highly delocalized π -bonding. As expected, all C-C, C-N, and N-N bond lengths show typical values intermediate between single and double bonds. Bond angles within the aromatic ring of the styphnate anion indicate a significant distortion with larger angles (122.04(18)–125.96(18) Å) at the carbons bearing the nitro groups, and smaller ones (113.30(17) and 114.07(17) Å) at the C-O⁻ carbon atoms.

Figure 3 shows the crystal packing of compound **2** in the solid state. The crystal structure is dominated by an extensive network of N-H \cdots O hydrogen bonds between NH₂ groups of the aminoguanidinium cation and the negatively charged oxygens of the styphnate anion. This leads to the formation of layers of alternating cations and anions. The layers are again interconnected by N-H \cdots N hydrogen bonds between neighboring aminoguanidinium cations (Table 3).

Figure 3. Crystal packing of the title compound aminoguanidinium styphnate, [H₂NNHC(NH₂)₂]₂[C₆HO₂(NO₂)₃] (**2**).

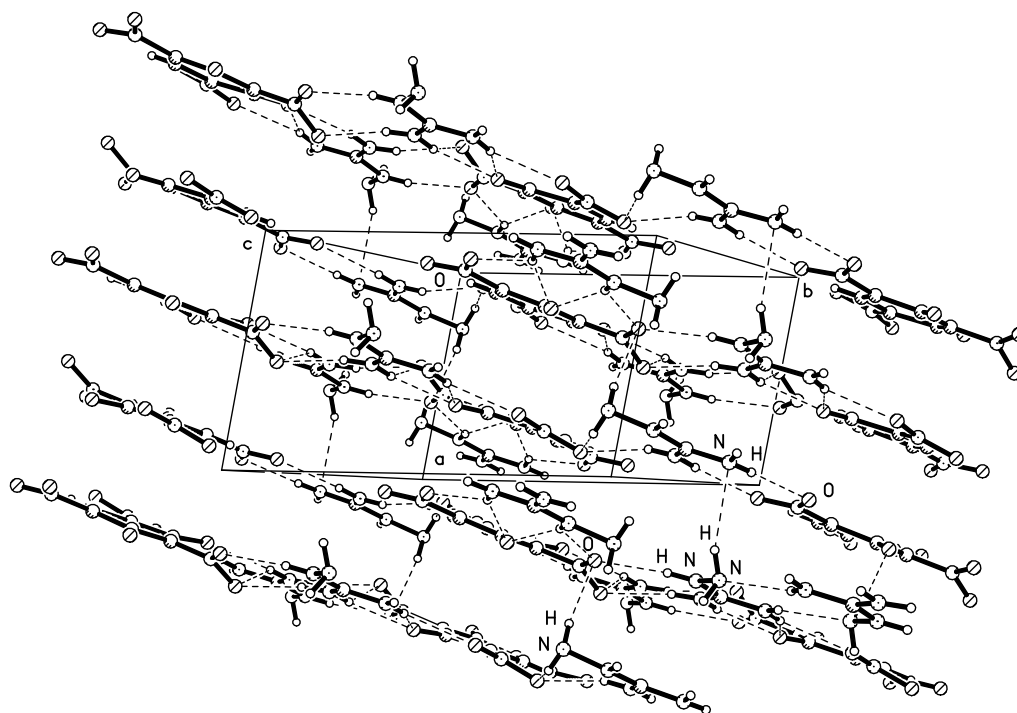


Table 1. Crystal data and structure refinement for aminoguanidinium styphnate, $[\text{H}_2\text{NNHC}(\text{NH}_2)_2]_2[\text{C}_6\text{HO}_2(\text{NO}_2)_3]$ (**2**).

Identification code	magd09
Empirical formula	$\text{C}_8\text{H}_{15}\text{N}_{11}\text{O}_8$
Formula weight	393.31
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P -1
Unit cell dimensions	$a = 6.7224(3)$ Å
	$b = 10.7473(4)$ Å
	$c = 11.9604(5)$ Å
Volume	$779.68(6)$ Å ³
Z	2
Density (calculated)	1.675 mg/m ³
Absorption coefficient	0.148 mm ⁻¹
F(000)	408
Crystal size	$0.26 \times 0.21 \times 0.13$ mm ³
Theta range for data collection	2.17 to 28.28°
Index ranges	$-8 \leq h \leq 8, -14 \leq k \leq 14, -15 \leq l \leq 15$
Reflections collected	12676
Independent reflections	3857 [$R(\text{int}) = 0.0335$]
Completeness to theta = 28.00°	99.8%
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3857/86/313
Goodness-of-fit on F^2	0.862
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0398, wR2 = 0.0916$
R indices (all data)	$R1 = 0.0627, wR2 = 0.0964$
Largest diff. peak and hole	0.540 and -0.330 e.Å ⁻³

Table 2. Selected bond lengths [Å] and angles [°] for aminoguanidinium styphnate, [H₂NNHC(NH₂)₂]₂[C₆HO₂(NO₂)₃] (2).

O(1)-C(1)	1.2559(18)	N(5)-C(7)	1.317(2)
O(2)-C(3)	1.2394(18)	N(6)-C(7)	1.339(2)
O(5)-N(2)	1.2269(16)	N(6)-N(7)	1.4073(19)
O(6)-N(2)	1.2423(16)	N(8)-C(8)	1.330(2)
O(7)-N(3)	1.2429(16)	N(9)-C(8)	1.320(2)
O(8)-N(3)	1.2403(16)	N(10)-C(8)	1.3343(19)
N(1)-O(3)	1.220(3)	N(10)-N(11)	1.4099(18)
N(1)-O(4)	1.2646(19)	C(1)-C(2)	1.443(2)
N(1)-O(3')	1.296(14)	C(1)-C(6)	1.455(2)
N(1)-C(2)	1.4223(19)	C(2)-C(3)	1.449(2)
N(1)-O(4')	1.443(7)	C(3)-C(4)	1.461(2)
N(2)-C(4)	1.4309(19)	C(4)-C(5)	1.376(2)
N(3)-C(6)	1.4285(19)	C(5)-C(6)	1.371(2)
N(4)-C(7)	1.324(2)		
O(3)-N(1)-O(4)	117.1(3)	O(2)-C(3)-C(2)	123.57(14)
O(3)-N(1)-O(3')	7.8(16)	O(2)-C(3)-C(4)	122.97(13)
O(4)-N(1)-O(3')	124.7(14)	C(2)-C(3)-C(4)	113.36(13)
O(3)-N(1)-C(2)	123.8(3)	C(5)-C(4)-N(2)	116.37(14)
O(4)-N(1)-C(2)	118.43(14)	C(5)-C(4)-C(3)	122.20(13)
O(3')-N(1)-C(2)	116.0(13)	N(2)-C(4)-C(3)	121.31(13)
O(3)-N(1)-O(4')	99.3(4)	C(6)-C(5)-C(4)	122.18(15)
O(4)-N(1)-O(4')	65.7(3)	C(5)-C(6)-N(3)	116.17(14)
O(3')-N(1)-O(4')	103.6(13)	C(5)-C(6)-C(1)	122.21(14)
C(2)-N(1)-O(4')	110.3(3)	N(3)-C(6)-C(1)	121.61(13)
O(5)-N(2)-O(6)	120.23(13)	N(5)-C(7)-N(4)	120.64(15)
O(5)-N(2)-C(4)	121.26(13)	N(5)-C(7)-N(6)	119.38(14)
O(6)-N(2)-C(4)	118.51(12)	N(4)-C(7)-N(6)	119.98(14)
O(8)-N(3)-O(7)	120.45(12)	N(9)-C(8)-N(8)	120.45(14)
O(8)-N(3)-C(6)	120.50(13)	N(9)-C(8)-N(10)	121.21(14)
O(7)-N(3)-C(6)	119.04(12)	N(8)-C(8)-N(10)	118.28(14)
C(7)-N(6)-N(7)	118.14(13)		
C(8)-N(10)-N(11)	124.15(13)		
O(1)-C(1)-C(2)	123.60(14)		
O(1)-C(1)-C(6)	122.47(13)		
C(2)-C(1)-C(6)	113.88(13)		
N(1)-C(2)-C(1)	117.63(13)		
N(1)-C(2)-C(3)	116.48(13)		
C(1)-C(2)-C(3)	125.89(13)		

Table 3. Hydrogen bond lengths [Å] and angles [°] for aminoguanidinium styphnate, [H₂NNHC(NH₂)₂]₂[C₆HO₂(NO₂)₃] (**2**).

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(4)-H(4A)...O(2)#1	0.861(13)	2.090(15)	2.8484(18)	146.5(18)
N(4)-H(4B)...O(4)#2	0.848(13)	2.192(14)	3.021(2)	165.7(18)
N(5)-H(5A)...N(7)#3	0.872(13)	2.302(14)	3.0538(19)	144.5(15)
N(5)-H(5B)...O(2)#1	0.867(13)	1.967(15)	2.7539(18)	150.3(17)
N(5)-H(5B)...O(5)#1	0.867(13)	2.244(16)	2.8868(17)	130.9(16)
N(6)-H(6)...O(3)#2	0.828(13)	2.359(15)	3.141(5)	157.8(15)
N(7)-H(7A)...O(1)#3	0.880(13)	2.099(14)	2.9737(19)	172.7(17)
N(7)-H(7B)...O(5)#4	0.876(13)	2.614(18)	3.0480(17)	111.6(14)
N(8)-H(8A)...O(8)#5	0.862(13)	2.086(13)	2.9407(17)	171.3(17)
N(8)-H(8B)...O(1)	0.866(13)	2.039(15)	2.8104(18)	147.9(17)
N(8)-H(8B)...O(8)	0.866(13)	2.203(16)	2.8673(18)	133.2(16)
N(9)-H(9A)...O(7)#5	0.836(13)	2.222(13)	3.0458(18)	168.8(16)
N(9)-H(9B)...O(6)#6	0.825(13)	2.110(14)	2.9156(19)	165.4(19)
N(10)-H(10)...O(1)	0.828(13)	2.030(15)	2.7668(18)	147.8(17)
N(10)-H(10)...O(3)	0.828(13)	2.371(16)	3.029(4)	136.9(15)
N(11)-H(11A)...O(6)#6	0.855(14)	2.530(17)	3.1708(19)	132.5(16)

Symmetry transformations used to generate equivalent atoms: #1 $-x + 1, -y + 1, -z + 1$; #2 $x, y - 1, z$; #3 $-x + 1, -y + 1, -z + 2$; #4 $x, y, z + 1$; #5 $-x, -y + 1, -z + 2$; #6 $x, y + 1, z + 1$

2.3. Sensitivity

For initial safety testing, the impact and friction sensitivities of the new styphnate was tested according to established BAM methods [1] using the BAM drophammer and BAM friction tester as well as a simple combustion test (Table 4). The title compound was found to be insensitive towards impact (<40 Nm) and friction (<360 N) and showed deflagration upon combustion. Long-term stability tests over a period of 30 days showed no changes in these data.

Table 4. Energetic Properties of **2**.

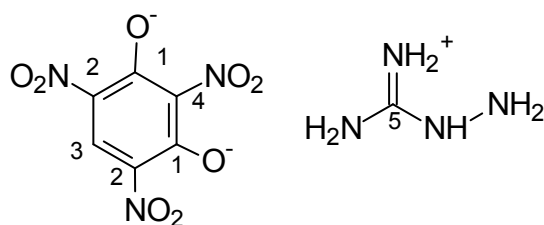
Compound	2
<i>M</i> (g/mol)	393.27
ρ , g/cm ³	1.844
Impact/Nm	>40
Friction Sensitivity (N)	>360
Combustion Test	Deflagration
N content (%)	39.18
Ω (%)	-26.15

3. Experimental Section

Aminoguanidinium nitrate was obtained from Aldrich and used as received. Sodium styphnate was prepared as described in [6]. The X-ray diffraction data for compound **2** were measured at -173 °C on a Stoe IPDS diffractometer. Structure solution and refinement were carried out using the programs SHELXS-97 [12] and SHELXL-97 [13].

Preparation of Aminoguanidinium-styphnate, $[H_2NNHC(NH_2)_2]_2[C_6HO_2(NO_2)_3]$ (2). Sodium styphnate (0.58 g, 2.0 mmol) was dissolved in a minimum amount of warm (*ca.* 40 °C) water and combined with an aqueous solution of aminoguanidinium nitrate (0.30 g, 2.2 mmol). Crystallization at room temperature for 24 h afforded 0.67 g (85% yield) bright yellow-orange, compact crystals of **2**. m.p. 220 °C. Anal. Calcd. for $C_8H_{15}N_{11}O_8$ (393.27 g/mol): C 24.43, H 3.84, N 39.18%. Found: C 23.65, H 3.89, N 38.39%. IR (KBr, cm^{-1}): ν_{max} 3422 (m, ν_{NH}), 3128 (vs), 2232 (w), 1725 (s), 1636 (m), 1575 (vs, ν_{C-NO_2}), 1539 (vs), 1515 (vs), 1417 (m), 1399 (s), 1355 (m), 1314 (vs), 1275 (m), 1231 (m), 1211 (m), 1132 (m), 1090 (m), 979 (m), 961 (m), 905 (m), 859 (w), 797 (m), 715 (m), 665 (m), 621 (m), 529 (w), 488 (m), 467 (m), 414 (w). ^{13}C -NMR (20°C, D_2O , 100 MHz): δ [ppm] 154.1 (C1), 127.2 (C2), 125.5 (C3), 135.1 (C4), 163.3 (C5) (Fig. 4).

Figure 4. Numbering scheme of the carbon atoms in aminoguanidinium styphnate, $[H_2NNHC(NH_2)_2]_2[C_6HO_2(NO_2)_3]$ (**2**).



4. Conclusions

Aminoguanidinium styphnate, $[H_2NNHC(NH_2)_2]_2[C_6HO_2(NO_2)_3]$ (**2**), was prepared in 85% yield by treatment of sodium styphnate with 2 equivalents of aminoguanidinium nitrate, followed by crystallization from aqueous solution. In the solid state structure of **2**, no water of crystallization is present. Bond angles within the aromatic ring of the styphnate anion indicate a significant distortion with larger angles (122.04(18)–125.96(18) Å) at the carbons bearing the nitro groups, and smaller ones (113.30(17) and 114.07(17) Å) at the $C-O^-$ carbon atoms. The crystal structure of **2** consists of layers interconnected by an extensive network of $N-H\cdots O$ hydrogen bonds between NH_2 groups of the aminoguanidinium cation and the negatively charged oxygens of the styphnate anion. The layers are again interconnected by $N-H\cdots N$ hydrogen bonds between neighboring aminoguanidinium cations.

Acknowledgements

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