Energetic salt of guanidinium 3,7-Bis(dinitromethylene)-octahydro-[1,2,4]-triazino-[6,5-e][1,2,4]triazine and its crystal structure

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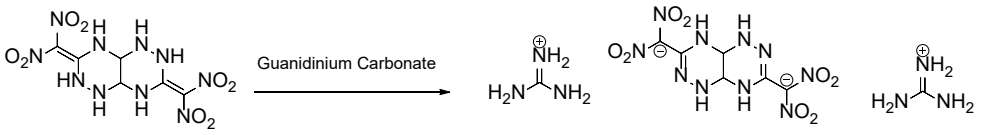
Abstract. Energetic salt of guanidinium 3,7-Bis(dinitromethylene)-octahydro-[1,2,4]-triazino-[6,5-e][1,2,4]triazine(**1**) was prepared through the reaction of 3,7-Bis(dinitromethylene)-octahydro-[1,2,4]-triazino-[6,5-e][1,2,4]triazine with guanidinium carbonate. The crystal structure of **1** was characterized. It is the first bicyclic energetic salt based on 3,7-Bis(dinitromethylene)-octahydro-[1,2,4]-triazino-[6,5-e][1,2,4]triazine.

1 Introduction

The design and synthesis of high-energy density materials is an important area in the finding of new explosive materials. Fused cyclic energetic materials are the promising backbone of some novel energetic materials. Fused heterocycles such as [5,5]-Bicyclic, [5,6]-bicyclic, [6,6]-bicyclic, [5,6,5]- Tricyclic, [5,7,5]-Tricyclic and Tetracyclic heterocyclic have all found extensive use in the design of new energetic materials. Nitrogen-rich salts based on Nitrogen-rich Fused heterocycles are a promising strategy for preparing high-performing, dense, thermally stable and environmentally friendly energetic materials.

Here, we synthesized the energetic salt of guanidinium 3,7-Bis(dinitromethylene)-octahydro-[1,2,4]-triazino-[6,5-e][1,2,4]triazine(**1**) (Scheme 1) and studied its crystal structure is shown in Figure 1.



(**1**)

Scheme 1 Synthesis of 1.

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2 Experiments and results

Treating 3,7-Bis(dinitromethylene)-octahydro-[1,2,4]-triazino-[6,5-e][1,2,4]triazine with guanidine carbonate in minimum water, **1** was synthesized.

Single crystals of guanidinium 3,7-Bis(dinitromethylene)-octahydro-[1,2,4]-triazino-[6,5-e][1,2,4]triazine ($C_8H_{22}N_{16}O_{10}$) was collected through the slow evaporation of its aqueous solution. A suitable crystal was selected and data for it was collected with **a** 'Bruker APEX-II CCD' **diff**ractometer. The crystal was kept at 170.0 K during data collection. Using Olex2 [1], the structure was solved with the ShelXT [2] structure solution program using Intrinsic Phasing and refined with the ShelXL [3] refinement package using Least Squares minimisation.

Crystal Data for **1**($C_8H_{22}N_{16}O_{10}$): (M =502.41 g/mol): triclinic, space group P-1 (no. 2), a = 9.278(9) Å, b = 10.255(8) Å, c = 11.396(7) Å, α = 75.99(2)°, β = 76.97(3)°, γ = 82.51(4)°, V = 1021.7(14) Å^3, Z = 2, T = 170.0 K, μ(MoKα) = 0.146 mm^{-1}, $Dcalc$ = 1.633 g/cm^3, 28236 reflections measured (4.52° ≤ 2Θ ≤ 54.292°), 4473 unique (R_{int} = 0.0286, R_{sigma} = 0.0191) which were used in all calculations. The final R_1 was 0.0705 (I > 2σ(I)) and wR_2 was 0.1669 (all data). (Details see Table 1 to 8)

Table 1. Crystal data and structure refinement for **1**.

Identification code	**1**
Empirical formula	$C_8H_{22}N_{16}O_{10}$
Formula weight	502.41
Temperature/K	170.0
Crystal system	triclinic
Space group	P-1
a/Å	9.278(9)
b/Å	10.255(8)
c/Å	11.396(7)
α/°	75.99(2)
β/°	76.97(3)
γ/°	82.51(4)
Volume/Å^3	1021.7(14)
Z	2
ρ_{calc}g/cm^3	1.633
μ/mm^{-1}	0.146
F(000)	524.0
Crystal size/mm^3	0.45 × 0.38 × 0.35
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.52 to 54.292
Index ranges	-11 ≤ h ≤ 11, -13 ≤ k ≤ 13, -14 ≤ l ≤ 14
Reflections collected	28236
Independent reflections	4473 [R_{int} = 0.0286, R_{sigma} = 0.0191]
Data/restraints/parameters	4473/30/361
Goodness-of-fit on F^2	1.245
Final R indexes [I>=2σ (I)]	R_1 = 0.0705, wR_2 = 0.1664
Final R indexes [all data]	R_1 = 0.0717, wR_2 = 0.1669
Largest diff. peak/hole / e Å^{-3}	0.55/-0.56

Table 2. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **1**. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O1	7268(3)	3846(3)	8057(2)	27.5(6)
O2	7673(3)	2670(3)	6650(2)	27.8(6)
O3	5495(3)	2745(2)	5543(2)	27.1(6)
O4	3618(3)	4192(3)	5981(2)	27.0(5)
O5	5547(3)	10665(2)	8704(2)	25.6(5)
O6	7831(3)	10312(2)	8926(3)	27.8(6)
O7	9198(3)	7999(3)	8606(3)	32.1(6)
O8	7875(3)	6651(2)	8148(2)	21.6(5)
N1	6848(3)	3442(3)	7250(2)	18.4(5)
N2	4866(3)	3592(3)	6167(2)	17.9(5)
N3	4351(3)	6214(3)	7077(2)	15.8(5)
N4	3974(3)	4488(3)	8890(2)	15.2(5)
N5	3017(3)	5449(3)	9478(2)	14.9(5)
N6	4544(3)	7348(3)	9150(2)	16.3(5)
N7	5037(3)	8835(3)	7196(2)	17.3(5)
N8	3619(3)	8559(3)	7073(2)	15.4(5)
N9	6726(3)	9923(3)	8715(3)	18.9(5)
N10	7991(3)	7772(3)	8415(2)	18.2(5)
C1	5419(3)	3926(3)	7051(3)	16.1(6)
C2	4523(3)	4915(3)	7736(3)	14.1(6)
C3	3200(3)	6879(3)	8984(3)	14.1(6)
C4	3241(3)	7179(3)	7594(3)	13.9(6)
C5	5362(3)	8246(3)	8250(3)	14.6(6)
C6	6734(3)	8629(3)	8501(3)	17.3(6)
O11	10559(3)	4975(3)	8509(3)	36.5(7)
N11	2601(3)	11804(3)	8368(3)	26.5(7)
N12	1113(3)	10194(3)	8316(3)	27.5(7)
N13	63(3)	12272(3)	8627(3)	24.4(6)
C7	1255(4)	11419(3)	8439(3)	19.4(6)
O9	7666(10)	6721(9)	5663(9)	31.6(19)
O10	7174(11)	10373(14)	5501(13)	19(2)
N14	7557(11)	10323(18)	5636(17)	24(3)
N15	9895(10)	11046(12)	5027(15)	41(3)
N16	9530(10)	8907(11)	4977(15)	41(3)
C8	8988(7)	10083(6)	5214(6)	23.1(13)
N17	10371(11)	5322(10)	5975(9)	37(2)
N18	9582(10)	5174(10)	4253(8)	30.0(19)
N19	8072(11)	6265(11)	5663(11)	30(2)
C9	9331(7)	5578(7)	5307(6)	23.3(14)

Table 3. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for mo_210507_SF1120102880656_0m. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	21.9(12)	38.0(14)	29.3(13)	-16.1(11)	-13.2(10)	3.6(10)
O2	19.9(12)	30.4(13)	35.4(14)	-19.2(11)	-2.4(10)	6.5(10)
O3	43.6(15)	21.5(12)	20.7(12)	-12.6(10)	-12.3(11)	6.6(11)
O4	26.4(13)	26.1(13)	34.7(14)	-10.4(11)	-18.2(11)	3.0(10)

O5	17.8(11)	20.5(12)	42.7(15)	-12.6(11)	-12.2(10)	4.7(9)
O6	19.1(12)	21.9(12)	49.5(16)	-11.4(11)	-16.4(11)	-3.9(9)
O7	19.0(12)	29.1(13)	57.8(18)	-20.2(13)	-18.5(12)	3.1(10)
O8	24.6(12)	16.9(11)	26.1(12)	-7.8(9)	-7.8(10)	-1.4(9)
N1	17.0(13)	18.4(13)	19.1(13)	-5.1(10)	-2.7(10)	1.2(10)
N2	24.0(14)	14.7(12)	15.9(12)	-3.0(10)	-6.0(10)	-1.4(10)
N3	17.9(13)	14.8(12)	13.6(12)	-2.8(10)	-1.6(10)	0.2(10)
N4	15.2(12)	15.7(12)	15.0(12)	-5.0(10)	-3.0(10)	0.6(10)
N5	16.2(12)	15.3(12)	12.5(12)	-3.4(9)	-1.0(9)	-1.3(10)
N6	17.5(13)	17.9(13)	15.1(12)	-1.6(10)	-6.1(10)	-6.2(10)
N7	16.6(13)	15.9(12)	20.8(13)	-2.4(10)	-7.2(10)	-3.0(10)
N8	14.9(12)	15.5(12)	17.0(12)	-1.7(10)	-7.5(10)	-1.8(10)
N9	16.3(13)	17.5(13)	24.1(14)	-5.1(11)	-5.9(11)	-1.8(10)
N10	18.9(13)	16.6(12)	21.3(13)	-4.3(10)	-8.2(11)	-1.4(10)
C1	17.0(14)	16.4(14)	15.6(14)	-4.7(11)	-4.0(11)	-0.3(11)
C2	12.4(13)	15.4(14)	16.5(14)	-5.3(11)	-5.5(11)	-0.4(11)
C3	13.4(14)	14.3(14)	14.7(14)	-4.4(11)	-2.1(11)	-1.0(11)
C4	14.6(14)	13.4(13)	14.4(13)	-2.9(11)	-4.6(11)	-0.7(11)
C5	12.3(13)	14.9(13)	17.3(14)	-5.0(11)	-3.4(11)	-0.3(11)
C6	16.8(15)	15.6(14)	21.0(15)	-3.9(12)	-6.1(12)	-2.9(11)
O11	22.3(13)	23.1(13)	65(2)	-10.4(13)	-11.0(13)	1.0(10)
N11	14.6(13)	21.1(14)	42.8(18)	-5.3(13)	-4.2(12)	-3.7(11)
N12	16.1(14)	22.2(14)	46.9(19)	-15.2(13)	-4.5(13)	-0.1(11)
N13	14.7(13)	20.6(14)	41.1(17)	-12.3(12)	-7.9(12)	1.3(11)
C7	16.2(15)	20.1(15)	21.0(15)	-2.0(12)	-4.8(12)	-0.7(12)
O9	27(5)	43(6)	30(3)	-15(4)	-5(3)	-11(4)
O10	16(4)	17(3)	21(4)	-4(3)	0(4)	2(3)
N14	20(6)	22(4)	27(5)	-6(3)	-3(5)	0(5)
N15	28(6)	33(4)	55(5)	-11(4)	12(6)	-3(5)
N16	28(6)	25(4)	62(6)	-16(4)	9(6)	6(4)
C8	24(3)	22(3)	21(3)	-2(3)	-4(3)	-2(3)
N17	29(4)	55(7)	30(5)	-8(4)	-13(3)	-6(4)
N18	22(3)	47(6)	24(4)	-12(4)	-6(3)	-1(4)
N19	30(6)	36(6)	27(4)	-9(4)	-10(4)	-5(4)
C9	24(3)	29(3)	18(3)	2(3)	-7(3)	-12(3)

Table 4. Bond Lengths for **1**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	N1	1.248(4)	N7	N8	1.425(4)
O2	N1	1.244(4)	N7	C5	1.289(4)
O3	N2	1.257(4)	N8	C4	1.452(4)
O4	N2	1.275(4)	N9	C6	1.405(4)
O5	N9	1.249(4)	N10	C6	1.366(4)
O6	N9	1.238(4)	C1	C2	1.483(4)
O7	N10	1.248(4)	C3	C4	1.531(4)
O8	N10	1.282(4)	C5	C6	1.485(4)
N1	C1	1.402(4)	N11	C7	1.338(4)
N2	C1	1.357(4)	N12	C7	1.324(4)
N3	C2	1.371(4)	N13	C7	1.329(4)
N3	C4	1.459(4)	N14	C8	1.319(11)

N4	N5	1.426(4)	N15	C8	1.328(9)
N4	C2	1.287(4)	N16	C8	1.311(10)
N5	C3	1.455(4)	N17	C9	1.322(9)
N6	C3	1.459(4)	N18	C9	1.326(8)
N6	C5	1.361(4)	N19	C9	1.317(9)

Table 5. Bond Angles for **1**.

Atom	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
N1	C1	116.2(3)	N4	C2	C1	117.8(3)
N1	O1	121.2(3)	N5	C3	N6	115.4(2)
N1	C1	122.6(3)	N5	C3	C4	108.2(2)
N2	O4	119.3(3)	N6	C3	C4	107.4(2)
N2	C1	124.5(3)	N3	C4	C3	107.4(2)
N2	C1	116.1(3)	N8	C4	N3	111.9(2)
N3	C4	120.1(3)	N8	C4	C3	108.2(2)
N4	N5	115.5(2)	N6	C5	C6	117.9(3)
N5	C3	119.1(2)	N7	C5	N6	126.0(3)
N6	C3	122.2(3)	N7	C5	C6	116.1(3)
N7	N8	113.4(3)	N9	C6	C5	118.2(3)
N8	C4	115.1(2)	N10	C6	N9	121.9(3)
N9	C6	117.3(3)	N10	C6	C5	119.6(3)
N9	O5	120.9(3)	N12	C7	N11	120.0(3)
N9	C6	121.7(3)	N12	C7	N13	120.1(3)
N10	O8	119.4(3)	N13	C7	N11	119.8(3)
N10	C6	124.6(3)	N14	C8	N15	119.5(10)
N10	C6	116.0(3)	N16	C8	N14	121.0(9)
C1	C2	120.3(3)	N16	C8	N15	119.4(7)
C1	N1	121.3(3)	N17	C9	N18	119.5(7)
C1	C2	118.2(3)	N19	C9	N17	120.4(8)
C2	C1	116.7(3)	N19	C9	N18	120.1(7)
C2	N3	125.6(3)				

Table 6. Torsion Angles for **1.**

A	**B**	**C**	**D**	**Angle/°**	**A**	**B**	**C**	**D**	**Angle/°**
O1	N1	C1	N2	177.7(3)	N5	N4	C2	C1	-174.7(2)
O1	N1	C1	C2	2.9(4)	N5	C3	C4	N3	-51.7(3)
O2	N1	C1	N2	-1.1(5)	N5	C3	C4	N8	-172.6(2)
O2	N1	C1	C2	-175.9(3)	N6	C3	C4	N3	73.4(3)
O3	N2	C1	N1	6.9(5)	N6	C3	C4	N8	-47.5(3)
O3	N2	C1	C2	-178.2(3)	N6	C5	C6	N9	-107.3(3)
O4	N2	C1	N1	-173.3(3)	N6	C5	C6	N10	78.2(4)
O4	N2	C1	C2	1.6(4)	N7	N8	C4	N3	-56.2(3)
O5	N9	C6	N10	175.8(3)	N7	N8	C4	C3	61.8(3)
O5	N9	C6	C5	1.4(4)	N7	C5	C6	N9	70.9(4)
O6	N9	C6	N10	-5.4(5)	N7	C5	C6	N10	-103.6(4)
O6	N9	C6	C5	-179.7(3)	N8	N7	C5	N6	5.6(4)
O7	N10	C6	N9	5.7(5)	N8	N7	C5	C6	-172.4(2)
O7	N10	C6	C5	179.9(3)	C2	N3	C4	N8	155.1(3)
O8	N10	C6	N9	-176.1(3)	C2	N3	C4	C3	36.5(4)
O8	N10	C6	C5	-1.9(4)	C2	N4	N5	C3	-26.0(4)

N1	C1	C2	N3	107.2(3)	C3	N6	C5	N7	3.7(5)
N1	C1	C2	N4	-72.8(4)	C3	N6	C5	C6	-178.3(3)
N2	C1	C2	N3	-67.8(4)	C4	N3	C2	N4	-13.2(4)
N2	C1	C2	N4	112.2(3)	C4	N3	C2	C1	166.8(3)
N4	N5	C3	N6	-70.0(3)	C5	N6	C3	N5	139.2(3)
N4	N5	C3	C4	50.2(3)	C5	N6	C3	C4	18.5(4)
N5	N4	C2	N3	5.2(4)	C5	N7	N8	C4	-39.8(4)

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References

1. Gao, H., Zhang, Q. & Shreeve, J.M. J. Mater. Chem. A, 2020, 8, 4193–4216
2. Gao, H. & Shreeve, Angew.Chem.Int.Ed. 2015, 54, 6335–6338.
3. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. J. Appl. Cryst. 2009, 42, 339-341.
4. Sheldrick, G.M. Acta Cryst. 2015. A71, 3-8.