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The crystal structure of 3-amino-(2,4-dioxopent-3-yl)-4,5-dihydro-1,2,4-triazinium nitrate, $C_8H_{13}N_5O_5$

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Abstract

$C_8H_{13}N_5O_5$, triclinic, $P\bar{1}$ (no. 2), $a = 9.1462(4)$ Å, $b = 9.9732(5)$ Å, $c = 13.5252(6)$ Å, $\alpha = 90.098(2)^\circ$, $\beta = 91.031(2)^\circ$, $\gamma = 109.874(2)^\circ$, $V = 1160.02(9)$ Å³, $Z = 4$, $R_{gt}(F) = 0.0392$, $wR_{ref}(F^2) = 0.1015$, $T = 150(2)$ K.

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The asymmetric unit of the title crystal structure is shown in the upper part of the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Colourless-yellow prism
Size:	$0.38 \times 0.19 \times 0.14$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	0.12 mm^{-1}
Diffractometer, scan mode:	Bruker D8 VENTURE, φ and ω
$\theta_{\max}$, completeness:	27.5° , $>99\%$
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	32137, 5341, 0.030
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 4575
$N(\text{param})_{\text{refined}}$:	329
Programs:	SHELX [1, 2], Bruker [3, 4], Platon [5]

Source of material

In a typical experiment 0.48 g of the recrystallized (heated water solution) 3-amino-1,2,4-triazine (Aldrich, 97%) was mixed with acetylacetone (Carlo Erba, 0.51 mL), 2.5 mL of 2 M nitric acid (Merck, p.a.) and water (1 mL). The mixture was left to crystallize (298 K) after stirring and dissolving. The first crystals obtained were removed from the solution, left to dry and further characterized. **FT-IR** (DRIFTS, KBr), cm^{-1} : 572m, 595m, 629m, 710m, 782m, 824m ($\nu_2 \text{ NO}_3^-$), 1051w ($\nu_1 \text{ NO}_3^-$), 1154m, 1185m, 1247m, 1272m, 1364s ($\nu_3 \text{ NO}_3^-$), 1490m, 1574m, 1664s ($\delta \text{ NH}_2$), 1678s ($\delta \text{ NH}_2$, $\nu \text{ C=O}$), 1706s ($\nu \text{ C=O}$), 1727m ($\nu \text{ C=N}$, $\nu \text{ C=O}$), 2914m ($\nu \text{ CH}_3$), 2949m ($\nu \text{ CH}_3$), 3062m

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
N11	0.07188(13)	0.84121(13)	1.03654(8)	0.0221(2)
H11	0.093938	0.856608	1.102858	0.027*
N12	−0.07681(13)	0.83526(13)	1.00836(9)	0.0233(2)
N13	0.15658(12)	0.84569(12)	0.87653(8)	0.0191(2)
H13	0.236090	0.850786	0.831735	0.023*
N14	0.32727(13)	0.87093(12)	1.00865(8)	0.0221(2)
H14A	0.398989	0.859077	0.966846	0.027*
H14B	0.340689	0.876677	1.073246	0.027*
C11	0.18675(15)	0.85368(13)	0.97311(9)	0.0163(2)
C12	−0.10714(16)	0.82704(15)	0.91600(10)	0.0227(3)
H12	−0.208996	0.822400	0.896344	0.027*
C13	0.00122(14)	0.82390(13)	0.83493(9)	0.0174(2)
H13A	0.009455	0.905770	0.790187	0.021*
C14	−0.06299(14)	0.68521(13)	0.77226(9)	0.0171(2)
H14	−0.177294	0.663106	0.761627	0.020*
C15	0.01346(15)	0.70511(15)	0.67135(10)	0.0198(3)
C16	−0.0582(2)	0.59032(19)	0.59664(12)	0.0366(4)
H16A	−0.008713	0.618939	0.532722	0.055*
H16B	−0.169644	0.574576	0.589963	0.055*
H16C	−0.043171	0.502013	0.618119	0.055*
C17	−0.03804(17)	0.55934(14)	0.82490(11)	0.0242(3)
C18	−0.1612(2)	0.47663(18)	0.89403(14)	0.0440(4)
H18A	−0.250151	0.413479	0.855890	0.066*
H18B	−0.194729	0.542659	0.933864	0.066*
H18C	−0.119386	0.419485	0.937675	0.066*
O11	0.12435(11)	0.80945(11)	0.65418(7)	0.0261(2)
O12	0.07754(15)	0.53010(14)	0.81088(11)	0.0456(3)
N15	0.15407(13)	0.84161(12)	1.28614(8)	0.0207(2)
O13	0.05087(11)	0.87001(12)	1.23703(7)	0.0271(2)
O14	0.28201(12)	0.85659(13)	1.24740(8)	0.0320(3)
O15	0.12733(13)	0.79755(14)	1.37221(8)	0.0374(3)
N21	0.62712(13)	0.82879(13)	0.53521(8)	0.0239(3)
H21	0.611322	0.818373	0.600234	0.029*
N22	0.78364(13)	0.86826(13)	0.51078(9)	0.0251(3)
N23	0.54699(13)	0.86083(12)	0.37750(8)	0.0182(2)
H23	0.465426	0.863377	0.336370	0.022*
N24	0.37641(13)	0.82233(12)	0.50727(8)	0.0221(2)
H24A	0.298105	0.821662	0.464577	0.027*
H24B	0.366405	0.820462	0.570976	0.027*
C21	0.51564(15)	0.83697(13)	0.47247(9)	0.0172(2)
C22	0.81237(16)	0.88381(16)	0.41914(10)	0.0242(3)
H22	0.918469	0.912672	0.401154	0.029*
C23	0.69402(14)	0.86076(14)	0.33657(9)	0.0177(3)
H23A	0.731544	0.944345	0.291443	0.021*
C24	0.67734(14)	0.72543(14)	0.27463(9)	0.0179(3)
H24	0.783668	0.721151	0.264340	0.022*
C25	0.58185(17)	0.59060(15)	0.32842(11)	0.0254(3)
C26	0.6696(3)	0.51314(19)	0.38435(15)	0.0471(5)
H26A	0.601029	0.449352	0.432123	0.071*
H26B	0.758133	0.582007	0.419534	0.071*
H26C	0.707517	0.457060	0.338232	0.071*
C27	0.60359(15)	0.73172(15)	0.17345(10)	0.0215(3)
C28	0.5928(2)	0.61157(18)	0.10337(12)	0.0358(4)
H28A	0.519546	0.522516	0.128735	0.054*
H28B	0.695602	0.602323	0.097340	0.054*

Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
H28C	0.556323	0.631498	0.038310	0.054*
O21	0.44111(14)	0.55221(12)	0.32541(10)	0.0428(3)
O22	0.55938(13)	0.82922(12)	0.15185(8)	0.0309(2)
N25	0.52308(14)	0.81248(13)	0.78554(8)	0.0233(2)
O23	0.53071(14)	0.80797(17)	0.87741(8)	0.0462(3)
O24	0.41608(11)	0.84244(12)	0.74288(7)	0.0269(2)
O25	0.62414(14)	0.78572(15)	0.73631(8)	0.0407(3)

(ν NH), 3138m (ν NH), 3199m (ν NH), 3262m (ν NH), 3374m (ν NH). **FT Raman** (1064 nm excitation), cm^{−1}: 113s, 144s, 170m, 572m, 632m, 787m, 1051vs (ν₁ NO₃[−]), 1162m, 1667m (δ NH₂), 1703w (ν C=O), 1727m (ν C=N, ν C=O), 2917m (ν CH₃), 2964w (ν CH₃), 3069w (ν NH).

Experimental details

The hydrogen atoms on carbons were fixed into idealised positions (riding model) and assigned temperature factors either $H_{iso}(H) = 1.2 U_{eq}$ (pivot atom) or $H_{iso}(H) = 1.5 U_{eq}$ for methyl moiety. The hydrogen atoms on nitrogen were found on difference Fourier maps and refined under rigid-body assumptions with assigned temperature factors $H_{iso}(H) = 1.2 U_{eq}$ (pivot atom).

Comment

Polarizable nitrogen-containing heteroaromatic rings are the promising molecules for crystal engineering of novel nonlinear optical materials [6, 7]. Triazines in particular are known to undergo nucleophilic addition reactions leading to chiral products [8], which can be utilized for preparation of desired crystalline products. These reactions occur not only with common nucleophiles, such as water or alcohols, but also with β-diketones (e.g. acetylacetone).

The crystal structure of the studied product contains two crystallographically independent 3-amino-5-(2,4-dioxopent-3-yl)-4,5-dihydro-1,2,4-triazinium(1+) cations (one of each enantiomer) and two nitrate anions in asymmetric unit. The heteroaromatic character of the triazine ring is affected, resulting in prolongation of N13–C13, N23–C23 and C12–C13, C22–C23 bonds. Shorter C12–N12 and C22–N22 bonds are close to imine double bond. The “guanidine” motifs (formed by N11, C11, N13, N14 and N21, C21, N23, N24 atoms) are virtually unchanged in the product and remain almost planar. In general, bond lengths and angles are all within the expectations [9]. The crystal packing involves a complex system of classical N–H⋯O and weak, non-classical C–H⋯O hydrogen bonds (lower part of the figure).

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