Supplemental Data (3 pages)

1-Butyl-3-methylimidazolium 3,5-dinitro-1,2,4-triazolate: A novel ionic liquid containing a rigid, planar energetic anion

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- 1. Experimental Details
- 2. Crystallographic details and packing diagram from crystal structure of tetrethylammonium 3,5dinitro-1,2,4-triazolate
- 3. Ab Initio computational Details for optimization of the 3,5-dinitro-1,2,4-triazolate anion

<u>1. Experimental Procedures</u>

Melting points were determined on a hot-stage apparatus and are uncorrected. Microanalyses were performed on an EA-1108 elemental analyzer. All of the chemicals were employed as supplied.

<u>Potassium 3,5-dinitro-1,2,4-triazolate</u> was prepared according to the published one-pot procedure by the reaction of cyanoguanidine with hydrazine followed by diazotization of intermediate 3,5-diamino-1*H*-triazole and substitution at the diazonium group in 46% yield.

1-Butyl-3-methylimidazolium 3,5-dinitro-1,2,4-triazolate (I). Potassium 3,5-dinitro-1,2,4-triazolate (591 mg, 3 mmol) was dissolved in acetone (20 ml) followed by the addition of dichloromethane (10 ml). 1-Methyl-3-butyl-imidazolium chloride (525 mg, 3 mmol) was dissolved in dichloromethane (20 mL) followed by the addition acetone (10 mL). The two solutions were mixed and stirred for 3 h. The resultant precipitate of potassium chloride was removed by filtration and the solvent was evaporated and the residue was dried *in vacuo*. The crude product was then extracted with acetone, the extract was filtered and the solvent was removed to give the product as a low melting pale yellow solid (690 mg, 78%). Mp 35-36 °C, (Found: C, 40.40; H, 5.10; N, 32.58. C₁₀H₁₅N₇O₄ requires C, 40.80; H, 5.09; N, 32.98), $\delta_{\rm H}$ (300 MHz; solvent CDCl₃) 0.91 (3H, t, *J* 7.4 Hz), 1.35 (2H, sex, *J* 7.3 Hz), 1.90 (2H, pen, *J* 7.4Hz), 4.13 (3H, s), 4.36 (2H, t, *J* 7.4 Hz), 7.56, 7.61 (2H, 2×s), 9.72 (1H, s), $\delta_{\rm C}$ (75 MHz; solvent CDCl₃) 13.1, 19.2, 31.9, 36.4, 49.8, 122.3, 123.8, 136.9, 163.0.

Tetramethylammonium 3,5-dinitro-1,2,4-triazolate (II). Obtained from potassium 3,5-dinitro-1,2,4-triazolate (250 mg, 1.27 mmol) in acetone/dichloromethane (1:1 ratio, 20 ml) and tetramethylammonium chloride (140 mg, 1.27 mmol) in acetone/dichloromethane (1:1 ratio, 20 ml) and isolated as a microcrystalline solid (250 mg, 84%). Mp 219-221 °C, (Found: C, 31.41; H, 5.17; N, 36.20. C₆H₁₂N₆O₄ requires C, 31.04; H, 5.21; N, 36.19), $\delta_{\rm H}$ (300 MHz; solvent CDCl₃) 3.13 (12H, s), $\delta_{\rm C}$ (75 MHz; solvent CDCl₃) 54.4 (4C, t, *J* 4 Hz), 162.9.

Tetraethylammonium 3,5-dinitro-[1,2,4]-triazolate (III). Obtained from potassium 3,5-dinitro-1,2,4-triazolate (197 mg, 1 mmol) in acetone/dichloromethane (1:1 ratio, 5 ml) and tetraethylammonium bromide (210 mg, 1 mmol) in acetone/dichloromethane (1:1 ratio, 15 ml) and isolated as a microcrystalline solid (270 mg, 94%). Colorless crystals suitable for X-ray diffraction were obtained upon recrystallization from dichloromethane/diethylether. Mp, 104-106 °C, (Found: C, 41.79; H, 7.12; N, 27.34. C₁₀H₂₀N₆O₄ requires C, 41.66; H, 6.99; N, 29.15), $\delta_{\rm H}$ (300 MHz; solvent CDCl₃) 1.40 (12H, tt, *J*₁ 7.3 Hz, *J*₂ 1.6Hz), 3.46 (8H, q, *J* 7.3 Hz), $\delta_{\rm C}$ (75 MHz; solvent CDCl₃) 7.5, 52.6 (4C, t, *J* 2.9 Hz), 163.3.

Tetrabutylammonium 3,5-*dinitro-1,2,4-triazolate* (**IV**). Obtained from potassium 3,5-*dinitro-1,2,4-triazole* (197 mg, 1.0 mmol) in acetone/dichloromethane (2:1 ratio, 15 mL) and tetrabutylammonium chloride (278 mg, 1.0 mmol) in acetone/dichloromethane (1:2 ratio, 15 mL) and tetrabutylammonium chloride (278 mg, 1.0 mmol) in acetone/dichloromethane (1:2 ratio, 15 mL) and was isolated as microcrystals (380 mg, 95%). Mp, 136–138 °C (Found: C, 53.36; H, 9.07; N, 21.51. C₁₈H₃₆N₆O₄ requires C, 53.98; H, 9.06; N, 20.98), $\delta_{\rm H}$ (300 MHz; solvent CDCl₃) 0.96 (12H, t, *J* 7.3 Hz), 1.39 (8H, sextet, *J* 7.3 Hz), 1.65–1.75 (8H, m), 3.30–3.36 (8H, m), $\delta_{\rm C}$ (75 MHz; solvent CDCl₃) 13.4, 19.6, 23.8, 58.8, 163.3.

2. Crystal Structure of III

X-ray data was collected on a Siemens CCD area detector-equipped diffractometer with Mo-K α ($\lambda = 0.71073$ Å) radiation and solved using the SHELXTL software package. All non-hydrogen atoms were anisotropically refined and all hydrogen atoms were isotropically refined. Crystal data: formula $C_{10}H_{20}N_6O_4$, M = 288.3, orthorhombic, a = 6.9962(17), b = 12.148(3) c = 16.572(4), Å, V = 1408.5(6) Å³, T = 173 K, space group $P2_12_12_1$ (no. 19), Z = 4, μ (Mo-K α) = 0.107 mm⁻¹, R1 = 0.0198, wR2 = 0.0486 (I > 2 σ (I)).



Packing diagram for **III** showing the relatively open structure. Hydrogens on the cation have been removed for clarity.

3. Ab Initio computational Details for Optimization of the 3,5-dinitro-1,2,4-triazolate anion

Ab initio calculation: Gamess Geometry Optimization, GAMESS VERSION = 12 DEC 2003 (R2)

TOTAL ENERGY = -647.3889117243 au

xyz coordinates

Atom	Туре	х	У	Z	Mulliken		
					charge		
1	N	0.0000864031	-0.6978875665	0.0050473066	-0.236235		
2	N	0.6575820731	1.4323547331	-0.0124920527	-0.171963		
3	N	-0.6579337662	1.4321562922	-0.0122496506	-0.171834		
4	N	-2.3806236868	-0.2587866222	0.0015455396	-0.306792		
5	N	2.3806660878	-0.2583830119	0.0035070576	-0.306903		
6	0	-3.2180604684	0.5863789716	0.0265844995	-0.032774		
7	0	-2.6048413455	-1.4268116798	-0.0210547911	-0.081871		
8	0	2.6046477788	-1.4266324525	0.0099298486	-0.081830		
9	0	3.2182947291	0.5869547256	0.0009201775	-0.032790		
10	С	-0.9949882444	0.1620754041	-0.0018844186	0.211413		
11	С	0.9950068393	0.1623779480	-0.0015021359	0.211579		

BOND ORDER AND VALENCE ANALYSIS BOND ORDER THRESHOLD=0.050

BOND							BOND					BOND
4 PAI	R DIST	ORDER		ATOM	PAI	R DIST	ORDER	A	MOTA	PAI	R DIST	ORDER
4	2.421	-0.058		1	5	2.421	-0.058		1	10	1.315	1.430
11	1.315	1.430		2	3	1.316	1.551		2	5	2.414	-0.072
10	2.084	-0.103		2	11	1.314	1.652		3	4	2.414	-0.072
10	1.314	1.652		3	11	2.084	-0.103		4	6	1.190	2.073
7	1.190	2.028		4	10	1.448	0.693		5	8	1.190	2.028
9	1.190	2.073		5	11	1.448	0.693		6	7	2.105	0.052
10	2.263	-0.140		7	10	2.262	-0.150		8	9	2.105	0.052
11	2.262	-0.151		9	11	2.263	-0.141		10	11	1.990	-0.307
			FOTAL		BOI	NDED	FI	REE				
ATOM		VZ	ALENCE	2	VAL	ENCE	VALEN	ICE				
Ν			2.830)	2	.830	0.0	000				
Ν			3.106	5	3	.106	0.0	000				
Ν			3.106	5	3	.106	0.0	000				
Ν			4.660)	4	.660	0.0	000				
Ν			4.660)	4	.660	0.0	000				
0			2.038	3	2	.038	0.0	000				
0			2.042	2	2	.042	0.0	000				
0			2.042	2	2	.042	0.0	000				
0			2.038	3	2	.038	0.0	000				
С			3.097	7	3	.097	0.0	000				
С			3.097	7	3	.097	0.0	000				
	M PAI 4 11 10 7 9 10 11 ATOM N N N N N N N O O O C C	<pre>M PAIR DIST 4 2.421 11 1.315 10 2.084 10 1.314 7 1.190 9 1.190 10 2.263 11 2.262 ATOM N N N N N N O O O O O O C C C C</pre>	BOND M PAIR DIST ORDER 4 2.421 -0.058 11 1.315 1.430 10 2.084 -0.103 10 1.314 1.652 7 1.190 2.028 9 1.190 2.073 10 2.263 -0.140 11 2.262 -0.151 M N N N N N N N N N O O O C C C	BOND M PAIR DIST ORDER 4 2.421 -0.058 11 1.315 1.430 10 2.084 -0.103 10 1.314 1.652 7 1.190 2.028 9 1.190 2.073 10 2.263 -0.140 11 2.262 -0.151 TOTAL ATOM VALENCH N 2.830 N 3.106 N 4.660 O 2.038 O 2.042 O 2.042 O 2.042 O 2.038 O 2.042 O 2.042 O 2.038 O 2.042 O 2.042 O 2.038 O 2.042 O 2.042 O 2.038 O 2.042 O 2.038 O 2.042 O 2.042 O 2.038 O 2.042 O 2.038 O 2.042 O 2.042	BOND M PAIR DIST ORDER ATOM 4 2.421 -0.058 1 11 1.315 1.430 2 10 2.084 -0.103 2 10 1.314 1.652 3 7 1.190 2.028 4 9 1.190 2.073 5 10 2.263 -0.140 7 11 2.262 -0.151 9 TOTAL ATOM VALENCE N 2.830 1.06 N 2.830 3.106 N 3.106 1.4660 N 4.660 2.038 O 2.038 2.042 O 2.038 2.042 O 2.038 2.038 C 3.097 3.097	BOND M PAIR DIST ORDER ATOM PAIR 4 2.421 -0.058 1 5 11 1.315 1.430 2 3 10 2.084 -0.103 2 11 10 1.314 1.652 3 11 7 1.190 2.028 4 10 9 1.190 2.073 5 11 10 2.263 -0.140 7 10 11 2.262 -0.151 9 11 TOTAL BOY ATOM VALENCE VAL N 2.830 2 N 3.106 3 N 4.660 4 N 2.038 2 0 2.042 2 0 2.042 2 0 2.042 2 0 2.042 2 0 2.042 2 0 2.038 2 0 2.042 2 0 2.042 2 0 2.042 2 0 2.042 3 0 3.097 3	BOND M PAIR DIST ORDER ATOM PAIR DIST 4 2.421 -0.058 1 5 2.421 11 1.315 1.430 2 3 1.316 10 2.084 -0.103 2 11 1.314 10 1.314 1.652 3 11 2.084 7 1.190 2.028 4 10 1.448 9 1.190 2.073 5 11 1.448 10 2.263 -0.140 7 10 2.262 11 2.262 -0.151 9 11 2.263 TOTAL BONDED ATOM XALENCE VALENCE N 2.830 2.830 N 3.106 3.106 N 3.106 3.106 N 4.660 4.660 N 4.660 4.660 N 4.660 4.660 Q 2.042 2.042 O 2.042 2.042 0	BOND BOND M PAIR DIST ORDER ATOM PAIR DIST ORDER 4 2.421 -0.058 1 5 2.421 -0.058 11 1.315 1.430 2 3 1.316 1.551 10 2.084 -0.103 2 11 1.314 1.652 10 1.314 1.652 3 11 2.084 -0.103 7 1.190 2.028 4 10 1.448 0.693 9 1.190 2.073 5 11 1.448 0.693 10 2.263 -0.140 7 10 2.262 -0.150 11 2.262 -0.151 9 11 2.263 -0.141 TOTAL BONDED FH ATOM VALENCE VALENCE VALEN N 2.830 2.830 0.00 N 3.106 3.106 0.00 N 3.106	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	BOND BOND M PAIR DIST ORDER ATOM PAIR DIST ORDER 1 10 1.315 14 2.421 -0.058 1 5 2.421 -0.058 1 10 1.315 11 1.315 1.430 2 3 1.316 1.551 2 5 2.414 10 1.314 1.652 3 11 2.084 -0.103 4 6 1.190 7 1.190 2.028 4 10 1.448 0.693 6 7 2.105 10 2.263 -0.140 7 10 2.262 -0.150 8 9 2.105 11 2.263 -0.140 7 10