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

1. Experimental Procedures

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.

Potassium 3,5-dinitro-1,2,4-triazolate 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. $C_{10}H_{15}N_7O_4$ requires C, 40.80; H, 5.09; N, 32.98), δ_H (300 MHz; solvent $CDCl_3$) 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), δ_C (75 MHz; solvent $CDCl_3$) 13.1, 19.2, 31.9, 36.4, 49.8, 122.3, 123.8, 136.9, 163.0.

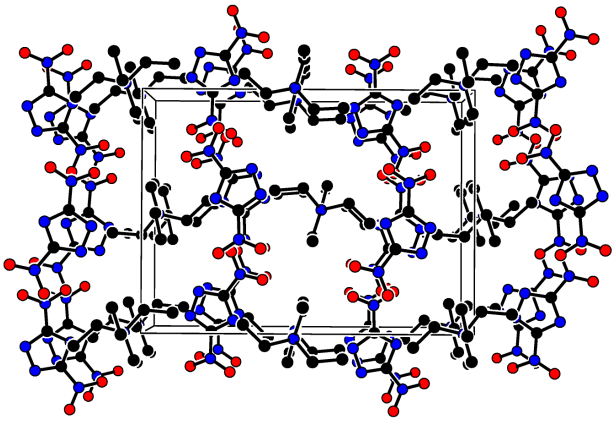
Tetramethylammonium 3,5-dinitro-1,2,4-triazolate (**II**). Obtained from potassium 3,5-dinitro-1,2,4-triazolate (250 mg, 1.27 mmol) in acetone/dichloromethane (1:1 ratio, 20 ml) and tetramethylammonium chloride (140 mg, 1.27 mmol) in acetone/dichloromethane (1:1 ratio, 20 ml) and isolated as a microcrystalline solid (250 mg, 84%). Mp 219-221 °C, (Found: C, 31.41; H, 5.17; N, 36.20. $C_6H_{12}N_6O_4$ requires C, 31.04; H, 5.21; N, 36.19), δ_H (300 MHz; solvent $CDCl_3$) 3.13 (12H, s), δ_C (75 MHz; solvent $CDCl_3$) 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, 1mmol) 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. $C_{10}H_{20}N_6O_4$ requires C, 41.66; H, 6.99; N, 29.15), δ_H (300 MHz; solvent $CDCl_3$) 1.40 (12H, tt, J_1 7.3 Hz, J_2 1.6Hz), 3.46 (8H, q, *J* 7.3 Hz), δ_C (75 MHz; solvent $CDCl_3$) 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 was isolated as microcrystals (380 mg, 95%). Mp, 136–138 ºC (Found: C, 53.36; H, 9.07; N, 21.51. $C_{18}H_{36}N_6O_4$ requires C, 53.98; H, 9.06; N, 20.98), δ_H (300 MHz; solvent $CDCl_3$) 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), δ_C (75 MHz; solvent $CDCl_3$) 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-Kα (λ = 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) $Å^3$, T = 173 K, space group $P2_12_12_1$ (no. 19), Z = 4, μ(Mo-Kα) = 0.107 mm^{-1}, R1 = 0.0198, wR2 = 0.0486 ($I > 2\sigma(I)$).



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	Type	x	y	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	O	-3.2180604684	0.5863789716	0.0265844995	-0.032774
7	O	-2.6048413455	-1.4268116798	-0.0210547911	-0.081871
8	O	2.6046477788	-1.4266324525	0.0099298486	-0.081830
9	O	3.2182947291	0.5869547256	0.0009201775	-0.032790
10	C	-0.9949882444	0.1620754041	-0.0018844186	0.211413
11	C	0.9950068393	0.1623779480	-0.0015021359	0.211579

BOND ORDER AND VALENCE ANALYSIS BOND ORDER THRESHOLD=0.050

ATOM	PAIR	DIST	BOND ORDER	ATOM	PAIR	DIST	BOND ORDER	ATOM	PAIR	DIST	BOND ORDER
1	4	2.421	-0.058	1	5	2.421	-0.058	1	10	1.315	1.430
1	11	1.315	1.430	2	3	1.316	1.551	2	5	2.414	-0.072
2	10	2.084	-0.103	2	11	1.314	1.652	3	4	2.414	-0.072
3	10	1.314	1.652	3	11	2.084	-0.103	4	6	1.190	2.073
4	7	1.190	2.028	4	10	1.448	0.693	5	8	1.190	2.028
5	9	1.190	2.073	5	11	1.448	0.693	6	7	2.105	0.052
6	10	2.263	-0.140	7	10	2.262	-0.150	8	9	2.105	0.052
8	11	2.262	-0.151	9	11	2.263	-0.141	10	11	1.990	-0.307

	ATOM	TOTAL VALENCE	BONDED VALENCE	FREE VALENCE
1	N	2.830	2.830	0.000
2	N	3.106	3.106	0.000
3	N	3.106	3.106	0.000
4	N	4.660	4.660	0.000
5	N	4.660	4.660	0.000
6	O	2.038	2.038	0.000
7	O	2.042	2.042	0.000
8	O	2.042	2.042	0.000
9	O	2.038	2.038	0.000
10	C	3.097	3.097	0.000
11	C	3.097	3.097	0.000