The synthesis and energetic properties of pyridinium and triazolium *N*-(nitrobenzoyl)-imides

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Abstract
Syntheses of nitrogen rich, energetic *N*-(nitro-substituted-benzoylimino)pyridinium and *N*-(nitro-substituted-benzoylimino)1,2,4-triazolium imides are reported and their energetic properties calculated/determined in terms of heats of formation (HOF), densities, detonation parameters, heats of decomposition and heats of combustion.

Keywords: Synthesis, pyridinium nitrobenzoyl imide, triazolium nitrobenzoyl imide, energetic properties

Introduction

During the last 60 years substantial efforts have been made to synthesize insensitive, high energy materials as alternatives to existing high explosives such as RDX (cyclotrimethylene-trinitramine), HMX (1,3,5,7-tetranitrooctahydro-1,3,5,7-tetrazocine), PETN (pentaerythritol tetranitrate), and CL20 (hexanitrohexaazaisowurtzitane).[1] Insensitive, mechanically and thermally stable explosives are required for use as ammunition and in technical areas such as nuclear fission, space, oil and ore exploration.[2-4] To this end many compounds such as PYX [3,5-dinitro-2,6-bis(picrylamino)pyridine], NTO (3-nitro-1,2,4-triazol-5-one), ONC (octanitro-cubane), TATB (1,3,5-triamino-2,4,6-trinitrobenzene) and DATB (1,3-diamino-2,4,6-trinitro-

benzene) have been synthesized and tested. TATB and DATB have been known since the 1880s, but ignored due to their large critical diameter and insensitivity to initiation which made efficient detonation almost impossible. The performance of TATB and DATB-based compositions may be modified by addition of more energetic explosives such as RDX, HMX and/or CL-20 thus enabling the compositions to be detonated.[4,5] Another way to solve the problem is to develop PBXs (plastic-bonded explosives) for military and civilian purposes by de-sensitization of HMX and PETN with appropriate plasticizers and binders. Among approaches towards Insensitive High Explosives (IHEs), raising nitrogen content by the use of heterocyclic nuclei instead of carbocyclic structures improves oxygen balance and forms N_2 as a product of explosion. Consequently, studies based on heterocyclic nitrogen compounds for IHEs have become popular.[6]

Benzotriazole is a synthetic auxiliary that offers many advantages in organic synthesis since it is easy to introduce, activates molecules towards numerous transformations, and can be removed easily at the end of a reaction.[7] In a continuing effort to explore the chemistry of compounds that are safe to handle and more cost-efficient to produce, we investigated the synthesis of nitro-substituted *N*-benzoylimides as potential candidates for energetic materials using acylbenzotriazoles rather than acid chlorides as the reactive starting materials.[8]

Results and Discussion

Preparation of intermediate acyl benzotriazoles **2a-e** was achieved by a one-step reaction as shown in Scheme 1.[9,10]

R = **a**, 2-nitro, **b**, 3-nitro, **c**, 4-nitro, **d**, 2,4-dinitro, **e**, 3,5-dinitro
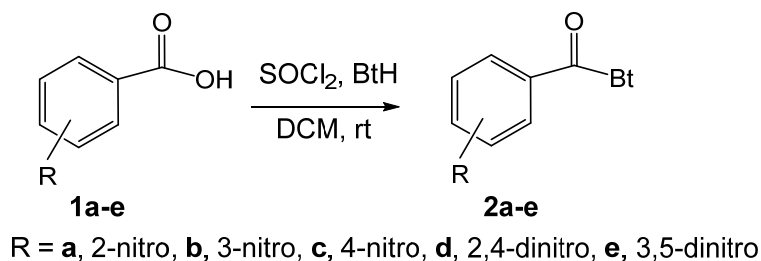
**Scheme 1.** Synthesis of acylbenzotriazoles **2a-e**.

The target heterocyclic nitro-substituted benzoylimides were prepared *via* the acylbenzotriazole method, which was much more convenient than the previously used acid chloride route[8] and gave almost quantitative yields. In a typical example, potassium carbonate was added to a solution of 1-aminopyridinium iodide or 4-amino-1-methyl-1*H*-1,2,4-triazol-4-ium iodide in acetonitrile. The reaction mixture was stirred at room temperature and then the appropriate aroylbenzotriazole was added in one portion. After one hour stirring, the inorganic salts were filtered off through celite and the filtrate was concentrated *in vacuo* to give the crude product, which was purified by column chromatography over silica gel with ethyl

acetate/hexanes and then acetonitrile/methanol as eluents to afford pure material (Schemes 2 and 3).
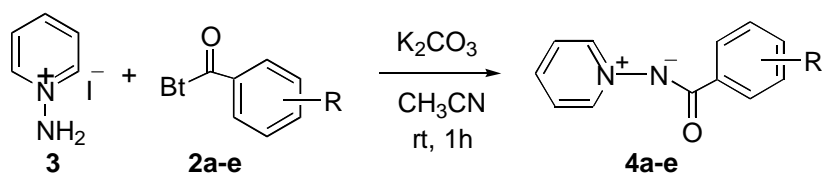
R = **a**, 2-nitro; **b**, 3-nitro; **c**, 4-nitro; **d**, 2,4-dinitro; **e**, 3,5-dinitro

Scheme 2. Synthesis of nitrobenzoyl pyridin-1-ium-1-yl imides **4a-e**.
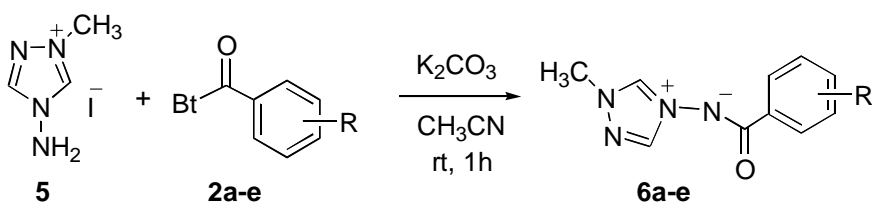
R = **a**, 2-nitro; **b**, 3-nitro; **c**, 4-nitro; **d**, 2,4-dinitro; **e**, 3,5-dinitro

Scheme 3. Synthesis of 1-methyl-1*H*-1,2,4-triazol-4-ium-4-yl nitrobenzoyl imides **6a-e**.

Table 1 shows the melting points, heats of decomposition (ΔH_d) and heats of combustion (ΔH_c) of the pyridinium (**4a-e**) and triazolium (**6a-e**) aroyl ylides as determined by differential scanning calorimetry (for ΔH_d) or adiabatically in a Parr Oxygen Bomb Calorimeter (for ΔH_c).
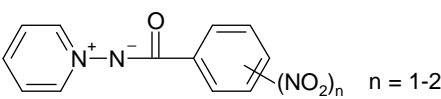
Table 2 shows the energetic properties of **4a-e** and **6a-e** including calculated heats of formation (ΔH_f) and densities (ρ), experimental densities determined by gas pycnometer and explosion parameters as calculated by Explo5 v.6.01 software.

The data in Table 1 and 2 are insufficient to determine whether or not a correlation exists between ΔH_d and ΔH_f but Table 2 reveals that both $\rho_{(calcd)}$ and $\rho_{(exp)}$ increase with the number of nitro groups present in the molecules. There is however, a distinct difference between the HOF values of the pyridinium and triazolium ylides with the latter some 90 kJ mol^{-1} higher in energy. Although the data are limited it is clear that addition of an *ortho*-nitro group over *meta* or *para* analogues adds ca.16–18 kJ mol^{-1} in both series. In comparison with RDX however, the densities, detonation pressures (P_D), detonation velocities (V_D) and specific impulses (Isp) are all greatly inferior. Thus it is expected that none of these compounds would afford useful explosives. On the basis of the correlation between $\rho_{(calcd)}$ and $\rho_{(exp)}$, the predicted density for 2,4,6-trinitroaroyl triazolium ylid **6f** is ca. 1.70 g/cm^3 and calculated HOF = 310 kJmol^{-1}, still

well short of RDX values. Considering the hazards associated with the use of trinitrobenzoic acid we decided not to attempt a synthesis of **6f** (Figure 1).
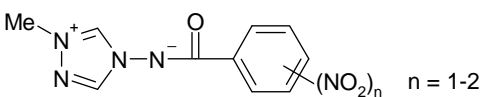
Table 1. Melting points, heats of decomposition and heats of combustion of pyridinium (**4a-e**) and triazolium (**6a-e**) nitrobenzoyl ylides

Pyridinium imides:

Compound	DSC mp ($\circ$C)	ΔH_d (exp.) (kJ mol^{-1})	ΔH_c (exp.) (kJ mol^{-1})
4a	136.2^a	-37.0	-7989
4b	168.1	-24.7	-5100
4c	257.3^a	-95.6	-6464
4d	220.6	-134	-4663
4e	213.1	-52.2	-2897

Triazolium imides:

Compound	DSC mp (^{o}C)	ΔH_d (exp.) (kJ mol^{-1})	ΔH_c (exp.) (kJ mol^{-1})
6a	183.6	-39.4	-5100
6b	245.4^a	-65.3	-5300
6c	231.5^a	-80.0	-5399
6d	203.3	-192	-5195
6e	232.2^a	-141	-4900

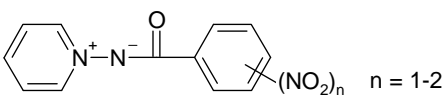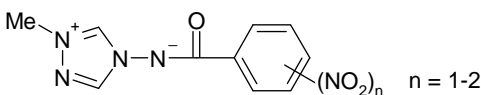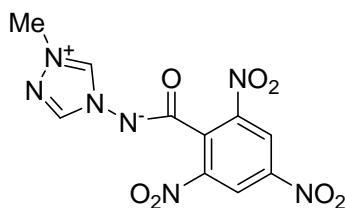^{a} Samples decomposed on melting.

Figure 1. Structure of **6f**.

Table 2. Heats of formation, densities and explosion parameters for pyridinium and triazolium ylides

Pyridinium imides:

Compound	ΔH_f (calc.)[a] (kJ mol^{-1})	ρ		P_D (calc.) (GPa)	V_D (calc.) (m/s)	I_{sp} (calc.) (s)
		calc	exp			
4a	184	1.128	1.39	8.69	5323	175.5
4b	166	1.125	1.51	10.69	5812	174.1
4c	171	1.126	1.50	10.60	5775	174.4
4d	177	1.240	1.58	12.51	6090	191.6
4e	161	1.230	1.57	13.93	6373	190.2

Triazolium imides:

Compound	ΔH_f (calc.)[a] (kJ mol^{-1})	ρ		P_D (calc.) (GPa)	V_D (calc.) (m/s)	I_{sp} (calc.) (s)
		calc.	exp.			
6a	276	1.174	1.51	13.26	6360	190.5
6b	258	1.166	1.55	14.01	6518	188.9
6c	262	1.168	1.55	14.13	6524	189.2
6d	262	1.276	1.62	17.82	7042	204.1
6e	251	1.275	1.61	17.43	6987	203.2
RDX	80	–	1.82	34.9	8748	258

[a] Determined by PM6.

The structures of ylides **4e** and **6d** were confirmed by X-ray crystallography (Figure 2) and in both cases the densities as determined by X-ray crystallography at 120K (1.585 and 1.669 respectively) were in good agreement with the pycnometer results. The most noteworthy features of the structures concern the relative orientations of the rings. In the case of **4e** the amide function is almost coplanar with the dinitrophenyl ring (angle between mean planes = 7.2 °) whereas the pyridinium ring is almost orthogonal (74.6 °) to the nitroaromatic ring. However, due to the presence of the *ortho* nitro group, in **6d** the amide group is highly twisted (65.3 °) out of the plane of the dinitrophenyl ring. In this case the two rings are inclined at an angle of 43.4 °.
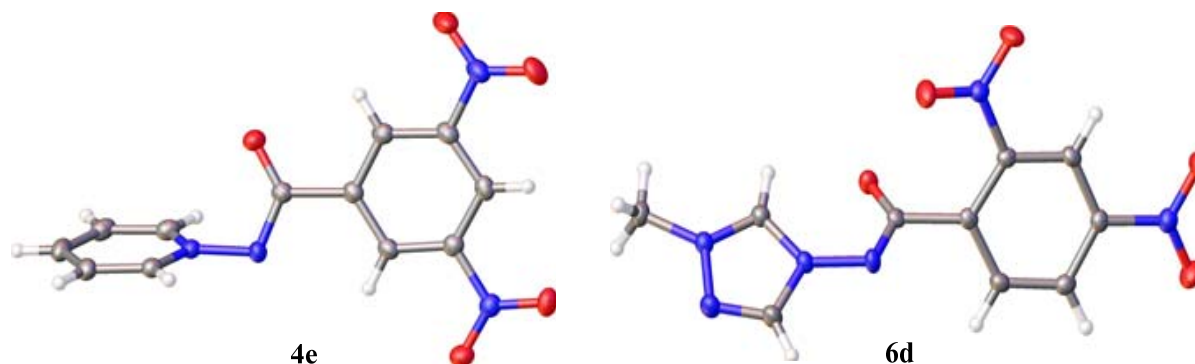
Figure 2. X-ray crystal structures of **4e** and **6d**.

Conclusions

In conclusion we have developed general conditions for the synthesis of energetic, nitrogen rich *N*-(nitro-substituted-benzoylimino)pyridinium and 1,2,4-triazolium imides *via* readily available acylbenzotriazoles. This strategy provides unprecedented synthetic advantages including shorter reaction times, higher yields and easier purification than the acid chloride method. However, the energetic parameters of the compounds synthesized fall short of those required for an effective explosive.

Experimental Section

Caution. Although we encountered no difficulties with the preparation or isolation of these compounds, synthetic work was restricted to the millimolar scale and care was taken to avoid impact, friction or overheating.

General. Melting points were determined on a capillary tube melting point apparatus equipped with a digital thermometer and are uncorrected. NMR spectra were recorded in DMSO-d_6 with TMS as the internal standard for [1]H (300 MHz) or in DMSO-d_6 with the residual solvent peak as the internal standard for [13]C (75 MHz), unless otherwise specified. Chemical shifts were reported in parts per million relative to the residual solvent peak. Individual peaks were reported as multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet) and coupling constants in Hertz (Hz). Elemental analyses were performed on a Carlo Erba EA 1108 elemental analyzer, Dept. of Chem., University of Florida. All reactions were carried out under nitrogen atmosphere. All reagents were purchased from commercial sources and used without treatment unless otherwise indicated. Column chromatography was performed with S733-1 silica gel (200–425 mesh). Combustion analysis was performed using a Parr Oxygen Bomb Calorimeter, under an atmosphere of excess oxygen at approximately 25 atm. All combustion residues were titrated as nitric acid to account for the formation of NO_x as a combustion by-product. Determination of

heats of decomposition was conducted using a DuPont Instruments DSC 2910 differential scanning calorimeter. Samples were heated from 100 ºC–500 ºC in hermetic aluminum pans, with helium as the purge gas. All sample pan lids were perforated to allow venting of gaseous products.

Densities were determined at room temperature by employing a Micromeritics AccuPyc 1330 gas pycnometer. The mass of the samples were determined on a Mettler Toledo AB104-S balance, and the volumes of the samples were measured by using the pycnometer - an average of 3 measured volumes was used to calculate the density. Sample density was calculated from the ratio of *mass* (m) to *volume* (V). ($d(g/cm^3) = m(g)/V(cm^3)$).

The detonation velocity (V_D), detonation pressure (P_D) and specific impulse (I_{Sp}) were calculated based on the calculated heat of formation values using Explo5 v.6.01.

Calculation of heats of formation and densities. The compounds were drawn in ChemDraw followed by 2D to 3D conversion using MM2[11] minimization in Chem3D.[12] The 3D geometries were parameterized using PM6[13] for further semi-empirical calculation. Geometry optimization followed by frequency calculation was performed using AMPAC software.[14] The geometries were optimized to their energy minima using Trust algorithm which reduces the number of cycles and refines the precision of the calculation at each step. The optimized geometries were loaded to Codessa III[15] and MOE-2014[16] software for the calculation of van der Waal's volume, densities and heats of formation.

General method for the preparation of (nitrobenzoyl)(pyridin-1-ium-1-yl)-imides 4a-e. Potassium carbonate (7.5 mmol) was added to a solution of *N*-aminopyridinium iodide **3** (2.5 mmol) in acetonitrile (25 mL) and the reaction mixture was stirred vigorously for 20 min at room temperature to give a purple solution, to which each acylbenzotriazole (**2a–e**, 2.5 mmol) was added in one portion. The mixtures were stirred at 20 °C for 1 h. The inorganic salts were filtered through celite and the filtrate was evaporated to dryness to give solids, which were purified by column chromatography over silica gel using first a gradient mixture of ethyl acetate/hexanes (1/10–1/2, v/v) as eluent to remove benzotriazole and then a mixture of acetonitrile/methanol (10/1, v/v) as eluent to give the products. Samples for elemental analysis were recrystallized from a mixture of acetonitrile and ethanol (1/1, v/v).

(2-Nitrobenzoyl)(pyridin-1-ium-1-yl)imide (4a). Yield 99%, off-white needles, mp 101–103 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.72 (d, *J* 5.7 Hz, 2H), 8.23 (t, *J* 7.88 Hz, 1H), 7.95 (t, *J* 7.10 Hz, 2H), 7.82 (d, *J* 8.1, 2H), 7.69 (t, *J* 7.7 Hz, 1H), 7.59 (t, *J* 8.3 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 168.1, 149.0, 142.9, 139.2, 133.9, 132.2, 129.7, 129.6, 127.1, 123.2. Anal. Calcd. for $C_{12}H_9N_3O_3$: C, 59.26; H, 3.73; N, 17.28. Found: C, 58.94; H, 3.47; N, 17.21 %.

(3-Nitrobenzoyl)(pyridin-1-ium-1-yl)imide (4b). Yield 98%, colorless microcrystals, mp 174–176 °C [lit.[8] mp 175.5–176.0 °C]. ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.86 (d, *J* 6.3 Hz, 2H), 8.79 (s, 1H), 8.43 (d, *J* 7.5 Hz, 1H), 8.30 (d, *J* 8.1 Hz, 1H), 8.23 (t, *J* 8.0 Hz, 1H), 7.94 (t, *J* 6.9 Hz,

2H) 7.71 (t, *J* 8.0 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 166.5, 147.5, 143.4, 139.6, 139.0, 133.9, 129.5, 126.9, 124.5, 122.1.

(4-Nitrobenzoyl)(pyridin-1-ium-1-yl)imide (4c). Yield 90%, colorless solids, mp 260–262 °C [lit.[16] mp 253 °C]. ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.86 (dd, *J* 6.9, 1.2 Hz, 2H), 8.26 (s, 4H), 8.23 (t, *J* 7.8 Hz, 1H), 7.94 (t, *J* 7.4 Hz, 2H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 166.8, 148.2, 144.1, 143.3, 139.0, 128.8, 126.9, 123.0.

(2,4-Dinitrobenzoyl)(pyridin-1-ium-1-yl)imide (4d). Yield 95%, colorless solid, mp 222–224 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.76 (dd, *J* 6.8, 1.4 Hz, 2H), 8.67 (d, *J* 2.4 Hz, 1H), 8.53 (dd, *J* 8.4, 2.1 Hz, 1H), 8.27 (tt, *J* 7.8, 1.4 Hz, 1H), 8.09 (d, *J* 8.4 Hz, 1H), 7.98 (t, *J* 7.1 Hz, 2H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 166.5, 148.6, 147.2, 142.9, 139.7, 139.2, 131.2, 127.2, 126.9, 119.0. Anal. Calcd. for $C_{12}H_8N_4O_5$: C, 50.01; H, 2.80; N, 19.44. Found: C, 50.06; H, 2.48; N, 19.13 %.

(3,5-Dinitrobenzoyl)(pyridin-1-ium-1-yl)imide (4e). Yield 99%, colorless prisms, mp 216–218 °C [lit.[8] mp 215–217 °C]. ^{1}H NMR (300 MHz, DMSO-d_6): δ 9.07 (d, *J* 2.1 Hz, 2H), 8.92-8.80 (m, 3H), 8.27 (tt, *J* 7.7, 1.4 Hz, 1H), 8.01-7.95 (m, 2H) ^{13}C NMR (75 MHz, DMSO-d_6): δ 164.7, 147.9, 143.2, 141.2, 139.5, 127.2, 127.0, 119.5.

General method for the preparation of (1-methyl-1*H*-1,2,4-triazol-4-ium-4-yl) (nitrobenzoyl)-imides 6a-e. Potassium carbonate (6.0 mmol) was added to a solution of 4-amino-1-methyl-1*H*-1,2,4-triazol-4-ium iodide **5** (2.0 mmol) in acetonitrile (20 mL) and the reaction mixture was stirred vigorously for 20 min at room temperature and each (1*H*-benzo[d][1,2,3]triazol-1-yl) (nitrophenyl)methanone **2a-e** (2.0 mmol) was added in one portion. The mixtures were stirred at rt for 1 h. The inorganic salts were filtered off through celite and the filtrates concentrated in vacuo to give the crude products, which were purified by column chromatography over silica gel using first a mixture of ethyl acetate/hexanes (1/10-1/2, v/v) as eluent to remove free benzotriazole and then a mixture of acetonitrile/methanol (10/1, v/v) as eluent to give the product. Samples for elemental analysis were recrystallized from ethyl acetate.

(1-Methyl-1*H*-1,2,4-triazol-4-ium-4-yl)(2-nitrobenzoyl)imide (6a). Yield 98%, colorless prisms, mp 185–187 °C [lit.[8] mp 180–182 °C]. ^{1}H NMR (300 MHz, DMSO-d_6): δ 10.58 (s, 1H), 9.15 (s, 1H), 7.79–7.74 (m, 2H), 7.64 (td, *J* 7.5, 1.5 Hz, 1H), 7.56 (tt, *J* 7.5, 1.5 Hz, 1H), 4.02 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 166.5, 149.2, 142.3, 139.6, 133.7, 131.8, 129.6, 129.5, 123.0, 38.4. Anal. Calcd. for $C_{10}H_9N_5O_3$: C, 48.59; H, 3.67; N, 28.33. Found: C, 48.53; H, 3.42; N, 28.62 %.

(1-Methyl-1*H*-1,2,4-triazol-4-ium-4-yl)(3-nitrobenzoyl)imide (6b). Yield 94%, colorless microcrystals, mp 244–246 °C [lit.[8] mp 243–245 °C] ^{1}H NMR (300 MHz, DMSO-d_6): δ 10.65 (s, 1H), 9.27 (s, 1H), 8.77–8.75 (m, 1H), 8.42–8.38 (m, 1H), 8.29–8.24 (m, 1H), 7.69 (t, J 8.0 Hz, 1H), 4.04 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 165.4, 147.5, 142.6, 139.8, 139.8, 133.7, 129.5, 124.2, 121.8, 38.5. Anal. Calcd. for $C_{10}H_9N_5O_3$: C, 48.59; H, 3.67; N, 28.33. Found: C, 48.70; H, 3.41; N, 28.70 %.

(1-Methyl-4*H*-1,2,4-triazol-1-ium-4-yl)(4-nitrobenzoyl)imide (6c). Yield 92%, colorless solid, mp 234–236 °C [lit.[8] mp 235–237 °C]. ^{1}H NMR (300 MHz, DMSO-d_6): δ 10.65 (s, 1H), 9.25 (s, 1H), 8.24 (d, *J* 8.7 Hz, 2H), 8.20 (d, *J* 8.7 Hz, 2H), 4.04 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d6): δ 165.8, 148.1, 144.3, 142.6, 139.8, 128.6, 123.0, 38.5.

(2,4-Dinitrobenzoyl)(1-methyl-1*H*-1,2,4-triazol-4-ium-4-yl)imide (6d). Yield 96%, beige prisms, mp 208–210 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 10.61 (s, 1H), 9.21 (s, 1H), 8.63 (d, *J* 2.4 Hz, 1H), 8.48 (dd, *J* 8.4, 2.4 Hz, 1H), 8.04 (d, *J* 8.4 Hz, 1H), 4.03 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 164.7, 148.9, 147.2, 142.3, 139.7, 138.9, 131.1, 126.5, 118.8, 38.5. Anal. Calcd. for $C_{10}H_8N_6O_5$: C, 41.10; H, 2.76; N, 28.76. Found: C, 41.47; H, 2.53; N, 28.34 %.

(3,5-Dinitrobenzoyl)(1-methyl-1*H*-1,2,4-triazol-4-ium-4-yl)imide (6e). Yield 97%, colorless solid, mp 235–236 °C;[lit.[8] mp 235–236 °C] ^{1}H NMR (300 MHz, DMSO-d_6): δ 10.71 (s, 1H), 9.35 (s, 1H), 9.03 (d, *J* 2.4 Hz, 2H), 8.86 (t, *J* 2.1 Hz, 1H), 4.06 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 163.2, 147.9, 142.5, 141.3, 139.8, 126.9, 119.2, 38.5.

X-Ray crystallography
The X-ray single crystal diffraction data for **4e** and **6d** were collected at 120 K on an Agilent SuperNova instrument with focussed microsource Cu Kα radiation (λ = 1.5418 Å) and ATLAS CCD area detector. The structures were solved using direct methods with SHELXS[17] and refined on F^2 using all data by full–matrix least square procedures with SHELXL–97.[17] Multiscan absorption corrections were done using SCALE3 ABSPACK. The non–hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were included in calculated positions with isotropic displacement parameters 1.2 times the isotropic equivalent of their carrier atoms.

Crystal data for **4e (CCDC 1429989)**: $C_{12}H_8N_4O_5$, FW 288.22, monoclinic, space group P2$_1$/c, *a* = 12.5016(4), *b* = 5.7712(2), *c* = 16.7640(6) Å, β = 93.206(3)^o, V = 1207.61(7)Å^3, F(000) = 592, Z = 4, T = -153 ^{o}C, μ(MoKα) = 1.092 mm^{-1}, ρ_{calcd} = 1.585 g.cm^{-3}, 2θ_{max} 134°, GOF = 1.08, wR(F^2) = 0.0943 (all 2162 data), R = 0.0361 (1924 data with I > 2σI).

Crystal data for **6d (1429990)**: $C_{10}H_8N_6O_5$, FW 292.21, triclinic, space group P-1, *a* = 7.1633(4), *b* = 8.0803(5), *c* = 11.2680(7) Å, α = 69.534(6), β = 72.136(5)^o, γ = 85.275(5)^o, V = 581.36(7)Å^3, F(000) = 300, Z = 2, T = -153 ^{o}C, μ(MoKα) = 1.191 mm^{-1}, ρ_{calcd} = 1.669 g.cm^{-3}, 2θ_{max} 135°, GOF = 1.07, wR(F^2) = 0.0959 (all 2101 data), R = 0.0361 (1972 data with I > 2σI).

Supplementary Material

[1]H, ^{13}C spectra, elemental analyses for all obtained compounds. CIF files for compounds **4e**, **6d**.

Acknowledgements

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