Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic Supplementary Information

Exploiting the Potential of Energetic 1,2,4-Oxadiazole Derivatives: Combining the Benefits of 1,2,4-Oxadiazole Framework with Various Energetic Functionalities

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1. The crystallographic data and crystal structure

Table S1. X-ray data and parameters of energetic salts **5**, **6a**, **6c**, **8** and **8a.**

	5	**6a**	**6c**	**8**	**8a**
Chemical formula	$C_3H_1N_4O_5K$	$C_3H_5N_5O_5$	$C_3H_5N_5O_6$	$C_3H_2N_6O_2$	$C_3H_5N_7O_2$
Formula mass	212.18	191.10	207.12	154.09	171.12
Crystal system	triclinic	triclinic	triclinic	orthorhombic	monoclinic
a/Å	6.8618(10)	7.0339(14)	6.7360(7)	9.0167(19)	3.7059(9)
b/Å	7.1833(10)	7.2398(14)	8.1254(9)	10.224(2)	25.344(6)
c/Å	7.7371(11)	7.9636(15	8.4748(9)	13.146(3)	7.2132(17)
α/°	84.776(3)	84.593(3)	62.402(2)	90	90
β/°	82.401(3)	83.386(4)	83.171(2)	90	101.824(4)
γ/°	64.520(2)	64.874(3)	65.905(2)	90	90
Volume/Å^3	341.00(8)	364.26(12)	373.84(7)	1211.9(4)	663.1(3)
Temperature/K	173	173	173	173	173
Space group	*P*-1	*P*-1	*P* -1	*Pbca*	*Cc*
Z	2	2	2	8	4
Radiation type	Mo-Ka	Mo-Ka	Mo-Ka	Mo-Ka	Mo-Ka
μ/mm^{-1}	0.778	0.164	0.177	0.144	0.145
Density$_{calcd}$/g cm^{-3}	2.066	1.743	1.840	1.689	1.714
F(000)	212.0	196.0	212.0	624.0	352.0
2Θ range for data collection/°	5.316 to 55.064	5.156 to 54.102	5.444 to 55.008	6.198 to 54.966	6.43 to 54.856
Index ranges	-	-8/9;-8/9; -9/10	-8:8; -10:9; -9:11	-11/11;-10/13; -17/17	-4/4;-32/32; -8/ 9
Reflections collected	1511	3072	4266	8094	2873
Independent reflections	1511	1544	1699	1385	1420
R$_{int}$	-	0.0263	0.0186	0.0315	0.0294
Data/restraints/ parameters	1511/0/122	1544/0/134	1699/0/133	1385/0/108	1420/5/124
R_1 / wR_2 [all data]	0.0343/0.1055	0.0585/0.1530	0.0367/0.0995	0.0422/0.0933	0.0409/0.0776
R_1 / wR_2 [I > 2σ(I)]	0.0330/0.1038	0.0516/0.1467	0.0333/0.0961	0.0368/0.0900	0.0354/0.0746
Goodness-of-fit on F^2	1.157	1.056	1.071	1.120	1.032
CCDC number	1558516	1558515	1558514	1558528	1558529

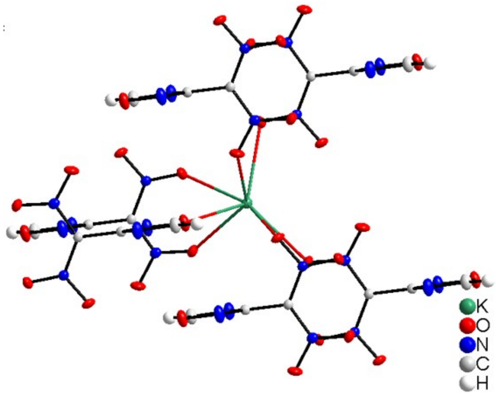


Figure S1. The coordination mode of potassium atom in compound **5**.

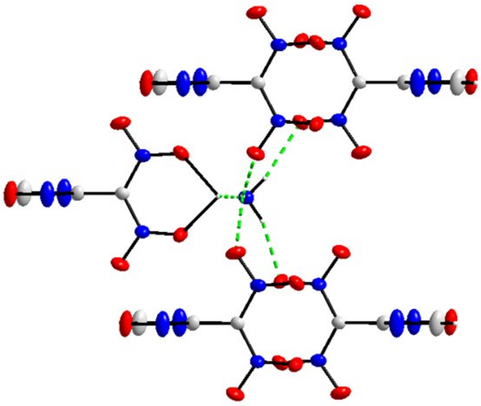


Figure S2. The hydrogen bonds between ammonium and surrounding energetic ligands in **6a**.

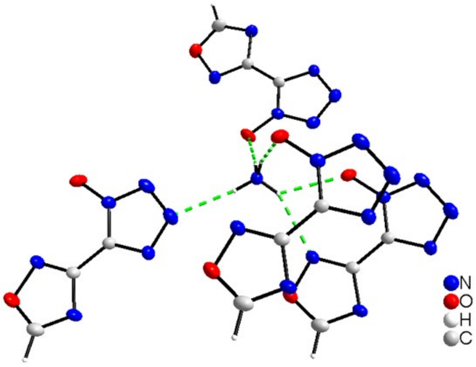


Figure S3. The hydrogen bonds between ammonium and surrounding energetic ligands contained in **8a**.

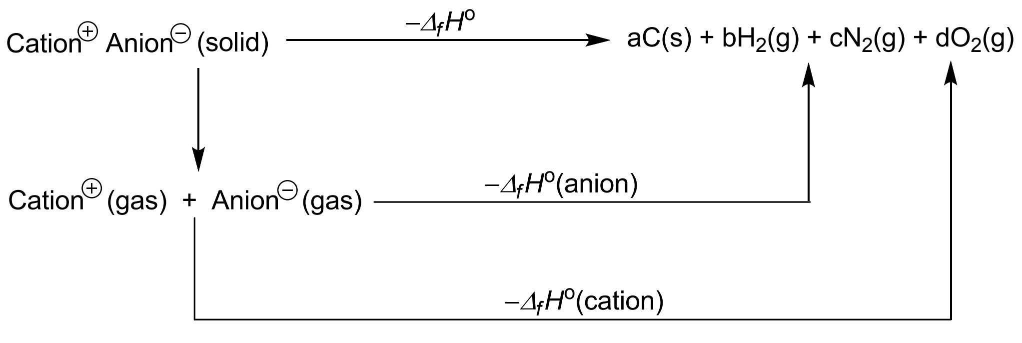
2. Theoretical study

Theoretical calculations were performed by using the Gaussian 09 (Revision D.01) suite of programs.[1] The geometric optimization and frequency analyses were conducted by using the B3LYP functional with the 6-31+G** basis set. Single energy points were calculated at the MP2/6-311++G** level of theory.[2] For all of the compounds, the optimized structures were characterized to be true local energy minima on the potential-energy surface without imaginary frequencies. Five explicit applications of isodesmic reactions were carried out to obtain the gas-phase heats of formation of the neutral compounds and the anion. The gas-phase enthalpies of the building-block molecules were obtained by using the atomization method with the G2 ab initio calculations. Then the remaining task is to determine the solid-state heats of formation for the synthesized compounds.

The solid-state enthalpy of formation for neutral compound can be estimated by subtracting the heat of sublimation from gas-phase heat of formation. On the basis of the literature,[3] the heat of sublimation can be estimated with Trouton's rule according to eq 1, where T represents either the melting point or the decomposition temperature when no melting occurs prior to decomposition:

$$\Delta H_{\mathrm{sub}} = 188/\mathrm{J\ mol^{-1}K^{-1}} \times \mathrm{T} \qquad (1)$$

For energetic salts, the heats of formation (HOF, $\Delta_f H°$) were calculated based on a Born–Haber energy cycle (Scheme S1).



Scheme S1. Born–Haber cycle for the formation of ionic salts.

For all the ionic salts, calculation of the HOFs was simplified by using Equation (2).

$$\Delta_f H^\circ\text{ (ionic salts, 298K)} = \Sigma\Delta_f H^\circ\text{(cation, 298K)} + \Sigma\Delta_f H^\circ\text{(anion, 298K)} - \Delta H_L \quad (2)$$

In eq 2, ΔH_L is the lattice energy of the ionic salts, which could be predicted by using the equation (3) suggested by by Jenkins et al.[4]

$$\Delta H_L = U_{POT} + [p(n_M/2 - 2) + q(n_x/2\text{-}2)]RT \quad (3)$$

In this equation, n_M and n_X depended on the nature of ions Mp^+ and Xq^-, respectively, and are equal to 3 for monoatomic ions, 5 for linear polyatomic ions, and 6 for nonlinear polyatomic ions.

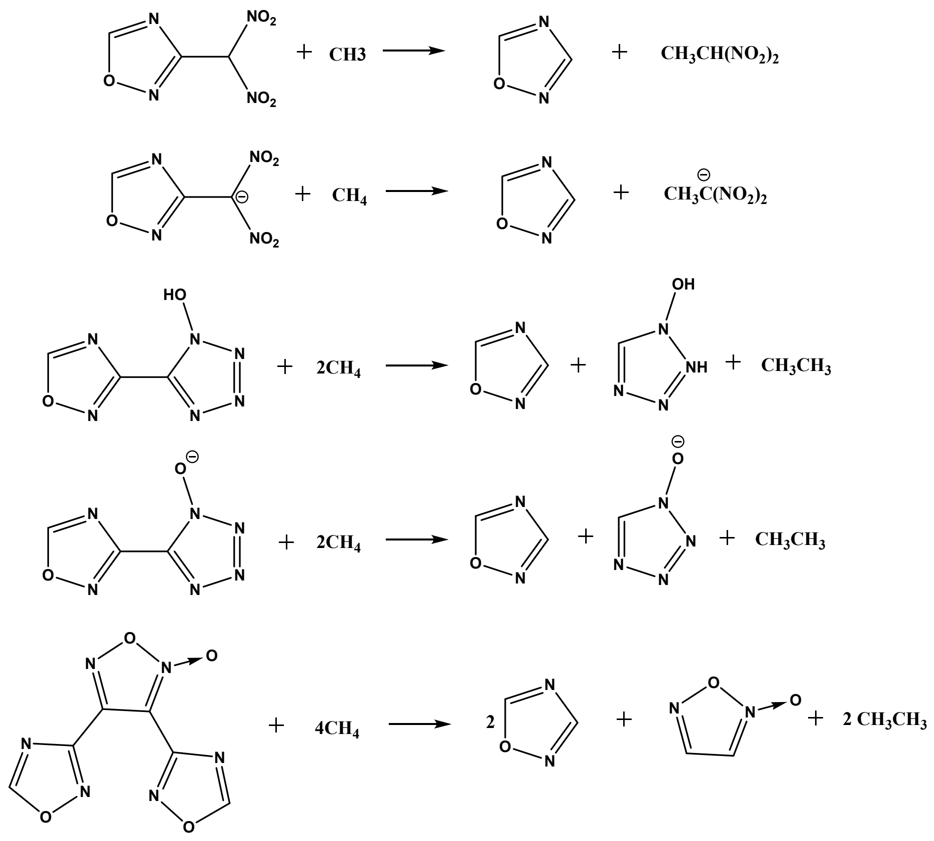
The lattice-potential energy (U_{POT}) was calculated according to Equation (4), in which ρ_m is the density (in g/cm^3) and M_m is the chemical formula mass of the ionic material; the coefficients γ and δ were taken from the literature.[4]

$$U_{POT}\text{ (kJ/mol)} = \gamma\ (\rho_m/M_m)^{1/3} - \delta \quad (4)$$

$$\Delta_f H^\circ(C^+, g) = \Delta_f H^\circ(C, g) + IE_C \quad (5)$$

$$\Delta_f H^\circ(A^-, g) = \Delta_f H^\circ(A, g) + EA_A \quad (6)$$

The heats of formation (HOFs) of the ionic salts were obtained by computing the component cations and anions. Specifically, the computation of HOFs for both cations and anions was performed according to literature methods[], that is, the gas-phase HOFs of the ions were determined by using Equations (5) and (6) (IE=ionization energy; EA=electron affinity). In Equations (5) and (6), additional calculations for the corresponding neutral molecules ($\Delta_f H^\circ$(C, g) and $\Delta_f H^\circ$(A, g) were performed for the atomization reaction $C_aH_bN_cO_d \rightarrow aC(g) + bH(g) + cN(g) + dO(g)$ by using G2 theory. Based on the results from Equation (5) and (6), the HOFs of the cations and anion were obtained.



Scheme S2. Isodesmic reactions

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[3] (a) F. Trouton, *Philos. Mag.***1884**, *18*, 54-57; (b) M. S. Westwell, M. S. Searle, D.J. Wales, D. H. Wiliams, *J. Am. Chem. Soc.* **1995**, *117*, 5013-5015.

[4] H. D. B. Jenkins, D. Tudela, L. Glasser, *Inorg. Chem.* **2002**, *41*, 2364-2367.