



ARL-TN-0927 • Nov 2018



Experimental Determination of Physical Properties of 1-Propyl-2-Nitroguanidine (PrNQ)

by RA Pesce-Rodriguez, C Munson, L Giri, and LB Blaudeau

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Experimental Determination of Physical Properties of 1-Propyl-2-Nitroguanidine (PrNQ)

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REPORT DOCUMENTATION PAGE				Form Approved OMB No. 0704-0188	
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1. REPORT DATE (DD-MM-YYYY) November 2018		2. REPORT TYPE Technical Note		3. DATES COVERED (From - To) 1 July–31 August 2018	
4. TITLE AND SUBTITLE Experimental Determination of Physical Properties of 1-Propyl-2-Nitroguanidine (PrNQ)				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) RA Pesce-Rodriguez, C Munson, L Giri, and LB Blaudeau				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) US Army Research Laboratory ATTN: RDRL-WML-B Aberdeen Proving Ground, MD 21005-5066				8. PERFORMING ORGANIZATION REPORT NUMBER ARL-TN-0927	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution is unlimited.					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT Chemical characterization of 1-propyl-2-nitroguanidine (PrNQ) was performed. Spectra (UV, Fourier transform IR, Raman) are presented along with results of elemental analysis, pH, and thermal analysis (thermogravimetric analysis and ambient and high-pressure differential scanning calorimetry). Based on determination of PrNQ's solubility, K_{ow} , K_{oc} , vapor pressure, and observed hydrolytic stability in neutral water, it was concluded that it will be highly mobile and persistent in ground water. PrNQ's low vapor pressure ($HMX < PrNQ < RDX$) in combination with its melting temperature ($\sim 100^\circ C$) makes it an attractive candidate for melt-cast formulations.					
15. SUBJECT TERMS 1-propyl-2-nitroguanidine, propyl nitroguanidine, PrNQ, fate and transport, F&T, fate and transport, K_{ow} , K_{oc} , solubility, vapor pressure, heat of sublimation, FTIR, Fourier transform IR, Raman, TGA, thermogravimetric analysis, DSC, differential scanning calorimetry, UV					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT UU	18. NUMBER OF PAGES 21	19a. NAME OF RESPONSIBLE PERSON Rose A Pesce-Rodriguez
a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified			19b. TELEPHONE NUMBER (Include area code) 410-306-1877

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Acknowledgments

The authors gratefully acknowledge Dr Michael Simini (Edgewood Chemical Biological Center) for generously providing characterized Sassafras sandy loam soil for K_{oc} determinations and Dr Bill Eck (US Army Public Health Center) and the Strategic Environmental Research and Development Program for funding of project #WP18-C3-1299.

1. Introduction

Cyclotrimethylenetrinitramine (RDX) and trinitrotoluene (TNT), the energetic constituents composing the melt-cast formulation Comp B, present an environmental risk toward the contamination of soils and ground water. Because of their widespread use in military munitions, contamination of training areas as well as worker exposure are significant concerns, and continuing efforts have been made to discover replacements with a lower health and environmental impact. The recently fielded formulations IMX-101 and IMX-104 were designed to be insensitive high-explosive-fill melt-cast alternatives with a detonation performance equivalent to TNT and Comp B for use in fragmenting warheads (Samuels et al. 2012). While now approved for use, concerns have arisen regarding the environmental and health impact related to the formulation components 3-nitro-1,2,4-triazol-5-one (NTO) and 2,4-dinitroanisole (DNAN) used in IMX-101 and 104 (Johnson et al. 2016; Williams et al. 2014). Toxicological assays of NTO have demonstrated negative effects on the male reproductive system, while DNAN exposure can result in anemia and neurotoxicity. Furthermore, DNAN exhibits a high vapor pressure (1.38×10^{-4} Torr at 25 °C) posing increased risk of industrial inhalation exposure during processing and handling.

Further experimental results indicate that the mixture of DNAN and NTO in IMX-101 produces a synergistic effect, reducing the amount of exposure needed to manifest ill effects (Johnson et al. 2016). Low-order detonations of insensitive formulations, such as IMX-104, can result in significant unreacted energetic residues introduced into the environment. During blow-in-place tests performed using IMX-104, up to 95% of the NTO load was found to deposit into the environment during the event (Walsh et al. 2014). Because NTO has high water solubility and becomes acidic in water, contamination and metals leeching in the vicinity of ranges and battlefields are of high concern.

1-propyl-2-nitroguanidine (PrNQ), an alkyl-substituted nitroguanidine, was first synthesized by Davis and Luce (1927), and was synthesized and scaled up to multikilogram quantities by a new method at the US Army Research Laboratory (ARL) in 2012 for investigation as a melt-cast binder for use in insensitive energetic formulations (Sherrill and Johnson 2012; Sherrill et al. 2013). PrNQ has many favorable characteristics: 1) in small-scale testing, PrNQ demonstrates significantly reduced sensitivity to impact, friction, and electrostatic discharge relative to RDX while having a predicted explosive performance comparable to TNT, 2) the melting point of PrNQ (~99 °C) and its low vapor pressure are ideal for melt-casting operations, 3) the synthesis is not difficult and has been scaled to 100s of pounds,

4) the material is relatively low cost, and 5) PrNQ is thermally compatible with common military energetics, such as RDX, HMX, and nitroguanidine.

The impacts of PrNQ toward human health and the environment, however, have not yet been completely investigated. PrNQ is expected to have minimal toxicological and environmental impact due to its chemical similarity to the molecules 2-nitroguanidine (NQ) and 1-methyl-2-nitroguanidine, both of which are known to be relatively benign (Williams and Eck 2010). In this work, we report on the probable environmental interactions of PrNQ.

2. Experimental

A sample of PrNQ (Fig. 1) was synthesized and provided by the Explosives Technology Branch of ARL.

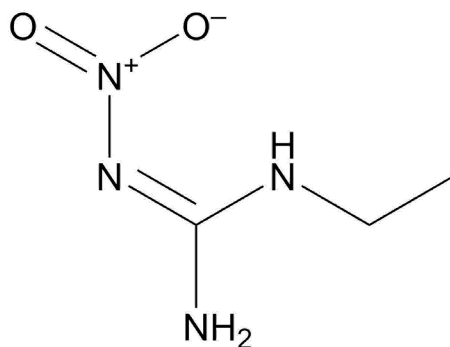


Fig. 1 Structure of PrNQ

Estimations of pH were obtained by placing solid material directly onto pH indicator strips (EMD Chemicals, Inc., Gibbstown, New Jersey) that had been pre-moistened with distilled, deionized water. Determination of pH was through visual comparison of the resulting strip color with a color chart provided by the manufacturer.

Elemental analysis was conducted using a Perkin Elmer Model 2400 Series II CHN analyzer.

Differential scanning calorimetry (DSC) analyses were carried out using a TA Instruments (New Castle, Delaware) Q2000 instrument operating under TA Universal Analysis software. All samples were run in both standard pans and hermetic pans with pinhole lids at a heating rate of 10 °C/min under nitrogen (50 mL/min). High-pressure DSC (HP-DSC) was run in a TA Instruments Q20 calorimeter at a heating rate of 10 °C/min under 500-psi nitrogen.

Thermogravimetric analysis (TGA) was performed using a TA Q500 TGA. All analyses were run under an inert atmosphere (nitrogen flowing at 60 mL/min), in platinum pans, and at a heating rate of 10 °C/min at 25–450 °C. Vapor pressure was estimated using the method given in Pesce-Rodriguez and Klier (2014). Heat of evaporation/sublimation was estimated by a Clausius–Clapeyron plot of estimated vapor pressures at 25, 70, and 100 °C.

Attenuated total reflectance (ATR)-Fourier transform IR (FTIR) spectra were obtained using a Nicolet is50 spectrometer with an onboard ATR accessory. For each spectrum, 128 scans were collected at a resolution of 4 cm⁻¹. Raman spectra were obtained using a Nicolet is50 Raman system with a 1064-nm laser operating at a power of 50 mW. For each spectrum, 32 scans were collected at a resolution of 8 cm⁻¹. Spectral collection and analysis with these instruments were performed using Nicolet Omnic software.

Solubility determination was performed on saturated solutions of each material at ambient temperature (23 °C). Saturation was insured by adding material to high-performance liquid chromatography (HPLC)-grade water and shaking for a minimum of 8 h. If solid material remained in the solution after that time, no further material was added. If all of the solid material had dissolved, more material was added and the solution was stirred for a minimum of an additional 8 h. The process was discontinued when solid material remained in the flask after an 8-h dissolution period. At this point, the solution was centrifuged (3000 rpm, 20 min at 23 °C) to separate any suspended solids. Supernatant solution was collected and analyzed by HPLC. Dilution was performed, if necessary, to prevent saturation of the detector. Quantitation was accomplished by means of a calibration curve constructed based on the HPLC peak areas of standard solutions prepared by adding preweighed, as-received material into known volumes of HPLC-grade water. Measurements of solubility were performed periodically over a two-week period (minimum) to establish equilibrium solubility.

The absorbance maximum for each compound was determined from a UV spectrum obtained on a USB4000 Ocean Optics UV/visible spectrometer. Concentration was determined in milligrams per milliliter.

For HPLC analysis, an Agilent Technologies 1200 Series HPLC with UV detection was used. The mobile phase consisted of 60% acetonitrile and 40% water at a constant flow rate of 1 mL/min. The column, an Agilent Technologies Pinnacle II C18 5-μm (250 × 4.6 mm) was maintained at a constant temperature of 23 °C. A sample injection volume of 20 μL was used.

K_{ow} determination was based on the Office of Prevention, Pesticides, and Toxic Substances (OPPTS) 830.7550, Partition Coefficient (n-Octanol/Water), Shake Flask Method (1996). Analytical-grade octanol and water were mutually presaturated by stirring at 23 °C. The solvents were then allowed to stand to permit phase separation and achieve a saturated state. For each sample, stock solutions were prepared by adding the minimum amount of analyte to water (presaturated with octanol). Samples were prepared based on the guidance in OPPTS 830.7550 that the maximum concentration in either phase could not exceed 0.01 mol/L. Samples were then prepared (in duplicate) by mixing aqueous stock solution and 1-octanol (presaturated with water) in the following proportions 2:1, 1:1, 1:2. All samples were prepared in 4-mL vials with white, snap-in polyethylene caps. All phases of the analysis were conducted at 23 °C. The test vessels were manually shaken by quickly rotating the vials through 180° about their transverse axis so that trapped air rose through the two phases. No fewer than 100 rotations in 5 min were performed, as per the guidance in OPPTS 830.7550. All vials were subsequently centrifuged at 3000 rpm for 10 min at 23 °C. After centrifugation, the phases were separated and analyzed by HPLC as described earlier for solubility samples.

K_{ow} was determined using Eq. 1:

$$K_{ow} = \frac{\text{Concentration of analyte in n-octanol (presaturated with water)}}{\text{Concentration of analyte in water (presaturated with 1-octanol)}} \quad (1)$$

Determination of K_{oc} was performed in accordance with ASTM E1195-01, *Standard Test Method for Determining a Sorption Constant (K_{oc}) for an Organic Chemical in Soil and Sediments* (2001). Soil-to-sample ratios were selected to achieve between 20% and 80% sorption. Analyses were conducted in 4-mL glass vials (with white, snap-in polyethylene lids) containing 2 mL of sample solution and 1 g of Sassafra sandy loam (SSL) soil. Results of the physical and chemical characterization of the SSL soil material are given in Table 1. As per ASTM E1195-01, the initial analyte concentration in should not exceed 0.5 times the given compound's water solubility. For this analysis, the initial concentration was reduced to not more than 0.1 times the water solubility in an attempt to increase the percentage of material sorbed. Control samples consisted of an aqueous solution of analyte with no soil and distilled water (no analyte) with soil. All samples were prepared in duplicate. Samples were agitated on a wrist-action shaker for a minimum time of 48 h and then centrifuged (3000 rpm, 20 min at 23 °C) before being analyzed by HPLC using the same conditions used for solubility determination.

Table 1 Information on SSL (SSL provided by Dr Michael Simini, Edgewood Chemical Biological Center [2015])

Soil Testing Results											
Sassafras Soil Characterization			SSL2007d								
Sieved 5mm; air dried			Collected from M-Field 6/21/2007								
		</									

Note: OM = organic matter

K_d , the sorption coefficient, factors in the organic matter (OM) content of the soil sample and is estimated from Eq. 2:

$$K_d = (K_{oc}) (\% \text{ organic carbon}/100). \quad (2)$$

Experimental K_d and K_{oc} values are calculated using Eqs. 3 and 4:

$$K_d = \frac{\mu\text{gs chemical/g solids}}{\mu\text{gw chemical/g H}_2\text{O}}, \quad (3)$$

where K_d = sorption coefficient, μgs = chemical sorbed, μg , and μgw = chemical in solution at equilibrium, μg , and

$$K_{oc} = K_d \times 100\% \text{ OC}, \quad (4)$$

where K_{oc} = organic carbon (OC) normalized sorption constant, K_d = sorption distribution coefficient, and % OC = percentage of organic carbon in solids.

3. Results and Discussion

General characterization of the PrNQ used in this study was performed to document purity and avail the information to the energetic community. Elemental analysis results are as follows: Found, C 32.90, H 6.95, N 38.66, [O 21.43, by difference]; Expected, C 32.87, H 6.90, N 38.34, O 21.89. The pH of a saturated solution was observed to be approximately 7. UV, Raman, and ATR-FTIR spectra of the material are given in Figs. 2–4. The FTIR spectrum is consistent with that reported by Sherrill and Johnson (2012).

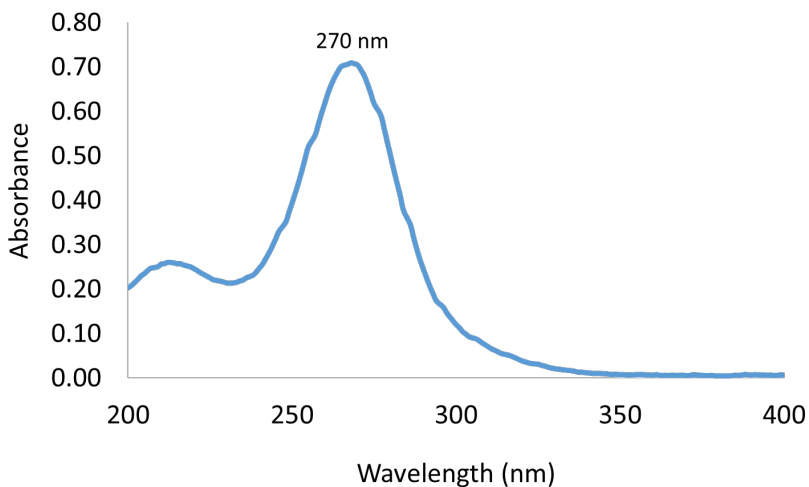


Fig. 2 UV spectrum of PrNQ

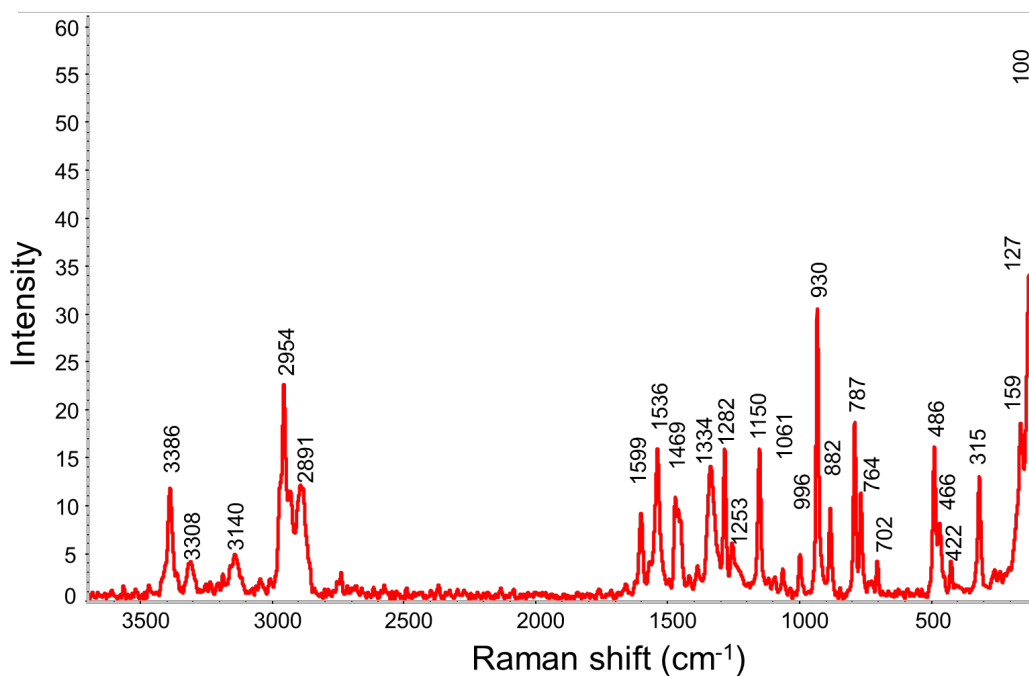


Fig. 3 Raman spectrum of PrNQ

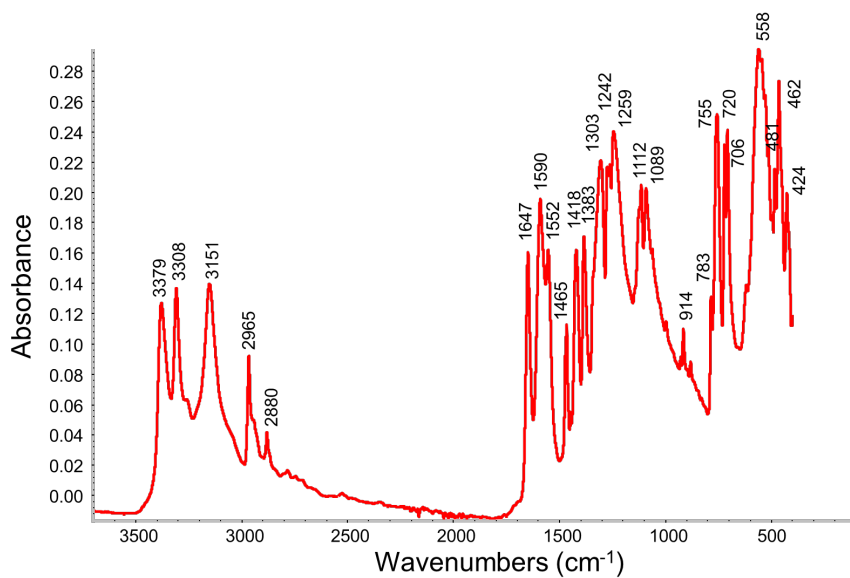


Fig. 4 ATR-FTIR spectrum of PrNQ

Thermal analysis of PrNQ resulted in the DSC and TGA traces given in Figs. 5 and 6. The DSC trace (Fig. 5) shows an endotherm assigned to melting (177 J/g) and an exotherm assigned to decomposition (796 J/g). The TGA trace for PrNQ is given in Fig. 6 and shows an onset of mass loss at approximately 177 °C. Mass loss

is rapid until approximately 250 °C, then slows until approximately 350 °C when the residual mass drops to zero. Estimation of vapor pressure and heat of vaporization, as described in Pesce-Rodriguez and Klier (2014), yields the data given in Table 2. Values for TNT, RDX, and HMX are given for comparison. It is interesting to note that the vapor pressure of PrNQ is not only lower than TNT, but than RDX as well. Dynamic and isothermal TGA of PrNQ and RDX (Fig. 7) are consistent with this conclusion.

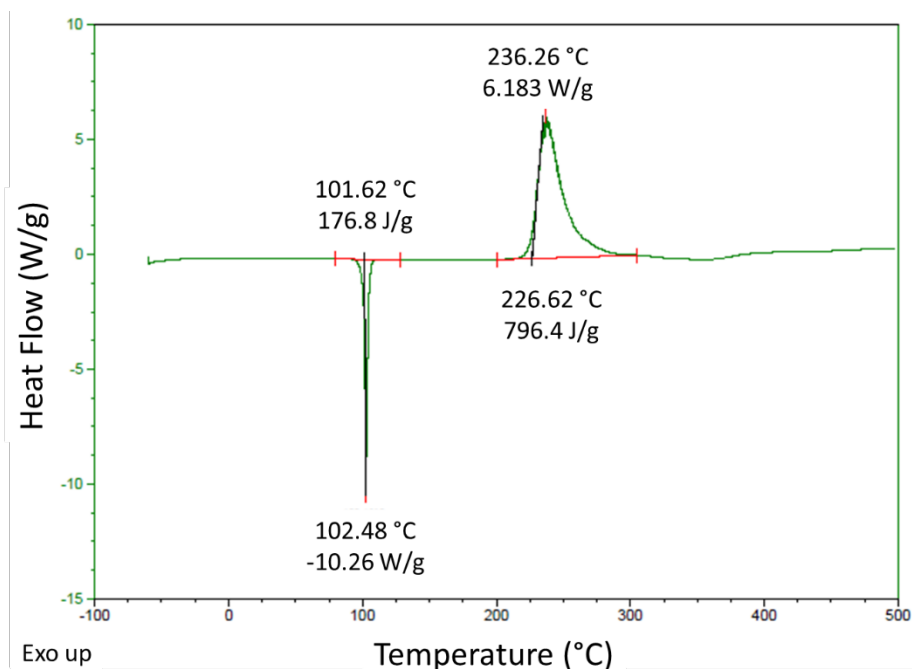


Fig. 5 DSC trace of PrNQ; heating rate: 10 °C/min under nitrogen

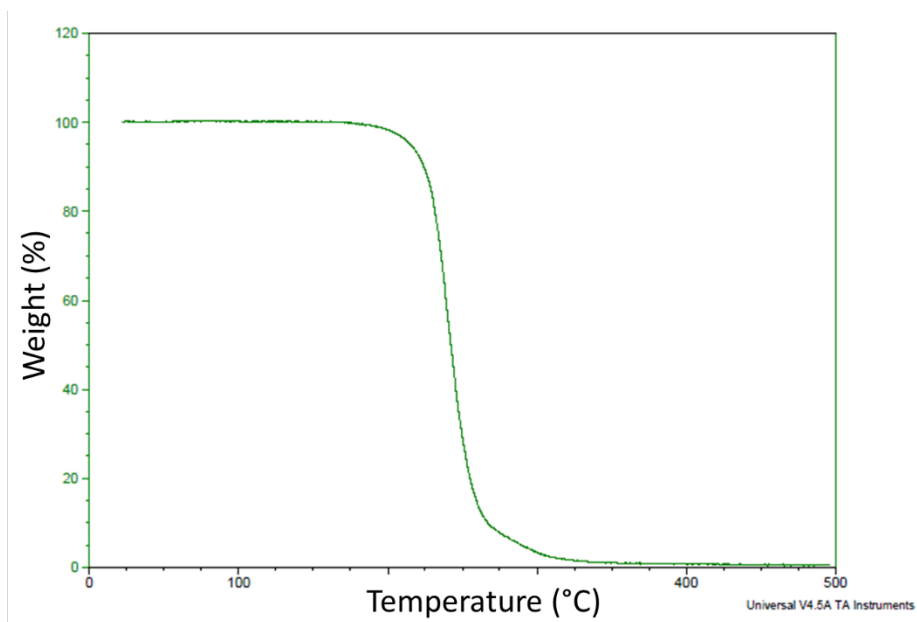


Fig. 6 TGA trace of PrNQ; heating rate: 10 °C/min under nitrogen

Table 2 Summary of estimated vapor pressures and heats of vaporization (ΔH_{vap}) (estimations made using method reported in Pesce-Rodriguez and Klier [2014]). Values for TNT, RDX, and HMX given for comparison.

Sample	VP (Torr)			ΔH_{vap} (kJ/mol)
	25 °C	70 °C	100 °C	
PrNQ	1.48×10^{-11}	9.85×10^{-09}	1.52×10^{-06}	139.7
TNT ^a	5.50×10^{-06}	2.31×10^{-03}	5.77×10^{-02}	114.1
RDX ^a	3.30×10^{-09}	2.76×10^{-06}	9.92×10^{-05}	127.1
HMX ^a	3.01×10^{-15}	3.14×10^{-11}	4.37×10^{-09}	174.7

^a Ostmark et al. (2012).

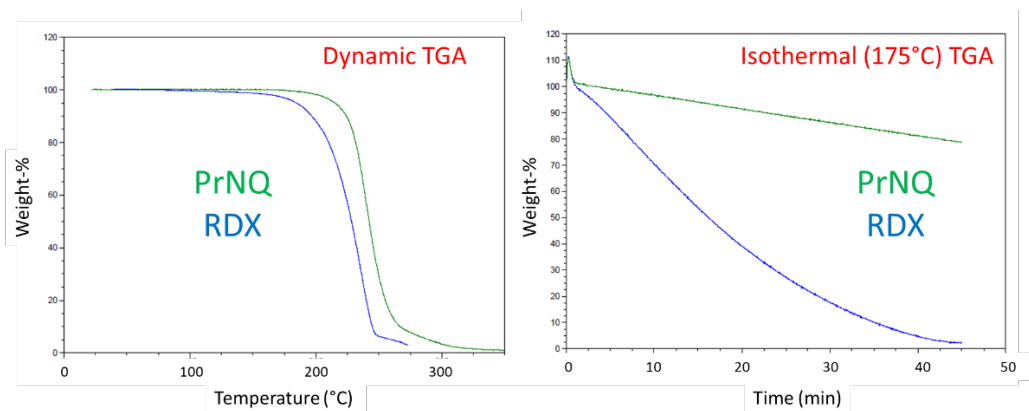


Fig. 7 TGA traces of PrNQ and RDX. Left: 10 °C/min under nitrogen dynamic. Right: isothermal at 175 °C.

Results for determination of solubility, K_{ow} , and K_{oc} are given in Table 3 along with values for TNT, RDX, and HMX for comparison. Predictions for all three PrNQ values calculated by EpiSuite (version 4.11 [USEPA 2013]; Eck [2018]) are in fair agreement with experimental values. A predicted solubility of 7.81×10^4 mg/L compares fairly well with the experimental value of 1.64×10^4 mg/L. While formal hydrolysis studies were not conducted, it was observed that PrNQ was stable in neutral water over a period of several weeks. Predicted K_{ow} and $\log K_{ow}$ (0.83 and -0.19, respectively) compare well with experimental values (1.35 and 0.13, respectively), and suggest that PrNQ will likely not bioconcentrate and will be highly mobile in ground water. Predicted values for K_{oc} and $\log K_{oc}$ (15.1 and 0.97, respectively) compare very well with experimental values (9.57 and 0.98, respectively). The low K_{oc} value is consistent with the conclusion that PrNQ will be highly mobile in soil.

Table 3 Summary of solubility, K_{ow} , and K_{oc} results for PrNQ. Literature values for TNT, RDX, and HMX shown for comparison.

Sample	Solubility (mg/L)	K_{ow}	Log K_{ow}	K_d	K_{oc}	log K_{oc}
PrNQ	$1.6 \times 10^{+04}$	1.35	0.13	0.223	9.57	0.98
TNT ^a	1.5×10^{-01}	100	2.0	12.1	524	2.72
RDX ^a	6.0×10^{-02}	7.41	0.87	0.023	100	2.0
HMX ^a	5.0×10^{-03}	1.82	0.26	0.054	3.46	0.54

^a Burrows et al. 1989.

4. Conclusion

PrNQ's high water solubility, low K_{ow} and K_{oc} , stability against hydrolysis in neutral water, and low vapor pressure suggest that the energetic material will be highly mobile and persistent in ground water.

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List of Symbols, Abbreviations, and Acronyms

ARL	US Army Research Laboratory
ATR	attenuated total reflectance
DNAN	2,4-dinitroanisole
DSC	differential scanning calorimetry
F&T	fate and transport
FTIR	Fourier transform IR
HPLC	high-performance liquid chromatography
IR	infrared
K _{oc}	soil sorption coefficient
K _{ow}	octanol/water partition coefficient
NTO	3-nitro-1,2,4-triazol-5-one
OC	organic carbon
OM	organic matter
OPPTS	Office of Prevention, Pesticides, and Toxic Substances
PrNQ	propyl nitroguanidine
RDX	cyclotrimethylenetrinitramine
SSL	sassafras sandy loam
TGA	thermogravimetric analysis
TNT	trinitrotoluene
UV	ultraviolet

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