

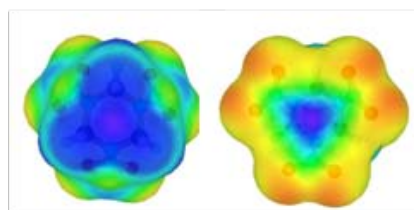


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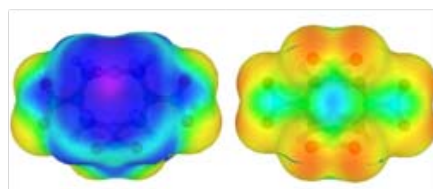
Prediction of Physicochemical Properties of Energetic Materials for Identification of Treatment Technologies for Waste Streams

Veera M. Boddu, Stephen W. Maloney,
Rebecca K. Toghiani, and Hussein Toghiani,

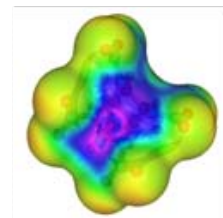
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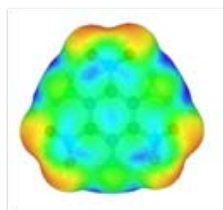
RDX



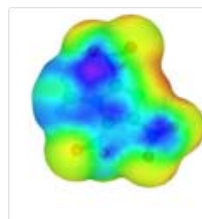
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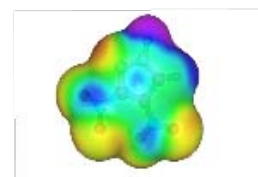
ε-CL20



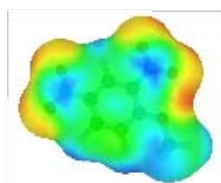
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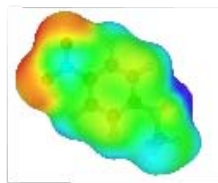
MTNI



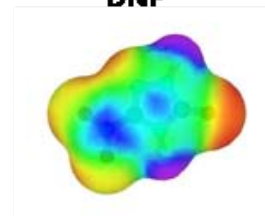
DNP



DNAN



MNA



NTO

Prediction of Physicochemical Properties of Energetic Materials for Identification of Treatment Technologies for Waste Streams

Veera M. Boddu and Stephen W. Maloney

*Construction Engineering Research Laboratory (CERL)
U.S. Army Engineer Research and Development Center
2902 Newmark Dr.
Champaign, IL 61822-1076*

Rebecca K. Toghiani and Hussein Toghiani

Mississippi State University

Final Report

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Abstract

This objective of this work was to predict the physicochemical properties of six energetic materials. The energetic materials of interest were 2,4-Dinitroaniline (DNAN), 3,4-Dinitropyrazole (DNP), n-Methyl-p-nitroaniline (MNA), 1-Methyl-2,4,5-trinitroimidazole (MTNI), 3-Nitro-1,2,4-triazol-5-one (NTO), and 1,3,5-Triamino-2,4,6-trinitrobenzene (TATB). The physicochemical properties of interest were the aqueous solubility, the octanol-water partition coefficient and Henry's constant. Three reference compounds were chosen to provide validation of the proposed approach: cyclotrimethylene-trinitramine (RDX), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), and ϵ -CL20.

Group contribution methods available in the literature were used for predictions. In addition, a number of physical properties were required, including critical temperature and pressure, normal boiling point, melting point, heat of fusion, and vapor pressure. These were also predicted using the chemical structure of the energetic compounds. Where literature data were available, comparisons with predictions were performed.

Another purely predictive method, based on chemical structure, was also employed for the estimation of physicochemical properties. This method, based on the “Conductor-like Screening Model for Real Solvents,” required quantum chemical calculations performed using TURBOMOLE to obtain the optimized electrostatic potential surface of each energetic material. The resulting surface was then used within the COSMOtherm software to predict solution behavior, including aqueous solubility, octanol-water partition coefficient, Henry's constant, and vapor pressure.

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Preface

This study was conducted for the Environmental Processes Branch of Engineering Research Development Center, Construction Engineering Research Laboratory (ERDC-CERL) under contract number W9132T-06-2-0027, by the Department of Chemical & Materials Science Engineering, Wayne State University, Detroit, MI. The technical monitor for this study was Dr. Reddy, Picatinny Arsenal, NJ (U.S. Armament Research, Development, and Engineering Center [ARDEC]).

The work was performed by the Environmental Process Branch (CN-E) of the Installations Division (CN), Construction Engineering Research Laboratory (CERL). The CERL Principal Investigator was Dr. Veera Boddu. Deborah R. Curtin is Chief, CN-E, and Dr. John T. Bandy is Chief, CN. The associated Technical Director was Alan Anderson. The Director of CERL is Dr. Ilker R. Adiguzel.

CERL is an element of the U.S. Army Engineer Research and Development Center (ERDC), U.S. Army Corps of Engineers. The Commander and Executive Director of ERDC is COL Kevin J. Wilson, and the Director of ERDC is Dr. Jeffery P. Holland.

1 Introduction

Background

The use of chemical structure as a means to predict physical and transport properties and physicochemical properties has been the subject of intense research in recent years. Physical and transport properties examined include melting point and density (Trohalaki et al. 2005), and viscosity, surface tension and thermal conductivity (Kauffman and Jurs 2001). Physicochemical properties examined include the octanol-water partition coefficient (Marrero and Gani 2002; Derawi et al. 2001), aqueous solubility (McElroy and Jurs 2001, Ran et al. 2001; Liu and So 2001), soil-sorption coefficient (Delgado et al. 2003), vapor pressure (Basak and Mills, 2001), and Henry's law constant (English and Carroll 2001). Two primary approaches have been taken in the prediction of physicochemical parameters based on the structure of a material: (1) group contribution methods, and (2) quantitative structure-property/activity relationships (QSPR/QSAR). The group contribution methods are primarily based on the numbers and types of molecular groups that form the compound (Poling et al. 2001); thus, the first order group contribution methods fail to distinguish between isomers that contain the same numbers and types of groups. Second order group contribution methods incorporate interactions between next nearest neighbors in an attempt to address the existence of isomers and their influence on the properties of interest.

Quantitative structure-property/activity relationships connect physical or chemical properties to a set of molecular descriptors. An extensive body of research in this area has focused on development of these relationships for use in the pharmaceutical industry, where aqueous solubility and lipophilicity are used to estimate the pharmacokinetics of potential drugs (Horning and Klamt 2005). QSPR/QSARs also have potential applications in the fuel science field (Katritzky and Fara 2005).

The molecular descriptors can be constitutional (depend on compound's composition), geometric (depend on 3D orientation of atoms in compound), electrostatic (depend on partial charge), or quantum-chemical (depend on compound's electron wave functions) (Katritzky and Fara 2005). What is critical in the development of QSPR/QSARs is the identification of the appropriate set of descriptors that allow the desired attribute of the compound to be adequately predicted. A key limitation to the use of QSPR/QSARs is

that the set of compounds used to develop the relationship should be similar to those compounds for which predictions are desired.

A third approach (Klamt and Eckert 2000) provides for *a priori* predictions of thermophysical data for chemical systems. Based on “Conductor-like Screening Model for Real Solvents,” COSMO-RS has a strong quantum chemical and statistical thermodynamics basis, which allows a physically meaningful description of the interactions between molecules in a solution. It has been used to predict a number of physicochemical properties including aqueous solubility (Klamt et al. 2002), soil sorption coefficients (Klamt et al. 2004), gas solubilities, and partition coefficients (Maassen et al. 1995).

These methods are challenged when little or no experimental data are available, often the case for particularly complex compounds, or compounds in the early stages of development. One must develop a means to validate the predictions, often by predicting similar compounds’ properties for which experimental data are available. Compounds chosen to serve this function in this work were ϵ -CL20 (2,4,6,8,10,12-Hexanitro-2,4,5,8,10,12-hexaazaisowurtzitane), cyclotrimethylene-trinitramine (RDX), and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX). All three structures contain multiple nitro functional groups and also contain cyclic nitrogen groups. The structures of the compounds of interest in this work, which contain these functional groups—either cyclic nitrogen atoms or nitro groups attached to the ring, or both—are:

- dinitroanisole (DNAN)
- n-methyl-p-nitroaniline (MNA)
- nitro-triazolene (NTO)
- triaminotrinitrobenzene (TATB)
- dinitro pyrazole (DNP)
- and m-trinitro imidazole (MTNI).

Objectives

The objective of this work was to develop a means to validate the predictions of physical and transport properties, and of physicochemical properties through prediction of similar compounds’ properties for which experimental data are available, specifically, ϵ -CL20 (2,4,6,8,10,12-Hexanitro-2,4,5,8,10,12-hexaazaisowurtzitane), RDX, and HMX.

Approach

This work was accomplished in the following steps:

1. Six compounds of interest in this work were specified and three reference compounds along with their Chemical Abstracts Service (CAS) registry numbers were identified.
2. The molecular structure of each compound was used to generate a mapping of atoms in each molecule in a Cartesian coordinate system.
3. Physical properties for the compounds of interest were estimated and the reference compounds was undertaken. In addition to the conventional physical properties estimated from molecular structure, the Abraham descriptors were computed.
4. Physicochemical and physical properties for the compounds of interest were also estimated.
5. Based on these estimates, a variety of treatment technologies was examined for the remediation of waste streams containing energetic compounds.

Mode of technology transfer

This report will be made accessible through the World Wide Web (WWW) at URLs:

<http://www.cecer.army.mil>

<http://libweb.erdclib.usace.army.mil>

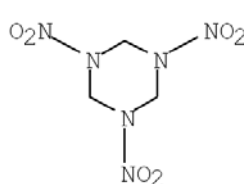
2 Computational Approach and Results

Molecular structures

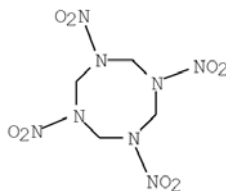
Table 1 lists the six compounds of interest in this work and three reference compounds along with their CAS registry numbers. The reference compounds were chosen based on the availability of literature data that could be used to validate the estimation approach and their inclusion of relevant molecular groups, in particular, the nitro (-NO₂) molecular group (Figure 1). Figure 2 shows the molecular structures for the six compounds of interest and the three reference compounds, obtained from the Scifinder Scholar database (ACS 2007).

Table 1. Compounds of interest and reference compounds.

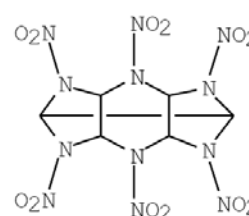
Compound Name	Acronym	Reference (Yes/No)	Molecular Formula	CAS Registry Number
2,4-Dinitroanisole	DNAN		C ₇ H ₆ N ₂ O ₅	119-27-7
3,4-Dinitropyrazole	DNP		C ₃ H ₂ N ₄ O ₄	38858-92-3
n-Methyl-p-nitroaniline	MNA		C ₇ H ₈ N ₂ O ₂	100-15-2
1-Methyl-2,4,5-trinitroimidazole	MTNI		C ₄ H ₃ N ₅ O ₆	19183-20-1
3-Nitro-1,2,4-triazol-5-one	NTO		C ₂ H ₂ N ₄ O ₃	932-64-9
1,3,5-Triamino-2,4,6-trinitrobenzene	TATB		C ₆ H ₆ N ₆ O ₆	3058-38-6
2,4,6,8,10,12-hexanitro-2,4,5,8,10,12-hexaazaisowurtzitane	ϵ -CL20	Yes	C ₆ H ₆ N ₁₂ O ₁₂	135285-90-4
1,3,5-Trinitro-1,3,5-triazacyclohexane	RDX	Yes	C ₃ H ₆ N ₆ O ₆	121-82-4
1,3,5,7-Tetranitro-1,3,5,7-tetrazacyclooctane	HMX	Yes	C ₄ H ₈ N ₈ O ₈	2691-41-0



RDX



HMX



ϵ -CL20

Figure 1. Structure of compounds used for validation.

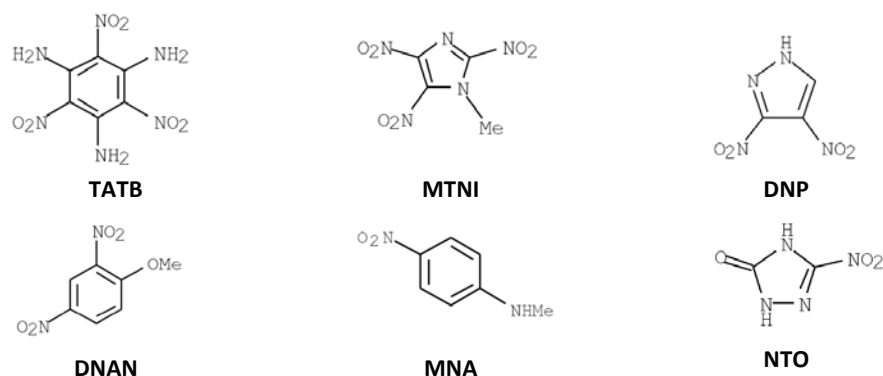


Figure 2. Structures of compounds of interest in this work.

TURBOMOLE computations

The molecular structure was used to generate a mapping of atoms in each molecule in a Cartesian coordinate system. This mapping used several programs available as freeware/shareware:

- *Chemdraw* – for drawing molecules and generating SMILES code (**S**implified **M**olecular **I**nput **L**ine **E**nter **S**pecification)
- *Corina* – for conversion of SMILES code to a PDB (protein databank) format file, containing 3D coordinates of all atoms and bonding information
- *Babel* for conversion of the PDB format file to XYZ format (listing of Cartesian coordinates for each atom in the compound).

The XYZ format file is then converted to the required format for TURBOMOLE using a utility provided with the TURBOMOLE software. A sample of the PDB and XYZ file contents are shown in Appendix A for the reference compound, ϵ -CL20.

For each compound, density functional theory (DFT) calculations were performed using TURBOMOLE (Version 5.9) (Ahlich et al. 1989, Trentler and Ahlich 1995, Sierka et al. 2003). The DFT computation resulted in an optimized structure for each compound. A second DFT computation was performed to yield the input geometry and energy required as input to the COSMOtherm program. The TZVP (triple zeta valence Gaussian) basis set was employed (Schafer et al. 1994). These computations were performed on a Next Dimension Next Demand-II computer system equipped with dual Advanced Micro Devices, Inc. (AMD) Opteron processors. COSMOtherm (Version 1.06) was used to predict physico-chemical properties.

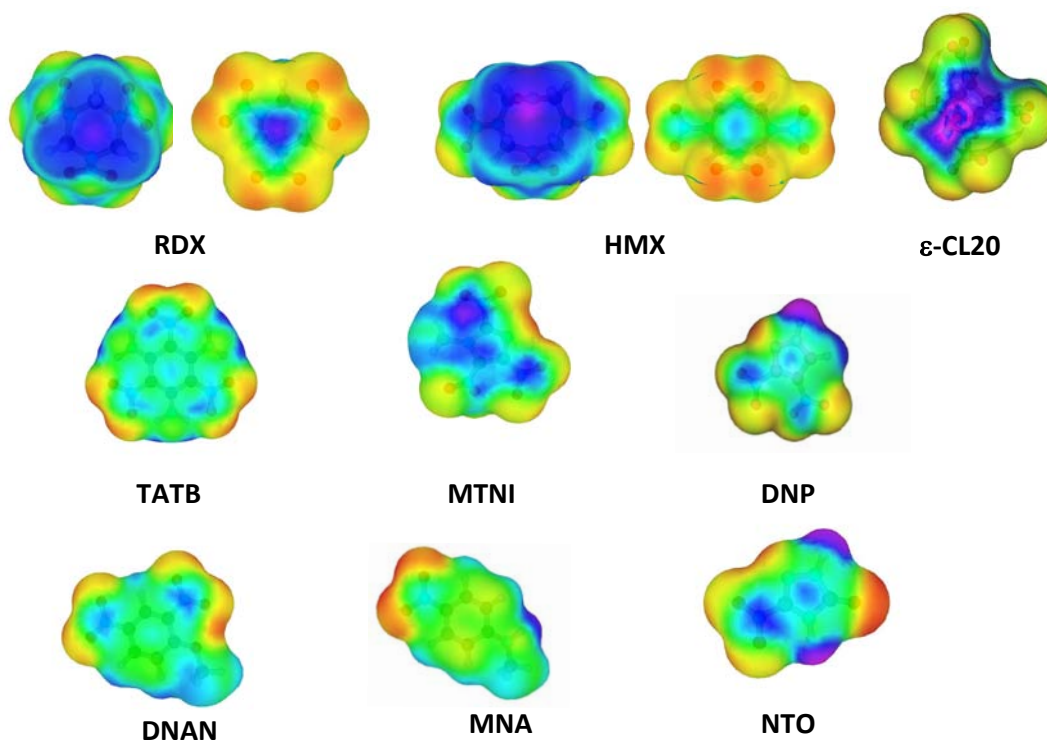


Figure 3. Electrostatic potential surfaces of compounds examined in this work.

The *.cosmo file used as input for COSMOtherm is generated using the TURBOMOLE software. Examples of these input files will be provided electronically on request. The contents of the *.cosmo file provide a mapping of the electrostatic potential on the surface of the molecule. Figure 3 shows these surfaces for the reference compounds and the compounds of interest.

Estimation of physical properties

The development of estimation techniques for physical and thermodynamic properties often relies on data specific to the substance of interest. Often used in correlation are the critical point of a substance (critical temperature, critical pressure), the normal boiling point, the acentric factor, the melting point and enthalpies of fusion and vaporization, and the vapor pressure of the pure component. For the compounds of interest in this work, very limited data were available for these physical properties. The following paragraphs review means to estimate values for these properties from readily available information such as molecular structure.

Estimation of physical properties for the compounds of interest and the reference compounds was undertaken. Experimental data for these physical properties are sparse. These limited data were used, where available, to

validate the predictive approach. The program, Cranium (Molecular Knowledge, Inc., Version 1.0.3) was used to predict critical properties (temperature, pressure, volume compressibility), the acentric factor, normal boiling point, melting point, heat of formation, free energy of formation, heat of fusion at the melting point, and latent heat of vaporization at the normal boiling point.

Critical properties

Using the molecular structure to estimate critical properties is the basis of group contribution methods. These methods, which were used to estimate critical temperature, critical pressure and critical volume, are based on correlative approaches using experimental data coupled with regression to obtain the contributions to a given property from a particular functional group. The widely used Joback method (Poling et al. 2001), which has been the historical method of choice, includes contributions for all functional groups of interest in the present work. The Joback method uses the normal boiling point and contributions from the representative functional groups to estimate critical temperature. In recent years, a number of alternate group contribution methods have been proposed for estimation of critical properties; these methods are based on more extensive databases, in attempts to address issues associated with first order group contributions methods such as failure to distinguish between isomers. The method of Constantinou and Gani (1994) is a second order group contribution method that allows isomers to be distinguished through the inclusion of the second order groupings. However, in this method, contributions for nitro groups ($-\text{NO}_2$) bonded to a nitrogen atom in a ring are not included; thus, this method will not be applicable for RDX and HMX, which were chosen as validation molecules in this work. The method of Valderrama and Alvarez (2006) was developed to be applicable to high molecular weight compounds, such as large, multifunctional compounds and biomolecules. The Joback method and the Valderrama/Alvarez methods were evaluated in the present effort for critical property evaluation.

In a previous effort (Boddu et al. 2004), the Joback method (Joback and Reid 1987) was used to estimate critical temperature and critical pressure for the three reference compounds, with normal boiling point estimated with the Joback method as modified by Stein and Brown (1994). The Joback method uses the following expressions to evaluate critical temperature, T_c , critical pressure, P_c , and critical volume, V_c :

$$T_c (K) = T_b \left[0.584 + 0.965 \left\{ \sum_k N_k (tc_k) \right\} - \left\{ \sum_k N_k (tc_k) \right\}^2 \right]^{-1} \quad \text{Eq 1}$$

$$P_c (\text{bar}) = \left[0.113 + 0.0032 * N_{\text{atoms}} - \left\{ \sum_k N_k (pc_k) \right\} \right]^{-2} \quad \text{Eq 2}$$

$$V_c (\text{cm}^3 / \text{mol}) = 17.5 + \sum_k N_k (vc_k) \quad \text{Eq 3}$$

where:

- N_k = the number of functional groups of type k in the molecule
- tc_k , pc_k and vc_k = the contributions to the critical temperature, critical pressure, and critical volume from functional group k
- N_{atoms} = the total number of atoms in the molecule
- T_b = the normal boiling point of the substance, and can be estimated if an experimental value is not available.

Values for the critical temperature and pressure were also estimated using the method of Valderrama and Alvarez (2006). This method does not require use of the normal boiling point in its estimation of critical temperature. It is based on the “idea of group contributions applied to estimate the force and the volume constants of the van der Waals equation of state” and “could be applied to large complex substances as those present in many natural products” (Valderrama and Alvarez 2006). Functional group contributions for the quantities $T_c / \sqrt{P_c}$, T_c / P_c , and V_c are given by Valderrama and Alvarez. These are combined using the following expressions:

$$\frac{T_c}{\sqrt{P_c}} = \alpha_1 + \left\{ \sum_i n_i \left[\frac{T_c}{\sqrt{P_c}} \right]_i \right\}^{\beta_1} \quad \text{Eq 4}$$

$$\frac{T_c}{P_c} = \alpha_2 + \left\{ \sum_i n_i \left[\frac{T_c}{P_c} \right]_i \right\}^{\beta_{21}} \quad \text{Eq 5}$$

$$V_c = \alpha_3 + \left\{ \sum_i n_i [V_c]_i \right\}^{\beta_{31}} \quad \text{Eq 6}$$

where:

- n_i is the number of functional groups of type i in the molecule
- $(T_c / \sqrt{P_c})_i$, $(T_c / P_c)_i$, and $(V_c)_i$ are the contributions to the respective functionals from functional group i
- a_i and b_i are specified constants.

Table 2 lists the estimated critical temperature and pressure from both methods. Experimental critical temperatures were available for HMX and RDX. Using the Stein-Brown modification of the Joback method, the critical temperature for RDX was estimated at 842.7 K compared to the experimental value of 840 K (Maksimov 1992); for HMX, the estimated critical temperature was 913.5 K compared to the experimental value of 927 K (Maksimov 1992). The method of Valderrama and Alvarez estimated critical temperatures for RDX and HMX that were much greater than the values reported in the literature: for RDX, 1112.3 K; and for HMX 1234.4 K.

The values estimated using the Joback method as modified by Stein and Brown were in better agreement with the available literature data for the reference compounds. The values for critical temperature and pressure estimated using the Stein-Brown modification of the Joback method were used in further computations.

Normal boiling point and acentric factor

The estimation of the normal boiling point and the acentric factor are also of interest in this work. The Stein-Brown method (1994) was used to estimate the normal boiling point of both reference compounds and compounds of interest in this work. This method uses the same functional groups as the Joback method, but applies a correction to estimated boiling temperatures above 800 K. This correction is in essence responsible for the difference observed in the predicted critical temperatures listed in Table 2. The acentric factor is estimated using its definition, along with the estimated critical temperature, critical pressure and normal boiling point. Table 3 lists predictions of normal boiling point and acentric factor for the compounds of interest and reference compounds.

Table 2. Critical properties.

	Literature Data	Joback/Stein Method		Valderrama/Alveraz Method	
Compound	T _c (K)	T _c (K)	P _c (bar)	T _c (K)	P _c (bar)
DNAN		806.3	39.9	938.9	34.67
DNP		816.8	69.33	1036.4	59.72
MNA		747.5	41.68	845.8	41.34
MTNI		845.0	54.71	1105.8	37.21
NTO		828.5	86.05	1291.6	145.15
TATB		912.7	56.45	1189.0	31.14
ε-CL20		1058.0	48.90	1539.4	21.96
RDX	840 ^a	842.7	58.01	1112.3	35.31
HMX	927 ^a	913.5	52.97	1234.4	28.83

^a Maksimov (1992).

Table 3. Estimated normal boiling point and acentric factor.

Compound	Estimated Normal Boiling Point T_{nbp} (K) Stein-Brown Method	Estimated Acentric Factor ω Definition of Acentric Factor
DNAN	587.6	0.858
DNP	574.5	0.307
MNA	527.3	0.659
MTNI	629.1	0.707
NTO	568.4	0.798
TATB	711.6	1.802
ϵ -CL20	861.8	2.547
RDX	626.6	1.252
HMX	709.5	1.700

Vapor pressure

There are very few experimental data available for the vapor pressure (over liquid or solid phases) for the compounds of interest and the reference compounds. Rosen and Dickenson (1969) reported on vapor pressure and heat of sublimation for high melting organic explosives, including reference compounds RDX and HMX, and one compound of interest, TATB.

Taylor and Crookes (1976) also reported on these properties for HMX. Cundall et al. (1978) provided measurements of vapor pressure for a slate of compounds including RDX and HMX. Dionne et al. (1986) measured the vapor pressure of RDX. Sinditskii et al. (2006) reported the vapor pressure over both liquid and solid phase NTO, fitting their data to a simple Claperyon relationship. These data were used, where possible, for comparison with predictions of vapor pressure for the compounds of interest and the reference compounds.

COSMOtherm was used to predict the vapor pressure for each reference compound and for the compounds of interest. Table 4 lists Antoine coefficients for the COSMOtherm vapor pressure predictions. For those compounds where experimental data were available in the literature, a comparison was made with COSMOtherm predictions. For RDX, literature data were available from three independent sources. Figure 4 shows these data with the COSMOtherm prediction. The COSMOtherm predictions are much larger than the reported experimental vapor pressures, and there is considerable scatter among the three literature data sets. The scatter among these measurements is indicative of the difficulty in measuring vapor pressure for compounds exhibiting very low volatility.

Table 4. Antoine coefficients generated using COSMOtherm.

Compound	A _i	B _i	C _i
DNAN	18.01	7087.5	-43.94
DNP	17.72	7092.4	-60.25
MNA	18.19	6757.9	-61.43
MTNI	17.99	7080.5	-41.10
NTO	20.63	7334.04	-76.29
TATB	18.27	6756.2	-62.45
ε-CL20	18.74	9247.9	-38.79
RDX	18.56	7718.5	-42.65
HMX	20.24	11881.4	-35.96

Where $\ln[P(\text{mbar})] = A_i - [B_i / (T(K) + C_i)]$

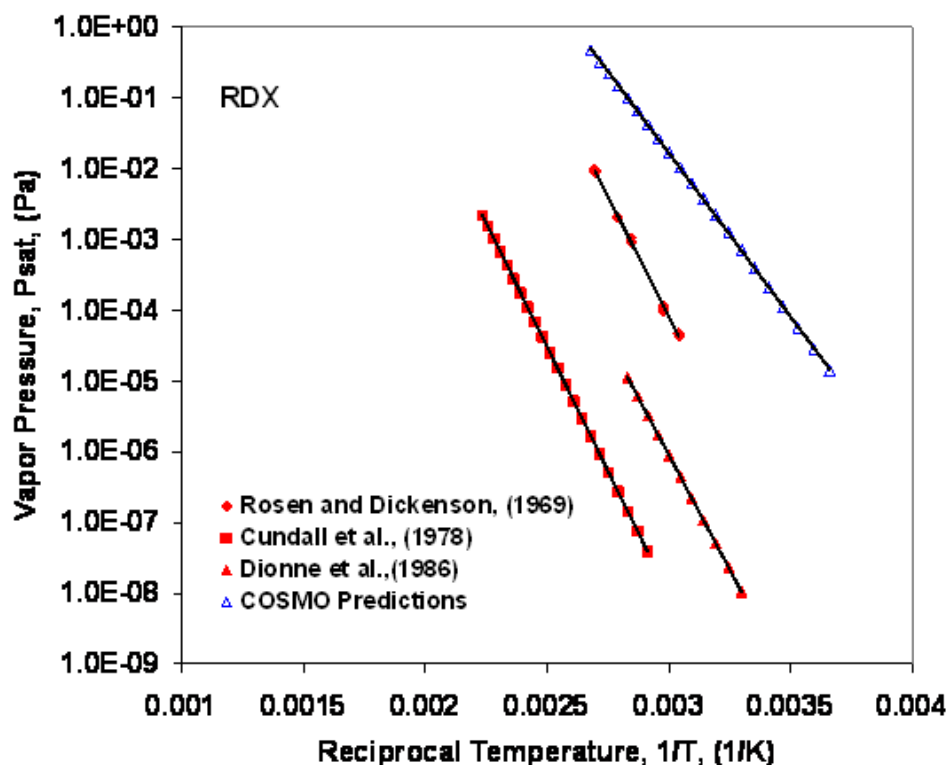


Figure 4. Vapor pressure of RDX shown with literature data.

Figure 5 shows HMX with experimental data available in three independent sources. Again, COSMOtherm predicts much larger vapor pressure at a given temperature compared to the experimental data. Figure 6 shows the vapor pressure of TATB as measured by Rosen and Dickenson (1969) against the COSMOtherm prediction.

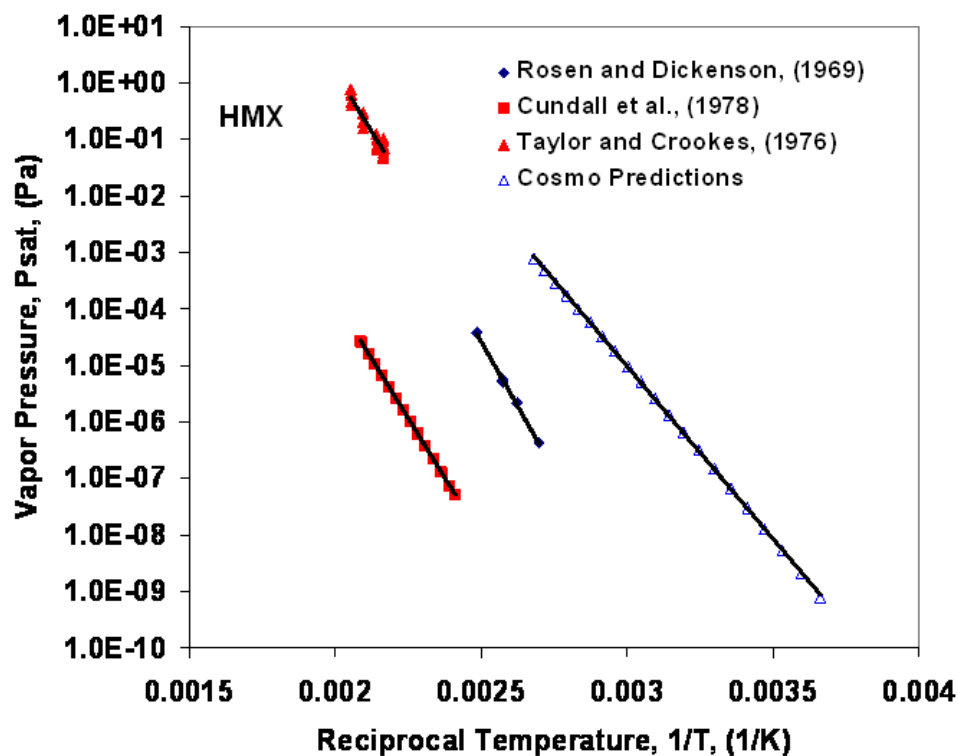


Figure 5. Vapor pressure of HMX shown with literature data.

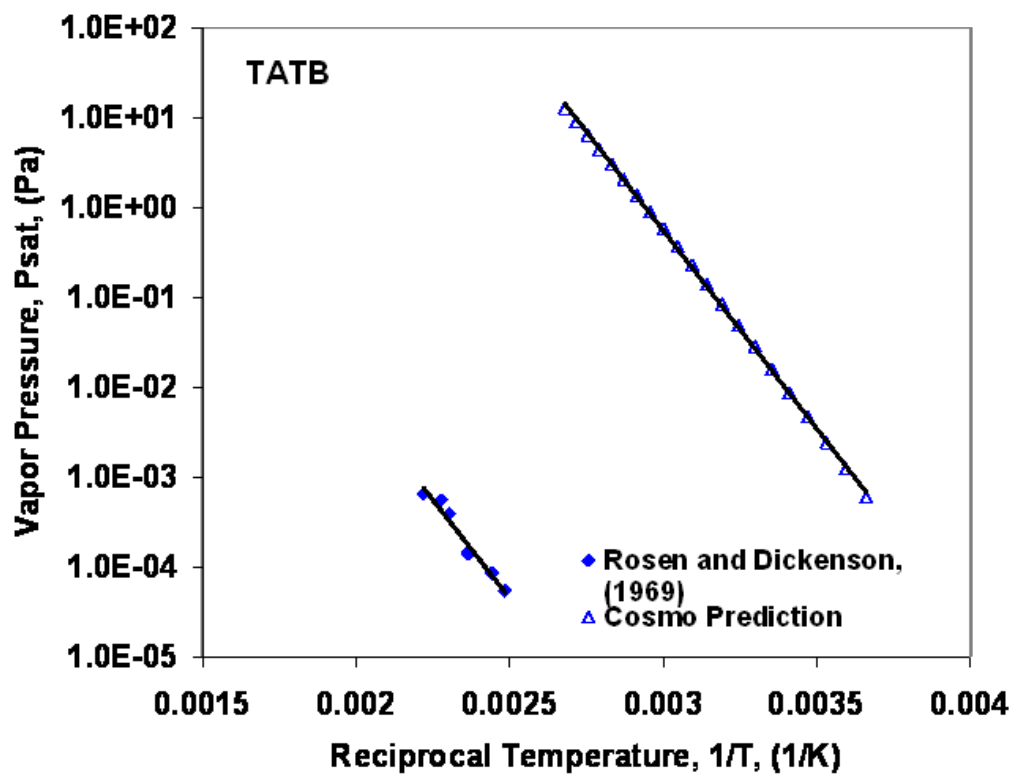


Figure 6. Vapor pressure of TATB shown with literature data.

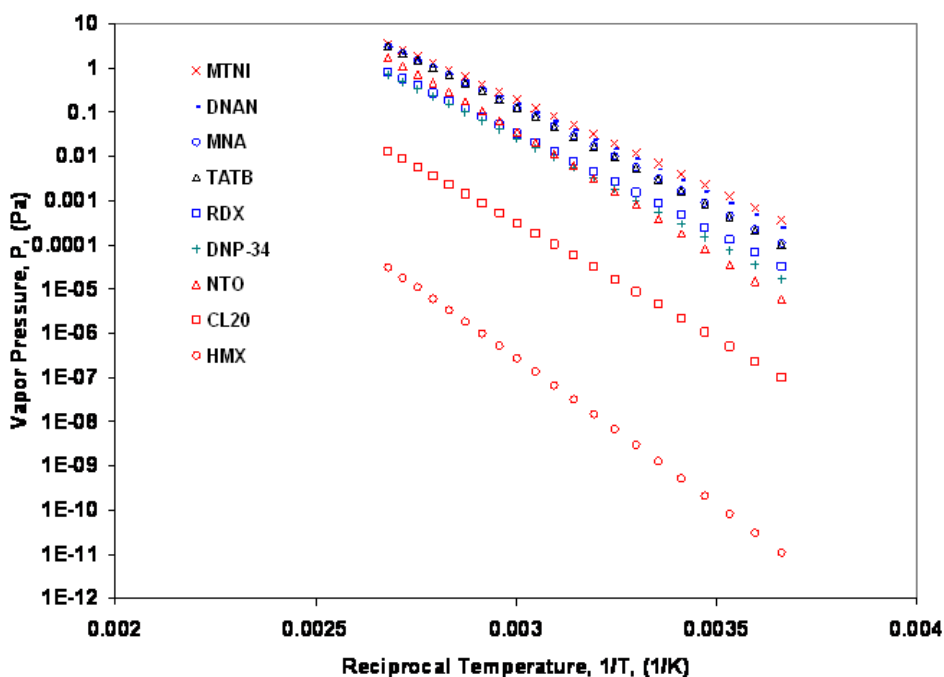


Figure 7. COSMOtherm predictions of vapor pressure for all compounds examined in this work.

Again, the experimental data from the literature are much smaller than the COSMOtherm predictions. Figure 7 shows COSMOtherm predictions for all compounds of interest and for the reference compounds. COSMOtherm predicts the trend in decreasing volatility to be:

$$\text{MTNI} > \text{DNAN} > \text{MNA} > \text{TATB} > \text{RDX} > \text{DNP} > \text{NTO} \gg \epsilon\text{-CL20} \gg \text{HMX}.$$

Melting point and enthalpy of fusion

The melting point for each of the compounds of interest and the reference compounds were available from the literature. Literature enthalpy of fusion data were available for only three compounds (RDX, NTO, and ϵ -CL20). Domalski and Hearing (1996) reported the enthalpy of fusion of RDX as 37.66 kJ/gmol. For NTO, the reported values of 27 kJ/mol (Liu et al. 1995) and 92.8 kJ/mol (Kim et al. 1998) differ by a factor of 4. For ϵ -CL20, the reported enthalpy of fusion value was 42.7 kJ/mol, estimated from data for similar nitro compounds (Zeman and Jalovy 2000); it was not an experimentally determined value.

The method of Chickos et al. (1999) was employed for estimation of the total phase change entropy at the melting point. In this group contribution method, the total entropy of fusion becomes numerically equivalent to the

entropy of fusion when there is a single solid-liquid phase transition. Enthalpy of fusion was then computed from the predicted entropy of fusion and the literature melting point for each compound. Table 5 summarizes the estimated enthalpy of fusion for the compounds in this work, and (if available) the literature data for melting point and enthalpy of fusion.

The estimated enthalpy of fusion for RDX at 39.52 kJ/mol is in good agreement with the experimental value of 37.66 (Domalski and Hearing 1996). For ϵ -CL20, the estimated value is much lower at 13.7 kJ/mol compared to the literature value of 42.7 (Zeman and Jalovy 2000). For NTO, the estimated value of 20.17 kJ/mol was comparable to the reported literature value of 27 kJ/mol. The estimated enthalpy of fusion values were used in all further predictive efforts.

Table 5. Melting point and enthalpy of fusion.

Compound	Melting Point T_m (K) (reference)	Estimated Enthalpy of Fusion, ΔH_m (kJ/mol)	Literature Enthalpy of Fusion, ΔH_m (kJ/mol) (reference)
DNAN	359.9 ^a	19.91	
DNP	363-364 ^b	27.6	
MNA	425.15 ^c	18.85	
MTNI	355.15 ^d	19.82	
NTO	539.35 ^e , 547.9 ^f	20.17	27 ^e , 92.8 ^f
TATB	594-599 ^g	43.0	
ϵ -CL20	513 ^h	13.7	42.7 ^j
RDX	478.5 ⁱ	39.52	37.66 ^k
HMX	553.15 ^a	45.0	

^a Maksimov (1992).

^b Beringer et al. (1953).

^c Katritzky et al. (2005), p 179.

^d Material Safety Data Sheet [OSHA] (MSDS) for N-methyl-4-nitroaniline, <http://ptcl.chem.ox.ac.uk/MSDS/ME/N-methyl-4-nitroaniline.html>, accessed 01/05/07.

^e Liu et al. (1995).

^f Kim et al. (1998).

^g Cho et al. (2002).

^h Andelkovic (2000).

ⁱ Hall (1971).

^j Zeman and Jalovy (2000).

^k Domalski and Hearing (1996).

Table 6. Abraham descriptors for compounds of interest and reference compounds.

Compound	Excess Molar Refraction R_2	Polarity/ Polarizability π_2^H	Hydrogen Bond Acidity $\sum \alpha_2^H$	Hydrogen Bond Basicity $\sum \beta_2^H$	McGowan Characteristic Volume V_x
DNAN	1.7059	1.9993	0.0057	0.6140	1.3289
DNP	1.7891	1.8702	1.2048	0.3796	0.9655
MNA	0.9795	1.4126	1.4126	0.6339	1.1521
MTNI	3.5180	3.0367	0.0845	0.4823	1.2902
NTO	0.9991	1.5359	1.5333	0.5891	0.8093
TATB	1.8381	2.3187	0.3112	0.8470	1.4534
ϵ -CL20	7.0001	5.1712	1.0047	0.3969	2.1330
RDX	3.0962	2.9028	0.2393	0.5430	1.2475
HMX	4.0232	3.8679	0.6605	0.7576	1.5855

Computation of molecular descriptors

In addition to the conventional physical properties estimated from molecular structure, the Abraham descriptors were computed. These descriptors are the foundation of the Abraham method (Abraham 1993) that correlates solvent-solute interactions using a solvation parameter approach. The solvation property (SP) is a linear combination of solute specific descriptors, as shown in equation (7):

$$\log(\text{SP}) = c + rR_2 + s\pi_2^H + a\sum \alpha_2^H + b\sum \beta_2^H + vV_x \quad \text{Eq 7}$$

where:

- R_2 = the excess molar refraction (molar refraction of the solute minus the molar refraction of an alkane of equivalent volume)
- π_2^H = the descriptor for combined dipolarity/polarizability
- $\sum \alpha_2^H$ = the overall solute hydrogen bond acidity
- $\sum \beta_2^H$ = the overall solute hydrogen bond basicity
- V_x = McGowan's characteristic volume (Abraham and McGowan 1987).

Table 6 lists the Abraham descriptors as computed in COSMOtherm.

Estimation of physicochemical properties

Physicochemical properties include aqueous solubility, octanol-water partition coefficient, and Henry's constant (among others). These properties determine how a particular compound partitions in the environment and distributes among phases. Key to these properties is an understanding of their influence on potential treatment technologies. For example, alkaline

hydrolysis is often used to remediate contaminated water streams, but the solubility of the contaminant in the stream is critical; alkaline hydrolysis may not be the preferred method of remediation for compounds exhibiting extremely low solubilities in aqueous solution.

Aqueous solubility

Monteil-Rivera et al. (2004) reported experimental measurements for the aqueous solubility as a function of temperature, the 1-octanol/water partition coefficient at 21 °C, and the soil-water distribution coefficient at 21 °C, for ϵ -CL20, RDX and HMX. Aqueous solubility for ϵ -CL20 has also been reported by Karakaya et al. (2005). Lynch et al. (2001) measured the solubility of three energetic compounds, trinitrotoluene (TNT), RDX and HMX over a moderate temperature range (2–38 °C) as a function of solution pH (4.2-6.2). Aqueous solubility increased with temperature increase. Monteil-Rivera et al. (2004) also reported aqueous solubility measurements for RDX, HMX, and ϵ -CL20 over the temperature range of 5 to 60 °C. These data provide the means for validating the estimation techniques.

For the compounds of interest, experimental aqueous solubility data have only been reported for NTO, MNA, and DNAN. Kim et al. (1998) reported measurements of aqueous solubility of NTO in water over a fairly wide temperature range of 284.65 to 367.55 K. Boddu et al. (2008a) reported experimental measurements of aqueous solubility for DNAN. Experimental solubility measurements for MNA were also reported by Boddu et al. (2008b).

Group contribution methods for the estimation of aqueous solubility at 25 °C are numerous and vary in their complexity. The methods applicable in this work are limited as many of the reported methods do not include a functional group for nitrogen in a ring structure in their development. The widely-used methods of Klopman (1992) contain this required functional group in Model II of Klopman. In Klopman's Model II, 67 different functional groups are considered. The general form of the Klopman model is:

$$\log_{10} \left[S_w \left(\frac{g}{L} \right) \right] = C_0 + \sum_i g_i G_i \quad \text{Eq 8}$$

where:

- S_w = the aqueous solubility in g/L
- C_0 = a constant
- G_i = the contribution to the solubility due to functional group i
- g_i = the number of functional group i contained in the molecule.

The solubility of a solid solute in a liquid is given by (Poling et al. 2001):

$$\ln(\gamma_2 x_2) = -\frac{\Delta S_m}{R} \left(\frac{T_m}{T} - 1 \right) = -\frac{\Delta H_m}{RT} \left(1 - \frac{T}{T_m} \right) \quad \text{Eq 9}$$

where:

- x_2 = the mole fraction of the solute in the solution
- ΔS_m = the entropy of fusion, ΔH_m is the enthalpy of fusion
- T_m = the melting point in K
- R = the gas constant
- T = the temperature of interest in K.

The ideal solubility is obtained when γ_2 , the activity coefficient of the solute in the solution, is set to unity.

Table 7 lists a compilation of aqueous solubility predictions using the method of Klopman et al., COSMOtherm, and the ideal solubility (equation [8]). The predictions using the method of Klopman and from COSMOtherm are in excellent agreement with one another for every compound examined. The ideal solubility predicted for each compound is much greater (often 3 to 4 orders of magnitude greater) compared to predictions of Klopman and of COSMOtherm. These results indicate that aqueous solutions containing these energetic compounds exhibit extremely large deviations from ideal behavior.

Also of interest in the present work is the temperature dependence of aqueous solubility. No group contribution methods exist to predict said temperature dependence. Thus, an alternate approach was undertaken using COSMOtherm. Aqueous solubility data as a function of temperature were available for all three reference compounds. Predictions for these provide a means to assess estimation of temperature dependent aqueous solubility and were compared with available literature data where possible.

Aqueous solubility over the temperature range of 273.15 K to 373.15 K was estimated using COSMOtherm for each of the compounds of interest and for the reference compounds. For both RDX and HMX, the aqueous solubilities predicted using COSMOtherm were smaller than the literature data (Figures 8 and 9, RDX and HMX, respectively). The experimental data of Lynch et al. (2001) and of Monteil-Rivera et al. (2004) are in excellent agreement. Figure 10 shows aqueous solubility data for ϵ -CL20; the literature data of Monteil-Rivera et al. (2004) and of Karakaya et al. (2005) are shown as are the COSMOtherm predictions. The data of Karakaya et al.

(2005) extend over a fairly broad temperature range (273 – 338 K). The predictions from COSMOtherm reflect the general trends exhibited by the experimental data.

Table 7. Comparison of predictive methods for aqueous solubility at 298.15 °K.

Compound	Aqueous Solubility, S (g/L) from literature	Aqueous Solubility, S (g/L) Method of Klopman et al. (1992)	Aqueous Solubility, S (g/L) COSMOtherm prediction	Ideal Solubility, S (g/L) Equation (8)
DNAN	0.276 ^a	0.14	0.159	3706.5
DNP		0.51	0.733	1390.7
MNA	0.085 ^b	1.17	0.347	971.3
MTNI		0.23	0.291	4619.9
NTO	9.99 at 11.5 °C ^c 19.99 at 33.9 °C ^c	7.56	9.97	55.8
TATB		0.16	0.197	2.5
ϵ -CL20	3.65×10^{-3} ^d	3.86×10^{-3}	2.91×10^{-3}	17.9
RDX	56.35×10^{-3} ^d	14.2×10^{-3}	12.6×10^{-3}	40.3
HMX	4.46×10^{-3} ^d	2.7×10^{-3}	2.16×10^{-3}	3.81

^a Boddu et al. (2008a).
^b Boddu et al. (2008b).
^c Kim et al. (1998).
^d Monteil-Rivera et al. (2004).

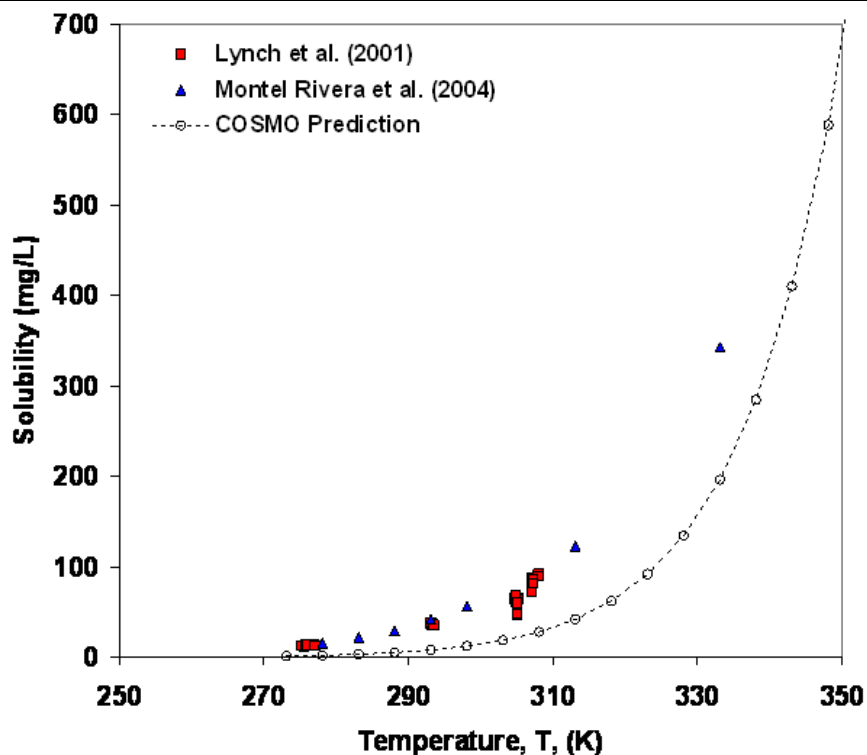


Figure 8. Aqueous solubility of RDX; literature data shown with COSMOtherm predictions.

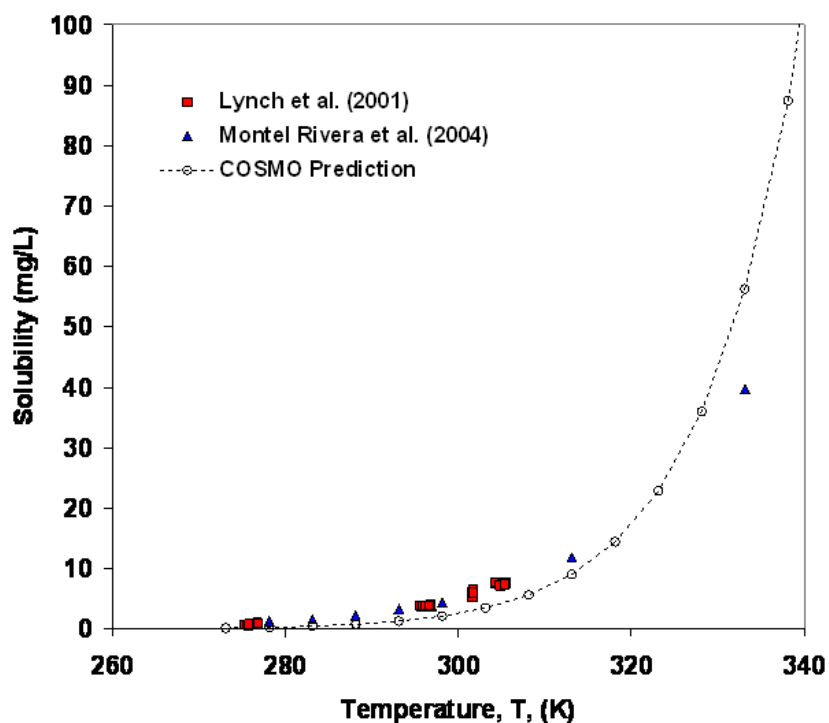


Figure 9. Aqueous solubility of HMX; literature data shown with COSMOtherm prediction.

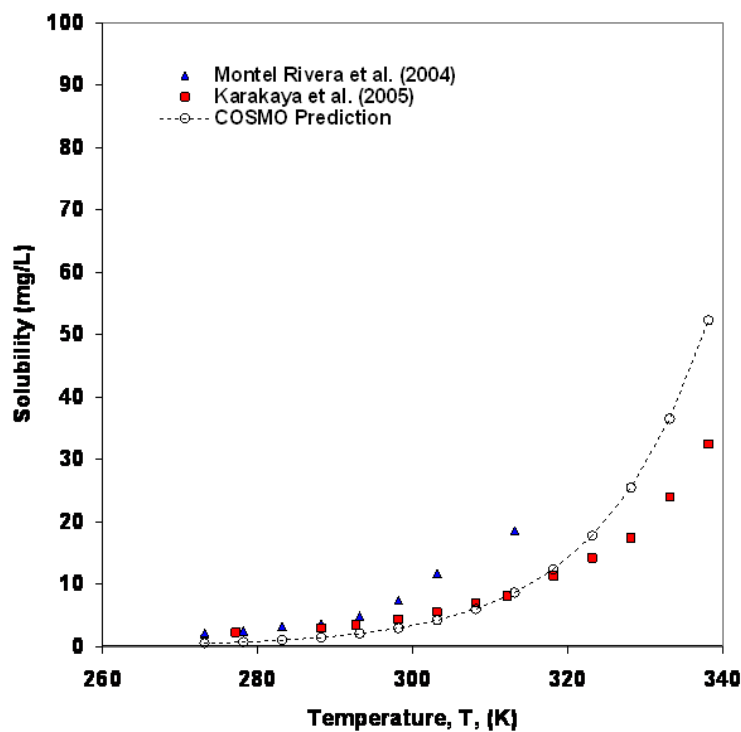


Figure 10. Aqueous solubility of ε-CL20; literature data shown with COSMOtherm predictions.

Figure 11 shows the experimental data of Kim et al. (1998) for the aqueous solubility of NTO. Again, the general trend of the experimental data is well predicted by COSMOtherm. The COSMOtherm predictions are slightly lower than the experimental data.

Figures 12 and 13 provide a comparison of recently reported experimental data for DNAN (Boddu et al. 2008a) and MNA (Boddu et al. 2008b), respectively. The COSMOtherm predictions for DNAN reflect the appropriate temperature dependence over the small temperature range examined (298.15 – 318.15 K) compared to the literature data, but predictions are slightly lower than the experimental data. For MNA, the experimental aqueous solubility is smaller, and COSMOtherm predictions are in good agreement with the experimental data. At 298.15 K, the experimental solubility for DNAN is 0.276 g/L while COSMOtherm predicts 0.159 g/L. At 298.15 K, the experimental solubility for MNA is 0.085 g/L while the COSMOtherm prediction is slightly larger at 0.347 g/L.

In general, COSMOtherm predictions of aqueous solubility are quite good, considering that these are *a priori* estimates based on molecular structure and on physical properties predicted using a variety of group contribution methods. COSMOtherm predictions were within 10 percent of the experimental data values, where available.

Figure 14 shows COSMOtherm predictions for all compounds of interest and for the reference compounds. The aqueous solubility for all compounds shows strong temperature dependence. NTO is predicted to be extremely soluble in water, with solubilities on the order of ~ 10 g/L at ambient temperature. The other compounds of interest are all predicted to be more soluble than the three reference compounds, by as much as 3 orders of magnitude.

Octanol-water partition coefficient

The octanol-water partition coefficient provides a measure of the hydrophobicity of a compound in addition to serving as a measure of the affinity of a solute to solubilize in an organic-rich (1-octanol) phase compared to in an aqueous phase (water). The partition coefficient is often reported as $\log_{10}(K_{ow})$, with a positive value indicating that a solute preferentially partitions into the organic phase, while a negative value indicates that the solute preferentially partitions into the aqueous phase. A positive octanol-water partition coefficient also indicates that the particular solute would have an affinity for organic matter in soil.

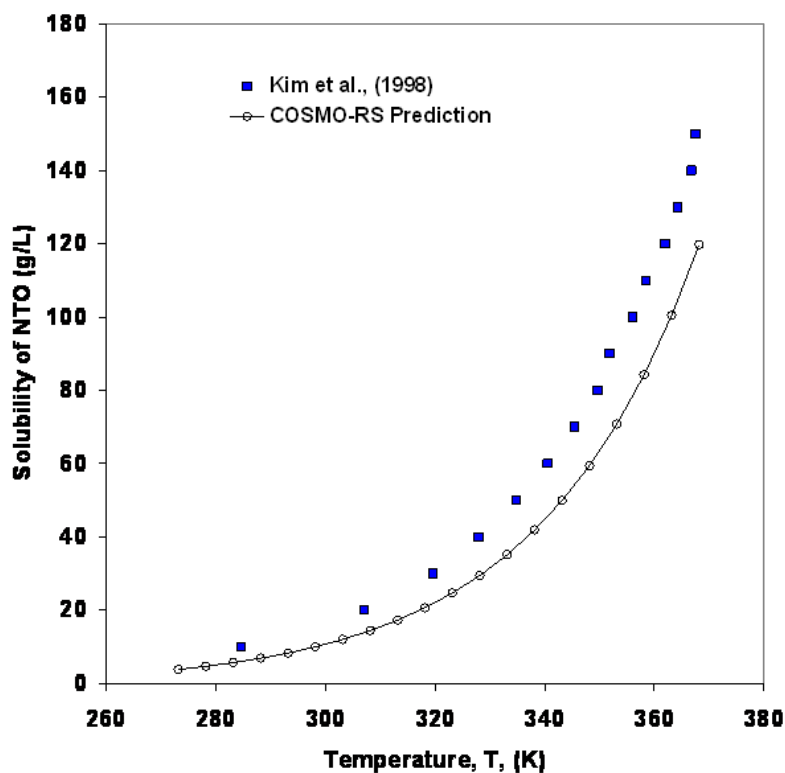


Figure 11. Aqueous solubility of NTO; literature data shown with COSMOtherm predictions.

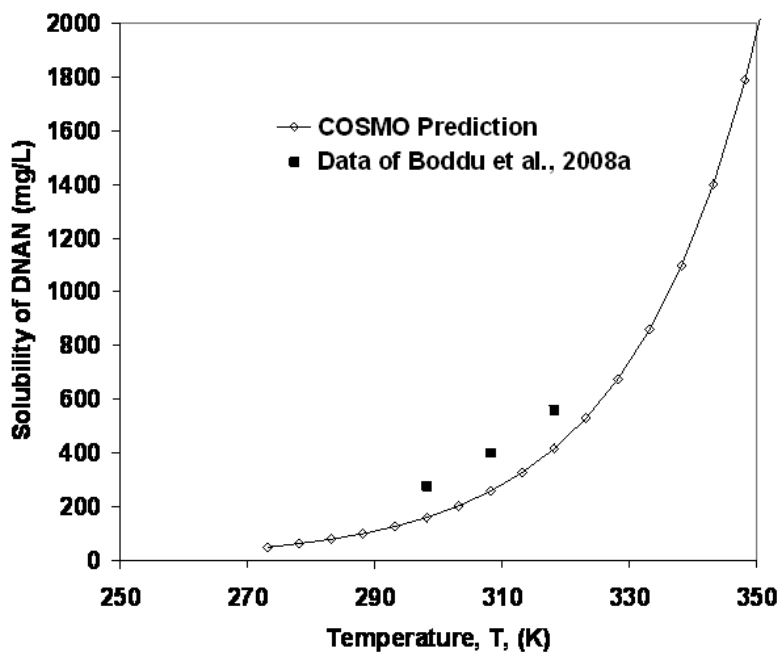


Figure 12. Aqueous solubility of DNAN; literature data shown with COSMOtherm predictions.

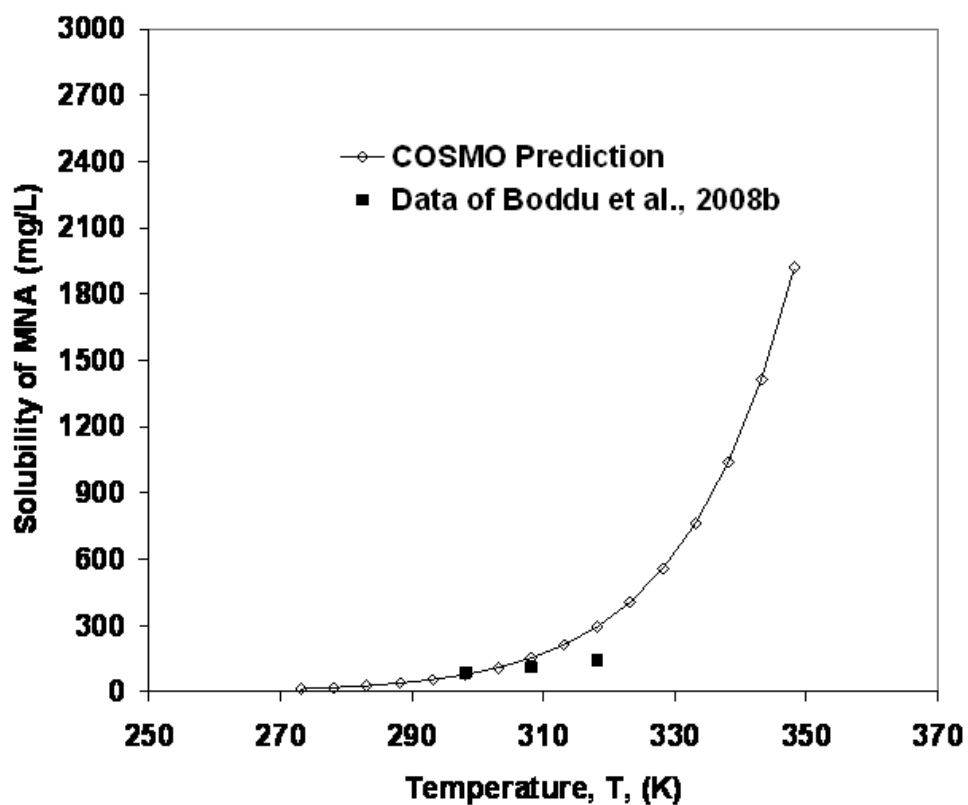


Figure 13. Aqueous solubility of MNA; literature data shown with COSMOtherm predictions.

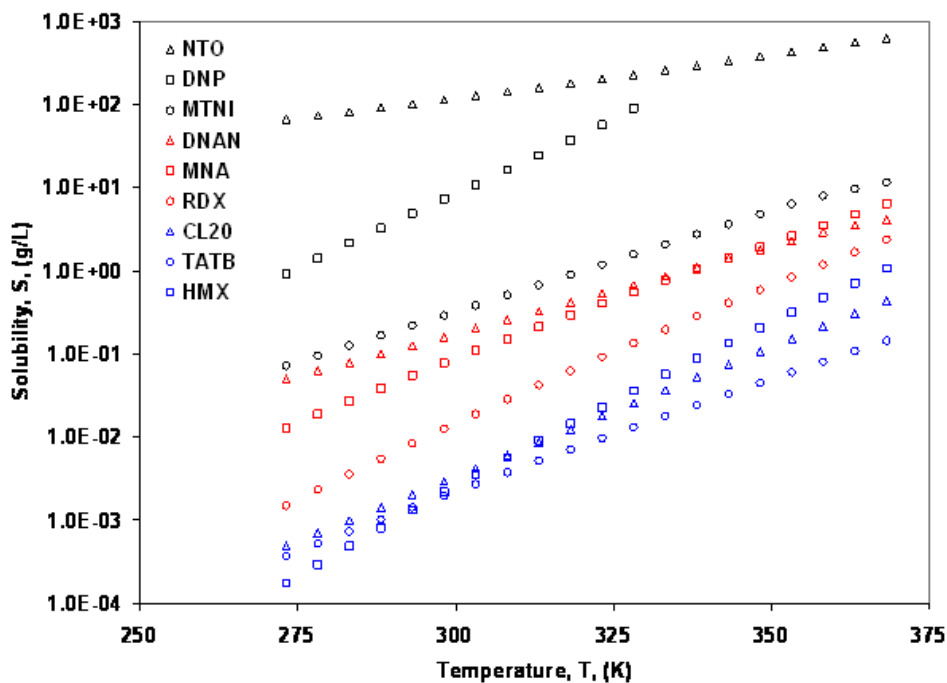


Figure 14. Solubilities of compounds of interest and reference compounds.

Two group contribution methods were examined for prediction of the octanol-water partition coefficient: the method of Broto et al. (1984) and the method of Ghose et al. (1988). These methods are atom contribution methods, wherein contributions from each atom are combined with contributions dependent on hybridization and the presence of heteroatoms as neighbors. These methods both used extensive training sets, composed of both a diversity of atoms and atomic environments. The Broto method is reported to provide K_{OW} values precise to 0.4 log units, while the precision of the Ghose method is reported as 0.496 log units (Ghose et al. 1988).

COSMOtherm predictions for the octanol-water partition coefficient were also performed. Table 8 lists the available experimental data, the predictions using the group contribution methods, and the COSMOtherm predictions at 298.15 K. For the majority of compounds, the predictions from the group contribution methods are in agreement. For DNP, the methods provide estimates that are similar in magnitude, but opposite in sign. For RDX, the values predicted using the group contribution methods and using COSMOtherm are in good agreement with the available literature values. The predictions for MNA using either group contribution method or COSMOtherm are significantly smaller than the experimentally determined values of 2.1028 ± 0.02 and 2.04. A difference of 1 unit in $\log_{10}(K_{OW})$ translates into an order of magnitude difference in the partition coefficient.

Based on the experimental data available in the literature, DNAN, MNA, and ϵ -CL20 would preferentially partition in the organic (1-octanol) phase to a greater extent than either RDX or HMX. MTNI is predicted to also partition into the organic phase. Both TATB and NTO are predicted to preferentially partition into the aqueous phase.

Henry's constant

The partitioning of a solute between the gas phase and the aqueous phase is described using the Henry's constant. This physicochemical parameter was evaluated using COSMOtherm results for the aqueous solubility and the vapor pressure of the solute over the temperature range 273.15 to 373.15 K. Figure 15 shows the resulting predictions for all compounds examined. With the exception of TATB, the Henry's constant values indicate that the compounds prefer to partition into the aqueous phase, rather than into a gas phase.

Table 8. Octanol-water partition coefficient at 298.15 °K.

Compound	Experimental Data	Method of Broto et al.	Method of Ghose et al.	COSMOtherm Prediction
DNAN	1.612 ^a	1.38	1.70	1.92
DNP		0.9	-0.99	0.37
MNA	2.1028 + 0.02 ^b 2.04 ^c	1.47	1.57	0.81
MTNI		-	0.48	1.64
NTO		-0.82	-	-1.19
TATB		-1.5	-0.44	4.74
ε-CL20	1.92 ^d at 21 °C	-	1.38	4.14
RDX	0.87 ^e 0.90 ^d at 21 °C	0.85	1.04	0.90
HMX	0.165 ^d at 21 °C	1.13	1.39	0.42

^a Boddu et al. (2008).
^b Boddu et al. (2008).
^c Banerjee et al. (1980).
^d Monteil-Rivera et al. (2004). Measurements at 21 °C.
^e Hansch (1979).

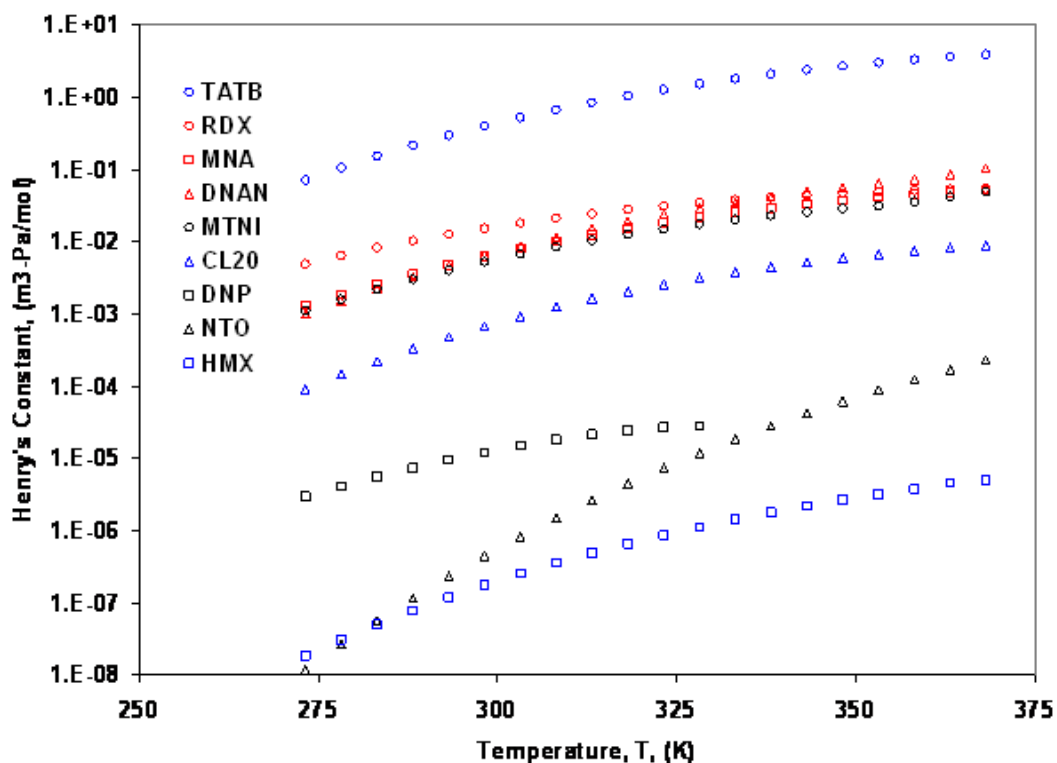


Figure 15. Predicted temperature dependence of Henry's Constant.

The extremely low volatility of the compounds is the dominant factor in determining Henry's constant. Table 9 lists the predictions for Henry's constant using COSMOtherm along with available experimental data for MNA and DNAN (Boddu et al. 2008a, 2008b). The estimated values are greater than the predicted values, by at least one order of magnitude. The influence of vapor pressure (estimated using COSMOtherm) on the predicted values warrants investigation. Accurate measurement of vapor pressure for the compounds of interest over the temperature range 283 K to 333 K would provide for improved estimates of the Henry's constant.

Table 9. Henry's constant at 298.15 °K.

Compound	Experimental Data (m ³ -Pa/mol)	COSMOtherm Prediction (m ³ -Pa/mol)
DNAN	1.366 ^a	6.37 x 10 ⁻³
DNP		1.20 x 10 ⁻⁵
MNA	0.61 ^b	6.18 x 10 ⁻³
MTNI		5.26 x 10 ⁻³
NTO		4.45 x 10 ⁻⁷
TATB		0.397
ε-CL20		6.73 x 10 ⁻⁴
RDX		0.153
HMX		1.75 x 10 ⁻⁷
a Boddu et al. (2008).		
b Boddu et al. (2008).		

3 Discussion

This work completed the estimation of physical properties and physico-chemical properties for the compounds of interest and for the reference compounds. One of the critical variables in the predictive approach is the vapor pressure (or sublimation pressure). Predictions of vapor pressure by COSMOtherm were compared with experimental data where available. For RDX, HMX, and TATB, the estimated vapor pressures were larger than the literature data by at least two orders of magnitude. Even where multiple data sets are available (for example, RDX, Figure 4; HMX, Figure 5), there are significant discrepancies between the data sets that cannot be attributed to experimental error. The influence of vapor/sublimation pressure on the physicochemical properties, in particular, on Henry's constant is significant. One recommendation to improve the quality of predictions is to expand the existing experimental program at CERL to measure the vapor/sublimation pressure of the energetic compounds of interest and the reference compounds. Establishing an experimental protocol for the accurate measurement of the vapor/sublimation pressures of materials with extremely low volatility would be of great benefit to the present work.

Results for the aqueous solubility as a function of temperature for the reference compounds provide a measure of validation for the predictive approach undertaken. With this approach, it is possible to predict aqueous solubility to within 10 percent of the experimental data using the molecular structure alone. The influence of the vapor/sublimation pressure on aqueous solubility should be examined as more accurate data become available for this property. An examination of the influence on aqueous solubility of salt addition, or the presence of caustic in the aqueous solution would also be beneficial, as data of this nature could be used to further enhance predictive capabilities using molecular structure alone.

The efforts at CERL undertaken in recent years to measure the physico-chemical properties as a function of temperature for these energetic compounds of interest will provide additional experimental data that may be used to validate and further refine the predictive techniques. Boddu et al. (2008a, 2008b) reported the influence of various inorganic salts on the solubility of DNAN and MNA; a demonstration of predictive capabilities that can reproduce the effects of salt addition on aqueous solubility would

be beneficial. Such predictive capabilities could then be used to examine/estimate the behavior of energetic compounds developed in the future. Data for the partition coefficients may also be used to examine whether other techniques provide more accurate predictions. It is difficult to assess the accuracy of the current predictive approach with the sparse amount of experimental data available at the present time, in particular for Henry's constant.

4 Treatment Technologies

A variety of treatment technologies have been examined for the remediation of waste streams containing energetic compounds. Rodgers and Bunce (2001) published a review of the major technologies employed for remediation of nitroaromatic explosives. The majority of published studies have examined the remediation of waste streams containing TNT or TNT-related compounds. A few have examined remediation of RDX- and HMX-contaminated streams, and still fewer have examined treatment of streams containing ϵ -CL20. The primary focus of this effort is on waste water streams containing energetic compounds, which are generated during production of the compounds of interest. These streams may contain an energetic compound at or below its solubility limit, and may also contain small amounts of the compound in the solid phase. In the present effort, it is assumed that only a single contaminant is present in a given waste water stream.

A stream may be remediated by the destruction of the contaminant into less problematic compounds; technologies resulting in destruction of the contaminant include advanced oxidation processes, chemical reduction processes, and bioremediation processes. Alkaline hydrolysis has been examined as a treatment method for streams contaminated with energetic materials, including RDX, HMX, and ϵ -CL20. Remediation may also be accomplished with the recovery of the contaminant to a sufficient degree from the waste stream so that the wastewater may safely be released to the environment. The recovery is accomplished through separation processes such as extraction, stripping, adsorption or filtration. In some instances, it may be beneficial to combine distinct recovery and destruction steps in a process so as to improve the overall efficiency of the remediation process.

Hwang et al. (2005) examined remediation of TNT-contaminated water by alkaline hydrolysis. Batch reactor studies conducted over a range of pH (11–12) and over a range of initial contaminant concentrations (5–25 mg/L) yielded kinetic rate information. Using a pseudo first-order rate constant to describe the dependence on TNT concentration, Hwang et al. concluded that the destruction proceeded at a greater rate when the pH was greater (i.e., more alkaline). Balakrishnan et al. (2003) examined the alkaline hydrolysis of RDX, HMX, and ϵ -CL20 in two solutions of differing pH (10 versus 12.3). They found that ϵ -CL20 was degraded much more quickly in the alkaline environment compared to RDX or HMX and con-

cluded that this was due to the susceptibility of the polycyclic nitramine cage in ϵ -CL20 to nucleophilic attack.

Heilman et al. (1996) also examined the alkaline hydrolysis of RDX and HMX in aqueous solution and adsorbed to activated carbon. They demonstrated that elevated temperature (80 °C) and high pH (12) provided for increased hydrolysis reaction rate. Karakaya et al. (2005) examined the alkaline hydrolysis of ϵ -CL20 in both homogeneous and heterogeneous environments. Other process variables examined included caustic concentration (i.e., pH), and temperature (15 to 40 °C). Karakaya et al. also found that increased temperature and higher caustic loading (high pH) increased the rate of degradation by alkaline hydrolysis.

Comparison of rate constants determined from both homogeneous alkaline hydrolysis experiments and from heterogeneous experiments (conducted with an excess of ϵ -CL20 in solution) indicated that rate constants were approximately four times larger for the homogeneous reaction compared to the heterogeneous reaction. Key here are the findings that the homogeneous reaction rates were significantly larger than the heterogeneous reaction rates indicating that species with greater aqueous solubility may be better suited to treatment by alkaline hydrolysis. The influence of pH is also significant, with higher pH leading to a greater concentration of free hydroxide in the solution to participate in the hydrolysis reaction. Thus, alkaline hydrolysis may have the potential for treatment of NTO-contaminated waste. It may also be effective, but to a lesser degree, for those species exhibiting moderate aqueous solubility, including DNAN, DNP, MNA, MTNI, and TATB. It is essential for the validation of the predictive approach to incorporate such process variables as pH, or the presence of inorganic salt (salting out) to adequately capture their impact. Examination of the susceptibility to nucleophilic attack of particular bonds in the structure of the energetic material may also provide valuable information.

Chen et al. (2007a) examined recovery of nitrotoluenes from an aqueous stream using toluene as the solvent. They examined numerous process variables including temperature, solvent/wastewater ratio, wastewater acidity and agitation time. They demonstrated that recovery was strongly influenced by extraction temperature, and increased as temperature increased. They also found that low pH and a solvent/wastewater ratio of 2 enhanced recovery. In a subsequent effort, Chen et al. (2007b) also examined the enhancement of the extraction process through the addition of inorganic salts, and found sodium chloride to be most effective. The use of

solvent extraction relies on the affinity of a compound for the organic phase; thus, extraction may be a suitable treatment method for DNAN, MNA, and ϵ -CL20, and to a lesser extent, DNP and MTNI. However, with the affinity of both NTO and TATB for the aqueous phase, solvent extraction would not be suitable for remediation of streams contaminated with these energetic materials.

Adsorption of energetic materials using activated carbon or similar materials was also examined in the literature (Rodgers and Bunce 2001, Tomaszewski et al. 2003, Rajagopal and Kapoor 2001). However, a review of these and other efforts indicate that assessment of adsorption as a remediation method for energetic materials is not solely a function of the structure of the energetic material. Indeed, the structure of the adsorbent and the implementation of the adsorption process influence the process performance.

Table 10 lists potential treatment technologies for waste streams containing individual energetic materials. The potential for a particular treatment technology was assessed on the basis of the predictions carried out in this work for the various physicochemical properties of the energetic materials.

Table 10. Potential of existing treatment technologies.

Compound	Treatment Approach			
	Chemical Processes		Physical Separation Processes	Bioremediation
	Oxidation	Reduction	Adsorption, Extraction, Membrane	
DNAN	AH (M)		Ex (H); Ad(I)	I
DNP	AH (M)		Ex (M); Ad(I)	I
MNA	AH (M)		Ex (H); Ad(I)	I
MTNI	AH (M)		Ex (M); Ad(I)	I
NTO	AH (H)		Ex (L); Ad(I)	I
TATB	AH (M)		Ex (L); Ad(I)	I
L - low possibility; M-Medium possibility; H-High possibility; I - Insufficient information Ex - Extraction; Ad - Adsorption; AH - Alkaline Hydrolysis				

5 Conclusion

This work used the molecular structures of six compounds of interest and three reference compounds to estimate the physical properties including critical temperature and pressure, normal boiling point, vapor pressure, and enthalpy of fusion that are essential when using group contribution methods for estimation of partition coefficients. TURBOMOLE (a quantum chemical software package that allows DFT computations to be readily performed) was used to optimize geometry for each compound's molecular structure. The result of the DFT computation was an input file containing a numerical description of the electrostatic potential surface of the given compound.

This work concluded that, when these electrostatic potential surface descriptions are incorporated into the COSMOtherm program along with estimated physical property values, it is possible to *a priori* predict solute partitioning into the aqueous phase (aqueous solubility), between organic and aqueous phases (octanol-water partition coefficient), into the gas phase (vapor pressure) and between gas and aqueous phases (Henry's constant). In the majority of cases where experimental data were available, the *a priori* estimates were within experimental error, excepting for vapor pressure estimates.

This work recommends that further efforts be directed at experimental determination of vapor pressure, aqueous solubility, partition coefficients over a wider range of temperatures, so that more meaningful assessment of waste treatment technologies may be realized.

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Acronyms and Abbreviations

<u>Term</u>	<u>Spellout</u>
ACS	American Chemical Society
AMD	Advanced Micro Devices, Inc.
CAS	Chemical Abstracts Service
CERL	Construction Engineering Research Laboratory
COSMO	<u>C</u> onductor-like <u>S</u> creening <u>M</u> odel
DFT	density functional theory
DNAN	2,4-dinitroanisole
DNP	3,4-Dinitropyrazole
ERDC	Engineer Research and Development Center
HMX	octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine
MNA	N-methyl-4-nitroaniline
MSDS	Material Safety Data Sheet
MTNI	1-Methyl-2,4,5-trinitroimidazole
NTO	3-Nitro-1,2,4-triazol-5-one
PDB	protein databank
QSPR/QSAR	quantitative structure-property/activity relationships
RDX	cyclotrimethylene-trinitramine
SMILES	S implified M olecular I ntput L ine E ntry S pecification
SP	solvation property
TATB	2,4,6-Triamino-1,3,5-trinitrobenzene
TNT	trinitrotoluene
TR	Technical Report
TZVP	triple zeta valence Gaussian
URL	Universal Resource Locator
WWW	World Wide Web

Appendix A: Reference Compound ϵ -CL20 - *.pdb and *.xyz file contents.

CL20.PDB File Contents

HEADER	CL20								NONE	1
ATOM	1	O	0	-2.420	-2.518	1.782	0.00	0.00		O+0
ATOM	2	N	0	-2.335	-1.303	1.815	0.00	0.00		N+0
ATOM	3	N	0	-1.165	-0.670	1.375	0.00	0.00		N+0
ATOM	4	C	0	-0.800	0.784	1.307	0.00	0.00		C+0
ATOM	5	C	0	0.745	0.883	1.313	0.00	0.00		C+0
ATOM	6	N	0	1.221	1.344	-0.012	0.00	0.00		N+0
ATOM	7	C	0	0.790	0.610	-1.198	0.00	0.00		C+0
ATOM	8	C	0	-0.746	0.695	-1.228	0.00	0.00		C+0
ATOM	9	N	0	-1.245	1.312	0.008	0.00	0.00		N+0
ATOM	10	N	0	-2.136	2.392	-0.049	0.00	0.00		N+0
ATOM	11	O	0	-2.545	2.899	0.980	0.00	0.00		O+0
ATOM	12	O	0	-2.501	2.824	-1.128	0.00	0.00		O+0
ATOM	13	N	0	-1.158	-0.697	-1.241	0.00	0.00		N+0
ATOM	14	C	0	-0.084	-1.561	-0.652	0.00	0.00		C+0
ATOM	15	N	0	1.117	-0.823	-1.219	0.00	0.00		N+0
ATOM	16	N	0	2.310	-1.400	-1.677	0.00	0.00		N+0
ATOM	17	O	0	3.201	-0.692	-2.111	0.00	0.00		O+0
ATOM	18	O	0	2.455	-2.608	-1.641	0.00	0.00		O+0
ATOM	19	C	0	0.094	-1.227	0.838	0.00	0.00		C+0
ATOM	20	N	0	1.227	-0.524	1.312	0.00	0.00		N+0
ATOM	21	N	0	2.482	-1.024	1.684	0.00	0.00		N+0
ATOM	22	O	0	3.349	-0.263	2.074	0.00	0.00		O+0
ATOM	23	O	0	2.706	-2.219	1.617	0.00	0.00		O+0
ATOM	24	N	0	-2.384	-1.165	-1.733	0.00	0.00		N+0
ATOM	25	O	0	-2.638	-2.356	-1.700	0.00	0.00		O+0
ATOM	26	O	0	-3.195	-0.382	-2.194	0.00	0.00		O+0
ATOM	27	N	0	2.063	2.457	-0.124	0.00	0.00		N+0
ATOM	28	O	0	2.446	2.824	-1.221	0.00	0.00		O+0
ATOM	29	O	0	2.413	3.060	0.875	0.00	0.00		O+0
ATOM	30	O	0	-3.269	-0.639	2.227	0.00	0.00		O+0
ATOM	31	H	0	-1.233	1.338	2.140	0.00	0.00		H+0
ATOM	32	H	0	1.130	1.484	2.137	0.00	0.00		H+0
ATOM	33	H	0	1.200	1.083	-2.090	0.00	0.00		H+0
ATOM	34	H	0	-1.096	1.234	-2.108	0.00	0.00		H+0
ATOM	35	H	0	-0.154	-2.621	-0.893	0.00	0.00		H+0
ATOM	36	H	0	0.168	-2.201	1.322	0.00	0.00		H+0
CONNECT	1	2	0	0					NONE	41
CONNECT	2	1	3	30	0				NONE	42
CONNECT	3	2	19	4	0				NONE	43
CONNECT	4	3	9	5	31				NONE	44
CONNECT	5	4	20	6	32				NONE	45
CONNECT	6	5	7	27	0				NONE	46
CONNECT	7	6	15	8	33				NONE	47
CONNECT	8	7	9	13	34				NONE	48
CONNECT	9	8	4	10	0				NONE	49
CONNECT	10	9	11	12	0				NONE	50
CONNECT	11	10	0	0	0				NONE	51
CONNECT	12	10	0	0	0				NONE	52
CONNECT	13	8	14	24	0				NONE	53
CONNECT	14	13	15	19	35				NONE	54
CONNECT	15	14	7	16	0				NONE	55
CONNECT	16	15	17	18	0				NONE	56
CONNECT	17	16	0	0	0				NONE	57
CONNECT	18	16	0	0	0				NONE	58
CONNECT	19	14	3	20	36				NONE	59
CONNECT	20	19	5	21	0				NONE	60
CONNECT	21	20	22	23	0				NONE	61
CONNECT	22	21	0	0	0				NONE	62
CONNECT	23	21	0	0	0				NONE	63
CONNECT	24	13	25	26	0				NONE	64

CONNECT	25	24	0	0	0	NONE	65
CONNECT	26	24	0	0	0	NONE	66
CONNECT	27	6	28	29	0	NONE	67
CONNECT	28	27	0	0	0	NONE	68
CONNECT	29	27	0	0	0	NONE	69
CONNECT	30	2	0	0	0	NONE	70
END						NONE	71

CL20.XYZ File Contents

```

36
Energy:      0.0000000
O      -2.42036      -2.52717      1.76569
N      -2.33536      -1.31217      1.79869
N      -1.16536      -0.67917      1.35869
C      -0.80036      0.77483      1.29069
C      0.74464      0.87383      1.29669
N      1.22064      1.33483      -0.02831
C      0.78964      0.60083      -1.21431
C      -0.74636      0.68583      -1.24431
N      -1.24536      1.30283      -0.00831
N      -2.13636      2.38283      -0.06531
O      -2.54536      2.88983      0.96369
O      -2.50136      2.81483      -1.14431
N      -1.15836      -0.70617      -1.25731
C      -0.08436      -1.57017      -0.66831
N      1.11664      -0.83217      -1.23531
N      2.30964      -1.40917      -1.69331
O      3.20064      -0.70117      -2.12731
O      2.45464      -2.61717      -1.65731
C      0.09364      -1.23617      0.82169
N      1.22664      -0.53317      1.29569
N      2.48164      -1.03317      1.66769
O      3.34864      -0.27217      2.05769
O      2.70564      -2.22817      1.60069
N      -2.38436      -1.17417      -1.74931
O      -2.63836      -2.36517      -1.71631
O      -3.19536      -0.39117      -2.21031
N      2.06264      2.44783      -0.14031
O      2.44564      2.81483      -1.23731
O      2.41264      3.05083      0.85869
O      -3.26936      -0.64817      2.21069
H      -1.23336      1.32883      2.12369
H      1.12964      1.47483      2.12069
H      1.19964      1.07383      -2.10631
H      -1.09636      1.22483      -2.12431
H      -0.15436      -2.63017      -0.90931
H      0.16764      -2.21017      1.30569

```

Appendix B: Cranium Predictions – Output for Compounds of Interest and Reference Compounds

HNIW

Descriptive Information:

Formula: C₆H₆N₁₂O₁₂

CAS #: 135285-90-4

Similar To: ---

Synonyms:

CL20

Structure Information:

Sym Num: ---

Opt Iso: ---

Chemical Families:

Oxygenated

Unsaturated

Molecular Structure:

Constant Properties:

Property	Data	Ref	Ests	Ref	Units
Mw:	---	---	4.3819E+02	[000]	---
dpm:	---	---	---	---	C m
rg:	---	---	---	---	m
Tm:	---	---	---	---	K
Tb:	8.6200E+02	[002]	8.6176E+02	[002]	K
Tc:	---	---	1.0580E+03	[003]	K
Pc:	---	---	4.8902E+06	[004]	Pa
Vc:	---	---	2.2274E-03	[005]	m ³ /kg
Zc:	---	---	5.4258E-01	[006]	---
acf:	---	---	2.5472E+00	[007]	---
Cp,298:	---	---	---	---	J/kg K
Hf,298:	---	---	---	---	J/kg
S,298:	---	---	---	---	J/kg K
Gf,298:	---	---	---	---	J/kg
Hvb:	4.7101E+05	---	4.4607E+05	[008]	J/kg
Hm:	---	---	---	---	J/kg
Hc,298:	---	---	---	---	J/kg
Tf:	---	---	---	---	K
LFL:	---	---	1.9223E+00	[009]	Vol %
UFL:	---	---	---	---	Vol %

hmx**Descriptive Information:**Formula: C₄H₈N₈O₈

CAS #: 2691-41-0

Similar To: ---

Synonyms:

Structure Information:

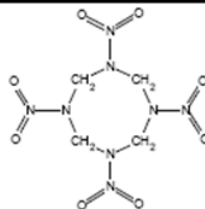
Sym Num: ---

Opt Iso: ---

Chemical Families:

Oxygenated

Unsaturated

Molecular Structure:**Constant Properties:**

Property	Data	Ref	Ests	Ref	Units
Mw:	---	---	2.9616E+02	[000]	---
dpm:	---	---	---	---	C m
rg:	---	---	---	---	m
Tm:	---	---	---	---	K
Tb:	---	---	7.0954E+02	[001]	K
Tc:	---	---	9.1345E+02	[002]	K
Pc:	---	---	5.2970E+06	[003]	Pa
Vc:	---	---	2.2218E-03	[004]	m ³ /kg
Zc:	---	---	4.5894E-01	[005]	---
acf:	---	---	1.7002E+00	[006]	---
Cp,298:	---	---	---	---	J/kg K
Hf,298:	---	---	---	---	J/kg
S,298:	---	---	---	---	J/kg K
Gf,298:	---	---	---	---	J/kg
Hvb:	---	---	4.2007E+05	[007]	J/kg
Hm:	---	---	---	---	J/kg
Hc,298:	---	---	---	---	J/kg
Tf:	---	---	---	---	K
LFL:	---	---	2.3063E+00	[008]	Vol %
UFL:	---	---	---	---	Vol %

RDX

Descriptive Information:

Formula: C₃H₆N₆O₆

CAS #: 121-82-4

Similar To: ---

Synonyms:

Structure Information:

Sym Num: ---

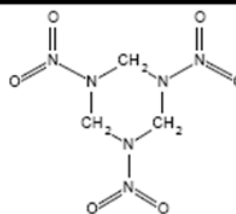
Opt Iso: ---

Chemical Families:

Oxygenated

Unsaturated

Molecular Structure:



Constant Properties:

Property	Data	Ref	Ests	Ref	Units
Mw:	---	---	2.2212E+02	[000]	---
dpm:	---	---	---	---	C m
rg:	---	---	---	---	m
Tm:	---	---	---	---	K
Tb:	6.2660E+02	[002]	6.2656E+02	[002]	K
Tc:	---	---	8.4274E+02	[003]	K
Pc:	---	---	5.8006E+06	[004]	Pa
Vc:	---	---	2.0777E-03	[005]	m ³ /kg
Zc:	---	---	3.8207E-01	[006]	---
acf:	---	---	1.2524E+00	[007]	---
Cp,298:	---	---	---	---	J/kg K
Hf,298:	---	---	---	---	J/kg
S,298:	---	---	---	---	J/kg K
Gf,298:	---	---	---	---	J/kg
Hvb:	---	---	4.1894E+05	[008]	J/kg
Hm:	---	---	---	---	J/kg
Hc,298:	---	---	---	---	J/kg
Tf:	---	---	---	---	K
LFL:	---	---	3.0750E+00	[009]	Vol %
UFL:	---	---	---	---	Vol %

Dinitroaniso

Descriptive Information:

Formula: C₇H₆N₂O₅

CAS #: 119-27-7

Similar To: ---

Synonyms:

benzene, 1-methoxy-2,4-dinitro- (9CI)

DNAN

Structure Information:

Sym Num: ---

Opt Iso: ---

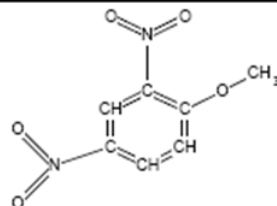
Chemical Families:

Aromatic

Ether

Oxygenated

Molecular Structure:



Constant Properties:

Property	Data	Ref	Ests	Ref	Units
Mw:	---	---	1.9814E+02	[000]	---
dpm:	---	---	---	---	C m
rg:	---	---	---	---	m
Tm:	---	---	5.2906E+02	[001]	K
Tb:	---	---	5.8757E+02	[002]	K
Tc:	---	---	8.0625E+02	[003]	K
Pc:	---	---	3.9956E+06	[004]	Pa
Vc:	---	---	2.4731E-03	[005]	m ³ /kg
Zc:	---	---	2.9208E-01	[006]	---
acf:	---	---	8.5766E-01	[007]	---
Cp,298:	---	---	9.2217E+02	[008]	J/kg K
Hf,298:	---	---	-6.4582E+05	[009]	J/kg
S,298:	---	---	---	---	J/kg K
Gf,298:	---	---	4.1245E+05	[010]	J/kg
Hvb:	---	---	3.5512E+05	[012]	J/kg
Hm:	---	---	1.5671E+05	[011]	J/kg
Hc,298:	---	---	---	---	J/kg
Tf:	---	---	---	---	K
LFL:	---	---	1.5133E+00	[013]	Vol %
UFL:	---	---	---	---	Vol %

Dinitro pyrazole

Descriptive Information:

Formula: C₃H₂N₄O₄

CAS #: 38858-92-3

Similar To: ---

Synonyms:

DNP

1H-Pyrazole, 1,4-dinitro- (9CI)

Structure Information:

Sym Num: ---

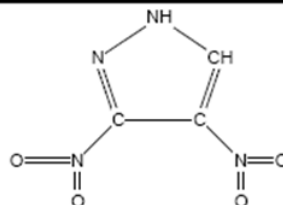
Opt Iso: ---

Chemical Families:

Oxygenated

Unsaturated

Molecular Structure:



Constant Properties:

Property	Data	Ref	Ests	Ref	Units
Mw:	---	---	1.5807E+02	[000]	---
dpm:	---	---	---	---	C m
rg:	---	---	---	---	m
Tm:	---	---	6.2856E+02	[001]	K
Tb:	---	---	5.7448E+02	[002]	K
Tc:	---	---	8.1676E+02	[003]	K
Pc:	---	---	6.9329E+06	[004]	Pa
Vc:	---	---	2.3249E-03	[005]	m ³ /kg
Zc:	---	---	3.7521E-01	[006]	---
acf:	---	---	3.0709E+00	[007]	---
Cp,298:	---	---	7.8012E+02	[008]	J/kg K
Hf,298:	---	---	7.4187E+05	[009]	J/kg
S,298:	---	---	---	---	J/kg K
Gf,298:	---	---	1.9584E+06	[010]	J/kg
Hvb:	---	---	4.4846E+05	[012]	J/kg
Hm:	---	---	2.2456E+05	[011]	J/kg
Hc,298:	---	---	---	---	J/kg
Tf:	---	---	---	---	K
LFL:	---	---	3.7821E+00	[013]	Vol %
UFL:	---	---	---	---	Vol %

N-methyl-*p*-nitroaniline

Descriptive Information:

Formula: C7H8N2O2

CAS #: 99-52-5

Similar To: ---

Synonyms:

MNA

2-methyl-4-nitro-benzenamine

2-amino-5-nitrotoluene

Structure Information:

Sym Num: ---

Opt Iso: ---

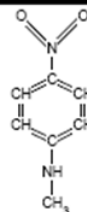
Chemical Families:

Amine

Aromatic

Oxygenated

Molecular Structure:



Constant Properties:

Property	Data	Ref	Ests	Ref	Units
Mw:	---	---	1.5215E+02	[000]	---
dpm:	---	---	---	---	C m
rg:	---	---	---	---	m
Tm:	---	---	4.0336E+02	[001]	K
Tb:	---	---	5.2730E+02	[002]	K
Tc:	---	---	7.4754E+02	[003]	K
Pc:	---	---	4.1677E+06	[004]	Pa
Vc:	---	---	2.8261E-03	[005]	m ³ /kg
Zc:	---	---	2.8835E-01	[006]	---
acf:	---	---	6.5881E-01	[007]	---
Cp,298:	---	---	1.0160E+03	[008]	J/kg K
Hf,298:	---	---	5.2552E+05	[009]	J/kg
S,298:	---	---	---	---	J/kg K
Gf,298:	---	---	1.6443E+06	[010]	J/kg
Hvb:	---	---	3.7552E+05	[012]	J/kg
Hm:	---	---	1.5707E+05	[011]	J/kg
Hc,298:	---	---	---	---	J/kg
Tf:	---	---	---	---	K
LFL:	---	---	1.2745E+00	[013]	Vol %
UFL:	---	---	---	---	Vol %

1H-Imidazole, 1-methyl-2,4,5-trinitro-

Descriptive Information:

Formula: C₄H₃N₅O₆

CAS #: 19183-20-1

Similar To: ---

Synonyms:

Imidazole, 1-methyl-2,4,5-trinitro-

1-Methyl-2,4,5-trinitroimidazole

MTNI

Structure Information:

Sym Num: ---

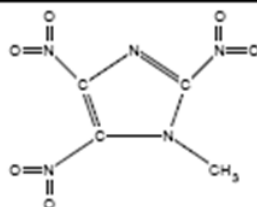
Opt Iso: ---

Chemical Families:

Oxygenated

Unsaturated

Molecular Structure:



Constant Properties:

Property	Data	Ref	Ests	Ref	Units
Mw:	---	---	2.1710E+02	[000]	---
dpm:	---	---	---	---	C m
rg:	---	---	---	---	m
Tm:	---	---	7.2892E+02	[001]	K
Tb:	---	---	8.2907E+02	[002]	K
Tc:	---	---	8.4501E+02	[003]	K
Pc:	---	---	5.4707E+08	[004]	Pa
Vc:	---	---	2.2778E-03	[005]	m ³ /kg
Zc:	---	---	3.8507E-01	[006]	---
acf:	---	---	7.0669E-01	[007]	---
Cp,298:	---	---	---	---	J/kg K
Hf,298:	---	---	---	---	J/kg
S,298:	---	---	---	---	J/kg K
Gf,298:	---	---	---	---	J/kg
Hvb:	---	---	4.2413E+05	[008]	J/kg
Hm:	---	---	---	---	J/kg
Ho,298:	---	---	---	---	J/kg
Tf:	---	---	---	---	K
LFL:	---	---	2.9847E+00	[009]	Vol %
UFL:	---	---	---	---	Vol %

Nitro Triazolene

Descriptive Information:

Formula: C₂H₂N₄O₃

CAS #: 932-64-9

Similar To: ---

Synonyms:

NTO

5-oxo-3-nitro-1,2,4-triazole

3-nitro-1,2,4-triazol-5-one

Structure Information:

Sym Num: ---

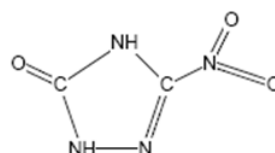
Opt Iso: ---

Chemical Families:

Oxygenated

Unsaturated

Molecular Structure:



Constant Properties:

Property	Data	Ref	Ests	Ref	Units
Mw:	---	---	1.3006E+02	[000]	---
dpm:	---	---	---	---	C m
rg:	---	---	---	---	m
Tm:	---	---	6.3365E+02	[001]	K
Tb:	---	---	5.6841E+02	[002]	K
Tc:	---	---	8.2852E+02	[003]	K
Pc:	---	---	8.6052E+06	[004]	Pa
Vc:	---	---	2.2105E-03	[005]	m ³ /kg
Zc:	---	---	3.5916E-01	[006]	---
acf:	---	---	7.9831E-01	[007]	---
Cp,298:	---	---	7.6850E+02	[008]	J/kg K
Hf,298:	---	---	1.8991E+04	[009]	J/kg
S,298:	---	---	---	---	J/kg K
Gf,298:	---	---	1.6176E+06	[010]	J/kg
Hvb:	---	---	4.7765E+05	[012]	J/kg
Hm:	---	---	2.7550E+05	[011]	J/kg
Hc,298:	---	---	---	---	J/kg
Tf:	---	---	---	---	K
LFL:	---	---	4.9950E+00	[013]	Vol %
UFL:	---	---	---	---	Vol %

Triaminotrinitrobenzene

Descriptive Information:

Formula: C₆H₃N₆O₆

CAS #: 3058-38-6

Similar To: ---

Synonyms:

TATB

1,3,5-triamino-2,4,6-trinitrobenzene

s-triaminotrinitrobenzene

Structure Information:

Sym Num: ---

Opt Iso: ---

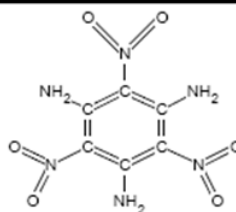
Chemical Families:

Amine

Aromatic

Oxygenated

Molecular Structure:



Constant Properties:

Property	Data	Ref	Ests	Ref	Units
Mw:	---	---	2.5815E+02	[000]	---
dpm:	---	---	---	---	C m
rg:	---	---	---	---	m
Tm:	---	---	9.2651E+02	[001]	K
Tb:	---	---	7.1158E+02	[002]	K
Tc:	---	---	9.1266E+02	[003]	K
Pc:	---	---	5.6447E+06	[004]	Pa
Vc:	---	---	2.3107E-03	[005]	m ³ /kg
Zc:	---	---	4.4375E-01	[006]	---
acf:	---	---	1.8023E+00	[007]	---
Cp,298:	---	---	9.4180E+02	[008]	J/kg K
Hf,298:	---	---	3.1416E+05	[009]	J/kg
S,298:	---	---	---	---	J/kg K
Gf,298:	---	---	1.4887E+06	[010]	J/kg
Hvb:	---	---	4.5020E+05	[012]	J/kg
Hm:	---	---	2.0551E+05	[011]	J/kg
Hc,298:	---	---	---	---	J/kg
Tf:	---	---	---	---	K
LFL:	---	---	1.6717E+00	[013]	Vol %
UFL:	---	---	---	---	Vol %

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13. SUPPLEMENTARY NOTES					
14. ABSTRACT This objective of this work was to predict the physicochemical properties of six energetic materials. The energetic materials of interest were 2,4-Dinitroanisole (DNAN), 3,4-Dinitropyrazole (DNP), n-Methyl-p-nitroaniline (MNA), 1-Methyl-2,4,5-trinitroimidazole (MTNI), 3-Nitro-1,2,4-triazol-5-one (NTO), and 1,3,5-Triamino-2,4,6-trinitrobenzene (TATB). The physicochemical properties of interest were the aqueous solubility, the octanol-water partition coefficient and Henry's constant. Three reference compounds were chosen to provide validation of the proposed approach: cyclotrimethylene-trinitramine (RDX), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), and ε-CL20. Group contribution methods available in the literature were used for predictions. In addition, a number of physical properties were required, including critical temperature and pressure, normal boiling point, melting point, heat of fusion, and vapor pressure. These were also predicted using the chemical structure of the energetic compounds. Where literature data were available, comparisons with predictions were performed. Another purely predictive method, based on chemical structure, was also employed for the estimation of physicochemical properties. This method, based on the "Conductor-like Screening Model for Real Solvents," required quantum chemical calculations performed using TURBOMOLE to obtain the optimized electrostatic potential surface of each energetic material. The resulting surface was then used within the COSMOtherm software to predict solution behavior, including aqueous solubility, octanol-water partition coefficient, Henry's constant, and vapor pressure.					
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