

COMMON TRENDS IN THE RELATIONSHIPS BETWEEN CHEMICAL AND PHYSICAL PROPERTIES AND MOLECULAR STRUCTURE OF NITRAMINE, CAGE NITRAMINE, AND NITROAROMATIC ENERGETICS

¹Dr. Mohammad (Mo) Qasim*; ¹Dr. Minoru Uchimiya; ^{1,2}Dr. Leonid Gorb; ^{1,3}Dr. Jerzy Leszczynski;
^{1,4}Brett Moore; ^{1,4}Lyssa Taylor; ^{1,5}Matthew Middleton

¹USACE ERDC, 3909 Halls Ferry Rd., Vicksburg, MS 39180; ²SpecPro, Inc., Huntsville, AL; ³Computational Center for Molecular Structure and Interactions (CCMSI), Jackson State University, Jackson, MS; ⁴Mississippi College, Jackson, MS; ^{1,5}Mississippi State University, Starkville, MS

ABSTRACT

Chemical and physical properties of nitroaromatic and nitramine explosives were related to their molecular structure with the objective of predicting types, sites and rates of reactivity as well as prediction of transformation intermediate and final products, stability, and toxicity potential. Understanding these relationships is intrinsic to the development of computational chemistry (CC) protocols for basic research into new compounds as well as for specific applications to military sites. Our comparisons manifested new trends in fundamental relationships of these energetic compounds, including emergent compounds and their reactivities in the environment.

Three classes of nitro compounds of military interest were compared computationally and verified spectroscopically: i) nitroaromatic: trinitrotoluene (TNT) and derivatives; ii) cyclic nitramines: hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and octahydro-1,3,5,7-tetrazocine (HMX); and iii) cage nitramine: 2,4,6,8,10,12-hexanitrohexaazoisowurtzitane (CL-20). Hypothesis and methodology were extended to include emerging nitro compounds: dinitroanisole (DNAN); octonitrocubane (ONC); and tetranitrotetra-aminocubane (TNTAC).

1. INTRODUCTION

1.1 Background

Widespread presence and potential toxicity of nitro compounds, their derivatives, and products of their environmental transformation require CC prediction and analysis of chemical/physical properties in relation to molecular structure as well as development of new CC protocols applicable to emerging compounds of military interest [Kholod, Y., et al., 2008; Qasim, M., Kolod, Y. et al., 2007; Qasim, M., Moore, B., 2007].

1.2 Goal

The hypothesis that *the environmental fate and effects of energetic materials can be predicted from their molecular structures* was applied to emerging compounds. Thus, the theme throughout this research comprised defining direct relationships between molecular structure and quantum chemical calculations as related to chemical and physical properties. These properties dictate chemical and physical reactivities, as in the scheme below:

Structure → quantum mechanical
predictions → physical and chemical properties →
reactivities.

2. APPROACH

Since CC in combination with experimental verification is useful both in proving concepts and ascertaining the chemically feasible, our methodology involved a *theoretical* approach and *spectroscopic* support. Values generated via Advanced Chemistry Development (ADC/LABS) were added as supplemental verification and for providing context to our research.

Theoretical study involved MOPAC quantum mechanical and classical force field mechanics to predict most likely bond lengths and angles, heat of formation, steric energy, dipole moments, solvent accessibility and electrostatic potential surfaces, partial charges and HOMO/LUMO energies. Since compounds of similar structures were compared, MOPAC gave reliable information quickly with accuracy corresponding to the requirements of these comparisons [Qasim, M., Moore, B. et al., 2007]. Correlations between compound chemical/ physical properties and molecular structure were then examined to discover possible trends.

Report Documentation Page				Form Approved OMB No. 0704-0188	
Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.					
1. REPORT DATE DEC 2008		2. REPORT TYPE N/A		3. DATES COVERED -	
4. TITLE AND SUBTITLE Common Trends In The Relationships Between Chemical And Physical Properties And Molecular Structure Of Nitramine, Cage Nitramine, And Nitroaromatic Energetics				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) USACE ERDC, 3909 Halls Ferry Rd., Vicksburg, MS 39180				8. PERFORMING ORGANIZATION REPORT NUMBER	
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 unlimited					
13. SUPPLEMENTARY NOTES See also ADM002187. Proceedings of the Army Science Conference (26th) Held in Orlando, Florida on 1-4 December 2008, The original document contains color images.					
14. ABSTRACT					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT UU	18. NUMBER OF PAGES 6	19a. NAME OF RESPONSIBLE PERSON
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified			

Spectroscopic tools included:

- UV/Vis to measure rates and reactions of nucleophilic / base reactions of nitro compounds;
- Stopped Flow (SF) to follow rates of reaction intermediates to alkaline hydrolysis. UV/Vis and SF also verified selected CC data for chemical feasibility and were used to distinguish trends evinced by reactivities of these explosives.

3. RESULTS

Both tables and figures generate observations of trends pertaining to their subject compounds. For example, as seen in Figs. 1 and 2, SF shows that HMX is less reactive than RDX, and Table 1 reveals that this reactivity trend can also be seen from the HMX larger HOMO/LUMO gap as well as from the SF rates of reaction to alkaline hydrolysis.

Table 1. MOPAC Quantum Mechanical calculations

MOPAC CALCULATIONS									
Compounds			MM2 Total Steric Energy (kcal/mole)	AM1 Minimal Energy				Heat of Formation (kcal/mole)	
				Orbital Levels	HOMO / LUMO Energies (eV)	Gap	Dipole Charge (debye)		
		RDX	19.9	N=42 N=43	HOMO -11.7 LUMO -2.1	9.60	2.092	104.9	
		HMX	40.0	N=56 N=57	HOMO -11.7 LUMO -1.1	10.60	10.315	142.7	
		TNT	5.9	N=42 N=43	HOMO -11.7 LUMO -2.4	9.30	1.391	41.0	
		TNA	14.5	N=45 N=46	HOMO -11.8 LUMO -2.5	9.30	2.146	12.3	
		TNTAC	228.8	N=52 N=53	HOMO -13.1 LUMO -2.8	10.30	1.515	367.0	
		CL-20	46.8	N=81 N=82	HOMO -12.0 LUMO -2.7	9.30	2.89	277.9	
		ONC	45.6	N=84 N=85	HOMO -12.7 LUMO -1.2	11.50	1.309	949.0	

Table 2. Advanced Chemistry Development (ACD/LABS) physical property results

ACD Calculated Physical Properties							
Compounds	RDX	HMX	TNT	TNA	TNTAC	CL-20	ONC
							
							
Log P	-2.19	-2.92	1.68	1.04	38.38	0.03	20.85
Henry's Law	7.08	9.44	0.53	0.53	15.6	3.9	0.35
Molar Refractivity (cm ³)	43.65	58.2	50.71	52.56	50.06	81.04	77.25
Molar Volume (cm ³)	117	151.7	141.2	148.9	78.2	167.3	165.5
Surface Tension (dyne/cm ²)	106.6	119	71.9	69.6	492.5	229	229
Density (g/cm ³)	1.89	1.95	1.608	1.632	3.68	2.61	2.8
Polarizability (x10 ⁻²⁴ cm ³)	17.3	23.07	20.1	20.83	19.84	30.62	30.62
Average Mass (Da)	222.1163	296.1551	227.1311	243.1305	288.0916	464.1296	464.1296

The following trends in properties and reactivities can be seen from Table 2.

LogP: RDX, HMX, TNT, TNA and CL-20 all have low LogP values, indicating aqueous solubility and, thus, possibility of ground water contamination. ONC and TNTAC have high LogP values, indicating hydrophobicity.

Henry's Law: TNT, TNA and ONC have low Henry's Law constants, indicating that they tend to remain in the gaseous phase, whereas RDX, HMX, TNTAC and CL-20 have higher Henry's Law constants, indicating easier dissolution.

Density: As predicted, RDX, HMX, TNT and TNA have lower densities than the cage molecules ONC, TNTAC and CL-20.

Three different comparisons were made within each class of compounds: a) nitramine (RDX and HMX); b) nitroaromatic (TNT and TNA); c) cage nitro compounds (TNTAC, CL-20 and ONC).

a) RDX/HMX: Based on CC alone, HMX is less reactive than RDX, as revealed by the larger HMX HOMO/LUMO gap. The HMX larger size is represented by its higher heat of formation, larger molar volume, larger parachor and greater surface tension. HMX contains an additional nitrogen in its ring system as well as an additional nitro group attached to that nitrogen. This results in HMX having higher steric energy due to HMX collapsing back on itself. HMX is more polar than RDX as seen by its larger dipole charge and higher polarizability due to the increased number of nitrogens in the molecule. Both molecules are highly similar in their LogP, pKa, index of refraction and density. Comparisons of RDX and HMX charges are represented in Fig. 3. Noticeable changes are seen between the negative oxygen atoms of RDX and HMX.

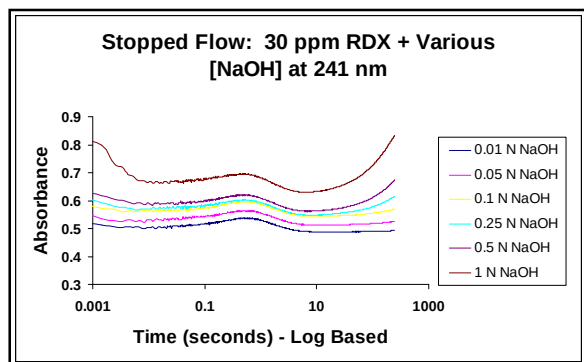


Figure 1. Alkaline hydrolysis of RDX via sodium hydroxide (NaOH)

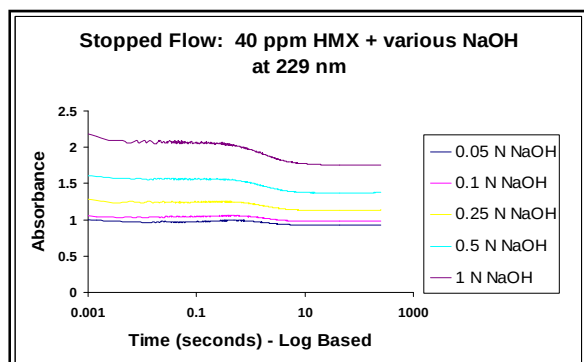


Figure 2. Alkaline hydrolysis of HMX

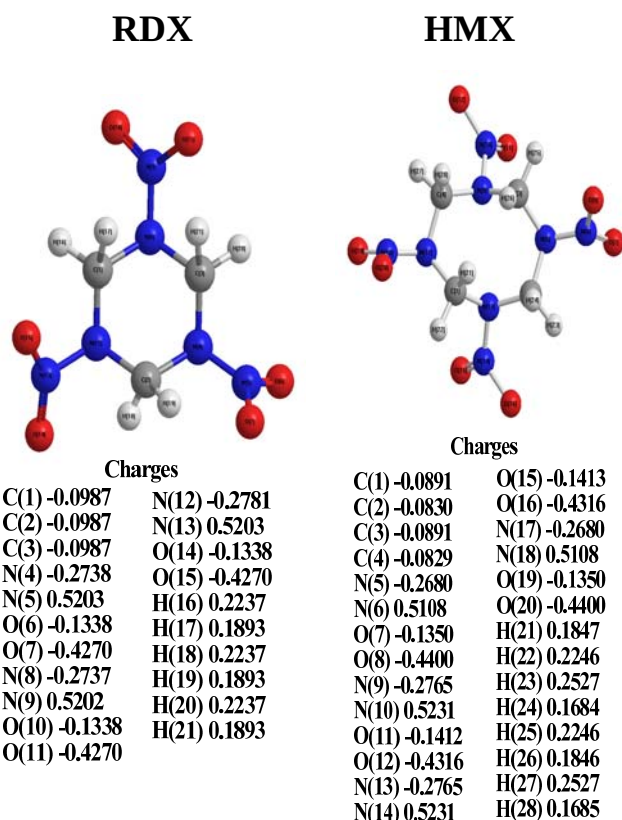


Figure 3. Comparison of charge densities for RDX and HMX

b) TNT/TNA: TNA is more sterically hindered than TNT due to the oxygen of the methoxy group. This oxygen also gives TNA a larger dipole charge and causes a decrease in the heat of formation. TNA is slightly less reactive than TNT due to interaction between the hydrogen atoms of the methoxy group with the oxygens of the nitro groups. It is also less reactive with environmental media due to more electrons in the π system. The TNA methoxy group inductively stabilizes the molecule. The TNA methoxy group also renders TNA a larger molecule than does the methyl group of TNT. This is evident in larger molar volume, parachor and average mass data. Spectroscopic studies were conducted using 2,4-dinitroanisole because of its classification as an emerging compound of military interest. Nucleophilic reactions carried out via alkali hydrolysis at various concentrations of NaOH were performed using TNT and DNAN and are represented by the corresponding UV/Vis and SF spectra, Figs. 4 and 5. SF spectra of TNT and DNAN show mirror-image correspondence of appearance/disappearance of final products. Further, SF spectra show alkali hydrolysis rates of TNT reactions are faster compared to DNAN. Slower rates

are expected in DNAN because of the methoxy's effect to the ring compared to the methyl of TNT. Also, the additional nitro group found in TNT increases the rate of the alkali hydrolysis reaction.

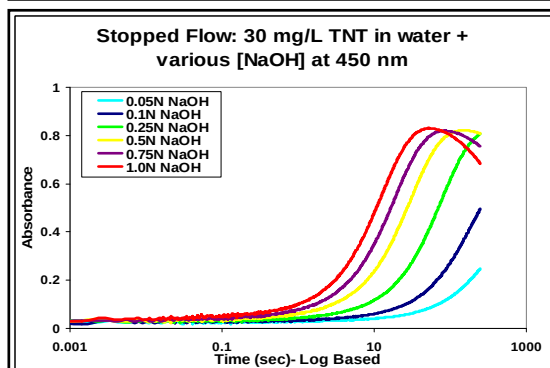
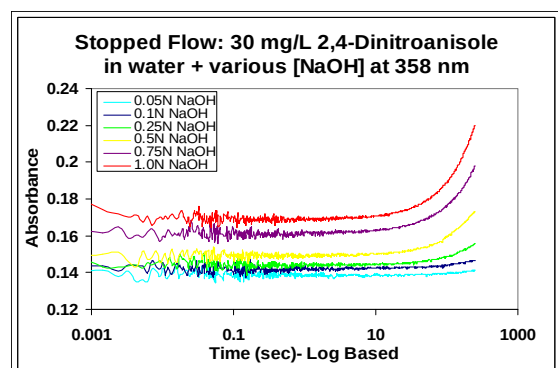
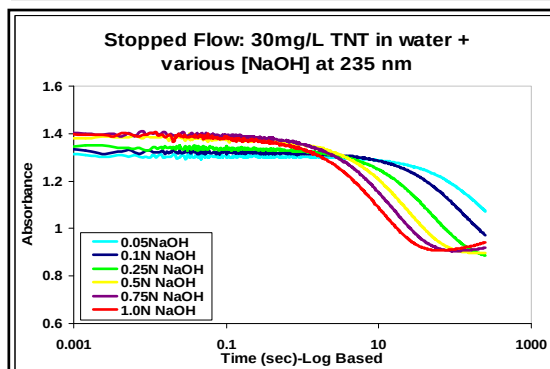
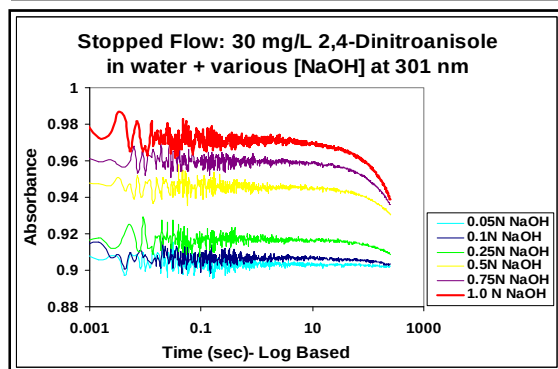
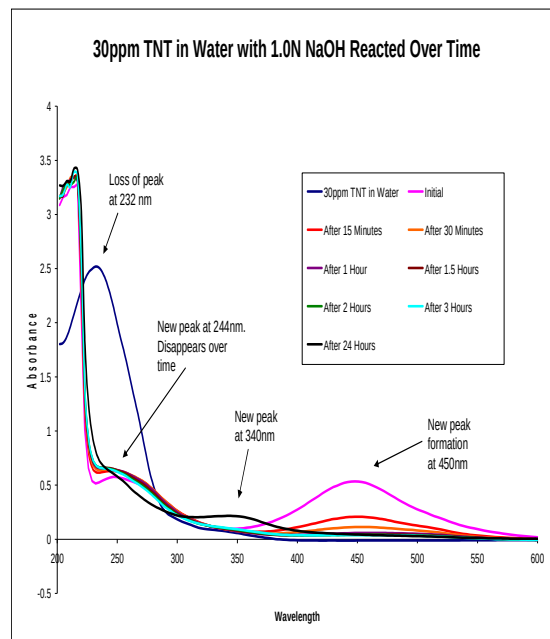
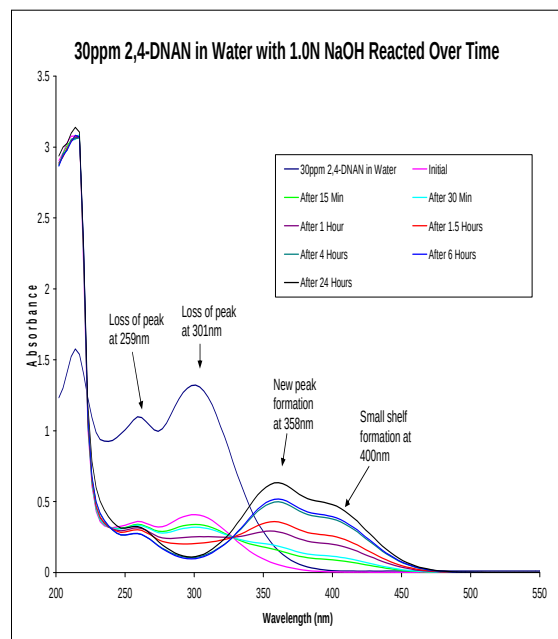


Figure 4. UV/Vis and Stopped Flow spectra of 2,4-dinitroanisole (DNAN) comprise Figure 4.

Figure 5. UV/Vis and Stopped Flow spectra of 2,4,6-Trinitrotoluene (TNT) comprise Figure 5

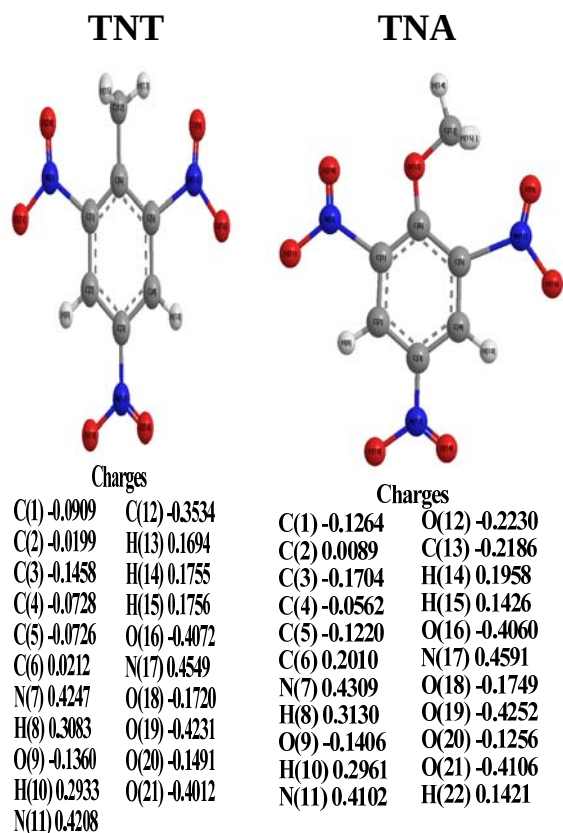


Figure 6. Comparison of charge densities for TNT and TNA

TNAN, not physically available, was studied via CC to compare the methoxy group on its ring vs. the methyl group on the ring of TNT. DNAN was studied due to military interest as to its possible replacement of TNT

c) TNTAC/CL-20/ONC: Of the cage nitroaromatics, TNTAC is more sterically hindered than either CL-20 or ONC. ONC is the least reactive, as seen by the HOMO/LUMO gap. Also, ONC is almost impossible to form as seen by its high heat of formation. ONC has the smallest dipole moment when compared to the other cage explosives. This is due to its molecular symmetry. This symmetry renders ONC susceptible to free radical attack as opposed to electrophilic attack. ONC structure allows for a much larger surface area. However, CL-20 has greater molar volume and a larger parachor than the others. TNTAC has much more surface tension and is far more dense than the other molecules. All three molecules possess high MM2 and heat of formation, which is due to the cage effect and the crowdedness of the nitro groups branching from the main ring system.

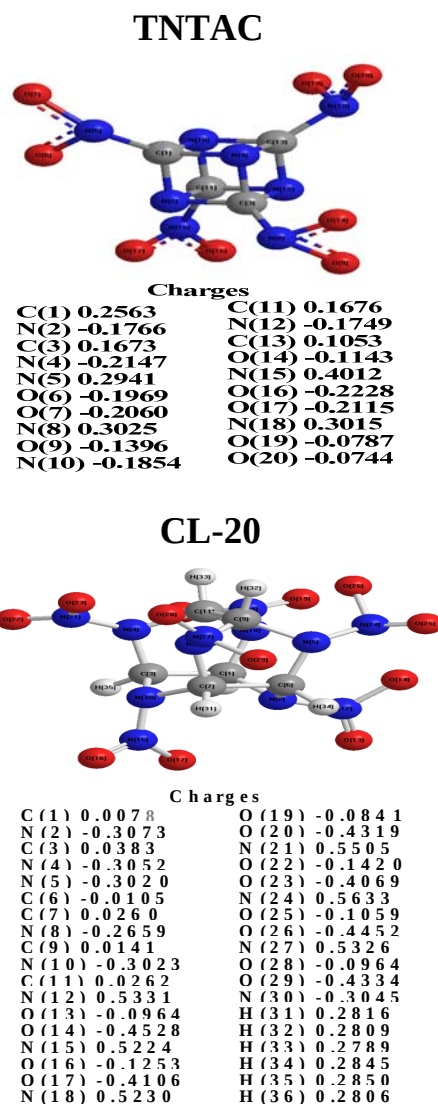


Figure 7. Comparison of charge densities for TNTAC, CL-20, and ONC comprise Figure 7.

4. CONCLUSIONS

From observing a), b) and c), it can be generalized that most physical property values are dependent on molecular size. Data demonstrated that small changes in molecular structure can greatly affect the chemical/physical properties of a molecule.

This study resulted in predicting potential transformation trends in reactivity with environmental media.

ACD/LABS provided correlation and context to our combined use of CC and spectroscopic tools. In summary, this study, through comparing our CC, ACD/LABS, and spectroscopic data—thereby examining trends—proved hypothesis and revealed specific ways in which molecular structure is related to physical and chemical properties.

Basic understanding was provided of nitramine, cage nitramine and nitroaromatic compounds of military interest, including emergent nitro compounds and their potential interactions with the environment. Discovering trends due to molecular structure, also to type, position and size of substituents contributes to: i) basic and applied research into new energetics; ii) bases for development of new CC protocols; and iii) development of applications specific to military sites and purposes.

ACKNOWLEDGEMENTS

MOPAC calculations and spectroscopic studies were conducted at the U. S. Army Environmental Quality Technology program at the USACE Engineer Research and Development Center (ERDC), Environmental Laboratory, Vicksburg, MS.

We thank Dr. John Cullinane, ERDC Technical Director for Military Environmental Engineering and Science; and Dr. Richard E. Price, Environmental Division Chief for their support of this research.

REFERENCES

- Kholod, Y., Kosenkov, D., Okovytyy, S., Gorb, L., Qasim, M. and Leszczynski, J., CL-20 photodecomposition: *Ab initio* foundations for identification of products, *Spectrochimica Acta, Part A*, 2008, **71A**, 1386-1425.
- Qasim, M., Kholod, Y., Gorb, L., Magers, D., Honea, P. and Leszczynski, J., Application of quantum-chemical approximations to environmental problems: Prediction of physical and chemical properties of TNT and related species, *Chemosphere, Environmental Chemistry*, Issue 7, Nov. 2007 **69**:1144-1150.
- Qasim, M., Moore, B., Taylor, L., Gorb, L., Leszczynski, J. and Honea, P., Structural Characteristics and Reactivity Relationships of Nitroaromatic and Nitramine Explosives — A Review of Our Computational Chemistry and Spectroscopic Research, *Int. J. Mol. Sci.*, 2007, **8**: 1422-0067.