

OFFICE OF NAVAL RESEARCH

CONTRACT N00014-95-1-0028

R&T Code 33e 1806

Dr. Richard S. Miller

Technical Report No. 92

COMPUTED HEATS OF FORMATION OF DIFLUORAMINE  
ANALOGUES OF RDX AND HMX

by

Peter Politzer, M. Edward Grice and Pat Lane

Department of Chemistry  
University of New Orleans  
New Orleans, LA 70148

19960715 069

June 18, 1996

Reproduction in whole or in part is permitted for any purpose of the United States Government.

This document has been approved for public release and sale; its distribution is unlimited.

DTIC QUALITY INSPECTED 1

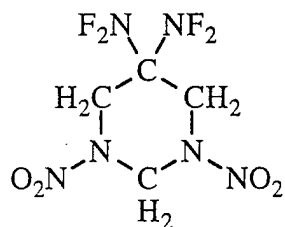
# REPORT DOCUMENTATION PAGE

Form Approved  
OMB No. 0704-0188

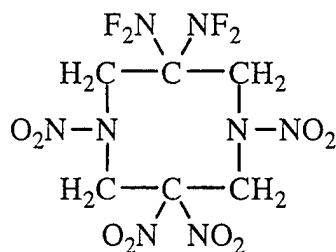
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments 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, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE June 18, 1996	3. REPORT TYPE AND DATES COVERED Technical Report	
4. TITLE AND SUBTITLE Computed Heats of Formation of Difluoramine Analogues of RDX and HMX		5. FUNDING NUMBERS N00014-95-1-0028  Dr. Richard S. Miller  R&T Code 33e 1806	
6. AUTHOR(S) Peter Politzer, M. Edward Grice and Pat Lane			
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) University of New Orleans Department of Chemistry New Orleans, Louisiana 70148		8. PERFORMING ORGANIZATION REPORT NUMBER  92	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research Code 333 800 N. Quincy Street Arlington, VA 22217		10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES			
12a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release. Unlimited distribution.		12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words)  We have used our density functional procedure to compute the heats of formation of three difluoramine analogues of RDX and HMX, 1 - 3.			
<p>Results:</p> <p>1: <math>\Delta H_f^{298K}(\text{gas}) = 11 \text{ kcal/mole} = 38 \text{ cal/g}</math>    <math>\Delta H_f^{298K}(\text{solid}) = -21 \text{ kcal/mole} = -75 \text{ cal/g}</math></p> <p>2: <math>\Delta H_f^{298K}(\text{gas}) = 5 \text{ kcal/mole} = 13 \text{ cal/g}</math>    <math>\Delta H_f^{298K}(\text{solid}) = -39 \text{ kcal/mole} = -99 \text{ cal/g}</math></p> <p>3: <math>\Delta H_f^{298K}(\text{gas}) = -24 \text{ kcal/mole} = -58 \text{ cal/g}</math>    <math>\Delta H_f^{298K}(\text{solid}) = -67 \text{ kcal/mole} = -165 \text{ cal/g}</math></p> <p>For comparison, the experimental gas phase <math>\Delta H_f^{298K}</math> value for RDX is 206 cal/g.</p>			
14. SUBJECT TERMS difluoramine analogues of RDX and HMX, heats of formation		15. NUMBER OF PAGES 4	
		16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT Unlimited

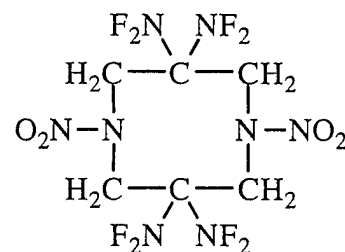
We have used our density functional procedure [1] to compute the heats of formation of three difluoramino analogues of RDX and HMX, **1** - **3**. The vibrational energies were determined from the molecular stoichiometries [2].



**1**



**2**



**3**

The density functional calculations give the gas phase heat of formation, which we convert to the solid state value by subtracting the heat of sublimation. We obtain the latter by means of the relationship that we have developed between the heat of sublimation and the computed electrostatic potential on the molecular surface [3].

The heat of formation of **3** was calculated for four different molecular geometries. Three of these were DF/BP86/6-31G\*\* re-optimizations of HF/6-31G\* structures sent by H. L. Ammon, University of Maryland, who imposed  $C_1$ ,  $C_2$  and no symmetry, to correspond to three polymorphs of **3**. We maintained the same constraints in the re-optimizations. The fourth geometry was computed directly at the DF/BP86/6-31G\*\* level, with no imposed symmetry. Since the heats of formation obtained for these four structures covered a range of less than 4 kcal/mole, we will report only the results corresponding to the one with lowest energy; this is the density functional re-optimization of the HF/6-31G\* geometry with no symmetry imposed.

Results:

$$\begin{aligned} \mathbf{1:} \quad \Delta H_f^{298K}(\text{gas}) &= 11 \text{ kcal/mole} = 38 \text{ cal/g} \\ \Delta H_f^{298K}(\text{solid}) &= -21 \text{ kcal/mole} = -75 \text{ cal/g} \end{aligned}$$

$$\begin{aligned} \mathbf{2:} \quad \Delta H_f^{298K}(\text{gas}) &= 5 \text{ kcal/mole} = 13 \text{ cal/g} \\ \Delta H_f^{298K}(\text{solid}) &= -39 \text{ kcal/mole} = -99 \text{ cal/g} \end{aligned}$$

$$\begin{aligned} \mathbf{3:} \quad \Delta H_f^{298K}(\text{gas}) &= -24 \text{ kcal/mole} = -58 \text{ cal/g} \\ \Delta H_f^{298K}(\text{solid}) &= -67 \text{ kcal/mole} = -165 \text{ cal/g} \end{aligned}$$

For comparison, the experimental gas phase  $\Delta H_f^{298K}$  value for RDX is 206 cal/g [4, 5].

References:

1. D. Habibollahzadeh, M. E. Grice, M. C. Concha, J. S. Murray and P. Politzer, *J. Comp. Chem.* **16**, 654 (1995).
2. M. E. Grice and P. Politzer, *Chem. Phys. Lett.* **244**, 295 (1995).
3. M. DeSalvo, E. Miller, J. S. Murray and P. Politzer, unpublished work.
4. D. R. Stull, E. F. Westrum and G. C. Sinke, *The Chemical Thermodynamics of Organic Compounds*, Wiley, New York, 1969.
5. J. M. Rosen and C. Dickinson, *J. Chem. Eng. Data* **14**, 120 (1969).