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COMPUTED HEATS OF FORMATION OF DIFLUORAMINE ANALOGUES OF RDX AND HMX

by

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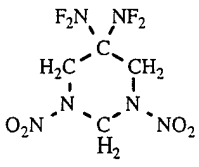
13. ABSTRACT *(Maximum 200 words)*

We have used our density functional procedure to compute the heats of formation of three difluoramine analogues of RDX and HMX, **1** - **3**.



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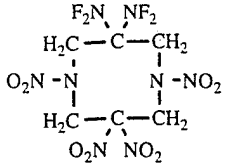

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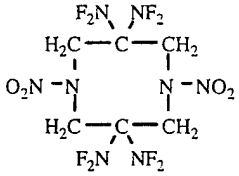

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Results:

1: ΔH_f^{298K} (gas) = 11 kcal/mole = 38 cal/g ΔH_f^{298K} (solid) = −21 kcal/mole = −75 cal/g

2: ΔH_f^{298K} (gas) = 5 kcal/mole = 13 cal/g ΔH_f^{298K} (solid) = −39 kcal/mole = −99 cal/g

3: ΔH_f^{298K} (gas) = −24 kcal/mole = −58 cal/g ΔH_f^{298K} (solid) = −67 kcal/mole = −165 cal/g

For comparison, the experimental gas phase ΔH_f^{298K} value for RDX is 206 cal/g.

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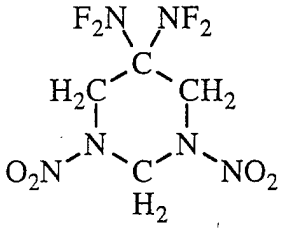
We have used our density functional procedure [1] to compute the heats of formation of three difluoramine analogues of RDX and HMX, **1** - **3**. The vibrational energies were determined from the molecular stoichiometries [2].



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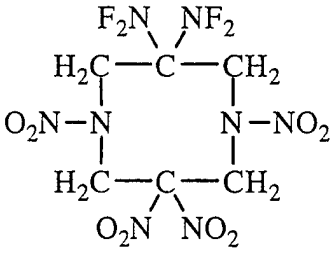

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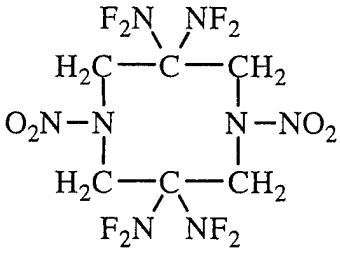

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The density functional calculations give the gas phase heat of formation, which we convert to the solid state value by subtracting the heat of sublimation. We obtain the latter by means of the relationship that we have developed between the heat of 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_i, 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:

1:

$$\Delta H_f^{298K}(\text{gas}) = 11 \text{ kcal/mole} = 38 \text{ cal/g}$$

$$\Delta H_f^{298K}(\text{solid}) = -21 \text{ kcal/mole} = -75 \text{ cal/g}$$

2:

$$\Delta H_f^{298K}(\text{gas}) = 5 \text{ kcal/mole} = 13 \text{ cal/g}$$

$$\Delta H_f^{298K}(\text{solid}) = -39 \text{ kcal/mole} = -99 \text{ cal/g}$$

3:

$$\Delta H_f^{298K}(\text{gas}) = -24 \text{ kcal/mole} = -58 \text{ cal/g}$$

$$\Delta H_f^{298K}(\text{solid}) = -67 \text{ kcal/mole} = -165 \text{ cal/g}$$

For comparison, the experimental gas phase ΔH_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).