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COMPUTATIONAL DETERMINATION OF HEATS OF FORMATION OF ENERGETIC COMPOUNDS

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ABSTRACT

A recently-developed density functional procedure for computing gas phase heats of formation is briefly described and results for several categories of energetic compounds are summarized and discussed. Liquid and solid phase values can be obtained by combining the gas phase data with heats of vaporization and sublimation estimated by means of other relationships. Some observed functional group effects upon heats of formation are noted.

INTRODUCTION

The heat of formation is frequently viewed as a measure of the energy content of a compound. As such, it is an important factor to consider in designing new energetic materials or evaluating existing ones. For example, the heat of formation enters into the calculation of such key explosive and propellant properties as detonation velocity [1,2], detonation pressure [1,2] and specific impulse [3].

We have recently developed a nonlocal density functional procedure for computing gas phase heats of formation [4]. The advantages of a computational approach are of course that it can be applied to suggested target molecules prior to undertaking syntheses, and to newly-prepared compounds even when the available amount is insufficient for laboratory characterization. We have now applied our technique to a variety of molecules that are of potential interest as energetic materials [5-8]. These as well as more recent results will be summarized and discussed.

THEORY

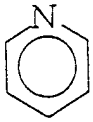
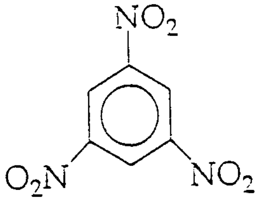
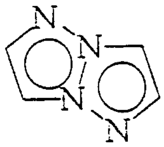
Our procedure [4] involves calculating ΔE for the formation of the molecule from its elements at 0 K followed by conversion to ΔH at 298 K by assuming ideal behavior and adding the translational, rotational and vibrational energies. Empirical correction terms corresponding to the various coordination states of the carbons, nitrogens and oxygens are also added.

ΔE is computed by a nonlocal density functional procedure (Gaussian 94 [9], Becke exchange and Perdew correlation functionals [10,11], 6-31G** basis set), using optimized geometries. The vibrational energy was originally determined from the normal mode frequencies, the calculation of which can be quite demanding in terms of computer resources. We have found, however, that this energy can be estimated accurately from stoichiometry-based relationships [12]; accordingly we now compute the frequencies only when we wish to confirm that the geometry corresponds to a local minimum in the energy (indicated by the absence of imaginary frequencies [13]).

In Table I, our calculated heats of formation are compared to the experimental values for some compounds relevant to the area of energetic materials. Additional comparisons have been presented elsewhere [4]. The average absolute error in the test cases is 3.4 kcal/mole, indicating very satisfactory agreement.

The procedure that has been described yields gas phase heats of formation, and these will be the primary subject of this paper. For practical purposes, however, liquid and solid phase values are often of greater interest; these can be obtained if the heats of vaporization and sublimation are known, using eqs. (1) and (2):

Table I. Comparison of Some Calculated and Experimental Gas Phase Heats of Formation

	Molecule	Heat of formation, kcal/mole	
		Calculated	Experimental
1	$(H_3C)_2N-NO_2$	-2.7[a]	-1.1[b]
2		31.4[c]	33.56[b]
3		18.2[c]	14.9[b]
4		124.3[d]	130[e]
5		125.1[d]	124[g]

[a] Reference 6. [b] Reference 45.

[c] Reference 4. [d] Reference 8.

[e] Extrapolated from the experimental values for the dibenzo- and monobenzo-derivatives, which are 142.8 and 136.4 kcal/mole, respectively.[f]

[f] Y. T. Chia and H. E. Simmons, J. Am. Chem. Soc. 89, 2638 (1967).

[g] Extrapolated from the experimental values for the dibenzo- and monobenzo-derivatives, which are 132.1 and 128.2 kcal/mole, respectively.[f]

$$\Delta H_f^{298}(\text{liquid}) = \Delta H_f^{298}(\text{gaseous}) - \Delta H_{vap}^{298} \qquad (1)$$

$$\Delta H_f^{298}(\text{solid}) = \Delta H_f^{298}(\text{gaseous}) - \Delta H_{sub}^{298} \qquad (2)$$

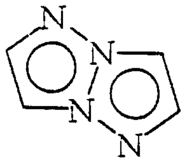
We have recently developed quantitative representations of both ΔH_{vap}^{298} and ΔH_{sub}^{298} in terms of computed quantities related to electrostatic potentials on molecular surfaces [14,15]; the approach is one that we have used successfully to relate a variety of liquid, solid and solution properties to quantities calculated for individual molecules [14,16,17]. These expressions for ΔH_{vap}^{298} and ΔH_{sub}^{298} can accordingly be used in conjunction with ΔH_f^{298}(gaseous) to obtain liquid and solid phase heats of formation, via eqs. (1) and (2).

RESULTS AND DISCUSSION

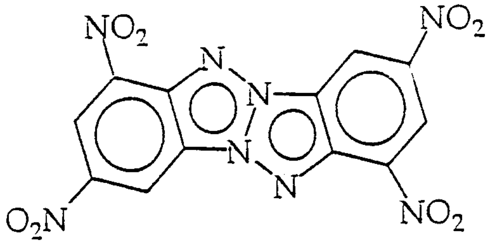
We will present and discuss our computed gas phase heats of formation for several classes of compounds that are currently of interest as potential energetic materials. Some of these data have been published elsewhere, as will be indicated. We will also mention two solid phase heats of formation that we have recently obtained, using eq. (2) and our expression for ΔH_{sub}^{298}.

1. Tetraazapentalenes

The presence of several linked nitrogens in a molecule (nitrogen catenation) is frequently associated with instability [18]. It is therefore notable that certain derivatives of the tetraazapentalene 4 show unexpected stability [19-21]; of particular interest in the present context is TACOT, 6, which has a melting/decomposition temperature of 378° C [22]. We have recently speculated that the surprising stability that has been observed experimentally for the molecular framework 4 may be due to the relatively positive character that we have found for the two triply-coordinated nitrogens [8].



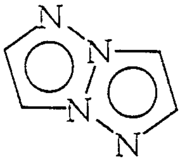
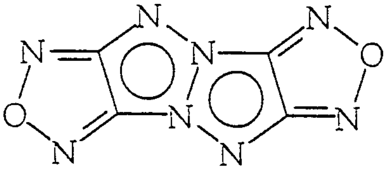
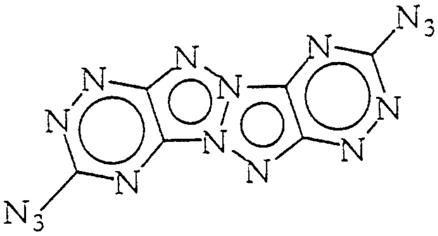
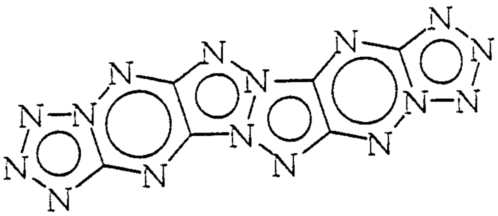
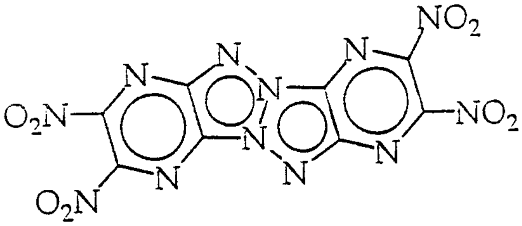
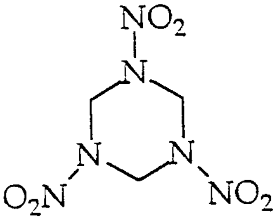
4



6

In Table II are listed our computed gas phase heats of formation for the two isomeric tetraazapentalenes 4 and 5 and for three of their derivatives. None of these compounds are known at present, although various other derivatives have been prepared [19-21,23,24], including 6 [22]. 7 [25] and 8 and 9 [26] have been proposed as target energetic materials, and synthesis efforts have been undertaken.

Table II. Calculated Gas Phase Heats of Formation of Some Tetraazapentalenes[a]

	Molecule	ΔH_f^{298} kcal/mole	ΔH_f^{298} cal/g
4		124	1151
5		125	1158
7		253	1318
8		426	1439
9		442	1493
10		247	630
11 RDX		45.7 (experimental value[b])	206

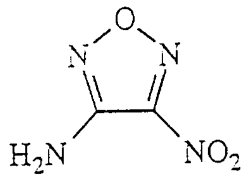
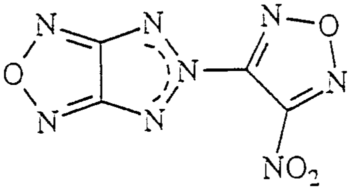
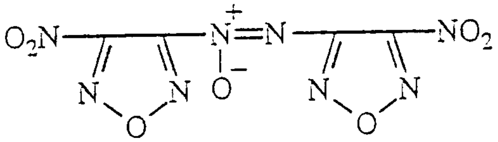
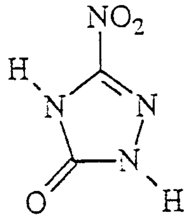
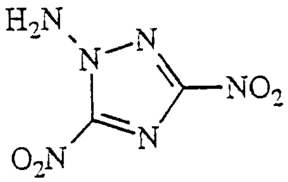
[a] The values for all of the tetraazapentalenes except 10 are from reference 8.

[b] References 27 and 28.

The data in Table II are given in both kilocalories/mole and calories/gram; it is the latter that is relevant for predicting detonation performance [1-3]. In order to provide a basis for comparison, the experimentally-determined gas phase heat of formation of RDX, 11, a prominent military explosive, is also included [27,28].

Most of the tetraazapentalenes in Table II have quite large positive heats of formation, greater by at least a factor of five, in calories/gram, than that of RDX; the high values obtained for the unsubstituted molecules 4 and 5 are particularly striking. The relatively low ΔH_f^{298} found for 10 may indicate that

Table III. Calculated Gas Phase Heats of Formation of Some Furazans and Triazoles[a]

	Molecule	ΔH_f^{298} kcal/mole	ΔH_f^{298} cal/g
12		43	330
13 NOTO		202	903
14 DNAF		169	621
15 NTO		-5.7	-44
16 ADNT		87	502
11	RDX	45.7	206
		(experimental value[b])	

[a] The value for NOTO, 13, is from reference 8.

[b] References 27 and 28.

framework nitrogens are more effective than nitro groups in producing a large heat of formation. The diazide 8 and the ditetrazole 9 are tautomers, which are expected to be related through a tautomeric equilibrium, 8 $\rightleftharpoons$ 9. Our results show the diazide to be the more stable, by about 16 kcal/mole. This could be a matter for concern, from the standpoint of an energetic material, because of the tendency of many azides toward facile decomposition [29].

2. Furazans and Triazoles

Like the tetraazapentalenes, the furazans and triazoles in Table III fit into the category of high-nitrogen compounds. However these have actually been synthesized: 12 [30,31], NOTO, 13 [32], DNAF, 14 [33], NTO, 15 [34,35], ADNT, 16 [36]. NOTO has the interesting feature of being a liquid at room temperature [32]. Table III shows that all of these compounds except NTO have positive heats of formation which are considerably larger, on a calories/gram basis, than that of RDX but much smaller than those of most of the tetraazapentalenes in Table II.

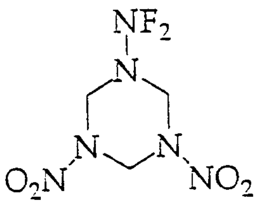
3. Nitramines and Difluoramines

The difluoramino group, $-NF_2$, continues to be of interest as an ingredient of energetic materials, particularly propellants [2,3,37,38]. A judicious combination of nitro and difluoramino substituents offers the possibility of enhanced propellant performance due to an increased number of moles of gaseous combustion products per gram of material (provided that some hydrogens are present) [3,6,39].

In conjunction with recent computational studies of various existing or proposed nitramine and difluoramine systems [6,40], we have calculated the gas phase heats of formation of the compounds in Table IV. While most of them are positive, only 18 has a gas phase value (in calories/gram) greater than that of RDX.

A consistent pattern in Table IV is that ΔH_f^{298} is lower (less positive) for the difluoramine than for its nitramine analogue. (Leroy *et al* have observed the same to be true when the $-NF_2$ and $-NO_2$ are attached to carbons [41], as we do also for the pair 20, 22.) However the difluoramine may still have a higher specific impulse (a measure of propellant thrust [3,22,39]) due to producing more moles of gaseous products per gram upon combustion. Thus the specific impulse of 23 is predicted to be higher than that of RDX, 11, despite having a lower estimated heat of formation [3].

23



11, RDX

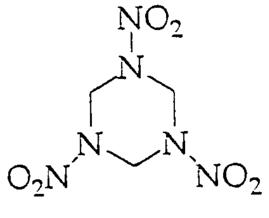
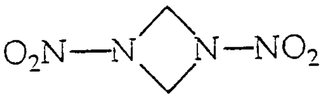
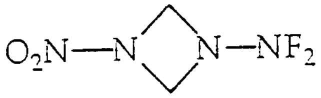
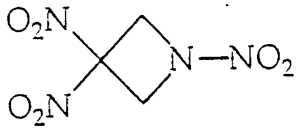
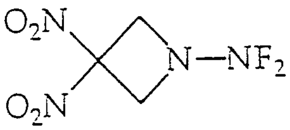
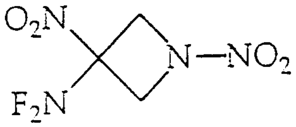


Table IV. Calculated Gas Phase Heats of Formation of Some Nitramines and Difluoramines[a]

	Molecule	ΔH_f^{298} kcal/mole	ΔH_f^{298} cal/g
1	$(H_3C)_2N-NO_2$	-2.7	-30
17	$(H_3C)_2N-NF_2$	-20	-206
18		44	297
19		29	186
20 TNAZ		31	160
21		16	79
22		7.4	38
11	RDX	45.7 (experimental value[b])	206

[a] All of these calculated results except that for 22 are from reference 6.

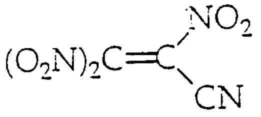
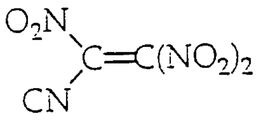
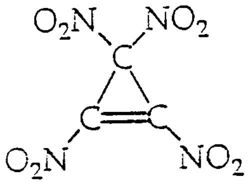
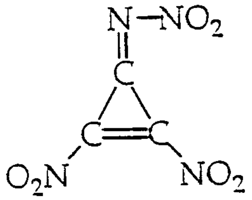
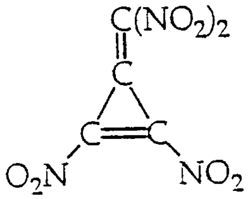
[b] References 27 and 28.

4. Some C, N, O, F Compounds

We have investigated computationally a group of 19 unsaturated molecules that contain only the elements C, N, O and F (Table V) [7]. Their high N/C and O/C ratios suggest that these are potential energetic molecules or precursors. To the best of our knowledge, most of these molecules are presently unknown, an exception being **26** [42,43].

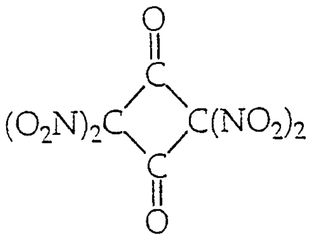
The calculated gas phase heats of formation are given in Table V. These were obtained by a slightly modified version of the method described earlier, in that *ab initio* HF/6-31G* optimized geometries and vibrational frequencies were used and ΔE was computed with the density functional program DeMon [44]. Structures **26A**, dinitrosoacetylene, and **26B**, which is more accurately designated as dinitrile-di-N-oxide, were both found to correspond to energy minima at the *ab initio* HF/6-31G*

Table V. Calculated Gas Phase Heats of Formation of Some C, N, O, F Compounds[a]

	Molecule	ΔH_f^{298} kcal/mole	ΔH_f^{298} cal/g
24	$O_2N{-}C{\equiv}C{-}NO_2$	89	763
25	$O_2N{-}C{\equiv}C{-}NO$	100	1004
26A	$ON{-}C{\equiv}C{-}NO$	130	1550
26B	$ON{\equiv}C{-}C{\equiv}NO$	73	868
27	$O_2N{-}C{\equiv}C{-}NF_2$	74	606
28	$ON{-}C{\equiv}C{-}NF_2$	95	901
29	$N_3{-}C{\equiv}C{-}NO_2$	144	1287
30	$OCN{-}C{\equiv}C{-}NO_2$	54	486
31	 $(O_2N)_2C{=}C(NO_2)(CN)$	80	426
32	 $(O_2N)(CN)C{=}C(NO_2)_2$	108	572
33	$(O_2N)_2C{=}C{=}O$	3	22
34	$O_2N{-}N{=}C{=}N{-}NO_2$	87	659
35	$(O_2N)_2C{=}C{=}C{=}O$	39	274
36	$(O_2N)_2C{=}C{=}C{=}N{-}NO_2$	115	613
37	$O_2N{-}N{=}C{=}C{=}N{-}NO_2$	128	888
38	$O_2N{-}N{=}C{=}C{=}C{=}N{-}NO_2$	136	870
39		102	465
40		135	716
41		130	559

(continued)

Table V. Calculated Gas Phase Heats of Formation of Some C, N, O, F Compounds[a] (continued)

	Molecule	ΔH_f^{298} kcal/mole	ΔH_f^{298} cal/g
42		9	35
11	RDX	45.7	206
		(experimental value[b])	

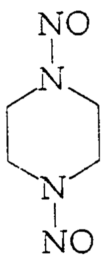
[a] The results for 24 - 30, 33-35, 37 and 38 are in reference 7.

[b] References 27 and 28.

level [7]. Table V shows that **26B** is the more stable, which is consistent with experimental evidence [42,43].

Most of these compounds are predicted to have rather large positive heats of formation (calories/gram). One of the highest, not surprisingly, is the azide **29**. The pairs **24**, **27** and **25**, **28** show again that replacing $-NO_2$ by $-NF_2$ lowers ΔH_f^{298}, as observed above when these groups were on nitrogens.

Particularly striking, especially on a calories/gram basis, is the *increase* in ΔH_f^{298} that occurs when the nitro group is replaced by the nitroso. This can be seen in **24**, **25** and **26A** and again in **27** and **28**. (**26B** is more nitrile-N-oxide than nitroso in character, as mentioned above.) This effect has also been observed experimentally; the heat of formation of **43** is 46.44 kcal/mole (322.5 cal/g) vs. 13.9 kcal/mole (79.0 cal/g) for **44** [45]. In view of these findings, it is interesting to note evidence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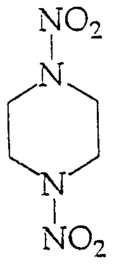
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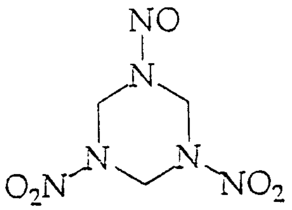
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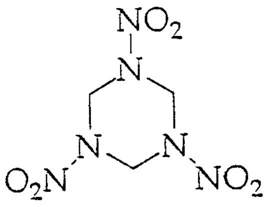
11, RDX

suggesting the possibility of another desirable consequence of substituting $-NO$ for $-NO_2$; an experimental study showed that the impact sensitivity of **45** is significantly less than that of RDX, **11**, while the explosive power (measured by dent depth) is essentially the same [46].

A further comparison of interest is between $=C(NO_2)_2$ compounds and their $=N(NO_2)$ analogues. The latter have the greater heats of formation, as can be seen from the pairs **36**, **37** and **40**, **41**.

5. Solid Phase Heats of Formation

As was pointed out earlier in this paper, we now have the means for reliably estimating heats of vaporization and sublimation [14,15]. These permit us to convert our computed gas phase heats of formation to liquid and solid phase values, using eqs. (1) and (2), respectively. We have thus far applied this procedure to two compounds, 1,3,3-trinitroazetidine (20, TNAZ) and DNAF (14).

For TNAZ, we find ΔH_{sub}^{298} = 22 kcal/mole; when combined with ΔH_f^{298}(gaseous) = 31 kcal/mole (Table IV) via eq. (2), the result is ΔH_f^{298}(solid) = 9 kcal/mole. This is in excellent agreement with the experimental value, 8.7 kcal/mole [38]. For DNAF, we obtain ΔH_{sub}^{298} = 32 kcal/mole. Using ΔH_f^{298}(gaseous) = 169 kcal/mole (Table III), eq. (2) gives ΔH_f^{298}(solid) = 137 kcal/mole.

CONCLUSIONS

We have presented and discussed the results of density functional calculations of gas phase heats of formation for several categories of energetic compounds. We have also demonstrated the feasibility of converting these to solid phase values.

For the systems investigated, some key observations are:

(1) The tetraazapentalenes have particularly large positive heats of formation (calories/gram).

(2) Replacement of a nitro by a difluoramino group, whether on a carbon or on a nitrogen, lowers the heat of formation.

(3) Replacement of a nitro by a nitroso group increases the heat of formation.

(4) Replacement of $=C(NO_2)_2$ by $=N{-}NO_2$ increases the heat of formation.

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