

## MOLECULAR LEVEL STUDIES OF POLY-NITROGEN EXPLOSIVES

P J Haskins, J Fellows, M D Cook and A Wood  
QinetiQ Ltd., Fort Halstead,  
Sevenoaks, Kent TN14 7BP, England

This paper describes a range of theoretical studies into the likely properties of poly-nitrogen molecules ( $N_n$ ,  $n>3$ ). In particular, we describe the approach we have used to assess the potential detonation performance of this class of material, and illustrate this with a number of example calculations. We also discuss the implications and limitations of these predictions. In addition, we describe some calculations of decomposition pathways for  $N_4$  and  $N_8$ , and ab-initio molecular dynamics simulations of  $N_4$ . From these we draw some tentative conclusions with regard to the likely stability/sensitivity of these materials.

### INTRODUCTION

Poly-nitrogen molecules ( $N_n$ ,  $n>3$ ) have been proposed and discussed as potential high energy-density materials for a number of years<sup>1</sup>. However, with the exception of the  $N_5^+AsF_6^-$  salt recently synthesised<sup>2</sup>, no poly-nitrogen syntheses have been reported to date. Our purpose in this paper is to report theoretical studies aimed at predicting the performance and properties of a range of these materials, which can serve to focus synthetic efforts.

Although poly-nitrogen molecules are iso-electronic with their C-H counterparts they are potentially considerably more energetic. This is primarily a result of the large difference in energy between the single and double N-N bonds in the molecules and the very strong triple bond in  $N_2$ , the principal, or only, reaction

product. As a consequence a large number of poly-nitrogen species have been proposed as energetic materials. However, it is not our intention to review all the possibilities here, rather we intend to illustrate the potential of these materials by way of a few examples, and to describe the theoretical methods we have adopted.

In the first part of the paper we describe some detonation performance predictions on a number of simple poly-nitrogen species, and discuss the implications and limitations of these calculations. In the second part of the paper we report some ab-initio quantum chemistry studies we have made on possible decomposition pathways for  $N_4$  and  $N_8$  to help assess their likely stability/sensitivity. Finally, in the third main section of the report we describe some preliminary ab-initio molecular

dynamics simulations aimed at obtaining further information on the likely reactivity of  $N_4$ .

## PERFORMANCE PREDICTIONS

The method we have adopted for the prediction of performance can be divided into three principal steps, namely:

1. Ab-initio quantum chemistry calculations of the electronic structure, optimised geometry and heat of formation.
2. Crystal packing calculations to estimate the density.
3. Equilibrium thermodynamic code calculations of the ideal detonation performance.

We have used the GAUSSIAN 98 code<sup>3</sup> at the ub31yp/6-31+g\* level of theory to carry out the electronic structure and geometry optimisation calculations. The MOPAC code<sup>4</sup> was then used for the heat of formation predictions. The densities (at 0K) were predicted with the MOLPAK crystal packing code<sup>5</sup>, using the optimised geometry and atomic charges from the GAUSSIAN 98 calculation.

In the final step, the density, heat of formation and chemical formula were used in CHEETAH (v2.0)<sup>6</sup> with the BKWC equation of state, to predict the ideal detonation performance. Although not considered further in this paper, it is worth noting that poly-nitrogen materials also have potential as high-energy propellants, and that a similar approach may be adopted to predict their specific impulse.

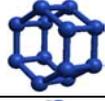
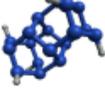
The results of our predictions for some simple poly-nitrogen species are illustrated in Table 1. It can clearly be seen that all the molecules listed in the table have exceptionally high detonation parameters.

Typically, the detonation velocities are in excess of 12 mm/ $\mu$ s and the detonation pressures are 2-3 times that of HMX (39 GPa). Although not listed in the table it is also important to note that the predicted detonation temperatures are also very high (7000-8000K), as a result of the highly exothermic reactions to form  $N_2$ .

The predictions in Table 1 would appear to suggest that many poly-nitrogen species would be extremely powerful explosives if they could be synthesised. However, it is important here to interject a few words of caution.

Firstly, from a practical viewpoint it is important to consider the physical properties of the materials at normal temperatures and pressures. For most purposes it is desirable to have a solid material, and this is assumed implicitly in the calculation of the crystal density at 0K. However, for pure (no atoms other than N) poly-nitrogen molecules the lack of a dipole, and low polarizability would suggest that many of the lower molecular weight species will not be solids at STP. A number of routes suggest themselves to overcome this problem. One approach is to prepare salts incorporating a poly-nitrogen ion (e.g.  $N_5^+AsF_6^-$ ). The disadvantages of this route are that empirical evidence suggests that salts are likely to be sensitive, and unless both ions are energetic the energy density will be reduced. However, the recently proposed  $N_5^+N_5^-$  species<sup>7</sup> would certainly avoid the later problem. Alternative routes are to increase the molecular weight (and generally the polarizability with it), and/or to add other atoms, and thus create a dipole. In the last row of Table 1 we show an example of this type of approach with the species  $N_{18}H_6$ . Many structures of this kind can be devised, either terminated by hydrogen, as in this example, or by other atoms/groups.

**TABLE 1. PREDICTED PERFORMANCE OF SOME POLY-NITROGEN SPECIES.**

No of Nitrogen Atoms	Electronic Energy (Hartrees)	Geometry	Heat of Formation (kcal/mol)	Density (g/cc)	Velocity of Det. (km/s)	C-J Pressure (GPa)	Polarizability
4	-218.781		268.77	1.752	13.24	77.02	23.464
6	-328.102		345.58	1.974	14.04	93.32	36.426
8	-438.440		406.69	2.151	14.86	108.39	45.987
10	-546.875		473.42	2.211	12.08	58.05	59.45
12	-656.170		579.82	2.283	12.53	64.07	76.891
N <sub>18</sub> H <sub>6</sub>	-988.349		669.121	2.191	17.653	133.07	110.834

An additional variation on this theme is to complex the poly-nitrogen entities to a metal atom, and this approach may also have advantages from the synthetic standpoint.

A second consideration of some concern is the validity of the ideal detonation code predictions for such high performance materials. In particular, the equations of state used are not validated at the extreme temperatures and pressures predicted for the CJ state of these explosives. In fact it is known from shock compression experiments<sup>8</sup> that N<sub>2</sub> begins to dissociate into atomic nitrogen at 30GPa and 7000K. As the calculated CJ states are in excess of these conditions, it follows that there will be a mixture of molecular and atomic nitrogen at the real CJ states, which will exhibit a lower pressure and temperature than predicted. It would then be expected that exothermic reaction of

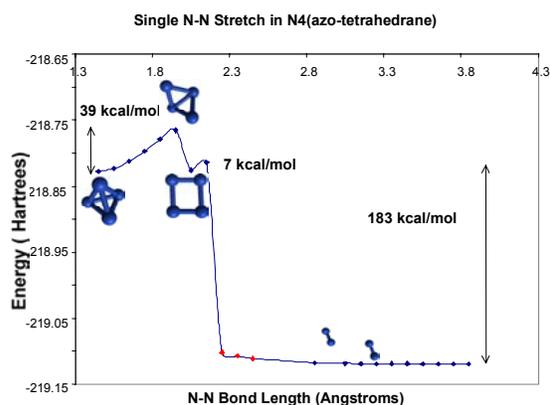
atomic nitrogen to form N<sub>2</sub> would occur behind the CJ plane, contributing to the blast performance.

## REACTION PATHWAYS

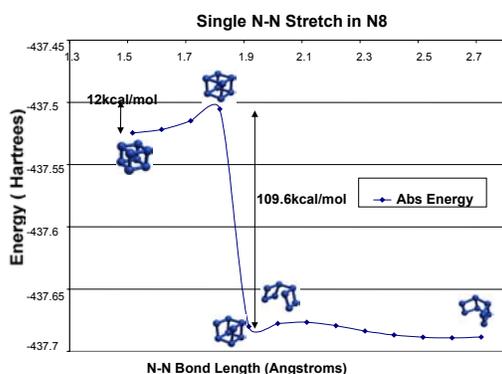
In addition to predicting their likely performance it is clearly of great interest to assess the likely stability and sensitivity of potential poly-nitrogen explosives. One simple approach to gaining information on their likely stability is to calculate the energy required for uni-molecular dissociation. In Figures 1 and 2 we show relaxed potential scans in which a single N-N bond has been stretched in N<sub>4</sub> and N<sub>8</sub> respectively.

Although these potential scans only represent one possible mode of decomposition they do provide some interesting information. In particular, it can

be seen that there is a relatively low barrier of 12kcal/mol for  $N_8$  dissociation. This clearly gives rise to concerns over the thermal stability of  $N_8$ . For this simple mode of decomposition  $N_4$  appears to be considerably more stable, with an activation barrier of 39 kcal/mol.



**FIGURE 1. RELAXED POTENTIAL SCAN OF  $N_4$  (CALCULATED AT UB3LYP/6-311+G\*\*).**



**FIGURE 2. RELAXED POTENTIAL SCAN OF  $N_8$  (CALCULATED AT UB3LYP/6-311+G\*\*).**

## MOLECULAR DYNAMICS STUDIES

In an attempt to gain further understanding of the reactivity of these materials we have carried out some

preliminary ab-initio molecular dynamics simulations on  $N_4$ . We have carried out simulations using our ab-initio MD code, QUASIMODO<sup>9</sup> at the UHF/6-31G\*\* level of theory. A maximum time-step size of one femtosecond was chosen in order to accurately describe molecular bond vibrations and to conserve the total energy of the system.

In the first phase of these simulations we allowed two molecules of  $N_4$  to collide in various orientations, and at various impact velocities. The orientations chosen were:

(a) Apex into centre of face.

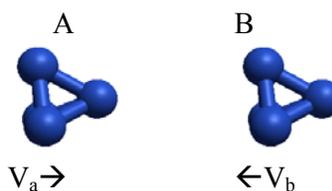


Table 2 details the results of simulations over a range of impact velocities. Possible outcomes ranged from prompt reaction after collision, as in the 12kms<sup>-1</sup> impact, through late reaction, as in the 9.5kms<sup>-1</sup> impact, to no reaction as in the 6kms<sup>-1</sup> impact.

It appears that the decomposition of one of the  $N_4$  molecules takes place after collision when different vibrational modes of the now excited molecule couple, allowing the formation of two  $N_2$  molecules. No reactions are observed to take place after the vibrational modes in the excited molecules have equilibrated.

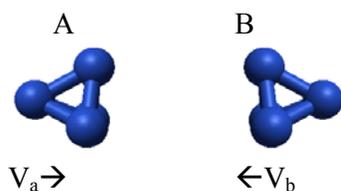
The high velocities needed to achieve reaction, especially in comparison to previous studies with nitromethane<sup>9</sup> can be put down to the environment of this idealised experiment, the strength of the N=N bond, and the fact that no local neighbouring atoms/molecules are present.

If the reaction were in a condensed phase, we would expect the velocity threshold to reaction to be much lower than the 9-9.5kms<sup>-1</sup> observed here. This follows since it would be expected that energy would be more readily localised (i.e. put into bond vibrational energy), rather than largely appearing as translational kinetic energy, as in these simulations.

**TABLE 2. N<sub>4</sub> APEX TO CENTRE OF FACE IMPACT.**

Impact Velocity (kms <sup>-1</sup> )	Result
6	No reaction
8	No reaction
9	No reaction
9.5	Reaction ~1000fs
10	Reaction ~1300fs
12	Reaction ~50fs

(b) Face into face (symmetric).



In this orientation no reactions were observed with impact velocities up to 12kms<sup>-1</sup>. The results are given in Table 3.

(c) Apex into apex (symmetric).

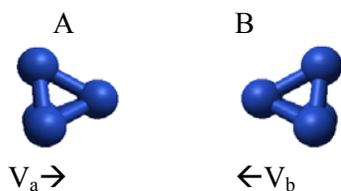
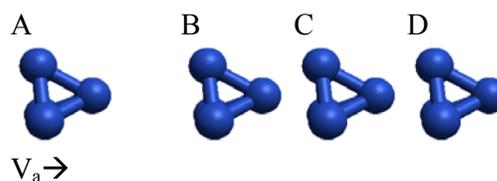


Table 4 details the results of simulations over a range of impact velocities. A reaction threshold of 8.5-9kms<sup>-1</sup> was observed. It would thus appear that collisions involving an apex are more sensitive.

In order to investigate the possible affect of temperature in reducing the

reaction threshold, the apex into centre of face simulations were repeated with a fixed impact velocity of 9kms<sup>-1</sup> and over a range of vibrationally excited states. These were achieved by randomly choosing the atomic Cartesian velocity components such that the energy was equivalent to that of a thermalised system of a given *temperature*. Table 5 details the results of these simulations. The effect of increasing the *temperature* of the molecules in the simulation is, as expected, to reduce the reaction impact velocity.

To increase the effect of energy localisation, a system of four molecules of N<sub>4</sub> has also been studied. In these simulations one molecule impacted a line of three stationary molecules, giving the molecules the possibility of experiencing multiple collisions.



The simulations detailed in Table 6 show the effects of both thermalisation and multiple impacts. As before the effect of an increase in the initial temperature is to reduce the threshold velocity for reaction. However, the additional collisions appear to have had only an effect on the time to reaction at 10kms<sup>-1</sup>, and not to have reduced the thresholds any further.

Finally we studied a single N<sub>4</sub> molecule constrained in a 5Å<sup>3</sup> cubic box. These results are detailed in Table 7. The affect of the rigid boundary conditions is to dramatically reduce the reaction impact velocity threshold to between 3.5kms<sup>-1</sup> and 3.75kms<sup>-1</sup>.

**TABLE 3. N<sub>4</sub> FACE TO FACE IMPACT**

Impact Velocity (kms <sup>-1</sup> )	Result
9	No reaction
10	No reaction
12	No reaction

**TABLE 4. N<sub>4</sub> APEX TO APEX IMPACT**

Impact Velocity (kms <sup>-1</sup> )	Result
8	No reaction
8.5	No reaction
9	Reaction~ 80fs

**TABLE 5. THERMALISED N<sub>4</sub> IMPACTS**

Temperature(K)	Result
300	No reaction
500	No reaction
625	No reaction
750	Reaction ~100fs
1000	Reaction ~350fs

**TABLE 6. N<sub>4</sub> IMPACTS: 3 x N<sub>4</sub>**

Temperature(K)	Velocity(kms <sup>-1</sup> )	Result
0	8	No reaction
300	8	No reaction
0	9	No reaction
300	9	Reaction~700fs
0	10	Reaction~350fs

**TABLE 7. N<sub>4</sub> CONSTRAINED IN A CUBIC BOX**

Velocity(kms <sup>-1</sup> )	Result
3	No reaction
3.5	No reaction
3.75	Reaction ~450fs
4	Reaction ~700fs
4.5	Reaction ~100fs
5	Reaction ~70fs

## CONCLUSIONS

In this paper we have demonstrated how theoretical techniques may be used to study the likely properties of novel polynitrogen materials. In addition we have shown that this class of molecules offers

the potential for very high energy-density materials.

We have also indicated certain reservations regarding the likely physical state of some of the lower molecular weight species, and the probability that the detonation performances are likely to be lower than predicted, due to N<sub>2</sub> dissociation.

The stability and sensitivity of this novel class of materials is only just beginning to be studied. Our preliminary molecular dynamics and potential scan calculations at least indicate that N<sub>4</sub> is not abnormally reactive. Clearly further work is needed in this area to more accurately reproduce the condensed environment.

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