



Prediction of unusual curled nitrogen oligomers



Frank J. Owens

Department of Physics, Hunter College and the Graduate Center, City University of New York, 695 Park Ave., New York, NY 10065, United States

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ABSTRACT

Density Functional Theory is used to predict the possibility of single chain nitrogen oligomers containing more than 10 nitrogen atoms. Calculation of the frequencies of the normal modes for various chain lengths show no imaginary frequencies indicating the structures are at a minimum on the potential energy surface. While shorter oligomers are shown to be near linear, longer polymer chains are predicted to have an unusual curled structure. It is predicted that the longer oligomers could be semiconductors. The calculations show that the decomposition reaction to $n[\text{N}_2]$ is exothermic. Bond dissociation energies are calculated to assess the stability of the oligomers.

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1. Introduction

A number of calculations have indicated that molecules or clusters containing only nitrogen atoms such as N_8 , N_{10} , N_{12} and N_{20} would be very energetic materials releasing much more energy on exothermic reaction compared to presently used materials [1,2]. For example the exothermic reaction of the cubic N_8 molecule is predicted to release 3.8 Kcal/g compared to 1.48 kcal/g for HMX ($\text{C}_4\text{H}_8\text{N}_8\text{O}_8$), the most energetic material in wide use today. However, none of these structures have yet been synthesized and their synthesis remains a challenge. These would also be environmentally friendly because the products of their decomposition are nitrogen molecules. Further they could be quite stable because of the strength of the N–N bond. Recently attention has turned to polymeric nitrogen as a high energy material because of two reports of its possible existence [3,4]. Polymeric nitrogen would also be expected to be a very energetic material. In one report a polymeric form of nitrogen having an unusual cubic gauche structure (cg-N) was synthesized from molecular nitrogen by high pressure and temperature, (2000 K and 110 GPa). Another report suggested the existence of polymeric nitrogen in sodium azide, (NaN_3) subjected to a pressure of 160 GPa at temperatures ranging from 120 to 3300 K. The pressure induced an interaction between the linear N_3^- azide ions as indicated by the emergence of new lines in the Raman spectra possibly forming some polymeric structure of nitrogen perhaps a linear chain. However, the structure of this polymer in NaN_3 has not been determined. More recently Density Functional Theory (DFT) has been used to show that a N_8 single zigzag chain of nitrogens is stable inside carbon nanotubes and between sheets of graphene [5–7]. Nitrogen clusters have also been

predicted to be stable inside C_{60} [8]. It has also been shown that a double nitrogen chain oligomer is stable as a free standing entity [9]. There is some recent evidence for the formation of nitrogen oligomers on carbon nanotube sheets by electrochemical deposition. It was shown that these sheets catalyze the oxygen reduction reaction when used as electrodes in fuel cells [10].

In this work DFT is used to obtain the structure of larger nitrogen single chains having more than 10 nitrogen atoms. The chains are found to be stable free standing structures. The possibility of a free standing single nitrogen molecular chains having length longer than 10 nitrogens has not previously been considered. There have been molecular orbital calculations on smaller nitrogen linear chain having less than 10 nitrogens such as N_6 , N_8 , and N_{10} [11–14]. Raman active vibrational frequencies, electronic energy levels, bond dissociation energies and energy released in unimolecular decomposition to N_2 molecules are calculated as a function of the number of nitrogens in the chains to assess their potential as an energetic materials.

2. Methods and results

The optimized structure of the nitrogen chain oligomers at different lengths is obtained employing Density Functional Theory (DFT) at the B3LYP/6-31G* level using GAUSSIAN 03 software [15]. The frequencies at each length were calculated to verify that the structures are at a minimum on the potential energy surface. The energy levels of the structures are obtained by performing a single point calculation on the B3LYP/6-31G* optimized structure using the local spin density approximation employing the Slater exchange functionals and the VWN correlation function. The energy gap is obtained by taking the difference in energy between the highest occupied molecular orbital (HOMO) and the lowest

E-mail address: owensfj@gmail.com

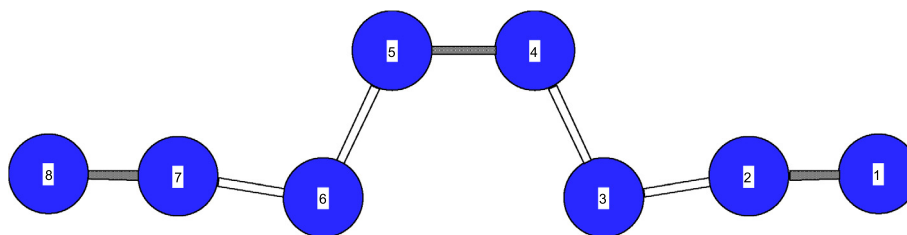


Figure 1. Minimum energy structure of N_8 calculated by 3 different molecular orbital methods.

Table 1

Comparison of bond lengths in angstroms and bond angles in degrees of optimized structure of the N_8 oligomer calculated by using B3LYP DFT, Hartree-Fock and MP2 methods employing a 6-31G* basis set. Numbers refer to nitrogen atoms labeled in Figure 1.

Bonds and angles	B3LYP	MP2	HF
8–7	1.135	1.125	1.093
7–6	1.255	1.271	1.259
6–5	1.421	1.418	1.386
5–4	1.240	1.242	1.210
4–3	1.421	1.418	1.387
3–2	1.255	1.271	1.259
2–1	1.15	1.125	1.093
3–4–5	115.36°	114.94°	116.45°
4–5–6	115.40°	114.94°	116.33°

unoccupied molecular orbital (LUMO). Previous calculations of energy levels in materials indicate this approach is necessary to obtain reliable energy gaps [16].

In order to test the validity of using DFT at the B3LYP/6-31G* level to calculate the minimum energy structure of linear nitrogen polymers, the minimum energy structure of the singlet state of N_8 was calculated using Hartree Fock and MP2 using a 6-31G* basis set and compared with the results of the same calculation using B3LYP/6-31G*. All methods yielded a similar minimum energy structure for N_8 , which is illustrated in Figure 1, and had no imaginary frequencies. The different methods yielded slightly different bond lengths and angles for the structure which are compared with the B3LYP/6-31G* results in Table 1. The comparison indicates that the B3LYP/6-31G* method can reliably predict the structure of the linear nitrogen oligomers. Also the structures are in good agreement with a previous calculation at the B3LYP/aug-cc-eVDZ level [11]. Interestingly the structure shown in Figure 1 has a lower energy than the previously reported cubic N_8 structure [2]. However, both have no imaginary frequencies indicating they are minimum energy structures.

Figure 2a shows the calculated minimum energy structure of the singlet nitrogen oligomer, N_{18} . The minimum energy structures were also obtained for triplet state oligomers. The results indicated that all single chain oligomers had a singlet ground state. While the figure does not clearly show it, the nitrogen atoms do not all lie in one plane. This can be readily seen from the coordinates of the optimized structure shown in Table 2. When the length of the chain is increased beyond 18 nitrogen atoms, the calculations indicate that the minimum energy structures are curled geometries as shown in Figure 2b.

The vibrational frequencies of the normal modes as well as the Raman activity were calculated as a function of the number of nitrogens in the chain. At all lengths calculated there were no imaginary frequencies indicating that the structures are at a minimum on the potential energy surface. This means the structures are stable as free standing entities not requiring encapsulation in carbon nanotubes or between sheets of graphene for stability as

has previously been reported [5–7]. The most intense Raman lines have frequencies in the vicinity of 1225 and 2259 cm^{-1} for the N_{10} chain. There is some dependency of the frequencies on the chain length, as shown in Figure 3 for the 1225 cm^{-1} vibration which is an N–N stretch vibration.

The energy gap determined by the difference in the calculated HOMO and LUMO energy levels calculated as a function of chain length, is plotted in Figure 4. There appears to be some oscillation between large energy gap and small gaps with chain length. It has been shown that for case of covalently bonded solids such as diamond and silicon, a molecular orbital calculation of the HOMO–LUMO energy gap on a sufficiently large cluster having the structure of the solid can provide an approximation to the band gap at the center of the Brillouin zone [17,18]. Thus associating the energy gap with the band gap at $K=0$ for the larger nitrogen oligomers suggests they could be semiconducting.

One of the possible uses of nitrogen containing oligomers could be as energetic materials. Thus it is of interest to determine the energy released and how the length of the chain affects it. It is assumed that the final products of the exothermic reaction of the polymer are nitrogen molecules, i.e. that the reaction is;



The energy released is calculated by taking the difference between then total electronic energy including the zero point vibrational energy of the parent and the products,

$$\Delta Q = [E_e([N_2]_n) + E_{zpe}([N_2]_n)] - n[E_e(N_2) + E_{zpe}(N_2)] \quad (2)$$

Figure 5 shows the calculated energy output versus number of nitrogens in the oligomer showing a systematic increase in the energy with the number of atoms. The oligomers are predicted to release more energy per gram than HMX. For example the N_{24} chain is predicted to release 2.01 Kcal/gm compared to 1.48 for HMX. However, the nitrogen oligomers will release less energy per unit volume than HMX because of the lower density of the oligomers. The densities were estimated by calculating the van der Waals volume of the chains and dividing it into the molecular weight.

In order to assess the stability of the oligomers the bond dissociation energy (BDE) of some of the bonds was calculated. The BDE to remove an N_2 from the end of N_{18} is given by,

$$BDE = [E(N_{16}) + E(N_2)] - E(N_{18}) \quad (3)$$

where E is the electronic energy plus the zero point vibrational energy.

The calculation yields a value -59.27 Kcal/mol. However the BDE for the reaction step $N_{18} \rightarrow 2N_9$ is obtained to be -9.22 Kcal/mol which means this oligomer is metastable. It is found that this is true of all of the oligomers considered. The minus signs mean the reaction is exothermic. This interpretation of a minus BDE has previously been reported and discussed [19,20].

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