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Ab Initio Study of Nitrogen−Oxygen Clusters: N_8O_3, N_4O_6, and N_8O_{12}

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An ab initio study on three hypothetical nitrogen−oxygen clusters is presented. The investigated systems are N_2O_3, N_4O_6, and N_8O_{12} with highly symmetric geometries, D_{3h}, T_d, and O_h symmetry, respectively. Calculations were performed at SCF and MP2 level (MP2, for the two smallest clusters only). Several basis sets were used, from 3s2p to 4s3p2d1f, depending on the cluster size. These structures were found to have local minima, with energies very high above the products of a fragmentation reaction (N_2 and O_2). According to these calculations, NO clusters are potentially interesting as high-energy-density materials.

1. Introduction

There is currently a great deal of interest in finding new compounds that can be used to store large amounts of energy. From a purely energetic point of view, the crucial characteristic is the ratio of the energy released in a fragmentation reaction and the specific weight. Compounds with a high value of this ratio have been called high-energy-density materials (HEDM), and a considerable literature exists on this subject. Nitrogen clusters, the most studied among these systems, have been considered for a long time.[1−7] As interesting candidates for possible HEDM's, many nitrogen structures have been theoretically investigated: N_4,[8−12] N_6,[13−16] N_8,[17−27] and N_{20}.[28] Also oxygen[29−31] and, more recently, heteronuclear compounds have been studied: in particular, CO[32,33] and CNO clusters.[34]

In the present work, three hypothetical systems composed of nitrogen and oxygen are theoretically considered. They are N_2O_3, N_4O_6, and N_8O_{12} with highly symmetric structures: D_{3h}, T_d, and O_h symmetry, respectively. The three structures are characterized as having single bonds only, and being relatively unstrained. Therefore, their electronic wave function at the equilibrium geometry should be largely dominated by a single Slater determinant. For this reason, and considering the relatively large size of some of the clusters, they were investigated at SCF and MP2 level only. This approach permits one to address the problem of their local stability, i.e., the presence or absence of a local minimum on the potential-energy surface (PES). However, with these methods, one can expect to obtain essentially qualitative results: more sophisticated methods, such as configuration interaction (CI) or coupled cluster (CC), are usually needed to obtain results of quantitative accuracy. Moreover, the investigation concerning the heights of the barriers between the hypothetical local minima and the fragmented system (or other less energetic conformational isomers) usually requires multireference methods, like complete active space SCF (CAS-SCF) and related methods. The problem of barrier heights is not considered in the present work. It is worth noting, however, that recent investigations on the N_8 cluster at CAS-SCF and CAS-PT2 levels,[24,26,27] gave results in essential agreement with previous investigations, performed with different methods.

Formally, nitrogen−oxygen (NO) clusters can be generated from single-bonded nitrogen clusters by inserting one oxygen atom on some N−N single bonds. The most symmetric forms are obtained when exactly one oxygen is inserted on each N−N bond. Since each nitrogen forms three single bonds, and each oxygen can be bonded to two nitrogens, by starting from a hypothetical N_{2n} cluster (with $n = 1, 2, 3$, etc.) we will obtain an NO cluster with the stoichiometry $N_{2n}O_{3n}$. According to simple bond-energy considerations, such NO clusters are expected to have a rather large energy content. Indeed, the N−O single bond is a very weak bond (only about 39 kcal/mol[35]). On the other hand, both O_2 and N_2 are strongly bonded molecules, their dissociation energies being about 119 and 226 kcal/mol, respectively.[35] Therefore, an $N_{2n}O_{3n}$ cluster should lie about $(3/2) \times 119 + 226 - 6 \times 39 = 170$ kcal/mol higher than $nN_2 + (3n/2)O_2$ *for each n*.[36] According to these simple considerations, NO clusters are candidates to be HEDM, and it is worthwhile to perform *ab initio* investigations on these systems.

It should be noted that the smallest NO cluster (i.e., diatomic nitric oxide) is also a very energetic molecule, although not having the same stoichiometry as the clusters studied in the present work. In fact, diatomic NO is known experimentally to be an explosive in the liquid state, with an enthalpy of about 21.6 kcal/mol relative to N_2 and O_2 products at 298 K.[37]

2. Computational Details

Ab initio SCF and MP2 calculations were performed on N_2O_3 (D_{3h} symmetry), N_4O_6 (T_d symmetry), and N_8O_{12} (O_h symmetry, SCF only). The atomic basis sets used were the correlation-consistent vdzp and vtzp basis sets (i.e., valence double- and triple-zeta plus polarization), optimized by Dunning.[38] These are Gaussian basis sets of (9s4p1d)/[3s2p1d] and (10s5p2d1f)/[4s3p2d1f] quality on each atom, respectively. For the sake of completeness, also the two intermediate contractions [3s2p] and [4s3p2d] were used, when possible, in this investigation.

For each basis set the geometries were optimized at the SCF level and, whenever possible, also at the MP2 level. The optimizations were performed with the constraints of the full symmetry group at SCF level, while the largest abelian subgroup was used at MP2 level (C_{2v} for N_2O_3 and C_s for N_4O_6). With all the basis sets considered, the SCF orbital energies at equilibrium show a rather large HOMO−LUMO gap. Moreover, the weight of the SCF wave function on the perturbed

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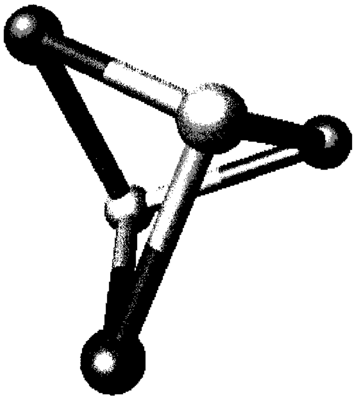

Figure 1. Equilibrium geometry for N_2O_3 at MP2 level, using the [3s2p1d] basis set. Dark gray, oxygen atoms; light gray, nitrogen atoms.

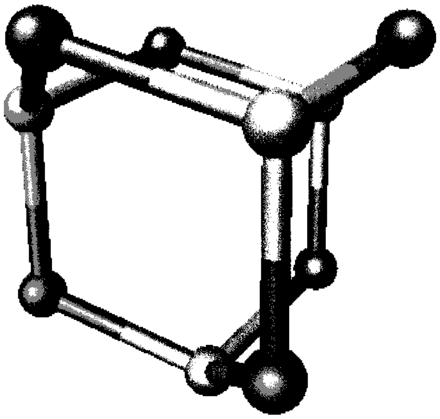

Figure 2. Equilibrium geometry for N_4O_6 at MP2 level, [[3s2p1d] basis set.

MP2 function is rather large, once the cluster size is taken into account. These facts support the intuitive feeling that these clusters admit a description in terms of saturated single bonds. Therefore, in a first approximation, it seems appropriate to describe these systems using a closed-shell single determinant.

The SCF and MP2 harmonic frequencies were computed analytically for the two smallest clusters with the [3s2p] and [3s2p1d] basis sets. Since no imaginary frequency appears, at this level of description the three clusters are local minima on the corresponding PES. Because of its size, the computation of analytical second derivatives for N_8O_{12} is beyond the scope of the present investigation and would require the use of more powerful computer resources.

The results presented were obtained using the ab initio package CADPAC.[39] All the calculations were done on IBM RISC workstations, with the exception of the second-derivative calculation at vdzp/MP2 level for the cluster N_4O_6, done on the CRAY C90 of CINECA.

3. Results and Discussion

As a first step of investigation, the geometries of the clusters were optimized, subject to the symmetry constraints. The equilibrium-geometry structures of two clusters N_2O_3 and N_4O_6, computed at [3s2p1d]/MP2 level, are shown in Figures 1 and 2. In Figure 3 the equilibrium structure of N_8O_{12}, computed at the [3s2p1d]/SCF level, is shown.

In Table 1 the values of the geometric parameters at equilibrium, obtained with the different levels of approximation, are reported. In the three clusters all the N atoms and all the O atoms are equivalent by symmetry, and there is only one type of N−O bond. As expected, the bond length b is longer at MP2 than SCF level, as normally happens in most molecules. Because of the importance of polarization functions, b tends to become shorter when larger basis sets are used. On the basis of the general trend shown in Table 1, one could expect for b a “limit” value in the range 2.7−2.8 bohr for N_2O_3, and 2.6−2.7 bohr for N_4O_6. For a comparison, b is 2.746 bohr in H_2NOH.[40] We see that the bond length in these NO clusters is close to the typical length of N−O single bonds.

On the other hand, because of the closed structure of the clusters, the angles in $N_{2n}O_{3n}$ structures are distorted with respect to the “typical” bond angles formed by nitrogen or oxygen atoms. For instance, bond angles are 104.51° in H_2O and 106.7°

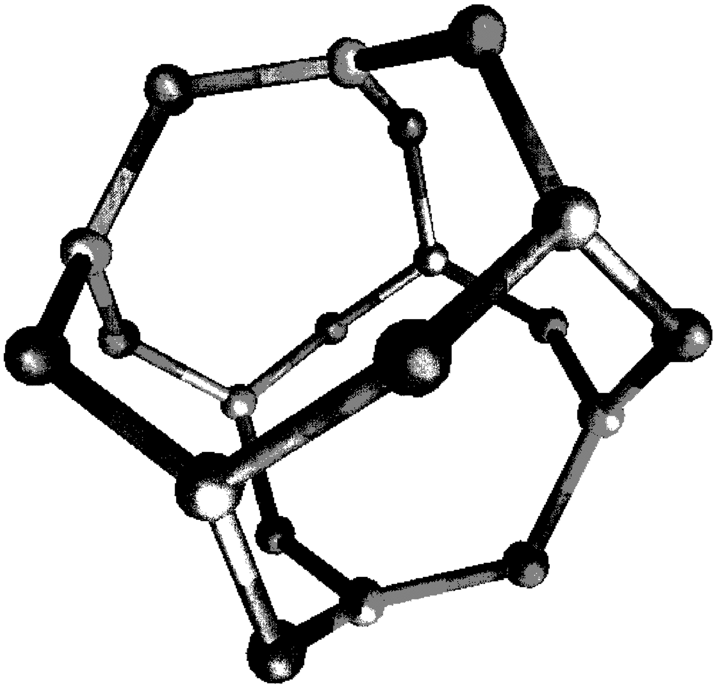

Figure 3. Equilibrium geometry for N_8O_{12} at SCF level, [3s2p1d] basis set.

TABLE 1: Equilibrium Geometries for N_2O_3, N_4O_6, and N_8O_{12}: Bond Length (*b*), ONO and NON Angles (θ_N and θ_O)[a]

cluster	method		*b*	θ_N	θ_O
N_2O_3	3s2p	SCF	2.841	85.28	77.08
		MP2	3.138	87.08	74.61
	3s2p1d	SCF	2.680	86.28	75.72
		MP2	2.821	87.32	74.27
	4s3p2d	SCF	2.679	86.30	75.69
		MP2	2.826	87.34	74.26
	4s3p2d1f	SCF	2.671	86.34	75.62
		MP2	2.789	87.42	74.14
N_4O_6	3s2p	SCF	2.700	107.71	112.88
		MP2	2.910	107.14	113.95
	3s2p1d	SCF	2.592	108.05	112.27
		MP2	2.695	107.85	112.57
	4s3p2d	SCF	2.590	108.14	112.07
	4s3p2d1f	SCF	2.583	108.12	112.12
N_8O_{12}	3s2p	SCF	2.642	117.76	126.87
	3s2p1d	SCF	2.557	117.60	127.46
	unstrained		2.746	106.7	104.51

[a] Distances are in bohr and angles in degrees. The "unstrained" values are experimental values obtained from H_2NOH (*b*), NH_3 (θ_N), and H_2O (θ_O); all values taken from ref 40.

in NH_3.[40] From Table 1, we note that the difference is considerable, particularly in the case of N_2O_3 and N_8O_{12}. The cluster N_4O_6, on the other hand, seems to have a less strained structure, a fact that is in agreement with the shortest bond lengths predicted for this species.

An important indicator of the closed-shell character of a molecular wave function is the HOMO−LUMO gap. The gaps for the three clusters are similar and rather large in value, being in the range of 0.56-0.71 hartree. The gap tends to become more narrow as the size of the cluster increases. It is essentially independent of the basis set, with the exception of the [3s2p] basis set, which gives a value of about 0.06 hartree smaller than the results obtained with the larger basis sets. This last fact can be explained by the stabilizing effect of the introduction of polarization functions in the basis set. The values of the gap are compatible with a closed-shell wave function. The HOMO and LUMO energies, together with the HOMO−LUMO gap, obtained at the SCF equilibrium geometry are reported in Table 5 (available as Supporting Information).

In order to evaluate the energy content of the clusters, and verify their possible interest as HEDM's, one must consider the energy release associated with the possible fragmentation reactions. In the present work, only the fragmentations leading to the appropriate number of N_2 and O_2 molecules were considered. This is because this fragmentation should be the most energetic one, and therefore gives an upper bound to the energy that could be extracted from these systems. The three clusters can fragment into N_2 and O_2 with ratio 2:3. Therefore, $E(N_2O_3)$ must be compared to $E(N_2) + (3/2)E(O_2)$. In a similar way, $E(N_4O_6)$ is compared to $2E(N_2) + 3E(O_2)$, and $E(N_8O_{12})$ to $4E(N_2) + 6E(O_2)$. Table 2 shows the total energies of the three clusters as a function of the method and basis set used. Note that zero-point energies are not taken into account.

The values of the fragmentation energies are larger at the SCF level than at the MP2 level, as one could expect on the basis of the general behavior of similar molecules. More sophisticated methods, such as multireference configuration interaction (MRCI) or coupled cluster (CC), usually give dissociation energies situated between the SCF and MP2 results, and closer to MP2. Enlarging the basis set decreases the fragmentation energy: again, this can be explained as due to a better capability of larger basis sets to describe strained structures, as these clusters are.

Let us consider the vdzp/SCF fragmentation energies (the best values available for all the three clusters). Divided by *n*, these energies are about 200, 130, and 170 kcal/mol for $n = 1, 2, 3$, respectively. These are probably upper bounds to what one would obtain by using MRCI or CC methods and larger basis sets. On the basis of the results reported in Table 2, we can expect for $E(N_2O_3)$ an extrapolated fragmentation energy of about 180 kcal/mol, and of 240 kcal/mol for $E(N_4O_6)$. The first value is close to the rough estimate done on the basis of bond energies, while the second one is only about 70% of this value. In fact, as discussed in the Introduction, simple bond-energy considerations lead to an estimate for $E(N_{2n}O_{3n})$ of about 170 times *n* kcal/mol. Since all the structures are strained (the first one is considerably strained), we conclude that these clusters have an energy content significantly smaller than what could be expected. The results reported in Table 2 are consistent with the N−O bonds being more energetic than the typical bonds between these two species. However, the reason for such a difference is at the moment unclear.

The above discussion is based on the hypothesis that the reaction products from an NO−cluster fragmentation would consist solely of N_2 and O_2, which is certainly not the case. In fact, as pointed out by one of the referees, there exist other NO clusters with low heats of formation: e.g., 2.7 kcal/mol for N_2O_4, and 3.2 kcal/mol for N_2O_5.[40] The existence of these low-energy multiatom molecules probably would seriously degrade the explosive performance of the NO clusters. Indeed, high pressure would favor the existence of these molecules, and thus the quantities of gas produced initially would be reduced when the materials were detonated. This fact is less important if the materials were used as propellants, since combustion normally occurs in relatively low pressure conditions. High temperatures and low pressures would probably lead to a complete fragmentation of the low-energy species.

The Mulliken population analysis indicates that the electrons move from nitrogen to oxygen, as one could predict on the basis of electronegativities of the two species. The amount of transfer is rather small, being in the range 0.18−0.30 for nitrogen and between −0.12 and −0.20 for oxygen. (Because of the

TABLE 2: SCF and MP2 Energies with the Different Basis Sets: for $n = 1, 2, 3$, the Total Energies $E(N_{2n}O_{3n})$ (in hartrees), and the Fragmentation Energies, $D = E(N_{2n}O_{3n}) - (3n/2)E(O_2) - nE(N_2)$ (in kcal/mol) (Zero-Point Energies Are Not Taken into Account)

method		$E(N_2O_3)$	$E(N_4O_6)$	$E(N_8O_{12})$	$D(N_2O_3)$	$D(N_4O_6)$	$D(N_8O_{12})$
3s2p	SCF	−332.8450	−665.9470	−1331.7072	219.22	277.23	671.52
	MP2	−333.5596	−667.2529		201.26	318.59	
3s2p1d	SCF	−333.0571	−666.3447	−1332.4315	202.12	259.60	681.11
	MP2	−333.9918	−668.1582		178.86	248.19	
4s3p2d	SCF	−333.1525	−666.5291		194.75	248.87	
	MP2	−334.2648			171.72		
4s3p2d1f	SCF	−333.1650	−666.5564		195.29	248.51	
	MP2	−334.3740			164.08		

TABLE 3: Weight of the SCF Determinant in the Optimized MP2 Wave Function (Normalized to a Single N_2O_3 Unit)

	N_2O_3	N_4O_6
3s2p	0.8522	0.8938
3s2p1d	0.8769	0.8994
4s3p2d	0.8676	
4s3p2d1f	0.8681	

TABLE 4: Smallest Analytical Frequency (in cm^{-1}) for N_2O_3 and N_4O_6 (All Frequencies Are Real)

		N_2O_3	N_4O_6
3s2p	SCF	703	431
	MP2	439	102
3s2p1d	SCF	837	496
	MP2	520	411

stoichiometry of the clusters, the charge transfer value for oxygen is equal to $-{}^{2}/_{3}$ the corresponding value for nitrogen.) The charge transfer is substantially reduced by increasing the basis set, and by going from SCF to MP2. A similar behavior was observed in analogous calculations on CO clusters.[33] The Mulliken charge transfer is reported in Table 6 (available as Supporting Information).

In order to trust the MP2 results, one must verify that the SCF determinant is dominant in the MP2 wave function. Since N_2O_3 and N_4O_6 have a different number of atoms, the weights in the two cases are not directly comparable, but must first be normalized. The choice adopted here was to take the square root of the weight of N_4O_6. This makes the result directly comparable to the weight of N_2O_3, which is left unchanged. The normalized weights of the SCF determinants in the MP2 wave functions are reported in Table 3. They are never smaller than 0.85 which, considering the size of the systems, is a rather large value. For a comparison, the analogous weight for the N_8 cluster using a [3s2p1d] is 0.8246. Once this weight is normalized, by taking into account the different number of electrons of the two species, we obtain a value of 0.8773. This value is very close to the weights of the NO clusters obtained using the same basis set.

The analytical derivatives of the energy at SCF and MP2 level were computed using the [3s2p] and [3s2p1d] basis sets for both N_2O_3 and N_4O_6 at their equilibrium geometries. All the frequencies are real, which means that there is a minimum on the Born−Oppenheimer PES. The smallest frequency obtained for each structure, using the different approximations, is reported in Table 4. The minimum frequency is greatly reduced in going from SCF to MP2, which is the typical behavior. The introduction of polarization functions has the opposite effect, presumably because of the importance of these functions in describing the strained bonds of these two clusters. Because of its size, frequencies could not be computed for the N_8O_{12} cluster.

4. Conclusions

NO clusters, N_2O_3, N_4O_6 and N_8O_{12}, with D_{3h}, T_d, and O_h symmetries, respectively, were investigated at SCF and MP2 levels. Basis sets of different quality were used, ranging from [3s2p] to [4s3p2d1f]. At this level of description, these systems possess local minima on the PES, lying considerably higher than the products of a fragmentation reaction. Therefore, they show characteristics of HEDM's, similarly to the previously proposed O, N, and CO clusters. Their energy content is smaller than in the N or CO clusters, and is more similar to that of O clusters. This seems to indicate that the N−O bonds are somewhat stronger than the typical N−O single bonds. This fact could be a reason for relatively high barriers to fragmentation, and therefore NO clusters may be good candidates for metastable HEDM's. The results presented in the present work, however, need to be be confirmed by more accurate quantum chemistry approximations.

None of the proposed HEDM clusters (O, N, CO, NO) has ever been synthesized, and there is no direct or indirect experimental evidence of their existence. Indeed, it could be that none of them is experimentally a local minimum on the PES and that the minima are artifacts of the SCF/MP2 description. However, this possibility seems rather unlikely. Or it could be that there is indeed a minimum, but it is too shallow to permit the existence of a metastable species at room temperature for a significant amount of time. Therefore, a study of these clusters at more sophisticated levels is highly desirable, as is a systematic investigation of the activation energies toward fragmentation or rearrangement of the atoms. Such an investigation could help to single out those forms that are more likely to be metastable, and therefore of possible practical interest.

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Supporting Information Available: Energies of the HOMO and LUMO orbitals (Table 5) and Mulliken total charges on nitrogen and oxygen (Table 6) (2 pages). Ordering information is given on any current masthead page.

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