Stability of Polynitrogen Compounds: The Importance of Separating the σ and π Electron Systems[†]

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Planar N_x systems such as cyclo-N_5^- and N_5^+ tend to be more stable than nonplanar systems such as the neutral cyclo-N_6. It is proposed that the key to stabilization is the separation of the σ and π electron systems. In both cyclo-N_5^- and N_5^+, a six-π-electron system is created upon either adding to or removing from the cyclo-N_5 radical one electron. Judicious addition of oxygen atoms to polynitrogen ring compounds such as cyclo-N_4 and cyclo-N_6 can increase their thermodynamic and kinetic stabilities, accompanied by only a small reduction in their efficiency as high energy density materials (HEDMs). The properties of some of these compounds are calculated and compared with the parent all-nitrogen compounds. Coordination of one or more oxygen atoms to the ring leads to effective separation of the σ and π electron systems helping to stabilize the systems. Natural bond analysis indicates that the exocyclic NO bonds can assume a single or double bond character, depending on the ring system.

1. Introduction

The quest for HEDMs based on nitrogen atoms has produced hundreds of theoretical papers, but so far, only one solid-state material containing a N_5^+ cation and a gas phase N_5^- anion was reported experimentally in addition to the well-known N_3^- anion and N_3 radical. (Other species, such as N_4,[1] were only observed as short-lived transients.) The difficulty in preparing all nitrogen compounds has been portrayed in several topical reviews.[2−4] The conclusions are that the goal is achievable, although criteria for this optimistic view were mostly based on computations, whereas predictive tools for establishing which design principles should be used are still limited. Christe and coworkers recently reported two breakthroughs in the field: the synthesis of the N_5^+ cation in a salt[5] and of the cyclo-N_5^- anion in the gas phase.[6] The cation is V-shaped, whereas the anion is cyclic, according to theoretical calculations.[3] Although the stability of the cyclo-N_5^- anion was known for many years, on the basis of calculations, its preparation was achieved only recently and only in the gas phase by the selective dissociation of the C−N bond in substituted phenylpentazole anions.[6,7] As detailed in a recent summary by Christe,[8] preparation of neutral N_x compounds in the bulk is yet to be achieved.

Two conflicting design parameters must be balanced: The system should have high energy content, which in N_x systems is brought about by the repulsion between neighboring atoms carrying more p electrons than carbon atoms. At the same time, it should be stable enough to maintain a crystal structure and not to be oversensitive to shocks and temperature rise. Some criteria and guidelines for the design of all-nitrogen HEDMs have been proposed. The idea of aromatic stabilization was put forward to explain the stability of the cyclo-N_5^- anion,[9] but the instability of the isoelectronic neutral cyclo-N_6[10−13] remains to be accounted for.[14] Several authors suggested that the inclusion of oxygen, either as N−O−N bonds[15] or exocyclic to ring systems,[16] might increase the stability of the N_x systems without appreciably reducing their efficiency as HEDMs. A recurring problem in these endeavors has been the inconsistency of the results upon using different computational approximations.[13] In this work, we explore the factors affecting the stability of N_x compounds and their oxygen derivatives by considering their electronic structure as reflecting in their frontier orbitals. It is proposed that planar systems are stabilized because of the separation of their π and σ electron systems. Both thermodynamic and kinetics aspects are considered. We start with the cyclo-N_5^- anion, which is reported to be one of the most stable N_x structures, continue to show that the V-shaped N_5^+ cation is also a planar system stabilized by having six π electrons, and explain how the addition of oxygen atoms can stabilize the neutral cyclo-N_4 and cyclo-N_6 system as well as the N_8 azapentalene system.

2. Proposed Model: N_x Molecules Possessing a Strong Second-Order Jahn−Teller Effect

The fact that the cyclo-N_5^- anion is much more stable than the cyclo-N_5 radical may be correlated with its electronic structure: It is a closed shell system having six π electrons in a ring system, as in aromatic systems. However, the corresponding cyclic N_6 molecule, with the same number of π electrons in a ring, is unstable. The difference between the two is in the number of lone pair electrons: 10 in cyclo-N_5^- versus 12 in N_6. This suggests that a proper analysis must be based on both σ and π electrons.

The design of new N_x compounds often tended to be founded on hydrocarbon analogues on the basis of the fact that the nitrogen atom is isoelectronic with the CH group. A major difference is due to the fact that in hydrocarbons with multiple bonds, the separation between σ and π electrons is justified by the fact that the energy of occupied σ orbitals is usually much lower than that of π orbitals. Therefore, the frontier orbitals responsible for the chemical stability and reactivity are usually π orbitals. Furthermore, both HOMO and LUMO are π orbitals so that only an in-plane distortion can mix them. This state of

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affairs does not apply to N_x molecules. Let us consider the binding nature of a N_x ring compound. The symmetry of the system suggests sp^2 hybridization: each nitrogen atom is bound to its two nearest neighbors by a two-electron σ bond using two of the three sp^2 hybrid orbitals. The p electrons can form π orbitals across the ring system, as in the corresponding $(CH)_x$ ring systems. However, the third sp^2 hybrid orbital is filled with two σ-type electrons and in principle does not tend to form bonding or antibonding orbitals. In ammonia, this is the lone pair orbital, whereas in the present case, symmetry dictates the formation of σ orbitals across the whole molecular system whose energies are comparable to those of the π orbitals. When such fully occupied atomic orbitals interact, the effect of the resulting antibonding interactions is usually larger than that of the bonding ones. This is the origin of the “repulsive forces” in polynitrogen compounds that contribute to their efficiency as HEDMs. Despite their antibonding character, the energy of these MOs is commensurate with that of the π orbitals because of their partial σ character. Because these orbitals are of only minor binding power, we keep on using the term “nonbonding” with them, using the quotation marks to recall their special character. Fabian and Lewars,[14] in their study of the aromaticity of $(CH)_xN_{6-x}$ ring molecules, noted that increasing nitrogen substitution causes a steady decrease in the kinetic and thermodynamic stability. This was ascribed to electrostatic repulsion between “lone pair” electrons. However, their suggested interactions between lone pair and σ^* orbitals cannot lead to out-of-plane distortion, which is the most prominent manifestation of the instability of the N_6 system.

The “nonbonding” MOs are distinguishable from the π ones only if the molecules are planar; in a nonplanar configuration, they mix strongly. This situation leads to a major distinction compared with planar $(CH)_x$ systems: here the HOMO and LUMO can be of different nature (σ or π) so that they can be mixed by out-of-plane vibrations. This can cause the molecule to lose its planarity and become less stable because of reduced or complete loss of π conjugation. For instance, if the HOMO is a σ orbital and the LUMO is a π^* orbital, then strong interaction between the two leads to weak bonding and easily disruptive bond.

For instance, calculations indicate that in neutral cyclo-N_6, the HOMO is a σ orbital and the LUMO is a π^* orbital; strong interaction between the two leads to weak bonding and easily disruptive bonds. In cyclo-N_5^-, however, the π and σ systems are separated, with both the HOMO and the LUMO being π orbitals. The stability of the latter may thus be related to the reduced interaction between the π HOMO and π^* LUMO orbitals. The neutral cyclo-N_5 molecule is a Jahn−Teller system that spontaneously distorts to a nonplanar structure, making it highly reactive, for instance, by having a small barrier to dissociation. The neutral cyclo-N_6 is a Jahn−Teller of the second-order system[17] that also tends to out-of-plane distortions with similar consequences. (See the Results Section.) It is proposed that to achieve stability, N_x systems must be constructed so as to minimize the mixing between π and σ electrons; this is possible only if the system is planar. In this article, we discuss two feasible mechanisms. One involves the creation of a stable six-π-electron system by either adding an electron to a five-π-electron system or by converting σ electrons to π electrons by breaking a σ bond. The other involves binding an atom to the frontier “nonbonding” σ orbitals, causing them to become bonding at a much lower energy, making a π orbital the HOMO with consequent stabilization of a planar structure. As noted by ref 16, adding an O atom to the cyclo-N_4 or cyclo-N_6 systems leads to planarization of the molecules and considerable stabilization. The authors noted that this result cannot be associated with aromaticity but did not offer a model for the effect. As shown here, the oxygen atom binds to the nonbonding orbital of the nitrogen atom, reducing the electrostatic repulsion and resulting in separation of the σ and π systems. It is proposed that this is the underlying mechanism for the special stabilization of cyclo-N_6O_3.

3. Details of the Calculation

All calculations were performed using the Gaussian 2003 program suite.[18] Geometries for ionic and neutral species were optimized, and harmonic vibrational frequencies were calculated at the B3LYP/cc-pVDZ, MP2/cc-pVDZ, and CCSD/cc-pVDZ levels of theory. MO correlations were based on the HF (closed shell) or ROHF (open shell) calculations. Transition states were located using the transit-guided quasi-Newton (STQN) method implemented by Schlegel et al.[19,20] Natural bond order (NBO) calculations[21,22] were used to estimate the bond orders and the charge distribution among the atoms.

4. Results

4.1. Cyclo-N_5^- and Derivatives. The cyclo-N_5^- anion is considered to be one of the most stable N_x species. We have chosen it to be a standard for estimating the relative kinetic stability of several of its oxygenated derivatives. The calculated structures of the molecules dealt with in this work are shown in Figure 1, along with the natural charge distribution and the NBO bond orders. It is seen that the NO bond in all molecules has a length of 1.260 ± 0.005 Å and two bonding electrons; that is, a single bond is formed.

In this work only unimolecular reactions are considered. Possible bimolecular mechanisms are disregarded at this time. The rationale for this choice is the belief that the initial step in the dissociation of N_x compounds is a bond breaking reaction: either a single N−N bond or a concerted extrusion of a N_2 molecule. Table 1 summarizes the data obtained for some unimolecular dissociation pathways. Both the free enthalpy change (ΔH_f) and the barrier (E_{act}) for the reaction are listed.

Inspection of Table 1 shows that the addition of oxygen to the N_5^- ring leads to relatively stable products. The energy release is smaller than that of cyclo-N_5^- itself when singlet NO^- is formed. However, the ground state of NO^- is a triplet ($^3\Sigma$) that lies at a much lower energy (32.5 kcal/mol). If the triplet is formed, then the reactions of the oxygenated molecules are more exothermic than that of the parent. The barriers for unimolecular dissociation are on the same order as that of the parent for singlet reactions. The reaction leading to the triplet may have an even higher barrier. In the case of 1,2-$N_5O_2^-$, it is found that the likely dissociation channels exhibit a higher barrier than that of cyclo-N_5^- using the MP2 calculation and one on the same order upon using DFT. As in previously reported calculations on reaction barriers, different methods lead to numerically different results, but the trends are similar: oxygenation does not significantly mitigate the stability of the cyclic N_5 anion framework. Figure S1 in the Supporting Information shows the calculated structures of some different transition states.

4.2. Neutral Systems. The calculated structures of the neutral molecules considered in this work are shown in Figure 2. Details of the calculations are reported in Table S1 of the Supporting Information. The data obtained for the cyclo-N_4 and cyclo-N_6 derivatives were in complete agreement with those of ref 16 and are not repeated.

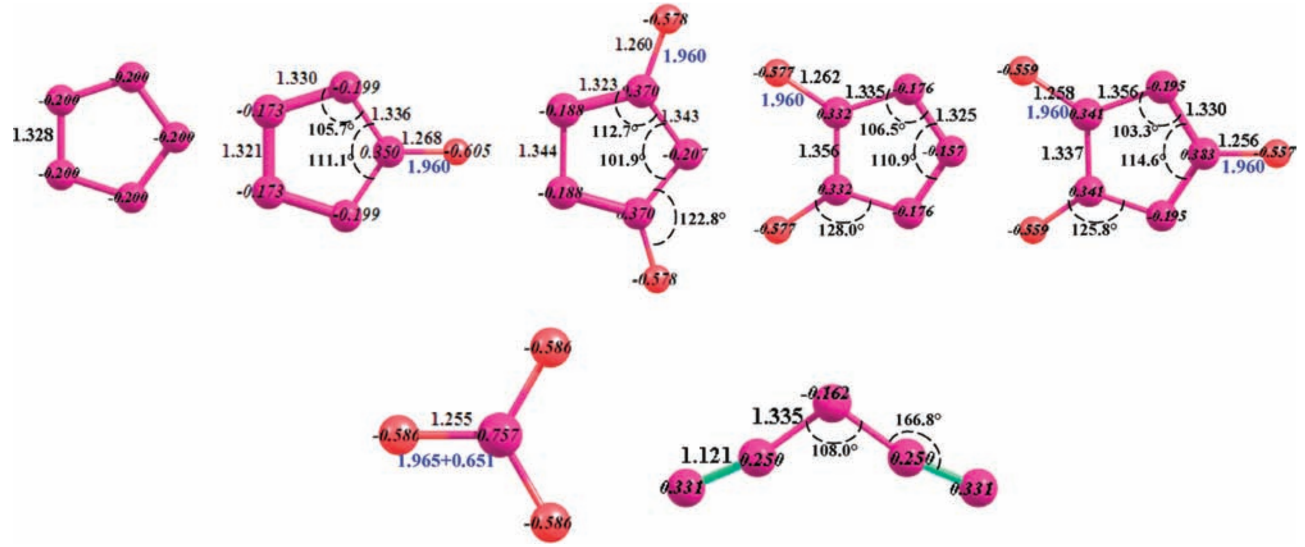

Figure 1. CCSD/cc-pVDZ-calculated structures and natural charge distribution of N_5^-, N_5O^-, 1,3-$N_5O_2^-$, 1,2-$N_5O_2^-$, and 1,2,4-$N_5O_3^-$. Bond lengths are in angstroms and NBO occupancy of the NO bonds is in terms of electron occupancy (blue). Bottom line: calculated structures of the NO_3^- anion and of the N_5^+ cation.

TABLE 1: Reaction Enthalpies and Activation Barriers (kcal/mol) Calculated for Some N_5 Anion Derivatives[a,b]

	CCSD/ccpVDZ	MP2/cc-pVDZ		B3LYP/cc-pVDZ	
reaction	ΔH_f	ΔH_f	E_{act}	ΔH_f	E_{act}
$N_5^- \rightarrow N_3^- + N_2$	−8.9	−16.6	28.3	−2.7	28.4
$N_5O^- \rightarrow N_3^- + N_2O$	14.7	1.2	38.1	15.7	37.2
$N_5O^- \rightarrow N_3O^- + N_2$	8.9	15.0	23.3	17.8	29.1
$N_5O^- \rightarrow NO^- + 2N_2$	−6.0	11.8	37.6	27.4	25.2
$N_5O^- \rightarrow {}^3NO^- + 2N_2$	−38.5	−19.8		7.5	
1,2-$N_5O_2^- \rightarrow N_3O^- + N_2O$	22.7	22.7	31.2	27.7	27.8
1,2-$N_5O_2^- \rightarrow NO^- + N_2O + N_2$	7.7	19.5	36.2	37.0	30.5
1,2-$N_5O_2^- \rightarrow {}^3NO + N_2O + N_2$	−24.8	−12.1		3.1	
1,3-$N_5O_2^- \rightarrow N_3O^- + N_2O$	30.1	40.0	26.6	33.9	41.8
1,3-$N_5O_2^- \rightarrow NO^- + N_2O + N_2$	15.1	25.4	26.4	43.2	27.6
1,3-$N_5O_2^- \rightarrow {}^3NO^- + N_2O + N_2$	−17.4	−6.2		8.3	
1,2,4-$N_5O_3^- \rightarrow NO^- + 2N_2O$	25.9	31.0	24.7	50.3	20.3
1,2,4-$N_5O_3^- \rightarrow {}^3NO^- + 2N_2O$	−6.6	−0.6		15.4	

[a] $\Delta H_f = H_f{}^0{}_{product} - H_f{}^0{}_{reactant}$. [b] E_{act} is the barrier from the side of the cyclic compound.

TABLE 2: Calculated Barriers for the N_8, N_8O, and N_8O_2 Ring-Opening Reactions (kcal/mol) at the MP2/cc-pVDZ and B3LYP/cc-pVDZ Levels

molecule	product(s)	MP2	B3LYP
N_8	N_5N_3	20.6	12.3
N_8O	$N_3N(O)N_4$	33.0	34.4
N_8O	1-O-3-N_3N_5	17.9	11.3
N_8O_2	$N_3N(O)N_2N_2O$	18.0	21.3

Inspection of Figure 2 reveals some interesting trends. In the case of cyclic N_4 and N_6 compounds, the addition of one or more oxygen atoms results in the formation of a double NO bond on the basis of NBO analysis. This is in contrast with the case of the cyclo-N_5 anions and also with aza-pentalene-N_8, where only a single bond is indicated. In N_2O and pyridine oxide, the NO bond is also essentially a single bond. It is noticed that the NO bond length is not a useful indicator for the bond order in this case; for instance, the calculated bond length in N_6O (1.205 Å) is only slightly shorter than that in N_8O (1.210 Å). The single NO bond length in pyridine oxide shown for comparison is 1.269 Å; this indicates a special type of bonding in the polynitrogen case. An additional difference between the N_4 and N_6 compounds and the N_8 compound is the amount of charge transferred to the oxygen atom; it is significantly smaller for N_4 and N_6.

The barriers for dissociation of the aza-pentalene derivatives are shown in Table 2. It is found that the barrier for the ring-opening reaction of the oxo compounds is on the same order as that of the parent aza-pentalene. Therefore, coordination of oxygen atoms to the aza-pentalene molecule did not change the kinetic stability of the system, similar to the case of cyclo-N_5^- anion (Table 1).

Table 3 summarizes the calculated thermodynamic properties of these molecules and also the energy released per gram (ERPG) of the HEDM. Clearly, the energy release per gram is larger for N_x species. However, in the case of N_8O, the ERPG is substantial (83% of N_8 itself), whereas the barrier for dissociation is over 30 kcal/mol. This result may be compared with the much higher barrier for the unimolecular dissociation of sym-N_6O_3, 60 kcal/mol, calculated by Wilson et al. at the CCSD level.[16]

For propellants, the material's potential is best measured by its specific impulse, Isp. The specific impulse in units of seconds can be approximated with the following equation[16]

$$\text{Isp (seconds)} = 265\sqrt{\frac{\Delta H_f\ (\text{kcal/mol})}{\text{MW (g/mol)}}}$$

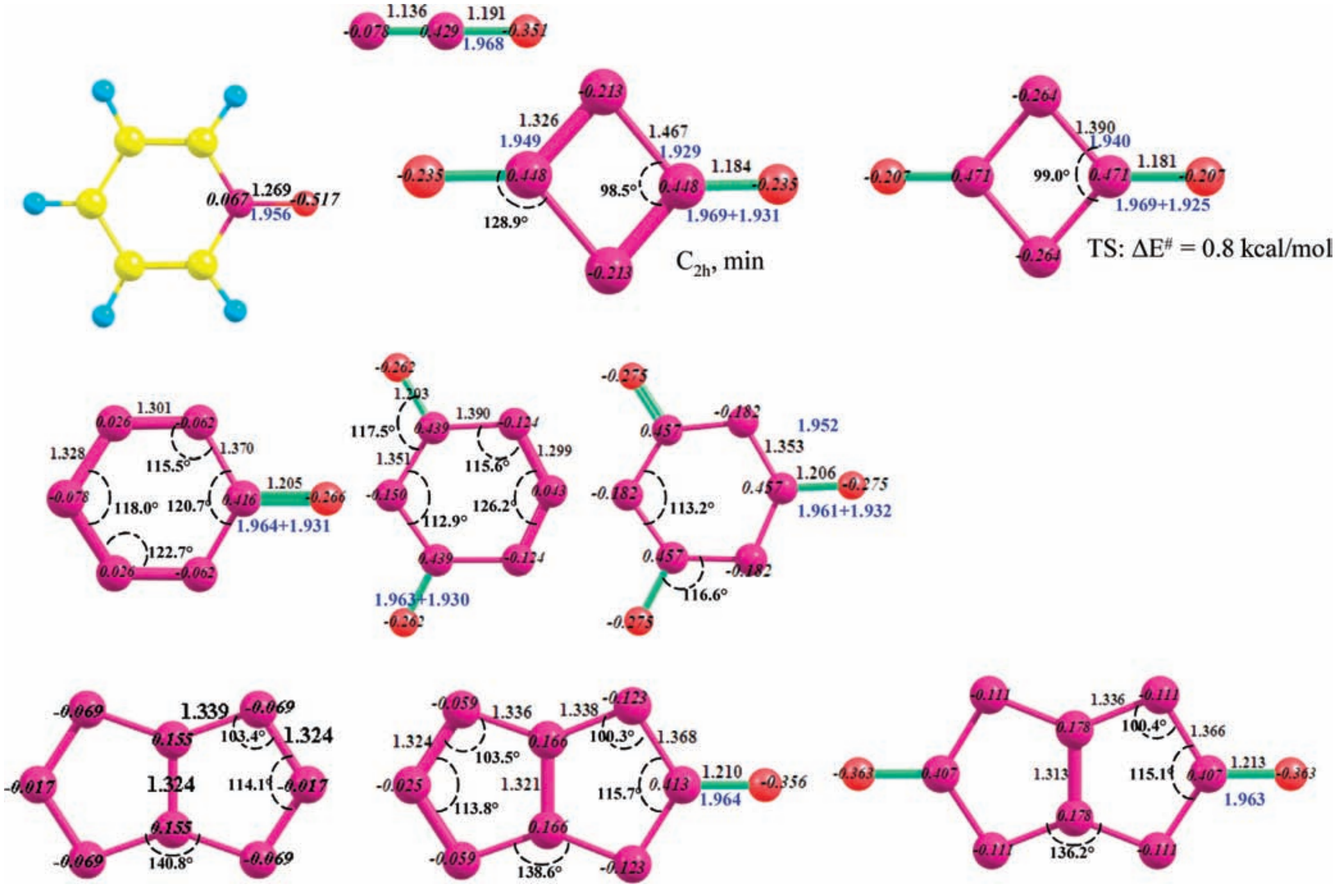

Figure 2. CCSD/cc-pVDZ-calculated structures, natural charges, and NBO occupancy of the NO bonds (blue) of stable minima of some N_x and N_xO_y compounds. In the top row, the calculated structures of pyridine-oxide and N_2O are shown for comparison. Top row: the minimum structure of 1,3-dioxo tetrazene has a distorted C_{2h} symmetry. The symmetric D_{2h} structure, also shown, is a transition state between two C_{2h} structures, lying only 0.8 kcal/mol higher in energy. Middle row, left to right: oxo-cyclo-N_6 (C_{2v}), 1,3-dioxo-cyclo-N_6 (C_{2v}), 1,3,5-trioxo-cyclo-N_6 (D_{3h}). Bottom row, left to right: Aza-pentalene, oxo-aza-pentalene(C_{2v}), 1,5-dioxo-aza-pentalene (D_{2h}).

TABLE 3: Calculated Energy Released in Several Dissociation Reactions of Neutral N_x and N_xO_y Molecules[a]

	CCSD/cc-pVDZ				MP2/cc-pVDZ		B3LYP/cc-pVDZ	
reaction	ΔE^*	ΔH_f	Isp	ΔH/gram	ΔE^*	ΔH_f	ΔE^*	ΔH_f
$N_4 \rightarrow 2N_2$	163.6	162.2	450	2.89	194.1	195.8	174.4	176.3
$N_4O_2 \rightarrow 2N_2O$	105.6	106.8	292	1.21	119.1	121.7	92.9	94.5
1,3-$N_6O_2 \rightarrow 2N_2O + N_2$	155.1	159.1	310	1.37	163.2	168.4	126.5	130.1
$N_6O_3 \rightarrow 3N_2O$	128.7	133.2	267	1.0	142.6	147.8	106.1	109.8
$N_8O \rightarrow N_2O + 3N_2$	241.4	250.3	370	1.95	227.9	238.2	189.7	198.5
$N_8O_2 \rightarrow 2N_2O + 2N_2$	230.6	239.1	335	1.66	221.2	230.6	183.1	190.9
$N_8 \rightarrow 4N_2$	255.7	264.9	400	2.36	237.5	248.7	200.1	209.7

[a] ΔE^* is the difference between the total energies of the reactant and product, and ΔH_f is the energy difference with the zero-point energy contribution included (the negative of the reaction enthalpy). Energies are in kcal/mol. Isp is in seconds.

One finds that for N_8O, Isp = 370 s, as compared with 288 and 311 s for N_6O_3 and N_6O, respectively. For N_6O, the calculated barrier, however, was only 1.1 kcal/mol. The Isp compares quite well to that calculated for N_8 itself, 400 s.

5. Discussion

5.1. Importance of σ−π Separation. The design of new N_x compounds often tended to begin with hydrocarbon analogues on the basis of the fact that the nitrogen atom is isoelectronic with the CH group. As discussed in Section 2, a major difference is due to the fact that in hydrocarbons having multiple bonds, the separation between σ and π electrons is justified by the fact that the energy of occupied σ orbitals is usually much lower than that of π orbitals.

This may be demonstrated by considering the three N_5 molecules N_5^+, N_5 radical, and N_5^-. The calculated MO energies of these species are shown in Figure 3; a presentation of the frontier orbitals is shown schematically in Figure S2 in the Supporting Information.

Consider first the cyclo-N_5 radical. The hypothetical D_{5h} symmetric Jahn−Teller system is distorted into two C_{2v} structures of A_2 and B_1 symmetry that are the structures of minimum energy. The HOMO (which is a SOMO in this case) undergoes strong interaction with the HOMO-1 (a σ MO), tending to distort the molecule from planarity. As a result, the neutral N_5 system is unstable. Two ways may be advanced to increase the stability of the system. Adding an extra electron yields the cyclo-N_5^- anion. In it, the HOMO is a doubly degenerate π orbital, which is fully occupied. Therefore, the π* LUMO can only weakly interact with the σ HOMO-2, leading to a stable system. There is a price to pay: the repulsive interaction between the two electrons occupying the same MO

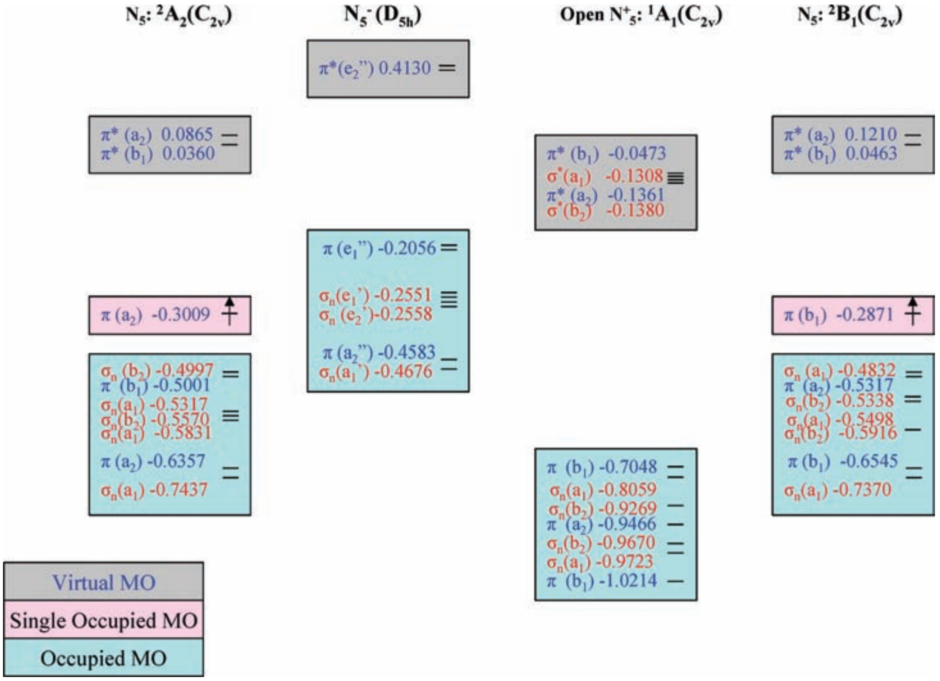

Figure 3. HF(ROHF)/cc-pVDZ: MO correlation diagrams between the cyclo-N_5 anion, N_5 cation, and two degenerate states of the cyclo-N_5 radical.

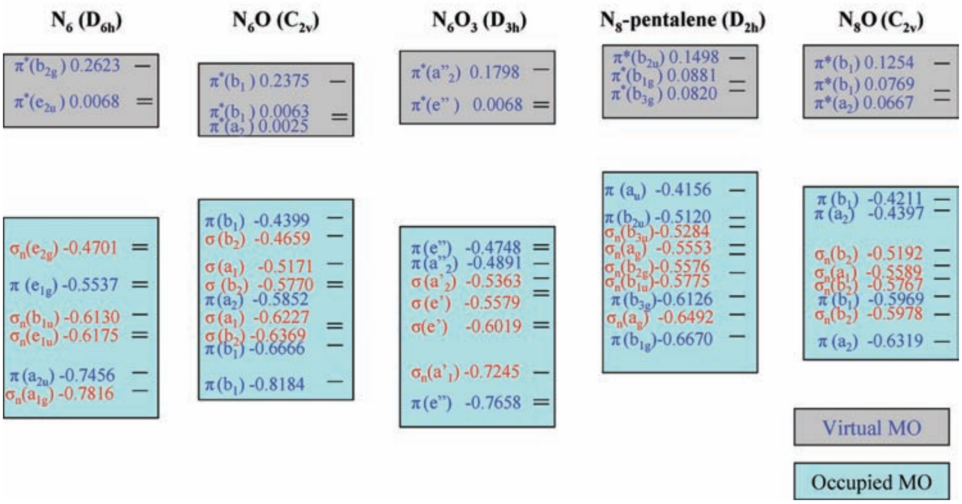

Figure 4. HF/cc-pVDZ: MO diagrams of the frontier orbitals of (left to right) cyclo-N_6, cyclo-N_6O, 1,3,5-trioxo-cyclo-N_6, aza-pentalene, and 1-oxo-aza-pentalene.

results in a higher energy of this orbital, by about 0.1 hartree compared with the SOMO of the N_5 radical. However, the resulting symmetric species is kinetically more stable than the open shell radical.

One can also remove one electron, forming the N_5 cation. In this case the system can be significantly stabilized by opening one of the N−N stable σ bonds, forming an open chain. The two electrons that had formed the σ bond now occupy the highest π orbital (b_1 symmetry, Figure 3), also forming in this case a six-π-electron system, which is quite stable. As shown in Figure 3, there are now two low-lying unoccupied σ orbitals; they replace the two σ orbitals (one strongly bonding, the other strongly antibonding) that disappeared when the NN σ bond was broken.

A similar analysis can be applied to other systems. Figure 4 compares the cyclo-N_6 and aza-pentalene-N_8 systems.

In the D_{6h} cyclo-N_6 system, the HOMO is a nonbonding σ orbital that can mix with the LUMO π^* orbital and lead to distortion. Therefore, the system does not tend to form a stable planar minimum, as verified by many computations. Binding a single nitrogen atom to an oxygen atom changes the order, and now the HOMO is a π MO. The reason is the stabilization of the σ orbital, which is now a bonding one, reducing its energy. However, the energy gap between the π HOMO and the σ HOMO-1 is quite small on the HF level. By adding two more O atoms and forming the 1,3,5-trioxo derivative, a stable planar system is obtained.

5.2. Use of Oxygenated N_x Compounds as High Energy Density Materials. As previously noted,[16] binding an oxygen atom to a cyclic N_x structure is expected to stabilize it because of the resulting reduction in the large lone-pair repulsion in the ring. It was suggested that the new bond is a N → O coordinate bond, but the exact nature of the bond remains to be established. At the HF level, the N_6O molecule is found, in contrast with the cyclo-N_6 compound, to be a planar molecule of C_{2v} symmetry. This can be correlated with the fact that both HOMO

TABLE 4: Isodesmic Reaction Energies (kcal/mol) for the Reaction $N_xO_y + N_2O \rightarrow N_xO_{y+1} + N_2$[a]

reaction	CCSD/ cc-pVDZ ΔE	MP2/ cc-pVDZ ΔE	B3LYP/ cc-pVDZ ΔE
N_2O + Pyr → N_2 + PyrO	−20.7	−13.3	−15.2
$N_4 + 2N_2O \rightarrow N_4O_2 + 2N_2$	−83.0	−75.1	−56.0
$C_3H_3N_3 + 3\ N_2O \rightarrow C_3H_3N_3O_3 + 3N_2$	−34.8	−16.2	−21.0
$N_6 + N_2O \rightarrow N_6O + N_2$	−32.6	−29.1	−30.4
$N_6O + N_2O \rightarrow$ 1,3-$N_6O_2 + N_2$	−32.0	−24.0	−26.6
1,3-$N_6O_2 + N_2O \rightarrow$ 1,3,5-$N_6O_3 + N_2$	−26.4	−20.6	−20.4
$N_6 + 3N_2O \rightarrow N_6O_3 + 3N_2$	−91.0	−73.6	−77.4
$N_8 + N_2O \rightarrow N_8O + N_2$	−14.3	−9.6	−10.4
$N_8O + N_2O \rightarrow N_8O_2 + N_2$	−10.7	−6.7	−6.7
$N_5^- + N_2O \rightarrow N_5O^- + N_2$	−23.6	−15.4	−18.2
$N_5O^- + N_2O \rightarrow$ 1,2-$N_5O_2^- + N_2$	−13.7	−7.7	−9.9
$N_5O^- + N_2O \rightarrow$ 1,3-$N_5O_2^- + N_2$	−21.2	−13.7	−16.1
1,3-$N_5O_2^- + N_2O \rightarrow$ 1,2,4-$N_5O_3^- + N_2$	−10.7	−5.6	−6.9

[a] $\Delta E = E_{\mathrm{abs}}{}^{0}{}_{\mathrm{product}} - E_{\mathrm{abs}}{}^{0}{}_{\mathrm{reactant}}$.

and LUMO are π orbitals (Figure 4). However, when electron correlation is considered (for instance, by applying MP2, CCSD, or DFT methods) the molecule distorts from planarity to Cs structure because of interaction with the nearby σ HOMO-1. When more oxygen atoms are added, as in the symmetric exoaddition of three oxygen atoms to form 1,3,5-trioxo-cyclo-N_6, a planar ring results and is maintained at higher levels of theory including electron correlation. Using natural bond orbital (NBO) formalism,[23] it has also been found that the oxygen atoms in N_6O_3 are negatively charged and that charge alternation occurs in the ring. A more detailed analysis, as presented here, reveals considerable variations in the nature of the bonding in oxygenated N_x molecules. The N−N bond in N_4O_2 and N_6O_3 is a single bond, according to NBO analysis. This holds even for the distorted C_{2h} structure of N_4O_2; despite the large difference in bond length (1.467 vs 1.326 Å), the bond occupation numbers are very similar: 1.929 versus 1.949, respectively. The bonding in the symmetric D_{2h} structure, in which the bond length and occupation number are 1.390 Å and 1.940, respectively, is essentially the same; it transpires that the molecule occupies a shallow minimum and is expected to alternate rapidly between the two C_{2h} equivalent structures. The N−O bond in this molecule, as well as in N_6O and N_6O_3, is essentially a double bond. In contrast, the N−O bond in N_8O and N_8O_2 is a single bond, notwithstanding the fact that the bond lengths in these molecules (1.210 and 1.213 Å) are only slightly longer than those in N_6O_3 (1.205 Å). These results also show that the cyclic molecules N_4O_2 and N_6O_3 are neither aromatic nor antiaromatic; they do not possess a conjugate π system. It is concluded that bond lengths are not a useful measure of the nature of bonding in these N_xO_y molecules, and other means of characterizing the bonding stability are required. In an attempt to make extrapolations to other molecular structures possible, we present a potential rationale for the computational results on the basis of the nature of the N_x ring systems.

Isodesmic reactions have often been used to quantify differences between similar bonds in different molecules. Table 4 presents the results of the calculated isodesmic reactions of N_xO_y molecules with N_2O to produce ^3O atoms. The Table can be used to estimate the relative stability of the NO bond in the HEDMs compared with that of N_2O. It is seen that little energy is released in the reaction of N_2O with pentalene N_8O, pentalene-N_8, and N_5O^- to form 1,2-N_5O_2, more in cyclo-N_5 and N_5O to form 1,3-N_5O_2, and still more with cyclo-N_4 and cyclo-N_6. This order correlates with the energy release of the HEDMs; it also shows that the molecules releasing a small amount of energy are expected to be stable.

The role of oxygen can be rationalized using a VB model with canonical Lewis and increased VB structures, similar to one applied to N_2O.[24,25] Figure 5 shows the main VB structures of N_2O, N_5O^-, N_8O, N_8O_2 and compares them with N_4O_2 and N_6O_3. In the first group, the dominant structures exhibit a single NO bond, whereas in the second group, the dominant structures carry a double bond. The case of cyclo-N_5O^- may be taken up first. In the three equivalent structures having a single NO bond,

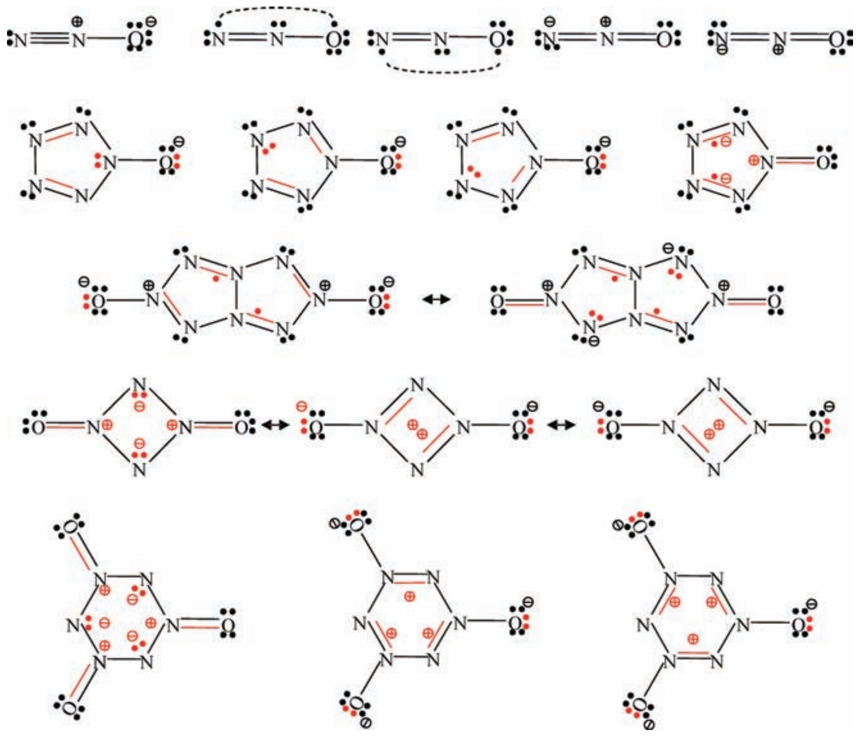
Figure 5. VB representation of some N_xO_y structures.

the negative charge is located mainly on the O atom, and six π electrons remain in the ring. In contrast, having a double NO bond forces six electron to be localized on the smaller N4 fragment, resulting in destabilization due to extra repulsion.

A similar case is found for the neutral N_8O based on N_8-pentalene. The two main VB structures of N_8-pentalene are shown in Figure S3 in the Supporting Information. The 10 π electrons are located within the double-ring system. In the presence of an O atom, the nitrogen atom donates charge to the more electronegative oxygen, relieving the electrostatic repulsion. If a double bond had been formed, then back-donation to the ring would have increased the electron density, causing extra repulsion.

Considering the utilization of the oxygenated N_x species as HEDMs, the preceding analysis reveals a difference between cyco-N_5^- and aza-pentalene on one hand and cyclo-N_4 or cyclo-N_6 on the other. If N_2O is one of the end products of the dissociation of these species, then the extra stabilization of the NO bond in cyclo-N_6O and cyclo-N_6O_3 compared with the same bond in N_2O results in lower energy release. This effect is much smaller in cyclo-N_5O^- and aza-pentalene-O, making them almost as efficient as their all-nitrogen parents.

6. Summary

The properties of all-nitrogen HEDMs are discussed in terms of their frontier MOs. In distinction with the $(CH)_x$ compounds, a major role is played by the somewhat antibonding orbitals formed by σ orbitals of the nitrogen atoms, analogous to the nonbonding MO of ammonia. These "nonbonding" MOs are high-lying and can interact with π MOs of similar energy. The interaction, induced by out-of-plane vibrations, can lead to nonplanar molecules of reduced stability. It is shown that both the cyclo-N_5^- anion and the N_5^+ cation, systems that are known experimentally, can be viewed as a stabilized cyclo-N_5 radical in which $\sigma-\pi$ separation was imposed on the system. It is also noted that previous theoretical work showed that linear structures of N_4,[26] N_6,[13] and N_8[27] are stable species;[28] all are planar and also conform to the idea of $\sigma-\pi$ separation. Another way of inducing $\sigma-\pi$ separation is by localizing the "nonbonding" σ electrons by attaching oxygen atoms to them. The same strategy can also be used with other electron-attracting agents. Bond-order analysis shows that the NN bonds in cyclo-N_4O_2 and cyclo-N_6O_3 are single, and the π-electron contribution to their bonding is minimal. In contrast, the NO bond in these molecules is essentially a double bond. In pentalene-N_8O and pentalene-N_8O_2, the NO bond is a single, as in N_2O. This fact makes it a more suitable HEDM material than either cyclo-N_4O_2 or cyclo-N_6O_3.

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Supporting Information Available: MP2-calculated structures of transition states of several unimolecular dissociation channels of cyclo-$N5^-$ derivatives, schematic presentation of the frontier orbitals of the cyclo-$N5^-$ anion and the $N5^+$ cation, canonical Lewis and increased VB structures for the N8-pentalene$-\pi$ system, and results of MP2-cc-pVDZ and B3LYP/cc-pVDZ calculations on minima and transition states of all systems. This material is available free of charge via the Internet at http://pubs.acs.org.

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