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Stabilization of the Pseudo-Benzene N_6 Ring with Oxygen

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The long sought N_6 ring that is isoelectronic with benzene can be formed by adding coordinate-covalent bonds from oxygen. Optimized structures, normal infrared harmonic frequencies, heats of formation, and activation energies for unimolecular dissociation are presented for the N_4O, N_4O_2, N_6O, N_6O_2, and N_6O_3 systems. By increasing the number of oxygen atoms adjacent to the ring, a nitrogen ring with alternating positive and negative atomic charges can be created. In fact, the N_4O_2 and N_6O_3 systems have completely planar structures and computed heats of formation of 125.0 and 154.7 kcal mol^{-1}, respectively. Furthermore, these systems appear kinetically stable with barriers to unimolecular dissociation of 44.8 and 62.4 kcal mol^{-1}, respectively.

I. Introduction

One of the goals for the development of new high-energy-density molecules has been to explore the prospects for making novel polynitrogen compounds. Since the generation of N_2 as a propulsion or explosion product is highly recommended by its very strong triple bond, such processes offer very attractive energetics in an environmentally friendly way. Hence, guided by isovalent analogies with carbon and phosphorus compounds, we[1−7] have used predictive quantum chemical techniques to investigate the structure, stability, spectra, and decomposition paths of experimentally unknown polynitrogen molecules, as have others.[8−12] (See ref 6 for an extensive survey of pure nitrogen species, from 2 to 12 atoms, their cations, anions, and low-lying excited states). It is apparent that if −CH groups could be replaced by isovalent −N, there will be a large increase in the amount of energy stored by virtue of the standard state of nitrogen, N_2, and also in the repulsion of electron lone pairs on adjacent nitrogens. However, we pay a price for this endothermicity, since to retain the energy for use as a fuel, we must have sufficiently high activation barriers to unimolecular decomposition as well, and we have also to address the question of whether nonradiative transitions can play a role in the molecule's decomposition.[10] We have considered the molecule N_4 in a tetrahedral arrangement,[1,2,7] as well as the N_8 analogue of cubane.[2,13] In both cases, the high symmetry indicates that any decomposition to N_2 would be Woodward−Hoffmann forbidden, suggesting significant barriers to decomposition. Numerical investigation of the barriers shows that N_4's is 62 kcal mol^{-1} [4,8] though its effective barrier is close to 40 (because of a low-lying triplet state[4,10]) and N_8's is 19.[11,12] We have also investigated the other azacubanes where 1−7 of the −CH units have been replaced by −N, and the nitroazacubanes.[13] More energy per molecule can be gained from single rather than double-bonded nitrogen linkages, recommending N_4 and N_8 if they could be synthesized and stabilized, but at the cost of the stability offered by the double-bonded −N═N− structures. In addition, to impose some organization of proposed energetic species, we here considered dimers, trimers, etc. of highly energetic units such as O_2NCN and other units.[53] In this paper the unit is N_2O.

Beyond N_2 and N_3^-, there is little experimental evidence to date that nitrogen can form stable homonuclear molecules. Just recently, Christe and co-workers have reported the synthesis of $N_5^+AsF_6^-$,[14] while N_3^+,[15] $N_4{}^+$,[16−18] and the diazidyl N_6^- complex[19,20] have been detected spectroscopically as short-lived species. Notable in the series of homoleptic polynitrogen systems is the absence of the N_6 ring. The N_6 ring, analogous to benzene, is not a minimum on the potential energy surface as a planar, hexagonal ring. Instead, including correlation, the D_{6h} structure is a second-order saddle point with the closest minimum, a nonplanar boat-type D_2 structure.[21] This feature might be attributed to the large lone-pair repulsion in the ring. However, we might expect to reduce some of this repulsion by forming coordinate covalent bonds, −N→O. In fact, such bonds are found in explosives[22−25] and suggest some interesting consequences for the formation of novel polynitrogen rings.

II. Computational Methods

All the ab initio calculations in this report were performed with the ACES II program system[26] while the density functional calculations used the Q-CHEM computer program.[27] The well-known hierarchy of ab initio methods ranging from Hartree−Fock self-consistent field (SCF), second-order many-body perturbation theory (MBPT(2)), coupled-cluster singles and doubles (CCSD), to coupled-cluster singles and doubles with a perturbative inclusion of triples (CCSD(T)) were employed to show the importance of higher dynamic correlation. Density functional theory with the empirical Becke three-parameter Lee, Yang, and Parr (B3LYP) exchange correlation functional was also used. Both the ab initio and DFT calculations were performed in the 6-31G* one-particle basis set using Cartesian Gaussians.[28] This basis corresponds to a modest 15 functions per heavy atom, but is largely sufficient for the whole series of molecules ranging up to nine heavy atoms, studied here. To obtain better energetics, single-point energies were computed

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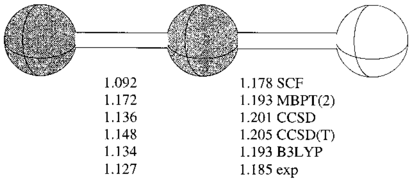


Figure 1. Computed and experimental structure for N_2O.

TABLE 1: Computed Electronic Energies in Hartrees with the 6-31G* Basis for the Nitrogen Ring Systems Considered in This Work along with Their Transition States for Unimolecular Dissociation and the Reference Systems (N_2, O_2, and N_2O)

	sym	SCF	MBPT(2)	CCSD	CCSD(T)	B3LYP
N_4O	C_{3v}	−292.24948	−293.14183	−293.11678	−293.16431	−293.74738
N_4O TS	C_s		−293.12807	−293.10008	−293.15494	−293.73555
N_4O_2	C_{2h}	−367.18793	−368.22286	−368.21021	−368.26495	−369.00953
N_4O_2 TS	C_s	−367.08451	−368.11780	−368.13412		−368.94015
N_6O	C_s	−401.23971	−402.41983	−402.40314	−402.46850	−403.27751
N_6O TS	C_1	−401.20786	−402.41173	−402.39816	−402.46492	−403.27193
N_6O_2	C_{2v}	−476.03554	−477.40901	−477.38679	−477.46083	−478.42721
N_6O_2 TS	C_1	−476.00358	−477.37440	−477.36196	−477.43747	−478.40574
N_6O_3	D_{3h}	−550.82526	−552.39317	−552.36192	−552.44360	−553.56742
N_6O_3 TS	C_1	−550.65752	−552.28431	−552.23772	−552.33575	−553.44754
N_2	$D_{\infty h}$	−108.94395	−109.25528	−109.25579	−109.26852	−109.47195
O_2	$D_{\infty h}$	−149.61791	−149.94973	−149.95176	−149.96178	−150.26010
N_2O	$C_{\infty v}$	−183.68012	−184.20414	−184.18702	−184.21223	−184.57778

with the aug-cc-pVDZ basis set[29] at the optimized 6-31G* geometries (see Table 1). Total atomic charges were computed with the natural bond orbital (NBO) procedure of Weinhold et al.[30] A spin unrestricted wave function was used to describe the $^3\Sigma_g^-$ state of O_2 which showed little evidence of spin contamination. All transition states were confirmed by the presence of only one negative eigenvalue in the computed Hessian matrix. All core electrons were omitted from the correlation procedure; however, the virtuals corresponding to the core electrons were included in the correlated calculation.

III. Results and Discussion

In this section, we begin by checking the reliability of our methods by calculations on the N_2O molecule. Then, we explore the trends in structures and energetics for its dimers and trimers plus related species as a function of increasing the number of coordinate−covalent bonds. The first series is based on a four-membered nitrogen ring system and contains N_4O and N_4O_2. In the second series, we consider the six-membered nitrogen ring systems: N_6O, N_6O_2, and N_6O_3.

The computed and experimental geometries of N_2O are shown in Figure 1. The SCF method slightly underestimates both bond lengths, while all other methods predict bond lengths longer than their experimental values. The computed CCSD(T) N−N bond length of 1.148 Å and N−O bond distance of 1.205 Å compare to the experimental values of 1.127 Å and 1.185 Å, respectively. The error is due in large part to the use of the small 6-31G* one-particle basis set, as the larger cc-pVTZ[28] basis gives 1.132 Å and 1.189 Å. However, the predicted B3LYP bond lengths seem slightly better in the 6-31G* small basis. The computed and experimental harmonic frequencies are presented in Table 2. Here, the CCSD(T) computed frequencies are slightly better than the B3LYP computed values. The largest difference is for the second Σ_g^+ normal mode which CCSD(T) underestimates by 6 cm^{-1} and the B3LYP method overestimates by 88 cm^{-1}.

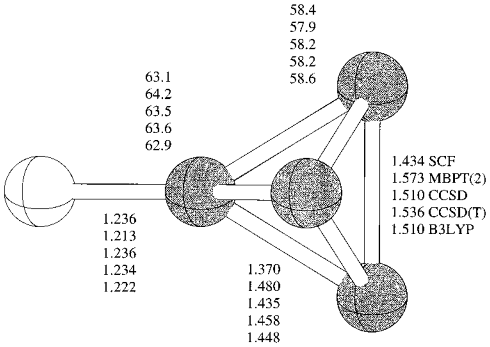


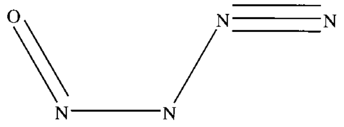
Figure 2. Computed structure for N_4O.

TABLE 2: Computed Harmonic Vibrational Frequencies in cm^{-1} and Infrared Intensities in Parentheses with Units of km mol^{-1} for the N_2, O_2, and N_2O Molecules[a]

	sym	SCF	MBPT(2)	CCSD	CCSD(T)	B3LYP	expt[50,51]
$^1\Sigma_g^+$ N_2 ($D_{\infty h}$)	Σ_g^+	2758	2175	2411	2341	2457	2358.57
$^3\Sigma_g^-$ O_2 ($D_{\infty h}$)	Σ_g^+	1998	1410	1650	1578	1658	1580.19
	Π	689	575	597	573(6.8)	603(9.0)	596.3
$^1\Sigma_g^+$ N_2O ($C_{\infty v}$)	Σ_g^+	1393	1288	1319	1292(42.4)	1342(49.9)	1298.3
	Σ_g^+	2633	2247	2353	2276(287.5)	2370(308.9)	2282.1

[a] All computed values are from the 6-31G* basis.

The first member of the N_4 series is the N_4O system and its computed lowest-energy structure is shown in Figure 2. The four-membered nitrogen ring is not a minimum for this molecule which instead adopts a C_{3v} structure similar to that of the tetrahedral isomer of N_4. One of the N−N bond lengths is on the order of a single bond (1.45 Å)[31] with its CCSD(T) predicted value of 1.458 Å and the other one that is not equivalent by symmetry has a slightly longer value of 1.536 Å. Other isomers of N_4O have been considered including a C_{2v} ring structure with oxygen as part of the ring.[32] However, the transition state for the unimolecular dissociation of this C_{2v} molecule was located which indicated a barrier between 1 and 2 kcal mol^{-1}. A somewhat more stable and experimentally observed[33] isomer is the *trans*-chain nitrosyl azide.



Prompted by its Raman characterization, Klapötke and Schulz considered two dissociation pathways for this molecule.[34] The first pathway involved conversion into a cis isomer, then a cyclic form, followed by its dissociation into N_2 and linear N_2O. The highest barrier for this process computed at the MP2/6-31+G* level was 6.7 kcal mol^{-1}. A transition state for the direct dissociation into N_2 and cyclic N_2O was also found which indicated a barrier of 24.2 kcal mol^{-1}.

The transition state structure for the loss of NO from our C_{3v} structure is shown in Figure 3. It has C_s symmetry with the major difference that one of the N−N bonds is broken. It is worth noting that the differences between the MBPT(2), CCSD, CCSD(T) and B3LYP methods are slightly larger than those for the structure shown in Figure 2, indicating that more sophisticated treatments of electron correlation are needed to describe transition states. The barriers, shown in Table 3, differ at most by 7 kcal mol^{-1} from our most reliable estimate, the CCSD(T) value of 5.6 kcal mol^{-1}. Such a small value suggests that it may be possible to observe this N_4O isomer only as a short-lived species, rather than being suitable for preparation and handling in bulk quantities.

The addition of a second oxygen atom to the N_4 ring leads to the completely planar N_4O_2 structure shown in Figure 4. The optimized SCF structure belongs to the D_{2h} point group while

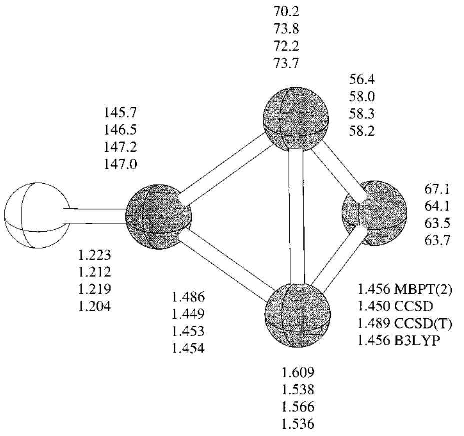


Figure 3. Computed transition state structure for N_4O.

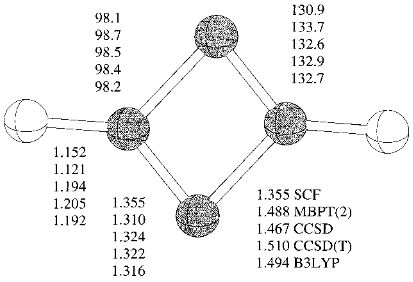


Figure 4. Computed structure for N_4O_2.

TABLE 3: Activation Energies in kcal mol^{-1} for Unimolecular Dissociation[a]

	SCF	MBPT(2)	CCSD	CCSD(T)	B3LYP
N_4O		8.6 (9.3)	9.3 (10.0)	5.0 (5.6)	6.4 (−1.0)
N_4O_2	60.1 (60.1)	65.0 (65.4)	44.8 (45.6)		41.1 (41.4)
N_6O	17.9 (18.5)	3.4 (4.0)	1.8 (1.8)	1.1 (1.2)	2.3 (2.8)
N_6O_2	18.4 (19.2)	20.4 (21.3)	13.9 (14.5)	13.1 (13.8)	12.0 (12.6)
N_6O_3	101.2 (86.3)	64.9 (66.6)	74.1	62.4	71.9 (74.7)

[a] Values not in parentheses are from the 6-31G* basis, and values in parentheses are from the aug-cc-pVDZ basis at the 6-31G* optimized geometries. All values include electronic energy differences as well as zero-point vibrational energy differences and thermodynamic corrections for 298 K.

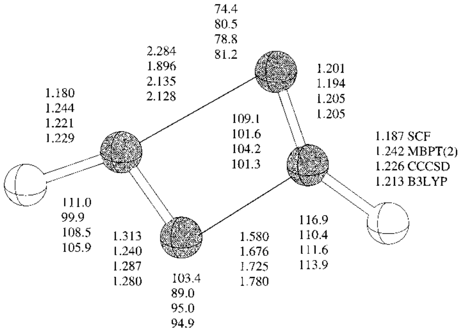


Figure 5. Computed transition state structure for N_4O_2.

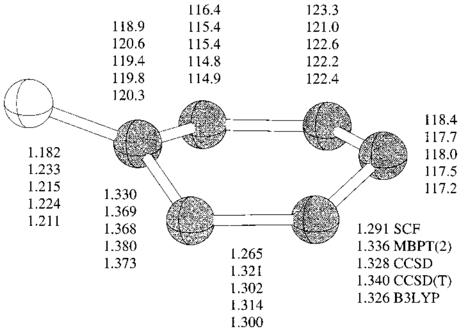


Figure 6. Computed structure for N_6O.

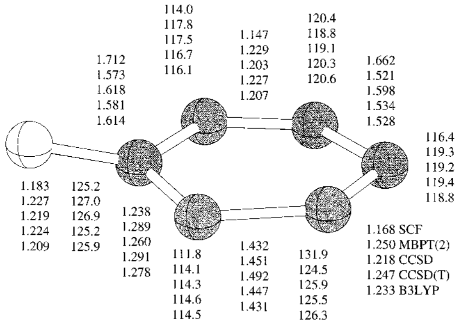


Figure 7. Computed transition state structure for N_6O.

all other methods predict a less symmetric C_{2h} structure. One N−N bond length is between that of a single (1.45 Å) and double (1.25 Å) bond and the other, not equivalent by symmetry, is slightly longer than a typical single bond. Previously, Manaa and Chabalowski have considered another cyclic isomer of N_4O_2 where the oxygen atoms were members of the ring.[35] This structure does not allow for oxygen to remove as much charge from the nitrogen atoms and hence is not as stable kinetically.[36] For the linear N_4O_2 isomer, there have been two reports of its synthesis.[37,38]

The addition of the second coordinate covalent bond to the four-membered ring significantly increases its kinetic stability. The transition state structure for the loss of N_2O is presented in Figure 5. This structure has C_s symmetry and two considerably longer N−N bonds. The large differences between the SCF and CCSD structures demonstrate the importance of electron correlation in describing the transition state. Furthermore, there is a 14 kcal mol^{-1} difference in activation energies with the SCF-computed value of 60.1 kcal mol^{-1} and the CCSD value of 45.6 kcal mol^{-1}. We were unable to converge the CCSD(T) method on this transition state.

The N_6O molecule is the first member of the second series with a six-membered ring. Its structure is nonplanar with C_s symmetry as shown in Figure 6. All N−N bond lengths are greater than that of a double bond (1.25 Å) but shorter than a single bond (1.45 Å).[31] One interesting aspect of the frequencies and intensities in Table 6 is the substantial difference in the B3LYP and CCSD(T) intensities. Particularly, the three A′ modes near 1000 cm^{-1} have a different distribution of intensities, though the total intensity in that symmetry is comparable. The transition state for the unimolecular dissociation of N_6O is shown in Figure 7 which corresponds to loss of N_2. Our best estimate of the barrier for this process is 1.2 kcal mol^{-1} at the CCSD(T)/aug-cc-pVDZ//CCSD(T)/6-31G* level of theory.

Addition of another oxygen atom to the previous structure results in the planar N_6O_2 system shown in Figure 8. This molecule has C_{2v} symmetry and all N−N bond lengths are between those of a double and single bond. Again, the IR intensities vary greatly between CCSD(T) and B3LYP. The transition state for unimolecular dissociation is shown in Figure 9 and corresponds to loss of N_3. The barrier for this process is 13.8 kcal mol^{-1} at the CCSD(T)/aug-cc-pVDZ//CCSD(T)/6-31G* level. Although this value is somewhat larger than that for N_6O, it is still too low to facilitate handling on a bulk scale. Other transitions might occur to products involving N_3^- and N_3O^+, the latter isovalent with N_4.

Addition of another oxygen results in the highly symmetric N_6O_3 structure shown in Figure 10, the trimer of N_2O. This

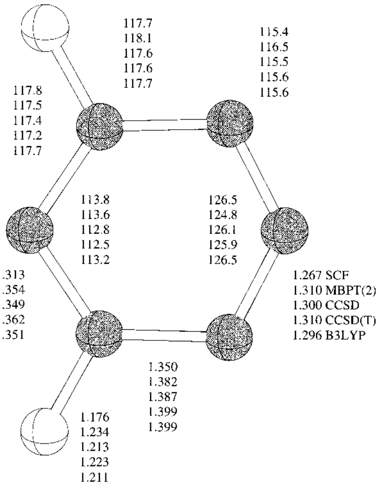


Figure 8. Computed structure for N_6O_2.

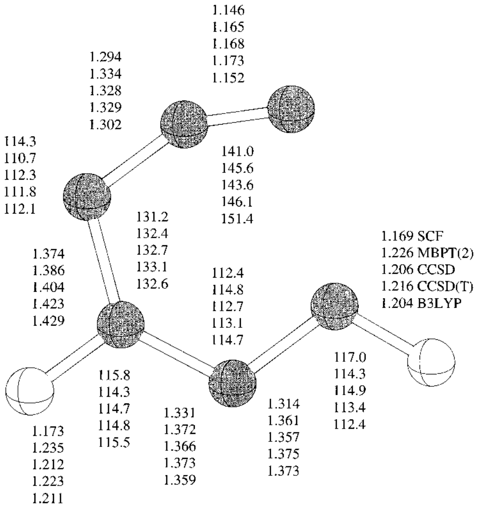


Figure 9. Computed transition state structure for N_6O_2.

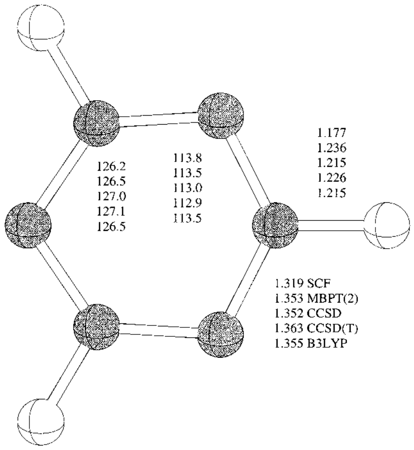


Figure 10. Computed structure for N_6O_3.

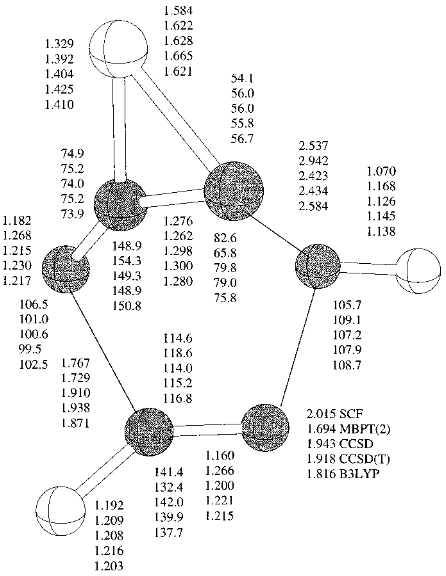


Figure 11. Computed transition state structure for N_6O_3.

molecule has D_{3h} symmetry with all N−N bond lengths equal to 1.363 Å at the CCSD(T) level of theory. This distance is almost exactly between that of a double and single bond, attesting to benzene-like delocalization (though no resonance stabilization as discussed below). Unlike N_6O and N_6O_2, N_6O_3 has comparable IR intensity patterns between B3LYP and CCSD(T). The transition state for unimolecular dissociation is shown in Figure 11. Our best estimate at the CCSD(T)/6-31G* level for the barrier of this process is 62.4 kcal mol^{-1}. Being the trimer of N_2O, there could be an alternative dissociation path to 3 N_2O's, somewhat analogous to the concerted triple dissociation of s-tetrazine,[39] however all attempts to locate other transition states along different dissociation pathways were unsuccessful. Initial indications are that such a N_6O_3 species should be capable of being synthesized.

A. Atomic Charges. One property which can be related to the computed activation energies is the atomic charge or rather the arrangement of the atomic charges. These were computed with the natural bond orbital (NBO) formalism[40] within the 6-31G* basis and are presented in Figure 12. In all structures, oxygen has a large negative charge. However, in the stable structures (N_4O_2 and N_6O_3), the nitrogen ring is composed of alternating charges. For example, in N_4O_2 the smallest charge difference on adjacent nitrogens is 0.60 at the B3LYP level of theory. In N_6O and N_6O_2, the charge on adjacent nitrogens is not as well separated with the smallest B3LYP differences being 0.07 and 0.13, respectively. Figure 12 shows a perfectly alternating NBO charge on the six-membered ring of N_6O_3 with the smallest charge difference being 0.56.

B. Resonance Stabilization? Another interesting concept with the proposed highly energetic molecules is their resonance energy and whether they are resonance stabilized. Early calculations on planar-hexagonal N_6 based on Shaik's quantum-mechanical resonance energy[41] and Dewar's π-resonance energy[42] indicated that hexazine was even more aromatic than benzene. However, Glukhovtsev and Schleyer later reported homodesmic and hyperhomodesmic reactions for hexazine which showed a destabilizing resonance energy of 17.6 kcal mol^{-1} and 10.4 kcal mol^{-1}, respectively.[43,44]

Gimarc and Zhao have offered an explanation of nitrogen's destabilizing resonance energy as opposed to that of carbon, which is based on average bond energies.[45,46] In this approximation, the total energy of a molecule is the sum of its bond energies. Since the average carbon−carbon single bond energy is 83 kcal mol^{-1} which is more than half of the carbon−carbon double bond energy of 144 kcal mol^{-1}, carbon structures with pairs of single bonds rather than double bonds are lower in energy. For nitrogen, the situation is reversed. The average nitrogen−nitrogen single bond energy is 43 kcal mol^{-1}, which is less than half of the nitrogen−nitrogen double bond energy of 100 kcal mol^{-1}. Hence, nitrogen prefers double bonds rather than pairs of single bonds.

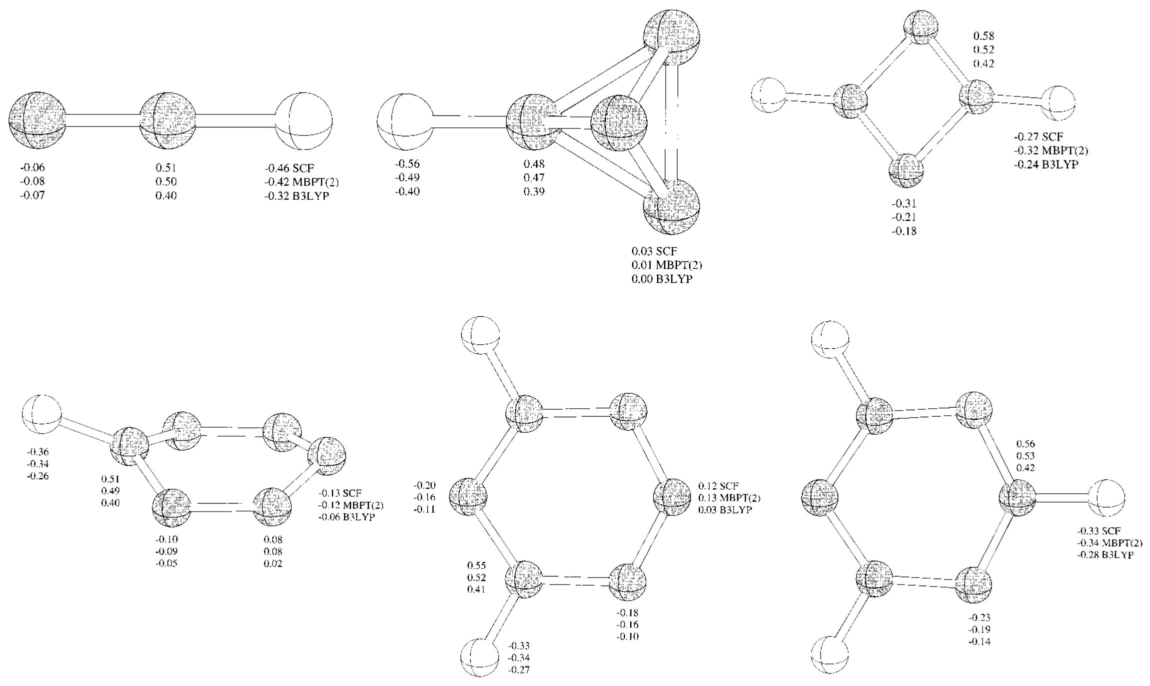


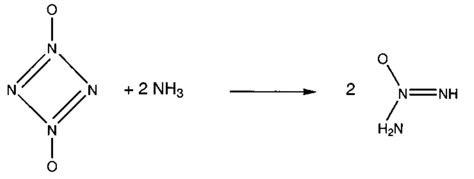
Figure 12. Computed NBO natural charges.

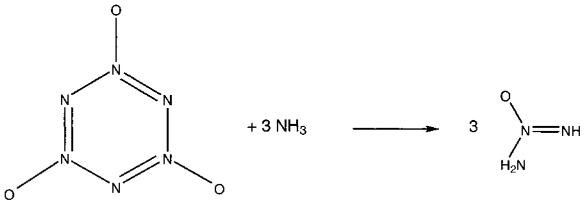
TABLE 4: Resonance Energies in kcal mol^{-1} for Isodesmic Reactions[a]

	SCF	MBPT(2)	CCSD	CCSD(T)	B3LYP
N_4O_2	−38.5 (−34.4)	−36.4 (−32.1)	−36.5 (−31.6)	−32.3 (−27.6)	−35.2 (−32.5)
N_6O_3	−32.1 (−26.2)	−18.6 (−10.7)	−26.5 (−18.1)	−22.0 (−13.9)	−20.3 (−15.9)
$N_6(D_{6h})$		−17.6[b]			
$(CH)_6$		23.9[b]			

[a] Values not in parentheses are from the 6-31G* basis, and values in parentheses are from the aug-cc-pVDZ basis at the 6-31G* optimized geometries. All values include electronic energy differences as well as zero-point vibrational energy differences and thermodynamic corrections for 298 K. [b] These values were computed with the MBPT(4)/6-31G*//MBPT(2)/6-31G* formalism.[43,44]

To estimate the amount of resonance energy in the novel N_4O_2 and N_6O_3 molecules, we have used the following isodesmic reactions, in analogy to $N_6 + 3NH_3 \rightarrow 3H_2N{-}N{=}NH$.





Based upon the energies of the above isodesmic reactions, both ring structures have a destabilizing resonance energy. For N_4O_2, the CCSD(T)/aug-cc-pVDZ//CCSD(T)/6-31G* value is 27.6 kcal mol^{-1} and for N_6O_3 it is 13.9 kcal mol^{-1}. Other quantum mechanical methods predict values which agree closely with CCSD(T) and they are presented in Table 4. We also present the resonance energy for N_6 in the D_{6h} conformation. In fact, the value of −17.6 is very close to our MBPT(2)/6-31G* value for N_6O_3 of −18.6 kcal mol^{-1}. For N_4O_2, the resonance energy is slightly more destabilizing, numerically being −36.4 kcal mol^{-1}.

TABLE 5: Enthalpy of Formation (ΔH_f) and Specific Impulse (I_{sp}) Values for the Ring Species Considered in This Work[a]

	ΔH_f		I_{sp}	
	B3LYP	expt[52]	B3LYP	expt[b]
N_2O	16.7 (17.3)	19.61	163.2 (166.3)	176.9
N_4O	205.2 (206.4)		447.3 (448.6)	
N_4O_2	125.4 (125.0)		316.3 (315.8)	
N_6O	169.1 (169.3)		344.5 (344.7)	
N_6O_2	160.4 (160.2)		311.5 (311.4)	
N_6O_3	155.6 (154.7)		287.7 (286.8)	

[a] ΔH_f is in units of kcal mol^{-1} and I_{sp} is in seconds. Values not in parentheses are from the 6-31G* basis, and values in parentheses are from the aug-cc-pVDZ basis at the 6-31G* optimized geometries. All values include electronic energy differences as well as zero-point vibrational energy differences and thermodynamic corrections for 298 K. [b] Calculated using the experimental ΔH_f and eq 1.

C. Enthalpy of Formation and Specific Impulse. One useful figure of merit for potential fuels and explosives is the material's enthalpy of formation, ΔH_f, or energy relative to the elements in their standard states. It has been shown for molecules that do not contain fluorine, that ΔH_f largely parallels the heat of combustion.[47] In Table 5, we present ΔH_f's for the ring molecules considered in this work and the N_2O test system. For N_2O, the ΔH_f computed from B3LYP/aug-cc-pVDZ//B3LYP/6-31G* is 17.3 kcal mol^{-1} which is in excellent agreement with the experimental value of 19.61 kcal mol^{-1}. For propellants, the molecular weight is also important and a material's potential is best measured by its specific impulse, I_{sp}. The specific impulse in units of seconds can be approximated with the following equation:

$$I_{sp}(\text{seconds}) = 265\sqrt{\frac{\Delta H_f\ (\text{kcal mol}^{-1})}{\text{MW (grams mol}^{-1})}} \qquad (1)$$

where MW is the molecular weight in grams per mol. The I_{sp}'s for the ring species considered in this work are presented in Table 5. The prospective HEDMs that are stable with respect to unimolecular dissociation, N_4O_2 and N_6O_3, have I_{sp}'s of 315.8 and 286.8 s, respectively. Both of these offer an improvement to the 224 s I_{sp} for hydrazine, the most frequently used monopropellant. A survey of possible generalizations of the basic hydrazine molecular structure has been considered elsewhere.[48]

TABLE 6: Computed Normal Harmonic Vibrational Frequencies and Infrared Intensities in Parentheses for Various Nitrogen Ring Structures within the 6-31G* Basis[a]

	point group	sym	SCF	MBPT(2)	CCSD	CCSD(T)	B3LYP
N_4O	C_{3v}	E	522	382	465	430(2.4)	453(2.9)
		E	841	558	659	584(6.7)	604(10.0)
		A_1	834	710	772	730(1.1)	778(2.3)
		E	1173	762	932	845(15.2)	884(15.7)
		A_1	1378	912	1156	1059(1.8)	1149(1.1)
		A_1	1726	1703	1603	1579(344.7)	1657(347.3)
N_4O TS	C_s	A'		732i	683i	599i (38.8)	612i (49.1)
N_4O_2	C_{2h}	A_u	251	224	228	222(2.2)	228(2.1)
		B_u	443	372	372	328(4.8)	343(4.2)
		A_g	575	558	519	486	498
		B_g	782	656	666	622	664
		A_g	805	690	714	702	725
		A_g	894	908	898	870	876
		A_u	931	737	772	704(14.6)	743(19.5)
		B_u	969	866	853	789(93.6)	813(102.0)
		A_g	1260	1183	1130	1147	1133
		B_u	1450	1346	1356	1292(57.8)	1315(74.0)
		B_u	1931	1795	1726	1673(617.8)	1706(758.0)
		A_g	2217	1879	1935	1865	1904
N_4O_2 TS	C_s	A'	1063i	1417i	1070i (73.4)		801i (23.5)
N_6O	C_s	A'	130	153	114	136(0.5)	148(0.5)
		A''	451	322	260	313(2.9)	318(1.0)
		A''	494	490	358	425(19.1)	493(5.1)
		A'	690	516	549	514(17.3)	532(19.2)
		A'	693	669	665	651(0.7)	674(1.0)
		A''	675	673	574	569(32.2)	573(24.7)
		A'	924	752	789	746(4.5)	774(2.6)
		A''	793	827	710	692(5.5)	711(7.3)
		A'	965	857	859	821(19.1)	835(30.4)
		A'	1167	1055	1091	1049(12.3)	1066(30.1)
		A'	1294	1138	1115	1073(23.7)	1091(2.0)
		A''	1493	1166	1266	1173(0.0)	1172(1.4)
		A''	1589	1262	1340	1257(11.6)	1284(23.6)
		A'	1715	1299	1440	1340(31.2)	1390(38.4)
		A'	1835	1717	1672	1609(201.6)	1648(269.0)
N_6O TS	C_1	A	882i	649i	511i	416i (51.5)	448i (52.9)
N_6O_2	C_{2v}	A_2	168	98	113	98	90
		B_1	194	145	149	141(0.4)	146(0.4)
		A_1	518	439	458	438(4.1)	445(2.9)
		B_1	569	462	482	453(16.0)	458(17.9)
		B_2	663	541	489	486(17.5)	536(13.4)
		A_1	672	591	600	578(1.7)	583(2.8)
		B_2	703	605	612	595(1.9)	606(33.3)
		B_2	811	706	643	616(48.8)	628(13.4)
		A_2	868	714	747	709	738
		B_1	877	722	751	714(14.3)	745(18.2)
		A_1	861	768	754	713(2.2)	706(4.2)
		A_1	1092	1041	1010	992(11.8)	986(7.9)
		B_2	1249	1085	1088	1036(30.1)	1060(36.3)
		A_1	1443	1211	1259	1193(1.6)	1237(14.7)
		A_1	1484	1294	1295	1226(22.3)	1200(22.0)
		B_2	1664	1413	1451	1367(133.4)	1409(175.8)
		B_2	1812	1653	1628	1565(447.0)	1596(522.6)
		A_1	1909	1681	1702	1633(65.6)	1672(84.7)
N_6O_2 TS	C_s	A'	474i	541i	448i	446i (94.9)	319i (49.0)
N_6O_3	D_{3h}	E''	166	131	131	$127^{\dagger}$	128
		A_2''	236	207	206	201(3.3)	202(4.5)
		E'	512	442	456	442(7.6)	444(5.7)
		E'	633	575	572	552(12.9)	562(14.7)
		A_1'	791	674	697	662	679
		A_2'	822	628	648	602	690
		A_2''	830	670	704	669(33.7)	695(38.6)
		E''	840	689	721	701	712
		A_1'	1038	988	956	938	943
		A_2'	1134	957	916	875	915
		E'	1252	1092	1102	1052(41.3)	1064(34.7)
		E'	1510	1364	1346	1283(175.0)	1271(218.4)
		E'	1788	1645	1610	1559(469.5)	1572(508.9)
		A_1'	1930	1687	1720	1660	1682
N_6O_3 TS	C_1	A	638i	364i	604i	420i (146.8)	293i (114.2)

[a] Frequencies are in units of cm^{-1}, intensities are in km mol^{-1}. [b] The CCSD(T) frequencies of the N_6O_3 isomer were computed with the larger cc-pVDZ basis set.

IV. Conclusions

In this work, we have quantitatively shown how four- and six-membered nitrogen rings can be stabilized by coordinate covalent bonds to oxygen. Other potentially interesting coordinate covalent structures would include those to BH_3. Our analysis is based on locating the lowest energy transition state for unimolecular dissociation. Although we believe we have done this effectively, we realize that with large molecules, and hence high-dimensional potential energy surfaces, other decomposition routes may exist. Similarity-transformed equation-of-motion (STEOM) calculations[49] of the vertical excitation energies at the singlet optimized geometries of N_4O_2 and N_6O_3 show the lowest triplet states to be at 60.4 and 56.1 kcal mol^{-1}, respectively. Since both of the triplets are high in energy, singlet−triplet crossings should not significantly lower the activation energies. In light of the stability characteristics of the N_2O dimer and trimer, the tetramer of N_2O might be expected to have similar properties. Our preliminary investigations show that N_8O_4 has a S_4-type structure. Although the smallest charge difference on adjacent nitrogens of the tetramer is 0.54 at the B3LYP level of theory, the structure is highly nonplanar. We have not investigated its transition states for unimolecular dissociation, and therefore cannot comment on its kinetic stability. All told, N_4O_2 and N_6O_3 are highly energetic molecules which appear to be stable. They are indeed worth attempts to synthesize. To facilitate their identification, we present harmonic infrared vibrational frequencies and their associated intensities in Table 6.

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