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Do Nitrogen-Containing Oxocarbons Exist? Predictions of Their Stability and Aromaticity

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Density functional theory has been used to investigate the structure, stability and aromaticity of a series of nitrogen-containing oxocarbons, which are related to $C_nO_n^{2-}$ ($n = 3-6$). We have identified a large number of minimum-energy species which might be synthesized and calculated their aromaticity using the nucleus-independent chemical shift method of Schleyer. Successive substitution of carbon by nitrogen reduces their stability, as reflected in the calculated bond orders and dissociation energies. In general, there is no close correlation between the stability and π-aromaticity of the species studied.

Introduction

Aromaticity is one of the most quoted and controversial theoretical concepts at present because of the fact that it is not possible to measure it directly. Among different definitions of such a term, the computational nucleus-independent chemical shift (NICS) method has been proved by Schleyer et al. to be an efficient aromaticity probe.[1] In this method, a negative NICS value implies aromaticity, a positive value antiaromaticity, and a value close to zero a lack of aromaticity. The NICS values (NICS(r)) are calculated at various distances (r, Å) above the molecular plane. Schleyer et al. have recently applied this criterion to the oxocarbons ($C_nO_n^{2-}$, $n = 3, 6$) and found that deltate ($C_3O_3^{2-}$, NICS(1): −11 ppm) and squarate ($C_4O_4^{2-}$, NICS(1): −9 ppm) dianions are both moderately aromatic, while croconate ($C_5O_5^{2-}$, NICS(1): −6 ppm) and rhodizonate ($C_6O_6^{2-}$, NICS(1): −4 ppm) are less aromatic.[2] We have recently studied the chemistry of nitrogen oxides and their anions,[3] particularly their possible involvement in the reduction of NO to N_2, a process of importance in the removal of pollutants from the environment. Since it is often possible in the field of heterocyclic chemistry to successively replace carbon by nitrogen atoms,[4] we may ask whether it is possible to replace carbon by nitrogen in the oxocarbons. This would give an interesting bonding situation where nitrogen would have a formal valency greater than three, not unlike amine oxides. In addition, complete substitution of carbon would give novel nitrogen oxide species.

There is another aspect of oxocarbon chemistry that is of interest, arising from substituting benzene with six O^- atoms. This yields a system with four more electrons than the $C_6O_6^{2-}$ oxocarbon ion. A comparison of species isoelectronic with these two ions ($C_6O_6^{2-}$ and $C_6O_6^{6-}$) allows aromaticity to be studied in the same nuclear framework, but with a differing number of π-electrons.

We report herein the theoretical analysis of the isoelectronic nitrogen analogues of the aforementioned oxocarbons to explore the structure and stability of these species, as well as their aromaticity as reflected in the corresponding NICS values.

Theoretical Approach

We have used the B3LYP density functional approach[5] and the aug-cc-pVXZ (X = D and T) basis sets,[6,7] with the Gaussian suite of programs.[8] Stationary structures were characterized by calculation of harmonic frequencies (B3LYP/aug-cc-pVDZ). These minima were then located with the larger aug-cc-pVTZ basis set to yield the energetics which are reported here. Bond orders were calculated with the natural bond orbital (NBO) method,[9] and the NICS were computed by means of the gauge-independent atomic orbital (GIAO) approach at the B3LYP/aug-cc-pVDZ level.[10] We have used bond orders rather than bond lengths to discuss changes in bonding resulting from nitrogen substitution, as the inherent differences in C−C, C−N, and N−N bond lengths obscure the changes in bonding taking place. All calculated reaction energies include zero point effects.

Computational Results

We first compare our calculated NICS(0) values with those of Schleyer et al.[2] who used a 6-31+G* basis. For $C_3O_3^{2-}$ (**1**), their value (−36 ppm) is very close to the value we obtain (−33 ppm) with an aug-cc-pVDZ basis. Additionally, we have used the HF/6-31+G* level to determine NICS values for comparison to our B3LYP/aug-cc-pVDZ values for the three- and four-membered rings (see Supporting Information). There is generally good agreement between the two sets of data.

Three-Membered Rings. We find $C_3O_3^{2-}$ (**1**), $C_2NO_3^-$ (**2**), and CN_2O_3 (**3**) (Figure 1) to be stable, with planar structures, while the ion $N_3O_3^+$ was not stable under the constraint of D_{3h} symmetry. The bonding in the oxocarbon series is best understood by considering the neutral cyclic structures (C_xO_x), where there are formally carbonyl and cyclic single C−C bonds. In addition, the π^* orbitals of the carbonyl groups, mainly located on carbon, interact to produce a C−C bonding orbital, which gives the oxocarbon series ($C_xO_x^{2-}$) when doubly occupied. The change in geometry caused by the addition of the two electrons is to decrease the C−C bonds and increase the C−O bonds in length. We find that the effect on this bonding arrangement of successive replacement of carbon by nitrogen is to increase the bond order of the C−O and N−O bonds and to decrease that of the C−C and C−N bonds (Figure 1). This bond order change is so significant for $N_3O_3^{+1}$ that it renders it unstable.

We can further examine the effect of replacing carbon with nitrogen by considering the energy changes associated with

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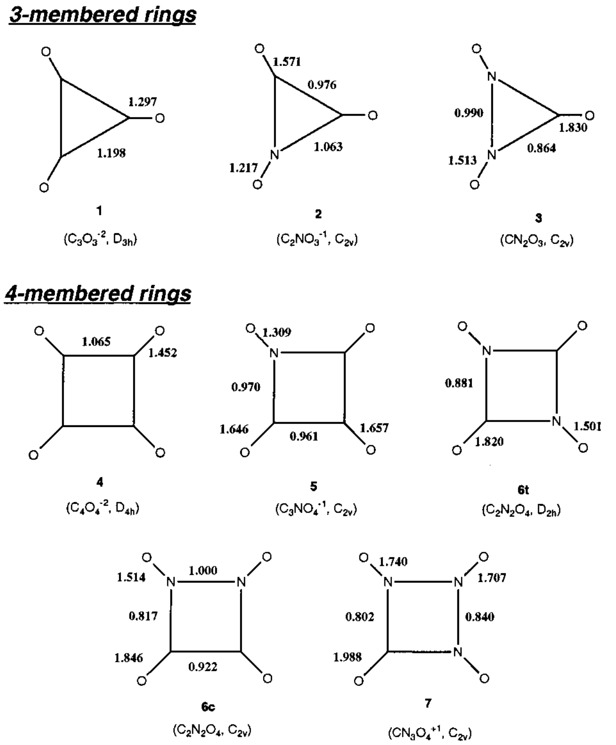

Figure 1. Bond orders of the three- and four-membered rings.

dissociation reactions that give the constituent diatomic species(CO, NO and NO^{-1}), i.e.

$$C_2NO_3^{-1} = 2CO + NO^{-1} \qquad (\Delta E = 142 \text{ kJ mol}^{-1})$$

$$CN_2O_3 = CO + 2NO \qquad (\Delta E = -136 \text{ kJ mol}^{-1})$$

Clearly, the products of such reaction schemes may exist in a variety of electronic configurations having different charges and spin multiplicities leading to different estimates of the dissociation energy. In all schemes reported here, we have chosen the lowest-energy reaction products. The energy changes clearly show that the monoaza oxocarbon is stable to dissociation, while the dissociation of the diaza species is exothermic, confirming the increased instability caused by successively replacing carbon by nitrogen.

We find NICS(0) values of −33, −27, and −31 ppm for **1**, **2**, and **3** respectively at the plane ring point of the electron density (Figure 2A). For three-membered rings, the NICS value in the molecular plane is influenced by local effects from σ-bonds[11] and therefore may not reflect π-aromaticity. We thus compute the NICS values along the z-axis (perpendicular to molecular plane). This will enable us to evaluate the effect of σ-aromaticity that is known to occur in related three-membered rings.[12,13] From Figure 2A it is clear that the diamagnetic shielding is a maximum in the molecular plane associated with in plane aromaticity.[14] Thus **1**, **2**, and **3** have a high σ-contribution to their total aromaticity. The NICS(0) values of **1**, **2**, and **3** imply that **1** is most aromatic, **3** is the next most aromatic, and **2** is least aromatic. We note that the order of aromaticity does not follow the extent of nitrogen substitution in contrast to the situation found for substituted phosphinines.[15] In summary, we find both $C_2NO_3^-$ and CN_2O_3 to be stable species, with a high degree of aromaticity, which has a large σ-contribution. Both the related species $C_3O_3^{2-}$ and amine oxides have been prepared, which leads us to suggest that $C_2NO_3^-$ and CN_2O_3 may be synthesized.

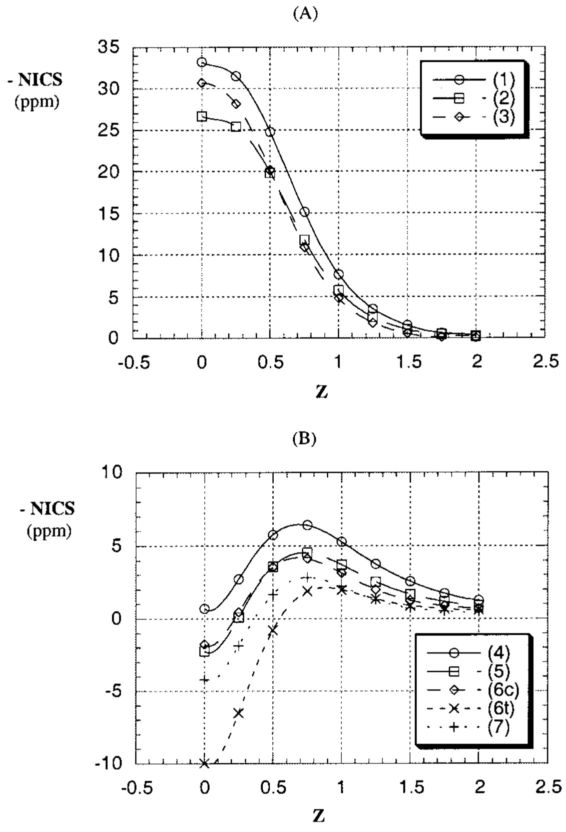

Figure 2. NICS values for the three- and four-membered rings.

Four-Membered Rings. We now consider the four-membered rings systems $C_4O_4^{2-}$ (**4**), $C_3NO_4^-$ (**5**), *trans*-$C_2N_2O_4$ (**6t**), *cis*-$C_2N_2O_4$ (**6c**), and $CN_3O_4^{+1}$ (**7**) (Figure 1), which are all found to be minimum-energy species. The D_{4h} structure of $N_4O_4^{+2}$ was found to be a transition state, which dissociates on removal of symmetry constraints. When compared to the parent squarate dianion (**4**), the effect of aza substitution in the four substituted squarates (**5**, **6c**, **6t**, and **7**) is to increase the bond order in the C−O and N−O bonds and reduce it in the ring bonds. Similar bond order changes were observed for the three-membered rings (**1**, **2**, and **3**).

The reaction energies for dissociation into the constituent diatomic species

$$C_3NO_4^{-1} = 3CO + NO^{-1} \qquad (\Delta E = 292 \text{ kJ mol}^{-1})$$

$$C_2N_2O_4\,(t) = 2CO + 2NO \qquad (\Delta E = 14 \text{ kJ mol}^{-1})$$

show the four-membered rings (**5** and **6t**) to be stable to dissociation into the corresponding diatomic species. With the two diaza species (**6c** and **6t**), it is possible to calculate the isomerization energy and thus obtain a measure of the instability associated with the N−N bond

$$C_2N_2O_4\,(c) = C_2N_2O_4\,(t) \qquad (\Delta E = -33 \text{ kJ mol}^{-1})$$

The NICS values for these four-membered rings (Figure 2B) are qualitatively different from those for the three-membered rings (**1**, **2** and **3**). In the molecular plane, the NICS values are now positive or close to zero rather than negative and become more negative with the increasing distance above the ring. Thus, the σ-bonds contribute paramagnetically and the π-bonds diamagnetically to the ring current,[16] in contrast to the results for the three-membered rings. These paratropic effects fall off

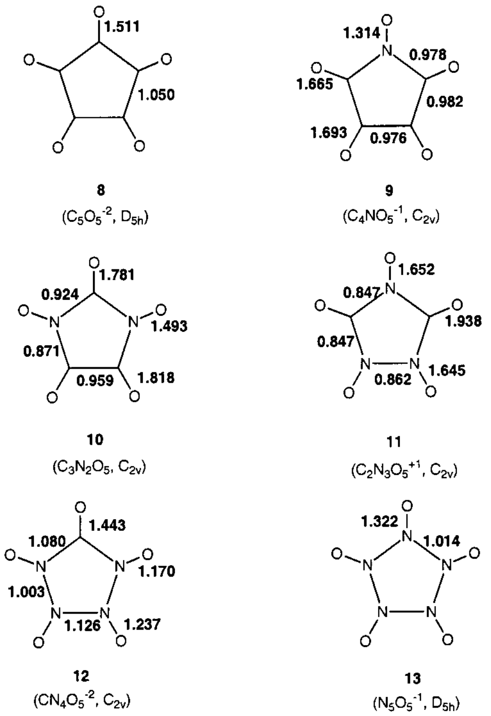

Figure 3. Bond orders of the five-membered rings.

more rapidly than the diatropic effect away from the center, with the maximum NICS value being ~0.75 Å above the ring. This height (0.7−1.0 Å) has been suggested to be the most appropriate position for the interpretation of π-aromaticity.[2,17] While NICS(0) values show a large spread (10 to −1 ppm), the values some 0.75 Å above the ring show less variation (−2 to −6 ppm), indicating a slight π-aromatic character. As we found for the three-membered rings, the sequential aza substitution does not correlate with the corresponding aromaticity. (The supplementary information contains the numeric NICS values at all levels of theory used for both 3- and four-membered rings.) It is worth mentioning that although **6t** is 33 kJ mol^{-1}more stable than the isomer **6c**, the latter is in fact more aromatic than **6t**, as judged by the NICS values.[18]

Five-and Six-Membered Rings. We have not investigated all the possible isomers of the five- and six-membered rings, but given our results for the three- and four-membered rings, we have considered only those with the minimal number of N−N bonds. Thus, the species considered are $C_5O_5^{2-}$ (**8**), $C_4NO_5^-$ (**9**), $C_3N_2O_5$ (**10**), $C_2N_3O_5^+$ (**11**), $CN_4O_5^{2-}$ (**12**), $N_5O_5^-$ (**13**), $C_6O_6^{2-}$ (**14**), $C_5NO_6^-$ (**15**), $C_4N_2O_6$ (**16**), $C_3N_3O_6^+$ (**17**), $C_3N_3O_6^-$ (**18**), $C_3N_3O_6^{3-}$ (**19**), and $C_2N_4O_6^{2-}$ (**20**) (Figures 3 and 4). All species were found to be stable minima and with the exception of **14** and **15** were also found to be planar. For a number of species with more N−N bonds, $N_5O_5^{3+}$, $N_6O_6^{4+}$, $CN_5O_6^-$, and N_6O_6, no stable cyclic structures could be found.

Five-Membered Rings. We first consider the isoelectronic series $C_5O_5^{2-}$ (**8**), $C_4NO_5^-$ (**9**), $C_3N_2O_5$ (**10**), and $C_2N_3O_5^+$ (**11**), which behave very much as the three- and four-membered rings that we have already considered. Thus, the successive introduction of nitrogen atoms into the ring gives rise to larger C−O and N−O bonds orders and reduced bond orders between ring atoms. Again, no stable structure for the totally substituted species ($N_5O_5^{3+}$) could be found.

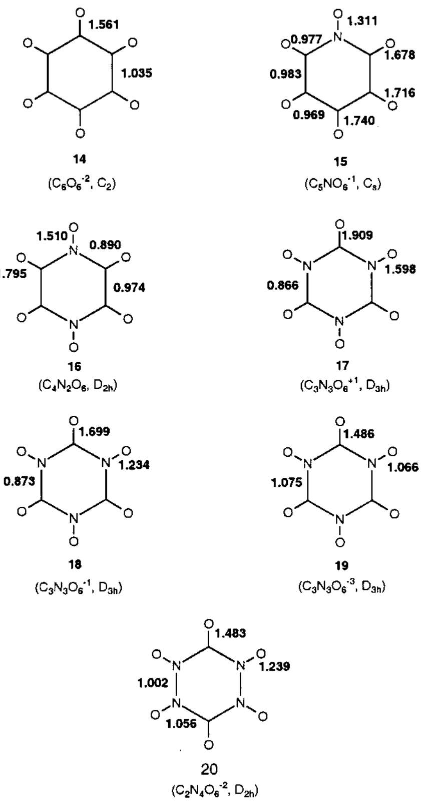

Figure 4. Bond orders of the six-membered rings.

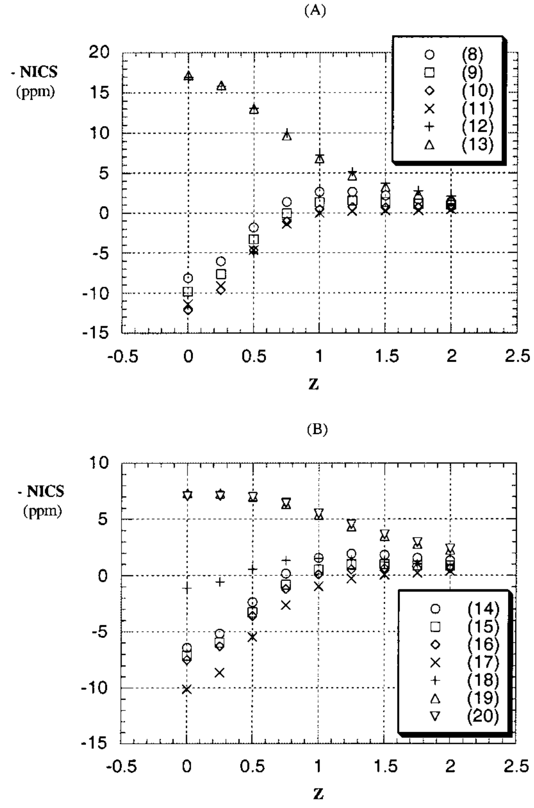

Figure 5. NICS values for the five- and six-membered rings.

The NICS values for these molecules at the electronic center of the ring show an antiaromatic character mainly due to the paramagnetic effects of the σ bonds. The corresponding NICS values 1 Å above the plane of the ring (which avoid such effects) indicate nonaromatic or slight aromatic character in all molecules (Figure 5A). In this case, the successive substitution of carbon by nitrogen around the ring does correlate with their magnetic properties, contrary to our findings for the three- and four-membered rings.

The energies of the dissociative reactions clearly indicate the

$$C_4NO_5^{-} = NO^{-} + 4CO \qquad (\Delta E = 334\ \mathrm{kJ\ mol^{-1}})$$

$$C_3N_2O_5 = 2NO + 3CO \qquad (\Delta E = 22\ \mathrm{kJ\ mol^{-1}})$$

stability to dissociation into the constituent diatomics and the preference for smaller degrees of nitrogen substitution.

Two other five-membered rings ($CN_4O_5^{2-}$ (**12**) and $N_5O_5^{-}$ (**13**)) have been found to be minimum-energy structures. $N_5O_5^{-}$ is stable to dissociation into its constituent diatomic species

$$N_5O_5^{-} = NO^{-} + 4NO \qquad (\Delta E = 58\ \mathrm{kJ\ mol^{-1}})$$

while the dissociation of $CN_4O_5^{2-}$ is exothermic

$$CN_4O_5^{2-} = 2NO^{-} + 2NO + CO \qquad (\Delta E = -13\ \mathrm{kJ\ mol^{-1}})$$

However, the latter reaction involves dissociation of a doubly charged species into two singly charged species, which may cast doubt on the validity of the calculated energetics.[19] These two structures, which contain more nitrogen atoms than the previous ones, are isoelectronic with $C_5O_5^{6-}$, which can be pictured as the well-known aromatic ion $C_5H_5^{-}$ substituted with five O^{-} atoms. Although $N_5O_5^{3+}$ was found to be unstable, the additional four electrons in $N_5O_5^{-}$ now renders the molecule stable. This pentazole pentoxide ion has a single bond between the nitrogens of the ring (the NBO analysis gives a value of 1.01 for this bond order, Figure 3) and a bond order of 1.32 between nitrogen and oxygen. This analysis is supported by the vibrational frequencies where the N−N stretches are found at 646, 967 (E), and 1076 (E) $\mathrm{cm^{-1}}$ and the N−O stretches at 1419 (E), 1462 (E), and 1539 $\mathrm{cm^{-1}}$. For $CN_4O_5^{2-}$, the corresponding frequencies are not too different from $N_5O_5^{-}$, implying a similar bonding scheme (see supplementary information). The NICS values for both **12** and **13** (Figure 5A) show both σ- and π-contributions to aromaticity. The values in the molecular plane of −17 ppm ($CN_4O_5^{2-}$) and −17 ppm ($N_5O_5^{-}$) clearly demonstrate aromatic character. However, the NICS values fall as one moves above the ring (Figure 5A), implying σ-aromaticity, but the significant value at 1 Å above the molecular plane shows there is also a nonnegligible π-contribution to the aromaticity.

Six-Membered Rings. The analysis of the aromaticity in the isoelectronic six-membered rings (**14**−**17**) (Figure 5B) reveals behavior similar to that seen in the five-membered rings (**8**−**11**) with all four species displaying antiaromaticity in the molecular plane and nonaromaticity or slight π-aromaticity 1 Å above it. Addition of four electrons to **17** gives the ion $C_3N_3O_6^{3-}$ (**19**), which is isoelectronic with $C_6O_6^{6-}$ (benzene substituted with six O^{-} atoms). This ion (**19**) and the related ion $C_2N_4O_6^{2-}$ (**20**) are more aromatic than the other six-membered rings we have considered, with NICS(0) values of −7 ppm. A similar increase in aromaticity accompanying the addition of four electrons was observed for the related five-membered rings. Addition of two electrons to $C_3N_3O_6^{+}$ (**17**) gives triplet $C_3N_3O_6^{-}$ (**18**) with a NICS(0) value of 1 ppm, which is, as expected, between that of $C_3N_3O_6^{+}$ (**17**) (+10 ppm) and $C_3N_3O_6^{3-}$ (**19**) (−7 ppm). However, a previous study found that the rules for aromaticity can be reversed for triplet states, with 4nπ annulenes being aromatic.[20]

The bond orders follow the trend found for the five-membered rings. The substitution of carbon by nitrogen causes a reduction in bond order between ring atoms and an increased bond order for interactions involving exocyclic atoms. For the series **17**−**19** $C_3N_3O_6^{-x}$ ($x = -1$, 1, and 3), the successive addition of electrons leads to increased ring bonding and a decrease in the bond order between the ring atoms and the oxygen atoms (Figure 4). The parent acid of $C_3N_3O_6^{-3}$, $(CO)_3(NOH)_3$, is known, and hence, the charged species may be not too difficult to prepare.[21]

TABLE 1: Energies (kJ mol^{-1}) for Loss of CO from the Substituted and Unsubstituted Oxocarbons (reactions 1−4)

ring size of the reactant	6	5	4
$C_xO_x^{-2} = C_{x-1}O_{x-1}^{-2} + CO$	6	128	250
$C_xNO_{x+1}^{-1} = C_{x-1}NO_x^{-1} + CO$	−56	43	150
$C_xN_2O_{x+2} = C_{x-1}N_2O_{x+1} + CO$	−83	8	149
$C_xN_3O_{x+3}^{+1} = C_{x-1}N_3O_{x+2}^{+1} + CO$	−32	63	−

Stability and Ring Size

We have so far discussed the relative stability of each particular ring size, with respect to nitrogen substitution. It is of interest to assess the relative stability of different ring sizes having the same degree of nitrogen substitution. We can examine this by considering a series of reactions involving the removal of a CO molecule, thus reducing the size of ring, while maintaining the same degree of nitrogen subtitution. To do this, we consider the following reactions, whose energetics are given in Table 1:

$$C_xO_x^{2-} = C_{x-1}O_{x-1}^{2-} + CO \qquad (1)$$

$$C_xNO_{x+1}^{-} = C_{x-1}NO_x^{-} + CO \qquad (2)$$

$$C_xN_2O_{x+2} = C_{x-1}N_2O_{x+1} + CO \qquad (3)$$

$$C_xN_3O_{x+3}^{+} = C_{x-1}N_3O_{x+2}^{+} + CO \qquad (4)$$

It can be seen that the loss of CO from nitrogen-containing species is favored for the six-membered rings, but not for the smaller rings, suggesting that the five-membered rings are the most stable species and that the stability is associated with the presence of nitrogen rather than carbon in the ring. This is in line with the low energy (8 kJ mol^{-1}) needed to remove CO from $C_3N_2O_5$.

Conclusions

We have identified a range of cyclic nitrogen-containing oxocarbons, which we predict to be stable species. For a given ring size, an increase in the degree of nitrogen substitution leads to a decrease in stability of these molecules. We have used NICS values to estimate the degree of aromaticity of these species. The values 1 Å above the molecular plane indicate all species are nonaromatic or have a small degree of aromaticity. A close correlation between stability and π-aromaticity, as reflected in the NICS(1) values, is not observed in general. Thus, it appears that stability is determined by ring strain, nitrogen substitution, and σ-aromaticity. We believe that a number of species we have studied could well be synthesized or perhaps be observed as products of surface reactions involving NO and CO.

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Supporting Information Available: Numeric NICS values at all levels of theory used for both three- and four-membered rings. This material is available free of charge via the Internet at http://pubs.acs.org.

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