

Are Neutral Oxocarbons Stable?

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A set of novel oligomeric polycyclic neutral oxocarbons has been computed at the B3LYP level of density functional theory. On the basis of the calculated dissociation enthalpies, the most stable structures are C₉O₉ and C₁₂O₁₂ with benzene-like central ring, in agreement with the experimental finding, and the enhanced stability is due to their aromaticity. Several other oxocarbons also have been identified as stable and are targets for further experimental investigations.

Introduction

Oxocarbons, in which the ring carbons are attached to carbonyl or enolic oxygens or to their hydrated equivalent,¹ have been investigated with structure, bonding, stability and aromaticity.^{2–5} The monocyclic oxocarbon dianions and the neutral cyclic compounds are two representative subgroups of the oxocarbon family. In contrast to the well-known monocyclic dianions (C_nO_n²⁻, n = 3,⁶ 4,⁷ 5,⁸ 6⁹), the corresponding neutral compounds (C_nO_n) are experimentally still unknown, and attempts to prepare these species were unsuccessful so far. High-level computations show that monocyclic C₃O₃ does not exist on the potential energy surface at all, and the other monocyclic structures (C_nO_n, n = 4, 5, 6) are highly unstable as a result of their great exothermic tendency toward dissociation into carbon monoxide,³ as supported by mass spectrometric studies.¹⁰ In addition, oligomeric carbon monoxides have also been studied theoretically.¹¹ Recent theoretical investigation on stability and aromaticity of the unknown nitrogen-containing oxocarbons

shows that the stability decreases with successive substitution of carbon by nitrogen.¹² The structural related cyclic carbon cluster dianions and their aromaticity have also been reported.¹³

In this paper, we present our theoretical investigations on the structure and stability of a set of novel neutral oligomeric polycyclic oxocarbons. Indeed, “organic carbon oxides” (**1–4**, Scheme 1) have been synthesized from tetrahydroxy-1,4-benzoquinone and hexahydroxybenzene with carbonyl chloride or oxalyl chloride by Nallaiah (**1**, **2**)¹⁴ and by Verter (**3**, **4**).¹⁵ It is found that **1** and **2** are extremely sensitive to heat and moisture and darken and decompose on heating at 45–53 °C with brisk evolution of gas,¹⁴ and **3** as well as **4** decompose easily under reduced pressure upon removal of the solvent.¹⁵ The structure of **1** was computed at the HF/6-31G* level by Kwon and Koo.¹⁶ Nevertheless, we thought that this conceptual possibility¹⁵ should be applicable to other neutral oxocarbons deduced from the stability of the parent oxocarbon dianions or their precursors and also to carboxyl-rich chemistry.

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Computational Details

For convenience, we used the R_mC_nO_n nomenclature in which R_m is the ring size of the parent monocyclic dianion and C_nO_n represents the designed neutral oxocarbons. The structures of R_mC_nO_n were optimized at the B3LYP/6-311+G(d) level of density functional theory as implemented in the Gaussian 98 program.¹⁷ Frequency calculations at the same level determined the nature of the stationary points and gave the zero point energies (ZPE).¹⁸ However, because of the huge convergence problem at the B3LYP/6-311+G* level, the structure of R₉-C₁₂O₁₂ (**3**) was only optimized at the B3LYP/6-31G*

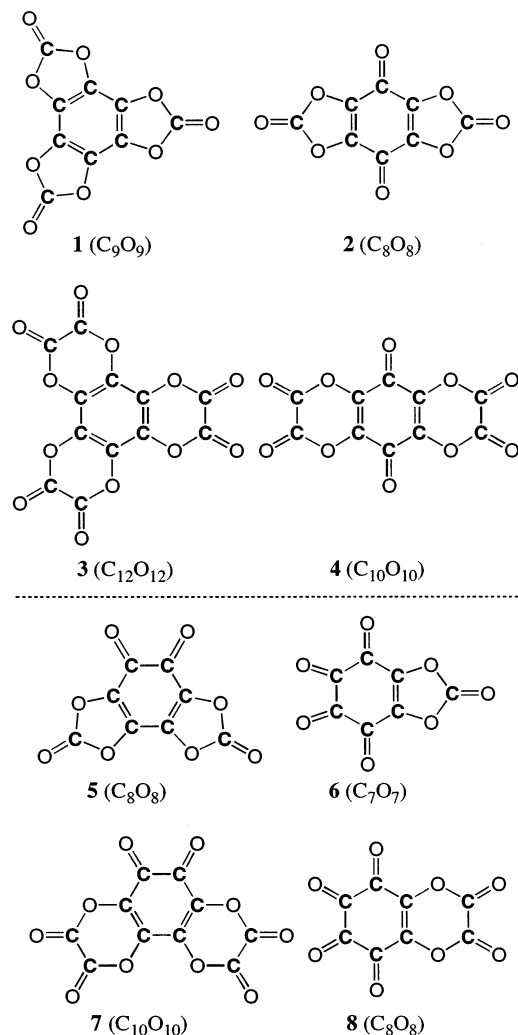
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SCHEME 1. Experimentally Known (1–4) and Proposed (5–8) Oxocarbons ($R_6-C_nO_n$)


level and the related frequency calculation was only done at HF/6-31G* rather than at B3LYP/6-31G* because of the CPU limitation. Energy minima have real frequencies and transition states have only one imaginary frequency. It was found that the B3LYP functional is appropriate for oxocarbon chemistry.¹⁹ Nucleus-independent chemical shifts (NICS)²⁰ were computed at GIAO-HF/6-31+G(d) on the B3LYP/6-

311+G(d) geometries for selected compounds (GIAO-HF/6-31G*//B3LYP/6-31G* for **3**). The computed total electronic energies, zero-point energies (ZPE), and the optimized Cartesian coordinates are summarized in Supporting Information.

Results and Discussion

$R_6-C_nO_n$ (1–8). Oxocarbons (1–8) in Scheme 1 are molecules with a monocyclic $C_6O_6^{2-}$ dianionic nucleus. Although 1–4 are known experimentally, no structural information is available, and the corresponding compounds 5–8 are as yet unknown. As shown in Figure 1, **1** and **3** have benzene-like central six-membered rings, and the planar forms (D_{3h}) are minimum structures. It is also shown that the central C–C bond lengths of **1** (1.397/1.373 Å; 1.400/1.377 Å at B3LYP/6-31G*) and **3** (1.389/1.400 Å at B3LYP/6-31G*) are equalized. Oxocarbons **2** and **4** in D_{2h} symmetry as energy minima mimic the *p*-benzoquinone form, while **5** and **7** in C_{2v} symmetry are similar to that of *o*-benzoquinone.

Experimentally, both para and ortho benzoquinones are known and the former is computed to be 7.5 kcal/mol more stable than the latter. This energetic order is also found for **2** and **5**, as well as for **4** and **7**, e.g., **2** is 7.2 kcal/mol more stable than **5**, and **4** is 7.0 kcal/mol more stable than **7** at B3LYP/6-311+G*. Since **2** and **4** have been synthesized using tetrahydroxy-1,4-benzoquinone, **5** and **7** should be available from 3,4,5,6-tetrahydroxy-1,2-benzoquinone.²¹

In addition to the tri- (**1**, **3**) and diannelated (**2**, **4**, **5**, **7**) oxocarbons, we have also calculated the monoannelated analogues **6** and **8**. The optimized structures are shown in Figure 1. The ground states of **6A** and **8A** are C_2 symmetrical, and the C_{2v} structures (**6B**, **8B**) having one imaginary frequency are transition states for the twisting of the two >C=O groups at the trans position of the R_6 -ring. The barriers are negligible (<0.1 kcal/mol). They might have planar structures in the solid state as in case of biphenyl. Both **6A** and **8A** should be available from 5,6-dihydroxycyclohex-5-ene-1,2,3,4-tetraone.

$R_5-C_nO_n$ (9–12). Oxocarbons with a monocyclic $C_5O_5^{2-}$ nucleus are shown in Scheme 2 (top) with two monoannelated (**9**, **11**) and two diannelated (**10**, **12**) structures. At B3LYP/6-311+G*, **9**, **11** and **12** in C_{2v} symmetry are minimum structures, while diannelated **10A** is C_2 symmetrical. The C_{2v} structure (**10B**) with one imaginary frequency is the transition state for the twisting of the central five-membered ring. The twisting barrier is only 2.4 kcal/mol. The optimized structures are shown in Figure 2. Both the di- and monoannelated compounds should be accessible from tetrahydroxycyclopentadienone²² and 4,5-dihydroxycyclopent-4-ene-1,2,3-trione (croconic acid).

$R_4-C_nO_n$ (13–16). Oxocarbons with a monocyclic $C_4O_4^{2-}$ unit are shown Scheme 2 (middle). As with the monocyclic $C_5O_5^{2-}$, it is also possible to diagram two mono- (**13**, **15**) and two diannelated oxocarbons (**14**, **16**). At B3LYP/6-311+G*, both **13** and **15** are minimum structures in C_{2v} symmetry.

In contrast, one would expect problems associated with the central cyclobutadiene rings of diannelated **14** and

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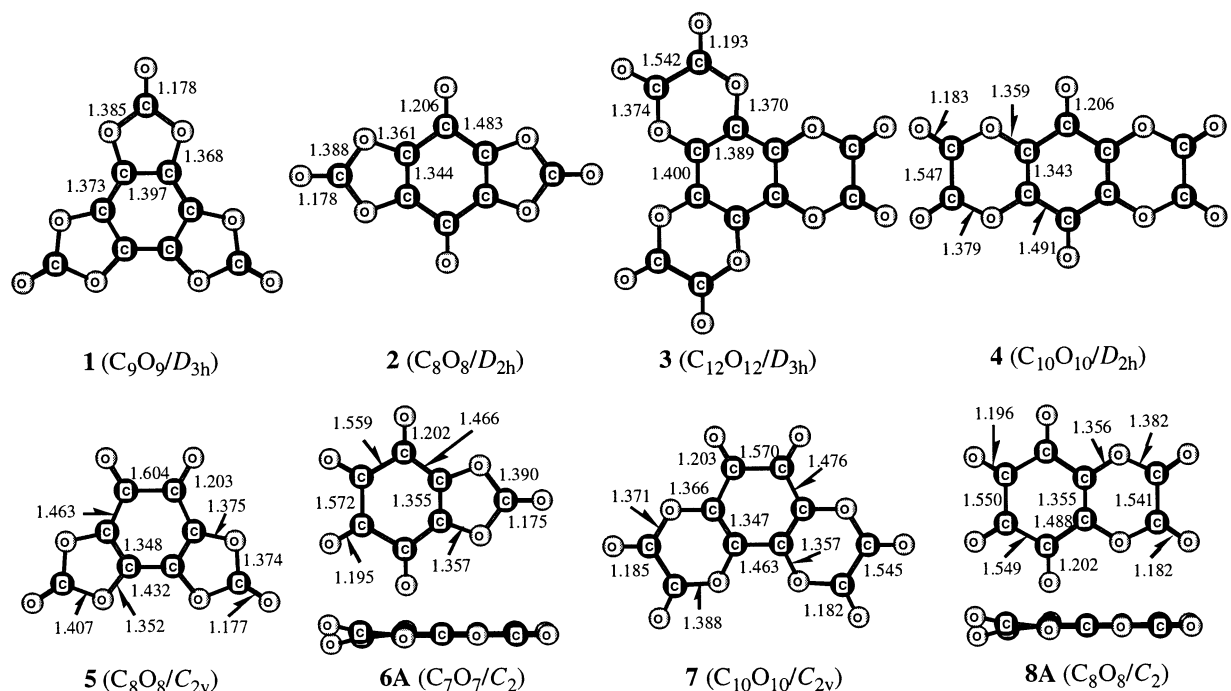


FIGURE 1. B3LYP/6-311+G* optimized bond lengths (Å) of $R_6-C_nO_n$ (**3**//B3LYP/6-31G*).

SCHEME 2. Proposed Oxocarbons 9–18

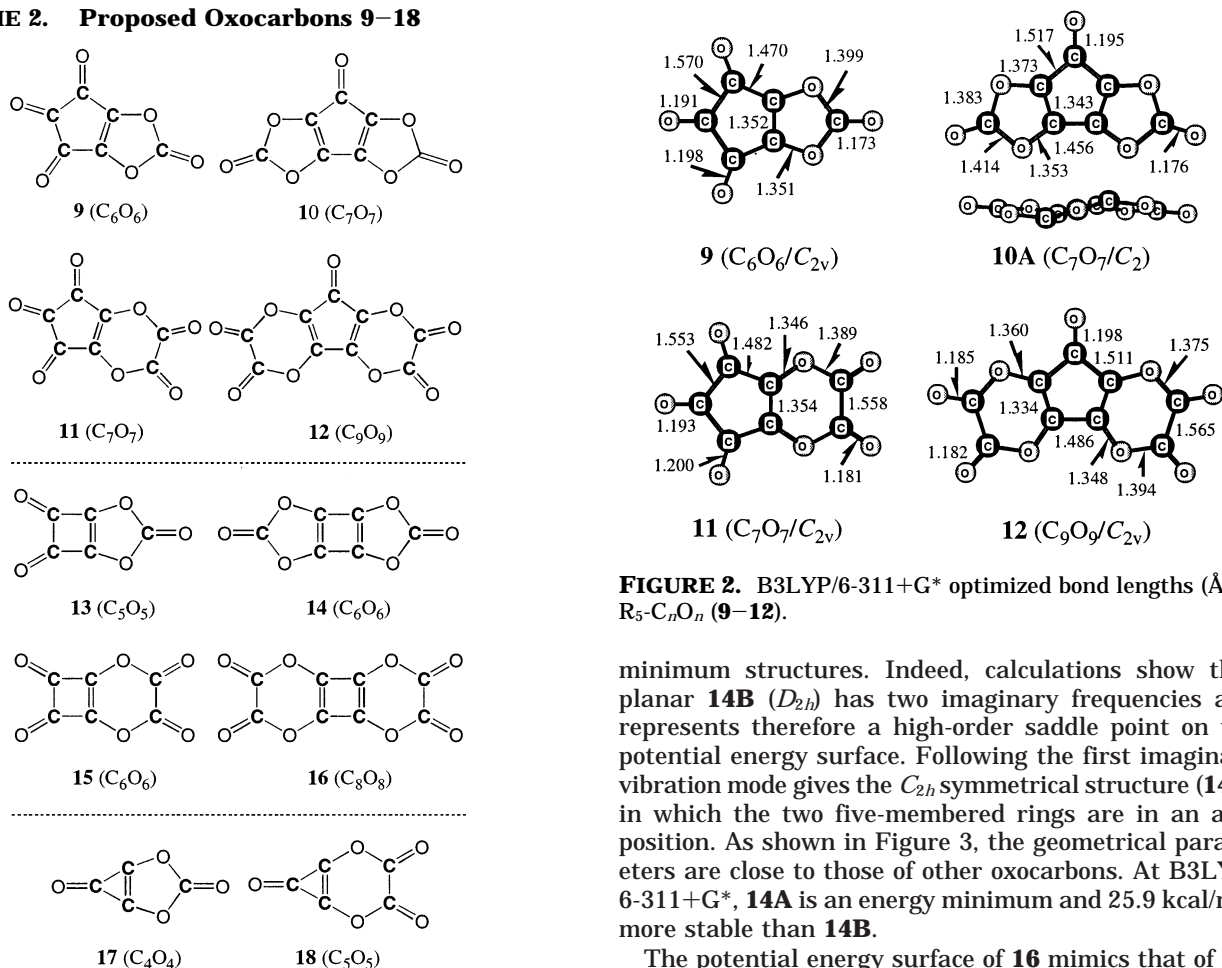


FIGURE 2. B3LYP/6-311+G* optimized bond lengths (Å) of $R_5-C_nO_n$ (**9–12**).

minimum structures. Indeed, calculations show that planar **14B** (D_{2h}) has two imaginary frequencies and represents therefore a high-order saddle point on the potential energy surface. Following the first imaginary vibration mode gives the C_{2h} symmetrical structure (**14A**) in which the two five-membered rings are in an anti position. As shown in Figure 3, the geometrical parameters are close to those of other oxocarbons. At B3LYP/6-311+G*, **14A** is an energy minimum and 25.9 kcal/mol more stable than **14B**.

The potential energy surface of **16** mimics that of **14**. The D_{2h} form **16B** has one imaginary frequency, and

16, since cyclobutadiene is antiaromatic and only bulky substituted structures are experimentally known.²³ On this basis, it is unlikely for **14** and **16** to have planar

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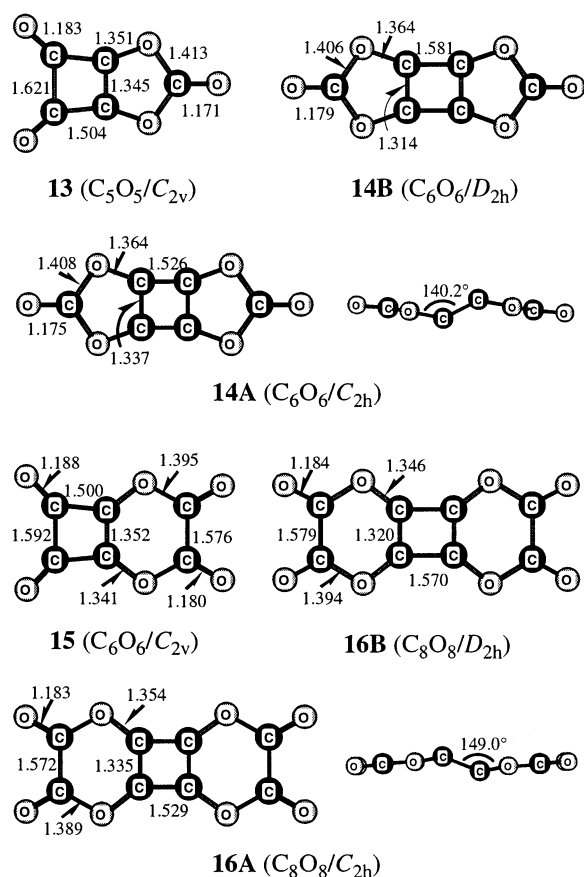


FIGURE 3. B3LYP/6-311+G* optimized bond lengths (Å) of $R_4-C_nO_n$ (**13**–**16**).

further optimization following the negative vibration mode gives the C_{2h} structure **16A** as minimum. At B3LYP/6-311+G*, **16A** is 8.6 kcal/mol more stable than **16B**. The synthetic precursor should be squaric acid.

$R_3-C_nO_n$ (**17**, **18**). Oxocarbons deduced from monocyclic $C_3O_3^{2-}$ are shown in Scheme 2 (bottom) with **17** being the smallest oxocarbon (C_4O_4). At B3LYP/6-311+G*, the planar form (**17B**, C_{2v}) with one imaginary frequency is the transition state for the ring bending on the PES. From the displacement of the negative mode, a nonplanar form in C_s symmetry as minimum structure (**17A**) is found, and **17A** is 8.2 kcal/mol lower in energy than **17B**. As shown in Figure 4, the five-membered ring in **17A** is slightly bent, and the dihedral angle between the two rings is 132.6° . A similar PSE is found for **18**, e.g., planar **18B** (C_{2v}) has one imaginary frequency, while the nonplanar **18A** (C_s) is the minimum structure and 0.2 kcal/mol more stable. The synthetic precursor should be dihydroxycyclopropanone.

Stability. The stability of the monocyclic neutral oxocarbons has been judged from the dissociation enthalpy into carbon monoxide,³ and the large exothermicities of these decomposition reactions rationalize the failures to prepare and to observe such carbon monoxide oligomers. Using the same criterion, the stability of polycyclic neutral oxocarbons representing minimum structures is analyzed, and the calculated dissociation enthalpies are summarized in Table 1.

As expected from monocyclic neutral oxocarbons, some of our examples, especially those with small parent rings

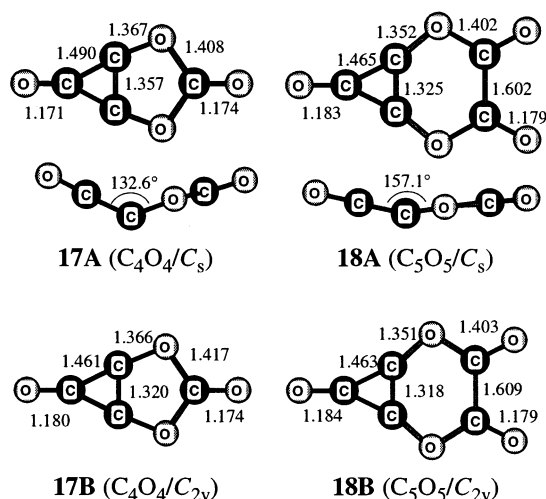


FIGURE 4. B3LYP/6-311+G* optimized bond lengths (Å) of $R_3-C_nO_n$ (**17**, **18**).

TABLE 1. Computed $R_m-C_nO_n \rightarrow nCO$ Dissociation Enthalpies (ΔE , kcal/mol) and NICS (ppm)

$R_m-C_nO_n$	ΔE^a	NICS(0) ^b	NICS(1) ^b
$R_6-C_6O_6$	-45.6		
1 (C_9O_9)	+31.0 (+73.5) ^c	-17.9	-12.7
2 (C_8O_8)	+7.4	+2.8	-0.2
3 ($C_{12}O_{12}$)	(+79.0) ^c	-17.4 ^d	-12.6 ^d
4 ($C_{10}O_{10}$)	+3.7	+1.5	-1.0
5 (C_8O_8)	+0.4	+4.6	+1.0
6A (C_7O_7)	-11.7	+7.9	+0.3
7 ($C_{10}O_{10}$)	-3.1	+3.1	+0.2
8A (C_8O_8)	-16.4	+7.5	+0.3
$R_5-C_5O_5$	-37.2		
9 (C_6O_6)	-11.5	+7.6	-1.9
10A (C_7O_7)	-28.6	+1.2	0.0
11 (C_7O_7)	-9.1	+7.7	-1.9
12 (C_9O_9)	-17.0	+1.8	+2.2
$R_4-C_4O_4^e$	-46.6		
13 (C_5O_5)	-33.8	-5.9	-2.8
14B (C_6O_6)		+18.2	+16.4
14A (C_6O_6)	-100.5	+7.3	+6.5
15 (C_6O_6)	-24.6	-1.5	-5.4
16B (C_8O_8)		+8.2	+13.1
16A (C_8O_8)	-82.2	+1.0	+7.6
17A (C_4O_4)	-73.2	-32.1	-5.7
18A (C_5O_5)	-61.2	-32.8	-8.6

^a B3LYP/6-311+G* + ZPE (B3LYP/6-311+G*). ^b GIAO-HF/6-31+G**/B3LYP/6-311+G*. ^c B3LYP/6-31G* + ZPE (HF/6-31G*). ^d GIAO-HF/6-31G**/B3LYP/6-31G*. ^e Singlet state.

(R_m , $m = 3, 4$), have large exothermic dissociation enthalpies (up to -100 kcal/mol), while those of bicyclic **13** ($R_4-C_5O_5$, -33.8 kcal/mol) and **15** ($R_4-C_6O_6$, -24.6 kcal/mol) are relatively small, and they are also smaller than that of monocyclic C_4O_4 (-46.6 kcal/mol). With increased parent ring size ($R_5-C_nO_n$), the dissociation enthalpies of **9** and **11** (-11.5, -9.1 kcal/mol) are only moderately exothermic, as compared to that of monocyclic C_5O_5 (-37.2 kcal/mol), indicating the increased stability of the polycyclic oxocarbons. This must mainly be attributed to the reduced strain energy with increased ring size. With $m = 6$ ($R_6-C_nO_n$), the dissociation enthalpy changes from highly exothermic for a monocyclic ring (-45.6 kcal/mol) to less exothermic (**6A**/-11.7; **7**/-3.1; **8A**/-16.4 kcal/mol) or even endothermic for the polycyclic rings (**1**–**5**). The

calculated dissociation enthalpy at B3LYP/6-31G* + ZPE (HF/6-31G*) for **1** of 73.5 kcal/mol is comparable to that (79.0 kcal/mol) of **3** at the same level. The huge difference (42.5 kcal/mol) in dissociation enthalpy of **1** at B3LYP/6-311+G* and B3LYP/6-31G* indicates the effect of basis set.²⁴ The largest endothermicities are found for R₆-C₁₂O₁₂ (**3**) and R₆-C₉O₉ (**1**). Apart from the reduced strain energy, this is probably due to its benzene-like structure and therefore its aromatic stabilization. On this basis, one might also expect the higher stable homologues of **3** with additional carbonyl (>C=O) or oxalyl (C₂O₂) coupling.

Aromaticity. Since the aromaticity of the monocyclic oxocarbon dianions has been successfully characterized with the nucleus-independent chemical shift (NICS) calculated at ring center (NICS(0)) and 1 Å above the center of the ring (NICS(1)),^{3,4} we used the same methodology for these neutral systems. It is found that NICS(0) are influenced by the local effects of the C–C(σ) and CO bonds, and NICS(1) values are better suited for the interpretation of π contributions perpendicular to the ring plane.³

As given in Table 1, most stable R₆-C₉O₉ (**1**) and R₆-C₁₂O₁₂ (**3**) have NICS(1) values of –12.7 and –12.6, which are larger than the benzene value (–10.6) at the same level. The other NICS(1) values (–0.2, –1.0, 1.0, 0.2, 0.3 and 0.3) of **2**, **4**, **5** and **7**, and **6A** and **8A** are very close to those (1.9, 0.3, and –1.0) of 1,3- and 1,4-cyclohexadiene and cyclohexene.^{20c} These indicate **1** and **3** to be highly aromatic, while the others are nonaromatic. On the basis of the same criterion, **9–12** are also nonaromatic.

However, the deformed cyclobutadiene-like R₄-C₆O₆ (**14A**) and R₄-C₈O₈ (**16A**) are only weakly antiaromatic with NICS(1) values of 6.5 and 7.6, which are smaller

than those of the planar forms (16.4/**14B**, 13.1/**16B**). It is also important to note that the bicyclic **13** and **15** have small negative NICS values (–2.8 and –5.4) which might be attributed to the delocalized σ framework of the parent rings,³ as indicated by the much longer C–C bond of the parent four-membered rings (1.621 Å/**13** and 1.592 Å/**15**). In addition, the R₃-C₄O₄ (**17A**) and R₃-C₅O₅ (**18A**) are highly unstable toward dissociation by 73.2 and 61.2 kcal/mol, respectively.

Conclusion

B3LYP density functional theory has been used to investigate a set of polycyclic neutral oxocarbons. In full agreement with the experimental findings, oxocarbons **1–4** are found to be stable toward dissociation into CO. The additional stability of structures R₆-C₉O₉ (**1**) and R₆-C₁₂O₁₂ (**3**) can be ascribed to its aromaticity, which has been analyzed on the basis of the calculated NICS values. The calculated NICS(1) value for R₆-C₉O₉ (**1**) and R₆-C₁₂O₁₂ (**3**) are larger than the benzene value. As compared to the neutral monocyclic structures, some of the proposed structures have enhanced stability toward dissociation and they should be targets for further synthetic investigations.

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Supporting Information Available: Total electronic energies, zero-point energies for all systems, and Cartesian coordinates are summarized. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(24) As a result of the convergence problem, it was unable to get the optimization or single point calculation of energy for **3** at the B3LYP/6-311+G* level of theory.