Are Oxocarbon Dianions Aromatic?

Paul von Ragué Schleyer,*[†,‡] Katayoun Najafian,[‡] Boggavarapu Kiran,[‡] and Haijun Jiao[‡]

Computational Chemistry Annex, University of Georgia, Athens, Georgia 30602-2525, and Institut für Organische Chemie der Universität Erlangen-Nürnberg, Henkestrasse 42, D-91054 Erlangen, Germany

Received August 10, 1999

Assessment of the cyclic electron delocalization of the oxocarbon dianions, $C_nO_n^{2-}$ and their neutral counterparts C_nO_n ($n = 3-6$), by means of structural, energetic, and magnetic criteria, shows that $C_3O_3^{2-}$ is doubly aromatic (both σ and π cyclic electron delocalization), $C_4O_4^{2-}$ is moderately aromatic, but $C_5O_5^{2-}$, as well as $C_6O_6^{2-}$, are less so. Localized orbital contributions, computed by the individual gauge for localized orbitals method (IGLO), to the nucleus-independent chemical shifts (NICS) allow π effects to be disected from the σ single bonds and other influences. The C−C(π) contribution to (NICS(0,π) (i.e., at the center of the ring) in oxocarbon dianions decreases with ring size but shows little ring size effect at points 1.0 Å above the ring. On the basis of the same criteria, C_4O_4 exhibits cyclic electron delocalization due to partial occupancy of the σ CC bonds. However, the dissociation energies of all the neutral oxocarbons, C_nO_n, are highly exothermic.

Introduction

Many investigations have been concerned with the structure and bonding of oxocarbons,[1−3] in which the carbon atoms are attached to carbonyl or enolic oxygens or to their hydrated equivalents.[4] The monocyclic oxocarbon dianions ($C_nO_n^{2-}$) and the neutral cyclic compounds (C_nO_n) comprise two prototypal subgroups within the oxocarbon family. Although both croconate ($C_5O_5^{2-}$)[5] and rhodizonate ($C_6O_6^{2-}$)[6] have been known for more than 160 years, the lower analogues, squarate ($C_4O_4^{2-}$)[7] and deltate ($C_3O_3^{2-}$),[8] were synthesized more recently. Extensive literature and reviews[9] on oxocarbons center on experimental aspects, such as improved synthesis,[10−15] and their photochemical behavior[16] and physical properties. In contrast, the neutral C_nO_n species are not known experimentally.

In the early 1960s, West suggested that the monocyclic $C_nO_n^{2-}$ should constitute a new series of "aromatic" compounds.[17] The IR and Raman spectra, along with the deduced force constants, indicated $C_4O_4^{2-}$ and $C_5O_5^{2-}$ to have D_{nh} symmetry,[18] and this was confirmed later by X-ray analysis.[19,20] The Urey−Bradly force fields of $C_nO_n^{2-}$ ($n = 3$,[21] 4, and 5[18]) were compared with those of aromatic species such as benzene, the cyclopentadienyl anion, and the cyclopropenyl cation. The CC stretching force constants for $C_4O_4^{2-}$ and $C_5O_5^{2-}$ are greater than those for a CC single bond and, for the $C_3O_3^{2-}$ dianion, are as large as those of benzene. This indicates extensive electron delocalization over the oxocarbon rings. West found that $C_nO_n^{2-}$ exhibit behavior of diamagnetic anisotropy like benzene and furan;[4] e.g., a large diamagnetic anisotropy and the diamagnetic susceptibility exaltation of $C_5O_5^{2-}$ (−15 ppm cgs) were ascribed to the diatropic ring current.

Simple Hückel π electron-type calculations provided estimates of the electron delocalization energies. These dropped off sharply from $C_3O_3^{2-}$ to $C_4O_4^{2-}$ and then decreased further steadily with increasing ring size ($n = 4-6$).[22] However, Dewar[23] as well as Hess and Schaad[24]

[†] University of Georgia.

[‡] Universität Erlangen-Nürnberg.

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10.1021/jo991267n CCC: $19.00

argued that “this delocalization energy cannot be used as a measure of aromaticity, but the aromaticity index of cyclic conjugated system must be related to thermodynamic stability estimated relative to an appropriate olefinic reference structure”. Using graph theory, Aihara[25] calculated the topological resonance energy (TRE) and diamagnetic susceptibilities of $C_nO_n^{2-}$ and found also that the degree of aromaticity decreases with increasing ring size. Only $C_3O_3^{2-}$, which has a much larger TRE[25] and magnetic susceptibility[4] than the other members in the family, is highly diatropic. These conclusions were supported further by Ha et al.’s semiempirical and ab initio results on the IR frequencies and diamagnetic anisotropies of $C_nO_n^{2-}$.[26] Using bond orders as an alternative approach, Jug[27] reached similar conclusions. Note that $C_nO_n^{2-}$ have only 2π electrons assigned to the carbon rings, and one would expect decreasing aromaticity with the ring size on this basis.

We have been employing three sets of criteria to evaluate the aromaticity[28,29] of a compound: geometric (bond length equalization, bond order indices),[30] energetic (aromatic stabilization energies),[31] and magnetic (^{1}H NMR chemical shifts,[32] magnetic susceptibility anisotropies[33] and exaltations,[34] and nucleus-independent chemical shifts (NICS)[35]). Excellent correlation among these criteria were demonstrated for a wide-ranging set of five-membered heterocycles.[36] However, such parallel behavior is not found in more complicated polycyclic systems, when other interactions dominate.[37−40]

As $C_nO_n^{2-}$ do not have hydrogens and ^{13}C NMR chemical shifts are not informative, the applicable magnetic criteria have focused in the past on the assessment of the exaltation of the diamagnetic susceptibility, Λ, and its anisotropy. However, Λ depends not only on the square of the ring size[29] but also on the number of delocalized electrons. An alternative efficient and simple criterion, computed easily, is NICS.[35] This method is based on the negative of the magnetic shielding computed, e.g., in the center of rings. Significantly negative NICS values imply aromaticity (diatropic ring currents dominate), and positive NICS values correspond to antiaromaticity (paratropic ring currents dominate). NICS, as an criteria of aromaticity, agrees well with the energetic, geometric, and magnetic criteria in five-membered heterocycles.[35] It also is not dependent on ring size[41] and is an “absolute” method, in the sense that NICS does not require an increment system or reference molecules for evaluation. However, NICS(0) (at the geometrical center of the ring) is influenced by the local effects arising mainly from the σ bonds. Our experience has shown that NICS(1) (1 Å above the plane of the ring) mainly reflects π effects and often is a better indicator of the ring current than the value in the center.[42]

Earlier conclusions on aromaticity of $C_nO_n^{2-}$ are divergent—all agree that $C_3O_3^{2-}$ is aromatic, but differ in their assessment of the higher members of the series. We now analyze the degree of aromaticity in $C_nO_n^{2-}$ ($n = 3-6$) based on magnetic properties.

Computational Methods

The geometries of $C_nO_n^{2-}$ ($n = 3-6$) were optimized first at B3LYP/6-31G* and then at B3LYP/6-311+G* levels of density functional theory as implemented in the Gaussian 94 program.[43] Frequency calculations, carried out at B3LYP/6-31G*, determined the nature of the stationary points and gave the zero point energies (ZPE).[44] Minima have only real frequencies and transition states one imaginary frequency. NICS were computed at GIAO-HF/6-31+G*[45] on the B3LYP/6-311+G* geometries. The magnetic susceptibilities were calculated at HF/6-31+G*//B3LYP/6-311+G* by using the CSGT (continuous set of gauge transformations) method.[46] We have also carried out NICS calculations on $C_nO_n^{2-}$ systems at the SOS-DFPT-IGLO[47] level using the Perdew-Wang-91 exchange-correlation functional and the IGLO III TZ2P basis set as implemented in the deMon NMR program using Pipek-Mezey localization procedure for analyzing the σ and π contributions.[48]

Results and Discussion

Table 1 summarizes the computed total energies and ZPE for all systems, and the optimized structures are

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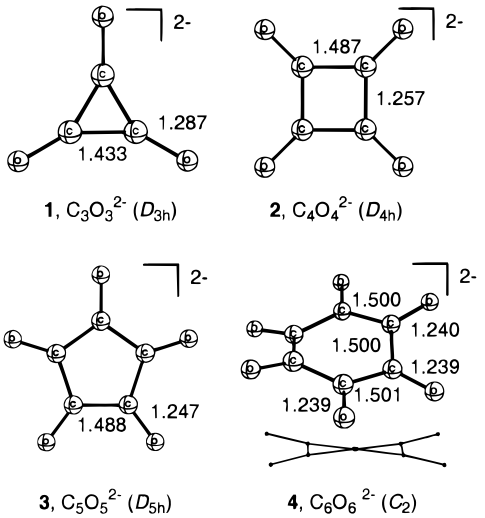
Table 1. Total Electronic Energies (au) for $C_nO_n^{2-}$ (n = 3−6)

molecule	symmetry	ZPE (NImag)[a]	E_{tot}[b]
$C_3O_3^{2-}$	D_{3h}	14.82(0)	−339.965 11
$C_4O_4^{2-}$	D_{4h}	21.62(0)	−453.416 96
$C_5O_5^{2-}$	D_{5h}	27.91(0)	−566.819 77
$C_6O_6^{2-}$	D_{6h}	33.40(3)	−680.175 19
$C_6O_6^{2-}$	C_2	33.54(0)	−680.175 74

[a] Zero-point energy (kcal/mol), calculated at B3LYP/6-31G(d); in parentheses: number of imaginary frequencies (NImag). [b] At B3LYP/6-311+G*.



1, $C_3O_3^{2-}$ (D_{3h})

2, $C_4O_4^{2-}$ (D_{4h})

3, $C_5O_5^{2-}$ (D_{5h})

4, $C_6O_6^{2-}$ (C_2)

Figure 1. Geometries of oxocarbon dianions at the B3LYP/6-311+G* level.

shown in Figure 1. The oxocarbon dianions, $C_nO_n^{2-}$ (n = 3−5), favor D_{nh} symmetry (Figure 1). However, the $C_6O_6^{2-}$ energy minimum has C_2 symmetry, and other symmetrical isomers as D_{6h}, D_{3d}, O_h, and C_{2h} are transition states or higher order saddle points. However, the energy difference between various isomers is very small, e.g., 0.34 kcal/mol between the D_{6h} and C_2 forms.

As shown in Figure 1 and given in Table 2, the lengths of CC and CO bonds increase and decrease as the ring size increases. The computed bond lengths agree well with the experimental values for $C_nO_n^{2-}$ (Table 2); $C_3O_3^{2-}$ has the shortest C−C (1.433 Å) and the longest C−O (1.287 Å) bond lengths compared to other members of the set. The C−C bonds in $C_3O_3^{2-}$ are slightly shorter than the conjugated single bond (1.466 Å) in butadiene, but considerably longer than the C−C (1.362 Å) bond in $C_3H_3^+$. The CO bond lengths (1.240−1.287 Å) also are longer than computed for acetone (1.212 Å). The calculated CC Wiberg bond indices (WBI), 1.195 for $C_3O_3^{2-}$ and 1.062−1.023 for the other dianions, indicate the C−C bonds to have very little double bond character. The CO Wiberg bond indices, which range from 1.312 for $C_3O_3^{2-}$ to 1.462−1.584 for the rest (compare with WBI = 1.8 for C=O in acetone), indicate delocalization. The calculated charges on carbon and oxygen show the same differences: the positive charges are the smallest on carbon and the negative charges on oxygen are the largest for $C_3O_3^{2-}$ and change gradually with increasing ring size, from $C_4O_4^{2-}$ to $C_6O_6^{2-}$.

The infrared frequencies computed at B3LYP/6-31G* for $C_nO_n^{2-}$ agree well with the experimental results (Table 3). The computed ^{13}C chemical shifts of $C_nO_n^{2-}$ also agree well with experiment[49] (Table 4).

Table 2. B3LYP/6-311+G* Bond Lengths (in Å) of $C_nO_n^{2-}$ (n = 3−6) Compared with the X-ray Values (in Parentheses), Wiberg Bond Indices (WBI), and Natural Charges (q)

	C−C	C−O	WBI_{C-C}	WBI_{C-O}	q_C	q_O
$C_3O_3^{2-}$	1.433	1.287	1.195	1.312	+0.228	−0.895
$C_4O_4^{2-}$	1.487	1.257	1.062	1.462	+0.289	−0.789
	(1.469)[a]	(1.259)[a]				
$C_5O_5^{2-}$	1.488	1.247	1.046	1.532	+0.308	−0.708
	(1.457)[b]	(1.262)[b]				
$C_6O_6^{2-}$	1.500	1.239	1.029	1.578	+0.316	−0.652
	1.501	1.240	1.023	1.584	+0.320	−0.651
	(1.488)[c]	(1.213)[c]				

[a] Reference 20. [b] Reference 19. [c] Reference 18.

Aromatic Stabilization Energy (ASE). If $C_nO_n^{2-}$ (n = 3−6) are aromatic, they should have large aromatic stabilization energies like other aromatic species. The evaluation of ASE depends on the choice of reference molecules. We have considered three types of reactions for evaluating the ASE of $C_nO_n^{2-}$ (n = 3−6). Although logically conceived, all these reaction types have drawbacks. Energetic relationships are revealed, but none yield ASEs that we consider to be free from other influences. The first sets of eqs, 1−4, involve the neutral oxocarbons, C_nO_n (n = 3−6) and acyclic dianions **5a**−**8a** as well as polyketones **5b**−**8b** as given; see Scheme 1 for the reference compounds.

$$C_3O_3 + \mathbf{5a} \rightarrow C_3O_3^{2-} + \mathbf{5b} \quad E_1 = -60.65 \text{ kcal/mol} \tag{1}$$

$$C_4O_4 + \mathbf{6a} \rightarrow C_4O_4^{2-} + \mathbf{6b} \quad E_2 = -66.31 \text{ kcal/mol} \tag{2}$$

$$C_5O_5 + \mathbf{7a} \rightarrow C_5O_5^{2-} + \mathbf{7b} \quad E_3 = -71.21 \text{ kcal/mol} \tag{3}$$

$$C_6O_6 + \mathbf{8a} \rightarrow C_6O_6^{2-} + \mathbf{8b} \quad E_4 = -64.29 \text{ kcal/mol} \tag{4}$$

The second series of equations, 5−8, employs the cycloalkenes, C_nH_{2n-2} (n = 3−6) with **5a**−**8a** (see Scheme 1) as reference species.

$$\text{cyclopropene} + \mathbf{5a} \rightarrow C_3O_3^{2-} + 2\text{-}\mathit{trans}\text{-pentene} \quad E_5 = -43.79 \text{ kcal/mol} \tag{5}$$

$$\text{cyclobutene} + \mathbf{6a} \rightarrow C_4O_4^{2-} + 3\text{-}\mathit{trans}\text{-hexene} \quad E_6 = -60.82 \text{ kcal/mol} \tag{6}$$

$$\text{cyclopentene} + \mathbf{7a} \rightarrow C_5O_5^{2-} + 3\text{-}\mathit{trans}\text{-heptene} \quad E_7 = -56.16 \text{ kcal/mol} \tag{7}$$

$$\text{cyclohexene} + \mathbf{8a} \rightarrow C_6O_6^{2-} + 3\text{-}\mathit{trans}\text{-octene} \quad E_8 = -54.94 \text{ kcal/mol} \tag{8}$$

The third type of equation, 9, is based on carbon monoxide and the smallest member of this family, $C_2O_2^{2-}$,

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[49] Städeli, W.; Hollenstein, R.; Philipsborn, W. *Helv. Chim. Acta* **1977**, *60*, 948.

Table 3. B3LYP/6-31G* IR Frequencies (cm-1) for $C_nO_n^{2-}$ Compared with the Experimental Data in Parentheses

$C_3O_3^{2-}$	$C_4O_4^{2-}$	$C_5O_5^{2-}$	$C_6O_6^{2-}$
236 (313)	259 (262)	248 (260)	235 (238)
(323)	350 (331)	374 (349)	386 (336−364; 435−449; 461−591)
995 (1077)	1090 (1070)	1100 (1098)	1051 (1041, 1046)
1470 (1608)	1530 (1575)	1570 (1589)	1449 (1596, 1599; 1618)

[a] From ref 21. [b] From ref 4b, pp 131−132.

Table 4. Computed Magnetic Susceptibility (χ, ppm cgs), Diamagnetic Susceptibility Exaltation (Λ, ppm cgs), NICS (ppm), and ^{13}C Chemical Shifts (relative to TMS) Compared with the Experimental Data Given in Parentheses

	χ^a	Λ^b	Λ^c	Λ^d	NICS(0)^e	NICS(1)^e	13C^{f,g}
$C_3O_3^{2-}$	−44.6	−15.6	−10.1	2.76	−36.2	−11.0	139.1 (140.0)
$C_4O_4^{2-}$	−46.3	−8.5	−10.6	12.5	−5.0	−8.6	207.4 (204.2)
$C_5O_5^{2-}$	−51.6	−6.5	−9.2	18.9	3.9	−5.8	191.5 (189.3)
$C_6O_6^{2-}$	−58.7	−5.7	−10.1	23.3	+7.9	−4.4	178.8 (174.2) 182.83 182.72

[a] At CSGT-HF/6-31+G*//B3LYP/6-311+G*. [b] Using eqs 1−4. [c] Using eqs 5−8. [d] Using eq 9. [e] At GIAO-HF/6-31+G*//B3LYP/6-311+G*. [f] Computed at GIAO-HF/6-31+G*//B3LYP/6-311+G*. [g] Reference 49.

as the reference molecules:

$$C_2O_2^{\,2-} + (n-2)CO \rightarrow C_nO_n^{\,2-}\ (n = 3-6) \qquad (9)$$

$$E_9\ (\text{kcal/mol}) = -63.3\ (n = 3);\ -127.8\ (n = 4);\ -161.5\ (n = 5);\ -165.9\ (n = 6)$$

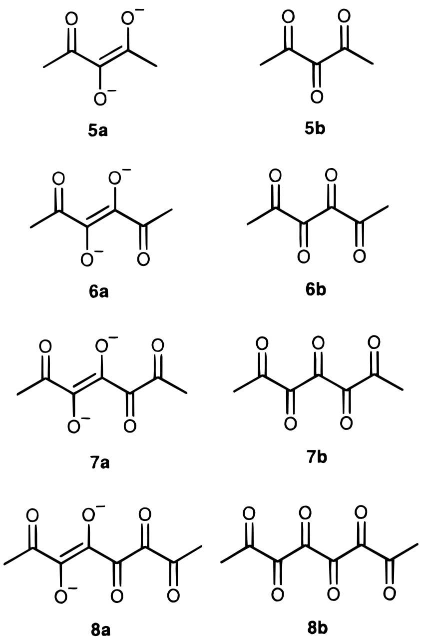
In the first set of reactions (eqs 1−4), all the carbons and oxygens in the cyclic neutral reference oxocarbons C_nO_n match those in $C_nO_n^{2-}$. Likewise, the acyclic dianion **5a**−**8a** equivalents are the same polyketones **5b**−**8b** (Scheme 1). However, such comparisons are imperfect, since the acyclic reference molecules (**5a**−**8a**), unlike the cyclic $C_nO_n^{2-}$, do not distribute the charge to the oxygens equally. Consequently, the energies of eqs 1−4 are all quite exothermic and do not show any regular trend with ring size.

Cycloalkenes (C_nH_{2n-2}) are the reference structures used to estimate the ASE in the second type of reactions (eqs 5−8). In effect, the oxygens in the acyclic polyoxodianions **5a**−**8a** are transferred to the cycloalkenes and to give $C_nO_n^{2-}$ and acyclic alkenes (C_2H_{2n-2}). The energies given by eqs 5−8 are quite different and even more exothermic than those of eqs 1−4. The energy increases sharply from $C_3O_3^{2-}$ to $C_4O_4^{2-}$ and further increases smoothly from $C_4O_4^{2-}$ to $C_6O_6^{2-}$. Again, the acyclic polyoxygen dianions **5a**−**8a** do not model the $C_nO_n^{2-}$ satisfactorily.

The third type of equation (eq 9), which uses the high energy $C_2O_2^{2-}$ as the basis and incorporates carbon monoxide sequentially, yields the largest exothermicities. Reflecting the overall stability and decrease in ring strain as well as formation of additional new bonds, these increase with increasing the ring size of $C_nO_n^{2-}$.

The consistent picture from various energetic evaluations of $C_nO_n^{2-}$ is that they appear to be aromatic. Though none of the equations model the strain and charge effects satisfactorily, eqs 5−8 appear to us to be the best set.

Scheme 1



Diamagnetic Susceptibility Exaltation (Λ). The diamagnetic susceptibility exaltation, Λ, is the measurable property most directly associated with aromaticity.[34] Generally, Λ is defined as $\Lambda = \chi_m - \chi_m'$ where χ_m is the bulk magnetic susceptibility of conjugated compound and χ_m' the susceptibilities estimated via increment systems for the same structure without the ring current contribution. A negative Λ value for a compound implies that it is "aromatic"; antiaromatic compounds have positive Λs. The magnitude of Λ can be expected to depend on the square of the ring area.[41] The three types of equations used for energy calculations (eqs 1−9) can also be applied to evaluate the Λ values of $C_nO_n^{2-}$.

It is illustrative to compare the magnetic susceptibility exaltations of three sets of reactions. According to the first set (eqs 1−4), the calculated Λ of −15.6 for $C_3O_3^2$ is quite large, but drops sharply to $\Lambda = -8.5$ for $C_4O_4^{2-}$ and decreases further smoothly with increased ring size (Table 4). This trend toward decreasing Λ of $C_nO_n^{2-}$ with ring size confirms the earlier conclusions that the smallest member of this family, $C_3O_3^{2-}$ is highly diatropic.[3a,25−27] Hence, the first type of reaction (eqs 1−4) performs well in this respect. However, Λ, based on the second type of reaction (eqs 5−8), are nearly the same in all the oxocarbon dianions (Table 4). Equation 9 is not suitable to compute Λ due to the exceptional character of CO used as a reference.

Nucleus-Independent Chemical Shift (NICS). In addition to the geometric, energetic properties and the dimagnetic susceptibility exaltations, we also calculated NICS at both the ring center NICS(0) and 1 Å over the each ring NICS(1) (Table 4) for analyzing the aromaticity. However, NICS values in the molecular planes are influenced by the local contributions of the C−C(σ) and CO bonds.[42] Hence, NICS(1) values are better suited for the interpretation of π contributions perpendicular to the ring plane and to answer the question whether $C_nO_n^{2-}$ ($n = 3-6$) are really aromatic.

As shown in Table 4, the NICS(1) value is appreciable in $C_3O_3^{2-}$ (−11.0) and is larger than in $C_4O_4^{2-}$ (−8.6), comparable to the benzene value (−10.0). Furthermore,

Table 5. NICS(tot), NICS(σ), and NICS(π), NICS(C−O), and Lone Pair Contribution at the Center of the Ring and 1.0 Å above the Ring (in Parentheses)[a] for $C_nO_n^{2-}$ and References Systems

	NICS(tot)	C−C(σ)	C−C(π)	C−O	LP (O)
$C_3O_3^{2-}$	−35.1	−11.7	−27.9	7.2	−1.8
	(−8.3)	(−5.1)	(−6.9)	(5.8)	(−0.7)
$C_4O_4^{2-}$	−2.4	14.8	−22.8	6.4	0.0
	(−5.4)	(−1.6)	(−7.9)	(5.6)	(−1.4)
$C_5O_5^{2-}$	6.9	16.5	−17.4	5.5	1.0
	(−2.6)	(1.5)	(−7.9)	(5.0)	(−1.0)
$C_6O_6^{2-}$	4.8	12.0	−13.0	5.4	1.2
	(−2.0)	(3.6)	(−7.4)	(3.0)	(−0.8)
$C_3H_3^+$	−23.5	10.2	−26.0	−6.6	
	(−15.0)	(−5.7)	(−4.6)	(−4.5)[b]	
$C_3F_3^+$	−34.6	−9.3	−27.0	5.1	−2.5
	(−8.8)	(−3.9)	(−5.0)	(0.7)[b]	(−0.3)[c]

[a] The remaining contributions are due to core orbitals. [b] Contributions from C−H or C−F bonds. [c] Contributions from F lone pair.

NICS(1) of −5.8 and −4.4 for $C_5O_5^{2-}$ and $C_6O_6^{2-}$, show both dianions to have a small degree of aromaticity. The trends of the NICS(1) values and the Λ values based on eqs 1−4 compared in Table 4 are remarkably similar (high NICS(1) and Λ value for $C_3O_3^{2-}$), and both agree with some of the earlier conclusions, e.g., aromaticity decreases with increasing $C_nO_n^{2-}$ ring size of n = 3−6.[3a,25−27]

Further understanding comes from NICS computations by the IGLO method, which allows NICS shielding tensors to be computed in terms of localized orbitals, e.g., the contributions from C−C(σ), C−C(π), C−O(σ), C−O(π), and lone pairs as well as core orbitals.[47] The Pipek−Mezey[48] localization procedure implemented in the deMon program[47] allows the σ and π separation and facilitates to understand the origin of the ring current. Usually, the σ bonds contribute paramagnetic and π bonds diamagnetic to the ring current.[33,42] We have computed NICS for $C_nO_n^{2-}$ using the SOS-PW91-IGLO/III method (Table 5). The exceptionally high NICS(0) for $C_3O_3^{2-}$ is due to the diatropic contributions from both σ and π electrons to the ring current (Table 5). The change in the magnetic behavior of C−C(σ) bonds for $C_3O_3^{2-}$ is mainly due to the high electronegativity of the oxygen atoms. This assertion can be verified by comparing with $C_3H_3^+$ and $C_3F_3^+$. For $C_3H_3^+$ NICS(0) is −23.5 with the C−C(σ, +10.2), C−C(π, −26.0), and C−H (−6.6), whereas for $C_3F_3^+$ NICS(0) is −34.6 with C−C (σ, −9.3), C−C (π, −27.0), +5.1(C−F), and fluorine lone pair. Thus, $C_3O_3^{2-}$ and $C_3F_3^+$ are *both* σ and π aromatic. For the higher analogues, at NICS(0), σ bonds contribute paramagnetically (Table 5). As the ring size increases, the π contributions decrease, but are sufficiently diamagnetic for all to be classified as aromatic (Table 5). Note that this trend is not reflected in the total NICS(0) values.

However, NICS(1) values for the $C_nO_n^{2-}$ (n = 3−6) show all the oxocarbon dianions exhibit diatropic ring currents, but the extent decreases with the increasing ring size. However, the C−C(σ) contribution to the NICS(1), i.e., 1 Å above the ring, drops off, regardless of the ring size, while the π contribution to the NICS(1) is very similar (Table 5). Therefore, considering the π contribution both at NICS(0,π) and NICS(1,π), all $C_nO_n^{2-}$ have substantial ring current.

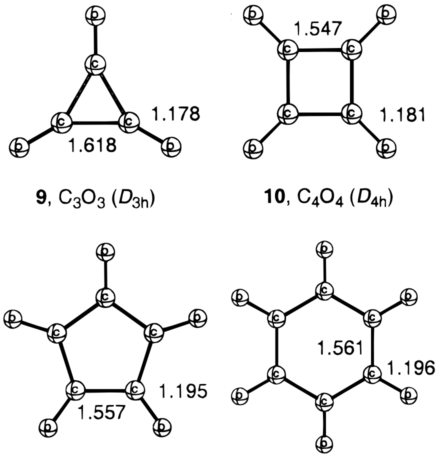
Table 6. Total Energies (au) for C_nO_n (n = 3−6) Structures at B3LYP/6-311+G*

	symmetry	ZPE(NImag)[a]	E_{tot}
C_3O_3[b]	D_{3h}	12.67(2)	−339.939 67
C_4O_4	D_{4h}	20.58(0)	−456.340 71
C_5O_5	D_{5h}	27.68(0)	−566.704 24
C_6O_6	D_{6h}	33.99(2)	−680.044 60
C_6O_6	C_{2v}	34.00(0)	−680.044 66

[a] Zero-point energy (kcal/mol), calculated at B3LYP/6-31G(d). In parentheses: number of imaginary frequencies NImag. [b] Following the imaginary frequency leads to dissociation into CO molecules.

Table 7. B3LYP/6-311+G* Bond Lengths (Å) of C_nO_n (n = 3−6), Wiberg Bond Indices (WBI), and Natural Charges (q)

	C−C	C−O	WBI_{C-C}	WBI_{C-O}	q_C	q_O
C_3O_3	1.618	1.178	0.858	1.959	0.403	−0.403
C_4O_4	1.547	1.181	0.882	1.764	0.371	−0.371
C_5O_5	1.557	1.195	0.906	1.915	0.391	−0.391
C_6O_6	1.561	1.196	0.910	1.911	0.389	−0.389



9, C_3O_3 (D_{3h}) **10**, C_4O_4 (D_{4h})

11, C_5O_5 (D_{5h}) **12**, C_6O_6 (C_{2v})

Figure 2. Geometries of neutral oxocarbon at the B3LYP/6-311+G* level.

Neutral Oxocarbons, C_nO_n (n = 3−6). The neutral oxocarbons, C_nO_n (n = 3−6) have received less attention[1,24,50,51] than the oxocarbon dianions, $C_nO_n^{2-}$ (n = 3−6). Attempts to prepare these neutral species have been unsuccessful. Our computational examination at B3LYP/6-311+G* assumed high symmetry point groups, e.g., C_3O_3 (D_{3h}), C_4O_4 (D_{4h}), C_5O_5 (D_{5h}), C_6O_6 (D_{6h}) (Table 6). Frequency analyses established C_4O_4 (D_{4h}) and C_5O_5 (D_{5h}) to be minima. In contrast, C_3O_3 (D_{3h}) and C_6O_6 (D_{6h}) are second-order saddle points (NIMAG = 2). Reduction of the D_{6h} symmetry of C_6O_6 resulted in a C_{2v} minimum with nearly the same energy (Table 6), while C_3O_3 collapses directly into three COs in all geometries examined.

The optimized geometries of the neutral oxocarbons, C_nO_n (n = 3−6), are shown in Figure 2 and Table 7. The smallest member of this family, C_3O_3, has the longest C−C and shortest C−O bond lengths, in contrast to the trend of $C_nO_n^{2-}$. Neutral oxocarbons are nonaromatic, since there are no π bonds in the ring. Small NICS(1) values show the presence of no ring current with the exception of C_4O_4 (Table 8). Contrary to the expectations,

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(50) (a) Frenking, G. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1410. (b) Evangelisti, S. *Chem. Phys. Lett.* **1996**, *259*, 261.

(51) Gleiter, R.; Hyla-Kryspin, I.; Pfeifer, K.-H. *J. Org. Chem.* **1995**, *60*, 5878.

Table 8. NICS(tot), NICS(σ), and C−O and Lone Pair Contributions at the Center of the Ring and 1.0 Å above the Ring (in Parentheses)[a] for Neutral Oxocarbons

	NICS(tot)	C−C(σ)	C−O	LP(O)
$C_3O_3(D_{3h})$	98.6 (4.0)	87.9 (3.0)	7.2 (5.8)	−1.8 (−1.8)
$C_4O_4\ (D_{4h})$	−32.0 (−8.9)	−36.3 (−12.5)	6.4 (5.6)	−1.7 (−1.6)
$C_5O_5\ (D_{5h})$	27.6 (4.5)	28.0 (5.0)	5.5 (5.0)	−0.1 (−1.2)
$C_6O_6\ (D_{6h})$	13.6 (3.1)	14.8 (4.0)	5.4 (3.0)	2.9 (0.7)

[a] The remaining contributions are due to core orbitals.

large diatropic NICS(0) (−32.0) and NICS(1) (−8.9) values of C_4O_4 indicate the presence of cyclic electron delocalization. Since there are no π bonds, the ring current must be due to σ bonds. NBO analysis shows that the C−C bonds of C_4O_4 are not 2c−2e bonds but are only partially occupied (1.318 e instead of 2.000 e). This is responsible for the diatropic NICS, since the C−O π^* bonds are populated by remaining electrons. Both C_5O_5 and C_6O_6 have the expected electronic structure, i.e., 2c−2e C−C and σ C−O bonds. The dissociation energies of neutral oxocarbon minima into carbon monoxide (eq 10) are

$$C_nO_n \rightarrow nCO \qquad (10)$$

$$E_{10}\ (\text{kcal/mol}) = -34.8\ (n = 4);\ -25.7\ (n = 5);\ -31.2\ (n = 6)$$

The large exothermicities of these decomposition reactions rationalize the failures to prepare and to observe such "carbon monoxide oligomers."

Concluding Remarks

The aromaticity of the $C_nO_n^{2-}$ ($n = 3-6$) decreases with increasing ring size. $C_3O_3^{2-}$ is both σ and π aromatic, and $C_4O_4^{2-}$ is moderately aromatic, while $C_5O_5^{2-}$ and $C_6O_6^{2-}$ are less aromatic. The double aromaticity as $C_3O_3^{2-}$ is observed in $C_3F_3^+$, but not in $C_3H_3^+$.

The localized orbital contribution to the NICS shieldings, computed by the IGLO method, gives a more detailed picture of the nature of the ring currents in the $C_nO_n^{2-}$ ($n = 3-6$) set. While NICS(π, 0) shows a gradational decrease with the ring size, the NICS(π, 1) is nearly constant for all the systems. The same criteria reveal cyclic electron delocalization in C_4O_4. Nevertheless, the dissociation of all the neutral oxocarbons into carbon monoxide is highly exothermic.

Acknowledgment. This work is supported by Deutsche Forschungsgemeinschaft (DFG) and Fonds der Chemischen Industrie (Erlangen) and the University of Georgia. B.K. and H.J. thank the DFG for financial support. K.N. thanks the Deutscher Akademischer Austauschdienst (DAAD) for a doctoral fellowship.

JO991267N