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First-principles investigations on $C_5O_5^{-/0}$ and $C_6O_6^{-/0}$ oxocarbons

Jin-Chang Guo [a,b], Hai-Gang Lu [a,*], Si-Dian Li [a,*]

[a] Institute of Molecular Science, Shanxi University, Taiyuan 030001, Shanxi, People's Republic of China
[b] Institute of Materials Science and Department of Chemistry, Xinzhou Teachers' University, Xinzhou 034000, Shanxi, People's Republic of China

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ABSTRACT

Comprehensive first-principles calculations on the geometrical and electronic properties of $C_5O_5^{-/0}$ and $C_6O_6^{-/0}$ oxocarbons have been performed in this work. Both $C_5O_5^-$ monoanion and C_5O_5 neutral are found to possess perfect planar pentagonal structures at their ground states D_{5h} $C_5O_5^-$ ($^2A_2''$) (1) and D_{5h} C_5O_5 ($^1A_2'$) (2), while $C_6O_6^-$ and C_6O_6 appear to favor the slightly distorted quasi-planar C_{2v} $C_6O_6^-$ ($^2A_1$) (3) and C_{2v} C_6O_6 ($^1A_1$) (4), respectively. Adaptive natural density partitioning (AdNDP) analyses clearly reveal the σ- and π-bonding patterns of the monocyclic $C_nO_n^{2-/-/0}$ oxocarbons (n = 5 and 6). The adiabatic detachment energies (ADEs) and low-lying vertical detachment energies (VDEs) of the monoanions have been calculated at the coupled cluster level with triple excitations (CCSD(T)), with ADE = 3.723 and VDE = 3.776 eV for $C_5O_5^-$ and ADE = 3.629 eV and VDE = 3.679 eV for $C_6O_6^-$ CCSD(T)//MP2. The first excited states of the neutrals are predicted to have the approximate term values of T_1 = 1.08 eV ($^3A_2$) for C_5O_5 and T_1 = 1.22 eV ($^3B_1$) for C_6O_6. The predictions made in this work may help facilitate experimental characterizations of $C_5O_5^-$ and $C_6O_6^-$ monoanions.

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1. Introduction

Oxocarbons C_nO_n (n = 3–6), the cyclic polymers of carbon monoxide, have attracted considerable attention in the past several decades [1–42]. The well-known $C_nO_n^{2-}$ dianions (n = 3–6) have been extensively studied in chemistry due to their π-aromaticity, capacity as either bridging ligands or building blocks in interesting materials and usefulness in analytic applications [27–42]. In contrast, much less attention has been paid to C_nO_n neutrals and $C_nO_n^-$ monoanions which started to arouse the curiosity of chemists in the past decade. The main theoretical investigations in this aspect are focused on the unusual electronic structure of C_4O_4 which was predicted to have a triplet ground state at coupled cluster level with triple excitations (CCSD(T)) [27–31]. This prediction was confirmed in 2012 by photoelectron spectroscopy (PES) measurements coupled with an electrospray ionization (ESI) source of $C_4O_4^-$ clusters generated from squaric acid solution of $C_4O_4H_2$, combined with CCSD(T) calculations [32]. Shortly after this report, a comprehensive molecular orbital (MO) analysis for the whole oxocarbon neutral series $(CO)_n$ (n = 2–6) appeared very recently [33].

At the best of our knowledge, limited investigations have been reported for $C_nO_n^-$ monoanions and their neutrals C_nO_n (n = 5, 6) [28–42]. Experimentally, $C_5O_5^-$ radical was firstly observed in ESR measurements by oxidation of bis(tripheny1phosphine) iminium croconate in 1973 [12]. Trace amounts of $C_5O_5^-$ and $C_6O_6^-$ monoanions in gas phases were observed in mass spectrum in 1999 [41]. $C_6O_6^-$ monoanion was also recently produced from oligomerization of CO on molybdenum anions in 2006 [42]. As a powerful experimental technique, PES can be used to directly probe the electronic states of both monoanions and their neutrals. But only very accurate theoretical calculations at coupled cluster levels are expected to provide reliable theoretical predictions to assign the PES spectra of $C_nO_n^-$ monoanions, as noticed in the case of $C_4O_4^-$ [32]. The ground states of C_nO_n (n = 5, 6) neutrals are known to be singlet [17,33]. However, the ground states of $C_nO_n^-$ (n = 5, 6) monoanions and the exited states of their neutrals still remain unknown to date. In this work, we present comprehensive first-principles investigations on the geometrical and electronic structures of $C_5O_5^{-/0}$ and $C_6O_6^{-/0}$ and predict the low-lying one-electron detachment energies of $C_5O_5^-$ and $C_6O_6^-$ to facilitate their experimental characterizations. We also provide detailed molecular orbital analyses for $C_nO_n^{2-/-/0}$ clusters (n = 5, 6) to help understand their σ- and π-bonding patterns and probe the one-electron detachment channels from $C_nO_n^-$ monoanions to their C_nO_n neutrals.

2. Computational methodology

The geometries of C_nO_n neutrals and $C_nO_n^-$ monoanions (n = 5, 6) were fully optimized at both B3LYP [43–44] and MP2 [45–46] levels with the Dunning's correlation consistent basis sets (aug-cc-pVTZ) [47] for both carbon and oxygen. Vibrational analyses at

* Corresponding authors.
E-mail addresses: haigang_lu@yahoo.com.cn (H.-G. Lu), lisidian@yahoo.com (S.-D. Li).

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B3LYP level were carried out to ensure that all of the optimized geometries were true minima on potential energy surfaces of the systems. Natural bond orbital (NBO) analyses were performed to gain insight into the bonding characters of these species. In addition, chemical bonding analyses of $C_5O_5^{2-/1-/0}$ and $C_6O_6^{2-/1-/0}$ were performed utilizing the recently proposed adaptive natural density partitioning (AdNDP) method [48–50] with the 6-31G basis set. It has been shown that the AdNDP results are not sensitive to the level of theory or basis set used. Molecular visualization was performed using Molekel 5.4 [51]. Adiabatic detachment energies (ADEs) were calculated as the energy differences between the anions and the corresponding neutrals at their ground-state structures, while the vertical detachment energies (VDEs) as the energy differences between the anions and their neutrals at the ground-state structures of the anions. CCSD(T) [52–54] single-point energy calculations were performed at both B3LYP and MP2 geometries. One-electron detachment energies of the monoanions were also approximated with the outer valence Green function approach (OVGF) [55]. All the calculations in this work were performed using the Gaussian 03 software package [56].

3. Results and discussion

3.1. Structures and stabilities

The optimized structures of $C_nO_n^-$ monoanions (n = 5,6) and their neutrals are shown in Fig. 1, with the C–C and C–O bond lengths at both B3LYP and MP2 levels indicated. Both $C_5O_5^-$ (1), monoanion and C_5O_5 (2), neutral are found to take perfect planar D_{5h} structures, while $C_6O_6^-$ (3) and C_6O_6 (4) possess the slightly distorted quasi-planar C_{2v} geometries. The C_{2v} conformation of $C_6O_6^-$ (3) is a true minimum on the potential energy surface of the monoanion without imaginary frequencies (see Table 1), while other isomers such as D_{6h}, D_{3d}, D_2, C_2, and C_s turn out to be transition states or high-order saddle points lying slightly higher than C_{2v} $C_6O_6^-$ (3) (by less than 0.16 kcal/mol, see Fig. S1 in Supplementary information). These results indicate that the potential energy surface of $C_6O_6^-$ is very flat and its isomers obtained in Fig. S1 are practically isoenergetic with one another. While the energetically nearly degenerate α-HOMO (a_{2u}) and α-HOMO-1 (b_{1g}) make it difficult to determine the ground state of $C_4O_4^-$ theoretically [28,31–33], the energy gaps between the α-HOMO and α-HOMO-1 of $C_5O_5^-$ and $C_6O_6^-$ appear to be big enough (60.2 and 69.3 kcal/mol at CCSD(T)//B3LYP, respectively) to ensure that the doublet D_{5h} $C_5O_5^-$ ($^2A_2''$) (1) and C_{2v} $C_6O_6^-$ ($^2A_1$) (3) be the ground states of the systems without ambiguity. This situation greatly simplifies the theoretical calculations on $C_5O_5^{-/0}$ and $C_6O_6^{-/0}$. The optimized singlet ground states of D_{5h} C_5O_5 ($^1A_1'$) (2) and C_{2v} C_6O_6 ($^1A_{1g}$) (4) in Fig. 1 well agree with the prediction of Schleyer and coworkers [17].

As can be seen from Fig. 1, B3LYP and MP2 methods produced similar geometries and bond parameters for the concerned oxocarbons. It is interesting to notice that the periphery C–C bond lengths of the monoanions are systematically shorter than the corresponding values of their neutrals (by about 0.037 Å in average) due to the fact that the extra electron on $C_nO_n^-$ occupies the totally delocalized bonding π-HOMO of the systems over the oxocarbon rings (see Fig. 3). It is this delocalized multi-center-one-electron π-HOMO that makes $C_nO_n^-$ monoanions thermodynamically more stable than their C_nO_n neutrals. The highly stable $C_nO_n^{2-}$ dianions are produced with one more extra electron in the π-HOMO of $C_nO_n^-$. In addition, it is expected that the symmetric ring breathing modes of the neutrals to be excited upon detaching one electron from the monoanions. The calculated symmetrical breathing modes (a_1) of C_5O_5 (2) and C_6O_6 (4) have the vibrational frequencies of 1754 cm^{-1} and 1742 cm^{-1} (after the 0.97 scaling) at B3LYP/aug-cc-pVTZ level, respectively, which appear to be 70–80 cm^{-1} lower than the ring breathing frequency of 1824 cm^{-1} calculated for C_4O_4 at the same theoretical level [32].

As demonstrated in Table 1, NBO analysis indicates that C and O atoms in oxocarbons well follow the octet rule with the total Wiberg atomic bond indices of WBI_C = 3.87–3.89 and WBI_O = 1.93–2.17. The C–C Wiberg bond indices of WBI_{C-C} = 0.89–0.97 calculated for (1–4) clearly indicate that C–C bonds are typical covalent single bond. We notice the C–C bond indexes ($WBI_{C-C} \approx 0.97$) of the monoanions are clearly higher than their neutrals with $WBI_{C-C} \approx 0.89$–0.90, in consistent with the shorter C–C bond lengths in the monoanions than in their neutrals discussed above. The C–O Wiberg bond indices with the bond orders of WBI_{C-O} = 1.71–1.92 for (1–4) show that the C–O bonds are typical double bonds in these species. Given the fact that oxygen is more electronegative than carbon, it is easy to understand that O atoms in oxocarbons carry negative net atomic charges ($q_O = -0.37|e| \sim -0.53|e|$), while C atoms are positively charged with $q_C = +0.33|e| \sim +0.38|e|$.

The singlet ground states of C_nO_n neutrals (n = 5, 6) have been predicted to be unstable with respect to dissociation to n CO molecules [17,29,37]. Schleyer and coworkers [17] proposed that the exothermicities of C_nO_n (−25.7 kcal/mol for n = 5 and −31.2 kcal/mol for n = 6 at B3LYP/6-311+G* level) in the decomposition reactions ($C_nO_n \rightarrow nCO$) rationalize the failures to prepare and to observe these "neutral carbon monoxide oligomers". To evaluate the thermodynamic stabilities of their monoanions, we calculate the energy changes of the following processes at CCSD(T)//B3LYP level at 298.15 K and 1 atm:

$$nCO \rightarrow C_nO_n \rightarrow C_nO_n^- \ (n = 4, 5, 6)$$

With zero-point corrections included, ΔE_1 = +53.88, +46.49, and +54.42 kcal/mol, ΔE_2 = −80.49, −86.87, and −85.59 kcal/mol, and the overall $\Delta E = \Delta E_1 + \Delta E_2$ = −26.61, −40.38 and −31.17 kcal/mol for D_{4h} $C_4O_4^-$ ($^2A_{2u}$), D_{5h} $C_5O_5^-$ ($^2A_2''$) (1), and C_{2v} $C_6O_6^-$ ($^2A_1$) (3), respectively. Obviously, with positive formation energies (ΔE_1), C_4O_4, C_5O_5, and C_6O_6 neutrals are unstable with respect to dissociations to 4CO, 5CO, and 6CO (in consistent with the prediction of Schleyer and coworkers [17]). However, these unstable neutrals possess huge electron affinities (ΔE_2) upon one-electron attach-

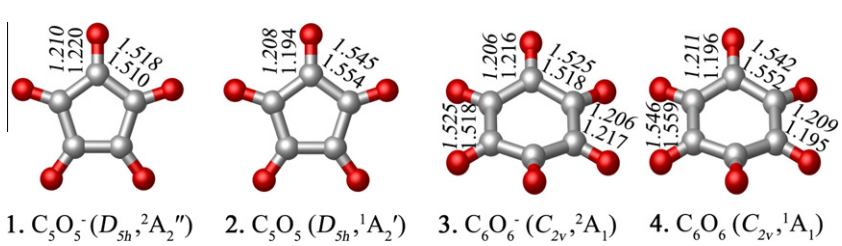

Fig. 1. Optimized ground-state structures of monocyclic $C_5O_5^-$ (1), C_5O_5 (2), $C_6O_6^-$ (3) and C_6O_6 (4) with bond lengths indicated in Å at both B3LYP (in normal mode) and MP2 (in *italic* mode).

Table 1
Calculated natural atomic charges (q/|e|) and total Wiberg bond indices (WBI) of oxygen and carbon atoms, Wiberg bond indices of the C–C bonds (WBI_{C-C}) and the C–O bonds (WBI_{C-O}), and the lowest vibrational frequencies (ν_{min}/cm^{-1}) of $C_5O_5^{-/0}$ and $C_6O_6^{-/0}$ at B3LYP/aug-cc-pVTZ.

	Symm	State	q_C	q_O	WBI_C	WBI_O	WBI_{C-C}	WBI_{C-O}	ν_{min}
$C_5O_5^-$	D_{5h}	$^2A_2''$	+0.33	−0.53	3.87	1.93	0.97	1.71	+68
C_5O_5	D_{5h}	$^1A_1'$	+0.37	−0.37	3.89	2.17	0.90	1.92	+33
$C_6O_6^-$	C_{2v}	$^2A_1$	+0.33, +0.35	−0.50	3.87	1.97	0.97	1.74	+2
C_6O_6	C_{2v}	$^1A_1$	+0.38	−0.38	3.89	2.17	0.89, 0.90	1.92	+4

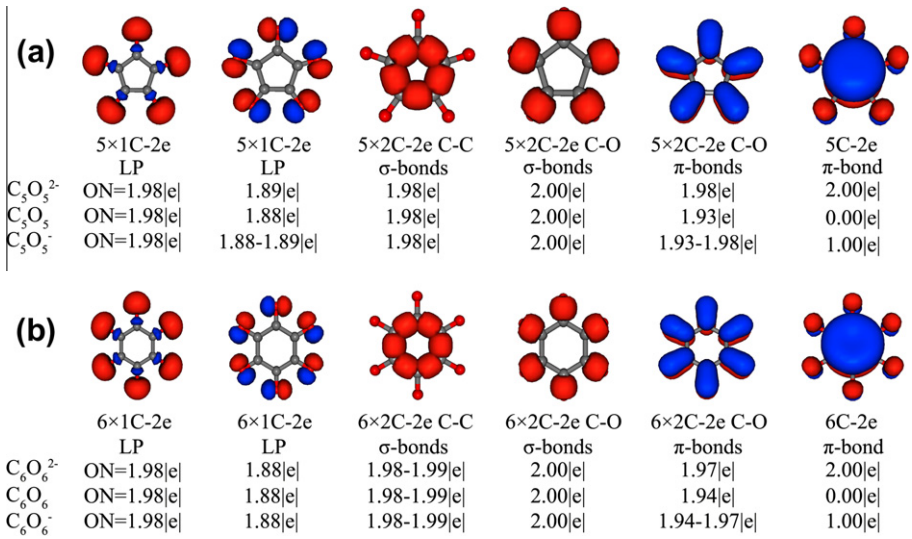

Fig. 2. AdNDP σ- and π-bonding patterns of $C_5O_5^{2-/-/0}$ (a) and $C_6O_6^{2-/-/0}$ (b) at the ground state structures of the monoanions, with occupation numbers (ONs) indicated.

ment, making their monoanions $C_4O_4^-$, $C_5O_5^-$, and $C_6O_6^-$ thermodynamically stable with considerable negative overall formation energies (ΔE). In these monoanions, $C_5O_5^-$ appears to be the most favorable species in thermodynamics. Given the fact that monocyclic D_{4h} $C_4O_4^-$ was generated from squaric acid solution of $C_4O_4H_2$ and characterized in PES measurements [32], it is reasonable to expect that monocyclic $C_5O_5^-$ (1) and $C_6O_6^-$ (3) to be produced from croconic acid ($C_5O_5H_2$) and rhodizonic acid ($C_6O_6H_2$) or their salts (like $C_5O_5Na_2$ and $C_6O_6Na_2$) and characterized in PES spectral measurements.

3.2. AdNDP analyses

In order to understand the bonding nature of these oxocarbon species, we performed detailed chemical bonding analyses for D_{5h} $C_5O_5^-$ ($^2A_2''$) (1) and C_{2v} $C_6O_6^-$ ($^2A_1$) (3) using the AdNDP approach [48–50]. As an extension of the natural bond orbital analysis, AdNDP is a very efficient and visual approach to interpretation of the molecular orbital-based wave functions. The current version of the AdNDP program can only deal with closed-shell systems. Therefore, in order to assess chemical bonding in the open-shell $C_nO_n^-$ (n = 5, 6) anions, we performed AdNDP analyses on both the closed-shell $C_nO_n^{2-}$ dianions and C_nO_n neutrals (n = 5, 6) at the geometries of their monoanions (see Fig. 2). The AdNDP σ- and π-bonding patterns of $C_nO_n^-$ (n = 5, 6) monoanions are shown in Fig. 2 as intermediates between the $C_nO_n^{2-}$ dianions and C_nO_n neutrals with averaged occupation numbers (ONs).

We discuss the results obtained for D_{5h} $C_5O_5^-$ (1) first. Of the 51 valence electrons, 20 electrons are for the ten 1c–2e lone-pairs (LPs) on O atoms, 10 electrons for the five periphery 2c–2e C–C σ single bonds, and 20 electrons for the five 2c–2e C=O double bonds (in which 10 electrons are for the five 2c–2e C–O σ bonds and 10 electrons for the five 2c–2e C–O π bonds). The remaining one extra electron occupies the totally delocalized 5c–1e bonding π-bond with the ON = 1.0|e|. The σ - and π-bonding patterns of C_{2v} $C_6O_6^-$ (3) are similar with D_{5h} $C_5O_5^-$ ($^2A_2''$) (1), except the fact that it possesses a singly occupied 6c–1e π-bond over the molecular plane with the ON = 1.0|e|. We stress here that it is the singly occupied delocalized π-bonds (the π-HOMOs) that makes $C_5O_5^-$ (1) and $C_6O_6^-$ (3) π-aromatic in nature and provides extra stabilization energies to stabilize these monoanions, similar to the situation in $C_4O_4^-$ [27–32].

3.3. ADEs and VDEs

Under the single-particle approximation (Koopmans's theorem), vertical electronic detachments can be viewed as removing one electron from each respective occupied MO of the anion. We performed CCSD(T) single-point energy calculations on the ground states of $C_nO_n^{-/0}$ (n = 5, 6) and the first two excited states of the neutrals at both the B3LYP and MP2 geometries of the monoanions to predict their ADEs and low-lying VDEs. We also calculated the first three VDEs of $C_5O_5^-$ and $C_6O_6^-$ using the (U)OVGF approach.

As shown in Fig. 3a, the HOMO (a_2'') of D_{5h} $C_5O_5^-$ ($^2A_2''$) (1) is a typical singly occupied delocalized π MO, while the degenerate HOMO-1 (e_2') includes two doubly occupied σ MOs. One-electron detachment from $C_5O_5^-$ results in three electron states for neutral C_5O_5. The first VDE corresponds to detaching one electron vertically from the singly occupied π-HOMO with the final neutral singlet state of $^1A_1'$, while the second and third VDEs correspond to detachment of a β or α electron from HOMO-1 (e_2') which leads to the final neutral triplet $^3A_2$ and singlet $^1A_2$ state, respectively. As listed in Table 2, $C_5O_5^-$ has the calculated first detachment energies of ADE = 3.780 eV and VDE = 3.874 eV at ΔCCSD(T)//B3LYP and ADE = 3.723 eV and VDE = 3.776 eV at ΔCCSD(T)//MP2. This gives an approximate electron affinity value of EA = 3.72–3.78 eV for

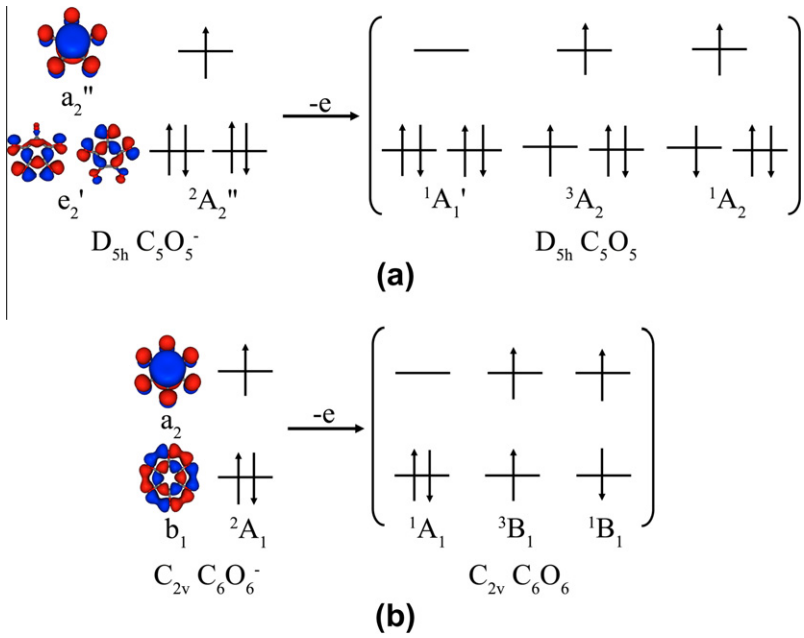

Fig. 3. (a) Three low-lying electronic states of C_5O_5 formed upon detachment of one electron from D_{5h} $C_5O_5^-$. The ground state uses the description of D_{5h} symmetry, while the first and second excited states use the descriptions of C_{2v} symmetry (the real electronic structures of these excited states possess C_{2v} symmetry). (b) Three low-lying electronic states of C_6O_6 formed upon detachment of one electron from C_{2v} $C_6O_6^-$.

Table 2
Calculated ADEs/eV and VDEs/eV of D_{5h} $C_5O_5^-$ ($^2A_2''$) and C_{2v} $C_6O_6^-$ ($^2A_1$) at various theoretical levels. The first and second excited states of C_5O_5 use C_{2v} descriptions because their real electronic structures possess C_{2v} symmetry. Values in parentheses represent the pole strength values obtained in (U)OVGF calculations.

	Final state	At B3LYP geometry		At MP2 geometry	
		ΔCCSD(T)	(U)OVGF	ΔCCSD(T)	(U)UOVGF
$C_5O_5^-$ (D_{5h}, $^2A_2''$)					
ADE		3.780		3.723	
VDE	$^1A_1'$	3.874	3.818 (0.90)	3.776	3.938 (0.90)
A	$^3A_2$	4.951	5.050 (0.88)	4.859	4.936 (0.88)
B	$^1A_2$	5.181	5.226 (0.87)	5.069	5.108 (0.88)
$C_6O_6^-$ (C_{2v}, $^2A_1$)					
ADE		3.715		3.629	
VDE	$^1A_1$	3.771	3.879 (0.90)	3.679	3.735 (0.90)
A	$^3B_1$	4.999	4.959 (0.87)	4.896	4.841 (0.90)
B	$^1B_1$	5.073	5.113 (0.87)	4.969	4.984 (0.87)

C_5O_5 neutral at CCSD(T). The small ADE–VDE difference (<0.10 eV) well demonstrates the minor structural relaxation from D_{5h} $C_5O_5^-$ (1) to D_{5h} C_5O_5 (2) (see Fig. 1) upon one-electron detachment. The first $^3A_2$ and second $^1A_2$ excited states of the neutral appear to be very close in energy, with the second and third VDE = 4.951 and 5.181 eV at ΔCCSD(T)//B3LYP and VDE = 4.859 and 5.069 eV at ΔCCSD(T)//MP2, respectively. These values define an approximate term value of T_1 = 1.08 eV for the first ($^3A_2$) excited state of D_{5h} C_5O_5. This value turns out to be much higher than the corresponding measured term value of T_1 = 0.065 eV ($^1A_{1g}$) measured for C_4O_4 in PES experiments [32]. Interestingly, simple (U)OVGF calculations also produce VDE values well comparable with the more accurate ΔCCSD(T) method at both B3LYP and MP2 geometries (see Table 2). The high pole strengths (>0.87) of the electron detachment channels for $C_5O_5^-$ (and $C_6O_6^-$) strongly suggest that multireference interactions be most likely negligible for the monoanions concerned in this work.

Similar situation occurs to $C_6O_6^-$. As demonstrated in Fig. 3b, the HOMO (a_2) of C_{2v} $C_6O_6^-$ ($^2A_1$) (3) is a typical singly occupied π molecular orbital, while its HOMO-1 (b_1) is a doubly occupied σ molecular orbital. One-electron detachment from $C_6O_6^-$ results in three electronic states for C_6O_6, including $^1A_1$, $^3B_1$, and $^1B_1$ which are responsible for the three PES bands (X, A and B), respectively. The first one-electron detachment (X) from the singly occupied HOMO (a_2) produces the singlet final state of $^1A_1$, with ADE = 3.715 eV and VDE = 3.771 eV at CCSD(T)//B3LYP and ADE = 3.629 eV and VDE = 3.679 eV CCSD(T)//MP2, respectively. These values produce an approximate electron affinity of EA = 3.62–3.72 eV for C_6O_6 at CCSD(T). The second (A) and third (B) VDEs correspond to detaching a β or α electron from the HOMO-1 (b_1) which leads to the neutral triplet ($^3B_1$) and singlet ($^1B_1$) final state, respectively, with the second and third VDE = 4.999 and 5.073 eV at CCSDF(T)//B3LYP and VDE = 4.896 eV and 4.969 eV at CCSD(T)//MP2. These VDE values define an approximate term value of T_1 = 1.22 eV for the first excited state ($^3B_1$) of C_6O_6. As shown in Table 2 (U)OVGF calculations also produce VDE values well in agreement with the more accurate CCSD(T) method for $C_6O_6^-$.

4. Summary

We have performed comprehensive first-principles calculations on the geometrical and electronic structures of $C_5O_5^{-/0}$ and $C_6O_6^{-/0}$

oxocarbons in this work to complete CCSD(T) calculations on the whole monocyclic $C_nO_n^{-/0}$ series (n = 3–6) [28,31–33]. The ground state of $C_5O_5^-$ anion favors perfect planar D_{5h} symmetry, while $C_6O_6^-$ anion possesses a quasi-planar C_{2v} symmetry. The electron affinities of C_5O_5 and C_6O_6 calculated at CCSDF(T) appear to be about 0.2–0.3 eV higher than the corresponding value (3.475 eV) of C_4O_4 [19]. The term values of the first excited states of C_5O_5 and C_6O_6 neutrals are predicted to be much higher than the corresponding value of C_4O_4 [19]. The symmetrical ring breathing frequencies of C_5O_5 and C_6O_6 are predicted to be around 1750 cm^{-1}, slightly lower than that of smaller-sized C_4O_4 [19].

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.comptc.2012.12.003.

References

[1] R. West, J. Niu, in: J. Snyder (Ed.), Non-Benzenoid Aromatic Compounds, vol. I, Academic Press, New York, 1969, p. 312.
[2] R. West (Ed.), Oxocarbons, Academic Press, New York, 1980.
[3] B.F. Abrahams, M.G. Haywood, R. Robson, An unexpected network in guanidinium rhodizonate, CrystEngComm 7 (2005) 629–632.
[4] C.C. Wang, C.T. Kuo, P.T. Chou, G.H. Lee, The first rhodizonate metal complex with a novel 2D chair-like M_6 metal organic framework: $[M(C_6O_6)(bpym)(H_2O)]$ nH_2O (M = Cd (1), n = 1; M = Mn (2), n = 2; bpym = 2,2′-bipyrimidine) and associated luminescence properties, Angew. Chem. Int. Ed. 4 (2004) 4507–4510.
[5] H. Chen, M. Armand, M. Courty, M. Jiang, C.P. Grey, F. Dolhem, J.-M. Tarascon, P. Poizot, Lithium salt of tetrahydroxybenzoquinone: toward the development of a sustainable Li-Ion battery, J. Am. Chem. Soc. 131 (2009) 8984–8988.
[6] A.C. Stott, T.P. Vaid, E.J. Bylaska, D.A. Dixon, Tuning band gap energies in $Pb_3(C_6X_6)$ extended solid-state structures, J. Phys. Chem. C 116 (2012) 8370–8378.
[7] R. West, H.-Y. Niu, D.L. Powrll, M.V. Evans, Symmetrical resonance stabilized anions $C_nO_n^{2-}$, J. Am. Chem. Soc. 82 (1960) 6204–6205.
[8] R. West, D.L. Powrll, New aromatic anions. III. Molecular orbital calculations on oxygenated anions, J. Am. Chem. Soc. 85 (1963) 2577–2579.
[9] R. West, H.-Y. Niu, Symmetrical resonance stabilized anions, $C_nO_n^{m-}$. II. $K_4C_6O_6$ and evidence for $C_6O_6^{3-}$, J. Am. Chem. Soc. 84 (1962) 1324–1325.
[10] M. Ito, R. West, New Aromatic Anions. IV. Vibrational spectra and force constants for $C_4O_4^{2-}$ and $C_5O_5^{2-}$, J. Am. Chem. Soc. 85 (1963) 2580–2584.
[11] R. West, H.-Y. Niu, M. Ito, New Aromatic Anions. V. The synthesis of diketocyclobutenediol and its conversion to octahydroxycyclobutane, J. Am. Chem. Soc. 85 (1963). 2584–2584.
[12] E.V. Patton, R. West, New aromatic anions. IX. Anion radicals of the monocyclic oxocarbons, J. Phys. Chem. 77 (1973) 2652–2654.
[13] R. West, D. Eggerding, J. Perkins, D. Handy, E.C. Tuazon, New Aromatic Anions. II. Vibrational spectra and force constants for Deltate Ion, $C_3O_3^{2-}$, J. Am. Chem. Soc. 101 (1979) 1710–1714.
[14] G. Seitz, P. Imming, Oxocarbons and pseudooxocarbons, Chem. Rev. 92 (1992) 1227–1260.
[15] M.B. Rubin, R. Gleiter, The chemistry of vicinal polycarbonyl compounds, Chem. Rev. 100 (2000) 1121–1164.
[16] J. Aihara, Are the oxocarbon dianions really aromatic?, J Am. Chem. Soc. 103 (1981) 1633–1635.
[17] P.V.R. Schleyer, K. Najafian, B. Kiran, H.J. Jiao, Are oxocarbon dianions aromatic?, J Org. Chem. 65 (2000) 426–431.
[18] E. Coronado, P. Day, Chem. Rev. 104 (2004) 5419–5448.
[19] T. Enoki, A. Miyazaki, Magnetic TTF-based charge-transfer complexes, Chem. Rev. 104 (2004) 5449–5477.
[20] H. Kobayashi, H. Cui, A. Kobayashi, Organic metals and superconductors based on BETS (BETS = bis(ethylenedithio)tetraselenafulvalene), Chem. Rev. 104 (2004) 5265–5288.
[21] A.W. Graham, M. Kurmoo, P. Day, β″-(BEDT-TTF)$_4$[$(H_2O)Fe(C_2O_4)_3$]·PhCN: the first molecular superconductor containing paramagnetic metal ions, J. Chem. Soc., Chem. Commun. (1995) 2061–2062.
[22] M. Kurmoo, A.W. Graham, P. Day, S.J. Coles, M.B. Hursthouse, J.L. Caulfield, J. Singleton, F.L. Pratt, W. Hayes, Superconducting and semiconducting magnetic charge transfer salts: (BEDT-TTF)$_4$AFe$(C_2O_4)_3$·CsHsC(N A = H_2O, K, NH_4), J. Am. Chem. Soc. 117 (1995) 12209–12217.
[23] T.G. Prokhorova, L.I. Buravov, E.B. Yagubskii, L.V. Zorina, S.S. Khasanov, S.V. Simonov, R.P. Shibaeva, A.V. Korobenko, V.N. Zverev, Effect of electrocrystallization medium on quality, structural features, and conducting properties of single crystals of the (BEDT-TTF)$_4$A^I[$Fe^{III}(C_2O_4)_3$]·G family, CrystEngComm 13 (2011) 537–545.
[24] H. Akutsu, A. Akutsu-Sato, S.S. Turner, D. Le Pevelen, P. Day, V. Laukhin, A. Klehe, J. Singleton, D.A. Tocher, M.R. Probert, J.A.K. Howard, Effect of included guest molecules on the normal state conductivity and superconductivity of a β″-(ET)$_4$[$(H_3O)Ga(C_2O_4)_3$]·G (G = Pyridine, Nitrobenzene), J. Am. Chem. Soc. 124 (2002) 12430–12431.
[25] E. Coronado, S. Curreli, C. Gimenez-Saiz, C.J. Gomez-Garcia, The series of molecular conductors and superconductors ET$_4$[AFe$(C_2O_4)_3$]·PhX (ET = bis(ethylenedithio)tetrathiafulvalene; $(C_2O_4)_2$ = oxalate; $A^+ = H_3O^+$, K^+; X = F, Cl, Br, and I): influence of the halobenzene guest molecules on the crystal structure and superconducting properties, Inorg. Chem. 51 (2012) 1111–1126.
[26] M. Atzori, E. Sessini, F. Artizzu, L. Pilia, A. Serpe. C.J. Gomez-Garcia, C. Gimenez-Saiz, P. Deplano, M.L. Mercuri, Synthesis and physical properties of $K_4[Fe(C_5O_5)_2(H_2O)_2](HC_5O_5)_2{\cdot}4H_2O$ ($C_5O_5^{2-}$ = Croconate): a rare example of ferromagnetic coupling via H-bonds, Inorg. Chem. 51 (2012) 5360–5367.
[27] R. Gleiter, I. Hyla-Kryspin, K.-H. Pfeifer, On the stability of the tetramers of carbon monoxide, hydrogen isocyanide, and vinylidene. A molecular orbital theoretical rationalization, J. Org. Chem. 60 (1995) 5878–5883.
[28] H.-J. Jiao, G. Frapper, J.-F. Halet, J.-Y. Saillard, Stability of tetraoxocyclobutane revised: perturbation theory and density functional scheme, J. Phys. Chem. A 105 (2001) 5945–5947.
[29] H.-J. Jiao, H.-S. Wu, Are neutral oxocarbons stable?, J Org. Chem. 68 (2003) 1475–1479.
[30] X. Zhou, D.A. Hrovat, R. Gleiter, W.T. Borden, Reinvestigation of the ordering of the low-lying electronic states of cyclobutanetetraone with CASPT2, CCSD(T), G3B3, ccCA, and CBS-QB3 calculations, Mol. Phys. 107 (2009) 863–870.
[31] X. Zhou, D.A. Hrovat, W.T. Borden, Calculations of the relative energies of the $^2B_{1g}$ and $^2A_{2u}$ states of cyclobutanetetraone radical cation and radical anion provide further evidence of a $^3B_{2u}$ ground state for the neutral molecule: a proposed experimental test of the prediction of a triplet ground state for $(CO)_4$, J. Phys. Chem. A 114 (2010) 1304–1308.
[32] J.-C. Guo, G.-L. Hou, S.-D. Li, X.-B. Wang, Probing the low-lying electronic states of cyclobutanetetraone (C_4O_4) and its radical anion: a low-temperature anion photoelectron spectroscopic approach, J. Phys. Chem. Lett. 3 (2012) 304–308.
[33] X.-G. Bao, X. Zhou, C.F. Lovitt, A. Venkatraman, D.A. Hrovat, R. Gleiter, R. Hoffmann, W.T. Borden, Molecular orbitals of the oxocarbons $(CO)_n$, n = 2–6. Why does $(CO)_4$ have a triplet ground state?, J Am. Chem. Soc. 134 (2012) 10259–10270.
[34] J.J. Kaufman, LCAO–MO–SCF calculations of C_6O_6 systems, J. Phys. Chem. 68 (1964) 2648–2651.
[35] G. Frenking, Die Struktur von cyclischem C_6S_6 and C_6O_6, Angew. Chem. 102 (1990) 1516–1517.
[36] L. Farnell, L. Radom, M.A. Vincent, The geometric and electronicstructures of oxocarbons. An abinitiomolecularorbitalstudy, J. Mol. Struct. Theochem. 76 (1981) 1–10.
[37] H. Sabzyan, M.R. Noorbala, Ab initio and DFT study of carbon monoxide cyclic oligomers, $(CO)_2$ to $(CO)_6$, J. Mol. Struct. Theochem. 626 (2003) 143–158.
[38] G. Corkran, D.W. Ball, The relative energies of cyclopropanone, cyclopropanedione, and cyclopropanetrione. Hartree–Fock, density-functional, G2, and CBS calculations, J. Mol. Struct. Theochem. 668 (2004) 171–178.
[39] P.K. Sahu, S.-L. Lee, Many-body interactions of carbon monoxide cyclic oligomers: a computational study, Int. J. Quantum Chem. 103 (2005) 314–321.
[40] F. Nazari, Stable structures of oxocarbons and pseudooxocarbons of group VI, J. Mol. Struct. Theochem. 760 (2006) 29–37.
[41] D. Schröder, H. Schwarz, S. Dua, S.J. Blanksby, J.H. Bowie, Mass spectrometric studies of the oxocarbons C_nO_n (n = 3–6), Int. J. Mass Spectrom. 188 (1999) 17–25.
[42] R.B. Wyrwas, C.C. Jarrold, Production of $C_6O_6^-$ from oligomerization of CO on molybdenum anions, J. Am. Chem. Soc. 128 (2006) 13688–13689.
[43] A.D. Beck, Density functional thermochemistry. III. The role of exact exchange, J. Chem. Phys. 98 (1993) 5648–5659.
[44] C. Lee, W. Yang, R.G. Parr, Development of the Colle–Salvetti correlation-energy formula into a functional of the electron density, Phys. Rev. B 37 (1988) 785–791.
[45] M. Head-Gordon, J.A. Pople, M.J. Frisch, MP2 energy evaluation by direct methods, Chem. Phys. Lett. 153 (1988) 503–506.
[46] M. Head-Gordon, T. Head-Gordon, Analytic MP2 frequencies without fifth-order storage: theory and application to bifurcated hydrogen bonds in the water hexamer, Chem. Phys. Lett. 220 (1994) 122–128.
[47] R.A. Kendall, T.H. Dunning, R.J. Harrison, Electron affinities of the first-row atoms revisited. Systematic basis sets and wave functions, J. Chem. Phys. 96 (1992) 6796–6806.
[48] D.Y. Zubarev, A.I. Boldyrev, Developing paradigms of chemical bonding: adaptive natural density partitioning, Phys. Chem. Chem. Phys. 10 (2008) 5207–5217.
[49] D.Y. Zubarev, A.I. Boldyrev, Revealing intuitively assessable chemical bonding patterns in organic aromatic molecules via adaptive natural density partitioning, J. Org. Chem. 73 (2008) 9251–9258.

[50] D.Y. Zubarev, A.I. Boldyrev, Deciphering chemical bonding in golden cages, J. Phys. Chem. A 113 (2009) 866–868.
[51] U. Varetto, Molekel 5.4.0.8, Swiss National Supercomputing Centre, Manno.
[52] J.A. Pople, M. Head-Gordon, K. Raghavachari, Quadratic configuration interaction. A general technique for determining electron correlation energies, J. Chem. Phys. 87 (1987) 5968–5975.
[53] G.E. Scuseria, H.F. Schaefer III, Is coupled cluster singles and doubles (CCSDs) more computationally intensive than quadratic configuration interaction (QCISD)?, J Chem. Phys. 90 (1989) 3700–3703.
[54] G.E. Scuseria, C.L. Janssen, H.F. Schaefer III, An efficient reformulation of the closed-shell coupled cluster single and double excitation (CCSD) equations, J. Chem. Phys. 89 (1988) 7382–7387.
[55] J.V. Ortiz, Toward an exact one-electron picture of chemical bonding, Adv. Quantum Chem. 35 (1999) 33–52.
[56] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, Gaussian 03, Revision B.03, Gaussian Inc., Pittsburgh, PA, 2003.