Electronic Structures of the Oxocarbon Anions[1]

K. Sakamoto and Y. J. I'Haya[2]

Contribution from the Department of Chemistry, Tokyo Kyoiku University,
Otsuka, Tokyo, Japan, and the Department of Materials Science,
The University of Electro-Communications, Chofu-shi, Tokyo, Japan.
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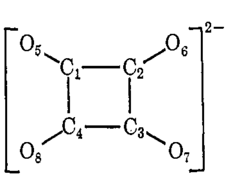
Abstract: The lower π electronic states of the oxocarbon anions, $(C_4O_4)^{2-}$, $(C_5O_5)^{2-}$, and $(C_6O_6)^{2-}$, are calculated by the semiempirical VESCF-CI and the SCF-CI methods. The degenerate SCF MO's for $(C_4O_4)^{2-}$ are transformed by a unitary transformation to determine its electronic excited state symmetries. Various kinds of approximations for estimating electronic repulsion integrals and resonance integrals are compared. The importance of doubly excited configurations in configuration-interaction calculations is shown. In order to reduce sizes of the configuration-interaction matrices, criteria for the truncation of configuration interaction are set up. The calculated lowest transition energies for these anions are in good agreement with observed values.

Although the aromatic oxocarbons have recently attracted the attention of many investigators, their origin is quite historic. In particular, the croconate ion was isolated as its potassium salt in the year when benzene was discovered, and the synthesis of croconic acid, which is now known to be a bacterial metabolic product, was prior to that of urea. Having been ignored for a long time, the oxocarbons became the subject of systematic investigations about 10 years ago. Since then, analyses of the ultraviolet, infrared, and Raman spectra together with X-ray analyses for the dianions of squarate $(C_4O_4)^{2-}$ (I), croconate $(C_5O_5)^{2-}$ (II), and rhodizonate $(C_6O_6)^{2-}$ (III)[3-12] have been carried out, all indicating that these anions have planar and symmetrical delocalized structures. However, little work has been done so far on the theoretical treatment of the oxocarbons. A simple Hückel-type calculation carried out by West and Powell[13] is apparently the only one applied to the entire series of $(C_nO_n)^{m-}$ anions. For the croconate anion, a few more elaborate theoretical studies have been carried out, *i.e.*, Baenziger and Hegenbarth's Hückel calculation including overlap,[14] Cignitti's SCF treatment[15] with a Pariser–Parr approximation,[16] and the authors' previous communication.[17] In the last (hereafter called part I), the authors employed the VESCF[18-20] (variable electronegativity self-consistent field) method including up to the doubly excited configurations and showed that the doubly excited configuration interaction plays a major part in producing a singlet ground state for the croconate anion. The Hückel and SCF methods were applied to the rhodizonate anion by Kaufman.[21] The importance of the doubly excited configurations within the framework of a Pariser–Parr approximation in aromatic hydrocarbons has also been emphasized in several other articles, for example, the recent work of Allinger and Stuart.[22] To make a step further toward understanding the role of the doubly excited configurations in heteronuclear conjugated systems, we shall here treat the above-mentioned three oxocarbon anions, making a careful comparison between different methods of calculation in regard to the available spectral data.



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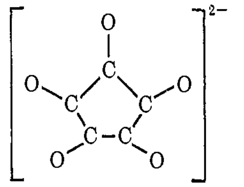

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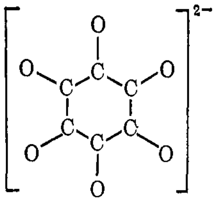

III

Method of Calculation

The three oxocarbon anions considered are assumed to have planar and regular polygonal structures, namely $(C_4O_4)^{2-}$ D_{4h}, $(C_5O_5)^{2-}$ D_{5h}, and $(C_6O_6)^{2-}$ D_{6h} symmetry, each atom contributing one π electron to the ring. The bond lengths used for the calculation are listed in Table I.

For comparison, two kinds of SCF MO methods within the framework of a Pariser–Parr approxima-

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[2] To whom all correspondence should be addressed at the Department of Materials Science, The University of Electro-Communications, Chofu-shi, Tokyo 182, Japan.

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Table I. Bond Lengths, Å[a]

	$(C_4O_4)^{2-}$	$(C_5O_5)^{2-}$	$(C_6O_6)^{2-}$
C-C	1.457[b]	1.460[c]	1.457[d]
C-O	1.259[b]	1.260[c]	1.262[d]

[a] The values only for the nearest neighbors are given. [b] Reference 12. [c] Average values taken from ref 8. [d] Assumed values.

tion[16] are used. One is the usual SCF LCAO MO method in which we use constant values for the sp^2 hybrid state ionization potential and electron affinity taken from Hinze and Jaffé's work.[23] The other is the VESCF method which has been fully described in part I.[17] In both treatments, the following approximations for the molecular integrals are considered: (a) a Pariser–Parr-type quadratic equation (P-P) for the two-center electronic repulsion integrals γ_{pq}; (b) the Mataga–Nishimoto equation (M-N)[24] for γ_{pq}; (c) only nearest neighbor resonance integrals taken (β_{near}); (d) nonnearest neighbor β's included (β_{all}).[20,25,26] The nearest neighbor penetration integrals are calculated purely theoretically using Slater-type AO's and are assumed to be constant throughout the whole SCF routine (see part I).

In the process of the CI calculation, the symmetry of the state produced by excitation of an electron between degenerate MO's can not be explicitly determined for the squarate anion. To remove this difficulty, unitary transformed MO's are used. For example, consider the four singly excited configurations in the squarate anion, ψ_2^6, ψ_2^7, ψ_3^6, and ψ_3^7 [27] in which the degenerate MO's (φ_2 and φ_3, φ_6 and φ_7) all belong to the same symmetry, e_g. The pairs of the degenerate SCF MO's belonging to the D_{4h} symmetry in the real form are

$$\begin{aligned}\varphi_i &= +a(\chi_1 - \chi_3) + b(\chi_2 - \chi_4) + \\ &\qquad c(\chi_5 - \chi_7) + d(\chi_6 - \chi_8) \\ \varphi_j &= -b(\chi_1 - \chi_3) + a(\chi_2 - \chi_4) - \\ &\qquad d(\chi_5 - \chi_7) + c(\chi_6 - \chi_8)\end{aligned} \tag{1}$$

The numbering of the AO's χ_k follows the numbering of the atoms shown on the structural formula of the squarate anion (I). We transform these degenerate MO's by the unitary transformation as follows

$$\begin{aligned}\varphi_2 &= +k_1(\chi_1 + \chi_2 - \chi_3 - \chi_4) + \\ &\qquad k_2(\chi_5 + \chi_6 - \chi_7 - \chi_8) \\ \varphi_3 &= -k_1(\chi_1 - \chi_2 - \chi_3 + \chi_4) - \\ &\qquad k_2(\chi_5 - \chi_6 - \chi_7 + \chi_8) \\ \varphi_6 &= +k_2(\chi_1 + \chi_2 - \chi_3 - \chi_4) - \\ &\qquad k_1(\chi_5 + \chi_6 - \chi_7 - \chi_8) \\ \varphi_7 &= +k_2(\chi_1 - \chi_2 - \chi_3 + \chi_4) - \\ &\qquad k_1(\chi_5 - \chi_6 - \chi_7 + \chi_8)\end{aligned} \tag{2}$$

where the numbering of the degenerate MO's is in order of increasing energy, and the relationships between the coefficients k_1 and k_2 above and a, b, c, and d which appeared in eq 1 are given by $k_1 = (a^2 + b^2)^{1/2}/2$, $k_2 = (c^2 + d^2)^{1/2}/2$. Using these transformed MO's, symmetries of the excited states are uniquely determined

$$\psi_2^6 - \psi_3^7 \subset A_{1g} \qquad \psi_2^6 + \psi_3^7 \subset B_{1g}$$
$$\psi_2^7 + \psi_3^6 \subset A_{2g} \qquad \psi_2^7 - \psi_3^6 \subset B_{2g}$$

The excitation energies and oscillator strengths are independent of whether transformed MO's are used. Symmetries of the degenerate SCF MO's of the croconate anion are determined by the method described in part I, while symmetries of the SCF MO's for other molecules are easily obtained.

Although one of our present purposes is to check an extensive CI effect in the oxocarbon series, it is not possible to include all the configurations for each electronic state due to the limit of our matrix diagonalization routine. In order to select more important singly and doubly excited configurations, therefore, we adopt the following procedure. First, we search for the lowest member among both the singly and doubly excited configurations belonging to the same symmetry group, except for the state including the ground configuration ψ_0, in which case ψ_0 of course is the lowest member of this symmetry group. Second, in order to make a rough estimate for the extent of CI, we solve 2×2 matrices constructed from the lowest member selected and each excited configuration belonging to the same symmetry group. If the lowest member or the excited configurations concerned are degenerate, the matrix to be solved should contain all the degenerate configurations. These procedures are carried out for all the possible configuration species up to doubly excited configurations. The excited configurations whose energetic contribution is more than 1% of the eigenvalue of the lowest member of a symmetry group are selected. For the state including ψ_0, excited configurations which push down the eigenvalue of ψ_0 more than 0.01 eV are taken.

Having carefully analyzed the result obtained by the above-mentioned procedures, we select the more important doubly excited configurations and compare the CI calculation including these with that including only singly excited configurations.

Results and Discussion

In 1967, Allinger and Stuart[22] studied the effect of doubly excited configurations for aromatic hydrocarbons within the framework of the VESCF method. They proved that the cut-off point for 0.2-eV consistency was at approximately 20 eV measured from the ground configuration. We examine a cut-off criterion for the oxocarbon series by a somewhat different procedure as described in the previous section.

The results are shown in Table II, where the number of singly and doubly excited configurations considered is given in parentheses. The entries in the table show the eigenvalue of the highest energy configuration (the cut-off level) relative to the energy of the lowest member of the state. As the table shows, the values of these cut-off levels and the numbers of configurations used

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(27) The subscript on ψ means an occupied MO in the ground configuration, and superscript a virtual or vacant MO.

Table II. Effect of Excited Configurations upon the Ground and First Singlet Excited States, eV[a]

State	Energy criterion	$(C_4O_4)^{2-}$	$(C_5O_5)^{2-}$	$(C_6O_6)^{2-}$
		$^1A_{1g}$	$^1A_1'$	$^1A_{1g}$
Ground	0.01[b]	22.2	24.1	27.8
		(0 + 46)	(0 + 115)	(0 + 117)
	0.03[b]	19.2	18.5	19.0
		(0 + 28)	(0 + 97)	(0 + 94)
		^1E_u	$^1E_1'$	$^1E_{1u}$
Excited	1[c]	14.2	17.2	11.0
		(6 + 18)	(10 + 48)	(10 + 46)
	3[c]	10.7	11.2	10.9
		(6 + 18)	(4 + 22)	(4 + 24)

[a] Under the approximation (P–P, β_{near}, VESCF). Each figure denotes the highest eigenvalue; Figures in parentheses are the numbers of configurations; the first corresponds to the singly, the next the doubly excited configurations (see text). [b] In eV. [c] Per cent.

depend on the energy criteria, the molecular species, and the electronic states considered.

If the energy criterion is restricted within 1% against the lowest eigenvalue of each state (or 0.01 eV), the maximum cut-off level is 27.8 eV above the reference state. When the restriction is relaxed to 3% (or 0.03 eV), the value comes down to 19.2 eV and the secular equations to be solved can be reduced to the 30 × 30 size at the largest for every excited state. Although there are so many configurations in the 15–19-eV region for the ground-state CI calculation, their total contribution to the ground configuration was found to be only about one-tenth of the contribution due to the whole configuration in the 0–19-eV region. Therefore, we tentatively set up the following criteria for each molecular electronic state. (a) 15 eV is chosen as a cut-off level, beyond which the effect of configurations is ignored. (b) Even below this level configurations whose energetic contributions are less than 3% of the corresponding lowest member or 0.03 eV are omitted.

The cut-off level 15 eV thus fixed, of course, has a range of about 1 eV depending on the approximations adopted for molecular integrals. Even if the usual SCF method is employed instead of the VESCF, 15 eV is found to be a reasonable cut-off level.

Table III. Comparison of the Lowest Excitation Energies of $(C_4O_4)^{2-}$ Calculated by Different Procedures[a]

Method and approximation[b]	$^1E_u \leftarrow {}^1A_{1g}$ excitation energy, eV SCI[c]	DCI[d]
	VESCF-CI	
P–P, β_{near}	3.277	3.205 (−1.075)[e]
P–P, β_{all}	3.595	3.259 (−0.854)
M–N, β_{near}	2.988	2.948 (−1.507)
M–N, β_{all}	3.244	2.872 (−1.251)
	SCF-CI	
P–P, β_{all}	4.379	4.060 (−0.560)
M–N, β_{all}	3.877	3.383 (−0.894)

[a] Observed value 4.60 eV. [b] See text. [c] All the singly excited configurations are included. [d] CI calculation including both singly and doubly excited configurations. [e] Energy depression of the lowest $^1A_{1g}$ state relative to its SCF energy due to DCI.

Table III shows the result of the preliminary calculation for the ^1E_u state of $(C_4O_4)^{2-}$, in which comparison of the calculation schemes and approximations for molecular integrals is made. In the second column are listed the results obtained when all the singly excited configurations are included irrespective of the cut-off level criterion (SCI). The third column gives the results of calculations including 6 singly and 18 doubly excited configurations chosen according to the abovementioned criteria (DCI) (note that the lowest member is doubly degenerate). It is seen from the table that the energies of the lowest singlet excited state relative to the ground state calculated with SCI and DCI are slightly, but not negligibly, affected by the approximations adopted for the resonance integral, β_{near} or β_{all}. The energies are also influenced by the choice of the usual SCF or the VESCF methods and by the approximations for the two-center electronic repulsion integrals. Another remarkable point is that the first excited ^1E_u state is lowered more by DCI than by SCI. In order to reproduce more closely the only experimental value, the $^1E_u \leftarrow {}^1A_{1g}$ excitation energy 4.60 eV, the P–P approximation for γ_{pq} and the β_{all} approximation for the resonance integrals are best.

It should be noted that the usual SCF-CI method gives better agreement with experimental values in each molecular electronic state than the VESCF-CI. A similar tendency is found in other oxocarbon anions, II and III.[28] This is quite surprising, as it is expected that the VESCF-CI would be indispensable for such aromatics containing many heteroatoms. On the basis of these preliminary calculations, all the lower electronic states of the oxocarbon series were calculated by the usual SCF-CI method with the approximation (P–P, β_{all}). The results are listed in Tables IV–VI.

Table IV. Lower Electronic States of Squaric Anion, eV[a]

Singlet state SCI	f	DCI	f	Triplet state SCI	DCI
	$^1A_{1g}$			$^3A_{1g}$	
0		0 (ref)		5.693	6.753
8.268		6.719		10.854	9.782
10.894		9.184			
(3)		(0 + 16)		(3)	(3 + 6)
	^1E_u			^3E_u	
4.379	0.710	4.060	0.420	1.864	2.250
7.267	0.418	6.753	0.473	6.101	6.556
(8)		(8 + 18)		(8)	(4 + 22)
	$^1B_{1g}$			$^3B_{1g}$	
8.217[c]		5.732		8.217[c]	7.841
(2)		(2 + 16)		(2)	(2 + 8)
	$^1A_{2g}$			$^3A_{2g}$	
8.217[c]		7.486		8.217[c]	7.882
(2)		(2 + 14)		(2)	(2 + 18)
	$^1B_{2g}$			$^3B_{2g}$	
6.259		4.583		4.779	5.135
7.910		7.123		6.618	7.083
(4)		(4 + 16)		(4)	(4 + 20)

[a] Under the approximation (P–P, β_{all}, SCF). Observed value 4.60 eV (oscillator strength $f = 0.367$).[b] Figures in parentheses indicate the numbers of the configurations taken; the first corresponds to the singly excited configurations, the next the doubly excited ones. [b] Our observed values (unpublished). [c] Accidentally degenerate.

The main role of DCI for the oxocarbon series is tentatively concluded to be as follows. The energies

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(28) With the approximation (P–P, β_{all}) and DCI, the $^1E_1' \leftarrow {}^1A_1'$ excitation energy for the croconate anion and the $^1E_{1u} \leftarrow {}^1A_{1g}$ excitation energy for the rhodizonate anion are calculated to be 3.031 and 2.266 eV, respectively, by the VESCF-CI.

Table V. Lower Electronic States of Croconate Anion, eV[a]

Singlet state SCI	Singlet state f	Singlet state DCI	Singlet state f	Triplet state SCI	Triplet state DCI
	$^1A_1'$			$^3A_1'$	
0		0 (ref)		5.591	6.512
8.999		6.023		10.098	8.200
10.229		8.281			
(8)		(0 + 14)		(8)	(8 + 10)
	$^1E_1'$			$^3E_1'$	
3.288	0.739	3.354	0.368	0.489	1.291
7.029	1.032	7.312	0.686	5.418	6.177
10.257	0.008	9.475	0.034	9.375	8.101
(16)		(6 + 22)		(16)	(6 + 21)
	$^1E_2'$			$^3E_2'$	
5.461		3.783		4.142	5.123
6.920		5.504		5.607	7.412
8.226		7.092		7.820	8.850
(16)		(6 + 23)		(16)	(2 + 24)
	$^1A_2'$			$^3A_2'$	
8.190[c]		7.727		8.190[c]	8.147
11.732[c]		11.039		11.732[c]	9.541
(8)		(8 + 10)		(8)	(8 + 10)

[a] See footnote *a* of Table IV. Observed value 3.40 eV.[b] [b] Reference 3. [c] See footnote *c* of Table IV.

Table VI. Lower Electronic States of Rhodizonate Anion, eV[a]

Singlet state SCI	Singlet state f	Singlet state DCI	Singlet state f	Triplet state SCI	Triplet state DCI
	$^1A_{1g}$			$^3A_{1g}$	
0		0 (ref)		5.350	6.660
9.154		4.794		9.472	7.534
(9)		(0 + 20)		(9)	(9 + 10)
	$^1E_{1u}$			$^3E_{1u}$	
2.555	0.739	2.615	0.221	−0.420	0.754
6.779	1.498	5.877	0.690	4.851	5.923
(16)		(6 + 24)		(16)	(8 + 19)
	$^1E_{2g}$			$^3E_{2g}$	
4.363		2.373		3.174	3.890
6.215		4.585		4.633	5.426
(16)		(12 + 16)		(16)	(13 + 12)
	$^1A_{2g}$			$^3A_{2g}$	
8.078[c]		7.980		8.078[c]	7.610
10.702[c]		10.133		10.702[c]	9.257
(8)		(8 + 8)		(8)	(8 + 12)
	$^1B_{1u}$			$^3B_{1u}$	
5.631		5.352		4.009	4.234
6.577		9.103		5.332	6.155
(10)		(4 + 22)		(10)	(6 + 16)
	$^1B_{2u}$			$^3B_{2u}$	
6.501[c]		5.593		6.501[c]	4.815
12.185		7.597		12.236	6.245
(10)		(4 + 14)		(10)	(4 + 17)

[a] See footnote *a* of Table IV. Observed value 2.56 eV.[b] [b] Reference 13. [c] See footnote *c* of Table IV.

calculated for the allowed state are not very much improved by DCI, while the effect of DCI is quite large in the symmetrically forbidden states and in most of the triplet states. The spin-degenerate configurations of the type ψ_{ij}^{kl} are found to have an effect on lowering the lowest excited state energies as well as other configurations of the types ψ_{ii}^{kk}, ψ_{ii}^{kl}, and ψ_{ij}^{kk}.

The lowest triplet state energies calculated by the DCI approximation for the three anions are higher than the corresponding lowest singlet state energies; that is, these levels never come to be ground states. This result is in accord with the magnetic experiments.[10,11] It should be noted, however, that the calculation including only singly excited configurations yields a triplet ground state for the rhodizonate anion (Table VI). In part I, a similar situation was demonstrated to occur in the croconate anion when the VESCF method was used and the doubly excited configurations were neglected. As seen from Table V, the usual SCF method with SCI predicts the lowest triplet state to lie above the singlet ground state but the singlet–triplet separation is too small.

It should be added, finally, that the oscillator strengths of the squarate anion are well explained by the inclusion of the limited number of doubly excited configurations.

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