[Contribution from the Department of Chemistry, the University of Wisconsin, Madison 6, Wis.]

New Aromatic Anions. IV. Vibrational Spectra and Force Constants for $C_4O_4^{-2}$ and $C_5O_5^{-2}$

By Mitsuo Ito and Robert West

The infrared spectra of solid $K_2C_4O_4$ and $K_2C_5O_5$ and the Raman spectra of their aqueous solutions have been investigated. The spectra indicate planar symmetrical structures (D_{4h} and D_{5h}) for the ions. Vibrational assignments were made on the basis of these structures and a normal coordinate treatment was carried out using a Urey–Bradley force field. The resulting force constants support the view that these ions constitute members of an aromatic series.[1,2]

The $C_nO_n^{-2}$ series of ions is of interest in that it has recently been recognized as a new class of aromatic substances.[1,2] In 1958, Hirata and his co-workers first suggested that the croconate ion $C_5O_5^{-2}$ had a symmetrical resonance-stabilized structure. This conclusion was based mainly on the observation that in the infrared spectra of croconate salts, no absorption occurred in the region near 1700 cm.$^{-1}$ normally expected for the C=O group, but instead a very broad band was found at lower frequency.[3] Similar observations on the dianion of diketocyclobutenediol, $C_4O_4^{-2}$, by Cohen, Lacher, and Park led them to propose a planar resonance-stabilized structure for this anion also.[4]

This paper reports a more complete investigation of the Raman and infrared spectra for $C_4O_4^{-2}$ and $C_5O_5^{-2}$ ions, undertaken to provide definite evidence for the structures of these anions. A normal coordinate treatment has been carried out on the vibrational data. The resulting force constants provide evidence concerning the nature of the bonds in the two anions.

Experimental

Preparation of samples used in these studies is described elsewhere.[1,5,6]

Raman Spectra.—A Cary model 81 automatic recording Raman spectrophotometer was used to determine the spectrum of solid $K_2C_4O_4$ and a 10% by weight aqueous solution of this salt. Rhodamin 5-GDN extra and Wratten 2A filters were used to remove ultraviolet light. The results obtained are shown in the first column of Table I.

Table I
Vibrational Frequencies of the $C_4O_4^{-2}$ Ion

Raman, cm.$^{-1}$	Infrared, cm.$^{-1}$	Adjustment (D_{4h})
	259s	$\nu_4(A_{2u})$ out-of-plane CO bending
294w dp		$\nu_6(B_{1g})$ in-plane CO bending
	350m	$\nu_{14}(E_u)$ in-plane CO bending
647s dp		$\nu_{10}(B_{2g})$ ring bending
(662)vw[a]		$\nu_{11}(E_g)$ out-of-plane CO bending
723s p		$\nu_2(A_{1g})$ ring breathing
	1090s	$\nu_{13}(E_u)$ CC stretching
1123vs dp		$\nu_5(B_{1g})$ CC stretching
1329vw		$\nu_2 + \nu_{11}$
	1530vs, v. broad	$\nu_{12}(E_u)$ CO stretching
1593s dp		$\nu_3(B_{2u})$ CO stretching
	1700vw	
1794w p		$\nu_1(A_{1g})$ CO stretching
	2200w	$\nu_5 + \nu_{13}$

[a] Observed only in the solid.

The Raman spectrum of $K_2C_5O_5$ was obtained on a 7% by weight aqueous solution, using a spectrometer at the Mellon Institute in Pittsburgh, Pa.[7,8] Because croconate ion has a yellow

(1) R. West, H. Y. Niu, D. L. Powell, and M. V. Evans, *J. Am. Chem. Soc.*, **82**, 6204 (1960).

(2) R. West and D. L. Powell, *ibid.*, **85**, 2577 (1963).

(3) K. Yamada, N. Mizuno, and Y. Hirata, *Bull. Chem. Soc. Japan*, **31**, 543 (1958).

(4) S. Cohen, J. R. Lacher, and J. D. Park, *J. Am. Chem. Soc.*, **81**, 3480 (1959).

(5) R. West, H. Y. Niu, and M. Ito, *ibid.*, **85**, 2584 (1963).

(6) H. Y. Niu, Thesis, University of Wisconsin, 1962.

(7) F. A. Miller and R. G. Inskeep, *J. Chem. Phys.*, **18**, 1519 (1950).

(8) F. A. Miller, L. R. Cousins, and R. B. Hannan, *ibid.*, **23**, 2127 (1955).

color in solution, the 5461 Å. mercury line was used for excitation. Other experimental conditions were as described by Miller and Carlson.[9] Results are given in Table II.

Table II
Vibrational Frequencies of the $C_5O_5^{-2}$ Ion

Raman, cm.$^{-1}$	Infrared, cm.$^{-1}$	Assignment (D_{5h})
	248s	$\nu_4(A'')$ out-of-plane CO bending
	350vw	
	374m	$\nu_7(E_1')$ in-plane CO bending
555s dp		$\nu_{11}(E_2')$ ring bending
637m p		$\nu_2(A_1')$ ring breathing
	795w	$\nu_4 + \nu_{11}$
	1100w	$\nu_8(E_1')$ CC stretching
1243m dp		$\nu_{10}(E_2')$ CC stretching
	1325w	
	1570vs, v. broad	$\nu_2(E_1')$ CO stretching
1591s dp		$\nu_9(E_2')$ CO stretching
	1660w	$\nu_{11} + \nu_6$
1718w p		$\nu_1(A_1')$ CO stretching
	1740w	$\nu_2 + \nu_6$
	2120vw	$\nu_5 + \nu_{11}$
	3150vw	$\nu_5 + \nu_9$ or $2 \times \nu_5$

Infrared Spectra.—A Baird model 4-55 infrared spectrometer was used for the sodium chloride region, a Beckman model IR-4 with a cesium bromide prism was used for the region 660–300 cm.$^{-1}$, and a small grating instrument at the Mellon Institute was used for the region 300–185 cm.$^{-1}$.[10] The spectra of the solid potassium salts were observed as mulls in Nujol. The results obtained are given in the second column of Tables I and II. The spectra of $K_2C_4O_4$ and $K_2C_5O_5$ are very similar and are quite simple, showing only four strong bands over the entire range from 200 to 4000 cm.$^{-1}$. The band near 1500 cm.$^{-1}$ is very strong and extremely broad; this type of absorption is characteristic of salts of the $C_nO_n^{-2}$ ions.

The infrared spectra of $Na_2C_4O_4$ and $Na_2C_5O_5$ were also studied briefly. These spectra were generally similar to those of the corresponding dipotassium salts, but contained a few extra bands. It therefore seemed likely that the local symmetry of the anions was lower in the sodium than in the potassium salts, and it was assumed that the spectrum of the latter would most nearly represent that of the anion itself.

Vibrational Assignments.—Assignments were made on the basis of D_{4h} and D_{5h} symmetry for $C_4O_4^{-2}$ and $C_5O_5^{-2}$, respectively (see Discussion section). The distribution of normal vibrations among various symmetry species, their approximate vibrational modes, and the selection rules are given for $C_4O_4^{-2}$ and $C_5O_5^{-2}$ in Tables III and IV.

(1) **$C_4O_4^{-2}$ Ion. A_{1g} Species.**—The totally symmetric vibrations are easily identified from the polarized Raman lines which fall at 723 and 1794 cm.$^{-1}$. The former is assigned to the ring breathing vibration ν_2 and the latter to the symmetrical CO stretching vibration ν_1. A totally symmetric fundamental vibration usually gives a strong Raman line because it is generally accompanied with a great change in polarizability. However, in the $C_4O_4^{-2}$ ion, the ν_1 vibration of 1794 cm.$^{-1}$ was observed as a rather weak Raman line. An unusual weak Raman intensity was also observed for the corresponding totally symmetric vibration of the $C_5O_5^{-2}$ ion.

B_{1g} Species.—The vibrations in this species, ν_5 and ν_8, are active only in the Raman spectrum and the corresponding Raman lines should be depolarized. A strong Raman line of 1123 cm.$^{-1}$ is reasonably assigned to the C–C stretching vibration ν_5. The in-plane CO bending vibration, ν_6, will be expected to give the lowest frequency in the Raman spectrum, and a Raman line of 294 cm.$^{-1}$ was assigned to this mode.

(9) F. A. Miller and G. L. Carlson, *Spectrochim. Acta*, **17**, 977 (1961).

(10) F. A. Miller, G. L. Carlson, and W. B. White, *ibid.*, **15**, 709 (1959).

Table III
Normal Vibrations of the $C_4O_4^{-2}$ Ion

Symmetry species (D_{4h})	Selection rule	Number of normal vibration	Vibrational mode
A_{1g}	R.(p)	ν_1	Symmetrical CO stretching
		ν_2	Ring breathing
A_{2g}	Inactive	ν_3	In-plane CO bending
A_{2u}	I.R.	ν_4	Out-of-plane CO bending
B_{1g}	R.(dp)	ν_5	CC stretching
		ν_6	In-plane CO bending
B_{1u}	Inactive	ν_7	Out-of-plane CO bending
		ν_8	Ring twisting
B_{2g}	R.(dp)	ν_9	CO stretching
		ν_{10}	Ring bending
E_g	R.(dp)	ν_{11}	Out-of-plane CO bending
E_u	I.R.	ν_{12}	CO stretching
		ν_{13}	CC stretching
		ν_{14}	In-plane CO bending

Table IV
Normal Vibrations of the $C_5O_5^{-2}$ Ion

Symmetry species (D_{5h})	Selection rule	Number of normal fundamental	Vibrational mode
A_1'	R.(p)	ν_1	Symmetrical CO stretching
		ν_2	Ring breathing
A_2'	Inactive	ν_3	In-plane CO bending
A_2''	I.R.	ν_4	Out-of-plane CO bending
E_1'	I.R.	ν_5	CO stretching
		ν_6	CC stretching
		ν_7	In-plane CO bending
E_1''	R.(dp)	ν_8	Out-of-plane CO bending
E_2'	R.(dp)	ν_9	CO stretching
		ν_{10}	CC stretching
		ν_{11}	Ring bending
		ν_{12}	In-plane CO bending
E_2''	Inactive	ν_{13}	Ring twisting
		ν_{14}	Out-of-plane CO bending

Table V
Symmetry Coordinates for In-Plane Vibrations of the $C_4O_4^{-2}$ Ion

Symmetry species (D_{4h})		Symmetry coordinate
A_{1g}	S_1	$(\Delta s_1 + \Delta s_2 + \Delta s_3 + \Delta s_4)/2$
	S_2	$(\Delta t_1 + \Delta t_2 + \Delta t_3 + \Delta t_4)/2$
A_{2g}	S_3	$s_0(\Delta\beta_1 + \Delta\beta_2 + \Delta\beta_3 + \Delta\beta_4)/2$
B_{1g}	S_4	$(\Delta t_1 - \Delta t_2 + \Delta t_3 - \Delta t_4)/2$
	S_5	$s_0(\Delta\beta_1 - \Delta\beta_2 + \Delta\beta_3 - \Delta\beta_4)/2$
B_{2g}	S_6	$(\Delta s_1 - \Delta s_2 + \Delta s_3 - \Delta s_4)/2$
	S_7	$t_0(\Delta\alpha_1 - \Delta\alpha_2 + \Delta\alpha_3 - \Delta\alpha_4)/2$
E_u	S_8	$(\Delta s_1 - \Delta s_3)/\sqrt{2}$
	S_9	$(\Delta t_1 - \Delta t_2 - \Delta t_3 + \Delta t_4)/2\sqrt{2} - t_0(\Delta\alpha_1 - \Delta\alpha_2)/2$
	S_{10}	$s_0(\Delta\beta_2 - \Delta\beta_4)/\sqrt{2}$

B_{2g} **Species.**—There are two vibrations in this species, ν_9 and ν_{10}, and they also should give depolarized Raman lines. A depolarized Raman line at 1593 cm.$^{-1}$ is readily assigned to the CO stretching vibration ν_9. Only one Raman line with a moderate intensity remains unassigned, at 647 cm.$^{-1}$, and it may be assigned to the ring bending vibration ν_{10}.

E_u **Species.**—The vibrations of ν_{12}, ν_{13}, and ν_{14} belong to this species and they are active only in the infrared spectrum. The very strong and very broad infrared band centered at 1530 cm.$^{-1}$ and a band at 1090 cm.$^{-1}$ should be assigned to the CO stretching vibration ν_{12} and the CC stretching vibration ν_{13}, respectively. One of the two strong bands at 259 and 350 cm.$^{-1}$ should be ν_{14}. According to normal coordinate calculations for the $C_4O_4^{-2}$ ion, ν_{14} always has a higher frequency than ν_6 for sets of reasonable values of the force constants. Therefore, the 350 cm.$^{-1}$ band was tentatively assigned as ν_{14}.

Out-of-Plane CO Bending Vibrations.—Two out-of-plane CO bending vibrations are expected to appear in the spectrum. One of them is ν_{11} of species E_g and the other is ν_4 of species A_{2u}. The former is Raman active and the latter infrared active. A very weak Raman line of 662 cm.$^{-1}$ which was observed in the solid state is tentatively assigned as ν_{11}. In the CH_3COO^- ion, the corresponding out-of-plane vibration was found at 616 cm.$^{-1}$.[11] A strong infrared band of 259 cm.$^{-1}$ which remained unassigned is tentatively assigned to ν_4.

The assignments thus obtained are also summarized in the last column of Table I.

(2) **$C_5O_5^{-2}$ Ion.**—On the bases of the close similarities in the selection rules and the spectra between the $C_4O_4^{-2}$ and $C_5O_5^{-2}$ ions, the vibrational assignment for $C_5O_5^{-2}$ was carried out along the same lines as indicated above for the $C_4O_4^{-2}$ ion. The assignments obtained are given in the last column of Table II.

Normal Coordinate Treatment of In-Plane Vibrations of the $C_4O_4^{-2}$ and $C_5O_5^{-2}$ Ions.—Normal coordinate treatments for the in-plane vibrations of these ions were carried out using the basic Urey–Bradley force field. The standard FG matrix method was used for the calculation of the normal coordinates.[12] The internal coordinates are shown in Fig. 1. By using these internal coordinates, sets of symmetry coordinates were constructed on the basis of D_{4h} and D_{5h} symmetries. These are given in Tables V and VI, where the coordinates β_i have the same meaning as defined by Crawford and Miller,[13] that is

$$\beta_1 = \frac{1}{2}(\phi_1 - \phi_2)$$
$$\beta_2 = \frac{1}{2}(\phi_3 - \phi_4)$$

According to Califano and Crawford,[14] for species containing redundant coordinates, symmetry coordinates were chosen orthogonal to them.

The Urey–Bradley potentials can be expressed in the form

For $C_4O_4^{-2}$

$$2V = \sum_{i=1}^{4}[K_{co}(\Delta s_i)^2 + 2\sum_{i=1}^{4}K_{co}'s_0\Delta s_i + \sum_{i=1}^{4}K_{cc}(\Delta t_i)^2 +$$

$$2\sum_{i=1}^{4}K_{cc}'t_0\Delta t_i + \sum_{i=1}^{4}H_{ccc}(t_0\Delta\alpha_i)^2 + 2\sum_{i=1}^{4}H_{ccc}'t_0^2\Delta\alpha_i +$$

$$\sum_{i=1}^{4}H_{cco}(s_0\Delta\beta_i)^2 + 2\sum_{i=1}^{4}H_{cco}'s_0^2\Delta\beta_i + \sum_{i=1}^{4}F_{co}[(\Delta q_{c_jc_{j+1}})^2 +$$

$$(\Delta q_{c_jo_{j-1}})^2] + 2\sum_{i=1}^{4}F_{co}'q_{co}(\Delta q_{c_jo_{j+1}} + \Delta q_{c_jo_{j-1}}) +$$

$$\sum_{i=1}^{4}F_{oo}(\Delta q_{o_jo_{i+1}})^2 + 2\sum_{i=1}^{4}F_{oo}'q_{oo}\Delta q_{o_jo_{i+1}} +$$

$$\frac{1}{2}\sum_{i=1}^{4}F_{cc}(\Delta q_{c_jc_{i+2}})^2 + \sum_{i=1}^{4}F_{cc}'q_{cc}(\Delta q_{c_jc_{i+2}})]$$

For $C_5O_5^{-2}$

$$2V = \left[\sum_{i=1}^{5}K_{co}(\Delta s_i)^2 + 2\sum_{i=1}^{5}K_{co}'s_0\Delta s_i +\right.$$

$$\sum_{i=1}^{5}K_{cc}(\Delta t_i)^2 + 2\sum_{i=1}^{5}K_{cc}'t_0\Delta t_i + \sum_{i=1}^{5}H_{ccc}(t_0\Delta\alpha_i)^2 +$$

$$2\sum_{i=1}^{5}H_{ccc}'t_0^2\Delta\alpha_i + \sum_{i=1}^{5}H_{cco}(s_0\Delta\beta_i)^2 +$$

$$2\sum_{i=1}^{5}H_{cco}'s_0^2\Delta\beta_i + \sum_{i=1}^{5}F_{co}[(\Delta q_{c_jo_{j+1}})^2 + (\Delta q_{c_jo_{j-1}})^2] +$$

$$2\sum_{i=1}^{5}F_{co}'q_{co}(\Delta q_{c_jo_{j-1}} + \Delta q_{c_jo_{j-1}}) +$$

$$\sum_{i=1}^{5}F_{oo}(\Delta q_{o_jo_{j+1}})^2 + 2\sum_{i=1}^{5}F_{oo}'q_{oo}\Delta q_{o_jo_{j+1}} +$$

$$\left.\sum_{i=1}^{5}F_{cc}(\Delta q_{c_jc_{j+2}})^2 + 2\sum_{i=1}^{5}F_{cc}'q_{cc}\Delta q_{c_jc_{j+2}}\right]$$

(11) K. Nakamura, *J. Chem. Soc. Japan, Pure Chem. Sect.*, **79**, 1411 (1958).

(12) E. B. Wilson, J. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw–Hill Book Co., Inc., New York, N. Y., 1955.

(13) B. L. Crawford and F. A. Miller, *J. Chem. Phys.*, **17**, 249 (1949).

(14) S. Califano and B. L. Crawford, *Spectrochim. Acta.* **16**, 889 (1960).

TABLE VI

SYMMETRY COORDINATES FOR IN-PLANE VIBRATIONS OF THE $C_5O_5^{-2}$ ION

Symmetry species (D_{5h})		Symmetry coordinate
A_1'	S_1	$(\Delta s_1 + \Delta s_2 + \Delta s_3 + \Delta s_4 + \Delta s_5)/\sqrt{5}$
	S_2	$(\Delta t_1 + \Delta t_2 + \Delta t_3 + \Delta t_4 + \Delta t_5)/\sqrt{5}$
A_2'	S_3	$s_0(\Delta\beta_1 + \Delta\beta_2 + \Delta\beta_3 + \Delta\beta_4 + \Delta\beta_5)/\sqrt{5}$
E_1'	S_4	$(\Delta s_1 + \cos \varphi\Delta s_2 + \cos 2\phi\Delta s_3 + \cos 2\phi\Delta s_4 + \cos \phi\Delta s_5)\sqrt{2/5}$
	S_5	$0.2533[(1 + \cos \phi)\Delta t_1 + (\cos \phi + \cos 2\phi)\Delta t_2 + 2\cos 2\phi\Delta t_3 + (\cos \phi + \cos 2\phi)\Delta t_4 + (1 + \cos \phi)\Delta t_5] - 0.7617 t_0[\Delta\alpha_1 + \cos 2\phi\Delta\alpha_2 + \cos 2\phi\Delta\alpha_3 + \cos \phi\Delta\alpha_5]\sqrt{2/5}$
	S_6	$0.3326 s_0[(1 - \cos 2\phi)\Delta\beta_2 + (\cos \phi - \cos 2\phi)\Delta\beta_3 + (\cos 2\phi - \cos \phi)\Delta\beta_4 + (\cos 2\phi - 1)\Delta\beta_5]$
E_2'	S_7	$(\Delta s_1 + \cos 2\phi\Delta s_2 + \cos \phi\Delta s_3 + \cos \phi\Delta s_4 + \cos 2\phi\Delta s_5)\sqrt{2/5}$
	S_8	$1.023[(1 + \cos 2\phi)(\Delta t_1 + \Delta t_5) + (\cos \phi + \cos 2\phi) \times (\Delta t_2 + \Delta t_4) + 2\cos \phi\Delta t_3]$
	S_9	$t_0[\Delta\alpha_1 + \cos 2\phi(\Delta\alpha_2 + \Delta\alpha_5) + \cos \phi(\Delta\alpha_3 + \Delta\alpha_4)]\sqrt{2/5}$
	S_{10}	$0.538 s_0[(1 - \cos \phi)(\Delta\beta_2 - \Delta\beta_5) + (\cos 2\phi - \cos \phi) \times (\Delta\beta_3 - \Delta\beta_4)]$

$\phi = 72°$

where K_{co}, K_{cc}, H_{ccc}, and H_{cco} have the usual meanings, F_{co}, F_{oo}, and F_{cc} are repulsion terms between nonbonded atoms, s_0 and t_0 are the bond distances of the CO and CC bonds, and q_{co}, q_{oo}, and q_{cc} are the distances between nonbonded atoms. The linear terms are indicated with a prime. The potential function was rewritten in terms of the internal coordinates, and the F matrix obtained was factored using the same symmetry coordinates as employed for the construction of the symmetrized G matrix.[15]
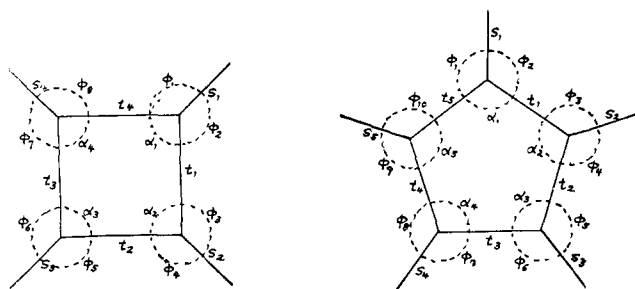

Fig. 1.—Internal coordinates.

In the calculation, the usual assumption was made that linear terms are -0.1 of the corresponding quadratic terms.[16] Bond lengths are not available for these ions, and so distances $s_0 = 1.22$ Å. and $t_0 = 1.47$ Å. were assumed. It was found that small changes in the bond distances do not greatly affect the calculated frequencies. The force constants were refined by the least-squares method.[17] The calculated results are given in Tables VII and

TABLE VII

CALCULATED AND OBSERVED FREQUENCIES FOR IN-PLANE VIBRATIONS OF THE $C_4O_4^{-2}$ ION

Species (D_{4h})	Number of normal vibration	ν_{obsd}, cm.$^{-1}$	ν_{calcd}, cm.$^{-1}$	Difference, %
A_{1g}	ν_1	1794	1778	-0.9
	ν_2	723	730	$+1.0$
B_{1g}	ν_5	1123	1128	$+0.5$
	ν_6	294	299	$+1.7$
B_{2g}	ν_9	1593	1633	$+2.5$
	ν_{10}	647	635	-1.9
E_u	ν_{12}	1530	1544	$+1.0$
	ν_{13}	1090	1070	-1.8
	ν_{14}	350	354	$+1.1$

VIII together with the observed frequencies. Agreement between observed and calculated results is very good. Maximum deviation of the calculated from the observed frequencies is less than 3% for $C_4O_4^{-2}$ and about 4% for $C_5O_5^{-2}$. The force constants used in the calculations are listed in Table X.

Discussion

Structures of the $C_4O_4^{-2}$ and $C_5O_5^{-2}$ Ions.—Some possible structures for $C_4O_4^{-2}$ are shown in Fig. 2. In model I one of the C–C bonds is shorter than the others, and two of the C–O bonds are shorter than the other two. This model belongs to point group C_{2v} if all

(15) J. R. Scherer and J. Overend, *Spectrochim. Acta*, **17**, 719 (1961).

(16) Y. Morino, K. Kuchitsu, and T. Shimanouchi, *J. Chem. Phys.*, **20**, 726 (1952).

(17) D. E. Mann, L. Fano, J. H. Meal, and T. Shimanouchi, *ibid.*, **27**, 51 (1957).

TABLE VIII

CALCULATED AND OBSERVED FREQUENCIES FOR IN-PLANE VIBRATIONS OF THE $C_5O_5^{-2}$ ION

Species (D_{5h})	Number of normal vibration	ν_{obsd}, cm.$^{-1}$	ν_{calcd}, cm.$^{-1}$	Difference, %
A_1'	ν_1	1718	1652	-3.8
	ν_2	637	655	$+2.8$
E_1'	ν_5	1570	1605	$+2.2$
	ν_6	1100	1087	-1.2
	ν_7	374	372	-0.5
E_2'	ν_9	1591	1584	-0.4
	ν_{10}	1243	1223	-1.6
	ν_{11}	555	558	$+0.5$
	ν_{12}	..	357	...

the atoms are in the same plane. In models II–V, all of the C–C bonds and all of the C–O bonds are assumed to be equivalent; atoms lying above or below the plane are indicated by plus and minus signs. The symmetrical planar model V, of point group D_{4h}, has the highest
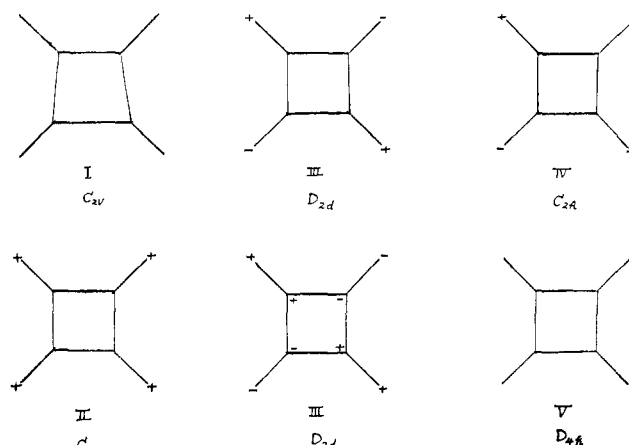

Fig. 2.—Possible structures of $C_4O_4^{-2}$ ion.

symmetry of all the models shown. The numbers of polarized Raman active fundamentals, the total number of infrared active and Raman active fundamentals, and the number of infrared–Raman coincidences were predicted from the selection rules for each of the models. These predictions are given in Table IX.

Eight lines are observed in the Raman spectrum of $C_4O_4^{-2}$ (Table I), of which two are polarized. The very weak line at 1329 cm.$^{-1}$ is most likely due to an overtone or combination, giving seven as the probable number of Raman active fundamentals. Similarly, the two weak bands in the infrared spectrum are best interpreted as combination or overtone bands, leaving four infrared active fundamentals. There is no vibrational frequency which appears both in the infrared and the Raman spectrum. The results are summarized in Table IX.

Comparison with predictions for the various models shows that model V gives a reasonable fit with the experimental data while all other models are excluded. Other highly unsymmetrical models for $C_4O_4^{-2}$ could have been assumed, but these would give an even larger number of frequencies than the models assumed here, and so are also excluded. It can therefore be concluded that $C_4O_4^{-2}$ has the symmetrical planar structure of the D_{4h} point group.

TABLE IX

COMPARISON OF PREDICTED AND OBSERVED BANDS FOR $C_4O_4^{-2}$ AND $C_5O_5^{-2}$

	$C_4O_4^{-2}$, predicted					$C_4O_4^{-2}$, $C_5O_5^{-2}$, $C_5O_5^{-2}$,		
						obsd.	pred.	obsd.
Model	I	II	III	IV	V			
Symmetry	C_{2v}	C_{4v}	D_{2d}	C_{2h}	D_{4h}		D_{5h}	
Polarized Raman fundamentals	7	3	4	5	2	2	2	2
Total Raman fundamentals	18	13	13	9	7	7	7	5
Total infrared fundamentals	15	7	7	9	4	4	4	3 or 4
Raman–infrared coincidences	15	7	7	0	0	0	0	0

The symmetrical planar model for $C_5O_5^{-2}$ belongs to point group D_{5h}. It is interesting that the predicted numbers of bands for this model are the same as for the symmetrical $C_4O_4^{-2}$ ion (Table IX). In fact, any ion $C_nO_n^{-m}$ with symmetrical planar structure should have seven Raman active fundamentals of which two should be polarized, four infrared active fundamentals, and no coincidences. If both $C_4O_4^{-2}$ and $C_5O_5^{-2}$ have symmetrical planar structures their spectra should be closely similar, and comparison of data in Tables I and II shows that this is indeed the case. Moreover, reasonably good agreement of the prediction based on D_{5h} symmetry with the observed numbers of bands (Table IX) further indicates that $C_5O_5^{-2}$ also has the symmetrical planar structure.

Force Constants and Bonding.—Urey–Bradley force constants for these ions and for some related species are shown in Table X. The CO stretching force constant, K_{co}, of $C_4O_4^{-2}$ is close to the value expected for a single C–O bond (5–6 mdynes/Å.)[18]; K_{co} increases to 6.72 mdynes/Å. in $C_5O_5^{-2}$, indicating an increase in the C–O bond order. However, the value found is lower than that for K_{co} in carboxylate ions.[11,19]

TABLE X

UREY–BRADLEY FORCE CONSTANTS IN MDYNES/Å.

	$C_4O_4^{-2}$	$C_5O_5^{-2}$	$C_2O_4^{-2}$	$OH_3CO_2^{-2}$	C_6H_6	$C_5H_5^{-}$
K_{oo}	5.60	6.72	7.60	7.20	..	..
K_{cc}	3.95	3.50	2.10	2.46	5.59	3.89
F_{oo}	0.45	0.38	0.60	0.50	..	..
F_{cc}	3.91	1.52	..	..	0.54[a]	0.70
F_{oo}	−0.09	−0.12	2.76	3.00	..	..
H_{occ}	0.14	0.24	0.28[c]	0.15[c]	..	..
H_{cco}	1.38	1.46	0.34	0.307	..	..
Data ref.	[b]	[b]	19	11	15	20

[a] For carbon atoms in *meta* positions.   [b] This work.   [c] H_{oco}.

The C–C stretching force constant K_{cc} decreases from $C_4O_4^{-2}$ to $C_5O_5^{-2}$, indicating that the double bond character of the C–C bonds decreases with increase of ring size. The opposite trends in K_{co} and K_{cc} with ring size are in agreement with molecular orbital calculations,[3] which predict increasing C–O bond order and decreasing C–C bond order with increasing ring size.

It is of special interest to compare the C–C force constants with those for other aromatic systems. As shown in Table X, K_{cc} for the oxocarbon anions is lower than that for benzene,[14] but is decidedly greater than

that for a single C–C bond. The observed C–C force constants are about equal to that obtained by a simple valence force field calculation for the aromatic cyclopentadienide ring in ferrocene.[20] These results support our view that these anions constitute a new aromatic series.[2,3]

The force constants show other unusual features. The repulsion force constant for the transannular carbon atoms in $C_4O_4^{-2}$ is very large (F_{cc} = 3.91). Such a large repulsion constant may be reasonable for non-bonded atoms constrained to short internuclear distances, particularly when they bear partial negative charges. As shown in Table X, large repulsion constants are also found for the nonbonded oxygen atoms in carboxylate anions. For $C_5O_5^{-2}$, F_{cc} drops to 1.52, indicating that the nonbonded repulsion drops off rapidly with increasing ring size. The repulsion force constant for nonbonded oxygen atoms is found to be negative for both $C_4O_4^{-2}$ and for $C_5O_5^{-2}$. Negative values were also reported by Califano and Crawford[14] for the interaction terms between two atoms in the *para* positions of benzene and *s*-triazine. As previously explained by these workers, negative terms are not unreasonable if we assume for the force between nonbonded oxygen atoms a model such as the Lennard-Jones potential, in which the repulsive term becomes negligible at long distances while the attractive term is still appreciable.

Comparing the values of bending force constants with those of the related substances, H_{cco} is found to be abnormally large. This may be due to a misassignment of the bending vibrations, or to unsuitability of the basic Urey–Bradley force field for bending vibrations in these ions. In order to check the latter possibility, several improvements of the Urey–Bradley force field were attempted. Recently, Overend and Wu[21] showed that an additional force constant, the intramolecular tension constant κ, is important to account for the observed frequencies of diborane, which contains a four-membered ring. This force constant might be important also for the oxocarbon ions, especially for $C_4O_4^{-2}$. Another important contribution to the force field may be the effect of resonance.[22] This effect may be taken into consideration by including additional interaction terms for the various pairs of the bonds. However, calculations showed that inclusion of these interaction and intramolecular tension terms does not greatly change the bending force constants H_{oco} and H_{cco}.

Recently, Shimanouchi[23] introduced the idea of bond flexibility in his work on the normal coordinate treatment of ethylene. It might be important to include bond flexibility in the potentials of $C_4O_4^{-2}$ and $C_5O_5^{-2}$ ions, in which the C–C bonds may be regarded as bent bonds. According to the method proposed by Shimanouchi,[23] we assumed four weightless atoms at the midpoints of the C–C bonds of $C_4O_4^{-2}$. The flexibility of the C–C bond is expressed by means of bending force constant for the angles made by the assumed weightless atoms. The inclusion of bond flexibility slightly improved the values of the bending force constants, raising H_{oco} to 0.2 and lowering H_{cco} to 1.1, but the values are still unusual.[24]

(18) M. Margottin-Maclou, *J. phys. radium*, **21**, 634 (1960); C. Tanaka, K. Kuratani, and S. Mizushima, *Spectrochim. Acta*, **9**, 265 (1957).

(19) H. Murata and K. Kawai, *J. Chem. Phys.*, **25**, 589 (1956).

(20) E. R. Lippincott and R. D. Nelson, *Spectrochim. Acta*, **10**, 307 (1958).

(21) Private communication from Drs. Overend and Wu of the University of Minnesota.

(22) J. R. Scherer and J. Overend, *Spectrochim. Acta*, **17**, 719 (1961).

(23) T. Shimanouchi, *J. Chem. Phys.*, **26**, 594 (1957).

(24) NOTE ADDED IN PROOF.—A recent communication on the crystal structure of diammonium croconate (N. C. Baenziger, J. J. Hegenbarth, and D. G. Williams, *J. Am. Chem. Soc.*, **85**, 1539 (1963)) shows that the croconate ion is symmetrical and planar in this salt, with bond distances 1.45 (C–C) and 1.25 (C–O) Å., quite close to those used in our normal coordinate treatment.


New Aromatic Anions. V. The Synthesis of Diketocyclobutenediol and its Conversion to Octahydroxycyclobutane

BY ROBERT WEST, HSIEN YING NIU, AND MITSUO ITO

Mild oxidation of diketocyclobutenediol (1) with nitric acid at 0° yields the compound octahydroxycyclobutane IV. The infrared and Raman spectra of IV and its octadeuterio analog indicate that it has the planar D_{4h} structure. The preparation of I from 1,2-dichloro-3,3,4,4-tetrafluorocyclobutene is also discussed, and structures are presented for intermediate compounds in this synthesis.

Following publication of the synthesis of diketocyclobutenediol ("squaric acid," I) by Cohen, Lacher, and Park,[1] the relationship of this substance to the five- and six-ring compounds croconic acid (II) and rhodizonic acid (III) was pointed out and it was suggested
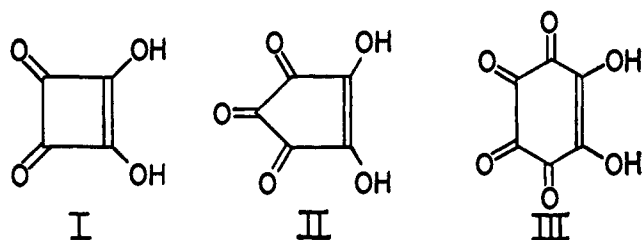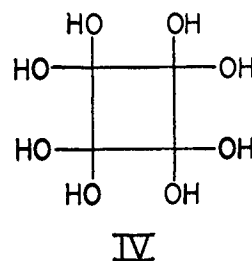

that the dianions of these enols represent a series of totally delocalized aromatic anions.[2] Compounds II and III, when treated with nitric acid, give rise to the interesting oxidation products leuconic acid, C_5O_5·$5H_2O$,[3] and triquinoyl octahydrate, C_6O_6·$8H_2O$.[4] The structure of these substances has been controversial for many years.[5,6] Person and Williams found no absorption in the carbonyl region of the infrared spectra of leuconic acid and triquinoyl, and on that basis favored totally hydroxylated structures for these compounds.[7]

In view of the relationship of diketocyclobutenediol (I) to II and III, it was of interest to determine whether compound I would yield a related oxidation product. Treatment of I with nitric acid or bromine at room temperature or above converted it to carbon dioxide and oxalic acid. At 0°, however, brief treatment with dilute nitric acid or bromine oxidized I smoothly to a colorless crystalline substance with the composition $C_4H_8O_8$. This compound could be reduced back to I by sulfur dioxide.

A study of the infrared spectrum of solid $C_4H_8O_8$ and the Raman spectrum of its acidic aqueous solution was undertaken to determine its structure. The octadeuterio analog $C_4D_8O_8$, obtained by oxidation of deuterated I with bromine, was also studied by these tech-

niques. The results and tentative assignments are shown in Table I. The data indicate that $C_4H_8O_8$ has the octahydroxycyclobutane structure IV, with a planar or nearly planar ring configuration. No ab-

sorption bands other than the O–H stretching mode appear above 1300 cm.$^{-1}$ so the compound cannot have a free carbonyl group either in the solid or in aqueous acidic solution. The infrared spectra are extremely simple, showing only five bands above 400 cm.$^{-1}$, of which three are associated with the motion of the hydrogen atoms. There are no coincidences between the Raman and infrared spectra, indicating by the rule of mutual exclusion that the molecule has a center of symmetry. Two polarized Raman lines are found in the expected region.[8] The findings are all consistent with a planar symmetrical D_{4h} model, but a slight torsional deformation of the ring cannot definitely be excluded.

TABLE I
VIBRATIONAL FREQUENCIES IN CM.$^{-1}$ FOR OCTAHYDROXYCYCLOBUTANE[a]

$C_4(OH)_8$	$C_4(OD)_8$	Assignment (D_{4h} model)
165 R	166 R	
405 R,p	390 R,p	OCO scissoring, A_{1g}
465 R,d	455 R,d	
707 R,p	682 R,p	C–C stretching, A_{1g}
900 IR	805 IR	O–H deformation
1080 IR,s	1065 IR,s	C–O stretching, A_{2u} or E_u
1160 IR,s	1150 IR,s	C–O stretching, A_{2u} or E_u
1215 R	1225 R	C–O stretching
1300 IR	960 IR	O–H deformation
3250 IR,s	2450 IR,s	O–H stretching

[a] R = Raman, IR = infrared, s = strong, p = polarized, d = depolarized.

Octahydroxycyclobutane decomposes at about 140° with liberation of carbon dioxide. Aqueous solutions

(1) S. Cohen, J. R. Lacher, and J. D. Park, *J. Am. Chem. Soc.*, **81**, 3480 (1959).

(2) R. West, H. Y. Niu, D. L. Powell, and M. V. Evans, *ibid.*, **82**, 6204 (1960).

(3) H. Will, *Ann.*, **118**, 177 (1858).

(4) J. U. Lerch, *ibid.*, **124**, 20 (1862).

(5) R. Nietzki and T. Benckiser, *Ber.*, **18**, 499 (1885); **19**, 293 (1886); R. Nietzki and H. Rosemann, *ibid.*, **22**, 916 (1889).

(6) R. P. Temple, *Research* (London), **1**, 280 (1948); P. Souchay and F. Tatibouet, *J. chim. phys.*, **49**, C108 (1952).

(7) W. B. Person and D. G. Williams, *J. Phys. Chem.*, **61**, 1016 (1957). We find that triquinoyl octahydrate has a band of medium intensity at 1650 cm.$^{-1}$, and that leuconic acid has a weak band at 1625 cm.$^{-1}$. However, it is probable that these bands do not represent carbonyl stretching modes.

(8) The D_{4h} model is predicted to have three polarized Raman lines; reasonable structures with lower symmetry should have a larger number of polarized Raman lines. See G. Herzberg, "Molecular Spectra and Molecular Structure," Vol. II, D. Van Nostrand Co., Inc., Princeton, N. J., 1945, Chapter II.