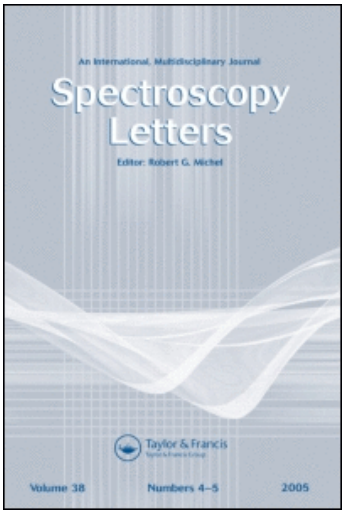

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Molecular Vibrational Constants and Chemical Bonding in the Cyclic Oxocarbon Dianions $C_n0_n^{-2}$ (n=3, 4 and 5)

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MOLECULAR VIBRATIONAL CONSTANTS AND CHEMICAL BONDING IN THE CYCLIC OXOCARBON DIANIONS $C_nO_n^{-2}$ (n=3, 4 and 5)

Key words: oxocarbons, force constants.

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ABSTRACT

By means of an **ab initio** force field and the mean amplitudes of vibration of the cyclic oxocarbon dianions $C_nO_n^{-2}$ with n= 3, 4 and 5, it has been found that the ground-state aromaticity order in the series is: deltate (n=3) > squarate (n=4) > croconate (n=5) ion. The reactivity of these molecules with respect to an electrophilic attack follows the order croconate > squarate > deltate ion.

INTRODUCTION.

The observation of a vibrational frequency is just a simple criterion for the detection of a chemical bond. Chemical bonds, characteriyed by a relatively high vibrational frequency, a small mean amplitude of vibration and a large force constant value, may be regarded as pure covalent bonds. They will be highly directional, or rigid, in comparison to ionic bonds which become more flexible with increasing ioni-

TABLE 1
Most relevant force constants f (mdyn. $\AA^{-1}$)

	$C_3O_3^{-2}$	$C_4O_4^{-2}$	$C_5O_5^{-2}$
f(C-O)	8.18	9.16	10.59
f(C-C)	6.60	5.80	5.45
f(CCO)	1.49	1.57	1.95
f(CCC)	8.30	12.06	16.16
f(CCCO)	0.20	1.49	2.26
f(OCCO)	-	1.05	1.10
f(CCCC)	-	0.96	0.86

city. As a result, the chemical bonds associated with the lowest force constant value, corresponding to the largest mean amplitude, will have the greatest reactivity [1].

In the present work the characteristics of the chemical bonds in the aromatic series [2,3] $C_3O_3^{-2}$, $C_4O_4^{-2}$ and $C_5O_5^{-2}$ are discussed in terms of their fundamental frequencies, the ab-initio force constants and the mean amplitudes of vibration.

CALCULATIONS.

Normal coordinate analysis.

The fundamental frequencies of $C_3O_3^{-2}$, $C_4O_4^{-2}$ and $C_5O_5^{-2}$ were selected from vibrational data previously reported [4,5]; the analysis of the infrared and Raman spectra confirm their predicted D_{3h}, D_{4h} and D_{5h} symmetries. However, the solid state spectra of $C_3O_3^{-2}$ contains very weak extra bands which can be assigned as effects of reduced symmetry. The normal coordinate treatment for the three molecules was carried out using the ab-initio geometrical parameters and force fields reported by Puebla and Ha [6]. The most relevant force constants **f**, which are in good agreement with other published data for similar molecules [4,5,7], are shown in Table 1.

The Wilson matrix G was set up in the internal coordinate representation [8]. The internal coordinate sets were chosen conforming to satisfy the requirements that they must be the most complete, representative and symmetrically compatible; the elimination of certain groups of symmetrically equivalent internal coordinates does not result in a loss of generality [9]. For the deltate dianion (symmetry D_{3h}), twelve internal coordinates were chosen: the changes in 5 bonds, 3 CO (q) and 2 CC (D), four in-plane angles, 1 CCC (α) and 3 CCO (ß), and three out-of-plane angles CCCO (ρ) (see Fig. 1). In the case of squarate dianion $C_4O_4^{-2}$, the eighteen internal coordinates were chosen as follows: 3 D, 4 q, 2α, 4 ß, and only one ρ, three external torsions described by the diedral angles $O_1C_2\widehat{C_3}C_2C_3O_4$ (τ), and one internal torsion corresponding to the diedral angle $C_1C_2\widehat{C_3}C_2C_3C_4$ (χ). Twenty four internal coordinates describe the expected 14 normal modes for the croconate dianion $C_5O_5^{-2}$. They are displayed in Fig. 1. The results of the secular equation are in agreement with both the expected E modes degeneracy and the observed frequencies (see Table 2). The theoretical assignment was carried out using the normal vibration modes form matrix (L) and the Potential Energy Distribution (P.E.D.).

MEAN AMPLITUDES OF VIBRATION.

The potential fields previously reported [6] were used to calculate the mean amplitudes (ℓ) for the principal interactions. The ℓ values were obtained according to well established methods [10,11]. The results at 298 K are given in Table 3, along with the interatomic distances [6]. Experimental ℓ values have not been published for the present dianions, but several other independent studies of molecules with similar chemical groups are available [7,12].

DISCUSSION.

A qualitative band assignment based mainly on the frequencies normally associated with the CO and CC bonds will probably lead to an erroneus interpretation of these vibrational modes in the molecules $C_3O_3^{-2}$, $C_4O_4^{-2}$ and $C_5O_5^{-2}$. In fact, these molecules have no infrared absorptions in the usual carbonyl region, but instead they show a very broad and strong band centered near 1500 cm^{-1}. On the other hand,

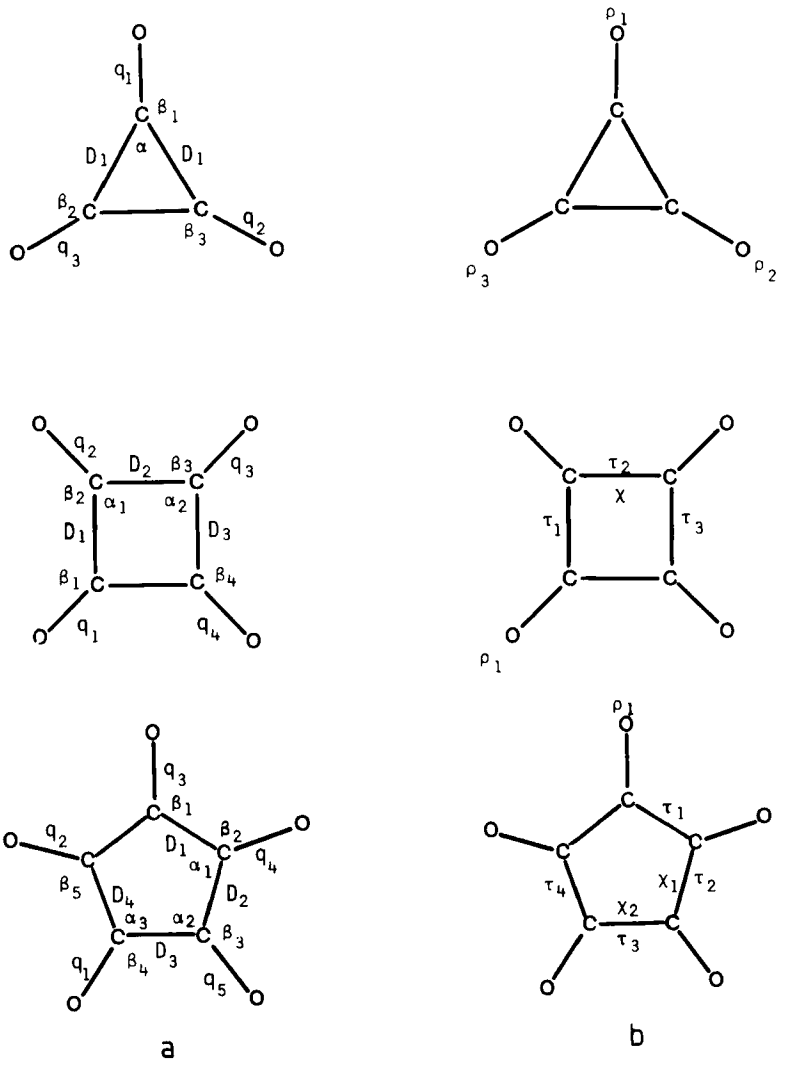

Fig. 1.- Internal coordinates. a) in-plane vibrations b) out-of-plane vibrations.

TABLE 2

Observed[a,b] and Calculated Frequencies for $C_3O_3^{-2}$, $C_4O_4^{-2}$ and $C_5O_5^{-2}$ ions.

$C_3O_3^{-2}$					$C_4O_4^{-2}$					$C_5O_5^{-2}$				
$\nu_{exp.}$[a]	$\nu_{calc.}$		Assign.	Sym.	$\nu_{exp.}$[b]	$\nu_{calc.}$		Assign.	Sym.	$\nu_{exp.}$[b]	$\nu_{calc.}$		Assign.	Sym.
1835 IR,Rp	1784		νCC+νCO	A_1'	1794 Rp	1781		νCC+νCO	A_{1g}	1718 Rp	1872		νCO+νCC	A_1'
					1593 Rdp	1654		α+νCO	B_{2g}	1591 Rdp	1756	1773 1740	νCO+νCC+α	E_2'
1470 IR,Rdp	1466	1473 1459	νCC+νCO+α	E'	1530 IR	1412	1422 1403	νCC+νCO	E_u	1570 IR	1578	1503 1575	νCO+νCC	E_1'
										1243 Rdp	1307	1315 1298	νCC	E_2'
					1123 Rdp	1159		νCC	B_{1g}					
995 IR,Rdp	995	999 991		E'	1090 IR	1065	1085 1042	νCO+α+νCC	E_u	1100 IR	1141	1141 1141	νCC+δCO	E_1'
											1130	1130 1130	δCO	E_2'
					647 Rdp	643		α	B_{2g}	555 Rdp	591	584 579	α	E_2'
	863		δCO	A_2''		879		δCO	A_{2g}		924		δCO	A_2''
803 IR,Rdp	782		νCC+νCO	A_1'	723 Rp	710		νCC+νCO	A_{1g}	637 R	640		νCC+νCO	A_1'
689 IR,Rdp	596	674 517	ρCO	E''	662 R	672	737 607	ρCO+τ	E_g		501	501 501	τ+ρCO	E_2''
						519		τ+ρCO	B_{1u}		350	370 331	ρCO+τ	E_1''
341 IR,Rdp	321	345 340	δCO+α	E'	350 IR	322	324 320	δCO+α	E_u	374 IR	365	366 364	δCO+α	E_1'
					294 Rdp	286		δCO	B_{1g}					
258 IR	365		ρCO	A_2''	259 IR	167		τ+χ	A_{2u}	248 IR	287		τ+ρCO	A_2''
											100	146 54	χ+ρCO	E_2''

[a] Ref. [5]

[b] Ref. [4]

TABLE 3

Mean amplitudes of vibration ℓ (Å) at 298 K and the interatomic distances r_e (Å)

	$C_3O_3^{-2}$	$C_4O_4^{-2}$	$C_5O_5^{-2}$
ℓ (C-C)	0.0416	0.0433	0.0460
ℓ (C-O)	0.0414	0.0405	0.0350
r_e (C-C)	1.4284	1.4783	1.4628
r_e (C-O)	1.2847	1.2573	1.2484

TABLE 4

Potential energy distribution among the internal coordinates.

	ν_{exp}	ν_{calc}	Assign. (P.E.D.)	#[a]
$C_3O_3^{-2}$	1835	1784	47 ν_{CC} + 36 ν_{CO}	ν_1
	803	782	40 ν_{CC} + 20 ν_{CO}	ν_2
$C_4O_4^{-2}$	1794	1781	22 ν_{CC} + 32 ν_{CO}	ν_1
	723	710	50 ν_{CC} + 10 ν_{CO}	ν_2
$C_5O_5^{-2}$	1718	1872	12 ν_{CC} + 30 ν_{CO}	ν_1
	637	640	60 ν_{CC} + 8 ν_{CO}	ν_2

[a]Number of normal fundamental

unusual weak and polarized Raman lines have been observed near 1800 and 720 cm^{-1} [4,5]. For the three dianions, the PED indicates that most of the vibrational modes are highly coupled, particularly the totally symmetric vibrations ν_1 and ν_2 (see Table 4). The frequency drop of ν_1 and ν_2 can be explained directly from the changes in the force constants associated to the stretching C-C (ν_{CC}) and C-O (ν_{CO}). In fact, the opposite trends if f (CO) and f(CC) predict increasing CO bond order and decreasing CC bond order with increasing ring size (see Table 1). Thus, the relative increasing in the term ν_{CO} for the ν_1 modes makes the drop in frequency more smooth than expected. The drastic frequency drop of the ν_2 modes arises from the increasing in the term ν_{CC} (or the decreasing in the term ν_{CO}).

From these results one may infer that in the oxocarbon series $C_nO_n^{-2}$ with $n \geq 6$ the ν_1 mode will be less coupled and then it can be associated to the stretching CO vibration. The ν_2 mode could be associated to a coupled vibration (ν_{CC} and ν_{CO}) in $C_3O_3^{-2}$, but assigned to a ring breathing mode in the dianions with $n \geq 5$ in concordance with West et al. [4,5].

The above results suggest that C-C π bonding in the deltate dianion is more pronounced than in the other two members of the series. The

extent of electron delocalization involving the carbonyl group and ring in $C_3O_3^{-2}$ is also reflected in the lower value of the f(CO), compared to that of $C_4O_4^{-2}$ and $C_5O_5^{-2}$ and the general range of 9-11 mdyn Å^{-1} for the C=O double bond in the other cyclic ketones [7]. The values for the force constants f(CCO), f(CCCO), f(CCC) and f(CCCC), summarized in Table 1 are consistent with the pattern of increase C-O bond order and decrease C-C bond order with increasing ring size. Thus, the vibrational frequencies involving mainly the δ_{CCO} and ρ modes will increase and the frequencies for the χ mode decrease when the ring size increases (see Table 2).

Although the f(CCC) values are found to be abnormally large (see Table 1), the calculated frequencies involving the α modes are in good agreement with both the experimental ones and other published data concerning related molecules: pyrrole ca. 870 cm^{-1} [13] and benzene ca. 640 cm^{-1} [14] (see Table 2). The trend in the frequencies with ring size also agree with the decreasing C-C bond order. These unexpected results could arise from the internal consistency of the potential force field.

The breakdown of D_{3h} symmetry for the $C_3O_3^{-2}$ dianion has been evidenced in the solid state [5] by the presence of some unexpected active bands: 1830, ca. 1500, 801, 681 cm^{-1}, the splitting of the E′ mode at ca. 1000 cm^{-1} into a double-peaked band in IR and a very weak Raman line at ca. 1550 cm^{-1}. In order to explain these effects the D_{3h} force field was constrained to a C_{2v} symmetry: only some interaction force constants were modified, within normal values, to be symmetrically compatible with a C_{2v} symmetry. The C_{2v} force field interpretates quite well the above mentioned frequencies (see Table 5).

Thecalculated mean amplitudes agree well with the available experimental and other published data [7,11,12] (see Table 3). The present calculation confirms the characteristic values for the C-C and C-O mean amplitudes as Cyvin and Vizi [15] pointed out. The trend obtained in the ℓ values for the series is the expected one according to the opposite trend in the force constants.

VIBRATING CHEMICAL BOND AND CHEMICAL REACTIVITY

From the force constants and ℓ values in Tables 1 and 3 we could infer that the C-C bond in $C_3O_3^{-2}$ will be highly directional and

TABLE 5

Calculated and observed[a] frequencies for the $C_3O_3^{-2}$ ion. (C_{2v} symmetry)

ν_{exp}	ν_{calc}	Assign.(P.E.D.)	Species	N° of normal vibration
1835 R(p) 1830 IR	1842	$\nu_{CC} + \nu_{CO}$	A_1	ν_1
1550 IR,R	1546	$\nu_{CO} + \nu_{CC}$	B_1	ν_9
1446 R(dp) 1470 IR	1430	$\nu_{CO} + \alpha$	A_1	ν_5
992 R(dp)	998	$\nu_{CC} + \nu_{CO}$	B_1	ν_{10}
985 995 IR	980	α	A_1	ν_6
?	856	δ_{CO}	A_1	ν_3
803 R(p) broad 801 IR	761	$\nu_{CC} + \nu_{CO}$	A_1	ν_2
696 R(dp) 681 R,IR	675	ρ_{CO}	B_2	ν_8
520 IR	517	ρ_{CO}	A_2	ν_{11}
346 R(dp) broad	365	ρ_{CO}	B_2	ν_4
341 IR	322	δ_{CO}	A_1	ν_{12}
258 IR	320	$\delta_{CO} + \alpha$	B_1	ν_7

[a]Ref. 5

more rigid than the C-C bond in $C_5O_5^{-2}$. The values f= 6.6 mdyn.$\mathring{A}^{-1}$ and ℓ = 0.0416 $\mathring{A}$ (r_e(C-C)= 1.428 $\mathring{A}$) for the C-C bond in $C_3O_3^{-2}$ will be consistent with a bond of intermediate character between C-C and C=C : a single C-C bond with f ~ 4.5 mdyn. $\mathring{A}^{-1}$ and ℓ ~ 0.050 $\mathring{A}$ and a C=C (benzene) with f(CC) close to 7.62 mdyn. $\mathring{A}^{-1}$ and ℓ~0.046 $\mathring{A}$ (r_e(C-C)= 1.434 $\mathring{A}$). Thus, the adquired covalency degree of the C-C bond will decrease in the series when passing from $C_3O_3^{-2}$ to $C_5O_5^{-2}$.

The force constant of the symmetric stretching of the C-C bond increases in the oreder $C_5O_5^{-2}$ to $C_3O_3^{-2}$. The increase in frequency of the corrsponding mode may be caused by the change in the same order, towards a situation of higher aromaticity, following a greater delocalization of the C-C bond. Thus, $C_3O_3^{-2}$ will be more aromatic than $C_5O_5^{-2}$ but the former less aromatic than benzene. This result agrees with the reported data [6,16].

The substantial differences in the ℓ values for the C-O bond in the series here considered suggest a loose vibration in $C_3O_3^{-2}$ (low force constant value) compared to the rigid C-O bond in $C_5O_5^{-2}$. If these molecules are predicted to be reactive to an electrophilic attack it will preferentially take place through a highly negative charged atom, which is the case in the oxygen atoms in $C_5O_5^{-2}$. Thus, the order of reactivity respect to an electrophilic attack follows the order $C_5O_5^{-2} > C_4O_4^{-2} > C_3O_3^{-2}$. This result is in concordance with the observed dissociation constants for the acids $H_2C_6O_6$, $H_2C_5O_5$ and $H_2C_4O_4$ which increase in this order [16].

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