# The Crystal Structure of Squaric Acid

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The crystal structure of squaric acid (3,4-dihydroxy-3-cyclobutene-1,2-dione) has been determined from three-dimensional X-ray diffraction data measured by counter methods. The compound crystallizes in the space group $P2_1/m$. The symmetry is pseudotetragonal with cell dimensions $a = 6.129(3)$, $b = 5.273(2)$, $c = 6.140(3)$ Å and $\beta = 90.00(1)°$. The data were corrected for extinction effects and refined by least-squares techniques to a conventional R factor of 0.049. Hydrogen bonds of length 2.55 Å link the molecules into infinite sheets. The bond lengths indicate a high degree of conjugation in the molecule: $C=O$ 1.229(1) Å, $C-O$ 1.291(1) Å, $C=C$ 1.409(1) Å, $C-C$ 1.458(1) Å, $C-C$ 1.501(1) Å.

Squaric acid, $C_4H_2O_4$, (I), the smallest known member of the cyclic oxocarbon acids, was first synthesized by Cohen, Lacher and Park.[1]

I
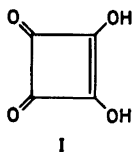
In view of the bond-angle strain associated with a four-membered ring, the squaric acid molecule is surprisingly stable: cyclobutene decomposes at room temperature, whereas squaric acid is stable up to 290°C. The molecule is unique among the oxocarbon acids in having an equal number of groups acting as donors and acceptors for hydrogen bonding. The compound is a strong acid ($pK_1 = 0.5$, $pK_2 = 3.5$), and the dianion $C_4O_4^{2-}$ has been shown to have a symmetrical structure,[2] indicating a substantial delocalization. The crystal structure analysis of squaric acid was carried out in order to obtain information about the influence of conjugation in the molecular system and to examine the hydrogen bonding properties of the compound. A brief description of the results of the X-ray crystal structure analysis has been published.[3]

EXPERIMENTAL

Well developed bipyramidal crystals were obtained from an aqueous solution of commercially available squaric acid. Preliminary film investigations with $CuK\alpha$ radiation suggested the Laue symmetry to be $4/m$. However, photographs from small crystals showed unexpected splitting of reflections with high θ values into triple spots instead of the normal α_1, α_2 pairs. Similar splittings were observed by scanning along 2θ with a manual Picker diffractometer, using both α and β components of the radiation. 2θ scans with the latter showed doublets instead of triplets. At high 2θ angles splitting was generally observed except for reflections corresponding to the unique axis and the diagonals in the plane normal to this axis. The observations were interpreted as due to twinning, thus implying a lower symmetry than tetragonal. After some effort a true single crystal was found, and this specimen was used in the following X-ray experiments.

The crystal was of rectangular shape with dimensions $0.59 \times 0.22 \times 0.60$ mm³. The Weissenberg and precession photographs showed systematic absences only for $(0k0)$, $k = 2n + 1$. It was further evident from these photographs that only a pseudo fourfold axis was present. The space group is hence either $P2_1$ or $P2_1/m$. The latter was assumed and proved to be correct by the structure refinement. Cell dimensions were determined on a manual four-circle diffractometer using CuK radiation. Three-dimensional intensity data were recorded on an automatic Picker four-circle diffractometer using graphite crystal monochromated $MoK\alpha$ radiation, $(\lambda = 0.71069)$. Integrated intensities were collected using the $\omega - 2\theta$ scan technique with a scan rate of $1°/min$. The scan range was $0.7°$ below $2\theta(\alpha_1)$ and $0.7°$ above $2\theta(\alpha_2)$. Background counts were taken for 15 sec at each end of the scan range limits. The standard reflections measured after every 50 reflections declined in intensity by less than 4 % during the data collection and 2178 reflections within the sphere for 2θ less than $75°$ were measured. Two quadrants $(\pm h, k, \pm l)$ of the reciprocal space were examined and a total of 1849 reflections with intensities greater than $2\sigma(I)$ were obtained. The remaining 329 reflections were excluded from the structure refinement procedure. The intensities were corrected for Lorentz and polarization effects, assuming an ideal mosaic monochromator crystal. The standard reflections were used for scaling and a 2 % uncertainty in scaling and diffractometer stability was included in the standard deviations. Atomic scattering factors were those of Hanson et al.[4] except for hydrogen.[5] All programs applied are written or revised for CD-3300 by Dahl et al.[6]

CRYSTAL DATA

Squaric acid, $C_4H_2O_4$, F.W. 114.1, monoclinic. $a = 6.129(3)$, $b = 5.273(2)$, $c = 6.140(3)$ Å, $\beta = 90.00(1)°$, $V = 198.4$ Å³, $F(000) = 116$, $Z = 2$, $\varrho_{obs} = 1.90$ g cm⁻³, $\varrho_{calc} = 1.908$ g cm⁻³. Space group $P2_1/m$.

STRUCTURE DETERMINATION

There are two non-centrosymmetric molecules in the unit cell. Each molecule is thus constrained to lie on a mirror plane. From inspection of the intensity data it was evident that reflections with $h + k + l = 2n + 1$ were weak or absent, suggesting an approximately body-centered lattice. The orientation of the molecule was found from a three-dimensional Patterson synthesis. A trial parameter set in accordance with the above considerations was refined by the "minimum residual method".[7] The R value for 100 low order reflections dropped from 0.20 to 0.13 during refinement. Full matrix least-squares refinements of positional and anisotropic thermal parameters gave $R_w = 0.093$ and $R = 0.072$. At this stage the positions for the hydrogen atoms could be calculated and refinement including positional and isotropic thermal param-

Table 1. Observed and calculated structure factors. (The five columns list values of h, k, l, $10F_o$, and $10F_c$.)

Table 2. Positional and thermal parameters ($\times 10^5$) with estimated standard deviations. The temperature factor is given by $\exp-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl)$.

Atom	x	y	z	B_{11}(B)	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C1	19994	25000	9806	504	1555	513	0	− 47	0
	13		14	17	34	18		25	
C2	10677	25000	30788	511	1556	517	0	− 54	0
	13		13	18	34	18		25	
C3	32099	25000	41085	579	1488	484	0	7	0
	13		14	18	34	18		25	
C4	42040	25000	18737	512	1509	521	0	− 10	0
	14		13	17	33	18		25	
O1	11415	25000	− 9386	706	2433	445	0	−213	0
	11		10	17	35	16		23	
O2	− 8699	25000	39065	459	2445	687	0	189	0
	10		10	15	34	17		23	
O3	39265	25000	59777	767	2295	469	0	−209	0
	11		10	17	34	16		23	
O4	60567	25000	11132	461	2305	737	0	138	0
	11		11	15	33	18		23	
H1	23029	25000	− 21688	4.88					
	212		260	.53					
H2	− 21550	25000	26307	4.96					
	228		229	.54					

eters for all atoms gave $R_w = 0.086$ and $R = 0.072$. A comparison of observed and calculated structure factors revealed the presence of extinction effects. Isotropic secondary extinction corrections [6] were carried out giving $R_w = 0.076$ and $R = 0.064$.* However, it is evident that some structure factors had been undercorrected while others had been overcorrected, suggesting anisotropic extinction effects. Symmetry related reflections were then averaged. The total number of independent reflections observed twice became 898. The standard deviations for these reflections were taken as the average of the individual standard deviations. Another 52 reflections were also included in the data, increasing their standard deviations arbitrarily by 10 %. Further refinement decreased the residuals to $R_w = 0.062$ and $R = 0.049$.

The weight analysis showed negligible intensity dependence except for the smaller F-values. Observed and calculated structure factors are listed in Table 1 and atomic and thermal parameters in Table 2. Bond distances and angles are listed in Table 3, as well as in Fig. 1. The standard deviations in bond lengths and angles were calculated from the correlation matrix of the final least-squares cycle. Fig. 2 is a schematical drawing of the structure as viewed along the b axis.

Successive least-squares refinements with increasing inner cut-off limits in $\sin \theta/\lambda$ were finally applied to the intensity data. A summary of these calculations is given in Table 4.

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* The strong 020 reflections was omitted from refinement at this stage, being less than 2/3 of their calculated value after correction.

Table 3. Bond distances, bond angles, hydrogen bond lengths and angles (uncorrected values).

Bond lengths (Å)	e.s.d. ($\times 10^4$)	Bond angles (°)	
C1 – C2	1.409 (11)	C1 – C2 – C3	91.8(.07)
C2 – C3	1.457 (11)	C2 – C3 – C4	88.2(.07)
C3 – C4	1.501 (11)	C3 – C4 – C1	88.2(.07)
C1 – C4	1.458 (11)	C4 – C1 – C2	91.8(.07)
C1 – O1	1.290 (10)	O1 – C1 – C2	132.0(.08)
C2 – O2	1.292 (10)	O1 – C1 – C4	136.1(.08)
C3 – O3	1.229 (10)	O2 – C2 – C3	131.1(.08)
C4 – O4	1.228 (10)	O2 – C2 – C1	137.1(.08)
O1 – H1	1.108(150)	O3 – C3 – C4	135.1(.08)
O2 – H2	1.040(140)	O3 – C3 – C2	136.7(.08)
		O4 – C4 – C1	135.6(.08)
		O4 – C4 – C3	136.3(.08)

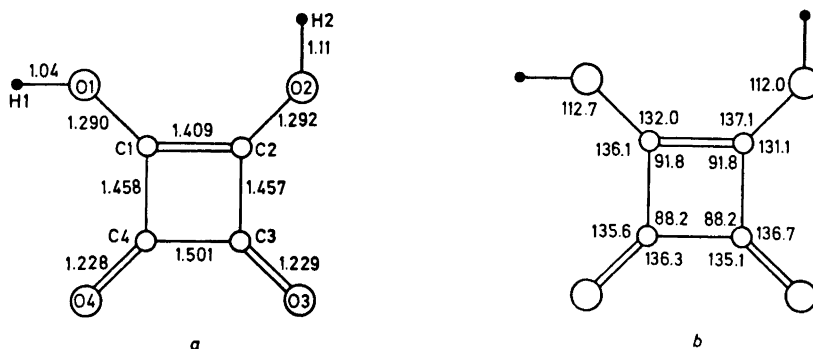| Hydrogen bond lengths (Å)		Hydrogen bond angles (°)	
O1···O3	2.549 (10)	O1 – H1···O3	177.9(1.2)
O2···O4	2.548 (10)	O2 – H2···O4	175.6(1.2)
O3···H1	1.510(160)	C1 – O1 – H1	112.7(0.7)
O4···H2	1.441(140)	C1 – O1···O3	113.9(0.06)
		C2 – O2 – H2	112.0(0.7)
		C2 – O2···O4	114.5(0.05)
		C3 – O3···H1	117.9(0.5)
		C3 – O3···O1	117.0(0.06)
		C4 – O4···H2	117.2(0.5)
		C4 – O4···O2	115.3(0.6)

Fig. 1. Schematical drawings of the molecule showing (*a*) bond lengths (Å), (*b*) angles (°) (uncorrected values).

DAG SEMMINGSEN

Table 4. Intramolecular distances (Å) as found with increasing inner cut-off in sin θ/λ were employed in the least-squares refinements.

sin θ/λ lower limit	R_1	R_2	R_w	N	k	s	C1–O1	C2–O2	C3–O3	C4–O4	C1–C4	C2–C3	C1–C2	C3–C4	Average e.s.d. ($\times 10^4$)
0.0	.049	.049	.062	950	.984	3.72	1.290	1.292	1.229	1.228	1.458	1.457	1.409	1.501	10
0.4	.049	.040	.051	840	.982	3.03	1.290	1.289	1.229	1.230	1.458	1.460	1.412	1.500	11
0.5	.049	.033	.041	732	.972	2.39	1.290	1.290	1.230	1.231	1.459	1.460	1.414	1.501	9
0.6	.049	.029	.031	573	.954	1.73	1.289	1.289	1.231	1.232	1.459	1.459	1.413	1.497	8

R_1 and R_2 include all data and data used in the refinement, respectively. N denotes the number of data in the refinement procedure and k is the scale factor from the refinement. The standard deviation of an observation of unit weight is $s = (\sum w\Delta F^2/N - m)^{\frac{1}{2}}$ where m is the number of parameters.
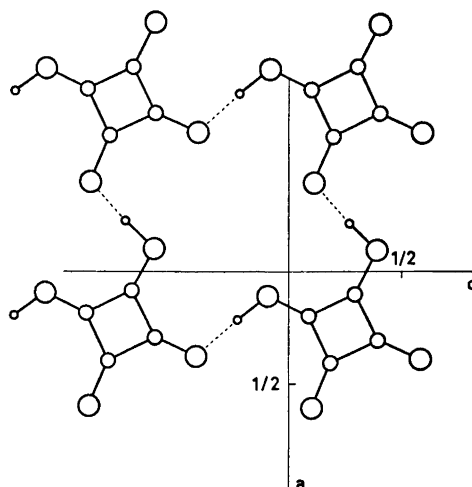
Fig. 2. Schematical drawing of molecules at $y = 1/4$ as viewed along the b axis.

The thermal parameters of Table 1 were applied in the thermal analysis. Root-mean-square amplitudes and corresponding B-values for the atomic anisotropic thermal vibration along the principal axes together with the components of these axes along the crystal axes are given in Table 5. Largest component of the thermal motion is normal to the plane of the molecule. The carbon atoms in the ring have almost isotropic motion in this plane, whereas the oxygen atoms show small deviations from isotropic motion and have the larger component in the plane normal to the $C-O$ bonds.

Table 5. R.m.s. amplitudes of vibration $(\overline{u^2})^{\frac{1}{2}}$ (Å) and B-values (Å^2) along the principal axes of vibration given by the components of a unit vector **e** in fractional coordinates ($\times$ 10^3).

Atom	$(\overline{u^2})^{\frac{1}{2}}$	B	e_x	e_y	e_z	Atom	$(\overline{u^2})^{\frac{1}{2}}$	B	e_x	e_y	e_z
	.184	2.68	0	190	0		.147	1.71	0	190	0
O1	.118	1.11	− 154	0	55	C1	.100	.79	− 100	0	129
	.087	.60	55	0	153		.095	.71	129	0	100
	.185	2.70	0	190	0		.147	1.71	0	190	0
O2	.117	1.08	55	0	154	C2	.100	.80	− 104	0	126
	.089	.63	− 154	0	55		.095	.72	126	0	104
	.179	2.53	0	190	0		.144	1.63	0	190	0
O3	.123	1.19	− 156	0	49	C3	.104	.85	163	0	5
	.090	.65	49	0	155		.095	.72	− 51	0	163
	.179	2.54	0	190	0		.145	1.65	0	190	0
O4	.119	1.12	37	0	159	C4	.099	.77	− 59	0	152
	.091	.66	− 159	0	37		.097	.75	152	0	59

Table 6. Components of molecular translational $(T_{ij} \times 10^4 \text{ Å}^2)$ and librational $[L_{ij} \, (°)^2]$ tensors referred to the crystal axes, standard deviations in parentheses.

	11	22	33	12	13	23
T	80	171	78	0	− 3	0
	(2)	(3)	(2)	(2)	(3)	(3)
L	8.5	3.5	9.9	0.0	− 0.6	0.0
	(10.4)	(0.2)	(10.4)	(0.3)	(10.8)	(0.3)

Principal axes of **T** (Å) and **L** (°) and their direction cosines

T	0.131	0.0	1.0	0.0
	0.091	0.7993	0.0	− 0.6010
	0.087	0.6009	0.0	0.7993
L	3.18	0.3553	0.0	− 0.9347
	2.89	0.9347	0.0	0.3553
	1.88	0.0	1.0	0.0

With the molecular center of mass as origin, the tensors of librational and vibrational motion with respect to the crystal axes were also derived in a rigid-body analysis [8] (Table 6). The root-mean-square deviation is 0.0004 Å². The atoms in the molecule lie, however, very close to the asymptotes of a hyperbola and thus approximately along a quadratic curve.[8] The two largest components in the libration tensor **L** occurring in the molecular plane have large standard deviations, probably indicating that the motion perpendicular to the molecular plane is poorly resolved. The two largest librational amplitudes occur around axes nearly parallel with the C − C bonds, while the two smaller amplitudes of the translational motion coincides nearly with the directions of the hydrogen bonds. As is expected for an approximately centrosymmetric molecule, the components of the correlation tensor **S** are very small. Similarly the **T** and **L** tensors are approximately diagonal. The "center of reaction" lies within 0.06 Å from the center of mass of the molecule.

Corrections in bond lengths for rigid-body motion are small and amount to 0.002 Å for the four terminal C − O bonds and about 0.004 Å for the C − C bonds. Owing to the large standard deviations in the **L** tensor these corrections may be rather uncertain. Corrections in bond lengths for "riding" motion [9] have been calculated for the terminal carbon oxygen bonds and amount to 0.007 Å.

DISCUSSION

Refinement using different inner cut-off limits yielded only minor differences in the structural parameters. However, it will be seen from Table 4 that R, R_w, and s continuously decrease with increasing inner cut-off. The

maximum difference of 0.004 Å in bond lengths is barely outside the experimental error. However, most of the variations in bond lengths (Table 4) are as expected, taking into consideration effects from lone pairs and bonding electrons.[10] In the following the values obtained from the refinement including all observed intensities will be discussed.

The molecular point group is C_{2v}, but only one mirror plane is retained in the crystal. The values found for chemically equivalent bonds agree very well, the largest deviation being only 0.0014 Å while standard deviations range from 0.0010 to 0.0012 Å.

Table 7. Bond distances in squaric acid and some related compounds.

	C1 − C2	C1 − C4	C3 − C4	C1 − O1	C3 − O3	Ref.
1-Cyclohexeneyl-1-cyclobutenedione	1.395(18)	1.483(18)	1.547(18)	1.198(18)	—	11
Phenylcyclobutenedione	1.358(6)	1.485(6)	1.543(6)	1.205(10)	—	12
Benzocyclobutenedione	1.384(10)	1.493(10)	1.569(13)	1.197(12)	—	13
1,2-Dichloro-1-cyclobutenedione	1.41(2)	1.46(2)	1.56(2)	1.20(2)	—	14
3,4-Dimethylenecyclobutene	1.357(5)	1.488(9)	1.516(20)	—	—	15
This investigation	1.409(1)	1.458(1)	1.501(1)	1.229(1)	1.291(1)	—

The bond lengths in the cyclobutene ring show significant departures from those found in other investigations of the cyclobutenedione moiety. Table 7 contains a summary of relevant bond lengths in some similar molecules.[11-15] The single bonds C1 − C4 and C2 − C3 (1.458 Å) are appreciably shorter than corresponding bonds commonly found in cyclobutenediones. Similarly, the formal double bond C1 − C2 (1.409 Å) is longer than those listed in Table 7. Furthermore, the formal single bond distance in the diketonic group (1.501 Å) is shorter than the C − C distance in glyoxal [1.525(3) Å] [16] and even shorter than similar bonds in pure hydrocarbons containing strained four-membered rings such as biphenylene [1.514(3) Å] [17] and dimethylenecyclobutene [1.516(20) Å].[15] Thus it seems that the conjugation is higher in squaric acid than ordinarily found in cyclobutenediones and related conjugated systems. The conjugation in the molecule seems to extend to the C = O and C − O bonds, the two C = O bonds (1.229 Å) being longer than similar distances in other cyclobutenedione moieties. In investigations of acireductones (− CO − COH = COH −) the values of the C − O bonds range from 1.361(2) Å [18] in ascorbic acid to 1.308 Å [19] (1.297 Å neutron diffraction) [20] in dialuric acid. The C − O bond in squaric acid is probably somewhat shorter than that in dialuric acid. The values of the carbon-oxygen bonds in squaric acid are, however, comparable with those commonly found among the carboxylic acids: C = O 1.228(2) − 1.211(4) Å and C − O 1.278(2) − 1.322(4) Å.[21,22]

The high degree of conjugation revealed in the bond lengths is probably connected with the strong hydrogen bonding.

Striking examples of the influence of hydrogen bonding on electronic structure are found in recent investigations of the monomers and dimers of formic,[23] acetic,[24] and propionic acids [25] by electron diffraction in the vapour phase where the $C-O$ bond on average is 0.035 Å shorter in the dimer than in the monomer, whereas the $C=O$ bond on average is 0.014 Å longer in the dimer.

The bond angles within the ring closely conform to the C_{2v} symmetry of the molecule and agree fairly well with corresponding angles in previous investigations of the cyclobutenedione moiety. The angles involving the hydroxylic oxygens and the carbon atoms in the ring depart, however, markedly from this symmetry, the angle on the same side as the hydrogen atom being expanded. Small distortions are also found in the external angles involving the carbonyl groups. Similar distortions have been found in several phenols [26] and may be explained by intramolecular non-bonded repulsions between the hydrogen bonded proton and the carbon atom carrying the hydroxyl group.[27] However, effects associated with the hydrogen bond formation may also be of importance.

The two short O···O distances of 2.549 Å indicate the presence of strong *inter*molecular hydrogen bonds. They are shorter than corresponding bonds found in the free carboxylic acids (2.63 – 2.67 Å).[28,29] As expected from the incomplete delocalization of the π electrons between the heavy atoms, the hydrogen bonds are of the asymmetric type. The protons are located 1.04 Å and 1.11 Å from their respective hydroxyl oxygen atoms, the average bond length being slightly longer than the value (1.03 Å) predicted from the Naka-moto-Margoshes-Rundle curve of Hamilton and Ibers.[30] The hydrogen bonds are nearly linear, the $O-H\cdots O$ angles being 177.8° and 175.6°. The values are in good agreement with that of 176° calculated from the linear empirical relation between $O-H\cdots O$ angles and O···O distances of Hamilton.[31] The hydrogen atoms make angles with the carbonyl groups of 117.9° and 117.2°, respectively.

The four oxygen atoms in a molecule are linked to four other molecules by hydrogen bonds across pseudo fourfold inversion axes (see below). There are two crystallographically independent hydrogen bonds per molecule, and the molecules thus form infinite planar networks lying in the crystallographic mirror planes. Molecules in one layer are related to the layers above and below by screw axes. Thus they are fitted into the open regions in and between the layers above and below, in such a way that each oxygen atom in a molecule is situated between two $O-C-C-O$ fragments from molecules in neighbouring sheets. This produces a very efficient stacking along the b axis which partly explains the high density of the crystals.

As implied by the lattice constants and intensity symmetry the crystal structure is pseudo tetragonal. In addition to the space group symmetry operations there are approximate fourfold axes parallel to the b axis through the molecules at $x=z=1/4$ and approximate fourfold inversion axes at $x=-z=1/4$, and the pseudo space group is therefore $I4/m$.

The most probable explanation of the reflection splitting observed in twinned crystals is an interchange of the a axis with the slightly longer (0.01 Å) c axis and *vice versa*, arising from a twin axis or twin plane along the diagonal

in the $a-c$ plane, or from a 90° rotation about the b axis. The latter explanation is in accordance with the pseudosymmetry found in the single crystal investigation (while the former is not), and therefore seems to be the most probable one, although this kind of twin growth does not give a normal rotational twin.[32]

A final electron-density difference synthesis was calculated with the contributions from all atoms subtracted and with the scale factor and parameters given in Table 1. The resulting map is shown in Fig. 3. The highest peaks
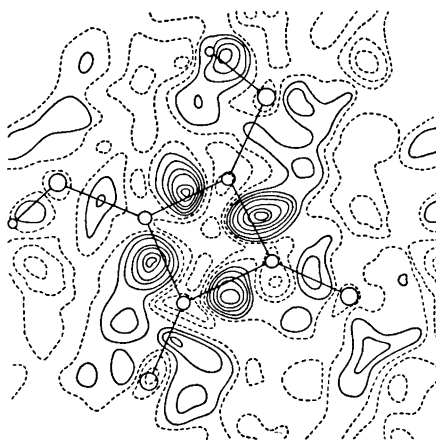

Fig. 3. Final electron density difference synthesis through the molecular plane. Contours at 0.05 eÅ⁻³. Zero and negative contours dotted.

are found in the regions between the $C-C$ bonds, the terminal $C-O$ bonds having smaller residuals. The positions of the maxima of the residual electron density in the $C-C$ single bonds lie about 0.2 Å outside the lines joining the atomic centers, while that of the double bond lies less than 0.1 Å outside. The positions of these maxima seem to support the concept of bent bonds in strained rings, but the data in the present work are probably too inaccurate to warrant a detailed study of the residual electron density.

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