

Is Squaric Acid Square? A Combined X-Ray and Neutron Diffraction Study of 3,4-Dihydroxycyclobut-3-ene-1,2-dione

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The single-crystal structure of the title compound has been studied by both X-ray and neutron diffraction. The space group is $P2_1/m$ with $Z = 2$ in a unit cell of dimensions (X-ray data): $a = 6.119(3)$, $b = 6.133(3)$, $c = 5.297(3)$, $\beta = 90.05(3)^\circ$, $\lambda = 0.7107 \text{ \AA}$. The final weighted discrepancy factors, R^1 , obtained after anisotropic full-matrix least-squares refinement were: X-ray 0.069 (2717 reflections) and neutron, extinction-corrected, 0.038 (714 reflections). The squaric acid molecule is asymmetric with two types of hydrogen bonding to the four oxygen atoms. The two O...O distances are 2.532(4) and 2.544(4) Å (neutron data). The molecules are planar and located at mirror-plane special positions. Strong intermolecular hydrogen bonding between the molecules in the plane results in the formation of an infinite plane sheet structure. The layers are parallel to the ab plane and the distance between layers is $c/2$, 2.649 Å.

ALTHOUGH square acid was first synthesized nearly fifteen years ago,¹⁻³ the structure is still disputed. The anion derived from it, $C_4O_4^{2-}$, is considered to be one of a new series of aromatic anions, $C_nO_n^{2-}$, and its i.r. and Raman spectra⁴ indicate it to be planar with D_{4h} symmetry. Simple Hückel LCAO-MO calculations⁵ show that there is an unusually high resonance energy for $C_4O_4^{2-}$, which is consistent with the observation that squaric acid is a very strong acid with pK_1 1.2(2) and pK_2 3.48(2).^{6,7} The i.r. spectrum of the acid shows a very broad line at 4.3 μm which was interpreted in terms of strong hydrogen bonds.¹ A single-crystal i.r. and Raman spectrum study of squaric acid was recently reported by Baglin and Rose,⁸ who assumed that the molecule possessed C_{2v} symmetry. From the temperature independence of the intensity of hydrogen-bond absorption, they suggested that the hydrogen atoms were bonded within a very asymmetric double minimum potential well.⁹ This would imply possible nonequivalence of the oxygen atoms and that the molecule might not possess a four-fold axis. The results of X-ray and neutron diffraction studies of this system are now reported.

EXPERIMENTAL

3,4-Dihydroxycyclobut-3-ene-1,2-dione (Aldrich) crystallized from water as colourless tetragonal-bipyramidal prisms. Precession and Weissenberg photographs showed systematic absences $00l$ where $l \neq 2n$ with pseudo-body centering (see later).

Crystal Data.— $C_4H_2O_4$, $M = 114.06$. Monoclinic, $a = 6.119(3)$, $b = 6.133(3)$, $c = 5.297(3)$, $\beta = 90.05(3)$, $U = 198.785 \text{ \AA}^3$, $D_m = 1.82(3)$ (by flotation), $Z = 2$, $D_c = 1.88$, $F(000) = 166$. Space group $P2_1/m$ (see later). Mo- K_α x-radiation, $\lambda = 0.7107 \text{ \AA}$; $\eta(\text{Mo-}K_\alpha) = 1.824 \text{ cm}^{-1}$. Neutron diffraction, $\lambda = 1.142 \text{ \AA}$, $\mu = 1.101 \text{ cm}^{-1}$, assuming cross-section of H atom to be 37.5 barn.

Crystallographic Measurements.—(a) X-ray. A square-pyramidal shaped crystal with dimensions 0.15 × 0.15 × 0.3 mm was mounted on a glass fibre along [211] for diffractometer data collection. A computer-controlled four-circle Picker diffractometer with Mo- K_α radiation and a highly oriented graphite monochromator were used for all intensity measurements. Pulse-height discriminator settings for 95% peak acceptance and background rejection were obtained from a pulse-height distribution curve for the K_α component of a typical reflection. The take-off angle was 1.6°. Integrated intensities were collected, by the θ — 2θ scan technique at a rate of 1° min⁻¹. Each reflection was taken using a dispersion-corrected 1.5° scan on 2θ , with 10 s background counts taken at both sides of the peak.

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

² R. West, H. Y. Niu, and M. Ito, *J. Amer. Chem. Soc.*, 1963, **85**, 2584.

³ G. Haahs and P. Hegenberg, *Angew. Chem. Internat. Edn.*, 1966, **5**, 888.

⁴ M. Ito and R. West, *J. Amer. Chem. Soc.*, 1963, **85**, 2580.

⁵ R. West and D. L. Powell, *J. Amer. Chem. Soc.*, 1963, **85**, 577.

⁶ D. T. Ireland and H. F. Walton, *J. Phys. Chem.*, 1967, **71**, 751.

⁷ D. J. MacDonald, *J. Org. Chem.*, 1968, **33**, 4559.

⁸ F. G. Baglin and C. B. Rose, *Spectrochim. Acta*, 1970, **26**, A, 2293.

⁹ R. L. Somorjai and D. F. Hornig, *J. Chem. Phys.*, 1962, **36**, 570.

A full sphere of data, 2717 unique reflections, was collected. Among the four forms, two symmetry-equivalent forms were collected up to 20 110°, while the other two were collected to 70°. Intensities were corrected for background and Lorentz and polarization effects. Scattering factors for all atoms were taken from ref. 10.

(b) *Neutron*. A well-formed tetragonal-bipyramidal shaped crystal, grown by the very slow evaporation from a saturated aqueous solution and weighing 16 mg was mounted on a lead glass capillary along the *c*-axis for data collection. In order to reduce multiple scattering, the crystal *c* axis was offset 2° from the ϕ -axis of the diffractometer. Full three-dimensional data were collected, using an Electronics and Alloys four-circle diffractometer at the CP 5 reactor (Argonne National Laboratory). The fully automated diffractometer operates under remote Sigma V computer control. Data collection was *via* the θ —2 θ scan technique, employing 0.1° step intervals, with backgrounds obtained by taking readings on both sides of the peak. Scan ranges of 40—60 steps were found suitable for data collection. Full three-dimensional data (714 unique reflections) were collected up to 20 110°. Two reference reflections were monitored every 20 reflections and their integrated intensities were found to vary no more than 2% during data collection. Observed integrated intensities were corrected for background, Lorentz, and absorption effects. All intensities were placed on an absolute scale by calibration with a well characterized standard NaCl crystal, using the data reduction and absorption correction program, DATALIB. The scattering amplitudes of carbon, oxygen, and hydrogen were taken to be 0.6626, 0.5750, and —0.3723. Since there was a space group ambiguity,¹¹ refinements in different space groups are reported here. Results are compared and summarized in Table 1.

TABLE 1

Comparison of refinement in different space groups

Space group	<i>R'</i>	Comments
<i>(a) Tetragonal</i>		
<i>I4/m</i>	0.043	Most $h + k + l \neq 2n$ weak, but obs. H symmetrically disordered along O...O vector.
<i>P4₂/m</i>	0.079 ^a	H symmetrically disordered along O...O vector.
	0.094 ^b	H symmetrically disordered along O...O vector.
<i>P4/m</i>	0.060 ^a	Unreasonable temp. factors; see text.
	0.072 ^b	H symmetrically disordered along O...O vector.
<i>(b) Monoclinic</i>		
<i>P2₁/m</i>	0.069 ^a	Positive-definite temp. factors.
	0.038 ^b	H symmetrically bonded along O...O vector, agreeing with i.r. and Raman data. Would not refine.

^a X-Ray. ^b Neutron.

Solution and Refinements.—(a) *Refinement in tetragonal space groups.* Precession and Weissenberg photographs showed Laue symmetry *4/m* with systematic absences $h + k + l \neq 2n$ with only a few weak exceptions. A statistical test on *4/m* symmetry-equivalent reflections from neutron data gave only 3% violations (the F_o of two

¹⁰ H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Cryst.*, 1964, **17**, 1040.

¹¹ C. M. Bock, Summer Meeting Amer. Cryst. Assoc., 1967, abstract p. 100.

symmetry-related reflections differed by $>3\sigma$). The first trial space-group was therefore *I4/m* with 1/4 of the molecule comprising the asymmetric unit. Least-squares refinement on the X-ray data excluding those reflections, $h + k + l \neq 2n$, converged to a final weighted agreement factor, R' of 0.043, where $R' = (\sum \omega |F_o - F_c|^2 / \sum \omega F_o^2)^{1/2}$ and $\omega = 1/\sigma^2(F)$ (population weights).¹² The second trial space group was *P4₂/m* with 1/2 of the molecule comprising the asymmetric unit and included reflections $h + k + l \neq 2n$. Least-squares refinements of the X-ray data converged to R' 0.079, while that on the neutron data (unit weights) converged to R' 0.094. The third trial space group was *P4/m* with two independent molecules per unit cell situated about the special positions *4/m*. This model converged to R' 0.060 (X-ray) and 0.072 (neutron). However, the two molecules at $Z = 0$ and 1/2 gave completely different thermal parameters, and six out of ten atoms had non-positive-definite temperature factors.

(b) *Refinement in monoclinic space groups.* All tetragonal space groups required hydrogen atoms to be either bonded symmetrically between two oxygen atoms or disordered symmetrically along the O...O vectors. Taking into account the i.r. and Raman spectral study⁸ and the O...O distance derived from the neutron data (2.53 Å), the hydrogen atoms were assumed to be bonded in an ordered and asymmetric fashion along the O...O vectors.

TABLE 2

Bond distances (Å) and angles (deg.) *

<i>(a) Distances</i>			
C(4)—C(3)	1.458(3)	C(1)—O(1)	1.257(2)
	1.470(7)		1.250(6)
C(3)—C(2)	1.405(3)	O(3)—H(3)	1.118(38)
	1.427(6)		1.104(9)
C(2)—C(1)	1.454(3)	O(2)—H(4)	0.720(26)
	1.441(6)		1.028(7)
C(1)—C(4)	1.496(3)	O(3)—O(1'')	2.544(1)
	1.486(6)		2.532(4)
C(4)—O(4)	1.232(2)	O(2')—O(4)	2.545(1)
	1.237(7)		2.544(4)
C(3)—O(3)	1.259(2)	H(3)—O(1'')	1.507(36)
	1.271(6)		1.435(9)
C(2)—O(2)	1.285(2)	H(4)—O(4'')	1.825(26)
	1.277(7)		1.516(7)
<i>(b) Angles</i>			
C(1)—C(4)—C(3)	88.4(1)	O(3)—C(3)—C(2)	135.6(2)
	88.2(4)		136.5(5)
C(2)—C(1)—C(4)	88.0(1)	O(2)—C(2)—C(3)	132.3(2)
	89.5(3)		131.7(5)
C(1)—C(2)—C(3)	92.2(1)	O(2)—C(2)—C(1)	135.5(2)
	91.7(4)		136.6(4)
C(2)—C(3)—C(4)	91.4(1)	O(1)—C(1)—C(2)	134.7(2)
	90.6(4)		134.9(4)
O(4)—C(4)—C(3)	136.8(2)	O(1)—C(1)—C(4)	137.3(2)
	136.1(5)		135.6(5)
O(4)—C(4)—C(1)	134.8(2)	O(4)—H(4)—O(2')	179.8(3.0)
	135.6(5)		178.8(9)
O(3)—C(3)—C(4)	133.1(2)	O(3)—H(3)—O(1'')	151.2(3.1)
	132.8(4)		171.8(9)

* Upper value from X-ray and lower from neutron data.

Tetragonal symmetry had therefore to be ruled out. The required decrease in symmetry suggested the next possible space groups to be *P2₁/m* or *P2₁*. In *P2₁/m*, there is one molecule per asymmetric unit and the centre of the ring is at 1/4, 1/4, 1/4. Subsequent least-squares refinement (see later) including all the atoms gave all positive-definite and physically meaningful temperature factors.

¹² G. H. Stout and L. H. Jensen, 'X-Ray Structure Determination, A Practical Guide,' Macmillan, New York, p. 454.

The statistical $N(Z)$ test suggested a centric distribution curve and a least-squares refinement in the acentric space group $P2_1$ was unsuccessful.

(i) *Neutron*. From the neutron data, least-squares refinement including anisotropic thermal parameters yielded a final R' of 0.059 based on F^2 . Several weighting schemes (counting statistics, Hughes',¹³ and Cruickshank's¹⁴) were tried, but only unit weights showed no significant variation of $w|F_o - F_c|$ vs. the magnitude of F_o and $\sin \theta/\lambda$. When F_o and F_c were compared, some reflections obviously suffered from extinction and a correction¹⁵ was applied.¹⁶ An isotropic extinction correction gave R' 0.043 based on

DISCUSSION

The di-anion, $C_4O_4^{2-}$, has complete π -electron delocalization with D_{4h} symmetry and therefore equivalent C-C 1.457(8) and C-O 1.259(7) Å bonds.¹⁷ The data of Cohen *et al.*¹ indicated that the functional groups were ketone C=O, carbon-hydroxy C-OH, and a C-C double bond in the ring. From the neutron data (see the Figure), we did find a variation of C-C bond lengths in the ring with C(3)-C(2) (Table 1) being the shortest [1.427(6) Å], and close to a C-C double-bond length, whereas C(1)-C(4) is much longer [1.486(6) Å] and close

TABLE 3
Fractional co-ordinates and thermal parameters * all $\times 10^4$, with estimated standard deviations in parentheses

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}
C(4)	4148(3)	1820(3)	2500	54(3)	67(3)	115(8)	-11(3)
	4138(5)	1810(5)	2500	98(6)	74(5)	163(11)	18(4)
C(3)	3126(3)	3967(3)	2500	71(4)	55(3)	142(8)	-5(3)
	3124(5)	3982(4)	2500	98(6)	48(5)	158(11)	-4(4)
C(2)	1028(3)	3034(3)	2500	75(4)	69(3)	147(9)	22(3)
	1003(5)	3021(4)	2500	44(4)	58(5)	148(10)	-5(4)
C(1)	1911(3)	834(3)	2500	77(4)	75(4)	129(8)	21(3)
	1911(4)	853(4)	2500	60(6)	86(5)	154(11)	14(4)
O(4)	6022(2)	1088(2)	2500	73(3)	79(3)	244(9)	22(2)
	6021(6)	1083(5)	2500	69(6)	97(7)	245(17)	10(5)
O(3)	3882(2)	5877(2)	2500	90(3)	46(3)	240(9)	-15(2)
	3906(5)	5903(5)	2500	85(6)	45(6)	227(17)	-26(5)
O(2)	-895(2)	3874(2)	2500	29(3)	89(3)	239(9)	-03(2)
	-901(5)	3865(5)	2500	49(6)	82(6)	222(16)	09(5)
O(1)	1092(2)	-1047(2)	2500	87(3)	53(3)	216(8)	-16(2)
	1135(5)	-1033(5)	2500	103(7)	80(7)	233(18)	-12(6)
H(4)	8230(41)	3075(44)	2500		16008		
	7869(6)	2726(9)	2500	59(11)	168(13)	307(13)	6(10)
H(3)	2316(64)	6793(56)	2500		53668		
	2594(13)	7137(12)	2500	360(17)	258(28)	246(12)	-247(23)

* Upper value for X-ray, lower for neutron (after extinction); $\beta_{13} = \beta_{23} = 0.000$ due to mirror symmetry. The form of the thermal parameter is: $\exp[-(\beta_{11}h^2 + \dots + 2\beta_{12}hk + \dots)]$.

F^2 , while a Type I (Mosaic spread) anisotropic extinction correction gave R' 0.038. The final R was 0.062, and S was 0.33 [$S = \sum_w(F_o - F_c)^2 / (N_o - N_v)$, where N_o = number of observations (714), and N_v = number of variables (67)].

(ii) *X-Ray refinement*. Two symmetry-related data sets with 20 up to 110° were averaged. Based on this average data, R' converged to 0.069 on F (all data) after several cycles of least-squares refinement with anisotropic thermal parameters.¹⁶ Counting statistic weights were used with $w = 1/\sigma^2(F)$ where $\sigma(F) = \frac{F}{2I}[(CN + 1/4) \left(\frac{T_G}{T_B}\right)^2(B_1 + B_2) (kI)^2]^{1/2}$ where CN = total counts, T_G = total scan time for the reflection, T_B = time for background counts taken, B_1, B_2 = background counts on each side of the reflection, I = net counts of the reflection, and k = constant = 0.01. This weighting scheme gave no significant variation of $w(F_o - F_c)$ with the magnitude of F_o and $\sin \theta/\lambda$. The final R is 0.071 [observed reflections $I > 2\sigma(I)$ only], $S = 1.85$ with $N_o = 2717$, $N_v = 55$.

Bond distances and angles obtained from both X-ray and neutron data¹⁶ are listed in Table 2, and atom positional parameters in Table 3, are listed in Supplementary Publication No. SUP 20821 (5 pp., 1 microfiche).*

* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue.

¹³ E. W. Hughes, *J. Amer. Chem. Soc.*, 1941, **63**, 1737.

¹⁴ D. W. J. Cruickshank, 'X-ray Crystal Analysis,' eds. R. Pepinsky, J. M. Robertson, and J. C. Speakman, Pergamon, New York, 1961, p. 45.

¹⁵ W. H. Zachariasen, *Acta Cryst.*, 1967, **23**, 558.

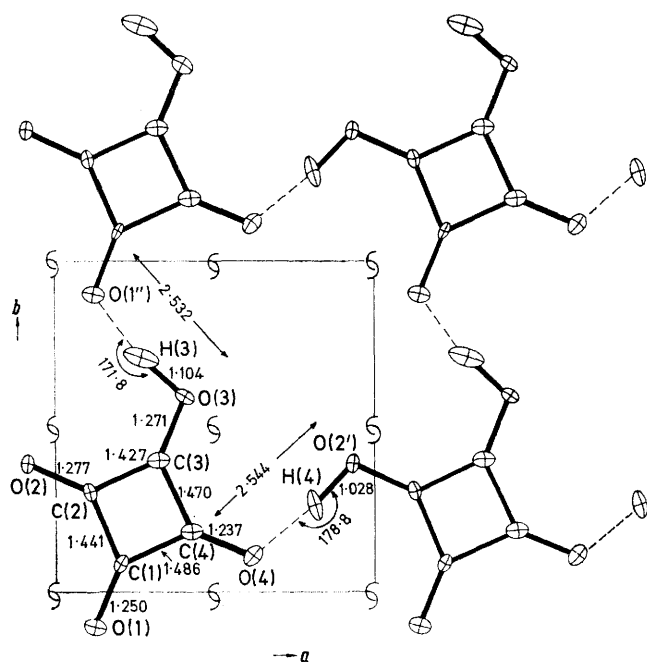
to a C-C single-bond distance. C(1)-C(2) and C(4)-C(3) are intermediate. Some variation among the C-O bond lengths was also found, C(4)-O(4) being the shortest [1.237(7) Å] and C(2)-O(2) the longest [1.277(7) Å]. The data can be interpreted in terms of the π -electron delocalization being through the O(1)-C(1)-C(2)-C(3)-O(3)-H(3) chain, so that C(4)-O(4) is best described as a carbonyl group, while C(2)-O(2)-H(4) is a carbinol group. The shortening of C(1)-C(2), the lengthening of C(4)-C(3), and the fact that the thermal parameter of H(3) is larger than that of H(4), are all in agreement with this assumption. According to Hamilton and Ibers,¹⁸ the O-H bond length usually increases as the O...O distance decreases. Although the O(4)...O(2)' distance [2.544(4) Å] is not significantly different from the O(3)...O(1)'' distance [2.532(4) Å], O(2)-H(4) [1.028(7) Å] appears to be significantly shorter than O(3)-H(3) distance [1.104(9) Å] from both the neutron and X-ray data. However, the anisotropic thermal

¹⁶ W. R. Busing, K. D. Martin, and H. A. Levy, ORXFLS3, A Fortran Crystallographic Least-Square Program, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1971; ORFFE, A Fortran Crystallographic Least-Square Function and Error Program, 1962; ORFLSD, A Fortran Crystallographic Least-Square Program, 1962.

¹⁷ W. M. Macintyre and M. S. Werkema, 1964, *J. Chem. Phys.*, **40**, 3563.

¹⁸ W. C. Hamilton and J. A. Ibers, 'Hydrogen Bonding in Solids,' Benjamin, New York, 1968, p. 53.

parameters of the two hydrogen atoms, H(4) and H(3), are very different, with the largest root-mean-square displacement of H(3) being directed more nearly along



Molecular structure and crystal packing for $c = \frac{1}{4}$ plane of squaric acid

$O(1'') \cdots O(3)$ vector and that of H(4) being more nearly perpendicular to the $O(2') \cdots O(4)$ vector. We are

therefore not convinced that there is a physically significant difference in the $O(2)-H(4)$ and $O(3)-H(3)$ bond lengths.

The results obtained here do show that the hydrogen atoms of the squaric acid molecule in the solid state are asymmetrically hydrogen bonded between two oxygen atoms. The asymmetric double minimum potential predicted earlier⁸ due to the lack of change in intensity of antisymmetric stretching vibration $\nu(\text{OH})$ between 296 and 77 K is thereby confirmed by this crystallographic data. As noted previously, it was necessary⁸ to assume symmetry lower than D_{4h} (as observed here) in order to assign all the i.r. and Raman absorption shifts.

Crystallographically, this is a very interesting structure, since the four-membered carbon ring has very nearly four-fold symmetry. However, the hydrogen atom locations destroy the four-fold symmetry making it very difficult to determine the space group with X-ray data. Even the interference figure suggests a uniaxial pattern. The foregoing results are consistent, however, for neutron, X-ray, i.r. and Raman data.

Added in proof: A preliminary single crystal X-ray structure of squaric acid which is essentially in agreement with our findings has recently appeared (D. Semmingsen, *Tetrahedron Letters*, 1973, 807).

We thank Dr. S. Peterson for helpful discussion, L. Fuchs for taking the interference figure, the National Science Foundation for financial support of this work, and the U.S. Atomic Energy Commission for the neutron diffraction facilities.

[3/266 Received, 5th February, 1973]