washed well with methanol and air-dried. Yield 0.89 g (91 %). (Found: N 19.34; H 4.60; Cl 36.62. Calc. for *cis*-$[RhCl_2(NH_3)_4]Cl.\frac{1}{2}H_2O$: N 19.54; H 4.57; Cl 37.16).

3. cis-*Tetraamminedibromorhodium(III) bromide hemihydrate, cis*-$[RhBr_2(NH_3)_4]Br.\frac{1}{2}H_2O$. $[Rh(ox)(NH_3)_4]ClO_4.H_2O$ (0.70 g, 1.86 mmol) was boiled with 5 M hydrobromic acid (30 ml) until all the complex had dissolved (*ca.* 2 – 3 min). The resulting orange solution was allowed to cool to room temperature and then kept in a freezer at – 15 °C overnight. The product was isolated by filtration, washed with 96 % ethanol and air-dried. Yield 0.68 g. Recrystallisation was performed as for the *cis*-dichloro chloride (prep. 2), using 3 M hydrobromic acid (30 ml) in place of hydrochloric acid. The orange crystals were filtered off, washed with 96 % ethanol and air-dried. Yield 0.60 g (77 %). (Found: N 13.48; H 3.08; Br 57.25. Calc. for *cis*-$[RhBr_2(NH_3)_4]Br.\frac{1}{2}H_2O$: N 13.33; H 3.12; Br 57.10).

4. cis-*Tetraamminedichlororhodium(III) dithionate, cis*-$[RhCl_2(NH_3)_4]_2S_2O_6$. $[RhCl_2(NH_3)_4]Cl.\frac{1}{2}H_2O$ (0.25 g, 0.87 mmol) was dissolved in water (20 ml) at room temperature and the solution filtered. A solution of sodium dithionate dihydrate (0.5 g, 2.1 mmol) in water (10 ml) was added, whereupon crystals of the desired product began to form immediately. After cooling the solution overnight at 0 °C the fine pale-yellow crystals were isolated by filtration, washed well with ice-cold water and then 96 % ethanol, and air-dried. Yield 0.21 g (75 %). (Found: N 17.58; H 3.45; S 9.88. Calc. for *cis*-$[RhCl_2(NH_3)_4]_2S_2O_6$: N 17.39; H 3.76; S 9.93).

5. cis-*Tetraamminedibromorhodium(III) dithionate, cis*-$[RhBr_2(NH_3)_4]_2S_2O_6$. This complex was prepared in the same way as the *cis*-dichloro dithionate (prep. 4), using *cis*-$[RhBr_2(NH_3)_4]Br.\frac{1}{2}H_2O$ (0.30 g, 0.71 mmol) dissolved in water (25 ml). The shiny orange crystals were filtered off, washed with ice-cold water and 96 % ethanol, and air-dried. Yield 0.23 g (78 %). (Found: N 13.78; H 2.83; S 7.89. Calc. for *cis*-$[RhBr_2(NH_3)_4]_2S_2O_6$: N 13.63; H 2.94; S 7.80).

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Received February 20, 1975.

On the Structure of Deuterated Squaric Acid, $C_4D_2O_4$, at Room Temperature

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The crystal structure of 3,4-dihydroxy-3-cyclobutene-1,2-dione (Squaric acid, hereafter denoted H_2SQ) as determined by X-ray diffraction has been reported previously.[1] Interest in this compound developed recently due to the discovery of a continuous phase transition in both H_2SQ ($T_C = 97$ °C) and D_2SQ ($T_C = 243$ °C).[2] The magnitude of the isotope effect in the transition temperatures of these compounds suggests that the hydrogen bonds are essential to the dynamics of the transition. Since the length of the hydrogen bonds in H_2SQ lie in the range where isotope effects in these bonds are to be expected, it was considered of importance to acquire exact information of the crystal structure of D_2SQ.

Squaric acid (H_2SQ) has also been independently examined by X-ray and neutron diffraction.[3] However, there are some points of disagreement between that work and our X-ray study.[2] In our X-ray study squaric acid crystals were found almost invariably to be twinned, and it was only after considerable effort that an untwinned sample could be found. Such difficulties were apparently not encountered in the combined X and N study.[3] A high degree of consistency was obtained between chemically equivalent but crystallographically independent bonds in our X-ray study,[1] but not in the combined study.[3] In the latter study poor agreement was also obtained for certain bond distances between the X-ray and neutron results. The X-ray structure determination of D_2SQ was therefore also undertaken in order to establish the validity of our previous X-ray work.[1]

Table 1. Fractional atomic coordinates and thermal parameters with estimated standard deviations ($\times 10^5$), isotropic temperature factor and positional parameters ($\times 10^4$) for the deuterium atoms. The anisotropic 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	B11	B22	B33	B12	B13	B23
O1	11398(8)	25000(0)	-9234(8)		795(9)	2532(24)	548(8)	0(0)	-214(13)	0(0)
O2	-8493(8)	25000(0)	39140(8)		539(8)	2544(24)	809(10)	0(0)	178(13)	0(0)
O3	39328(8)	25000(0)	59650(8)		864(10)	2374(24)	574(9)	0(0)	-228(14)	0(0)
O4	60539(8)	25000(0)	11080(8)		557(8)	2363(23)	855(10)	0(0)	143(13)	0(0)
C1	20859(9)	25000(0)	9895(9)		581(9)	1558(22)	562(10)	0(0)	-47(14)	0(0)
C2	10834(9)	25000(0)	30799(9)		555(9)	1577(23)	599(10)	0(0)	-11(14)	0(0)
C3	32237(9)	25000(0)	41073(10)		617(9)	1536(22)	564(10)	0(0)	-33(14)	0(0)
C4	42136(9)	25000(0)	18711(9)		558(9)	1534(22)	618(10)	0(0)	-19(15)	0(0)
D1	2318(22)	2500(0)	-2060(27)	5.7(.4)						
D2	-2043(25)	2500(0)	2730(28)	6.5(.5)						

A single crystal with the dimensions $0.4 \times 0.1 \times 0.4$ mm was cut from a larger specimen and thoroughly examined by optical methods, before and after collection of intensity data. Details of the crystallization procedure will be published later. Scans along 2θ and ω on a four circle diffractometer for several highorder reflections revealed only $\alpha_1-\alpha_2$ splitting,[1b] confirming the absence of twinning. Intensity data were collected at room temperature (19 ± 1 °C) on a SYNTEX P$\bar{1}$ diffractometer with graphite monochromated Mo$K\alpha$ radiation ($\lambda = 0.71069$ Å) in two steps. One hemisphere of the reciprocal lattice ($h, \pm k, \pm l$) was examined with $2\theta \leq 55°$ and one quadrant ($h,k, \pm l$) was recorded with $55° < 2\theta \leq 110°$. In the latter shell, an instrumental threshold value was applied to avoid measurements of reflections with intensities less than $3\sigma(I)$. A total of 2271 reflections were measured, of which 146 had intensities less than $2\sigma(I)$ and were classified as unobserved. Equivalent reflections were averaged to yield about 1720 independent reflections. The average disagreement between equivalent reflections was 2.0 % [$Rc = \sum|F_o^2 - F^2|/\sum F_o^2$]. The average disagreement between pseudo-equivalent reflections, *i.e.* (hkl) and ($lk\bar{h}$) pairs was 10 %. The conditions for systematically absent reflections indicate the space group to be $P2_1$ or $P2_1/m$ in agreement with the previous X-ray determination. The cell dimensions were determined by a least-squares adjustment of 30 high-angle reflections giving:

$a = 6.152(1)$, $b = 5.269(1)$, $c = 6.165(1)$ Å, $\beta = 89.92(1)°$

The atomic parameters of the non-hydrogen atoms from the H_2SQ investigation [1b] were used as the starting point in full-matrix least-squares refinements, assuming the space group to be $P2_1/m$. The D atoms were included in the final cycles with a variable isotropic temperature factor. The weights used were those from counting statistics including a 2 % uncertainty in instrument stability. The final values for the residuals are $R = 0.041$ and $R_w = 0.051$. The positional and thermal parameters are given in Table 1. Tables of measured and calculated structure amplitudes are available from the author, on request.

The molecular geometry of D_2SQ is shown in Fig. 1, together with that of H_2SQ.[1b] Hydrogen bond distances and angles are given in Table 2.

The e.s.d. in bond distances between heavy atoms as calculated from the correlation matrix from the final L.S.R. refinement are 0.0008 Å or less. Crystallographically independent, but chemically equivalent bonds differ by a maximum of 0.0017 Å. The results from the previous X-ray determination are fully confirmed. The independent study of H_2SQ by neutron and X-ray diffraction [3] has therefore probably been carried out on twinned crystals.

H_2SQ and D_2SQ are closely isostructural. Thus the conclusions previously drawn for H_2SQ [1] in general also apply to D_2SQ: The deuterium atoms are asymmetrically located in

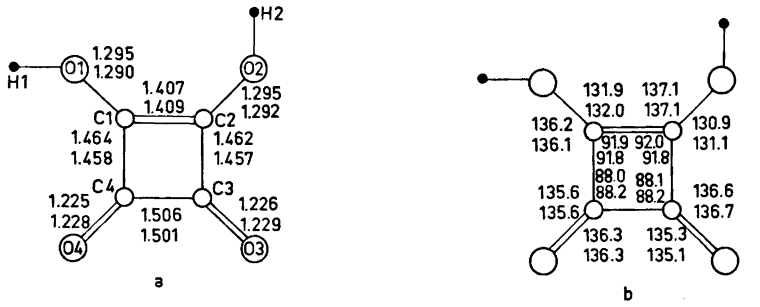

Fig. 1. Bond distances (a) and angles (b) uncorrected for thermal motion (upper values D_2SQ, lower values H_2SQ).

Table 2. Hydrogen bond distances and angles.

Bond lengths (Å)		Bond angles (°)	
O1···O3	2.5731(7)	O1–D1···O3	174.0(1.0)
O2···O4	2.5751(7)	O2–D2···O4	176.0(2.0)
O3···D1	1.56(2)	C1–O1–D1	110.4(0.8)
O4···D2	1.54(2)	C1–O1···O3	113.8(0.1)
O1–D1	1.01(2)	C2–O2–D2	111.8(0.9)
O3–D2	1.04(2)	C2–O2···O4	114.4(0.1)
		C3–O3···D1	119.5(0.5)
		C3–O3···O1	117.3(0.1)
		C4–O4···D2	117.0(0.6)
		C4–O4···O2	115.2(0.1)

the hydrogen bonds (Fig. 2). Each C_4O_4 unit is thus surrounded by two close and two distant deuterium atoms. The structure is built up from two-dimensional hydrogen-bonded layers perpendicular to the unique (*b*) axis. The stacking sequence may be described by a translation $\frac{1}{2}(\mathbf{a}+\mathbf{b}+\mathbf{c})$ of a layer with respect to that below or above. However, the directions of hydrogen bonds in neighbouring layers are opposite each other. The crystal structure is therefore pseudo-body-centered tetragonal with approximate fourfold rotation and screw (4_2) axes.

The O···O distances found in this study (2.575(1) and 2.573(1) Å) are longer than those found in the H_2SQ crystal (2.548(1) and 2.549(1) Å) by an average amount of 0.025 Å. This is highly significant, and is comparable with the figure (0.03 Å) estimated from expansions of the *a* and *c* axis (0.023 and 0.025 Å) on deuteration. According to calculations [4] an increase in the O···O distance is to be expected if the potential energy function is of the symmetric or asymmetric double minimum type. It has been suggested [5] that this isotope effect is at maximum for hydrogen bonds at a range (2.50–2.56 Å) closely centered around the values found in H_2SQ. Isotope effects of comparable magnitudes have previously been found in single crystal studies of $NaHC_2O_4.H_2O$ (0.022 Å) [6] and $(COOH)_2.2H_2O$ (0.012 Å).[7] These structures are, however, rather complicated in comparison to the H_2SQ structure, so that secondary effects may also be of importance.[6,7] In the $(COOH)_2.2H_2O$ structure [7] large isotope effects are even found in the weaker hydrogen bonds, which are not in agreement with predictions from the theory.[4,5] In the layers of molecules in D_2SQ and H_2SQ the intermolecular approaches are almost entirely dominated by the attractive hydrogen-bonding forces, whereas interplanar forces are predominantly of van der Waals nature and presumably much weaker, as is shown by the prominent cleavage along (010).[2]

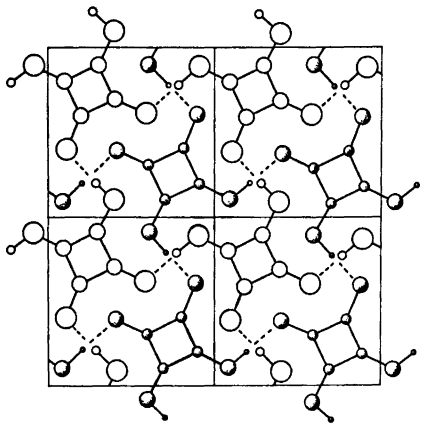

Fig. 2. The content of four unit cells of D_2SQ as viewed along the *b*-axis. Open circles: molecules at $y = 1/4$. Shaded circles: molecules at $y = 3/4$.

A very interesting feature in the H_2SQ [1b] and D_2SQ structures is that isotope effects in the hydrogen bonds seem to be transmitted to the molecule itself. Although differences in the corresponding bond distances in the two structures are of marginal significance, there appears to be slightly less delocalization of π-bonding in the deuterated material. This is in keeping with the results from the H_2SQ investigation [1b] where the high degree of conjugation found in the molecule was judged to be partly due to the strong hydrogen bonding.

The standard deviations and systematic errors in the parameters of the light atoms, (H and D) in X-ray determinations are large, and a full discussion of the hydrogen bond geometry and isotope effects will be given in a forthcoming neutron diffraction analysis.

Finally, an additional striking isotope effect in this material which is worth mentioning, is the large observed difference in domain wall mobility in H_2SQ and D_2SQ. Crystals of H_2SQ and D_2SQ show ferroelastic twinning,[8] and samples of H_2SQ have been successfully detwinned by application of uniaxial stress along the *a* and *c* axes. The motion of the domain walls is easily followed under a polarizing microscope. Similar attempts with D_2SQ have so far resulted in breakdown of the crystal before detwinning occurs.

Acknowledgements. The author is indebted to S. C. Abrahams at Bells Laboratories for his suggestion that the twinning in squaric acid crystals could be of ferroelastic origin.

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Received March 19, 1975.

On the Formation of Phosgene and Trichloroacetyl Chloride in the Non-sensitized Photo-oxidation of Perchloroethylene in Air

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The non-sensitized photo-oxidation of trichloroethylene (tri) and 1,1,1-trichloroethane in the gas phase have earlier been reported.[1,2] In this paper the non-sensitized photo-oxidation of perchloroethylene (per) at low vapour pressures in air is described. The experimental technique has been described in the paper on photo-oxidation of trichloroethylene by Dahlberg.[1]

In the tri case the initiating step was shown to be a reaction between one tri molecule in the excited state and one in the ground state in competition with a pseudo first-order deactivation step.[1] However, for perchloroethylene we have shown that the initiating step is a dissociation of a per molecule upon light absorption. It is further shown that phosgene is probably formed not only according to the scheme by Huybrecht *et al.*[3] for the chlorine-sensitized photo-oxidation, but also by a parallel chain mechanism.

The results of the kinetic measurements are shown in Figs. 1 and 2. Obviously there are linear relationships between the rates of formation (v) of trichloroacetyl chloride (TCAC) and phosgene, respectively, and the absorbed light (I_{abs}). Thus all measurements made at the oxygen pressure 0.2 atm and at I_{abs} above 8.5×10^{-13} einstein/s fit well to the following equations calculated by the method of least squares:

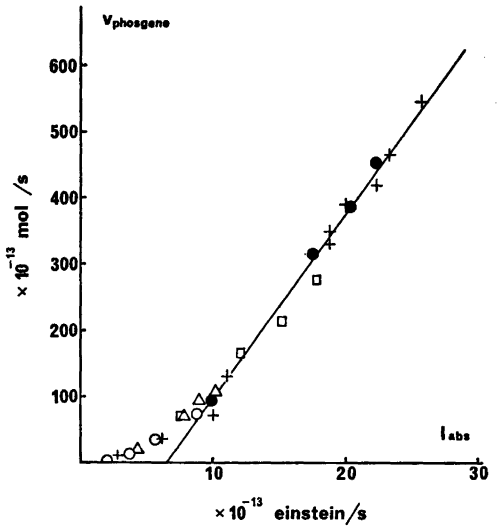

Fig. 1. $v_{phosgene}$ (measured) plotted *vs.* I_{abs} at different p_{per}. ○, $p_{per} = 5$ Pa; △, $p_{per} = 10$ Pa; □, $p_{per} = 30$ Pa; ●, $p_{per} = 50$ Pa; +, $p_{per} = 100$ Pa.

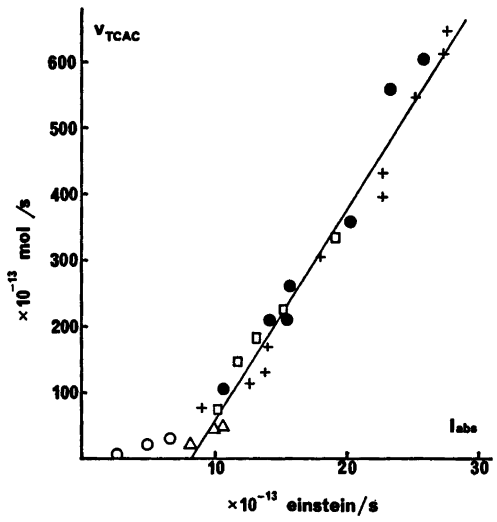

Fig. 2. v_{TCAC} (measured) plotted *vs.* I_{abs} at different p_{per}. ○, $p_{per} = 5$ Pa; △, $p_{per} = 10$ Pa; □, $p_{per} = 30$ Pa; ●, $p_{per} = 50$ Pa; + $p_{per} = 100$ Pa.

$$v_{TCAC} = 31.9\ I_{abs} - 263 \times 10^{-13} \text{ mol s}^{-1}$$
$$v_{phosgene} = 27.6\ I_{abs} - 177 \times 10^{-13} \text{ mol s}^{-1}$$

The slopes of these lines, *i.e.* the quantum yields, seem to be independent of the per pres-