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The Crystal Structure of L-Ascorbic Acid, 'Vitamin C'. II. The Neutron Diffraction Analysis*

BY JAN HVOSLEF

Universitetets Kjemiske Institutt, Blindern, Oslo, Norway

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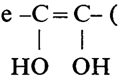
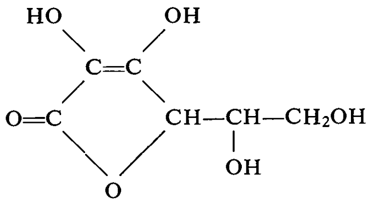
This work is a supplement to the X-ray diffraction determination of L(+)-ascorbic acid, and comprises neutron diffraction studies of single crystals of the normal and of the partly deuterated substance. Refinement was confined to positional and thermal analysis of the hydrogen atoms, resulting in an average standard deviation of 0·019 Å for C–H and O–H bonds, and of 1·3° in the angles involving hydrogen. The average C–H distance was found to be 1·100 Å while the different O–H distances varied according to the empirical curve for the O···O hydrogen bond lengths. The actual values as found by X-ray diffraction are smaller than the neutron diffraction values by 0·148 Å for O–H and 0·083 Å for C–H bonds. The average C–O–H angle in the  $-\underset{\displaystyle \mathrm{HO}}{\underset{|}{\mathrm{C}}}=\underset{\displaystyle \mathrm{OH}}{\underset{|}{\mathrm{C}}}-$ (enediol) group is 113·9°, while the alcoholic C–O–H angle is 109·2°. The average C–C–H and O–C–H angle was found to be 109·2°. All the C–O–H···O systems were non-planar.

Introduction

A substance with the formula $C_6H_8O_6$ was isolated by Szent-Györgyi (1928). The original name was hexuronic acid, but this was changed to L(+)-ascorbic acid or vitamin C because of its healing effect on scurvy. The chemical constitution was determined by Herbert, Hirst, Percival, Reynolds & Smith (1933). They proposed the structural formula



An incorrect crystal structure was proposed by Cox & Goodwin (1936), and no further progress was made until the crystal structure was determined by means of 1640 X-ray reflexions (Hvoslef, 1968). The average standard deviation was 0·004 Å for the C–C and C–O bonds and 0·030 Å for the C–H and O–H bonds.

The intention of this work was to establish more precise hydrogen parameters by means of neutron data and to compare the results with the values found by X-ray diffraction. In order to assist the interpretation, two kinds of crystal were used. The first specimen was the usual ascorbic acid, while the second had been treated with D_2O in order to exchange all the hydroxyl hydrogen atoms with deuterium atoms. This double set of data was desirable in order to improve the ratio of independent structure factors to the number of parameters.

The unit cell contains two molecules *A* and *B* in the asymmetric unit, and although about 400 neutron reflexions were recorded for each crystal it was realized that we could not attain the same accuracy in the heavy atom parameters as was possible from the three-dimensional X-ray data. The carbon and oxygen parameters were consequently kept unchanged throughout the neutron analysis.

Experimental

Crystals of L(+)-ascorbic acid were grown from aqueous solutions by slow evaporation at room temperature. Care had to be taken to avoid oxidation of the substance. The first crystal was a relatively large, tabular and slightly elongated specimen with the dimensions $0{\cdot}23 \times 0{\cdot}65 \times 0{\cdot}30$ cm^3 weighing 525 mg. This crystal was used in its original form for the collection of the data in the *h*0*l* zone, but was later slightly modified for the collection of the *hk*0 intensities. The size was now $0{\cdot}20 \times 0{\cdot}52 \times 0{\cdot}30$ cm^3 and the weight 425 mg.

In preparing the second crystal, vitamin C had been dissolved in pure D_2O and twice evaporated to dryness. Finally a large specimen was grown by slow evaporation at room temperature. The size of this crystal was $0{\cdot}50 \times 0{\cdot}63 \times 0{\cdot}20$ cm^3 and the weight 842 mg.

Both crystals were checked for single-crystallinity by means of X-rays.

The neutron source was the Norwegian reactor 'JEEP I' at Kjeller. The central flux was 10^{12} neutrons cm^{-2} sec^{-1}, giving a moderate counting rate. The weak intensities at higher scattering angles were uncertain because of the large incoherent scattering from hydrogen which tended to obscure the peaks.

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* Neutron diffraction data collected at IFA, Kjeller, Norway

The *h*0*l* intensities for both crystals were measured on an integrating step-scan goniometer which was coupled in the usual θ-2θ mode, and constructed for recording intensities in one zone. Neutrons of wavelength 1·020 Å were obtained by means of a lead monochromator crystal. Later the *hk*0 intensities for both crystals were measured on a new automatic spectrometer 'KANDI' (Kjeller Report 57, 1963). This was also constructed for collection of data in one zone only, but allowed programming of crystal and counter angles as well as counting time to be introduced by means of punched tape. In this case the wavelength was 1·222 Å, obtained with a copper monochromator crystal.

The two sets of data have been labeled F^{H} and F^{D} for the normal and for the deuterated substances, respectively. The zero observed reflexions were included according to Hamilton (1955) by taking one-quarter of the minimum observable intensity in the *h*0*l* zone and one-third in the *hk*0 zone.

The absorption coefficients for the two kinds of crystal were measured by direct transmission experiments, and found to be 1·87 cm^{-1} for the usual acid and 1·78 cm^{-1} for the deuterated acid. The data were subsequently corrected for absorption by means of a computer program written by T. Dahl at this institute.

Unit cell and space group

$a = 17{\cdot}299$ (8) $V = 688{\cdot}59$ Å^3
$b = 6{\cdot}353$ (3) $d_{\mathrm{calc}} = 1{\cdot}699$ g.cm^{-3}
$c = 6{\cdot}411$ (3) $M = 176{\cdot}13$
$\beta = 102°11'$ (08) $Z = 4$
Space group $P2_1$

The four molecules in the unit cell were related in pairs by pseudo screw axes along [010] in the positions $(x=\frac{1}{4}, z=\frac{5}{8})$ and in $(x=\frac{3}{4}, z=\frac{3}{8})$. This operation gave rise to a set of near-absences in the *hk*0 and *h*0*l* zones which were distinct in the X-ray case, but less obvious in the neutron case, especially for the *h*0*l* intensities. This indicated that at least some hydrogen atoms were violating the pseudosymmetry considerably when seen along [010].

The idea of utilizing the isomorphous replacement of the hydrogen isotopes as a means of solving the structure from the start was abandoned, since eight instead of four atomic sites had to be determined first.

Refinement of the hydrogen parameters

The conventional *R* index for the F^{H} and F^{D} data was calculated using the set of parameters found from the X-ray analysis. The value was satisfactory for the nor-

Table 1. *Hydrogen parameters*

The first entry gives the F^{H} results. The second entry for the hydroxyl hydrogen atoms gives the results from the combination of F^{H} and F^{D} data. For the other hydrogen atoms the second entry gives the results from the F^{D} data. All values are multiplied by 10^4. Standard deviations in parentheses.

	x	y	z	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}
O(2)–H	−1050 (11)	9366 (67)	6243 (32)	26 (5)	211 (81)	161 (41)	66 (57)	102 (28)
	−1081 (16)	9385 —	6261 (36)	16 (9)		31 (42)		49 (35)
O(3)–H	0449 (12)	9381 (67)	2738 (34)	28 (6)	126 (67)	163 (47)	−29 (52)	−16 (30)
	0467 (17)	9400 —	2747 (42)	22 (11)		70 (52)		−24 (44)
O(5)–H	1196 (12)	5101 (74)	7120 (35)	28 (6)	253 (111)	145 (43)	−41 (63)	−8 (30)
	1179 (15)	5067 —	7170 (40)	10 (8)		86 (56)		−87 (37)
O(6)–H	3670 (18)	9878 (71)	9960 (46)	48 (11)	260 (136)	230 (64)	−143 (83)	−80 (45)
	3635 (26)	9890 —	9984 (58)	43 (16)		183 (89)		−117 (64)
C(4)–H	1753 (13)	0968 (46)	7737 (49)	31 (7)	27 (47)	290 (72)	−83 (39)	−115 (43)
	1715 (18)	0992 (53)	7858 (53)	35 (9)	64 (70)	242 (71)	−118 (54)	−85 (48)
C(5)–H	2211 (8)	7815 (51)	6245 (21)	21 (4)	154 (77)	33 (26)	50 (49)	62 (19)
	2211 (14)	7649 (81)	6250 (31)	38 (7)	355 (145)	175 (38)	214 (83)	128 (30)
C(6)–H(1)	2564 (19)	8516 (105)	1070 (39)	60 (12)	340 (144)	137 (45)	−205 (100)	−28 (42)
	2549 (19)	8564 (122)	1072 (40)	41 (11)	530 (255)	140 (46)	−250 (118)	31 (39)
C(6)–H(2)	3101 (14)	6537 (76)	9587 (59)	28 (7)	217 (94)	403 (97)	−67 (67)	44 (47)
	3089 (20)	6661 (95)	9786 (84)	30 (10)	229 (127)	465 (136)	20 (76)	20 (62)
O(2)*–H	5999 (10)	5146 (69)	6118 (41)	16 (4)	246 (92)	314 (69)	−32 (47)	114 (32)
	6012 (12)	5165 —	6100 (72)	0 (6)		525 (151)		14 (50)
O(3)*–H	4531 (10)	4551 (64)	9704 (30)	21 (5)	132 (69)	119 (37)	−43 (50)	34 (25)
	4550 (20)	4530 —	9734 (34)	40 (12)		0 (38)		16 (30)
O(5)*–H	3317 (18)	0504 (92)	6408 (32)	63 (12)	247 (128)	77 (36)	−88 (92)	−23 (37)
	3332 (16)	0470 —	6407 (38)	16 (9)		52 (51)		−73 (34)
O(6)*–H	1690 (18)	4969 (81)	1050 (58)	47 (10)	308 (155)	338 (95)	−183 (85)	66 (55)
	1677 (23)	5033 —	0942 (69)	33 (13)		291 (110)		84 (63)
C(4)*–H	3222 (11)	6145 (63)	4612 (32)	26 (5)	193 (98)	151 (42)	−57 (56)	80 (28)
	3262 (16)	6155 (57)	4613 (44)	43 (9)	69 (65)	198 (64)	−80 (54)	117 (45)
C(5)*–H	2612 (8)	3247 (67)	5996 (28)	14 (4)	310 (143)	124 (33)	−118 (59)	75 (21)
	2623 (12)	3201 (93)	6028 (24)	22 (6)	408 (193)	21 (25)	−194 (82)	64 (22)
C(6)*–H(1)	2569 (11)	2722 (72)	1228 (30)	28 (5)	228 (90)	127 (40)	75 (60)	35 (26)
	2584 (10)	2857 (77)	1282 (37)	7 (5)	245 (124)	228 (53)	52 (57)	23 (28)
C(6)*–H(2)	1932 (10)	1533 (41)	2736 (21)	30 (5)	30 (46)	8 (22)	−123 (35)	−59 (19)
	1888 (12)	1571 (36)	2776 (41)	12 (6)	0 (42)	286 (49)	−51 (31)	−30 (32)

Table 2. *Structure factors for the usual crystal*

The observed values are corrected for absorption.

h	k	l	F^H_{obs}	$\lvert F^H_{calc}\rvert$
1	0	0	.1	.1
2	0	0	7.9	7.7
3	0	0	.2	.2
4	0	0	2.5	2.0
5	0	0	.1	.1
6	0	0	2.4	2.3
7	0	0	.2	.1
8	0	0	1.5	1.0
9	0	0	.3	.6
10	0	0	6.4	5.7
11	0	0	.4	.3
12	0	0	4.3	3.8
13	0	0	1.7	1.5
14	0	0	7.8	7.1
15	0	0	.4	.4
16	0	0	1.7	1.3
17	0	0	.4	.2
18	0	0	1.0	1.2
19	0	0	2.3	2.3
20	0	0	2.6	2.8
21	0	0	2.4	2.2
0	2	0	16.0	16.6
0	4	0	12.8	12.1
0	6	0	13.9	13.5
0	8	0	7.4	8.5
1	1	0	.5	.5
1	2	0	.8	.7
1	3	0	.7	.6
1	4	0	.8	.9
1	5	0	.4	.4
1	6	0	.4	.4
1	7	0	.4	.4
1	8	0	.4	.4
2	1	0	8.0	7.7
2	2	0	8.8	8.4
2	3	0	9.9	9.8
2	4	0	10.3	10.5
2	5	0	5.7	5.7
2	6	0	4.1	4.1
2	7	0	2.0	2.0
2	8	0	3.2	3.4
3	1	0	.2	.2
3	2	0	.6	.8
3	3	0	.3	.3
3	4	0	.4	.4
3	5	0	.4	.4
3	6	0	.8	.9
3	7	0	.4	.4
3	8	0	.9	.8
4	1	0	7.7	7.6
4	2	0	.8	.8
4	3	0	1.0	1.0
4	4	0	1.8	1.7
4	5	0	3.3	2.8
4	6	0	.9	.9
4	7	0	3.1	3.3
4	8	0	2.2	2.4
5	1	0	.3	.3
5	2	0	.3	.4
5	3	0	.3	.3
5	4	0	.4	.6
5	5	0	.4	.5
5	6	0	.4	.4
5	7	0	.4	.5
6	1	0	9.0	8.7
6	2	0	2.6	2.5
6	3	0	4.4	3.9
6	4	0	1.6	1.6
6	5	0	3.0	3.1
6	6	0	1.1	1.1
6	7	0	1.9	1.8
7	1	0	.3	.3
7	2	0	.3	.3
7	3	0	.3	.3
7	4	0	.9	.9
7	5	0	.4	.6
7	6	0	.4	.5
7	7	0	.4	.6
8	1	0	3.7	3.2
8	2	0	1.4	1.4
8	3	0	1.4	1.4
8	4	0	4.8	4.5
8	5	0	2.9	2.9
8	6	0	1.7	1.8
8	7	0	1.0	1.1
9	1	0	.4	.4
9	2	0	.4	.2
9	3	0	.9	.9
9	4	0	1.1	1.0
9	5	0	1.3	1.3
9	6	0	.4	.6
9	7	0	.9	.8
10	1	0	7.4	6.7
10	2	0	5.7	5.3
10	3	0	3.8	3.6
10	4	0	3.0	2.9
10	5	0	3.8	3.4
10	6	0	2.2	2.4
10	7	0	1.8	1.8
11	1	0	1.2	1.2
11	2	0	.7	.3
11	3	0	.4	.5
11	4	0	.4	.4
11	5	0	.9	.9
11	6	0	.5	.5
11	7	0	.4	.6
12	1	0	6.1	6.2
12	2	0	8.0	7.0
12	3	0	1.7	1.9
12	4	0	6.1	6.0
12	5	0	1.9	1.9
12	6	0	2.8	2.9
13	1	0	1.0	.9
13	2	0	1.2	1.1
13	3	0	1.4	1.5
13	4	0	1.2	1.0
13	5	0	.5	.6
13	6	0	1.4	1.4
14	1	0	4.4	4.4
14	2	0	4.5	4.1
14	3	0	8.5	8.1
14	4	0	2.9	2.7
14	5	0	2.8	3.2
14	6	0	3.7	3.5
15	1	0	2.1	2.0
15	2	0	1.3	1.4
15	3	0	1.7	1.6
15	5	0	1.3	1.5
16	1	0	6.1	5.6
16	2	0	2.6	2.5
16	3	0	2.1	2.3
16	4	0	1.9	1.7
16	5	0	2.9	3.0
17	1	0	.9	1.2
17	2	0	2.0	1.5
17	3	0	1.4	1.5
17	4	0	1.1	1.1
17	5	0	.4	.5
18	1	0	6.2	6.0
18	2	0	3.6	3.4
18	3	0	.9	.7
18	4	0	3.6	3.6
19	1	0	1.7	1.5
19	2	0	2.5	2.2
19	3	0	1.6	1.2
20	1	0	1.3	.9
20	2	0	2.2	2.1
20	3	0	2.3	2.3
21	1	0	1.0	1.0
21	2	0	1.5	1.3
0	0	1	4.1	3.9
1	0	1	5.9	5.7
2	0	1	.1	.1
3	0	1	1.9	1.8
4	0	1	.9	.9
5	0	1	3.1	3.1
6	0	1	1.1	.9
7	0	1	5.8	6.6
8	0	1	7.9	8.4
9	0	1	2.1	1.7
10	0	1	4.7	4.3
11	0	1	2.1	2.3
12	0	1	1.8	1.9
13	0	1	.2	1.6
14	0	1	8.8	9.1
15	0	1	3.9	3.3
16	0	1	1.1	1.4
17	0	1	.2	.1
18	0	1	.7	1.1
19	0	1	.2	.4
20	0	1	2.1	1.6
21	0	1	.4	.9
- 1	0	1	2.7	2.8
- 2	0	1	4.8	4.9
- 3	0	1	1.6	1.6
- 4	0	1	.1	.2
- 5	0	1	3.6	3.6
- 6	0	1	.1	.1
- 7	0	1	2.9	2.6
- 8	0	1	2.8	2.3
- 9	0	1	1.6	1.5
-10	0	1	1.0	1.4
-11	0	1	3.6	3.8
-12	0	1	2.1	1.7
-13	0	1	5.9	6.7
-14	0	1	1.6	2.0
-15	0	1	2.5	3.4
-16	0	1	3.4	3.5
-17	0	1	5.4	5.4
-18	0	1	5.5	5.0
-19	0	1	3.1	4.1
-20	0	1	2.7	2.4
-21	0	1	3.3	3.6
-22	0	1	.7	1.0
0	0	2	.8	.8
1	0	2	12.8	13.7
2	0	2	1.4	1.1
3	0	2	5.0	4.7
4	0	2	.1	.6
5	0	2	5.6	5.7
6	0	2	1.2	.8
7	0	2	.2	.8
8	0	2	.2	.4
9	0	2	1.6	1.6
10	0	2	.2	.1
11	0	2	2.9	3.1
12	0	2	1.7	1.2
13	0	2	1.8	1.2
14	0	2	.9	1.0
15	0	2	.2	.0
16	0	2	.2	.1
17	0	2	.2	.0
18	0	2	.2	.2
19	0	2	.7	1.6
20	0	2	.2	.5
- 1	0	2	2.9	2.8
- 2	0	2	.3	.2
- 3	0	2	8.6	9.2
- 4	0	2	.8	.5
- 5	0	2	7.9	8.7
- 6	0	2	1.0	.5
- 7	0	2	1.8	1.8
- 8	0	2	.5	.8
- 9	0	2	2.9	3.5
-10	0	2	1.3	1.1
-11	0	2	2.3	2.3
-12	0	2	.7	1.2
-13	0	2	4.7	4.9
-14	0	2	.2	.2
-15	0	2	.2	.2
-16	0	2	3.4	3.2
-17	0	2	5.1	4.4
-18	0	2	1.4	1.7
-19	0	2	.6	.6
-20	0	2	1.4	2.0
-21	0	2	.7	.8
-22	0	2	.7	.5
0	0	3	2.8	2.7
1	0	3	3.9	3.7
2	0	3	3.5	3.5
3	0	3	.2	.3
4	0	3	4.3	4.2
5	0	3	3.8	3.8
6	0	3	3.6	3.3
7	0	3	2.2	2.4
8	0	3	5.7	5.7
9	0	3	1.8	1.8
10	0	3	2.6	2.9
11	0	3	4.4	4.3
12	0	3	3.6	3.2
13	0	3	6.3	5.9
14	0	3	1.1	1.1
15	0	3	2.4	2.1
16	0	3	.6	.2
17	0	3	.2	.1
18	0	3	1.7	2.2
- 1	0	3	2.2	1.8
- 2	0	3	5.4	5.2
- 3	0	3	1.9	2.1
- 4	0	3	4.8	4.6
- 5	0	3	1.6	.8
- 6	0	3	4.8	4.0
- 7	0	3	6.5	6.8
- 8	0	3	.1	.1
- 9	0	3	2.9	3.1
-10	0	3	1.3	1.5
-11	0	3	3.3	2.7
-12	0	3	.6	.9
-13	0	3	3.7	4.5
-14	0	3	1.4	1.2
-15	0	3	3.1	3.3
-16	0	3	3.5	3.2
-17	0	3	.7	.5
-18	0	3	.2	.2
-19	0	3	3.0	2.6
-20	0	3	2.6	2.4
-21	0	3	4.9	4.7
-22	0	3	.2	.3
0	0	4	3.8	3.7
1	0	4	.2	.2
2	0	4	7.9	7.3
3	0	4	2.5	2.7
4	0	4	7.7	7.0
5	0	4	.8	.8
6	0	4	.3	.2
7	0	4	2.7	1.9
8	0	4	6.3	5.9
9	0	4	.2	.2
10	0	4	.2	.4
11	0	4	.2	.8
12	0	4	4.9	4.5
13	0	4	.7	.9
14	0	4	2.6	2.4
15	0	4	1.1	1.6
16	0	4	.2	.4
- 1	0	4	.2	.1
- 2	0	4	9.5	9.7
- 3	0	4	1.4	1.5
- 4	0	4	6.3	5.5
- 5	0	4	1.1	1.2
- 6	0	4	.3	.7
- 7	0	4	.8	.5
- 8	0	4	1.5	1.5
- 9	0	4	.6	.2
-10	0	4	1.1	.8
-11	0	4	.4	.5
-12	0	4	6.9	7.0
-13	0	4	.9	1.2
-14	0	4	.6	.9
-15	0	4	.6	.7
-16	0	4	.7	1.1
-17	0	4	.7	.2
-18	0	4	1.2	2.1
-19	0	4	.7	1.0
-20	0	4	.6	.6
-21	0	4	1.1	1.3
0	0	5	.8	.6
1	0	5	2.9	3.0
2	0	5	4.4	4.4
3	0	5	8.2	7.6
4	0	5	3.6	3.3
5	0	5	2.8	2.9
6	0	5	2.8	2.7
7	0	5	.8	.8
8	0	5	1.9	2.1
9	0	5	.6	.6
10	0	5	.2	.9
11	0	5	4.0	4.1
12	0	5	.7	1.1
13	0	5	.7	1.4
14	0	5	.7	.7
- 1	0	5	6.5	6.0
- 2	0	5	1.6	1.2
- 3	0	5	5.5	5.3
- 4	0	5	.5	.2
- 5	0	5	3.2	2.7
- 6	0	5	3.4	3.9
- 7	0	5	3.9	4.3
- 8	0	5	5.0	4.8
- 9	0	5	6.1	6.6
-10	0	5	2.3	1.9
-11	0	5	1.7	1.5
-12	0	5	4.2	3.7
-13	0	5	.2	.5
-14	0	5	4.9	4.9
-15	0	5	.7	.8
-16	0	5	.7	1.6
-17	0	5	.2	.3
-18	0	5	2.4	2.5
-19	0	5	.7	.6
-20	0	5	.7	1.3
0	0	6	.6	.6
1	0	6	.6	.8
2	0	6	.6	.8
3	0	6	5.0	4.8
4	0	6	.2	.4
5	0	6	2.8	2.8
6	0	6	.8	.8
7	0	6	2.9	2.2
8	0	6	.2	.3
9	0	6	.2	.9
10	0	6	.5	.5
11	0	6	2.7	3.1
12	0	6	2.2	2.1
- 1	0	6	2.8	3.6
- 2	0	6	.8	.6
- 3	0	6	.2	.0
- 4	0	6	.6	.8
- 5	0	6	6.1	5.6
- 6	0	6	1.1	1.1
- 7	0	6	9.2	9.0
- 8	0	6	.9	1.0
- 9	0	6	2.4	2.3
-10	0	6	.9	.7
-11	0	6	.2	.1
-12	0	6	.2	.2
-13	0	6	1.8	2.1
-14	0	6	.2	.2
-15	0	6	.7	.5
-16	0	6	.2	.7
-17	0	6	2.4	2.8
-18	0	6	.7	.8
0	0	7	1.8	1.8
1	0	7	.6	.5
2	0	7	3.2	2.7
3	0	7	.2	.6
4	0	7	3.5	2.9
5	0	7	.7	.7
6	0	7	3.6	2.5
7	0	7	4.1	4.1
- 1	0	7	.2	.1
- 2	0	7	.7	.8
- 3	0	7	2.5	3.0
- 4	0	7	.2	.9
- 5	0	7	1.3	1.8
- 6	0	7	3.7	4.0
- 7	0	7	.6	1.0
- 8	0	7	.2	.1
- 9	0	7	.2	.2
-10	0	7	.2	.4
-11	0	7	.7	1.4
-12	0	7	.7	.7
-13	0	7	.2	.3
-14	0	7	2.1	2.2
0	0	8	1.2	1.4
1	0	8	.7	.3
- 1	0	8	.7	.5
- 2	0	8	.2	.5
- 3	0	8	.7	.7
- 4	0	8	3.3	3.1
- 5	0	8	.7	.7
- 6	0	8	2.3	2.9
- 7	0	8	.2	.1
- 8	0	8	.2	.1
- 9	0	8	.7	1.1
-10	0	8	3.7	3.5

mal crystal (20%), but surprisingly bad for the deuterated crystal (45%). A preliminary Fourier analysis using the F^D structure factors indicated absent or very weak scattering densities in the hydroxyl hydrogen (deuterium) positions. The obvious explanation for this would be that the crystal was only partly deuterated at these sites, since a mixture of the two isotopes will give a scattering density that varies according to the mixture ratio. This is a consequence of the opposite sign of the scattering lengths of the two isotopes. These were taken to be $-0{\cdot}378 \times 10^{-12}$ cm for H and $+0{\cdot}650 \times 10^{-12}$ cm for D (Bacon 1962).

The failure to produce a total replacement of the hydroxyl hydrogen atoms by deuterium is not yet fully understood. The simplest explanation would of course be an experimental accident at some stage in the crystallization process, but the failure may also be caused by the fact that L-ascorbic acid contains dimers of the substance in aqueous solutions, as stated by Ulmgren & Wahlberg (private communication). Similar failure in total isotopic exchange has been reported by O'Connor & Dale (1966) for $NiSO_4.6H_2O$.

Since the extent of the isotopic exchange in the crystal was unknown, it was decided to analyse the normal crystal first.

The normal crystal

Both zones were refined simultaneously, using a full-matrix least-squares program. This was originally written by Gantzel, Sparks & Trueblood (1965), but later revised and adapted for 'UNIVAC 1107' and 'CDC 3300' by C. Rømming at this institute. The function to be minized was

$$\sum_{hkl} w_{hkl}^2(|F_{\rm obs}| - G|F_{\rm calc}|)^2$$

where w_{hkl} is the weight function and G is the reciprocal scale factor. Various weight schemes were tried,

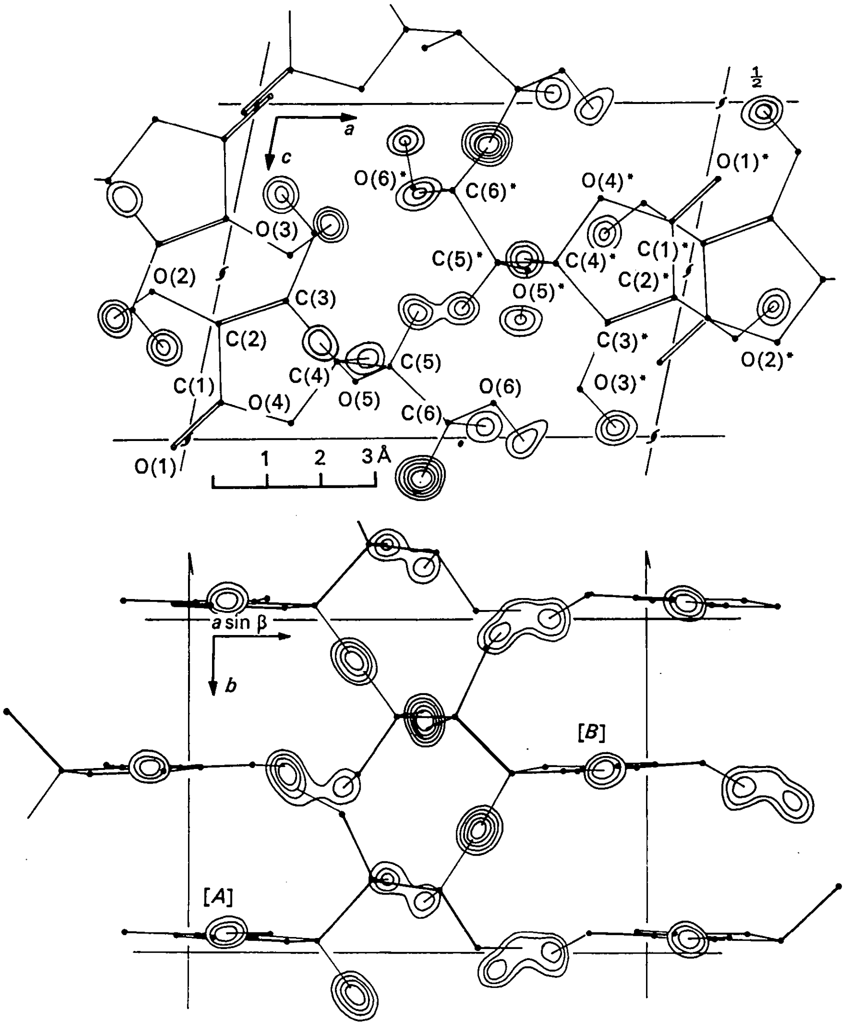

Fig. 1. Difference-Fourier maps along [010] (upper part) and [001] indicate the hydrogen contents in one half of the unit cell. Contours are drawn at intervals of $0{\cdot}25 \times 10^{-12}$ cm. Å^{-2}, starting at $0{\cdot}50 \times {}^{-12}$ cm. Å^{-2}. Full lines are negative.

Table 3. *Structure factors for the deuterated crystal*

The observed values are corrected for absorption.

h	k	l	F^D_{obs}	$\lvert F^D_{calc}\rvert$
1	0	0	.1	.1
2	0	0	7.9	8.6
3	0	0	.6	.3
4	0	0	1.3	.9
5	0	0	.6	.3
6	0	0	2.8	2.3
7	0	0	.3	.0
8	0	0	.9	1.1
9	0	0	.3	.2
10	0	0	5.9	5.7
11	0	0	.3	.1
12	0	0	3.1	2.4
13	0	0	.9	1.1
14	0	0	5.2	5.2
15	0	0	.4	.3
16	0	0	1.9	1.7
17	0	0	.4	.6
18	0	0	.4	.2
19	0	0	1.7	2.2
20	0	0	1.6	2.4
21	0	0	1.5	1.4
0	2	0	19.8	21.4
0	4	0	14.1	14.0
0	6	0	14.5	14.1
0	8	0	9.5	9.2
1	1	0	.5	.4
1	2	0	.5	.1
1	3	0	.6	.6
1	4	0	.6	.4
1	5	0	.4	.6
1	6	0	.4	.3
1	7	0	.4	.3
1	8	0	.4	.3
2	1	0	5.8	5.6
2	2	0	9.5	9.6
2	3	0	9.2	8.7
2	4	0	11.7	12.2
2	5	0	6.2	5.6
2	6	0	4.9	4.9
2	7	0	3.6	3.2
2	8	0	4.4	4.0
3	1	0	.4	.2
3	2	0	.7	.6
3	3	0	.3	.3
3	4	0	.3	.3
3	5	0	.4	.3
3	6	0	.4	.6
3	7	0	.4	.4
3	8	0	.4	.8
4	1	0	9.2	9.2
4	2	0	3.0	2.6
4	3	0	2.1	2.1
4	4	0	.9	.4
4	5	0	3.3	3.6
4	6	0	1.9	1.9
4	7	0	3.6	3.6
4	8	0	2.1	2.2
5	1	0	.4	.2
5	2	0	.3	.3
5	3	0	.3	.3
5	4	0	1.0	1.1
5	5	0	.4	.4
5	6	0	.4	.3
5	7	0	.4	.4
6	1	0	5.7	4.7
6	2	0	2.8	2.5
6	3	0	2.0	1.5
6	4	0	2.4	2.2
6	5	0	1.9	1.8
6	6	0	.7	.9
6	7	0	1.7	1.6
7	1	0	.6	.1
7	2	0	.5	.5
7	3	0	.6	.2
7	4	0	1.0	.8
7	5	0	.4	.6
7	6	0	.4	.6
7	7	0	.4	.7
8	1	0	3.2	2.9
8	2	0	1.6	1.6
8	3	0	1.6	1.4
8	4	0	4.1	4.2
8	5	0	2.4	2.7
8	6	0	1.2	1.3
8	7	0	.4	.5
9	1	0	.4	.5
9	2	0	.8	.5
9	3	0	.4	.3
9	4	0	.4	.6
9	5	0	.9	1.0
9	6	0	.4	.5
9	7	0	.9	1.1
10	1	0	7.3	6.7
10	2	0	5.0	5.0
10	3	0	3.2	3.3
10	4	0	2.5	2.2
10	5	0	3.3	3.4
10	6	0	2.3	2.7
10	7	0	1.7	1.9
11	1	0	1.1	1.3
11	2	0	.8	.8
11	3	0	.4	.7
11	4	0	.4	1.2
11	5	0	.4	.8
11	6	0	.4	.6
11	7	0	.4	.6
12	1	0	6.6	5.6
12	2	0	7.5	6.2
12	3	0	2.3	2.3
12	4	0	5.1	4.8
12	5	0	1.3	1.2
12	6	0	1.8	2.2
13	1	0	.9	.8
13	2	0	.8	.6
13	3	0	1.7	1.8
13	4	0	1.1	1.1
13	5	0	.4	.6
13	6	0	.7	1.1
14	1	0	4.6	3.4
14	2	0	4.4	4.0
14	3	0	8.6	7.8
14	4	0	2.0	1.7
14	5	0	2.9	3.0
14	6	0	3.0	3.0
15	1	0	1.6	1.1
15	2	0	1.4	1.3
15	3	0	1.4	1.5
15	4	0	1.7	1.8
15	5	0	1.3	1.2
16	1	0	7.5	5.7
16	2	0	2.9	2.4
16	3	0	2.9	2.6
16	4	0	2.1	1.9
16	5	0	2.7	3.0
17	1	0	1.5	1.3
17	2	0	1.6	1.4
17	3	0	1.2	1.1
17	4	0	1.2	1.4
17	5	0	.4	.8
18	1	0	8.4	6.5
18	2	0	3.2	2.4
18	3	0	.4	.4
18	4	0	3.5	3.3
19	1	0	1.1	.9
19	2	0	2.4	2.2
19	3	0	1.5	1.2
20	1	0	2.0	1.4
20	2	0	1.9	1.4
20	3	0	3.2	2.7
21	1	0	.4	.8
21	2	0	2.5	2.1
0	0	1	3.7	3.6
1	0	1	4.8	4.5
2	0	1	.5	.5
3	0	1	.3	.1
4	0	1	1.6	1.6
5	0	1	2.8	2.9
6	0	1	.5	.4
7	0	1	5.4	6.3
8	0	1	5.5	6.4
9	0	1	1.7	1.6
10	0	1	3.3	3.3
11	0	1	.3	.5
12	0	1	2.0	2.3
13	0	1	1.4	1.1
14	0	1	8.0	8.5
15	0	1	1.7	2.3
-1	0	1	2.0	1.9
-2	0	1	3.1	3.9
-3	0	1	1.8	1.6
-4	0	1	.2	.2
-5	0	1	5.7	5.6
-6	0	1	2.8	2.7
-7	0	1	2.9	2.4
-8	0	1	1.5	1.5
-9	0	1	.3	.7
-10	0	1	1.3	1.3
-11	0	1	.3	1.5
-12	0	1	2.5	3.1
-13	0	1	5.2	5.4
-14	0	1	.4	.8
-15	0	1	4.1	3.8
-16	0	1	3.9	3.9
-17	0	1	7.0	6.7
-18	0	1	4.8	4.5
-19	0	1	3.0	3.1
0	0	2	.6	.7
1	0	2	10.1	10.7
2	0	2	.9	.6
3	0	2	6.0	6.1
4	0	2	.9	.4
5	0	2	3.2	3.2
6	0	2	1.1	.6
7	0	2	2.1	2.3
8	0	2	.4	.2
9	0	2	.5	1.3
10	0	2	1.3	.7
11	0	2	5.5	5.8
12	0	2	1.7	1.5
13	0	2	.4	.6
14	0	2	1.5	1.4
15	0	2	.4	.7
16	0	2	1.2	.1
-1	0	2	4.6	4.8
-2	0	2	.2	.8
-3	0	2	8.1	7.3
-4	0	2	.9	.8
-5	0	2	9.5	9.7
-6	0	2	1.0	.8
-7	0	2	.3	.4
-8	0	2	1.4	1.1
-9	0	2	3.1	3.1
-10	0	2	1.0	.6
-11	0	2	2.7	2.6
-12	0	2	1.3	.7
-13	0	2	3.8	4.0
-14	0	2	.4	.3
-15	0	2	.4	.4
-16	0	2	3.0	3.6
-17	0	2	4.9	4.7
-18	0	2	1.8	1.6
-19	0	2	1.7	1.7
0	0	3	1.0	.8
1	0	3	2.5	2.3
2	0	3	3.2	3.1
3	0	3	.3	.4
4	0	3	3.7	3.3
5	0	3	3.9	4.9
6	0	3	2.7	2.4
7	0	3	3.3	3.7
8	0	3	5.9	5.8
9	0	3	3.5	3.5
10	0	3	2.0	2.6
11	0	3	3.1	4.0
12	0	3	1.6	1.8
13	0	3	3.3	4.6
-1	0	3	.7	1.7
-2	0	3	7.7	7.4
-3	0	3	.3	.8
-4	0	3	2.5	1.8
-5	0	3	1.4	1.3
-6	0	3	3.9	5.2
-7	0	3	4.8	4.2
-8	0	3	1.7	1.4
-9	0	3	3.5	3.5
-10	0	3	1.8	2.1
-11	0	3	4.0	4.0
-12	0	3	.3	.3
-13	0	3	3.7	3.6
-14	0	3	2.5	2.6
-15	0	3	3.1	3.7
-16	0	3	2.2	2.1
-17	0	3	.4	.1
-18	0	3	1.4	1.5
-19	0	3	1.7	2.0
-20	0	3	1.9	1.5
-21	0	3	3.4	4.3
0	0	4	3.6	3.7
1	0	4	.3	1.1
2	0	4	7.8	6.9
3	0	4	2.0	2.2
4	0	4	8.1	7.6
5	0	4	1.2	.8
6	0	4	1.6	1.3
7	0	4	2.8	2.5
8	0	4	4.7	5.2
9	0	4	.4	.1
10	0	4	.7	.8
11	0	4	.4	.2
12	0	4	2.4	2.7
-1	0	4	.3	1.1
-2	0	4	8.3	8.1
-3	0	4	.8	.8
-4	0	4	4.6	4.1
-5	0	4	1.2	.5
-6	0	4	1.1	.6
-7	0	4	.3	.5
-8	0	4	1.8	2.0
-9	0	4	.3	.3
-10	0	4	3.8	3.3
-11	0	4	.3	.5
-12	0	4	9.1	8.6
-13	0	4	1.5	1.4
-14	0	4	1.4	1.5
-15	0	4	.3	.3
-16	0	4	2.0	2.1
0	0	5	.3	.6
1	0	5	1.1	1.1
2	0	5	4.9	5.4
3	0	5	6.8	6.0
4	0	5	1.7	1.7
5	0	5	2.5	2.1
6	0	5	4.5	4.5
7	0	5	2.8	2.8
8	0	5	1.5	1.6
9	0	5	.4	.4
10	0	5	.4	.2
11	0	5	3.9	5.1
12	0	5	1.2	1.7
13	0	5	.4	.6
14	0	5	.4	.4
15	0	5	1.5	2.0
-1	0	5	4.7	4.4
-2	0	5	.3	.9
-3	0	5	6.3	5.6
-4	0	5	.3	.1
-5	0	5	2.5	2.8
-6	0	5	4.6	4.5
-7	0	5	4.0	3.7
-8	0	5	6.9	5.7
-9	0	5	6.7	5.8
-10	0	5	2.6	2.9
-11	0	5	1.6	1.6
-12	0	5	3.7	3.1
-13	0	5	.4	.4
-14	0	5	4.0	3.7
-15	0	5	1.6	1.9
-16	0	5	2.3	2.4
-17	0	5	.4	.2
-18	0	5	2.1	2.1
-19	0	5	.4	.5
-20	0	5	1.4	2.3
0	0	6	.3	.5
1	0	6	.3	.3
2	0	6	.4	.3
3	0	6	5.2	5.0
4	0	6	1.4	.1
5	0	6	2.4	2.9
6	0	6	.4	.2
7	0	6	4.8	4.3
8	0	6	.4	.6
9	0	6	1.7	1.3
-1	0	6	5.2	5.3
-2	0	6	1.1	.6
-3	0	6	1.7	1.5
-4	0	6	1.2	.9
-5	0	6	5.2	4.4
-6	0	6	.3	.3
-7	0	6	7.1	6.0
-8	0	6	.3	.3
-9	0	6	3.3	2.9
-10	0	6	.4	.0
-11	0	6	1.9	1.5
-12	0	6	.4	.6
-13	0	6	3.3	3.6
-14	0	6	.4	.5
-15	0	6	.4	.6
-16	0	6	.4	.3
-17	0	6	3.0	2.2
-18	0	6	.4	.7
0	0	7	1.3	1.1
1	0	7	.4	1.1
2	0	7	3.8	3.3
3	0	7	.4	.8
4	0	7	3.8	3.4
5	0	7	2.2	2.2
6	0	7	2.2	2.8
7	0	7	4.5	4.2
8	0	7	.4	.3
-1	0	7	.4	.4
-2	0	7	.4	.6
-3	0	7	1.1	1.6
-4	0	7	1.7	1.6
-5	0	7	1.9	1.7
-6	0	7	4.0	3.6
-7	0	7	1.9	1.5
-8	0	7	.4	.0
-9	0	7	.4	.6
-10	0	7	.4	.5
-11	0	7	1.3	1.6
-12	0	7	1.6	2.2
-13	0	7	1.5	1.0
0	0	8	.3	.1
1	0	8	.4	.2
-1	0	8	.9	1.2
-2	0	8	.4	.2
-3	0	8	.3	.3
-4	0	8	2.9	3.0
-5	0	8	1.1	1.3
-6	0	8	4.4	4.1
-7	0	8	.4	.8
-8	0	8	.4	.3
-9	0	8	1.7	1.7
-10	0	8	5.1	4.0

and the apparent best was the following: for $F_{\rm obs}$ less than 2·00, $w_{hkl}=6{\cdot}0$, and for larger values $w_{hkl}=8{\cdot}5/(F_{\rm obs})^{1/2}$.

Although possibly unjustified, the analysis of the hydrogen atoms was finally extended to include anisotropic thermal vibrations. Only eight atoms could be varied simultaneously in order to avoid overlap in any projection. Carbon and oxygen remained fixed with parameters as determined from the X-ray data.

After several cycles of least-squares refinement the final R index for all reflexions was 11·1% while the observed value was 9·2%. The corresponding positional and thermal parameters are given in the first entry in Table 1. Table 2 shows the observed and calculated structure factors. The data were finally used to check for any significant shift in the 'heavy' atom parameters, but none was found.

Difference-Fourier maps (Fig. 1) show the hydrogen atoms in the unit cell as seen along [001] and [010].

The deuterated crystal

The extent of isotopic replacement of H by D atoms could now be analysed by assigning tentative scattering lengths to the 'atoms' in the hydroxyl hydrogen positions. The residual scattering densities in those areas in conjunction with the R indices were used as criteria for this assignment, and the best fit was found when we assumed an equal exchange of 42% for all the atoms in question. This value is certainly not accurate, but a considerable improvement in the R value resulted. Thus the resultant scattering length for this isotopic mixture became $+0{\cdot}054\times10^{-12}$ cm, *i.e.* less than one tenth of the values for oxygen and carbon. We could not expect precise parameters for these 'atoms' from analysing the $F^{\rm D}$ data, and it was decided to use the values found from the $F^{\rm H}$ data. The only atoms left to be refined by means of the $F^{\rm D}$ data were in fact those attached to carbon.

In the subsequent least-squares refinement the same weight scheme was used as for the normal crystal. The final R index became 13·2% for all reflexions and

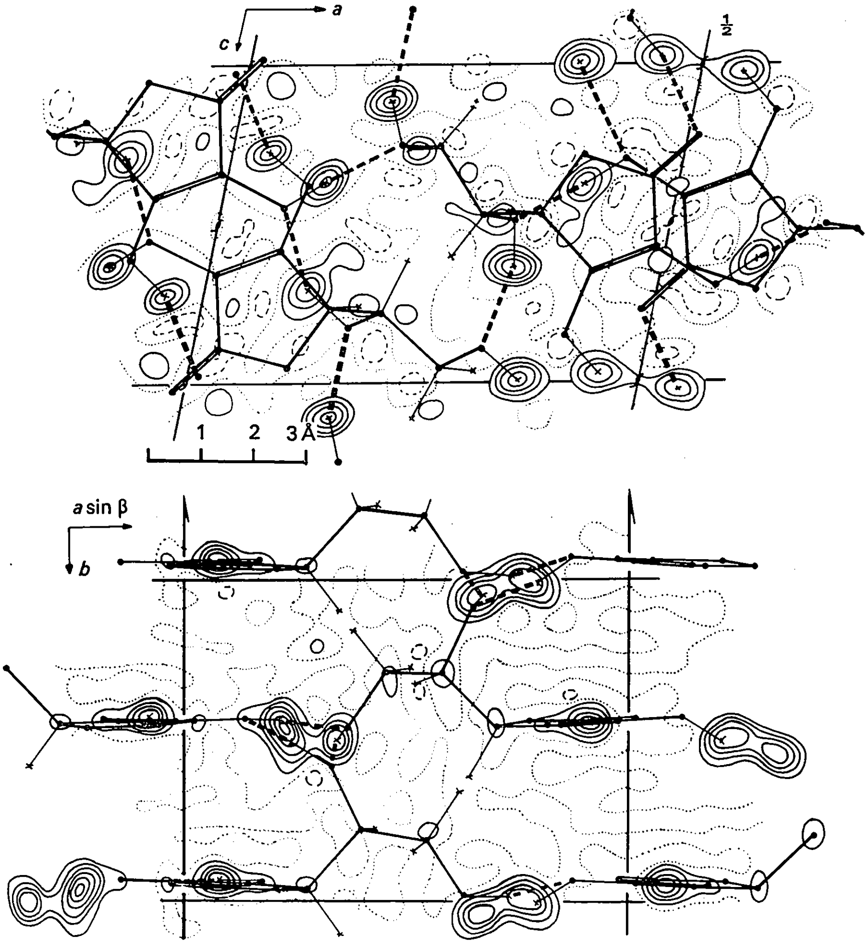

Fig. 2. Neutron scattering density projections along [010] and [001] constructed by subtracting the density for the $F^{\rm H}$ data from the density for the $F^{\rm D}$ data. Intervals at $0{\cdot}25\times10^{-12}$ cm. Å^{-2}. Full lines are positive, dotted lines zero and stippled lines are negative. Heavily stippled lines indicate hydrogen bonds.

11·7% for those observed. The final (C)–H parameters are included in the second entry in Table 1, while the observed and calculated structure factors are given in Table 3.

It was, however, possible to study the hydroxyl hydrogen atoms by a combination of the two sets of data. The Fourier syntheses in Fig. 2 show the differential scattering densities for the two cases. Only the exchanged 'hydrogens' show up, since all the other atoms cancel out.

The differential structure factors $[F^{\mathrm{D}}(h0l)-F^{\mathrm{H}}(h0l)]$ have been used to refine the x and z parameters for these 'hydrogen' atoms by least-squares methods. The results are included in the second entry in Table 1. The y coordinates were obtained from Fourier analyses.

The difference Fourier maps show reasonably low densities outside the (O)–H atomic sites as shown in Fig. 2. It is therefore difficult to reconcile this observation with Weigi's (1952) findings in his infrared study which indicated that L-ascorbic acid should contain one labile hydrogen atom attached to carbon atom number 4.

Discussion

A survey of the distances and angles in the L-ascorbic acid molecule is given in Table 4. It includes the values

Table 4. *Distances* (Å) *and angles* (°) *in the two independently determined molecules of* L-*ascorbic acid*

For the bonds involving hydrogen atoms the two entries correspond to the parameters in Table 1. Standard deviations are given in parentheses.

Distance	Molecule *A*	Molecule *B*	Average
C(1)–O(1)	1·218 (3)	1·213 (3)	1·216 (2)
C(2)–O(2)	1·361 (3)	1·362 (3)	1·361 (2)
C(3)–O(3)	1·327 (4)	1·326 (4)	1·326 (3)
C(1)–O(4)	1·352 (3)	1·358 (3)	1·355 (2)
C(4)–O(4)	1·441 (4)	1·448 (4)	1·444 (2)
C(5)–O(5)	1·421 (5)	1·434 (5)	1·427 (3)
C(6)–O(6)	1·434 (5)	1·429 (5)	1·431 (4)
C(2)–C(3)	1·341 (3)	1·335 (4)	1·338 (2)
C(1)–C(2)	1·457 (4)	1·448 (4)	1·452 (3)
C(3)–C(4)	1·493 (4)	1·494 (4)	1·493 (3)
C(4)–C(5)	1·521 (5)	1·521 (5)	1·521 (4)
C(5)–C(6)	1·521 (4)	1·521 (5)	1·521 (3)
Angle			
C(4)–O(4)–C(1)	109·2 (2)°	109·0 (2)°	109·1 (2)°
O(4)–C(1)–C(2)	109·6 (2)	109·4 (2)	109·5 (2)
C(1)–C(2)–C(3)	107·5 (2)	108·1 (2)	107·8 (2)
C(2)–C(3)–C(4)	109·4 (2)	109·5 (2)	109·5 (2)
C(3)–C(4)–O(4)	104·2 (2)	103·7 (2)	104·0 (2)
O(4)–C(1)–O(1)	121·9 (3)	120·9 (3)	121·4 (3)
O(1)–C(1)–C(2)	128·4 (2)	129·7 (2)	129·1 (2)
C(1)–C(2)–O(2)	124·7 (2)	124·5 (2)	124·6 (2)
O(2)–C(2)–C(3)	127·7 (3)	127·3 (3)	127·5 (2)
C(2)–C(3)–O(3)	133·7 (3)	133·3 (3)	133·5 (2)
O(3)–C(3)–C(4)	116·9 (2)	117·2 (2)	117·1 (2)
C(3)–C(4)–C(5)	114·8 (3)	114·8 (3)	114·8 (2)
O(4)–C(4)–C(5)	110·5 (3)	110·3 (3)	110·4 (2)
C(4)–C(5)–O(5)	111·6 (2)	111·8 (2)	111·7 (2)
C(4)–C(5)–C(6)	112·5 (3)	112·8 (3)	112·7 (2)
O(5)–C(5)–C(6)	106·1 (3)	107·6 (3)	106·9 (2)
C(5)–C(6)–O(6)	108·1 (3)	107·8 (3)	108·0 (2)

Bond	O–H	H...O	O···O	O–H···O	C–O–H
O(2)—H···O(6)*	0·876 (17)	1·748 (18)	2·612 (3)	168·6 (3·1)°	113·5 (1·3)°
	0·929 (23)	1·691 (24)		170·4 (3·7)	114·8 (1·4)
O(2)*–H···O(5′)*	1·045 (27)	1·628 (19)	2·645 (3)	162·6 (3·0)	105·8 (1·2)
	1·074 (35)	1·600 (25)		162·8 (3·6)	106·1 (1·8)
O(3)—H···O(1′)	0·949 (20)	1·729 (21)	2·656 (3)	164·6 (1·7)	117·7 (1·1)
	0·926 (26)	1·746 (26)		166·6 (2·4)	118·9 (1·6)
O(3)*–H···O(1′)*	0·978 (17)	1·719 (18)	2·666 (3)	162·2 (1·8)	117·3 (0·9)
	1·011 (26)	1·689 (23)		161·3 (2·7)	116·7 (1·6)
O(5)—H···O(2′)	1·082 (27)	1·764 (24)	2·786 (4)	155·6 (2·0)	120·3 (2·0)
	1·093 (30)	1·777 (27)		151·3 (2·2)	122·5 (2·2)
O(5)*–H···O(6)	0·935 (24)	1·787 (25)	2·707 (4)	167·2 (2·6)	105·7 (3·3)
	0·937 (26)	1·792 (26)		164·7 (2·2)	107·6 (2·8)
O(6)—H···O(2′)*	0·945 (27)	2·083 (29)	2·935 (3)	149·1 (2·6)	108·2 (2·4)
	0·908 (37)	2·095 (37)		153·4 (3·6)	106·7 (2·9)
O(6)*–H···O(5′)	0·956 (37)	1·846 (38)	2·769 (4)	161·2 (3·2)	100·3 (2·8)
	1·029 (43)	1·773 (44)		161·7 (3·1)	102·0 (2·6)

Table 4 (*cont.*)

	C–H	C(3)–C(4)–H	C(5)–C(4)–H	O(4)–C(4)–H
C(4)–H	1·057 (26)	113·8 (1·6)°	107·1 (1·1)°	106·1 (1·6)°
	1·035 (32)	114·8 (1·8)	111·0 (1·5)	100·3 (1·8)
*	1·113 (36)	112·5 (1·2)	107·2 (1·2)	108·2 (1·1)
	1·087 (34)	110·5 (1·5)	110·6 (1·3)	106·4 (1·4)
		C(4)–C(5)–H	C(6)–C(5)–H	O(5)–C(5)–H
C(5)–H	1·139 (13)	104·3 (1·4)°	106·5 (0·7)°	115·8 (1·6)°
	1·137 (20)	108·5 (2·1)	107·2 (1·1)	110·8 (2·5)
*	1·096 (17)	107·6 (1·9)	105·9 (0·8)	110·9 (2·1)
	1·097 (19)	108·1 (2·6)	107·3 (0·9)	109·0 (2·8)
		C(5)–C(6)–H	O(6)–C(6)–H	H(1)–C(6)–H(2)
C(6)–H(1)	1·107 (30)	109·3 (1·5)°	105·8 (3·1)°	117·6 (3·5)°
	1·128 (33)	108·3 (1·4)	105·0 (3·6)	112·9 (4·2)
*	1·135 (19)	109·9 (0·9)	110·3 (2·1)	108·7 (2·3)
	1·116 (20)	108·1 (0·9)	107·3 (2·3)	116·7 (2·6)
C(6)–H(2)	1·149 (41)	105·1 (1·7)	110·7 (1·5)	
	1·065 (52)	110·1 (2·6)	112·2 (2·1)	
*	1·055 (23)	106·7 (0·9)	113·4 (1·1)	
	1·088 (20)	107·4 (1·3)	109·2 (1·0)	

Table 5. *X-ray results involving hydrogen atoms*

Bond	O–H	H···O	O···O	O–H···O	C–O–H
O(2)—H···O(6)*	0·89 (2)	1·75 (2)	2·612 (3)	165 (3)°	112 (2)°
O(2)*–H···O(5′)*	0·87 (3)	1·77 (3)	2·645 (3)	179 (3)	115 (2)
O(3)—H···O(1′)	0·83 (3)	1·87 (4)	2·656 (3)	158 (3)	113 (2)
O(3)*–H···O(1′)*	0·92 (4)	1·84 (5)	2·666 (3)	148 (4)	107 (3)
O(5)—H···O(2′)	0·81 (4)	2·01 (5)	2·786 (4)	160 (5)	104 (4)
O(5)*–H···O(6)	0·74 (4)	2·05 (4)	2·707 (4)	149 (4)	100 (4)
O(6)—H···O(2′)*	0·82 (3)	2·23 (4)	2·935 (3)	144 (3)	111 (3)
O(6)*–H···O(5′)	0·77 (5)	2·02 (5)	2·769 (4)	162 (4)	114 (3)

	C–H	C(3)–C(4)–H	C(5)–C(4)–H	O(4)–C(4)–H
C(4)–H	1·10 (3)	111 (2)°	107 (1)°	109 (1)°
*	1·03 (4)	112 (2)	109 (2)	106 (2)
		C(4)–C(5)–H	C(6)–C(5)–H	O(5)–C(5)–H
C(5)–H	0·95 (3)	107 (2)°	109 (2)°	111 (2)°
*	1·01 (3)	105 (2)	109 (1)	110 (2)
		C(5)–C(6)–H	O(6)–C(6)–H	H(1)–C(6)–H(2)
C(6)–H(1)	1·00 (3)	113 (2)°	109 (2)°	108 (3)°
*	0·98 (2)	111 (1)	114 (2)	107 (2)
C(6)–H(2)	1·02 (3)	117 (2)	101 (2)	
*	1·05 (3)	112 (2)	105 (2)	

for C–C and C–O bonds as found by X-ray diffraction, and the O–H and C–H bonds as determined by neutron diffraction. For comparison the corresponding hydrogen distances from the X-ray analysis are given in Table 5. The standard deviations are given in parentheses. Note that the asterisks refer to molecule *B*, and that the two entries in Table 4 refer to different sets of data or refinement procedures as described above.

A perspective drawing of the molecule is shown in Fig. 3. The hydrogen atoms are identified by the C or O atom to which they are attached. Since molecules *A* and *B* have marked differences in the orientations of their alcoholic hydrogen atoms, their positions in molecule *B* are indicated by the letter *B*.

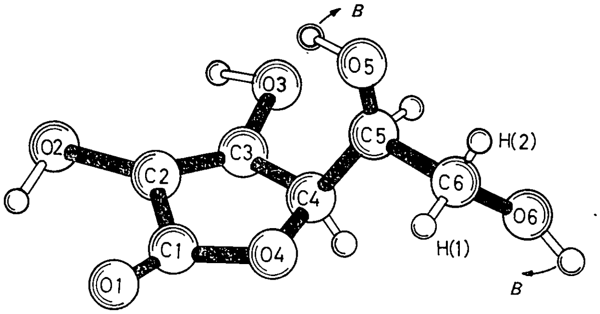

Fig. 3. Perspective drawing of the L-ascorbic acid molecule. The letter *B* indicates the hydroxyl hydrogen position in molecule *B*.

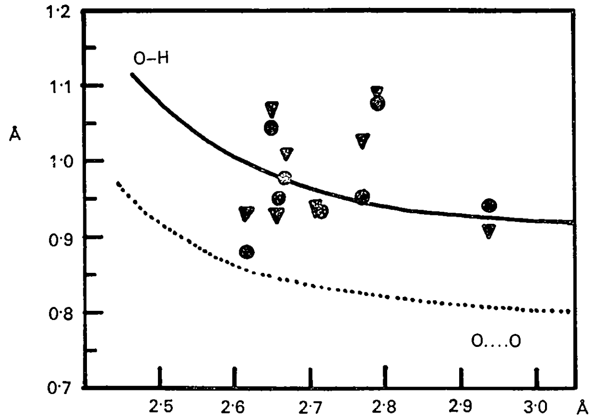

Fig. 4. Correlation diagram between the O–H and O...O distances. Black spots indicate the results from the F^H data, and triangles the results from the combination of the F^H and the F^D data. Full curve represents the empirical function given by Nakamoto *et. al.* (1955), dotted curve the best adapted curve for the present X-ray results.

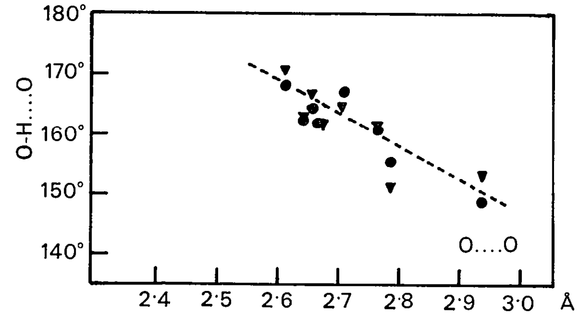

Fig. 5. Correlation diagram between O–H...O angles and O...O distances. Black spots from F^H data, triangles from the combination of F^H and F^D.

Under the assumption that the difference between an O–H and an O–D distance was well within the standard deviation for the present determination, it was decided to accept the respective mean values as given in Table 6. In this Table the standard deviations are multiplied by a factor of $1/\sqrt{2}$ for each additional determination of a bond length. Even under these conditions the results for the O–H and C–H bonds proved to be less accurate than the C–C or C–O bonds when these were determined by three-dimensional X-ray methods. Nevertheless, the neutron results for bonds involving hydrogen are certainly an improvement on the X-ray determination of these bonds.

A point of considerable interest was the systematic comparison between the actual bonding distances in the X-ray and the neutron cases. It was found that in the former case the least-squares procedure led to a systematic shortening in the bonding distances involving hydrogen atoms. The decrements were 0·148 Å for O–H and 0·083 Å for C–H. This is in good agreement with the theoretical results of Stewart, Davidson & Simpson (1965). The average C–H distance of 1·100 Å as determined by neutron diffraction is only slightly shorter than expected, but this may be attributed to the lack of correction for anisotropic thermal vibration.

Fig. 4 shows the variation in O–H bond lengths as a function of O···O distances in hydrogen bonds. The full curve represents the function given by Nakamoto, Margoshes & Rundle (1955), while the dotted curve represents the X-ray results for L-ascorbic acid. Most of the neutron diffraction results agree with this empirical function within three times their standard deviation. Exceptions occur, however, for O(2)–H, O(3)*–H and O(5)–H, but only O(2)–H and O(5)–H seem to fall outside the correlation band suggested by Atoji & Rundle (1958).

In this connexion it should be mentioned that the C(5)–O(5)–H angle is as high as 121·4° while the average for the three other alcoholic angles is 105·1°. The

Table 6. *Average neutron diffraction results*

Bond	O–H	H···O	O···O	O–H···O	C–O–H
O(2)—H···O(6)*	0·903 (14)	1·720 (15)	2·612 (3)	169·5 (2·4)°	114·2 (0·9)°
O(2)*–H···O(5′)*	1·060 (22)	1·614 (16)	2·645 (3)	162·7 (2·3)	106·0 (1·1)
O(3)—H···O(1′)	0·938 (16)	1·738 (16)	2·656 (3)	165·6 (1·4)	118·3 (0·9)
O(3)*–H···O(1′)*	0·995 (15)	1·704 (14)	2·666 (3)	161·8 (1·6)	117·0 (0·9)
O(5)—H···O(2′)	1·088 (20)	1·771 (18)	2·786 (4)	153·5 (1·5)	121·4 (1·5)
O(5)*–H···O(6)	0·936 (17)	1·790 (18)	2·707 (4)	166·0 (1·7)	106·7 (2·2)
O(6)—H···O(2′)*	0·927 (22)	2·089 (23)	2·935 (3)	151·3 (2·2)	107·5 (1·9)
O(6)*–H···O(5′)	0·993 (28)	1·810 (29)	2·769 (4)	161·5 (2·2)	101·2 (1·9)

	C–H	C(3)–C(4)–H	C(5)–C(4)–H	O(4)–C(4)–H
C(4)–H	1·073 (22)	112·9 (1·1)°	109·0 (0·9)°	105·3 (1·0)°
		C(4)–C(5)–H	C(6)–C(5)–H	O(5)–C(5)–H
C(5)–H	1·117 (12)	107·1 (1·4)°	106·7 (0·6)°	111·6 (1·6)°
		C(5)–C(6)–H	O(6)–C(6)–H	H(1)–C(6)–H(2)
C(6)–H(1)	1·122 (18)	108·9 (0·8)°	107·1 (2·0)°	114·0 (2·2)°
C(6)–H(2)	1·089 (24)	107·3 (1·2)	111·4 (1·0)	—

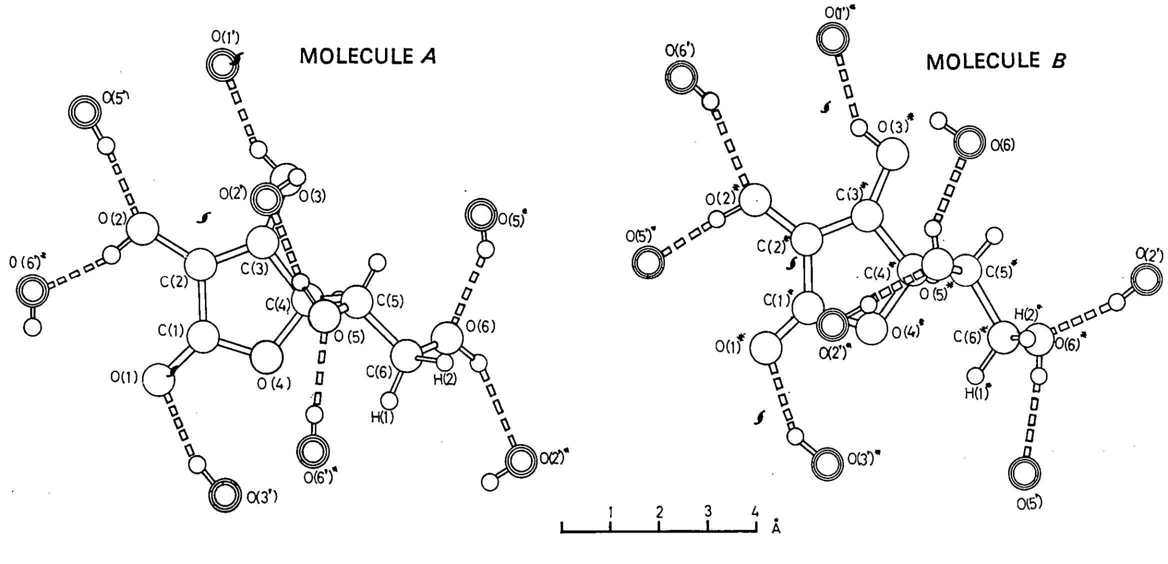

Fig. 6. Environments and hydrogen bonding for molecules *A* and *B*.

opening of this angle may be explained by repulsion effects from C(3) and C(4) in molecule *A*, and the increment of 0·14 Å in the O–H bond length may have some bearing on this. For comparison the average enediol C–O–H angle is 113·7°.

The different C–O–H···O systems have been tested for planarity, and the H atoms can lie out of the planes, defined by the heavy atoms, by up to a maximum of 0·16 Å. In this structure there seems to be however, a certain correlation between the O–H···O angle and the O···O distance, as indicated in Fig. 5.

Only intermolecular hydrogen bonds are present in these crystals. Some of them form helices running along [001], and some form bonds between O(3)–H and O(1) in a neighbouring molecule. This is illustrated in Fig. 2 by the heavily stippled lines, while the environments of the two independent molecules are given in Fig. 6.

The mean value for all the C–H bonds is 1·100 Å, and there seems to be no significant deviation from this value, nor from the average C–C–H and O–C–H angle of 109·2°.

No correction has been made for the apparent anisotropic movement of the hydrogen atoms because of the lack of three-dimensional data and the relatively large standard deviations in the thermal parameters for these atoms.

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