Acta Cryst. (1972). B28, 916

Structure of the Crystalline Dimer of Dehydro-L-Ascorbic Acid

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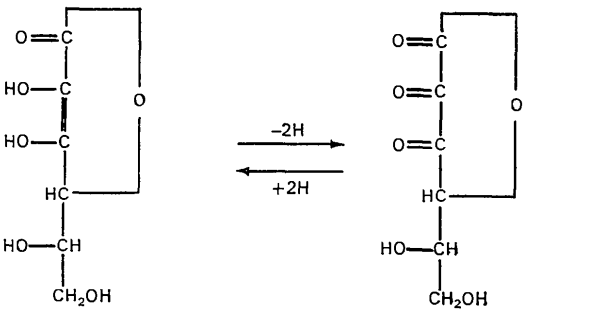
(*Received* 28 *June* 1971)

The first oxidation product of vitamin C is dehydro-L-ascorbic acid, $C_{12}H_{12}O_{12}$, which is dimeric in the crystalline state. The molecular and crystal structure has been determined by means of three-dimensional X-ray data and the parameters have been refined to a final R index of 5·6% for the observed reflexions. The monoclinic unit cell (space group $C2$) contains two molecules and has the lattice parameters $a=15{\cdot}728$, $b=5{\cdot}530$, $c=9{\cdot}453$ Å and $\beta=130{\cdot}56°$. The molecule has twofold symmetry and comprises a system of five fused rings; non-planar γ-lactone and furanose rings are attached to a central dioxan ring in the 'twisted boat' conformation. The C–O distances within the rings vary between 1·338 and 1·448 Å, while the C–C distances have a mean value of 1·524 Å. The external, axially bonded C–OH groups have relatively short C–O distances and contain, in addition to the carbonyl groups, the only oxygen atoms taking part in hydrogen bonding. Each molecule is linked to eight others by one such bond to each of them.

Introduction

It is generally accepted that an important property of vitamin C is its function as a reducing agent. This is attributed to the structure of the five-membered ring which includes a lactone and an enediol group (Euler & Eistert, 1957). The latter group is also responsible for the acidity of the compound. During a reversible oxidation two hydrogen atoms are removed from the molecule. The process is usually described by the equation



L-Ascorbic acid Dehydro-L-ascorbic acid

This structural formula of dehydro-L-ascorbic acid has been criticized by several authors because the three carbonyl groups in the ring are hardly compatible with the colourlessness of the crystalline solid (Albers, Müller & Dietz, 1963). Teichmann & Ziebarth (1966*a*) based their criticism on the properties of the infrared spectrum of the solid, and proposed a polymer form. Molecular weight determinations are complicated by the low solubility in most solvents, but cryoscopic measurements in dimethyl sulphoxide led Teichmann & Ziebarth (1966*b*) to the conclusion that the molecule is a monomer in solution. For several solid derivatives of dehydroascorbic acid, however, a dimeric form seems to be established (Albers, Müller & Dietz, 1963; Dietz, 1964). In a recent communication, Müller-Mulot (1970) proposes an equilibrium in solution between a monomeric and a dimeric form, and bases his conclusion upon the dependence on time of the optical rotatory power. Dietz (1970) emphasizes the role of the solvent in the dehydroascorbic acid solutions. Apparently the crystalline dimer can only be precipitated when certain acids are added to the solutions of the monomeric dehydroascorbic acid. It should be mentioned that we have obtained soft crystals, presumably of dehydroascorbic acid, which give X-ray diagrams typical of a polymer. These were produced by dissolving crystalline dehydroascorbic acid in dimethyl sulphoxide and adding acetonitrile. The analysis of these diagrams will be given elsewhere.

The structure of the monomeric dehydroascorbic acid is not yet known with certainty, mainly due to the difficulty of producing the pure substance. Pecherer (1951) has, however, succeeded in isolating a crystalline methanol complex from which the dimer may be regenerated on heating. These crystals are now being studied in our laboratory.

The present study is intended to clarify the structure of crystalline dehydroascorbic acid in order to contribute to the understanding of the chemistry of vitamin C.

Experimental

Commercially available dehydro-L-ascorbic acid (Koch–Light) was recrystallized from a mixture of 0·2*N* HCl and glacial acetic acid in a ratio of 5:95 by weight as recommended by Staudinger & Weis (1964). Very small, but well developed colourless monoclinic prisms [melting point 225–235° (decomp.)] were obtained in which the needle axis coincided with the b axis of the unit cell. In the base of the prism one edge is parallel to the a axis whereas the c axis forms the diagonal.

Two crystals were selected for the collection of three-dimensional X-ray data. Although they were the largest we could find, their dimensions were only 0·005 × 0·018 × 0·005 cm and 0·004 × 0·025 × 0·004 cm. Neither was well suited for data collection on an automatic diffractometer, and we therefore regretfully decided to use film technique in order to obtain a maximum number of observed intensities. The exposure time per layer varied between one and two weeks, using an integrating Weissenberg camera and Ni-filtered Cu $K\alpha$ radiation ($\lambda = 1{\cdot}5418$ Å). The smaller crystal was mainly used to check the interlayer scaling factors and to obtain a consistent set of data in the ($hk0$) zone. The intensities were recorded photometrically, and the weak reflexions which could not even be observed visually were included by taking one third of the minimum observable value, except for the centrosymmetric b projection where one quarter was used (Hamilton, 1955).

For the present spectra ($h+k=2n$) the only acceptable space group was $C2$ because of the optically active molecules.

The axial lengths were determined by means of Guinier photographs, using KCl as standard. The linear absorption coefficient for Cu $K\alpha$ radiation was 14·7 cm^{-1}, and for these small crystals no correction for absorption was considered to be necessary.

Crystal data

a	15·728 (9) Å	$C_{12}H_{12}O_{12}$	(dimeric form)
b	5·530 (2)	M.W.	348·220 (dimer)
c	9·453 (5)	d_{obs}	1·8 g.cm^{-3} (flotation)
β	130·56 (4)°	d_{calc}	1·836 g.cm^{-3}
V	624·64 Å^3	Z	2 (dimer)
Space group $C2$		μ	14·7 cm^{-1}

Structure determination and refinement

The short b axis offered a convenient way of attacking the phase problem by means of direct methods as the ($h0l$) zone offers the only centrosymmetric projection for this space group. The advantage of using direct methods in this case is obvious, since the model was unknown. Harker–Kasper inequalities yielded no conclusions, but several phases could be determined by the use of standard computer versions of the symbolic addition procedure (Dahl, Gram, Groth, Klewe & Rømming, 1970). The resulting Fourier syntheses were blurred owing to a few wrong signs, but nevertheless indicated atomic concentrations around the twofold axes. Thus from the density of the compound, the space group symmetry and the dimensions of the unit cell it could be inferred that a dimeric model was probable. We therefore proceeded to test the model proposed by Albers *et al.* (1963) and by Dietz (1964) which implied a system of five rings. The crystallographic twofold axis would according to the space-group properties have to pass through the central dioxan ring of the dimer. The orientation of the molecule was soon found, and a subsequent least-squares refinement resulted in a conventional R index of 11 % for the 148 $h0l$ reflexions. The parameters stipulated from this model were used to analyse the three-dimensional data.

Table 1. *Fractional coordinates x, y and z of atoms in the asymmetric unit (moiety) of the dehydroascorbic acid unit cell* ($\times 10^3$)

Standard deviations in parentheses. The hydrogen atoms are identified by the C or O atoms to which they are attached.

	x	y	z
O(1)	79·2 (4)	187·9 (14)	−286·1 (5)
O(2)	31·1 (3)	559·8 (12)	−131·3 (5)
O(3)	58·3 (3)	198·8 (12)	177·1 (4)
O(4)	188·7 (3)	52·6 (12)	4·1 (4)
O(5)	381·4 (3)	4·9 (13)	480·1 (5)
O(6)	186·9 (3)	474·5 (11)	228·2 (5)
C(1)	102·7 (4)	183·0 (14)	−137·5 (7)
C(2)	44·9 (4)	323·1 (14)	−85·8 (7)
C(3)	120·6 (4)	275·4 (13)	126·6 (6)
C(4)	199·9 (4)	76·1 (14)	167·9 (6)
C(5)	316·5 (4)	168·4 (14)	333·6 (6)
C(6)	289·1 (4)	383·5 (13)	396·5 (7)
C(4)H	186 (5)	−91 (14)	182 (9)
C(5)H	355 (4)	240 (13)	297 (7)
C(6)H(1)	344 (6)	528 (17)	447 (10)
C(6)H(2)	288 (5)	270 (15)	496 (9)
O(2)H	−17 (9)	567 (27)	−247 (17)
O(5)H	419 (6)	−83 (16)	463 (10)

Table 2. *Thermal parameters, b_{ij}, of the atoms in the asymmetric unit of the dehydroascorbic acid unit cell*

Standard deviations in parentheses. All b_{ij} values are multiplied by 10^4. The hydrogen atoms are identified by the C or O atoms to which they are attached, and only their isotropic B values are given.

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
O(1)	76 (3)	485 (23)	107 (7)	68 (15)	104 (7)	48 (22)
O(2)	58 (3)	214 (13)	122 (6)	−8 (11)	71 (7)	95 (18)
O(3)	40 (2)	239 (13)	111 (6)	−21 (9)	60 (6)	26 (16)
O(4)	54 (2)	309 (15)	102 (6)	64 (12)	72 (6)	26 (19)
O(5)	62 (3)	339 (19)	122 (7)	131 (13)	69 (7)	145 (20)
O(6)	46 (2)	207 (14)	112 (6)	−42 (10)	43 (6)	−11 (17)
C(1)	43 (3)	286 (22)	118 (8)	68 (15)	75 (8)	65 (24)
C(2)	34 (3)	238 (19)	94 (8)	−3 (12)	45 (8)	9 (22)
C(3)	40 (3)	192 (18)	82 (7)	26 (12)	45 (8)	−10 (19)
C(4)	52 (3)	196 (18)	111 (8)	48 (13)	91 (9)	47 (22)
C(5)	43 (3)	279 (20)	99 (8)	16 (15)	67 (8)	35 (24)
C(6)	51 (3)	215 (19)	106 (9)	−34 (14)	41 (9)	−28 (22)

Table 2 (*cont.*)

Hydrogen atoms	*B*
C(4)–H	2·7 (1·3)
C(5)–H	2·1 (1·1)
C(6)–H(1)	3·9 (1·6)
C(6)–H(2)	3·7 (1·6)
O(2)–H	8·7 (3·2)
O(5)–H	4·0 (1·8)

Throughout the refinement the scaling factors between the different layers were checked from time to time, but as a start the absolute F values were established from crossing layers and from the calculated values in the ($h0l$) zone. The initial refinements were restricted to block-diagonal least-squares calculations using isotropic thermal parameters and including only the carbon and oxygen atoms. The form factors for these atoms were those of Hanson, Herman, Lea & Skilman (1964). The hydrogen atoms were included in the calculations as soon as they were located in difference Fourier maps ($R=11\%$). The hydrogen form factor was that of Stewart, Davidson & Simpson (1965). Correction for secondary extinction was performed at an R index of 8%, and gave as a result a value of $C=1{\cdot}3\times10^{-4}$ in the Zachariasen (1963) formula. The last stages of refinement included full-matrix least-squares refinements with anisotropic thermal parameters for the oxygen and carbon atoms. The following weight scheme was used: for F_{obs} less than 4·00, $w=8{\cdot}0$, and for larger values $w=16{\cdot}0\,(F_{obs})^{-1/2}$. No further shifts were found at R equal to 5·6% for the observed

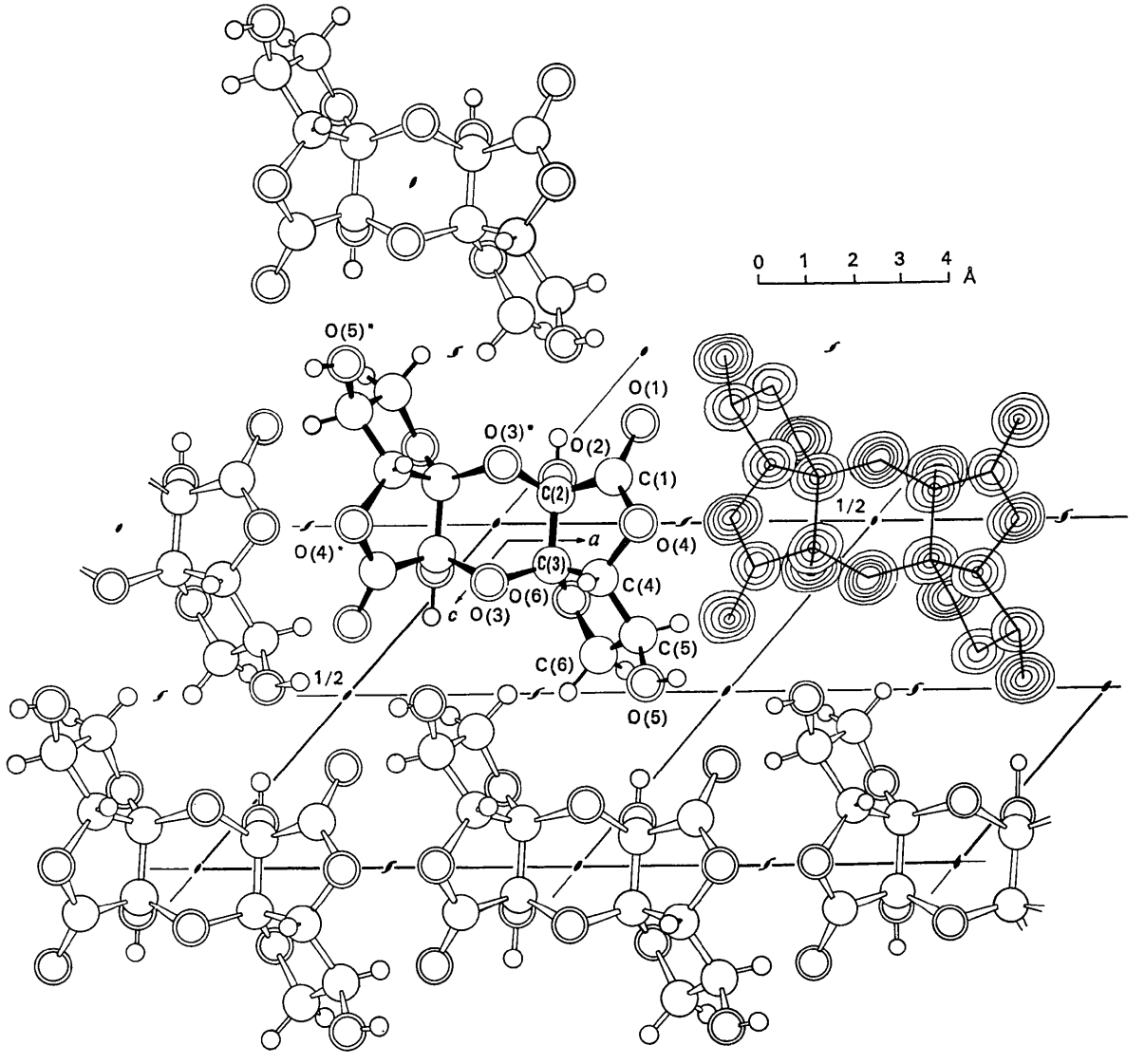


Fig. 1. View of the structure of dehydroascorbic acid along [010]. The reference molecule is indicated by solid lines. The electron density contours start at 2 e.Å^{-3} and have intervals of 2 e.Å^{-3}. Atoms marked by asterisks are symmetry equivalents of the asymmetric unit through the twofold axis. The positive direction of **b** is into the paper.

Table 3. *Observed and calculated structure factors*

F_{obs} are corrected for secondary extinction effects, and the zero observed reflexions (indicated by U) are included by taking one-third of the minimum observable intensity, except for the ($h0l$) zone, where one-quarter was taken.

h	k	l	$10*F_o$	$10*F_c$
2	0	0	23	22
4	0	0	237	244
6	0	0	31	31
8	0	0	416	406
10	0	0	182	170
12	0	0	168	172
14	0	0	102	104
0	0	1	572	520
0	0	2	220	223
0	0	3	489	497
0	0	4	66	61
0	0	5	58	59
0	0	6	199	205
0	0	7	124	132
0	0	8	98	102
0	0	9	9	11 U
-2	0	1	204	203
-4	0	1	195	197
-6	0	1	173	182
-8	0	1	208	213
-10	0	1	103	103
-12	0	1	88	95
-14	0	1	192	185
-16	0	1	22	25
-2	0	2	420	440
-4	0	2	717	729
-6	0	2	192	180
-8	0	2	47	50
-10	0	2	143	145
-12	0	2	141	142
-14	0	2	158	153
-16	0	2	22	26
-2	0	3	719	721
-4	0	3	316	315
-6	0	3	241	250
-8	0	3	357	356
-10	0	3	40	36
-12	0	3	108	105
-14	0	3	111	96
-16	0	3	38	37
-18	0	3	7	3 U
-2	0	4	639	605
-4	0	4	316	305
-6	0	4	385	381
-8	0	4	205	207
-10	0	4	395	377
-12	0	4	221	166
-14	0	4	130	141
-16	0	4	85	85
-18	0	4	76	55
-2	0	5	458	455
-4	0	5	43	46
-6	0	5	383	395
-8	0	5	271	257
-10	0	5	65	64
-12	0	5	208	206
-14	0	5	157	162
-16	0	5	39	37
-18	0	5	12	15 U
-2	0	6	192	202
-4	0	6	93	91
-6	0	6	188	189
-8	0	6	120	110
-10	0	6	50	21
-12	0	6	51	52
-14	0	6	17	26 U
-16	0	6	101	93
-18	0	6	13	12 U
-2	0	7	59	49
-4	0	7	85	73
-6	0	7	183	189
-8	0	7	22	19
-10	0	7	103	108
-12	0	7	81	71
-14	0	7	17	17 U
-16	0	7	16	9 U
-18	0	7	117	108
-2	0	8	16	21 U
-4	0	8	70	76
-6	0	8	83	75
-8	0	8	217	205
-10	0	8	202	184
-12	0	8	87	72
-14	0	8	241	227
-16	0	8	67	64
-18	0	8	13	7 U
-20	0	8	21	28
-2	0	9	57	57
-4	0	9	64	58
-6	0	9	196	194
-8	0	9	17	12 U
-10	0	9	17	11 U
-12	0	9	17	26 U
-14	0	9	181	172
-16	0	9	85	64
-18	0	9	12	17 U
-20	0	9	46	51
-4	0	10	12	11 U
-6	0	10	101	104
-8	0	10	93	89
-10	0	10	16	11 U
-12	0	10	16	19 U
-14	0	10	40	24
-16	0	10	14	12 U
-18	0	10	22	23
-6	0	11	48	45
-8	0	11	44	45
-10	0	11	65	62
-12	0	11	39	38
-14	0	11	53	50
-16	0	11	11	17 U
-12	0	12	28	24
-14	0	12	35	36
2	0	1	397	386
4	0	1	490	501
6	0	1	54	50
8	0	1	170	169
10	0	1	17	14 U
12	0	1	30	24
14	0	1	19	18
2	0	2	493	503
4	0	2	261	271
6	0	2	15	8 U
8	0	2	299	296
10	0	2	66	62
12	0	2	38	35
2	0	3	86	94
4	0	3	25	19
6	0	3	301	301
8	0	3	50	49
10	0	3	50	47
2	0	4	25	24
4	0	4	44	45
6	0	4	213	219
8	0	4	14	15 U
10	0	4	66	55
2	0	5	222	209
4	0	5	209	223
6	0	5	15	23 U
8	0	5	142	126
2	0	6	180	167
4	0	6	135	136
6	0	6	32	31
2	0	7	40	38
4	0	7	73	76
2	0	8	36	40
1	1	0	832	828
3	1	0	220	228
5	1	0	421	437
7	1	0	322	331
9	1	0	57	46
11	1	0	70	64
13	1	0	86	85
15	1	0	47	48
1	1	1	225	226
3	1	1	484	513
5	1	1	216	224
7	1	1	274	277
9	1	1	49	56
11	1	1	81	81
13	1	1	24	29 U
1	1	2	287	284
3	1	2	329	336
5	1	2	146	138
7	1	2	217	222
9	1	2	104	108
11	1	2	54	57
1	1	3	266	283
3	1	3	212	216
5	1	3	57	42
7	1	3	108	108
9	1	3	31	30 U
11	1	3	28	18
1	1	4	57	45
3	1	4	280	280
5	1	4	303	309
7	1	4	32	28 U
9	1	4	62	59
1	1	5	255	249
3	1	5	135	134
5	1	5	156	147
7	1	5	96	103
1	1	6	118	115
3	1	6	77	72
5	1	6	99	89
1	1	7	80	78
3	1	7	135	136
1	1	8	25	40 U
-1	1	1	738	741
-3	1	1	620	667
-5	1	1	87	66
-7	1	1	137	130
-9	1	1	190	194
-11	1	1	142	129
-13	1	1	172	177
-15	1	1	51	45
-1	1	2	234	252
-3	1	2	331	356
-5	1	2	1009	1067
-7	1	2	290	294
-9	1	2	90	94
-11	1	2	202	205
-13	1	2	156	159
-15	1	2	52	41
-1	1	3	448	475
-3	1	3	224	221
-5	1	3	111	103
-7	1	3	299	306
-9	1	3	77	66
-11	1	3	96	80
-13	1	3	92	84
-15	1	3	68	72
-17	1	3	23	33 U
-1	1	4	158	154
-3	1	4	294	258
-5	1	4	137	122
-7	1	4	269	262
-9	1	4	215	206
-11	1	4	177	164
-13	1	4	180	181
-15	1	4	73	64
-17	1	4	27	37 U
-1	1	5	223	205
-3	1	5	104	154
-5	1	5	115	105
-7	1	5	411	424
-9	1	5	170	172
-11	1	5	99	91
-13	1	5	168	167
-15	1	5	77	90
-17	1	5	29	41 U
-19	1	5	17	33 U
-1	1	6	98	94
-3	1	6	109	104
-5	1	6	203	220
-7	1	6	273	287
-9	1	6	276	261
-11	1	6	121	109
-13	1	6	98	92
-15	1	6	130	113
-17	1	6	30	17 U
-19	1	6	21	19 U
-1	1	7	265	262
-3	1	7	250	252
-5	1	7	57	43
-7	1	7	113	104
-9	1	7	170	166
-11	1	7	251	235
-13	1	7	135	131
-15	1	7	60	42
-17	1	7	75	76
-19	1	7	22	21 U
-1	1	8	45	58
-3	1	8	182	180
-5	1	8	35	27 U
-7	1	8	209	180
-9	1	8	217	198
-11	1	8	140	129
-13	1	8	168	160
-15	1	8	48	41
-17	1	8	30	43 U
-1	1	9	39	38
-3	1	9	41	40
-5	1	9	80	61
-7	1	9	149	127
-9	1	9	155	138
-11	1	9	35	39 U
-13	1	9	48	44
-15	1	9	32	38 U
-17	1	9	28	34 U
-19	1	9	20	14 U
-3	1	10	68	58
-5	1	10	92	90
-7	1	10	29	14 U
-9	1	10	70	57
-11	1	10	45	33
-13	1	10	34	41 U
-15	1	10	65	60
-17	1	10	25	40 U
-19	1	10	16	36 U
-11	1	11	57	57
-13	1	11	36	37
-15	1	11	23	28 U
-11	1	12	30	54
-13	1	12	20	36
2	2	0	405	423
4	2	0	130	129
6	2	0	340	339
8	2	0	141	142
10	2	0	147	132
12	2	0	55	54
14	2	0	48	44
0	2	1	297	300
0	2	2	352	362
0	2	3	122	111
0	2	4	313	304
0	2	5	158	164
0	2	6	258	264
0	2	7	139	135
0	2	8	76	77
2	2	1	350	362
4	2	1	502	535
6	2	1	128	133
8	2	1	89	92
10	2	1	148	145
12	2	1	52	51
2	2	2	225	245
4	2	2	49	31
6	2	2	74	73
8	2	2	80	87
10	2	2	118	124
12	2	2	35	41
2	2	3	299	296
4	2	3	72	68
6	2	3	60	67
8	2	3	34	30
10	2	3	25	26
2	2	4	253	249
4	2	4	312	309
6	2	4	37	31
8	2	4	42	49
2	2	5	147	155
4	2	5	79	70
6	2	5	39	44
2	2	6	144	143
4	2	6	57	50
6	2	6	9	22 U
2	2	7	41	40
4	2	7	130	128
2	2	8	9	23 U
-2	2	1	304	301
-4	2	1	80	74
-6	2	1	326	327
-8	2	1	303	331
-10	2	1	153	153
-12	2	1	194	211
-14	2	1	29	17
-2	2	2	185	186
-4	2	2	489	521
-6	2	2	359	361
-8	2	2	122	120
-10	2	2	75	86
-12	2	2	51	58
-14	2	2	88	92
-16	2	2	18	20
-2	2	3	253	271
-4	2	3	214	217
-6	2	3	302	316
-8	2	3	134	146
-10	2	3	62	58
-12	2	3	83	78
-14	2	3	61	60
-16	2	3	60	63
-2	2	4	247	242
-4	2	4	14	14 U
-6	2	4	222	216
-8	2	4	89	87
-10	2	4	155	153
-12	2	4	139	148
-14	2	4	143	151
-16	2	4	71	76
-18	2	4	31	40
-2	2	5	117	112
-4	2	5	112	96
-6	2	5	276	272
-8	2	5	73	75
-10	2	5	129	129
-12	2	5	35	27
-14	2	5	69	73
-16	2	5	19	21 U
-18	2	5	13	18 U
-2	2	6	105	95
-4	2	6	202	195
-6	2	6	129	111
-8	2	6	317	302
-10	2	6	205	199
-12	2	6	95	88
-14	2	6	100	89
-16	2	6	57	56
-18	2	6	20	19
-2	2	7	99	91
-4	2	7	112	111
-6	2	7	119	119
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-6	2	8	124	117
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-14	2	9	38	35
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-4	2	10	64	63
-6	2	10	80	73
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-10	2	10	36	33
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-14	2	11	62	63
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11	3	1	75	83
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3	3	5	83	73
5	3	5	79	75
7	3	5	43	49
1	3	6	50	56
3	3	6	25	19
5	3	6	126	137
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3	3	7	71	72
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6	4	2	157	155
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4	4	4	58	59
6	4	4	52	55
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-14	4	5	71	55
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1	5	1	142	136
3	5	1	146	138
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7	5	1	48	43
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1	5	3	95	100
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-3	5	3	113	128
-5	5	3	84	89
-7	5	3	101	97
-9	5	3	52	42
-11	5	3	57	51
-13	5	3	30	27
1	5	4	83	77
3	5	4	49	44
5	5	4	56	54
-1	5	4	22	18 U
-3	5	4	88	96
-5	5	4	121	104
-7	5	4	62	43
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-11	5	4	18	22 U
-13	5	4	91	70
1	5	5	68	61
3	5	5	29	22
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-3	5	5	92	89
-5	5	5	120	116
-7	5	5	34	35
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-11	5	5	42	31
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1	5	6	8	16 U
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-3	5	6	114	119
-5	5	6	41	37
-7	5	6	63	61
-9	5	6	85	89
-11	5	6	36	26
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4	6	0	78	62
6	6	0	21	25 U
0	6	1	58	48
2	6	1	92	93
4	6	1	22	31 U
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-4	6	1	70	64
-6	6	1	44	36
-8	6	1	17	18 U
2	6	2	65	64
4	6	2	28	16
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0	6	3	15	15
2	6	3	49	61
-2	6	3	91	103
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-4	6	4	84	92
-6	6	4	24	21
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-10	6	4	49	44
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-4	6	5	65	70
-6	6	5	30	27
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-10	6	5	51	61
-4	6	6	49	67
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0	4	0	141	148
0	6	0	114	102

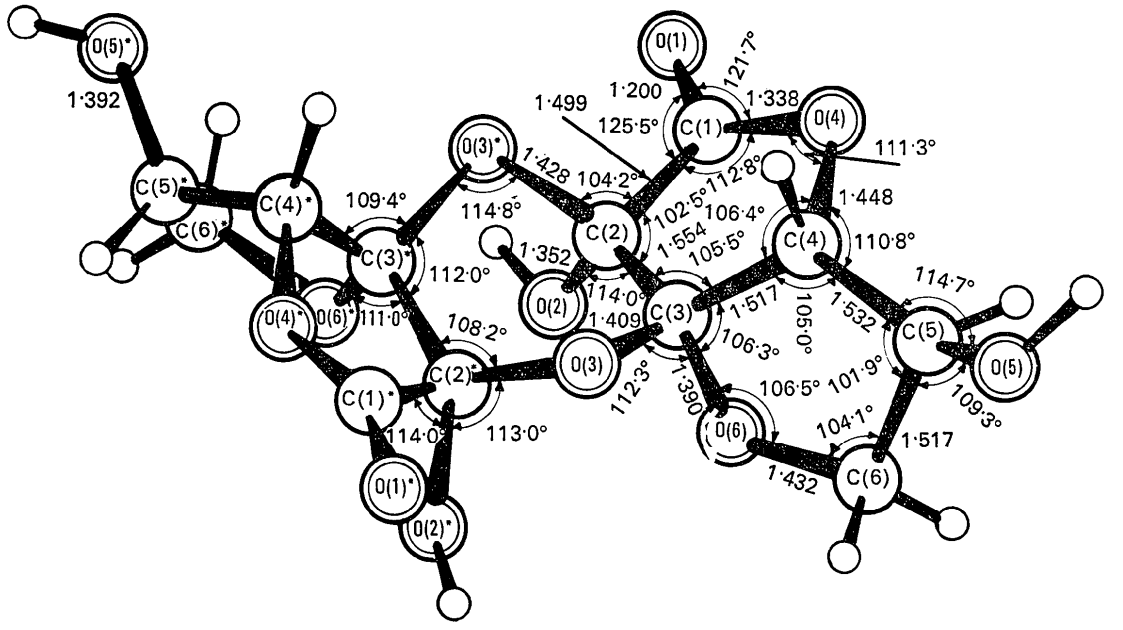


Fig. 2 Some bonding distances and in dehydroascorbic acid.

reflexions. The overall R value for 730 reflexions was then 6·1 %.

The atomic coordinates are given in Table 1, the thermal parameters in Table 2 and the observed and calculated structure factors in Table 3. Table 4 comprises the distances and angles, the corrected values and the standard deviations for dehydroascorbic acid, and also, for comparison, the relevant values in glucuronolactone. For the latter compound renumbering is performed in order to facilitate the comparison.

The thermal parameters have been used in a quantitative analysis of the molecular motion in terms of rigid-body modes of translation, libration and screw motion (Schomaker & Trueblood, 1968). We made two alternative assumptions. In the first, the dehydroascorbic acid moiety (*i.e.* the asymmetric unit as defined in Table 1) was considered to be a separate rigid body. In the second, the whole molecule was tested as such. Neither assumption was particularly successful, and the analysis did not favour any one of these assumptions. In both cases the corrections in bond lengths and angles were within the standard deviations. The corrected values in Table 4 are those where the whole molecule is considered to be a rigid body. These values form the basis of the subsequent discussion of the structure, and are also given in Fig. 2.

Discussion

A view of the structure is shown in Fig. 1. The positive direction of the b axis is into the paper, thus constituting a left-handed system where the choice of axes conforms with the absolute configuration of L-ascorbic acid.

Each molecule comprises one six-membered and

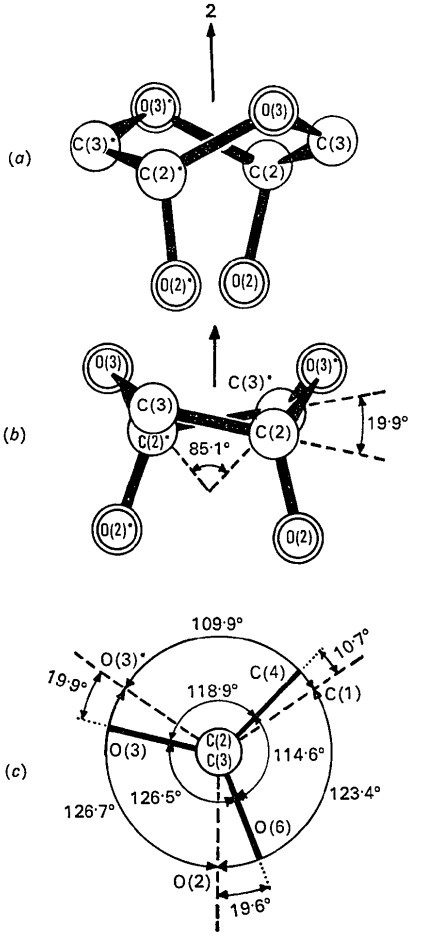


Fig. 3. Conformation of the dioxan ring. (*a*) shows the ring as seen along [001]. (*b*) is a view normal to the C–C bond. (*c*) is a Newman projection along C(2)–C(3).

four five-membered rings fused together as shown in Fig. 2. A central dioxan ring is linked to non-planar lactone and furanose rings. Our numbering of the atoms in the asymmetric unit corresponds to the convention for ascorbic acid. while the second half of the molecule which is generated by the operation of the twofold axis has atoms marked with asterisks.

Table 4. *Distances* (Å) *and angles* (°) *in dehydro*-L-*ascorbic acid and in glucuronolactone* (*Kim et al.*, 1967)

Standard deviations in parentheses. For dehydroascorbic acid the values in brackets are those corrected for thermal motions (TLS). Atoms indicated by * are obtained by the operation of the twofold symmetry axis on the asymmetric unit.

Distances	Dehydro-L-ascorbic acid	Glucurono-γ-lactone
C(1)–O(1)	1·199[1·200] (6) Å	1·215 (5) Å
C(2)–O(2)	1·350[1·352] (7)	1·416 (5)
C(3)–O(3)	1·406[1.409] (6)	–
C(1)–O(4)	1·336[1·338] (6)	1·340 (5)
C(4)–O(4)	1·446[1·448] (6)	1·475 (5)
C(5)–O(5)	1·392[1·392] (6)	1·409 (5)
C(6)–O(6)	1·429[1·432] (6)	1·424 (5)
C(3)–O(6)	1·386[1·390] (6)	1·446 (5)
C(2)–O(3)*	1·425[1·428] (6)	–
C(1)–C(2)	1·498[1·499] (7)	1·511 (6)
C(2)–C(3)	1·552[1·554] (6)	1·526 (6)
C(3)–C(4)	1·513[1·517] (6)	1·533 (6)
C(4)–C(5)	1·530[1·532] (6)	1·520 (6)
C(5)–C(6)	1·512[1·517] (8)	1·520 (6)
Angles		
C(4)–O(4)–C(1)	111·3[111·3] (4)°	111·0 (3)°
O(4)–C(1)–O(1)	121·8[121·7] (5)	120·0 (4)
O(4)–C(1)–C(2)	112·7[112·8] (4)	111·0 (3)
O(1)–C(1)–C(2)	125·5[125·5] (5)	128·9 (4)
C(1)–C(2)–O(2)	113·8[113·9] (5)	112·3 (3)
C(1)–C(2)–C(3)	102·5[102·5] (4)	104·0 (3)
C(1)–C(2)–O(3)*	104·3[104·2] (4)	–
O(2)–C(2)–O(3)*	113·0[113·0] (4)	–
C(3)–C(2)–O(3)*	108·3[108·2] (4)	–
O(2)–C(2)–C(3)	114·0[114·0] (4)	115·0 (3)
C(2)–C(3)–C(4)	105·5[105·5] (4)	104·9 (3)
C(2)–C(3)–O(6)	111·1[111·0] (4)	110·4 (3)
C(2)–C(3)–O(3)	111·9[112·0] (4)	–
O(3)–C(3)–C(4)	109·4[109·4] (4)	–
O(3)–C(3)–O(6)	112·4[112·3] (4)	–
C(4)–C(3)–O(6)	106·1[106·3] (4)	106·1 (3)
C(3)–O(6)–C(6)	106·6[106·5] (4)	108·7 (3)
O(6)–C(6)–C(5)	104·0[104·1] (4)	104·8 (3)
C(6)–C(5)–O(5)	109·4[109·3] (4)	112·0 (3)
C(6)–C(5)–C(4)	101·9[101·9] (4)	102·0 (3)
O(5)–C(5)–C(4)	114·7[114·7] (5)	106·0 (3)
C(5)–C(4)–C(3)	105·0[105·0] (4)	104·8 (3)
C(3)–C(4)–O(4)	106·5[106·4] (4)	106·2 (3)
C(5)–C(4)–O(4)	110·9[110·8] (4)	108·7 (3)
C(2)–O(3)*–C(3)*	114·9[114·8] (4)	–

The symmetry of the *dioxan* ring is restricted by the twofold axis of the space group, thus excluding a 'chair' conformation of this fragment. Further analysis revealed the presence of a 'twist-boat' conformation of dioxan, which to our knowledge has not been encountered before. To clarify the conformation Fig. 3 shows two additional views of the ring and a Newman projection along C(2)–C(3). The dihedral angle between C(2)–O(3)*–C(3)* and C(2)*–O(3)–C(3) is 85·1°

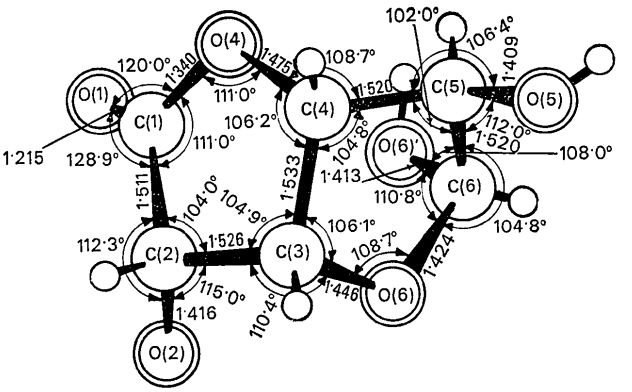
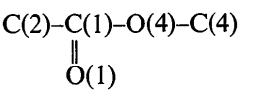


Fig. 4. Some bonding distances and angles in glucuronolactone. (Kim *et al.*, 1967). Atoms are renumbered to conform with dehydroascorbic acid.

and the angle between the two C–C bonds is 19·7°. The 'twist' angles about the C–C bond vary between 10·67° and 19·92°.

It should of course be born in mind that the angles and distances in the present dioxan ring (Table 4) reflect the strain introduced by the presence of the adjacent ring system, of which the lactone and dioxan rings have the C(2) and C(3) atoms in common. The furanose, dioxan and lactone rings have the C(3) atom in common. The long C(2)–C(3) distance of 1·554 Å may possibly be explained by the angular deformations at these atoms, the very short C(2)–O(2) bond (1·352 Å) and the number of oxygen atoms attached to these carbon atoms. Significance for the presence of an abnormally long C–C distance cannot be claimed, however, because of the magnitude of the standard deviation (0·006 Å). The variations in the internal and external C–O bond lengths are interesting in view of the anomer effects presumably present. That the two C–O bonds within the ring are significantly different is thus not surprising in view of the character of the adjacent groups. In gaseous dioxan Davis & Hassel (1963) determined the C–C and C–O bond lengths to be 1·523 and 1·423 Å, respectively, while in crystalline dichlorodioxanes Altona, Knobler & Romers (1963) and Altona & Romers (1963) found C–O distances that varied from 1·388 to 1·478 Å.

With the exception of C(3), the *lactone* ring is planar within ±0·010 Å which is less than three times the standard deviation. If we examine the actual coordinates, however, we observe a slightly puckered lactone group similar to that in ascorbic acid



(Hvoslef, 1968). C(3) is out of the plane through the other atoms by 0·192 Å, and a plane through C(2), C(3), C(4) forms an angle of 11·2° with the plane through the other ring atoms. The elevation of C(3) is smaller than usual for furanose or furanoid lactone rings. In

D-galactono-γ-lactone Jeffrey, Rosenstein & Vlasse (1967) report a deviation of 0·64 Å, while Berman, Rosenstein & Southwick (1971) find 0·58 Å in γ-D-gulonolactone. For the fused ring system of β-D-glucurono-γ-lactone Kim, Jeffrey, Rosenstein & Corfield (1967) found an elevation of 0·25 Å for a ring carbon atom which corresponds to C(2) in dehydroascorbic acid. In the ascorbate anion the deviation of C(3) is 0·152 Å (Hvoslef, 1970) even if the hybridization presumably is different. In dehydroascorbic acid the elevation of C(3) is determined by the presence of the adjacent dioxan ring, for which a 'twist' conformation has lower energy than a boat conformation. A completely planar lactone ring would necessarily imply a pure boat conformation for dioxan, while a 'normal' elevation of C(3) of 0·6 Å would impose upon the dioxan ring a twist angle beyond the energy minimum.

Except for the C(2)–C(3) and C(2)–O(2) distances the angles and bond lengths are in good agreement with the values found for glucuronolactone, and this comparison is highly relevant due to their close relationship, not only in molecular structure (Fig. 4) but also in biochemical context. Glucuronolactone is a precursor of ascorbic acid in the metabolic pathway in animals (Chatterjee, Chatterjee, Ghosh, Ghosh & Guha, 1960) and is converted to ascorbic acid in the human body (Baker, Bierman & Plough, 1960).

The very short axial C(2)–O(2) bond (1·352 Å) may possibly be explained by angular deformations at C(2) and anomer effect in the dioxan ring.

The *furanose* ring has an irregular envelope configuration where C(3), C(4), C(5) and O(6) deviate within ±0·07 Å in a zigzag manner from a least-squares plane through these atoms. C(6) has a 'normal' elevation of 0·550 Å from the plane, and deviates in the *exo* direction with respect to the lactone ring, contrary to the situation in glucuronolactone. The conformational angles for both substances are given in Table 5, and it is seen that the torsional angles are opposite in the two substances. A better fit is obtained if we perform a cyclic permutation so that O(6) in dehydroascorbic acid replaces C(6) in glucuronolactone and so on. Under this assumption the corresponding values of the torsion angles agree fairly well, although different bonds are compared.

The internal angles in the furanose ring are in good agreement with the values in glucuronolactone (Fig. 4), except for the C(3)–O(6)–C(6) angle where our value of 106·5° is smaller than usual for an oxygen atom at this site. The external angles at C(5) are different in the two substances, with one large and one small in each case, but in a different order. This difference is presumably an effect of intermolecular contacts and hydrogen bonding.

Table 5. *Conformational (torsional) angles in the furanose rings of dehydroascorbic acid and of glucuronolactone*

A positive sign is given to an anti-clockwise torsion when proceeding in the direction of the arrow.

	Dehydroascorbic acid	Glucuronolactone
C(4) → C(5)	+12·4 (5)°	−26·2°
C(5) → C(6)	−32·1 (5)	+35·8
C(6) → O(6)	+42·2 (5)	−32·1
O(6) → C(3)	−33·8 (5)	+14·7
C(3) → C(4)	+12·1 (5)	+ 8·7

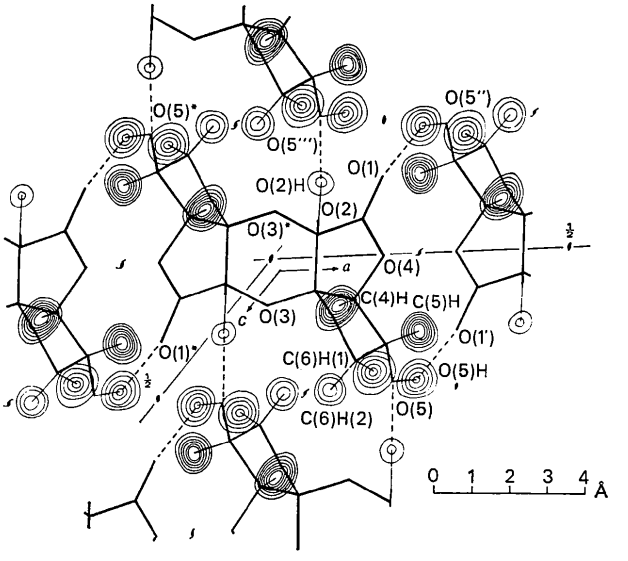


Fig. 5. Composite three-dimensional difference electron density map showing the hydrogen atoms as seen along [010]. Contours at intervals of 0·1 e.Å^{-3}, starting at 0·3 e.Å^{-3}. Broken lines indicate hydrogen bonds. O(1') and O(5'') belong to different molecules.

Table 6. *Distances* (Å) *and angles* (°) *involving hydrogen atoms*

Bond	O–H	H···O	O···O	O–H···O	C–O–H
O(2)–H···O(5')	0·83 (12) Å	1·99 (13) Å	2·808 (5) Å	166 (14)°	107 (10)°
O(5)–H···O(1'')	0·86 (8)	2·11 (8)	2·880 (7)	149 (6)	109 (5)

	C–H	O(4)–C(4)–H	C(3)–C(4)–H	C(5)–C(4)–H
C(4)–H	0·98 (7) Å	100 (4)°	120 (4)°	114 (4)°
	C–H	C(4)–C(5)–H	C(6)–C(5)–H	O(5)–C(5)–H
C(5)–H	0·96 (6) Å	113 (3)°	103 (4)°	114 (3)°
	C–H	C(5)–C(6)–H	O(6)–C(6)–H	H(2)–C(6)–H
C(6)–H(1)	1·04 (8) Å	115 (4)°	104 (4)°	120 (6)°
	C–H	C(5)–C(6)–H	O(6)–C(6)–H	
C(6)–H(2)	1·14 (8) Å	93 (4)°	120 (3)°	

The C–C and C–O distances are normal, but we have noted that the C(3)–O(6) bond is 0·042 Å shorter than O(6)–C(3). This difference was expected, but the position of the shorter bond is reversed compared to glucuronolactone, and this result very clearly demonstrates the effect of changing an oxygen substituent from the C(6) to the C(3) position.

The dihedral angle between the lactone ring and the furanose ring cannot be precisely defined due to the irregularities in both rings, but if we choose C(2), C(3), C(4) and O(6) as reference points, we find an angle of 118°. In glucuronolactone an angle of 111·3° was given, defined by the dihedral angle between the best planes through the planar parts of the rings.

Hydrogen bonding

The molecules are associated in the crystal by a fairly simple three-dimensional hydrogen bond network where each dimer is linked to eight others by one hydrogen bond to each of them.

As expected, no ring oxygen atom takes part in hydrogen bonding, and the only atom acting both as donor and acceptor for hydrogen bonds is O(5).

The sequence is O(2)–H···O(5)–H···O(1) where each oxygen atom belongs to a different molecule, as shown in Fig. 5. The O(5)–H···O(1) interaction is part of a helix running along the twofold screw axis, while O(2)–H···O(5) ties two layers of molecules together in a plane normal to the *b* axis. Neither interaction is strong, as inferred from the bonding distances and angles given in Table 6.

Det Norske Vitenskapsakademi has contributed to the research by a grant, which is gratefully acknowledged. The author is indebted to C. Rømming, P. Groth and B. Klewe for the use of their computer programs and for illuminating discussions. The author also would like to express his sincere thanks to Professor O. Hassel for his continued interest in this work, and for his invaluable advice and criticism.

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