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X-ray Crystal Analysis of the Substrates of Aconitase. IX. A Refinement of the Structure of Anhydrous Citric Acid*

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The structure of anhydrous citric acid was originally determined in this laboratory [Nordman, Weldon & Patterson, *Acta Cryst.* (1960) **13**, 418]. With the availability of improved instrumentation and computing facilities it was decided to collect more accurate data and to refine the structure further. The remeasured unit-cell dimensions are $a=12{\cdot}817$, $b=5{\cdot}628$, $c=11{\cdot}465$ Å $\pm 0{\cdot}13\%$, $\beta=111{\cdot}22\pm 0{\cdot}1°$. The space group is $P2_1/a$. Three-dimensional data were obtained with a General Electric XRD-5 diffractometer. All eight hydrogen atoms were located from a difference electron-density map after refinement of parameters. The final R value is 0·038. New bond lengths and angles and data on the thermal ellipsoids and the least squares planes through parts of the molecule are listed.

The structure of anhydrous citric acid, which crystallizes in the space group $P2_1/a$ with four molecules in the unit cell, was determined in this laboratory by Nordman, Weldon & Patterson (1960). Since that time data on molecular bond lengths and angles of certain other citrates and of citric acid monohydrate (Johnson, 1968) have been collected. It was felt that a further refinement of the structure of the anhydrous acid would be of value and therefore more accurate data were collected.

Experimental

Crystals of anhydrous citric acid were grown by slowly cooling a hot saturated aqueous solution. Cell dimensions were measured on a General Electric XRD-5 diffractometer and were found to be $a=12{\cdot}817$, $b=5{\cdot}628$, $c=11{\cdot}465$ Å, $\beta=111{\cdot}22°$. (Estimated standard deviations 0·13% for axial lengths, 0·1° for angles. $\lambda(\mathrm{Cu}\ K\alpha_1)=1{\cdot}5405$ Å, $\lambda(\mathrm{Cu}\ K\alpha_2)=1{\cdot}5443$ Å.) A crystal was ground to a sphere 0·0156 cm in radius. The $\theta/2\theta$ scan technique was used to collect three-dimensional diffraction data on the diffractometer with nickel-filtered Cu $K\alpha$ radiation and with a scintillation counter as detector. 1695 non-equivalent reflections were measured of which 145 were below the limit of possible measurement. The 'R' value between the present $|F|$ values and those of Nordman *et al.* (1960) is 11·5% for data observed in both sets. The data were corrected for the Lorentz and polarization factors and for absorption ($\mu=13{\cdot}98$ cm^{-1}).

Refinement of the structure

The parameters listed by Nordman *et al.* (1960) were used as input to a block-diagonal least-squares refinement. The initial R value was 22% which decreased to 14·5% after two stages of isotropic refinement and to 8·9% after three further stages of anisotropic refinement. Matrices for each atom were 3×3 for positional parameters, 6×6 for anisotropic and 1×1 for isotropic temperature factors. The weights were assigned on a statistical basis (Gabe, Glusker, Minkin & Patterson, 1967). In all the calculations the scattering factor curves employed were those given in *International Tables for X-ray Crystallography* (1962) except for

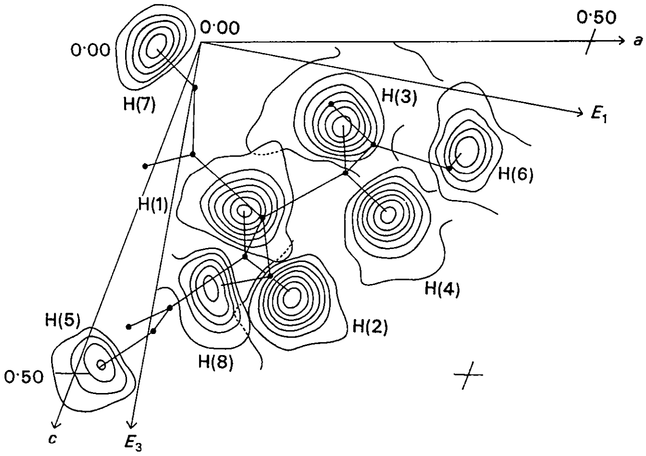

Fig. 1. Composite map of sections of the difference electron density map in three-dimensional space, made at intervals 0·02 b showing the eight hydrogen atoms. The nearest section to each peak is shown. The contour interval is 0·1 e.Å^{-3}. The zero contour is omitted. The axes of the E system are indicated. Solid circles show the final positions of the heavy atoms.

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Table 1. *Parameters of atoms for anhydrous citric acid*

Positional parameters are expressed as fractions of cell edges. Anisotropic temperature factors are expressed as

$$\exp\{-(h^2b^{11}+k^2b^{22}+l^2b^{33}+2hkb^{12}+2hlb^{13}+2klb^{23})\}.$$

Isotropic temperature factors for hydrogen atoms are of the form $\exp(-B\sin^2\theta/\lambda^2)$ and are given in Å². Standard deviations, determined from the inverted block-diagonal matrices, are listed below the parameters with respect to the last decimal place given.

	x	y	z	b^{11}	b^{22}	b^{33}	b^{12}	b^{13}	b^{23}
O(1)	0.0785	0.6717	0.4352	0.00551	0.01450	0.00641	0.00042	0.00314	-0.00062
	1	2	1	10	39	13	15	10	17
O(2)	0.0456	0.2812	0.4282	0.00788	0.01699	0.00867	-0.00242	0.00567	-0.00174
	1	3	1	13	43	15	19	12	20
O(3)	0.3773	-0.0760	0.1879	0.00345	0.02457	0.01430	0.00165	0.00176	-0.00691
	1	3	2	10	54	22	18	12	28
O(4)	0.1993	-0.1720	0.0903	0.00393	0.02312	0.00771	-0.00001	0.00102	-0.00350
	1	3	1	10	48	15	16	10	21
O(5)	0.0147	0.2716	0.0684	0.00440	0.02387	0.00592	0.00021	0.00068	0.00303
	1	3	1	10	50	13	17	9	20
O(6)	-0.0109	-0.0240	0.1846	0.00496	0.02602	0.00752	-0.00468	0.00195	0.00022
	1	3	1	11	54	15	19	10	22
O(7)	0.2003	0.0140	0.3517	0.00434	0.01634	0.00561	0.00065	0.00147	0.00214
	1	2	1	9	40	12	15	9	17
C(1)	0.0892	0.4572	0.3995	0.00404	0.01484	0.00453	-0.00006	0.00158	-0.00029
	2	3	2	12	50	15	19	11	21
C(2)	0.1599	0.4395	0.3207	0.00430	0.01363	0.00571	-0.00108	0.00238	-0.00126
	2	3	2	12	52	16	19	12	22
C(3)	0.1626	0.1945	0.2612	0.00335	0.01227	0.00474	0.00007	0.00168	0.00032
	1	3	2	11	46	14	18	10	20
C(4)	0.2475	0.2078	0.1956	0.00360	0.01620	0.00696	0.00007	0.00266	-0.00018
	2	3	2	11	52	18	21	12	25
C(5)	0.2698	-0.0328	0.1515	0.00334	0.01900	0.00537	0.00082	0.00183	0.00007
	2	3	2	11	56	16	20	11	24
C(6)	0.0456	0.1328	0.1675	0.00351	0.01496	0.00500	0.00024	0.00190	-0.00066
	1	3	2	11	50	15	19	11	22

Table 1 (*cont.*)

	x	y	z	B	attached to
H(1)	0.1373	0.5668	0.2562	3.1	C(2)
	20	48	22	6	
H(2)	0.2318	0.4780	0.3747	3.4	C(2)
	20	46	22	6	
H(3)	0.2214	0.3118	0.1214	4.0	C(4)
	25	50	25	6	
H(4)	0.3183	0.2720	0.2537	3.0	C(4)
	21	43	21	6	
H(5)	0.0282	0.6852	0.4918	7.0	O(1)
	30	63	29	10	
H(6)	0.3846	-0.2241	0.1641	5.7	O(3)
	29	52	30	9	
H(7)	-0.0557	0.2315	0.0135	4.4	O(5)
	24	50	24	7	
H(8)	0.1436	-0.0313	0.3659	5.0	O(7)
	27	57	28	8	

hydrogen atoms, for which the curve of Stewart, Davidson & Simpson (1965) was used.

The three-dimensional difference map computed at this stage revealed all eight hydrogen atoms. These are illustrated in Fig. 1. The R value was 6·8% when the hydrogen atoms were included in the structure factor calculation. After five cycles of refinement, when the R value was 4·7%, a secondary extinction correction was applied in the form

$$F_{\text{corr}}=F_{\text{obs}}\,[1+\alpha\beta(2\theta)\text{Lp}|F_{\text{obs}}|^2]$$

(Zachariasen, 1963*a*). Values of $\beta(2\theta)$ for $\mu r=0{\cdot}218$ are given by Zachariasen (1963*b*) and the experimental value of α was 8×10^{-6}. The R value was then 3·8% for all reflections.

The parameters from the least-squares refinement are listed in Table 1. The observed structure factors and those calculated from the parameters in Table 1 are listed in Table 2. The estimated standard deviations listed in Table 1 are obtained from the inverted block-diagonal least-squares matrices and lead to the standard deviations of positional coordinates, bond lengths, angles and temperature factors which are given in Table 3.

Discussion of the structure

The bond lengths and interbond angles in anhydrous citric acid are given in Fig. 2. No corrections for thermal motion have been made. The standard deviation between the present results and those of Nordman *et al.* (1960) is 0·014 Å for bonds not involving hydrogen atoms. The maximum deviation is 2·4 times the

Table 2. *Observed and calculated structure factors*

Each entry lists, in order, h, $|F_o|$, F_c. Values of $|F_o|$ have an extinction correction applied to them (see text). Unobserved reflections are indicated by an asterisk.

H	OBS	CALC
(H,0,0)		
2	14.3	14.4
4	40.0	40.3
6	10.6	11.0
8	0.5*	-0.4
10	6.1	6.0
12	3.1	3.2
14	0.5*	0.3
(H,0,1)		
-14	0.5*	0.1
-12	5.5	-6.2
-10	15.0	-15.5
-8	38.7	39.2
-6	72.6	72.5
-4	31.7	33.5
-2	48.6	49.8
0	5.6	5.2
2	76.4	-76.0
4	58.6	59.5
6	10.2	-10.2
8	17.3	17.5
10	22.2	23.5
12	6.2	-5.9
14	2.9	-2.8
(H,0,2)		
-14	2.3	-2.4
-12	2.1	2.3
-10	13.4	13.6
-8	11.6	-10.9
-6	15.7	-15.5
-4	0.5*	1.6
-2	23.5	-23.6
0	39.5	-41.2
2	117.6	118.6
4	21.3	20.2
6	23.6	-23.7
8	27.8	-27.8
10	8.5	9.4
12	6.4	-6.1
14	9.8	9.7
(H,0,3)		
-16	3.4	3.4
-14	1.0	-0.4
-12	17.2	17.5
-10	14.8	14.5
-8	45.3	-45.4
-6	75.0	74.1
-4	11.4	11.1
-2	27.9	28.9
0	51.8	-53.0
2	80.5	-81.9
4	49.7	-49.9
6	8.3	-9.2
8	9.4	-8.6
10	2.3	3.2
12	7.3	-7.0
(H,0,4)		
-16	6.2	6.6
-14	1.1	0.9
-12	22.4	22.9
-10	9.2	8.5
-8	20.2	20.6
-6	6.4	5.9
-4	108.3	-105.8
-2	31.3	33.0
0	55.7	-56.4
2	5.2	-4.6
4	33.2	33.8
6	9.1	9.8
8	1.2	1.1
10	22.6	-23.2
12	1.0	-1.3
(H,0,5)		
-16	6.4	6.0
-14	7.5	7.5
-12	1.2	-0.9
-10	0.6*	-0.6
-8	21.1	21.1
-6	36.0	-35.8
-4	35.8	35.0
-2	62.2	61.8
0	37.7	37.8
2	10.5	11.0
4	16.3	-16.5
6	22.6	-21.5
8	9.2	8.5
10	6.2	-6.7
12	1.6	2.1
(H,0,6)		
-16	5.1	4.2
-14	1.6	-0.6
-12	5.4	-5.5
-10	3.1	-2.5
-8	10.2	9.9
-6	12.9	13.2
-4	4.4	-2.6
-2	38.7	-37.8
0	6.3	-5.2
2	4.0	-3.9
4	12.2	12.3
6	6.0	-6.2
8	15.0	14.9
10	8.6	-8.7
(H,0,7)		
-16	11.9	-12.0
-14	3.7	-3.7
-12	3.7	-3.8
-10	29.6	-29.4
-8	6.4	-6.9
-6	20.9	-21.6
-4	10.4	-11.1
-2	4.7	4.5
0	3.4	-3.1
2	21.7	22.1
4	15.2	-15.6
6	16.3	-16.6
8	10.5	-10.4
10	7.9	-7.4
(H,0,8)		
-16	10.5	-10.5
-14	3.8	2.6
-12	6.3	-5.1
-10	3.6	-2.6
-8	3.7	3.0
-6	12.0	-12.0
-4	16.3	16.7
-2	31.5	-32.1
0	36.6	-36.4
2	21.8	-21.9
4	28.1	-29.5
6	6.7	6.7
8	12.1	-11.6
(H,0,9)		
-14	2.1	-1.8
-12	3.6	3.5
-10	3.8	1.4
-8	12.2	-11.9
-6	18.3	-18.5
-4	21.0	-20.7
-2	16.2	-16.1
0	6.9	-6.7
2	6.0	-6.2
4	0.5*	-0.2
6	3.8	3.9
8	8.3	-8.6
(H,0,10)		
-14	1.7	-1.4
-12	1.8	0.9
-10	1.0	0.6
-8	8.5	10.0
-6	7.0	-7.1
-4	5.0	5.3
-2	7.0	6.9
0	4.5	-4.6
2	1.3	-0.7
4	5.2	-5.3
6	1.9	1.5
(H,0,11)		
-14	3.6	4.4
-12	6.8	-6.2
-10	7.6	7.9
-8	11.7	-13.1
-6	5.9	-5.9
-4	0.6*	-0.3
-2	12.9	-13.4
0	10.7	10.5
2	7.6	7.1
4	7.4	7.3
(H,0,12)		
-12	11.0	-10.4
-10	6.0	-5.7
-8	15.5	-14.9
-6	16.3	16.9
-4	4.1	-4.0
-2	6.7	7.0
0	15.2	15.0
2	0.4*	0.2
4	0.3*	6.4
(H,0,13)		
-12	3.2	-2.8
-10	1.9	-1.0
-8	4.9	5.0
-6	1.0	-1.7
-4	3.7	-3.7
-2	4.8	5.3
0	3.8	-3.3
(H,0,14)		
-10	1.8	1.7
-8	1.3	-0.9
-6	2.8	-2.8
-4	10.3	10.7
-2	1.3	-1.1
(H,1,0)		
1	11.8	-12.4
2	29.6	-30.9
3	24.2	25.4
4	19.6	-19.2
5	60.5	61.8
6	4.6	-4.9
7	1.4	-0.9
8	30.2	-30.7
9	3.0	-3.2
10	14.2	-14.4
11	6.4	6.4
12	0.8*	1.4
13	9.3	-9.1
14	5.8	-5.9
15	7.3	7.2
(H,1,1)		
-15	9.8	-9.5
-14	13.0	12.9
-13	7.3	-7.0
-12	7.8	-8.0
-11	15.4	15.8
-10	20.8	21.3
-9	8.8	-9.9
-8	1.2	1.0
-7	11.5	-11.6
-6	20.9	-21.1
-5	9.0	-9.0
-4	0.4*	0.0
-3	7.9	-7.3
-2	3.3	-2.6
-1	81.5	81.8
0	42.0	-44.2
1	7.7	-7.8
2	2.7	-3.3
3	43.4	45.7
4	43.0	-45.2
5	8.1	-8.0
6	2.3	2.3
7	2.5	2.9
8	1.9	-0.4
9	6.1	-6.4
10	11.1	11.5
11	0.5*	-0.1
12	7.6	-7.4
13	11.1	11.6
14	0.4*	0.0
(H,1,2)		
-15	2.4	-2.1
-14	0.5*	0.3
-13	2.5	-2.5
-12	4.9	-4.7
-11	18.0	-18.0
-10	13.2	13.6
-9	7.0	6.3
-8	4.0	-4.3
-7	14.6	-14.6
-6	22.0	20.6
-5	5.9	-5.1
-4	1.1	-2.7
-3	9.8	-9.4
-2	64.8	-65.4
-1	16.3	17.3
0	9.2	9.3
1	60.5	-63.7
2	6.3	6.6
3	56.5	-56.9
4	30.0	-29.3
5	18.3	-18.6
6	2.3	3.0
7	19.7	19.4
8	11.9	-12.4
9	1.2	-0.7
10	1.6	-1.5
11	1.3	1.5
12	10.3	-10.3
13	2.1	-2.1
14	1.1	1.2
(H,1,3)		
-16	4.4	4.3
-15	3.0	2.7
-14	7.2	6.8
-13	10.4	-10.6
-12	12.2	12.4
-11	1.1	-0.7
-10	8.3	-8.3
-9	14.9	14.9
-8	17.9	-18.3
-7	7.6	-8.0
-6	12.7	-12.3
-5	17.0	-16.9
-4	36.7	-37.2
-3	86.6	-86.0
-2	66.9	-67.7
-1	15.5	-15.1
0	8.4	8.5
1	14.8	-14.7
2	48.5	-48.9
3	5.5	-6.1
4	8.6	-8.0
5	1.0	0.5
6	7.4	-6.6
7	25.1	-24.9
8	12.2	-12.1
9	9.7	10.0
10	5.5	5.0
11	9.7	-10.0
12	2.3	1.7
13	0.3*	-0.2
(H,1,4)		
-16	3.3	3.2
-15	0.4*	-0.9
-14	8.8	-8.9
-13	15.0	14.7
-12	11.6	-11.3
-11	7.3	7.2
-10	20.6	-20.9
-9	18.1	-20.8
-8	15.5	-15.7
-7	16.6	16.4
-6	22.6	-21.9
-5	1.2	-1.7
-4	1.2	-2.3
-3	8.7	8.6
-2	21.6	-22.3
-1	3.8	-3.5
0	6.8	-7.3
1	5.7	5.7
2	26.9	-25.8
3	2.7	2.7
4	29.5	29.2
5	22.1	-22.8
6	8.3	-8.2
7	5.6	-5.6
8	9.2	-9.7
9	14.8	14.7
10	2.8	-3.1
11	4.9	-5.0
12	6.6	-6.4
(H,1,5)		
-16	0.3*	-0.6
-15	1.6	1.3
-14	8.6	-8.2
-13	12.7	12.9
-12	1.1	0.3
-11	6.9	-7.1
-10	10.7	11.1
-9	0.5*	0.3
-8	16.2	-15.9
-7	23.4	23.7
-6	11.9	-11.8
-5	7.5	7.6
-4	14.2	-14.3
-3	23.4	23.8
-2	1.1	-1.0
-1	25.2	-26.1
0	12.2	-12.2
1	22.6	22.9
2	19.6	-19.4
3	14.9	15.2
4	4.9	-4.8
5	29.1	28.8
6	20.1	-20.4
7	8.2	7.7
8	2.1	-2.6
9	6.3	-6.3
10	2.7	-2.5
11	3.0	2.8
12	3.8	-3.5
(H,1,6)		
-16	1.0	-0.7
-15	0.4*	0.3
-14	6.6	-6.4
-13	8.9	-8.9
-12	9.6	-10.1
-11	9.9	9.3
-10	8.9	-8.9
-9	2.6	-1.9
-8	23.0	-23.6
-7	8.1	-8.1
-6	13.7	12.4
-5	6.2	-6.6
-4	25.9	-27.0
-3	32.8	32.2
-2	10.3	10.4
-1	31.6	31.6
0	13.0	-12.9
1	9.1	9.3
2	5.7	-6.2
3	19.2	19.5
4	4.7	-4.4
5	7.7	7.7
6	4.7	3.9
7	5.3	-5.8
8	7.5	7.1
9	1.6	1.7
10	1.3	-1.1
11	3.6	4.2
(H,1,7)		
-16	10.6	-9.9
-15	8.0	-7.6
-14	2.9	-2.9
-13	7.9	-7.7
-12	1.3	1.7
-11	1.6	1.8
-10	5.1	5.0
-9	9.6	-9.8
-8	10.9	11.1
-7	2.3	2.5
-6	14.8	14.6
-5	3.5	-3.7
-4	22.6	-23.1
-3	17.9	18.0
-2	7.2	7.5
-1	5.4	-5.6
0	3.1	-3.1
1	13.4	-13.2
2	3.3	3.0
3	3.6	3.3
4	2.8	-3.0
5	15.7	-15.2
6	2.3	-2.2
7	18.7	18.3
8	0.5*	0.6
9	3.1	-2.8
10	2.9	2.6
(H,1,8)		
-15	2.3	-1.7
-14	6.5	6.3
-13	0.5*	-0.9
-12	4.7	4.9
-11	9.4	-9.7
-10	12.7	-14.1
-9	7.9	7.5
-8	2.0	-1.9
-7	2.1	-1.8
-6	13.3	-13.5
-5	7.2	-7.1
-4	6.4	-6.3
-3	20.2	-20.5
-2	0.5*	-1.3
-1	4.7	-4.7
0	10.3	-10.3
1	6.6	6.6
2	0.8*	-1.1
3	11.9	-11.8
4	7.5	7.4
5	5.4	-5.0
6	1.8	1.7
7	0.6*	1.0
8	11.1	10.6
9	10.9	-11.0
(H,1,9)		
-15	9.2	8.5
-14	10.3	-10.1
-13	2.7	2.7
-12	0.5*	-0.8
-11	0.6*	-0.1
-10	8.1	-7.6
-9	9.2	9.1
-8	10.9	11.5
-7	1.4	-1.2
-6	9.9	-9.8
-5	3.5	3.7
-4	8.8	9.1
-3	7.6	-7.2
-2	2.1	-2.0
-1	4.7	4.9
0	0.5*	0.5
1	13.4	-13.2
2	13.9	13.8
3	5.3	-5.5
4	11.4	11.3
5	3.3	-3.2
6	1.3	1.1
7	8.2	-7.9
8	6.2	5.9
(H,1,10)		
-15	1.6	0.9
-14	3.1	2.8
-13	7.4	8.4
-12	7.9	7.3
-11	0.5*	1.2
-10	1.6	-0.9
-9	6.2	5.7
-8	4.4	-4.5
-7	1.5	-2.0
-6	9.4	-9.3
-5	5.9	5.9
-4	8.2	8.3
-3	3.6	3.8
-2	3.1	3.0
-1	12.7	-12.9
0	5.9	5.9
1	4.7	4.5
2	7.0	6.9
3	7.9	7.6
4	2.7	-2.4
5	1.4	1.3
6	5.1	4.9
(H,1,11)		
-14	2.2	-2.0
-13	5.5	4.8
-12	10.3	-9.6
-11	0.5*	-0.3
-10	3.6	-3.4
-9	1.4	2.2
-8	1.4	1.6
-7	4.3	-4.0
-6	11.1	11.4
-5	7.2	7.3
-4	4.6	4.4
-3	0.6*	0.2
-2	7.3	7.6
-1	3.3	3.3
0	5.8	5.8
1	15.3	14.9
2	7.5	7.3
3	5.2	-5.2
4	1.2	1.1
5	8.0	7.5
(H,1,12)		
-13	3.6	-3.8
-12	1.2	0.7
-11	0.4*	-0.1
-10	11.9	11.2
-9	6.9	-6.6
-8	8.8	8.8
-7	1.2	1.0
-6	3.8	3.7
-5	3.6	-4.4
-4	2.8	2.6
-3	3.1	2.6
-2	9.9	9.7
-1	6.4	6.6
0	2.9	2.7
1	4.4	-4.4
2	2.9	3.0
3	0.3*	-0.8
(H,1,13)		
-12	3.1	-3.0
-11	1.2	-1.4
-10	3.6	3.5
-9	2.7	-3.2
-8	1.0	0.6
-7	1.6	2.0
-6	1.8	1.8
-5	4.7	-4.6
-4	9.4	9.4
-3	3.7	3.8
-2	2.3	-2.4
-1	4.9	-5.4
0	1.6	-1.7
1	0.3*	-0.4
(H,1,14)		
-9	1.0	-0.4
-8	0.4*	2.4
-7	0.8	-0.6
-6	2.7	2.8
-5	2.1	1.9
-4	1.3	1.2
-3	5.5	-5.3
-2	6.6	-6.8
(H,2,0)		
0	4.0	-3.6
1	20.5	20.5
2	26.9	-27.9
3	7.9	-8.2
4	16.3	-17.2
5	19.1	-18.7
6	3.2	3.5
7	2.6	-2.6
8	9.8	9.8
9	1.4	0.6
10	12.5	13.0
11	12.3	12.4
12	3.7	-3.9
13	2.1	-2.0
14	4.1	4.0
(H,2,1)		
-15	0.3*	-0.2
-14	5.1	-4.0
-13	5.7	5.3
-12	1.0	-1.3
-11	4.9	5.0
-10	24.6	-24.8
-9	11.8	12.3
-8	7.9	-7.9
-7	5.1	5.0
-6	21.8	-22.1
-5	19.9	19.3
-4	24.2	-24.7
-3	13.4	13.4
-2	14.0	14.3
-1	34.4	-34.9
0	14.3	-15.3
1	7.7	7.0
2	32.9	32.0
3	5.9	5.4
4	8.6	9.2
5	14.3	14.6
6	5.7	-6.1
7	1.4	-1.5
8	8.3	8.8
9	7.1	-7.1
10	0.5*	1.0
11	13.7	14.0
12	2.4	-2.3
13	0.8	0.3
14	4.3	3.9
(H,2,2)		
-15	6.6	6.5
-14	9.7	-9.5
-13	0.5*	-0.5
-12	0.5*	-1.2
-11	13.0	12.9
-10	21.9	-22.7
-9	2.7	2.3
-8	8.2	8.4
-7	24.1	-24.0
-6	27.8	-28.3
-5	7.7	7.7
-4	19.9	19.5
-3	15.8	14.9
-2	73.1	-73.8
-1	13.0	-13.8
0	50.1	-51.4
1	3.5	-3.9
2	3.3	-2.9
3	13.5	-13.9
4	42.8	-42.8
5	24.1	23.4
6	3.7	4.0
7	4.0	4.7
8	9.9	-9.8
9	6.0	6.1
10	1.6	1.8
11	9.4	9.2
12	10.2	10.1
13	2.8	3.0
(H,2,3)		
-15	0.8	-0.7
-14	0.5*	0.5
-13	10.3	-10.3
-12	0.6*	0.8
-11	8.3	8.0
-10	9.2	-9.6
-9	1.0	0.9
-8	29.1	-28.9
-7	5.6	-6.4
-6	35.1	-34.8
-5	1.4	1.4
-4	27.8	-27.6
-3	25.9	-26.1
-2	39.4	-38.9
-1	14.3	14.9
0	9.1	9.0
1	14.0	12.9
2	23.3	-23.3
3	5.8	-5.6
4	4.3	4.5
5	23.1	23.2
6	9.3	9.3
7	10.7	11.1
8	11.5	-11.9
9	2.9	2.4
10	2.9	2.4
11	6.0	-6.0
12	1.0	0.9
13	1.0	-0.7
(H,2,4)		
-15	4.1	4.2
-14	1.7	-1.6
-13	1.9	2.2
-12	12.4	-12.2
-11	7.1	-7.2
-10	3.7	3.4
-9	2.8	-2.6
-8	3.3	3.6
-7	8.7	-7.8
-6	13.3	13.4
-5	9.9	-9.5
-4	9.8	9.6
-3	25.0	-24.0
-2	48.7	47.8
-1	46.3	45.5
0	30.9	-30.8
1	7.6	7.1
2	4.4	-4.8
3	10.0	-9.3
4	1.8	-2.3
5	1.3	1.5
6	3.6	-3.2
7	4.4	-5.4
8	1.4	1.0
9	1.0	0.8
10	2.9	-3.1
11	2.4	-2.2
12	0.8	0.8
(H,2,5)		
-15	0.4*	0.6
-14	5.9	5.7
-13	9.9	-9.5
-12	5.8	-5.6
-11	14.6	-14.6
-10	32.4	32.5
-9	1.7	0.9
-8	1.2	-1.4
-7	5.4	5.7
-6	2.1	-2.4
-5	22.1	22.0
-4	3.4	3.4
-3	4.8	-5.3
-2	12.2	-12.5
-1	11.7	11.6
0	18.6	18.3
1	10.1	-9.5
2	30.5	30.4
3	17.8	17.7
4	0.9	-0.2
5	0.5*	0.0
6	18.5	18.5
7	11.3	-11.5
8	8.8	8.4
9	5.2	5.3
10	5.8	6.1
11	4.6	-4.5
(H,2,6)		
-15	6.1	-5.9
-14	1.8	1.8
-13	4.0	4.3
-12	7.7	-6.8
-11	17.3	17.9
-10	3.6	-3.8
-9	1.6	-1.5
-8	17.4	-18.1
-7	8.1	8.0
-6	35.8	35.6
-5	16.3	16.7
-4	13.5	13.3
-3	4.1	4.0
-2	16.9	17.0
-1	2.8	3.2
0	53.8	53.1
1	4.1	4.2
2	7.0	-6.8
3	9.1	9.2
4	14.4	14.7
5	14.0	-13.9
6	9.0	8.9
7	8.2	-8.2
8	7.1	7.5
9	0.6*	1.2
10	7.3	7.0
(H,2,7)		
-15	0.5*	-0.5
-14	4.0	-3.9
-13	6.6	6.3
-12	4.4	4.2
-11	5.8	6.0
-10	8.5	-8.2
-9	12.2	-12.5
-8	27.1	28.3
-7	19.0	18.0
-6	1.3	1.3
-5	3.5	3.4
-4	8.8	-8.9
-3	9.2	9.3
-2	5.7	-5.9
-1	3.9	-3.5
0	6.4	-6.5
1	12.9	-13.1
2	2.0	-1.8
3	10.6	-10.6
4	22.3	22.2
5	5.3	5.2
6	3.1	-2.5
7	4.2	4.3
8	4.4	4.6
9	0.9	-0.7
(H,2,8)		
-15	1.0	1.2
-14	1.8	-1.7
-13	0.5*	-0.3
-12	3.8	3.3
-11	8.5	8.5
-10	6.6	-6.0
-9	10.2	10.5
-8	8.9	-8.5
-7	10.7	10.8
-6	27.3	-27.6
-5	25.9	-26.6
-4	21.9	22.0
-3	1.8	2.2
-2	0.5*	-0.9
-1	1.5	-1.7
0	9.8	9.7
1	7.9	-8.2
2	6.2	6.3
3	5.0	4.9
4	1.0	1.8
5	3.0	3.1
6	4.4	-4.5
7	2.3	-2.5
8	0.4*	0.7
(H,2,9)		
-14	8.9	-8.7
-13	0.5*	0.9
-12	9.2	8.6
-11	1.6	-2.2
-10	5.7	5.8
-9	5.6	-5.7
-8	1.5	1.8
-7	13.7	-13.7
-6	30.6	30.6
-5	10.9	-11.0
-4	4.0	4.2
-3	6.0	6.0
-2	0.6*	0.5
-1	7.0	-7.3
0	5.4	-4.9
1	4.0	-3.8
2	5.5	-5.3
3	2.1	2.3
4	1.6	-1.1
5	9.8	-9.6
6	2.1	2.3
7	6.9	6.5
(H,2,10)		
-14	8.5	8.2
-13	1.4	-2.2
-12	11.2	10.6
-11	9.2	-9.7
-10	4.2	3.9
-9	1.6	-1.5
-8	7.1	6.7
-7	0.6*	-0.7
-6	2.1	2.0
-5	3.6	3.6
-4	18.1	-18.2
-3	12.0	-12.2
-2	21.4	21.8
-1	4.0	-4.3
0	0.5*	0.8
1	7.6	7.6
2	12.0	11.8
3	3.9	3.8
4	2.6	-2.7
5	1.8	-1.9
6	2.7	2.6
(H,2,11)		
-13	7.8	7.5
-12	11.7	-11.2
-11	6.8	-6.2
-10	6.1	6.2
-9	0.5*	-0.7
-8	5.3	4.9
-7	3.8	-4.1
-6	8.8	8.7
-5	0.6*	-1.0
-4	14.8	15.0
-3	2.9	2.7
-2	12.4	12.6
-1	8.7	8.8
0	4.5	-4.1
1	0.5*	0.8
2	1.2	0.4
3	2.8	-2.9
4	1.8	-2.2
(H,2,12)		
-12	3.8	3.6
-11	5.3	-5.3
-10	8.4	7.7
-9	5.1	4.9
-8	0.5*	0.1
-7	2.9	2.5
-6	0.5*	0.2
-5	5.7	5.6
-4	6.2	-6.3
-3	8.2	8.0
-2	10.6	-10.6
-1	7.2	-7.4
0	0.5*	-0.5
1	2.3	-2.5
2	2.5	2.3
(H,2,13)		
-11	8.6	9.6
-10	12.7	-12.8
-9	4.0	4.7
-8	1.7	-1.7
-7	1.4	-1.5
-6	7.8	-7.9
-5	0.4*	-0.5
-4	3.8	4.2
-3	0.8	-0.9
-2	1.4	-1.7
-1	3.3	-3.4
0	1.6	2.5
(H,2,14)		
-7	0.3*	0.3
-6	2.6	-3.0
-5	0.3*	0.2
-4	0.3*	0.4
(H,3,0)		
1	20.0	19.3
2	20.8	-21.4
3	33.3	33.4
4	9.8	10.1
5	3.7	3.4
6	11.6	11.2
7	3.4	[illegible]
8	10.7	11.4
9	4.9	5.2
10	0.6*	-1.0
11	7.1	7.0
12	2.2	2.1
13	1.0	-0.8
(H,3,1)		
-14	7.1	-7.0
-13	1.7	-1.8
-12	4.0	-4.0
-11	10.0	10.1
-10	2.7	2.6
-9	5.9	-6.5
-8	20.5	20.9
-7	17.6	17.1
-6	4.5	4.0
-5	2.9	-2.8
-4	14.4	14.5
-3	10.3	11.0
-2	4.2	4.5
-1	23.8	-22.9
0	26.0	25.3
1	10.4	-10.7
2	1.5	0.9
3	16.9	18.1
4	2.5	3.0
5	10.0	-9.8
6	0.5*	-1.2
7	26.7	28.1
8	14.2	15.9
9	10.0	10.4
10	3.4	-3.4
11	1.1	-1.7
12	5.2	5.2
13	9.4	9.5
(H,3,2)		
-14	4.9	4.7
-13	9.5	9.6
-12	7.4	7.5
-11	11.7	-11.4
-10	0.7*	-0.9
-9	2.9	-2.8
-8	10.0	10.4
-7	20.9	-20.5
-6	1.6	-2.0
-5	26.9	-26.6
-4	6.2	-5.7
-3	4.4	-4.0
-2	22.4	-22.2
-1	7.0	-7.2
0	33.5	32.6
1	34.5	34.6
2	5.5	5.6
3	0.5*	-0.5
4	6.6	6.7
5	3.8	3.9
6	5.8	5.8
7	14.5	14.9
8	18.7	19.1
9	15.3	-15.6
10	13.1	12.9
11	2.7	2.4
12	7.8	7.6
(H,3,3)		
-14	4.1	4.2
-13	2.8	-3.0
-12	4.7	-5.0
-11	17.7	-17.5
-10	15.3	-15.3
-9	13.1	13.6
-8	1.4	-0.9
-7	10.3	-10.5
-6	11.0	10.8
-5	20.3	20.3
-4	10.9	12.0
-3	0.5*	-0.1
-2	17.1	16.8
-1	4.2	3.9
0	0.5*	-0.1
1	16.8	-16.5
2	21.4	21.6
3	25.7	-25.2
4	20.6	20.9
5	1.3	0.6
6	4.9	5.0
7	16.2	-16.1
8	0.5*	-0.7
9	5.9	-5.6
10	6.5	6.4
11	1.0	-0.7
12	1.8	-1.7
(H,3,4)		
-14	1.8	-2.2
-13	5.1	5.0
-12	3.1	3.0
-11	2.6	2.7
-10	10.5	10.5
-9	17.0	17.9
-8	3.3	-3.6
-7	6.2	-6.1
-6	0.5*	-0.7
-5	2.9	-2.4
-4	11.1	10.9
-3	3.8	-3.7
-2	2.3	3.0
-1	8.8	-8.9
0	18.0	-18.5
1	6.6	7.0
2	22.6	22.6
3	9.0	9.3
4	0.7*	-0.0
5	10.4	-11.2
6	3.8	4.1
7	6.9	-7.1
8	7.5	-7.4
9	3.1	-3.1
10	2.7	3.2
11	5.9	-5.7
(H,3,5)		
-14	2.3	-2.1
-13	3.3	2.9
-12	3.8	3.7
-11	1.8	-1.8
-10	0.6*	-0.1
-9	3.1	3.3
-8	16.0	-16.2
-7	3.6	3.2
-6	5.5	6.0
-5	33.2	32.7
-4	10.9	11.3
-3	24.1	23.3
-2	20.2	20.5
-1	4.9	-4.3
0	20.0	19.3
1	21.8	22.6
2	1.7	2.2
3	25.7	-26.2
4	3.5	-3.4
5	0.5*	-0.9
6	12.6	12.6
7	0.5*	0.1
8	2.4	-2.2
9	4.8	-4.7
10	5.1	-4.7
(H,3,6)		
-14	0.8	-0.4
-13	7.5	-7.1
-12	1.0	-0.4
-11	16.3	17.8
-10	8.2	8.4
-9	1.1	0.9
-8	28.6	28.8
-7	14.3	14.2
-6	16.1	16.5
-5	0.5*	0.0
-4	2.9	3.0
-3	26.1	-25.8
-2	17.4	17.5
-1	7.6	-7.2
0	6.6	7.1
1	3.3	-3.0
2	10.4	-10.3
3	7.4	-7.9
4	2.8	2.7
5	20.0	20.2
6	1.3	-0.9
7	6.8	-6.7
8	2.4	-2.1
9	4.2	4.2
10	3.8	-4.0
(H,3,7)		
-14	7.7	7.5
-13	2.1	-1.7
-12	0.6*	1.4
-11	2.9	2.7
-10	11.9	11.9
-9	20.7	-21.3
-8	8.1	7.9
-7	10.9	-11.0
-6	9.5	-9.7
-5	20.5	-20.7
-4	5.3	5.7
-3	4.0	4.3
-2	1.2	-1.0
-1	9.2	8.4
0	6.4	6.0
1	9.7	-9.7
2	4.3	4.1
3	3.2	3.6
4	1.1	1.3
5	3.4	-2.8
6	8.6	-8.5
7	0.5*	-0.8
8	6.2	6.0
(H,3,8)		
-14	0.7	0.8
-13	9.1	-8.9
-12	1.3	1.5
-11	6.5	-6.5
-10	1.0	0.8
-9	4.2	4.1
-8	4.4	-4.6
-7	6.8	-6.8
-6	19.0	19.0
-5	3.2	3.6
-4	9.0	9.1
-3	16.4	-16.6
-2	11.7	-11.6
-1	11.8	-12.1
0	1.3	1.3
1	12.8	-12.7
2	2.1	-2.4
3	0.5*	0.6
4	3.4	-3.2
5	0.5*	-0.3
6	2.3	-2.7
7	2.0	1.9
(H,3,9)		
-13	1.9	1.2
-12	7.7	7.1
-11	3.3	3.2
-10	3.6	-3.5
-9	6.5	-6.4
-8	1.2	-1.3
-7	14.6	-15.1
-6	2.9	-3.3
-5	2.4	-2.9
-4	17.9	-18.1
-3	16.1	-16.2
-2	6.6	-6.4
-1	19.6	19.9
0	4.2	-4.5
1	2.0	-1.6
2	3.7	-3.8
3	5.9	5.8
4	0.5*	0.1
5	6.3	-6.0
6	0.3*	0.3
(H,3,10)		
-13	3.3	3.2
-12	6.4	-6.3
-11	9.2	-9.0
-10	6.6	-6.3
-9	2.8	-2.5
-8	5.1	-5.3
-7	16.4	16.4
-6	12.0	-12.2
-5	10.9	10.4
-4	4.4	4.5
-3	11.0	11.1
-2	7.9	7.6
-1	2.7	3.1
0	6.0	-5.9
1	6.6	-6.5
2	3.5	-3.6
3	0.4*	0.8
4	0.9	-1.3
5	2.7	-2.9
(H,3,11)		
-12	2.7	2.4
-11	3.6	3.1
-10	3.4	3.4
-9	8.9	8.9
-8	0.5*	1.0
-7	5.0	5.3
-6	0.5*	0.5
-5	8.5	-8.5
-4	0.5*	0.2
-3	1.9	2.2
-2	5.7	-6.2
-1	4.0	-4.1
0	4.9	-4.8
1	8.3	8.3
2	0.4*	-0.2
3	1.3	1.4
(H,3,12)		
-10	6.0	-5.6
-9	8.0	-7.4
-8	1.4	-1.2
-7	0.5*	1.0
-6	0.5*	-0.7
-5	0.5*	-0.5
-4	4.9	-4.9
-3	12.0	12.0
-2	1.7	1.7
-1	0.9	-1.3
0	3.8	3.5
1	2.3	-2.0
(H,3,13)		
-8	3.4	3.2
-7	2.5	2.7
-6	2.7	3.0
-5	5.2	-5.4
-4	0.7	-0.5
-3	3.6	-4.1
(H,4,0)		
0	25.8	29.8
1	20.9	21.2
2	2.3	0.9
3	13.3	13.6
4	20.8	20.5
5	6.4	-6.5
6	6.3	6.2
7	17.3	-17.8
8	6.4	6.4
9	4.4	4.3
10	5.8	5.7
11	16.0	-15.8
12	5.4	5.3
(H,4,1)		
-13	12.7	13.2
-12	8.6	8.5
-11	6.8	6.9
-10	1.4	-1.3
-9	22.0	-22.9
-8	8.6	8.8
-7	8.6	8.9
-6	3.4	-2.2
-5	4.6	-4.1
-4	2.5	-1.6
-3	8.8	9.1
-2	12.6	12.2
-1	12.4	12.5
0	4.5	-4.6
1	1.3	-1.5
2	4.8	2.3
3	8.1	-8.3
4	14.3	13.9
5	0.6*	0.1
6	7.2	6.7
7	4.1	4.1
8	12.5	13.4
9	0.5*	-0.4
10	3.1	3.2
11	7.5	7.4
12	4.5	4.7
(H,4,2)		
-13	1.9	-1.9
-12	4.7	-4.7
-11	5.9	-5.9
-10	6.5	-6.2
-9	8.1	8.1
-8	2.0	2.1
-7	10.5	10.8
-6	17.4	-18.0
-5	1.8	1.1
-4	0.5*	0.4
-3	12.8	12.9
-2	1.5	0.2
-1	4.4	4.1
0	1.3	-1.3
1	29.4	-30.8
2	25.3	25.7
3	22.0	22.5
4	5.7	-5.4
5	10.6	10.6
6	16.3	15.6
7	1.5	-0.6
8	2.5	-2.6
9	11.7	-11.9
10	0.5*	-0.4
11	0.3*	-0.4
(H,4,3)		
-13	0.3*	-0.3
-12	3.1	-3.2
-11	6.8	6.7
-10	4.5	4.4
-9	7.5	7.5
-8	5.3	-5.2
-7	18.7	-19.9
-6	10.3	10.5
-5	17.7	-17.9
-4	1.0	1.2
-3	1.4	0.7
-2	2.3	1.9
-1	3.6	3.6
0	8.7	7.8
1	12.3	-12.7
2	0.7*	-0.7
3	6.9	6.9
4	13.3	-13.3
5	32.5	-32.3
6	4.2	-3.9
7	3.8	4.2
8	11.8	-11.9
9	1.2	-0.7
10	1.0	-0.9
11	0.3*	-0.7
(H,4,4)		
-13	2.9	-3.1
-12	4.2	4.0
-11	14.0	-13.8
-10	1.3	-1.3
-9	6.5	-6.8
-8	3.1	2.9
-7	0.6*	0.3
-6	12.2	12.5
-5	0.6*	0.5
-4	3.9	0.6
-3	4.9	-5.3
-2	9.2	9.1
-1	12.1	-12.2
0	9.5	-9.4
1	1.2	-0.5
2	2.2	2.2
3	15.3	-15.6
4	4.0	-3.7
5	7.7	-7.8
6	6.8	-6.6
7	15.4	15.8
8	4.2	-4.2
9	4.9	-4.7
10	8.1	-7.8
(H,4,5)		
-13	3.4	3.3
-12	1.1	1.1
-11	3.6	-3.4
-10	10.5	10.5
-9	7.5	7.1
-8	11.8	11.6
-7	6.0	6.1
-6	2.6	2.0
-5	13.8	-14.9
-4	19.9	21.0
-3	13.4	-13.4
-2	0.7*	-1.1
-1	12.0	-11.4
0	5.9	5.6
1	10.5	10.7
2	2.7	-2.3
3	8.4	-8.4
4	5.9	-5.8
5	2.2	2.5
6	5.1	-4.9
7	13.4	-13.0
8	6.9	-6.7
9	2.8	-2.5
(H,4,6)		
-13	3.6	3.5
-12	2.2	2.3
-11	6.7	-6.5
-10	9.6	10.1
-9	7.3	-7.2
-8	4.9	-4.9
-7	8.2	-8.1
-6	0.5*	-0.2
-5	1.3	0.5
-4	1.9	-1.2
-3	12.9	14.3
-2	10.7	-10.8
-1	10.1	-10.8
0	1.9	1.2
1	4.7	4.4
2	19.0	-18.9
3	2.1	-1.4
4	4.4	4.0
5	4.2	4.2
6	1.8	-1.7
7	0.4*	-0.5
8	4.2	4.2
(H,4,7)		
-13	0.4*	0.2
-12	2.9	-3.0
-11	1.3	1.1
-10	6.0	-6.1
-9	7.9	8.2
-8	2.5	-2.4
-7	1.4	-1.2
-6	7.5	-8.0
-5	10.9	11.0
-4	14.5	-14.7
-3	2.4	2.2
-2	6.9	-6.8
-1	7.1	-7.2
0	5.3	-5.0
1	8.1	8.9
2	0.6*	-0.2
3	3.7	3.6
4	1.3	1.0
5	8.3	8.2
6	0.4*	-0.4
7	2.5	2.3
(H,4,8)		
-12	1.5	-1.7
-11	4.0	3.5
-10	3.8	-4.0
-9	2.0	-1.8
-8	7.4	-6.8
-7	12.2	-12.0
-6	12.0	-11.7
-5	0.6*	0.7
-4	6.6	-6.5
-3	2.1	-2.5
-2	10.8	-10.8
-1	10.7	11.3
0	1.8	-1.5
1	0.5*	0.1
2	3.8	-3.7
3	2.4	-2.5
4	8.1	-7.7
5	1.3	1.2
6	1.4	1.2
(H,4,9)		
-12	3.9	-3.9
-11	0.4*	0.1
-10	8.0	-8.1
-9	2.9	-3.0
-8	8.8	-9.0
-7	4.2	4.2
-6	2.7	3.0
-5	4.3	4.5
-4	4.9	-5.3
-3	2.2	-1.7
-2	0.5*	-1.1
-1	4.6	4.6
0	2.0	-1.9
1	2.5	-2.6
2	2.3	-1.9
3	0.4*	0.4
4	3.8	3.5
(H,4,10)		
-11	2.4	2.3
-10	0.9	-0.6
-9	0.4*	0.2
-8	5.3	4.7
-7	3.8	3.8
-6	1.5	1.8
-5	3.2	-2.8
-4	1.3	1.2
-3	6.6	-6.2
-2	7.9	7.8
-1	3.5	3.4
0	2.7	-2.6
1	1.2	1.2
2	3.3	3.2
3	1.3	-1.1
(H,4,11)		
-10	0.3*	1.7
-9	0.4*	0.4
-8	1.4	-1.5
-7	1.0	1.1
-6	1.2	1.3
-5	2.2	2.5
-4	3.7	3.8
-3	2.5	2.8
-2	0.5*	0.0
-1	2.8	3.4
0	0.3*	-0.6
1	2.7	-2.8
(H,4,12)		
-7	0.3*	0.5
-6	4.0	3.7
-5	5.4	5.6
-4	6.5	-6.3
-3	1.6	1.3
(H,5,0)		
1	3.4	-3.1
2	21.0	-21.7
3	21.3	-21.5
4	0.7*	0.8
5	9.8	9.8
6	4.8	-4.8
7	6.5	6.5
8	7.7	7.7
9	1.0	1.2
10	0.8	-0.7
11	3.1	3.2
(H,5,1)		
-11	6.3	-6.3
-10	6.0	6.2
-9	5.9	-5.7
-8	8.2	8.4
-7	3.5	-3.6
-6	0.6*	-0.7
-5	11.7	-11.8
-4	8.0	-7.9
-3	16.0	-16.3
-2	3.8	-3.8
-1	19.3	19.4
0	3.4	-3.8
1	5.9	-6.1
2	12.8	12.7
3	20.0	20.3
4	14.7	14.6
5	0.6*	-0.8
6	0.5*	0.6
7	3.5	-3.1
8	5.2	5.7
9	2.3	2.4
10	8.6	-9.0
(H,5,2)		
-11	7.4	-7.5
-10	5.5	-5.6
-9	0.5*	-0.3
-8	2.1	-2.4
-7	12.0	-12.2
-6	0.6*	-0.3
-5	6.0	6.3
-4	4.4	4.5
-3	1.6	1.7
-2	9.9	9.7
-1	14.2	-14.0
0	22.9	22.7
1	15.4	-15.9
2	0.6*	1.1
3	3.7	4.0
4	12.2	-12.1
5	9.5	-9.3
6	12.8	-13.1
7	2.1	2.2
8	1.3	-1.1
9	3.2	3.4
(H,5,3)		
-11	7.3	7.2
-10	11.6	-11.3
-9	9.6	-9.3
-8	12.4	12.6
-7	10.9	-11.6
-6	6.7	7.1
-5	2.1	-1.7
-4	1.7	-2.5
-3	14.7	-15.1
-2	7.8	-7.7
-1	2.5	-2.4
0	21.8	-21.6
1	4.7	4.8
2	10.7	-10.8
3	2.2	2.0
4	0.6*	0.5
5	8.7	8.5
6	1.8	-1.7
7	5.0	-4.6
8	1.8	-1.7
9	0.3*	-0.5
(H,5,4)		
-11	2.2	2.0
-10	2.3	-2.0
-9	7.5	-7.5
-8	1.4	-1.0
-7	15.8	15.6
-6	18.0	-18.3
-5	4.2	-4.5
-4	1.2	-1.8
-3	16.3	16.4
-2	6.6	-5.9
-1	12.4	13.4
0	12.4	-12.1
1	3.6	-3.2
2	11.6	9.8
3	9.8	-9.8
4	10.3	-10.1
5	2.4	-2.0
6	10.1	-9.9
7	4.0	-3.7
8	9.0	-9.1
(H,5,5)		
-11	3.8	-3.6
-10	0.5*	-0.2
-9	12.7	12.4
-8	8.6	-8.2
-7	8.3	8.7
-6	2.1	2.2
-5	8.3	-8.4
-4	0.6*	2.0
-3	4.8	5.0
-2	7.6	-7.6
-1	7.2	-7.5
0	15.0	-14.7
1	4.3	4.1
2	11.6	-11.5
3	2.2	2.5
4	12.8	-12.8
5	5.5	5.3
6	7.3	7.5
7	4.4	4.3
(H,5,6)		
-11	1.6	-1.4
-10	2.3	2.1
-9	0.5*	0.7
-8	0.5*	-0.0
-7	3.4	-3.3
-6	6.9	-7.0
-5	7.3	7.2
-4	18.4	-18.1
-3	4.0	3.7
-2	1.6	1.1
-1	9.3	9.2
0	0.5*	-0.4
1	6.6	6.8
2	6.0	6.2
3	8.6	8.5
4	6.6	6.5
5	3.9	-3.8
6	7.4	7.4
(H,5,7)		
-11	0.3*	0.8
-10	3.3	3.0
-9	1.7	-1.9
-8	2.7	-2.7
-7	3.2	3.3
-6	6.8	-7.0
-5	1.6	2.4
-4	8.6	8.9
-3	2.7	-2.9
-2	5.9	6.1
-1	8.2	-7.9
0	6.3	5.8
1	4.3	-4.7
2	2.3	2.3
3	7.5	7.1
4	2.3	-2.6
5	3.1	-3.2
(H,5,8)		
-10	1.0	-0.9
-9	2.9	-3.0
-8	4.5	-4.2
-7	7.7	-7.9
-6	4.3	4.0
-5	3.2	-3.4
-4	3.5	3.5
-3	1.1	1.0
-2	12.4	-12.5
-1	0.5*	0.9
0	7.5	7.1
1	9.3	8.8
2	1.0	1.1
3	0.4*	-0.7
(H,5,9)		
-9	3.0	3.4
-8	2.5	2.4
-7	4.6	4.7
-6	0.8	0.9
-5	4.0	4.0
-4	1.4	1.5
-3	4.3	4.5
-2	0.4*	1.0
-1	4.2	4.1
0	7.1	7.5
1	3.6	-3.6
2	3.1	-3.3
(H,5,10)		
-7	0.3*	-0.5
-6	2.7	-2.3
-5	1.8	-2.2
-4	3.8	4.0
-3	3.1	3.2
-2	1.8	-1.8
-1	0.8	-1.0
(H,6,0)		
0	8.5	8.8
1	2.5	2.2
2	5.3	-5.4
3	11.7	11.4
4	4.7	4.7
5	6.9	7.0
6	2.4	-2.4
7	3.2	3.3
8	8.6	-8.3
(H,6,1)		
-8	5.5	-5.5
-7	1.8	1.3
-6	2.5	2.3
-5	0.5*	-0.1
-4	1.9	-1.6
-3	14.2	14.0
-2	3.1	2.9
-1	7.8	7.6
0	3.1	-2.8
1	9.0	8.7
2	10.7	-10.4
3	5.5	5.5
4	5.0	5.1
5	0.5*	-0.5
6	2.1	2.1
7	3.9	3.6
(H,6,2)		
-9	2.6	-2.5
-8	2.5	2.5
-7	1.8	1.7
-6	8.6	-8.2
-5	5.3	5.3
-4	8.9	-9.0
-3	6.4	5.8
-2	0.6*	-1.2
-1	4.1	-4.1
0	0.5*	0.4
1	4.7	4.1
2	3.5	-3.1
3	4.2	4.0
4	3.8	-3.8
5	8.3	8.2
6	0.4*	-0.3
7	2.8	2.9
(H,6,3)		
-9	4.6	-4.7
-8	5.3	-5.5
-7	3.6	3.6
-6	2.8	3.0
-5	4.0	4.0
-4	4.1	-4.3
-3	2.2	2.5
-2	2.9	-2.5
-1	10.2	10.2
0	2.0	-1.8
1	6.8	6.5
2	6.8	-6.6
3	0.5*	0.7
4	2.1	-2.1
5	3.4	-3.3
6	4.3	-4.3
(H,6,4)		
-8	1.6	1.3
-7	2.5	2.7
-6	8.8	8.7
-5	1.6	1.6
-4	10.0	-9.6
-3	3.6	-3.1
-2	1.8	-1.4
-1	2.7	2.1
0	4.4	-4.5
1	12.9	-12.6
2	6.8	6.7
3	8.8	-8.6
4	2.1	2.3
5	1.0	-1.2
(H,6,5)		
-8	0.4*	-0.4
-7	5.7	-6.1
-6	1.9	-2.1
-5	0.4*	-0.4
-4	2.2	2.7
-3	7.0	-6.9
-2	7.2	7.1
1	1.5	1.4
0	0.5*	-0.4
1	3.5	-3.1
2	2.1	1.9
3	9.4	9.2
4	1.7	2.1
(H,6,6)		
-8	0.3*	0.8
-7	0.4*	0.2
-6	1.4	-1.3
-5	4.2	4.3
-4	4.0	3.9
-3	2.9	2.8
-2	3.8	3.9
-1	1.0	-0.7
0	2.3	-2.2
1	5.5	5.2
2	2.5	2.4
3	1.3	1.6
(H,6,7)		
-7	7.5	7.3
-6	5.3	-5.4
-5	2.5	-2.2
-4	1.8	1.7
-3	2.5	1.8
-2	3.6	3.8
-1	3.4	-3.5
0	1.8	1.7
1	8.1	8.2
(H,6,8)		
-4	2.1	2.7
-3	8.8	9.0
-2	3.4	-3.5
(H,7,0)		
1	11.4	11.2
2	1.8	-1.7
3	1.6	1.6
(H,7,1)		
-3	4.2	4.4
-2	2.1	2.6
-1	0.3*	0.7
0	0.3*	-0.2
1	1.0	0.5
2	5.1	5.4
(H,7,2)		
-3	1.5	2.3
-2	7.8	-7.6
-1	6.8	-6.4
0	10.4	9.9
1	6.0	5.5
2	4.2	2.1
(H,7,3)		
-1	2.7	3.0
-2	2.3	3.0
0	8.2	7.3

Table 3. *Standard deviations of results*

(*a*) Standard deviations of positional coordinates:

oxygen	0·0016 Å
carbon	0·0019
methylene hydrogen	0·026
hydroxyl hydrogen	0·033

(*b*) Standard deviations of distances involving:

carbon and/or oxygen atoms only	0·003 Å
one hydrogen atom	0·03
two hydrogen atoms	0·04

(*c*) Standard deviations of interbond angles involving:

carbon and/or oxygen atoms only	0·2°
at least one hydrogen atom	3°

(*d*) Standard deviations of temperature factors:

carbon and oxygen atoms	0·06 Å^2
hydrogen atoms	0·6–0·8 Å^2

standard deviation given by these authors (0·008–0·012 Å) and therefore probably none of the deviations is significant.

The carbon–carbon bonds adjacent to the terminal carboxyl groups are significantly shorter (1·497, 1·509 Å) than those around the central carbon atom, C(3), (1·544, 1·532, 1·535 Å). In the carboxyl group O(2)C(1)O(1)H(5) the bonds O(1)C(1) and O(2)C(1) are closer in value (1·298, 1·239 Å) than in the other two carboxyl groups (1·310, 1·210; 1·316, 1·202 Å). This is the carboxyl group which is involved in the 'dimer' type hydrogen bonding and is also the acceptor of a hydrogen bond from the hydroxyl group, O(7)H(8).

The hydrogen bonding scheme is illustrated in Fig. 3 which shows stereodiagrams of one molecule and some neighboring atoms. The angles and distances involved are listed in Table 4. The superscript notation is given in this Table. As shown in Fig. 3 the atom H(8) is close

Table 4. *Distances and angles involved in possible hydrogen bonds*

Donor (*D*) (at *x,y,z*)	Acceptor (*A*)	*D*---*A* (Å)	H---*D* (Å)	H---*A* (Å)	∠*A*---H–*D* (degrees)	∠H–*D*---*A* (degrees)
O(1)–H(5)······	O(2^{i})	2·618	1·07	1·55	177	2
O(3)–H(6)······	O(6^{ii})	2·676	0·89	1·91	144	25
O(5)–H(7)······	O(4^{iii})	2·745	0·92	1·82	176	3
O(7)–H(8)······	O(1^{iv})	2·854	0·84	2·15	142	28
O(7)–H(8)······	O(6)	2·700*	0·84	2·29	110	53

* Not a hydrogen bond, see text.

Superscript notation (for Tables 4 and 6)

i	$-x$,	$1-y$,	$1-z$	iv	x,	$y-1$,	z
ii	$\frac{1}{2}+x$,	$-\frac{1}{2}-y$,	z	v	$x-\frac{1}{2}$,	$-\frac{1}{2}-y$,	z
iii	$-x$,	$-y$,	$-z$	vi	x,	$1+y$,	z

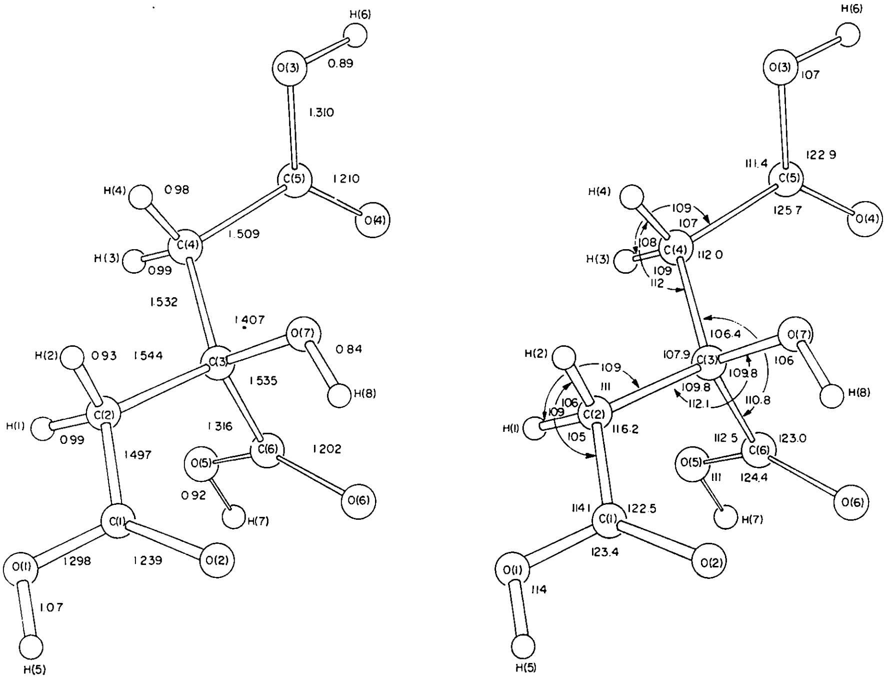

Fig. 2. Bond lengths in Å and interbond angles in degrees in one molecule of citric acid.

Table 5. *Principal axes of thermal ellipsoids*

Values of the temperature factors (B_i in Å^2) and the root mean square displacement (U_i in Å) along the major, intermediate and minor axes of the thermal ellipsoids are given together with the direction cosines of these axes (l_1, l_2 and l_3) with respect to the three axes (E_1, E_2 and E_3) of the orthonormal E system (Patterson, 1952) defined by the γ matrix below (E_2 coincides with b, E_1 and E_3 lie in the plane containing a and c at angles 10·02 and 11·20° to these axes respectively as shown in Fig. 1).

$$\begin{bmatrix} 12{\cdot}622 & 0 & -2{\cdot}228 \\ 0 & 5{\cdot}628 & 0 \\ -2{\cdot}228 & 0 & 11{\cdot}246 \end{bmatrix}$$

Atoms marked with an asterisk are probably not significantly anisotropic.

Atom	B_i	U_i	l_1	l_2	l_3
O(1)	3.42	0.208	0.767	0.001	0.641
	2.34	0.172	-0.583	-0.418	0.697
	1.73	0.148	0.269	-0.909	-0.320
O(2)	5.39	0.261	0.752	-0.201	0.628
	2.19	0.167	-0.394	0.627	0.672
	1.90	0.155	-0.529	-0.753	0.394
O(3)	7.87	0.316	0.177	0.380	-0.908
	2.65	0.183	0.507	0.755	0.415
	1.63	0.144	0.843	-0.534	-0.059
O(4)	4.51	0.239	0.284	0.491	-0.824
	2.49	0.178	-0.548	0.787	0.281
	2.12	0.164	0.787	0.372	0.493
O(5)	4.01	0.225	0.432	-0.576	-0.694
	2.80	0.188	0.721	0.683	-0.118
	1.94	0.157	0.542	-0.449	0.710
O(6)	4.55	0.240	-0.614	0.728	0.305
	3.41	0.208	0.224	-0.209	0.952
	1.72	0.148	0.757	0.652	-0.034
O(7)	2.97	0.194	-0.290	0.452	0.843
	2.54	0.180	0.936	0.318	0.151
	1.74	0.148	-0.200	0.833	-0.516
C(1)*	2.31	0.171	0.997	-0.017	0.072
	2.08	0.162	-0.073	-0.331	0.941
	1.86	0.153	0.007	-0.943	-0.331
C(2)	2.87	0.191	0.592	-0.298	0.749
	2.06	0.162	0.771	-0.063	-0.634
	1.61	0.143	0.236	0.952	0.193
C(3)*	2.19	0.167	0.368	0.115	0.923
	1.80	0.151	0.928	-0.099	-0.358
	1.54	0.140	0.051	0.988	-0.143
C(4)	3.21	0.202	-0.314	0.031	-0.949
	2.06	0.161	0.117	0.993	-0.006
	1.68	0.146	0.942	-0.112	-0.316
C(5)*	2.50	0.178	0.379	0.785	0.490
	2.44	0.176	0.019	-0.535	0.844
	1.71	0.147	0.926	-0.310	-0.218
C(6)*	2.36	0.173	-0.372	0.260	-0.891
	2.00	0.159	0.668	0.742	-0.062
	1.66	0.145	0.645	-0.618	-0.449

to two neighboring oxygen atoms, O(6) of the same molecule and $O(1^{iv})$ of another molecule. While the distance O(7)---O(6) is shorter than the distance $O(7)\text{---}O(1^{iv})$ (2·700 and 2·854 Å respectively), H(8) is nearer to $O(1^{iv})$ than to O(6) (2·15 and 2·29 Å respectively). The bond O(7)–H(8) deviates 28° from the line $O(7)\text{---}O(1^{iv})$ and 53° from the line O(7)---O(6) (see Table 4). This suggests an intermolecular hydrogen bond $O(7)H(8)\text{---}O(1^{iv})$ with H(8) close to O(6) of the same molecule for geometrical reasons. The atom H(8) is 0·28 Å from the plane $O(6)O(7)O(1^{iv})$. The hydrogen bonds $O(1)H(5)\text{---}O(2^{i})$ and $O(5)H(7)\text{---}O(4^{iii})$ are nearly linear but the hydrogen bond $O(3)H(6)\text{---}O(6^{ii})$ deviates 25° from linearity. Therefore each carboxyl group is involved in at least one hydrogen bond which is nearly linear.

The principal axes of the thermal ellipsoids which are shown in Fig. 3, are listed in Table 5. (The hydrogen atoms were refined only isotropically.) The atoms of a carboxyl group are vibrating with the major axis of each ellipsoid within 15° of the normal to the plane of the carboxyl group. The atom O(3) shows the most anisotropy with a root mean square displacement of 0·316 Å. The vibrations of most of the carbon atoms are probably not significantly anisotropic.

The equations of certain planes in the molecule are listed in Table 6. The angle between the plane of the central carboxyl group and the plane containing the oxygen atom of the adjacent hydroxyl group, C(6)C(3)O(7), is 11·97° and both planes are approximately perpendicular (94·48 and 87·58° respectively) to the plane of the backbone. [The plane of C(3)O(7)H(8) is 37·27° from the plane of C(6)C(3)O(7).] The plane of the terminal carboxyl group, O(2)C(1)O(1), is rotated 11·47° from the plane of the backbone while the plane of the other terminal carboxyl group O(4)C(5)O(3) is 47·62° from that of the backbone. The conformations of the carboxyl groups (Dunitz & Strickler, 1968) are shown in Fig. 4 which illustrates the torsion angles about certain bonds in the molecule. The torsion angle O(2)=C(1)–C(2)–C(3) is 8·2° while the torsion angle O(4)=C(5)–C(4)–C(3) is 50·4°. For the central carboxyl group the torsion angle O(6)–C(6)–C(3)–O(7) is 12·3°. The views down the bonds C(2)–C(3) and C(4)–C(3) show staggered conformations.

The deviations of atoms from the planes of the carboxyl group to which they are hydrogen bonded are also listed. This shows that the two carboxyl groups involved in the 'dimer' type hydrogen bonding are almost coplanar. The system $H(7)O(5)C(6)O(6)C(3)O(4^{iii})O(1^{iv})O(7)H(8)$ is also nearly planar.

Computations

Calculations were done on an IBM 1620 computer with programs written in this laboratory by D. van der Helm, C. K. Johnson, E. J. Gabe and the authors. We wish to thank C. K. Johnson, Oak Ridge National Laboratory, who prepared Fig. 3 with the computer program *ORTEP* (Johnson, 1965).

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Table 6. *Equations of some planes and perpendicular deviations of atoms from these planes*

The equations are expressed in the form

$$lX+mY+nZ=D$$

where distances are expressed in Å and X, Y, Z are coordinates in the E system (see Table 5). See Table 4 for superscript notation.

(*a*) *Equations of planes*

Designations and description of planes	Atoms in plane	l	m	n	D
(1) Center backbone	C(2), C(3), C(4)	0·5899	−0·2965	0·7511	2·4770
(2) Full backbone	C(1), C(2), C(3), C(4), C(5)	0·6482	−0·1929	0·7366	2·7576
(3) Hydroxyl	C(6), C(3), O(7)	−0·5564	0·4759	0·6811	1·4570
(4) Terminal carboxyl group	O(1), O(2), C(1), C(2)	0·6884	−0·1270	0·7140	2·9037
(5) Terminal carboxyl group	O(3), O(4), C(4), C(5)	−0·1971	−0·4134	0·8890	0·4520
(6) Central carboxyl group	O(5), O(6), C(6), C(3)	−0·5231	0·6422	0·5603	1·3759

(*b*) *Deviations* Δ (Å) *from these planes*

Atoms	$\Delta(1)$	Atoms	$\Delta(2)$	Atoms	$\Delta(3)$	Atoms	$\Delta(4)$	Atoms	$\Delta(5)$	Atoms	$\Delta(6)$
C(2)	0·000	C(1)	0·062	C(3)	0·000	O(1)	0·001	O(3)	0·000	O(5)	0·001
C(3)	0·000	C(2)	0·005	C(6)	0·000	O(2)	0·001	O(4)	0·000	O(6)	0·001
C(4)	0·000	C(3)	−0·119	O(7)	0·000	C(1)	−0·002	C(4)	0·000	C(6)	−0·003
		C(4)	−0·027			C(2)	0·001	C(5)	0·000	C(3)	0·001
		C(5)	0·079								
C(1)	0·125	O(1)	0·003	O(5)	−0·246	H(5)	0·00	H(6)	0·06	H(7)	0·00
C(5)	0·216	O(2)	0·164	O(6)	0·215	H(1)	−0·67	H(3)	−0·90	C(2)	1·352
C(6)	−1·241	O(3)	1·078	H(8)	0·49	H(2)	0·83	H(4)	0·14	C(4)	−1·107
		O(4)	−0·650			C(3)	−0·192	C(3)	1·095	O(7)	−0·272
		O(5)	−2·488							H(8)	0·12
		O(6)	−1·540			$O(2^{i})$	−0·026	$O(6^{ii})$	0·397		
		O(7)	0·943			$C(1^{i})$	−0·024			$O(4^{iii})$	0·136
		C(6)	−1·458			$O(1^{i})$	−0·026	$O(5^{iii})$	−0·468		
						$H(5^{i})$	−0·03	$H(7^{iii})$	−0·30	$O(1^{iv})$	0·071
										$O(3^{v})$	−0·542
						$O(7^{vi})$	0·078			$H(6^{v})$	−0·24
						$H(8^{vi})$	0·20				

(*c*) *Angles between these planes*

Planes	Angle (°)	Planes	Angle (°)	Planes	Angle (°)
1–6	94·48	2–3	87·17	1–5	47·62
2–6	92·88	5–6	70·38	3–6	11·97
4–6	92·38	3–5	58·77	1–4	11·47
1–3	87·58	4–5	56·52	1–2	6·87
3–4	87·55	2–5	52·63	2–4	4·70

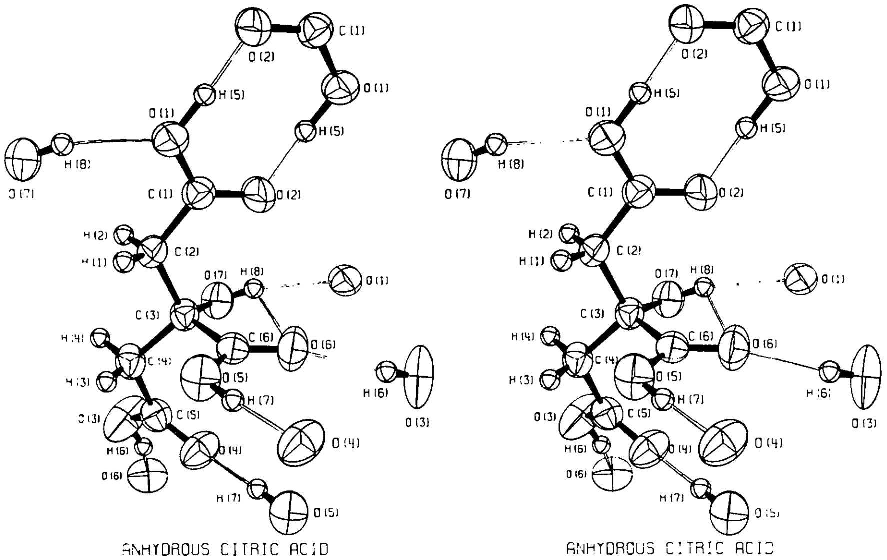

Fig. 3. Stereodiagrams of one molecule of citric acid with hydrogen-bonded nearest neighbors.

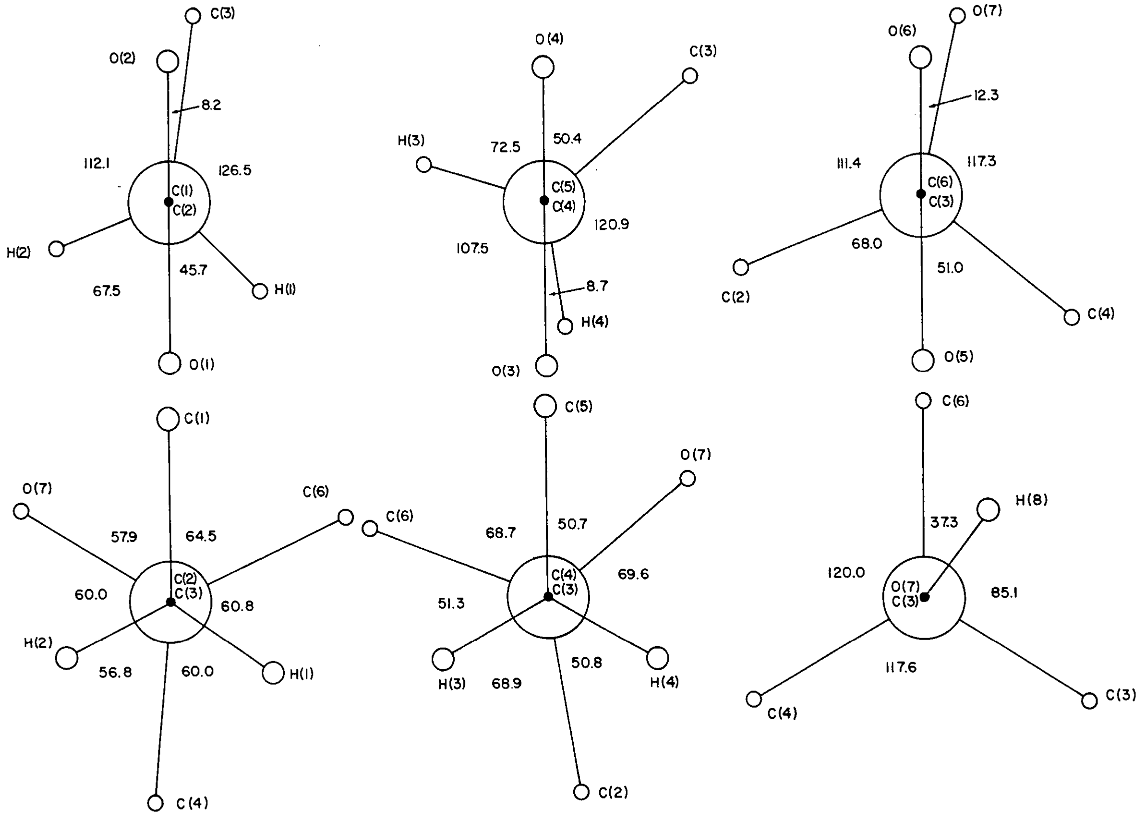

Fig. 4. Views down certain bonds in the molecule showing torsion angles. The bond down which the view is drawn is listed in the center of each diagram with the atom nearer the viewer listed above that of the atom farther from the viewer. The bond to the central black circle is to the uppermost atom.

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