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The Crystal Structure of *cis*-1,2-Cyclobutanedicarboxylic Acid*

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The crystal structure of *cis*-1,2-cyclobutanedicarboxylic acid, $C_6H_8O_4$, has been determined and refined by the three-dimensional least-squares techniques. The crystals are monoclinic, space group $P2_1/c$, with $a=10·710$ (3), $b=8·559$ (2), $c=7·343$ (2) Å and $\beta=95·03°$ (1). The final R value for 1256 reflections is 0·056. The cyclobutane ring is puckered with a dihedral angle of 156°. The longest and shortest bonds in the cyclobutane ring are 1·556 (4) and 1·526 (3) Å. The steric hindrance of the two carboxylic acid groups is decreased by deformation of bond angles and conformational angles. A librational temperature motion of the carboxylic acid groups around the C–C bonds of these groups is observed.

Introduction

The cyclobutane ring exists both in the planar and puckered conformation. In the solid state planar rings have been found in tetraphenylcyclobutane (Dunitz, 1949; Margulis, 1965), octahydroxycyclobutane (Bock, 1968), *trans*-1,3-cyclobutanedicarboxylic acid (Margulis & Fisher, 1967; Seigler, 1967), *cis,trans,cis*-1,2,3,4-tetracyanocyclobutane (Greenberg & Post, 1968) and *cis,trans,cis*-1,2,3,4-cyclobutanetetracarboxylic acid tetramethyl ester (Margulis, 1971). It is interesting to note that all of these molecules have a center of symmetry which is retained as a crystallographic element of symmetry. On the other hand, the structures of perchlorocyclobutane (Owen & Hoard, 1951; Margulis, 1965), *cis*- and *trans*-1,2-dibromo-1,2-dimethoxycarbonylcyclobutane (Karle, Karle & Britts, 1966), *cis*-1,3-cyclobutanedicarboxylic acid (Adman & Margulis, 1969), *trans*-1,2-cyclobutanedicarboxylic acid (Benedetti, Corradini & Pedone, 1970) and cyclobutane-1,1-dicarboxylic acid (Soltzberg & Margulis, 1969) provide examples of the puckered form. A surprising case has been reported by Adman & Margulis (1968) for the disodium salt of *trans*-1,3-cyclobutanedicarboxylic acid which crystallizes with two neutral acid molecules. The neutral acid previously found to have a planar conformation is found to be puckered, while the ring of the dianion is planar.

To gain more information about the cyclobutane ring, the diacid derivatives seem exceptionally well suited, because the thermal motion of the molecules should be low owing to the expected intermolecular hydrogen bonding. The accuracy of the structure determination should therefore be quite good. The present communication describes the structure determination of *cis*-1,2-cyclobutanedicarboxylic acid.

Experimental

Single crystals of *cis*-1,2-cyclobutanedicarboxylic acid, m.p. 139–140°, were kindly provided by Dr J. J. Bloomfield. A prismatic crystal, 0·17 × 0·35 × 0·27 mm, was used for this investigation. All measurements were made at room temperature (22°C). The crystal had a mosaic spread of about 0·5°. The crystal data are given in Table 1. The cell dimensions were calculated by a least-squares procedure from the 2θ values of 48 reflections. The crystal density was determined by flotation in a mixture of CH_2Cl_2 and CCl_4. The integrated intensities were taken on a General Electric XRD-5 diffraction unit using the θ–2θ scan technique and nickel-filtered Cu $K\alpha$ radiation. The diffraction unit was equipped with a single-crystal orienter, scintillation counter and pulse-height analyzer. In total, 1256 reflections, comprising all reflections with $2\theta \le 140°$, were measured, 81 of which did not show a peak on the

Table 1. *Crystal data for cis-1,2-cyclobutanedicarboxylic acid*

Throughout, estimated standard deviations for the last digit are given in parentheses.

Formula	$C_6H_8O_4$
F.W.	144·13
Systematic absences	$0k0,\ k=2n+1$ $h0l,\ l=2n+1$
Space group	$P2_1/c$
Cell dimensions	$a=10·710$ (3) Å $b=8·559$ (2) $c=7·343$ (2) $\beta=95·03°$ (1)
Cell volume	$V=670·5$ Å^3
Density, calculated	$\varrho_c=1·428$ g.cm^{-3}
Density, observed	$\varrho_o=1·423$
Number of molecules per unit cell	$Z=4$
Absorption coefficient	$\mu=10·59$ cm^{-1}
Wavelength	$\lambda=1·5418$ A°

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recorder while scanning through their diffraction position. These 81 reflections were tagged as unobserved, and assigned an intensity of 10 counts, which was one half the value of the lowest observable intensity. The intensity data were corrected for Lorentz and polarization factors and for absorption. For the absorption correction the program of Coppens, Leiserowitz & Rabinovich (1965) was used with 216 sampling points. The program uses the numerical integration method of Gauss.

Structure determination

The structure was solved by a symbolic addition process. The reflections 553, 630 and 281 were assigned positive signs to fix the origin. A total of 86 signed reflections with E values above 1·5 were used to calculate an E map. The oxygen and carbon peaks were identified from the map with the aid of a model. These atomic positions were refined, initially with isotropic temperature factors and in the later cycles with anisotropic ones, using block-diagonal least-squares computations until R $(=\sum||kF_o|-|F_c||/\sum|kF_o|)$ was reduced to 0·082. The function minimized in the least-squares calculations was $\sum w(|kF_o|-|F_c|)^2$, with $\sqrt{w}=|kF_o|/P$ if $|kF_o|\le P$, and $\sqrt{w}=P/|kF_o|$ if $|kF_o|>P$, using a value of 5 electrons for P, with the result that maximum weight was given to the most reliable data. A difference-Fourier synthesis using all the data revealed all the hydrogen atoms of the cyclobutane ring and two sets of disordered hydrogen atoms for the carboxyl groups. The peak heights of the latter hydrogen atoms were about half the height of those of the other hydrogen atoms (Table 2). A difference-Fourier synthesis of lower resolutions using only the data with $2\theta\le 60°$ showed only two hydrogen positions located equidistant from the oxygen atoms forming hydrogen bonds. A third difference-Fourier synthesis calculated after a few more cycles of least-squares refinement, which included the hydrogen atoms of the cyclobutane ring, once again, using all the data, revealed the fact that the hydrogen atoms of the carboxyl groups were disordered. In the final cycles of least-squares refinement these four hydrogen atoms were included with half-occupancy, and the refinement was terminated when all parameter shifts were less than $\frac{1}{6}$ the corresponding standard deviations. A final difference-Fourier synthesis showed no unusual features. The largest spurious peak was $-0·24$ e.Å^{-3}, and located between two oxygens of two different carboxyl groups in the same molecule.

Table 2. *Positions and peak heights of the disordered hydrogen atoms located from the first difference-Fourier synthesis*

	x	y	z	Peak height
H(1)	−0·02	0·61	0·40	0·30 e.Å^{-3}
H(2)	0·07	0·39	0·52	0·25
H(9)	0·40	0·60	0·47	0·19
H(10)	0·52	0·37	0·45	0·22

The final R value for all reflections was 0·056. The atomic scattering factors for C and O were taken directly from *International Tables for X-ray Crystallography* (1962). The scattering factors for H were those of Stewart, Davidson & Simpson (1965). The observed and calculated structure factors are given in Table 3. The positional and thermal parameters are presented in Tables 4 and 5.

Description and discussion of the structure

A projection of the structure down the b axis is shown in Fig. 1. Both acid groups form strong hydrogen bonds around two centers of symmetry, and the molecules form zigzag chains running parallel to the a axis. The carboxylic acid groups related to each other by a center of symmetry and forming the hydrogen bonds are not coplanar. The distances between the planes are 0·237 Å for O(1) O(2) C(3) C(4) and O(1′) O(2′) C(3′) C(4′), and 0·295 Å for O(10) O(9) C(8) C(7) and O(10′) O(9′) C(8′) C(7′). The shortest intermolecular distance is between O(2) and O(1) $(-x, -\frac{1}{2}+y, \frac{1}{2}-z)$ of 3·34 Å; all other intermolecular distances are larger than 3·4 Å. The equations of the planes are given in Table 6.

The cyclobutane ring of the present structure is puckered. The dihedral angle between the plane through C(4) C(5) C(6) and the plane through C(4) C(6) C(7) is 156°. This value is consistent with values reported for a puckered ring in other compounds containing a cyclobutane ring, which range from 145° in cyclobutane (Meiboom & Snyder, 1967) to 161° in perchlorocyclobutane (Margulis, 1965). The conformational angles of the bonds in the cyclobutane ring are given in Table 7. The average value is 17°.

The *cis* conformation of the two carboxylic acid groups bonded to adjacent carbon atoms results in considerable crowding of these two functional groups. This steric hindrance is relieved in the molecule in several ways: (1) By an additional twist of C(3) with respect to C(8) compared to C(5) with respect to C(6) of 16·5° [the conformational angles are C(3) C(4) C(7) C(8): −33·3° and C(5) C(4) C(7) C(6): −16·8°]. (2) By increasing the sum of the three C–C–C bond angles at C(4) to 332·8° and decreasing those at C(7) to 312·5°, which are respectively larger and smaller than those found in six other structures of cyclobutanedicarboxylic acids, in which these sums range from 314·4° to 325·8° for eight observations. (3) By rotating the carboxylic acid groups in the same directions around the C(3)–C(4) and C(7)–C(8) bonds, away from the preferred orientation (Dunitz & Strickler, 1968), in which the C=O bond (*vide infra*) of the acid group is *syn* planar with the C(4)–C(7) bond. It should be noted that all these adaptions of the molecule are angular deformations. The steric hindrance between the acid groups does not seem to influence the bond distances in the molecule. The C–H bond distances average 0·99 Å, with the extremes between 0·92 (3) Å for

Table 3. *Structure factors*

The values of $|10kF_o|$ and F_c are given. Unobserved reflections are indicated by an asterisk.

L	FO	FC
H= 0 K= 0		
2	8	12
4	159	-146
6	49	48
8	11	13
H= 0 K= 1		
1	2	-11
2	43	42
3	418	-447
4	51	52
5	82	79
6	36	35
7	142	-139
8	12	10
H= 0 K= 2		
0	941	1028
1	213	237
2	52	-54
3	215	215
4	34	27
5	49	-51
6	13	10
7	9	-8
8	7	7
H= 0 K= 3		
1	154	-157
2	180	-178
3	48	46
4	81	79
5	65	64
6	90	88
7	57	-54
8	2	-1*
H= 0 K= 4		
0	297	-304
1	31	-38
2	62	-63
3	25	23
4	64	61
5	35	35
6	12	-10
7	17	16
8	2	2*
H= 0 K= 5		
1	109	-113
2	202	-198
3	43	38
4	52	-52
5	36	35
6	62	65
7	30	27
H= 0 K= 6		
0	132	-125
1	39	36
2	11	-16
3	68	-69
4	5	6
5	13	12
6	13	16
7	30	31
H= 0 K= 7		
1	25	-31
2	19	13
3	24	-24
4	115	-115
5	9	-8
6	10	12
H= 0 K= 8		
0	13	7
1	90	86
2	26	26
3	32	-35
4	19	16
5	23	-20
H= 0 K= 9		
1	22	-28
2	39	36
3	2	9*
4	39	-39
H= 0 K= 10		
0	18	17
1	33	31
2	8	10
H= 1 K= 0		
0	67	63
2	106	105
-2	220	-233
4	156	156
-4	171	185
6	33	30
-6	186	-183
8	52	-53
-8	2	1*
H= 1 K= 1		
0	100	-101
1	614	653
-1	623	-685
2	11	17
-2	198	209
3	281	282
-3	110	-109
4	260	260
-4	76	-81
5	38	31
-5	146	156
6	2	2*
-6	41	43
7	95	-97
-7	37	-38
8	2	3*
-8	9	7
H= 1 K= 2		
0	159	161
1	437	-451
-1	119	123
2	61	-56
-2	257	-269
3	6	8
-3	420	-440
4	29	14
-4	26	2
5	37	-36
-5	142	-146
6	86	87
-6	99	-98
7	3	0*
-7	80	81
8	15	-14
-8	2	2*
H= 1 K= 3		
0	115	-117
1	135	132
-1	13	-3
2	150	153
-2	97	92
3	130	-126
-3	44	44
4	266	255
-4	87	-90
5	34	33
-5	107	113
6	19	-19
-6	80	81
7	18	-17
-7	38	40
8	26	25
-8	2	-3*
H= 1 K= 4		
0	8	-10
1	61	64
-1	25	22
2	150	-149
-2	80	-84
3	31	38
-3	302	-297
4	93	-97
-4	56	-56
5	148	-147
-5	61	-62
6	84	83
-6	20	-19
7	19	22
-7	56	55
8	31	33
-8	4	-4
H= 1 K= 5		
0	39	-36
1	113	-111
-1	28	23
2	135	130
-2	9	-14
3	72	-69
-3	136	137
4	2	-9*
-4	18	-17
5	10	9
-5	44	45
6	29	-26
-6	14	14
7	8	0
-7	26	28
H= 1 K= 6		
0	53	-56
1	118	114
-1	20	21
2	26	-21
-2	7	4
3	20	25
-3	12	14
4	41	-45
-4	2	-8*
5	90	-91
-5	21	-26
6	2	2*
-6	2	-7*
7	8	8
-7	10	9
H= 1 K= 7		
0	20	-16
1	40	-38
-1	28	25
2	5	-4
-2	90	90
3	28	-30
-3	29	34
4	37	-36
-4	8	5
5	10	8
-5	2	-3*
6	7	7
-6	46	-44
H= 1 K= 8		
0	69	67
1	11	10
-1	16	-16
2	22	-23
-2	2	6*
3	5	4
-3	68	63
4	5	-8
-4	7	-12
5	12	-15
-5	17	-20
H= 1 K= 9		
0	10	-6
1	41	40
-1	40	36
2	2	5*
-2	52	49
3	36	-34
-3	53	-53
4	2	1*
-4	24	24
H= 1 K= 10		
0	53	51
1	4	8
-1	45	-42
2	25	-28
-2	11	-4
H= 2 K= 0		
0	33	32
2	646	-686
-2	268	-280
4	78	76
-4	21	-23
6	54	54
-6	47	-47
8	78	-81
-8	17	-10
H= 2 K= 1		
0	30	-30
1	513	523
-1	499	533
2	31	27
-2	275	-285
3	131	-123
-3	272	-257
4	12	10
-4	54	51
5	207	203
-5	22	-29
6	18	-21
-6	117	117
7	39	38
-7	10	-10
8	17	16
-8	9	-10
H= 2 K= 2		
0	121	-120
1	380	-400
-1	197	-213
2	340	-316
-2	61	10
3	39	35
-3	134	-137
4	31	26
-4	113	111
5	94	95
-5	118	121
6	18	17
-6	60	-67
7	27	25
-7	18	-16
8	37	-36
-8	17	-14
H= 2 K= 3		
0	242	-254
1	39	39
-1	208	-214
2	112	-115
-2	248	-256
3	61	66
-3	96	103
4	130	125
-4	60	54
5	35	-38
-5	53	49
6	23	-24
-6	133	130
7	10	-8
-7	24	-23
8	8	9
-8	17	-19
H= 2 K= 4		
0	139	-143
1	303	-299
-1	97	94
2	45	-31
-2	161	168
3	17	21
-3	40	33
4	60	-63
-4	129	125
5	94	92
-5	41	40
6	21	22
-6	30	-32
7	2	-3*
-7	7	-7
8	11	10
-8	6	5
H= 2 K= 5		
0	155	-162
1	43	44
-1	144	-140
2	96	-93
-2	39	-39
3	8	-3
-3	78	75
4	95	91
-4	7	-6
5	97	-92
-5	31	34
6	2	-6*
-6	12	-13
7	11	-10
-7	2	6*
H= 2 K= 6		
0	30	28
1	75	76
-1	96	94
2	17	4
-2	35	31
3	27	-24
-3	44	42
4	103	-104
-4	9	2
5	9	-7
-5	16	15
6	33	32
-6	4	2
7	4	5
-7	17	14
H= 2 K= 7		
0	27	-27
1	115	112
-1	62	-61
2	34	32
-2	42	-44
3	5	6
-3	2	-9*
4	19	-15
-4	5	8
5	11	-9
-5	9	14
6	6	8
-6	42	-42
H= 2 K= 8		
0	7	-6
1	147	138
-1	15	12
2	46	43
-2	74	-70
3	29	-28
-3	8	-4
4	43	-42
-4	10	9
5	41	-39
-5	4	0
H= 2 K= 9		
0	26	-24
1	72	71
-1	36	-36
2	32	30
-2	8	-6
3	11	12
-3	6	-1
4	17	-14
-4	17	18
H= 2 K= 10		
0	11	-15
1	19	19
-1	2	1*
2	31	31
-2	51	-48
H= 3 K= 0		
0	123	124
2	354	356
-2	730	-823
4	20	-17
-4	167	161
6	38	37
-6	24	-20
8	21	-24
-8	24	23
H= 3 K= 1		
0	193	-195
1	415	430
-1	421	-438
2	382	-379
-2	268	274
3	149	-144
-3	164	-166
4	4	-1
-4	35	-36
5	34	34
-5	8	6
6	10	-8
-6	7	7
7	9	5
-7	41	-38
8	6	4
-8	23	20
H= 3 K= 2		
0	251	265
1	416	-432
-1	232	236
2	112	90
-2	217	-159
3	48	45
-3	179	178
4	36	-36
-4	124	123
5	56	54
-5	10	10
6	60	60
-6	21	-18
7	29	29
-7	6	3
8	32	-31
-8	19	22
H= 3 K= 3		
0	81	-87
1	131	130
-1	7	-10
2	319	-308
-2	200	209
3	244	-239
-3	139	-148
4	105	-100
-4	72	-71
5	44	-44
-5	117	-121
6	23	-19
-6	38	32
7	30	28
-7	10	-8
8	24	23
-8	30	29
H= 3 K= 4		
0	75	79
1	73	-68
-1	107	111
2	44	43
-2	307	313
3	40	-43
-3	49	46
4	7	0
-4	117	120
5	44	-49
-5	8	-10
6	32	31
-6	23	-20
7	54	54
-7	2	3*
-8	6	8
H= 3 K= 5		
0	43	40
1	19	-15
-1	30	-31
2	103	105
-2	6	5
3	50	-50
-3	40	38
4	108	-107
-4	18	-15
5	100	-102
-5	78	-84
6	26	-23
-6	14	8
7	13	18
-7	2	-1*
H= 3 K= 6		
0	152	-157
1	39	38
-1	7	10
2	85	84
-2	164	165
3	22	-20
-3	34	39
4	36	33
-4	93	101
5	46	-48
-5	78	-79
6	2	1*
-6	25	-20
-7	12	-8
H= 3 K= 7		
0	43	-45
1	20	-14
-1	50	-47
2	149	149
-2	2	2*
3	51	47
-3	61	62
4	6	-4
-4	27	24
5	33	-35
-5	11	-17
6	26	-27
-6	11	-14
H= 3 K= 8		
0	71	-75
1	15	-16
-1	7	13
2	10	8
-2	7	10
3	7	4
-3	55	57
4	6	6
-4	2	1*
5	7	7
-5	67	-68
H= 3 K= 9		
0	51	-46
1	17	-20
-1	2	-2*
2	51	53
-2	17	-15
3	12	11
-3	21	22
-4	18	15
H= 3 K= 10		
0	9	6
1	5	-3
-1	6	6
H= 4 K= 0		
0	337	-347
2	124	-111
-2	171	-154
4	119	119
-4	19	20
6	122	124
-6	22	-28
8	8	2
-8	21	15
H= 4 K= 1		
0	9	-4
1	160	-154
-1	211	-216
2	91	-93
-2	135	-131
3	77	-72
-3	128	129
4	30	-30
-4	34	-32
5	18	18
-5	54	54
6	38	-39
-6	62	60
7	14	16
-7	64	67
8	15	16
-8	39	-36
H= 4 K= 2		
0	344	-363
1	90	83
-1	327	332
2	171	169
-2	145	-140
3	50	-46
-3	137	-134
4	48	44
-4	66	67
5	91	-90
-5	143	147
6	23	11
-6	21	-25
7	2	4*
-7	45	45
8	8	6
-8	5	0
H= 4 K= 3		
0	15	-15
1	25	27
-1	52	-54
2	102	-101
-2	16	-7
3	61	60
-3	166	168
4	41	42
-4	60	-60
5	71	-72
-5	59	-59
6	93	-94
-6	85	82
7	34	35
-7	10	14
-8	47	-44
H= 4 K= 4		
0	141	-136
1	177	-176
-1	125	126
2	248	248
-2	12	9
3	97	97
-3	81	-80
4	50	-50
-4	2	7*
5	37	-35
-5	33	32
6	66	-66
-6	19	-19
7	37	-36
-7	24	24
-8	10	-11
H= 4 K= 5		
0	23	27
1	40	38
-1	160	157
2	58	59
-2	83	83
3	19	-22
-3	82	78
4	97	96
-4	57	-61
5	38	-37
-5	113	-112
6	63	-61
-6	60	58
7	39	40
-7	11	12
H= 4 K= 6		
0	28	29
1	128	-126
-1	29	-30
2	76	79
-2	34	33
3	70	71
-3	53	-56
4	40	-37
-4	53	-52
5	7	2
-5	55	-56
6	2	-4*
-6	6	-2
-7	12	-9
H= 4 K= 7		
0	89	93
1	24	24
-1	70	71
2	105	100
-2	2	2*
3	61	-62
-3	14	10
4	9	8
-4	57	-58
5	8	-9
-5	32	-34
-6	40	38
H= 4 K= 8		
0	24	22
1	46	-47
-1	39	-42
2	15	19
-2	19	-18
3	12	14
-3	2	-2*
4	11	-11
-4	6	-8
-5	28	-27
H= 4 K= 9		
0	30	29
1	21	21
-1	46	-42
2	27	27
-2	5	-2
3	13	-14
-3	2	-1*
H= 5 K= 0		
0	56	-54
2	102	-108
-2	87	-87
4	55	-52
-4	222	206
6	23	-24
-6	57	60
-8	2	-8*
H= 5 K= 1		
0	37	-35
1	90	-79
-1	123	115
2	61	-60
-2	89	90
3	206	-201
-3	35	32
4	82	80
-4	23	19
5	21	22
-5	25	21
6	32	-29
-6	24	-24
7	40	45
-7	27	-25
-8	32	-33
H= 5 K= 2		
0	14	12
1	304	-313
-1	255	265
2	124	-123
-2	23	-12
3	29	-30
-3	217	222
4	56	-54
-4	49	-31
5	36	39
-5	51	52
6	24	-27
-6	26	26
7	47	-51
-7	35	-40
-8	11	9
H= 5 K= 3		
0	57	56
1	51	-46
-1	266	263
2	117	-114
-2	56	57
3	24	26
-3	105	103
4	48	44
-4	25	20
5	58	54
-5	54	-57
6	21	-21
-6	5	-7
7	20	23
-7	2	1*
-8	47	-49
H= 5 K= 4		
0	39	-36
1	61	-61
-1	93	91
2	39	37
-2	4	-1
3	26	-22
-3	30	35
4	66	-67
-4	165	-173
5	37	38
-5	81	84
6	47	-48
-6	6	-5
7	11	-14
-7	22	-23
H= 5 K= 5		
0	63	64
1	28	31
-1	10	8
2	44	-39
-2	68	-66
3	189	189
-3	112	109
4	32	-32
-4	8	-10
5	2	-7*
-5	34	-36
6	20	16
-6	16	14
-7	2	1*
H= 5 K= 6		
0	100	-102
1	24	21
-1	90	-93
2	149	153
-2	21	-20
3	49	49
-3	12	-11
4	44	-45
-4	47	-50
5	30	27
-5	58	59
6	38	-36
-6	2	-2*
H= 5 K= 7		
0	25	-27
1	5	-5
-1	101	-102
2	23	-24
-2	21	-15
3	93	92
-3	57	59
4	12	-8
-4	20	-18
5	29	-27
-5	15	-12
H= 5 K= 8		
0	58	-61
1	2	1*
-1	65	-65
2	56	62
-2	22	20
3	46	47
-3	9	4
4	5	-7
-4	17	18
H= 5 K= 9		
0	2	0*
1	10	-9
-1	35	-33
2	19	-21
-2	10	13
-3	3	6
H= 6 K= 0		
0	277	261
2	47	46
-2	21	19
4	128	-133
-4	90	91
6	37	-32
-6	69	71
-8	59	54
H= 6 K= 1		
0	330	327
1	92	-86
-1	122	-118
2	19	-20
-2	97	94
3	52	-52
-3	57	52
4	56	-58
-4	96	-91
5	14	17
-5	34	-32
6	5	7
-6	15	13
7	4	-1*
-7	52	-55
-8	2	-3*
H= 6 K= 2		
0	128	118
1	36	38
-1	167	149
2	163	166
-2	30	-28
3	33	-33
-3	146	-147
4	79	-77
-4	30	25
5	65	-68
-5	15	-15
6	28	-37
-6	35	38
7	21	-24
-7	24	-22
-8	38	37
H= 6 K= 3		
0	271	276
1	5	6
-1	162	-165
2	27	-31
-2	170	168
3	124	122
-3	2	-6*
4	26	-29
-4	117	-117
5	62	-60
-5	11	-11
6	14	-13
-6	2	3*
7	5	-5
-7	2	-3*
H= 6 K= 4		
0	39	-43
1	43	-42
-1	77	83
2	117	115
-2	68	62
3	93	98
-3	10	-10
4	24	26
-4	87	-87
5	42	-42
-5	17	-17
6	10	-11
-6	20	-11
-7	12	-9
H= 6 K= 5		
0	57	-60
1	81	-78
-1	13	-19
2	49	-51
-2	100	104
3	110	110
-3	20	-20
4	12	9
-4	45	-47
5	19	-21
-5	48	-46
6	25	-25
-6	22	-20
-7	26	25
H= 6 K= 6		
0	40	-45
1	2	-2*
-1	10	13
2	44	-43
-2	145	141
3	79	78
-3	18	16
4	38	39
-4	78	-77
5	7	-4
-5	2	0*
-6	9	-7
H= 6 K= 7		
0	78	-79
1	84	-81
-1	39	36
2	43	-45
-2	9	10
3	22	23
-3	9	-9
4	14	-11
-4	2	-5*
-5	33	-34
H= 6 K= 8		
0	17	-17
1	30	30
-1	2	-1*
2	28	-26
-2	52	55
3	4	3
-3	16	-15
-4	2	-2*
H= 6 K= 9		
0	16	-17
1	28	-30
-1	9	13
-2	2	-2*
H= 7 K= 0		
0	50	49
2	129	-126
-2	103	101
4	41	-43
-4	33	-36
6	22	-16
-6	40	-39
H= 7 K= 1		
0	6	-2
1	91	-83
-1	15	-13
2	11	3
-2	63	61
3	125	122
-3	106	99
4	105	105
-4	32	36
5	16	-19
-5	111	113
6	30	-29
-6	2	-2*
7	48	-44
-7	8	3
H= 7 K= 2		
0	13	7
1	25	27
-1	10	-12
2	112	-108
-2	138	138
3	114	110
-3	200	-200
4	55	52
-4	81	-81
5	14	-16
-5	6	-3
6	9	3
-6	16	-15
-7	27	-31
H= 7 K= 3		
0	84	84
1	185	-177
-1	43	43
2	31	-21
-2	27	32
3	65	62
-3	31	-31
4	147	149
-4	5	13
5	5	-1
-5	2	0*
6	19	-22
-6	17	19
-7	54	49
H= 7 K= 4		
0	34	-35
1	44	43
-1	42	40
2	11	10
-2	68	71
3	11	8
-3	203	-202
4	91	88
-4	86	-85
5	5	-5
-5	34	37
6	10	8
-6	23	23
-7	4	-2
H= 7 K= 5		
0	52	51
1	59	-57
-1	8	-10
2	45	-47
-2	41	-40
3	29	29
-3	82	-80
4	63	62
-4	2	2*
5	39	-39
-5	22	-21
-6	27	33
H= 7 K= 6		
0	28	-31
1	2	3*
-1	6	11
2	65	66
-2	26	-19
3	21	-22
-3	54	-59
4	10	4
-4	29	-26
5	2	3*
-5	21	36
H= 7 K= 7		
0	21	-20
1	25	22
-1	2	-5*
2	18	-21
-2	17	-19
3	7	9
-3	12	-12
4	18	17
-4	24	24
H= 7 K= 8		
0	2	0*
1	19	-20
-1	8	-5
2	2	4*
-2	7	-4
-3	7	7
H= 8 K= 0		
0	126	123
2	243	-244
-2	27	30
4	26	21
-4	37	-37
6	14	11
-6	108	-102
H= 8 K= 1		
0	35	32
1	193	196
-1	222	215
2	34	-33
-2	71	-69
3	43	-44
-3	78	-76
4	10	11
-4	22	-25
5	5	-2
-5	53	57
6	7	6
-6	10	7
-7	2	-1*
H= 8 K= 2		
0	74	68
1	47	46
-1	128	133
2	119	-124
-2	20	-21
3	54	-57
-3	82	-83
4	5	5
-4	8	-9
5	61	63
-5	31	-35
6	2	-4*
-6	35	-27
-7	2	-2*
H= 8 K= 3		
0	33	-32
1	43	42
-1	6	7
2	24	-22
-2	83	-81
3	36	40
-3	75	-77
4	42	42
-4	18	11
5	16	-16
-5	40	47
6	2	1*
-6	7	-12
-7	2	3*
H= 8 K= 4		
0	42	-46
1	14	-20
-1	24	27
2	28	-23
-2	2	-4*
3	23	-25
-3	21	20
4	21	24
-4	6	-3
5	24	26
-5	11	-12
-6	52	49
H= 8 K= 5		
0	78	-79
1	119	-115
-1	16	-16
2	7	7
-2	7	-10
3	64	70
-3	2	-2*
4	33	35
-4	57	58
5	7	6
-5	2	3*
-6	26	-28
H= 8 K= 6		
0	65	-67
1	13	-15
-1	20	-17
2	28	-25
-2	44	44
3	42	-44
-3	51	54
4	33	31
-4	36	-35
-5	8	10
H= 8 K= 7		
0	9	-5
1	62	-63
-1	20	20
2	2	-6*
-2	2	5*
3	37	40
-3	25	24
-4	28	30
H= 8 K= 8		
0	27	-28
1	34	33
-1	10	-10
-2	12	16
H= 9 K= 0		
0	53	51
2	157	159
-2	123	-117
4	60	58
-4	74	77
-6	8	2
H= 9 K= 1		
0	25	-21
1	94	91
-1	34	-30
2	17	16
-2	77	-77
3	17	-20
-3	94	-92
4	10	8
-4	49	-47
5	23	-23
-5	47	-46
-6	9	14
H= 9 K= 2		
0	16	-14
1	31	-32
-1	24	23
2	32	16
-2	22	-6
3	79	77
-3	2	-6*
4	73	74
-4	49	54
5	26	29
-5	20	26
-6	17	13
H= 9 K= 3		
0	19	19
1	44	-45
-1	24	26
2	12	-12
-2	85	-90
3	15	13
-3	55	-49
4	2	-3*
-4	93	-92
5	18	18
-5	26	-23
-6	37	39
H= 9 K= 4		
0	27	-29
1	24	-26
-1	83	86
2	98	-104
-2	76	72
3	2	-3*
-3	33	-33
4	37	41
-4	11	8
-5	10	-9
-6	33	32
H= 9 K= 5		
0	40	42
1	34	-35
-1	26	30
2	8	-8
-2	6	1
3	2	2*
-3	48	-44
4	18	-17
-4	33	-39
-5	15	17
H= 9 K= 6		
0	20	17
1	6	-6
-1	38	43
2	53	-57
-2	34	34
3	30	-31
-3	2	-3*
-4	9	-7
H= 9 K= 7		
0	17	-13
1	3	-3
-1	20	22
-2	24	22
H= 10 K= 0		
0	55	54
2	42	-39
-2	19	-24
4	103	97
-4	2	-4*
-6	13	8
H= 10 K= 1		
0	29	29
1	89	-87
-1	28	31
2	53	-51
-2	26	-23
3	63	-63
-3	49	-47
4	19	20
-4	12	-8
5	67	64
-5	2	-2*
-6	10	10
H= 10 K= 2		
0	55	55
1	28	-30
-1	36	-41
2	33	-32
-2	53	-54
3	23	-21
-3	59	-57
4	54	51
-4	8	6
-5	71	67
-6	21	18
H= 10 K= 3		
0	21	22
1	2	3*
-1	59	59
2	43	-42
-2	54	-52
3	57	-57
-3	29	-30
4	27	29
-4	16	17
-5	40	37
H= 10 K= 4		
0	24	-21
1	20	-21
-1	66	-66
2	26	-25
-2	37	-35
3	10	10
-3	23	-22
-4	18	21
-5	46	47
H= 10 K= 5		
0	10	11
1	8	8
-1	52	52
2	21	19
-2	29	-29
3	20	-22
-3	2	0*
-4	34	36
H= 10 K= 6		
0	27	-26
1	7	-6
-1	17	-17
-2	2	4*
-3	12	11
H= 11 K= 0		
0	76	76
2	6	5
-2	151	-150
4	46	-55
-4	32	32
H= 11 K= 1		
0	23	-24
1	110	112
-1	38	-41
2	10	7
-2	11	9
3	58	-57
-3	26	-26
4	8	9
-4	37	35
-5	27	29
H= 11 K= 2		
0	37	38
1	41	-42
-1	18	-22
2	7	-8
-2	90	-89
3	29	-28
-3	6	8
-4	17	18
-5	6	9
H= 11 K= 3		
0	20	-20
1	5	-6
-1	43	39
2	14	-15
-2	36	36
3	32	-34
-3	49	48
-4	28	28
H= 11 K= 4		
0	8	10
1	30	-30
-1	17	16
2	10	-13
-2	27	-24
-3	26	26
-4	2	-4*
H= 11 K= 5		
0	2	2*
1	21	-24
-1	57	58
-2	26	29
H= 12 K= 0		
0	62	-60
2	10	13
-2	44	-41
-4	39	38
H= 12 K= 1		
0	35	32
1	15	-15
-1	52	-54
2	29	-25
-2	7	7
-3	22	28
-4	4	-1
H= 12 K= 2		
0	16	12
1	28	-29
-1	38	39
2	17	16
-2	27	-23
-3	19	-17
H= 12 K= 3		
0	43	42
1	7	6
-1	30	-30
-2	2	0*
-3	2	-1*
H= 12 K= 4		
0	63	66
-1	15	16
H= 13 K= 0		
0	55	55

Table 4. *Positional and isotropic thermal parameters*

	x	y	z	B(A^2)
O(1)	0·0132 (2)	0·5897 (2)	0·2923 (2)	
O(2)	0·1233 (1)	0·3956 (2)	0·4261 (2)	
C(3)	0·0977 (2)	0·4851 (3)	0·2940 (3)	
C(4)	0·1631 (2)	0·4700 (3)	0·1250 (3)	
C(5)	0·2009 (2)	0·6140 (3)	0·0204 (3)	
C(6)	0·3185 (2)	0·5249 (4)	−0·0237 (3)	
C(7)	0·2985 (2)	0·4063 (3)	0·1317 (3)	
C(8)	0·3809 (2)	0·4453 (3)	0·2999 (3)	
O(9)	0·3678 (2)	0·5696 (2)	0·3812 (3)	
O(10)	0·4667 (1)	0·3467 (2)	0·3467 (3)	
H(1)*	−0·013 (4)	0·600 (5)	0·390 (6)	4·1 (10)
H(2)*	0·076 (4)	0·395 (5)	0·500 (6)	3·7 (9)
H(4)	0·108 (2)	0·402 (3)	0·038 (3)	4·2 (5)
H(5)1	0·227 (2)	0·702 (3)	0·094 (3)	5·2 (5)
H(5)2	0·137 (2)	0·645 (3)	−0·082 (3)	5·3 (5)
H(6)1	0·406 (3)	0·584 (4)	−0·004 (5)	7·5 (7)
H(6)2	0·317 (3)	0·474 (4)	−0·135 (5)	8·5 (8)
H(7)	0·303 (2)	0·296 (3)	0·103 (3)	3·5 (4)
H(9)*	0·422 (6)	0·584 (8)	0·431 (9)	8·0 (16)
H(10)*	0·521 (6)	0·398 (7)	0·452 (9)	7·7 (15)

* Occupancy factor = ½.

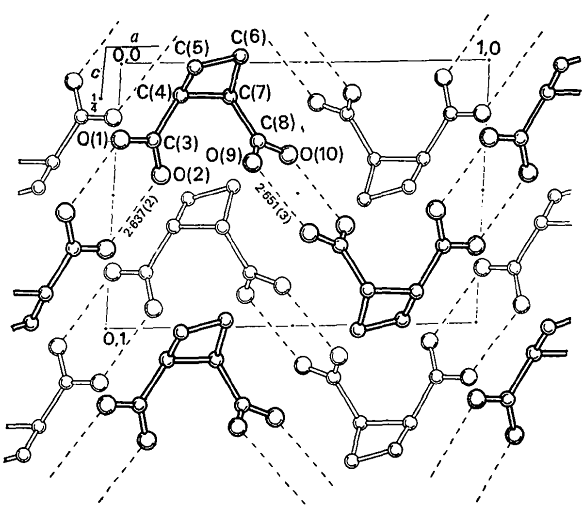

Fig. 1. Projection of the structure down the b axis

C(6)–H(6)2 and 1·07 (3) Å for C(6)–H(6)1. The distances between the oxygen atoms and the disordered hydrogen atoms vary between 0·67 (7) Å and 1·03 (6) Å. The bond angles involving the hydrogen atoms have an average value of 112·4°.

The bond distances and bond angles involving the C and O atoms are shown in Fig. 2. From both the observations in the difference-Fourier syntheses and least-squares refinement, indicating 1:1 disorder of the hydrogen atom in the carboxylic acid groups, we expected the C–O bond distances in each acid group to be equal in length. It is, however, obvious that both the C(3)–O(2) and C(8)–O(9) bonds are significantly shorter than the C(3)–O(1) and C(8)–O(10) distances. Some disorder for the hydrogen atoms, although not 1:1, is clearly indicated by the fact that the C(3)–O(1) and C(8)–O(10) distances are shorter than the C–O length, and that the C(3)–O(2) and C(8)–O(9) distances are longer than the C=O length in normal carboxylic acid groups. The bond angles around C(3) and C(8)

Table 5. *Anisotropic thermal parameters* (×10^4) *in the form* $\exp[-(b_{11}h^2+b_{22}k^2+b_{33}l^2+b_{23}kl+b_{13}hl+b_{12}hk)]$

	b_{11}	b_{22}	b_{33}	b_{23}	b_{13}	b_{12}
O(1)	94 (2)	188 (3)	218 (4)	71 (5)	42 (4)	78 (3)
O(2)	90 (1)	185 (3)	229 (4)	119 (5)	61 (4)	60 (3)
C(3)	58 (2)	124 (3)	182 (4)	−2 (6)	−16 (4)	−11 (4)
C(4)	66 (2)	144 (4)	177 (4)	−7 (6)	−9 (4)	−5 (4)
C(5)	97 (2)	173 (4)	221 (5)	55 (7)	36 (5)	5 (5)
C(6)	105 (2)	222 (5)	198 (5)	36 (8)	82 (5)	17 (6)
C(7)	77 (2)	138 (4)	198 (5)	−42 (6)	13 (5)	13 (4)
C(8)	63 (2)	132 (3)	205 (4)	2 (6)	42 (4)	−1 (4)
O(9)	90 (2)	183 (3)	312 (4)	−157 (6)	−67 (4)	41 (3)
O(10)	92 (2)	169 (3)	289 (4)	−26 (6)	−46 (4)	53 (4)

Table 6. *Least-squares planes*

The equations of the planes are expressed in the form $Ax+By+Cz=D$, where x, y and z are fractional coordinates and D is the distance from the origin in Å. The method of Schomaker, Waser, Marsh & Bergman (1959) was used to calculate the least-squares planes.

Plane	Atoms	A	B	C	D
1	O(1) O(2) C(3) C(4)	7·049	5·593	2·311	4·070
2	O(10) O(9) C(8) C(7)	7·287	3·948	−4·604	3·168
3	C(4) C(5) C(6)	−4·502	−3·055	−5·831	−2·899
4	C(4) C(6) C(7)	2·544	5·914	4·842	3·800
5	C(4) C(5) C(6) C(7)	3·583	4·613	5·439	3·548

	Δ(1)		Δ(2)		Δ(5)
O(1)	−0·004 Å	O(10)	0·005 Å	C(4)	−0·115 Å
O(2)	−0·004	O(9)	0·006	C(5)	0·116
C(3)	0·011	C(8)	−0·015	C(6)	−0·114
C(4)	−0·003	C(7)	0·004	C(7)	0·113

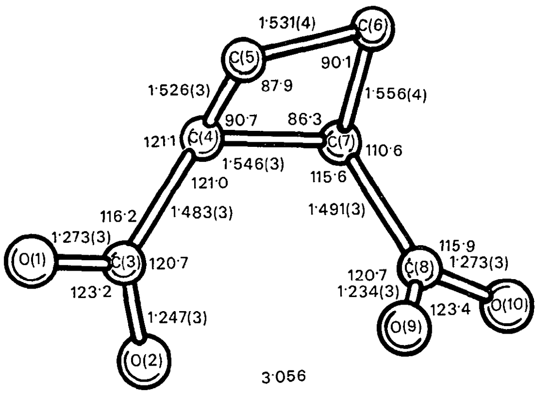

Fig. 2. Bond distances and bond angles. Standard deviations for the bond angles are 0·2°

are in agreement with this conclusion. Disorder in hydrogen bonding was also observed in *cis*-1,3-cyclobutanedicarboxylic acid (Adman & Margulis, 1969). The average of the bond distances in the cyclobutane ring is normal (1·540 Å°), the shortest and longest bond [C(4)–C(5) and C(7)–C(6) respectively] differ, however, significantly by 8 estimated standard deviations. We are unable to explain this observation. Although long bonds are not unusual in cyclobutane rings, short bonds are less common. An even shorter bond (1·517 Å) was observed in *trans*-1,2-cyclobutanedicarboxylic acid (Benedetti, Corradini & Pedone, 1970).

A rationale of long bonds in cyclobutane rings was given by Dunitz & Schomaker (1952). The bond distances in the cyclobutane ring can be corrected for thermal motion. The riding model of Busing & Levy (1964) gives the following corrected distances while the rigid-body motion of Schomaker & Trueblood (1969) for atoms C(3), C(7), C(5), C(6), C(7) and C(8) yields the distances in parentheses: C(4)–C(5) 1·538 (1·532) Å: C(4)–C(7), 1·548 (1·550) Å: C(5)–C(6), 1·536 (1·536) Å: C(6)–C(7), 1·571 (1·562) Å. Both corrections eliminate the short bonds but the large difference between long and short bonds remains. The rigid-body motion seems appropriate for the six carbon atoms because the largest difference between calculated and observed values for any thermal parameter is 4·5σ. This value increases to 15σ when all ten atoms are used as the rigid body, indicating an independent motion of the carboxylic acid groups (see below).

The principal axes of the vibration ellipsoids, along with the direction cosines, are presented in Table 8. A stereoscopic view of the molecule is shown in Fig. 3. It is sometimes assumed that the ring atoms in a cyclobutane ring should show a large thermal motion perpendicular to the ring. This is not the case, and as a matter of fact they show little anisotropy in the present structure. The largest thermal motion for the ring atoms is observed for C(6). This atom, however, has no intermolecular contacts smaller than 3·9 Å, while each of the other three atoms has intermolecular contacts between 3·4 and 3·5 Å. All oxygen atoms, on the other hand, show anisotropy, but not the carbon atoms of the carboxylic acid groups. This indicates a librational motion around the C(3)–C(4) and C(8)–C(7) bonds. This is supported by the fact that the main axes of the thermal ellipsoids of the oxygen atoms are approximately parallel to the normals of the planes through the respective carboxylic acid groups. The angles are 14, 23, 21 and 18° for O(1), O(2), O(9) and O(10).

Table 7. *Conformational angles*

The *cis* conformation is 0°. The angles given in the Table are the right handed rotations to obtain the observed conformation from the *cis* conformation for the atoms.

Atoms	Angle	Atoms	Angle
C(5) C(4) C(7) C(6)	−16·8°	C(3) C(4) C(7) C(8)	−33·3°
C(4) C(7) C(6) C(5)	16·8	O(2) C(3) C(4) C(7)	−29·1
C(7) C(6) C(5) C(4)	−16·9	O(9) C(8) C(7) C(4)	−32·3
C(6) C(5) C(4) C(7)	17·1		

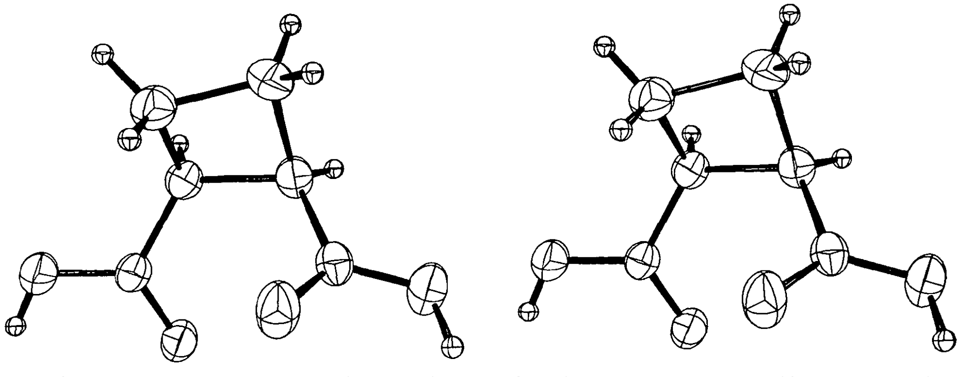

Fig. 3. Steroscopic diagram of the molecule using the *ORTEP* program (Johnson, 1965).

Table 8. *Vibration ellipsoids*

Principle axes and direction cosines with respect to the real axes.

	B (Å^2)	l_1	l_2	l_3
O(1)	6·74	0·466	0·791	0·355
	4·35	−0·414	−0·202	0·921
	3·32	0·782	−0·578	0·164
O(2)	7·04	0·334	0·734	0·559
	3·84	0·647	0·277	−0·764
	3·43	0·685	−0·620	0·321
C(3)	4·15	−0·402	0·100	0·942
	3·67	−0·106	0·982	−0·145
	2·47	0·909	0·159	0·303
C(4)	4·23	0·026	0·973	−0·231
	4·01	−0·452	0·216	0·901
	2·84	0·891	0·082	0·366
C(5)	5·61	0·099	0·778	0·609
	4·42	0·924	−0·303	0·151
	4·15	−0·369	−0·550	0·779
C(6)	6·68	0·237	0·937	0·236
	5·18	0·756	−0·345	0·489
	3·49	−0·611	−0·063	0·840
C(7)	4·76	−0·255	−0·642	0·743
	3·66	0·434	0·592	0·638
	3·39	0·864	−0·487	−0·203
C(8)	4·43	0·162	0·038	0·968
	3·88	−0·029	0·999	−0·031
	2·75	0·986	0·023	−0·249
O(9)	8·86	−0·383	−0·528	0·789
	4·03	−0·370	0·840	0·428
	3·50	0·846	0·129	0·441
O(10)	7·12	−0·498	−0·348	0·835
	5·06	0·251	0·819	0·492
	3·38	0·830	−0·457	0·246

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