The Crystal Structure of Cyclooctatetraenecarboxylic Acid[1]

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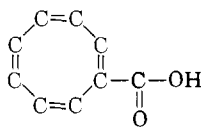
The crystal structure of 1,3,5,7-cyclooctatetraenecarboxylic acid has been determined by X-ray diffraction analysis. The crystals are monoclinic, space group C_{2h}^5-$P2_1/c$ (with a_0 = 6.76, b_0 = 14.64, and c_0 = 8.37 Å.; β = 110° 9.5′) and the unit cell contains four molecules. The cyclooctatetraene ring is tub form, conforming closely to the D_{2d} symmetry found by gas phase electron diffraction work. The mean double-bond and single-bond distances in the ring are 1.322 and 1.470 Å., respectively, with estimated standard deivations of 0.005 Å., and the mean interbond angle in the ring is 126.4°, with an e.s.d. of 0.4°. The molecules are present as hydrogen-bonded dimers, with an O–H···O distance of 2.604 Å.

Introduction

This study of the crystal structure of 1,3,5,7-cyclooctatetraenecarboxylic acid[3] (hereinafter referred to as



COT acid) was undertaken in 1952 in view of the then current interest and controversy concerning the shape of the cyclooctatetraene (COT) ring in the hydrocarbon itself. That controversy is now history; notwithstanding infrared and Raman spectroscopic evidence adduced for a crown configuration of D_4 symmetry in the vapor state,[4] there now seems to be little doubt that a "tub" configuration of D_{2d} symmetry with alternating single and double bonds is the correct one. This has been shown by electron diffraction studies in the vapor state[5–7] and by X-ray diffraction studies in the solid state.[8] Our early results for COT acid[9] showed indeed that the COT ring in this compound has the "tub" configuration.

Refinement of this structure took place sporadically over an unusually long period. It is now as complete as could reasonably be desired and the results are reported here.

Experimental

A sample of COT acid was kindly provided by Professor A. C. Cope. Crystals, grown by sublimation onto the walls of a test tube, were in the form of monoclinic plates or laths perpendicular to the *b* axis and with the longest direction parallel to *c*, showing good (001) cleavage. Crystals or cleaved fragments were mounted on glass fibers and reduced to cylinders about 0.2 mm. in diameter by rotating them in contact with filter

Table I. Atomic Positional Coordinates

Atom No.	Atom Kind	X / Y / Z	σ × 10⁵	Final shift × 10⁵
1	C(1)	0.23518	58	5
		0.19092	26	−15
		0.42007	48	−2
2	C(2)	0.44308	68	−2
		0.19468	27	−5
		0.46905	57	5
3	C(3)	0.56964	68	−9
		0.26831	34	−16
		0.43536	60	0
4	C(4)	0.56371	74	−16
		0.35525	32	9
		0.47711	69	18
5	C(5)	0.43044	82	9
		0.39593	30	−20
		0.56145	68	7
6	C(6)	0.22139	87	8
		0.39340	27	8
		0.51120	69	8
7	C(7)	0.08106	69	35
		0.34704	29	−3
		0.35493	64	−25
8	C(8)	0.08733	62	−25
		0.26045	29	3
		0.31732	53	19
9	C(9)	0.13403	62	−9
		0.10704	24	−15
		0.45367	51	−2
10	O(1)	−0.06329	48	−1
		0.10006	20	−6
		0.40268	47	−1
11	O(2)	0.25589	48	−23
		0.04298	20	1
		0.53736	50	21

Hydrogen positions

Atom	X	Y	Z
H(2)	0.5377	0.1394	0.5416
H(3)	0.6743	0.2459	0.3706
H(4)	0.6657	0.4042	0.4475
H(5)	0.5192	0.4314	0.6771
H(6)	0.1377	0.4263	0.5843
H(7)	−0.0341	0.3920	0.2695
H(8)	−0.0217	0.2336	0.2004
H	0.1624	−0.0040	0.5486

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(2) Participation in this work was sponsored by the Foreign Student Summer Project, Massachusetts Institute of Technology.

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Table II. Anistropic Thermal Parameters[a]

Atom	$\beta_{ij} \times 10^3$			Axes of vibration ellipsoid: Smallest U_1	Smallest u_1, v_1, w_1	Intermediate U_2	Intermediate u_2, v_2, w_2	Largest U_3	Largest u_3, v_3, w_3
C(1)	28.3	−1.0	6.1	0.229	0.64	0.244	0.34	0.265	−0.69
		5.3	0.0		0.67		−0.70		0.26
			20.3		0.39		0.63		0.67
C(2)	32.1	−0.4	8.2	0.239	0.19	0.256	0.87	0.287	−0.45
		5.3	−0.2		0.97		−0.22		−0.02
			25.2		0.12		0.44		0.89
C(3)	33.5	−2.0	6.4	0.250	0.80	0.262	0.22	0.321	−0.57
		7.2	1.9		0.57		−0.58		0.58
			25.6		0.20		0.79		0.58
C(4)	36.9	−1.8	6.7	0.244	−0.37	0.269	0.73	0.338	−0.58
		6.3	2.5		−0.90		−0.13		0.41
			29.6		0.22		0.67		0.70
C(5)	40.2	−1.9	5.3	0.237	0.29	0.272	0.60	0.337	−0.75
		5.5	0.8		0.96		−0.20		0.21
			28.7		0.03		0.78		0.63
C(6)	49.3	0.7	13.2	0.216	0.01	0.300	−0.26	0.317	0.97
		4.4	1.3		−0.98		0.17		0.05
			28.7		0.18		0.95		0.26
C(7)	36.1	0.8	10.8	0.226	−0.03	0.271	0.98	0.313	−0.18
		5.5	3.1		−0.90		0.05		0.43
			28.3		0.44		0.17		0.88
C(8)	31.5	−0.2	6.8	0.235	0.05	0.252	0.87	0.294	−0.48
		6.0	2.2		−0.77		0.34		0.54
			22.7		0.64		0.34		0.69
C(9)	29.9	−0.9	5.7	0.226	0.39	0.247	0.63	0.280	−0.67
		4.9	−0.5		0.85		−0.53		0.00
			22.2		0.36		0.57		0.74
O(1)	30.9	−1.9	5.7	0.232	0.66	0.258	0.57	0.343	−0.49
		5.9	2.0		0.75		−0.59		0.30
			32.2		0.12		0.57		0.82
O(2)	36.7	0.8	10.9	0.226	0.04	0.274	0.96	0.359	−0.29
		5.2	3.2		−0.96		0.11		0.25
			38.2		0.27		0.27		0.92
$\bar{\sigma}_0$	1.2	0.4	0.8						
		0.2	0.3						
			0.8						
$\bar{\sigma}_0$	0.9	0.3	0.7						
		0.2	0.3						
			0.8						

[a] Values of U_i, the r.m.s. vibrational amplitudes, are given in Ångstrøm units. The direction cosines, u, v, and w, are taken with respect to a set of Cartesian coordinates with the X' axis codirectional with a, the Y' axis codirectional with b, and the Z' axis making an angle of 20° 9.5′ with c. Thus in Figure 2, the X' and Y' axes lie in the plane of the paper and the Z' axis comes perpendicularly out of the paper.

paper moistened with alcohol. Lattice constants were determined by means of Cu Kα rotation photographs, with NaCl powder lines on them for calibration. The values obtained were $a_0 = 6.76 \pm 0.01$, $b_0 = 14.64 \pm 0.02$, and $c_0 = 8.37 \pm 0.01$ Å.; $\beta = 100° 9.5' \pm 5'$. These values lead to a calculated density of 1.255 g. cm.$^{-3}$ on the assumption of four molecules per unit cell; the observed density is 1.256 ± 0.005 g. cm.$^{-3}$ by flotation in heptane–carbon tetrachloride mixtures. The absence of (0k0) reflections with k odd and of ($h0l$) with l odd indicated the space group C_{2h}^5-$P2_1/c$. Intensity data for about 1650 planes were obtained by visual estimation with calibrated film strips from multiple-film equi-inclination Weissenberg photographs taken with copper Kα radiation. No absorption corrections were made.

Determination of the Structure

The structure was solved with a three-dimensional Patterson function, consisting of sections computed on the analog computer XRAC at Pennsylvania State University. A reasonably well resolved peak about 2.25 Å. from the origin was ascribed to the O···O intracarboxyl vector. With the use of required relations among peak positions for non-Harker and Harker peaks, it was possible to assign positions to the two oxygen atoms in the asymmetric unit. These positions, with their symmetry equivalents, were used as origins of eight shifted Patterson functions in an objective "Patterson superposition" or "vector convergence" procedure.[10] Carbon atoms were taken to be at positions where all eight shifted Patterson functions were above a preselected minimum value. Only two such positions were found in the asymmetric unit that could not reasonably be interpreted as atom positions; these were assumed to result from accidental congruences. The other nine, with the two oxygen positions first found, defined a chemically reasonable COT acid molecule with a tub-form COT ring.

The structure was refined by least squares.[11] The initial refinement was done on an IBM 704 computer with program NYXR1.[12] Unit weights were used, off-diagonal normal equation matrix elements were

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(11) E. W. Hughes, *J. Am. Chem. Soc.*, **63**, 1737 (1941).
(12) Program NYXR1 was written by D. Sayre, IBM Company. We used a modification made by V. Vand, Pennsylvania State University.

Table III. Observed and Calculated Structure Factors

L	FOBS	FCAL
0 0 L		
2	693	1128X
4	98	88
6	18	-15
8	52	-46
0 1 L		
1	171	-193
2	592	689
3	71	-88
4	153	136
5	82	74
6	56	51
7	44	37
8	9	12*
9	9	5*X
0 2 L		
0	292	-358
1	121	-127
2	118	129
3	291	-315
4	52	61
5	140	-127
6	9	-4*X
7	9	4*X
8	32	29
9	9	13*
0 3 L		
1	183	-224
2	170	-193
3	20	-26
4	68	-63
5	91	-88
6	101	-85
7	50	-47
8	9	-9*
9	9	1*X
0 4 L		
0	409	-463
1	146	-147
2	291	-342
3	22	-22
4	12	-13
5	75	65
6	9	9*
7	9	-2*X
8	27	-24
9	9	-6*X
0 5 L		
1	221	-229
2	117	-110
3	199	-224
4	119	-98
3	63	-65
6	9	-8*Z
7	9	-8*Z
8	28	-19
9	9	-9*
0 6 L		
0	301	-331
1	63	67
2	55	-54
3	120	136
4	10	16
5	76	69
6	28	29
7	32	25
8	27	24
9	9	-2*X
0 7 L		
1	180	185
2	119	-124
3	55	48
4	11	-11
5	19	-7
6	9	-12*
7	23	22
8	9	4*X
9	9	8*X
0 8 L		
0	136	136
1	155	166
2	11	-0
3	206	225
4	17	17
5	25	70X
6	27	23
7	27	21
8	9	-2*X
9	17	15
0 9 L		
1	94	87
2	9	-15*
3	83	83
4	91	-86
5	38	36
6	9	-11*
7	11	-8
8	9	6*X
0 10 L		
0	98	97
1	50	46
2	139	133
3	42	42
4	9	14*
5	9	12*
6	41	-44
7	9	2*X
8	9	-6*X
0 11 L		
1	88	-87
2	9	-4*X
3	42	38
4	61	62
5	23	23
6	9	6*X
7	9	6*X
8	9	-8*X
0 12 L		
0	38	-34
1	143	-129
2	109	-96
3	166	-173
4	32	-32
5	72	-68
6	9	2*X
7	26	-27
0 13 L		
1	163	150
2	46	45
3	9	12*
4	9	-5*X
5	9	-3*X
6	9	2*X
7	14	-11
0 14 L		
0	140	-126
1	26	31
2	78	-72
3	9	14*
5	9	1*X
6	9	10*
0 15 L		
1	25	-26
2	9	8*X
3	9	4*X
4	9	0*X
5	9	-9*
0 16 L		
0	26	-29
1	9	-4*X
2	9	-14*
3	9	12*
4	9	5*X
5	9	7*X
0 17 L		
1	9	6*X
2	9	9*
3	9	1*X
4	18	18
0 18 L		
0	23	9
1	9	6*X
2	9	10*
1 0 L		
-8	9	13*
-6	43	41
-4	77	-79
-2	412	-483
0	54	57
2	406	-406
4	276	-285
6	9	-2*X
8	9	-1*X
1 1 L		
-10	9	10*
-9	9	4*X
-8	30	28
-7	53	31
-6	34	31
-5	115	111
-4	92	95
-3	70	-91
-2	390	-443
-1	329	-409
0	317	-534
1	268	-314
2	58	46
3	85	-99
4	128	-122
5	9	3*X
6	48	-42
7	22	16
8	9	7*X
9	9	5*X
1 2 L		
-10	9	-11*
-9	23	-19
-8	9	8*2
-7	60	-53
-6	9	-8*X
-3	64	67
-4	125	135
-3	233	293
-2	439	661X
-1	69	83
0	146	178
1	118	129
2	87	90
3	18	-19
4	15	-23
5	61	-59
6	73	-68
7	25	-24
8	9	4*X
9	9	-7*X
1 3 L		
-10	9	7*X
-9	9	3*X
-8	9	-0*X
-7	65	-65
-6	35	-38
-3	226	-200
-4	336	-401
-3	90	-96
-2	507	-733X
-1	27	2
0	270	-314
1	138	150
2	22	22
3	253	293
4	122	116
3	94	92
6	16	13
7	12	-6
8	9	-3*X
9	9	-3*X
1 4 L		
-10	9	10*
-9	9	3*X
-8	9	-0*X
-7	37	34
-6	31	39
-5	32	28
-4	175	156
-3	31	31
-2	80	-82
-1	24	23
0	132	-139
1	179	-190
2	73	-73
3	81	-78
4	46	45
5	69	69
6	42	42
7	9	13*
8	9	-14*
9	9	-12*
1 5 L		
-9	29	-27
-8	9	1*X
-7	60	-53
-6	34	-33
-5	32	-36
-4	22	-15
-3	89	81
-2	18	4
-1	377	410
0	99	-100
1	295	342
2	126	-132
3	12	-8
4	119	-113
5	9	4*X
6	9	5*X
7	29	28
8	9	8*X
9	9	6*X
1 6 L		
-9	9	-4*X
-8	9	10*
-7	39	-37
-6	9	-5*X
-5	44	-42
-4	236	-147
-3	84	88
-2	180	-196
-1	316	326
0	147	-139
1	308	349
2	85	90
3	132	138
4	33	33
5	9	9*
6	34	-30
7	12	12
8	9	-9*
1 7 L		
-9	9	1*X
-8	9	10*
-7	9	-0*X
-6	98	95
-5	78	-82
-4	143	146
-3	134	-138
-2	101	114
-1	27	-33
0	116	-112
1	18	14
2	190	-197
3	42	-36
4	19	-15
5	60	-48
6	9	1*X
7	10	-11
8	9	-3*X
1 8 L		
-9	9	8*X
-8	17	-17
-7	33	33
-6	9	12*
-3	38	56
-4	38	64
-3	10	4
-2	22	12
-1	38	64
0	104	101
1	193	193
2	58	-45
3	133	131
4	36	-32
5	9	12*
6	27	22
7	12	-8
8	9	6*X
1 9 L		
-9	9	19*
-8	23	-22
-7	32	50
-6	35	-41
-5	114	117
-4	62	62
-3	42	47
-2	79	80
-1	130	-138
0	33	30
1	182	-183
2	44	42
3	86	-81
4	46	-43
5	9	-2*X
6	23	-20
7	9	-2*X
8	9	4*X
1 10 L		
-8	9	3*X
-7	12	12
-6	37	-59
-3	38	37
-4	75	-78
-3	53	54
-2	43	42
-1	9	8*2
0	19	18
1	9	3*X
2	84	76
3	9	-10*Y
4	74	71
5	22	-21
6	9	0*X
7	9	-7*X
1 11 L		
-8	9	9*
-7	20	20
-6	9	-10*Y
-5	64	71
-4	134	-136
-3	122	136
-2	146	-135
-1	32	31
0	100	-94
2	94	-91
3	9	6*X
4	24	22
5	9	-3*X
6	17	12
7	9	-12*
1 12 L		
-7	20	-19
-6	9	10*
-5	57	-63
-4	9	15*
-3	41	-43
-2	9	-14*
-1	34	26
0	57	58
2	9	2*X
3	26	-27
4	9	-9*Y
5	31	29
6	27	22
7	9	2*X
1 13 L		
-7	9	-4*X
-6	33	-33
-3	16	-7
-4	31	-50
-3	78	-73
-2	69	-74
-1	29	-30
0	28	-27
2	36	32
3	30	-32
4	9	-9*
5	12	-12
6	9	3*X
1 14 L		
-6	9	1*X
-5	34	38
-4	27	-28
-3	36	32
-2	30	-27
-1	36	-60
0	39	-39
1	47	-45
2	9	-8*X
3	27	-21
4	13	-13
5	21	-20
6	9	-10*
1 15 L		
-6	17	19
-5	32	-36
-4	38	39
-3	33	28
-2	54	31
-1	68	62
0	68	65
1	44	36
2	46	45
3	28	26
4	9	7*X
5	9	-11*
1 16 L		
-5	9	0*X
-4	9	-10*
-3	26	-21
-2	28	-24
-1	9	3*X
0	19	-20
1	9	6*X
2	9	12*
3	23	19
4	30	27
1 17 L		
-4	46	40
-3	9	0*X
-2	53	33
-1	9	-5*X
0	23	25
1	9	-4*X
2	9	0*X
3	9	-8*X
1 18 L		
-2	43	31
-1	9	-3*X
0	18	16
1	9	2*X
2 0 L		
-10	9	4*X
-8	37	-38
-6	70	-71
-4	132	-130
-2	442	-451
0	222	239
2	120	117
4	25	-28
6	72	59
8	9	12*
2 1 L		
-10	9	-7*X
-9	18	-15
-8	22	-15
-7	9	-9*
-6	89	-88
-5	31	36
-4	14	-15
-3	66	-75
-2	190	-174
-1	32	53
0	324	-358
1	276	278
2	100	96
3	123	129
4	18	10
5	9	1*X
6	9	-3*X
7	24	-19
8	37	34
2 2 L		
-10	9	-6*X
-9	18	-17
-8	9	-1*X
-7	39	-35
-6	63	-66
-5	24	23
-4	212	-200
-3	121	139
-2	22	22
-1	207	-207
0	315	-328
1	184	-183
2	293	-299
3	11	-12
4	33	-53
5	25	-18
6	41	-38
7	30	-24
8	9	9*
2 3 L		
-10	9	2*X
-9	20	20
-8	23	-19
-7	48	44
-6	23	-24
-3	68	64
-4	217	-207
-3	230	268
-2	200	-214
-1	180	189
0	164	168
1	99	-103
2	14	-2
3	20	13
4	40	-39
5	42	40
6	49	-46
7	9	2*X
8	27	-22
2 4 L		
-10	19	15
-9	36	-34
-8	26	21
-7	7	-2*X
-6	53	50
-5	100	103
-4	136	131
-3	241	293
-2	132	-132
-1	346	358
0	160	-163
1	34	-41
2	48	-46
3	130	-122
4	25	-24
5	9	3*X
6	9	1*X
7	13	9
8	23	-23
2 5 L		
-10	9	3*X
-9	9	-11*
-8	35	36
-7	72	-69
-6	19	-19
-5	88	-82
-4	78	-81
-3	33	27
-2	17	-11
-1	212	206
0	16	15
1	174	169
2	121	119
3	38	-29
4	61	60
5	9	-5*X
6	33	33
7	28	26
8	9	10*
2 6 L		
-9	47	50
-8	23	30
-7	76	68
-6	128	135
-5	9	4*X
-4	124	119
-3	93	-89
-2	68	64
-1	83	-82
0	81	-79
1	37	-40
2	22	19
3	23	-17
4	38	31
5	37	-30
6	9	-5*X
7	9	-6*X
8	9	10*
2 7 L		
-9	9	1*X
-8	47	-44
-7	44	42
-6	9	6*X
-5	45	45
-4	71	74
-3	17	21
-2	109	105
-1	12	10
0	68	70
1	11	10
2	9	3*X
3	9	12*Y
4	75	68
5	9	4*X
6	47	42
7	17	16
8	9	9*
2 8 L		
-9	9	5*X
-8	40	-37
-7	15	11
-6	96	-92
-5	20	17
-4	71	-60
-3	54	-52
-2	47	-44
-1	61	-62
0	146	142
1	28	8
2	109	101
3	9	1*X
4	9	-11*
5	23	-29
6	9	-4*X
7	14	-12
2 9 L		
-9	9	6*X
-8	9	7*2
-7	9	-3*X
-6	25	-28
-5	19	-17
-4	17	-12
-3	89	-86
-2	101	-93
-1	138	-141
0	159	-165
1	76	-64
2	19	21
3	9	1*X
4	27	29
5	9	-2*X
6	9	-1*X
7	16	-17
2 10 L		
-8	9	3*X
-7	9	-4*X
-6	27	-29
-5	9	4*X
-4	30	-31
-3	9	15*
-2	114	112
-1	26	-19
0	9	12*
1	19	-10
2	33	-36
3	9	-3*X
4	23	22
5	9	-7*X
6	9	-2*X
7	9	4*X
2 11 L		
-8	9	-9*
-7	9	-2*X
-6	9	5*X
-5	33	-33
-4	30	-28
-3	46	-50
-2	27	25
-1	100	-102
0	82	86
1	133	-119
2	35	-38
3	37	-34
4	21	-20
5	19	-20
6	9	4*X
2 12 L		
-8	9	-8*X
-7	9	2*X
-6	9	-8*2
-5	9	2*X
-4	16	14
-3	37	23
-2	9	1*X
-1	93	88
0	73	69
1	35	32
2	33	30
3	23	-23
4	21	-20
5	9	1*X
6	9	6*X
2 13 L		
-7	9	5*X
-6	9	-5*X
-5	30	30
-4	9	4*X
-3	27	-24
-2	9	9*
-1	27	-28
0	9	5*X
1	37	41
2	21	14
3	9	11*
4	27	-30
5	13	16
2 14 L		
-6	38	40
-5	9	-5*X
-4	36	37
-3	32	26
-2	51	53
-1	25	-28
0	44	45
1	9	-7*X
2	34	38
3	28	29
4	13	13
5	9	11*
2 15 L		
-6	9	6*X
-5	25	-25
-4	9	2*X
-3	9	10*
-2	24	-22
-1	23	21
0	9	-10*
1	30	-28
2	9	4*X
3	9	-12*
4	9	7*X
2 16 L		
-5	9	-11*
-4	38	38
-3	42	-40
-2	16	12
-1	23	-18
0	9	-14*
1	9	-8*X
2	9	-3*X
3	9	-2*X
2 17 L		
-4	9	26*X
-3	9	-1*X
-2	32	32
-1	9	-0*X
0	9	4*X
1	9	-3*X
2	9	-10*
2 18 L		
-1	9	-8*X
3 0 L		
-10	9	-11*
-8	65	-57
-6	65	-64
-4	89	92
-2	183	-173
0	211	-203
2	187	-190
4	173	-164
6	9	13*
8	9	37*X
3 1 L		
-10	9	10*
-9	9	2*X
-8	9	16*
-7	53	47
-6	44	-49
-5	161	142
-4	81	74
-3	56	57
-2	261	253
-1	68	-73
0	73	88
1	13	14
2	113	118
3	9	-13*
4	31	-29
5	60	-60
6	81	-69
7	32	-31
8	9	-3*X
3 2 L		
-10	9	4*X
-9	9	1*X
-8	9	8*X
-7	9	6*X
-6	39	-42
-5	100	101
-4	203	-190
-3	156	162
-2	44	50
-1	135	-144
0	34	51
1	68	-67
2	44	37
3	153	145
4	108	97
5	119	110
6	9	4*X
7	33	31
3 3 L		
-10	22	18
-9	9	-9*
-8	35	33
-7	28	-21
-6	92	91
-5	75	-65
-4	60	52
-3	55	61
-2	43	-42
-1	73	86
0	171	179
1	126	-107
2	63	57
3	38	-33
4	26	29
5	41	41
6	34	36
7	21	22
3 4 L		
-10	9	1*X
-9	9	-5*X
-8	9	8*X
-7	9	-9*Y
-6	9	-4*X
-5	36	-31
-4	71	62
-3	131	-138
-2	13	7
-1	170	-180
0	70	73
1	155	-140
2	129	122
3	110	-97
4	38	30
5	9	-1*X
6	28	22
7	9	8*X
3 5 L		
-10	9	-16*
-9	28	28
-8	9	2*X
-7	9	6*X
-6	23	-20
-5	9	0*X
-4	48	-38
-3	41	43
-2	78	81
-1	75	70
0	73	90
1	73	69
2	71	66
3	9	-6*X
4	21	-13
5	9	-1*X
6	17	-13
7	9	7*X
3 6 L		
-10	9	-6*X
-9	9	1*X
-8	9	-2*X
-7	9	1*X
-6	50	54
-5	64	-57
-4	26	-26
-3	104	-94
-2	72	-69
-1	72	-67
0	20	-15
1	62	-55
2	60	57
3	40	-46
4	44	42
5	36	-36
6	19	-15
7	9	-7*X
3 7 L		
-9	9	-12*
-8	40	-40
-7	9	-9*
-6	25	-24
-5	23	-28
-4	53	47
-3	72	-62
-2	57	48
-1	21	-18
0	51	45
1	9	1*X
2	9	-9*
3	9	-2*X
4	9	3*X
5	9	-6*X
6	9	-2*X
7	9	-0*X
3 8 L		
-9	9	10*
-8	9	15*
-7	9	-9*X
-6	9	11*
-5	18	-13
-4	46	49
-3	53	-44
-2	38	-34
-1	54	-51
0	28	-27
1	40	-34
2	29	-26
3	46	-48
4	51	-51
5	38	-42
6	9	-13*
7	23	-18
3 9 L		
-9	9	-6*X
-8	9	1*X
-7	9	-8*X
-6	9	9*
-5	9	6*X
-4	94	91
-3	9	-0*X
-2	130	119
-1	9	-12*
0	9	7*X
1	9	0*X
2	91	81
3	9	-2*X
4	68	69
3	9	-8*X
6	9	12*
3 10 L		
-8	9	-14*
-7	9	-8*X
-6	29	-26
-5	17	-23
-4	33	-30
-3	9	10*
-2	71	62
-1	24	24
0	41	-50
1	23	16
2	123	-129
3	9	9*
4	19	-16
5	12	-11
6	9	10*
3 11 L		
-8	9	13*
-7	9	1*X
-6	28	30
-5	32	-34
-4	17	-12
-3	38	-41
-2	29	-22
-1	9	13*
0	38	37
1	39	39
2	43	-41
3	67	61
4	31	-29
5	29	29
3 12 L		
-8	9	4*X
-7	15	13
-6	9	9*
-5	22	14
-4	49	54
-3	46	-45
-2	33	29
-1	41	-38
0	27	28
1	9	-12*
2	9	8*X
3	9	10*
4	33	-30
5	52	47
3 13 L		
-7	17	-16
-6	9	-5*X
-5	20	20
-4	26	-26
-3	9	1*X
-2	9	-11*
-1	36	-41
0	9	-10*
1	9	1*X
2	9	11*
3	9	-10*
4	9	-10*
3 14 L		
-6	40	33
-5	16	-10
-4	9	5*X
-3	44	45
-2	9	-2*X
-1	19	12
0	9	16*
1	9	-10*
2	30	30
3	9	6*X
4	9	13*
3 15 L		
-6	9	3*X
-5	30	-25
-4	14	12
-3	9	-13*
-2	9	-14*
-1	18	20

neglected, and positional and isotropic thermal parameters were refined for nonhydrogen atoms. In the later stages ring hydrogen atoms were introduced in expected positions but not refined. After shifts in successive cycles had become small in comparison to standard deviations, the agreeement factor

$$R = \Sigma|F_o - F_c|/\Sigma F_o$$

excluding unobserved reflections was 0.15. A three-dimensional Fourier electron-density synthesis was calculated with program MIFR1.[13] All hydrogen atoms were found with fairly well-defined peaks at roughly the expected positions, except the carbonyl hydrogen (H) which was on a rather poorly defined peak. This peak was roughly on a straight line between its associated oxygen atom and the double-bonded oxygen of the centrosymmetrically related molecule, so as to

(13) D. P. Shoemaker and W. G. Sly, *Acta Cryst.*, 14, 552 (1961).

Table III (*Continued*)

L	FOBS	FCAL
0	9	-13*
1	9	1*X
2	9	3*X
3	9	13*
3 16 L		
-4	9	-1*X
-3	9	8*X
-2	9	-2*X
-1	19	19
0	9	-8*Z
1	9	12*
2	9	-1*X
3 17 L		
-3	9	9*Y
-2	9	-11*
-1	9	2*X
0	9	-14*
4 0 L		
-10	23	17
-8	9	-9*
-6	42	-42
-4	132	123
-2	83	80
0	68	49
2	93	77
4	18	-9
6	9	4*X
4 1 L		
-10	9	9*
-9	9	-6*X
-8	14	39X
-7	11	-8
-6	19	-14
-5	29	-26
-4	16	-10
-3	172	-169
-2	144	138
-1	188	-165
0	10	9
1	40	43
2	28	28
3	95	93
4	25	22
5	35	32
6	35	-29
7	7	6*X
4 2 L		
-10	9	-9*
-9	9	-5*X
-8	9	-1*X
-7	34	-31
-6	58	49
-5	24	-23
-4	9	2*X
-3	17	16
-2	100	100
-1	154	-133
0	78	65
1	147	-125
2	58	-53
3	24	24
4	26	28
5	33	32
6	18	15
7	9	5*X
4 3 L		
-10	9	9*
-9	9	10*
-8	9	-10*
-7	26	23
-6	9	2*X
-5	9	-2*X
-4	89	68
-3	64	57
-2	95	93
-1	87	81
0	192	172
1	102	-95
2	9	-3*X
3	114	-112
4	78	-73
5	36	-40
6	25	-27
7	15	-17
4 4 L		
-10	9	2*X
-9	9	-8*X
-8	9	18*
-7	21	-13
-6	28	-24
-5	29	-14
-4	9	1*X
-3	56	-47
-2	10	10
-1	78	65
0	42	46
1	178	161
2	88	79
3	104	100
4	9	-2*X
5	46	41
6	9	-1*X

L	FOBS	FCAL
4 5 L		
-10	9	-8*Z
-9	9	4*X
-8	27	27
-7	18	-18
-6	64	59
-5	25	-14
-4	9	9*
-3	31	-11X
-2	43	38
-1	125	-116
0	20	-17
1	128	-122
2	25	-21
4	9	-10*
3	9	-3*X
6	9	-3*X
4 6 L		
-9	9	-1*X
-8	30	-25
-7	15	13
-6	26	23
-5	19	-14
-4	9	8*X
-3	33	-24
-2	9	2*X
-1	21	-16
0	60	52
1	53	-49
2	33	30
3	40	-39
4	9	-5*X
5	20	-19
6	31	-27
4 7 L		
-9	9	-14*
-8	9	-7*X
-7	14	-12
-6	9	-6*X
-5	26	22
-4	9	-1*X
-3	60	58
-2	93	-90
-1	63	61
0	60	-57
1	9	16*
2	9	9*Y
3	25	-15
4	24	29
5	19	-21
6	18	19
4 8 L		
-9	9	-2*X
-8	19	13
-7	30	-30
-6	9	-10*
-5	43	-41
-4	9	-13*
-3	27	-17
-2	100	-101
-1	9	15*
0	97	-101
1	9	14*
2	9	11*
3	9	-12*
4	26	25
5	16	-15
4 9 L		
-9	9	5*X
-8	9	-1*X
-7	9	-5*X
-6	9	5*X
-5	19	-23
-4	25	23
-3	9	-2*X
-2	9	-10*
-1	57	58
0	163	-154
1	110	101
2	109	-98
3	74	68
4	17	-16
5	17	18
4 10 L		
-8	9	10*
-7	9	5*X
-6	9	12*
-5	17	-19
-4	14	-8
-3	25	-23
-2	49	51
-1	9	-13*
0	9	5*X
1	9	1*X
2	89	-77
3	28	22
4	20	-21
5	9	12*
4 11 L		
-8	9	-1*X
-7	17	20
-6	21	12
-5	14	12

L	FOBS	FCAL
-4	23	22
-3	9	-1*X
-2	41	37
-1	31	29
0	133	114
1	23	24
2	50	47
3	22	22
4	9	-9*Y
4 12 L		
-7	9	-0*X
-6	22	-22
-5	30	30
-4	19	-13
-3	9	7*X
-2	51	-42
-1	21	11
0	44	-41
1	29	24
2	9	-1*X
3	9	-4*X
4	9	-7*X
4 13 L		
-7	15	-10
-6	9	2*X
-5	17	17
-4	9	-5*X
-3	27	24
-2	40	39
-1	19	-12
0	36	40
1	9	11*
2	29	28
3	9	-3*X
4 14 L		
-5	9	1*X
-4	21	-19
-3	26	25
-2	34	-29
-1	9	-2*X
0	9	-10*
1	17	-15
2	9	1*X
4 15 L		
-5	9	6*X
-4	15	-15
-3	9	8*Z
-2	30	-30
-1	18	13
0	9	-28*X
1	24	-26
4 16 L		
-3	9	-3*X
-2	14	11
-1	9	-11*
0	19	8
5 0 L		
-10	9	9*
-8	9	12*
-6	22	14
-4	184	171
-2	161	136
0	21	-20
2	13	11
4	30	-27
5 1 L		
-10	9	-3*X
-9	9	-2*X
-8	9	13*
-7	9	-5*X
-6	28	-25
-5	9	11*
-4	60	-61
-3	9	10*
-2	48	44
-1	17	21
0	21	-26
1	71	70
2	20	-24
3	51	45
4	29	27
5	9	-1*X
5 2 L		
-10	9	3*X
-9	9	4*X
-8	9	9*
-7	9	1*X
-6	70	63
-5	10	13
-4	22	29
-3	62	54
-2	14	15
-1	11	-1
0	19	-9
1	26	-29
2	96	-85
3	43	20X
4	17	-17
5	17	19

L	FOBS	FCAL
5 3 L		
-10	9	5*X
-9	9	-5*X
-8	9	-3*X
-7	21	-16
-6	9	-2*X
-5	105	-89
-4	65	58
-3	111	-111
-2	25	27
-1	17	-16
0	41	40
1	9	6*X
2	23	-28
3	9	10*
4	47	-51
5	26	23
5 4 L		
-10	9	-10*
-9	9	4*X
-8	9	-3*X
-7	28	25
-6	65	-59
-5	50	48
-4	73	-78
-3	61	-55
-2	31	-35
-1	118	-119
0	9	7*X
1	49	-52
2	48	48
3	21	-18
4	9	3*X
5	9	5*X
5 5 L		
-9	9	-1*X
-8	9	-2*X
-7	9	4*X
-6	9	-5*X
-5	55	47
-4	84	-81
-3	88	78
-2	59	-56
-1	32	-35
0	29	-24
1	101	-99
2	12	-10
3	67	-65
4	9	-5*X
5	20	-20
5 6 L		
-9	13	-15
-8	14	-9
-7	17	-16
-6	9	-9*
-5	9	-2*X
-4	71	-71
-3	88	83
-2	103	-96
-1	180	161
0	14	14
1	114	104
2	53	51
3	30	20
4	40	39
5	16	-16
5 7 L		
-9	9	0*X
-8	9	8*X
-7	9	-5*X
-6	9	-1*X
-5	9	9*
-4	23	-23
-3	9	3*X
-2	145	-128
-1	9	-2*X
0	128	-107
1	9	5*X
2	24	-19
3	16	14
4	12	13
5	9	9*
5 8 L		
-9	9	5*X
-8	14	10
-7	13	-10
-6	28	26
-5	9	-2*X
-4	88	78
-3	74	58
-2	59	54
-1	92	82
0	29	-25
1	52	52
2	23	-22
3	12	15
4	28	-24
5 9 L		
-8	9	-7*X
-7	9	7*X
-6	9	-14*
-5	9	-0*X
-4	32	-1X

L	FOBS	FCAL
-3	13	14
-2	60	54
-1	39	39
0	18	15
1	38	33
2	13	12
3	11	10
4	30	22
5 10 L		
-8	9	-3*X
-7	11	10
-6	9	-1*X
-5	9	-7*X
-4	29	-23
-3	15	-13
-2	13	12
-1	9	-3*X
0	30	30
1	9	-2*X
2	14	-16
3	14	12
4	9	5*X
5 11 L		
-7	16	14
-6	9	6*X
-5	12	10
-4	16	9
-3	12	-11
-2	38	-32
-1	9	8*Z
0	12	-11
1	9	-0*X
2	17	-19
3	12	-12
5 12 L		
-7	10	8
-6	21	-21
-5	29	24
-4	9	4*X
-3	15	-18
-2	12	10
-1	45	-43
0	9	-6*X
1	15	-16
2	15	11
5 13 L		
-6	9	-1*X
-5	9	5*X
-4	13	-10
-3	17	13
-2	19	17
-1	19	-20
0	10	5
1	9	-3*X
2	9	-9*
5 14 L		
-5	16	-12
-4	14	-15
-3	13	-11
-2	18	-20
-1	28	-24
0	9	2*X
1	9	-30*X
5 15 L		
-2	24	22
-1	9	-8*Z
6 0 L		
-8	38	28
-6	9	11*
-4	18	15
-2	72	-66
0	204	-166
2	57	-54
4	9	4*X
6 1 L		
-9	9	-0*X
-8	9	-2*X
-7	27	-18
-6	45	10X
-5	39	-33
-4	15	10
-3	34	-27
-2	95	84
-1	9	-3*X
0	9	15*
1	28	24
2	51	-46
3	30	22
4	9	-2*X
6 2 L		
-9	9	12*
-8	9	-26*X
-7	10	8
-6	9	-5*X
-5	42	-39
-4	9	-0*X
-3	62	-65
-2	9	10*

L	FOBS	FCAL
-1	78	-69
0	52	43
1	73	-50
2	9	-15*
3	9	-5*X
4	9	-12*
6 3 L		
-9	9	6*X
-8	9	-24*X
-7	52	41
-6	104	-85
-5	38	52
-4	55	-57
-3	42	27
-2	9	-16*
-1	53	34
0	41	40
1	9	9*
2	48	41
3	9	-12*
4	9	1*X
6 4 L		
-9	9	-5*X
-8	9	20*
-7	11	10
-6	9	-10*
-5	58	53
-4	52	-47
-3	9	26*X
-2	9	-14*
-1	25	-21
0	9	4*X
1	9	-1*X
2	9	24*X
3	9	-0*X
4	9	6*X
6 5 L		
-9	9	-8*X
-8	9	-6*X
-7	14	-14
-6	26	15
-5	22	17
-4	24	-22
-3	77	77
-2	9	-11*
-1	47	47
0	9	11*
1	9	7*X
2	9	8*X
3	9	0*X
4	9	12*
6 6 L		
-8	9	-10*
-7	9	8*X
-6	17	-9
-5	9	7*X
-4	13	-12
-3	9	13*
-2	9	-31*X
0	9	10*
1	28	6X
2	9	9*
3	9	-2*X
6 7 L		
-8	9	17*
-7	12	-9
-6	25	22
-5	9	5*X
-4	45	38
-3	9	-1*X
-2	9	-7*X
0	20	-23
1	9	-21*X
2	9	1*X
3	9	-5*X
6 8 L		
-8	9	-6*X
-7	9	-1*X
-6	15	-12
-5	9	4*X
-4	15	10
-3	45	43
-2	9	27*X
0	9	-5*X
1	9	7*X
2	9	5*X
3	9	-10*
6 9 L		
-7	9	6*X
-6	9	-5*X
-5	37	-29
-4	43	-30
-3	60	-50
-2	9	-14*
-1	42	-33
0	24	-19
1	24	-8
2	9	-16*
6 10 L		
-7	8	8*X

L	FOBS	FCAL
-6	38	32
-5	9	7*Z
-4	38	25
-3	9	1*X
-2	9	8*X
-1	9	-0*X
0	9	8*Z
1	9	-18*
2	9	-17*
6 11 L		
-6	17	-10
-5	9	-10*
-4	18	15
-3	28	-22
-2	9	3*X
-1	9	8*X
0	9	15*
1	9	15*
6 12 L		
-5	29	-17
-4	29	14
-3	55	-44
-2	9	26*X
-1	58	-38X
0	9	1*X
6 13 L		
-4	9	-8*X
-3	9	1*X
-2	9	14*
-1	9	-34*X
7 0 L		
-8	9	-18*
-6	27	-15
-4	43	39
-2	87	74
0	9	7*X
2	9	13*
7 1 L		
-8	9	-19*
-7	9	-2*X
-6	41	-27
-5	21	-15
-4	53	-40
-3	9	-7*X
-2	9	25*X
-1	9	2*X
0	38	34

L	FOBS	FCAL
1	9	3*X
2	9	-10*
7 2 L		
-8	9	-4*X
-7	9	27*X
-6	9	-1*X
-5	9	12*
-4	18	-13
-3	9	-10*
-2	61	-39X
-1	9	-10*
0	9	1*X
1	9	-10*
2	9	-1*X
7 3 L		
-8	9	-0*X
-7	14	11
-6	9	-10*
-5	32	26
-4	46	36
-3	9	1*X
-2	67	44X
-1	9	-6*X
0	9	15*
1	9	-7*X
2	9	6*X
7 4 L		
-8	9	7*X
-7	10	-11
-6	9	-9*Y
-5	9	4*X
-4	48	-37
-3	9	-4*X
-2	9	-6*X
-1	34	-24
0	9	1*X
1	9	-8*Z
2	9	4*X
7 5 L		
-8	9	-1*X
-7	8	6*X
-6	24	18
-5	9	6*X
-4	9	3*X
-3	9	16*
-2	9	-3*X
-1	9	0*X
0	9	11*
1	9	-5*X

L	FOBS	FCAL
2	9	3*X
7 6 L		
-7	9	2*X
-6	9	8*X
-5	19	-6
-4	18	17
-3	9	-20*
-2	9	-7*X
-1	17	-13
0	9	-1*X
1	9	-3*X
7 7 L		
-7	9	-3*X
-6	9	-6*X
-5	31	15
-4	9	6*X
-3	9	20*
-2	9	4*X
-1	9	2*X
0	9	-1*X
1	9	-4*X
7 8 L		
-6	9	-2*X
-5	42	-24X
-4	9	-4*X
-3	9	-4*X
-2	9	13*
-1	9	2*X
0	9	1*X
7 9 L		
-6	26	20
-5	9	-22*X
-4	9	-2*X
-3	9	-17*
-2	9	-2*X
-1	9	5*X
0	9	5*X
7 10 L		
-5	9	-10*
-4	27	20
-3	9	-10*
-2	9	-1*X
-1	9	3*X
8 0 L		
-6	9	-3*X

L	FOBS	FCAL
-4	9	4*X
-2	9	18*
0	9	-18*
8 1 L		
-7	9	3*X
-6	16	9
-5	17	-11
-4	9	-3*X
-3	9	-13*
-2	9	11*
-1	9	-13*
0	9	20*
8 2 L		
-6	9	3*X
-5	9	6*X
-4	15	14
-3	9	-3*X
-2	9	-1*X
-1	9	6*X
0	9	16*
8 3 L		
-6	20	-10
-5	9	2*X
-4	9	-2*X
-3	9	-3*X
-2	9	-2*X
-1	9	3*X
8 4 L		
-6	9	12*
-5	9	-5*X
-4	9	-2*X
-3	9	-6*X
-2	9	11*
-1	9	-4*X
8 5 L		
-6	9	7*X
-5	9	5*X
-4	19	12
-3	9	2*X
-2	9	2*X
-1	9	-4*X
8 6 L		
-5	9	-2*X
-4	9	-4*X
-3	9	-2*X
-2	9	-1*X

NOTES

*=UNOBSERVED REFLECTIONS.VALUE LISTED IS ESTIMATE OF MINIMUM OBSERVABLE.

X=OBSERVED REFLECTIONS OMITTED FROM REFINEMENT ON SUSPICION OF ABNORMAL ERROR.

*X=UNOBSERVED REFLECTIONS OMITTED FROM REFINEMENT FOR THEIR FCAL BEING LESS THAN ESTIMATED MINIMUM OBSERVABLE OR ON SUSPICION OF ABNORMAL ERROR.

*Y=UNOBSERVED REFLECTIONS WHICH WERE NOT INCLUDED (*X) IN THE LAST TWO CYCLES OF REFINEMENT BUT WITH THE FINAL PARAMETERS THEIR FCAL CAME OUT TO BE LARGER THAN THE MINIMUM OBSERVABLE.

*Z=UNOBSERVED REFLECTIONS WHICH WERE INCLUDED (*) IN THE LAST TWO CYCLES OF REFINEMENT BUT WITH THE FINAL PARAMETERS THEIR FCAL DROPPED BELOW THE ESTIMATED MINIMUM OBSERVABLE.

suggest an O–H···O hydrogen bond of length 2.6 Å. The hydrogen peaks were not sufficiently good to merit individual positional refinement but collectively they suggested small shifts in their relation to the ring carbon atoms which were made before continued refinement. Strong indications of anisotropic thermal motion of the nonhydrogen atoms were also shown by the electron density function.

Further least-squares refinement was done on an IBM 7094 computer using the program ORFLS.[14] All positional and anisotropic thermal parameters for all nonhydrogen atoms were refined with the full normal equation matrix. Ring hydrogen positions were assigned so that each C–H bond was 1.08 Å. in length and was coplanar with the adjacent ring bonds, and so that the ratio of the angle made with the double bond to that made with single bond was a constant, taken to be 1.062. The carbonyl hydrogen atom H was assigned a position at a distance of 0.96

(14) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFLS, a Fortran Crystallographic Least-Squares Program," Oak Ridge National Laboratory, ORNL-TM-305 Aug. 1962.

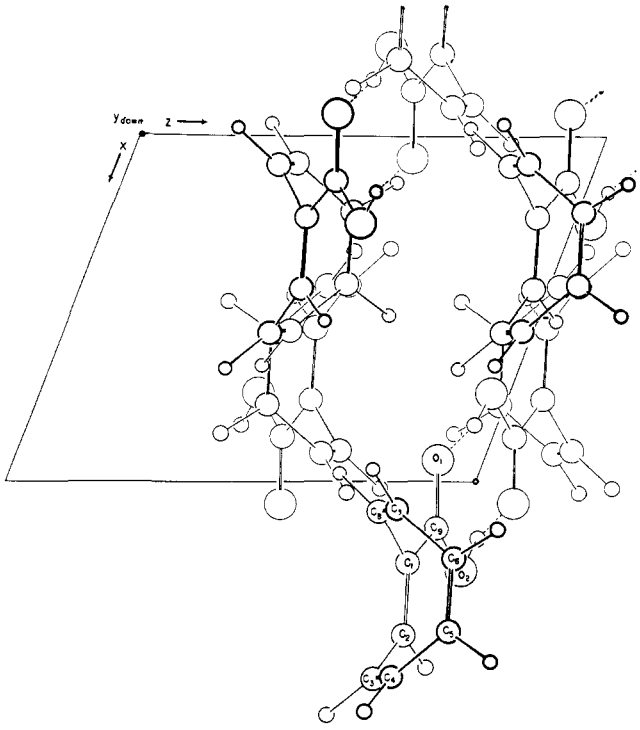

Figure 1. The crystal structure as viewed along the crystallographic *b* axis (*y* going into the paper). Molecules at the left edge of the unit cell outline are omitted.

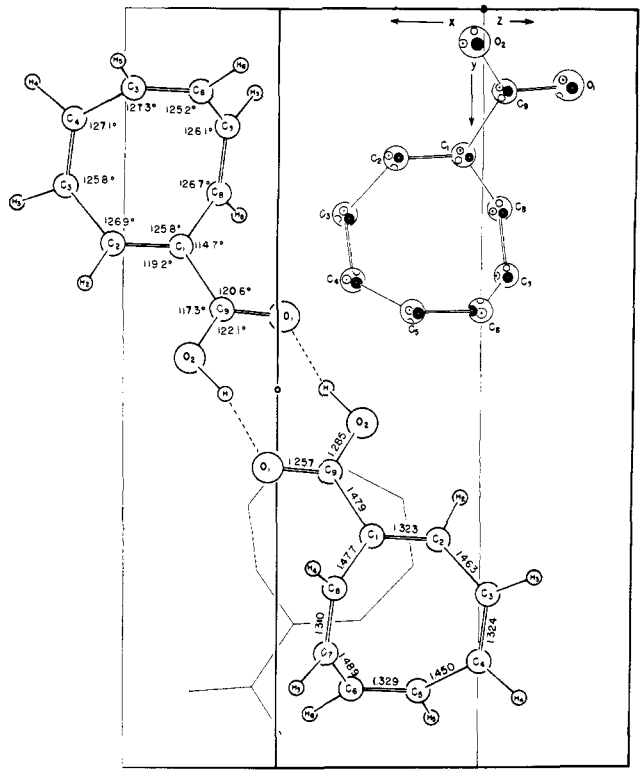

Figure 2. The crystal structure as viewed *perpendicular* to the crystallographic (001) plane (*z* coming at an angle out of the paper). The molecule at upper left is the same one as is labeled in Figure 1. The two molecules forming one dimer are labeled with angles and distances (in Ångstrøm units). The molecule at upper right is the one which corresponds to parameter values given in Table I. The atom circles outline *stereographic projections* of the poles of the principal thermal parameters of the nonhydrogen atoms. The black circle with white dot represents the axis of strongest thermal motion (3), the open circle with black dot represents the next strongest (2), and the open circle represents with its center the least strong (1). The diameters of these symbols are proportional to the respective estimated r.m.s. vibration amplitudes.

Å. from its oxygen atom, O(2), and as close as possible to the straight line connecting O(2) with O(1) of the centrosymmetrically related molecule, subject to an imposed C(9)–O(2)–H angle of 105°. Hydrogen atoms were given thermal parameters computed from an arbitrarily assigned isotropic temperature factor B = 5.0 in the usual units of (0.5 Å.)^2. Weights were assigned to the structure factors by the method of Hughes.[11] In the final stages, unobserved reflections were included in refinement where calculated values of structure factors exceeded the assigned lower limits of observability. A few reflections were omitted from the refinement because of extinction or suspicion of highly abnormal error; these and other special cases are indicated in the structure factor table (Table III) and its footnotes. Refinement was continued until parameter shifts were small in comparison to the indicated standard deviations. The final value of the agreement factor R, including all unobserved reflections used in the last refinement cycle, was 0.101.

The final values of the atomic coordinates are given in Table I, and the bond distances and interbond angles calculated from them are shown in Figure 2. In Table II are given the thermal parameters (β_{ij} in the temperature factor expression exp $-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)$. Also given are vibration amplitudes (U) in Ångstrøm units for the three principal axes of the thermal ellipsoid, and also the orientations of these axes (direction cosines u, v, and w). The distances, angles, and ellipsoid parameters were computed by the IBM 7094 with programs DISTAN and VIBELL.[15] The observed and final calculated structure factors are given in Table III.

Description of the Structure

The crystal structure is shown in two projections in Figures 1 and 2. The molecules are clearly present as hydrogen-bonded dimers, as in benzoic acid[16] and in many other crystalline carboxylic acids. The COT ring is nearly perpendicular to the *c* axis of the crystal; packing is good, the COT rings being about 4 Å. apart in the *c* direction. Interatomic distances and bond angles shown in Figure 2 are as calculated directly from the lattice constants and positional parameters; they were not corrected for thermal motion since no sound basis for making such corrections seemed apparent.

The COT ring has the tub form and conforms very closely with D_{2d} symmetry. The standard error in a positional parameter of an atom, as computed from least-squares residuals, is about 0.005 Å. for a carbon atom and a little less for an oxygen atom; this leads to an estimated standard error of 0.007 Å. in a C–C interatomic distance and 0.5° in a C–C–C angle. It would seem wise to raise our estimates to perhaps 0.010 Å. and 0.7° in view of possible systematic errors

(15) D. P. Shoemaker, "DISTAN Criptallographic Bond Distance, Bond Angle, and Dihedral Angle Computer Program," M.I.T., April 1963; D. P. Shoemaker and R. C. Srivastava, "VIBELL Anisotropic Thermal Parameter Interpreting Program," M.I.T., June 1963. Fortran decks are available from the first-named author on request.

(16) G. A. Sim, J. M. Robertson, and T. H. Goodwin, *Acta Cryst.*, **8**, 157 (1955).

Table IV. Average Values of COT Ring Parameters

Ref.	Substance	Method	Double bond, Å.	Single bond, Å.	Angle, degrees
This work	COT acid	X-Ray	1.322 ± 0.005	1.470 ± 0.005	126.4 ± 0.4
W, S, S[17]	CaCOT	X-Ray	1.337	1.464	126.3
K, F, M[8]	COT	X-Ray	(1.34)	(1.54)	(125)
B, H, H[7]	COT	E.d.	1.334 ± 0.001	1.462 ± 0.001	126.46 ± 0.23

arising from the arbitrary assignment of weights and hydrogen positions, as well as uncertainties in the lattice parameters. The four ring double-bond distances show a maximum deviation of 0.012 Å. from the average of 1.322 Å., and the four ring single-bond distances show a maximum deviation of 0.020 Å. from their average of 1.470 Å. The eight ring angles average to 126.4°, with a maximum deviation of 1.2° from the average. It appears, then, that the small apparent deviations of ring carbon atoms from a strict D_{2d} configuration are not significant.

The dihedral angles between ring bond planes intersecting in a double bond have a maximum of 1.29° and an average of 0.77°, indicating a high degree of planarity in the double bonds. The dihedral angles between planes intersecting in a single bond average 57.12° and have a total spread of 1.26°.

In Table IV the average COT ring parameters obtained in this work are compared with those published previously and with values obtained in as yet unpublished work on calcium 2,4,6,8-cyclooctatetraene-1,2-dicarboxylate dihydrate ("CaCOT").[17] The standard deviations given for our averages are those for individual values divided by $\sqrt{4}$, but the values are still possibly subject additionally to subtle systematic errors resulting from somewhat arbitrary placement of ring hydrogens. Such possible errors might account in part for the disagreements with the electron diffraction results, but they cannot easily account for the disagreements with the CaCOT results since in these the hydrogen contributions were assigned in a substantially identical way (except for somewhat different temperature factors). It would appear that these differences are possibly significant although no explanation is readily apparent.

The bond to the carboxyl group is bent away from the plane of the double bond so as to be more nearly parallel with the mean plane of the COT ring; the three bond–plane dihedral angles are roughly the same and average 6.1°. The carboxyl group itself is very nearly planar (the dihedral angles between bond planes in the carboxyl group do not exceed 0.55°) and is closely coplanar (within 2.5°) with the adjacent double bond in the ring. The C—C, C=O, and C—O distances and the C—C=O, C—C—O, and O=C—O bond angles are in reasonable agreement with respective values of 1.48 Å., 1.24 Å., 1.29 Å., 122°, 118°, and 122° in benzoic acid,[16] and with 1.46 Å., 1.24 Å., 1.33 Å., 123°, 117°, and 120° in salicylic acid.[18] The O–H···O hydrogen bond distance between oxygen pairs in the dimer, 2.604 Å., is in the range covered by such distances in typical carboxylic acid crystals such as benzoic acid (dimer), 2.64 Å.,[16] acetic acid (chain), 2.61 Å.,[19] and formic acid (chain), 2.58 Å.[20]

The molecule shows its strongest thermal motions roughly normal to the plane of the ring (Table II, Figure 2). Only on C(6) is this apparently not the case, but the difference between the values given for U_2 and U_3 is presumably smaller than the uncertainties in these qualities, and the true order may in fact be reversed. The largest vibrations are on the carboxyl oxygens (corresponding presumably in part to a libration about the C(1)–C(9) bond) and on the ring carbon atoms farthest from the carboxyl group (corresponding presumably in part to a wagging of the ring). The actual r.m.s. magnitudes of the thermal motion are more of relative than of absolute significance, since systematic errors in the temperature factor magnitudes arise from visual estimation of intensities (due to variable spot shape) and uncorrected absorption.

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(17) D. A. Wright, K. Seff, and D. P. Shoemaker, to be published.

(18) W. Cochran, *Acta Cryst.*, **6**, 260 (1953).

(19) R. E. Jones and D. H. Templeton, *ibid.*, **11**, 487 (1958).

(20) F. Holtzberg, B. Post, and I. Fankuchen, *ibid.*, **6**, 127 (1953).