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Refinement of the Structure of Salicylic Acid

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The crystal structure of salicylic acid has been refined with the use of unidimensionally-integrated photometric three-dimensional Weissenberg data. Positional and anisotropic thermal parameters of the non-hydrogen atoms and positional and isotropic thermal parameters of the hydrogen atoms were refined by the least-squares method. The R index for observed reflections is 5·9 %, excluding a number of reflections suffering varying degrees of secondary extinction. Average standard deviations in atomic positions are: O 0·0024, C 0·0035, H 0·040 Å. Hydrogen atom thermal parameters are, on the average, slightly smaller than those of the non-hydrogen atoms. Bond lengths between non-hydrogen atoms are in good agreement with the previous two-dimensional studies of Cochran, but the average C–H bond length of 0·973 Å is about 0·1 Å longer than reported in that work.

Previous work by Cochran (1953) on the crystal structure of salicylic acid* was done in projection on (010) and along [001] with photographic and Geiger-counter data. The estimated standard deviations in the C–C bond lengths averaged 0·009 Å. Our purpose was to obtain more accurate parameters, especially for the hydrogen atoms, by refinement based on three-dimensional data.

Experimental

Salicylic acid crystallizes in space group $P2_1/a$ with unit-cell parameters:

$$a=11\cdot52\pm0\cdot012,\ b=11\cdot21\pm0\cdot011,\ c=4\cdot92\pm0\cdot005\ \text{Å},$$
$$\text{and } \beta=90^\circ\ 50'\pm2'\ \text{(Cochran, 1953).}$$

Unidimensionally-integrated equi-inclination c-axis Weissenberg photographs of the zero through the fourth levels were collected by the multiple-film technique. Intensities were measured with a recording microdensitometer scanning at right angles to the direction of integration on the camera. Within the linear response range of the film, the area under the trace may be taken as proportional to the integrated intensity. Photographs were taken using three different needle-like crystals *ca.* 0·2 mm in diameter.

The structure factors were brought to a common scale from zero and first-level data of a fourth crystal set to rotate about [$\bar{1}$10]. The errors in interlayer scale factors are estimated to be less than 5%. Of the approximately 1460 reflections accessible with Cu $K\alpha$ radiation, 732 (50%) were measured.

The refinement

The refinement was carried through on an IBM 709 computer using Busing & Levy's (1959) full-matrix least-squares program. A total of 115 parameters were varied: 48 positional parameters for the 16 atoms, 60 anisotropic thermal parameters for the non-hydrogen atoms, 6 isotropic thermal parameters for the hydrogen atoms and one scale factor. The weighting function used was essentially that suggested by Hughes (1941):

$$\sqrt{w}=7/F_o \text{ if } F_o>7\cdot0$$
$$\sqrt{w}=1\cdot0 \text{ if } F_o\leq7\cdot0$$

The scattering factors for carbon and oxygen were those of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) and those for hydrogen were from McWeeny (1951).

Refinement began with the coordinates reported by Cochran (1953). In the initial stages, the hydrogen parameters were fixed, and the non-hydrogen parameters and the scale factor were refined, first with isotropic temperature factors, then with anisotropic temperature factors. Next the non-hydrogen parameters were fixed and the hydrogen parameters were refined; in the first few cycles only the positions were refined, then both position and thermal parameters were refined. A similar series of refinement cycles was repeated twice to insure complete refinement. In the last refinement cycle, no shift of a hydrogen parameter exceeded 0·1 of the standard deviation of that parameter. The final R index is 5·9%, based on 732 observed reflections from which were excluded 24 reflections suffering various degrees of secondary extinction. If F_o is taken equal to F_c for these reflections, R is reduced to 5·0%.

In Table 1 are listed observed and calculated structure factors, and in Tables 2 and 3 the atomic parameters and their standard deviations. The average standard deviations in the positional parameters are 0·0024 Å for oxygen, 0·0035 Å for carbon and 0·040 Å for hydrogen.

Discussion

The bond lengths and angles (Fig. 1) involving non-hydrogen atoms agree well with Cochran's two-dimensional analysis, except for the lengths of the C(2)–C(3)

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* After the experimental work reported here had been completed, we learned that Dr G. S. Pawley had also carried out a three-dimensional refinement at the University of Cambridge, England.

Table 1. *Observed and calculated structure factors*

In each group of three columns h, 10 F_o and 10 F_c are listed successively. An asterisk indicates that the reflection was given zero weight in the refinement.

h	10 F_o	10 F_c
0,K,0		
2	187	-206
4	250*	-277
6	133	124
8	87	87
1,K,0		
1	331*	398
2	173	-179
3	66	69
4	153	-160
5	52	42
6	245	-254
7	146	142
9	30	23
10	77	79
2,K,0		
0	223*	256
1	449*	-591
2	41	-33
3	60	-62
4	228	-249
6	184	181
7	114	-118
8	115	115
10	122	-128
12	122	-118
3,K,0		
2	306*	350
3	79	-78
4	95	87
5	244	-256
6	167	-169
7	79	99
12	121	-118
4,K,0		
0	259	274
1	102	100
2	137	-135
3	51	-53
4	76	-77
5	136	-139
6	252	-256
9	73	95
11	147	-150
5,K,0		
1	194	-199
3	95	-91
4	178	-182
5	192	-186
6	80	-78
8	68	67
9	63	-66
6,K,0		
0	287	-292
1	137	-137
2	191	-197
3	82	79
4	80	-80
6	76	76
7	80	74
7,K,0		
1	162	-168
2	200	194
3	117	114
5	85	-79
6	75	81
8,K,0		
0	128	-124
2	116	111
4	158	155
5	83	75
6	87	-94
8	68	-61
9,K,0		
3	103	106
4	168	-169
5	69	56
6	63	51
8	61	59
10,K,0		
0	86	-75
4	170	180
5	77	-76
6	84	76
7	73	62
11,K,0		
5	93	93
6	72	72
8	66	-61
12,K,0		
7	67	-60
9	59	-65
13,K,0		
2	51	-52
14,K,0		
0	50	-53
1	40	-37
2	41	-36
0,K,1		
1	283*	-328
2	75	76
3	165	186
4	66	-64
5	53	-48
8	224	232
9	71	58
10	140	-131
11	101	111
1,K,1		
1	77	79
2	725*	1058
3	127	127
4	58	57
5	57	59
6	147	-146
7	100	103
8	55	58
9	146	125
10	84	74
11	55	-45
2,K,1		
0	196	-215
1	485*	584
2	572*	730
3	82	79
4	141	140
5	39	-37
6	44	-34
3,K,1		
1	521*	618
2	269*	306
3	153	-156
4	252	-265
5	132	122
6	137	-144
4,K,1		
0	60	-59
1	180	185
2	85	-86
4	215	220
5	268	-275
6	77	-69
7	74	-67
12	72	70
13	58	-45
5,K,1		
1	62	-58
2	48	42
3	79	-82
4	98	101
5	73	67
7	81	-87
8	100	-104
9	105	100
11	69	58
13	76	-74
6,K,1		
0	153	-149
1	60	61
2	93	98
3	51	50
4	93	-91
6	102	-99
7	56	-48
8	95	-94
13	28	-38
7,K,1		
2	61	-59
3	79	-75
4	73	-74
7	158	-159
8	83	84
8,K,1		
0	144	-140
2	128	-123
3	83	-72
6	60	-63
9,K,1		
2	123	-111
3	109	-103
4	152	126
10,K,1		
1	67	-66
2	78	72
5	62	54
11,K,1		
2	155	-151
3	94	94
12,K,1		
2	60	46
3	69	-77
8	60	72
-1,K,1		
1	31	-31
2	135	151
3	93	-94
4	63	62
5	71	-64
6	168	-174
7	115	-106
9	62	-58
10	196	204
12	51	43
-2,K,1		
0	127	136
1	199	217
3	184	189
4	415*	-480
5	83	69
7	91	-84
9	127	126
10	157	-154
11	89	-74
14	29	31
-3,K,1		
1	215*	-246
2	207	225
3	367*	-426
4	127	155
5	85	82
7	77	-86
-4,K,1		
0	316*	-365
1	313*	-341
2	167	-168
4	141	-134
5	178	-180
8	57	64
12	54	-57
-5,K,1		
2	201	-190
3	71	-76
4	165	-152
5	60	64
7	57	-61
8	56	-55
-6,K,1		
0	169	178
1	187	-185
3	64	-57
5	166	171
7	119	-114
11	53	-54
-7,K,1		
2	89	-97
5	231	235
6	152	150
8	77	-68
10	75	-70
-8,K,1		
0	62	51
1	63	-63
3	76	-63
5	60	-61
6	179	184
7	97	93
-9,K,1		
1	38	64
2	118	-107
3	69	76
4	129	-117
6	195	193
-10,K,1		
4	105	106
5	107	-105
-11,K,1		
6	108	106
-12,K,1		
0	122	-119
1	77	-83
9	40	-26
-13,K,1		
4	42	-33
5	59	-54
0,K,2		
1	118	120
2	247	-257
3	203	216
4	93	82
5	36	-35
7	115	115
8	227	-246
9	54	-50
1,K,2		
1	36	35
2	100	105
3	132	-127
5	43	-58
6	56	-57
7	55	-67
8	145	165
9	135	-138
12	27	-23
13	37	20
2,K,2		
0	219*	-252
1	79	104
2	131	-206
3	62	-57
4	269*	307
6	54	52
7	97	-89
8	172	-189
9	171	174
11	45	47
12	46	19
3,K,2		
1	164	-192
2	174	-197
3	220	215
4	236*	271
5	98	85
7	76	72
4,K,2		
0	28	-27
1	21	20
2	103	110
3	258*	305
4	218	246
5	43	-38
7	37	-33
5,K,2		
1	41	-29
2	47	-52
3	360*	419
4	34	-33
7	40	-38
10	33	-39
11	26	16
6,K,2		
1	33	46
2	50	54
3	100	-101
4	45	45
5	34	-33
6	77	67
7	74	-74
9	13	21
7,K,2		
1	34	-36
2	38	37
3	45	42
7	62	69
8	63	-64
10	47	-47
8,K,2		
0	47	43
1	32	-31
2	57	-59
3	50	48
5	38	39
6	65	-66
7	32	-32
9	67	-75
10	33	24
9,K,2		
5	89	-47
6	32	41
7	30	-25
9	62	-65
10,K,2		
2	33	-27
4	77	-79
11,K,2		
2	54	56
3	35	-42
4	29	-20
6	27	23
12,K,2		
0	122	114
2	52	-54
4	39	-45
5	18	17
13,K,2		
1	56	60
3	10	-16
14,K,2		
1	57	-54
-1,K,2		
1	336*	-433
2	207	214
4	95	-93
5	69	-67
6	101	-101
7	94	-37
9	80	75
12	51	-56
13	46	-61
-2,K,2		
0	54	-64
1	141	139
2	277*	-325
3	304*	-331
4	77	67
5	126	-134
8	42	-36
10	33	-38
11	48	-57
-3,K,2		
1	212	229
2	75	-80
3	50	-55
4	75	-73
5	100	-77
6	109	-100
9	59	-55
13	32	25
-4,K,2		
0	157	164
1	164	162
2	137	133
3	45	-40
4	57	-55
5	57	-52
6	107	109
7	87	71
9	17	-88
11	57	-56
13	60	-63
-5,K,2		
1	132	132
2	145	136
4	91	-87
5	34	35
6	54	-50
7	129	214
8	76	73
9	50	56
10	40	-42
11	33	-40
12	30	-35
-6,K,2		
0	176	190
1	55	-52
2	85	83
3	190	-203
7	99	101
8	161	173
-7,K,2		
1	151	151
2	72	-67
3	111	110
4	72	72
5	123	-120
8	70	63
9	35	42
10	45	46
-8,K,2		
0	128	119
2	70	62
4	185	-194
5	155	158
8	67	67
-9,K,2		
2	104	-108
3	122	-124
4	141	140
-10,K,2		
0	43	54
2	81	-85
4	54	-87
5	49	-42
6	36	-34
7	31	29
9	26	21
-11,K,2		
2	44	-45
3	70	-74
5	39	-43
7	49	-52
-12,K,2		
4	31	-29
5	58	53
6	38	-37
7	31	-38
-13,K,2		
4	32	27
5	27	26
0,K,3		
0	227	-222
1	142	-148
2	141	139
3	72	-74
4	62	-60
5	60	-57
6	60	-55
7	50	-50
8	41	-45
12	30	31
1,K,3		
1	178	-191
2	161	-170
3	45	-41
4	78	-74
6	102	109
8	41	-41
10	38	-34
2,K,3		
0	255	-268
1	67	66
2	37	-38
5	52	53
6	174	-186
7	52	45
8	60	59
11	38	-39
3,K,3		
1	95	-96
2	68	-67
3	41	42
4	55	-51
6	195	205
7	171	-168
9	21	-23
10	51	-51
11	16	18
12	30	35
4,K,3		
1	61	-61
2	18	19
3	75	-71
4	105	-107
5	26	-23
6	44	43
7	140	150
8	31	-23
10	37	-10
5,K,3		
1	50	-46
2	29	-30
3	43	-39
4	36	-35
5	164	179
6	68	71
7	44	-42
8	19	20
9	21	-24
11	36	34
6,K,3		
0	93	71
1	96	-74
3	59	-52
4	37	15
5	165	167
6	56	53
8	20	20
9	18	-24
7,K,3		
1	78	77
2	58	-46
4	59	53
5	85	85
8	17	-15
10	14	16
8,K,3		
0	47	-45
1	89	-86
2	64	63
4	54	51
5	32	-33
8	16	18
9,K,3		
5	42	43
6	43	-44
7	31	23
8	18	-20
10,K,3		
1	22	26
4	31	-31
6	39	39
7	28	-30
11,K,3		
3	22	-21
4	31	31
6	32	-37
12,K,3		
0	43	-45
-1,K,3		
1	101	105
2	30	30
3	77	74
4	121	-122
5	46	-47
7	71	-71
8	28	22
10	59	-58
11	29	34
12	63	-68
-2,K,3		
0	37	37
1	37	37
2	68	63
3	158	165
4	109	103
5	90	-89
6	31	-29
7	34	-38
8	94	92
11	77	-78
12	54	41
-3,K,3		
1	31	32
2	20	-20
3	145	146
4	38	-38
5	27	-28
6	39	-34
7	40	47
9	104	105
10	27	25
11	25	19
12	19	-18
-4,K,3		
0	47	48
2	149	152
3	46	45
4	54	53
7	88	-98
9	144	158
10	59	59
-5,K,3		
1	215	228
2	101	101
3	111	-112
4	60	58
5	30	-28
10	57	62
-6,K,3		
0	71	85
2	115	-119
3	191	206
6	33	31
8	31	-35
9	27	23
10	15	25
11	15	17
-7,K,3		
1	26	-28
2	121	198
3	133	-138
4	104	-101
5	31	-31
6	34	-35
7	33	38
8	27	35
9	23	19
10	39	44
-8,K,3		
0	37	36
1	62	60
2	73	-72
3	51	-47
4	81	-83
5	24	-26
7	25	-13
9	17	21
-9,K,3		
2	82	42
5	85	-88
7	28	-31
8	57	-53
-10,K,3		
2	38	-19
3	61	67
4	53	-53
6	27	22
7	21	-20
-11,K,3		
3	27	-22
5	15	14
7	53	68
-12,K,3		
0	47	57
3	22	-43
4	21	24
0,K,4		
1	33	30
2	54	51
3	36	-32
4	52	47
5	68	72
6	13	16
7	58	-60
8	19	18
9	47	-47
10	14	74
1,K,4		
1	49	45
2	27	-26
3	34	34
4	78	72
6	34	-33
7	19	-18
8	39	-38
9	25	-21
10	41	-44
11	74	30
2,K,4		
0	167	182
1	32	-32
2	47	-47
3	41	-37
4	41	-37
5	42	-39
6	42	-40
7	19	23
8	15	13
9	28	-27
10	18	18
3,K,4		
1	28	-27
2	38	-31
3	35	-34
4	55	51
5	36	-49
6	69	-63
8	15	-15
4,K,4		
1	32	-84
2	42	-39
3	36	-31
4	130	-129
5	106	104
6	57	27
7	17	-17
8	13	12
9	27	-38
5,K,4		
4	59	61
5	141	-139
7	18	17
8	21	20
9	26	25
6,K,4		
0	13	5
1	14	-22
3	54	-51
4	15	11
5	47	47
6	76	-83
7	39	45
8	16	23
7,K,4		
1	17	23
3	15	-14
4	40	-17
5	69	-65
6	21	24
7	62	69
8	14	14
8,K,4		
0	22	22
1	18	14
5	20	-21
6	47	46
7	46	48
9,K,4		
1	38	41
2	18	-19
4	11	-9
6	13	13
10,K,4		
0	56	59
2	14	-16
3	29	-29
4	76	26
-1,K,4		
1	21	16
2	47	-44
3	72	76
4	17	17
5	98	101
6	58	-55
9	19	16
11	24	29
-2,K,4		
0	167	165
1	14	13
2	28	27
3	14	10
4	33	28
6	28	28
7	33	34
8	36	-38
9	41	-38
10	12	14
11	77	77
-3,K,4		
1	29	-10
2	94	90
3	73	68
4	46	38
5	51	54
6	39	33
7	76	-76
9	25	-27
10	9	-9
-4,K,4		
0	149	-147
1	235	237
2	26	-26
3	32	10
4	32	33
5	31	-28
6	25	-25
7	21	20
9	15	15
-5,K,4		
1	140	-140
2	17	-16
3	40	19
4	15	-2
5	15	-13
6	29	-26
7	21	20
9	17	-18
-6,K,4		
0	187	-176
1	26	25
2	50	47
3	42	44
5	50	-28
6	81	-75
7	22	-21
8	48	-50
-7,K,4		
1	29	-30
2	34	34
3	32	-37
4	43	40
5	17	-16
6	51	-21
7	30	-31
-8,K,4		
0	73	-68
1	69	47
2	52	-50
4	34	32
6	39	31
7	46	-45
-9,K,4		
4	35	-35
5	42	40
6	65	-75
-10,K,4		
2	67	64
5	47	-45

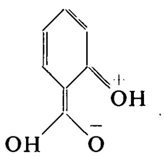
Table 2. *Parameters and (in parentheses) their standard deviations*

Thermal parameters, β_{ij}, are defined by the equation:

Temperature factor $=\exp\{-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})\}$.

Atom	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
O(1)	−0·05050 (0·00022)	0·13729 (0·00021)	0·83797 (0·00046)	0·00647 (0·00022)	0·00673 (0·00024)	0·04132 (0·00118)	0·04132 (0·00017)	0·00592 (0·00035)	0·00305 (0·00034)
O(2)	0·09881 (0·00020)	0·01676 (0·00022)	0·77027 (0·00043)	0·00577 (0·00020)	0·00580 (0·00023)	0·04095 (0·00117)	0 ·00089 (0·00016)	0·00450 (0·00034)	0·00308 (0·00032)
O(3)	0·25092 (0·00023)	0·07103 (0·00025)	0·39921 (0·00052)	0·00674 (0·00025)	0·00797 (0·00027)	0·05629 (0·00143)	0·00103 (0·00019)	0·00737 (0·00042)	0·00492 (0·00043)
C(1)	0·08361 (0·00027)	0·19261 (0·00029)	0·50601 (0·00059)	0·00577 (0·00027)	0·00537 (0·00030)	0·03088 (0·00149)	−0·00041 (0·00021)	0·00036 (0·00041)	0·00041 (0·00042)
C(2)	0·18470 (0·00029)	0· 16977 (0·00032)	0·35871 (0·00062)	0·00535 (0·00026)	0·00628 (0·00033)	0·03587 (0·00157)	−0·00088 (0·00023)	0·00059 (0·00043)	0·00076 (0·00046)
C(3)	0·22036 (0·00033)	0·25058 (0·00035)	0·16466 (0·00070)	0·00705 (0·00032)	0·00913 (0·00042)	0·03741 (0·00169)	−0·00177 (0·00028)	0·00251 (0·00050)	0·00202 (0·00057)
C(4)	0·15721 (0·00036)	0·35264 (0·00034)	0·11374 (0·00075)	0·00939 (0·00039)	0·00716 (0·00038)	0·04315 (0·00186)	−0·00237 (0·00028)	−0·00089 (0·00060)	0·00423 (0·00054)
C(5)	0·05729 (0·00040)	0·37610 (0·00033)	0·25742 (0·00075)	0·01058 (0·00041)	0·00670 (0·00034)	0·04272 (0·00188)	−0·00085 (0·00031)	−0·00133 (0·00060)	0·00413 (0·00057)
C(6)	0·02141 (0·00033)	0·29689 (0·00032)	0·45012 (0·00069)	0·00731 (0·00033)	0·00643 (0·00034)	0·04008 (0·00171)	0·00015 (0·00025)	0·00087 (0·00050)	0·00151 (0·00048)
C(7)	0·04504 (0·00028)	0·10881 (0·00027)	0·71260 (0·00060)	0·00512 (0·00026)	0·00538 (0·00029)	0·03103 (0·00146)	−0·00021 (0·00021)	0·00142 (0·00039)	0·00022 (0·00042)

and C(7)–O(1) bonds. The benzene ring is distorted from hexagonal symmetry, and the bond lengths, as indicated by Cochran, suggest that the quinoid structure



is the major valence-bond structure contributing to the over-all resonance state of the molecule (see Cochran (1953) for the other canonical structures). Thermal motion alone could not account for the observed shortening of the C–C bonds.

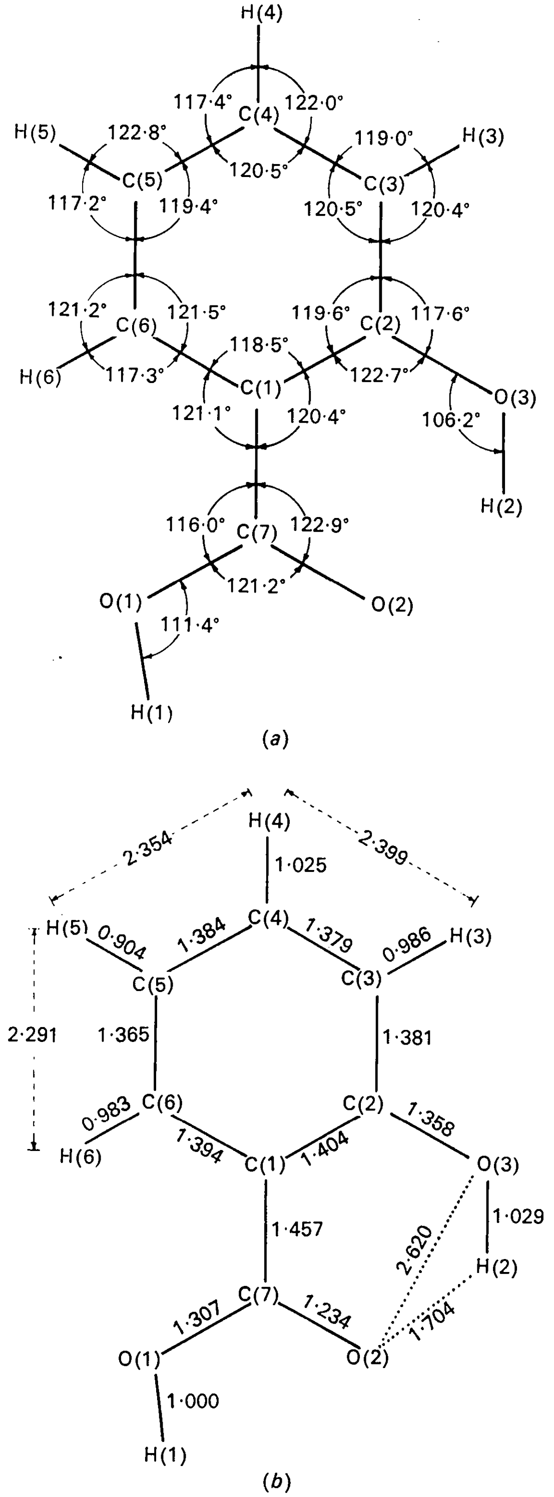


Fig. 1. (a) Bond angles and (b) bond lengths (Å) in salicylic acid. (Uncorrected for thermal motion).

Table 3. *Parameters of hydrogen and (in parentheses) their standard deviations*

	x/a	*y/b*	*z/c*	*B*
H(1)	−0·0692	0·0781	0·9828	2·73
	(0·0034)	(0·0034)	(0·0078)	(0·84)
H(2)	0·2096	0·0213	0·5449	3·28
	(0·0038)	(0·0039)	(0·0073)	(0·93)
H(3)	0·2936	0·2380	0·0674	2·94
	(0·0035)	(0·0036)	(0·0081)	(0·85)
H(4)	0·1801	0·4123	−0·0338	4·05
	(0·0041)	(0·0040)	(0·0085)	(1·01)
H(5)	0·0085	0·4365	0·2139	3·28
	(0·0037)	(0·0036)	(0·0077)	(0·90)
H(6)	−0·0511	0·3094	0·5489	2·41
	(0·0033)	(0·0035)	(0·0069)	(0·79)

The precise determination of the structure of 2-amino-3-methylbenzoic acid by Brown & Marsh (1963) shows many bond lengths which are similar to those in salicylic acid. This is to be expected since the electronic properties of the OH and NH_2 groups are quite similar. In 2-amino-3-methylbenzoic acid the resonance interaction of the amino group with the benzene ring and the *ortho* carboxylic group probably arrests the inductive and hyperconjugative effects of the methyl group which is *meta* to the carboxyl substituent. The largest difference between the C–C bond lengths in salicylic acid and 2-amino-3-methylbenzoic acid is in the C(2)–C(3) bond and is probably due to the presence of the methyl substituent adjacent to the amino group in the latter compound.

In salicylic acid the angle C(1)–C(7)–O(1) of 116·0° is significantly less than the 120° angle between the bonds of a trigonal carbon atom, and the angle C(1)–C(7)–O(2) of 122·8° is significantly greater. This feature is observed in both aliphatic and carboxylic acids (see Table 4 of Higgs & Sass (1962) and Table 7 of Nardelli, Fava & Giraldi (1962)). Angle O(2)–C(7)–O(1) is a little greater than 120°, as commonly observed in other carboxylic acids.

It is evident in Fig. 1(*a*) that all the substituent atoms on the ring are displaced slightly counterclockwise so that angles on either side of the ring atom-substituent atom bonds are systematically different. No single difference is significant except the 5·1° between the angles on either side of the C(2)–O(3) bond. The fact that the differences are systematic, however, would seem to indicate that they are real.

The six carbon atoms in the benzene ring are coplanar within experimental error (plane 1, Table 4). The mean deviation of the ring atoms is 0·001 Å. Of the non-hydrogen atoms in the molecule, only O(2) deviates significantly from the benzene plane. All hydrogen atoms are at distances from plane 1 within experimental error, with the possible exception of H(5), which is displaced by 0·12 Å. It is this atom which is involved in the shortest C–H bond, 0·904 Å, and the shortest H · · · H intermolecular distance, 2·55 Å.

Plane 2 in Table 4 is the least-squares plane through the ten non-hydrogen atoms in the molecule. Atom O(2) is significantly displaced from this plane, and the mean deviation of the other nine atoms is more than three times their mean deviation from plane 1.

Plane 3 in Table 4 is the least-squares plane through the six non-hydrogen atoms of the centrosymmetrically related carboxyl groups. The mean deviation of the atoms from the plane is over five times the mean standard deviation of coordinates of the atoms involved. These large deviations stem from the fact that the individual planes through each of the centrosymmetrically related carboxyl groups are separated by a distance of 0·15 Å, a feature which is the rule rather than the exception (Jeffrey & Sax, 1963; Robertson, 1964). It should also be noted that O(2) is displaced by 0·045 Å from the plane through C(7), O(3), O(1′).

The plane of the carboxyl group is inclined at 1·1° to the benzene plane. In 2-amino-3-methylbenzoic acid, Brown & Marsh (1963) report a value of 3° for the corresponding angle.

Table 4. *Displacements from least-squares planes through various atoms*

Atoms with displacements shown in parentheses were not included in calculation of the least-squares plane. O(1′), O(2′) and C(7′) are the atoms centrosymmetrically related to O(1), O(2) and C(7).

Atom	Plane 1	Plane 2	Plane 3
O(1)	(0·001) Å	0·008 Å	0·011 Å
O(2)	(−0·028)	−0·016	0·013
O(3)	(−0·003)	0·006	
C(1)	−0·001	0·003	
C(2)	0·002	0·006	
C(3)	−0·002	−0·001	
C(4)	0·001	−0·003	
C(5)	0·000	−0·005	
C(6)	0·000	−0·001	
C(7)	(−0·006)	0·002	−0·016
H(1)	(−0·05)	(−0·04)	
H(2)	(0·03)	(−0·02)	
H(3)	(−0·05)	(−0·05)	
H(4)	(0·03)	(0·03)	
H(5)	(0·12)	(0·11)	
H(6)	(0·04)	(0·04)	
O(1′)			−0·011
O(2′)			−0·013
C(7′)			0·016

Equation of least-squares planes in coordinate system with axes *a*, *b*, *c**:

Plane 1: $-0{\cdot}1621x-0{\cdot}1493y-0{\cdot}2115z+1=0$
Plane 2: $-0{\cdot}1626x-0{\cdot}1487y-0{\cdot}2123z+1=0$
Plane 3: $-0{\cdot}1619x-0{\cdot}1666y-0{\cdot}2057z+1=0$

Table 5. *Description of the thermal ellipsoids*

$B_i=8\pi^2 u_i^{-2}$ where u_i is the root-mean-square displacement corresponding to the *i*th axis of the ellipsoid. C_{ia}, C_{ib}, C_{ic} are the direction cosines of the *i* axis with respect to the crystal *a*, *b*, *c*.

Atom	Axis *i*	B_i	u_i	C_{ia}	C_{ib}	C_{ic}
O(1)	1	5·41 Å²	0·26 Å²	0·5728	0·4033	0·7052
	2	2·38	0·17	−0·7953	0·0627	0·6145
	3	2·99	0·19	−0·1984	0·9129	−0·3537
O(2)	1	4·90	0·25	0·4943	0·3794	0·7748
	2	2·43	0·18	−0·8636	0·1117	0·5041
	3	2·58	0·18	−0·0992	0·9185	−0·3814
O(3)	1	6·85	0·29	0·4465	0·3883	0·7996
	2	2·62	0·18	−0·8450	−0·0843	0·5258
	3	3·51	0·21	−0·2673	0·9177	−0·2900
C(1)	1	2·58	0·18	−0·4073	−0·8834	0·2375
	2	3·16	0·20	−0·9057	0·4233	0·0348
	3	3·01	0·20	−0·1174	−0·2008	−0·9708
C(2)	1	2·48	0·18	−0·7956	−0·5826	0·1775
	2	3·58	0·21	−0·2939	0·6108	0·7395
	3	3·40	0·21	−0·5297	0·5362	−0·6494
C(3)	1	2·66	0·18	−0·6765	−0·4571	0·5872
	2	5·18	0·26	−0·5144	0·8544	0·0813
	3	4·09	0·23	−0·5270	−0·2471	−0·8054
C(4)	1	6·00	0·28	−0·7533	0·5356	0·3926
	2	2·56	0·18	−0·3767	−0·8271	0·4227
	3	4·20	0·23	−0·5392	−0·1705	−0·8168
C(5)	1	2·75	0·19	−0·0648	−0·8412	0·5377
	2	5·90	0·27	−0·9017	0·2798	0·3426
	3	4·48	0·24	−0·4274	−0·4627	−0·7704
C(6)	1	3·09	0·20	0·0160	−0·9221	0·3863
	2	4·12	0·23	0·5399	0·3334	0·7650
	3	3·77	0·22	0·8415	−0·1964	−0·5154
C(7)	1	3·17	0·20	0·5208	−0·0331	0·8454
	2	2·48	0·18	−0·7629	−0·4665	0·4587
	3	2·77	0·19	0·3830	−0·8839	−0·2738

The greatest difference between the present analysis and Cochran's is in the C–H bond lengths, which now are found to be almost 0·1 Å longer (Fig. 1(*b*)). The shortest C–H bond, C(5)–H(5), was also the shortest in Cochran's work. The average C–H bond distance of 0·973 Å is appreciably less than the theoretical distance of 1·04 Å for a C(sp^2)–H bond (Cochran, 1956). This may be due in part to the effect of thermal oscillation.

The bond angles involving hydrogen are indicated in Figs. 1(*a*) and 2. The C–C–H angles are close to 120° and the C–O–H angles do not deviate greatly from the tetrahedral value. The C=O · · · H angles, however, are very different from 120°, a fact that must be considered in postulating models for hydrogen-bonded structures.

There are 5 H · · · H intermolecular distances less than 3·0 Å. The closest H · · · H approach is 2·55 Å between H(5) and the centrosymmetrically related H(5′). Of the six non-bonded C · · · H distances less than 3·3 Å, the shortest is 3·18 Å and occurs between C(2) of one molecule and H(6) of a glide related molecule. There are just two non-bonded O · · · H distances less than 3·0 Å. The shortest is 2·66 Å between O(3) of one molecule and H(6) of a glide-related molecule; the next shortest is 2·74 Å between O(3) and H(6) of a different glide related molecule.

In Table 5 are listed B_i, $\bar{u}_i$ and the direction cosines of the principal axes of the thermal ellipsoids with respect to the crystal axes *a*, *b*, *c*. A 'rigid body' refinement based on the data of Table 1 has been done elsewhere (Pawley, 1963).

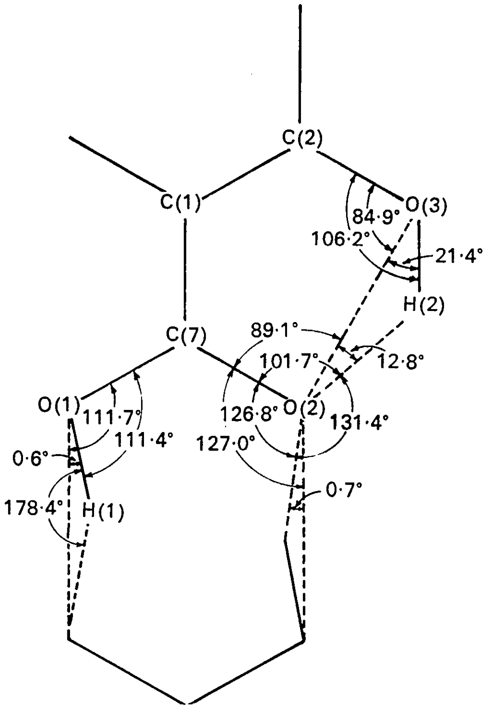


Fig. 2. Bond angles around the intermolecular and intramolecular O–H · · · O bonds.

The average of the isotropic thermal parameters for the hydrogen atoms is 3·1 Å^2, somewhat less than the mean value of B_{ii} ($B_{ii}=4\beta_{ii}/a_i^{*2}$ where $a_i^*=a^*$, b^*, c^* for $i=1, 2, 3$) of 4·0 Å^2 for the non-hydrogen atoms to which the hydrogen atoms are bonded. Although the mean B_{ii} is not exactly equal to the equivalent isotropic B, it is a close approximation since β does not differ much from 90°. (See also Jensen & Sundaralingam, 1964).

Fig. 3(*a*) is a composite ΔF synthesis showing the hydrogen atoms, and Fig. 3(*b*) is the corresponding F_o synthesis where the hydrogen atoms appear as small peaks just resolved from the atoms to which they are bonded.

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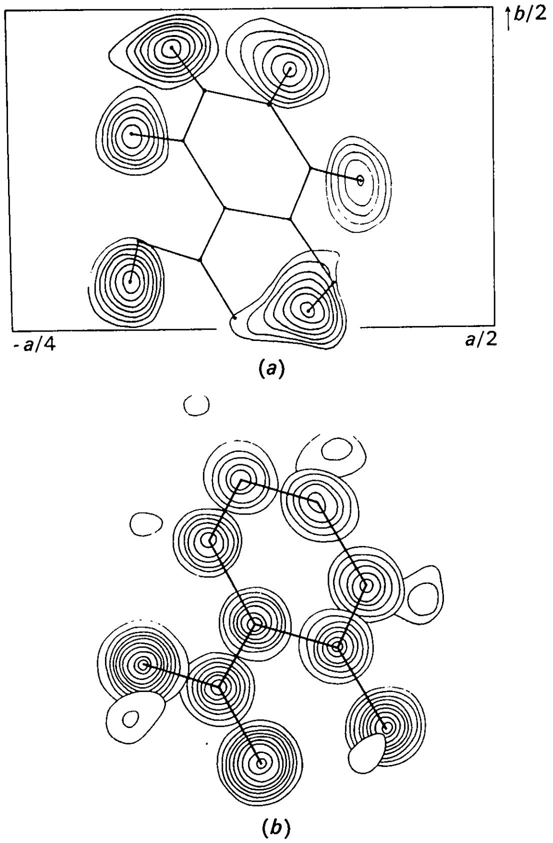

(*a*)

(*b*)

Fig. 3. (*a*) Composite ΔF synthesis showing hydrogen atoms based on reflections with $\sin\theta/\lambda<0·48$. Contour interval 0·05 e.Å^{-3} beginning at 0·1 e.Å^{-3}. (*b*) Composite F_o synthesis; non-hydrogen atom contours at intervals of 1 e.Å^{-3} beginning at 2 e.Å^{-3}, hydrogen atom contours at 0·75 and 1·0 e.Å^{-3}.

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Topochemistry. XI. The Crystal Structures of Methyl *m*- and *p*-Bromocinnamates

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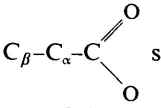
The packing arrangements of methyl *m*- and *p*-bromocinnamates have been determined from zonal and partly three-dimensional photographic data. The molecular shape of these esters, in particular the conformation of the  $C_\beta\text{–}C_\alpha\text{–}C\begin{smallmatrix}\nearrow O\\ \searrow O\end{smallmatrix}$ system is discussed in terms of non-bonded interactions between C_β and the oxygen atoms of the carboxyl group, and compared with the configuration of this system in unsaturated and saturated acids and amides.

Introduction

In part III (Schmidt, 1964) of this series we have discussed the relationship between the photochemical behaviour of some ring-substituted cinnamic acids and their crystal structures. We have pointed out that these acids occur in three packing types (α, β, γ) with several acids crystallizing in more than one such type (dimorphism, trimorphism), that these packing types differ in the geometry of contact between neighbouring $>C=C<$ groups, and that the photochemical behaviour of the three types is explicable in terms of this geometry.

We have now begun an investigation of the crystal chemistry of the esters of cinnamic acids. The photochemistry of methyl cinnamate has been studied by Liebermann & Zsuffa (1911) and by de Jong (1923) who isolated small amounts of an oligomer ($n=3,4$) and the centric dimer (dimethyl α-truxillate) respectively. It would appear from the work of these authors that the ratio of the two products is temperature dependent, and that the yield of the dimer increases at lower temperatures; in view of the low melting point of methyl cinnamate (33°) the possibility could not be excluded that oligomerization takes place in the melt rather than in the crystalline state. In addition to this complication the cell dimensions of methyl cinnamate (Table 1) measured on a crystal grown by evaporation of an ether solution and photographed in a Lindemann capillary, are not suited to a structure analysis. Three heavy-atom derivatives of the ester were therefore prepared and their crystallographic constants determined (Table 1). The present paper presents the structure

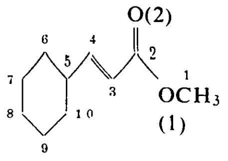


Fig. 1. Numbering of atoms in the present analysis.

Table 1. *Crystallographic constants of some methyl cinnamates*

	a	*b*	*c*	β	Space group	*n*	d_{calc}
Methyl cinnamate	21·9	5·8	20·99	104°	$P2_1/c$	12	1·25
Methyl *p*-chlorocinnamate	8·77	5·84	18·75	95·6°	$P2_1/n$	4	1·37
Methyl *m*-bromocinnamate	7·830	5·976	21·208	99°31′	$P2_1/a$	4	1·64
Methyl *p*-bromocinnamate	8·485	20·703	5·764	92·2°	$P2_1/n$	4	1·58