Acta Cryst. (1974). **B30**, 1249

A Refinement of the Crystal Structure of Maleic Acid

BY M. N. G. JAMES AND G. J. B. WILLIAMS*

Department of Biochemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2E1

(*Received* 19 *November* 1973; *accepted* 16 *January* 1974)

Room temperature diffractometer data for maleic acid were collected to $2\theta = 75°$ using graphite-monochromated Mo $K\alpha$ radiation. There are 4 molecules in a $P2_1/c$ cell with dimensions $a = 7{\cdot}473$ (1), $b = 10{\cdot}098$ (2), $c = 7{\cdot}627$ (2) Å, $\beta = 123{\cdot}59$ (2)°. Full-matrix least-squares refinement has yielded weighted and unweighted R values of 0·073 and 0·050 respectively. The intramolecular hydrogen bond is 2·502 (2) Å long and is asymmetric. The intermolecular hydrogen bond is linear, not bifurcated, and of length 2·643 (2) Å. Electron density maxima of heights 0·25, 0·30 and 0·30 e Å^{-3} are observed between the carbon atoms in a difference synthesis. Much smaller residual density is observed in the carbon-oxygen bonds. A brief comparison of the molecular geometries of several maleic acid/maleate ion species is presented.

Introduction

Interest in the structural chemistry of maleic acid and related substances stems from the fact that these species possess short but highly strained hydrogen bonds. Evidence for a central position for the acidic hydrogen atom in the maleate monoanion has been provided by studies using the methods of: (i) infrared spectroscopy (Cardwell, Dunitz & Orgel, 1953); (ii) X-ray crystallography (Darlow & Cochran, 1961; Ellison & Levy, 1965; Glusker, Orehowsky, Casciato & Carrell, 1972) and (iii) molecular orbital theory (Murthy, Bhat & Rao, 1970). Contra-indications have, however, been provided in the form of two crystal structures in which it was shown that the hydrogen atom of the intramolecular hydrogen bond was definitely not centred between the oxygen atoms (James & Williams, 1971, 1974*a*). There seems therefore to be a fine energy balance between the two types of hydrogen bond in this system with only few of those factors which determine the configuration adopted known. It was thought that by performing an accurate study of the parent substance, maleic acid, some information may be gleaned which related to this problem. Another reason for this reinvestigation was to settle the question of the existence of a bifurcated intermolecular hydrogen bond. In Shahat's original paper (Shahat, 1952) one hydrogen-bearing oxygen atom was found to be 2·75 and 2·98 Å from two other oxygen atoms and hydrogen-bond cross linkages between the ribbons of molecules were postulated. In a re-interpretation of this structure Donohue (1968) concluded that the hydrogen atom in question was shared by two, rather than three, oxygen atoms and that the inter-ribbon linkages were of the normal van der Waals type.

Experimental

A single-crystal specimen was cleaved from a large twinned crystal grown by cooling a warm saturated solution of the compound in acetone. The crystal was mounted about the monoclinic b axis and then encapsulated in Canada balsam to avoid atmospheric effects.

Table 1. *The unit-cell constants and some other quantities relating to the crystal structure analysis of maleic acid*

Molecular formula	$C_4H_4O_4$
Molecular weight	116·07
Space group	$P2_1/c$
a	7·473 (1) Å
b	10·098 (2)
c	7·627 (2)
β	123·59 (2)°
V	478·92 Å^3
Z	4
ϱ_{obs}	1·590 g cm^{-3}
ϱ_{calc}	1·610 g cm^{-3}
$\bar{\mu}$(Mo K)	1·6 cm^{-1}
Number of variable parameters	89
Ratio observations/parameters	20·3
Mean σ in C–C bond distance	0·002 Å
Mean σ in C–C–C angle	0·1°
Standard deviation of difference electron-density map	0·032 e Å^{-3}

The unit-cell constants, given in Table 1, were obtained during the alignment process on a Picker FACS-1 diffractometer. With the exception of the b repeat distance these are insignificantly different from those reported by Shahat (1952). Three-dimensional diffraction data out to a minimum d spacing of 0·584 Å ($2\theta_{max} = 75°$) were gathered using graphite-monochromated Mo $K\alpha$ radiation and a $\theta/2\theta$ scan mode. The scan speed was 2° min^{-1} over a basic peak width of 1·8° in 2θ; this width was modified as a function of θ to cope with the dispersion of the $K\alpha$ doublet (Arndt &

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* Present address: Department of Chemistry, Brookhaven National Laboratories, Upton, Long Island, New York 11973, U.S.A.

Table 2. *A listing of the observed structure amplitudes and the final calculated structure factors*

Excluded reflexions are marked with an asterisk. These amplitudes have been multipled by 10.

L	FO	FC
H= 0, K= 0		
2	930*	-1535
4	494*	559
6	161	-179
8	47	52
10	13	-14
H= 0, K= 1		
1	5	4
2	9	-9
3	4	-6
4	8	6
5	4*	2
6	4*	-3
7	5*	0
8	5*	1
9	6*	0
10	6*	1
H= 0, K= 2		
0	419*	-549
1	363*	431
2	333	366
3	202	-207
4	137	-135
5	85	89
6	40	38
7	35	-37
8	9	-10
9	13	13
10	6*	2
H= 0, K= 3		
1	2*	-2
2	17	16
3	3*	3
4	12	-11
5	4*	-1
6	4*	4
7	5*	0
8	5*	-1
9	6*	0
10	6*	0
H= 0, K= 4		
0	39	38
1	412*	465
2	19	-20
3	232	-238
4	7	-4
5	79	81
6	9	9
7	22	-22
8	6	-5
9	6*	5
10	6*	2
H= 0, K= 5		
1	3*	-1
2	6	-9
3	3*	1
4	6	7
5	4*	0
6	5*	-4
7	5*	0
8	5*	1
9	6*	0
10	6*	0
H= 0, K= 6		
0	332	-340
1	41	-36
2	254	254
3	22	20
4	120	-120
5	9	-8
6	44	44
7	5*	3
8	14	-14
9	6*	-1
10	7	4
H= 0, K= 7		
1	5	-6
2	4*	2
3	8	9
4	4*	-3
5	5	-6
6	5*	2
7	5*	2
8	6*	-1
9	6*	0
H= 0, K= 8		
0	100	99
1	131	-122
2	76	-78
3	79	78
4	40	40
5	33	-35
6	16	-16
7	11	12
8	7	6
9	6*	-3
H= 0, K= 9		
1	4*	3
2	4*	-6
3	4*	-5
4	5*	5
5	5*	3
6	5*	-3
7	6*	-1
8	6*	1
9	6*	0
H= 0, K= 10		
0	141	-149
1	66	-68
2	114	122
3	41	41
4	65	-69
5	17	-15
6	28	25
7	6	3
8	11	-10
H= 0, K= 11		
1	5*	-1
2	5*	-2
3	5*	1
4	5*	2
5	5*	-1
6	6*	-1
7	6*	0
8	6*	0
H= 0, K= 12		
0	117	119
1	5*	0
2	95	-96
3	5*	6
4	59	56
5	7	-9
6	23	-23
7	6*	7
H= 0, K= 13		
1	5*	2
2	5*	1
3	5*	-3
4	6*	-1
5	6*	3
6	6*	1
7	6*	-1
H= 0, K= 14		
0	29	30
1	6*	-5
2	24	-25
3	6*	1
4	15	15
5	6*	3
6	6	-7
H= 0, K= 15		
1	6*	0
2	6*	1
3	6*	1
4	6*	-2
5	6*	-1
H= 0, K= 16		
0	23	-25
1	16	15
2	22	21
3	10	-8
4	15	-12
H= 0, K= 17		
1	6*	0
2	6*	0
H= 1, K= 0		
0	46	41
2	10	-11
4	6	-4
6	6	5
8	5*	-3
10	6*	1
H= -1, K= 0		
2	49	-51
4	22	24
6	9	-5
8	5*	0
10	6*	0
H= 1, K= 1		
0	157	241
1	6	6
2	137	-139
3	10	-3
4	63	62
5	15	-11
6	27	-25
7	10	9
8	8	5
9	6*	-4
10	6*	-2
H= -1, K= 1		
1	26	28
2	179	185
3	25	-24
4	82	-80
5	26	26
6	35	36
7	18	-19
8	13	-15
9	5	9
10	6*	5
11	6*	-3
H= 1, K= 2		
0	227	223
1	215	229
2	119	-123
3	89	-92
4	46	47
5	27	28
6	17	-16
7	7	-8
8	5*	5
9	6*	2
10	6*	-1
H= -1, K= 2		
1	2*	303
2	160	-166
3	172	-185
4	64	83
5	67	71
6	31	-31
7	21	-23
8	11	11
9	8	7
10	6*	-3
11	6*	-2
H= 1, K= 3		
0	190	156
1	169	-195
2	86	-76
3	74	82
4	27	33
5	19	-22
6	16	-15
7	5*	4
8	6	6
9	6*	0
10	6*	-2
H= -1, K= 3		
1	224	236
2	161	160
3	119	-134
4	50	-90
5	34	42
6	42	40
7	5	-6
8	16	-15
9	5*	1
10	6*	5
11	6*	0
H= 1, K= 4		
0	112	-110
1	94	83
2	68	69
3	32	-28
4	35	-35
5	4*	4
6	17	17
7	5*	1
8	7	-7
9	6*	-1
10	6*	2
H= -1, K= 4		
1	121	113
2	90	96
3	70	-71
4	52	-59
5	27	29
6	26	27
7	5*	-4
8	10	-12
9	6*	0
10	6*	4
11	6*	0
H= 1, K= 5		
0	193	-171
1	68	62
2	94	94
3	38	-39
4	24	-25
5	19	21
6	5*	2
7	8	-9
8	6*	2
9	6*	3
H= -1, K= 5		
1	78	-70
2	150	-150
3	53	50
4	63	64
5	29	-29
6	19	-13
7	13	14
8	5*	0
9	6	-6
10	6*	1
H= 1, K= 6		
0	28	-20
1	152	-139
2	8	-4
3	71	70
4	25	23
5	24	-25
6	20	-14
7	7	8
8	7	9
9	6*	-2
H= -1, K= 6		
1	178	-166
2	24	22
3	113	110
4	4*	1
5	47	-47
6	13	-13
7	16	16
8	10	10
9	6	-5
10	6*	-4
H= 1, K= 7		
0	83	75
1	53	52
2	43	-42
3	31	-33
4	10	11
5	18	18
6	5*	8
7	7	-8
8	6*	-1
9	6*	2
H= -1, K= 7		
1	69	-65
2	64	66
3	55	57
4	26	-27
5	35	-35
6	5*	3
7	17	17
8	5*	2
9	6*	-6
10	6*	-2
H= 1, K= 8		
0	109	-110
1	175	174
2	75	80
3	106	-108
4	41	-41
5	50	51
6	18	17
7	19	-20
8	6*	-6
9	6*	6
H= -1, K= 8		
1	186	195
2	89	99
3	137	-145
4	56	-60
5	75	78
6	27	27
7	33	-33
8	10	-10
9	12	11
10	6*	3
H= 1, K= 9		
0	16	19
1	26	-25
2	12	-15
3	12	12
4	6	6
5	5*	-4
6	5*	-1
7	6*	1
8	6*	0
H= -1, K= 9		
1	33	33
2	8	11
3	26	-27
4	5*	-1
5	15	15
6	5*	-2
7	6*	-6
8	6*	2
9	6*	2
H= 1, K= 10		
0	17	10
1	136	-137
2	5*	0
3	76	80
4	7	-7
5	32	-34
6	6*	7
7	10	11
8	6*	-3
H= -1, K= 10		
1	150	-157
2	12	-6
3	111	110
4	5*	-1
5	57	-61
6	5*	5
7	23	23
8	6*	-4
9	7	-7
H= 1, K= 11		
0	33	-28
1	5*	0
2	25	24
3	5*	0
4	16	-16
5	6*	0
6	9	8
7	6*	0
H= -1, K= 11		
1	5*	-1
2	27	-25
3	5*	1
4	18	17
5	5*	-1
6	8	-10
7	6*	0
8	6*	4
H= 1, K= 12		
0	18	-15
1	18	-19
2	15	11
3	17	16
4	9	-6
5	11	-11
6	6*	2
7	8	5
H= -1, K= 12		
1	17	-17
2	15	13
3	15	16
4	10	-8
5	13	-12
6	6*	4
7	8	7
8	6*	-1
H= 1, K= 13		
0	18	-18
1	11	11
2	14	14
3	20	-20
4	8	-7
5	9	7
6	6*	2
H= -1, K= 13		
1	34	-35
2	14	-10
3	22	22
4	9	5
5	7	-8
6	6*	-3
7	6*	1
H= 1, K= 14		
0	74	68
1	18	-16
2	56	-53
3	10	11
4	33	31
5	7	-6
H= -1, K= 14		
1	17	-17
2	63	-63
3	13	13
4	49	43
5	6*	-7
6	29	-22
H= 1, K= 15		
0	8	9
1	14	-15
2	6*	-6
3	9	11
4	6*	3
H= -1, K= 15		
1	14	14
2	6*	5
3	7	-8
4	6*	-5
5	6*	3
H= 1, K= 16		
0	13	-9
1	57	59
2	6*	7
3	37	-36
H= -1, K= 16		
1	55	59
2	11	8
3	46	-46
4	6*	-5
H= 1, K= 17		
0	24	-22
1	19	-19
H= -1, K= 17		
1	19	21
2	20	-19
H= 2, K= 0		
0	314	292
2	140	-135
4	47	48
6	15	-17
8	7	6
H= -2, K= 0		
2	311	-321
4	174	172
6	65	-64
8	21	21
10	6	-6
H= 2, K= 1		
0	86	-82
1	66	61
2	39	40
3	22	-21
4	18	-20
5	7	6
6	8	-4
7	5*	-1
8	6*	-1
9	6*	0
H= -2, K= 1		
1	97	-95
2	97	-101
3	60	61
4	64	66
5	19	-21
6	33	-33
7	4*	5
8	14	14
9	5*	-1
10	6*	-5
11	6*	0
H= 2, K= 2		
0	416	-384
1	59	57
2	202	193
3	25	-25
4	76	-75
5	10	11
6	26	27
7	5*	-4
8	8	-8
9	6*	2
H= -2, K= 2		
1	85	89
2	388	404
3	67	-68
4	210	-215
5	32	31
6	81	84
7	11	-12
8	28	-30
9	6	4
10	9	4
11	6*	-1
H= 2, K= 3		
0	464	-429
1	79	73
2	210	210
3	23	-24
4	58	-62
5	5*	4
6	12	12
7	5*	0
8	6*	-1
9	6*	0
H= -2, K= 3		
1	124	-116
2	424	-433
3	89	91
4	203	212
5	34	-37
6	55	-59
7	8	9
8	8	10
9	5*	-1
10	6*	0
11	6*	0
H= 2, K= 4		
0	251	228
1	138	-58
2	113	-118
3	62	60
4	36	40
5	30	-30
6	9	-10
7	12	12
8	6*	2
9	6*	-4
H= -2, K= 4		
1	126	-115
2	234	-231
3	90	81
4	119	122
5	48	-46
6	39	-42
7	24	25
8	9	11
9	17	-11
10	6*	-3
11	6*	4
H= 2, K= 5		
0	209	191
1	121	-113
2	101	-101
3	46	50
4	31	33
5	14	-17
6	7	-7
7	6*	5
8	6*	1
9	6*	-1
H= -2, K= 5		
1	171	161
2	190	192
3	128	-124
4	99	-101
5	56	58
6	31	32
7	19	-20
8	6	-6
9	6	6
10	6*	0
11	6*	-1
H= 2, K= 6		
0	95	-84
1	86	-84
2	36	36
3	49	42
4	5	-6
5	18	-16
6	5*	-2
7	6*	5
8	6*	1
H= -2, K= 6		
1	108	-114
2	97	92
3	87	90
4	49	-49
5	47	-45
6	11	12
7	19	17
8	5*	0
9	6	-5
10	6*	-1
11	6*	1
H= 2, K= 7		
0	16	-11
1	153	-148
2	7	-6
3	73	71
4	15	15
5	27	-25
6	11	-11
7	6*	7
8	6*	5
H= -2, K= 7		
1	190	193
2	14	-9
3	145	-147
4	10	-10
5	70	70
6	19	14
7	24	-24
8	13	-11
9	7	7
10	6*	6
H= 2, K= 8		
0	116	125
1	106	99
2	87	-88
3	53	-52
4	43	44
5	20	20
6	17	-18
7	6*	-6
8	6*	6
H= -2, K= 8		
1	128	124
2	124	-124
3	101	-90
4	82	81
5	52	52
6	40	-42
7	21	-21
8	16	17
9	7	7
10	6*	-5
H= 2, K= 9		
0	77	72
1	131	129
2	44	-40
3	76	-77
4	17	17
5	36	35
6	6	-5
7	13	-12
8	5*	1
H= -2, K= 9		
1	149	-155
2	69	70
3	123	129
4	38	-40
5	75	-78
6	12	13
7	36	36
8	6*	-3
9	13	-14
10	6*	0
H= 2, K= 10		
0	54	-48
1	5*	-1
2	37	35
3	9	-7
4	19	-20
5	7	8
6	8	9
7	6*	-4
H= -2, K= 10		
1	8	-10
2	50	49
3	8	7
4	35	-37
5	5*	1
6	20	22
7	5*	-5
8	10	-10
9	6*	3
H= 2, K= 11		
0	15	-15
1	41	38
2	14	14
3	22	-21
4	11	-11
5	9	9
6	6*	6
7	6*	-3
H= -2, K= 11		
1	50	-49
2	12	-13
3	43	43
4	11	12
5	26	-26
6	9	-9
7	12	11
8	6*	5
9	6*	-4
H= 2, K= 12		
0	10	10
1	5*	-3
2	5*	-6
3	5*	6
4	6*	3
5	7	-5
6	6*	-2
H= -2, K= 12		
1	5*	-1
2	11	-13
3	5*	2
4	9	12
5	6	-5
6	6*	-7
7	6*	5
8	6*	1
H= 2, K= 13		
0	48	-42
1	15	-15
2	34	32
3	9	9
4	19	-19
5	6*	-5
H= -2, K= 13		
1	20	19
2	45	-43
3	20	-20
4	13	14
5	15	15
6	20	-21
7	7	-8
8	10	10
H= 2, K= 14		
0	6*	-2
1	18	16
2	6*	2
3	13	-13
4	6*	-1
5	9	8
H= -2, K= 14		
1	14	17
2	6*	1
3	15	-15
4	6*	0
5	13	12
6	6*	-1
7	6*	-7
H= 2, K= 15		
0	26	-26
1	31	-28
2	16	16
3	22	20
4	6*	-6
H= -2, K= 15		
1	28	30
2	24	-27
3	26	-25
4	16	17
5	17	18
6	8	-7
H= 2, K= 16		
0	19	-18
1	10	6
2	15	13
H= -2, K= 16		
1	11	12
2	18	19
3	11	-11
4	16	-15
H= 2, K= 17		
0	24	22
H= -2, K= 17		
1	8	-6
2	21	23
H= 3, K= 0		
0	271	241
2	106	-99
4	30	30
6	6	-8
8	6*	2
H= -3, K= 0		
2	332	-328
4	223	224
6	91	-91
8	28	28
10	7	-7
12	6*	2
H= 3, K= 1		
0	87	75
1	59	59
2	59	-53
3	13	-12
4	31	31
5	5*	0
6	14	-19
7	6*	2
8	6*	5
H= -3, K= 1		
1	119	-107
2	76	79
3	106	101
4	56	-54
5	44	-46
6	36	35
7	11	11
8	20	-21
9	5*	0
10	8	5
11	6*	-1
12	6*	-3
H= 3, K= 2		
0	339	-308
1	111	-109
2	131	131
3	30	33
4	35	-38
5	5*	-3
6	7	8
7	6*	-2
8	6*	-1
H= -3, K= 2		
1	197	-191
2	390	392
3	165	160
4	245	-247
5	64	-64
6	89	91
7	11	10
8	24	-24
9	5*	2
10	5*	5
11	6*	-2
12	6*	-1
H= 3, K= 3		
0	103	-52
1	33	31
2	50	49
3	23	-23
4	19	-20
5	13	13
6	8	7
7	6*	-6
8	6*	-2
H= -3, K= 3		
1	33	-36
2	113	-108
3	29	31
4	74	71
5	23	-22
6	33	-33
7	15	15
8	13	13
9	9	-8
10	6*	-5
11	6*	3
12	6*	1
H= 3, K= 4		
0	63	-57
1	9	-7
2	49	48
3	10	11
4	31	-32
5	7	-7
6	16	15
7	6*	3
8	6*	-5
H= -3, K= 4		
1	5	6
2	61	56
3	11	-13
4	53	-49
5	4*	5
6	39	39
7	4*	2
8	23	-24
9	5*	-3
10	10	10
11	6*	1
H= 3, K= 5		
0	139	-127
1	13	-10
2	60	55
3	4*	2
4	19	-19
5	5*	0
6	5*	5
7	6*	0
8	6*	-1
H= -3, K= 5		
1	20	25
2	161	-162
3	32	-29
4	112	114
5	18	18
6	48	-49
7	7	-8
8	16	15
9	5*	3
10	6*	-3
11	6*	-1
H= 3, K= 6		
0	121	105
1	99	-95
2	73	-71
3	53	52
4	35	35
5	22	-23
6	14	-13
7	6*	8
8	6*	4
H= -3, K= 6		
1	130	-133
2	120	-114
3	123	126
4	84	80
5	62	-82
6	43	-42
7	42	42
8	18	19
9	17	-17
10	7	-7
11	6*	6
H= 3, K= 7		
0	4*	1
1	83	-76
2	13	14
3	35	36
4	14	-14
5	12	-12
6	9	8
7	6*	3
H= -3, K= 7		
1	118	115
2	18	16
3	104	-102
4	9	-11
5	54	55
6	5*	-1
7	19	-21
8	6	5
9	6	6
10	6*	-3
11	6*	-1
H= 3, K= 8		
0	121	117
1	29	26
2	67	-66
3	15	-14
4	27	28
5	7	6
6	7	-9
7	6*	-2
H= -3, K= 8		
1	35	34
2	129	-137
3	31	-30
4	99	104
5	19	18
6	53	-54
7	9	-8
8	22	21
9	6*	3
10	7	-7
11	6*	-1
H= 3, K= 9		
0	70	64
1	24	-24
2	43	-41
3	17	17
4	19	20
5	9	-9
6	9	-8
7	6*	4
H= -3, K= 9		
1	25	30
2	72	72
3	28	-32
4	57	-58
5	25	27
6	31	34
7	18	-16
8	15	-15
9	9	7
10	6*	6
H= 3, K= 10		
0	45	-42
1	22	22
2	20	20
3	11	-11
4	6*	-5
5	6*	6
6	6*	0
H= -3, K= 10		
1	23	25
2	48	51
3	19	-20
4	33	-34
5	11	13
6	12	13
7	5*	-6
8	6*	-2
9	6*	3
10	6*	-1
H= 3, K= 11		
0	32	28
1	5*	4
2	17	-16
3	6	-3
4	6	6
5	6*	2
6	6*	-1
H= -3, K= 11		
1	13	-8
2	32	32
3	10	12
4	22	-22
5	17	-12
6	10	9
7	8	5
8	6*	-2
9	7	-4
H= 3, K= 12		
0	12	10
1	70	65
2	7	-4
3	36	-34
4	6*	1
5	13	13
H= -3, K= 12		
1	89	89
2	13	-14
3	86	-86
4	11	12
5	58	58
6	6	-7
7	29	-28
8	6*	2
9	11	10
H= 3, K= 13		
0	5*	2
1	24	24
2	6*	-4
3	11	-10
4	6*	4
5	6*	2
H= -3, K= 13		
1	34	-35
2	5*	0
3	30	31
4	6*	-2
5	15	-16
6	6*	3
7	8	5
8	6*	-3
H= 3, K= 14		
0	12	-13
1	21	-20
2	7	8
3	9	8
4	6*	-4
H= -3, K= 14		
1	29	-30
2	12	14
3	27	27
4	9	-11
5	15	-15
6	6*	7
7	7	5
H= 3, K= 15		
0	9	9
1	16	13
2	8	-6
3	11	-10
H= -3, K= 15		
1	15	-15
2	8	9
3	15	15
4	7	-7
5	13	-12
6	6*	4
H= 3, K= 16		
0	48	-44
1	6*	1
H= -3, K= 16		
1	6*	3
2	43	49
3	6*	-4
4	40	-41
5	6*	3
H= 4, K= 0		
0	217	-191
2	80	75
4	21	-19
6	6*	3
8	6*	0
H= -4, K= 0		
2	303	282
4	229	-215
6	95	92
8	26	-26
10	5*	5
12	6*	-1
H= 4, K= 1		
0	127	121
1	62	58
2	44	-46
3	21	-21
4	9	5
5	5*	6
6	6*	0
7	6*	-1
8	6*	-1
H= -4, K= 1		
1	118	-114
2	172	165
3	132	128
4	119	-115
5	77	-76
6	38	39
7	29	30
8	5*	-5
9	7	-5
10	5*	-1
11	6*	2
12	6*	1
H= 4, K= 2		
0	51	-44
1	27	-24
2	24	24
3	7	8
4	11	-11
5	5*	-2
6	6*	5
7	6*	0
8	6*	-1
H= -4, K= 2		
1	48	-46
2	63	60
3	50	46
4	51	-51
5	25	-23
6	30	30
7	6	6
8	13	-14
9	5*	-1
10	5*	6
11	6*	0
12	6*	-2
H= 4, K= 3		
0	70	-64
1	4*	-5
2	19	20
3	4*	-3
4	5*	-1
5	5*	4
6	6*	-2
7	6*	-2
H= -4, K= 3		
1	12	15
2	102	-97
3	10	-11
4	74	70
5	5	-2
6	23	-23
7	6	8
8	5*	0
9	5*	-6
10	5*	1
11	6*	2
12	6*	-2
H= 4, K= 4		
0	90	75
1	100	-94
2	40	-38
3	42	41
4	14	14
5	15	-15
6	6*	-4
7	6*	4
H= -4, K= 4		
1	154	-159
2	117	-111
3	163	167
4	96	93
5	103	-107
6	50	-49
7	47	45
8	19	19
9	17	-18
10	7	-6
11	6*	5
12	6*	1
H= 4, K= 5		
0	116	-108
1	40	37
2	69	67
3	17	-17
4	34	-34
5	6	6
6	13	14
7	6*	-2
H= -4, K= 5		
1	60	-57
2	134	-138
3	56	53
4	123	127
5	32	-30
6	84	-86
7	14	13
8	44	45
9	5*	-5
10	19	-18
11	6*	2
12	7	6
H= 4, K= 6		
0	66	66
1	27	-27
2	46	-47
3	6	7
4	20	19
5	6*	0
6	8	-7
7	6*	0
H= -4, K= 6		
1	52	-57
2	96	-106
3	58	65
4	76	83
5	38	-41
6	42	-44
7	15	16
8	18	18
9	5*	-4
10	6	-7
11	6*	0
H= 4, K= 7		
0	12	-8
1	78	-76
2	5*	1
3	41	41
4	5*	3
5	17	-17
6	6*	-2
7	6*	6
H= -4, K= 7		
1	104	111
2	15	-11
3	107	-115
4	7	4
5	81	84
6	5*	4
7	46	-47
8	6	-5
9	21	21
10	6*	3
11	6*	-7
H= 4, K= 8		
0	6	2
1	122	119
2	5*	0
3	52	-54
4	5*	0
5	16	14
6	6*	0
H= -4, K= 8		
1	109	109
2	7	-4
3	190	-195
4	7	4
5	133	137
6	5*	-3
7	66	-65
8	5*	1
9	25	24
10	6*	2
11	8	-7
H= 4, K= 9		
0	52	50
1	5*	0
2	25	-20
3	5*	-1
4	8	5
5	6*	1
6	6*	-2
H= -4, K= 9		
1	6	1
2	63	65
3	7	-3
4	54	-55
5	6	4
6	29	30
7	5*	-2
8	10	-11
9	6*	1
10	6*	3
H= 4, K= 10		
0	29	-25
1	8	-9
2	22	21
3	6*	3
4	11	-14
5	6*	-1
H= -4, K= 10		
1	13	-15
2	27	24
3	17	19
4	24	-22
5	15	-16
6	16	19
7	6	9
8	11	-12
9	6*	-3
10	6*	6
H= 4, K= 11		
0	8	7
1	37	-34
2	6*	-6
3	20	17
4	7	4
5	7	-7
H= -4, K= 11		
1	48	48
2	9	8
3	46	-46
4	10	-11
5	33	32
6	12	12
7	17	-17
8	9	-8
9	7	7
H= 4, K= 12		
0	42	-39
1	33	-29
2	20	19
3	21	19
4	7	-5
H= -4, K= 12		
1	37	-34
2	49	51
3	36	33
4	41	-43
5	29	-27
6	24	23
7	19	18
8	8	-8
9	11	-9
H= 4, K= 13		
0	17	16
1	37	35
2	10	-10
3	18	-17
4	6*	4
H= -4, K= 13		
1	52	-52
2	18	18
3	53	54
4	14	-15
5	39	-39
6	8	9
7	20	20
8	6*	-4
H= 4, K= 14		
0	24	19
1	12	-5
2	15	-13
3	6*	1
H= -4, K= 14		
1	10	-10
2	21	-23
3	9	10
4	21	21
5	7	-6
6	16	-15
7	6*	2
H= 4, K= 15		
0	21	21
1	6*	-1
2	17	-15
H= -4, K= 15		
1	6*	4
2	25	25
3	6*	-3
4	23	-23
5	6*	0
6	16	14
H= 4, K= 16		
0	6*	5
H= -4, K= 16		
1	14	15
2	6*	-4
3	16	-15
4	6*	6
H= 5, K= 0		
0	158	143
2	73	-66
4	24	26
6	16	-15
H= -5, K= 0		
2	221	-226
4	217	214
6	113	-115
8	61	62
10	23	-23
12	7	7
H= 5, K= 1		
0	98	94
1	29	-28
2	46	-45
3	4	4
4	17	16
5	6*	-1
6	6*	-6
7	6*	0
H= -5, K= 1		
1	53	57
2	129	133
3	73	-66
4	114	-116
5	45	47
6	65	64
7	15	-16
8	28	-27
9	5*	2
10	12	10
11	6*	0
12	6*	-4
H= 5, K= 2		
0	103	-97
1	33	31
2	11	31
3	23	-23
4	5*	-6
5	11	11
6	6*	0
7	6*	-4
H= -5, K= 2		
1	29	31
2	176	176
3	21	-23
4	172	-171
5	21	20
6	92	91
7	21	-20
8	31	-30
9	13	14
10	7	7
11	6	-6
12	6*	-1
H= 5, K= 3		
0	125	-118
1	55	51
2	60	59
3	24	-21
4	24	-24
5	7	8
6	6*	6
7	6*	-3
H= -5, K= 3		
1	92	-90
2	166	-170
3	114	110
4	163	171
5	87	-85
6	106	-110
7	46	47
8	52	-53
9	19	-14
10	21	-21
11	7	7
12	7	7
H= 5, K= 4		
0	60	54
1	4*	-1
2	13	-14
3	5*	-3
4	5*	-2
5	6*	2
6	6*	2
H= -5, K= 4		
1	15	-10
2	108	-106
3	20	13
4	107	105
5	8	-4
6	54	-54
7	4*	-4
8	14	15
9	6	4
10	5*	-1
11	6*	-2
12	6*	-1
H= 5, K= 5		
0	114	106
1	15	-14
2	45	-46
3	11	14
4	11	13
5	6*	-6
6	6*	-1

Table 2 (*cont.*)

L	FO	FC
H= -5, K= 5		
1	14	13
2	162	164
3	18	-17
4	152	-152
5	25	25
6	84	84
7	23	-24
8	32	-31
9	15	15
10	7	8
11	6	-7
12	6*	-2
H= 5, K= 6		
0	41	-39
1	12	-12
2	21	19
3	5*	4
4	9	-7
5	6*	-1
6	6*	2
H= -5, K= 6		
1	21	-24
2	51	57
3	27	30
4	50	-54
5	22	-23
6	33	33
7	13	11
8	16	-14
9	5*	-4
10	6*	5
11	6*	1
12	6*	-1
H= 5, K= 7		
0	52	-51
1	46	-44
2	22	22
3	20	19
4	8	-6
5	8	-6
6	6*	1
H= -5, K= 7		
1	72	77
2	69	-76
3	85	-92
4	64	69
5	68	73
6	36	-38
7	38	-40
8	13	14
9	16	16
10	6*	-3
11	7	-5
H= 5, K= 8		
0	40	39
1	24	21
2	14	-14
3	8	-7
4	6*	3
5	6*	2
H= -5, K= 8		
1	42	40
2	60	-63
3	53	-51
4	59	61
5	42	40
6	34	-34
7	22	-20
8	12	12
9	8	7
10	6*	-2
11	6*	-2
H= 5, K= 9		
0	34	34
1	43	40
2	22	-23
3	18	-16
4	10	12
5	6*	5
H= -5, K= 9		
1	68	-68
2	38	41
3	79	79
4	39	-41
5	61	-60
6	31	33
7	32	31
8	18	-21
9	12	-12
10	9	10
11	6*	3
H= 5, K= 10		
0	49	-46
1	7	-3
2	23	22
3	6*	3
4	9	-8
H= -5, K= 10		
1	6	-3
2	64	67
3	6	3
4	69	-66
5	6	-4
6	44	45
7	5*	4
8	22	-22
9	6*	-2
10	9	8
H= 5, K= 11		
0	25	-22
1	14	13
2	17	15
3	9	-10
4	8	-8
H= -5, K= 11		
1	19	-19
2	26	-25
3	17	16
4	25	23
5	19	-19
6	18	-17
7	18	17
8	12	11
9	12	-11
10	6*	-6
H= 5, K= 12		
0	6*	5
1	11	-12
2	6*	-3
3	6*	7
H= -5, K= 12		
1	14	-14
2	8	-7
3	13	13
4	9	8
5	12	-12
6	7	-6
7	7	9
8	6*	4
9	6*	-5
H= 5, K= 13		
0	6*	-4
1	33	-30
2	6*	3
H= -5, K= 13		
1	42	45
2	6*	-5
3	46	-50
4	6*	5
5	42	42
6	6*	-5
7	28	-27
8	6*	3
H= 5, K= 14		
0	6*	0
1	8	-7
H= -5, K= 14		
1	14	-15
2	6*	3
3	18	19
4	6*	-2
5	16	-16
6	6*	0
7	10	9
H= 5, K= 15		
0	6*	7
H= -5, K= 15		
1	6*	0
2	8	8
3	6*	0
4	8	-7
5	6*	-1
6	6*	5
H= 6, K= 0		
0	50	50
2	26	-25
4	9	10
6	6*	-3
H= -6, K= 0		
2	69	-76
4	74	82
6	57	-61
8	33	33
10	15	-14
12	6*	5
H= 6, K= 1		
0	71	67
1	62	-60
2	31	-30
3	27	26
4	11	10
5	9	-10
6	6*	-3
H= -6, K= 1		
1	97	102
2	108	107
3	120	-126
4	115	-112
5	102	106
6	76	73
7	64	-64
8	34	-34
9	30	30
10	11	12
11	11	-12
12	6	-3
13	6*	4
H= 6, K= 2		
0	25	24
1	5*	5
2	15	-14
3	7	-7
4	7	6
5	6*	4
6	6*	-2
H= -6, K= 2		
1	13	-8
2	27	-28
3	29	24
4	24	23
5	24	-21
6	16	-15
7	6	5
8	10	9
9	6	4
10	6	-6
11	6*	-4
12	6*	2
H= 6, K= 3		
0	133	129
1	8	-5
2	65	-64
3	5*	-2
4	25	26
5	6*	2
6	7	-8
H= -6, K= 3		
1	24	23
2	183	197
3	40	-40
4	154	-209
5	34	33
6	144	150
7	15	-13
8	79	-79
9	5*	1
10	34	33
11	6*	1
12	12	-11
H= 6, K= 4		
0	65	-63
1	30	29
2	31	31
3	11	-12
4	11	-12
5	6*	4
H= -6, K= 4		
1	49	53
2	88	93
3	63	-68
4	91	-95
5	56	59
6	65	66
7	35	-36
8	39	-35
9	16	17
10	14	15
11	7	-6
12	6*	-5
H= 6, K= 5		
0	39	-36
1	72	71
2	20	20
3	29	-29
4	8	-9
5	9	10
H= -6, K= 5		
1	121	-121
2	51	-54
3	156	166
4	58	62
5	135	-143
6	49	-52
7	80	83
8	32	32
9	35	-36
10	16	-15
11	12	12
12	6*	5
H= 6, K= 6		
0	35	33
1	7	-7
2	14	-13
3	6*	3
4	7	4
5	6*	-1
H= -6, K= 6		
1	13	-14
2	56	-56
3	20	20
4	61	60
5	18	-20
6	41	-40
7	12	13
8	17	17
9	6	-7
10	6*	-5
11	6*	3
12	6*	1
H= 6, K= 7		
0	11	9
1	5*	-1
2	5*	-4
3	6*	2
4	6*	2
5	6*	-2
H= -6, K= 7		
1	5*	-3
2	17	15
3	6	7
4	20	-19
5	5*	-5
6	18	17
7	5*	1
8	13	-11
9	5*	2
10	6*	5
11	6*	-2
H= 6, K= 8		
0	18	-17
1	5*	-3
2	11	10
3	6*	1
4	6*	-4
H= -6, K= 8		
1	5*	-6
2	19	21
3	5*	4
4	16	-19
5	5*	0
6	11	13
7	5*	-2
8	7	-7
9	6*	1
10	6*	4
11	6*	-1
H= 6, K= 9		
0	35	-33
1	26	25
2	16	15
3	12	-11
4	6*	-5
H= -6, K= 9		
1	42	-42
2	50	-51
3	52	50
4	52	54
5	45	-42
6	38	-38
7	27	25
8	21	19
9	13	-12
10	9	-7
11	6*	4
H= 6, K= 10		
0	10	-10
1	11	-11
2	6*	5
3	6*	5
H= -6, K= 10		
1	17	-17
2	17	16
3	19	21
4	19	-19
5	18	-20
6	15	15
7	12	14
8	9	-6
9	8	-6
10	6*	3
H= 6, K= 11		
0	16	-15
1	29	-28
2	8	7
3	10	11
H= -6, K= 11		
1	49	50
2	22	-22
3	64	-63
4	24	23
5	54	54
6	16	-17
7	31	-31
8	9	9
9	13	13
10	6*	-3
H= 6, K= 12		
0	6*	6
1	9	8
2	6*	-4
H= -6, K= 12		
1	17	18
2	7	-6
3	25	-26
4	6	5
5	23	24
6	6*	-4
7	14	-15
8	6*	2
9	6*	6
H= 6, K= 13		
0	14	-11
1	6*	6
H= -6, K= 13		
1	11	-12
2	16	-16
3	14	16
4	15	16
5	13	-14
6	12	-12
7	10	8
8	8	7
H= 6, K= 14		
0	14	11
H= -6, K= 14		
1	17	-18
2	15	-15
3	24	25
4	16	16
5	23	-24
6	13	-12
7	16	15
H= -6, K= 15		
2	34	37
3	28	-31
4	35	-39
5	28	27
H= 7, K= 0		
0	22	-20
2	10	9
4	6*	-3
H= -7, K= 0		
2	33	36
4	40	-44
6	35	37
8	21	-21
10	9	9
12	6*	-2
H= 7, K= 1		
0	113	112
1	30	-31
2	45	-46
3	12	12
4	14	15
5	6*	-4
H= -7, K= 1		
1	56	60
2	186	199
3	82	-86
4	225	-239
5	82	85
6	174	165
7	55	-58
8	96	-58
9	28	29
10	38	30
11	10	-11
12	12	-12
13	6*	4
H= 7, K= 2		
0	21	-20
1	5*	4
2	13	12
3	6*	1
4	7	-6
5	6*	-1
H= -7, K= 2		
1	18	18
2	26	27
3	33	-31
4	32	-32
5	30	28
6	33	32
7	13	-12
8	25	-25
9	5*	1
10	15	14
11	6*	2
12	7	-6
13	6*	-1
H= 7, K= 3		
0	22	-19
1	5*	2
2	7	7
3	6*	-3
4	6*	-2
H= -7, K= 3		
1	5*	3
2	40	-38
3	10	-10
4	48	45
5	10	8
6	35	-32
7	5*	0
8	16	13
9	5*	-4
10	5*	-3
11	6*	3
12	6*	0
H= 7, K= 4		
0	42	39
1	28	-27
2	18	-18
3	11	12
4	6*	7
H= -7, K= 4		
1	45	-47
2	66	-66
3	61	63
4	64	63
5	63	-64
6	73	-73
7	46	47
8	46	45
9	26	-26
10	21	-21
11	10	11
12	8	8
H= 7, K= 5		
0	53	51
1	13	13
2	18	-19
3	6*	-3
4	6*	5
H= -7, K= 5		
1	28	-33
2	91	94
3	45	53
4	112	-114
5	94	-51
6	88	88
7	28	31
8	45	-44
9	10	-12
10	17	16
11	6*	3
12	6*	-4
H= 7, K= 6		
0	14	-12
1	5*	3
2	6*	2
3	6*	-2
4	6*	1
H= -7, K= 6		
1	5*	0
2	27	29
3	5	4
4	37	-37
5	6	-5
6	29	28
7	5*	1
8	11	-12
9	5*	1
10	6*	1
11	6*	-2
12	6*	0
H= 7, K= 7		
0	21	-24
1	6*	8
2	7	8
3	6*	-3
4	6*	-1
H= -7, K= 7		
1	16	-17
2	43	-46
3	26	25
4	54	60
5	26	-25
6	42	-47
7	17	17
8	21	23
9	6	-8
10	6	-8
11	6*	3
H= 7, K= 8		
0	9	8
1	15	14
2	6*	-5
3	8	-6
H= -7, K= 8		
1	28	28
2	12	-13
3	42	-43
4	15	16
5	46	47
6	15	-16
7	35	-35
8	11	11
9	20	19
10	6*	-6
11	9	-7
H= 7, K= 9		
0	24	23
1	23	20
2	11	-11
3	9	-8
H= -7, K= 9		
1	35	-36
2	33	35
3	47	48
4	39	-39
5	45	-46
6	31	32
7	32	31
8	19	-19
9	17	-15
10	9	9
11	6*	6
H= 7, K= 10		
0	7	-4
1	6*	2
2	6*	4
H= -7, K= 10		
1	6*	-1
2	6*	2
3	5*	5
4	5*	-1
5	7	-6
6	6*	4
7	6*	2
8	6*	-6
9	6*	1
10	6*	5
H= 7, K= 11		
0	52	-49
1	6*	3
2	24	23
H= -7, K= 11		
1	6*	2
2	73	-76
3	7	-7
4	93	86
5	7	7
6	69	-70
7	6*	-2
8	42	41
9	6*	-2
H= 7, K= 12		
0	6*	1
1	14	-13
H= -7, K= 12		
1	22	-22
2	6*	1
3	26	28
4	6*	-2
5	27	-27
6	6*	3
7	21	20
8	6*	-2
9	11	-11
H= 7, K= 13		
0	6*	-2
H= -7, K= 13		
1	29	22
2	6*	-1
3	25	-27
4	6*	1
5	25	26
6	6*	-1
7	19	-20
8	6*	2
H= -7, K= 14		
2	6*	-1
3	21	-23
4	6*	1
5	19	21
6	6*	-1
H= 8, K= 0		
0	12	12
2	6*	0
H= -8, K= 0		
2	36	-36
4	58	57
6	51	-50
8	26	24
10	7	-5
12	6*	-1
H= 8, K= 1		
0	7	-7
1	7	-6
2	6*	2
3	6*	2
H= -8, K= 1		
1	15	16
2	12	-14
3	28	-28
4	16	19
5	33	33
6	14	-17
7	24	-25
8	9	10
9	11	12
10	5*	-4
11	6*	-4
12	6*	1
13	6*	1
H= 8, K= 2		
0	5*	6
1	6*	7
2	6*	-4
3	6*	-2
H= -8, K= 2		
1	16	16
2	5	-3
3	22	-24
4	7	-4
5	21	22
6	12	8
7	13	-12
8	5*	-4
9	6	4
10	6*	0
11	6*	-1
12	6*	1
H= 8, K= 3		
0	5*	0
1	15	15
2	6*	0
3	6*	-6
H= -8, K= 3		
1	27	-28
2	5*	1
3	40	41
4	5*	-4
5	43	-44
6	5*	5
7	34	34
8	6	-3
9	19	-19
10	6*	2
11	9	8
12	6*	-1
H= 8, K= 4		
0	29	-28
1	6*	5
2	14	14
3	6*	-1
H= -8, K= 4		
1	13	14
2	40	40
3	26	-26
4	46	-44
5	29	29
6	41	38
7	22	-20
8	28	-27
9	11	9
10	15	15
11	6*	-3
12	8	-7
H= 8, K= 5		
0	10	-10
1	6*	0
2	9	8
3	6*	1
H= -8, K= 5		
1	5*	-4
2	6	-7
3	10	11
4	5*	2
5	12	-14
6	5*	-2
7	8	9
8	6	5
9	5*	-2
10	6*	-6
11	6*	0
12	6*	4
H= 8, K= 6		
0	6*	-1
1	16	-15
2	6*	-2
3	7	7
H= -8, K= 6		
1	26	-26
2	10	10
3	35	35
4	18	-17
5	38	-38
6	14	13
7	32	32
8	5*	-3
9	21	-21
10	6*	-3
11	11	10
12	6*	3
H= 8, K= 7		
0	13	11
1	27	-26
2	7	-6
H= -8, K= 7		
1	50	51
2	15	15
3	74	-75
4	16	-16
5	79	78
6	15	15
7	60	-59
8	12	-12
9	34	32
10	8	8
11	15	-14
H= 8, K= 8		
0	10	8
1	9	-7
2	6*	-4
H= -8, K= 8		
1	17	-18
2	16	-16
3	26	28
4	21	21
5	28	-28
6	20	-21
7	19	18
8	14	14
9	9	-8
10	7	-7
11	6*	2
H= 8, K= 9		
0	6*	2
1	22	21
H= -8, K= 9		
1	43	-45
2	6*	-2
3	66	68
4	8	7
5	74	-74
6	9	-7
7	56	56
8	6*	3
9	31	-30
10	6*	0
H= 8, K= 10		
0	17	15
1	6*	0
H= -8, K= 10		
1	6*	-2
2	22	-21
3	6*	4
4	24	22
5	7	-5
6	21	-19
7	6*	3
8	15	14
9	6*	-1
10	9	-8
H= 8, K= 11		
0	6*	2
H= -8, K= 11		
1	6*	1
2	6*	5
3	6*	-5
4	7	-8
5	6*	7
6	6*	6
7	6*	-4
8	6*	-3
9	6*	0
H= -8, K= 12		
1	24	24
2	13	-13
3	33	-33
4	16	19
5	36	36
6	13	-16
7	31	-30
8	9	9
H= -8, K= 13		
3	10	-9
4	22	25
5	10	11
6	20	-22
H= 9, K= 0		
0	12	11
2	6*	-5
H= -9, K= 0		
2	17	-19
4	26	28
6	27	-30
8	23	24
10	14	-14
12	6*	6
H= 9, K= 1		
0	29	29
1	6*	0
2	10	-11
H= -9, K= 1		
1	6	-5
2	55	58
3	13	11
4	81	-83
5	16	-14
6	83	84
7	12	9
8	59	-59
9	5*	-2
10	30	30
11	6*	-1
12	12	-11
H= 9, K= 2		
0	6*	1
1	6*	0
2	6*	2
H= -9, K= 2		
1	5*	2
2	11	-11
3	5*	-5
4	19	20
5	6	6
6	18	-18
7	5*	-5
8	7	6
9	5*	2
10	6*	2
11	6*	0
12	6*	-3
H= 9, K= 3		
0	10	-10
1	9	8
2	6*	3
H= -9, K= 3		
1	10	-10
2	21	-23
3	9	8
4	31	34
5	5*	-5
6	30	-30
7	6	5
8	16	16
9	7	-7
10	6*	-5
11	7	6
12	6*	0
H= 9, K= 4		
0	6*	-3
1	6*	2
2	6*	-1
H= -9, K= 4		
1	8	10
2	14	17
3	20	-21
4	28	-30
5	27	27
6	27	29
7	22	-21
8	13	-14
9	10	10
10	6*	2
11	6*	-3
12	6*	2
H= 9, K= 5		
0	23	-20
1	6*	5
2	10	9
H= -9, K= 5		
1	11	-10
2	34	-33
3	17	18
4	43	41
5	22	-24
6	43	-41
7	21	22
8	34	32
9	15	-14
10	22	-19
11	8	7
12	11	9
H= 9, K= 6		
0	6*	-3
1	9	7
H= -9, K= 6		
1	14	15
2	6*	2
3	22	-22
4	5*	-1
5	23	23
6	5*	3
7	18	-18
8	6*	-5
9	12	11
10	6*	5
11	6*	-5
H= 9, K= 7		
0	10	-9
1	15	-13
H= -9, K= 7		
1	26	27
2	15	-16
3	38	-40
4	21	21
5	43	43
6	20	-20
7	35	-35
8	15	15
9	22	21
10	8	-8
11	10	-10
H= 9, K= 8		
0	6*	-4
H= -9, K= 8		
1	21	-22
2	10	12
3	34	36
4	17	-18
5	41	-42
6	15	16
7	34	34
8	9	-7
9	20	-20
10	6*	1
11	10	9
H= 9, K= 9		
0	16	17
H= -9, K= 9		
1	7	8
2	30	32
3	12	-11
4	42	-43
5	13	12
6	40	41
7	12	-12
8	29	-28
9	8	5
10	15	14
H= -9, K= 10		
1	6*	1
2	6*	0
3	6*	0
4	6*	2
5	6*	-2
6	6*	-2
7	6*	2
8	6*	0
9	6*	0
H= -9, K= 11		
2	6*	-2
3	12	-11
4	6*	5
5	14	14
6	6*	-5
7	12	-13
8	6*	3
H= -9, K= 12		
4	16	17
5	6*	-3
6	17	-16
H= 10, K= 0		
0	13	-12
H= -10, K= 0		
2	19	20
4	24	-24
6	24	24
8	21	-20
10	15	14
12	7	-6
H= 10, K= 1		
0	10	9
1	6*	5
H= -10, K= 1		
1	14	-14
2	20	20
3	25	25
4	34	-33
5	32	-32
6	38	38
7	29	27
8	30	-29
9	18	-16
10	16	16
11	8	6
12	6*	-6
H= 10, K= 2		
0	13	13
1	6*	1
H= -10, K= 2		
1	6*	6
2	21	-23
3	16	-16
4	29	30
5	24	25
6	31	-30
7	23	-23
8	25	24
9	13	13
10	16	-15
11	6*	-4
12	9	8
H= 10, K= 3		
0	21	-20
H= -10, K= 3		
1	8	-8
2	45	-45
3	11	11
4	72	71
5	13	-12
6	80	-78
7	13	12
8	61	56
9	11	-9
10	13	-30
11	6*	6
12	13	11
H= 10, K= 4		
0	6*	3
H= -10, K= 4		
1	6*	4
2	10	-10
3	7	-5
4	20	20
5	6	6
6	24	-24
7	6*	-6
8	19	18
9	6	5
10	8	-9
11	6*	-3
12	6*	3
H= 10, K= 5		
0	6*	-6
H= -10, K= 5		
1	12	13
2	6*	-7
3	21	-22
4	6*	5
5	26	26
6	6*	-2
7	24	-23
8	6*	2
9	16	15
10	6*	-3
11	7	-8
H= 10, K= 6		
0	6*	-4
H= -10, K= 6		
1	8	8
2	12	13
3	11	-12
4	25	-26
5	14	14
6	31	32
7	11	-12
8	24	-24
9	7	7
10	12	11
11	6*	-3
H= -10, K= 7		
1	20	21
2	6*	2
3	36	-38
4	6*	0
5	47	48
6	6*	-3
7	43	-43
8	6*	3
9	29	27
10	6*	-1
H= -10, K= 8		
2	17	18
3	14	-13
4	22	-23
5	17	16
6	24	24
7	17	-16
8	20	-19
9	14	12
10	13	11
H= -10, K= 9		
2	27	28
3	16	15
4	40	-42
5	21	-20
6	45	45
7	19	18
8	35	-34
9	13	-12
H= -10, K= 10		
3	15	17
4	6*	0
5	21	-22
6	6*	0
7	21	21
8	6*	1
H= -11, K= 0		
2	13	-13
4	20	20
6	26	-25
8	25	26
10	23	-20
H= -11, K= 1		
1	7	4
2	8	-7
3	6	-5
4	16	16
5	6*	4
6	21	-21
7	6*	-4
8	18	18
9	6*	4
10	11	-10
11	6*	-3
H= -11, K= 2		
1	6*	4
2	7	-5
3	6*	-5
4	9	9
5	6*	6
6	10	-10
7	7	-6
8	8	7
9	6*	6
10	6*	-3
11	6*	-4
H= -11, K= 3		
1	7	-8
2	6*	5
3	13	13
4	7	-4
5	18	-18
6	6*	4
7	17	17
8	6*	-4
9	13	-13
10	6*	4
11	6*	7
H= -11, K= 4		
2	6*	3
3	11	-12
4	9	-8
5	17	17
6	12	10
7	19	-19
8	10	-8
9	16	16
10	6*	3
11	8	-10
H= -11, K= 5		
2	9	-11
3	6*	1
4	15	16
5	6*	-1
6	17	-18
7	6*	1
8	15	15
9	6*	-1
10	9	-10
H= -11, K= 6		
3	12	-14
4	9	-10
5	18	18
6	12	11
7	17	-18
8	12	-12
9	12	12
10	11	11
H= -11, K= 7		
3	29	-30
4	14	-14
5	43	44
6	17	17
7	45	-45
8	16	-14
9	32	32
H= -11, K= 8		
4	6*	-3
5	29	-30
6	6*	4
7	31	31
8	6*	-3
H= -12, K= 0		
4	41	-42
6	52	53
8	48	-47
10	33	31
H= -12, K= 1		
3	10	-9
4	48	-48
5	11	10
6	65	64
7	12	-9
8	63	-61
9	10	8
10	44	41
H= -12, K= 2		
4	13	12
5	29	-29
6	16	-16
7	32	31
8	15	15
9	25	-24
10	11	-10
H= -12, K= 3		
4	11	11
5	6*	0
6	18	-19
7	6*	-2
8	17	18
9	6*	1
10	10	-10
H= -12, K= 4		
4	6*	-3
5	10	-10
6	6*	5
7	10	10
8	6*	-4
9	6*	-6
H= -12, K= 5		
5	9	-9
6	14	12
7	10	9
8	13	-11

Willis, 1966). Three standard reflexions were monitored periodically and showed no change during the course of data collection. A total of 2534 unique and space-group-permissible reflexions were measured; of these 727 (28·7%) had net intensities less than 3σ net and so were excluded from all subsequent calculations. 72 reflexions suffered from coincidence loss so were remeasured with a diffracted beam attenuator in position. An absorption profile of the encapsulated crystal was prepared by examining the net intensities of three $0k0$ reflections as a function of φ. Only minor variation with Bragg angle was found and the average curve used to correct the intensities (North, Phillips & Mathews, 1968) is given in Fig. 1. Data reduction procedures included: (i) application of the appropriate Lorentz and polarization corrections (Arndt & Willis, 1966); (ii) the calculation of observational weights according to $\sqrt{w}=2F_o/[T+(kI)^2+B]^{1/2}$ (Peterson &

Levy, 1957) where T, I and B are the total, net and background counts and k is a small constant, 0·04 in this case, which is included to allow for minor experimental errors; (iii) derivation of interpolated form factors. The curves for carbon and oxygen were obtained from analytical coefficients (Cromer & Mann, 1968) and modified by the constant terms $\Delta f'_C = 0{\cdot}005$ electrons and $\Delta f'_O = 0{\cdot}015$ electrons (Cromer & Libermann, 1970); the hydrogen-atom curve used was that of Stewart, Davidson & Simpson (1965).

Individual atom isotropic temperature factors of 3·5 Å^2 were assigned to carbon and oxygen atoms with the coordinates of Shahat, and least-squares refinement initiated. Three unit-weighted block-diagonal cycles followed by one unit-weighted full-matrix least-squares calculation resulted in convergence of this model at $R[=\sum||F_o|-|F_c||/\sum|F_o|$ for the reflexions $I>3\sigma(I)]$ $=0{\cdot}248$. Two subsequent cycles with the reflexion data weighted as before, but allowing the atoms anisotropic motion, reduced this residual to 0·087. The four hydrogen atoms were found with peak heights of 0·45 to 0·67 e Å^{-3} in a ΔF map calculated at this stage. These atoms were assigned the final isotropic temperature factors of the atoms to which they were bonded and included, with fixed parameters, in the next two cycles. Six reflexions of exceptionally high intensity and small scattering angle were deemed to be suffering from secondary extinction and so were excluded from subsequent cycles. Two further cycles in which the hydrogen-atom parameters were allowed to vary, resulted in final convergence of the model with $R=0{\cdot}050$. The weighted discrepancy index $R_w=[(\sum w\Delta^2/\sum wF_o^2)^{1/2}]$ has the value 0·073. The shifts in the atomic parameters from the final cycle were all less than one tenth of the associated estimated standard deviation.

Results and discussion

The observed structure amplitudes and the calculated structure factors based on the final model with $R=$ 0·050 are given in Table 2. The positional parameters and the thermal motion parameters with their corresponding e.s.d.'s are in Table 3.

The final R index is perhaps not as low as one would expect for such an overly determined structure (ratio of observations to parameters is 20:1). There are several possible sources of error, either in the data or in the model. The absorption correction that was used (Fig. 1) displays an unsymmetrical profile and could account for minor systematic errors. The data collected were from the hkl and $\bar{h}kl$ octants, so in order to determine the internal consistency of the data the equivalent re-

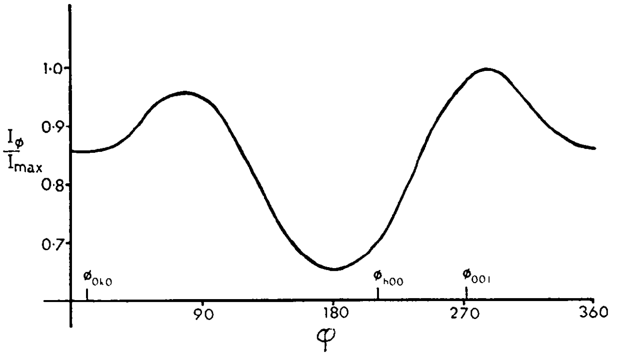


Fig. 1. A plot of the mean relative intensities of three 0k0 reflexions *versus* the diffractometer φ angle at $\chi=90°$.

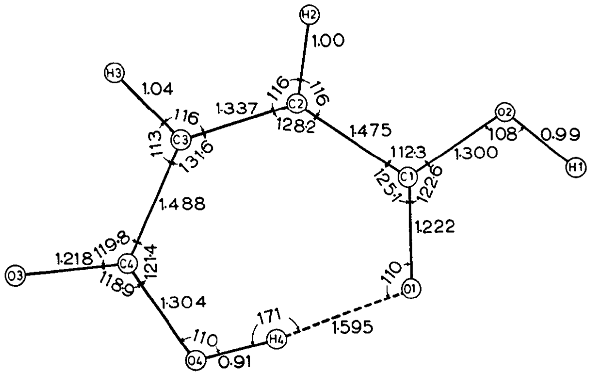


Fig. 2. Bond distances and angles for the maleic acid molecule. The atomic numbering scheme is also shown.

Table 3. *Positional and thermal parameters for one maleic acid molecule*

Thermal parameters are terms in the expression $\exp[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})]$. Anisotropic thermal parameters are $\times 10^5$.

	x/a	y/b	z/c	β_{11} or (B_{iso})	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	0·9702 (1)	0·3502 (1)	0·2500 (2)	1729 (19)	488 (7)	2872 (25)	−30 (8)	1527 (19)	−9 (9)
C(2)	0·8087 (2)	0·4346 (1)	0·2492 (2)	1962 (20)	411 (6)	3138 (28)	22 (9)	1683 (21)	−11 (10)
C(3)	0·6366 (2)	0·3969 (1)	0·2482 (2)	1910 (20)	477 (6)	3001 (26)	114 (9)	1631 (20)	12 (11)
C(4)	0·5530 (2)	0·2634 (1)	0·2493 (2)	1762 (19)	553 (7)	2847 (26)	54 (9)	1566 (19)	13 (10)
O(1)	0·9664 (1)	0·2292 (1)	0·2441 (2)	2419 (22)	471 (6)	4792 (33)	38 (8)	2599 (24)	−38 (10)
O(2)	1·1199 (1)	0·4191 (1)	0·2551 (2)	2305 (20)	593 (7)	4778 (33)	−139 (9)	2535 (23)	−44 (12)
O(3)	0·3915 (2)	0·2534 (1)	0·2510 (2)	2403 (22)	766 (8)	5029 (35)	−6 (9)	2788 (25)	−14 (13)
O(4)	0·6510 (1)	0·1558 (1)	0·2518 (2)	2454 (20)	468 (5)	4424 (30)	4 (8)	2513 (22)	42 (10)
H(1)	1·2193 (24)	0·3568 (18)	0·2516 (17)	3·68 (28)					
H(2)	0·8375 (26)	0·5322 (22)	0·2602 (17)	4·65 (35)					
H(3)	0·5351 (22)	0·4729 (18)	0·2349 (16)	3·66 (29)					
H(4)	0·7627 (27)	0·1765 (21)	0·2397 (21)	5·08 (39)					

flexions from the $hk0$ zone ($hk0$ and $\bar{h}k0$) were examined. A discrepancy index of 0·014 was calculated from $\sum||F_{hk0}|-|F_{\bar{h}k0}||/\sum|F_{hk0}|$ for the 122 pairs of reflexions. This relatively small index indicates that random errors of measurement are not contributing significantly to the relatively high final R index. The largest effect that we propose is the systematic error inherent in the use of the individual atom spherically symmetrical form factors for the description of the model. The final difference electron-density map indicates that rather large concentrations of bonding electron density are present in C–C bonds in addition to concentrations of positive density in the region of the oxygen atoms. The shortcomings of a spherical scattering factor model may be enhanced in this structure because of the large amount of strain in the molecule (see below) hence removing the atomic centres further than usual from the bonding electron density.

Figs. 2, 3 and 4 show that the gross features of Shahat's (1952) analysis are substantially correct. That Donohue's (1968) postulate regarding the simple character of the intermolecular hydrogen bond O(2)–H· · ·O(3) is also verified can be seen in Fig. 4.

The covalent bond lengths and interbond angles for maleic acid are shown in Fig. 2 which also contains the atomic numbering scheme used in this analysis. The estimated standard deviations in these molecular parameters were derived by the independent atom method (Ahmed, Hall, Pippy & Huber, 1966) and are summarized as follows: if X denotes a C or O atom the distances X–X and X–H have average e.s.d.'s of 0·002 and 0·02 Å respectively; the angles X–X–X, X–X–H, X–H–X have e.s.d.'s of 0·1, 1·0, 1·7° respectively.

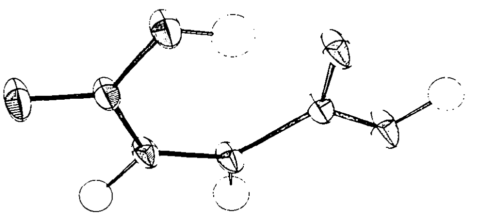


Fig. 3. Thermal-ellipsoid representational surfaces enclosing 25 % probability for maleic acid. This diagram clearly shows that the maximum vibrational amplitudes of thermal motion are perpendicular to the molecular plane and parallel to the crystallographic c^* axis.

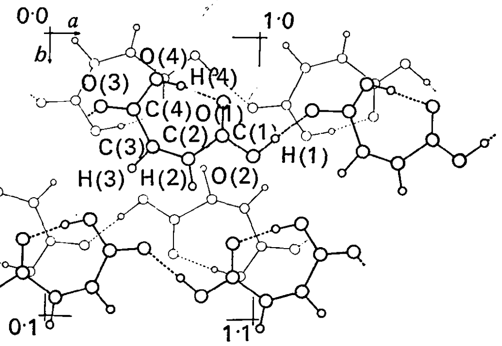


Fig. 4. Molecular packing viewed parallel to the **c*** direction.

(*a*) *Bond lengths*

The ethylenic linkage of 1·337 Å [C(2)–C(3)] is a normal length for bonds of this type: *cf.* Sutton (1965), who quotes 1·335 Å for simple C=C double bonds. Comparison of the two C(sp^2)–C(sp^2) single bonds to the carboxyl groups [C(2)–C(1) and C(3)–C(4)] shows that these two are not identical (6σ difference). It is of interest to note that the shorter (1·475 Å) of these linkages is to the carboxyl group having a C=O *cis* to the ethylene π system and the longer (1·488 Å) is to the carboxyl group with the *trans* relationship of these two π systems. These bond orders are much closer to unity than they are to two, implying little delocalization of π density between the ethylene and the carboxyl double-bond system.

The two carboxyl groups have identical carbon–oxygen bond-length sums of 2·522 Å, a value which is quoted by Manojlović & Speakman (1967) from a wide survey of carboxyl groups. In addition, individual bonds of the same type in these two carboxyl groups are of identical length. The mean values for a variety of carboxyl groups given by Dunitz & Strickler (1968) for the C=O distance (1·229 Å) and C–OH distance (1·309 Å) agree with the observations here, thus indicating that even in this highly strained system (see below) the bond lengths are not unusual and compare well with those in the unstrained isomer, fumaric acid (Brown, 1966; Bednowitz & Post, 1966).

Although the C–H and O–H bond lengths are of lower precision than the C–C and C–O bonds discussed above, they are close to accepted values.

(*b*) *Bond angles*

Darlow (1961) has quoted 121·5° as the average value for bond angles of the type C–C–COOH in unstrained molecules. The two angles C(1)–C(2)–C(3) and C(2)–C(3)–C(4) are of this type but are considerably larger than this value. These two angles, 128·2 and 131·6° respectively, indicate in part the high degree of strain in this molecule. An explanation for the 3·4° (34σ) difference is not apparent.

Whereas the two carboxyl groups are virtually identical when considering bond lengths, they are very different from the point of view of the inter-bond angles. If one takes the mean values for the bond angles at the central carbon atom in carboxyl groups tabulated by Dunitz & Strickler (1968), this molecule demonstrates two types of distortion. Angle O(1)–C(1)–O(2) retains its expected value of 122·6°, but the strain imposed by the short O(1)· · ·O(4) contact produces a 2·4° opening of the C(2)–C(1)=O(1) angle with a concomitant 2·7° closure of the C(2)–C(1)–O(2)H angle. In the other carboxyl group the 6·4° opening of the C(3)–C(4)–O(4)H angle is compensated by a 2·9° closure of the C(3)–C(4)=O(3) angle and a 3·4° closure of the O(3)–C(4)–O(4)H angle. The largest distortion

(6·4°) is associated with the antiplanar carboxyl group and this may be due to a result of more facile distortion of the C–C–OH angle over that for the C–C=O angle.

The two C–O–H bond angles do not differ significantly from the tetrahedral value. The four C–C–H angles do not significantly differ from one another but are all less than the expected 120° and this is presumed to be a consequence of the angle opening at atoms C(2) and C(3).

(*c*) *Hydrogen bonding*

There are two hydrogen bonds in this structure; one is of normal length, distance 2·643 Å, and links the molecules into infinite ribbons parallel to the crystallographic *a* axis. This length is within the range 2·56 to 2·69 Å tabulated by Donohue (1968) for hydrogen bonds between a carboxylic OH donor and a carboxylic carbonyl oxygen acceptor. The angle O(2)–H(1)···O(3) is 178 (2)°.

The second is the intramolecular hydrogen bond between atoms O(1) and O(4) which is confirmed as asymmetric, in agreement with the results of Hechtfischer, Steigemann & Hoppe (1970) in their study of a tricyclic alkene *cis*-dicarboxylic acid. The inter-oxygen distance, 2·502 Å, is not particularly short in comparison with the similar linkages in the monoanionic forms of maleic acid (see Table 5). Angle O(4)–H(4)···O(1) is 171 (2)° and indicates that H(4) is not exactly on the line between the two oxygen atoms. This observation is only marginally significant.

Table 4. *A results summary for the least-squares planes calculations of maleic acid*

(*a*) Distances from the planes (Å × 10^4)

	I	II	III	IV
C(1)	13*	7*	−44*	−132
C(2)	106*	−19*	14*	−139
C(3)	154*	19*	−248	−16*
C(4)	23*	−9*	−776	57*
O(1)	332*	438	16*	361
O(2)	−275*	−307	12*	−539
O(3)	−91*	−155	−1129	−21*
O(4)	−190*	−97	−1089	−14*
H(1)	−83	−31	207	−269
H(2)	−549	−759	−402	−938
H(3)	1033	805	667	767
H(4)	593	696	−103	723

* Atoms used to define the plane.

(*b*) Equations of the form $1x+my+nz-p=0$ and χ^2 values for the planes

Plane	l	m	n	p	χ^2
I	−0·0001	0·0046	−1·0000	−1·5723	2538·1
II	0·0034	−0·0046	−1·0000	−1·5830	7·4
III	0·0179	0·0257	−0·9995	−1·3802	23·8
IV	−0·0018	0·0097	−1·0000	−1·6191	34·9

(*c*) Dihedral angles between the planes (°)

Plane	I	II	III	IV
I	0	1·926	0·417	0·939
II		0	2·322	0·0
III			0	2·267
IV				0

(*d*) *Least-squares planes and torsion angles*

Table 4 contains the results from the least-squares planes calculations for maleic acid. Plane I in Table 4 shows that the non-hydrogen atoms do not constitute a good plane ($\chi^2 = 2538$). There are, however, three planar regions of this molecule defined by planes II, III and IV, *viz.* the four carbon atoms and the two carboxyl groups. The torsion angle between planes II and IV is essentially 0° whereas that between planes II and III is 2·32°. Whether or not this distortion from coplanarity of the entire molecule is a molecular characteristic or due to the packing cannot be ascertained. It does appear, however, that deviations from coplanarity are the rule rather than the exception for maleic acid/maleate ion systems.

(*e*) *Molecular packing*

The molecular packing viewed down the *c** axis is shown in Fig. 4. The infinite ribbons of molecules parallel to the *a* axis pack together edge to edge forming sheets. This layer structure explains the extremely facile cleavage of the crystals parallel to (001) as well as the extraordinarily large intensity and extinction associated with reflexion 002 (Yardley, 1925). The separation of the molecular layers, 3·144 Å, is relatively small in comparison with stacking interactions between aromatic molecules (Prout & Wallwork, 1966; Bugg, Thomas, Sundaralingam & Rao, 1971). It is clear that the maleic acid molecule is not aromatic but does contain π electron density and polarized multiple bonds. Although the interlayer separation is much shorter than the stacking distance in aromatic molecules, the interlayer attractive forces are not necessarily as strong in

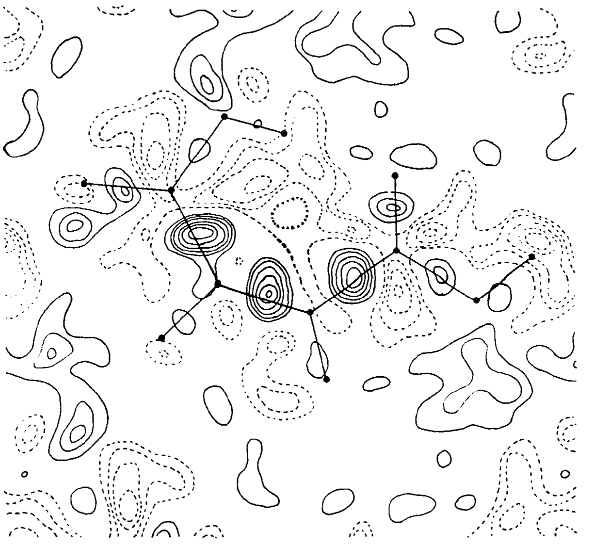


Fig. 5. A section of the final difference electron density map through the mean molecular plane. Contours start at ±0·05 e Å^{-3} and are in equal increments of this value.

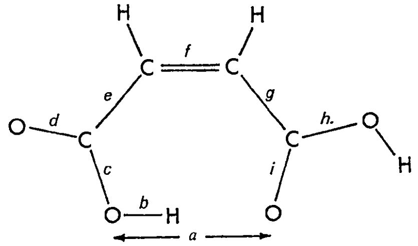
maleic acid because of the facile cleavage parallel to (001).

(*f*) *Residual electron density*

The section $z=\frac{1}{4}$ through the molecular plane of the final difference synthesis is shown in Fig. 5. The estimated standard deviation of difference electron density (Cruickshank, 1967) is 0·032e Å^{-3}. The contour level on this map starts at 1·5σ and the most important features are approximately 5–10 times the standard deviation. The bonding electron densities in the three carbon–carbon bonds are the most prominent positive peaks on the map and are extended perpendicular to the molecular plane. The regions of charge deficiency are mainly concentrated near carbon atoms C(1) and C(4) opposite to the three bonding directions for these two atoms. Similar features to the above have been described by others in more sophisticated analyses

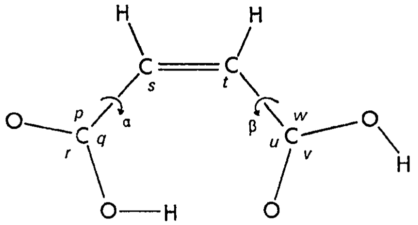
Table 5. *A summary of the molecular geometry for maleic acid/maleate ion species*

(*a*) Distances



Compound	*a*	*b*	*c*	*d*	*e*	*f*	*g*	*h*	*i*	Ref.*
Maleic acid	2·502 (1)	0·91 (2)	1·304 (2)	1·218 (2)	1·488 (2)	1·337 (2)	1·475 (2)	1·300 (2)	1·222 (1)	
Tricyclic alkene 1	2·472 (3)	0·78 (5)	1·297 (4)	1·225 (4)	1·492 (3)	1·349 (4)	1·485 (4)	1·300 (3)	1·221 (3)	*a*
Tricyclic alkene 2	2·512 (3)	1·03 (4)	1·305 (2)	1·219 (2)	1·503 (3)	1·344 (4)	1·487 (2)	1·310 (2)	1·225 (2)	
Weighted mean	2·500 (1)	0·92 (2)	1·304 (1)	1·219 (1)	1·492 (1)	1·340 (2)	1·481 (1)	1·304 (1)	1·222 (1)	
Bromphen HMal	2·417 (4)	1·08 (5)	1·292 (6)	1·209 (6)	1·497 (7)	1·329 (7)	1·481 (6)	1·230 (6)	1·265 (6)	*b*
Chlorphen HMal	2·444 (4)	0·87 (3)	1·280 (4)	1·209 (4)	1·489 (5)	1·331 (5)	1·486 (4)	1·236 (4)	1·266 (4)	*c*
KHMal	2·437 (4)	1·22 (4)	1·284 (3)	1·235 (3)	1·498 (3)	1·348 (4)	1·498 (3)	1·235 (3)	1·284 (3)	*d*
KHClMal	2·411 (3)	1·207 (5)	1·284 (3)	1·230 (2)	1·524 (2)	1·349 (3)	1·512 (2)	1·244 (2)	1·288 (3)	*e*
cis-Aconitate	2·425 (2)	1·13 (7)	1·291 (2)	1·235 (2)	1·485 (2)	1·345 (2)	1·519 (2)	1·230 (2)	1·287 (2)	*f*
Weighted mean	2·425 (1)		1·287 (1)	1·230 (1)	1·502 (1)	1·344 (1)	1·509 (1)	1·236 (1)	1·283 (1)	
Na_2Mal	3·151 (1)		1·293 (1)	1·281 (1)	1·506 (1)	1·336 (1)	1·495 (1)	1·250 (1)	1·264 (1)	*g*
Li_2Mal	2·999 (2)		1·273 (2)	1·252 (2)	1·505 (3)	1·330 (3)	1·495 (3)	1·252 (2)	1·277 (2)	*h*

(*b*) Angles



Compound	*p*	*q*	*r*	*s*	*t*	*u*	*v*	*w*	*α*	*β*	Ref.*
Maleic acid	119·8 (1)	121·4 (1)	118·9 (1)	131·6 (1)	128·2 (1)	125·1 (1)	122·6 (1)	112·3 (1)	0·0	2·3	
Tricyclic alkene 1	118·8 (3)	121·4 (3)	119·7 (2)	131·1 (3)	127·3 (2)	124·9 (3)	121·4 (3)	113·7 (2)	5·1	4·0	*a*
Tricyclic alkene 2	119·0 (2)	120·6 (1)	120·4 (1)	130·5 (2)	127·3 (2)	124·2 (1)	122·3 (1)	113·5 (1)	17·7	19·5	
Weighted mean	119·6 (1)	121·0 (1)	119·7 (1)	131·4 (1)	127·9 (1)	124·7 (1)	122·4 (1)	113·0 (1)			
Bromphen HMal	118·6 (5)	119·3 (4)	122·1 (5)	131·0 (5)	130·2 (5)	119·9 (4)	123·2 (5)	116·9 (4)	8·4	6·7	*b*
Chlorphen HMal	118·8 (4)	120·3 (3)	120·9 (4)	131·5 (3)	129·3 (5)	120·0 (3)	123·4 (3)	116·7 (3)	1·5	7·4	*c*
KHMal	117·0 (3)	120·3 (3)	122·7 (3)	130·4 (2)	130·4 (2)	120·3 (3)	122·7 (3)	117·0 (3)	0·0	0·0	*d*
KHClMal	118·6 (2)	118·0 (1)	123·3 (2)	130·6 (1)	129·5 (1)	120·3 (2)	122·7 (2)	117·0 (2)	8·5	9·0	*e*
cis-Aconitate	117·1 (2)	120·9 (1)	122·0 (2)	132·9 (2)	126·9 (1)	119·6 (1)	121·7 (2)	118·7 (1)	12·5	7·1	*f*
Weighted mean	117·8 (1)	119·5 (1)	122·5 (1)	131·0 (1)	128·5 (1)	119·8 (1)	122·5 (1)	118·0 (1)			
Na_2Mal	113·2 (1)	120·6 (1)	126·1 (1)	129·5 (1)	126·5 (1)	118·6 (1)	125·2 (1)	116·2 (1)	66·3	−16·9	*g*
Li_2Mal	116·8 (2)	119·1 (2)	124·1 (2)	127·4 (2)	125·1 (2)	119·2 (2)	123·5 (2)	117·3 (2)	81·4	7·0	*h*

* (*a*) Hechtfischer *et al.* (1970). (*b*) James & Williams (1971). (*c*) James & Williams (1974*a*). (*d*) Darlow & Cochran (1961). (*e*) Ellison & Levy (1965). (*f*) Glusker *et al.* (1972). (*g*) James & Williams (1974*b*). (*h*) Town & Small (1973).

(*e.g.* Hirshfeld, 1971; O'Connell, Rae & Maslen, 1966; Coppens & Vos, 1971).

Bonding electron density that is displaced from the internuclear line has been observed in *cis*-1,2,3-tricyanocyclopropane (Hartman & Hirshfeld, 1966). In their case, the density lay outside the strained ring system. In the present molecule, the three maxima between the carbon atoms are all displaced towards the molecular centre and occur at the position where sp^2-hybridized orbitals would be expected to overlap. The angles between these maxima and the atomic positions are 120°, as measured from a large-scale version of the map. Even though the internuclear angles are approximately 10° larger than 120° because of the molecular strain, it appears that the orbital directions at sp^2 carbon atoms are retained.

Fig. 5 also shows that the residual electron density in the carbon–oxygen bonds is lower than that in the carbon–carbon bonds. This phenonemon has been described previously (Hanson, Sieker & Jensen, 1973; James & Matsushima, 1973; Delbaere & James, 1973). A simplified explanation for this observation could be that the relatively high electronegativity of oxygen atoms contracts the valence electron cloud making it more closely approximate the spherical atom model used.

(*g*) *Comparison with other maleic acid systems*

Table 5 contains a summary of the bond distances and angles for the maleic/maleate systems thus far reported. Certain consistencies and trends may be noted. In all these systems, the C=C double-bond length is normal and it is thought that little π-electron delocalization occurs in any of them. In only two of these eight structures is the intramolecular hydrogen bond symmetrical. The intramolecular hydrogen bond length contracts on removal of the first base-dissociable proton and it appears that the position of the minimum of the potential well shifts towards the centre of the $O–H\cdots O$ contact in agreement with an earlier deduction (Coulson, 1961).

The internal C=C–C angles are consistently greater than 120° and that angle involving the carboxyl group bearing the intramolecular hydrogen bonded hydrogen atom is always the larger. This discrepancy between the two angles is found even when the intramolecular hydrogen bond does not exist as in the di-ionized species Na_2Mal and Li_2Mal.

When the first base-dissociable proton is removed, bonds h and i interchange their bond orders. Thus bonds c and i assume a more similar character providing a more equal bonding potential for the internal proton.

In those cases where packing interactions are thought to be small, the torsional angles α and β in both the maleic acid and monoanionic maleates are not large. However in the diionized forms Li_2Mal and Na_2Mal ionic repulsions between the carboxylates cause a large rotation of one from the mean plane of the carbon atoms.

This paper is abstracted from the Ph.D. thesis of G.J.B.W., who thanks the University of Alberta for financial support. Mr L. Goulden did most of the photography for the diagrams. The crystallographic programs of Ahmed *et al.* (1966) were used in this study. Financial support, grant MA-3406 to M.N.G.J. from the Medical Research Council of Canada, is gratefully acknowledged.

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The Crystal and Molecular Structure of Disodium Maleate Monohydrate

By M. N. G. James and G. J. B. Williams*

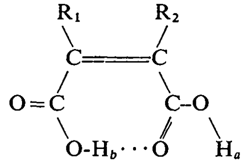
Department of Biochemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2E1

(*Received* 19 *November* 1973; *accepted* 16 *January* 1974)

Disodium maleate monohydrate crystallizes from DMSO/H_2O in the form of thick plates. The space group is $C2/c$ and the cell dimensions are $a=20{\cdot}979$ (4), $b=10{\cdot}004$ (3), $c=6{\cdot}369$ (1) Å, $\beta=100{\cdot}15$ (1)°. Diffractometer data to $2\theta=80°$ (Mo $K\alpha$) were collected. The structure was solved by symbolic addition and refined by full-matrix least-squares methods to final weighted and unweighted R values of 0·048 and 0·033 respectively. The four atoms of the carbon spine are nearly coplanar. One carboxylate ion is twisted by 66·0° about its C–C bond and the other is rotated −16·9°. Bond lengths within and between the carboxyl groups are dissimilar. Both sodium ions have five oxygen atoms as coordinators in a distorted square-pyramidal arrangement. The water molecule links the organic di-ions together in a hydrogen-bonded helical array. A comparison is made with the recently reported structure of Li_2 maleate.$2H_2O$.

Introduction

The conformation adopted by a *cis*-dicarboxylic alkene structural unit (I) represents a compromise between the attractive forces arising from the presence of an intramolecular hydrogen bond and the repulsions which are engendered by the unusual shortness of the O–H···O linkage.



(I)

(*a*) $R_1=R_2=H$: maleic acid.
(*b*) R_1, $R_2\cdots C_6H_8$: bicyclo[2,2,2]octa-2,5-diene-2,3-dicarboxylic acid.
(*c*) $R_1=R_2=H$, H_a absent: maleate monoanion.
(*d*) $R_1=H$, $R_2=Cl$, H_a absent: chloromaleate monoanion.
(*e*) $R_1={}^-OOCCH_2$, $R_2=H$, H_a absent: *cis*-aconitate dianion.
(*f*) $R_1=R_2=H$, H_a, H_b absent: maleate di-anion.

In the fully protonated forms I(*a*) (Shahat, 1952; James & Williams, 1974*b*) and I(*b*) (Hechtfischer, Steigemann & Hoppe, 1970) the internal angles of the quasi-cyclic system are considerably opened, the internal hydrogen bond is asymmetric and the carboxyl groups are slightly twisted out of the plane of the double bond. The maleate monoanion has been shown to have its internal bond angles similarly opened and the carboxyl groups similarly twisted so that the two central oxygen atoms are on the same side of the plane of the carbon atoms. A central position for the hydrogen atom of the internal hydrogen bond has been demonstrated in two cases (Ellison & Levy, 1965; Darlow & Cochran, 1961) and implied in one other (Glusker, Orehowsky, Casciato & Carrell, 1972). The results of Darlow and Cochran on potassium hydrogen maleate have been confirmed at a higher precision by a recent refinement based on diffractometer data by Dr P. W. Codding in this laboratory. That intermolecular interactions are important in determining whether or not the internal hydrogen bond is symmetric is demonstrated by the fact that short but definitely asymmetric hydrogen bonds have been found in two further structural studies of the maleate monoanion (James & Williams, 1971; 1974*a*). The only unequivocal demonstration of a centred hydrogen bond in the unsubstituted hydrogen maleate anion is that of Darlow and Cochran. However this ion is present in the crystals in a symmetric environment and the space-group symmetry of the environment creates the centred hydrogen bond, *cf.* brom-

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* Present address: Department of Chemistry, Brookhaven National Laboratory, Upton, Long Island, New York, 11973, U.S.A.