The Crystal Structure of 5-Halogeno-2-phthalimidobenzoic Acid Monohydrate

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The crystal structures of the isomorphous 5-iodo- and 5-bromo-2-phthalimidobenzoic acid mono-hydrates ($C_{15}H_8NO_4I.H_2O$ & $C_{15}H_8NO_4Br.H_2O$) have been determined by two-dimensional Fourier methods. The space group is $P\bar{1}$ with two molecules in the unit cell. The use of generalized and modulus projections based on $hk\bar{l}$ reflexions led to the solution of the structure. A suspected ring closure was found not to occur. In addition, the molecule of water, not initially revealed by chemical analysis, was identified.

Introduction

From certain chemical experiments (Lamchen, 1961), the accepted structure (*A*) of 2-phthalimidobenzoic acid was considered unlikely. The alternative structures (*B*) and especially (*C*) were thought to be more in accordance with the results obtained. To allow a direct structure determination to be undertaken, both an iodine and a bromine derivative were prepared in which the halogen atom had most probably been substituted at the position indicated.

(*A*)

(*B*)

(*C*)
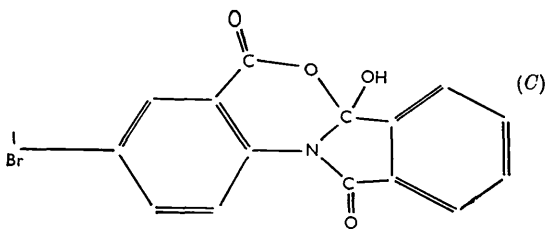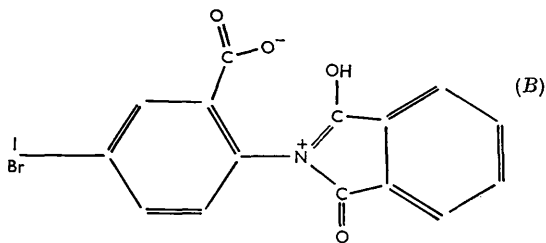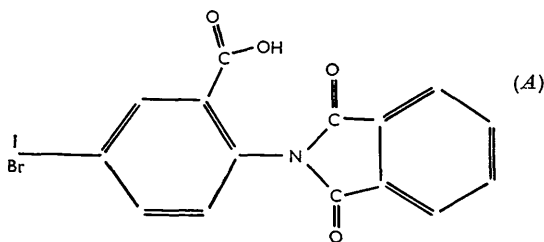
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Experimental

Crystals of the two compounds were obtained in the form of colourless needles from dilute solutions in ethyl alcohol. X-ray oscillation and Weissenberg photographs showed them to be triclinic with the shortest crystal axis parallel to the needle axis. The unit cells chosen were such that *a* and *b* had the shortest translations in real space. The directions of the **a**, **b** and **c** axes were chosen so as to make the cell angles in real space obtuse. This fixed the unit cells (Table 1) uniquely.

Table 1. *Crystal data*

	$C_{15}H_8NO_4I.H_2O$	$C_{15}H_8NO_4Br.H_2O$
a	$11{\cdot}06 \pm 0{\cdot}05$ Å	$10{\cdot}91 \pm 0{\cdot}05$ Å
b	$11{\cdot}29 \pm 0{\cdot}05$ Å	$11{\cdot}15 \pm 0{\cdot}05$ Å
c	$6{\cdot}42 \pm 0{\cdot}03$ Å	$6{\cdot}42 \pm 0{\cdot}03$ Å
α	$104° \ 55' \pm 20'$	$106° \ 24' \pm 30'$
β	$105° \ 49' \pm 20'$	$102° \ 35' \pm 30'$
γ	$97° \ 37' \pm 20'$	$97° \ 30' \pm 30'$
D_m	$1{\cdot}86 \pm 0{\cdot}02$ g.cm^{-3}	$1{\cdot}70 \pm 0{\cdot}02$ g.cm^{-3}
D_x	$1{\cdot}88$ g.cm^{-3}	$1{\cdot}69$ g.cm^{-3}

Since no computer was available when this work was started, it was necessary to proceed by two-dimensional methods.

Crystals, close to the optimum size, having the following cross-sections were used:

Br $\quad 0{\cdot}33 \times 0{\cdot}10$ mm^2

I $\quad 0{\cdot}10 \times 0{\cdot}06$ mm^2.

The $hk0$ intensities for both derivatives were measured from multiple-film Weissenberg photographs with Cu $K\alpha$ radiation. Because the shape of the spots on the bromine films was poor, the analysis was concentrated on the iodine derivative. The $hk\bar{l}$ intensities for this compound were obtained from equi-inclination Weissenberg photographs.

The intensities were estimated visually. For the first-layer spectra, only the peak intensities of the elongated spots were measured and subsequently a correction for the elongation (a geometrical factor) was made (Phillips, 1956). For this purpose, two sets

of films were needed to cover the reciprocal-lattice section. The number of observed intensities and the total number of intensities within the limiting sphere for each layer are given in Table 2.

Table 2. *Observed intensities*

Layer	n_{obs}	n_{total}
Br $(hk0)$	212	293
I $(hk0)$	198	290
I $(hk\bar{1})$	496	590

Since the linear absorption coefficients were high ($\mu_{Br} = 44$ cm^{-1} and $\mu_{I} = 193$ cm^{-1}), absorption corrections were applied to the intensities. Albrecht's (1939) method was used and the graphical aids suggested by Rogers & Moffet (1956) speeded up the calculations considerably. The correction factor was calculated as a function of the rotation angle for several values of $\xi = 2 \sin \theta$, and the results were contoured on the actual Weissenberg photograph scale. The ratios of the maximum to the minimum correction factor were 1·7 and 1·4 for the iodine and bromine derivatives respectively. Because the equi-inclination angle was small ($\mu = 7°$), the absorption corrections did not vary rapidly with μ and it was therefore assumed that the correction factors for the first and zero layers were the same.

Wilson plots were used to put the intensities on an approximately absolute scale. A statistical survey of the intensities gave an $N(z)$ distribution favouring the theoretical curve for a centrosymmetric structure (Howells, Phillips & Rogers, 1950), especially when allowance was made for the predominant heavy atoms (Sim, 1958). Since there were two molecules in the unit cell, it was assumed that the space group was $P\bar{1}$.

In the structure-factor calculations, the atomic form factors employed were those of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) for carbon, nitrogen and oxygen and those of Thomas & Umeda (1957) for bromine and iodine.

Structure determination

hk0 projections

The $hk0$ Patterson projections confirmed that the two compounds were isomorphous, the halogen atom having (x, y) coordinates equal to $(0·125, 0·116)$. Isomorphous replacement was used to determine the phases in the first instance. Since the halogen atom was almost in the position $x \approx y \approx \frac{1}{8}$, its contribution to some structure factors was small. Only 70% of the signs could be determined with any certainty and the corresponding electron-density projections showed too much false detail to be interpreted.

A survey of the $hk0$ Patterson function was then undertaken to see if any additional information could be obtained. This included the use of the Buerger minimum function (Buerger, 1959) and the difference Patterson function. The modified Patterson projection

(White & Clews, 1956) proved to be more successful. Iodine $F^2(hk0)$ terms having $\sin \theta < 0·3$ were omitted to strengthen the scattering power of the iodine atom relative to the light atoms. A Patterson projection, computed with the use of the remaining terms, was considerably sharper than the normal Patterson projection. The modified Patterson projection was vector shifted and the Buerger minimum function drawn. The resulting map was an improvement on the initial projection and gave some indication of possible atom sites.

Iodine hk̄1 projection

Generalized and modulus projections used in conjunction have much greater power than the normal zero-layer projections because of the possibility of obtaining all three coordinates (Buerger, 1960). The resolving power of the generalized electron-density projection is also usually greater (Phillips, 1954).

The components of the generalized Patterson projection, $_cP_{\bar{1}}$ and $_sP_{\bar{1}}$, defined by

$$_cP_{\bar{1}} = \frac{1}{A} \sum_{hk} F^2(hk\bar{1}) \cos 2\pi(hx + ky)$$

$$_sP_{\bar{1}} = -\frac{1}{A} \sum_{hk} F^2(hk\bar{1}) \sin 2\pi(hx + ky)$$

gave the z coordinate of the iodine atom as (0·317). The modulus Patterson projection

$$|P_{\bar{1}}| = \sqrt{(_cP_{\bar{1}}^2 + _sP_{\bar{1}}^2)}$$

resembled the modified, rather than the normal, $hk0$ Patterson projection.

The heavy-atom method was used to allocate the signs of $F(hk\bar{1})$. Owing to the addition of the third coordinate of the heavy atom, no less than 90% of the phases could be determined, of which 95% proved to be correct. The components of the complex generalized electron-density projection

$$\varrho_{\bar{1}} = _c\varrho_{\bar{1}} + i_s\varrho_{\bar{1}}$$

were then calculated. From these, the modulus projection $|\varrho_{\bar{1}}|$ was obtained, which was more promising than the corresponding $hk0$ projection. With the aid of the component projections, a model was made of all the likely atomic sites and the approximate position of the molecule was derived.

Initial refinement

Initial refinement began on the $hk0$ data using Fourier and difference Fourier syntheses. Structure factors were calculated by the use of 3° Beevers–Lipson strips (Beevers & Lipson, 1951). Successive syntheses indicated that individual temperature factors were necessary, viz. $B = 3$ Å^2 for the light atoms and $B = 5$ Å^2 for the heavy atom.

The third difference Fourier synthesis showed the position of the oxygen atoms to be such that they

could not close the ring in structure (C). This structure could not therefore be the correct one. The atoms were then placed according to the available evidence without reference to any particular assumed structure. The residual $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ was 25% for the iodine compound and 36% for the bromine compound. The corresponding Fourier and difference Fourier syntheses both suggested that a molecule of water was also present. This was later confirmed by chemical analysis of the crystals used in the investigation; the initial chemical analysis had been carried out, however, on dried crystals.

Final refinement

The final stages of the refinement were carried out on the STANTEC ZEBRA computer of the C.S.I.R. using the diagonal approximation of the least squares (Schoone, ZK 22). Successive cycles reduced the residual factor to 15% for the iodine data and to 25% for the bromine data. Difference syntheses suggested considerable anisotropic motion of both halogen atoms. Splitting the heavy atom into two atoms of half weight placed 0·2 Å apart (Vos & Smits, 1961), reduced each R value by another 3%. One refinement cycle, including the temperature factors, reduced the residuals to 9·6% and 17% for the iodine and bromine structure factors respectively.

The resulting (x, y) coordinates were used to calculate approximate z coordinates. First, the two sets of $(hk\bar{l})$ reflexions were put on a common scale by

Table 3. *Atomic parameters for iodine derivative*

Atom	x/a	y/b	z/c	B
C1	0·8875	0·2517	0·733	4·0 Å²
C2	0·7632	0·2009	0·595	3·5
C3	0·7508	0·1222	0·372	5·3
C4	0·8496	0·1039	0·295	5·0
C5	0·9753	0·1459	0·467	4·3
C6	0·9974	0·2260	0·672	4·4
C7	0·9147	0·3273	0·955	3·6
C8	0·5900	0·3152	0·627	3·5
C9	0·4906	0·3159	0·760	4·0
C10	0·4071	0·3927	0·782	4·0
C11	0·3306	0·3735	0·910	4·4
C12	0·3370	0·2814	1·002	4·8
C13	0·4160	0·1986	0·977	4·9
C14	0·4915	0·2182	0·840	4·6
C15	0·5939	0·1532	0·750	3·9
N16	0·6546	0·2184	0·671	4·1
O17	0·6275	0·0636	0·830	4·7
O18	0·6260	0·3950	0·561	4·4
O19	0·8200	0·3593	1·024	4·6
O20	1·0263	0·3663	1·064	4·9
O21	0·8525	0·4898	0·472	4·6
I22	1·1308	0·0999	0·3364	5·4
I22	1·1397	0·1219	0·3380	5·4

calculating structure factors for each set and using the scale factors so obtained. Successive refinements of the positional parameters reduced R to 16%. From a comparison between the Fourier and least-squares z coordinates, a final set of z coordinates was

adopted. With one refinement cycle of the temperature factors, this set of coordinates (Table 3) gave a final residual of 13% (observed reflexions only).

Discussion

The atomic maxima of the iodine $hk\bar{l}$ modulus projection (Fig. 1) were more clearly resolved than in the corresponding $hk0$ projection owing in part to the larger number of reflexions with high $\sin \theta$. Final difference syntheses on the $hk0$ data were clean, showing that all the atoms had been correctly placed. Splitting the heavy atom into two did not compensate completely for its anisotropic vibration.
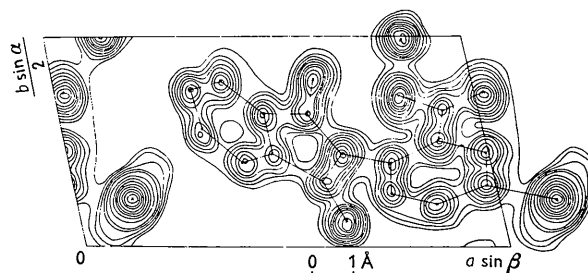
Fig. 1. Iodine $hk\bar{l}$ modulus electron-density projection. Contour intervals = 1 e.Å⁻² starting at 2 e.Å⁻², except that for I atom contour intervals = 2 e.Å⁻² and 10 e.Å⁻² above 10 e.Å⁻².

Fig. 2. Inter-atomic distances (Å) of iodine derivative.

The interatomic distances (Fig. 2) are within the range expected, taking into account the inaccuracies in the determination of the z coordinates. Cruickshank's (1960) formula gives the estimated standard

Table 4. *Direction cosines of best planes with respect to axes* a*, c ∧ a* *and* c

Plane 1 contains atoms 1–7, 16, 19, 20 and 22
Plane 2 contains atoms 8–18

	Plane 1	Plane 2
L	+0·010	+0·693
M	+0·813	+0·445
N	−0·582	+0·568
D	−0·131	+5·989

Table 5. *Observed and calculated structure factors for iodine derivative*

To put F_o and F_c on an absolute scale, divide by 5

0k0

K	Fo	Fc
1	271	278
2	214	-234
3	190	-180
4	465	-453
5	197	-222
6	91	-90
7	53	-80
8	126	138
9	107	93
10	50	45

1k0

K	Fo	Fc
0	251	226
1	183	233
2	85	-92
3	334	-341
4	229	-281
5	164	-164
6	98	112
7	136	125
8	132	140
9	75	81
12	27	-27
-1	244	203
-2	351	339
-3	18	15
-4	116	-133
-5	282	-315
-6	232	-209
-7	135	-142
-8	85	112
-9	76	83
-10	38	21
-11	60	62
-12	27	34

2k0

K	Fo	Fc
0	50	67
1	182	-251
2	599	-599
3	225	-262
4	60	-62
5	95	106
6	149	169
7	135	126
8	22	23
10	53	-60
11	42	-48
-1	114	104
-2	490	393
-3	477	470
-4	160	149
-6	109	-128
-7	158	-163
-8	97	-95
-10	42	43

3k0

K	Fo	Fc
0	204	-241
1	294	-311
2	292	-301
4	148	167
5	242	296
6	96	60
7	71	77
9	75	-70
10	42	-48
11	42	-46
-1	131	-121
-2	114	113
-3	424	370
-4	124	153
-5	229	248
-7	123	-136
-8	146	-156
-9	121	-132
-10	38	-43
-11	38	52
-12	47	43

4k0

K	Fo	Fc
0	499	-485
1	156	-164
3	101	91
4	160	164
5	191	206
6	71	70
8	99	-74
9	47	-36
-1	227	-223
-2	356	-324
-3	87	113
-4	320	297
-5	255	225
-6	185	181
-8	85	-85
-9	38	-19
-10	89	-109

5k0

K	Fo	Fc
0	18	00
1	24	30
2	239	250
3	149	153
4	71	53
5	33	35
6	80	-97
7	75	-75
8	42	-32
-1	228	-230
-2	296	-303
-3	111	-112
-4	68	-65
-5	293	279
-6	261	270
-7	96	84
-9	57	-66
-10	66	-77
-11	42	-49

6k0

K	Fo	Fc
0	139	157
1	204	197
2	203	213
3	121	140
5	87	-85
6	62	-80
7	65	-74
-1	163	-168
-2	231	-237
-3	214	-244
-4	107	-114
-6	52	54
-7	73	65
-8	125	130
-9	50	53
-11	27	-32

7k0

K	Fo	Fc
0	175	169
1	89	92
2	116	114
3	68	-64
4	126	-108
5	95	-99
6	42	-38
8	50	32
-1	154	163
-3	197	-204
-4	161	-147
-5	164	-149
-7	71	67
-8	107	131
-9	68	61

8k0

K	Fo	Fc
0	190	197
1	65	68
2	38	-31
3	112	-96
4	57	-50
5	42	-52
8	33	37
9	19	24
-1	170	173
-2	67	71
-3	33	-51
-4	98	-98
-5	111	-106
-6	91	-72
-7	47	-58
-9	53	48
-10	63	64

9k0

K	Fo	Fc
2	68	-68
3	82	-63
4	42	-38
8	19	22
-1	85	94
-2	50	31
-3	68	51
-4	100	94
-5	89	-69
-6	124	-118
-7	57	-40
-8	27	-27
-9	27	24
-10	33	33
-11	33	24

10k0

K	Fo	Fc
0	33	-37
1	112	-86
2	57	-46
5	38	40
6	30	16
-3	142	152
-4	78	85
-7	71	-61
-8	71	-63
-9	27	-19

11k0

K	Fo	Fc
0	91	-76
1	27	-43
-1	47	-38
-3	47	53
-4	75	61
-5	57	49
-8	47	-54
-9	47	-36

12k0

K	Fo	Fc
3	27	22
4	19	18
-1	63	-56
-2	65	-58
-5	19	37
-6	50	47

13k0

K	Fo	Fc
-1	19	-18
-2	27	-29
-3	27	-28

0k1̄

K	Fo	Fc
0	179	-219
1	388	-357
2	325	309
3	938	818
4	204	235
5	29	27
6	210	-207
7	217	-247
8	141	-151
9	42	-37
10	11	-35
11	69	81
12	82	66
13	13	14
-1	164	-152
-2	512	-516
-3	65	49
-4	45	-36
-5	253	266
-6	262	274
-7	113	87
-8	09	5
-9	42	-61
-10	50	-62
-11	22	-10
-12	24	-44

1k1̄

K	Fo	Fc
0	173	160
1	277	327
2	243	294
3	603	624
4	120	110
5	196	-191
6	188	-186
7	124	-146
8	84	-93
9	25	33
10	59	47
11	34	23
12	25	20
13	9	7
-1	293	-295
-2	427	-415
-3	310	-303
-4	306	-320
-5	121	130
-6	135	118
-7	105	100
-8	55	75
-9	30	40
-10	24	-39
-11	29	-27
-12	14	-9
-13	8	-5

2k1̄

K	Fo	Fc
0	361	375
1	326	379
2	31	-34
3	23	-31
4	197	-203
5	200	-248
6	86	-95
7	72	-78
8	69	85
9	69	85
10	68	63
11	35	44
13	15	-32
-1	41	-8
-2	67	56
-3	256	-280
-4	198	-256
-5	56	-60
-6	72	-100
-7	56	73
-8	142	121
-9	93	103
-10	49	60
-12	24	-40
-13	23	-26

3k1̄

K	Fo	Fc
0	477	519
1	69	71
2	28	-23
3	258	-321
4	149	-194
5	268	-287
6	49	-60
7	102	120
8	95	109
9	62	39
11	13	-14
13	11	-15
-1	580	507
-2	295	251
-3	105	87
-4	232	-230
-5	354	-360
-6	117	-96
-7	69	-86
-8	49	60
-9	74	59
-10	37	34
-11	34	47
-13	11	-20

4k1̄

K	Fo	Fc
0	178	159
1	262	-271
2	135	-179
3	144	-204
4	87	-122
5	38	55
6	68	67
7	100	94
8	108	125
9	22	7
-1	134	133
-2	390	-343
-3	235	206
-4	54	41
-5	146	-146
-6	247	-210
-7	218	-204
-8	42	-33
-9	34	41
-10	72	73
-11	51	40
-12	28	43

5k1̄

K	Fo	Fc
0	223	-236
1	286	-330
2	224	-281
3	146	-164
4	24	30
5	170	165
6	152	122
7	48	39
9	25	-28
10	49	-38
11	33	5
-1	29	45
-2	381	383
-3	402	363
-4	158	135
-5	18	-11
-6	41	-17
-7	141	-149
-8	101	-82
-9	63	-62
-10	7	3
-11	45	63
-12	21	25

6k1̄

K	Fo	Fc
0	158	-145
1	238	-240
2	61	-72
3	144	163
4	97	113
5	153	133
6	45	35
8	35	-38
9	40	-42
-1	34	-35
-2	125	-115
-3	20	-40
-4	217	193
-5	208	173
-6	89	83
-7	78	-85
-8	122	-103
-9	98	-89
-10	18	-15
-13	3	12

7k1̄

K	Fo	Fc
0	264	-251
2	88	103
3	116	145
4	88	93
5	106	116
6	21	-16
7	49	-43
8	57	-57
9	35	-41
11	4	24
-1	288	-246
-2	195	-155
-3	64	-62
-4	59	58
-5	263	228
-6	90	74
-7	68	56
-9	30	-25
-10	47	-48
-11	35	-31
-12	13	-24

8k1̄

K	Fo	Fc
0	81	-89
1	49	62
2	144	144
3	110	119
4	29	37
5	52	-50
6	52	-45
7	52	-43
8	25	-31
-1	39	-28
-2	204	-155
-3	125	-117
-4	23	-26
-5	21	24
-6	159	140
-7	153	141
-8	23	8
-10	27	-39
-11	43	-44
-12	24	-33

9k1̄

K	Fo	Fc
0	128	89
1	56	39
2	90	109
3	39	44
4	21	-16
5	49	-33
6	74	-68
7	19	-7
8	15	23
9	10	-16
-1	16	29
-2	72	-58
-3	116	-100
-4	154	-131
-5	40	-40
-7	30	31
-8	66	52
-9	38	37
-10	10	16
-11	5	-4
-12	7	-17

10k1̄

K	Fo	Fc
0	146	122
1	21	-19
2	48	-60
3	59	-53
4	32	-16
5	197	152
6	67	-64
-1	78	-46
-2	138	-109
-4	44	-28
-6	34	31
-8	88	68
-10	34	38

11k1̄

K	Fo	Fc
0	69	51
2	34	-26
3	75	-46
4	58	-42
5	17	-31
6	8	12
-1	62	53
-2	107	79
-3	56	52
-4	16	-24
-5	87	-79
-6	68	-43
-7	55	-49
-9	24	27
-10	19	19

12k1̄

K	Fo	Fc
0	16	15
1	75	-63
2	49	-41
3	16	-3
5	7	22
-1	24	22
-2	49	34
-3	66	53
-4	20	15
-6	48	-38
-7	58	-43
-8	30	-12
-9	8	-8

13k1̄

K	Fo	Fc
0	55	-44
1	35	-24
2	20	-26
-2	18	15
-3	41	35
-4	45	36
-5	9	-8
-6	8	15
-7	5	-3

1k1̄

K	Fo	Fc
0	512	-568
1	96	-104
2	116	101
3	673	585
4	64	67
5	192	197
6	151	133
7	32	-62
8	92	-77
9	126	-127
10	57	-53
11	30	62
13	14	17
-1	763	-852
-2	44	-54
-3	167	200
-4	118	131
-5	232	237
-6	110	112
-8	74	-49
-9	67	-35
-10	29	-34
-11	34	-34
-12	19	23

2k1̄

K	Fo	Fc
0	119	-155
1	688	-612
2	164	-111
3	121	-111
4	132	129
5	329	322
6	220	220
7	83	52
8	62	-66
9	59	-41
10	85	-74
11	5	-4
-1	261	296
-2	58	58
-3	146	154
-4	274	246
-5	62	49
-6	17	1
-7	122	-129
-8	135	-115
-9	67	-49

3k1̄

K	Fo	Fc
0	86	-99
1	313	-323
2	409	-380
3	426	-350
4	76	-66
5	12	18
6	184	200
7	182	169
8	128	124
10	27	-24
11	33	-28
12	31	-48
-1	70	110
-2	431	472
-3	230	257
-4	113	137
-5	62	-42
-6	116	-96
-7	120	-119
-8	81	-63
-10	44	47
-11	51	37
-12	4	9

4k1̄

K	Fo	Fc
0	132	163
1	44	23
2	155	-175
3	178	-163
4	242	-221
5	165	-159
6	123	127
7	111	77
8	234	208
9	120	118
11	48	-56
12	34	-31
13	23	-35
-1	96	117
-2	299	303
-3	9	-18
-4	73	-92
-5	114	-106
-6	114	-110
-7	20	-2
-10	53	51
-11	2	22

5k1̄

K	Fo	Fc
0	198	241
1	267	262
2	120	113
3	151	-147
4	183	-178
5	242	-219
6	143	-124
8	60	56
9	105	102
10	56	58
13	22	-40
-1	137	172
-2	17	21
-3	74	-75
-4	115	-136
-5	82	-65
-6	63	-62
-8	59	59
-9	29	21

6k1̄

K	Fo	Fc
0	75	86
1	193	208
2	115	119
3	186	198
4	99	-102
5	201	-202
6	185	-173
7	94	-80
8	39	67
9	32	43
10	47	36
11	69	74
12	9	5
-1	64	-67
-2	93	-112
-3	114	-120
-4	100	-92
-6	15	23
-7	62	61
-8	37	28

7k1̄

K	Fo	Fc
1	114	121
2	136	142
3	145	173
4	103	104
5	26	41
6	140	-109
7	96	-106
8	103	-105
9	30	-22
10	20	21
11	31	48
12	24	26
-1	102	-118
-2	142	-154
-3	81	-85
-4	26	-41
-5	50	55
-6	56	43
-7	32	32

8k1̄

K	Fo	Fc
0	128	-142
1	44	-40
2	50	53
3	133	139
4	156	165
5	32	21
6	64	-72
7	37	-46
8	75	-81
9	44	-40
12	23	28
-1	71	-62
-2	30	-44
-3	37	-34
-4	44	55
-5	84	76
-6	39	32

9k1̄

K	Fo	Fc
0	82	-82
1	62	-75
2	51	-65
3	39	55
4	47	70
5	20	6
6	90	82
7	73	59
9	43	-45
10	32	-34
11	16	-18
12	15	1
-1	72	-70
-2	21	31
-3	37	25
-4	34	35
-5	18	21
-6	15	20

10k1̄

K	Fo	Fc
2	41	-55
3	56	-54
4	63	-63
5	39	40
6	76	87
7	50	49
9	11	-16
10	24	-32
11	13	-28
-1	15	11
-2	67	64
-3	32	34
-4	24	14

11k1̄

K	Fo	Fc
2	47	64
3	34	-45
4	33	-36
5	32	-45
6	32	51
7	29	40
8	22	27
9	15	28
-1	22	25
-2	39	41
-3	15	15

12k1̄

K	Fo	Fc
0	20	28
3	17	-14
4	34	-44
5	16	-19
8	13	33
-1	23	34

13k1̄

K	Fo	Fc
1	10	39
2	11	28
4	8	-20
5	10	-29

deviation of the light and heavy atom coordinates as 0·015 and 0·006 Å respectively. Since the z coordinates are determined by only one non-zero layer line, the assumption of isotropic sampling is not really valid and the above values can be expected to apply only to the x and y coordinates. From the way in which the z coordinates were determined, the uncertainty in these coordinates seems to be about two to three times that of the other two coordinates.

Using the method of Schomaker, Waser, Marsh & Bergman (1959), the best planes were calculated through the two parts of the molecule. The direction cosines of these planes are given in Table 4. Atoms deviating furthest from their respective planes are (Fig. 2) C4, C5, Cl5 and O18 (0·10 Å). The two planes have twisted through an angle of 88° with respect to each other about the C–N bond. Since the acid grouping lies in the plane of the benzene ring, a relatively short distance results between N16 and O19 (2·48 Å). This approach is less than the sum of the effective van der Waals radii (2·9 Å), but more than the sum of the effective ionic radii (2·0 Å). This is mainly due to electrostatic attraction between the oppositely charged ions.
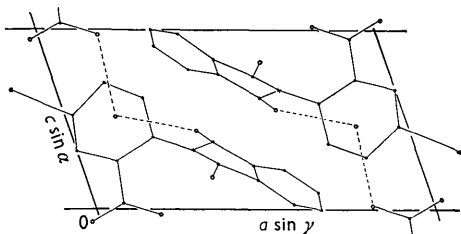
Fig. 3. Arrangement of molecules viewed down the b axis. The broken lines represent hydrogen bonds.

Hydrogen bonding (Fig. 3) between the molecule of water and O18 in one molecule (2.85 Å) and O19 in the molecule a $-c$ translation away (2·77 Å) helps bind the molecules within a stack while the stacks themselves are held together by forces of the van der Waals type. The bond angle between the oxygen atoms involved in the hydrogen bonding is 130°.

The individual isotropic temperature factors were obtained by least-squares refinement. Their standard deviation is about 0·5 Å². Atoms on the periphery of the molecule appear to execute thermal motion with a larger amplitude.

In the above analysis, extensive use of generalized functions has been made. The generalized Patterson projection was sharper than the corresponding zero-layer projection. The determination of the third coordinate, albeit roughly, from the initial generalized projection, allowed a successful trial structure to be found. Lastly, the final generalized projection gave a good check on the least-squares coordinates. The successful application of these methods shows that the scope and power of the generalized projection can, in general, considerably extend the range of molecules that can be solved by two-dimensional methods.

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