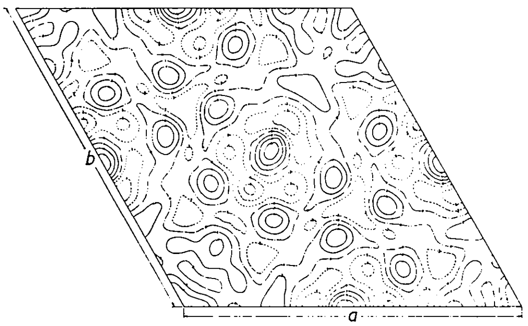

Fig. 10. α-Quartz ($F_o - F_c$) difference map at 155 °K. ——— Positive, - - - - negative, electron density in e.Å^{-2}.

and (220) reflections were omitted from the LS refinement and the difference map of Fig. 10. There are significantly large regions of negative and positive density in this map indicating that a relatively low R factor in the LS refinement does not necessarily mean that further adjustments may not be indicated by a difference map.

We are particularly grateful to Dr William R. Busing of the Oak Ridge National Laboratory for his services in providing us with all of the ORACLE computer results based on our data. We also wish to express our appreciation to the Georgia Institute of Technology for the donation of many hours of computer time (IBM 650) and to the staff of the Georgia Institute of Technology Computer Center for their aid in using the computer. We are pleased to thank Prof. I. Fankuchen of the Polytechnic Institute of Brooklyn for helpful discussions.

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X-ray Studies of Molecular Overcrowding. III. The Crystal and Molecular Structure of *o*-Bromobenzoic Acid.

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(*Received* 16 *May* 1961)

o-Bromobenzoic acid crystallizes in the monoclinic system, space group $C2/c$, with eight molecules in a unit cell of dimensions

$$a = 14{\cdot}82,\ b = 4{\cdot}10,\ c = 25{\cdot}90\ \text{Å};\ \beta = 118°\ 15'.$$

The final atomic coordinates were obtained from a three-dimensional least-squares refinement involving 1145 observed structure factors. The molecules occur as centrosymmetrical dimers with hydrogen bonds (2·64 Å) between adjacent carboxyl groups. The strain which would be imposed on an ideal planar molecule is relieved in a number of ways.

(i) The carboxyl group is rotated about the exocyclic carbon–carbon bond 18·3° out of the plane of the benzene ring.

(ii) The exocyclic substituents are deflected in opposite directions out of the aromatic plane, the bromine atom by $+0{\cdot}064$ Å and the exocyclic carbon atom by $-0{\cdot}057$ Å.

(iii) The exocyclic carbon–carbon and carbon–bromine bonds are displaced sideways so that the normal valency angles of 120° are increased to 123·4° and 124·9°, respectively.

1. Introduction

The previous paper in this series (Ferguson & Sim, 1961) gave a description of the molecular structure of *o*-chlorobenzoic acid in the solid state. Consideration of atomic sizes suggests that marked deviations from planarity should also occur in the molecule of *o*-bromobenzoic acid. A detailed structure analysis of this substance has therefore been carried out with three-dimensional X-ray data.

2. Crystal data

o-Bromobenzoic acid, $C_7H_5O_2Br$; *M*, 201·0; m.p. 150 °C.; *d*, calc. 1·926, meas. 1·929 g.cm.$^{-3}$ (Steinmetz, 1914). Monoclinic,

$$a = 14{\cdot}82 \pm 0{\cdot}04,\ b = 4{\cdot}10 \pm 0{\cdot}02,\ c = 25{\cdot}90 \pm 0{\cdot}05\ \text{Å},\ \beta = 118°\ 15'.$$

Space group deduced from absent reflexions either $Cc\text{–}C_s^4$ or $C2/c\text{–}C_{2h}^6$. Structure refinement confirms $C2/c$ as true space group. Eight molecules per unit cell. Volume of the unit cell, 1386 Å^3. Absorption coefficient for X-rays, $\lambda = 1{\cdot}542$ Å, $\mu = 77{\cdot}6$ cm.$^{-1}$. Total number of electrons per unit cell $= F(000) = 784$.

Crystallization from chloroform/ether solution gave single crystals of *o*-bromobenzoic acid in the form of thin, narrow laths elongated along *b*.

3. Experimental

Rotation, oscillation and moving-film photographic methods were used, with Cu $K\alpha$ radiation. The cell dimensions were determined from rotation and equatorial-layer-line Weissenberg photographs. The intensity data were obtained from multiple-film equi-inclination Weissenberg photographs of the *h*0*l*, *h*1*l*, *h*2*l* and *h*3*l* layers. The number of independent reflexions observed was 1145. The intensities were corrected for Lorentz, polarization and the rotation factors appropriate to upper layers (Tunell, 1939). A small crystal of cross-section 0·10 × 0·17 mm. was employed and absorption corrections were neglected. The scaling factor for each layer was adjusted during refinement to ensure that $\Sigma|F_o| = \Sigma|F_c|$. The values of the measured structure amplitudes on the final, absolute, scale are listed in Table 5.

4. Structure determination

The b-axis projection

Initially the *x* and *z* coordinates of the bromine atom were obtained from a Patterson projection (Fig. 1) and the carbon and oxygen atoms were placed by comparison with the *b*-axis projection of *o*-chlorobenzoic acid. These approximate atomic positions were refined by Fourier and least-squares methods, four rounds of calculations reducing the discrepancy factor *R* to 0·149. In the structure-factor calculations the atomic form factors employed were those of Berghuis *et al.* (1955) for carbon and oxygen, and the Thomas–Fermi values for bromine (*Internationale Tabellen zur Bestimmung von Kristallstrukturen*, Vol. II, 1935).

The final electron-density projection on (010) is shown in Fig. 2.

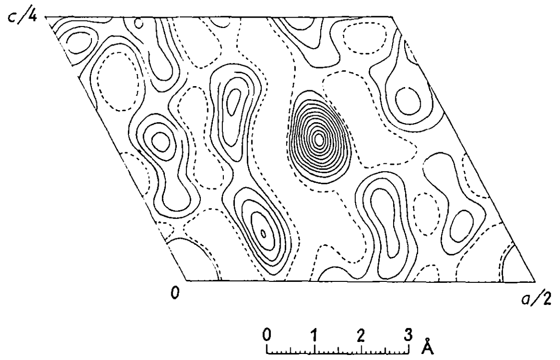

Fig. 1. Patterson projection along the *b* axis. Contours at equal arbitrary intervals, the lowest contour broken.

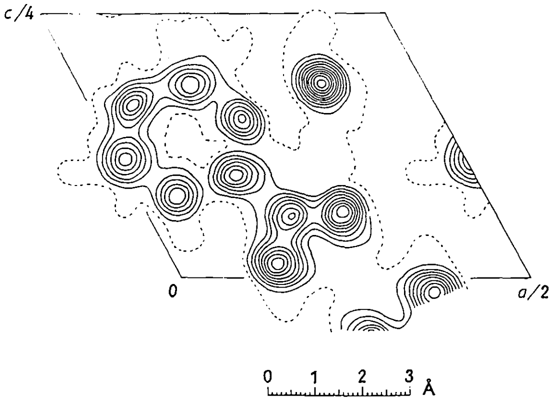

Fig. 2. Electron-density projection on (010). Contours at intervals of 1 e.Å^{-2} except around the bromine atom where the interval is 5 e.Å^{-2}. One-electron line broken.

Three-dimensional refinement

From the bond lengths measured on the *b*-axis projection the tilt of the benzene ring was deduced. Assuming that the bromine and carbon atoms are coplanar, the molecule was then moved along the *b* axis until a reasonably low discrepancy ($R = 0{\cdot}28$) was obtained between $|F_o|$ and $|F_c|$ values for the *h*1*l* reflexions. Line Fourier syntheses evaluated parallel to the *b* axis and passing close to the atom centres gave improved *y*-coordinates, the value of *R* for the *h*1*l* reflexions falling to 0·17.

Seven cycles of three-dimensional least-squares refinement (Rollett, 1961) were then carried out and the overall value of *R* for the 1145 observed reflexions was reduced to 0·132. The final calculated and measured structure factors are listed in Table 5.

5. Coordinates, molecular dimensions and estimates of accuracy

The final coordinates of the carbon, oxygen and bromine atoms and the final anisotropic temperature-factor parameters are shown in Tables 1 and 2, respectively. The average standard deviations of the positional parameters, calculated from the results of the final least-squares cycle, are $\sigma(x)=\sigma(z)=0{\cdot}013$, $\sigma(y)=0{\cdot}016$ Å for a carbon atom, $\sigma(x)=\sigma(z)=0{\cdot}009$, $\sigma(y)=0{\cdot}012$ Å for an oxygen atom and $\sigma(x)=\sigma(y)=\sigma(z)=0{\cdot}002$ Å for the bromine atom. From these results the estimated standard deviation of a carbon–carbon bond is about 0·020 Å, that of a carbon–oxygen bond is about 0·017 Å, and that of the carbon–bromine bond is 0·014 Å. The estimated standard deviation of bond angle is 1·3°.

Table 1. *Final atomic coordinates*

Coordinates *x*, *y*, *z* are referred to the monoclinic crystal axes and are expressed as fractions of the axial lengths, with origin at the centre of symmetry on glide plane *c*. Coordinates *X′*, *Y* and *Z′* are referred to orthogonal axes *a*, *b* and *c′*, *c′* being taken perpendicular to the *a* and *b* crystal axes, and are expressed in Å units

Atom	*x*	*y*	*z*	*X′*	*Y*	*Z′*
C_1	0·2029	0·3511	0·0567	2·312	1·440	1·293
C_2	0·1583	0·4335	0·0958	1·171	1·777	2·185
C_3	0·2117	0·5871	0·1484	1·319	2·407	3·385
C_4	0·1636	0·6701	0·1830	0·181	2·748	4·175
C_5	0·0611	0·5978	0·1629	−1·092	2·451	3·717
C_6	0·0078	0·4434	0·1104	−1·238	1·818	2·518
C_7	0·0560	0·3571	0·0753	−0·093	1·453	1·718
O_1	0·2801	0·4633	0·0596	3·421	1·899	1·360
O_2	0·1489	0·1268	0·0156	2·013	0·520	0·356
Br	0·3523	0·6911	0·1833	2·974	2·834	4·181

The bond lengths and valency angles in the molecule were calculated from the coordinates of Table 1 and are shown in Fig. 3. The shorter intermolecular contacts are listed in Table 4.

The plane through the carbon atoms of the benzene ring, derived by the method of Schomaker *et al.* (1959) is

$$0{\cdot}04782X'-0{\cdot}88713Y+0{\cdot}45903Z'+0{\cdot}51657=0\ .$$

The plane through the atoms of the carboxyl group (C_1, O_1 and O_2) and carbon atom C_2 of the benzene ring is

$$0{\cdot}26961X'-0{\cdot}73115Y+0{\cdot}62669Z'-0{\cdot}38458=0\ .$$

The displacements of the atoms from these planes are shown in Table 3. The angle between the planes is 18·3°.

6. Discussion

The $Br \cdots O_1$ (3·004 Å) and $Br \cdots C_1$ (3·275 Å) intramolecular separations are appreciably shorter than the sums of the van der Waals radii (3·35 and 3·95 Å, respectively).

Table 3. *Deviations from the mean planes*

(*a*) Plane through benzene ring atoms $C_2 \cdots C_7$
(*b*) Plane through C_1, C_2, O_1, O_2

Atom	(*a*)	(*b*)
C_1	−0·057 Å	−0·003 Å
C_2	−0·001	0·001
C_3	−0·002	—
C_4	0·005	—
C_5	−0·004	—
C_6	0·001	—
C_7	0·002	—
O_1	−0·380	0·001
O_2	0·315	0·001
Br	0·064	—

A number of distortions of the molecule from the ideal planar state with valency angles of 120° at the benzene carbon atoms are consequences of the steric

Table 4. *The shorter intermolecular contacts*

$O_1 \cdots O_2^{I}$	2·643 Å	$C_3 \cdots C_2^{II}$	3·675 Å
$O_1 \cdots O_2^{II}$	3·224	$C_4 \cdots C_7^{II}$	3·748
$O_1 \cdots O_1^{I}$	3·284	$Br \cdots C_6^{V}$	3·751
$C_1 \cdots O_2^{II}$	3·329	$Br \cdots C_5^{V}$	3·766
$C_1 \cdots O_1^{I}$	3·393	$C_6 \cdots O_2^{III}$	3·785
$C_7 \cdots O_2^{III}$	3·454	$C_4 \cdots C_4^{VIII}$	3·794
$C_6 \cdots O_2^{IV}$	3·459	$O_1 \cdots C_1^{II}$	3·806
$C_2 \cdots O_2^{II}$	3·484	$C_3 \cdots O_2^{II}$	3·815
$C_1 \cdots O_2^{I}$	3·498	$C_5 \cdots C_7^{II}$	3·832
$C_7 \cdots O_2^{IV}$	3·531	$C_3 \cdots C_7^{II}$	3·839
$O_1 \cdots C_6^{V}$	3·576	$C_4 \cdots C_2^{II}$	3·839
$O_2 \cdots O_2^{I}$	3·602	$C_4 \cdots C_6^{II}$	3·848
$C_7 \cdots C_7^{IV}$	3·635	$C_1 \cdots C_1^{I}$	3·890
$O_1 \cdots O_1^{VI}$	3·640	$C_3 \cdots C_1^{II}$	3·896
$C_6 \cdots O_1^{VII}$	3·668	$C_7 \cdots C_1^{IV}$	3·927
$C_5 \cdots C_6^{II}$	3·671	$Br \cdots C_5^{VIII}$	3·932
		$C_6 \cdots C_7^{II}$	3·998

The superscripts refer to the following positions

I	$\frac{1}{2}-x$	$\frac{1}{2}-y$	$\bar{z}$	V	$\frac{1}{2}+x$	$\frac{1}{2}+y$	z
II	x	$1+y$	z	VI	$\frac{1}{2}-x$	$1\frac{1}{2}-y$	$\bar{z}$
III	$\bar{x}$	$\bar{y}$	$\bar{z}$	VII	$-\frac{1}{2}+x$	$\frac{1}{2}+y$	z
IV	$\bar{x}$	$1-y$	$\bar{z}$	VIII	$\frac{1}{2}-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$

Table 2. *Anisotropic temperature-factor parameters*

Atom	B_{hh}	B_{kk}	B_{ll}	B_{kl}	B_{hl}	B_{hk}
C_1	0·00652	0·10898	0·00251	−0·00273	0·00415	−0·01475
C_2	0·00850	0·04668	0·00213	−0·00191	0·00550	0·00554
C_3	0·00912	0·05377	0·00293	0·00553	0·00574	0·00926
C_4	0·01194	0·08734	0·00293	−0·00173	0·00756	0·01398
C_5	0·01032	0·08000	0·00385	−0·00168	0·00871	0·00673
C_6	0·00836	0·13500	0·00289	0·00699	0·00530	0·01221
C_7	0·00730	0·15955	0·00271	−0·00419	0·00559	0·00705
O_1	0·01028	0·14574	0·00289	−0·01490	0·00709	−0·01210
O_2	0·01115	0·10024	0·00315	−0·00844	0·00648	−0·00457
Br	0·00827	0·11888	0·00283	−0·00937	0·00473	−0·01022

The temperature factor is expressed in the form

$$2^{-(B_{hh}h^2+B_{kk}k^2+B_{ll}l^2+B_{kl}kl+B_{hl}hl+B_{hk}hk)}$$

Table 5. *Measured and calculated structure factors*

o-BROMOBENZOIC ACID.

h	k	l	$10\lvert F_o\rvert$	$10 F_c$
0	0	2	337	-537
		4	978	-1095
		6	1438	1784
		8	2048	-2549
		10	745	684
		12	994	834
		14	1156	-1019
		16	1090	1030
		18	< 84	-49
		20	231	-235
		22	538	439
		24	604	-525
		26	< 71	-47
		28	121	147
2	0	-30	107	78
		-28	207	-171
		-26	555	488
		-24	173	93
		-22	319	-278
		-20	659	523
		-18	796	-678
		-16	< 73	86
		-14	1003	1026
		-12	827	-921
		-10	1251	1552
		-8	776	963
		-6	1251	-1609
		-2	344	-363
		0	1617	-1488
		2	342	340
		4	2249	-2430
		6	361	386
		8	1048	1005
		10	928	-874
		12	895	810
		14	734	-576
		16	867	-754
		18	645	579
		20	645	-516
		22	165	-188
		24	292	318
		26	163	-150
4	0	-30	278	254
		-28	< 74	-25
		-26	167	-149
		-24	291	271
		-22	1109	-827
		-20	228	253
		-18	1036	1068
		-16	949	-985
		-14	816	831
		-12	525	-423
		-10	2017	-2561
		-8	1313	1274
		-6	1445	-1341
		-4	1441	-1294
		-2	2221	1936
		0	1458	-1524
		2	497	419
		4	563	489
		6	1957	-1900
		8	1050	891
		10	126	-72
		12	950	-702
		14	1135	870
		16	340	-250
		18	< 87	-66
		20	377	361
		22	212	-254
		24	162	155
6	0	-30	228	-215
		-28	480	443
		-26	346	-359
		-24	422	-435
		-22	575	595
		-20	667	-737
		-18	109	154
		-16	379	431
		-14	1258	-1553
		-12	608	806
		-10	275	202
		-8	476	-461
		-6	1757	1452
		-4	1632	-1469
		-2	731	511
		0	1969	1713
		2	1889	-1664
		4	1014	900
		6	577	481
		8	810	-761
		10	1310	1213
		12	106	-114
		14	408	-410
		16	435	447
		18	247	-278
		20	81	78
		22	148	175
8	0	-32	213	214
		-30	151	-181
		-28	157	-183
		-26	351	383
		-24	317	-378
		-22	213	257
		-20	429	587
		-18	446	-579
		-16	638	750
		-14	143	-116
		-12	636	-726
		-10	1752	1514
		-8	519	-475
		-6	< 64	-5
		-4	2006	1555
		-2	987	-821
		0	199	247
		2	234	220
		4	1152	-1058
		6	666	628
		8	211	155
		10	197	-186
		12	229	276
		14	383	-436
		16	< 72	-8
		18	117	167
		20	103	-213
10	0	-32	153	-142
		-30	296	338
		-28	121	-156
		-26	< 83	48
		-24	185	187
		-22	482	-632
		-20	441	591
		-18	206	223
		-16	391	-467
		-14	781	958
		-12	620	-782
		-10	435	-366
		-8	1118	970
		-6	1557	-1233
		-4	< 77	34
		-2	381	322
		0	1047	-976
		2	627	678
		4	< 87	-30
		6	357	-393
		8	415	490
		10	450	-470
		12	166	-175
		14	198	249
		16	127	-191
12	0	-32	187	-209
		-30	< 61	-67
		-28	215	263
		-26	356	-446
		-24	239	249
		-22	275	361
		-20	422	-554
		-18	392	478
		-16	358	-474
		-14	979	-1074
		-12	771	621
		-10	240	-159
		-8	170	147
		-6	664	549
		-4	756	-639
		-2	290	244
		0	< 88	36
		2	445	-457
		4	379	407
		6	179	-185
		8	< 72	-35
		10	315	373
		12	121	-177
14	0	-26	< 71	51
		-24	301	-377
		-22	183	279
		-20	< 85	-86
		-18	193	-238
14	0	-16	418	492
		-14	215	-217
		-12	304	284
		-10	540	485
		-8	649	-615
		-6	194	156
		-4	< 85	24
		-2	339	-335
		0	563	579
		2	< 74	-15
		4	124	-145
		6	237	309
		8	101	-155
16	0	-28	150	-200
		-26	253	329
		-24	157	202
		-22	171	-241
		-20	304	345
		-18	202	-186
		-16	175	-165
		-14	273	299
		-12	325	-365
		-10	198	192
		-8	240	230
		-6	309	-336
		-4	228	272
		-2	< 63	-23
		0	172	-206
		2	136	190
18	0	-24	64	103
		-22	162	-202
		-20	104	-97
		-18	234	282
		-16	234	-275
		-14	< 57	29
		-12	200	241
		-10	189	-241
		-8	82	107
		-6	< 39	-40
1	1	-27	187	212
		-26	119	119
		-25	291	-272
		-24	167	-179
		-23	390	350
		-22	104	-54
		-21	< 31	53
		-20	104	63
		-19	468	-460
		-18	253	-232
		-17	729	776
		-16	459	481
		-15	593	-532
		-14	297	218
		-13	245	-241
		-12	136	21
		-11	1134	1257
		-10	908	943
		-9	1389	-1520
		-8	343	-373
		-7	724	688
		-6	123	217
		-5	1544	1485
		-4	1144	902
		-1	947	968
		0	331	-407
		1	709	-932
		2	1237	1436
		4	571	546
		5	1249	1510
		6	930	947
		7	607	-665
		8	225	-237
		9	107	-91
		10	602	-616
		11	681	797
		12	181	-105
		13	1024	-1201
		14	365	-406
		15	239	279
		16	146	91
		17	< 29	46
		18	88	-80
		19	466	-585
		20	178	-203
		21	373	419
		22	264	291
		23	108	-105
		24	< 26	-4
		25	75	-98
		26	81	-107
		27	226	274
3	1	-30	66	64
		-29	121	-161
		-28	81	-97
		-27	82	111
		-26	95	-67
		-25	130	-104
		-24	214	175
		-23	424	-419
		-22	178	182
		-21	433	445
		-20	358	369
		-19	298	-263
		-18	< 28	-105
		-17	157	-113
		-16	420	-358
		-15	783	714
		-14	175	116
		-13	1351	-1208
		-12	519	-537
		-11	149	55
		-10	147	13
		-9	312	284
		-8	632	484
		-7	1585	-1717
		-6	406	-409
		-5	1069	1025
		-4	507	474
		-3	312	-260
		-2	120	-202
		-1	957	-1149
		0	754	-883
		2	116	138
		3	849	-943
		4	782	-762
		5	< 37	39
		6	421	-492
		7	880	1101
		8	176	163
		9	936	-1058
		10	471	-473
		11	383	417
		12	312	307
		13	269	310
		14	258	271
		15	508	-576
		16	285	-334
		17	479	533
		18	119	93
		19	< 30	-3
		20	< 29	17
		21	95	-155
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		0	586	-654
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		2	57	60
		3	57	-106
		4	58	67
		5	117	-85
		6	276	-333
		7	162	217
		8	316	316
		9	56	-91
		10	54	-41
		11	142	-125
		12	49	-71
		13	96	108
		14	140	188
		15	72	-106
9	3	-26	199	-238
		-25	102	111
		-24	83	-37
		-23	49	-82
		-22	96	112
		-21	107	-126
		-20	249	-231
		-19	197	178
		-18	259	237
		-17	82	-58
		-16	< 32	9
		-15	124	-90
		-14	235	-242
		-13	154	153
		-12	309	311
		-11	148	-154
		-10	307	-289
		-9	71	-50
		-8	108	-103
		-7	107	82
		-6	231	249
		-5	232	-251
		-4	405	-384
		-3	< 32	17
		-2	203	188
		-1	58	14
		0	92	157
		1	214	-195
		2	199	-204
		3	216	245
		4	397	354
		5	78	42
		6	85	-70
		7	180	-168
		8	66	-112
		9	102	93
		10	149	181
		11	67	-95
		12	202	-159
11	3	-26	120	163
		-25	163	-161
		-24	131	-137
		-23	84	97
		-22	188	181
		-21	121	94
		-20	109	94
		-19	119	-79
		-18	283	-293
		-17	< 30	-43
		-16	248	263
		-15	114	-155
		-14	162	-117
		-13	58	-17
		-12	124	-140
		-11	164	117
		-10	424	383
		-9	71	-65
		-8	221	-220
		-7	63	83
		-6	220	160
		-5	70	28
		-4	252	270
		-3	145	-119
		-2	298	-302
		-1	179	190
		0	223	177
		1	57	1
		2	56	-17
		3	189	-151
		4	150	-173
		5	130	117
		6	226	214
		7	< 19	-27
		8	99	-105
13	3	-24	115	106
		-23	< 18	-14
		-22	113	-133
		-21	95	66
		-20	118	123
		-19	124	-150
		-18	< 26	-9
		-17	< 26	-3
		-16	113	-109
		-15	214	222
		-14	217	199
		-13	63	-39
		-12	142	-135
		-11	< 28	88
		-10	57	9
		-9	109	92
		-8	153	152
		-7	289	-257
		-6	206	-191
		-5	53	60
		-4	117	87
		-3	211	152
		-2	84	-54
		-1	146	-116
		0	162	-167
		1	42	60
		2	169	177
15	3	-19	73	85
		-18	149	156
		-17	75	-38
		-16	177	-155
		-15	35	7
		-14	< 20	-18
		-13	100	37
		-12	156	142
		-11	99	-114
		-10	215	-197
		-9	< 19	-2
		-8	107	87
		-7	80	43

strain. The carboxyl group is twisted out of the benzene plane by 18·3° while small out-of-plane and larger in-plane deflections of the exocyclic valency bonds are also evident. Thus the bromine atom and the exocyclic carbon atom are displaced from the plane of the aromatic ring by +0·064 and −0·057 Å, respectively, and two of the exocyclic valency angles are increased from the normal value of 120° to 124·9° and 123·4° while the adjacent angles are decreased to 114·4° and 116·4° (Fig. 3). These effects are very similar to, though slightly larger than, those observed in *o*-chlorobenzoic acid.

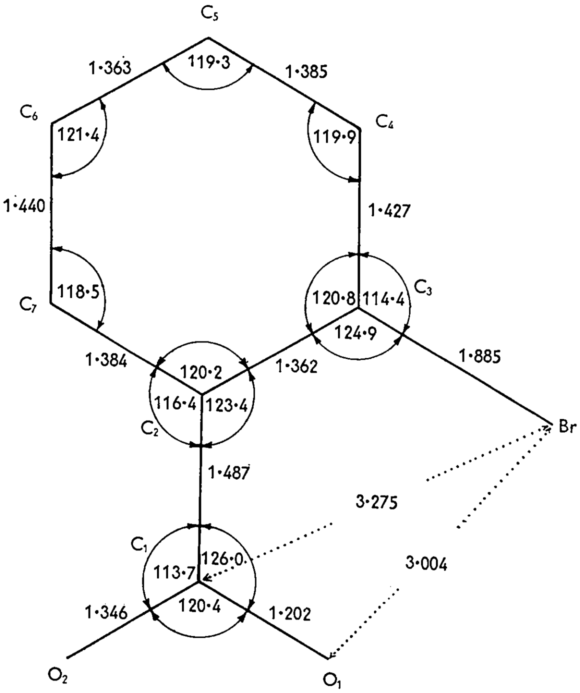

Fig. 3. Interatomic distances and valency angles in *o*-bromobenzoic acid.

The pattern of bond lengths and valency angles in the carboxyl group is as generally found in carboxylic acids. The angle C_2–C_1–O_1 (126·0°), however, is a little larger than usual; in view of the proximity of the bulky bromine atom this enlargement, if significant, may be a further steric effect.

The carbon-bromine distance of 1·885 Å appears to be slightly longer than the average value of 1·85 Å for aromatic carbon–bromine bonds (*Tables of Interatomic Distances and Configuration in Molecules and Ions*, 1958). As the estimated standard deviation of this bond length is 0·014 Å the difference may not be significant.

The closest intermolecular approach occurs between oxygen atoms of adjacent carboxyl groups related by a centre of symmetry. The OH ··· O distance here is 2·64 Å which is normal for this type of hydrogen bonding. All other intermolecular contacts (Table 4) are over 3 Å and correspond to normal van der Waals interactions.

The numerical calculations were carried out on the Glasgow University DEUCE computer using programmes devised by Dr J. S. Rollett and Dr J. G. Sime. We wish to express our thanks to Prof. J. Monteath Robertson, F.R.S., for his interest and to the Carnegie Trust for the award of a scholarship which enabled G. F. to participate in this work.

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