

## References

- BRITTON, D. & NOLAND, W. E. (1962a). *Chem. and Ind.* p. 563.
- BRITTON, D. & NOLAND, W. E. (1962b). *J. Org. Chem.* **27**, 3218.
- CADY, H. C., LARSON, A. C., & CROMER, D. T. (1966). *Acta Cryst.* **20**, 336.
- CORFIELD, P. W. R., DOEDENS, R. J. & IBERS, J. A. (1967). *Inorg. Chem.* **6**, 197.
- DONOHUE, J. (1968). In *Structural Chemistry and Molecular Biology*, p. 459. Edited by A. RICH & N. DAVIDSON. San Francisco: W. H. Freeman.
- International Tables for X-ray Crystallography* (1962). Vol. III, p. 202. Birmingham: Kynoch Press.
- MASLEN, E. N. (1968). *Acta Cryst.* **B24**, 1170.
- SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* **B24**, 63.
- ULKU, D., HUDDLE, B. P. & MORROW, J. C. (1971). *Acta Cryst.* **B27**, 432.

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## The Crystal Packing of 5-Bromo- and 5-Chlorobenzfurazan-1-oxide

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The packing of 5-bromobenzfurazan-1-oxide and 5-chlorobenzfurazan-1-oxide has been studied by refining single-crystal, film X-ray diffraction data treating the molecules as groups of known structure. Short intermolecular contacts,  $N \cdots Br$ ,  $3 \cdot 14 \text{ \AA}$ , and  $N \cdots Cl$ ,  $3 \cdot 20 \text{ \AA}$ , were found.

### Introduction

Several years ago three of us (GLH, RH, and GVN) undertook the structure determination of 5-bromobenzfurazan-1-oxide to determine the configuration of the benzfuroxan ring. With the publication of the structure of 5-chlorobenzfurazan-1-oxide (Britton & Noland, 1962) the determination was set aside. After the determination of the structure of 5-methylbenzfurazan-1-oxide [see the preceding article (Britton & Noland, 1972)] the structure of the chloro compound was re-examined to see whether there was any obvious reason why the packing in the chloro and methyl compounds was different. A previously overlooked short intermolecular  $N \cdots Cl$  distance was found; this is taken to indicate a weak acid-base interaction and presumably explains the difference in packing. It was then decided to continue with the determination of the structure of the bromo compound to a point where the intermolecular distances could be compared.

### Experimental

The unit-cell dimensions and space group for 5-bromobenzfurazan-1-oxide were reported earlier (Britton & Noland, 1962). The results here are in agreement with those,  $a = 12 \cdot 67$  (2),  $b = 7 \cdot 35$  (1),  $c = 7 \cdot 79$  (1)  $\text{\AA}$ ,  $\beta = 90 \cdot 0$  (1)° and space group  $P2_1/n$  ( $C_{2h}^5$ ). Crystals suitable for intensity measurements were grown from an ethanol solution. A crystal was cleaved to a roughly cubic shape and wedged in a thin-walled glass capillary tube, which

was then filled with water and sealed. Weissenberg photographs of layers  $hk0-hk3$  were collected and were measured by visual comparison with an intensity standard. There were 262 independent reflections of measurable intensity; these were corrected for Lorentz and polarization factors but not for absorption.\*

In view of the limited amount of data and the lack of absorption corrections (the crystal dimensions had not been recorded when the data were collected in 1962) it was decided to carry out the refinement treating the entire molecule as a rigid group of known dimensions. The dimensions for the molecule were taken from those of the corresponding methyl compound (see the preceding paper; values before libration corrections were used) except that the methyl group with the carbon atom  $1 \cdot 508 \text{ \AA}$  from the ring was replaced with a bromine atom  $1 \cdot 870 \text{ \AA}$  from the ring, and the molecule was made exactly planar. The initial position and orientation of the molecule were chosen to correspond to the known structure of the chloro compound. Scale factors for the individual layers were treated as independent variables. Convergence was reached after four cycles of refinement with  $r = 0 \cdot 185$  and  $R = 0 \cdot 200$ . The

\* The programs used were the same as those in the preceding paper (Britton & Noland, 1972), plus *GROUP*, a local modification of a group refinement program by R. J. Doedens based on *ORFLS*.  $R$  and  $r$  are defined as they were previously with the weights assigned according to:  $w = (F_w/F_o)^4$  for  $F_o > F_w$  and  $w = 1$  for  $F_o \leq F_w$ .  $F_w$  was 10.0 for the bromo compound and 8.0 for the chloro compound for the  $F_o$  on an absolute scale.

group parameters are given in Table 1, the atomic parameters in Table 2, and the observed structure factors in Table 3.

Table 1. *Group parameters*

The origin of the group is halfway between atoms C(5) and C(6) in each case. The angles are in radians.  $\delta$ ,  $\epsilon$  and  $\eta$  are angles that bring about alignment (except for translation) of an internal coordinate system within the group with a fixed external system. See La Placa & Ibers (1965) for the definitions.

Molecule	<i>x</i>	<i>y</i>	<i>z</i>
BrC <sub>6</sub> H <sub>3</sub> N <sub>2</sub> O <sub>2</sub>	0.4356 (8)	0.5048 (12)	0.2902 (21)
ClC <sub>6</sub> H <sub>3</sub> N <sub>2</sub> O <sub>2</sub>	0.4316 (5)	0.4998 (10)	0.2938 (11)
	$\delta$	$\epsilon$	$\eta$
BrC <sub>6</sub> H <sub>3</sub> N <sub>2</sub> O <sub>2</sub>	2.734 (10)	3.048 (19)	-2.692 (9)
ClC <sub>6</sub> H <sub>3</sub> N <sub>2</sub> O <sub>2</sub>	2.770 (5)	3.051 (8)	-2.652 (4)

Table 2. *Positional parameters*  $\times 10^3$  and *temperature factors for the atoms*

The parameters for the bromo compound are given on the first line in each case, for the chloro compound on the second.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
X=Br	374 (1)	774 (2)	399 (3)	7.7 (3)
=Cl	373 (1)	758 (1)	396 (1)	7.0 (3)
O(1)	644 (3)	47 (6)	38 (7)	12.7 (15)
	647 (2)	41 (3)	39 (3)	15.3 (12)
O(2)	732 (2)	319 (7)	50 (3)	11.6 (13)
	731 (1)	330 (4)	55 (1)	9.5 (7)
N(1)	640 (2)	208 (6)	81 (4)	15.0 (36)
	641 (1)	208 (3)	84 (2)	10.4 (9)
N(2)	713 (1)	494 (6)	108 (2)	9.2 (43)
	709 (1)	510 (3)	114 (1)	9.1 (8)
C(1)	569 (2)	315 (4)	155 (3)	20.3 (43)
	569 (1)	314 (2)	158 (1)	4.8 (6)
C(2)	615 (2)	488 (4)	169 (3)	8.7 (14)
	611 (1)	496 (2)	175 (1)	3.7 (5)
C(3)	557 (2)	632 (3)	244 (2)	7.3 (14)
	550 (1)	641 (1)	250 (1)	5.5 (6)
C(4)	458 (2)	595 (3)	299 (2)	10.1 (21)
	453 (1)	595 (1)	303 (1)	3.0 (5)
C(5)	413 (1)	415 (2)	282 (2)	7.7 (14)
	411 (1)	405 (1)	284 (2)	5.5 (7)
C(6)	467 (1)	275 (2)	211 (2)	7.5 (14)
	467 (1)	263 (1)	212 (2)	8.0 (9)

The structure of the chloro compound was also refined using the entire molecule as a rigid group. The same dimensions were used for this molecule as for the bromo molecule, except that the bromine atom was replaced with a chlorine atom 1.710 Å from the ring. Convergence was reached after four cycles with  $r=0.276$ ,  $R=0.259$ . Although the original refinement was carried further (to anisotropic individual atoms), the deviations from normal bond lengths were such that we feel the individual atomic positions are probably more accurate, on the average, from the group refinement, and therefore, that the group refinement gives a better estimate of the intermolecular distances. The group parameters are given in Table 1, the atomic par-

ameters from the group refinement in Table 2. Since the observed structure factors are available in the original paper (Britton & Noland, 1962), they are not repeated here.

## Results and discussion

The crystal structure is shown in Fig. 1. The molecules form layers parallel to the (101) plane. In the bromo compound the average distance between layers is 3.37 Å; the shortest interatomic distances between layers are 3.38, 3.39, 3.43 and 3.48 Å. In the chloro compound the average distance between layers is 3.23 Å; the shortest interatomic distances between layers are 3.24, 3.25, 3.31, and 3.36 Å. The intermolecular distances within a layer are indicated in the Figure and are given in Table 4; all distances shorter than 4.0 Å are shown. All of the distances correspond to normal van der

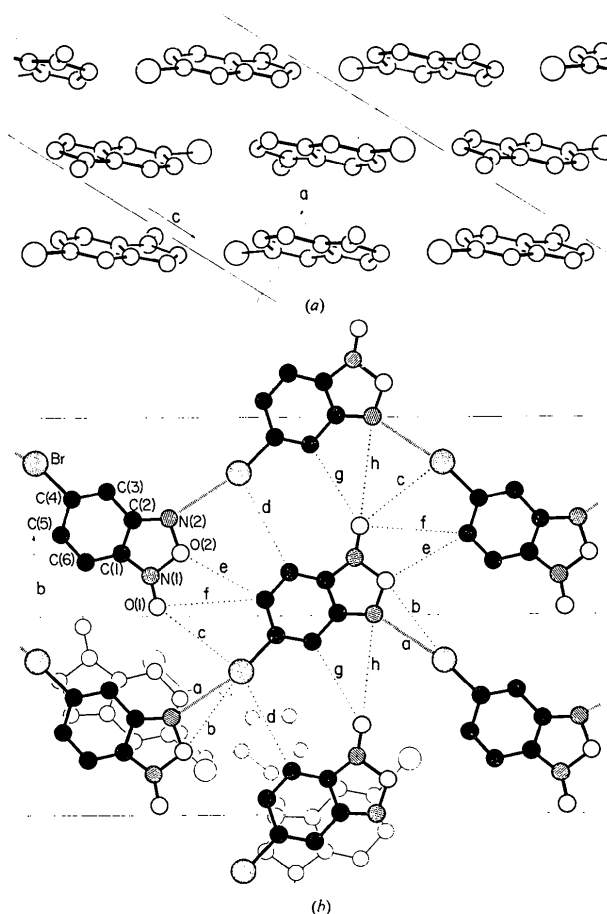


Fig. 1. The crystal structure of 5-bromobenzofuran-1-oxide. (a) Projection down **b**, (b) projection perpendicular to the layers of molecules shown in the top projection, *i.e.* perpendicular to (101). The lowest layer on the top projection is emphasized on the bottom projection. The dashed lines show the short N...Br distance; the dotted lines show the other intermolecular contacts under 4.0 Å. Values for both the bromo and chloro compounds are given in Table 4. In the lower left hand corner two molecules from the adjacent layer and one molecule from the layer below that are shown.

Table 3. Observed structure factors ( $\times 10$ ) for 5-bromobenzofurazan-1-oxide

L=0	H K	FO	H K	FO	H K	FO	H K	FO	H K	FO	H K	FO	H K	FO
	6 4	96	2 6	161	-3 1	1439	3 4	75	-6 1	132	2 3	379		
	6 5	157	3 0	1088	-3 2	346	3 5	297	-6 2	460	2 5	210		
0 2	773	7 1	305	3 1	373	-3 3	687	4 1	921	-6 3	77	3 2	121	
0 4	605	7 2	133	3 2	953	-3 4	48	4 2	222	-6 4	271	3 3	339	
0 6	129	7 3	131	3 3	134	-3 5	243	4 3	530	-6 5	91	3 4	116	
1 1	461	7 4	100	3 4	382	-4 2	247	4 5	196	-7 1	51	3 5	169	
1 2	232	7 5	80	3 6	198	-5 0	1052	5 2	475	-7 2	76	4 1	139	
1 3	147	7 6	97	4 1	200	-5 1	226	5 3	103	-7 3	186	4 4	254	
1 4	162	8 0	368	4 2	120	-5 2	823	5 4	253	-7 4	155	5 1	279	
1 5	232	8 2	293	4 3	291	-5 4	199	5 6	92	-8 0	260	5 2	440	
1 6	124	8 3	52	4 5	229	-6 1	178	6 2	489	-8 1	422	5 4	239	
1 7	90	8 4	216	5 0	134	-6 3	134	6 4	271	-8 2	31	5 5	173	
2 0	301	8 5	56	5 1	912	-7 1	500	6 6	82	-8 3	216	7 2	138	
2 2	137	8 6	65	5 3	604	-7 3	351	7 3	186	-8 5	92	7 3	302	
2 3	674	9 2	52	5 5	157	-7 4	109	7 5	131	-9 4	65	8 2	73	
2 5	275	9 3	165	6 1	124	-7 5	115	-1 1	426	-9 5	63	9 1	107	
2 6	67	10 0	93	6 2	149	-9 2	266	-1 2	236	-10 0	284	9 2	273	
3 1	227	10 1	259	6 4	128			-1 3	402	-10 1	63	11 3	158	
3 2	597	10 2	96	7 0	614			-1 4	175	-10 2	159	-1 4	1047	
3 3	316	10 5	52	7 1	89	L=2		-1 5	143	-10 4	91	-1 4	140	
3 4	291	11 3	40	7 2	464	0 2	288	-2 2	533	-11 3	91	-1 5	233	
3 5	136	12 0	170	7 4	155	0 3	490	-2 3	149	-12 0	64	-2 1	153	
3 6	148			8 1	97	0 4	200	-2 4	527	-12 1	91	-2 2	76	
4 0	1293	L=1		8 3	167	0 5	287	-2 5	83	-12 2	63	-3 0	852	
4 1	325			9 1	234	1 1	785	-3 1	113		-3 1	347		
4 2	585	0 1	223	9 3	288	1 2	169	-3 2	203	L=3	-3 2	797		
4 3	40	0 2	214	10 2	161	1 3	103	-3 3	329		-3 3	176		
4 4	415	0 3	370	11 0	162	1 4	237	-3 5	122	0 1	222	-3 4	235	
4 6	98	0 4	242	11 2	200	1 5	102	-3 6	92	0 2	344	-4 1	157	
5 1	139	0 5	261	-1 2	1420	1 6	183	-4 0	384	0 4	226	-5 0	291	
5 2	257	0 6	159	-1 3	189	2 1	686	-4 1	774	0 5	191	-5 1	559	
5 3	237	1 0	92	-1 4	282	2 2	854	-4 2	278	0 6	111	-5 2	210	
5 4	113	1 1	399	-1 6	163	2 3	149	-4 3	516	1 1	209	-5 3	307	
5 5	199	1 2	56	-2 1	47	2 4	413	-4 5	176	1 2	374	-5 4	126	
5 6	120	1 5	142	-2 2	259	2 5	75	-5 1	507	1 3	335	-5 1	185	
6 0	216	2 1	310	-2 3	233	2 6	159	-5 2	103	1 4	156	-7 2	243	
6 1	713	2 3	186	-2 4	187	3 1	185	-5 3	207	1 5	103	-8 1	100	
6 2	59	2 4	386	-2 5	240	3 2	143	-5 5	156	1 6	132	-9 0	94	
6 3	427	2 5	277	-3 0	584	3 3	183	-6 0	386	2 2	144	-9 1	181	

Waals distances except the  $N(2)\cdots X$  distances of 3.14 and 3.20 Å in the bromo and chloro compounds, respectively; these should be compared with the expected van der Waals distances of 3.45 and 3.30 Å, respectively. The distance in the chloro compound, by itself, might not be convincing, but the distance in the bromo compound is significantly shorter than the van der Waals distance and moreover is shorter than the dis-

tance in the chloro compound, which would not be expected in the absence of any interaction.

Table 4. Interatomic distances between molecules

Distance	Atoms	$BrC_6H_3N_2O_2$	$ClC_6H_3N_2O_2$
<i>a</i>	X-N(2)	3.14 Å	3.20 Å
<i>b</i>	X-O(2)	3.69	3.66
<i>c</i>	X-O(1)	3.92	3.74
<i>d</i>	X-C(6)	4.15	4.05
<i>e</i>	C(5)-O(2)	3.58	3.59
<i>f</i>	C(5)-O(1)	3.99	3.96
<i>g</i>	C(3)-O(1)	3.64	3.53
<i>h</i>	N(2)-O(1)	4.20	3.87

It appears to us that this specific acid-base interaction,  $N\cdots X$ , provides a likely explanation for the difference in packing between the halogen compounds and the corresponding methyl compound. What is surprising about the situation is that the melting points of these three compounds, Br, 69; Cl, 48;  $CH_3$ , 98°C, taken by themselves would seem to indicate stronger interactions in the methyl compound than in the other two. We can offer no explanation for this anomaly.

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#### References

- BRITTON, D. & NOLAND, W. E. (1962). *J. Org. Chem.* **27**, 3218.  
 BRITTON, D. & NOLAND, W. E. (1972). *Acta Cryst.* **B28**, 1116.  
 LA PLACA, S. J. & IBERS, J. A. (1965). *Acta Cryst.* **18**, 511.

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## The Crystal Structure of 5,6-Dichlorobenzofurazan-1-oxide

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5,6-Dichlorobenzofurazan-1-oxide is monoclinic with  $a=11.609$  (19),  $b=8.956$  (15),  $c=7.355$  (12) Å, and  $\beta=96.2$  (1)°, with four molecules in the unit cell. The measured density is 1.80 (2) g.cm<sup>-3</sup>; the calculated density is 1.790 (5) g.cm<sup>-3</sup>. The space group is  $C2/c$  ( $C_2^6$ ). The molecules are disordered with the pseudo-twofold axis of the molecule approximately aligned with the twofold axis in the crystal. The disorder precludes any accurate determination of the molecular parameters. The molecules lie in sheets parallel to the (10 $\bar{1}$ ) plane, and, within the sheets, in rows parallel to *b*. The  $O\cdots Cl$  contacts within the rows are approximately normal, near 3.2 Å. There is one short intermolecular distance in the structure, an  $O\cdots C$  distance of 3.16 or 3.33 Å depending on the disorder.

#### Introduction

Several years ago two of us (JH and LMT) undertook to determine the structure of 5,6-dichlorobenzofuroxan

(=5,6-dichlorobenzofurazan-1-oxide) in order to determine the configuration of the benzofuroxan ring. This work was set aside when the completed structure determination of 5-chlorobenzofuroxan (Britton & Noland,