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## The Crystal Packing of 4,7-Dibromobenzofurazan 1-Oxide

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**Abstract.**  $C_6H_2Br_2N_2O_2$ ,  $M_r = 293.90$ , monoclinic,  $C2/c$ ,  $a = 23.083$  (26),  $b = 7.842$  (3),  $c = 28.081$  (13) Å,  $\beta = 105.97$  (7)°,  $V/Z = 203.6$  (5) Å<sup>3</sup>,  $Z = 24$  (3 molecules in the asymmetric unit),  $D_x = 2.396$  (6) g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 98.1$  cm<sup>-1</sup>,  $F(000) = 3312$ ,  $T = 297$  (2) K,  $R = 0.079$  for 2187 unique observed reflections with  $I > \sigma(I)$ . Bond lengths and angles are normal. Each of the six independent Br atoms is close to either an O or an N atom on an adjacent molecule. These interactions organize the molecules into two-dimensional sheets. These sheets are of two different kinds, both involving the same kinds of intermolecular interactions, but with distinctly different overall patterns.

**Introduction.** Short intermolecular N...X distances were found in the crystal structures of 5-chloro- and 5-bromobenzofurazan 1-oxide (Britton & Noland, 1962; Britton, Hardgrove, Hegstrom & Nelson, 1972) and short O...I distances were found in the structure of 5-iodobenzofurazan 1-oxide (Gehrz & Britton, 1972). These were interpreted as Lewis acid–base interactions with the halogen atoms as the acids and the N and O atoms as the bases. Seeking another example where this sort of interaction is possible, we report here the crystal structure of one of the isomers of dibromobenzofurazan 1-oxide.

**Experimental.** A sample of the compound was prepared by Professor W. E. Noland and K. A. N. Juneau of this Department. Crystals suitable for X-ray diffraction were hard to obtain. The first eight crystals examined were of very poor quality: the

errors in the cell constants, measured in the usual way, were of the order of 1/500; the peaks were broad with peak widths of 2–3°; the intensities were low. Lowering the temperature did not improve the quality of the data. A slightly better crystal was eventually found and used for the data collection. It had been recrystallized from acetone and was a yellow prism 0.10 × 0.18 × 0.35 mm. Data were collected on an Enraf–Nonius CAD-4 diffractometer equipped with a graphite monochromator. 23 reflections with  $9 < \theta < 13^\circ$  were used to determine the cell parameters. Systematic extinctions ( $hkl$ ,  $h+k$  odd;  $h0l$ ,  $l$  odd) indicated the space group to be either  $Cc$  or  $C2/c$ . The latter was chosen on the basis of the eventual solution. Data were collected, using  $\omega$  scans, in the range  $0 < \theta < 24^\circ$  over one hemisphere (ranges:  $h - 26$  to  $26$ ;  $k 0$  to  $8$ ;  $l - 32$  to  $32$ ). The intensities of 7252 different reflections were measured. Three check reflections measured every 5000 s of exposure time showed a 5% linear decay over the entire data collection; this was corrected for. The structure was solved by direct methods (*MITHRIL*; Gilmore, 1984). After preliminary refinement, absorption corrections were made, using the program *DIFABS* (Walker & Stuart, 1983; transmission factors 0.64 to 1.32), and equivalent reflections were combined to give 3634 independent reflections ( $R_{\text{int}} = 0.052$ ), of which the 2187 with  $I > \sigma(I)$  were used in the calculations. The structure was refined by full-matrix least squares on  $F^2$ 's. Since the amount of data was limited, only the Br, O and N atoms were given anisotropic thermal parameters. The H atoms were included at idealized positions with isotropic  $B$

Table 1. Fractional atomic coordinates and equivalent (for N, O, Br) isotropic temperature factors

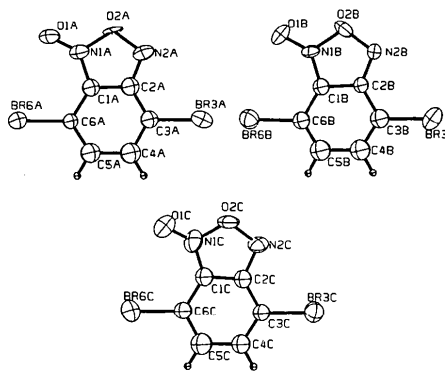
Isotropic temperature factors for C atoms.				
$B_{\text{eq}} = (8\pi^2/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$				
	x	y	z	$B_{\text{eq}}/B_{\text{iso}}(\text{\AA}^2)$
N1A	0.6115 (6)	0.517 (2)	0.6030 (5)	3.8 (7)
O1A	0.5849 (5)	0.618 (2)	0.5723 (4)	4.2 (6)
O2A	0.6549 (5)	0.578 (1)	0.6465 (4)	3.4 (5)
N2A	0.6808 (6)	0.445 (2)	0.6764 (4)	3.5 (7)
C1A	0.6135 (7)	0.343 (2)	0.6076 (5)	3.1 (3)
C2A	0.6555 (7)	0.306 (3)	0.6534 (5)	3.4 (3)
C3A	0.6653 (7)	0.137 (2)	0.6677 (5)	3.2 (3)
C4A	0.6356 (8)	0.006 (3)	0.6381 (6)	4.3 (4)
C5A	0.5926 (8)	0.049 (3)	0.5918 (6)	4.0 (4)
C6A	0.5810 (6)	0.212 (2)	0.5759 (5)	2.5 (3)
Br3A	0.72233 (9)	0.0815 (2)	0.72867 (6)	3.94 (8)
Br6A	0.52379 (8)	0.2703 (2)	0.51571 (5)	3.65 (8)
N1B	0.3811 (6)	0.623 (2)	0.2206 (4)	2.8 (6)
O1B	0.4072 (6)	0.731 (2)	0.2519 (4)	4.8 (6)
O2B	0.3400 (5)	0.690 (2)	0.1759 (3)	4.7 (6)
N2B	0.3154 (6)	0.557 (2)	0.1456 (4)	3.3 (6)
C1B	0.3796 (7)	0.452 (2)	0.2172 (5)	2.8 (3)
C2B	0.3379 (7)	0.419 (2)	0.1700 (5)	2.5 (3)
C3B	0.3279 (8)	0.249 (2)	0.1565 (6)	3.7 (4)
C4B	0.3560 (8)	0.128 (3)	0.1875 (6)	4.4 (4)
C5B	0.3983 (8)	0.168 (3)	0.2339 (6)	4.4 (4)
C6B	0.4109 (7)	0.321 (2)	0.2487 (5)	3.1 (3)
Br3B	0.27237 (8)	0.1955 (3)	0.09482 (6)	4.5 (1)
Br6B	0.46704 (8)	0.3815 (3)	0.30866 (6)	4.10 (9)
N1C	0.1412 (6)	-0.002 (2)	-0.0241 (5)	4.3 (7)
O1C	0.1715 (6)	0.071 (2)	0.0096 (4)	5.5 (7)
O2C	0.1030 (5)	0.081 (1)	-0.0669 (4)	3.8 (6)
N2C	0.0701 (6)	-0.029 (2)	-0.1006 (5)	3.7 (7)
C1C	0.1307 (7)	-0.169 (3)	-0.0348 (5)	3.3 (3)
C2C	0.0886 (7)	-0.185 (3)	-0.0809 (5)	3.2 (3)
C3C	0.0701 (7)	-0.343 (2)	-0.1018 (5)	3.3 (3)
C4C	0.0919 (8)	-0.487 (3)	-0.0755 (6)	3.6 (4)
C5C	0.1347 (8)	-0.480 (3)	-0.0278 (6)	4.7 (4)
C6C	0.1552 (7)	-0.321 (3)	-0.0083 (5)	3.3 (3)
Br3C	0.01312 (8)	-0.3500 (3)	-0.16486 (6)	4.9 (1)
Br6C	0.21403 (8)	-0.3156 (3)	0.05306 (6)	4.43 (9)

Table 2. Bond lengths (Å) and angles (°)

	Molecule A	Molecule B	Molecule C	Average
N1—O1	1.21 (2)	1.24 (1)	1.16 (2)	1.20
N1—O2	1.44 (2)	1.45 (1)	1.44 (2)	1.44
N1—C1	1.37 (2)	1.35 (2)	1.35 (2)	1.36
O2—N2	1.37 (1)	1.37 (2)	1.35 (1)	1.36
N2—C2	1.32 (2)	1.31 (2)	1.37 (2)	1.33
C1—C2	1.41 (2)	1.43 (2)	1.39 (2)	1.41
C1—C6	1.43 (2)	1.42 (2)	1.44 (2)	1.43
C2—C3	1.39 (2)	1.39 (2)	1.39 (2)	1.39
C3—C4	1.38 (2)	1.33 (2)	1.37 (2)	1.36
C3—Br3	1.90 (1)	1.90 (1)	1.89 (1)	1.90
C4—C5	1.44 (2)	1.43 (2)	1.43 (2)	1.43
C5—C6	1.36 (2)	1.28 (3)	1.40 (3)	1.35
C6—Br6	1.89 (1)	1.88 (1)	1.88 (1)	1.88
O1—N1—O2	119 (1)	116 (1)	123 (2)	119
O1—N1—C1	136 (1)	136 (1)	134 (2)	135
O2—N1—C1	105 (1)	108 (1)	103 (1)	105
N1—O2—N2	110 (1)	109 (1)	113 (1)	111
O2—N2—C2	106 (1)	106 (1)	104 (1)	105
N1—C1—C2	107 (2)	104 (1)	110 (2)	107
C2—C1—C6	122 (2)	123 (2)	119 (2)	121
N2—C2—C1	112 (2)	114 (2)	111 (2)	112
C1—C2—C3	118 (2)	116 (2)	122 (2)	119
C2—C3—C4	122 (2)	119 (2)	119 (1)	120
C3—C4—C5	118 (2)	122 (2)	122 (2)	121
C4—C5—C6	123 (2)	122 (2)	118 (2)	121
C1—C6—C5	117 (1)	116 (1)	120 (1)	118

Table 3. Short intermolecular contacts

	Br...X (Å)	C—Br...X (°)
C3A—Br3A...N2A	3.16 (1)	173 (1)
C6A—Br6A...O1A	3.12 (1)	170 (1)
C3B—Br3B...O1C	3.01 (1)	168 (1)
C6B—Br6B...N2C	3.19 (1)	171 (1)
C3C—Br3C...O1B	3.03 (1)	157 (1)
C6C—Br6C...N2B	3.14 (1)	160 (1)

Fig. 1. The three independent  $\text{C}_6\text{H}_2\text{Br}_2\text{N}_2\text{O}_2$  molecules. Thermal ellipsoids are drawn at the 50% probability level. H atoms are shown with arbitrary radius.

values 20% larger than the isotropic  $B$  of the attached C atom. Refinement converged with  $R = 0.079$ ,  $wR = 0.060$  and  $S = 1.48$ ;  $w = 1/\sigma^2(F)$  was calculated from  $\sigma^2(I) = \sigma^2(I)_c + (0.03I)^2$ , where  $\sigma(I)_c$  is the standard deviation in  $I$  based on counting statistics alone. In the final cycle of refinement,  $(\Delta/\sigma)_{\text{max}} = 0.17$ ,  $(\Delta\rho)_{\text{max}} = 1.67$  and  $(\Delta\rho)_{\text{min}} = -1.19 \text{ e \AA}^{-3}$ . Atomic scattering factors and anomalous-dispersion corrections for all atoms were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). The computer programs used were from *TEXSAN* (Molecular Structure Corporation, 1985).

**Discussion.** The final positional parameters are given in Table 1.\* The thermal ellipsoids and the labelling of the atoms are shown in Fig. 1. Bond lengths and angles are given in Table 2; they are normal within

the rather large experimental error. The molecules deviate only marginally from planarity.

The packing shows several interesting features. The short Br...N and Br...O distances that were being looked for are present; they are listed in Table 3. Every Br atom is close to either an N2 or an O1 atom on an adjacent molecule. Nyburg & Faerman (1985) give 3.08 Å as the shortest Br...O distance to be expected for axial approach to the Br and 3.14 Å for the corresponding Br...N distance. All of the distances in Table 3 are close to these values.

\* Lists of anisotropic thermal parameters, H-atom parameters, deviations from the mean planes of the molecules, intermolecular distances and observed and calculated structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54958 (29 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CR0354]

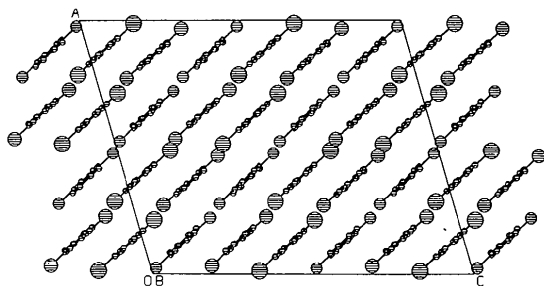


Fig. 2. The packing of  $C_6H_2Br_2N_2O_2$ . The view is down the  $b$  axis. The Br atoms are drawn with a larger radius than the other atoms. The  $A$  molecules are those with the smallest,  $B$  with the intermediate and  $C$  with the largest Br radii. There are two  $BC$  layers between every pair of  $A$  layers.

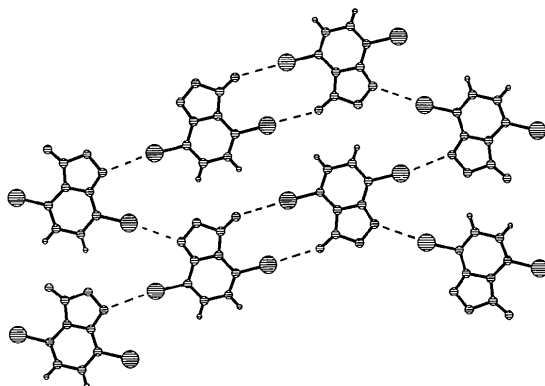


Fig. 3. The packing in the  $A$  layers. The view is along the normal to the  $(101)$  plane. The  $b$  axis is vertical. The first column is related to the second by a 2, screw axis, the second to the third by a center of symmetry and the third to the fourth by another screw axis. The fifth column (not shown) would be translationally equivalent to the first. The short  $Br\cdots N$  and  $Br\cdots O$  distances are shown by dashed lines.

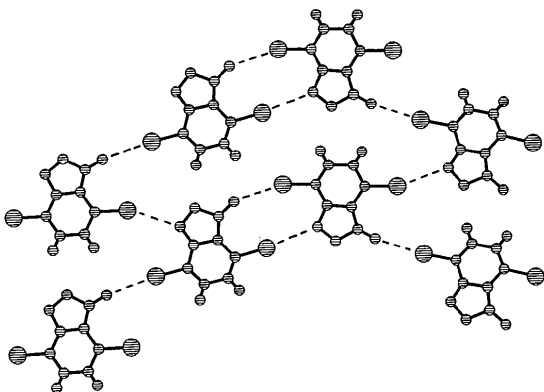


Fig. 4. The packing in the  $BC$  layers. View as in Fig. 3. The first and third columns are  $C$  molecules, the second and fourth  $B$ . The fifth column (not shown) would be translationally equivalent to the first.

The molecules pack in sheets parallel to the  $(101)$  plane as shown in Fig. 2. There are two types of sheet. The sheet through the origin is composed entirely of type  $A$  molecules and is shown in Fig. 3. The next two sheets in either direction are composed of equal numbers of type  $B$  and  $C$  molecules; this sheet is shown in Fig. 4. The molecules are tilted slightly with respect to the sheets. The angle between the mean plane of the molecule and the  $(101)$  plane is  $3.7(1)^\circ$  for molecule  $A$ ,  $3.9(1)^\circ$  for  $B$  and  $3.0(1)^\circ$  for  $C$ . The average distance between  $A$  and  $BC$  sheets is  $3.335 \text{ \AA}$ , between  $BC$  and  $BC$  sheets  $3.362 \text{ \AA}$ ; owing to the tilt of the molecules individual atoms may be nearer to or farther from adjacent sheets by up to  $0.1 \text{ \AA}$ .

Both sheets represent a solution to a two-dimensional packing problem. From the geometry of the crystal, both sheets fill 2D space equally well. Since both occur in the same crystal, it would appear that they are about equal energetically, which is reasonable since both sheets involve the same number and type of interactions. There are significant differences, however. The  $A$  sheets involve pairs of molecules held together by two identical  $Br\cdots O$  interactions (between columns 2 and 3 in Fig. 3) plus infinite chains held together by identical  $Br\cdots N$  interactions (between columns 1 and 2 or 3 and 4). The  $BC$  sheets involve pairs of molecules held together by one  $Br\cdots O$  and one  $Br\cdots N$  interaction (between columns 2 and 3 of Fig. 4) plus infinite chains held together by alternating  $Br\cdots O$  and  $Br\cdots N$  interactions (between columns 1 and 2 or 3 and 4).

In spite of their similarities, it is surprising that both types of sheet occur in the same structure. If the sheets are viewed along their normals, there do not appear to be any unusual intersheet interactions that would require both kinds to be present. A simpler structure, with only type  $A$  sheets, for example, would seem to represent an equally satisfactory and more economical packing. If the analogous dichloro and bromochloro compounds can be prepared, it is intended to pursue this problem further.

I thank Professor W. E. Noland for supplying the compound.

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