The crystal packing of 4,7-dichloro- and 4,7-dibromobenzo[c]furazan 1-oxide

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The molecular structures of 4,7-dichlorobenzo[c]furazan 1-oxide, $C_6H_2Cl_2N_2O_2$, (I), and 4,7-dibromobenzo[c]furazan 1-oxide, $C_6H_2Br_2N_2O_2$, (II), are normal. Compound (I) occurs in two polymorphic forms. One polymorph contains one molecule in the asymmetric unit, organized into two-dimensional sheets involving intermolecular N···Cl and O···Cl interactions. The second polymorph has three molecules in the asymmetric unit, organized into two crystallographically different two-dimensional sheets with similar interactions. Compound (II) is isomorphous with the second polymorph of (I). The three two-dimensional sheets in the two polymorphs comprise a set of three two-dimensional polymorphic arrangements.

Comment

In the structure of 4,7-dibromobenzo[c]furazan 1-oxide, DBR or (II), there are three crystallographically different DBR molecules (Britton, 1992). These pack in two similar but different kinds of layers, both characterized by Br···O and Br···N intermolecular interactions. The presence of two different kinds of layers was surprising, since either type of layer alone would appear to be a possible motif for a less

(I) X = Cl
(II) X = Br
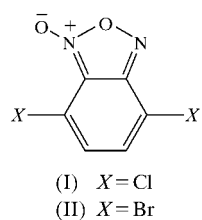
complex but satisfactory packing. To explore the question further, we have looked at the crystal structure of the corresponding dichloro compound, DCL or (I). Two polymorphs were found and these are described below. We also report a

redetermination of the structure of (II). A search for a second polymorph of (II) was unsuccessful.

Drawings of all the independent molecules in both polymorphs of (I) are shown in Fig. 1, while Fig. 2 shows the corresponding drawings for (II). The bond lengths and angles are all normal, and agree within experimental error, for all four independent molecules of (I) and for all three independent molecules of (II). In addition, the distances and angles between non-halogen atoms agree between the two compounds.

The packing in the two polymorphs of (I), denoted DCL-I and DCL-II, is shown in Figs. 3 and 4; the packing for (II) is the same as that shown in Fig. 4, and the discussion of the packing is the same as that for the second polymorph of (I), hence it is denoted DBR-II. In both polymorphs of (I), there are nearly planar layers. Between the two polymorphs, there are three different kinds of layers: those in polymorph I are denoted Cl-I layers, those in polymorph II involving A molecules are denoted Cl-IIA layers, and those in polymorph II involving B and C molecules are denoted Cl-IIBC layers.

Although the most important intermolecular interactions would appear to be those between the Cl atoms of one molecule and the N or O atoms of adjacent molecules, we will begin our discussion by focusing on the C—H···O intermolecular interactions that are also present. All three layers can be thought of as beginning with rows of molecules. These are parallel to [110] in polymorph I, with a repeat distance along the row of 7.820 (1) Å. They are parallel to [010] in polymorph II, with each of the A, B and C molecules forming its own row, with a repeat distance of 7.819 (2) Å. The geometric details along these rows are summarized in Table 1. The H···O distances are similar to those generally found; see Desiraju & Steiner (1999).
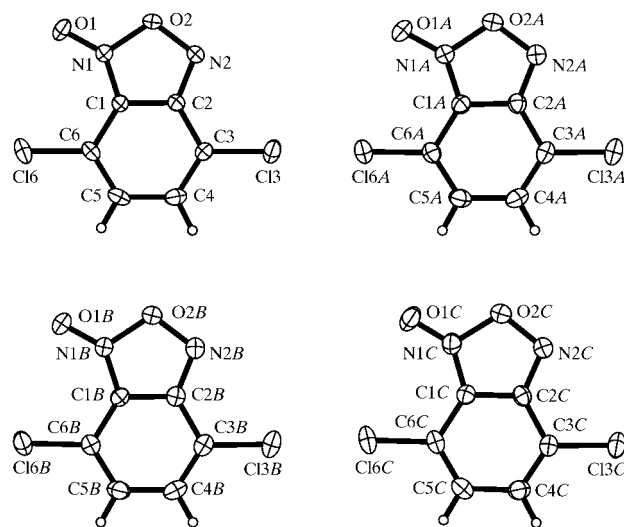

Figure 1
The four independent molecules of (I). Polymorph I is in the upper left corner; the remaining plots are for polymorph II. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.
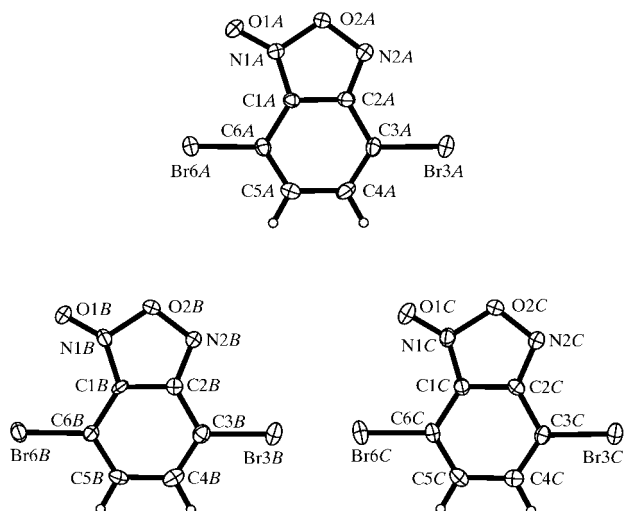
Figure 2
The three independent molecules of (II). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

The rows are combined in three different ways. In polymorph I, they are all parallel to each other and each molecule has contacts with two others on each side. In the two kinds of layers in polymorph II, each molecule has two contacts with the same antiparallel molecule on one side and contacts with two other parallel molecules on the other side. In the Cl-II*A*
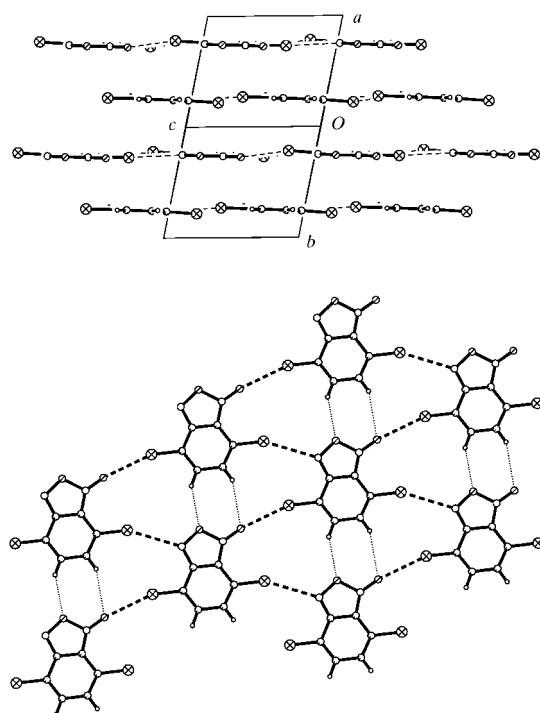
layers, the two molecules sharing two contacts are related by a center of symmetry, with both contacts being Cl···O. The contacts between parallel rows are all Cl···N. In the Cl-II*BC* layers, the two molecules sharing two contacts are one *B* and one *C*, with one Cl···O and one Cl···N contact. The contacts between parallel rows alternate between Cl···O and Cl···N. The geometric details for all these contacts are given in Table 2. For an extensive discussion of intermolecular inter-

Figure 3
The packing in (I), polymorph I (DCL-I). At the top is a view along the [110] direction. The bottom view is normal to (1$\overline{1}$0). The layer shown is that with four molecules in the top view. Heavy dashed lines indicate Cl···O and Cl···N interactions, and light dotted lines indicate C—H···O interactions.
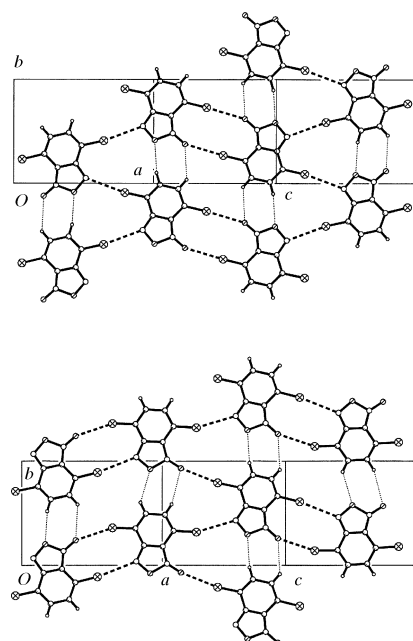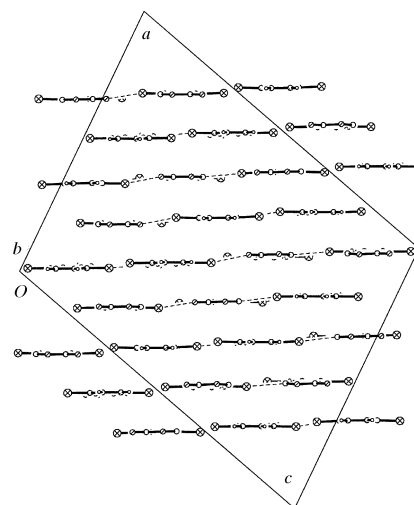
Figure 4
The packing in (I), polymorph II (DCL-II). The upper view is along the *b* axis. The top part of the lower view is normal to (10$\overline{1}$), and the layer shown contains the *A* molecules and passes through the origin in the upper view. The bottom part of the lower view is another view normal to (10$\overline{1}$). This layer contains the *B* (in the first and third columns) and *C* (in the second and fourth columns) molecules, and crosses the *c* axis at *c*/3 in the upper view. Heavy dashed lines indicate Cl···O and Cl···N interactions, and light dotted lines indicate C—H···O interactions. The packing in (II) is identical.

actions between halogens and N or O, see Lommerse *et al.* (1996).

These two polymorphs involve three two-dimensional polymorphic layers. As was mentioned earlier, it is surprising to have two different kinds of layers in polymorph II. If we consider the molecular volumes for (I), namely 187.9 Å³ for polymorph I and 188.7 Å³ for polymorph II, it seems likely that polymorph I is the more stable at low temperature (Dunitz, 1995). This is not inconsistent with the greater difficulty in obtaining crystals of DCL-II. On the other hand, the failure to grow crystals of DBR-I may be a consequence of the greater stability of DBR-II. It would be of interest to prepare 4,7-bromochlorobenzo[*c*]furazan 1-oxide to see which polymorphs would occur. It would also be of interest to see whether the Br and Cl atoms would be ordered or disordered.

Experimental

Samples of 4,7-dibromobenzo[*c*]furazan 1-oxide, (II), and 4,7-dichlorobenzo[*c*]furazan 1-oxide, (I), were prepared as described previously by Mallory *et al.* (1965). Compound (I) was recrystallized from acetone and the structure determined; the details are given below as DCL-I. Since the purpose of the study was to see whether (I) might be isomorphous with (II), a search was made for other polymorphs. Recrystallization of (I) from acetonitrile, acetone, benzene, methylene chloride, chloroform, carbon tetrachloride, methanol and ethanol all gave polymorph DCL-I. However, crystals of polymorph II were obtained from diethyl ether and propan-2-ol; the latter also gave polymorph I. A crystal from the propan-2-ol crystallization was used for the present structure determination and is reported below as DCL-II. Using the notation suggested by Zorky (1996), polymorph I is in space group $C2/c$ with $Z = 24$ (1^3), and polymorph II is in space group $P\bar{1}$ with $Z = 2$ (1). A similar search was made for polymorphs of (II). However, all of the solvents listed above produced only one polymorph, which is labeled polymorph II to be consistent with (I); no second polymorph of (II) could be found. A crystal grown from acetone was used for the structure determination; the data are given below as DBR-II.

Polymorph DCL-I

Crystal data

$C_6H_2Cl_2N_2O_2$	$Z = 2$
$M_r = 205.00$	$D_x = 1.812$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 7.357$ (2) Å	Cell parameters from 2332
$b = 7.667$ (2) Å	reflections
$c = 8.190$ (2) Å	$\theta = 2.7–27.5°$
$\alpha = 92.10$ (1)°	$\mu = 0.82$ mm^{-1}
$\beta = 109.81$ (1)°	$T = 173$ (2) K
$\gamma = 117.31$ (1)°	Prism, yellow
$V = 375.8$ (2) Å³	$0.3 \times 0.3 \times 0.1$ mm

Data collection

Siemens SMART CCD area-detector diffractometer	1447 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.021$
Absorption correction: multi-scan [*SADABS*; Sheldrick (1996) and Blessing (1995)]	$\theta_{max} = 27.5°$
	$h = -9 \rightarrow 9$
	$k = -9 \rightarrow 9$
	$l = -10 \rightarrow 10$
$T_{min} = 0.78$, $T_{max} = 0.92$	76 standard reflections
4117 measured reflections	frequency: 360 min
1695 independent reflections	intensity decay: <1%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0591P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.034$	$+ 0.0163P]$
$wR(F^2) = 0.095$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.09$	$(\Delta/\sigma)_{max} = 0.001$
1695 reflections	$\Delta\rho_{max} = 0.40$ e Å^{-3}
117 parameters	$\Delta\rho_{min} = -0.34$ e Å^{-3}
All H-atom parameters refined	

Polymorph DCL-II

Crystal data

$C_6H_2Cl_2N_2O_2$	$D_x = 1.804$ Mg m^{-3}
$M_r = 205.00$	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 1162
$a = 21.828$ (5) Å	reflections
$b = 7.819$ (2) Å	$\theta = 2.0–27.4°$
$c = 27.501$ (7) Å	$\mu = 0.81$ mm^{-1}
$\beta = 105.21$ (3)°	$T = 173$ (2) K
$V = 4529$ (2) Å³	Prism, yellow
$Z = 24$	$0.45 \times 0.20 \times 0.20$ mm

Table 1
Intermolecular C—H⋯O—N hydrogen-bond contacts in (I) and (II) (Å, °).

C—H⋯O—N	C—H	H⋯O	C⋯O	C—H⋯O	H⋯O—N
C4—H4⋯O2^i—N2^i	0.95	2.49	3.336 (2)	149	123
C5—H5⋯O1^i—N1^i	0.91	2.76	3.593 (2)	154	116
C4A—H4A⋯O2A^{ii}—N2A^{ii}	0.93	2.49	3.391 (2)	165	107
C5A—H5A⋯O1A^{ii}—N1A^{ii}	0.93	2.70	3.421 (2)	135	134
C4B—H4B⋯O2B^{ii}—N2B^{ii}	0.93	2.47	3.386 (2)	167	143
C5B—H5B⋯O1B^{ii}—N1B^{ii}	0.93	2.69	3.415 (2)	135	135
C4C—H4C⋯O2C^{ii}—N2C^{ii}	0.93	2.61	3.364 (2)	138	115
C5C—H5C⋯O1C^{ii}—N1C^{ii}	0.93	2.80	3.694 (2)	162	108
C4A—H4A⋯O2A^{ii}—N2A^{ii}	0.95	2.50	3.417 (5)	164	107
C5A—H5A⋯O1A^{ii}—N1A^{ii}	0.95	2.71	3.435 (5)	134	135
C4B—H4B⋯O2B^{ii}—N2B^{ii}	0.95	2.48	3.411 (4)	168	144
C5B—H5B⋯O1B^{ii}—N1B^{ii}	0.95	2.70	3.434 (4)	134	136
C4C—H4C⋯O2C^{ii}—N2C^{ii}	0.95	2.62	3.387 (5)	138	115
C5C—H5C⋯O1C^{ii}—N1C^{ii}	0.95	2.80	3.713 (4)	161	109

Symmetry codes: (i) $1 + x, 1 + y, z$; (ii) $x, y - 1, z$.

Table 2
Distances and angles in the C—X⋯Y—Z contacts in (I) and (II) (Å, °).

C—X⋯Y—Z	C—X⋯Y	X⋯Y	X⋯Y—Z
C3—Cl3⋯O1^i—N1^i	157.7 (2)	3.010 (2)	166.3 (2)
C6—Cl6⋯N2^{ii}—O2^{ii}	156.3 (2)	3.191 (2)	119.3 (2)
C3A—Cl3A⋯N2A^{iii}—O2A^{iii}	170.8 (2)	3.140 (2)	109.7 (2)
C6A—Cl6A⋯O1A^{iv}—N1A^{iv}	168.8 (2)	3.045 (2)	152.6 (2)
C3B—Cl3B⋯O1C—N1C	166.4 (2)	2.987 (2)	166.8 (2)
C6B—Cl6B⋯N2C^v—O2C^v	171.0 (2)	3.135 (2)	117.4 (2)
C3C—Cl3C⋯O1B^{vi}—N1B^{vi}	157.0 (2)	2.936 (2)	154.7 (2)
C6C—Cl6C⋯N2B^{vii}—O2B^{vii}	159.9 (2)	3.068 (2)	113.1 (2)
C3A—Br3A⋯N2A^{iii}—O2A^{iii}	172.3 (4)	3.131 (3)	110.1 (3)
C6A—Br6A⋯O1A^{iv}—N1A^{iv}	169.1 (4)	3.100 (3)	152.1 (3)
C3B—Br6B⋯O1C—N1C	167.4 (4)	2.982 (3)	163.4 (3)
C6B—Br6B⋯N2C^v—O2C^v	169.8 (4)	3.151 (3)	117.7 (3)
C3C—Br3C⋯O1B^{vi}—N1B^{vi}	155.9 (4)	2.995 (3)	152.2 (3)
C6C—Br6C⋯N2B^{vii}—O2B^{vii}	159.7 (4)	3.093 (3)	111.6 (3)

Symmetry codes: (i) $1 + x, 1 + y.1 + z$; (ii) $x, y, z - 1$; (iii) $\frac{3}{2} - x, y - \frac{1}{2}, \frac{3}{2} - z$; (iv) $1 - x, 1 - y, 1 - z$; (v) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; (vi) $x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$; (vii) $x, y - 1, z$.

organic compounds

Data collection

Siemens SMART CCD area-
detector diffractometer
ω scans
Absorption correction: multi-scan
[*SADABS*; Sheldrick (1996) and
Blessing (1995)]
$T_{min} = 0.72$, $T_{max} = 0.85$
13 985 measured reflections
5149 independent reflections

4301 reflections with $I > 2\sigma(I)$
$R_{int} = 0.020$
$\theta_{max} = 27.5°$
$h = -28 \rightarrow 24$
$k = -10 \rightarrow 8$
$l = -33 \rightarrow 35$
227 standard reflections
   frequency: 360 min
   intensity decay: <1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.081$
$S = 1.06$
5149 reflections
325 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.035P)^2$
   $+ 4.8P]$
   where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.42$ e Å^{-3}
$\Delta\rho_{min} = -0.29$ e Å^{-3}

Compound DBR-II

Crystal data

$C_6H_2Br_2N_2O_2$
$M_r = 293.92$
Monoclinic, $C2/c$
$a = 22.810 (6)$ Å
$b = 7.835 (2)$ Å
$c = 27.859 (7)$ Å
$\beta = 105.31 (2)°$
$V = 4802 (2)$ Å^3
$Z = 24$

$D_x = 2.439$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2707
   reflections
$\theta = 2.7–27.2°$
$\mu = 10.08$ mm^{-1}
$T = 175 (2)$ K
Prism, yellow
$0.25 \times 0.20 \times 0.15$ mm

Data collection

Siemens SMART CCD area-
detector diffractometer
ω scans
Absorption correction: multi-scan
[*SADABS*; Sheldrick (1996) and
Blessing (1995)]
$T_{min} = 0.10$, $T_{max} = 0.22$
27 206 measured reflections
5513 independent reflections

4095 reflections with $I > 2\sigma(I)$
$R_{int} = 0.052$
$\theta_{max} = 27.5°$
$h = -29 \rightarrow 29$
$k = -10 \rightarrow 10$
$l = -36 \rightarrow 36$
153 standard reflections
   frequency: 600 min
   intensity decay: <1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.058$
$S = 1.05$
5513 reflections
325 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.018P)^2$
   $+ 6.94P]$
   where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.92$ e Å^{-3}
$\Delta\rho_{min} = -0.66$ e Å^{-3}

For the triclinic polymorph of (I), H-atom parameters were
refined, giving C—H distances of 0.91 (2) and 0.95 (2) Å. For the
monoclinic polymorph of (I), and also for (II), H atoms were treated
as riding, with C—H distances of 0.93 and 0.95 Å, respectively.

For both compounds, data collection: *SMART* (Siemens, 1995);
cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT*;
program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997);
program(s) used to refine structure: *SHELXTL*; molecular graphics:
SHELXTL; software used to prepare material for publication:
SHELXTL.

Supplementary data for this paper are available from the IUCr electronic
archives (Reference: BK1639). Services for accessing these data are
described at the back of the journal.

References

Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–38.
Britton, D. (1992). *Acta Cryst.* C**48**, 1283–1285.
Desiraju, G. R. & Steiner, T. (1999). *The Weak Hydrogen Bond*. Oxford
   University Press.
Dunitz, J. D. (1995). *Acta Cryst.* B**51**, 619–631.
Lommerse, J. P. M., Stone, A. J., Taylor, R. & Allen, F. H. (1996). *J. Am. Chem.*
   Soc. **118**, 3108–3116.
Mallory, F. B., Manatt, S. L. & Wood, C. S. (1965). *J. Am. Chem. Soc.* **87**, 5433–
   5438.
Sheldrick, G. M. (1997). *SHELXTL*. Version 5.1. Siemens Analytical X-ray
   Instruments Inc., Madison, Wisconsin, USA.
Sheldrick. G. M. (1996). *SADABS*. University of Göttingen, Germany.
Siemens (1995). *SMART* and *SAINT*. Versions 4.0. Siemens Analytical X-ray
   Instruments Inc., Madison, Wisconsin, USA.
Zorky, P. M. (1996). *J. Mol. Struct.* **374**, 9–28.