research papers

5-Chloro- and 5-bromobenzfurazan 1-oxide revisited

Maren Pink and Doyle Britton*

Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455-0431, USA

Correspondence e-mail:
britton@chemsun.chem.umn.edu

At room temperature the two title compounds are isomorphous. Both have a disordered structure that includes a major component, one of the title compounds, and a minor component, the 6-halo isomer, occurring at the same site in the crystal. When the chloro compound is cooled to as low as 98 K, there is no change in the structure and no significant change in the degree of disorder. When the bromo compound is cooled, it undergoes a second-order phase transition at 282 K to a second polymorph, structurally very similar, but with two molecules in the asymmetric unit. In both isomorphs and both polymorphs the molecules occur in two-dimensional layers that are essentially the same. In the low-temperature form of the bromo compound the layers have shifted relative to each other by approximately 0.7 Å in y. In the low-temperature form the disorder, which is still present after the transition, decreases as the temperature is lowered.

1. Introduction

The structures of the title compounds were originally determined, using film data (Britton & Noland, 1962; Britton *et al.*, 1972), to confirm that *ortho*-dinitroso aromatic molecules in fact contained the heterocyclic ring system. During recent work on the disorder in 5,6-dichlorobenzfurazan 1-oxide polymorphs (Ojala *et al.*, 1999) improved metric data for the title compounds would have been useful and redeterminations of the two structures using area-detector data were begun. These were expected to be routine, but two unexpected results were obtained. First, both structures at room temperature were found to contain a disordered mixture of the two isomers with the halogen atoms at the 5- or 6- positions (see Fig. 1). We will abbreviate the isomers as 5-XBF and 6-XBF. Second, at low temperatures the bromo compound transformed to a second polymorph with a unit cell twice as large, but with essentially the same packing. The details of both these findings are reported here.

2. Experimental

Both compounds were synthesized by the hypochlorite oxidation of either the 4- or 5-halo-2-nitroaniline. In each case the same product was obtained from either starting isomer. Crystals of both compounds suitable for X-ray diffraction were obtained by recrystallization from ethanol.

2.1. Structure of the chloro compound

The structure of the chloro compound was first determined at 174 K and then, after the disorder (see below) was

Table 1
Experimental details.

	Cl 273 K	Cl 98 K	Br 299 K	Br 173 K
Crystal data				
Chemical formula	$C_6H_3ClN_2O_2$	$C_6H_3ClN_2O_2$	$C_6H_3BrN_2O_2$	$C_6H_3BrN_2O_2$
Chemical formula weight	170.55	170.55	215.01	215.01
Cell setting, space group	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$
a, b, c (Å)	7.973 (2), 7.0579 (15), 12.389 (3)	7.8317 (10), 7.0527 (9), 12.2576 (15)	7.954 (4), 7.297 (3), 12.574 (6)	14.5294 (3), 7.4121 (2), 14.5587 (3)
β (°)	92.683 (4)	93.612 (2)	90.124 (8)	115.676 (1)
V (Å^3)	696.4 (3)	675.70 (15)	729.9 (6)	1413.06 (6)
Z	4	4	4	8
D_x (Mg m^{-3})	1.627	1.677	1.957	2.021
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
No. of reflections for cell parameters	449	1621	1671	4919
θ range (°)	2.9–17.4	3.0–25.0	2.8–21.7	3.1–31.9
μ (mm^{-1})	0.490	0.505	5.576	5.761
Temperature (K)	273 (2)	98 (1)	299 (1)	173 (1)
Crystal form, colour	Prism, yellow	Prism, yellow	Prism, yellow	Prism, yellow
Crystal size (mm)	$0.50 \times 0.32 \times 0.21$	$0.26 \times 0.24 \times 0.22$	$0.35 \times 0.20 \times 0.10$	$0.45 \times 0.31 \times 0.18$
Data collection				
Diffractometer	Siemens *SMART*	Siemens *SMART*	Siemens *SMART*	Siemens *SMART*
Data collection method	ω scans	ω scans	ω scans	ω scans
Absorption correction	Multi-scan	Multi-scan	Multi-scan	Multi-scan
T_{min}	0.84	0.87	0.30	0.13
T_{max}	0.90	0.89	0.57	0.35
No. of measured, independent and observed parameters	3550, 1231, 620	3517, 1199, 971	5494, 1650, 896	25 565, 5442, 3583
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.0275	0.0214	0.0299	0.0395
θ_{max} (°)	25.05	25.06	27.51	33.52
Range of h, k, l	$-9 \rightarrow h \rightarrow 9$	$-9 \rightarrow h \rightarrow 5$	$-10 \rightarrow h \rightarrow 10$	$-22 \rightarrow h \rightarrow 22$
	$-8 \rightarrow k \rightarrow 7$	$-8 \rightarrow k \rightarrow 7$	$-9 \rightarrow k \rightarrow 9$	$-10 \rightarrow k \rightarrow 11$
	$-14 \rightarrow l \rightarrow 14$	$-14 \rightarrow l \rightarrow 14$	$-16 \rightarrow l \rightarrow 16$	$-22 \rightarrow l \rightarrow 18$
Refinement				
Refinement on	F^2	F^2	F^2	F^2
$R[F^2>2\sigma(F^2)]$, $wR(F^2)$, S	0.0341, 0.0747, 1.161	0.0356, 0.0973, 1.117	0.0464, 0.1271, 1.221	0.031, 0.0707, 1.125
No. of reflections and parameters used in refinement	1231, 165	1199, 165	1650, 135	5442, 268
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.037P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.062P)^2 + 0.113P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.084P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.039P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	0.003	0.013	0.001	0.004
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.134, −0.103	0.258, −0.197	0.567, −0.535	0.611, −0.773
Extinction method	None	None	*SHELXTL*	*SHELXTL*
Extinction coefficient	–	–	0.013 (3)	0.0076 (4)

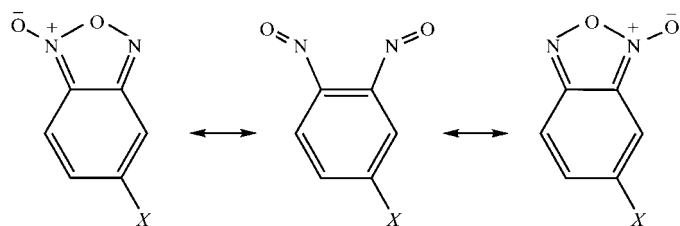Computer programs used: *SMART* and *SAINT* (Siemens, 1995), *SHELXTL* (Sheldrick, 1994).

Figure 1
Conversion of 5-halobenzfurazan 1-oxide (left) to 6-halobenzfurazan 1-oxide (right) through a dinitroso intermediate.

discovered, at several other temperatures to determine how the amount of disorder varied with temperature. The temperature was also taken as low as possible (98 K) to see whether the transformation found in the bromo compound took place at all; it did not. The itemized crystal data for the 98 K and one of the 273 K determinations are given in Table 1. The higher temperature determination was made at 273 K because the crystal decomposed too rapidly, through sublimation, at 298 K. The changes in cell constants with temperature are shown in Fig. 2; the values shown in Fig. 2

were all measured on the same crystal and differ slightly from the values in Table 1.

The results of the early structure determination (Britton & Noland, 1962) were taken as the trial structure. The initial refinement of the new data, which assumed an ordered structure of 5-ClBF, converged with an unacceptably high R value. The difference Fourier map showed peaks near the Cl atom and in the $(NO)_2$ region (see Fig. 3 for the difference map for the 98 K determination). These peaks were ultimately explained by assuming that the other isomer, 6-ClBF, was present to a significant extent. Since the positions of the two isomers overlapped almost completely, they could not be refined independently. The two $C_6H_3N_2O_2$ fragments were restrained to be the same within 0.001 Å and the C—Cl distances to be the same within 0.002 Å; the two C atoms in each of the overlapping pairs were constrained to have identical anisotropic displacement parameters (ADP's), although the N, O and Cl ADP's could be refined independently. With these restrictions, refinement converged smoothly at every temperature. Table 2 shows a comparison of the refinements assuming order and disorder for all the data sets collected. Less attention was paid to the cooling rate with the chloro compound than with the bromo (see below), but the structure determination at 98 K was on a sample that had been cooled
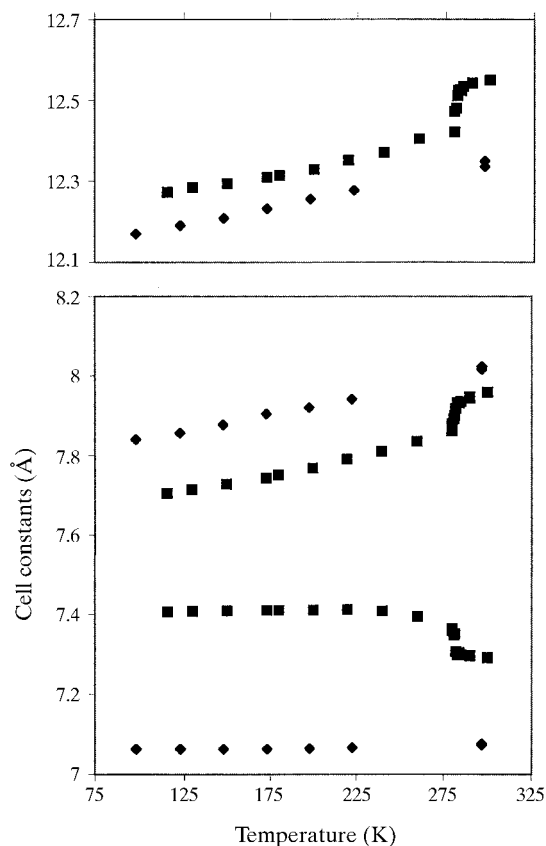
Table 2
Comparison of ordered and disordered models.

R = conventional R for data with $I > 2\sigma(I)$; ρ_{max} is the highest peak in the final difference Fourier map; disorder parameter: fractional occupancy of the minor component, 6-XBF.

Temperature (K)	Ordered		Disordered		
	R	ρ_{max} (e Å^{-3})	R	ρ_{max} (e Å^{-3})	Disorder parameter
$ClC_6H_3N_2O_2$					
273†	0.082	0.59	0.034	0.13	0.221 (5)
273	0.075	0.49	0.041	0.17	0.207 (8)
223	0.091	0.97	0.037	0.19	0.202 (4)
223	0.090	0.77	0.042	0.21	0.204 (4)
174	0.105	1.16	0.048	0.24	0.239 (5)
174	0.102	1.26	0.035	0.25	0.242 (4)
173	0.099	1.20	0.038	0.19	0.214 (3)
124	0.097	1.47	0.036	0.31	0.201 (4)
98†	0.101	1.59	0.036	0.26	0.211 (4)
High-temperature $BrC_6H_3N_2O_2$					
299†	0.075	1.12	0.046	0.57	0.143 (5)
297	0.077	1.32	0.055	0.57	0.138 (6)
284	0.065	0.97	0.047	0.35	0.118 (6)
Low-temperature $BrC_6H_3N_2O_2$					
280	0.054	0.89	0.044	0.51	0.074 (3)‡ 0.094 (4)‡
273	0.054	1.45	0.039	0.74	0.057 (2) 0.084 (2)
223	0.046	1.53	0.043	1.47	0.014 (1) 0.040 (2)
223	0.043	1.28	0.038	1.23	0.021 (2) 0.037 (2)
173§	0.054	1.80	0.035	1.17	0.123 (3) 0.125 (3)
173§	0.057	1.93	0.037	1.36	0.103 (3) 0.118 (3)
173	0.030	0.95	0.027	0.57	0.011 (1) 0.023 (1)
173†	0.034	1.31	0.031	0.61	0.011 (1) 0.027 (1)

† This sample is described fully in Table 1. ‡ First column refers to molecules 1 and 3, second column molecules 2 and 4. § Rapidly cooled – see text.

from room temperature in 25° steps over the course of 8 h and the degree of disorder was the same as in the 124 K determination on a sample that had been quickly cooled.

2.2. Structure of the bromo compound – general

The bromo compound was first examined at 173 K and found to have a unit cell different from the earlier room-temperature cell. Data were collected and the structure solved using direct methods. The crystal was then warmed to 297 K, where it was found to have the same structure as the earlier one. The transformation from room temperature to low temperature and back to room temperature did not appear to damage the single crystal at all; this would seem to be consistent with a second-order transformation. The high-temperature cell has $Z = 4$ (1), while the low-temperature form has $Z = 8$ (1^2), where the notation of Zorky (Zorky *et al.*, 1967; Belsky *et al.*, 1995; Zorky, 1996) has been used to show the structural class. The matrix $101/0\bar{1}0/10\bar{1}$ converts the cell constants of the high-temperature form to a new set very similar to those of the low-temperature form. The changes in the cell constants with temperature for the bromo compound are shown in Fig. 2, where the inverse transformation, $0.5,0,0.5/0,-1,0/0.5,0,-0.5$, was used so that all the cell constants are similar to the high-temperature values and to those of the chloro compound. As with the chloro compound,

Figure 2
Temperature dependence of the cell constants. Diamonds: $ClC_6H_3N_2O_2$; squares: $BrC_6H_3N_2O_2$. Top: *c*; center: *a*; bottom: *b*. The points for Cl-*c* have been displaced down by 0.1 Å to avoid overlap.

structures were determined at several temperatures to determine how the amount of disorder varied with temperature.

2.3. Structure of the bromo compound – high temperature

The same disorder problem was present in the high-temperature bromo structure as in the chloro structure. The difference maps assuming no disorder were not as clear cut as that shown in Fig. 3 for two reasons: first the larger scattering from the Br made the light atom contributions less clear, and second the amount of disorder was less. Nevertheless, there were clear peaks in the $(NO)_2$ region as well as near the Br.

As a consequence of the lower amount of disorder and the greater predominance of the Br atom more restraints had to be imposed. The ADP's for the N and O atoms in the minor constituent invariably had non-positive definite matrices. To avoid this, refinement with isotropic displacement parameters (IDP's) for the minor component was tried, as well as refinement with ADP's of the minor component atoms constrained to be the same as those of the nearest like atom of the major component. Both procedures gave essentially the same values for R and wR. Since the constrained ADP's involved fewer parameters, this was used for all the final calculations. For the Br atoms independent refinement of the ADP's sometimes converged satisfactorily, but sometimes not. Again it made very little difference in R and wR whether IDP's or constrained ADP's were used, and again constrained ADP's were used. Finally, the minor component molecules were restrained to be planar within 0.001 Å. It was felt necessary to use the same procedure in each final refinement in order to make the estimates of the degree of disorder comparable to each other since these estimates varied by up to ten s.u.'s depending on the restraints used. Table 2 includes the high-temperature bromo structure results for both ordered and disordered refinements. The data for a determination at 299 K are included in Table 1.
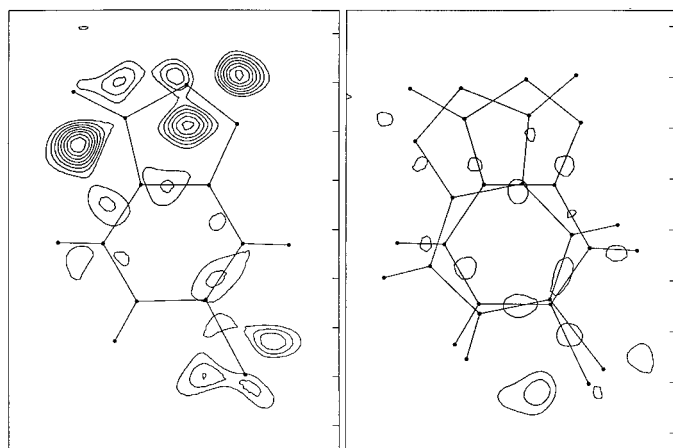
2.4. Structure of the bromo compound – low temperature

The first determination of this structure was made on a crystal that was placed directly in the cooling stream at 173 K. The direct method solution appeared to be straightforward and the refinement converged with $R = 0.054$ using the assumption that the structure was ordered 5-BrBF. After the disorder at higher temperatures was discovered, the data were reexamined and disorder was found to about the same extent as in the high-temperature form. Allowance for a fractional disorder of 0.124 (4) lowered the R value to 0.035. However, the situation was not this simple.

When the structure was determined on a sample at 280 K, just below the transition temperature, there appeared to be considerably less disorder. The difference map showed peaks near the Br atoms and, as might be expected, they were higher than the corresponding peaks in the Cl maps. However, there were no peaks in the $(NO)_2$ region and when refinement of the disordered model was attempted, depending on where the minor component was placed at the start of the refinement, its final position varied and the degree of disorder changed by more than five s.u.'s. We conclude from this that the disorder is at such a low level that it cannot be determined accurately from the data. Nevertheless, the disorder appeared to be real and, for the sake of consistency, each disordered refinement was begun at the final positions found at the next higher temperature. Determinations were also made at 273 and 223 K with essentially the same results as at 280 K. At 223 K the structure was determined on a freshly cooled sample. The crystal was held at 223 K for 24 h and the structure was redetermined. There were no significant changes in the results.

To address the apparently higher disorder found at 173 K, we first repeated the determination on a new crystal mounted directly in the cold stream, just as the first one had been. The results were essentially the same. Then a new crystal was cooled from 297 to 173 K at a rate of 5 K h^{-1} over the course of 24 h before the structure was determined. This set of data

Figure 3
Difference Fourier maps for $ClC_6H_2N_2O_2$ at 98 K. Left: map assuming structure with no disorder; contour interval 0.2 e Å^{-3}, lowest contour 0.2. Right: map allowing for disorder between the isomers; contour interval 0.1 e Å^{-3}, lowest contour 0.1.
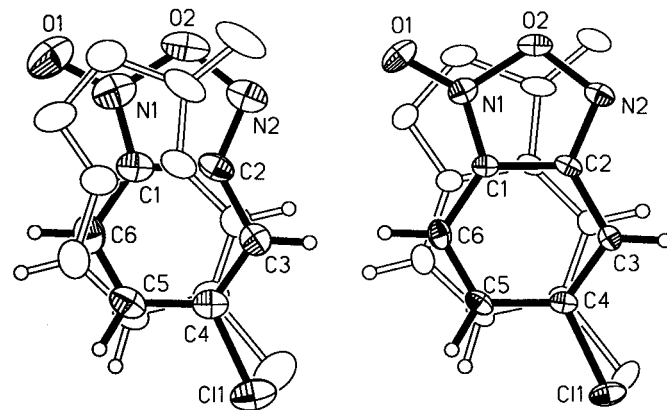

Figure 4
ClBF at 273 K (left) and 98 K (right). Displacement ellipsoids are shown at the 20% probability level to avoid excessive overlap. H atoms are shown as spheres of arbitrary radius. The two orientations are shown at the correct juxtaposition. The shaded molecule is the predominant component (78% at 273 K, 79% at 98 K).

Table 3
Selected geometric parameters (Å, °) for 5-chloro-, 5-bromo- and 5-methylbenzfurazan-1-oxide.

	Cl	Br1	Br2	CH_3[a]
$X-C4$	1.733 (3)	1.897 (2)	1.889 (2)	1.511
$C1-C2$	1.404 (4)	1.411 (3)	1.410 (3)	1.407
$C2-C3$	1.425 (4)	1.435 (2)	1.434 (2)	1.430
$C3-C4$	1.352 (4)	1.346 (2)	1.352 (2)	1.354
$C4-C5$	1.427 (3)	1.437 (2)	1.440 (2)	1.455
$C5-C6$	1.349 (4)	1.352 (3)	1.339 (3)	1.365
$C6-C1$	1.406 (4)	1.408 (3)	1.408 (2)	1.413
$C1-N1$	1.343 (5)	1.332 (2)	1.329 (2)	1.332
$C2-N2$	1.330 (4)	1.325 (2)	1.327 (2)	1.335
$N1-O1$	1.232 (4)	1.226 (2)	1.236 (2)	1.240
$N1-O2$	1.448 (4)	1.454 (2)	1.446 (2)	1.451
$N2-O2$	1.383 (4)	1.378 (2)	1.381 (2)	1.390
$C6-C1-C2$	123.3 (3)	123.1 (2)	123.1 (2)	123.3
$C1-C2-C3$	119.6 (2)	119.7 (2)	119.7 (2)	119.5
$C2-C3-C4$	115.4 (2)	115.7 (2)	115.6 (2)	117.8
$C3-C4-C5$	124.9 (3)	124.1 (2)	123.9 (2)	121.4
$C4-C5-C6$	120.2 (3)	121.1 (2)	121.3 (2)	122.3
$C5-C6-C1$	116.6 (3)	116.2 (2)	116.5 (2)	115.7
$C2-C1-N1$	106.7 (3)	107.2 (2)	106.9 (2)	107.2
$C1-C2-N2$	113.1 (3)	112.2 (2)	112.5 (2)	112.6
$C1-N1-O2$	106.1 (2)	106.0 (2)	106.5 (2)	106.5
$C2-N2-O2$	104.7 (3)	105.5 (2)	105.0 (2)	104.8
$N1-O2-N2$	109.5 (2)	109.1 (2)	109.2 (2)	109.0
$O1-N1-O2$	118.4 (3)	117.6 (2)	117.3 (2)	117.8

Reference: Britton & Noland (1972).

showed very little disorder. The first two samples at 173 K apparently had the disorder frozen in. Finally, to try to make the measurement of the disorder more certain, the data were recollected on the slowly cooled sample at 173 K out to a maximum theta of 33°, compared with the 25–26° limit that had been used with all the other data sets. The results for this last set of data are included in Table 1.

3. Discussion

3.1. General

The atom labeling and anisotropic displacement ellipsoids for the chloro compound at 273 and 98 K are shown in Fig. 4 and for the bromo compound at 299 and 173 K in Fig. 5. The final coordinates are provided in the supplementary material.[1] Bond lengths and angles for the chloro compound at 98 K and the bromo compound at 173 K are compared in Table 3 to related values from the corresponding methyl compound (Britton & Noland, 1972). The values, for the most part, agree well. There are significant differences in the ring angles at C3, C4, C5 and C6, but these are in the direction that would be expected from the replacement of the halogen by a methyl group (see Domenicano, 1992).

---

[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK0096). Services for accessing these data are described at the back of the journal.

3.2. The disorder

Both of these compounds have been studied in solution (Uematsu & Akahori, 1978) by NMR spectroscopy. Both show an equilibrium between 5-XBF and 6-XBF with the 5-XBF isomer as the major component. At 195 K the chloro mixture was 0.31 of the 6-ClBF isomer and at 243 K the bromo mixture was 0.40 of 6-BrBF. The temperature dependence of the equilibrium was not reported so the energy difference between the two forms in solution cannot be calculated.

The chloro compound in the crystalline state appears to have about the same amount of disorder at all temperatures measured (see Table 2). As in solution, the 5-ClBF is the major component. It is possible that the constancy of the disorder with temperature is a consequence of frozen-in disorder, but there is nothing in the data to confirm this (see §2).

The high-temperature form of the bromo compound is only stable down to 282 K. The range of accessible temperatures is too small to decide whether there is a temperature dependency in the disorder. Again, as in solution, the 5-BrBF is the major component. There is, however a significant difference between the solution and the crystalline state. In solution the
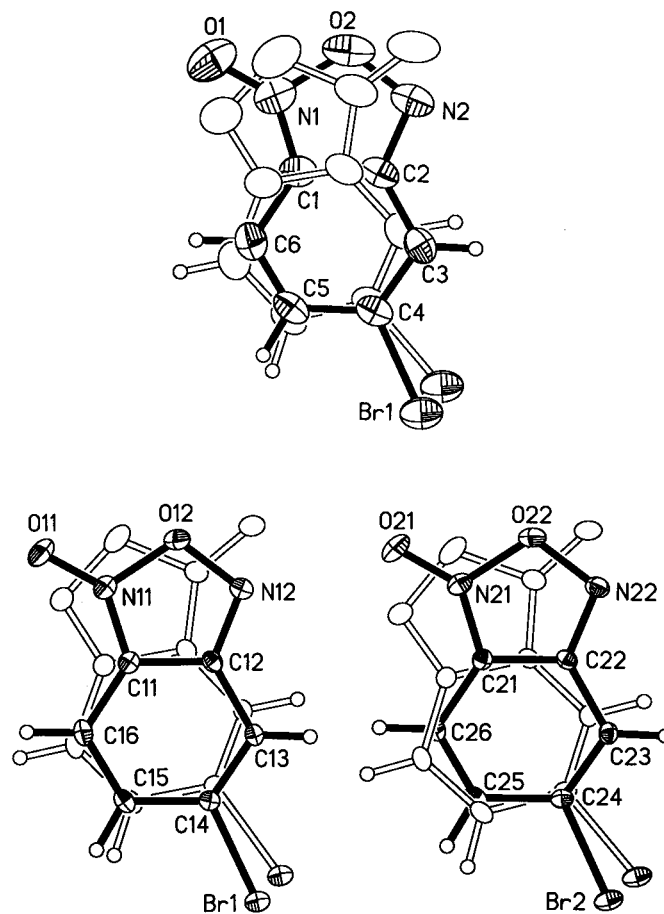

Figure 5
BrBF at 299 K (top) and 173 K (bottom). Displacement ellipsoids are shown at the 20% probability level. The two orientations are shown at the correct juxtaposition. The shaded molecule is the predominant component (86% at 299 K, 99% for molecule 1 and 97% for molecule 2 at 173 K).

Table 4
Intermolecular C—$X\cdots$N—O contacts.

C	X	N	O	C—$X\cdots$N (°)	$X\cdots$N (Å)	$X\cdots$N—O (°)
ClBF 273 K						
C4	Cl1	N2[i]	O2[i]	168.1	3.184	96.3
ClBF 98 K						
C4	Cl1	N2[i]	O2[i]	167.2	3.139	98.5
BrBF 299 K						
C4	Br1	N2[i]	O2[i]	168.9	3.167	104.4
BrBF 173 K molecule 1						
C14	Br1	N22[ii]	O22[ii]	171.6	3.098	112.2
BrBF 173 K molecule 2						
C24	Br2	N12[iii]	O12[iii]	165.6	3.138	105.9

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

The low-temperature form of the bromo compound shows less disorder than the high-temperature form and it also shows an unmistakable trend with temperature. The disorder in the high-temperature form at 284 K, 0.118 (6) 6-BrBF, is larger than that in the low-temperature form at 280 K, 0.074 (3), beyond experimental uncertainty. In the slowly cooled samples the disorder continues to decrease to the point at 173 K where one might question whether it is even measurable. Although the trend is clear, an Arrhenius plot of the data does not give a straight line, so it is not possible to estimate the enthalpy and entropy changes associated with the disorder. One other point does seem clear, however, and that is that the disorder at the molecule A position is always less than at the molecule B position, suggesting that the packing energy at the molecule A site is slightly larger.

If the constancy of the fraction of disorder in the ClBF is due to a frozen-in non-equilibrium, there is no apparent reason in the packing that would explain why the same frozen-

difference in the amounts of the two isomers is greater for the chloro than for the bromo compound, while in the crystals it is just the opposite. The bromo compound would be expected to have a larger packing energy and these results suggest that the packing energy difference between the two isomers favors the 5-XBF isomer just as the intrinisic energy between the isomers does.
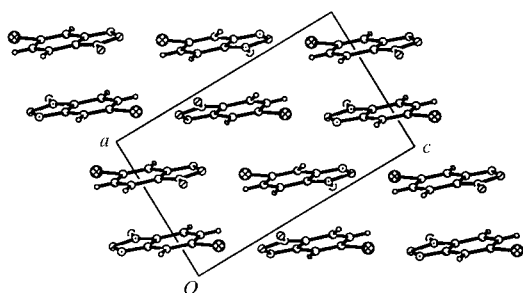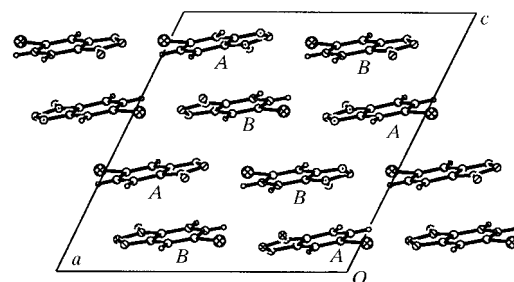

Figure 6
The packing of BrBF at 299 K. Above: view along **b**. Below: view perpendicular to the (101) plane. Only the bottommost layer in the upper view is shown in the lower view. Dotted lines show the short Br$\cdots$N contacts. Only the major component is shown. The packing of ClBF at all temperatures would look the same.

Figure 7
The packing of BrBF at 173 K. Above: view along **b**. Below: view perpendicular to the (001) plane. Only the bottommost layer in the upper view is shown in the lower view. The two sets of crystallographically independent molecules are labelled A and B. Dotted lines show the short Br$\cdots$N contacts. Only the major component is shown.

Table 5
Intermolecular C—H···Y—Z contacts less than 3.20 Å (Y = O, Cl, Br; Z = N, C).

In each section the entries above the rule are contacts within the layers shown in Figs. 6 and 7. The entries below the rule are contacts between layers.

C	H	Y	Z	C—H···Y ($°$)	H···Y (Å)	H···Y—Z ($°$)	C···Y (Å)
ClBF 273 K							
C3	H3	O1[i]	N1[i]	133.8	2.867	118.5	3.754
C5	H5	O1[ii]	N1[ii]	152.5	3.076	92.6	3.925
C5	H5	O2[ii]	N1[ii]	142.2	2.844	98.4	3.624
C6	H6	Cl1[iii]	C4[iii]	142.3	3.353	100.5	4.127
C3	H3	O2[iv]	N2[iv]	121.5	2.772	101.1	3.353
C5	H5	Cl1[v]	C4[v]	128.0	3.190	114.5	3.833
C6	H6	O1[vi]	N1[vi]	138.6	2.526	134.6	3.282
ClBF 98 K							
C3	H3	O1[i]	N1[i]	137.0	2.746	117.8	3.384
C5	H5	O1[ii]	N1[ii]	152.7	3.023	92.2	3.823
C5	H5	O2[ii]	N1[ii]	142.7	2.731	100.1	3.517
C6	H6	Cl1[iii]	C4[iii]	146.5	3.232	102.1	4.040
C3	H3	O2[iv]	N2[iv]	117.8	2.739	99.9	3.277
C5	H5	Cl1[v]	C4[v]	126.5	3.101	115.6	3.730
C6	H6	O1[vi]	N1[vi]	133.1	2.511	132.5	3.219
BrBF 299 K							
C3	H3	O1[i]	N1[i]	138.2	2.791	125.1	3.539
C5	H5	O1[ii]	N1[ii]	155.0	3.170	90.6	4.032
C5	H5	O2[iii]	N1[iii]	138.8	2.799	101.7	3.552
C6	H6	Br1[iv]	C4[iv]	145.2	3.310	105.8	4.108
C3	H3	O2[v]	N2[v]	122.2	2.816	98.2	3.404
C5	H5	Br1[vi]	C4[vi]	128.8	3.280	115.9	3.932
C6	H6	O1[vii]	N1[vii]	133.6	2.587	135.1	3.299
BrBF 173 K molecule 1							
C13	H13	O11[iii]	N11[iii]	145.1	2.625	131.2	3.448
C15	H15	O21[vii]	N21[vii]	159.1	3.107	86.5	4.008
C15	H15	O22[vii]	N21[vii]	141.9	2.522	108.1	3.322
C16	H16	Br1[i]	C14[i]	149.6	3.229	109.1	4.077
C13	H13	O22[viii]	N22[viii]	100.2	2.929	76.3	3.235
C15	H15	Br1[ix]	C14[ix]	124.4	3.274	113.1	3.891
C16	H16	O21[x]	N21[x]	128.5	2.580	133.9	3.257
BrBF 173 K molecule 2							
C23	H23	O21[i]	N21[i]	140.8	2.597	131.9	3.386
C25	H25	O11	N11	157.8	2.978	91.7	3.874
C25	H25	O12	N11	134.3	2.696	98.8	3.427
C26	H26	Br2[iii]	C24[iii]	147.9	3.170	112.9	4.006
C23	H23	O12[xi]	N12[xi]	137.0	2.920	113.5	3.672
C25	H25	Br2[xii]	C24[xii]	123.1	3.154	113.6	3.758
C26	H26	O11[xii]	N11[xii]	128.1	2.759	133.0	3.428

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

Fig. 7. In both forms the molecules are assembled in approximately planar layers. The details of the interactions within the layers between the halogen atom on one molecule and a nitrogen atom on the next are shown in Table 4. The distances are not especially short. The suggested van der Waals radii for non-spherical atoms (Nyburg & Faerman, 1985) would predict Cl···N distances of 3.18 Å and Br···N distances of 3.14 Å, which are about what is found. The geometries, however, are suggestive of Lewis acid–base interactions with the angle at the halogen (acid) near linear and the angle at the nitrogen (base) near tetrahedral. The change in the bromo distance between the two forms is what would be expected from the change in temperature.

The details of the intermolecular interactions involving hydrogen are given in Table 5. In Table 5 the interactions are separated into those within the layers and those between layers. The H3 atom is involved in two approximately equal interactions, one to an O1 atom in the same layer and the other to an O2 atom in an adjacent layer. The H5 atom is involved in a bifurcated interaction to an O1 atom and an O2 atom in an adjacent molecule in the same layer, as well as another to a halogen atom in an adjacent layer. The H6 atom is involved in one interaction to a halogen atom in the same layer and another to an O1 atom in the next layer. There are small changes in these interactions between the high- and low-temperature forms of the BrBF, as well as between the two independent low-temperature BrBF molecules, but none are particularly striking. Desiraju (1991) has pointed out that CH···X interactions occur over a broader range of distances than are usually found in NH···X or OH···X hydrogen bonds, but that there is a tendency towards linearity, regardless of the distance. In our compounds the in-layer interactions are closer to linear than the between-layer ones and would appear to be the more important ones.

In Fig. 8 the packing between layers is shown for the high-temperature BrBF polymorph and both molecules in the low-

in constancy does not occur in the low-temperature BrBF (see §3.3).

3.3. The packing

The chloro compound and the high-temperature form of the bromo compound have the same packing arrangement, which is shown in Fig. 6. The low-temperature form of the bromo compound has a closely related packing, which is shown in

temperature polymorph. They are similar but distinct differences can be seen among all three molecules. The picture for the ClBF molecule is virtually the same as for the high-temperature BrBF.

The pseudosymmetry in the low-temperature form is such that the A molecule nearest the origin in Fig. 7 is converted to molecule B in the same layer, in the next layer up, in the third layer up and in the top layer, by the relationships

$$0.507\,(3) + x,\ 0.386\,(7) - y,\ 0.017\,(7) + z;$$
$$0.493\,(3) - x,\ 0.886\,(7) - y,\ 0.483\,(7) - z;$$
$$0.507\,(3) + x,\ 0.114\,(7) + y,\ 0.517\,(7) + z;\ \text{and}$$
$$0.493\,(3) - x,\ 0.614\,(7) + y,\ 0.983 - z;$$

respectively. These correspond to a pseudo-a-glide at $y = 0.193$; a pseudo-center at 0.246, 0.443, 0.242; a pseudo-translation of 0.507, 0.114, 0.517; and a pseudo-screw axis at $x = 0.246$ and $z = 0.492$ with a translation of 0.614 in y, respectively. The numerical parameters are based on all the non-H atoms given equal weight and the uncertainties are the r.m.s. deviation of the individual atoms. These uncertainties correspond to 0.04 Å in x, 0.05 Å in y and 0.10 Å in z; they are all less than the r.m.s. values of the ADP's.

The difference between the two polymorphs can be summarized as follows. If we start the layers in the high-temperature form and leave the layers intact and virtually unchanged within the layer, the low-temperature form is produced by translating a pair of adjacent layers by ca −0.05 along y and then translating the next pair by +0.05 along y. This motion of entire layers by ca 0.7 Å relative to each other is not enough to powder the crystal or, as far as we can tell, not even enough to lower the quality of the crystal. Twice, cells were determined, the crystals cooled and then rewarmed, and the cells redetermined. The number of reflections found after the cooling–heating cycle was the same as the number found before with no change in the intensities.
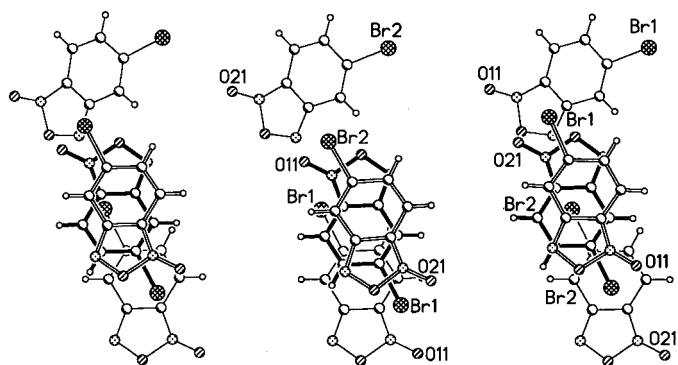
3.4. The interconversion between isomers

The reaction of the 5-XBF isomer to form the 6-XBF isomer has been studied in solution by following the change in the NMR spectra with temperature (Uematsu & Akahori, 1978). Activation energies were found of 44.3 (ClBF) and 58.6 (BrBF) kJ mol^{-1}. The half-life for the reaction in solution is of the order of hundredths of a second at room temperature and would be predicted to be of the order of hours at 173 K. At any given temperature below 260 K the half-life for the BrBF isomerization is longer than that for the ClCF isomerization.

A theoretical study of the reaction path of the parent compound, BF (Eckert *et al.*, 1999), gives an activation energy that is in good agreement with the experimental results. This study also indicates that the activation energy arises from the breaking of the N—O bond in the first step of the reaction and that the second step, the rotation of the NO group around the C—N bond, requires less energy. These results are for the isolated molecules.

In the crystals the breaking of the N—O bond, which leaves the molecule approximately planar, would probably be less affected by the packing than the rotation of the N—O group around the C—N bond. The rotation would surely require more energy to occur in the crystal than in the isolated molecule. The packing in the region of the $C_2N_2O_2$ fragment, where these out-of-plane rotations would have to occur, are shown in Fig. 8. It does not appear that the rotation would be particularly different in the ClBF and high-temperature form of the BrBF than in the low-temperature BrBF. This suggests that constancy with temperature of the amount of disorder in the ClBF is due to a near-zero difference in energy between the 5- and 6- isomers *in the crystal* and that the 5-isomer is favored by a small entropy difference.

Several readers of this manuscript have suggested that variable-temperature solid-state NMR measurements would be desirable here to give a better understanding of the disorder. We totally agree, but we do not have the capability to do this. We encourage anyone interested to take up the NMR studies.

Figure 8
The stacking of BrBF. The reference molecule is drawn with heavy bonds; the molecule above with open bonds; the molecule below with dashed bonds. Left: at 299 K. Center and right: the two independent molecules at 173 K.

References

Belsky, V. K., Zorkaya, O. N. & Zorky, P. M. (1995). *Acta Cryst.* A**51**, 473–481.
Britton, D., Hardgrove, G. L., Hegstrom, R. & Nelson, G. V. (1972). *Acta Cryst.* B**28**, 1121–1123.
Britton, D. & Noland, W. E. (1962). *J. Org. Chem.* **27**, 3218–3223.
Britton, D. & Noland, W. E. (1972). *Acta Cryst.* B**28**, 1116–1121.
Desiraju, G. R. (1991). *Acc. Chem. Res.* **24**, 290–296.

research papers

Domenicano, A. (1992). *Accurate Molecular Structures*, edited by A. Domenicano & I. Hargittai, pp. 437–468. Oxford University Press.

Eckert, F., Rauhut, G., Katritzky, A. R. & Steel, P. J. (1999). *J. Am. Chem. Soc.* **121**, 6700–6711.

Nyburg, S. C. & Faerman, C. H. (1985). *Acta Cryst.* B**41**, 274–279.

Ojala, C. R., Ojala, W. H. D. & Gougoutas, J. Z. (1999). *Acta Cryst.* B**55**, 530–542.

Sheldrick, G. M. (1994). *SHELXTL*, Version 5.0. Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin, USA.

Siemens (1995). *SMART and SAINT*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Uematsu, S. & Akahori, Y. (1978). *Chem. Pharm. Bull.* **26**, 25–32.

Zorky, P. M. (1996). *J. Mol. Struct.* **374**, 9–28.

Zorky, P. M., Belsky, V. K., Lazareva, S. G. & Porai-Koshits, M. A. (1967). *J. Struct. Chem.* **8**, 267–270.