

Packing similarities of three isosteric molecules: 4,5-dichlorophthalic anhydride, 4,5-dibromophthalic anhydride and 5,6-dichlorobenzfurazan 1-oxide, including three polymorphs of 5,6-dichlorobenzfurazan 1-oxide

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(Received 3 April 1998; accepted 6 January 1999)

Abstract

4,5-Dichlorophthalic anhydride (CPA) lies on a twofold axis in space group *C2/c*; the molecules pack as stacks of two-dimensional sheets. Polymorph A of 5,6-dichlorobenzfurazan 1-oxide (CBF; systematic name 5,6-dichloro-2,1,3-benzoxadiazole 1-oxide) is isomorphous with CPA with disordered CBF molecules being pseudo-isosteric with the CPA molecule. Polymorph C of CBF has similar unit-cell dimensions but the arrangement of the molecules in the cell is different. 4,5-Dibromophthalic anhydride occurs in space group *P1* in a structure derived from the CPA structure. The four structures all have similar two-dimensional sheets of molecules, but differ, in addition to the disorder of the CBF molecules, in the stacking of successive sheets. There are three polymorphs of 5,6-dichlorobenzfurazan 1-oxide. In all three the molecules are disordered about twofold or pseudo-twofold axes. In all three the molecules form chains involving similar Cl···O contacts along the direction of the twofold axis. In polymorphs A and C these chains form virtually identical two-dimensional sheets with inter-chain C—H···O, C—H···N and Cl···Cl contacts, but with different stacking arrangements between the sheets. In polymorph B the chains are associated in face-to-face pairs with the same face-to-face overlap as in A, at an average distance of 3.42 Å compared to an average distance of 3.38 Å in A (*cf.* Table 8); there are no two-dimensional sheets.

1. Introduction

The phenomenon of isomorphism (Mitscherlich, 1822) is a familiar one, and the idea that, in some cases at least, it is traceable to isosterism (having the same size and shape) is also long standing (Langmuir, 1919). For some time (Gougoutas, 1983; Ojala, 1985, 1986) we have been interested in using isosteres as a probe for electronic behavior. We feel there is as much interest in a pair of isosteres that do not have isomorphous crystals (and why they do not) as in a pair that do. The general aspects

of the question are discussed at greater length by Gougoutas (1983). This paper describes the similarities and differences in a set of related structures.

The original crystal structure of 5,6-dichlorobenzfurazan 1-oxide (CBF) showed disordered CBF molecules situated on a twofold axis in space group *C2/c* (Britton *et al.*, 1972). The CBF molecule disordered across a twofold axis is pseudo-isosteric with 4,5-dichlorophthalic anhydride (CPA). Photographic data showed the two compounds to have similar cell dimensions and similar intensity patterns, *i.e.* they are indeed isomorphous (Ojala, 1986). We report here the complete structure of 4,5-dichlorophthalic anhydride (CPA) in order to look at the details of the isomorphism. In addition, we report the structure of 4,5-dibromophthalic anhydride (BPA), which is approximately isosteric with CPA, for comparison.

As what was originally intended as a secondary part of this study we began a redetermination of the structure of CBF. In the course of this, however, we found two additional polymorphs of CBF. We report here the redetermined structure of CBF-A at 297 and 173 K to confirm that the structure is disordered in *C2/c* and not ordered in *Cc*. We also report the structures of CBF-B and CBF-C at 297 and 173 K.

2. Experimental

2.1. The polymorphs of CBF

CBF was prepared by hypochlorite oxidation of 4,5-dichloro-2-nitroaniline (Aldrich) and originally recrystallized from methanol. When it was recognized that two polymorphs were present in this sample, CBF was recrystallized from other solvents as well. Eventually three polymorphs were found; they are labeled CBF-A, -B and -C in the order from most dense to least dense, since this is probably the order from most to least stable at low temperature (Dunitz, 1995). Crystals of sufficient quality for single-crystal diffraction were obtained from the following solvents (identification of the polymorphs

was by unit-cell determination): methanol, a mixture of thick needles (A) elongated along **c** with faces {110} and {10 $\bar{1}$ }, thick plates (A) with faces (110) and ($\bar{1}\bar{1}0$), and plates (C) with plate faces {001}; 2-propanol, prisms (B) with faces {011}, {110} and {010}; ethanol/water, plates (C) with faces {001} and {110}; ethyl acetate, plates and sword-shaped (both A) elongated along **c** with faces {110} and {10 $\bar{1}$ } developed to different extents in the two habits; benzene, needles (A) elongated along **c**; acetone, needles (A) elongated along **c** and prisms (C) with faces {001} and {1 $\bar{1}\bar{1}$ }; chloroform, thick plates (A) with faces {100}; carbon tetrachloride, thick plates (C) with faces {001} and {110}. The needles, prisms and thick plates were yellow; the thin plates were so thin as to appear colorless.

CBF-A melted at 404–405 K after undergoing a transition to a second solid phase (turning opaque) at 359–366 K. CBF-B melted at 404–406 K after turning opaque at 368–376 K. CBF-C melted at 404–405 K. All three forms tended to sublime when the temperature neared 373 K. Since all three forms melted at the same temperature, we interpret these observations as indicating that A transforms to C at 359–366 K, and B transforms to C at 368–376 K.

The itemized crystal data, data collection and refinement details for all the polymorphs are given in Table 1. In each case data were collected first at room temperature and then, when refinement proved to be difficult, new data were collected at low temperature. Data collected on the CAD-4 diffractometer were processed using *CAD-4 Software* (Enraf-Nonius, 1989) and *TEXSAN* (Molecular Structure Corporation, 1985); data collected on the SMART system were processed using *ASTRO* and *SAINT* (Siemens, 1995). The trial structures for CBF-B and -C at low temperature were obtained, and all refinements were carried out, using *SHELXTL* (Sheldrick, 1994). Graphics were prepared using *SHELXTL* and *TEXSAN*.

For CBF-A the results from the previous determination were used as the trial structure for the low-temperature data. Unrestrained refinement in *C2/c* did not lead to reasonable results, so the following restraints were included: the C–C and C–Cl bond lengths related by the disorder were restrained to be approximately equal and the atoms involved in these bonds were restrained to have similar anisotropic displacement parameters. With these restraints refinement converged satisfactorily. To confirm that disorder in *C2/c* is the correct model, the final result for the *C2/c* refinement was used as the starting point for refinement of an ordered molecule in *Cc*; the same restraints were used. This refinement converged with $R(F)$ for the observed data of 0.073 and $wR(F^2)$ for all the data of 0.2395. These values are more than twice as large as the *C2/c* values. In addition, the final difference map showed large peaks for the two O-atom positions that corresponded to the disordered model. Thus, we reach the same conclusion

as previously but with much more assurance. The room-temperature data were refined with the same restraints using the low-temperature results as the starting parameters and again converged satisfactorily.

The trial structure for CBF-B was obtained by direct methods. The same kind of disorder is present as in CBF-A except that in the CBF-B structure the molecules do not lie on symmetry elements so that the two components of the disorder do not have to be present in equal amounts. Again unrestrained refinement was unsatisfactory. The restraints used in CBF-A were again used. In addition, the molecules in the two orientations of the disorder were constrained to have exactly the same bond lengths and angles. With these restraints refinement converged satisfactorily. With the same restraints, and using the low-temperature results as the trial structure, refinement of the room-temperature data also converged satisfactorily.

The trial structure for CBF-C was obtained by direct methods. The situation is the same as in CBF-A; there are four molecules in *Cc* or *C2/c* with the *C2/c* alternative requiring disorder. Refinement was carried out in the same manner as for CBF-A, with the same restraints, and assuming disorder in *C2/c*. Refinement converged satisfactorily. If refinement was carried out assuming ordered molecules in *Cc*, R and wR were again more than twice as large as for the *C2/c* refinement, so again the latter was accepted as the correct description of the structure. With the same assumption and restraints, and using the low-temperature results as the trial structure, refinement of the room-temperature data also converged satisfactorily.

For polymorphs A and C, refinements carried out assuming that the C, N and Cl atoms were exactly related by the twofold axis converged with R values less than 0.05 for the low-temperature data. Similarly, if B was assumed to be ordered, except for disorder in the O-atom positions, refinement converged with R less than 0.05. However, in all three cases the resulting anisotropic displacement ellipsoids were physically unreasonable, so that these partially ordered models were rejected in favor of the ones described above.

2.2. The dihalophthalic anhydrides

CPA was obtained from Aldrich Chemical Company and recrystallized from carbon tetrachloride to obtain crystals (needles) suitable for diffraction. The crystals melted at 458–460 K. The same crystal modification was also obtained from acetone (prisms and needles), benzene (prisms) and chloroform (prisms and plates). The needles were elongated along **c**. The prisms had faces {100}, {110} and {11 $\bar{1}$ }. The plates had plate faces ($\bar{1}\bar{1}\bar{1}$) and ($\bar{1}\bar{1}\bar{1}$), which is surprising in that only part of the {111} form was developed and this was not a form found in the prisms. The alcohols that were used for the

Table 1. *Experimental details*

	CBF-A		CBF-B	
Crystal data				
Chemical formula	C ₆ H ₂ Cl ₂ N ₂ O ₂	C ₆ H ₂ Cl ₂ N ₂ O ₂	C ₆ H ₂ Cl ₂ N ₂ O ₂	C ₆ H ₂ Cl ₂ N ₂ O ₂
Chemical formula weight	205	205	205	205
Cell setting	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	C2/c	C2/c	P2 ₁ /n	P2 ₁ /n
<i>a</i> (Å)	11.397 (2)	11.554 (2)	7.0679 (6)	7.1739 (2)
<i>b</i> (Å)	8.871 (2)	8.926 (2)	11.7502 (9)	11.8351 (2)
<i>c</i> (Å)	7.222 (4)	7.310 (6)	9.0114 (7)	9.0639 (1)
α (°)	90	90	90	90
β (°)	95.12 (3)	96.10 (4)	98.563 (1)	98.350 (1)
γ (°)	90	90	90	90
<i>V</i> (Å ³)	727.3 (5)	749.6 (7)	740.05 (10)	761.40 (3)
<i>Z</i>	4	4	4	4
<i>D_x</i> (Mg m ⁻³)	1.872	1.816	1.840	1.788
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
No. of reflections for cell parameters	25	24	3250	2148
θ range (°)	11–22	14–23	2–25	2–25
μ (mm ⁻¹)	0.842	0.817	0.827	0.804
Temperature (K)	173 (2)	297 (2)	173 (2)	297 (2)
Crystal form	Sword-shaped	Sword-shaped	Prism	Prism
Crystal size (mm)	0.50 × 0.28 × 0.12	0.50 × 0.28 × 0.12	0.50 × 0.35 × 0.30	0.50 × 0.35 × 0.30
Crystal color	Yellow	Yellow	Yellow	Yellow
Data collection				
Diffractometer	CAD-4	CAD-4	SMART	SMART
Data collection method	ω -2 θ scans	ω -2 θ scans	ω scans	ω scans
Absorption correction	ψ scan (North <i>et al.</i> , 1968)	ψ scan (North <i>et al.</i> , 1968)	SADABS (Sheldrick, 1996)	SADABS (Sheldrick, 1996)
<i>T</i> _{min}	0.74	0.74	0.63	0.47
<i>T</i> _{max}	0.90	0.90	0.81	0.82
No. of measured reflections	2528	1811	3699	3751
No. of independent reflections	1267	908	1305	1330
No. of observed reflections	1140	780	1145	1158
Criterion for observed reflections	<i>I</i> > 2 σ (<i>I</i>)	<i>I</i> > 2 σ (<i>I</i>)	<i>I</i> > 2 σ (<i>I</i>)	<i>I</i> > 2 σ (<i>I</i>)
<i>R</i> _{int}	0.026	0.024	0.016	0.015
θ _{max} (°)	32	28	25	25
Range of <i>h</i> , <i>k</i> , <i>l</i>	-16 → <i>h</i> → 16 0 → <i>k</i> → 13 -10 → <i>l</i> → 10	-15 → <i>h</i> → 15 0 → <i>k</i> → 11 -9 → <i>l</i> → 9	-8 → <i>h</i> → 8 -11 → <i>k</i> → 13 -10 → <i>l</i> → 10	-8 → <i>h</i> → 8 -13 → <i>k</i> → 14 -9 → <i>l</i> → 10
No. of standard reflections	3	3	150†	153†
Frequency of standard reflections (min)	50	50	360	360
Refinement				
Refinement on	<i>F</i> ²	<i>F</i> ²	<i>F</i> ²	<i>F</i> ²
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)]	0.029	0.035	0.038	0.036
<i>wR</i> (<i>F</i> ²)	0.076	0.085	0.110	0.107
<i>S</i>	1.131	1.105	1.044	1.687
No. of reflections used in refinement	1267	908	1305	1330
No. of parameters used	110	110	218	218
No. of restraints used	33	33	113	113
H-atom treatment	Placed in idealized positions	Placed in idealized positions	Placed in idealized positions	Placed in idealized positions
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.029P)^2 + 0.14P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.032P)^2 + 0.15P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.065P)^2 + 0.91P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.045P)^2 + 0.027P]$ where $P = (F_o^2 + 2F_c^2)/3$
(Δ/σ) _{max}	0.01	-0.02	0.03	0.04
$\Delta\rho$ _{max} (e Å ⁻³)	0.47	0.37	0.47	0.37
$\Delta\rho$ _{min} (e Å ⁻³)	-0.35	-0.21	-0.50	-0.31

Table 1 (cont.)

	CBF-A		CBF-B	
Extinction method	<i>SHELXL</i> (Sheldrick, 1994)	<i>SHELXL</i> (Sheldrick, 1994)	None	None
Extinction coefficient	0.039 (3)	0.055 (4)	—	—
Source of atomic scattering factors	<i>International Tables for Crystallography</i> (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)	<i>International Tables for Crystallography</i> (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)	<i>International Tables for Crystallography</i> (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)	<i>International Tables for Crystallography</i> (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
	CBF-C		CPA	BPA
Crystal data				
Chemical formula	C ₆ H ₂ Cl ₂ N ₂ O ₂	C ₆ H ₂ Cl ₂ N ₂ O ₂	C ₈ H ₂ Cl ₂ O ₃	C ₈ H ₂ Br ₂ O ₃
Chemical formula weight	205	205	217	305.92
Cell setting	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	<i>C2/c</i>	<i>C2/c</i>	<i>C2/c</i>	$\bar{C}1$
<i>a</i> (Å)	7.2233 (1)	7.293 (5)	11.987 (4)	12.923 (3)
<i>b</i> (Å)	9.0549 (3)	9.061 (6)	8.994 (3)	9.209 (2)
<i>c</i> (Å)	11.5700 (4)	11.618 (2)	7.423 (4)	7.6280 (15)
α (°)	90	90	90	105.08 (3)
β (°)	95.315 (2)	96.12 (3)	92.91 (4)	99.20 (3)
γ (°)	90	90	90	81.29 (3)
<i>V</i> (Å ³)	753.50 (4)	763.4 (12)	799.2 (6)	859.5 (3)
<i>Z</i>	4	4	4	4
<i>D_x</i> (Mg m ⁻³)	1.807	1.784	1.803	2.364
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
No. of reflections for cell parameters	1656	25	49	25
θ range (°)	2–25	14–22	11–29	13–22
μ (mm ⁻¹)	0.812	0.802	0.774	9.4
Temperature (K)	173 (2)	297 (2)	297 (2)	297 (2)
Crystal form	Thick plate	Thin plate	Thick needle	Plate
Crystal size (mm)	0.50 × 0.45 × 0.20	0.45 × 0.25 × 0.01	0.45 × 0.25 × 0.15	0.35 × 0.20 × 0.07
Crystal color	Yellow	Colorless	Colorless	Colorless
Data collection				
Diffractometer	SMART	CAD-4	CAD-4	CAD-4
Data collection method	ω scans	ω - 2θ scans	ω scans	ω - 2θ scans
Absorption correction	<i>SADABS</i> (Sheldrick, 1996)	ψ scan (North <i>et al.</i> , 1968)	ψ scan (North <i>et al.</i> , 1968)	ψ scan (North <i>et al.</i> , 1968)
<i>T</i> _{min}	0.67	0.82	0.76	0.23
<i>T</i> _{max}	0.85	0.99	0.89	0.52
No. of measured reflections	3292	1588	2336	4009
No. of independent reflections	659	747	1171	2058
No. of observed reflections	594	472	1041	1284
Criterion for observed reflections	<i>I</i> > 2σ(<i>I</i>)	<i>I</i> > 2σ(<i>I</i>)	<i>I</i> > 2σ(<i>I</i>)	<i>I</i> > 2σ(<i>I</i>)
<i>R</i> _{int}	0.024	0.079	0.015	0.050
θ _{max} (°)	25.05	26	30	28
Range of <i>h, k, l</i>	–8 → <i>h</i> → 8 –10 → <i>k</i> → 7 –13 → <i>l</i> → 13	–8 → <i>h</i> → 8 0 → <i>k</i> → 11 –14 → <i>l</i> → 14	–16 → <i>h</i> → 16 0 → <i>k</i> → 12 –10 → <i>l</i> → 10	–16 → <i>h</i> → 16 –12 → <i>k</i> → 12 –10 → <i>l</i> → 10
No. of standard reflections	150†	3	3	3
Frequency of standard reflections (min)	360	60	50	50
Refinement				
Refinement on	<i>F</i> ²	<i>F</i> ²	<i>F</i> ²	<i>F</i> ²
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)]	0.027	0.038	0.029	0.050
<i>wR</i> (<i>F</i> ²)	0.073	0.136	0.085	0.139
<i>S</i>	1.116	0.825	1.063	1.028
No. of reflections used in refinement	659	747	1171	2057

Table 1 (cont.)

	CBF-C		CPA	BPA
No. of parameters used	109	109	61	119
No. of restraints used	33	33	0	0
H-atom treatment	Placed in idealized positions	Placed in idealized positions	Not refined, placed in idealized positions	Placed in idealized positions
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.043P)^2 + 0.199P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.055P)^2 + 1.03P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.036P)^2 + 0.23P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.064P)^2 + 0.18P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$	0.02	0.01	0.01	0.01
$\Delta\rho_{\max}$ ($e \text{ \AA}^{-3}$)	0.18	0.18	0.43	0.80
$\Delta\rho_{\min}$ ($e \text{ \AA}^{-3}$)	-0.21	-0.15	-0.18	-0.74
Extinction method	None	None	<i>SHELXL</i> (Sheldrick, 1994)	<i>SHELXL</i> (Sheldrick, 1994)
Extinction coefficient	—	—	0.146 (7)	0.0047 (9)
Source of atomic scattering factors	<i>International Tables for Crystallography</i> (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)	<i>International Tables for Crystallography</i> (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)	<i>International Tables for Crystallography</i> (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)	<i>International Tables for Crystallography</i> (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

† The first N reflections were recollected at the end of the data collection.

recrystallization of CBF could not be used since they reacted with CPA to form esters.

BPA was prepared by oxidizing 4,5-dibromoxylene to 4,5-dibromophthalic acid with permanganate and then dehydrating the acid with thionyl chloride. Crystals suitable for diffraction were obtained by recrystallization from carbon tetrachloride (plates). The crystals melted at 493–495 K. The same crystal modification was also obtained from acetone and chloroform. The faces were not determined on the crystal used for the structure determination. Other crystals, examined later, were all twinned. *DIRAX* (Duisenberg, 1992) was used to sort out the twinning. The crystal was a perpendicular

(normal) twin with 180° rotation of the interface plane (001).

Crystal data, data collection and refinement details are given in Table 1. The same programs were used as above, plus *MITHRIL* (Gilmore, 1984) and *DIRDIF* (Beurskens, 1984) were used to obtain a trial structure for BPA.

The CPA structure was straightforward; the trial structure was taken from the CBF-A results. The BPA structure was solved by direct methods in space group $P\bar{1}$, but it is reported throughout the paper in $C\bar{1}$ for better comparison with the CPA structure. The matrix $-\frac{1}{22}, 0/0, 1/\frac{1}{22}, 0$ will convert the $C\bar{1}$ cell to the conven-

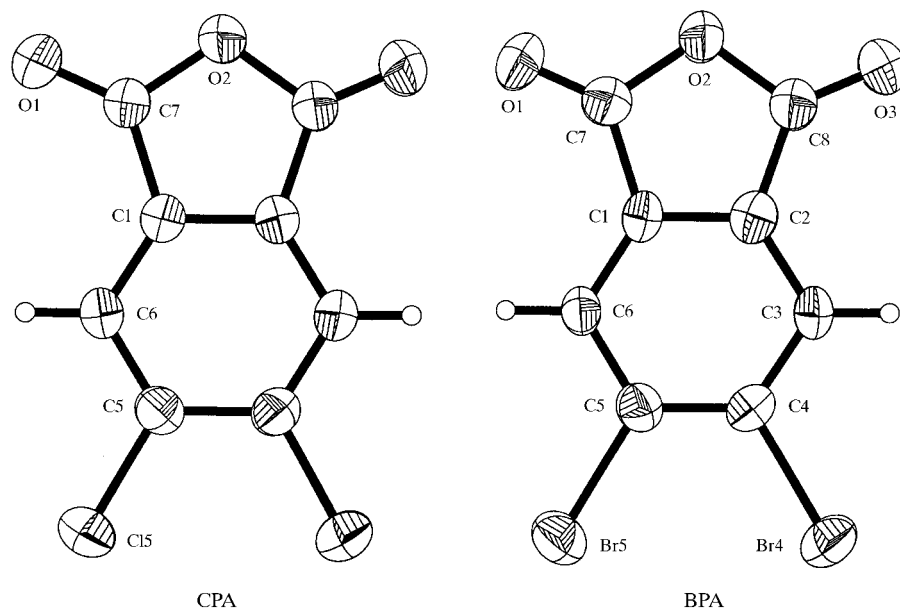


Fig. 1. The structures of CPA (left) and BPA (right). Displacement ellipsoids are shown at the 50% probability level. H atoms are shown with arbitrary radii. CPA lies on a crystallographic twofold axis; BPA does not.

Table 2. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)
$$U_{\text{eq}} = (1/3)\sum_i \sum_j U^{ij} a^i a^j \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U_{eq}
CPA				
Cl5	0.62077 (3)	0.67439 (4)	0.33897 (5)	0.0508 (2)
O1	0.66550 (9)	0.03635 (13)	0.4008 (2)	0.0646 (4)
O2	1/2	0.0016 (2)	1/4	0.0565 (4)
C7	0.58546 (11)	0.0907 (2)	0.3254 (2)	0.0461 (3)
C1	0.55276 (9)	0.24651 (14)	0.2933 (2)	0.0378 (3)
C5	0.55436 (10)	0.50873 (14)	0.2914 (2)	0.0384 (3)
C6	0.60860 (9)	0.3765 (2)	0.3361 (2)	0.0403 (3)
BPA				
Br4	0.37379 (6)	0.70771 (8)	0.16374 (12)	0.0508 (3)
Br5	0.62425 (6)	0.69818 (9)	0.35590 (12)	0.0518 (3)
O1	0.6722 (5)	0.0542 (6)	0.3695 (9)	0.063 (2)
O2	0.5069 (4)	0.0238 (5)	0.2304 (8)	0.0509 (13)
O3	0.3416 (5)	0.0645 (6)	0.0907 (9)	0.061 (2)
C7	0.5912 (6)	0.1096 (8)	0.3068 (11)	0.044 (2)
C8	0.4208 (6)	0.1150 (8)	0.1613 (11)	0.044 (2)
C1	0.5553 (5)	0.2655 (8)	0.2842 (9)	0.0378 (14)
C2	0.4529 (5)	0.2683 (8)	0.1995 (10)	0.0399 (15)
C3	0.3955 (5)	0.3988 (8)	0.1619 (9)	0.0368 (14)
C4	0.4498 (5)	0.5276 (7)	0.2125 (9)	0.0377 (14)
C5	0.5523 (5)	0.5250 (7)	0.2963 (10)	0.0382 (14)
C6	0.6090 (5)	0.3925 (7)	0.3352 (9)	0.0356 (13)
CBF-A 173 K				
C1	0.5438 (5)	0.2394 (5)	0.2850 (10)	0.0196 (6)
C2	0.4298 (4)	0.2469 (5)	0.1901 (10)	0.0216 (7)
C3	0.3798 (7)	0.3893 (12)	0.1527 (12)	0.0227 (9)
C4	0.4430 (9)	0.5146 (12)	0.2069 (15)	0.0202 (8)
C5	0.5623 (8)	0.5003 (12)	0.2997 (14)	0.0209 (8)
C6	0.6137 (7)	0.3655 (11)	0.3403 (12)	0.0238 (10)
N1	0.5718 (2)	0.0959 (2)	0.3104 (3)	0.0247 (4)
N2	0.3874 (2)	0.1079 (3)	0.1540 (4)	0.0272 (4)
O1	0.6566 (2)	0.0266 (2)	0.3865 (3)	0.0335 (4)
O2	0.47343 (13)	0.0101 (2)	0.2272 (3)	0.0299 (4)
Cl4	0.3794 (6)	0.6869 (7)	0.1563 (9)	0.0276 (5)
Cl5	0.6330 (5)	0.6699 (6)	0.3490 (9)	0.0257 (4)
CBF-B 173 K				
C1†	0.1896 (3)	0.4137 (4)	-0.2518 (6)	0.0242 (12)
C2†	0.0951 (3)	0.3091 (3)	-0.2555 (6)	0.0250 (11)
C3†	0.0561 (5)	0.2584 (5)	-0.1212 (7)	0.0273 (10)
C4†	0.1142 (6)	0.3157 (6)	0.0075 (7)	0.0242 (8)
C5†	0.2121 (6)	0.4240 (6)	0.0108 (7)	0.0211 (8)
C6†	0.2510 (5)	0.4745 (5)	-0.1173 (7)	0.0243 (10)
N1†	0.2067 (4)	0.4407 (4)	-0.3937 (6)	0.0343 (11)
N2†	0.0517 (4)	0.2686 (4)	-0.3948 (6)	0.0363 (11)
O1†	0.2753 (4)	0.5204 (3)	-0.4562 (4)	0.0460 (10)
O2†	0.1195 (3)	0.3488 (3)	-0.4852 (4)	0.0401 (10)
Cl4†	0.0718 (7)	0.2592 (5)	0.1750 (5)	0.0368 (7)
Cl5†	0.2816 (7)	0.4910 (5)	0.1826 (4)	0.0241 (5)
C21‡	0.1242 (4)	0.3440 (5)	-0.2617 (7)	0.0247 (13)
C22‡	0.2116 (4)	0.4509 (4)	-0.2462 (7)	0.0237 (14)
C23‡	0.2549 (7)	0.5019 (6)	-0.1032 (9)	0.0233 (12)
C24‡	0.2079 (9)	0.4425 (8)	0.0144 (8)	0.0206 (9)
C25‡	0.1173 (9)	0.3319 (8)	-0.0021 (8)	0.0240 (9)
C26‡	0.0744 (7)	0.2812 (6)	-0.1388 (8)	0.0274 (12)
N21‡	0.1008 (5)	0.3173 (4)	-0.4078 (6)	0.0338 (14)
N22‡	0.2445 (6)	0.4931 (4)	-0.3775 (7)	0.0340 (14)
O21‡	0.0338 (6)	0.2363 (4)	-0.4847 (5)	0.0381 (15)
O22‡	0.1769 (5)	0.4117 (4)	-0.4822 (5)	0.036 (2)
Cl24‡	0.2563 (12)	0.4991 (10)	0.1915 (7)	0.039 (2)
Cl25‡	0.0625 (13)	0.2623 (9)	0.1566 (6)	0.0410 (14)

Table 2 (cont.)

	x	y	z	U_{eq}
CBF-C 173 K				
C1	0.5311 (13)	0.2759 (6)	0.7869 (9)	0.028 (2)
C2	0.4322 (14)	0.2843 (7)	0.6770 (7)	0.028 (2)
C3	0.3963 (12)	0.4281 (16)	0.6298 (10)	0.0322 (14)
C4	0.4539 (16)	0.5510 (18)	0.6922 (9)	0.0286 (15)
C5	0.5525 (16)	0.5284 (18)	0.8080 (9)	0.0296 (15)
C6	0.5955 (12)	0.3957 (15)	0.8566 (10)	0.0328 (14)
N1	0.5552 (5)	0.1343 (5)	0.8159 (3)	0.0384 (8)
N2	0.3926 (5)	0.1483 (5)	0.6335 (4)	0.0410 (8)
O1	0.6282 (4)	0.0635 (4)	0.8995 (3)	0.0513 (7)
O2	0.4665 (4)	0.0517 (3)	0.7181 (2)	0.0431 (7)
Cl4	0.4124 (10)	0.7204 (9)	0.6282 (6)	0.0368 (7)
Cl5	0.6101 (10)	0.6932 (9)	0.8783 (6)	0.0372 (7)

† Site occupancy 0.622 (4). ‡ Site occupancy 0.378 (4).

tional $P\bar{1}$ cell [$a = 7.344$ (3), $b = 7.632$ (3), $c = 8.485$ (3) \AA , $\alpha = 105.25$ (3), $\beta = 109.26$ (4), $\gamma = 91.26$ (3) $^\circ$].

3. Discussion

3.1. General

The atom labeling and anisotropic displacement ellipsoids for CPA and BPA are shown in Fig. 1. The final coordinates are given in Table 2.† Bond lengths and angles are given in Table 3.

The bond lengths and angles are normal. There is good agreement between the chemically equivalent distances and angles in BPA, which in turn agree with the distances and angles in CPA. Both molecules deviate significantly from planarity. In both cases the benzene rings are close to planarity but the Cl and Br atoms are bent out of the plane in opposite directions by 0.02–0.07 \AA . The anhydride C atoms are bent out of the plane in a similar fashion and to about the same extent. Rudman (1971) found similar non-planarity in tetra-chlorophthalic anhydride.

The displacement ellipsoids and the atom labeling for the low-temperature structures of CBF are shown in Fig. 2, where the disorder is shown also. The final positional parameters are given in Table 2. Bond lengths and angles are given in Table 4.

As can be seen in Fig. 2, the relationship between the two orientations of the disordered molecules is similar in all three polymorphs. In A and C the two orientations are related by a crystallographic twofold axis and are equally populated. In B there is no crystallographic symmetry relating the two orientations; they are related by a rotation of 177.6 $^\circ$ around an axis that is 1.3 $^\circ$ away from being parallel to the c axis. This can be described as

† Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK0061). Services for accessing these data are described at the back of the journal.

Table 3. Selected geometric parameters (\AA , $^\circ$)

	CPA	BPA
C14(Br4)—C4		1.888 (6)
C15(Br5)—C5	1.718 (1)	1.885 (7)
C1—C7	1.471 (2)	1.486 (9)
C2—C8		1.476 (10)
C7—O1	1.191 (2)	1.179 (9)
C7—O2	1.395 (2)	1.403 (9)
C8—O2		1.408 (8)
C8—O3		1.179 (9)
C1—C2(C1')	1.389 (2)	1.376 (9)
C2—C3		1.385 (9)
C3—C4		1.405 (9)
C4(C5')—C5	1.412 (3)	1.376 (9)
C5—C6	1.388 (2)	1.401 (9)
C6—C1	1.376 (2)	1.386 (9)
C6—C1—C2(C1')	121.83 (7)	122.4 (6)
C1—C2—C3		122.4 (7)
C2—C3—C4		115.4 (6)
C3—C4—C5		122.3 (6)
C4(C5')—C5—C6	120.99 (7)	121.6 (6)
C5—C6—C1	117.15 (10)	115.9 (6)
C2(C1')—C1—C7	107.68 (7)	108.0 (6)
C1—C2—C8		108.5 (6)
C1—C7—O2	107.34 (11)	106.8 (6)
C2—C8—O2		106.8 (6)
C7—O2—C8(C7')	109.9 (2)	110.0 (5)
O1—C7—O2	120.69 (14)	121.2 (6)
O3—C8—O2		120.9 (7)
C5—C4(C5')—Cl4(Br4)		121.1 (5)
C4(C5')—C5—Cl5(Br5)	119.8 (2)	121.3 (5)

Table 4. Bond lengths (\AA) and angles ($^\circ$) in CBF at low temperature

	CBF-A	CBF-B	CBF-C	Average
Average values weighted to allow for the standard uncertainties in the individual values.				
C1—C2	1.415 (5)	1.397 (5)	1.403 (7)	1.405 (3)
C2—C3	1.402 (9)	1.413 (7)	1.427 (10)	1.413 (5)
C3—C4	1.363 (12)	1.351 (8)	1.370 (15)	1.357 (6)
C4—C5	1.467 (4)	1.447 (4)	1.472 (6)	1.460 (3)
C5—C6	1.352 (12)	1.361 (8)	1.350 (15)	1.357 (6)
C6—C1	1.411 (8)	1.418 (7)	1.405 (9)	1.412 (5)
C1—N1	1.321 (5)	1.340 (7)	1.332 (8)	1.328 (4)
C2—N2	1.341 (5)	1.335 (7)	1.350 (9)	1.341 (4)
N1—O1	1.233 (3)	1.230 (5)	1.237 (5)	1.233 (2)
N1—O2	1.441 (3)	1.440 (5)	1.454 (5)	1.444 (2)
N2—O2	1.378 (3)	1.377 (5)	1.383 (5)	1.379 (2)
C4—Cl4	1.717 (11)	1.716 (7)	1.717 (14)	1.716 (5)
C5—Cl5	1.729 (10)	1.740 (6)	1.732 (14)	1.736 (5)
C6—C1—C2	124.8 (7)	123.2 (6)	126.3 (9)	124.4 (4)
C1—C2—C3	118.4 (6)	120.3 (6)	117.1 (9)	118.9 (4)
C2—C3—C4	119.0 (8)	116.9 (5)	120.3 (11)	117.9 (4)
C3—C4—C5	120.4 (11)	122.7 (7)	117.6 (17)	121.6 (6)
C4—C5—C6	122.8 (11)	121.4 (6)	125.2 (17)	122.0 (5)
C5—C6—C1	114.7 (7)	115.5 (5)	113.4 (11)	115.0 (5)
C2—C1—N1	108.2 (4)	107.2 (5)	108.9 (5)	108.1 (3)
C1—C2—N2	110.5 (4)	112.2 (6)	111.2 (5)	111.1 (3)
C1—N1—O2	106.3 (3)	106.1 (4)	105.2 (4)	106.0 (2)
C2—N2—O2	105.8 (2)	105.1 (4)	105.0 (4)	105.6 (2)
N1—O2—N2	109.1 (2)	109.3 (3)	109.8 (3)	109.3 (1)
O1—N1—O2	118.2 (2)	118.2 (4)	117.8 (3)	118.1 (2)
C5—C4—Cl4	122.1 (10)	117.9 (6)	124.5 (16)	119.5 (5)
C4—C5—Cl5	114.5 (10)	119.1 (6)	112.5 (16)	117.9 (5)

rotation around a pseudo-twofold axis. The distribution between the two sites has the more populated orientation with an occupancy of 0.622 (4) at 173 K and 0.610 (3) at 298 K for the crystal reported in Table 1. The closeness of these two values suggests that the disorder might be frozen in, and that these two values are the

same within experimental error. To test this, complete data sets were collected at the same two temperatures on a different crystal. Using the same constraints, these refined to the same results within experimental error. In

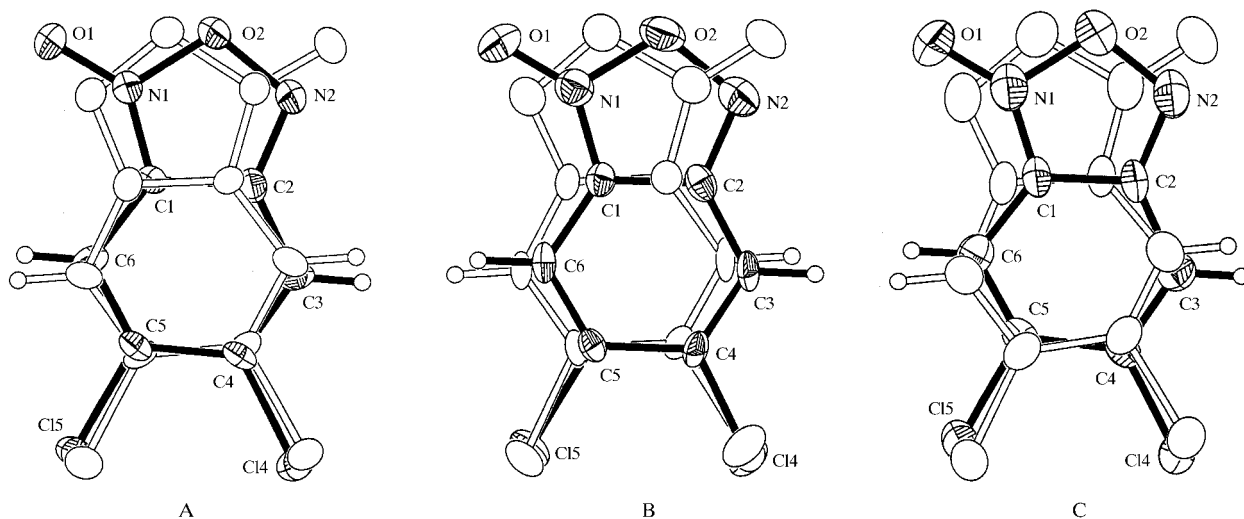


Fig. 2. Polymorphs A, B and C of CBF. Displacement ellipsoids are shown at the 50% probability level and H atoms are shown as spheres of arbitrary radii. The two orientations for each polymorph are shown in the correct juxtaposition. In A and C the molecules are located on a twofold axis and present in equal amounts. In B the shaded molecule is the predominant orientation (about 60%).

particular the occupancies were 0.624 (2) at 173 K and 0.611 (3) at 298 K. We conclude that the difference in the occupancy between the two temperatures, although small, is real. It should be mentioned that data for the first crystal were collected at room temperature first and low temperature next, while this order was reversed for the data collection on the second crystal. If we assume that there are no cooperative effects, then the enthalpy and entropy changes can be estimated in the usual way (Sim, 1990). For the reaction in which the major component converts to the minor one, using the averages of the occupancies quoted above, $\Delta H = +0.18$ (6) kJ mol^{-1} and $\Delta S = -3.1$ (3) $\text{J K}^{-1} \text{mol}^{-1}$. In any case, the molecules are similarly disordered in all three polymorphs, and there is no polymorph, discovered so far, in which the molecules are ordered.

It should be noted that the details of the disorder cannot be determined from the Bragg diffraction data. To illustrate, three simple models of the disorder are: (i) each molecule could have a random orientation unaffected by the orientations of adjacent molecules; (ii) in each ribbon (see §3.2) all the molecules could have the same orientation with adjacent ribbons oriented randomly; (iii) in each ribbon successive molecules could alternate between the two orientations

with adjacent ribbons oriented randomly. All three of these arrangements would give the same diffraction pattern. Welberry has described the use of diffuse scattering to obtain information about the short-range scattering (see Khanna & Welberry, 1990, and references therein). Such data would be necessary to say more about the details of the disorder.

In view of the disorder, it is to be expected that the bond lengths and angles have larger-than-usual errors. The results in Table 4 show that the constrained refinement does give reasonable values, values which agree, where comparison is possible, with those found in benzfuran 1-oxide (Britton & Olson, 1979) and 5-methylbenzofuran 1-oxide (Britton & Noland, 1972). Since the errors are large, we will not discuss these values at length, except to note that the difference between the two C—Cl bond lengths seems to be real.

3.2. Packing

3.2.1. Packing of CPA. We will start the discussion with the packing of CPA, since this is what Megaw (1973) calls the aristotype, the simplest and most

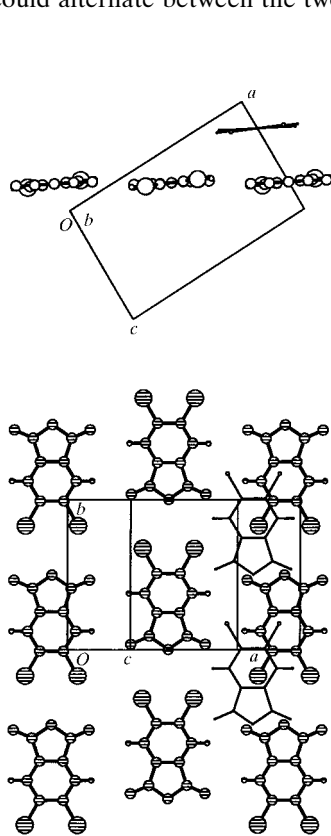


Fig. 3. The packing of CPA. Below: view perpendicular to the $(10\bar{1})$ plane showing a two-dimensional layer of molecules. Two molecules from the next layer are shown in outline. Above: view along the b axis showing the same molecules as the lower view.

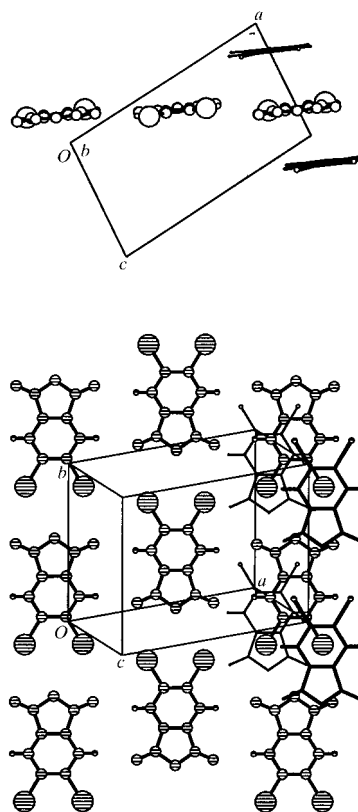


Fig. 4. The packing of BPA. Below: view perpendicular to the $(10\bar{1})$ plane showing a two-dimensional layer of molecules. Two molecules each from the next layers on either side are shown in outline. Above: view along the b axis showing the same molecules as the lower view.

symmetric of the five packings we will discuss here. A view of the packing is shown in Fig. 3. The molecules form two-dimensional layers parallel to the $(10\bar{1})$ plane; the molecular twofold axis coincides with the crystallographic twofold axis. In the b direction adjacent molecules interact to form ribbons through $\text{Cl}\cdots\text{O}$ contacts that are slightly longer than the usual van der Waals distance. In the direction at right angles to b adjacent ribbons of molecules interact through $\text{H}\cdots\text{O}$ contacts that are slightly shorter than the distance expected from the usual van der Waals radii of H and O, and which might be described as $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds. In addition there are $\text{Cl}\cdots\text{Cl}$ and $\text{Cl}\cdots\text{O}$ interactions between molecules in adjacent ribbons, although the distances here are larger than the usual van der Waals distances. The layers stack to form the three-dimensional structure, again with no unusually short distances between the layers.

We will compare the packing in the five structures reported here; first, with respect to the contacts along the ribbons of molecules parallel to the twofold or pseudo-twofold axes; second, with respect to the contacts at the edges of these ribbons; third, with respect to the face-to-face contacts between these ribbons. In each case the contact distances will be compared with

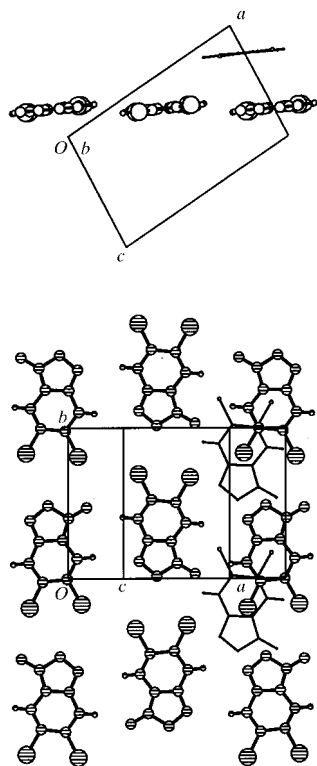


Fig. 5. The packing of CBF-A. Below: view perpendicular to the $(10\bar{1})$ plane showing a two-dimensional layer of molecules. Two molecules from the next layer are shown in outline. Above: view along the b axis showing the same molecules as the lower view.

the van der Waals distances suggested by Pauling (1960) and by Bondi (1964). The packings of BPA, CBF-A, CBF-B and CBF-C are shown, respectively, in Figs. 4, 5, 6 and 7. All of the comparisons will be made using the room-temperature distances since the structures of CPA and BPA were determined only at room temperature.

3.2.2. *Contacts along the ribbons.* All five of the structures have ribbons of molecules along the twofold or pseudo-twofold axes with halogen atoms in one molecule in contact with O atoms in the adjacent molecule. This is the one feature that all five structures have in common. The $\text{X}\cdots\text{O}$ distances and $\text{C}-\text{X}\cdots\text{O}$ angles are given in Table 5. For the CBF polymorphs, the two short distances between molecules with identical orientations with respect to the disorder are given first, followed by the two short distances between molecules with opposite orientations. If the distances are compared with the usual van der Waals distances ($\text{Cl}\cdots\text{O}$: Pauling 3.20 Å, Bondi 3.27 Å; $\text{Br}\cdots\text{O}$: Pauling 3.35 Å, Bondi 3.31 Å), the distances in CPA and BPA are slightly longer than usual and the shortest distances in all the CBF polymorphs are the usual length or slightly shorter. There are, however, two more $\text{Cl}\cdots\text{O}$ contacts in CPA and this may be the controlling factor since the melting point of CPA is about 50 K higher than that of CBF.

Allen *et al.* (1997) surveyed the Cambridge Crystallographic Database for $\text{Cl}\cdots\text{O}$ distances for O atoms in nitro groups. It is reasonable to expect similar interactions with O atoms in benzofurazan oxide groups, and this

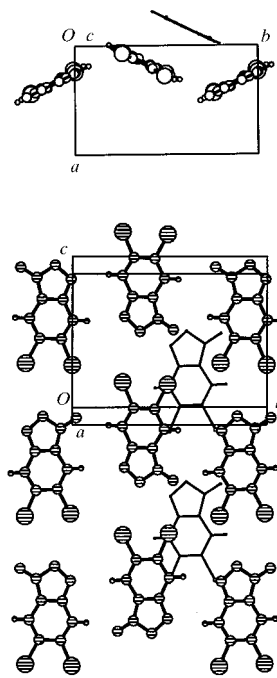


Fig. 6. The packing of CBF-B. Below: view perpendicular to the (011) plane showing a two-dimensional layer of molecules. Two molecules from the next layer are shown in outline. Above: view along the c axis showing the same molecules as the lower view.

Table 5. Distances (Å) and angles (°) in the Cl···O and Br···O contacts

	173 K	297 K		173 K	297 K
CPA					
Cl5···O1 ⁱ	—	3.33	C5—Cl5···O1 ⁱ	—	161
Cl5···O2 ⁱ	—	3.33	C5—Cl5···O2 ⁱ	—	122
BPA					
Br4···O3 ⁱ	—	3.43	C4—Br4···O3 ⁱ	—	156
Br4···O2 ⁱ	—	3.49	C4—Br4···O2 ⁱ	—	119
Br5···O1 ⁱ	—	3.40	C5—Br5···O1 ⁱ	—	159
Br5···O2 ⁱ	—	3.44	C5—Br5···O2 ⁱ	—	120
CBF polymorph A					
Cl4···O2 ⁱ	3.09	3.10	C4—Cl4···O2 ⁱ	131	133
Cl5···O1 ⁱ	3.19	3.26	C5—Cl5···O1 ⁱ	156	155
Cl4···O1 ⁱⁱ	3.05	3.07	C4—Cl4···O1 ⁱⁱ	162	162
Cl5···O2 ⁱⁱ	3.28	3.37	C5—Cl5···O2 ⁱⁱ	127	127
CBF polymorph B					
Cl4···O2 ⁱⁱⁱ	3.21	3.20	C4—Cl4···O2 ⁱⁱⁱ	135	138
Cl5···O1 ⁱⁱⁱ	3.28	3.36	C5—Cl5···O1 ⁱⁱⁱ	152	150
Cl4···O21 ⁱⁱⁱ	3.13	3.15	C4—Cl4···O21 ⁱⁱⁱ	161	164
Cl5···O22 ⁱⁱⁱ	3.35	3.47	C5—Cl5···O22 ⁱⁱⁱ	127	126
Cl24···O22 ⁱⁱⁱ	3.24	3.24	C24—Cl24···O22 ⁱⁱⁱ	133	136
Cl25···O21 ⁱⁱⁱ	3.28	3.38	C25—Cl25···O21 ⁱⁱⁱ	155	151
Cl24···O1 ⁱⁱⁱ	3.17	3.18	C24—Cl24···O1 ⁱⁱⁱ	159	162
Cl25···O2 ⁱⁱⁱ	3.35	3.47	C25—Cl25···O2 ⁱⁱⁱ	130	128
CBF polymorph C					
Cl4···O2 ⁱ	3.19	3.20	C4—Cl4···O2 ⁱ	134	138
Cl5···O1 ⁱ	3.36	3.41	C5—Cl5···O1 ⁱ	154	151
Cl4···O1 ⁱⁱ	3.13	3.16	C4—Cl4···O1 ⁱⁱ	160	164
Cl5···O2 ⁱⁱ	3.46	3.52	C5—Cl5···O2 ⁱⁱ	129	127

Symmetry codes: (i) $x, 1 + y, z$; (ii) $1 - x, 1 + y, \frac{1}{2} - z$; (iii) $x, y, 1 + z$. For contacts with (i) both molecules have the same orientation, for contacts with (ii) they have opposite orientations with respect to the twofold axis.

is what we find. In A the distances are toward the lower end of the range of values found by Allen *et al.*, while in B and C they are closer to the average values. The trends in the distances from A to B to C are consistent with the lengths of the axes in the repeat directions of the ribbons: in A $b = 8.871$ Å, in B $c = 9.011$ Å, in C $b = 9.055$ Å. It should also be noted that in all three polymorphs the shortest Cl···O distances, which presumably correspond to the strongest interactions, change the least on increasing the temperature.

3.2.3. *Contacts at the edges of the ribbons.* The existence of C—H···X ($X = N$ or O) hydrogen bonds has been the subject of some controversy, but the consensus is that they are real (see, for example, Taylor & Kennard, 1982; Berkovitch-Yellin & Leiserowitz, 1984; Desiraju, 1991). They are present in CPA and BPA with the graph-set motif $R_2^2(10)$ (Etter, 1990; Bernstein *et al.*, 1995) and in all three polymorphs of CBF with the graph-set motif $R_2^2(9)$. The motif occurs on both sides of the molecule in CPA, BPA, and CBF-A and -C and on one side in CBF-B. On the other side in CBF-B, there are similar contacts, but the C—H···X angles are much farther from the ideal of 180° . Details of these contacts are given in Table 6. If the distances are compared with

the usual van der Waals distances (H···O: Pauling 2.60 Å, Bondi 2.72 Å; H···N: Pauling 2.70 Å, Bondi 2.75 Å), it can be seen that in every structure there are H···O distances that are shorter than usual. However, the H···N distances that occur in all the CBF structures do not show any shortening even though they are as well aligned as the H···O distances.

Inspection of Figs. 3–7 suggests that $X···X$ and $X···O$, where X is Cl or Br, contacts between adjacent ribbons should also be considered. Table 7 shows the $X···X$ distances. These appear to be normal van der Waals distances or slightly larger (Cl···Cl: Pauling 3.60 Å, Bondi 3.52 Å; Br···Br: Pauling 3.90 Å, Bondi 3.70 Å). The $X···O$ distances (not given) are all 0.2 Å or more larger than the van der Waals distances.

3.2.4. *Face-to-face contacts between the ribbons.* In all of the structures except CBF-B the ribbons aggregate into two-dimensional layers that are approximately planar. In CBF-B the layers are considerably puckered. Table 8 gives the metrical details. Approximately parallel molecules in adjacent layers make partial face-to-face contacts. As can be seen in Figs. 3–7, it is in these contacts that the greatest differences between the structures occur.

Table 6. Distances (\AA) and angles ($^\circ$) in the $C-H \cdots O$ and $C-H \cdots N$ contacts at room temperature

	H...X distance	Angle	Symmetry code for N or O
CPA			
C6—H6...O1	2.46	156	$\frac{3}{2} - x, \frac{1}{2} - y, 1 - z$
BPA			
C3—H3...O3	2.46	166	$\frac{1}{2} - x, \frac{1}{2} - y, -z$
C6—H6...O1	2.45	159	$\frac{3}{2} - x, \frac{1}{2} - y, 1 - z$
CBF-A			
C3—H3...O1	2.28	161	$-\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$
C3—H3...N2	2.72	163	$-\frac{1}{2} - x, \frac{1}{2} - y, -z$
C6—H6...O1	2.51	148	$-\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$
C6—H6...N2	2.83	164	$\frac{3}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$
CBF-B			
C6—H6...O21	2.67	159	$\frac{1}{2} - x, \frac{1}{2} + y, -\frac{1}{2} - z$
C6—H6...N2	2.84	171	$-\frac{1}{2} - x, \frac{1}{2} + y, -\frac{1}{2} - z$
C23—H23...O21	2.29	174	$-\frac{1}{2} - x, \frac{1}{2} + y, -\frac{1}{2} - z$
C23—H23...N2	2.57	166	$-\frac{1}{2} - x, \frac{1}{2} + y, -\frac{1}{2} - z$
C3—H3...O1	2.67	113	$-\frac{1}{2} - x, -\frac{1}{2} + y, -\frac{1}{2} - z$
C3—H3...N22	3.03	112	$-\frac{1}{2} - x, -\frac{1}{2} + y, -\frac{1}{2} - z$
C26—H26...O1	2.77	120	$-\frac{1}{2} - x, -\frac{1}{2} + y, -\frac{1}{2} - z$
C26—H26...N22	3.02	122	$-\frac{1}{2} - x, -\frac{1}{2} + y, -\frac{1}{2} - z$
CBF-C			
C3—H3...O1	2.27	160	$-\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$
C3—H3...N2	2.74	153	$\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$
C6—H6...O1	2.41	165	$-\frac{1}{2} - x, \frac{1}{2} - y, 2 - z$
C6—H6...N2	2.77	172	$\frac{3}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$

In CPA a Cl atom in one molecule lies over the six-membered ring in the next; the other Cl atom lies under a six-membered ring on the opposite side. This arrangement is duplicated in CBF-A. In BPA one Br atom is similarly next to a six-membered ring, but the other is next to a five-membered ring. In CBF-C both Cl atoms are next to five-membered rings. In CBF-B a given molecule has a parallel neighbor on only one side, but, as can be seen in Fig. 8, the overlap on this side is virtually identical to that in CBF-A.

3.2.5. Summary. As stated above CPA is the aristotype of this series. The CPA molecule has its twofold axis coincident with the twofold axis of the space group. The molecules form two-dimensional layers with rectangular symmetry. Face-to-face molecules in adjacent layers are antiparallel to each other.

Again following Megaw (1973), the BPA structure is a hettotype (less symmetric variation) of the CPA structure. Again the molecules form two-dimensional layers with the molecular twofold axis now aligned with a pseudo-twofold axis in the layer. In this structure, however, there is no crystallographic twofold axis. The face-to-face interactions on opposite sides of the molecule are no longer equivalent and the molecular overlaps on the two sides are different. Thus, the interlayer contacts have changed considerably, leading to the lower symmetry for BPA, but the packing within the layers is

Table 7. Distances (\AA) in the $Cl \cdots Cl$ and $Br \cdots Br$ contacts at room temperature

		Symmetry code for second Cl/Br
CPA		
Cl5...Cl5	4.05	$\frac{3}{2} - x, \frac{3}{2} - y, 1 - z$
BPA		
Br4...Br4	3.85	$\frac{1}{2} - x, \frac{3}{2} - y, -z$
Br5...Br5	3.72	$\frac{3}{2} - x, \frac{3}{2} - y, 1 - z$
CBF-A		
Cl4...Cl4	3.79	$\frac{1}{2} - x, \frac{3}{2} - y, -z$
Cl4...Cl5	3.67	$-\frac{1}{2} + x, \frac{3}{2} - y, -\frac{1}{2} + z$
Cl5...Cl5	3.57	$\frac{3}{2} - x, \frac{3}{2} - y, 1 - z$
CBF-B		
Cl4...Cl5	3.57	$\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$
Cl4...Cl24	3.62	$\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$
Cl5...Cl25	3.49	$-\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$
Cl24...Cl25	3.53	$\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$
CBF-C		
Cl4...Cl4	3.73	$\frac{1}{2} - x, \frac{3}{2} - y, 1 - z$
Cl4...Cl5	3.56	$-\frac{1}{2} + x, \frac{3}{2} - y, -\frac{1}{2} + z$
Cl5...Cl5	3.41	$\frac{3}{2} - x, \frac{3}{2} - y, 2 - z$

virtually the same. The two-dimensional unit cell, which was rectangular in CPA, has a cell angle of 90.11° in BPA.

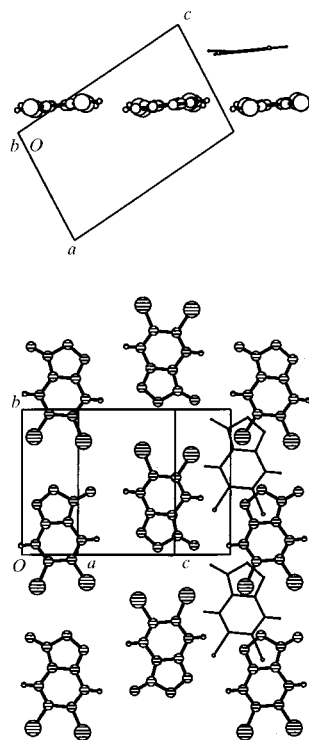


Fig. 7. The packing of CBF-C. Below: view perpendicular to the $(10\bar{1})$ plane showing a two-dimensional layer of molecules. Two molecules from the next layer are shown in outline. Above: view along the b axis showing the same molecules as the lower view.

Table 8. Distances between planes at room temperature

	Layer parallel to	Distance between layers (Å)	Angle between molecule and layer (°)	Perpendicular distance between molecules (Å)
CPA	10 $\bar{1}$	3.23	5.9	3.40
BPA	10 $\bar{1}$	3.35	5.9	3.45, 3.55
CBF-A	10 $\bar{1}$	3.23	5.7	3.38
CBF-B	011	3.65	27.2 \dagger	3.42 \dagger
CBF-C	10 $\bar{1}$	3.23	4.0	3.44

\dagger Based on the mean plane of the two disordered molecules.

The CBF-A structure is a hettotype of a different sort. It is a true isomorph of CPA, but the CBF molecule does not contain a twofold axis and disorder about a crystallographic twofold axis is required to make the molecules pseudo-isosteric. Similar intermolecular interactions occur in both structures along the ribbons and at the sides of the ribbons, although both the numbers and the types change. The face-to-face contacts between molecules in adjacent layers are quite similar to those in CPA.

The CBF-B structure is the most different of the five. It can be regarded as the CBF-A structure with the layers puckered to the extent that they are no longer close to planar. The end-to-end contacts in the ribbons stay the same, but the crystallographic twofold axis is replaced by a pseudo-twofold axis. Half of the edge-to-edge contacts of the ribbons are changed drastically and

the face-to-face interactions occur only on one side of the molecule. However, the remaining edge-to-edge and face-to-face contacts are virtually identical to those in CBF-A.

The structure of CBF-C at first glance might be regarded as isomorphous with CBF-A; they have very similar unit-cell dimensions and the same space group. However, the cell dimensions do not correspond without exchanging the *a* and *c* directions in CBF-C. If this is performed, the space group becomes *A2/a*, a nonstandard setting of *C2/c*. Nevertheless, CBF-C is still a variation of the CBF-A structure. The two dimensional layer in CBF-C is virtually identical to that in CBF-A. What is different is that the adjacent layers have been displaced so that the face-to-face molecules now have parallel rather than antiparallel orientations.

After accepting the disorder in the CBF molecules as making them pseudo-isosteric with CPA and BPA, we might summarize the overall relationships by noting that CPA, CBF-A, BPA and CBF-C are all isostructural in their two-dimensional layers, but only the first two are isostructural in three dimensions.

We thank Dr Victor G. Young Jr, Director of the University of Minnesota X-ray Diffraction Laboratory, for help in using the SMART system and the *SHELXTL* programs, and for determining the twin plane in BPA.

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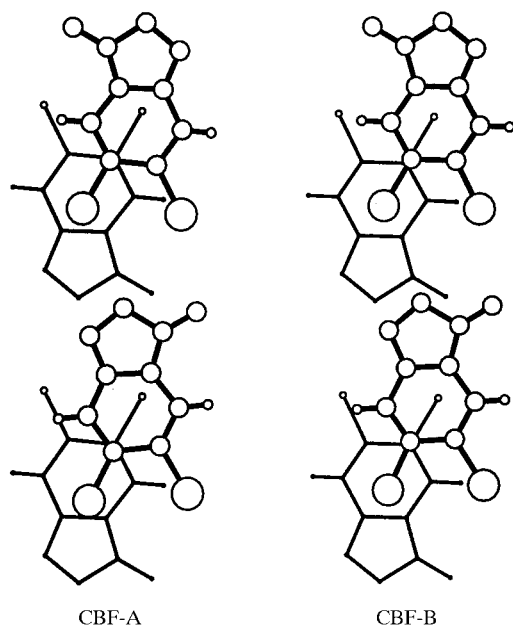


Fig. 8. Left: CBF-A. The four molecules in the upper right corner of Fig. 5 viewed from a direction perpendicular to the plane of the molecules. Right: CBF-B. Four molecules from two parallel ribbons are viewed from a direction perpendicular to the plane of the molecules.

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