organic compounds

o-Chloro- and o-bromobenzo-nitrile: pseudosymmetry and pseudo-isostructural packing

Doyle Britton

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

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

The structures of o-chlorobenzonitrile, C_7H_4ClN, (I), and o-bromobenzonitrile, C_7H_4BrN, (II), have similar packing arrangements, even though $Z' = 4$ in (I) and $Z' = 1$ in (II). Both structures involve $X \cdots N$ interactions, as well as weak C—H$\cdots X$ and C—H$\cdots$N hydrogen bonds. The four crystallographically independent molecules in (I) are related by pseudosymmetry.

Comment

The structures of the title compounds, (I) and (II), have been determined as part of a series of studies on halogen–nitrile intermolecular interactions. Although many examples of $X \cdots NC$ intermolecular interactions are known, in o-iodobenzonitrile (Lam & Britton, 1974) there are no I$\cdots$NC contacts, but short I$\cdots$I contacts are important. The question of interest was whether the same situation occurred with the lighter halogens.

Fig. 1 shows the atom labelling and displacement ellipsoids for one of the four crystallographically non-equivalent molecules in (I), and for a molecule of (II). The displacement ellipsoids in the remaining three independent molecules in (I) are similar. The bond lengths and angles are normal (Allen et al., 1987).
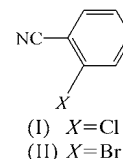
(I)   X=Cl
(II) X=Br

Fig. 2 shows one view of the packing in (I). The four crystallographically independent molecules, A, B, C and D, are tilted by 25.8 (1), 25.4 (1), 23.9 (1) and 24.1 (1)°, respectively, with respect to (010). Fig. 3 shows a view of the packing in (II). The molecules of (II) are all tilted by 27.5° with respect to the (100) plane. In both figures, the $X \cdots N$ interactions are shown as dashed lines. Geometric details are given in Table 1. The Cl$\cdots$N distances are not shorter than the usual van der Waals distances but the Br$\cdots$N distance is. The similarity in the geometries suggests that the same type of interaction is occurring in both cases. There are a number of C—H$\cdots X$ (X = N, Cl or Br) interactions which are not shown in the figures but are listed in Table 2. These are at about the normal van der Waals distances, but could be regarded as C—H$\cdots X$ hydrogen bonds. They are shown to emphasize the packing similarities
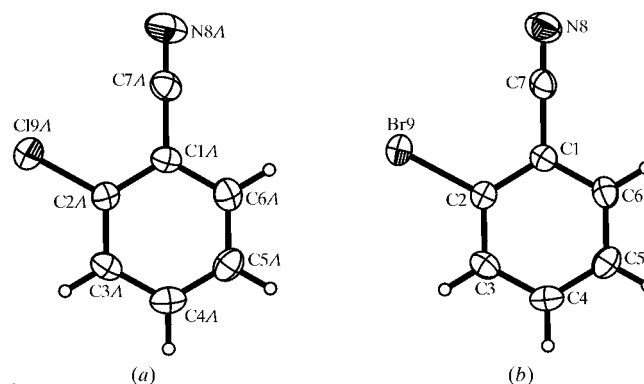
Figure 1
(a) Molecule A in (I); molecules B, C, and D are similar. (b) The molecule of (II). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.
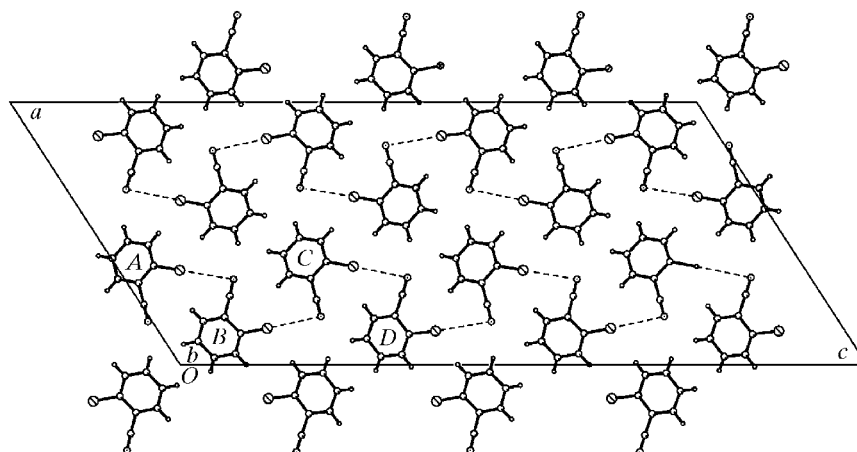
Figure 2
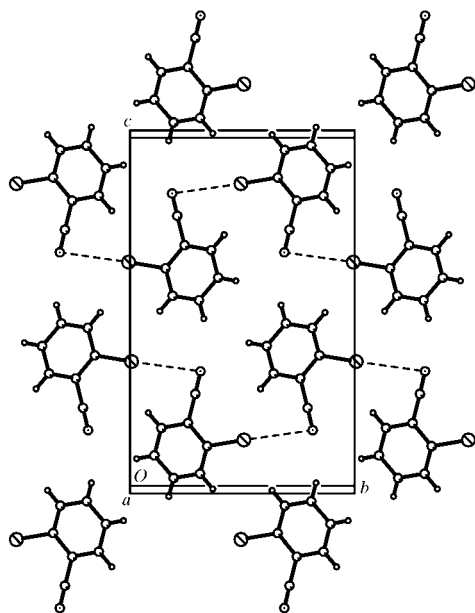The structure of (I), viewed along b. $X \cdots CN$ contacts are shown as dashed lines.

Figure 3
The structure of (II), viewed normal to (100). $X\cdots CN$ contacts are shown as dashed lines.

between (I) and (II), and also to show the extent of the differences between the four independent molecules of (I). There are $X\cdots X$ interlayer contacts separated by a in (I) and by b in (II); none is closer than the usual van der Waals distance.

The similarity in the packing for (I) and (II) (see Figs. 2 and 3) suggests that there are pseudosymmetric relationships between the independent molecules in (I). Closer inspection shows that this is, indeed, the case. The pseudo-conversions are shown in Table 3. As part of the pseudosymmetric relationship, the matrix (400/010/001) converts the cell in (I) to a nearly orthogonal cell, with $a' = 63.768\ (16)$ Å, $\simeq 4a(\sin\beta)$, $b' = b$, $c' = c$ and $\beta' = 89.89\ (1)°$. In this cell, the glide planes perpendicular to a^* are also perpendicular to a'.

Experimental

Both compounds were obtained from Aldrich Chemical Co. Inc. A crystal of (I) selected from the original sample and a crystal of (II) grown from an acetone solution were used for the data collection. Both (I) and (II), as well as the iodine analogue, were recrystallized from acetone, acetonitrile, benzene, dichloromethane, chloroform and carbon tetrachloride solutions in efforts to find additional polymorphs of the three compounds, but none was found.

Compound (I)

Crystal data

C_7H_4ClN	$Z = 16$
$M_r = 137.56$	$D_x = 1.432$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 18.999\ (4)$ Å	$\mu = 0.49$ mm^{-1}
$b = 3.8410\ (8)$ Å	$T = 174\ (2)$ K
$c = 41.690\ (8)$ Å	Needle, colourless
$\beta = 122.96\ (3)°$	$0.40 \times 0.10 \times 0.10$ mm
$V = 2552.7\ (12)$ Å^3	

Data collection

Bruker SMART 1K CCD area-detector diffractometer	27524 measured reflections
ω scans	5797 independent reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003; Blessing, 1995)	4186 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.052$
$T_{min} = 0.91$, $T_{max} = 0.95$	$\theta_{max} = 27.5°$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.041P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.048$	$+ 1.039P]$
$wR(F^2) = 0.102$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.03$	$(\Delta/\sigma)_{max} = 0.001$
5797 reflections	$\Delta\rho_{max} = 0.26$ e Å^{-3}
325 parameters	$\Delta\rho_{min} = -0.32$ e Å^{-3}
H-atom parameters constrained	

Compound (II)

Crystal data

C_7H_4BrN	$Z = 4$
$M_r = 182.02$	$D_x = 1.824$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 3.9247\ (10)$ Å	$\mu = 6.10$ mm^{-1}
$b = 10.348\ (3)$ Å	$T = 174\ (2)$ K
$c = 16.387\ (4)$ Å	Prism, colourless
$\beta = 95.011\ (4)°$	$0.40 \times 0.30 \times 0.20$ mm
$V = 663.0\ (3)$ Å^3	

Data collection

Bruker SMART 1K area-detector diffractometer	7557 measured reflections
ω scans	1518 independent reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003; Blessing, 1995)	1301 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.027$
$T_{min} = 0.15$, $T_{max} = 0.30$	$\theta_{max} = 27.5°$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.019P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.022$	$+ 0.386P]$
$wR(F^2) = 0.051$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.07$	$(\Delta/\sigma)_{max} = 0.001$
1518 reflections	$\Delta\rho_{max} = 0.31$ e Å^{-3}
83 parameters	$\Delta\rho_{min} = -0.29$ e Å^{-3}
H-atom parameters constrained	Extinction correction: *SHELXTL* (Sheldrick, 1997)
	Extinction coefficient: 0.0049 (8)

Table 1
A comparison of the geometry (Å, °) of the $X\cdots N$ contacts in compounds (I) and (II).

For comparison, the van der Waals contact distances are $Cl\cdots N = 3.30$ Å and $Br\cdots N = 3.40$ Å (Bondi, 1964; Rowland & Taylor, 1996).

	$X\cdots N$	$C-X\cdots N$	$X\cdots N$	$X\cdots N\equiv C$
(I)	Cl9$A$$\cdots$N8$B$	169.0 (2)	3.380 (2)	92.2 (2)
	Cl9$B$$\cdots$N8$C$	146.2 (2)	3.466 (2)	94.0 (2)
	Cl9$C$$\cdots$N8$D$	170.2 (2)	3.394 (2)	87.8 (2)
	Cl9$D$$\cdots$N8$A^i$	167.1 (2)	3.477 (2)	89.9 (2)
(II)	Br9$\cdots$N8^{ii}	170.4 (2)	3.327 (2)	90.5 (2)

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

H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C—H distances of 0.95 Å and with $U_{iso}(H) = 1.2U_{eq}(C)$.

Table 2
A comparison of the geometries (Å, °) of the C—H···X interactions in (I) and (II), where X = N, Cl or Br.

For comparison, the van der Waals contact distances are Cl···N = 3.30 Å and Br···N = 3.40 Å (Bondi, 1964; Rowland & Taylor, 1996).

H	X	C—H···X	H···X	H···X—C	C···X
o-Chlorobenzonitrile, (I)					
H3*A*	Cl9*C*[i]	138	3.03	97	3.788 (2)
H3*A*	Cl9*C*[ii]	144	3.10	119	3.908 (2)
H4*A*	N8*D*[ii]	161	2.68	164	3.592 (3)
H5*A*	N8*D*[iii]	141	2.71	121	3.496 (3)
H6*A*	Cl9*D*[iii]	143	3.17	98	3.969 (2)
H3*B*	Cl9*D*[iv]	134	3.26	124	3.978 (2)
H3*B*	Cl9*D*[v]	148	2.97	98	3.807 (2)
H4*B*	N8*A*[vi]	162	2.66	165	3.573 (3)
H5*B*	N8*A*[vii]	140	2.75	120	3.523 (3)
H6*B*	Cl9*A*[vii]	133	3.08	98	3.794 (2)
H3*C*	Cl9*A*[viii]	136	3.16	122	3.898 (2)
H3*C*	Cl9*A*[ix]	145	3.05	94	3.869 (2)
H4*C*	N8*B*[ix]	155	2.82	166	3.703 (3)
H5*C*	N8*B*[vii]	129	2.74	135	3.422 (3)
H6*C*	Cl9*B*[vii]	136	3.09	121	3.832 (2)
H3*D*	Cl9*B*[iv]	142	3.15	99	3.944 (2)
H3*D*	Cl9*B*[v]	145	3.29	121	4.107 (2)
H4*D*	N8*C*[iv]	146	2.62	158	3.443 (3)
H5*D*	N8*C*[x]	140	2.99	111	3.763 (3)
H6*D*	Cl9*C*[xi]	139	3.17	98	3.939 (2)
H6*D*	Cl9*C*	135	3.12	121	3.856 (2)
o-Bromobenzonitrile, (II)					
H3	Br9[vi]	130	3.14	90	3.822 (2)
H3	Br9[xii]	152	3.22	119	4.078 (2)
H4	N8[xiii]	152	2.80	155	3.670 (3)
H5	N8[iv]	133	2.82	131	3.535 (3)
H6	Br9[iv]	149	3.15	98	3.987 (2)

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

Table 3
Pseudo-conversions for the four independent molecules of (I).

Conversion	Pseudosymmetry element	Approximate translation	Average discrepancy between corresponding atoms
$A \rightarrow B$	Screw axis parallel to c	$c/8$	0.16 Å
$A \rightarrow C$	c glide perpendicular to b	$c/4$	0.14 Å
$A \rightarrow D$	c glide perpendicular to a^*	$3c/8$	0.13 Å
$B \rightarrow C$	c glide perpendicular to a^*	$c/8$	0.06 Å
$B \rightarrow D$	c glide perpendicular to b	$c/4$	0.23 Å
$C \rightarrow D$	Screw axis parallel to c	$c/8$	0.19 Å

For both compounds, data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); 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*.

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
Blessing, R. H. (1995). *Acta Cryst.* **A51**, 33–38.
Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.
Bruker (2002). *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Lam, S. & Britton, D. (1974). *Acta Cryst.* **B30**, 1119–1120.
Rowland, R. S. & Taylor, R. (1996). *J. Phys. Chem.* **100**, 7384–7391.
Sheldrick, G. M. (1997). *SHELXTL*. Version 5.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (2003). *SADABS*. Version 2.10. University of Göttingen, Germany.