

## 3,5-Dibromobenzonitrile

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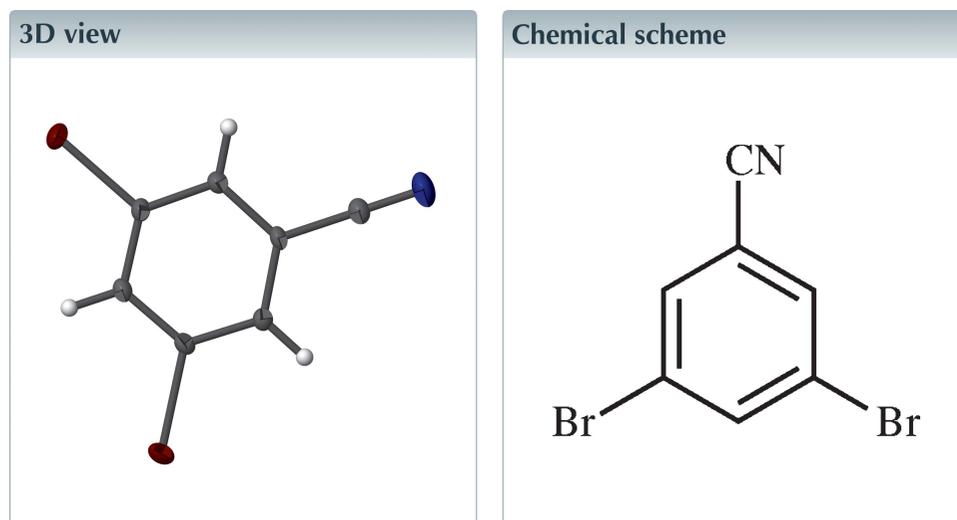
Edited by J. Simpson, University of Otago, New Zealand

Keywords: crystal structure; nitrile; C—H...N hydrogen bonds; C≡N...H contacts.

CCDC reference: 1580004

Structural data: full structural data are available from [iucrdata.iucr.org](http://iucrdata.iucr.org)

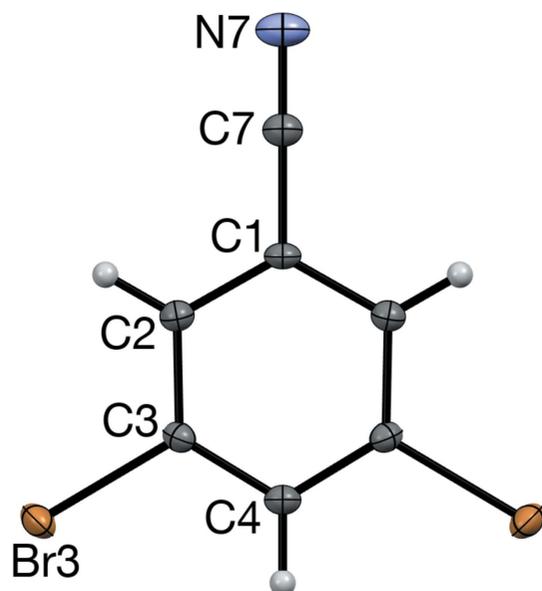
Molecules of the title compound (I), C<sub>7</sub>H<sub>3</sub>Br<sub>2</sub>N, lie on a crystallographic mirror plane that bisects the benzene ring and the cyano group. In the crystal, no C≡N...Br or Br...Br short contacts are observed. Head-to-tail C(7) chains form based on weak hydrogen bonding between the the *para* H atom and the cyano N atom. Although molecules of (I) pack differently than 3,5-difluorobenzonitrile, both compounds have similarly distorted benzene rings. For (I), the endocyclic bond angles are 121.16 (16)° and 117.78 (16)° about the *ipso* and *para* C atoms, respectively.



### Structure description

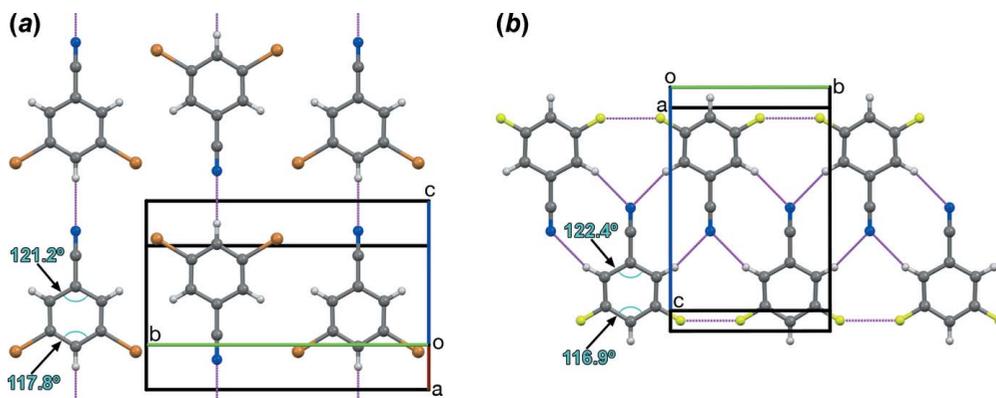
Cyano-halo (C≡N...X) short contacts are commonly observed in crystals of halogenated benzonitriles, especially when X = Br or I. The strength of these contacts correlates with halogen polarizability (Desiraju & Harlow, 1989). Depending on the nature of the 4-substituent, 2,6-dibromo-3,5-unsubstituted benzonitriles usually form sheet structures based on each cyano group being bisected by two C≡N...Br contacts (Noland & Tritch, 2017), or have Br...Br contacts as the primary supramolecular interaction (Noland *et al.*, 2017). As of the most recent update of the Cambridge Structural Database (Version 5.37, May 2017; Groom *et al.*, 2016), 3,5-difluorobenzonitrile is the only example with the X and H atoms transposed from the former arrangement (Britton, 2002). Our objective was to determine whether the title nitrile (I) would be isomorphous with 3,5-difluorobenzonitrile, or if a packing motif based on C≡N...Br or Br...Br interactions would be observed.

Although the planarity of molecules of (I) (Fig. 1) is not crystallographically imposed, the mean deviation of ring atoms (C1–C4) from the best-fit plane is less than 0.001 (1) Å. Interestingly, neither C≡N...Br nor Br...Br short contacts are observed in the crystal of (I). Instead, C(7) head-to-tail chains of weak C4–H4...N7 hydrogen bonds form (Table 1). Chains of this type are commonly observed from 4-halobenzonitriles as



**Figure 1**  
The molecular structure of (I), showing the atomic numbering and displacement ellipsoids at the 50% probability level. Unlabelled atoms are related by the  $(x, \frac{1}{2} - y, z)$  symmetry operation.

$C\equiv N \cdots X$  contacts (Desiraju & Harlow, 1989). In the title crystal, the  $C(7)$  chains form along  $[10\bar{1}]$  and align to form translationally stacked sheets parallel to  $(101)$  (Fig. 2*a*). Adjacent chains within each sheet are antiparallel (Fig. 3), whereas corresponding chains in adjacent sheets are parallel. This differs greatly from the packing of 3,5-difluorobenzonitrile (Fig. 2*b*), in which a sheet structure forms based on cyano  $N$  atoms bisected by weak  $C-H \cdots N$  hydrogen bonds with *ortho*  $H$  atoms. Weak  $F \cdots F$  contacts were observed in the difluoro analog, adding to the surprise that (I) does not form  $Br \cdots Br$  short contacts. Even though (I) and the difluoro analog pack differently, the benzene rings in both molecules are similarly distorted (Fig. 2), supporting Britton's hypothesis that these distortions are mainly due to intramolecular substituent effects, rather than supramolecular effects in the crystals (Britton, 2002).

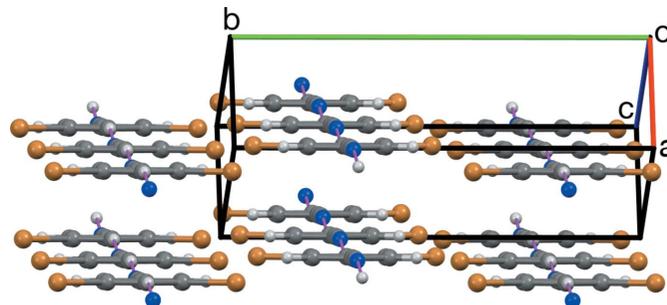


**Figure 2**  
The sheet structures in crystals of (a) compound (I), viewed along  $[301]$ ; (b) 3,5-difluorobenzonitrile, viewed roughly along  $[100]$ . Bond angles about the *ortho* and *meta*  $C$  atoms are denoted in light blue. Dashed magenta lines represent short contacts.

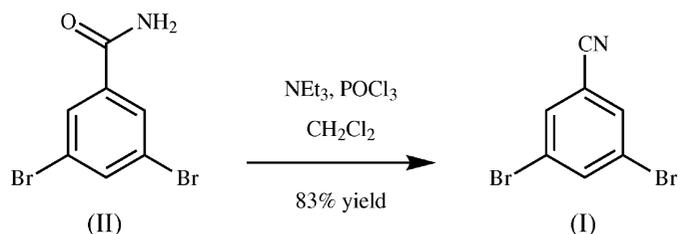
**Table 1**  
Contact geometry ( $\text{\AA}$ ,  $^\circ$ ).

D—H $\cdots$ A	D—H	H $\cdots$ A	D $\cdots$ A	D—H $\cdots$ A
C4—H4 $\cdots$ N7 <sup>i</sup>	0.95	2.51	3.443 (3)	168

Symmetry code: (i)  $1 + x, y, -1 + z$ .



**Figure 3**  
The arrangement of  $C(7)$  chains in the crystal of (I), viewed roughly along  $[101]$ . Dashed magenta lines represent short contacts.



**Figure 4**  
The synthesis of (I).

### Synthesis and crystallization

**3,5-Dibromobenzonitrile (I):** 3,5-Dibromobenzamide [(II), Fig. 4] (Sigma–Aldrich, Inc. No. 680389; 962 mg), dichloromethane (30 ml), and triethylamine (1.4 ml) were combined in a round-bottomed flask. The resulting mixture was stirred at 290 K.  $POCl_3$  (320  $\mu$ L) was added dropwise. After 4 h, the reaction mixture was washed with hydrochloric acid (1 *M*, 2  $\times$  25 ml), and then  $NaHCO_3$  solution (0.5 *M*, 50 ml). The organic

**Table 2**  
Experimental details.

Crystal data	
Chemical formula	C <sub>7</sub> H <sub>3</sub> Br <sub>2</sub> N
<i>M<sub>r</sub></i>	260.92
Crystal system, space group	Monoclinic, <i>P</i> 2 <sub>1</sub> / <i>m</i>
Temperature (K)	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	4.0047 (2), 13.2585 (8), 7.3356 (4)
$\beta$ (°)	97.440 (3)
<i>V</i> (Å <sup>3</sup> )	386.21 (4)
<i>Z</i>	2
Radiation type	Mo <i>K</i> $\alpha$
$\mu$ (mm <sup>-1</sup> )	10.41
Crystal size (mm)	0.20 × 0.07 × 0.05
Data collection	
Diffractometer	Bruker AXS VENTURE PHOTON-II
Absorption correction	Multi-scan ( <i>SADABS</i> ; Krause <i>et al.</i> , 2015)
<i>T</i> <sub>min</sub> , <i>T</i> <sub>max</sub>	0.231, 0.625
No. of measured, independent and observed [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] reflections	8873, 1945, 1696
<i>R</i> <sub>int</sub>	0.036
( $\sin \theta/\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )	0.834
Refinement	
$R[F^2 > 2\sigma(F^2)]$ , $wR(F^2)$ , <i>S</i>	0.024, 0.058, 1.07
No. of reflections	1945
No. of parameters	53
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\max}$ , $\Delta\rho_{\min}$ (e Å <sup>-3</sup> )	0.98, -0.49

Computer programs: *APEX3* and *SAINT* (Bruker, 2012), *SHELXT2014* (Sheldrick, 2015a), *SHELXL2014* (Sheldrick, 2015b), *Mercury* (Macrae *et al.*, 2008) and *publCIF* (Westrip, 2010).

portion was filtered through basic alumina (4 cm × 2 cm, length × diameter). The filter was washed with dichloromethane (20 ml). The combined filtrate was concentrated in a rotary evaporator, giving an off-white powder (750 mg, 83%). Crystals suitable for X-ray diffraction (colourless needles) were prepared by slow evaporation of a solution in chloroform and cyclohexane, followed by decantation, and then washing with pentane. M.p. 367–368 K (lit. 368–369 K; Ishii *et al.*, 2013); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.917 (*t*, *J* = 1.8 Hz, 1H, H4), 7.739 (*d*, *J* = 1.8 Hz, 2H, H2); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$

139.0 (1 C, C4), 133.6 (2 C, C2), 123.7 (2 C, C3), 116.0 (1 C, C7), 115.6 (1 C, C1); IR (KBr, cm<sup>-1</sup>) 3072, 2961, 2922, 2236, 1551, 1418, 1198, 1109, 864, 759, 666; MS (EI, *m/z*) *M*<sup>+</sup> calculated for C<sub>7</sub>H<sub>3</sub><sup>81</sup>Br<sup>79</sup>BrN 260.8606, found 260.8605.

## Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

## Acknowledgements

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## full crystallographic data

*IUCrData* (2018). 3, x180059 [https://doi.org/10.1107/S2414314618000597]

## 3,5-Dibromobenzonitrile

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## 3,5-Dibromobenzonitrile

*Crystal data*

$C_7H_3Br_2N$

$M_r = 260.92$

Monoclinic,  $P2_1/m$

$a = 4.0047$  (2) Å

$b = 13.2585$  (8) Å

$c = 7.3356$  (4) Å

$\beta = 97.440$  (3)°

$V = 386.21$  (4) Å<sup>3</sup>

$Z = 2$

$F(000) = 244$

$D_x = 2.244$  Mg m<sup>-3</sup>

Melting point: 367 K

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 2765 reflections

$\theta = 2.8$ – $36.4$ °

$\mu = 10.41$  mm<sup>-1</sup>

$T = 100$  K

Needle, colourless

$0.20 \times 0.07 \times 0.05$  mm

*Data collection*

Bruker AXS VENTURE PHOTON-II  
diffractometer

Radiation source: micro-focus

$\varphi$  and  $\omega$  scans

Absorption correction: multi-scan  
(SADABS; Krause *et al.*, 2015)

$T_{\min} = 0.231$ ,  $T_{\max} = 0.625$

8873 measured reflections

1945 independent reflections

1696 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.036$

$\theta_{\max} = 36.4$ °,  $\theta_{\min} = 2.8$ °

$h = -6 \rightarrow 6$

$k = -20 \rightarrow 22$

$l = -12 \rightarrow 12$

*Refinement*

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.024$

$wR(F^2) = 0.058$

$S = 1.07$

1945 reflections

53 parameters

0 restraints

Hydrogen site location: inferred from  
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0202P)^2 + 0.2462P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.98$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.49$  e Å<sup>-3</sup>

Extinction correction: SHELXL2014

(Sheldrick, 2015b),

$F_c^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.0102 (18)

*Special details*

**Experimental.** Dr. K. J. Tritch / Prof. W. E. Noland

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Br3	0.84613 (4)	0.46259 (2)	0.21614 (2)	0.02026 (6)
N7	0.2774 (5)	0.2500	0.8775 (3)	0.0261 (4)
C1	0.5455 (5)	0.2500	0.5751 (2)	0.0136 (3)
C2	0.6134 (3)	0.34183 (11)	0.49387 (18)	0.0148 (2)
H2	0.5664	0.4041	0.5495	0.018*
C3	0.7512 (3)	0.33975 (11)	0.32980 (18)	0.0143 (2)
C4	0.8227 (5)	0.2500	0.2449 (3)	0.0150 (3)
H4	0.9172	0.2500	0.1326	0.018*
C7	0.3995 (5)	0.2500	0.7444 (3)	0.0175 (3)

Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Br3	0.02244 (8)	0.01753 (8)	0.02213 (8)	-0.00043 (5)	0.00792 (5)	0.00604 (5)
N7	0.0229 (9)	0.0394 (12)	0.0169 (8)	0.000	0.0062 (7)	0.000
C1	0.0129 (7)	0.0181 (8)	0.0105 (6)	0.000	0.0039 (5)	0.000
C2	0.0148 (5)	0.0158 (6)	0.0141 (5)	0.0004 (4)	0.0036 (4)	-0.0005 (4)
C3	0.0139 (5)	0.0159 (6)	0.0136 (5)	-0.0001 (4)	0.0035 (4)	0.0021 (4)
C4	0.0151 (7)	0.0180 (8)	0.0123 (7)	0.000	0.0036 (6)	0.000
C7	0.0167 (8)	0.0213 (9)	0.0147 (8)	0.000	0.0031 (6)	0.000

Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

Br3—C3	1.8906 (13)	C2—C3	1.3878 (18)
N7—C7	1.147 (3)	C2—H2	0.9500
C1—C2 <sup>i</sup>	1.3977 (16)	C3—C4	1.3898 (17)
C1—C2	1.3977 (16)	C4—C3 <sup>i</sup>	1.3898 (17)
C1—C7	1.439 (3)	C4—H4	0.9500
C2 <sup>i</sup> —C1—C2	121.16 (16)	C2—C3—Br3	119.38 (11)
C2 <sup>i</sup> —C1—C7	119.42 (8)	C4—C3—Br3	118.37 (10)
C2—C1—C7	119.42 (8)	C3 <sup>i</sup> —C4—C3	117.78 (16)
C3—C2—C1	118.28 (13)	C3 <sup>i</sup> —C4—H4	121.1
C3—C2—H2	120.9	C3—C4—H4	121.1
C1—C2—H2	120.9	N7—C7—C1	178.8 (2)
C2—C3—C4	122.25 (13)		
C2 <sup>i</sup> —C1—C2—C3	-0.1 (3)	C1—C2—C3—Br3	180.00 (12)
C7—C1—C2—C3	-179.38 (17)	C2—C3—C4—C3 <sup>i</sup>	0.1 (3)
C1—C2—C3—C4	0.0 (2)	Br3—C3—C4—C3 <sup>i</sup>	-179.91 (9)

Symmetry code: (i) *x*, -*y*+1/2, *z*.