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Crystal structures of methyl 3,5-dibromo-4-cyanobenzoate and methyl 3,5-dibromo-4-isocyanobenzoate

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The title crystals, $C_9H_5Br_2NO_2$, are the first reported 2,6-dihalophenyl cyanide–isocyanide pair that have neither three- nor two-dimensional isomorphism. Both crystals contain contacts between the carbonyl O atom and a Br atom. In the crystal of the cyanide, $R_2^2(10)$ inversion dimers form based on C≡N···Br contacts, a common packing feature in this series of crystals. In the isocyanide, the corresponding N≡C···Br contacts are not observed. Instead, the isocyano C atom forms contacts with the methoxy C atom. RNC was refined as a two-component pseudo-merohedral twin.

1. Chemical context & database survey

The crystal packing of 2,6-dihalophenyl cyanides and isocyanides is commonly influenced by C≡N···*X* or N≡C···*X* contacts, especially when *X* is Br or I (Desiraju & Harlow, 1989). The crystal structures of isomeric, non-ligand cyanides and isocyanides are usually very similar. There are six reported 2,6-dihalophenyl cyanide–isocyanide pairs (Fig. 1). Three are in the most recent update of the Cambridge

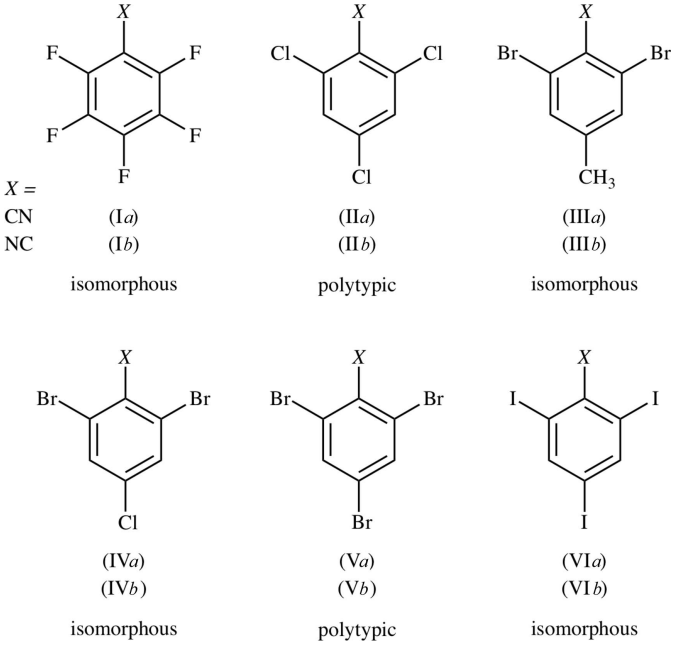
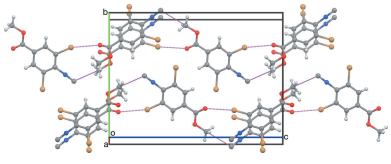
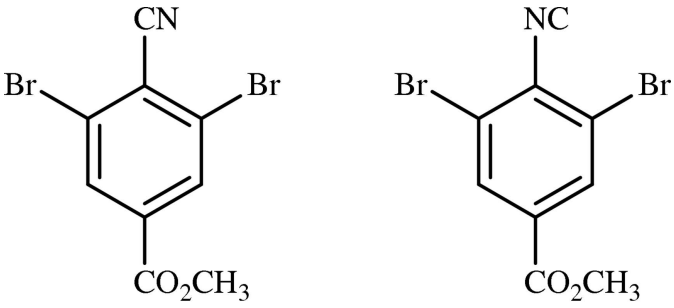


Figure 1
The six pairs of 2,6-dihalophenyl cyanides (_*a*) and isocyanides (_*b*) previously reported in the CSD. All corresponding crystal pairs are either isomorphous or polytypic.



Structural Database (CSD, Version 5.38, May 2017; Groom *et al.*, 2016), and three were recently completed by our group. The pentafluoro [(I*a*); Bond *et al.*, 2001) and (I*b*); Lentz & Preugschat, 1993)], 2,6-dibromo-4-methyl [(III*a*), (III*b*); Noland *et al.*, 2017*b*], 2,6-dibromo-4-chloro [(IV*a*); Britton, 2005 and (IV*b*); Noland & Tritch, 2018], and 2,4,6-triiodo [(VI*a*), (VI*b*); Noland *et al.* 2018] pairs are each isomorphous. The 2,4,6-trichloro [(II*a*), (II*b*); Pink *et al.*, 2000] and 2,4,6-tribromo [(V*a*), (V*b*); Britton *et al.*, 2016] pairs each have two-dimensional isomorphism and are polytypic.



RCN RNC

Two simple 3,5-dibromobenzoate esters were found in the CSD (Fig. 2). Crystals of (VII) contain *C*(6) chains of C═O···Br contacts (Saeed *et al.*, 2010), and crystals of (VIII) contain *C*(5) chains of Br···Br contacts (Reinhold & Rosati, 1994). A co-crystal of cyano acid (IX*a*) with anthracene was recently reported by our group (Noland *et al.* 2017*a*). The corresponding isocyano acid (IX*b*) was not observed, probably because of the acid sensitivity of isocyanides (Ugi *et al.*, 1965), preventing crystallographic comparison of (IX*a*) and (IX*b*). The title cyanide (RCN) and isocyanide (RNC) were synthetic intermediates to (IX*a*) and (IX*b*), and their crystals are presented instead.

2. Structural commentary

Molecules of RCN and RNC (Fig. 3) occupy general positions and have similar, typical geometry. Both benzene rings are nearly planar, with mean atomic deviations of 0.005 (2) and 0.002 (3) Å for RCN and RNC, respectively. The most prominent difference between the molecular conformations is the bond angles about the methoxy O atoms, which are 117.1 (2)° for C8—O2—C9, and 114.8 (3)° for C18—O12—

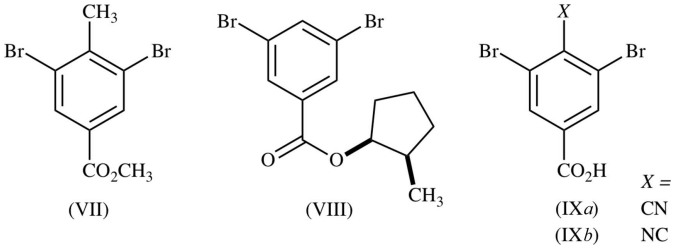


Figure 2
3,5-Dibromobenzoates (VII) and (VIII) in the CSD. We recently reported (IX*a*); isocyano acid (IX*b*) was not observed.

Table 1
Contact geometry for RCN and RNC (Å, °).

A—*B*···*C*	*A*—*B*	*B*···*C*	*A*—*B*···*C*
C1≡N1···Br2^{i}	1.138 (3)	3.041 (3)	128.6 (2)
C8═O1···Br6^{ii}	1.201 (3)	3.025 (2)	143.7 (2)
N11≡C17···C19^{iii}	1.162 (5)	3.240 (6)	112.9 (3)
C18═O11···Br16^{iv}	1.207 (5)	3.133 (3)	146.6 (3)

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

C19. In RNC, the compression about O12 is probably caused by repulsion between methyl groups in adjacent molecules, rather than the N11≡C17···C19 short contact (Table 1), because the C9—O2 and C19—O12 bond lengths are nearly identical.

3. Supramolecular features

Molecules of RCN form $R_2^2(10)$ inversion dimers based on C1≡N1···Br2 short contacts (Table 1), similar to the centric contacts found in crystals of (II) and (IV)–(VI). Adjacent dimers are connected along [201] by C8═O1···Br6 contacts similar to those found in (VII). Adjacent dimers are mutually inclined by 44.03 (7)°. The resulting sheet structure (Fig. 4) is staggered so that the methyl groups are spread apart to minimize steric congestion (Fig. 5). Crystals of RNC have a different packing motif, a slice of which is antiparallel ribbons parallel to [001] (Fig. 6). Each molecule of RNC participates in four short contacts between two pairs of molecules that are related by the $(x+1, y, z)$ translation, forming a three-dimensional network. Contacted molecules are mutually inclined by 42.0 (1)°. Half of the contacts are C18═O11···Br16 contacts, similar to those found in RCN and (VII). The other half are N11≡C17···C19 contacts, instead of the anticipated N11≡C17···Br12 contacts. It is interesting that the cyano group in RCN favors contacting a Br atom, but the isocyano group in RNC favors contacting the methoxy C atom.

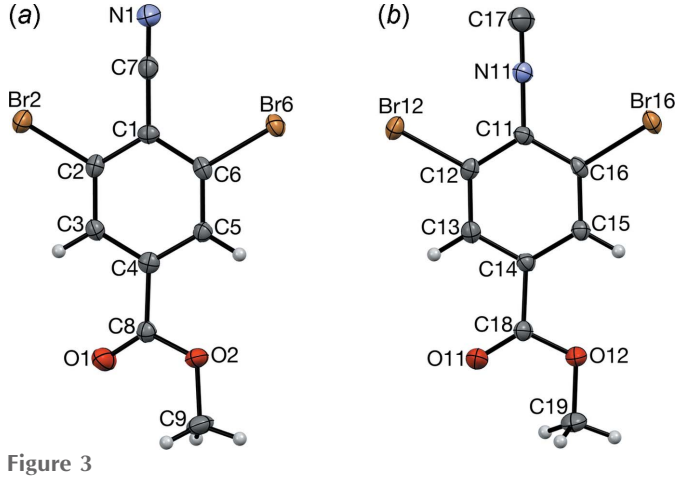


Figure 3
The molecular structures of (*a*) RCN and (*b*) RNC, with atom labeling and displacement ellipsoids at the 50% probability level.

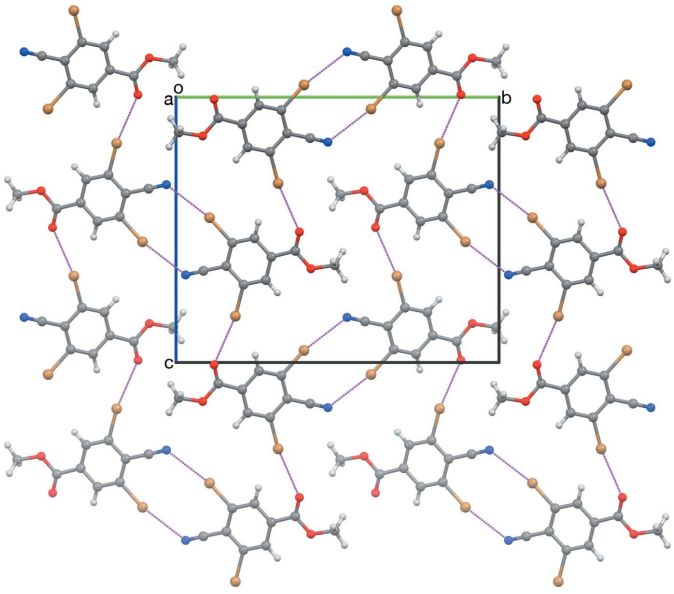


Figure 4
The sheet structure in a crystal of RCN, viewed along [100]. Dashed magenta lines represent short contacts.

4. Synthesis and crystallization

Methyl 4-amino-3,5-dibromobenzoate (RNH2) and **methyl 3,5-dibromo-4-cyanobenzoate (RCN)** were taken from material prepared in our recent study (Noland *et al.* 2017*a*; Fig. 7).

Methyl 3,5-dibromo-4-formamidobenzoate (RFA) was prepared from (RNH2, 1.24 g) by the formylation procedure described by Britton *et al.* (2016), with 1,2-dichloroethane in place of tetrahydrofuran, giving white needles (1.31 g, 97%). M.p. 489–490 K; ^{1}H NMR (300 MHz, $(CD_3)_2CO$) δ 9.203 (*s*, 1H), 8.441 (*s*, 1H), 8.226 (*s*, 2H), 3.928 (*s*, 3H); ^{13}C NMR (126 MHz, $(CD_3)_2SO$) δ 163.5 (1C), 160.2 (1C), 139.5 (1C), 132.5 (2C), 130.7 (1C), 123.5 (2C), 52.9 (1C); IR (KBr, cm^{-1}) 3153, 1727, 1664, 1524, 1282, 1154, 966, 765, 749; MS–ESI $[M + Na]^+$ calculated for $C_9H_7{}^{79}Br^{81}BrNO_3$ 359.8664, found 359.8662.

Methyl 3,5-dibromo-4-isocyanobenzoate (RNC) was prepared from (RFA, 594 mg) by the dehydration procedure described by Britton *et al.* (2016), giving a brown powder (490 mg), which was crystallized as described below (453 mg, 84%). M.p. 391–392 K; ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.278 (*s*, H13*A*, H15*A*), 3.930 (*s*, H19*A*, H19*B*, H19*C*); ^{13}C NMR (126 MHz, $(CD_3)_2SO$) δ 174.1 (C17), 163.0 (C18), 132.5 (C13, C15), 132.3 (C14), 130.1 (C11), 121.0 (C12, C16), 53.2 (C19); IR (KBr, cm^{-1}) 3073, 2961, 2853, 2122, 1722, 1426, 1275, 971, 764, 753; MS–EI $[M]^+$ calculated for $C_9H_5{}^{79}Br^{81}BrNO_2$ 316.8682, found 316.8699.

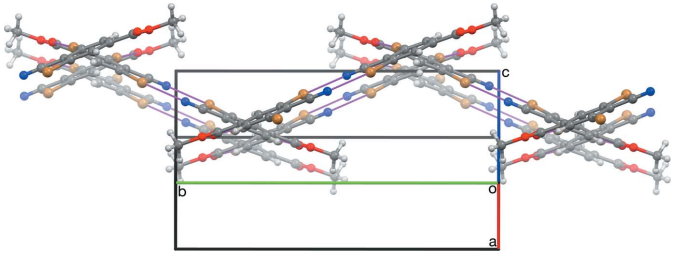


Figure 5
The sheet structure in a crystal of RCN, viewed along [503]. The same molecules are shown as in Fig. 4.

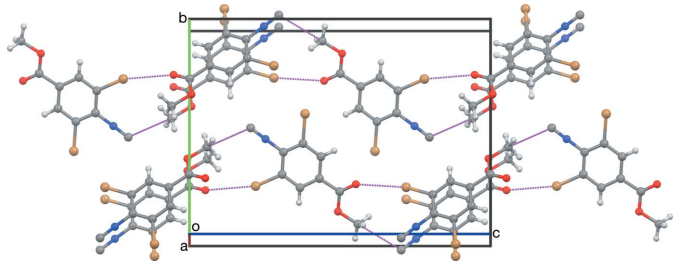


Figure 6
A slice of a crystal of RNC parallel to (100), viewed nearly along [100].

Crystallization: Crystals of RCN and RNC were grown by slow evaporation of solutions in dichloromethane–pentane, followed by decantation, washing with pentane, and then drying at room temperature and reduced pressure (10 Pa, 4 h). RCN was obtained as colorless blocks, and RNC was obtained as colorless needles.

5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. A direct-methods solution was calculated, followed by full-matrix least squares/difference-

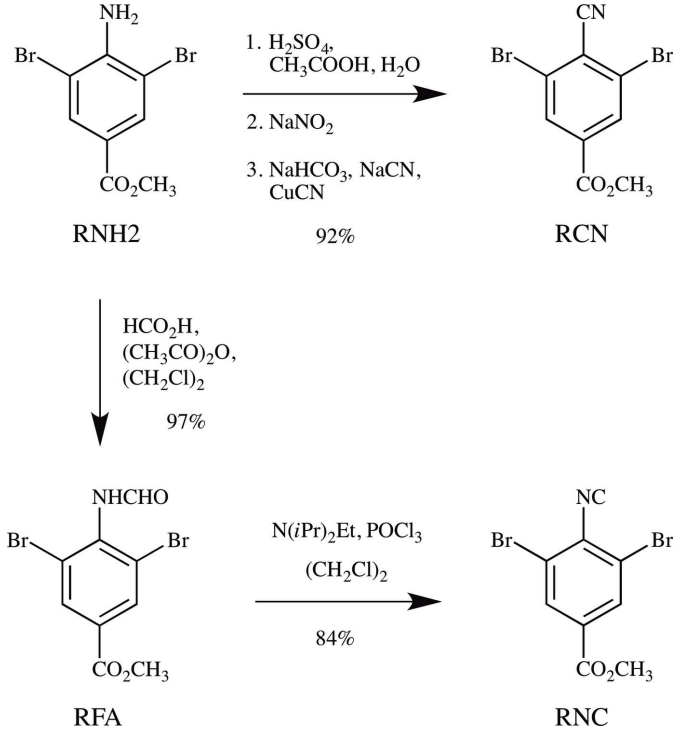


Figure 7
The synthesis of RCN and RNC.

Table 2
Experimental details.

	RCN	RNC
Crystal data		
Chemical formula	$C_9H_5Br_2NO_2$	$C_9H_5Br_2NO_2$
M_r	318.96	318.96
Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/n$
Temperature (K)	173	173
a, b, c (Å)	3.9273 (18), 17.881 (8), 14.739 (7)	3.9233 (9), 13.554 (3), 18.672 (4)
β (°)	93.757 (7)	90.002 (3)
V (Å^3)	1032.9 (8)	992.9 (4)
Z	4	4
Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	7.82	8.13
Crystal size (mm)	0.32 × 0.27 × 0.25	0.50 × 0.12 × 0.03
Data collection		
Diffractometer	Bruker APEXII CCD	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Sheldrick, 1996)	Multi-scan (*SADABS*; Sheldrick, 1996)
T_{min}, T_{max}	0.414, 0.746	0.418, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	11889, 2426, 2013	11400, 2277, 2132
R_{int}	0.043	0.053
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.657	0.650
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.026, 0.059, 1.07	0.029, 0.069, 1.02
No. of reflections	2426	2277
No. of parameters	128	129
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.37, −0.52	0.85, −0.65

Computer programs: *APEX2* and *SAINT* (Bruker, 2012), *SHELXT2014* (Sheldrick 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*), *Mercury* (Macrae *et al.*, 2008) and *publCIF* (Westrip, 2010).

Fourier cycles. All H atoms were placed in calculated positions and refined as riding atoms. For aryl H atoms, C—H = 0.95 Å and U_{iso}(H) = 1.2U_{eq}(C). For methyl H atoms, C—H = 0.98 Å and U_{iso}(H) = 1.5U_{eq}(C). RNC was refined as a two-component pseudo-merohedral twin in an 0.67:0.33 ratio, with a 180° rotation of [001] as the twinning symmetry element.

Acknowledgements

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supporting information

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Crystal structures of methyl 3,5-dibromo-4-cyanobenzoate and methyl 3,5-dibromo-4-isocyanobenzoate

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Computing details

For both structures, data collection: *APEX2* (Bruker, 2012); cell refinement: *SAINT* (Bruker, 2012); data reduction: *SAINT* (Bruker, 2012); program(s) used to solve structure: SHELXT2014 (Sheldrick 2015a); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015b); molecular graphics: *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Methyl 3,5-dibromo-4-cyanobenzoate (RCN)

Crystal data

$C_9H_5Br_2NO_2$
M_r = 318.96
Monoclinic, $P2_1/c$
a = 3.9273 (18) Å
b = 17.881 (8) Å
c = 14.739 (7) Å
β = 93.757 (7)°
V = 1032.9 (8) Å^3
Z = 4
$F(000)$ = 608
D_x = 2.051 Mg m^{-3}
Melting point: 410 K
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 2977 reflections
θ = 2.7–27.6°
μ = 7.82 mm^{-1}
T = 173 K
Block, colourless
0.32 × 0.27 × 0.25 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: sealed tube
φ and ω scans
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
T_{min} = 0.414, T_{max} = 0.746
11889 measured reflections
2426 independent reflections
2013 reflections with $I > 2\sigma(I)$
R_{int} = 0.043
θ_{max} = 27.8°, θ_{min} = 1.8°
h = −5→5
k = −23→23
l = −19→19

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.026
$wR(F^2)$ = 0.059
S = 1.07
2426 reflections
128 parameters
0 restraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0274P)^2 + 0.0295P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.37 e Å^{-3}
$\Delta\rho_{min}$ = −0.52 e Å^{-3}

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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.6370 (6)	0.65590 (14)	0.86321 (17)	0.0196 (5)
C2	0.7731 (6)	0.67398 (14)	0.95078 (16)	0.0199 (5)
Br2	0.74408 (8)	0.60384 (2)	1.04534 (2)	0.02954 (9)
C3	0.9245 (6)	0.74304 (14)	0.96807 (17)	0.0204 (5)
H3A	1.0169	0.7548	1.0275	0.024*
C4	0.9412 (6)	0.79516 (14)	0.89815 (17)	0.0197 (5)
C5	0.8100 (6)	0.77825 (14)	0.81049 (16)	0.0193 (5)
H5A	0.8216	0.8138	0.7629	0.023*
C6	0.6624 (6)	0.70889 (15)	0.79351 (16)	0.0193 (5)
Br6	0.49149 (7)	0.68383 (2)	0.67451 (2)	0.02395 (9)
C7	0.4695 (7)	0.58481 (16)	0.84529 (18)	0.0251 (6)
N1	0.3333 (6)	0.52966 (14)	0.82991 (16)	0.0359 (6)
C8	1.1066 (6)	0.86917 (14)	0.92064 (17)	0.0203 (5)
O1	1.2632 (5)	0.88220 (11)	0.99159 (14)	0.0357 (5)
O2	1.0590 (5)	0.91760 (10)	0.85308 (13)	0.0292 (5)
C9	1.2078 (8)	0.99150 (15)	0.8667 (2)	0.0326 (7)
H9A	1.1628	1.0215	0.8115	0.049*
H9B	1.4548	0.9868	0.8798	0.049*
H9C	1.1063	1.0161	0.9179	0.049*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0183 (13)	0.0179 (13)	0.0226 (13)	0.0008 (11)	0.0018 (10)	−0.0010 (11)
C2	0.0187 (13)	0.0237 (14)	0.0174 (12)	0.0018 (11)	0.0022 (10)	0.0039 (10)
Br2	0.03760 (18)	0.02881 (17)	0.02189 (15)	−0.00681 (12)	−0.00044 (12)	0.00724 (11)
C3	0.0225 (13)	0.0220 (14)	0.0164 (12)	0.0024 (11)	−0.0001 (10)	−0.0013 (10)
C4	0.0174 (13)	0.0198 (13)	0.0219 (13)	0.0036 (10)	0.0021 (10)	−0.0002 (10)
C5	0.0213 (14)	0.0189 (14)	0.0177 (13)	0.0009 (10)	0.0011 (10)	0.0011 (10)
C6	0.0164 (13)	0.0256 (14)	0.0158 (12)	0.0028 (10)	0.0002 (10)	−0.0029 (10)
Br6	0.02657 (15)	0.02717 (16)	0.01735 (14)	−0.00102 (11)	−0.00436 (10)	−0.00197 (10)
C7	0.0273 (15)	0.0289 (16)	0.0189 (13)	−0.0006 (12)	0.0009 (11)	0.0023 (11)
N1	0.0486 (17)	0.0303 (15)	0.0282 (13)	−0.0132 (12)	−0.0021 (11)	0.0024 (11)
C8	0.0214 (13)	0.0207 (14)	0.0187 (13)	0.0020 (11)	0.0014 (10)	0.0007 (10)
O1	0.0487 (13)	0.0283 (11)	0.0283 (11)	−0.0060 (10)	−0.0112 (10)	0.0008 (9)
O2	0.0403 (12)	0.0195 (10)	0.0270 (10)	−0.0074 (9)	−0.0036 (9)	0.0025 (8)
C9	0.0387 (17)	0.0196 (15)	0.0388 (17)	−0.0077 (12)	−0.0018 (13)	0.0053 (12)

Geometric parameters (Å, º)

C1—C2	1.402 (4)	C5—H5A	0.9500
C1—C6	1.406 (4)	C6—Br6	1.890 (2)
C1—C7	1.448 (4)	C7—N1	1.138 (3)
C2—C3	1.387 (3)	C8—O1	1.201 (3)
C2—Br2	1.884 (3)	C8—O2	1.324 (3)
C3—C4	1.394 (3)	O2—C9	1.454 (3)
C3—H3A	0.9500	C9—H9A	0.9800
C4—C5	1.393 (3)	C9—H9B	0.9800
C4—C8	1.502 (4)	C9—H9C	0.9800
C5—C6	1.385 (4)		
C2—C1—C6	118.4 (2)	C5—C6—C1	121.4 (2)
C2—C1—C7	120.8 (2)	C5—C6—Br6	119.93 (19)
C6—C1—C7	120.8 (2)	C1—C6—Br6	118.71 (19)
C3—C2—C1	120.5 (2)	N1—C7—C1	178.6 (3)
C3—C2—Br2	120.19 (19)	O1—C8—O2	124.6 (2)
C1—C2—Br2	119.32 (19)	O1—C8—C4	123.6 (2)
C2—C3—C4	120.0 (2)	O2—C8—C4	111.9 (2)
C2—C3—H3A	120.0	C8—O2—C9	117.1 (2)
C4—C3—H3A	120.0	O2—C9—H9A	109.5
C5—C4—C3	120.5 (2)	O2—C9—H9B	109.5
C5—C4—C8	121.6 (2)	H9A—C9—H9B	109.5
C3—C4—C8	117.8 (2)	O2—C9—H9C	109.5
C6—C5—C4	119.2 (2)	H9A—C9—H9C	109.5
C6—C5—H5A	120.4	H9B—C9—H9C	109.5
C4—C5—H5A	120.4		
C6—C1—C2—C3	0.9 (4)	C4—C5—C6—Br6	−178.62 (18)
C7—C1—C2—C3	−178.1 (2)	C2—C1—C6—C5	−1.6 (4)
C6—C1—C2—Br2	−179.76 (18)	C7—C1—C6—C5	177.4 (2)
C7—C1—C2—Br2	1.2 (3)	C2—C1—C6—Br6	178.18 (18)
C1—C2—C3—C4	0.2 (4)	C7—C1—C6—Br6	−2.8 (3)
Br2—C2—C3—C4	−179.11 (18)	C5—C4—C8—O1	−169.5 (3)
C2—C3—C4—C5	−0.7 (4)	C3—C4—C8—O1	10.1 (4)
C2—C3—C4—C8	179.8 (2)	C5—C4—C8—O2	10.4 (3)
C3—C4—C5—C6	0.0 (4)	C3—C4—C8—O2	−170.0 (2)
C8—C4—C5—C6	179.5 (2)	O1—C8—O2—C9	0.0 (4)
C4—C5—C6—C1	1.2 (4)	C4—C8—O2—C9	−179.9 (2)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C3—H3*A*···Br6^{i}	0.95	2.97	3.878 (3)	160

Symmetry code: (i) *x*+1, −*y*+3/2, *z*+1/2.

Methyl 3,5-dibromo-4-isocyanobenzoate (RNC)

Crystal data

$C_9H_5Br_2NO_2$
$M_r = 318.96$
Monoclinic, $P2_1/n$
$a = 3.9233$ (9) Å
$b = 13.554$ (3) Å
$c = 18.672$ (4) Å
$\beta = 90.002$ (3)°
$V = 992.9$ (4) Å^3
$Z = 4$
$F(000) = 608$
$D_x = 2.134$ Mg m^{-3}
Melting point: 391 K
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 2953 reflections
$\theta = 2.2$–$27.4°$
$\mu = 8.13$ mm^{-1}
$T = 173$ K
Needle, colourless
0.50 × 0.12 × 0.03 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: sealed tube
φ and ω scans
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
$T_{min} = 0.418$, $T_{max} = 0.746$
11400 measured reflections
2277 independent reflections
2132 reflections with $I > 2\sigma(I)$
$R_{int} = 0.053$
$\theta_{max} = 27.5°$, $\theta_{min} = 1.1°$
$h = -5 \rightarrow 5$
$k = -17 \rightarrow 17$
$l = -24 \rightarrow 24$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.069$
$S = 1.02$
2277 reflections
129 parameters
0 restraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0385P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.85$ e Å^{-3}
$\Delta\rho_{min} = -0.65$ e Å^{-3}

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.

Refinement. Refined as a 2-component pseudo-merohedral twin in an 0.67:0.33 ratio.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	y	z	U_{iso}*/U_{eq}
C11	0.5312 (10)	0.5930 (3)	0.6880 (2)	0.0187 (7)
C12	0.6653 (9)	0.5605 (2)	0.6228 (2)	0.0193 (7)
Br12	0.85319 (11)	0.43306 (2)	0.61597 (2)	0.02497 (11)
C13	0.6606 (10)	0.6211 (2)	0.5634 (2)	0.0216 (8)
H13A	0.7504	0.5983	0.5192	0.026*
C14	0.5246 (10)	0.7153 (2)	0.56835 (19)	0.0188 (8)
C15	0.3900 (9)	0.7501 (2)	0.63284 (19)	0.0185 (8)
H15A	0.2971	0.8147	0.6360	0.022*

C16	0.3944 (9)	0.6887 (3)	0.69219 (18)	0.0181 (7)
Br16	0.21859 (11)	0.73312 (2)	0.78028 (2)	0.02528 (11)
N11	0.5307 (9)	0.5321 (2)	0.74742 (17)	0.0240 (7)
C17	0.5282 (15)	0.4800 (3)	0.7968 (2)	0.0402 (11)
C18	0.5255 (11)	0.7760 (2)	0.5011 (2)	0.0210 (8)
O11	0.6712 (9)	0.75012 (19)	0.44732 (15)	0.0321 (7)
O12	0.3467 (8)	0.85902 (17)	0.50681 (14)	0.0270 (6)
C19	0.3135 (13)	0.9150 (3)	0.4408 (2)	0.0306 (9)
H19A	0.1794	0.9747	0.4498	0.046*
H19B	0.1984	0.8745	0.4046	0.046*
H19C	0.5404	0.9335	0.4234	0.046*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C11	0.0214 (19)	0.0192 (16)	0.0153 (18)	−0.0050 (15)	−0.0002 (15)	−0.0001 (14)
C12	0.0169 (19)	0.0166 (15)	0.0246 (19)	−0.0021 (13)	−0.0002 (18)	−0.0022 (13)
Br12	0.0280 (2)	0.01584 (15)	0.0310 (2)	0.00238 (13)	0.0011 (2)	−0.00255 (14)
C13	0.021 (2)	0.0209 (16)	0.0231 (19)	−0.0018 (15)	0.0031 (16)	−0.0034 (14)
C14	0.023 (2)	0.0176 (16)	0.0160 (18)	−0.0025 (14)	0.0008 (15)	−0.0007 (14)
C15	0.020 (2)	0.0185 (15)	0.0175 (19)	−0.0019 (13)	−0.0019 (15)	−0.0022 (13)
C16	0.0196 (19)	0.0210 (16)	0.0138 (16)	−0.0049 (14)	0.0001 (14)	−0.0060 (13)
Br16	0.0296 (2)	0.02670 (18)	0.01950 (19)	−0.00182 (15)	0.00484 (19)	−0.00694 (13)
N11	0.0310 (19)	0.0198 (15)	0.0213 (17)	−0.0029 (13)	0.0011 (14)	−0.0014 (13)
C17	0.065 (3)	0.028 (2)	0.027 (2)	−0.008 (2)	−0.003 (2)	−0.0025 (19)
C18	0.027 (2)	0.0172 (17)	0.0187 (19)	−0.0031 (14)	−0.0015 (16)	−0.0021 (14)
O11	0.048 (2)	0.0235 (12)	0.0245 (15)	0.0022 (14)	0.0087 (16)	0.0019 (10)
O12	0.0391 (17)	0.0219 (12)	0.0201 (13)	0.0055 (12)	0.0001 (13)	0.0016 (10)
C19	0.039 (3)	0.0269 (18)	0.026 (2)	0.0042 (19)	−0.003 (2)	0.0071 (15)

Geometric parameters (Å, º)

C11—N11	1.383 (5)	C15—H15A	0.9500
C11—C12	1.396 (5)	C16—Br16	1.882 (3)
C11—C16	1.407 (5)	N11—C17	1.162 (5)
C12—C13	1.379 (5)	C18—O11	1.207 (5)
C12—Br12	1.883 (3)	C18—O12	1.331 (4)
C13—C14	1.387 (5)	O12—C19	1.454 (4)
C13—H13A	0.9500	C19—H19A	0.9800
C14—C15	1.397 (5)	C19—H19B	0.9800
C14—C18	1.501 (5)	C19—H19C	0.9800
C15—C16	1.386 (5)		
N11—C11—C12	120.8 (3)	C15—C16—C11	120.9 (3)
N11—C11—C16	120.3 (3)	C15—C16—Br16	120.2 (3)
C12—C11—C16	118.9 (3)	C11—C16—Br16	118.9 (3)
C13—C12—C11	120.5 (3)	C17—N11—C11	179.1 (4)
C13—C12—Br12	119.8 (3)	O11—C18—O12	124.2 (4)

C11—C12—Br12	119.7 (3)	O11—C18—C14	122.6 (3)
C12—C13—C14	120.0 (3)	O12—C18—C14	113.2 (3)
C12—C13—H13A	120.0	C18—O12—C19	114.8 (3)
C14—C13—H13A	120.0	O12—C19—H19A	109.5
C13—C14—C15	120.9 (3)	O12—C19—H19B	109.5
C13—C14—C18	116.6 (3)	H19A—C19—H19B	109.5
C15—C14—C18	122.5 (3)	O12—C19—H19C	109.5
C16—C15—C14	118.8 (3)	H19A—C19—H19C	109.5
C16—C15—H15A	120.6	H19B—C19—H19C	109.5
C14—C15—H15A	120.6		

N11—C11—C12—C13	179.1 (3)	C14—C15—C16—Br16	179.5 (3)
C16—C11—C12—C13	−0.6 (6)	N11—C11—C16—C15	−179.3 (4)
N11—C11—C12—Br12	−0.8 (5)	C12—C11—C16—C15	0.4 (5)
C16—C11—C12—Br12	179.5 (3)	N11—C11—C16—Br16	1.1 (5)
C11—C12—C13—C14	0.6 (6)	C12—C11—C16—Br16	−179.2 (3)
Br12—C12—C13—C14	−179.5 (3)	C13—C14—C18—O11	−8.6 (6)
C12—C13—C14—C15	−0.3 (6)	C15—C14—C18—O11	172.4 (4)
C12—C13—C14—C18	−179.3 (4)	C13—C14—C18—O12	170.5 (3)
C13—C14—C15—C16	0.0 (6)	C15—C14—C18—O12	−8.5 (6)
C18—C14—C15—C16	179.0 (3)	O11—C18—O12—C19	4.8 (6)
C14—C15—C16—C11	−0.1 (6)	C14—C18—O12—C19	−174.2 (4)