

2,6-Dibromo-4-chlorophenyl isocyanide

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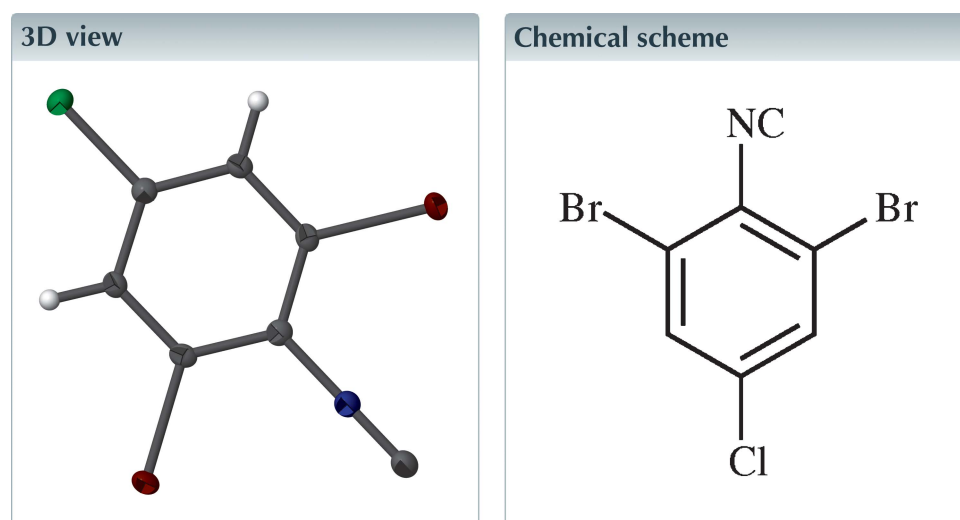
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Keywords: crystal structure; isocyanide; NC...Br contacts.

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Structural data: full structural data are available from iucrdata.iucr.org

Molecules of the title compound, C₇H₂Br₂ClN (RNC), are bisected by a mirror plane that passes through the chloro and isocyano groups. The isocyano C atom is bisected by two NC...Br contacts, one per Br atom. The resulting centric R₂²(10) rings form ribbons along [010], which align to form a nearly planar sheet structure that is very similar to the sheets observed in several related 2,6-dibromophenyl cyanides and isocyanides. The crystal of RNC is isomorphous with the corresponding cyanide, with solely translational stacking between sheets. This is in contrast to the 2,4,6-tribromophenyl cyanide and isocyanide, which occur as different polytypes.



Structure description

The title isocyanide (RNC) is presented to add to the library of corresponding cyanide/isocyanide pairs in the study of cyano/isocyano-halo short contacts. The molecular structure of RNC (Fig. 1) has typical geometry, with the largest distortion being displacement of C14 toward the center of the benzene ring such that the C13–C14–C13' angle is 122.2 (2)°. RNC is nearly planar, with a mean deviation of 0.002 (2) Å from the best-fit benzene plane for ring atoms (C11–C14), and 0.026 (3) Å for substituent atoms (Br11/Cl11/N11/C15). Centric N11≡C15...Br11 contacts are the main supramolecular interaction (Table 1). Two such contacts bisect each C15 atom, forming ribbons of R₂²(10) rings along [010]. Adjacent ribbons translate along [201], forming nearly-planar sheets parallel to (102), with no short contacts between ribbons (Fig. 2). Adjacent sheets stack translationally. RNC is isomorphous with 2,6-dibromo-4-chlorobenzonitrile (RCN; Britton, 2005). This outcome answers a question about the polytypism observed in this series of 2,6-dibromo compounds. The most common (Z = 2) polytype of 2,4,6-tribromobenzonitrile (Britton *et al.*, 2016) is isomorphous with RCN and RNC. However, 2,4,6-tribromophenyl isocyanide is exclusively reported as a Z = 8 polytype with mixed translational and centric stacking. It was therefore postulated that RNC might also occur

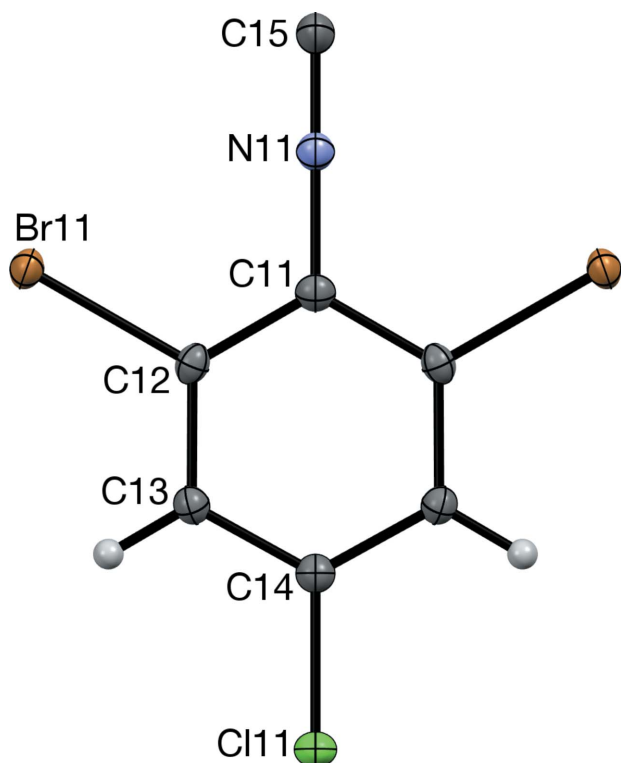


Figure 1
The molecular structure of RNC, showing the atomic numbering and displacement ellipsoids at the 50% probability level. Unlabelled atoms are related by the $(x, \frac{3}{2} - y, z)$ symmetry operation.

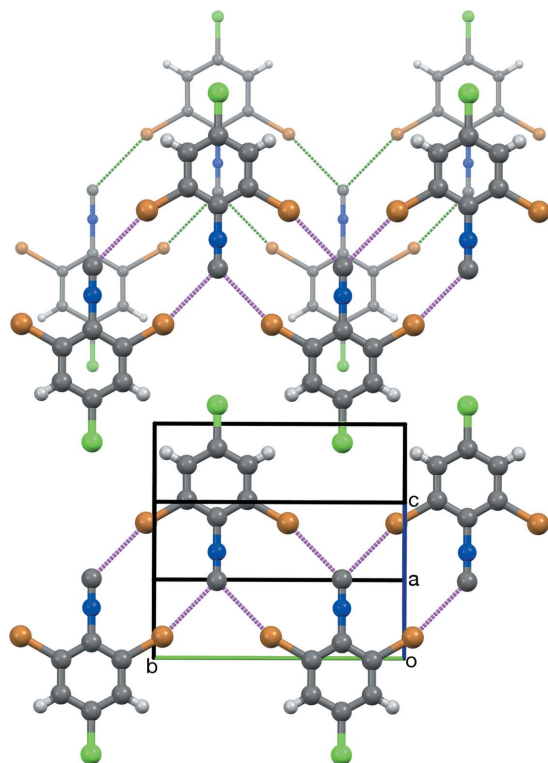


Figure 2
The sheet structure of RNC, viewed along $[20\bar{1}]$. For the four upper molecules, two adjacent layers are shown, illustrating the translational stacking mode. Dashed magenta lines represent short contacts in the front layer. Molecules in the rear layer are drawn with smaller balls and sticks, lower opacity, and green dashed lines representing short contacts.

Table 1
Contact geometry (\AA , $^\circ$).

$\text{N}\equiv\text{C}\cdots\text{Br}$	$\text{N}\equiv\text{C}$	$\text{C}\cdots\text{Br}$	$\text{N}\equiv\text{C}\cdots\text{C}$
$\text{N11}\equiv\text{C15}\cdots\text{Br11}^i$	1.161 (4)	3.125 (2)	135.95 (3)

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

mainly or exclusively as the $Z = 8$ polytype, however, that structure has not yet been observed.

Synthesis and crystallization

RNC was prepared over 3 steps (Fig. 3). 4-Chloroaniline (3.50 g; Acros Organics Co., No. 10859) was brominated according to the procedure described by Noland & Tritch (2017), giving 2,6-dibromo-4-chloroaniline (RNH2) as colourless needles [61% yield, m.p. 364–366 K (lit. 366–368 K; Miura *et al.*, 1998)]; ^1H NMR (500 MHz, CDCl_3) δ 7.39 (s, 2H), 4.54 (s, 2H); ^{13}C NMR (126 MHz, CDCl_3) δ 141.1, 131.4, 122.8, 108.6. A portion of the RNH2 (1.15 g) was formylated according to the procedure described by Britton *et al.* (2016), with dichloromethane in the place of tetrahydrofuran, giving 2,6-dibromo-4-chloroformanilide (RFA) as colourless needles (90% yield, m.p. 485–487 K dec.); ^1H NMR (500 MHz, $\text{DMSO-}d_6$, 2 conformers obs.) δ 10.12 (s, 1H, major), 9.89 (s, 1H, minor), 8.30 (s, 1H, major), 8.10 (s, 1H, minor), 7.93 (s, 2H, both); ^{13}C NMR (126 MHz, $\text{DMSO-}d_6$) δ 159.6, 134.1, 133.2, 131.7, 124.2. A portion of the RFA (313 mg) was dehydrated according to the procedure described by Britton *et al.* (2016), with dichloromethane in the place of 1,2-dichloroethane, giving RNC as a brown powder. Crystals suitable for X-ray diffraction (colourless needles) were prepared by slow

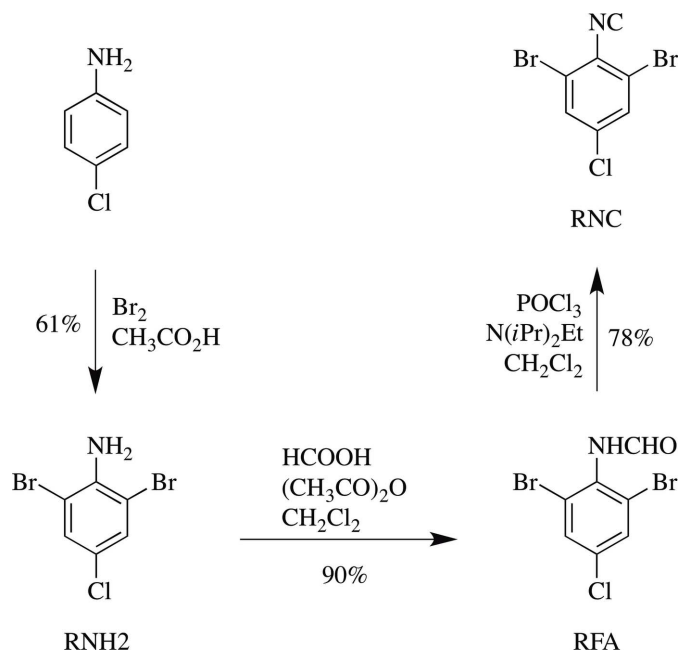


Figure 3
The synthesis of RNC.

Table 2
Experimental details.

Crystal data	
Chemical formula	C ₇ H ₂ Br ₂ ClN
<i>M_r</i>	295.37
Crystal system, space group	Monoclinic, <i>P</i> 2 ₁ / <i>m</i>
Temperature (K)	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	4.7215 (4), 10.0181 (9), 8.7689 (8)
β (°)	93.023 (4)
<i>V</i> (Å ³)	414.20 (6)
<i>Z</i>	2
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	10.03
Crystal size (mm)	0.20 × 0.20 × 0.12
Data collection	
Diffractometer	Bruker VENTURE PHOTON-II
Absorption correction	Multi-scan (<i>SADABS</i> ; Sheldrick, 1996)
<i>T</i> _{min} , <i>T</i> _{max}	0.057, 0.156
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	7071, 1334, 1239
<i>R</i> _{int}	0.037
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.715
Refinement	
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.021, 0.050, 1.08
No. of reflections	1334
No. of parameters	58
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	0.51, -0.90

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

evaporation of a solution in chloroform and cyclohexane, followed by decantation, and then washing with pentane (78% yield, m.p. 377–378 K); ¹H NMR (500 MHz, CD₂Cl₂) δ 7.69 (*s*, H13A); ¹³C NMR (126 MHz, CD₂Cl₂) δ 174.7 (C15), 136.4 (C14), 132.6 (C13), 127.4 (C11), 121.7 (C12); IR (KBr, cm⁻¹)

3074, 2132, 1578, 1561, 1540, 1433, 1375, 1117, 857, 840, 749, 661.

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, x171819 [https://doi.org/10.1107/S2414314617018193]

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2,6-Dibromo-4-chlorophenyl isocyanide

Crystal data

$C_7H_2Br_2ClN$

$M_r = 295.37$

Monoclinic, $P2_1/m$

$a = 4.7215$ (4) Å

$b = 10.0181$ (9) Å

$c = 8.7689$ (8) Å

$\beta = 93.023$ (4)°

$V = 414.20$ (6) Å³

$Z = 2$

$F(000) = 276$

$D_x = 2.368$ Mg m⁻³

Melting point: 377 K

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

Cell parameters from 2922 reflections

$\theta = 2.3$ – 30.5 °

$\mu = 10.03$ mm⁻¹

$T = 100$ K

Needle, colourless

$0.20 \times 0.20 \times 0.12$ mm

Data collection

Bruker VENTURE PHOTON-II
diffractometer

Radiation source: micro-focus

φ and ω scans

Absorption correction: multi-scan
(SADABS; Sheldrick, 1996)

$T_{\min} = 0.057$, $T_{\max} = 0.156$

7071 measured reflections

1334 independent reflections

1239 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.037$

$\theta_{\max} = 30.5$ °, $\theta_{\min} = 2.3$ °

$h = -6 \rightarrow 5$

$k = -14 \rightarrow 14$

$l = -12 \rightarrow 12$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.021$

$wR(F^2) = 0.050$

$S = 1.08$

1334 reflections

58 parameters

0 restraints

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0194P)^2 + 0.2636P]$

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

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

$\Delta\rho_{\max} = 0.51$ e Å⁻³

$\Delta\rho_{\min} = -0.90$ 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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Br11	0.34536 (4)	0.46686 (2)	0.69204 (2)	0.01601 (7)
Cl11	1.09879 (12)	0.7500	1.06960 (7)	0.01600 (12)
C11	0.3949 (5)	0.7500	0.7040 (3)	0.0141 (4)
N11	0.1793 (5)	0.7500	0.5901 (2)	0.0153 (4)
C12	0.5017 (3)	0.62936 (17)	0.76251 (19)	0.0136 (3)
C13	0.7193 (3)	0.62865 (17)	0.87580 (19)	0.0140 (3)
H13A	0.7934	0.5469	0.9156	0.017*
C14	0.8258 (5)	0.7500	0.9296 (3)	0.0140 (4)
C15	0.0001 (6)	0.7500	0.4941 (3)	0.0195 (5)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br11	0.02047 (10)	0.01162 (10)	0.01577 (10)	-0.00213 (6)	-0.00046 (7)	-0.00098 (6)
Cl11	0.0151 (3)	0.0176 (3)	0.0150 (3)	0.000	-0.0022 (2)	0.000
C11	0.0153 (10)	0.0157 (11)	0.0113 (10)	0.000	0.0019 (8)	0.000
N11	0.0185 (10)	0.0140 (9)	0.0134 (9)	0.000	0.0000 (8)	0.000
C12	0.0156 (7)	0.0125 (7)	0.0130 (7)	-0.0016 (6)	0.0030 (6)	-0.0017 (6)
C13	0.0155 (7)	0.0127 (7)	0.0139 (8)	0.0011 (6)	0.0014 (6)	0.0003 (6)
C14	0.0136 (10)	0.0149 (11)	0.0136 (10)	0.000	0.0016 (8)	0.000
C15	0.0253 (13)	0.0139 (10)	0.0189 (12)	0.000	-0.0036 (10)	0.000

Geometric parameters (\AA , $^\circ$)

Br11—C12	1.8785 (17)	N11—C15	1.161 (4)
Cl11—C14	1.733 (3)	C12—C13	1.391 (3)
C11—N11	1.388 (3)	C13—C14	1.389 (2)
C11—C12 ⁱ	1.397 (2)	C13—H13A	0.9500
C11—C12	1.397 (2)	C14—C13 ⁱ	1.389 (2)
N11—C11—C12 ⁱ	120.09 (11)	C14—C13—C12	118.60 (17)
N11—C11—C12	120.09 (11)	C14—C13—H13A	120.7
C12 ⁱ —C11—C12	119.8 (2)	C12—C13—H13A	120.7
C15—N11—C11	179.6 (3)	C13 ⁱ —C14—C13	122.2 (2)
C13—C12—C11	120.38 (17)	C13 ⁱ —C14—Cl11	118.90 (11)
C13—C12—Br11	119.55 (13)	C13—C14—Cl11	118.90 (11)
C11—C12—Br11	120.06 (14)		
N11—C11—C12—C13	179.51 (19)	C11—C12—C13—C14	0.4 (3)
C12 ⁱ —C11—C12—C13	-1.8 (3)	Br11—C12—C13—C14	-178.03 (15)
N11—C11—C12—Br11	-2.1 (3)	C12—C13—C14—C13 ⁱ	1.1 (3)
C12 ⁱ —C11—C12—Br11	176.61 (11)	C12—C13—C14—Cl11	-179.48 (14)

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