

Crystal structures of 2,6-dibromo-4-methylbenzo- nitrile and 2,6-dibromo-4-methylphenyl isocyanide

Wayland E. Noland,* Jessica E. Shudy, Janel L. Rieger, Zoe H. Tu and Kenneth J. Tritch

Department of Chemistry, University of Minnesota, 207 Pleasant St SE, Minneapolis, MN 55455, USA. *Correspondence e-mail: noland001@umn.edu

Received 27 October 2017

Accepted 15 November 2017

Edited by A. J. Lough, University of Toronto, Canada

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

CCDC references: 1525809; 1525810

Supporting information: this article has supporting information at journals.iucr.org/e

In the title crystals, $C_8H_5Br_2N$, which are isomorphous, the steric bulk of the methyl group causes neighboring molecules to become mutually inclined. This prevents the formation of planar or nearly planar sheets, which were observed in the trichloro and tribromo analogs. Instead of CN/NC...Br contacts, tetrameric Br...Br contacts are observed. These contacts form tetragonally puckered sheets parallel to (001). The CN/NC and methyl groups are grouped at the peaks and troughs. Both molecules lie across crystallographic mirror planes; thus, the methyl H atoms are disordered over two sets of sites with equal occupancy. The title nitrile is a redetermination. The refinement converged at $R[F^2 > 2\sigma(F^2)] = 0.020$, whereas the original determination [Gleason & Britton, (1976). *Cryst. Struct. Commun.* **5**, 229–232] had $R = 0.112$.

1. Chemical context

As part of an ongoing study of cyano–halo short contacts, the para-Br atom of 2,4,6-tribromobenzonitrile (van Rij & Britton, 1972) was replaced by a methyl group (Gleason & Britton, 1976), giving 2,6-dibromo-4-methylbenzonitrile (RCN). The methyl group was bulky enough to disrupt the planar sheet structure that was observed in the tribromo nitrile. As of the most recent update of the Cambridge Structural Database (CSD; Version 5.37, Feb 2017; Groom *et al.*, 2016), RCN remains the only example of a 2,6-dihalobenzonitrile with a methyl group at the 4-position. Most of the examples with polyatomic 4-substituents are fluorinated benzonitriles, with applications including tuning the fluoride affinity of phosphoranes (Solyntjes *et al.*, 2016), study of magnetostructural correlation (Thomson *et al.*, 2012), and use as metal ligands (Díaz-Álvarez *et al.*, 2006). The chlorinated and brominated entries are either *bis*(carbonitriles) [(I), Fig. 1; Britton, 1981; Hirshfeld, 1984; van Rij & Britton, 1981] or 4-carboxy analogs [(II); Britton, 2012; Noland *et al.*, 2017]. All of these 4-substituents have stronger interactions than a methyl group, and exhibit different packing motifs than RCN.

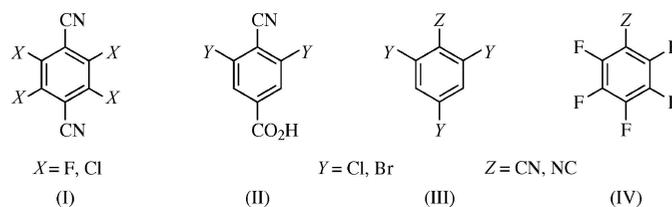
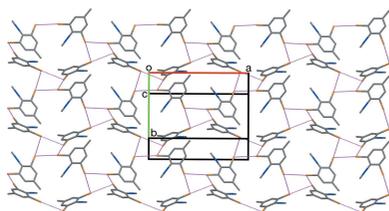
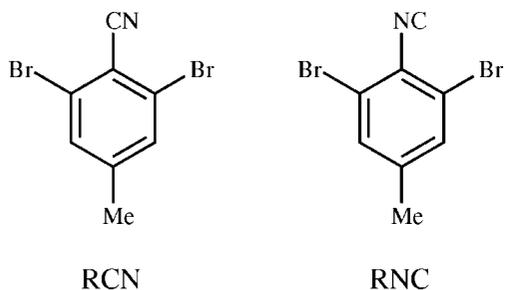


Figure 1
Contextual compounds.

The comparison of corresponding nitriles and isocyanides is a rare opportunity to explore the subtle differences between molecules that are both isomeric and isoelectronic. In the 2,6-dihaloaryl series, there are only three prior examples in the CSD. The trichloro and tribromo pairs [(III); Pink *et al.*, 2000; Britton *et al.*, 2016] are polytypic, and the pentafluoro pair [(IV), Fig. 1; Bond *et al.*, 2001; Lentz & Preugschat, 1993] is isomorphous. The question arose as to whether RCN and its isocyanide (2,6-dibromo-4-methylphenyl isocyanide, RNC) would be isomorphous, polytypic, or polymorphic. A single crystal of RNC and a redetermination of RCN are presented.



2. Structural commentary

RNC and the redetermination of RCN are isomorphous with the original RCN structure (Gleason & Britton, 1976). The molecular structures of RCN (Fig. 2*a*) and RNC (Fig. 2*b*) are nearly planar. The two crystals described herein were pseudo-enantiomorphous, roughly being enantiomorphs with swapped cyano C and N atoms, hence the reflected ellipsoid orientations between RCN and RNC. For RCN, the mean deviation from the plane of best fit for the benzene ring (C1–C4) is 0.002 (3) Å. For RNC, this deviation (C11–C14) is 0.001 (2) Å. These planes are roughly parallel to (33 $\bar{2}$).

3. Supramolecular features

The methyl group is sufficiently bulky to prevent planar ribbons or inversion dimers of the types found in the tribromo

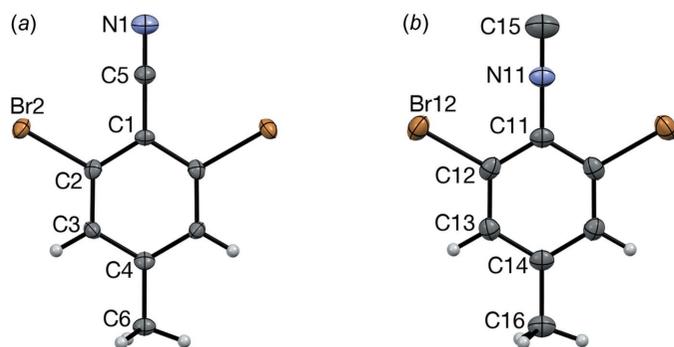


Figure 2

The molecular structures of (a) RCN and (b) RNC, with atom labeling and displacement ellipsoids at the 50% probability level. Unlabeled atoms are generated by the $(-\frac{1}{2} + y, \frac{1}{2} + x, z)$ and $(\frac{1}{2} - y, -\frac{1}{2} + x, z)$ symmetry operations, respectively. For the methyl H atoms, only one of the two mirror-related disorder sites is shown.

Table 1

Contact geometry (Å, °).

C–Br···Br	C–Br	Br···Br	C–Br···Br
C2–Br2···Br2 ⁱ	1.899 (5)	3.5575 (7)	96.8 (2)
C2–Br2···Br2 ⁱⁱ	1.899 (5)	3.5575 (7)	176.41 (7)
C12–Br12···Br12 ⁱ	1.895 (4)	3.575 (1)	97.8 (1)
C12–Br12···Br12 ⁱⁱ	1.895 (4)	3.575 (1)	175.7 (1)

Symmetry codes: (i) $1 - y, x, 1 - z$; (ii) $y, 1 - x, 1 - z$.

analogs. Instead, neighboring molecules of RCN and RNC adopt a mutually inclined arrangement. The inclination between best-fit planes for adjacent molecules of RCN is 38.3 (3)°, and 41.0 (2)° for RNC. This molecular arrangement prevents CN···Br and NC···Br contacts, but is probably affected by the formation of $R_4^4(4)$ rings of Br···Br contacts (Table 1). Each Br atom participates both as a donor (narrow C–Br···Br angle) and an acceptor (wide C–Br···Br angle). Each molecule participates in two such $R_4^4(4)$ rings, forming $R_4^4(24)$ rings. The result is a tetragonally puckered sheet structure parallel to (001) (Fig. 3). This is similar to the sheet structure reported for 2,6-dibromobenzonitrile (Britton *et al.*, 2000), although without the methyl group, the sheets were nearly planar. As future work, we plan to find whether this packing motif changes when the Br atoms are replaced with I atoms.

4. Synthesis and crystallization

The synthesis of RCN and RNC is shown in Fig. 4.

2,6-Dibromo-4-methylaniline (V) was prepared from 4-methylaniline based on the work of Olivier (1926).

RCN was prepared from (V) (980 mg) *via* the Sandmeyer cyanation procedure described by Britton *et al.* (2016; Fig. 4), as a tan powder (898 mg, 88%). M.p. 434–435 K (lit. 429–431 K; Gleason & Britton, 1976); $R_f = 0.49$ (SiO₂ in 2:1 hexane–ethyl acetate); ¹H NMR (500 MHz, CD₂Cl₂) δ 7.490 (*s*, 2H, H3A), 2.380 (*s*, 3H, H6A–C); ¹³C NMR (126 MHz, CD₂Cl₂) δ 147.1 (C4), 133.2 (C3), 126.6 (C2), 116.6 (C1 or C5), 116.1 (C5 or C1), 21.7 (C6); IR (KBr, cm⁻¹) 3062, 2231, 1582,

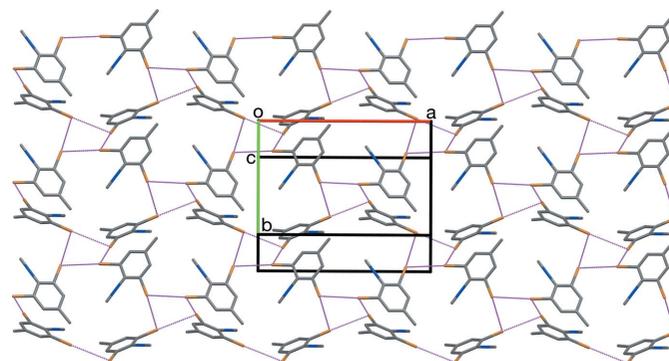


Figure 3

The sheet structure of RNC, viewed along [0 $\bar{1}$ 3]. The Br···Br contacts are represented as pink dotted lines.

Table 2
Experimental details.

	RCN	RNC
Crystal data		
Chemical formula	C ₈ H ₅ Br ₂ N	C ₈ H ₅ Br ₂ N
<i>M_r</i>	274.95	274.95
Crystal system, space group	Tetragonal, <i>P</i> $\bar{4}$ ₂ <i>m</i>	Tetragonal, <i>P</i> $\bar{4}$ ₂ <i>m</i>
Temperature (K)	123	173
<i>a</i> , <i>c</i> (Å)	14.6731 (5), 3.9727 (1)	14.690 (5), 4.0703 (15)
<i>V</i> (Å ³)	855.32 (6)	878.3 (7)
<i>Z</i>	4	4
Radiation type	Cu <i>K</i> α	Mo <i>K</i> α
<i>μ</i> (mm ⁻¹)	11.46	9.16
Crystal size (mm)	0.50 × 0.07 × 0.04	0.40 × 0.14 × 0.08
Data collection		
Diffractometer	Bruker Venture PHOTON-II	Bruker APEXII CCD
Absorption correction	Multi-scan (<i>SADABS</i> ; Sheldrick, 1996)	Multi-scan (<i>SADABS</i> ; Sheldrick, 1996)
<i>T_{min}</i> , <i>T_{max}</i>	0.314, 0.754	0.255, 0.746
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	8444, 904, 902	10248, 1074, 1001
<i>R_{int}</i>	0.039	0.045
(sin θ/λ) _{max} (Å ⁻¹)	0.624	0.652
Refinement		
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.020, 0.057, 1.27	0.023, 0.051, 1.14
No. of reflections	904	1074
No. of parameters	60	59
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.37, -0.32	0.30, -0.51
Absolute structure	Flack <i>x</i> determined using 348 quotients [[<i>I</i> ⁺)-(<i>I</i> ⁻)]/[<i>I</i> ⁺ +(<i>I</i> ⁻)] (Parsons <i>et al.</i> , 2013)	Flack <i>x</i> determined using 381 quotients [[<i>I</i> ⁺)-(<i>I</i> ⁻)]/[<i>I</i> ⁺ +(<i>I</i> ⁻)] (Parsons <i>et al.</i> , 2013)
Absolute structure parameter	-0.02 (3)	-0.024 (13)

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

1451, 1197, 857, 747; MS (EI, *m/z*) [*M*]⁺ calculated for C₈H₅Br₂N 274.8763, found 274.8766.

2,6-Dibromo-4-methylformanilide (VI) was prepared from (V) (997 mg) *via* the formylation procedure described by Britton *et al.* (2016), performed at 60% scale, with dichloromethane instead of tetrahydrofuran. The filter cake was recrystallized from toluene, giving white needles (1.00 g, 91%). M.p. 505–506 K; *R_f* = 0.27 (SiO₂ in 2:1 hexane–ethyl acetate); ¹H NMR (500 MHz, (CD₃)₂SO; 2 conformers obs.) δ 9.993 (*s*, 1H; major), 9.743 (*d*, *J* = 10.9 Hz, 1H; minor), 8.270 (*s*, 1H; major), 8.021 (*d*, *J* = 11.1 Hz, 1H; minor), 7.623 (*s*, 2H; minor), 7.571 (*s*, 2H; major), 2.303 (*s*, 3H; both); ¹³C NMR (126 MHz, (CD₃)₂SO; 2 conformers obs.) δ 164.5 (1C; minor), 159.6 (1C; major), 140.9 (1C; minor), 140.7 (1C; major), 133.0 (2C; minor), 132.6 (2C; major), 131.9 (1C; minor), 131.8 (1C; major), 123.3 (2C; minor), 123.2 (2C; major), 19.8 (1C; both); IR (KBr, cm⁻¹) 3247, 2927, 1656, 1511, 1152, 1060, 840, 747, 684; MS (ESI, *m/z*) [*M*-H]⁻ calculated for C₈H₇Br₂NO 289.8822, found 289.8814.

RNC was prepared from (VI) (254 mg) *via* the amide dehydration procedure described by Britton *et al.* (2016), performed at 15% scale, as a beige powder (190 mg, 81%). M.p. 401–402 K; *R_f* = 0.53 (SiO₂ in 3:1 hexane–ethyl acetate); ¹H NMR (400 MHz, CD₂Cl₂) δ 7.456 (*s*, 2H, H13), 2.346 (*s*, 3H, H16A–C); ¹³C NMR (101 MHz, CD₂Cl₂) δ 172.7 (C15), 142.9 (C14), 133.2 (C13), 126.0 (C11), 120.8 (C12), 21.2 (C16); IR (KBr, cm⁻¹) 3061, 2922, 2850, 2118, 1654, 1586, 1451, 1384,

1064, 857, 748, 701; MS (EI, *m/z*) [*M*]⁺ calculated for C₈H₅Br₂N 274.8783, found 274.8784.

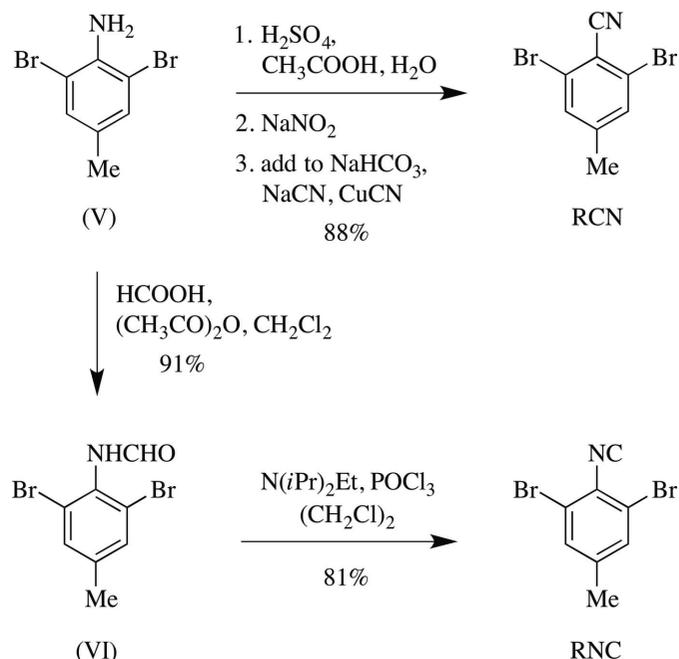


Figure 4
The synthesis of RCN and RNC.

Crystallization: RCN and RNC crystals were grown by slow evaporation of dichloromethane solutions under ambient conditions. Crystals were collected by suction filtration when a small portion of the original solvent remained, and then they were washed with pentane.

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-Fourier cycles. All H atoms were placed in calculated positions (C–H = 0.95 or 0.98 Å) and refined as riding atoms with $U_{\text{iso}}(\text{H})$ set to $1.2U_{\text{eq}}(\text{C})$ for aryl H atoms and $1.5U_{\text{eq}}(\text{C})$ for methyl H atoms. Because the molecules lie across mirror planes, the methyl H atoms are disordered across two sets of sites with 1:1 occupancy.

Acknowledgements

The authors thank Victor G. Young, Jr. (X-Ray Crystallographic Laboratory, University of Minnesota) for assistance with the crystallographic determination, the Wayland E. Noland Research Fellowship Fund at the University of Minnesota Foundation for generous financial support of this project, and Doyle Britton (deceased July 7, 2015) for providing the basis of this project. This work was taken in large part from the PhD thesis of KJT (Tritch, 2017).

References

Bond, A. D., Davies, J. E., Griffiths, J. & Rawson, J. M. (2001). *Acta Cryst.* **E57**, o231–o233.
 Britton, D. (1981). *Cryst. Struct. Commun.* **10**, 1501–1508.

Britton, D. (2012). *J. Chem. Crystallogr.* **42**, 851–855.
 Britton, D., Noland, W. E. & Pinnow, M. J. (2000). *Acta Cryst.* **B56**, 822–827.
 Britton, D., Noland, W. E. & Tritch, K. J. (2016). *Acta Cryst.* **E72**, 178–183.
 Bruker (2012). *APEX2* and *SAINT*. Bruker AXS, Inc., Madison, Wisconsin, USA.
 Díaz-Álvarez, A. E., Crochet, P., Zablocka, M., Cadierno, V., Duhayon, C., Gimeno, J. & Majoral, J.-P. (2006). *New J. Chem.* **30**, 1295–1306.
 Gleason, W. B. & Britton, D. (1976). *Cryst. Struct. Commun.* **5**, 229–232.
 Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* **B72**, 171–179.
 Hirshfeld, F. L. (1984). *Acta Cryst.* **B40**, 484–492.
 Lentz, D. & Preugschat, D. (1993). *Acta Cryst.* **C49**, 52–54.
 Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.
 Noland, W. E., Rieger, J. L., Tu, Z. H. & Tritch, K. J. (2017). *Acta Cryst.* **E73**, 1743–1746.
 Olivier, S. C. J. (1926). *Recl Trav. Chim. Pays Bas*, **45**, 296–306.
 Parsons, S., Flack, H. D. & Wagner, T. (2013). *Acta Cryst.* **B69**, 249–259.
 Pink, M., Britton, D., Noland, W. E. & Pinnow, M. J. (2000). *Acta Cryst.* **C56**, 1271–1273.
 Rij, C. van & Britton, D. (1981). *Cryst. Struct. Commun.* **10**, 175–178.
 Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
 Sheldrick, G. M. (2015a). *Acta Cryst.* **A71**, 3–8.
 Sheldrick, G. M. (2015b). *Acta Cryst.* **C71**, 3–8.
 Solyntjes, S., Neumann, B., Stammler, H.-G., Ignat'ev, N. & Hoge, B. (2016). *Eur. J. Inorg. Chem.* **2016**, 3999–4010.
 Thomson, R. I., Pask, C. M., Lloyd, G. O., Mito, M. & Rawson, J. M. (2012). *Chem. Eur. J.* **18**, 8629–8633.
 Tritch, K. J. (2017). PhD thesis, University of Minnesota, Minneapolis, MN, USA.
 Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

supporting information

Acta Cryst. (2017). E73, 1913-1916 [https://doi.org/10.1107/S2056989017016395]

Crystal structures of 2,6-dibromo-4-methylbenzotrile and 2,6-dibromo-4-methylphenyl isocyanide

Wayland E. Noland, Jessica E. Shudy, Janel L. Rieger, Zoe H. Tu and Kenneth J. Tritch

Computing details

For both structures, data collection: *APEX2* (Bruker, 2012); cell refinement: *SAINTE* (Bruker, 2012); data reduction: *SAINTE* (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).

3,5-Dibromo-4-methylbenzotrile (RCN)

Crystal data

$C_8H_5Br_2N$

$M_r = 274.95$

Tetragonal, $P4_2/m$

$a = 14.6731$ (5) Å

$c = 3.9727$ (1) Å

$V = 855.32$ (6) Å³

$Z = 4$

$F(000) = 520$

$D_x = 2.135$ Mg m⁻³

Melting point: 434 K

Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å

Cell parameters from 2980 reflections

$\theta = 4.3$ – 74.0°

$\mu = 11.46$ mm⁻¹

$T = 123$ K

Needle, colourless

$0.50 \times 0.07 \times 0.04$ mm

Data collection

Bruker Venture PHOTON-II
diffractometer

Radiation source: ImuS micro-focus

φ and ω scans

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

$T_{\min} = 0.314$, $T_{\max} = 0.754$

8444 measured reflections

904 independent reflections

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

$R_{\text{int}} = 0.039$

$\theta_{\max} = 74.2^\circ$, $\theta_{\min} = 6.0^\circ$

$h = -18 \rightarrow 18$

$k = -17 \rightarrow 17$

$l = -4 \rightarrow 4$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.020$

$wR(F^2) = 0.057$

$S = 1.27$

904 reflections

60 parameters

0 restraints

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + 2.1952P]$

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

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

$\Delta\rho_{\max} = 0.37$ e Å⁻³

$\Delta\rho_{\min} = -0.32$ e Å⁻³

Extinction correction: SHELXL2014
(Sheldrick, 2015b),

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

Extinction coefficient: 0.0055 (4)

Absolute structure: Flack x determined using
 348 quotients $[(F^-)-(F)]/[(F^+)+(F)]$ (Parsons *et al.*,
 2013)
 Absolute structure parameter: -0.02 (3)

Special details

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)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
C1	0.2722 (3)	0.7722 (3)	0.357 (2)	0.0156 (13)	
C2	0.2985 (3)	0.6837 (4)	0.2695 (13)	0.0177 (10)	
Br2	0.41762 (3)	0.64354 (3)	0.38319 (19)	0.0222 (2)	
C3	0.2404 (3)	0.6240 (3)	0.1067 (15)	0.0185 (9)	
H3A	0.2605	0.5645	0.0486	0.022*	
C4	0.1517 (3)	0.6517 (3)	0.0283 (18)	0.0189 (15)	
C5	0.3328 (4)	0.8328 (4)	0.532 (2)	0.0223 (17)	
N1	0.3806 (3)	0.8806 (3)	0.676 (2)	0.0309 (17)	
C6	0.0866 (3)	0.5866 (3)	-0.138 (2)	0.0212 (13)	
H6A	0.0306	0.6190	-0.1991	0.032*	0.5
H6B	0.0720	0.5369	0.0175	0.032*	0.5
H6C	0.1148	0.5615	-0.3417	0.032*	0.5

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0183 (18)	0.0183 (18)	0.010 (3)	-0.003 (2)	0.000 (2)	0.000 (2)
C2	0.015 (2)	0.019 (2)	0.019 (3)	0.0001 (19)	0.0034 (19)	0.0025 (19)
Br2	0.0147 (3)	0.0236 (3)	0.0282 (3)	0.00002 (17)	-0.0017 (2)	0.0042 (3)
C3	0.018 (2)	0.015 (2)	0.022 (2)	-0.0001 (17)	0.002 (3)	-0.003 (2)
C4	0.018 (2)	0.018 (2)	0.020 (4)	-0.005 (3)	0.0031 (18)	0.0031 (18)
C5	0.022 (2)	0.022 (2)	0.024 (4)	-0.002 (3)	0.000 (2)	0.000 (2)
N1	0.031 (2)	0.031 (2)	0.030 (4)	-0.009 (3)	-0.003 (2)	-0.003 (2)
C6	0.023 (2)	0.023 (2)	0.017 (3)	-0.005 (3)	0.000 (2)	0.000 (2)

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

C1—C2 ⁱ	1.399 (6)	C4—C3 ⁱ	1.398 (6)
C1—C2	1.399 (6)	C4—C6	1.505 (10)
C1—C5	1.437 (10)	C5—N1	1.145 (11)
C2—C3	1.383 (8)	C6—H6A	0.9800
C2—Br2	1.899 (5)	C6—H6B	0.9800
C3—C4	1.398 (6)	C6—H6C	0.9800
C3—H3A	0.9500		

C2 ⁱ —C1—C2	116.8 (7)	C3 ⁱ —C4—C6	120.3 (3)
C2 ⁱ —C1—C5	121.6 (3)	C3—C4—C6	120.3 (3)
C2—C1—C5	121.6 (3)	N1—C5—C1	179.0 (9)
C3—C2—C1	122.3 (5)	C4—C6—H6A	109.5
C3—C2—Br2	118.8 (4)	C4—C6—H6B	109.5
C1—C2—Br2	118.9 (4)	H6A—C6—H6B	109.5
C2—C3—C4	119.6 (5)	C4—C6—H6C	109.5
C2—C3—H3A	120.2	H6A—C6—H6C	109.5
C4—C3—H3A	120.2	H6B—C6—H6C	109.5
C3 ⁱ —C4—C3	119.5 (6)		
C2 ⁱ —C1—C2—C3	-0.5 (10)	C1—C2—C3—C4	-0.7 (9)
C5—C1—C2—C3	178.7 (7)	Br2—C2—C3—C4	178.5 (5)
C2 ⁱ —C1—C2—Br2	-179.7 (4)	C2—C3—C4—C3 ⁱ	1.9 (11)
C5—C1—C2—Br2	-0.5 (9)	C2—C3—C4—C6	-178.0 (6)

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

2,6-Dibromo-4-methylphenyl isocyanide (RNC)

Crystal data

C₈H₅Br₂N
M_r = 274.95
 Tetragonal, *P*4₂*m*
a = 14.690 (5) Å
c = 4.0703 (15) Å
V = 878.3 (7) Å³
Z = 4
F(000) = 520
D_x = 2.079 Mg m⁻³

Melting point: 401 K
 Mo *K*α radiation, $\lambda = 0.71073$ Å
 Cell parameters from 2995 reflections
 $\theta = 2.8\text{--}26.9^\circ$
 $\mu = 9.16$ mm⁻¹
T = 173 K
 Needle, colourless
 0.40 × 0.14 × 0.08 mm

Data collection

Bruker APEXII CCD
 diffractometer
 Radiation source: sealed tube
 φ and ω scans
 Absorption correction: multi-scan
 (SADABS; Sheldrick, 1996)
T_{min} = 0.255, *T_{max}* = 0.746
 10248 measured reflections

1074 independent reflections
 1001 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.045$
 $\theta_{\text{max}} = 27.6^\circ$, $\theta_{\text{min}} = 2.0^\circ$
 $h = -18 \rightarrow 19$
 $k = -19 \rightarrow 19$
 $l = -5 \rightarrow 5$

Refinement

Refinement on *F*²
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.023$
 $wR(F^2) = 0.051$
S = 1.14
 1074 reflections
 59 parameters
 0 restraints
 Hydrogen site location: inferred from
 neighbouring sites

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0267P)^2 + 0.0073P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.30$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.51$ e Å⁻³
 Absolute structure: Flack *x* determined using
 381 quotients $[(I^-)-(I)]/[(I^+)+(I)]$ (Parsons *et al.*,
 2013)
 Absolute structure parameter: -0.024 (13)

Special details

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>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Br12	0.64344 (3)	0.58324 (2)	0.38265 (14)	0.03268 (14)	
N11	0.8281 (2)	0.6719 (2)	0.5307 (11)	0.0278 (11)	
C11	0.7708 (2)	0.7292 (2)	0.3538 (15)	0.0228 (11)	
C12	0.6845 (3)	0.7013 (3)	0.2671 (9)	0.0245 (8)	
C13	0.6256 (2)	0.7587 (2)	0.0981 (10)	0.0243 (8)	
H13A	0.5664	0.7382	0.0402	0.029*	
C14	0.6535 (3)	0.8465 (3)	0.0132 (13)	0.0237 (11)	
C15	0.8753 (3)	0.6247 (3)	0.6829 (18)	0.0474 (18)	
C16	0.5894 (3)	0.9106 (3)	−0.1624 (14)	0.0328 (12)	
H16A	0.5318	0.8793	−0.2065	0.049*	0.5
H16B	0.6169	0.9300	−0.3703	0.049*	0.5
H16C	0.5781	0.9640	−0.0241	0.049*	0.5

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br12	0.0337 (2)	0.02125 (19)	0.0431 (2)	−0.00062 (15)	0.0071 (2)	0.0013 (2)
N11	0.0268 (15)	0.0268 (15)	0.030 (3)	0.009 (2)	0.0005 (13)	−0.0005 (13)
C11	0.0238 (15)	0.0238 (15)	0.021 (3)	0.0067 (19)	0.0031 (16)	−0.0031 (16)
C12	0.0267 (19)	0.0202 (18)	0.027 (2)	0.0008 (16)	0.0080 (16)	−0.0028 (15)
C13	0.0214 (17)	0.0240 (17)	0.0273 (19)	0.0001 (14)	0.0017 (18)	−0.0043 (19)
C14	0.0245 (16)	0.0245 (16)	0.022 (3)	0.007 (2)	0.0038 (14)	−0.0038 (14)
C15	0.048 (2)	0.048 (2)	0.046 (5)	0.016 (3)	−0.002 (2)	0.002 (2)
C16	0.0329 (18)	0.0329 (18)	0.033 (3)	0.009 (3)	−0.0013 (18)	0.0013 (18)

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

Br12—C12	1.896 (4)	C13—H13A	0.9500
N11—C15	1.161 (8)	C14—C13 ⁱ	1.396 (4)
N11—C11	1.391 (7)	C14—C16	1.511 (7)
C11—C12	1.379 (5)	C16—H16A	0.9800
C11—C12 ⁱ	1.379 (5)	C16—H16B	0.9800
C12—C13	1.389 (6)	C16—H16C	0.9800
C13—C14	1.396 (4)		
C15—N11—C11	178.9 (6)	C13—C14—C13 ⁱ	118.7 (5)
C12—C11—C12 ⁱ	118.7 (5)	C13—C14—C16	120.6 (2)
C12—C11—N11	120.6 (3)	C13 ⁱ —C14—C16	120.6 (2)
C12 ⁱ —C11—N11	120.6 (3)	C14—C16—H16A	109.5

C11—C12—C13	121.3 (4)	C14—C16—H16B	109.5
C11—C12—Br12	120.0 (3)	H16A—C16—H16B	109.5
C13—C12—Br12	118.7 (3)	C14—C16—H16C	109.5
C12—C13—C14	120.0 (4)	H16A—C16—H16C	109.5
C12—C13—H13A	120.0	H16B—C16—H16C	109.5
C14—C13—H13A	120.0		
<hr/>			
C12 ⁱ —C11—C12—C13	-0.5 (8)	C11—C12—C13—C14	-0.1 (6)
N11—C11—C12—C13	178.2 (4)	Br12—C12—C13—C14	179.2 (3)
C12 ⁱ —C11—C12—Br12	-179.8 (3)	C12—C13—C14—C13 ⁱ	0.7 (7)
N11—C11—C12—Br12	-1.1 (7)	C12—C13—C14—C16	-178.3 (4)

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