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Two new polytypes of 2,4,6-tribromobenzonitrile

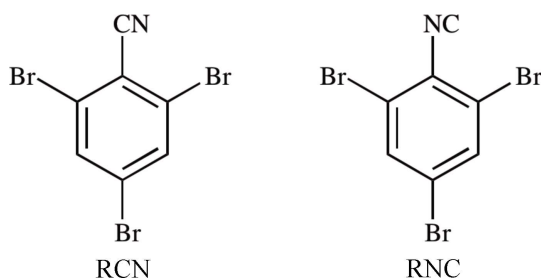
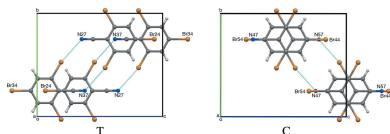
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Three polymorphs of 2,4,6-tribromobenzonitrile (RCN), $C_7H_2Br_3N$, two of which are novel and one of which is a redetermination of the original structure first determined by Carter & Britton [(1972). *Acta Cryst.* **B28**, 945–950] are found to be polytypic. Each has a layer structure which differs only in the stacking of the layers. Each layer is composed of molecules associated through $C\equiv N\cdots Br$ contacts which form $R_2^2(10)$ rings. Two such rings are associated with each N atom; one with each *ortho*-Br atom. No new polytypes of 1,3,5-tribromo-2-isocyanobenzene (RNC) were found but a re-determination of the original structure by Carter *et al.* [(1977). *Cryst. Struct. Commun.* **6**, 543–548] is presented. RNC was found to be isostructural with one of the novel polytypes of RCN. Unit cells were determined for 23 RCN samples and 11 RNC samples. Polytypes could not be distinguished based on crystal habits. In all four structures, each molecule of the asymmetric unit lies across a mirror plane.

1. Chemical context

The reported structures of 2,4,6-tribromobenzonitrile (RCN, Figs. 1 and 2; Carter & Britton, 1972) and 1,3,5-tribromo-2-isocyanobenzene (RNC, Figs. 1 and 3; Carter *et al.*, 1977) have two-dimensional layers of similarly arranged molecules, but the packing of adjacent layers is distinctly different. At the time, no explanation was offered. It was puzzling, given that the two compounds are isoelectronic, isosteric, and the principal intermolecular interactions, $C\equiv N\cdots Br$ and $N\equiv C\cdots Br$, are similar. Recent reports of polytype organic structures, such as picryl bromide (Parrish *et al.*, 2008) and 5,6-dimethylbenzofurazan 1-oxide (Britton *et al.*, 2012) led to the idea that RCN and RNC might occur as polytypes. Earlier, Bredig (1930) had determined the space group and unit cell of RCN with the same results as Carter & Britton. Bredig was trying to follow up on the goniometer studies of Jaeger (1909), but while he found the same *a:b* ratio as Jaeger in the RCN unit cell, he found a different *b:c* ratio.



Accordingly, a search was made for polytypes of RCN, and to a lesser extent, of RNC. Four different structures were identified. RCN-I is the original $Z = 2$ structure of RCN; RCN-II is a new $Z = 8$ polytype; RCN-III is a new $Z = 12$ polytype. No RNC counterparts to RCN-I or RCN-III were observed.

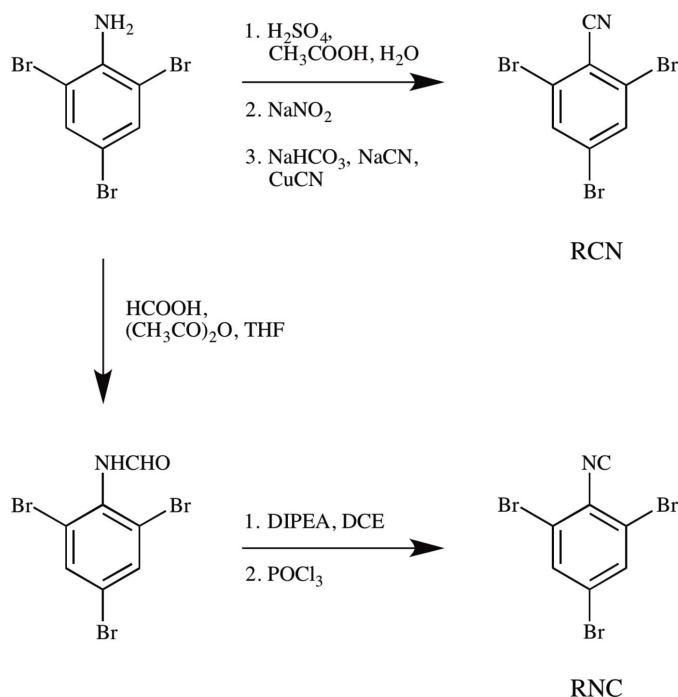


Figure 1
Synthesis of RCN and RNC.

RNC-II is the original $Z = 8$ structure. As the Z values suggest, RCN-II and RNC-II are isomorphs.

2. Structural commentary

Molecules of RCN and RNC are nearly planar. The average distance of atoms from the plane of best fit is 0.025 Å in RCN-I. For RCN-II, the average distances are 0.037 and 0.010 Å, for the (N27) and (N37) molecules, respectively. In RNC-II, the molecules are slightly more distorted, with average deviations of 0.043 and 0.017 Å for the (N127) and (N137) molecules, respectively. For RCN-III, the average distances are 0.009, 0.018, and 0.032 Å for the (N47), (N57), and (N67) molecules, respectively.

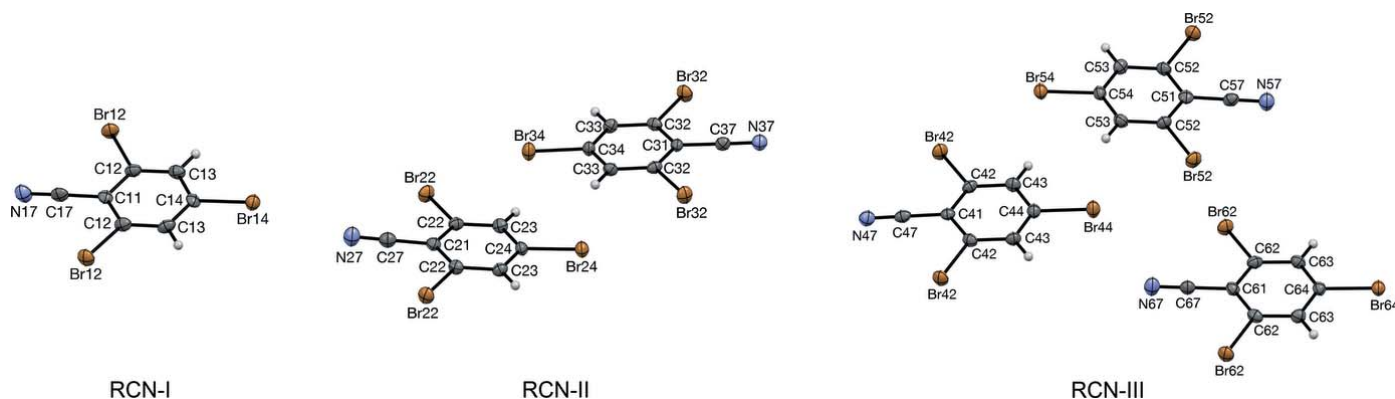


Figure 2
Molecular structures, with atom labeling, of RCN-I viewed along [111]; RCN-II viewed along [120]; RCN-III viewed along [120]. Displacement ellipsoids are drawn at the 50% probability level. In discussion, molecules are named by their respective nitrogen atoms. Each molecule lies across a crystallographic mirror plane.

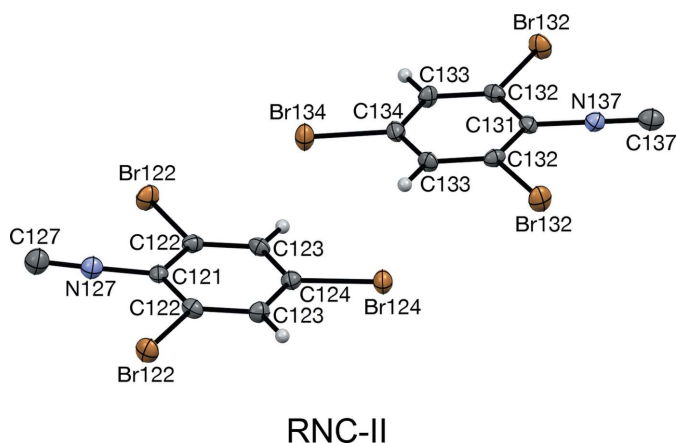


Figure 3
Molecular structure, with atom labeling, of RNC-II viewed along [120]. Displacement ellipsoids are drawn at the 50% probability level. Each molecule lies across a crystallographic mirror plane.

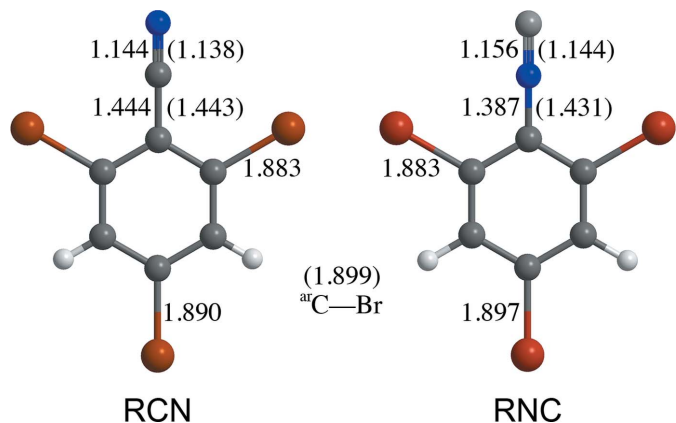


Figure 4
Selected bond lengths (Å) in RCN and RNC, averaged across all polytypes. The data shown in parentheses are the mean distances for each bond type reported by Allen *et al.* (1987).

The bond lengths in RCN and RNC are generally similar (Fig. 4). They are also similar to the mean bond distances reported for bonds of each type (Allen *et al.*, 1987). The N

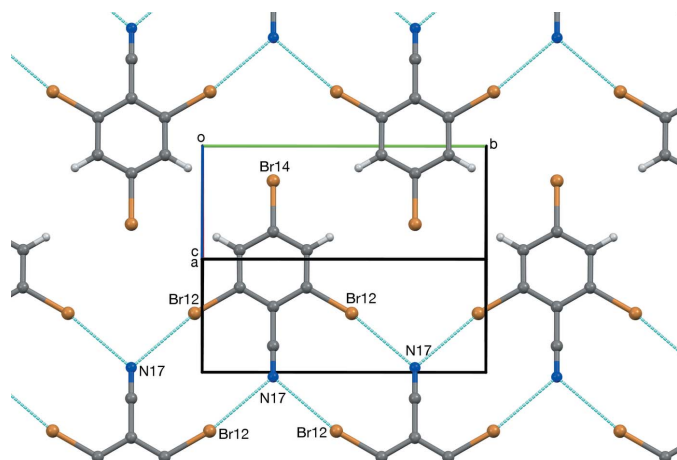


Figure 5
View of one layer of RCN-I along $[10\bar{1}]$. Dashed blue lines represent short contacts.

atom in RNC is displaced toward the aryl ring compared to the literature distances for aryl isocyanides.

3. Supramolecular features

Fig. 5 shows a two-dimensional layer of RCN-I. All of the structures are composed of similar layers. Adjacent molecules are associated through $C\equiv N\cdots Br$ interactions, arranged in $R_2^2(10)$ rings (Etter, 1990; Bernstein *et al.*, 1995). The $CN\cdots Br$ distances in these rings range between 3.053 and 3.077 Å (Table 1); these distances can be compared with the $N\cdots Br$ van der Waals distance of 3.40 Å (Bondi, 1964; Rowland & Taylor, 1996). Each layer in RCN-II is composed of alternating (N27) and (N37) molecules. RCN-III contains two layers of alternating (N47) and (N57) molecules for each layer composed entirely of (N67) molecules. Adjacent pairs of layers show translational or pseudotranslational, or pseudocentric stacking (Fig. 6). RCN-I shows translational stacking between all adjacent layers (Fig. 7). In RCN-II, alternating pairs of layers show pseudocentric and pseudotranslational stacking (Fig. 8). In RCN-III, each layer of (N67) molecules pseudotranslationally overlaps both neighboring (N47/N57) layers, while pairs of adjacent (N47/N57) layers, every third pair of layers, overlap pseudocentrically (Fig. 9).

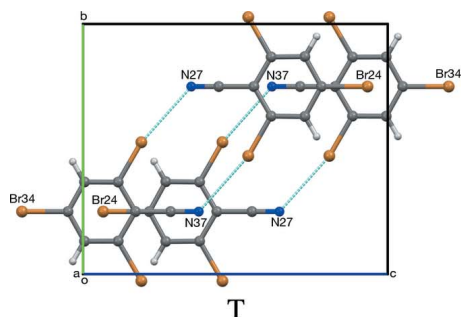


Figure 6
Pseudotranslational (T) and pseudocentric (C) stacking of layers in RCN-II and RCN-III, respectively. Both are viewed along $[100]$. The molecules shown are the second pair of layers from the top, in Fig. 7 and Fig. 8, respectively.

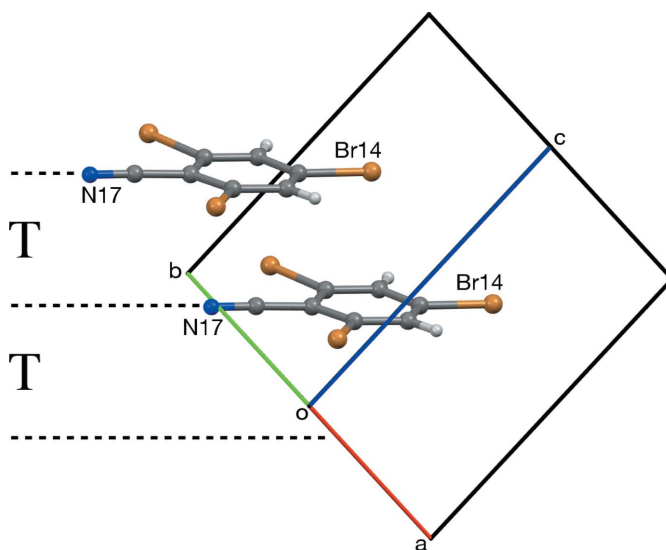


Figure 7
Translational (T) stacking of layers in $Z = 2$ RCN-I, viewed along $[110]$. If the unit cell of RCN-I is transformed by the matrix $[100/010/201]$, the dimensions of the projection become $10.247(3) \times 12.480(3)$ Å, which is similar to the corresponding $b \times c$ measurements, $10.2147(10) \times 12.4754(12)$ Å for RCN-II, and $10.2167(18) \times 12.493(2)$ Å for RCN-III.

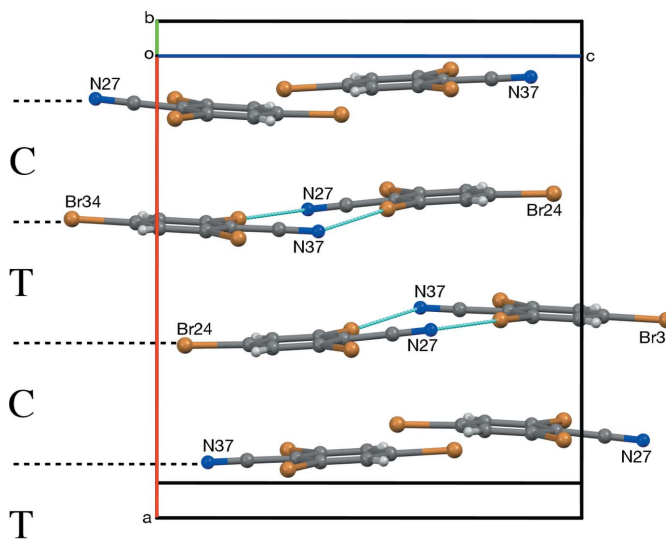
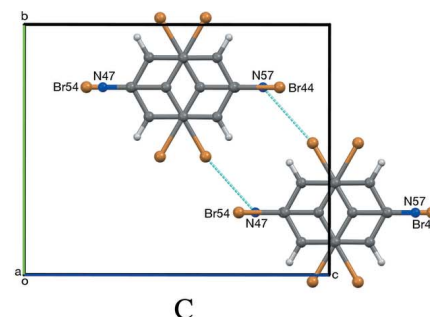


Figure 8
Pseudocentric (C) and pseudotranslational (T) stacking of layers in $Z = 8$ RCN-II, viewed roughly along $[010]$.



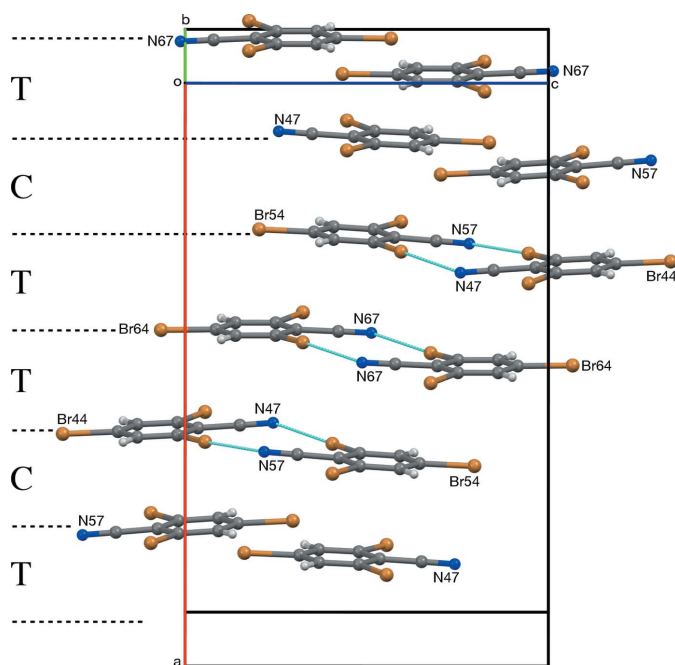


Figure 9
Pseudotranslational (T) and pseudocentric (C) stacking of layers in $Z = 12$ RCN-III, viewed roughly along [010].

The $\text{NC}\cdots\text{Br}$ contact distances in RNC-II are a smaller percentage of the van der Waals distance, 3.63 \AA , versus corresponding atoms in RCN-II. The contacts in RNC-II occur at slightly wider angles than those in RCN-II (Table 1).

In RCN-II, the planes of best fit of the two different molecules are inclined by 6.5° to each other; in RNC-II this inclination is 7.5° . In RCN-III, the relative inclination of planes of (N47) and (N57) molecules is 7.0° . These two planes are approximately bisected by the planes of (N67) molecules.

4. Database survey

A search of the Cambridge Structural Database (Version 5.36, update 3; Groom & Allen, 2014) for 2,4,6-trihalo-3,5-unsubstituted benzonitriles found nine entries: RCN; its trichloro analog, Gol'der *et al.* (1952), Carter & Britton (1972), Pink *et al.* (2000); its trifluoro analog, Britton (2008); four mixed-halogen entries, Gleason & Britton (1978), Britton (2005), Britton *et al.* (2002), and Britton (1997). Searching for the corresponding isocyanides found two entries: RNC and its trichloro analog (Pink *et al.*, 2000).

Layers of the type observed in RCN were reported in 2,6-dibromo entries with Cl, Br, or I at the 4-position. Other entries exhibit short contacts between the cyano- or isocyanogroup and one *ortho*-halogen atom of an intralayer molecule, with various interlayer contacts. Polymorphs are only reported for 2,4,6-trichlorobenzonitrile; those are not polytypic.

Expanding the search to include organometallic complexes found three more entries, with the cyano N or isocyanoc atom ligating gallium (trifluorobenzonitrile; Tang *et al.*, 2012),

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

$X\equiv Y\cdots\text{Br}$	$X\equiv Y$	$Y\cdots\text{Br}$	$X\equiv Y\cdots\text{Br}$
$\text{C17}\equiv\text{N17}\cdots\text{Br12}^{\text{i}}$	1.144 (10)	3.053 (4)	131.45 (9)
$\text{C27}\equiv\text{N27}\cdots\text{Br32}^{\text{ii}}$	1.132 (7)	3.059 (3)	131.76 (7)
$\text{N127}\equiv\text{C127}\cdots\text{Br132}^{\text{ii}}$	1.147 (6)	3.141 (4)	134.01 (8)
$\text{C37}\equiv\text{N37}\cdots\text{Br22}^{\text{iii}}$	1.156 (6)	3.077 (3)	130.68 (10)
$\text{N137}\equiv\text{C137}\cdots\text{Br122}^{\text{iii}}$	1.164 (6)	3.161 (4)	133.23 (11)
$\text{C47}\equiv\text{N47}\cdots\text{Br52}^{\text{ii}}$	1.146 (6)	3.072 (3)	130.95 (9)
$\text{C57}\equiv\text{N57}\cdots\text{Br42}^{\text{iii}}$	1.147 (6)	3.057 (3)	131.47 (7)
$\text{C67}\equiv\text{N67}\cdots\text{Br62}^{\text{iv}}$	1.139 (6)	3.065 (3)	131.96 (7)

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

rhodium (trichloroisocyanobenzene; Ko *et al.*, 2011), and ruthenium (RNC; Leung *et al.*, 2009).

5. Synthesis and crystallization

2,4,6-Tribromoaniline was prepared from aniline according to the work of Coleman & Talbot (1943).

RCN, adapted from the work of Toya *et al.* (1992): *Diazotization*: 2,4,6-Tribromoaniline (1.25 g), water (2.5 ml), and glacial acetic acid (4.4 ml) were combined in a round-bottomed flask. The resulting suspension was cooled in an ice bath, and then H_2SO_4 (98%, 1.0 ml) was added dropwise, followed by an ice-cold solution of NaNO_2 (520 mg) in water (4 ml). The resulting mixture was warmed to 310 K for 1 h, and then cooled in an ice bath. *Cyanide suspension*: CuCN (680 mg) and NaCN (1.12 g) were dissolved in water (20 ml). NaHCO_3 (10.9 g) and ethyl acetate (10 ml) were added, giving a suspension, which was cooled in an ice bath. *Cyanation*: The diazotization mixture was added dropwise to the cyanide suspension as quickly as possible without causing excessive foaming. The ice bath was removed and then the mixture was stirred overnight. The organic phase was set aside. The aqueous phase was extracted with ethyl acetate ($3 \times 10 \text{ ml}$). The combined organic portions were washed with brine (10 ml), dried with Na_2SO_4 , and concentrated at reduced pressure, giving a brown powder, which was purified by column chromatography (SiO_2 , hexane–ethyl acetate, gradient from 1:0 to 10:1). The desired fraction ($R_f = 0.61$ in 8:1) was concentrated at reduced pressure, giving beige needles (760 mg, 59%). M.p. 400–400.5 K (lit. 402 K; Giumanini *et al.*, 1996); $^1\text{H NMR}$ (300 MHz, CD_2Cl_2) δ 7.853 (s, H13); $^{13}\text{C NMR}$ (75 MHz, CD_2Cl_2) δ 135.3 (C13), 128.6 (C14), 127.4 (C12), 118.3 (C17), 116.0 (C11); IR (NaCl, cm^{-1}) 3095, 3068, 2921 (w), 2233 (s, $\text{C}\equiv\text{N}$; lit. 2232), 1716 (w), 1563 (s), 1527 (s), 1431 (s), 1410 (s), 1370 (s), 1353 (s), 1328, 1191 (s), 1109 (s), 1087, 1063 (s), 854 (s), 809 (s), 748 (s); MS (EI, m/z) $[M]^+$ calculated for $\text{C}_7\text{H}_2\text{Br}_3\text{N}$ 336.7732, found 336.7716.

2,4,6-Tribromofornanilide, adapted from the work of Krishnamurthy (1982): Acetic anhydride (3.2 ml) and tetrahydrofuran (THF, 5.0 ml) were combined in a round-bottomed flask. Formic acid (88% aq., 1.7 ml) was added dropwise. The resulting solution was stirred for 30 min at room temperature. A solution of 2,4,6-tribromoaniline (1.82 g) in

Table 2
Experimental details.

	RCN-I	RCN-II	RCN-III	RNC-II
Crystal data				
Chemical formula	C ₇ H ₂ Br ₃ N	C ₇ H ₂ Br ₃ N	C ₇ H ₂ Br ₃ N	C ₇ H ₂ Br ₃ N
<i>M_r</i>	339.83	339.83	339.83	339.83
Crystal system, space group	Monoclinic, <i>P</i> 2 ₁ / <i>m</i>	Orthorhombic, <i>Pnma</i>	Orthorhombic, <i>Pnma</i>	Orthorhombic, <i>Pnma</i>
Temperature (K)	173	173	173	173
<i>a</i> , <i>b</i> , <i>c</i> (Å)	4.8742 (15), 10.247 (3), 8.683 (3)	13.6183 (13), 10.2147 (10), 12.4754 (12)	20.399 (4), 10.2167 (18), 12.493 (2)	13.5916 (18), 10.1464 (13), 12.6158 (16)
α , β , γ (°)	90, 94.97 (1), 90	90, 90, 90	90, 90, 90	90, 90, 90
<i>V</i> (Å ³)	432.0 (2)	1735.4 (3)	2603.7 (8)	1739.8 (4)
<i>Z</i>	2	8	12	8
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α
μ (mm ⁻¹)	13.93	13.88	13.87	13.84
Crystal size (mm)	0.50 × 0.15 × 0.10	0.25 × 0.20 × 0.07	0.50 × 0.15 × 0.10	0.40 × 0.35 × 0.20
Data collection				
Diffractometer	Bruker 1K area detector	Bruker 1K area detector	Bruker 1K area detector	Bruker APEXII CCD
Absorption correction	Multi-scan (<i>SADABS</i> ; Bruker, 2002)	Multi-scan (<i>SADABS</i> ; Bruker, 2002)	Multi-scan (<i>SADABS</i> ; Bruker, 2002)	Multi-scan (<i>SADABS</i> ; Bruker, 2002)
<i>T</i> _{min} – <i>T</i> _{max}	0.080, 0.248	0.06, 0.37	0.054, 0.337	0.170, 0.333
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	4093, 1024, 856	16607, 2093, 1692	22804, 2691, 2165	19459, 2105, 1638
<i>R</i> _{int}	0.127	0.052	0.055	0.078
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.649	0.650	0.616	0.650
Refinement				
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.046, 0.116, 1.01	0.028, 0.063, 1.02	0.023, 0.046, 1.07	0.025, 0.055, 1.06
No. of reflections	1024	2093	2691	2105
No. of parameters	58	115	173	116
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	1.36, -1.28	0.44, -0.69	0.56, -0.49	0.44, -0.48

Computer programs: *SMART*, *APEX2* and *SAINT* (Bruker, 2002), *SHELXT* (Sheldrick, 2015a), *SHELXL2014* (Sheldrick, 2015b), *Mercury* (Macrae *et al.*, 2008), *SHELXTL* (Sheldrick, 2008), *enCIFer* (Allen *et al.*, 2004), and *pubCIF* (Westrip, 2010).

THF (20 ml) was added dropwise. The resulting mixture was stirred for 18 h. The resulting heterogeneous mixture was filtered through neutral alumina (Sigma–Aldrich 199974, 5 cm H × 3 cm D), with addition of sufficient THF to elute all product, as indicated by TLC. The filtrate was concentrated at reduced pressure. The resulting residue was washed with sat. NaHCO₃ solution (50 ml), and then filtered. The filter cake was recrystallized from acetone, giving white needles (1.72 g, 87%). M.p. 493–494 K (lit. 494.5 K; Chattaway *et al.*, 1899); *R_f* = 0.48 (SiO₂ in 1:1 hexane–ethyl acetate); ¹H NMR (300 MHz, (CD₃)₂SO) δ 10.192 (*s*, NH, *O*-*E* conformer, 0.87H), 8.522 (*s*, NH, *O*-*Z* conformer, 0.13H), 8.260 (*s*, CHO, 1H), 8.018 (*s*, CH, 2H); ¹³C NMR (75 MHz, (CD₃)₂SO) δ 165.9 (CO, *O*-*Z* conformer), 159.8 (CO, *O*-*E* conformer), 134.6 (*ipso*-C), 134.4 (CH), 124.5 (*ortho*-CBr), 121.1 (*para*-CBr); IR (NaCl, cm⁻¹) 3201, 3166, 1661 (*s*, C=O), 1558, 1154, 858, 810; MS (ESI, *m/z*) [*M* – H]⁻ calculated for C₇H₄Br₃NO 355.7750, found 355.7758. Analysis (MHW Laboratories, Phoenix, AZ, USA) calculated for C₇H₄Br₃NO: C 23.50, H 1.13, Br 66.99, N 3.91; found C 23.42, H 1.15, Br 66.71, N 3.57.

RNC, adapted from the work of Ugi *et al.* (1965): 2,4,6-Tribromoformanilide (1.96 g) and *N,N*-diisopropylethylamine (DIPEA, 3.4 ml) were added to 1,2-dichloroethane (75 ml). The resulting suspension was refluxed for 5 min, and then cooled to room temperature. POCl₃ (0.6 ml) was added

dropwise. The mixture was stirred for 18 h, cooled in an ice bath, and then filtered through neutral alumina (3 cm H × 3 cm D), with addition of sufficient dichloromethane (DCM) to elute all product as indicated by TLC. The filtrate was concentrated at reduced pressure. The resulting yellow residue was dissolved in DCM (25 ml), cooled in an ice bath, and washed with ice-cold acetic acid solution (0.025 M, 3 × 15 ml), and then ice-cold sat. NaHCO₃ solution (15 ml). The organic phase was collected, dried with Na₂SO₄, and then concentrated under a stream of nitrogen, giving beige needles upon filtration (630 mg, 34%). M.p. 390 K (lit. 394 K, Mironov & Mokrushin, 1999); *R_f* = 0.75 (Al₂O₃ in 2:1 hexane–ethyl acetate); ¹H NMR (300 MHz, CD₂Cl₂) δ 7.827 (*s*, H123); ¹³C NMR (75 MHz, (CD₃)₂CO) 159.7 (C127), 135.8 (C123), 135.4 (C121), 124.5 (C124), 122.0 (C122); IR (NaCl, cm⁻¹) 3162, 3068, 2921, 2128 (*s*, N≡C; lit. 2125), 1660 (*s*), 1555 (*s*), 1370 (*s*), 856 (*s*), 701 (*s*); MS (EI, *m/z*) [*M*]⁺ calculated for C₇H₂Br₃N 336.7732, found 336.7734.

Crystallization: RCN crystals were grown by slow evaporation of single-solvent solutions (290–295 K). RCN-I was obtained from acetonitrile, benzene, chloroform, or methylene chloride; RCN-II from mesitylene; RCN-III from benzene or chloroform. RNC-II crystals were obtained by sublimation (385 K, 0.05 torr), or by slow evaporation from the same solvents as RCN (268–295 K).

6. Refinement

Crystal data, data collection, and structure refinement details for RCN and RNC are summarized in Table 2. H atoms were placed in calculated positions and refined as riding atoms, with C–H = 0.95 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Acknowledgements

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supporting information

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Two new polytypes of 2,4,6-tribromobenzonitrile

Doyle Britton, Wayland E. Noland and Kenneth J. Tritch

Computing details

Data collection: *SMART* (Bruker, 2002) for RCN-I, RCN-II, RCN-III; *APEX2* (Bruker, 2002) for RNC-II. For all compounds, cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT* (Bruker, 2002). Program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008) for RCN-I, RCN-II, RCN-III; *SHELXT* (Sheldrick, 2015a) for RNC-II. Program(s) used to refine structure: *SHELXTL* (Sheldrick, 2008) for RCN-I, RCN-II, RCN-III; *SHELXL2014* (Sheldrick, 2015b) for RNC-II. For all compounds, molecular graphics: *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008), *enCIFer* (Allen *et al.*, 2004), and *publCIF* (Westrip, 2010).

(RCN-I) 2,4,6-Tribromobenzonitrile - polytype I

Crystal data

$C_7H_2Br_3N$

$M_r = 339.83$

Monoclinic, $P2_1/m$

Hall symbol: -P 2yb

$a = 4.8742$ (15) Å

$b = 10.247$ (3) Å

$c = 8.683$ (3) Å

$\beta = 94.97$ (1)°

$V = 432.0$ (2) Å³

$Z = 2$

$F(000) = 312$

$D_x = 2.612$ Mg m⁻³

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

Cell parameters from 2049 reflections

$\theta = 2.4$ – 27.4 °

$\mu = 13.93$ mm⁻¹

$T = 173$ K

Needle, colorless

$0.50 \times 0.15 \times 0.10$ mm

Data collection

Bruker 1K area-detector
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

ω scans

Absorption correction: multi-scan
(*SADABS*; Bruker, 2002)

$T_{\min} = 0.080$, $T_{\max} = 0.248$

4093 measured reflections

1024 independent reflections

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

$R_{\text{int}} = 0.127$

$\theta_{\max} = 27.5$ °, $\theta_{\min} = 2.4$ °

$h = -6 \rightarrow 6$

$k = -13 \rightarrow 13$

$l = -11 \rightarrow 11$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.046$

$wR(F^2) = 0.116$

$S = 1.01$

1024 reflections

58 parameters

0 restraints

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.069P)^2]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$

$$\Delta\rho_{\max} = 1.36 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -1.28 \text{ e } \text{\AA}^{-3}$$

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Br12	0.33356 (11)	0.47324 (5)	0.18676 (7)	0.0280 (2)
Br14	1.11323 (14)	0.7500	0.57820 (9)	0.0256 (3)
N17	-0.0263 (14)	0.7500	-0.0147 (8)	0.0313 (16)
C11	0.3828 (14)	0.7500	0.1960 (8)	0.0204 (15)
C12	0.4932 (10)	0.6324 (5)	0.2559 (6)	0.0224 (11)
C13	0.7107 (10)	0.6313 (5)	0.3688 (6)	0.0244 (11)
H13	0.7842	0.5512	0.4091	0.029*
C14	0.8200 (14)	0.7500	0.4224 (8)	0.0197 (15)
C17	0.1523 (16)	0.7500	0.0799 (9)	0.0241 (16)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br12	0.0334 (4)	0.0160 (3)	0.0337 (4)	-0.0043 (2)	-0.0015 (2)	-0.0016 (2)
Br14	0.0229 (4)	0.0239 (4)	0.0295 (5)	0.000	-0.0018 (3)	0.000
N17	0.041 (4)	0.021 (3)	0.031 (4)	0.000	-0.006 (3)	0.000
C11	0.022 (3)	0.025 (4)	0.015 (4)	0.000	0.005 (3)	0.000
C12	0.023 (2)	0.016 (2)	0.029 (3)	-0.0012 (19)	0.006 (2)	0.001 (2)
C13	0.024 (2)	0.017 (3)	0.033 (3)	0.004 (2)	0.007 (2)	0.004 (2)
C14	0.024 (3)	0.025 (4)	0.011 (3)	0.000	0.003 (3)	0.000
C17	0.030 (4)	0.011 (3)	0.032 (4)	0.000	0.004 (3)	0.000

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

Br12—C12	1.883 (5)	C12—C13	1.380 (8)
Br14—C14	1.881 (7)	C13—C14	1.391 (6)
C11—C12	1.401 (6)	C13—H13	0.9500
C11—C17	1.443 (10)	N17—C17	1.144 (10)
C12—C11—C12 ⁱ	118.6 (6)	C12—C13—H13	120.7
C12—C11—C17	120.7 (3)	C14—C13—H13	120.7
C13—C12—C11	121.2 (5)	C13—C14—C13 ⁱ	121.9 (6)
C13—C12—Br12	119.3 (4)	C13—C14—Br14	119.0 (3)
C11—C12—Br12	119.4 (4)	N17—C17—C11	178.4 (9)
C12—C13—C14	118.6 (5)		
C12 ⁱ —C11—C12—C13	-1.6 (11)	C11—C12—C13—C14	-0.2 (10)
C17—C11—C12—C13	-178.9 (7)	Br12—C12—C13—C14	-177.8 (5)
C12 ⁱ —C11—C12—Br12	176.0 (3)	C12—C13—C14—C13 ⁱ	2.0 (12)
C17—C11—C12—Br12	-1.3 (9)	C12—C13—C14—Br14	179.2 (5)

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

(RCN-II) 2,4,6-Tribromobenzonitrile - polytype II

Crystal data

C₇H₂Br₃N $M_r = 339.83$ Orthorhombic, *Pnma*

Hall symbol: -P 2ac 2n

 $a = 13.6183$ (13) Å $b = 10.2147$ (10) Å $c = 12.4754$ (12) Å $V = 1735.4$ (3) Å³ $Z = 8$ $F(000) = 1248$ $D_x = 2.601$ Mg m⁻³Mo *K*α radiation, $\lambda = 0.71073$ Å

Cell parameters from 3180 reflections

 $\theta = 2.9$ – 27.2° $\mu = 13.88$ mm⁻¹ $T = 173$ K

Plate, colorless

 $0.25 \times 0.20 \times 0.07$ mm

Data collection

Bruker 1K area-detector
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

 ω scansAbsorption correction: multi-scan
(*SADABS*; Bruker, 2002) $T_{\min} = 0.06$, $T_{\max} = 0.37$

16607 measured reflections

2093 independent reflections

1692 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.052$ $\theta_{\text{max}} = 27.5^\circ$, $\theta_{\text{min}} = 2.2^\circ$ $h = -17 \rightarrow 17$ $k = -13 \rightarrow 13$ $l = -16 \rightarrow 16$

Refinement

Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.028$ $wR(F^2) = 0.063$ $S = 1.02$

2093 reflections

115 parameters

0 restraints

Primary atom site location: structure-invariant
direct methodsSecondary atom site location: difference Fourier
mapHydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

 $w = 1/[\sigma^2(F_o^2) + (0.030P)^2 + 1.560P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\text{max}} = 0.001$ $\Delta\rho_{\text{max}} = 0.44$ e Å⁻³ $\Delta\rho_{\text{min}} = -0.69$ e Å⁻³Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Br22	0.13341 (3)	0.52761 (3)	0.04244 (3)	0.02658 (11)
Br24	0.14558 (4)	0.2500	0.43375 (4)	0.02477 (13)
C21	0.1318 (3)	0.2500	0.0608 (4)	0.0197 (10)
C22	0.1359 (2)	0.3683 (3)	0.1174 (3)	0.0206 (7)
C23	0.1418 (2)	0.3697 (3)	0.2282 (3)	0.0217 (7)
H23	0.1444	0.4500	0.2666	0.026*
C24	0.1437 (3)	0.2500	0.2821 (4)	0.0190 (10)
C27	0.1207 (4)	0.2500	-0.0545 (4)	0.0257 (11)
N27	0.1115 (3)	0.2500	-0.1447 (4)	0.0332 (11)
Br32	0.10699 (3)	0.47273 (3)	0.69146 (3)	0.02650 (11)
Br34	0.12804 (4)	0.7500	0.29979 (4)	0.02786 (13)
C31	0.1095 (3)	0.7500	0.6720 (3)	0.0175 (9)
C32	0.1116 (2)	0.6320 (3)	0.6155 (3)	0.0195 (7)
C33	0.1171 (2)	0.6315 (3)	0.5049 (3)	0.0201 (7)

H33	0.1189	0.5511	0.4666	0.024*
C34	0.1199 (3)	0.7500	0.4508 (4)	0.0196 (10)
C37	0.1056 (3)	0.7500	0.7873 (4)	0.0200 (10)
N37	0.1015 (3)	0.7500	0.8798 (3)	0.0255 (9)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br22	0.0364 (2)	0.01742 (19)	0.0259 (2)	−0.00058 (15)	−0.00196 (15)	0.00451 (14)
Br24	0.0303 (3)	0.0261 (3)	0.0179 (2)	0.000	0.00098 (19)	0.000
C21	0.018 (2)	0.021 (3)	0.021 (2)	0.000	0.0017 (19)	0.000
C22	0.0208 (16)	0.0182 (16)	0.0227 (17)	0.0016 (14)	−0.0003 (13)	0.0017 (14)
C23	0.0225 (16)	0.0186 (18)	0.0240 (17)	−0.0012 (14)	−0.0012 (14)	−0.0017 (14)
C24	0.021 (2)	0.021 (3)	0.015 (2)	0.000	0.0022 (18)	0.000
C27	0.028 (3)	0.020 (3)	0.029 (3)	0.000	0.000 (2)	0.000
N27	0.048 (3)	0.026 (2)	0.026 (3)	0.000	−0.002 (2)	0.000
Br32	0.0386 (2)	0.01618 (19)	0.02475 (19)	−0.00117 (15)	0.00205 (14)	0.00374 (14)
Br34	0.0418 (3)	0.0243 (3)	0.0174 (2)	0.000	−0.0003 (2)	0.000
C31	0.017 (2)	0.021 (2)	0.015 (2)	0.000	−0.0003 (17)	0.000
C32	0.0182 (15)	0.0163 (16)	0.0241 (17)	0.0004 (13)	−0.0006 (13)	0.0044 (14)
C33	0.0229 (17)	0.0157 (18)	0.0216 (17)	0.0015 (14)	−0.0009 (13)	−0.0018 (14)
C34	0.025 (2)	0.018 (2)	0.015 (2)	0.000	−0.0001 (18)	0.000
C37	0.023 (2)	0.014 (2)	0.023 (3)	0.000	−0.0009 (19)	0.000
N37	0.030 (2)	0.024 (2)	0.023 (2)	0.000	−0.0002 (17)	0.000

Geometric parameters (Å, °)

Br22—C22	1.877 (3)	Br32—C32	1.884 (3)
Br24—C24	1.892 (5)	Br34—C34	1.887 (4)
C21—C22	1.400 (4)	C31—C32	1.396 (4)
C21—C27	1.446 (7)	C31—C37	1.439 (6)
C22—C23	1.385 (5)	C32—C33	1.382 (5)
C23—C24	1.395 (4)	C33—C34	1.387 (4)
C23—H23	0.9500	C33—H33	0.9500
C27—N27	1.132 (7)	C37—N37	1.156 (6)
C22 ⁱ —C21—C22	119.3 (4)	C32 ⁱⁱ —C31—C32	119.3 (4)
C22—C21—C27	120.3 (2)	C32—C31—C37	120.3 (2)
C23—C22—C21	120.9 (3)	C33—C32—C31	120.6 (3)
C23—C22—Br22	119.3 (3)	C33—C32—Br32	120.0 (3)
C21—C22—Br22	119.8 (3)	C31—C32—Br32	119.4 (2)
C22—C23—C24	118.2 (3)	C32—C33—C34	118.9 (3)
C22—C23—H23	120.9	C32—C33—H33	120.5
C24—C23—H23	120.9	C34—C33—H33	120.5
C23 ⁱ —C24—C23	122.4 (4)	C33 ⁱⁱ —C34—C33	121.6 (4)
C23—C24—Br24	118.8 (2)	C33—C34—Br34	119.2 (2)
N27—C27—C21	179.7 (5)	N37—C37—C31	179.3 (5)

C22 ⁱ —C21—C22—C23	−1.4 (6)	C32 ⁱⁱ —C31—C32—C33	0.8 (6)
C27—C21—C22—C23	176.8 (4)	C37—C31—C32—C33	−178.9 (4)
C22 ⁱ —C21—C22—Br22	178.6 (2)	C32 ⁱⁱ —C31—C32—Br32	−179.2 (2)
C27—C21—C22—Br22	−3.2 (5)	C37—C31—C32—Br32	1.1 (5)
C21—C22—C23—C24	0.1 (5)	C31—C32—C33—C34	−0.3 (5)
Br22—C22—C23—C24	−179.9 (3)	Br32—C32—C33—C34	179.7 (3)
C22—C23—C24—C23 ⁱ	1.3 (7)	C32—C33—C34—C33 ⁱⁱ	−0.2 (7)
C22—C23—C24—Br24	−177.1 (2)	C32—C33—C34—Br34	179.7 (2)

Symmetry codes: (i) $x, -y+1/2, z$; (ii) $x, -y+3/2, z$.

(RCN-III) 2,4,6-Tribromobenzonitrile - polytype III

Crystal data

C₇H₂Br₃N

$M_r = 339.83$

Orthorhombic, *Pnma*

Hall symbol: -P 2ac 2n

$a = 20.399$ (4) Å

$b = 10.2167$ (18) Å

$c = 12.493$ (2) Å

$V = 2603.7$ (8) Å³

$Z = 12$

$F(000) = 1872$

$D_x = 2.601$ Mg m⁻³

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

Cell parameters from 2928 reflections

$\theta = 2.6$ – 26.7°

$\mu = 13.87$ mm⁻¹

$T = 173$ K

Needle, colorless

$0.50 \times 0.15 \times 0.10$ mm

Data collection

Bruker 1K area-detector
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

ω scans

Absorption correction: multi-scan
(*SADABS*; Bruker, 2002)

$T_{\min} = 0.054$, $T_{\max} = 0.337$

22804 measured reflections

2691 independent reflections

2165 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.055$

$\theta_{\max} = 26.0^\circ$, $\theta_{\min} = 2.6^\circ$

$h = -24 \rightarrow 24$

$k = -12 \rightarrow 12$

$l = -15 \rightarrow 15$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.023$

$wR(F^2) = 0.046$

$S = 1.07$

2691 reflections

173 parameters

0 restraints

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0096P)^2 + 3.390P]$

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

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

$\Delta\rho_{\max} = 0.56$ e Å⁻³

$\Delta\rho_{\min} = -0.49$ e Å⁻³

Extinction correction: *SHELXL*,

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

Extinction coefficient: 0.00028 (3)

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Br42	0.340999 (16)	0.52705 (3)	−0.05464 (3)	0.02707 (10)
Br44	0.32895 (2)	0.2500	0.33679 (4)	0.02913 (13)

Br52	0.332551 (16)	0.47245 (3)	0.59427 (3)	0.02775 (9)
Br54	0.32011 (2)	0.7500	0.20370 (3)	0.02542 (12)
Br62	0.511839 (16)	0.52774 (3)	0.67598 (3)	0.02743 (10)
Br64	0.50730 (2)	0.2500	1.06666 (4)	0.02435 (12)
C41	0.33919 (19)	0.2500	-0.0353 (3)	0.0182 (9)
C42	0.33772 (14)	0.3675 (3)	0.0214 (2)	0.0207 (7)
C43	0.33432 (14)	0.3686 (3)	0.1321 (2)	0.0226 (7)
H43	0.3331	0.4487	0.1706	0.027*
C44	0.3328 (2)	0.2500	0.1851 (4)	0.0219 (10)
C47	0.3440 (2)	0.2500	-0.1508 (4)	0.0218 (10)
N47	0.34814 (18)	0.2500	-0.2423 (3)	0.0272 (9)
C51	0.3338 (2)	0.7500	0.5758 (4)	0.0221 (10)
C52	0.33096 (14)	0.6320 (3)	0.5193 (2)	0.0211 (7)
C53	0.32641 (14)	0.6314 (3)	0.4085 (2)	0.0228 (7)
H53	0.3246	0.5512	0.3701	0.027*
C54	0.3245 (2)	0.7500	0.3549 (3)	0.0204 (10)
C57	0.3399 (2)	0.7500	0.6908 (4)	0.0225 (10)
N57	0.3445 (2)	0.7500	0.7823 (3)	0.0329 (10)
C61	0.5080 (2)	0.2500	0.6942 (4)	0.0204 (10)
C62	0.50889 (14)	0.3676 (3)	0.7509 (2)	0.0216 (7)
C63	0.50886 (14)	0.3686 (3)	0.8618 (2)	0.0218 (7)
H63	0.5092	0.4488	0.9002	0.026*
C64	0.5083 (2)	0.2500	0.9155 (4)	0.0200 (10)
C67	0.5049 (2)	0.2500	0.5783 (4)	0.0225 (10)
N67	0.5024 (2)	0.2500	0.4872 (3)	0.0329 (10)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br42	0.03864 (19)	0.01711 (17)	0.02545 (18)	-0.00178 (14)	0.00143 (15)	0.00391 (15)
Br44	0.0432 (3)	0.0252 (3)	0.0190 (3)	0.000	0.0007 (2)	0.000
Br52	0.03826 (19)	0.01818 (17)	0.02682 (18)	-0.00040 (15)	-0.00267 (15)	0.00467 (15)
Br54	0.0309 (3)	0.0270 (3)	0.0184 (2)	0.000	0.0017 (2)	0.000
Br62	0.03877 (19)	0.01736 (17)	0.02617 (18)	-0.00080 (15)	-0.00036 (15)	0.00376 (15)
Br64	0.0300 (2)	0.0243 (3)	0.0188 (2)	0.000	-0.00018 (19)	0.000
C41	0.016 (2)	0.017 (2)	0.022 (2)	0.000	-0.0010 (18)	0.000
C42	0.0214 (15)	0.0175 (17)	0.0233 (17)	-0.0001 (14)	-0.0011 (13)	0.0052 (14)
C43	0.0269 (16)	0.0160 (17)	0.0248 (17)	-0.0016 (14)	-0.0003 (14)	-0.0016 (15)
C44	0.023 (2)	0.024 (3)	0.019 (2)	0.000	0.0000 (19)	0.000
C47	0.020 (2)	0.016 (2)	0.029 (3)	0.000	-0.004 (2)	0.000
N47	0.033 (2)	0.022 (2)	0.026 (2)	0.000	-0.0017 (19)	0.000
C51	0.016 (2)	0.026 (3)	0.024 (2)	0.000	0.001 (2)	0.000
C52	0.0244 (15)	0.0154 (17)	0.0234 (16)	0.0002 (14)	-0.0002 (13)	0.0037 (14)
C53	0.0255 (16)	0.0198 (18)	0.0232 (17)	0.0025 (14)	0.0024 (14)	-0.0031 (15)
C54	0.020 (2)	0.024 (3)	0.017 (2)	0.000	0.0021 (18)	0.000
C57	0.025 (2)	0.015 (2)	0.027 (3)	0.000	-0.003 (2)	0.000
N57	0.048 (3)	0.027 (2)	0.024 (2)	0.000	-0.001 (2)	0.000
C61	0.020 (2)	0.022 (2)	0.020 (2)	0.000	0.0041 (19)	0.000

C62	0.0199 (15)	0.0188 (17)	0.0261 (17)	0.0017 (13)	0.0011 (13)	0.0047 (15)
C63	0.0236 (16)	0.0178 (18)	0.0239 (16)	0.0007 (14)	0.0018 (13)	-0.0028 (15)
C64	0.020 (2)	0.022 (2)	0.018 (2)	0.000	0.0017 (19)	0.000
C67	0.028 (2)	0.016 (2)	0.024 (3)	0.000	0.000 (2)	0.000
N67	0.055 (3)	0.021 (2)	0.024 (2)	0.000	-0.002 (2)	0.000

Geometric parameters (Å, °)

Br42—C42	1.888 (3)	C51—C52	1.399 (4)
Br44—C44	1.897 (5)	C51—C57	1.443 (6)
Br52—C52	1.880 (3)	C52—C53	1.387 (4)
Br54—C54	1.892 (4)	C53—C54	1.384 (4)
Br62—C62	1.885 (3)	C53—H53	0.9500
Br64—C64	1.889 (4)	C57—N57	1.147 (6)
C41—C42	1.394 (4)	C61—C62	1.395 (4)
C41—C47	1.447 (6)	C61—C67	1.450 (6)
C42—C43	1.384 (4)	C62—C63	1.386 (4)
C43—C44	1.381 (4)	C63—C64	1.385 (4)
C43—H43	0.9500	C63—H63	0.9500
C47—N47	1.146 (6)	C67—N67	1.139 (6)
C42—C41—C42 ⁱ	118.9 (4)	C54—C53—H53	120.6
C42—C41—C47	120.5 (2)	C52—C53—H53	120.6
C43—C42—C41	121.0 (3)	C53 ⁱⁱ —C54—C53	122.1 (4)
C43—C42—Br42	119.9 (2)	C53—C54—Br54	119.0 (2)
C41—C42—Br42	119.2 (2)	N57—C57—C51	179.8 (5)
C44—C43—C42	118.3 (3)	C62 ⁱ —C61—C62	119.0 (4)
C44—C43—H43	120.9	C62—C61—C67	120.5 (2)
C42—C43—H43	120.9	C63—C62—C61	120.9 (3)
C43 ⁱ —C44—C43	122.6 (4)	C63—C62—Br62	119.4 (3)
C43—C44—Br44	118.7 (2)	C61—C62—Br62	119.8 (2)
N47—C47—C41	179.7 (5)	C64—C63—C62	118.6 (3)
C52 ⁱⁱ —C51—C52	119.1 (4)	C64—C63—H63	120.7
C52—C51—C57	120.4 (2)	C62—C63—H63	120.7
C53—C52—C51	120.7 (3)	C63 ⁱ —C64—C63	122.0 (4)
C53—C52—Br52	119.7 (2)	C63—C64—Br64	119.0 (2)
C51—C52—Br52	119.7 (2)	N67—C67—C61	180.0 (5)
C54—C53—C52	118.7 (3)		
C42 ⁱ —C41—C42—C43	-0.5 (6)	C51—C52—C53—C54	-0.2 (5)
C47—C41—C42—C43	-178.8 (3)	Br52—C52—C53—C54	179.2 (3)
C42 ⁱ —C41—C42—Br42	179.07 (19)	C52—C53—C54—C53 ⁱⁱ	-0.6 (6)
C47—C41—C42—Br42	0.8 (5)	C52—C53—C54—Br54	178.7 (2)
C41—C42—C43—C44	0.4 (5)	C62 ⁱ —C61—C62—C63	-1.7 (6)
Br42—C42—C43—C44	-179.2 (3)	C67—C61—C62—C63	177.0 (3)
C42—C43—C44—C43 ⁱ	-0.2 (6)	C62 ⁱ —C61—C62—Br62	177.1 (2)
C42—C43—C44—Br44	179.4 (2)	C67—C61—C62—Br62	-4.2 (5)
C52 ⁱⁱ —C51—C52—C53	0.9 (6)	C61—C62—C63—C64	0.4 (5)

C57—C51—C52—C53	−178.7 (3)	Br62—C62—C63—C64	−178.4 (3)
C52 ⁱⁱ —C51—C52—Br52	−178.48 (19)	C62—C63—C64—C63 ⁱ	1.0 (6)
C57—C51—C52—Br52	1.9 (5)	C62—C63—C64—Br64	−179.3 (2)

Symmetry codes: (i) $x, -y+1/2, z$; (ii) $x, -y+3/2, z$.

(RNC-II) 1,3,5-Tribromo-2-isocyanobenzene - polytype II

Crystal data

$C_7H_2Br_3N$

$M_r = 339.83$

Orthorhombic, $Pnma$

$a = 13.5916$ (18) Å

$b = 10.1464$ (13) Å

$c = 12.6158$ (16) Å

$V = 1739.8$ (4) Å³

$Z = 8$

$F(000) = 1248$

$D_x = 2.595$ Mg m^{−3}

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

Cell parameters from 2721 reflections

$\theta = 3.0$ – 27.4°

$\mu = 13.84$ mm^{−1}

$T = 173$ K

Block, colourless

$0.40 \times 0.35 \times 0.20$ mm

Data collection

Bruker APEXII CCD
diffractometer

Radiation source: sealed tube

φ and ω scans

Absorption correction: multi-scan
(*SADABS*; Bruker, 2002)

$T_{\min} = 0.170$, $T_{\max} = 0.333$

19459 measured reflections

2105 independent reflections

1638 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.078$

$\theta_{\max} = 27.5^\circ$, $\theta_{\min} = 2.2^\circ$

$h = -17 \rightarrow 17$

$k = -13 \rightarrow 13$

$l = -16 \rightarrow 16$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.025$

$wR(F^2) = 0.055$

$S = 1.06$

2105 reflections

116 parameters

0 restraints

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0121P)^2 + 1.0004P]$

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

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

$\Delta\rho_{\max} = 0.44$ e Å^{−3}

$\Delta\rho_{\min} = -0.48$ e Å^{−3}

Extinction correction: *SHELXL*,

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

Extinction coefficient: 0.00269 (12)

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 (Å²)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C121	0.3678 (3)	0.7500	0.5680 (3)	0.0162 (9)
C122	0.3637 (2)	0.6315 (3)	0.6238 (2)	0.0176 (7)
C123	0.3573 (2)	0.6306 (3)	0.7332 (2)	0.0182 (7)
H123	0.3541	0.5499	0.7712	0.022*

C124	0.3559 (3)	0.7500	0.7858 (4)	0.0173 (9)
N127	0.3793 (3)	0.7500	0.4583 (3)	0.0215 (9)
C127	0.3909 (4)	0.7500	0.3682 (4)	0.0285 (12)
Br122	0.36763 (3)	0.47074 (3)	0.54952 (3)	0.02456 (11)
Br124	0.35282 (4)	0.7500	0.93610 (4)	0.02254 (13)
C131	0.3904 (3)	0.2500	0.1747 (3)	0.0161 (10)
C132	0.3885 (2)	0.3685 (3)	0.1192 (3)	0.0169 (7)
C133	0.3821 (2)	0.3691 (3)	0.0100 (2)	0.0179 (7)
H133	0.3806	0.4499	-0.0281	0.021*
C134	0.3781 (3)	0.2500	-0.0428 (4)	0.0190 (10)
N137	0.3955 (3)	0.2500	0.2840 (3)	0.0180 (8)
C137	0.3995 (3)	0.2500	0.3761 (4)	0.0246 (11)
Br132	0.39399 (3)	0.52885 (3)	0.19404 (3)	0.02480 (11)
Br134	0.36801 (4)	0.2500	-0.19267 (4)	0.02564 (14)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C121	0.013 (2)	0.019 (2)	0.016 (2)	0.000	0.0002 (19)	0.000
C122	0.0164 (16)	0.0157 (16)	0.0207 (17)	0.0016 (14)	-0.0016 (14)	-0.0031 (13)
C123	0.0191 (17)	0.0152 (17)	0.0202 (17)	0.0013 (14)	-0.0017 (14)	0.0039 (13)
C124	0.017 (2)	0.017 (2)	0.018 (2)	0.000	0.0003 (19)	0.000
N127	0.026 (2)	0.018 (2)	0.021 (2)	0.000	0.0008 (17)	0.000
C127	0.035 (3)	0.025 (3)	0.026 (3)	0.000	0.002 (2)	0.000
Br122	0.0339 (2)	0.01579 (18)	0.0239 (2)	-0.00052 (15)	0.00210 (15)	-0.00522 (14)
Br124	0.0290 (3)	0.0231 (3)	0.0155 (2)	0.000	-0.0005 (2)	0.000
C131	0.014 (2)	0.019 (2)	0.015 (2)	0.000	-0.0026 (17)	0.000
C132	0.0158 (16)	0.0138 (16)	0.0210 (17)	0.0001 (13)	0.0003 (13)	-0.0042 (13)
C133	0.0229 (18)	0.0132 (17)	0.0174 (17)	0.0014 (14)	-0.0001 (13)	0.0035 (13)
C134	0.018 (2)	0.024 (3)	0.015 (2)	0.000	-0.0016 (18)	0.000
N137	0.019 (2)	0.017 (2)	0.018 (2)	0.000	0.0008 (16)	0.000
C137	0.024 (3)	0.019 (3)	0.030 (3)	0.000	-0.001 (2)	0.000
Br132	0.0360 (2)	0.01500 (19)	0.0234 (2)	-0.00111 (15)	-0.00260 (14)	-0.00427 (14)
Br134	0.0393 (3)	0.0222 (3)	0.0154 (3)	0.000	0.0003 (2)	0.000

Geometric parameters (Å, °)

C121—N127	1.393 (6)	C131—N137	1.380 (6)
C121—C122 ⁱ	1.395 (4)	C131—C132 ⁱⁱ	1.392 (4)
C122—C123	1.382 (4)	C132—C133	1.380 (4)
C122—Br122	1.882 (3)	C132—Br132	1.883 (3)
C123—C124 ⁱ	1.381 (4)	C133—C134 ⁱⁱ	1.381 (4)
C123—H123	0.9500	C133—H133	0.9500
C124—Br124	1.897 (5)	C134—Br134	1.895 (4)
N127—C127	1.147 (6)	N137—C137	1.164 (6)
N127—C121—C122 ⁱ	120.4 (2)	N137—C131—C132 ⁱⁱ	120.3 (2)
C122—C121—C122 ⁱ	119.1 (4)	C132 ⁱⁱ —C131—C132	119.5 (4)

C123—C122—C121	120.8 (3)	C133—C132—C131	120.5 (3)
C123—C122—Br122	119.6 (2)	C133—C132—Br132	119.9 (2)
C121—C122—Br122	119.6 (2)	C131—C132—Br132	119.5 (2)
C124—C123—C122	118.3 (3)	C132—C133—C134	118.7 (3)
C124—C123—H123	120.8	C132—C133—H133	120.7
C122—C123—H123	120.8	C134—C133—H133	120.7
C123—C124—C123 ⁱ	122.5 (4)	C133 ⁱⁱ —C134—C133	122.1 (4)
C123 ⁱ —C124—Br124	118.7 (2)	C133 ⁱⁱ —C134—Br134	118.9 (2)
C127—N127—C121	178.5 (5)	C137—N137—C131	179.8 (4)
N127—C121—C122—C123	176.7 (3)	N137—C131—C132—C133	-179.2 (3)
C122 ⁱ —C121—C122—C123	-1.0 (6)	C132 ⁱⁱ —C131—C132—C133	1.6 (6)
N127—C121—C122—Br122	-3.0 (5)	N137—C131—C132—Br132	0.6 (5)
C122 ⁱ —C121—C122—Br122	179.30 (19)	C132 ⁱⁱ —C131—C132—Br132	-178.6 (2)
C121—C122—C123—C124	-0.5 (5)	C131—C132—C133—C134	-0.2 (5)
Br122—C122—C123—C124	179.2 (3)	Br132—C132—C133—C134	-179.9 (3)
C122—C123—C124—C123 ⁱ	2.1 (7)	C132—C133—C134—C133 ⁱⁱ	-1.3 (7)
C122—C123—C124—Br124	-177.4 (2)	C132—C133—C134—Br134	179.3 (3)

Symmetry codes: (i) $x, -y+3/2, z$; (ii) $x, -y+1/2, z$.

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C123—H123 ⁱⁱⁱ —Br134 ⁱⁱⁱ	0.95	3.08	3.976 (3)	157
C133—H133 ^{iv} —Br124 ^{iv}	0.95	3.10	3.995 (3)	157

Symmetry codes: (iii) $x, y, z+1$; (iv) $x, y, z-1$.