

Crystal structure of 2,3,5,6-tetrabromoterephthalonitrile

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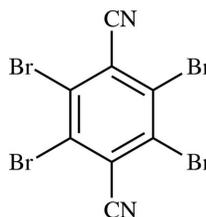
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Keywords: crystal structure; nitrile; N...Br contacts.**CCDC reference:** 1911575**Supporting information:** this article has supporting information at journals.iucr.org/e

The title crystal (systematic name: 2,3,5,6-tetrabromobenzene-1,4-dicarbonitrile), $C_8Br_4N_2$, is the first bromo analog in a study of cyano-halo ($C\equiv N\cdots X$) non-bonded contacts in crystals of halogenated dicyanobenzenes. The complete molecule is generated by a crystallographic center of symmetry. In the extended structure, each Br atom accepts one $C\equiv N\cdots Br$ interaction, and each N atom is bisected by two. This contact network forms a nearly planar sheet structure propagating in the $(\bar{1}01)$ plane, similar to that reported in hexamethylbenzene co-crystals of the tetrachloro analog.

1. Chemical context

The title crystal is part of a study of solid-state $C\equiv N\cdots X$ ($X = F, Cl, Br, I$) non-bonded contacts in substituted benzonitriles. The question is whether these contacts will form for a given nitrile, and whether they are isolated or extended to create ribbon or sheet structures in their crystals. The prevailing trend is that $C\equiv N\cdots F$ contacts do not form (Bond *et al.*, 2001), $C\equiv N\cdots Cl$ contacts form in isolation or as inversion dimers (Pink *et al.*, 2000), and $C\equiv N\cdots Br$ and $\cdots I$ contacts form networks (Noland *et al.*, 2018). Contact strength tends to increase with the polarizability of the halogen atom (Desiraju & Harlow, 1989).



The crystal structures of neat (*i.e.* not co-crystals, no solvent included in the crystal) halogenated terephthalodinitriles have followed this trend. The crystal of 2,3,5,6-tetrafluoro-terephthalodinitrile (F4TN) does not contain any $C\equiv N\cdots F$ contacts, with molecules adopting a sawtooth formation (Fig. 1*a*; Hirshfeld, 1984), similar to a crystal of pentafluorobenzonitrile (Bond *et al.*, 2001). The crystal of the tetrachloro analog (Cl4TN) contains one $C\equiv N\cdots Cl$ contact per N atom, forming staggered $C_2^2(14)$ chains (Britton, 1981*b*; Fig. 1*b*). In co-crystals of Cl4TN with anthracene (Britton, 2005*b*), phenanthrene, or pyrene (Britton, 2005*a*), no $C\equiv N\cdots Cl$ contacts are found. However, Cl4TN and the corresponding *ortho*- and *meta*-dicyano isomers each form co-crystals with hexamethylbenzene wherein $C\equiv N\cdots Cl$ -based sheets occur, in alternating layers with sheets of hexamethylbenzene (Britton, 2002). No crystals involving the title compound (Br4TN) have been reported previously.

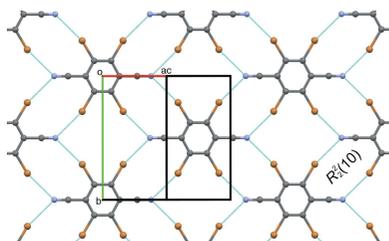


Table 1
Contact geometry for Br4TN (\AA , $^\circ$).

$\text{C}\equiv\text{N}\cdots\text{Br}$	$\text{C}\equiv\text{N}$	$\text{N}\cdots\text{Br}$	$\text{C}\equiv\text{N}\cdots\text{Br}$
$\text{C1}\equiv\text{N1}\cdots\text{Br1}^i$	1.139 (5)	3.015 (2)	135.48 (5)

Symmetry code: (i) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$.

2. Structural commentary

In the crystal of Br4TN, the molecules lie about an inversion center and a vertical mirror plane, and are almost planar (Fig. 2). The ring C2/C3 atoms have r.m.s. deviations of 0.002 (2) \AA from the plane of best fit. The Br1 and N1 atoms deviate from this plane by 0.038 (4) and 0.026 (9) \AA , respectively. This distortion is chair-like, with adjacent ring positions bent to opposite sides of the best-fit plane.

3. Supramolecular features

$\text{C}\equiv\text{N}\cdots\text{Br}$ contacts are the most prominent packing feature (Table 1). The length of these contacts is similar to 3.064 (4) \AA , the mean $\text{C}\equiv\text{N}\cdots\text{Br}$ distance found in crystals of 2,4,6-tribromobenzonitrile (Br3BN; Noland *et al.*, 2018). The N and *ortho*-Br atoms of Br3BN form a contact network similar to a half-molecule of Br4TN. Pairs of these contacts form centrosymmetric $R_2^2(10)$ rings (Fig. 3). Each molecule of Br4TN

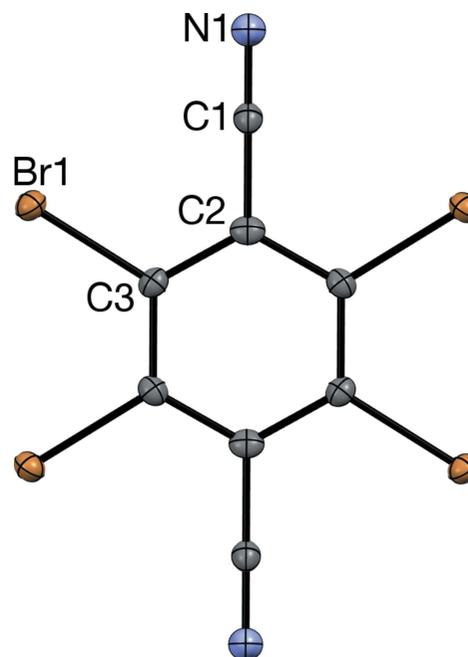


Figure 2
The molecular structure of Br4TN, with atom labeling and displacement ellipsoids at the 50% probability level. Unlabeled atoms are generated by the $(x, -y + 1, z)$, $(-x + 1, y, -z + 2)$, and $(-x + 1, -y + 1, -z + 2)$ symmetry operations.

participates in four such rings, generating a nearly planar sheet structure that is similar to Cl4TN layers in the Cl4TN-hexamethylbenzene co-crystal (Britton, 2002). In Br4TN, adjacent sheets stack roughly along $[70\bar{4}]$, and the $[001]$ translation relates molecules in neighboring sheets.

4. Database survey

A search of the Cambridge Structural Database (CSD, Version 5.40, November 2018; Groom *et al.*, 2016) found six additional reports similar to Br4TN. For F4TN, a co-crystal with 9-acetylanthracene (Wang *et al.*, 2018), and an η^2 -

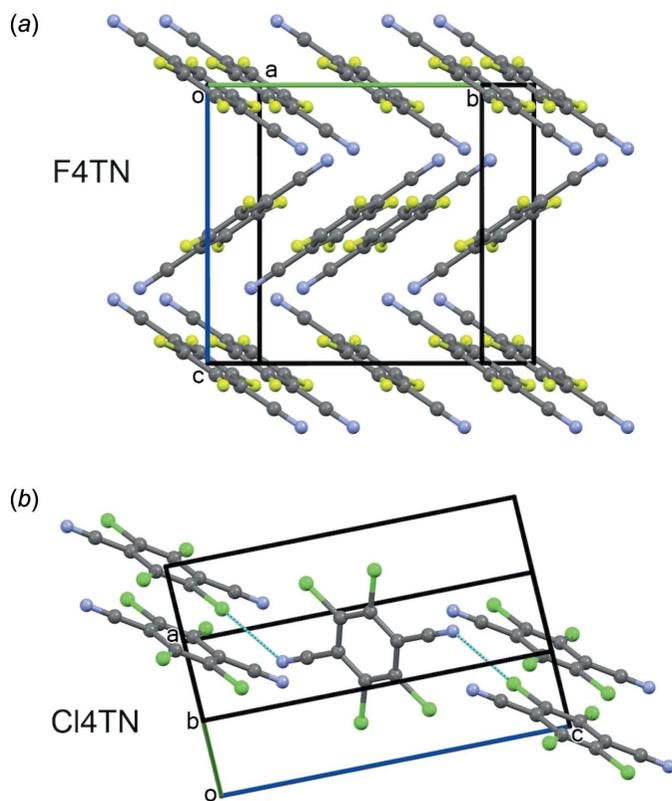


Figure 1
Packing in the crystals of (a) F4TN, viewed along $[5\bar{1}0]$; (b) Cl4TN, viewed along $[1\bar{2}0]$. The dashed blue lines represent short contacts.

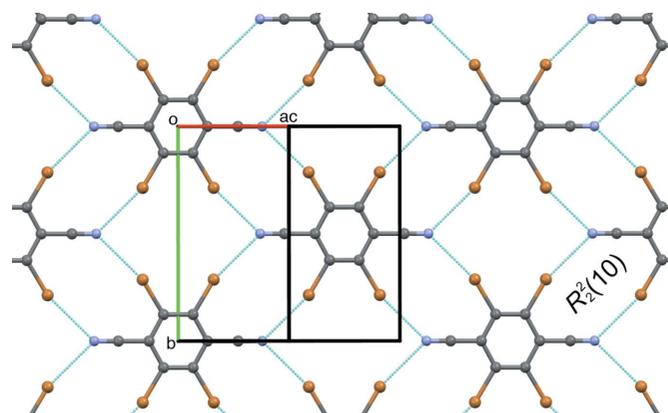


Figure 3
The nearly planar sheet structure in a crystal of Br4TN, viewed along $\bar{1}01$. The dashed blue lines represent short contacts.

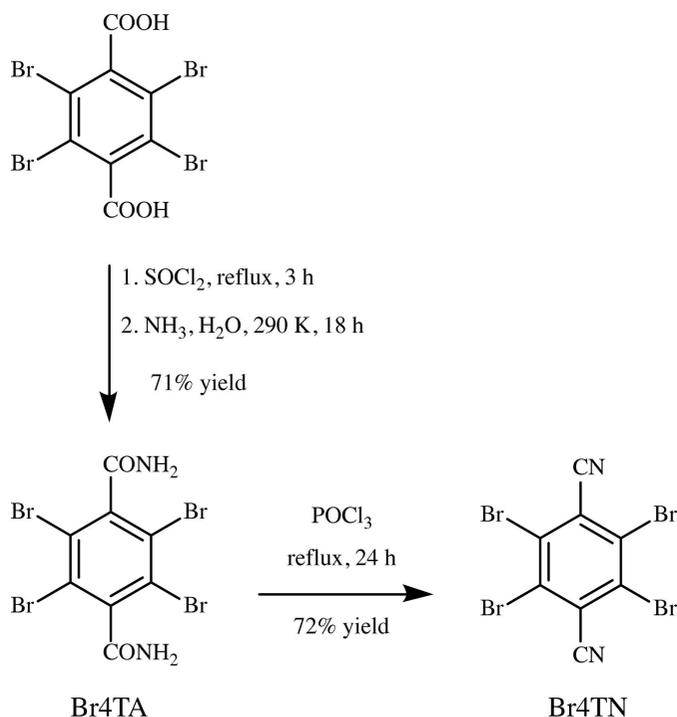


Figure 4
 The synthesis of Br4TN via amination of 2,3,5,6-tetrabromoterephthalic acid, followed by dehydration.

complex with tungsten(II) (Kiplinger *et al.*, 1997) are both given; these contain no $\text{C}\equiv\text{N}\cdots\text{F}$ contacts. Neat crystals are reported for the *ortho*- (Britton, 1981c) and *meta*-dicyano (Hu *et al.*, 2004) isomers of Cl4TN, and 2,4,6-trichlorotricyanobenzene (Britton, 1981a).

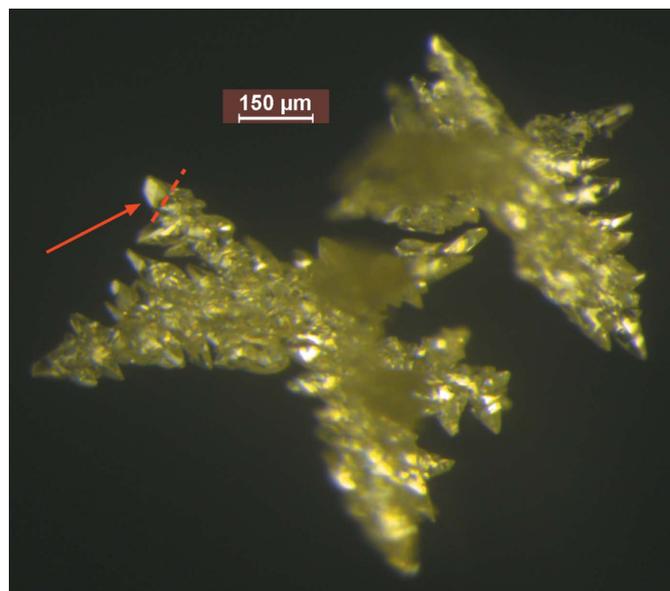


Figure 5
 A confocal micrograph showing two colorless crystals of Br4TN. The apparent yellow colour is caused by the lighting. The blurry portions are out of the focal plane toward the viewer. A prismatic tip similar to the one indicated by the red arrow was used for X-ray diffraction.

5. Synthesis and crystallization

2,3,5,6-Tetrabromoterephthaldiamide (Br4TA), adapted from the work of Schäfer *et al.* (2017): Tetrabromoterephthalic acid (4.01 g; Sigma–Aldrich, Inc., No. 524441) and thionyl chloride (24 mL) were combined in a round-bottomed flask. The resulting mixture was refluxed for 3 h, and then cooled to ambient temperature. The thionyl chloride was removed under reduced pressure. The resulting white solid was dissolved in 1,4-dioxane (60 mL). An ammonium hydroxide solution (15 M, 50 mL) was added and then the mixture was stirred for 18 h. Water (50 mL) and an Na_2CO_3 solution (2 M, 50 mL) were added, and then the mixture was stirred for 24 h. A precipitate was collected by suction filtration, and then washed with water, giving a white powder (5.71 g, 71%). A trace of ammonium chloride could not be removed, based on the MS results. M.p. 627 K (lit. 615 K; Knobloch & Ramirez, 1975); ^1H NMR (500 MHz, $\text{DMSO-}d_6$; 2 conformers obs.) δ 8.085 (s, 2H, both), 7.936 (s, 2H, minor), 7.889 (s, 2H, major); ^{13}C NMR (126 MHz, $\text{DMSO-}d_6$) δ 166.8 (2C), 143.4 (2C), 122.2 (4C); IR (KBr, cm^{-1}) 3292, 3158, 2966, 2907, 2853, 1679, 1427, 1315, 1287, 1252, 1114, 1089, 866; MS (ESI, m/z) [$M+^{35}\text{Cl}$] $^-$ calculated for $\text{C}_8\text{H}_4^{79}\text{Br}_2^{81}\text{Br}_2\text{N}_2\text{O}_2$ 514.6660, found 514.6672.

2,3,5,6-Tetrabromoterephthalodinitrile (Br4TN), adapted from the work of Schäfer *et al.* (2017) (Fig. 4): A portion of Br4TA (515 mg) and phosphorus oxychloride (16 mL) were combined in a round-bottomed flask. The resulting mixture was refluxed for 24 h, then cooled to ambient temperature, and then poured into ice–water (200 mL). This mixture was stirred until the ice melted, then a precipitate was collected by suction filtration, and then washed with water, giving a white powder (342 mg, 72%). M.p. 603 K; ^{13}C NMR (126 MHz, $\text{DMSO-}d_6$) δ 129.6 (4C, C3), 123.5 (2C, C2), 116.0 (2C, C1); IR (KBr, cm^{-1}) 2236, 1364, 1330, 1293, 1229, 1156, 1121, 732; MS (EI, m/z) [M] $^+$ calculated for $\text{C}_8^{79}\text{Br}_2^{81}\text{Br}_2\text{N}_2$ 443.6749, found 443.6764.

Crystallization: A solution of Br4TN (150 mg) in bis(2-methoxyethyl) ether (10 mL) at 425 K was cooled by 30 K h^{-1} until a precipitate began to form. The temperature was held for 1 h, and then cooled by 10 K h^{-1} to ambient temperature. After 24 h, colorless, highly twinned, prismatic crystals were collected by decantation and then washed with methanol. A monocrystalline tip similar to the one indicated in Fig. 5 was harvested for X-ray diffraction.

6. Refinement

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

Acknowledgements

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Table 2
Experimental details.

Crystal data	
Chemical formula	C ₈ Br ₄ N ₂
<i>M_r</i>	443.74
Crystal system, space group	Monoclinic, <i>C2/m</i>
Temperature (K)	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	7.8500 (6), 9.8330 (8), 6.7540 (6)
β (°)	90.202 (4)
<i>V</i> (Å ³)	521.33 (7)
<i>Z</i>	2
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	15.40
Crystal size (mm)	0.15 × 0.06 × 0.03
Data collection	
Diffractometer	Bruker VENTURE PHOTON-II area detector
Absorption correction	Multi-scan (<i>SADABS</i> ; Sheldrick, 1996)
<i>T_{min}</i> , <i>T_{max}</i>	0.253, 0.494
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	3324, 837, 741
<i>R_{int}</i>	0.063
(sin θ/λ) _{max} (Å ⁻¹)	0.715
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.029, 0.072, 1.04
No. of reflections	837
No. of parameters	38
Δρ _{max} , Δρ _{min} (e Å ⁻³)	1.09, -1.01

Computer programs: *APEX2* and *SAINT* (Bruker, 2012), *SHELXT2014/5* (Sheldrick, 2015a), *SHELXL2018/3* (Sheldrick, 2015b), *Mercury* (Macrae *et al.*, 2008) and *publCIF* (Westrip, 2010).

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supporting information

Acta Cryst. (2019). E75, 703-706 [https://doi.org/10.1107/S2056989019005486]

Crystal structure of 2,3,5,6-tetrabromoterephthalonitrile

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Computing details

Data collection: *APEX2* (Bruker, 2012); cell refinement: *SAINT* (Bruker, 2012); data reduction: *SAINT* (Bruker, 2012); program(s) used to solve structure: *SHELXT2014/5* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018/3* (Sheldrick, 2015b); molecular graphics: *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *publCIF* (Westrip, 2010).

2,3,5,6-Tetrabromobenzene-1,4-dinitrile

Crystal data

$C_8Br_4N_2$

$M_r = 443.74$

Monoclinic, $C2/m$

$a = 7.8500$ (6) Å

$b = 9.8330$ (8) Å

$c = 6.7540$ (6) Å

$\beta = 90.202$ (4)°

$V = 521.33$ (7) Å³

$Z = 2$

$F(000) = 404$

$D_x = 2.827$ Mg m⁻³

Melting point: 603 K

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

Cell parameters from 2993 reflections

$\theta = 3.0$ – 30.4 °

$\mu = 15.40$ mm⁻¹

$T = 100$ K

Prism, colourless

$0.15 \times 0.06 \times 0.03$ mm

Data collection

Bruker VENTURE PHOTON-II area detector diffractometer

Radiation source: micro-focus

φ and ω scans

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

$T_{\min} = 0.253$, $T_{\max} = 0.494$

3324 measured reflections

837 independent reflections

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

$R_{\text{int}} = 0.063$

$\theta_{\max} = 30.6$ °, $\theta_{\min} = 3.0$ °

$h = -11 \rightarrow 9$

$k = -13 \rightarrow 14$

$l = -9 \rightarrow 9$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.029$

$wR(F^2) = 0.072$

$S = 1.04$

837 reflections

38 parameters

0 restraints

Primary atom site location: dual

$w = 1/[\sigma^2(F_o^2) + (0.0175P)^2 + 0.7909P]$

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

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

$\Delta\rho_{\max} = 1.09$ e Å⁻³

$\Delta\rho_{\min} = -1.01$ e Å⁻³

Extinction correction: SHELXL2018/3

(Sheldrick 2015b),

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

Extinction coefficient: 0.0029 (10)

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>	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.40138 (3)	0.78605 (3)	0.77786 (4)	0.01672 (15)
N1	0.2553 (5)	0.500000	0.4857 (5)	0.0219 (7)
C1	0.3260 (5)	0.500000	0.6333 (6)	0.0158 (7)
C2	0.4158 (5)	0.500000	0.8209 (6)	0.0148 (7)
C3	0.4576 (3)	0.6237 (3)	0.9090 (4)	0.0142 (5)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0186 (2)	0.0174 (2)	0.0142 (2)	0.00120 (9)	0.00004 (12)	0.00249 (9)
N1	0.0253 (19)	0.0198 (18)	0.0204 (19)	0.000	-0.0045 (15)	0.000
C1	0.0190 (19)	0.0140 (19)	0.0144 (18)	0.000	0.0032 (14)	0.000
C2	0.0125 (17)	0.021 (2)	0.0113 (16)	0.000	0.0035 (13)	0.000
C3	0.0138 (12)	0.0151 (14)	0.0136 (13)	0.0007 (9)	0.0026 (10)	0.0018 (10)

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

Br1—C3	1.878 (3)	C2—C3	1.393 (3)
N1—C1	1.139 (5)	C2—C3 ⁱ	1.393 (3)
C1—C2	1.448 (5)	C3—C3 ⁱⁱ	1.395 (5)
N1—C1—C2	180.0 (4)	C2—C3—C3 ⁱⁱ	119.17 (17)
C3—C2—C3 ⁱ	121.7 (3)	C2—C3—Br1	119.1 (2)
C3—C2—C1	119.17 (17)	C3 ⁱⁱ —C3—Br1	121.75 (8)
C3 ⁱ —C2—C1	119.17 (17)		
C3 ⁱ —C2—C3—C3 ⁱⁱ	-0.5 (6)	C3 ⁱ —C2—C3—Br1	178.56 (19)
C1—C2—C3—C3 ⁱⁱ	179.2 (3)	C1—C2—C3—Br1	-1.7 (4)

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