

2,6-Dibromo-4-nitrobenzonitrile

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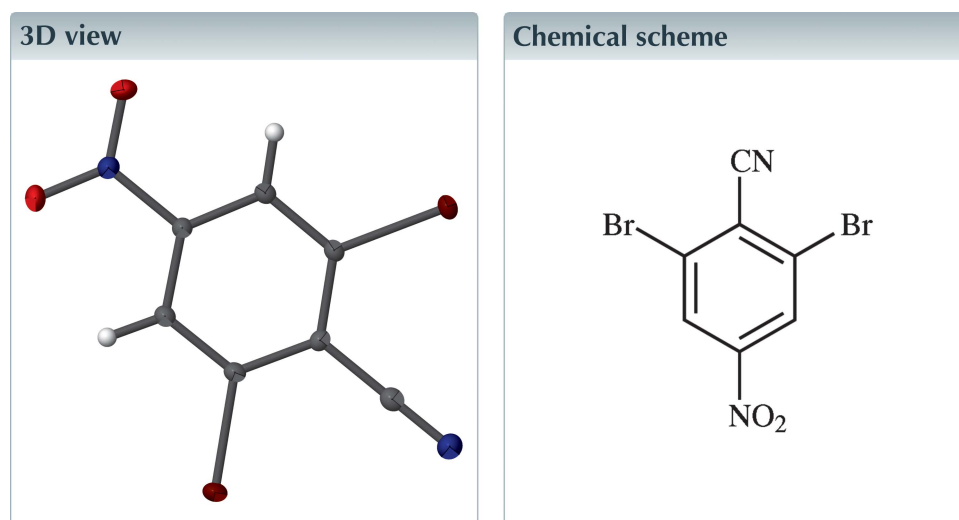
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Keywords: crystal structure; nitrile; $\text{CN}\cdots\text{Br}$ contacts; $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds.

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

Molecules of the title compound, $\text{C}_7\text{H}_2\text{Br}_2\text{N}_2\text{O}_2$, have C_{2v} symmetry and each lie on a twofold axis that bisects the benzene ring and its nitro and cyano substituents. The cyano N atom is bisected by two $\text{CN}\cdots\text{Br}$ contacts, and the nitro O atoms participate in weak $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds. These interactions form a planar sheet structure that stacks about a glide plane. This stacking mode has not been previously reported with cyano-halo-derived sheets of this type.



Structure description

The title nitrile (I) is presented as part of an ongoing packing study of 2,6-dihalobenzonitriles. Molecules of (I) have typical geometry (Fig. 1). The major axis of each molecule (connecting N4 and N7) lies on a twofold axis, two orthogonal mirror planes, and a glide plane. Thus, molecules have C_{2v} point symmetry and are planar. The cyano groups are bisected by two symmetry-related $\text{C7}\equiv\text{N7}\cdots\text{Br2}$ contacts (Table 1), forming ribbons of $R_2^2(10)$ inversion dimers along [001]. Adjacent ribbons are related by an [010] translation, giving a planar sheet structure parallel to (100) (Fig. 2a). This sheet is similar to those reported for 2,4,6-tribromobenzonitrile (II) (Fig. 2b; Britton *et al.*, 2016) and 2,6-dibromo-4-chlorobenzonitrile (III), (Fig. 2c; Britton, 2005). The relative displacement of molecules in the different sheets is consistent with the geometries of the 4-substituents. In (II) and (III), there are no short contacts between adjacent ribbons. By contrast, adjacent ribbons in (I) are connected by weak $\text{C3}-\text{H3A}\cdots\text{O1}$ hydrogen bonds that form chains of $R_2^2(10)$ inversion dimers along [001], informally mirroring the $\text{CN}\cdots\text{Br}$ contacts (Table 1). In the crystal of (I), sheets stack about glide planes (Fig. 3a), a stacking mode not yet observed in this series. Three polytypes of (II) were reported with combinations of centric (Fig. 3b) and translational stacking. Crystals of (III) had only translational (Fig. 3c) stacking.

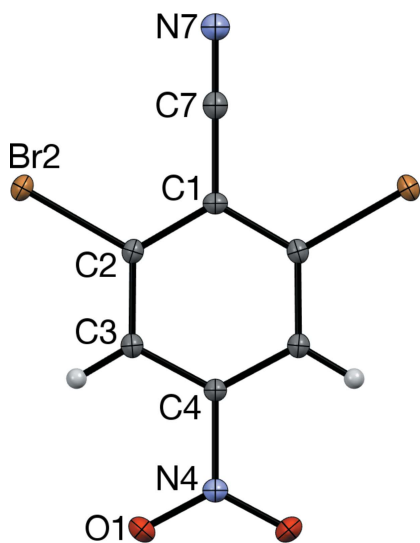


Figure 1
The molecular structure of (I), showing the atomic numbering and displacement ellipsoids at the 50% probability level. Unlabelled atoms are related by twofold and mirror symmetry.

Table 1
Contact geometry (Å, °)..

$A-B \cdots C$	$A-B$	$B \cdots C$	$A \cdots C$	$A-B \cdots C$
$C7 \equiv N7 \cdots Br2^i$	1.151 (3)	3.1508 (9)	3.8640 (1)	120.49 (3)
$C3-H3A \cdots O1^{ii}$	0.95	2.493	3.409 (2)	161.82

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

Synthesis and crystallization

4-Nitroaniline (2.57 g; Acros Organics Co., No. 12837) was brominated (Br_2 , 2.1 ml) in acetic acid (100 ml) at 350 K for 6 h. The resulting mixture was cooled to room temperature. A precipitate was collected by filtration, and then neutralized in a mixture of saturated aqueous $NaHSO_3$ (20 ml) and Na_2CO_3 (100 ml), water (50 ml), and ethyl acetate (300 ml). The organic portion was concentrated on a rotary evaporator, and then recrystallized from chloroform, giving 2,6-dibromo-4-nitroaniline as yellow needles [84% yield, m.p. 480–481 K (lit. 476–477 K; Podgoršek *et al.*, 2009)]. A portion (570 mg) was

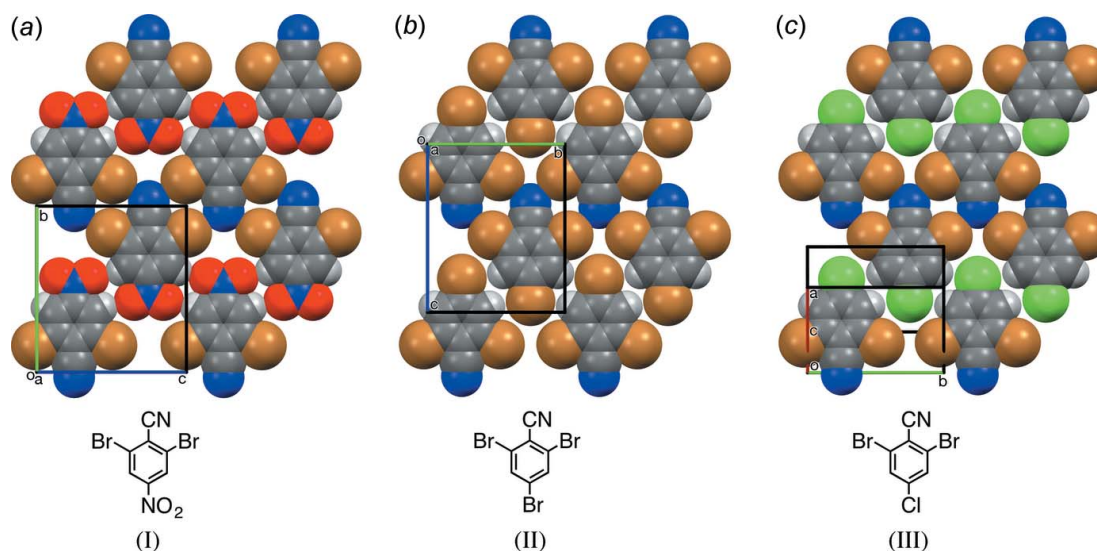


Figure 2
Space-filling drawings of the sheet structures in (a) 4-nitro nitrile (I), viewed along [100]; (b) the $Z = 8$ polytype of 4-bromo nitrile (II), viewed along [100]; (c) 4-chloro nitrile (III), viewed along $[\bar{1}02]$.

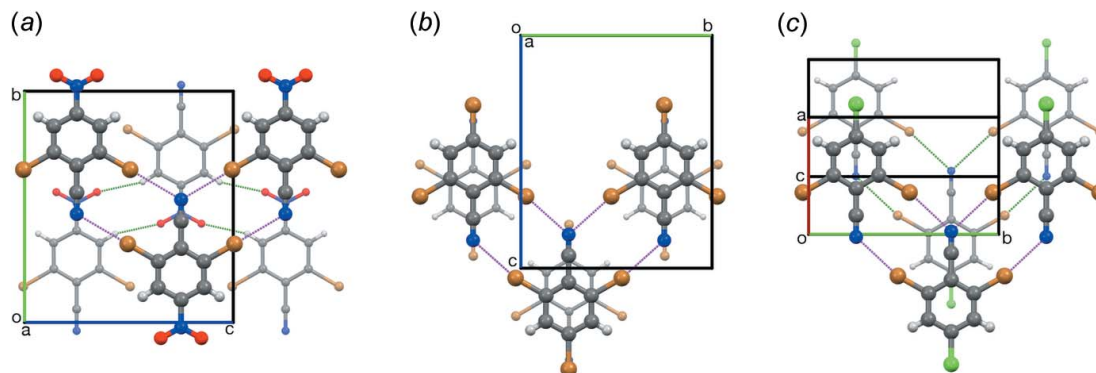


Figure 3
The three stacking modes observed for the given sheet structure: (a) glide stacking between adjacent sheets in (I), viewed along [100]; (b) centric stacking between alternating sheet pairs in the $Z = 8$ polytype of (II), viewed along [100]; (c) translational stacking between adjacent sheets in (III), viewed along $[\bar{1}02]$. 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 2
Experimental details.

Crystal data	
Chemical formula	C ₇ H ₂ Br ₂ N ₂ O ₂
<i>M_r</i>	305.93
Crystal system, space group	Orthorhombic, <i>Cmcm</i>
Temperature (K)	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	6.4256 (2), 12.3231 (5), 11.1117 (4)
<i>V</i> (Å ³)	879.86 (6)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	9.18
Crystal size (mm)	0.22 × 0.15 × 0.11
Data collection	
Diffractometer	Bruker VENTURE PHOTON-II
Absorption correction	Multi-scan (<i>SADABS</i> ; Sheldrick, 1996)
<i>T_{min}</i> , <i>T_{max}</i>	0.249, 0.344
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	10626, 1195, 1060
<i>R_{int}</i>	0.027
(sin θ/λ) _{max} (Å ⁻¹)	0.835
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.014, 0.035, 1.08
No. of reflections	1195
No. of parameters	46
H-atom treatment	H-atom parameters constrained
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.64, -0.43

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

cyanated according to the Sandmeyer procedure described by Britton *et al.* (2016), giving (I) as an off-white powder (35% yield, m.p. 466–467 K). ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.68 (*s*, H3A); ¹³C NMR (101 MHz, DMSO-*d*₆) δ 150.0 (C4), 127.3 (C2), 126.8 (C3), 122.9 (C1), 115.5 (C7); IR (KBr, cm⁻¹) 3098,

2232, 1525, 1345, 1278, 1095, 903, 783, 751, 621. Crystals were prepared by slow evaporation of a solution in chloroform, followed by decantation, and then washing with pentane.

Refinement

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

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full crystallographic data

IUCrData (2017). 2, x171617 [https://doi.org/10.1107/S2414314617016170]

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2,6-Dibromo-4-nitrobenzonitrile

Crystal data

$C_7H_2Br_2N_2O_2$

$M_r = 305.93$

Orthorhombic, *Cmcm*

$a = 6.4256$ (2) Å

$b = 12.3231$ (5) Å

$c = 11.1117$ (4) Å

$V = 879.86$ (6) Å³

$Z = 4$

$F(000) = 576$

$D_x = 2.309$ Mg m⁻³

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

Cell parameters from 2992 reflections

$\theta = 3.3$ – 36.1°

$\mu = 9.18$ mm⁻¹

$T = 100$ K

Square bipyramid, colorless

$0.22 \times 0.15 \times 0.11$ mm

Data collection

Bruker VENTURE PHOTON-II
diffractometer

Radiation source: micro-focus

φ and ω scans

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

$T_{\min} = 0.249$, $T_{\max} = 0.344$

10626 measured reflections

1195 independent reflections

1060 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.027$

$\theta_{\max} = 36.4^\circ$, $\theta_{\min} = 3.3^\circ$

$h = -10 \rightarrow 10$

$k = -20 \rightarrow 20$

$l = -18 \rightarrow 18$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.014$

$wR(F^2) = 0.035$

$S = 1.08$

1195 reflections

46 parameters

0 restraints

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0108P)^2 + 0.7137P]$

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

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

$\Delta\rho_{\max} = 0.64$ e Å⁻³

$\Delta\rho_{\min} = -0.43$ 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)

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>	$U_{\text{iso}}^*/U_{\text{eq}}$
Br2	0.5000	0.83929 (2)	0.49434 (2)	0.01475 (5)
O1	0.5000	0.43194 (8)	0.65277 (9)	0.0238 (2)
N4	0.5000	0.47860 (12)	0.7500	0.0148 (3)
N7	0.5000	1.03098 (14)	0.7500	0.0193 (3)
C1	0.5000	0.82086 (13)	0.7500	0.0118 (3)
C2	0.5000	0.76354 (9)	0.64089 (10)	0.01227 (19)
C3	0.5000	0.65122 (9)	0.63981 (10)	0.01287 (19)
H3A	0.5000	0.6119	0.5663	0.015*
C4	0.5000	0.59809 (13)	0.7500	0.0120 (3)
C7	0.5000	0.93761 (15)	0.7500	0.0146 (3)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br2	0.01902 (7)	0.01452 (6)	0.01072 (6)	0.000	0.000	0.00282 (4)
O1	0.0424 (6)	0.0139 (4)	0.0150 (4)	0.000	0.000	-0.0038 (3)
N4	0.0189 (6)	0.0118 (6)	0.0136 (6)	0.000	0.000	0.000
N7	0.0246 (8)	0.0154 (6)	0.0178 (6)	0.000	0.000	0.000
C1	0.0124 (6)	0.0099 (6)	0.0130 (6)	0.000	0.000	0.000
C2	0.0140 (4)	0.0128 (4)	0.0100 (4)	0.000	0.000	0.0010 (3)
C3	0.0153 (5)	0.0128 (5)	0.0105 (4)	0.000	0.000	-0.0002 (3)
C4	0.0142 (6)	0.0106 (6)	0.0110 (6)	0.000	0.000	0.000
C7	0.0140 (7)	0.0167 (7)	0.0130 (6)	0.000	0.000	0.000

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

Br2—C2	1.8770 (11)	C1—C2 ⁱ	1.4031 (14)
O1—N4	1.2239 (12)	C1—C7	1.439 (2)
N4—O1 ⁱ	1.2239 (12)	C2—C3	1.3842 (17)
N4—C4	1.473 (2)	C3—C4	1.3884 (13)
N7—C7	1.151 (3)	C3—H3A	0.9500
C1—C2	1.4031 (14)	C4—C3 ⁱ	1.3885 (13)
O1 ⁱ —N4—O1	123.96 (16)	C1—C2—Br2	119.95 (9)
O1 ⁱ —N4—C4	118.02 (8)	C2—C3—C4	117.63 (11)
O1—N4—C4	118.02 (8)	C2—C3—H3A	121.2
C2—C1—C2 ⁱ	119.55 (15)	C4—C3—H3A	121.2
C2—C1—C7	120.23 (7)	C3—C4—C3 ⁱ	123.74 (15)
C2 ⁱ —C1—C7	120.23 (7)	C3—C4—N4	118.13 (7)
C3—C2—C1	120.72 (11)	C3 ⁱ —C4—N4	118.13 (7)
C3—C2—Br2	119.32 (8)	N7—C7—C1	180.0
C2 ⁱ —C1—C2—C3	0.000 (1)	C2—C3—C4—C3 ⁱ	0.000 (1)
C7—C1—C2—C3	180.000 (1)	C2—C3—C4—N4	180.000 (1)
C2 ⁱ —C1—C2—Br2	180.000 (1)	O1 ⁱ —N4—C4—C3	180.000 (1)

C7—C1—C2—Br2	0.000 (1)	O1—N4—C4—C3	0.000 (1)
C1—C2—C3—C4	0.000 (1)	O1 ⁱ —N4—C4—C3 ⁱ	0.000 (1)
Br2—C2—C3—C4	180.000 (1)	O1—N4—C4—C3 ⁱ	180.000 (1)

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