

A 2:1 co-crystal of 3,5-dibromo-4-cyanobenzoic acid and anthracene

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The title co-crystal, $C_8H_3Br_2NO_2 \cdot 0.5C_{14}H_{10}$, was self-assembled from a 2:1 mixture of the components in slowly evaporating dichloromethane. The molecules adopt a sheet structure parallel to $(1\bar{1}2)$ in which carboxy hydrogen-bonded dimers and anthracene molecules stagger in both dimensions. Within the sheets, six individual cyano acid molecules surround each anthracene molecule. Cyano acid molecules form one of the two possible $R_2^2(10)$ rings between neighboring cyano and bromo groups. Compared to the dichloro analog [Britton (2012). *J. Chem. Crystallogr.* **42**, 851–855], the dihedral angle between the best-fit planes of acid and anthracene molecules has decreased from 7.1 to 0.9 (2)°.

1. Chemical context

Doyle Britton (1930–2015) published roughly 30 crystallographic articles on solid-phase cyano–halo interactions from variously substituted halobenzonitriles and isocyanides.

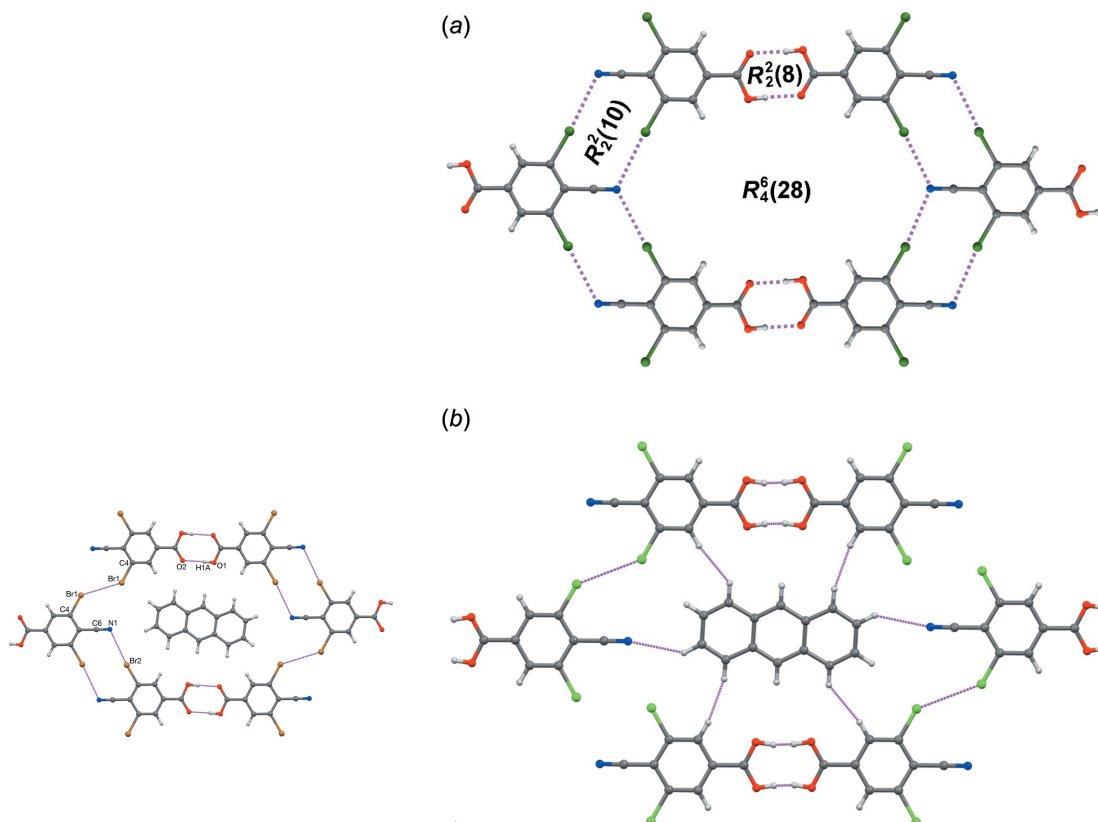
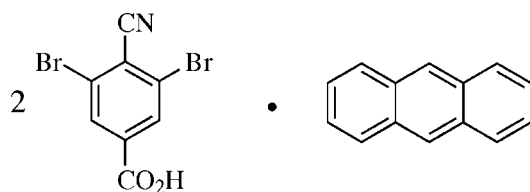


Figure 1

(a) The honeycomb-like structure envisioned by Doyle Britton. (b) A 2:1 co-crystal of 3,5-dichloro-4-cyanobenzoic acid with anthracene, viewed along $28\bar{1}$ (Britton, 2012). Magenta dashed lines represent short contacts.

Britton postulated that 3,5-dichloro-4-cyanobenzoic acid might assemble into a honeycomb-like sheet structure (Fig. 1*a*) via a combination of carboxy hydrogen-bond dimerization and $\text{CN}\cdots\text{Cl}$ short contacts. In 2012, he found that the cyano acid molecules alone do not pack in this way, but slow evaporation of mixtures containing naphthalene or anthracene afforded 2:1 acid:hydrocarbon co-crystals roughly matching his proposed structure (Britton, 2012). However, no $\text{CN}\cdots\text{Cl}$ contacts were observed (Fig. 1*b*). Anthracene was the better fit, although it was too large to allow the ideal molecular arrangement. There is no obvious substitute for anthracene or naphthalene. Thus, we have prepared anthracene co-crystals with the dibromo analog in hopes that the larger Br bond and contact radii might close the $\text{CN}\cdots\text{X}$ gaps observed with Cl.



2. Structural commentary

The benzene (C2–C5/C7/C8) and anthracene (C9–C15 and symmetry equivalents, Fig. 2) ring systems are nearly planar. The mean deviation of atoms from the planes of best fit are 0.0074 (17) Å and 0.0041 (14) Å, respectively, both of which are comparable to the corresponding values in the dichloro crystal. However, the dihedral angle between the carboxy group (O1–C1–O2) and the benzene ring is 3.2 (4)°, compared with 7.2° in the dichloro analog.

3. Supramolecular features

The dihedral angle between the benzene and anthracene planes is 0.9 (2)°, which is much lower than 7.1° of the dichloro

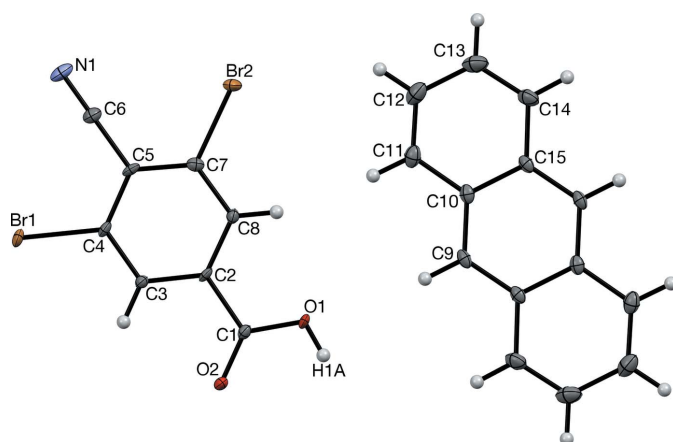


Figure 2
The molecular structures of the components of the title co-crystal, with atom labeling and displacement ellipsoids at the 50% probability level. Only the symmetry-unique 3,5-dibromo-4-cyanobenzoic acid molecule is shown. Unlabeled anthracene atoms are generated by the $(-x, -y, -z)$ symmetry operation.

Table 1
Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1–H1A \cdots O2 ⁱ	0.84	1.79	2.627 (2)	178

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

Table 2
Contact geometry (Å, °).

$C-X\cdots Br$	$C-X$	$X\cdots Br$	$C-X\cdots Br$
C6 \equiv N1 \cdots Br2 ⁱⁱ	1.143 (4)	3.307 (2)	115.9 (2)
C4–Br1 \cdots Br1 ⁱⁱⁱ	1.886 (2)	3.5534 (5)	133.43 (7)

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

analog. As expected, $R_2^2(8)$ carboxy hydrogen-bonded dimers are observed (Table 1); these are located on an inversion center. $R_2^2(10)$ rings form about another inversion center based on C6 \equiv N1 \cdots Br2 contacts (Table 2); however, the corresponding N1 \cdots Br1 contacts are not observed (Fig. 3). Instead, 3.5534 (5) Å Br1 \cdots Br1 contacts form, slightly closer than the 3.70 Å non-bonded contact diameter of Br (Rowland & Taylor, 1996). In the title co-crystal, two corners of the anthracene molecule contact the cyano acid network (Fig. 3), whereas all four corners made contact in the Cl analog (Fig. 1*b*). Overall, substitution of Cl atoms with Br atoms has facilitated the formation of half of the envisioned $\text{CN}\cdots\text{X}$ short contacts and also improved the coplanarity of the acid and hydrocarbon molecules, but anthracene is slightly too large to allow the ideal arrangement of cyano acid molecules. It is possible that upon substitution of Br atoms with I atoms, the improvements would continue and the envisioned sheet structure might occur. This possibility is currently being studied in our laboratory.

4. Database survey

A search of the Cambridge Structural Database (Version 5.38, update May 2017; Groom *et al.*, 2016) found no 4-cyano-3-halobenzoic acids other than the six structures reported by Britton (2012). Among 3-halobenzoic acids, no entries were found in which carboxy dimers formed and assembled into a

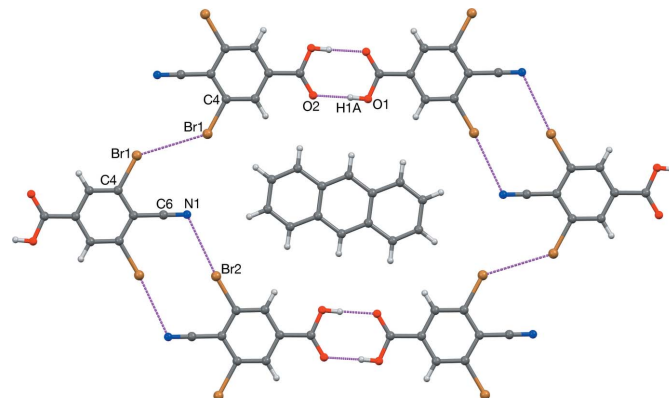


Figure 3
The sheet structure observed in the title co-crystal, viewed along [011].

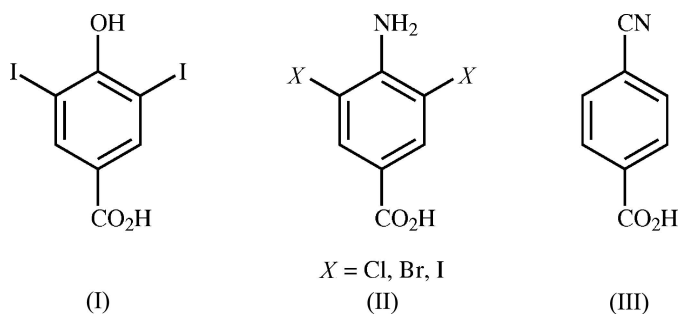


Figure 4
Selected structures from the database survey.

honeycomb-like sheet, with or without a co-former. Of the 40 entries for 3,5-dihalo-2,6-unsubstituted benzoic acids, 11 of them are co-crystals with carboxy monomers hydrogen-bonded to an O or N atom in the co-former (*i.e.*, Dubey & Desiraju, 2014; Back *et al.*, 2012). Hydroxy acid (I) (Prout *et al.*, 1988; Fig. 4) and amino acids (II) (Pant, 1965; Ueda *et al.*, 2014) form interlocking ribbons in which adjacent carboxy dimers are connected by I...I contacts, or amino-carboxy hydrogen-bonds, respectively. 4-Cyanobenzoic acid (III) forms a sheet structure in which carboxy dimers are connected lengthwise by $R_2^2(10)$ rings formed by $\text{CN}\cdots\text{H}$ contacts, and laterally by $R_3^3(7)$ rings formed by weak C—H...O bonds flanking each pair of carboxy groups (Higashi & Osaki, 1981).

5. Synthesis and crystallization

Methyl 4-amino-3,5-dibromobenzoate (V): Bromine (3.9 mL) and then pyridine (5.7 mL) were added dropwise to ice-cold

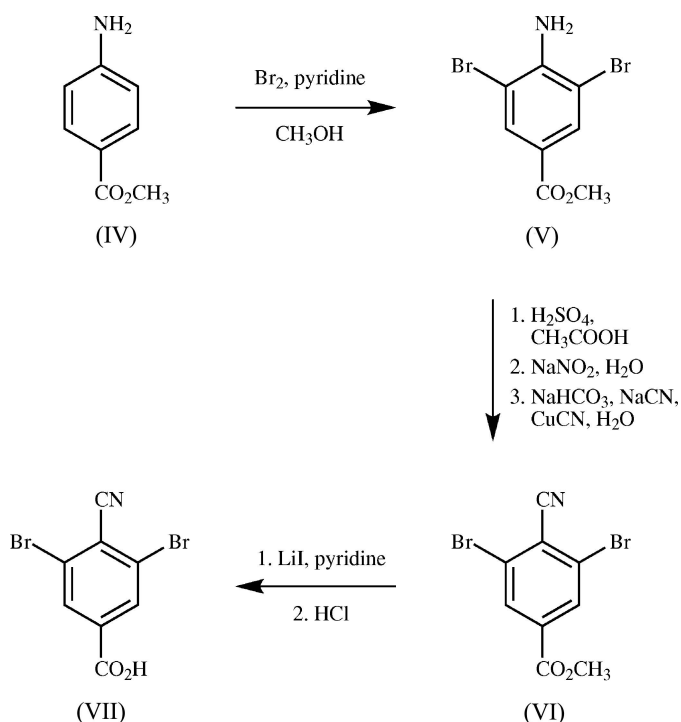


Figure 5
The three-step synthesis of the title cyano acid (VII).

methanol (35 mL). This mixture was added dropwise to a solution of methyl 4-aminobenzoate [(IV), commercially available, Fig. 5] in methanol (50 mL). The resulting mixture was refluxed for 4 h and then cooled to room temperature. The methanol was removed on a rotary evaporator. Dichloromethane (50 mL) and water (50 mL) were added. Aliquots (5 mL) of Na_2CO_3 solution (aq., sat.) were added until the aqueous phase remained slightly alkaline after 10 min. The organic phase was separated and then washed with $\text{Na}_2\text{S}_2\text{O}_3$ solution (aq., sat., 25 mL), water (25 mL), brine (25 mL), and was then concentrated on a rotary evaporator. The resulting brown residue was recrystallized from ethyl acetate, giving colorless needles (18.1 g, 93%). M.p. 406–408 K (lit. 404–406 K; Otto & Juppe, 1965); ^1H NMR (300 MHz, CDCl_3) δ 8.063 (*s*, 2H), 4.996 (*s*, 2H), 3.866 (*s*, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 165.1 (1C), 145.9 (1C), 133.5 (2C), 121.0 (1C), 107.5 (2C), 52.3 (1C); IR (NaCl, cm^{-1}) 3321, 3076, 2958, 1723, 1713, 1610, 1432, 1303, 1268, 975, 855, 761; MS (ESI, m/z) [$M+\text{Na}$] $^+$ calculated for $\text{C}_8\text{H}_7\text{Br}_2\text{NO}_2$ 331.8715, found 331.8709.

Methyl 3,5-dibromo-4-cyanobenzoate (VI), adapted from the work of Toya *et al.* (1992): *Cyanide suspension*: NaCN (680 mg) and CuCN (480 mg) and water (40 mL) were combined in a 400 mL beaker. After the solids dissolved, NaHCO_3 (6.5 g) was added. The resulting suspension was cooled in an ice bath. *Diazotization*: Dibromo ester [(V), 720 mg] was ground in a mortar and then combined with acetic acid (2.6 mL) in a round-bottomed flask. H_2SO_4 (0.6 mL) was added dropwise over 1 min, followed by a solution of NaNO_2 (313 mg) in water (1.5 mL) over 30 min. During the course of the additions, the reaction mixture was gradually warmed in an oil bath to 315 K. *Cyanation*: When no more starting material remained, as indicated by TLC, the diazotization mixture was removed from the heat and then added dropwise to the cyanide suspension. The ice bath was removed. The cyanation mixture was stirred overnight and then extracted with dichloromethane (3×20 mL). The combined organic portions were washed with water (20 mL), brine (20 mL), dried with Na_2SO_4 , filtered, and then concentrated on a rotary evaporator. The resulting brown residue was separated by column chromatography. The desired fraction ($R_f = 0.34$ in 3:1 hexane:ethyl acetate on SiO_2) was concentrated on a rotary evaporator, giving a tan powder (681 mg, 92%). M.p. 410–411 K; ^1H NMR (500 MHz, CDCl_3) δ 8.264 (*s*, 2H), 3.974 (*s*, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 163.4 (1C), 135.5 (1C), 132.6 (2C), 127.1 (2C), 122.5 (1C), 115.5 (1C), 53.5 (1C); IR (KBr, cm^{-1}) 3076, 2955, 2229, 1732, 1429, 1263, 1124, 971, 748; MS (ESI, m/z) [$M+\text{Na}$] $^+$ calculated for $\text{C}_9\text{H}_5\text{Br}_2\text{NO}_2$ 341.8559, found 341.8547.

3,5-Dibromo-4-cyanobenzoic acid (VII), adapted from the work of Lepage *et al.* (2004; especially compound 24): Cyano ester [(VI), 231 mg], lithium iodide (128 mg), and pyridine (10 mL) were combined in a round-bottomed flask. The resulting mixture was refluxed for 24 h and then cooled to room temperature. Chloroform (25 mL), water (25 mL), and hydrochloric acid (12 M, 25 mL) were added. After being stirred for 10 min, the resulting mixture was separated by suction filtration, giving a light-brown powder (217 mg, 99%).

M.p. 423–425 K; ^1H NMR (500 MHz, $(\text{CD}_3)_2\text{SO}$) δ 14.120 (s, H1A), 8.232 (s, H3A, H8A); ^{13}C NMR (126 MHz, $(\text{CD}_3)_2\text{SO}$) δ 163.9 (C1), 137.0 (C2), 132.1 (C3, C8), 126.7 (C4, C7), 120.6 (C5), 115.9 (C6); IR (KBr, cm^{-1}) 3421, 3077, 2128, 1811, 1662, 1537, 1371, 1296, 1025, 825, 770, 748; MS (ESI, m/z) $[M-\text{H}]^-$ calculated for $\text{C}_8\text{H}_3\text{Br}_2\text{NO}_2$ 303.8437, found 303.8443.

Crystallization: 3,5-Dibromo-4-cyanobenzoic acid (100 mg) and anthracene (29 mg) were dissolved in dichloromethane (25 mL) in a loosely covered beaker. Most of the solvent was allowed to evaporate gradually over 3 d. The resulting colorless or pale-orange plate-shaped crystals were collected after decantation and then washed with several drops of ice-cold 1:3 dichloromethane:pentane.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. A direct-methods solution was calculated, followed by full-matrix least squares/difference-Fourier cycles. All H atoms were placed in calculated positions ($\text{C}-\text{H} = 0.95 \text{ \AA}$, $\text{O}-\text{H} = 0.84 \text{ \AA}$) and refined as riding atoms with $U_{\text{iso}}(\text{H})$ set to $1.2U_{\text{eq}}(\text{C})$ and $1.5U_{\text{eq}}(\text{O})$.

Acknowledgements

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Table 3

Experimental details.

Crystal data	
Chemical formula	$\text{C}_8\text{H}_3\text{Br}_2\text{NO}_2 \cdot 0.5\text{C}_{14}\text{H}_{10}$
M_r	394.04
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	123
a, b, c (Å)	8.8963 (8), 9.4701 (9), 9.5839 (9)
α, β, γ (°)	115.356 (3), 106.876 (3), 94.119 (3)
V (Å ³)	680.03 (11)
Z	2
Radiation type	Cu $K\alpha$
μ (mm ⁻¹)	7.57
Crystal size (mm)	0.18 × 0.09 × 0.03
Data collection	
Diffractometer	Bruker VENTURE PHOTON-1000
Absorption correction	Multi-scan (<i>SADABS</i> ; Sheldrick, 1996)
$T_{\text{min}}, T_{\text{max}}$	0.509, 0.754
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	9139, 2745, 2607
R_{int}	0.035
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.625
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.026, 0.068, 1.06
No. of reflections	2745
No. of parameters	182
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	0.40, -0.53

Computer programs: *APEX2* and *SAINT* (Bruker, 2012), *SHELXS97* (Sheldrick 2015a), *SHELXL2014* (Sheldrick, 2015b), *Mercury* (Macrae *et al.*, 2008) and *pubCIF* (Westrip, 2010).

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supporting information

Acta Cryst. (2017). E73, 1743-1746 [https://doi.org/10.1107/S2056989017014815]

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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: *SHELXS97* (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-cyanobenzoic acid–anthracene (2/1)

Crystal data

$C_8H_3Br_2NO_2 \cdot 0.5C_{14}H_{10}$

$M_r = 394.04$

Triclinic, $P\bar{1}$

$a = 8.8963$ (8) Å

$b = 9.4701$ (9) Å

$c = 9.5839$ (9) Å

$\alpha = 115.356$ (3)°

$\beta = 106.876$ (3)°

$\gamma = 94.119$ (3)°

$V = 680.03$ (11) Å³

$Z = 2$

$F(000) = 382$

$D_x = 1.924$ Mg m⁻³

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

Cell parameters from 2967 reflections

$\theta = 5.3$ – 74.6 °

$\mu = 7.57$ mm⁻¹

$T = 123$ K

Plate, pale orange

$0.18 \times 0.09 \times 0.03$ mm

Data collection

Bruker VENTURE PHOTON-1000 diffractometer

φ and ω scans

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

$T_{\min} = 0.509$, $T_{\max} = 0.754$

9139 measured reflections

2745 independent reflections

2607 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.035$

$\theta_{\max} = 74.6$ °, $\theta_{\min} = 5.3$ °

$h = -11 \rightarrow 11$

$k = -11 \rightarrow 11$

$l = -11 \rightarrow 11$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.026$

$wR(F^2) = 0.068$

$S = 1.06$

2745 reflections

182 parameters

0 restraints

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0369P)^2 + 0.5603P]$

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

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

$\Delta\rho_{\max} = 0.40$ e Å⁻³

$\Delta\rho_{\min} = -0.53$ e Å⁻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)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.38562 (3)	0.12356 (3)	0.93908 (3)	0.01483 (9)
Br2	0.81803 (2)	0.51847 (3)	0.84679 (3)	0.01686 (9)
O1	0.21809 (18)	0.54610 (19)	0.5615 (2)	0.0154 (3)
H1A	0.1338	0.5671	0.5146	0.023*
O2	0.04198 (18)	0.38413 (18)	0.5858 (2)	0.0139 (3)
N1	0.8230 (2)	0.2641 (3)	1.0526 (3)	0.0211 (4)
C1	0.1800 (3)	0.4429 (2)	0.6097 (3)	0.0102 (4)
C2	0.3217 (2)	0.4018 (2)	0.7011 (2)	0.0092 (4)
C3	0.2929 (2)	0.2999 (2)	0.7650 (2)	0.0096 (4)
H3A	0.1859	0.2573	0.7495	0.011*
C4	0.4229 (3)	0.2615 (2)	0.8516 (2)	0.0100 (4)
C5	0.5815 (2)	0.3249 (2)	0.8767 (2)	0.0102 (4)
C6	0.7162 (3)	0.2888 (3)	0.9728 (3)	0.0135 (4)
C7	0.6057 (3)	0.4265 (3)	0.8107 (3)	0.0116 (4)
C8	0.4777 (3)	0.4647 (2)	0.7223 (2)	0.0103 (4)
H8A	0.4958	0.5328	0.6766	0.012*
C9	0.4142 (3)	0.8993 (2)	0.5372 (3)	0.0131 (4)
H9A	0.3562	0.8307	0.5622	0.016*
C10	0.5827 (3)	0.9268 (2)	0.5908 (3)	0.0126 (4)
C11	0.6714 (3)	0.8552 (3)	0.6831 (3)	0.0179 (5)
H11A	0.6149	0.7875	0.7102	0.022*
C12	0.8344 (3)	0.8823 (3)	0.7326 (3)	0.0230 (5)
H12A	0.8912	0.8345	0.7947	0.028*
C13	0.9206 (3)	0.9822 (3)	0.6915 (3)	0.0247 (5)
H13A	1.0347	0.9989	0.7249	0.030*
C14	0.8420 (3)	1.0540 (3)	0.6055 (3)	0.0198 (5)
H14A	0.9019	1.1211	0.5803	0.024*
C15	0.6700 (3)	1.0296 (2)	0.5522 (3)	0.0121 (4)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.01625 (14)	0.01597 (13)	0.01776 (14)	0.00482 (9)	0.00336 (10)	0.01426 (10)
Br2	0.00653 (13)	0.02493 (15)	0.02190 (14)	0.00266 (9)	0.00341 (10)	0.01464 (11)
O1	0.0098 (7)	0.0197 (8)	0.0244 (8)	0.0037 (6)	0.0021 (6)	0.0196 (7)
O2	0.0079 (7)	0.0163 (7)	0.0211 (8)	0.0027 (6)	0.0017 (6)	0.0141 (6)
N1	0.0163 (10)	0.0255 (10)	0.0221 (10)	0.0110 (8)	0.0021 (8)	0.0136 (9)
C1	0.0104 (10)	0.0099 (9)	0.0095 (9)	0.0028 (7)	0.0010 (7)	0.0053 (7)
C2	0.0092 (9)	0.0086 (9)	0.0081 (9)	0.0037 (7)	-0.0007 (7)	0.0046 (7)

C3	0.0084 (9)	0.0091 (9)	0.0107 (9)	0.0020 (7)	0.0014 (7)	0.0054 (7)
C4	0.0115 (10)	0.0100 (9)	0.0090 (9)	0.0045 (7)	0.0011 (8)	0.0062 (8)
C5	0.0080 (9)	0.0111 (9)	0.0082 (9)	0.0045 (7)	-0.0005 (7)	0.0035 (8)
C6	0.0117 (10)	0.0140 (10)	0.0131 (10)	0.0048 (8)	0.0025 (8)	0.0059 (8)
C7	0.0088 (9)	0.0128 (9)	0.0112 (9)	0.0016 (7)	0.0028 (8)	0.0044 (8)
C8	0.0113 (9)	0.0095 (9)	0.0108 (9)	0.0021 (7)	0.0025 (8)	0.0063 (8)
C9	0.0162 (10)	0.0082 (9)	0.0148 (10)	0.0001 (8)	0.0070 (8)	0.0047 (8)
C10	0.0172 (11)	0.0081 (9)	0.0113 (9)	0.0016 (8)	0.0056 (8)	0.0033 (8)
C11	0.0245 (12)	0.0125 (10)	0.0156 (10)	0.0033 (9)	0.0049 (9)	0.0069 (9)
C12	0.0257 (13)	0.0167 (11)	0.0196 (11)	0.0055 (9)	-0.0010 (10)	0.0082 (9)
C13	0.0135 (11)	0.0222 (12)	0.0276 (13)	0.0018 (9)	0.0007 (9)	0.0071 (10)
C14	0.0131 (11)	0.0152 (11)	0.0261 (12)	-0.0012 (8)	0.0052 (9)	0.0072 (9)
C15	0.0138 (10)	0.0073 (9)	0.0131 (9)	0.0000 (7)	0.0057 (8)	0.0027 (8)

Geometric parameters (Å, °)

Br1—C4	1.886 (2)	C8—H8A	0.9500
Br2—C7	1.890 (2)	C9—C15 ⁱ	1.394 (3)
O1—C1	1.309 (3)	C9—C10	1.400 (3)
O1—H1A	0.8400	C9—H9A	0.9500
O2—C1	1.224 (3)	C10—C11	1.432 (3)
N1—C6	1.142 (3)	C10—C15	1.432 (3)
C1—C2	1.493 (3)	C11—C12	1.356 (4)
C2—C3	1.390 (3)	C11—H11A	0.9500
C2—C8	1.391 (3)	C12—C13	1.423 (4)
C3—C4	1.386 (3)	C12—H12A	0.9500
C3—H3A	0.9500	C13—C14	1.359 (4)
C4—C5	1.402 (3)	C13—H13A	0.9500
C5—C7	1.394 (3)	C14—C15	1.433 (3)
C5—C6	1.446 (3)	C14—H14A	0.9500
C7—C8	1.381 (3)	C15—C9 ⁱ	1.394 (3)
C1—O1—H1A	109.5	C2—C8—H8A	120.5
O2—C1—O1	124.6 (2)	C15 ⁱ —C9—C10	121.3 (2)
O2—C1—C2	121.29 (19)	C15 ⁱ —C9—H9A	119.4
O1—C1—C2	114.08 (18)	C10—C9—H9A	119.4
C3—C2—C8	121.22 (19)	C9—C10—C11	122.1 (2)
C3—C2—C1	117.98 (18)	C9—C10—C15	119.3 (2)
C8—C2—C1	120.80 (19)	C11—C10—C15	118.6 (2)
C4—C3—C2	118.88 (19)	C12—C11—C10	121.2 (2)
C4—C3—H3A	120.6	C12—C11—H11A	119.4
C2—C3—H3A	120.6	C10—C11—H11A	119.4
C3—C4—C5	121.09 (19)	C11—C12—C13	120.0 (2)
C3—C4—Br1	119.34 (16)	C11—C12—H12A	120.0
C5—C4—Br1	119.57 (15)	C13—C12—H12A	120.0
C7—C5—C4	118.42 (19)	C14—C13—C12	121.0 (2)
C7—C5—C6	121.09 (19)	C14—C13—H13A	119.5
C4—C5—C6	120.47 (19)	C12—C13—H13A	119.5

N1—C6—C5	178.1 (2)	C13—C14—C15	120.7 (2)
C8—C7—C5	121.37 (19)	C13—C14—H14A	119.7
C8—C7—Br2	119.04 (16)	C15—C14—H14A	119.7
C5—C7—Br2	119.57 (16)	C9 ⁱ —C15—C10	119.5 (2)
C7—C8—C2	119.02 (19)	C9 ⁱ —C15—C14	122.1 (2)
C7—C8—H8A	120.5	C10—C15—C14	118.5 (2)
O2—C1—C2—C3	-2.9 (3)	Br2—C7—C8—C2	-177.60 (15)
O1—C1—C2—C3	176.48 (18)	C3—C2—C8—C7	-1.0 (3)
O2—C1—C2—C8	177.60 (19)	C1—C2—C8—C7	178.55 (18)
O1—C1—C2—C8	-3.1 (3)	C15 ⁱ —C9—C10—C11	179.81 (19)
C8—C2—C3—C4	0.2 (3)	C15 ⁱ —C9—C10—C15	-0.3 (3)
C1—C2—C3—C4	-179.35 (18)	C9—C10—C11—C12	179.4 (2)
C2—C3—C4—C5	0.6 (3)	C15—C10—C11—C12	-0.5 (3)
C2—C3—C4—Br1	179.97 (14)	C10—C11—C12—C13	-0.6 (4)
C3—C4—C5—C7	-0.7 (3)	C11—C12—C13—C14	1.2 (4)
Br1—C4—C5—C7	180.00 (14)	C12—C13—C14—C15	-0.7 (4)
C3—C4—C5—C6	177.55 (18)	C9—C10—C15—C9 ⁱ	0.3 (3)
Br1—C4—C5—C6	-1.8 (3)	C11—C10—C15—C9 ⁱ	-179.81 (19)
C4—C5—C7—C8	-0.1 (3)	C9—C10—C15—C14	-178.88 (19)
C6—C5—C7—C8	-178.35 (19)	C11—C10—C15—C14	1.0 (3)
C4—C5—C7—Br2	178.40 (14)	C13—C14—C15—C9 ⁱ	-179.6 (2)
C6—C5—C7—Br2	0.2 (3)	C13—C14—C15—C10	-0.4 (3)
C5—C7—C8—C2	1.0 (3)		

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1A ⁱⁱ —O2 ⁱⁱ	0.84	1.79	2.627 (2)	178

Symmetry code: (ii) $-x, -y+1, -z+1$.