



Anomalous halogen bonds in the crystal structures of 1,2,3-tribromo-5-nitrobenzene and 1,3-dibromo-2-iodo-5-nitrobenzene

José A. Romero,^a Gerardo Aguirre Hernández^a and Sylvain Bernès^{b*}Received 1 July 2015
Accepted 12 July 2015^aCentro de Graduados e Investigación en Química, Instituto Tecnológico de Tijuana, Apdo. Postal 1166, 22510 Tijuana, B.C., Mexico, and ^bInstituto de Física, Benemérita Universidad Autónoma de Puebla, Av. San Claudio y 18 Sur, 72570 Puebla, Pue., Mexico. *Correspondence e-mail: sylvain_bernes@hotmail.com

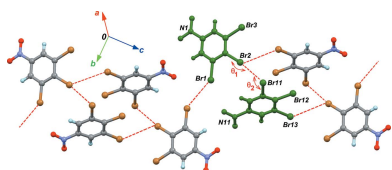
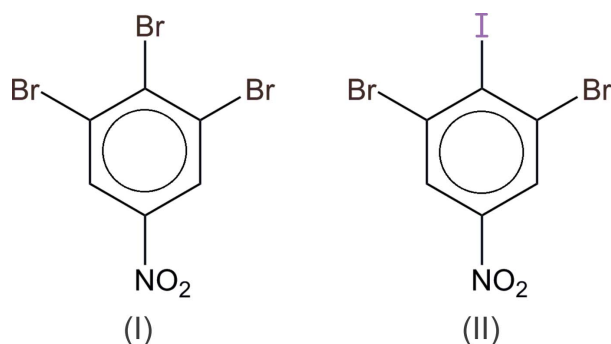
Edited by W. T. A. Harrison, University of Aberdeen, Scotland

Keywords: crystal structure; polyhalogenated benzene; halogen bond; bromine; iodine**CCDC references:** 1412444; 1412445**Supporting information:** this article has supporting information at journals.iucr.org/e

The title trihalogenated nitrobenzene derivatives, C₆H₂Br₃NO₂ and C₆H₂Br₂INO₂, crystallize in triclinic and monoclinic cells, respectively, with two molecules per asymmetric unit in each case. The asymmetric unit of the tribromo compound features a polarized Br^{δ+}···Br^{δ-} intermolecular halogen bond. After substitution of the Br atom in the *para* position with respect to the nitro group, the network of X···X halogen contacts is reorganized. Two intermolecular polarized halogen bonds are then observed, which present the uncommon polarization Br^{δ+}···I^{δ-}: the more electronegative site (Br) behaves as a donor and the less electronegative site (I) as an acceptor for the charge transfer.

1. Chemical context

Within the large class of non-covalent interactions studied in chemical crystallography, halogen bonds are of special interest in crystal engineering. The stabilizing interaction between a halogen atom and a Lewis base, X···B, shares many aspects with classical hydrogen bonds, but is more directional. On the other hand, halogen contacts X···X are more difficult to conceptualize (Wang *et al.*, 2014), for instance because the charge transfer in the Br···Br contact is not as obvious as in hydrogen bonds. Evidence supporting the importance of this topic is the recent organization of an international meeting dedicated to halogen bonding (Erdelyi, 2014).



In this context, we are engaged in the synthesis and structural characterization of a series of halogen-substituted nitrobenzenes. The present communication describes two closely related compounds in the series, which differ only by the halogen atom substituting at the ring position *para* to the nitro group. Despite the small chemical modification, the resulting crystal structures are very different, as a consequence of a different network of halogen bonds.

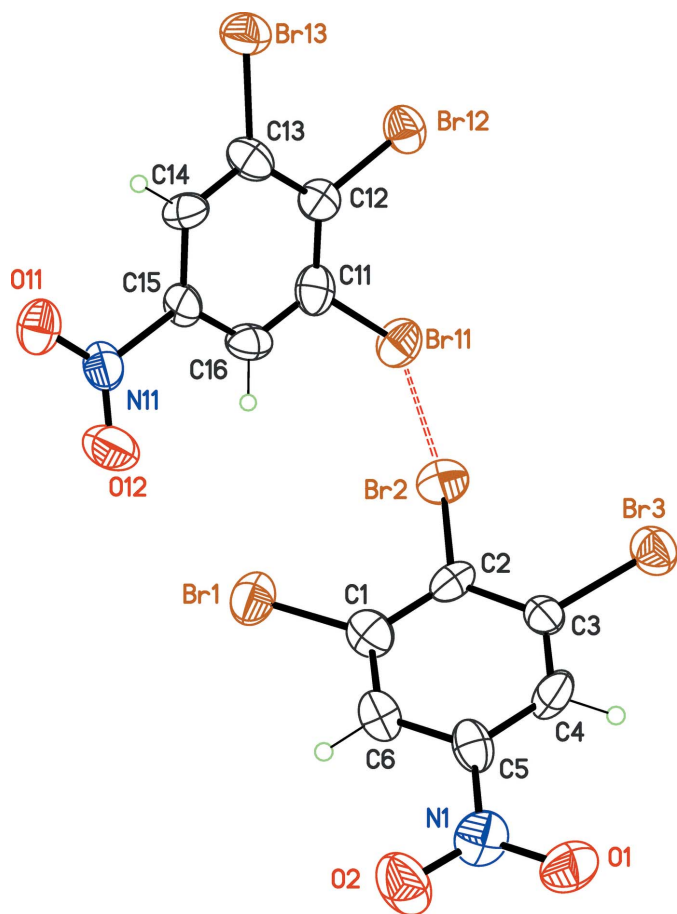


Figure 1
The asymmetric unit of (I), with displacement ellipsoids at the 30% probability level. The dashed bond connecting the independent molecules is a type-II halogen bond.

2. Structural commentary

Both compounds crystallize with two molecules in the asymmetric unit, but in different space groups. The tribromo derivative, (I, Fig. 1), is a $P\bar{1}$ crystal isomorphous to the chloro analogue (Bhar *et al.*, 1995), although the unit-cell parameters are significantly larger for (I) compared to the chloro compound: the cell volume is increased by more than 7%. In the present work, we retained the Niggli reduced triclinic cell ($a < b < c$), while Bhar *et al.* used a non-reduced cell. Moreover, the asymmetric unit content was defined in order to emphasize the strongest $\text{Br} \cdots \text{Br}$ bond in (I). The bromo-iodo derivative (II, Fig. 2) crystallizes in the monoclinic system and, in that case, the standard setting was used for space group $P2_1/c$.

The C–halogen bond lengths are as expected. In (I), C–Br distances are in the range 1.821 (12)–1.886 (11) Å, slightly shorter than C–Br bond lengths observed in hexabromobenzene, 1.881 Å ($T = 100$ K; Reddy *et al.*, 2006) or 1.871 Å (synchrotron study, $T = 100$ K; Brezgunova *et al.*, 2012). In (II), C–Br bond lengths are longer, 1.875 (13) to 1.895 (14) Å, while the C–I bond lengths, 2.088 (12) and 2.074 (14) Å, may be compared to bonds in hexaiodobenzene, 2.109 Å ($T = 100$ K; Ghosh *et al.*, 2007) or 1,2,3-triiodobenzene, 2.090 Å (T

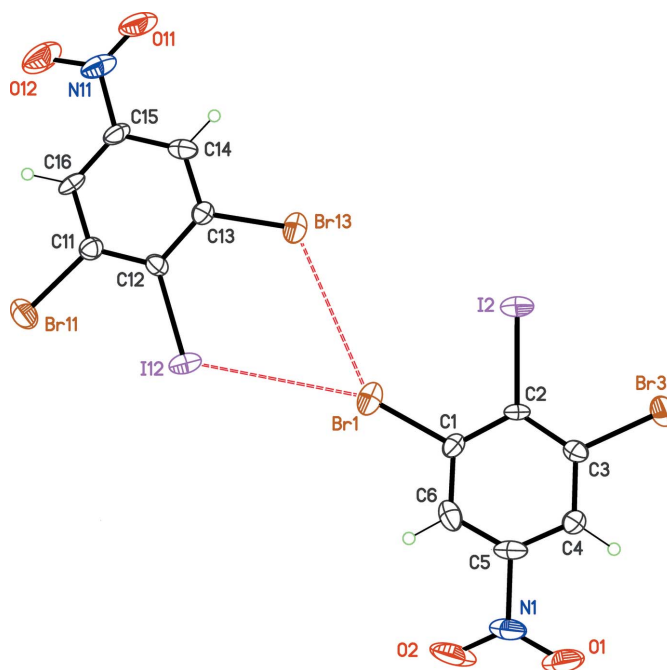


Figure 2
The asymmetric unit of (II), with displacement ellipsoids at the 30% probability level. The dashed bonds connecting the independent molecules are halogen contacts.

= 223 K, Novak & Li, 2007). Indeed, differences in bond lengths between perhalogenated and trihalogenated derivatives are within experimental errors, and the substitution of the 5-position by the nitro electron-withdrawing group in (I) and (II) has probably little influence on these bonds.

The important feature in these halogenated molecules is rather the possibility of steric repulsion between vicinal halogen atoms, which is related to the reduction of endocyclic angles. Regarding this point, it is worth reading the *Acta E* article about 1,2,3-triiodobenzene (Novak & Li, 2007). As in polyiodo derivatives, intramolecular steric crowding between the halogen atoms in (I) and (II) is offset by benzene ring distortion. As a consequence, the C1–C2–C3 and equivalent C11–C12–C13 angles are systematically less than 120° : 116.2 (11) and 118.8 (13) $^\circ$ in (I); 118.1 (12) and 117.3 (13) $^\circ$ in (II). Again, the nitro group has little influence on intramolecular halogen \cdots halogen contacts. For instance, in 1,3-dibromo-2-iodobenzene, the C1–C2–C3 angle is 118.0 $^\circ$ (Schmidbaur *et al.*, 2004), very close to that observed in (II), which presents the same halogen substitution.

The 5-nitro substituent is almost conjugated with the benzene nucleus in (I): the dihedral angle between the NO_2 plane and the benzene ring is 6(2) and 1(2) $^\circ$ for each independent molecule. For (II), twisting of the NO_2 groups is more significant, with dihedral angles of 10 (1) and 7(1) $^\circ$. This near planar conformation is identical to that observed for 1,2,3-trichloro-5-nitrobenzene (Bhar *et al.*, 1995), but contrasts with the twisted conformation observed in perhalogenated nitrobenzene derivatives: pentachloronitrobenzene (twist angle of NO_2 : 62 $^\circ$; Tanaka *et al.*, 1974) and 1-bromo-2,3,5,6-tetrafluoro-4-nitrobenzene (twist angle of NO_2 : 41.7 (3) $^\circ$; Stein *et al.*,

Table 1
Halogen-bond geometry (Å, °) for (I).

$X_1 \cdots X_2$	d	θ_1	θ_2	bond type
Br2 \cdots Br11	3.642 (3)	165.2 (5)	82.3 (5)	II-polarized
Br1 \cdots Br1 ⁱ	3.731 (4)	133.3 (4)	133.3 (4)	I-unpolarized
Br2 \cdots Br13 ⁱⁱ	3.781 (3)	126.8 (4)	129.6 (4)	I-unpolarized

Notes: d = separation $X_1 \cdots X_2$; θ_1 = angle $C-X_1 \cdots X_2$; θ_2 = angle $X_1 \cdots X_2-C$. For halogen bond types, see: Reddy *et al.* (2006). Symmetry codes: (i) $-x, 1-y, -z$; (ii) $-x, -y, 1-z$.

Table 2
Halogen-bond geometry (Å, °) for (II).

$X_1 \cdots X_2$	d	θ_1	θ_2	bond type
Br1 \cdots I12	3.813 (2)	161.2 (4)	117.2 (4)	II-polarized
I2 \cdots Br11 ⁱ	3.893 (2)	116.6 (4)	161.8 (4)	II-polarized
Br1 \cdots Br13	3.787 (2)	142.8 (4)	122.9 (4)	I-unpolarized
Br11 \cdots Br3 ⁱⁱ	3.858 (2)	143.9 (4)	124.4 (4)	I-unpolarized

Notes: d = separation $X_1 \cdots X_2$; θ_1 = angle $C-X_1 \cdots X_2$; θ_2 = angle $X_1 \cdots X_2-C$. For halogen bond types, see: Reddy *et al.* (2006). Symmetry codes: (i) $1+x, y, z$; (ii) $-1+x, y, z$.

2011). It thus seems clear that twisting of the nitro group with respect to the benzene ring in nitrobenzene derivatives is a direct consequence of intramolecular crowding with *ortho* substituents. For 1,2,3-halogenated-5-nitrobenzenes such as (I) and (II), a planar conformation should be expected as a rule.

3. Supramolecular features

The crystal structures are directed by intermolecular weak halogen bonds, also known as type-II interactions in the Desiraju classification scheme (Reddy *et al.*, 2006). Such a bond is present in the asymmetric unit of (I), between Br2 and Br11 (Fig. 3). The type-II arrangement is characterized by angles $\theta_1 = C2-Br2 \cdots Br11$ and $\theta_2 = C11-Br11 \cdots Br2$, which

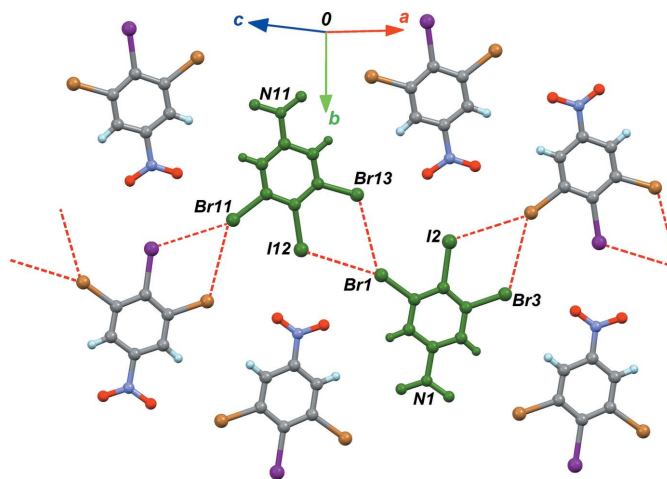


Figure 4
Part of the crystal structure of (II), emphasizing the halogen bonds (dashed lines). The green molecules correspond to the asymmetric unit.

should be close to 180 and 90°, respectively. For (I), observed angles are $\theta_1 = 165.2(5)^\circ$ and $\theta_2 = 82.3(5)^\circ$. The crystal packing thus polarizes the involved halogen atoms, forming the halogen bond $Br2^{\delta+} \cdots Br11^{\delta-}$. This dimolecular polar unit is connected *via* inversion centers to neighboring units in the cell, forming $C-H \cdots Br$ hydrogen bonds, and $O \cdots Br$ contacts. This packing motif induces secondary halogen \cdots halogen contacts, which are clearly unpolarized. These type-I interactions are characterized by angles $\theta_1 \simeq \theta_2$ (Table 1, entries 2 and 3) and display larger $Br \cdots Br$ separations compared to the polarized halogen bond (entry 1), in which electrostatic forces bring the atoms into close contact.

The substitution of one Br atom by I, to form crystal (II), changes dramatically the packing structure, affording a more complex network of halogen contacts (Fig. 4 and Table 2). Within the asymmetric unit, the type-II polarized contact is $Br1 \cdots I12$ (Table 2, entry 1). However, θ angles for this bond deviate from ideal values, and, surprisingly, the bond is

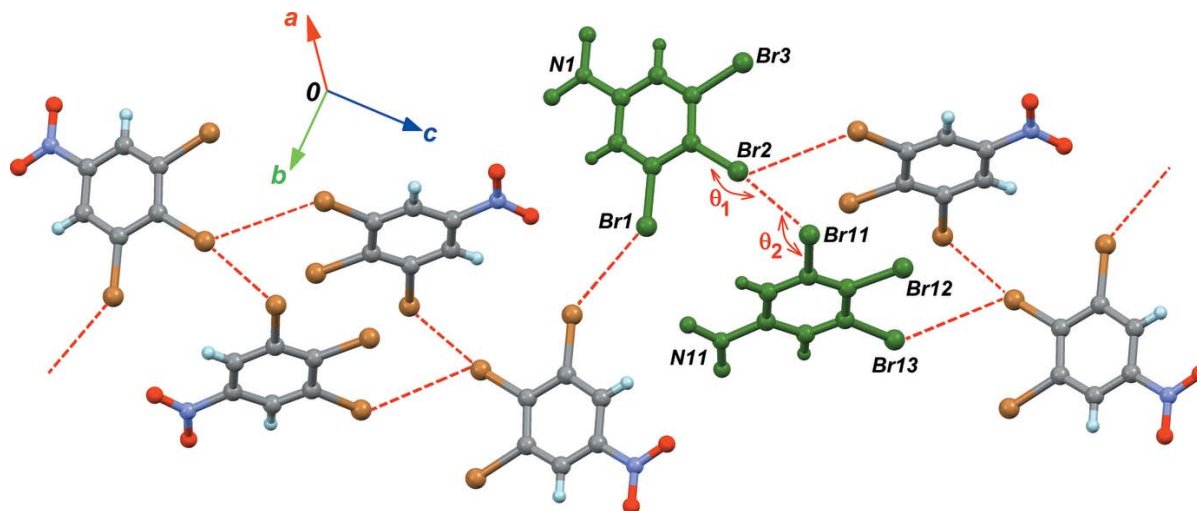


Figure 3
Part of the crystal structure of (I), emphasizing the halogen bonds (dashed lines). The green molecules correspond to the asymmetric unit.

polarized in the wrong way, $\text{Br}^{\delta+} \cdots \text{I}^{\delta-}$. The opposite polarization was expected for this bond, due to the lower electronegativity and higher polarizability of iodine compared to bromine. The other significant contact observed in the asymmetric unit is a $\text{Br} \cdots \text{Br}$ unpolarized contact. The network of halogen bonds is expanded in the [100] direction by Br11, which gives a bifurcated contact with I2 and Br3 (Table 2, entries 2 and 4). One contact is polarized, with the polarization, once again, oriented in the unexpected way, $\text{I2}^{\delta-} \cdots \text{Br11}^{\delta+}$. These anomalous halogen bonds are not present in other mixed halogen derivatives. Indeed, in 1,3-dibromo-2-iodobenzene (Schmidbaur *et al.*, 2004), the iodine atom is not engaged in halogen bonding.

4. Database survey

The current release of the CSD (Version 5.36 with all updates; Groom & Allen, 2014), contains many structures of halogen-substituted nitrobenzene, with Cl (*e.g.* Bhar *et al.*, 1995; Tanaka *et al.*, 1974), Br (*e.g.* Olaru *et al.*, 2014), and I (Thalladi *et al.*, 1996). This series is completed with nitrophenol derivatives, for example 2,3-difluoro-4-iodo-6-nitrophenol (Francke *et al.*, 2010). Structures of pentachlorophenol (Brezgunova *et al.*, 2012) and pentabromophenol (Betz *et al.*, 2008; Brezgunova *et al.*, 2012) are also available.

Regarding poly- and per-halogenated benzene structures, an impressive series of 23 compounds has been described, including Cl, Br, I and Me as substituents, generating a variety

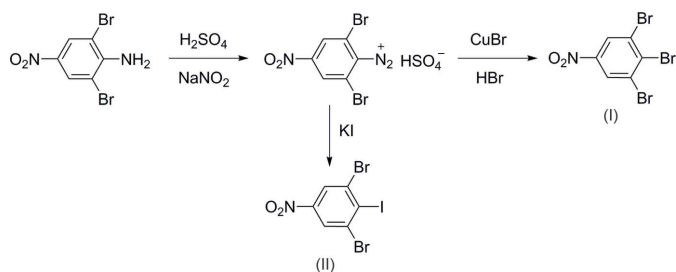


Figure 5
Synthetic scheme for (I) and (II).

of molecular symmetries (Reddy *et al.*, 2006). The structure of D_{6h} -perhalogenated benzene has been reported with F (Shorafa *et al.*, 2009), Cl (Brown & Strydom, 1974; Reddy *et al.*, 2006), Br (Baharie & Pawley, 1979; Reddy *et al.*, 2006; Brezgunova *et al.*, 2012) and I (Ghosh *et al.*, 2007). The former is a $Z' = 2$ crystal, while others are $Z' = 1$ crystals.

5. Synthesis and crystallization

Compounds (I) and (II) were synthesized from 2,6-dibromo-4-nitroaniline (Bryant *et al.*, 1998), as depicted in Fig. 5.

Synthesis of (I). A solution of 2,6-dibromo-4-nitroaniline (1.0 g, 3.38 mmol) in acetic acid (3 ml) was cooled to 278 K, and concentrated H_2SO_4 (7 ml) was carefully added under stirring. While ensuring that the temperature was still below 278 K, NaNO_2 (0.708 g, 10.26 mmol) was added in one batch. The reaction was stirred at this temperature for 2 h to afford

Table 3
Experimental details.

	(I)	(II)
Crystal data		
Chemical formula	$\text{C}_6\text{H}_2\text{Br}_3\text{NO}_2$	$\text{C}_6\text{H}_2\text{Br}_2\text{INO}_2$
M_r	359.82	406.81
Crystal system, space group	Triclinic, $P\bar{1}$	Monoclinic, $P2_1/c$
Temperature (K)	298	298
a, b, c (Å)	7.641 (5), 8.040 (5), 14.917 (6)	13.548 (3), 20.037 (3), 9.123 (2)
α, β, γ (°)	83.91 (3), 79.86 (4), 81.49 (4)	90, 130.37 (2), 90
V (Å ³)	889.2 (8)	1886.8 (8)
Z	4	8
Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ (mm ⁻¹)	13.57	11.82
Crystal size (mm)	0.42 × 0.40 × 0.30	0.50 × 0.22 × 0.12
Data collection		
Diffractometer	Bruker P4	Bruker P4
Absorption correction	Part of the refinement model (ΔF) (Walker & Stuart, 1983)	ψ scan (XSCANS; Bruker, 1997)
T_{\min}, T_{\max}	0.0002, 0.001	0.429, 0.988
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	6070, 3141, 1503	5716, 5407, 1968
R_{int}	0.120	0.058
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.596	0.703
Refinement		
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.066, 0.196, 1.47	0.061, 0.153, 0.95
No. of reflections	3141	5407
No. of parameters	218	218
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	0.79, -1.00	0.84, -0.84

Computer programs: XSCANS (Bruker, 1997), SHELXS2014 (Sheldrick, 2008), SHELXL2014 (Sheldrick, 2015) and Mercury (Macrae *et al.*, 2008).

the diazonium salt. An aqueous solution (17.67 ml) of CuBr (4.95 g, 34.54 mmol) and 47% HBr (17.67 ml) was warmed to 343 K, and the diazotization solution previously prepared was added in one batch with stirring. The mixture was kept at 343 K for 1 h, and then left to cool overnight. The reaction was neutralized with NaOH and extracted with CH₂Cl₂ (3 × 30 ml). The resulting solution was concentrated under vacuum and the crude material was purified by flash chromatography (petroleum ether/CH₂Cl₂ 8/2, R_f = 0.49) to give (I). Crystals were obtained by slow evaporation of a methanol/ethyl ether solution (yield: 0.952 g, 2.65 mmol, 78%). m.p. 380–382 K. IR (KBr, cm⁻¹): 3090 (Ar–H); 1583 (C=C); 1526, 1342 (N=O); 738 (C–Br). ¹H-NMR (600 MHz, CDCl₃): δ 8.43 (s, H-4, H-6). ¹³C-NMR (150 MHz, CDCl₃): δ 146.8, 135.7, 127.0, 126.9, 126.8. EIMS m/z: [M⁺] 357 (34), [M⁺+2] 359 (7), [M⁺+4] 361 (100), [M⁺+6] 363 (36) [M⁺-NO₂] 311 (12).

Synthesis of (II). A solution of 2,6-dibromo-4-nitroaniline (1.0 g, 3.38 mmol) in acetic acid (3 ml) was cooled to 278 K in an ice-salt bath, and concentrated H₂SO₄ (3 ml) was carefully added under stirring. While ensuring that the temperature was still below 278 K, NaNO₂ (0.242 g, 3.516 mmol) was added in one batch. The reaction was stirred at this temperature for 30 min to afford the diazonium salt. An aqueous solution (10 ml) of KI (5.635 g, 33.95 mmol) was prepared, and the diazotization solution previously prepared was added in one batch. The mixture was then further stirred for 1 h. The reaction was neutralized with NaOH, extracted with CH₂Cl₂ (3 × 30 ml), and concentrated under vacuum. The crude material was purified by flash chromatography (petroleum ether/CH₂Cl₂ 4/1, R_f = 0.31) to give (II). Crystals were obtained by slow evaporation of an acetone/methanol/CH₂Cl₂ solution (yield: 1.21 g, 2.98 mmol, 88%). m.p. 415–417 K. IR (KBr, cm⁻¹): 3010 (Ar–H); 1620, 1516 (C=C); 1336 (N=O). ¹H-NMR (600 MHz, CDCl₃): δ 8.38 (s, H-4, H-6). ¹³C-NMR (150 MHz, CDCl₃): δ 146.1, 142.4, 127.4, 124.1. EIMS m/z: [M⁺] 405 (42), [M⁺+2] 407 (100), [M⁺+4] 409 (48).

6. Refinement

Crystal data, data collection and structure refinement details for (I) and (II) are summarized in Table 3. The absorption correction for (I) was challenging, and eventually carried out by applying *DIFABS* on the complete isotropic model (Walker & Stuart, 1983). In the case of (II), measured ψ -scans were used. H atoms were refined as riding to their carrier C

atoms, with C–H bond lengths fixed at 0.93 Å and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{carrier atom})$.

Acknowledgements

We acknowledge the contribution of Angélica Navarrete to the synthesis of the reported compounds.

References

- Baharie, E. & Pawley, G. S. (1979). *Acta Cryst.* **A35**, 233–235.
 Betz, R., Klüfers, P. & Mayer, P. (2008). *Acta Cryst.* **E64**, o1921.
 Bhar, A., Aune, J. P., Benali-Cherif, N., Benmenni, L. & Giorgi, M. (1995). *Acta Cryst.* **C51**, 256–260.
 Brezgunova, M. E., Aubert, E., Dahaoui, S., Fertey, P., Lebègue, S., Jelsch, C., Ángyán, J. G. & Espinosa, E. (2012). *Cryst. Growth Des.* **12**, 5373–5386.
 Brown, G. M. & Strydom, O. A. W. (1974). *Acta Cryst.* **B30**, 801–804.
 Bruker (1997). *XSCANS*. Bruker Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
 Bryant, R., James, S. C., Norman, N. C. & Orpen, A. G. (1998). *Acta Cryst.* **C54**, 1113–1115.
 Erdelyi, M. (2014). *Nat. Chem.* **6**, 762–764.
 Francke, R., Schnakenburg, G. & Waldvogel, S. R. (2010). *Eur. J. Org. Chem.* pp. 2357–2362.
 Ghosh, S., Reddy, C. M. & Desiraju, G. R. (2007). *Acta Cryst.* **E63**, o910–o911.
 Groom, C. R. & Allen, F. H. (2014). *Angew. Chem. Int. Ed.* **53**, 662–671.
 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.
 Novak, I. & Li, D. (2007). *Acta Cryst.* **E63**, o438–o439.
 Olaru, M., Beckmann, J. & Rač, C. I. (2014). *Organometallics*, **33**, 3012–3020.
 Reddy, C. M., Kirchner, M. T., Gundakaram, R. C., Padmanabhan, K. A. & Desiraju, G. R. (2006). *Chem. Eur. J.* **12**, 2222–2234.
 Schmidbaur, H., Minge, O. & Nogai, S. (2004). *Z. Naturforsch. Teil B*, **59**, 264–268.
 Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
 Sheldrick, G. M. (2015). *Acta Cryst.* **C71**, 3–8.
 Shorafa, H., Mollenhauer, D., Paulus, B. & Seppelt, K. (2009). *Angew. Chem. Int. Ed.* **48**, 5845–5847.
 Stein, M., Schwarzer, A., Hulliger, J. & Weber, E. (2011). *Acta Cryst.* **E67**, o1655.
 Tanaka, I., Iwasaki, F. & Aihara, A. (1974). *Acta Cryst.* **B30**, 1546–1549.
 Thalladi, V. R., Goud, B. S., Hoy, V. J., Allen, F. H., Howard, J. A. K. & Desiraju, G. R. (1996). *Chem. Commun.* pp. 401–402.
 Walker, N. & Stuart, D. (1983). *Acta Cryst.* **A39**, 158–166.
 Wang, C., Danovich, D., Mo, Y. & Shaik, S. (2014). *J. Chem. Theory Comput.* **10**, 3726–3737.

supporting information

Acta Cryst. (2015). E71, 960-964 [doi:10.1107/S2056989015013377]

Anomalous halogen bonds in the crystal structures of 1,2,3-tribromo-5-nitrobenzene and 1,3-dibromo-2-iodo-5-nitrobenzene

José A. Romero, Gerardo Aguirre Hernández and Sylvain Bernès

Computing details

For both compounds, data collection: *XSCANS* (Bruker, 1997); cell refinement: *XSCANS* (Bruker, 1997); data reduction: *XSCANS* (Bruker, 1997); program(s) used to solve structure: *SHELXS2014* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *SHELXL2014* (Sheldrick, 2015).

(I) 1,2,3-Tribromo-5-nitrobenzene

Crystal data

$C_6H_2Br_3NO_2$

$M_r = 359.82$

Triclinic, $P1$

$a = 7.641$ (5) Å

$b = 8.040$ (5) Å

$c = 14.917$ (6) Å

$\alpha = 83.91$ (3)°

$\beta = 79.86$ (4)°

$\gamma = 81.49$ (4)°

$V = 889.2$ (8) Å³

$Z = 4$

$F(000) = 664$

$D_x = 2.688$ Mg m⁻³

Melting point: 380 K

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

Cell parameters from 48 reflections

$\theta = 4.8$ – 12.4 °

$\mu = 13.57$ mm⁻¹

$T = 298$ K

Irregular, colourless

$0.42 \times 0.40 \times 0.30$ mm

Data collection

Bruker P4

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

ω scans

Absorption correction: part of the refinement

model (ΔF)

(Walker & Stuart, 1983)

$T_{\min} = 0.0002$, $T_{\max} = 0.001$

6070 measured reflections

3141 independent reflections

1503 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.120$

$\theta_{\max} = 25.1$ °, $\theta_{\min} = 2.6$ °

$h = -8 \rightarrow 9$

$k = -9 \rightarrow 9$

$l = 0 \rightarrow 17$

3 standard reflections every 97 reflections

intensity decay: 1%

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.066$

$wR(F^2) = 0.196$

$S = 1.47$

3141 reflections

218 parameters

0 restraints

0 constraints

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

$$w = 1/[\sigma^2(F_o^2) + (0.050P)^2]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

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

$$\Delta\rho_{\max} = 0.79 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -1.00 \text{ e } \text{\AA}^{-3}$$

Extinction correction: *SHELXL2014* (Sheldrick, 2015), $F_c^* = kFc[1 + 0.001x Fc^2 \lambda^3 / \sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.0063 (12)

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.1438 (2)	0.3194 (2)	0.05082 (13)	0.0863 (6)
Br2	0.2958 (2)	0.0254 (2)	0.20089 (11)	0.0855 (6)
Br3	0.4312 (2)	-0.3604 (2)	0.13778 (10)	0.0791 (5)
C1	0.2177 (18)	0.1018 (19)	0.0215 (9)	0.070 (4)
C2	0.2831 (17)	-0.0235 (17)	0.0860 (9)	0.063 (3)
C3	0.3360 (14)	-0.1910 (16)	0.0555 (8)	0.056 (3)
C4	0.3227 (18)	-0.2259 (19)	-0.0296 (9)	0.069 (4)
H4	0.3573	-0.3355	-0.0465	0.083*
C5	0.2615 (17)	-0.1072 (16)	-0.0895 (10)	0.064 (3)
C6	0.2067 (16)	0.0562 (16)	-0.0661 (9)	0.059 (3)
H6	0.1619	0.1373	-0.1085	0.071*
N1	0.2502 (16)	-0.1453 (18)	-0.1809 (8)	0.075 (3)
O1	0.2967 (16)	-0.2925 (16)	-0.2012 (7)	0.094 (3)
O2	0.1923 (18)	-0.0342 (15)	-0.2318 (8)	0.105 (4)
Br11	0.3943 (2)	0.2012 (2)	0.39885 (13)	0.0891 (6)
Br12	0.1013 (2)	0.1170 (2)	0.58586 (10)	0.0795 (6)
Br13	-0.3231 (2)	0.2845 (2)	0.59130 (11)	0.0865 (6)
C11	0.151 (2)	0.2912 (18)	0.4092 (12)	0.077 (4)
C12	0.0303 (18)	0.2505 (18)	0.4860 (10)	0.064 (3)
C13	-0.150 (2)	0.323 (2)	0.4913 (9)	0.073 (4)
C14	-0.2002 (19)	0.4188 (19)	0.4208 (9)	0.070 (4)
H14	-0.3207	0.4619	0.4232	0.084*
C15	-0.079 (2)	0.4583 (18)	0.3427 (8)	0.068 (4)
C16	0.0943 (19)	0.3923 (18)	0.3375 (9)	0.068 (4)
H16	0.1756	0.4155	0.2850	0.082*
N11	-0.1327 (18)	0.5801 (16)	0.2644 (10)	0.076 (3)
O11	-0.2882 (14)	0.6432 (13)	0.2757 (7)	0.083 (3)
O12	-0.0224 (17)	0.5952 (18)	0.1956 (8)	0.110 (4)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0776 (11)	0.0671 (10)	0.1094 (12)	-0.0047 (8)	-0.0022 (9)	-0.0140 (8)
Br2	0.0876 (11)	0.0974 (13)	0.0716 (9)	-0.0124 (9)	-0.0075 (8)	-0.0164 (8)
Br3	0.0765 (10)	0.0789 (11)	0.0793 (10)	-0.0043 (8)	-0.0186 (8)	0.0070 (8)
C1	0.062 (8)	0.078 (10)	0.072 (9)	-0.013 (7)	-0.022 (7)	0.001 (7)
C2	0.058 (8)	0.068 (9)	0.062 (8)	-0.006 (7)	0.004 (6)	-0.026 (7)
C3	0.034 (6)	0.064 (8)	0.060 (7)	-0.001 (6)	0.001 (6)	0.012 (6)

C4	0.063 (8)	0.072 (9)	0.071 (9)	0.022 (7)	-0.018 (7)	-0.030 (7)
C5	0.056 (8)	0.051 (8)	0.087 (10)	-0.015 (6)	-0.021 (7)	0.009 (7)
C6	0.062 (8)	0.052 (8)	0.073 (8)	-0.019 (6)	-0.033 (7)	0.003 (6)
N1	0.079 (8)	0.081 (9)	0.080 (8)	-0.016 (7)	-0.036 (7)	-0.026 (7)
O1	0.119 (9)	0.095 (9)	0.071 (6)	-0.005 (7)	-0.017 (6)	-0.032 (6)
O2	0.151 (11)	0.087 (9)	0.089 (7)	-0.010 (8)	-0.061 (8)	0.004 (6)
Br11	0.0644 (10)	0.0993 (13)	0.1026 (12)	0.0018 (9)	-0.0185 (9)	-0.0137 (10)
Br12	0.0955 (12)	0.0701 (10)	0.0769 (9)	-0.0090 (8)	-0.0294 (9)	-0.0017 (7)
Br13	0.0785 (11)	0.0945 (13)	0.0808 (10)	-0.0202 (9)	0.0012 (8)	0.0067 (9)
C11	0.084 (10)	0.050 (8)	0.102 (11)	-0.013 (7)	-0.021 (9)	-0.015 (8)
C12	0.060 (8)	0.062 (8)	0.073 (9)	-0.018 (7)	-0.012 (8)	-0.008 (7)
C13	0.081 (10)	0.082 (10)	0.060 (8)	-0.020 (8)	-0.024 (7)	0.009 (7)
C14	0.056 (8)	0.080 (10)	0.065 (8)	-0.010 (7)	0.011 (7)	-0.007 (7)
C15	0.088 (10)	0.077 (10)	0.040 (6)	0.019 (8)	-0.034 (7)	-0.004 (6)
C16	0.070 (9)	0.072 (9)	0.062 (8)	-0.028 (8)	0.006 (7)	-0.003 (7)
N11	0.067 (8)	0.065 (8)	0.093 (10)	-0.005 (6)	-0.017 (7)	0.011 (7)
O11	0.074 (7)	0.079 (7)	0.099 (7)	0.003 (6)	-0.032 (6)	-0.014 (6)
O12	0.097 (8)	0.144 (12)	0.077 (7)	-0.012 (8)	-0.011 (7)	0.028 (7)

Geometric parameters (Å, °)

Br1—C1	1.831 (15)	Br11—C11	1.877 (15)
Br2—C2	1.821 (12)	Br12—C12	1.854 (14)
Br3—C3	1.886 (11)	Br13—C13	1.842 (15)
C1—C6	1.415 (18)	C11—C16	1.368 (19)
C1—C2	1.416 (18)	C11—C12	1.38 (2)
C2—C3	1.445 (18)	C12—C13	1.410 (19)
C3—C4	1.353 (17)	C13—C14	1.313 (18)
C4—C5	1.328 (17)	C14—C15	1.39 (2)
C4—H4	0.9300	C14—H14	0.9300
C5—C6	1.381 (19)	C15—C16	1.347 (19)
C5—N1	1.448 (18)	C15—N11	1.515 (16)
C6—H6	0.9300	C16—H16	0.9300
N1—O2	1.194 (15)	N11—O11	1.211 (15)
N1—O1	1.238 (16)	N11—O12	1.216 (16)
C6—C1—C2	119.0 (13)	C16—C11—C12	120.4 (14)
C6—C1—Br1	119.9 (9)	C16—C11—Br11	118.6 (13)
C2—C1—Br1	121.0 (10)	C12—C11—Br11	120.9 (11)
C1—C2—C3	116.2 (11)	C11—C12—C13	118.8 (13)
C1—C2—Br2	121.3 (10)	C11—C12—Br12	122.1 (10)
C3—C2—Br2	122.5 (9)	C13—C12—Br12	118.9 (10)
C4—C3—C2	121.8 (11)	C14—C13—C12	118.8 (14)
C4—C3—Br3	120.6 (10)	C14—C13—Br13	118.0 (11)
C2—C3—Br3	117.6 (9)	C12—C13—Br13	123.1 (10)
C5—C4—C3	121.5 (13)	C13—C14—C15	122.5 (13)
C5—C4—H4	119.3	C13—C14—H14	118.8
C3—C4—H4	119.3	C15—C14—H14	118.8

C4—C5—C6	120.7 (13)	C16—C15—C14	119.2 (11)
C4—C5—N1	121.1 (13)	C16—C15—N11	117.9 (13)
C6—C5—N1	118.2 (11)	C14—C15—N11	122.8 (12)
C5—C6—C1	120.8 (11)	C15—C16—C11	120.0 (14)
C5—C6—H6	119.6	C15—C16—H16	120.0
C1—C6—H6	119.6	C11—C16—H16	120.0
O2—N1—O1	123.6 (12)	O11—N11—O12	127.0 (13)
O2—N1—C5	118.3 (13)	O11—N11—C15	114.7 (13)
O1—N1—C5	118.1 (12)	O12—N11—C15	118.1 (12)
C6—C1—C2—C3	0.6 (19)	C16—C11—C12—C13	-4 (2)
Br1—C1—C2—C3	179.5 (9)	Br11—C11—C12—C13	179.1 (11)
C6—C1—C2—Br2	-178.5 (10)	C16—C11—C12—Br12	-178.9 (11)
Br1—C1—C2—Br2	0.3 (16)	Br11—C11—C12—Br12	4.0 (17)
C1—C2—C3—C4	-0.3 (19)	C11—C12—C13—C14	4 (2)
Br2—C2—C3—C4	178.8 (11)	Br12—C12—C13—C14	179.4 (12)
C1—C2—C3—Br3	178.0 (9)	C11—C12—C13—Br13	-178.0 (11)
Br2—C2—C3—Br3	-2.8 (14)	Br12—C12—C13—Br13	-2.7 (18)
C2—C3—C4—C5	1 (2)	C12—C13—C14—C15	-3 (2)
Br3—C3—C4—C5	-177.8 (11)	Br13—C13—C14—C15	178.7 (12)
C3—C4—C5—C6	-1 (2)	C13—C14—C15—C16	2 (2)
C3—C4—C5—N1	179.1 (13)	C13—C14—C15—N11	-174.8 (15)
C4—C5—C6—C1	1 (2)	C14—C15—C16—C11	-2 (2)
N1—C5—C6—C1	-178.8 (12)	N11—C15—C16—C11	175.4 (13)
C2—C1—C6—C5	-1 (2)	C12—C11—C16—C15	3 (2)
Br1—C1—C6—C5	-180.0 (10)	Br11—C11—C16—C15	179.8 (11)
C4—C5—N1—O2	179.2 (14)	C16—C15—N11—O11	-175.5 (13)
C6—C5—N1—O2	-1 (2)	C14—C15—N11—O11	1 (2)
C4—C5—N1—O1	1 (2)	C16—C15—N11—O12	10 (2)
C6—C5—N1—O1	-178.8 (13)	C14—C15—N11—O12	-173.5 (15)

(II) 1,3-Dibromo-2-iodo-5-nitrobenzene*Crystal data*

$C_6H_2Br_2INO_2$
 $M_r = 406.81$
 Monoclinic, $P2_1/c$
 $a = 13.548$ (3) Å
 $b = 20.037$ (3) Å
 $c = 9.123$ (2) Å
 $\beta = 130.37$ (2)°
 $V = 1886.8$ (8) Å³
 $Z = 8$
 $F(000) = 1472$

Data collection

Bruker P4
 diffractometer
 Radiation source: fine-focus sealed tube
 Graphite monochromator

$D_x = 2.864$ Mg m⁻³
 Melting point: 415 K
 Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
 Cell parameters from 43 reflections
 $\theta = 5.7$ – 12.5 °
 $\mu = 11.82$ mm⁻¹
 $T = 298$ K
 Prism, brown
 $0.50 \times 0.22 \times 0.12$ mm

$2\theta/\omega$ scans
 Absorption correction: ψ scan
 (*XSCANS*; Bruker, 1997)
 $T_{\min} = 0.429$, $T_{\max} = 0.988$

5716 measured reflections
 5407 independent reflections
 1968 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.058$
 $\theta_{\text{max}} = 30.0^\circ$, $\theta_{\text{min}} = 2.2^\circ$

$h = -14 \rightarrow 19$
 $k = 0 \rightarrow 28$
 $l = -12 \rightarrow 0$
 3 standard reflections every 97 reflections
 intensity decay: 1%

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.061$
 $wR(F^2) = 0.153$
 $S = 0.95$
 5407 reflections
 218 parameters
 0 restraints
 0 constraints
 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
 $w = 1/[\sigma^2(F_o^2) + (0.053P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.84 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.84 \text{ e } \text{\AA}^{-3}$
 Extinction correction: *SHELXL2014* (Sheldrick,
 2015), $F_c^* = kFc^*[1 + 0.001x\text{Fc}^2\lambda^3/\sin(2\theta)]^{-1/4}$
 Extinction coefficient: 0.00093 (11)

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.30362 (13)	0.43988 (8)	0.2401 (2)	0.0615 (4)
I2	0.54556 (10)	0.36925 (4)	0.26460 (13)	0.0583 (3)
Br3	0.73278 (12)	0.49074 (7)	0.26614 (18)	0.0561 (4)
C1	0.4175 (11)	0.4967 (7)	0.2453 (16)	0.035 (3)
C2	0.5191 (11)	0.4723 (6)	0.2535 (13)	0.033 (3)
C3	0.5960 (11)	0.5182 (6)	0.2557 (17)	0.038 (3)
C4	0.5754 (12)	0.5862 (6)	0.2478 (17)	0.040 (3)
H4A	0.6264	0.6171	0.2474	0.048*
C5	0.4763 (13)	0.6050 (7)	0.2405 (15)	0.046 (4)
C6	0.3965 (12)	0.5642 (7)	0.2397 (18)	0.048 (4)
H6A	0.3307	0.5809	0.2355	0.057*
N1	0.4555 (13)	0.6807 (6)	0.2380 (17)	0.065 (3)
O1	0.5145 (11)	0.7161 (5)	0.2088 (17)	0.085 (4)
O2	0.3795 (15)	0.6989 (5)	0.2557 (18)	0.105 (4)
Br11	-0.18918 (13)	0.30721 (8)	0.2488 (2)	0.0620 (4)
I12	0.04866 (10)	0.37922 (4)	0.26639 (13)	0.0593 (3)
Br13	0.24427 (12)	0.25893 (8)	0.2825 (2)	0.0588 (4)
C11	-0.0736 (11)	0.2509 (7)	0.2562 (17)	0.039 (3)
C12	0.0237 (12)	0.2769 (7)	0.2619 (14)	0.035 (3)
C13	0.1046 (11)	0.2312 (6)	0.2672 (18)	0.039 (3)
C14	0.0869 (13)	0.1639 (6)	0.2665 (18)	0.045 (4)
H14A	0.1429	0.1344	0.2736	0.054*
C15	-0.0137 (13)	0.1391 (8)	0.2553 (16)	0.045 (4)
C16	-0.0922 (13)	0.1829 (6)	0.2507 (18)	0.043 (4)
H16A	-0.1596	0.1668	0.2437	0.052*
N11	-0.0302 (15)	0.0681 (6)	0.2483 (17)	0.066 (4)
O11	0.0350 (12)	0.0323 (6)	0.2418 (18)	0.099 (4)

O12	-0.1106 (14)	0.0493 (6)	0.2609 (17)	0.099 (4)
-----	--------------	------------	-------------	-----------

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0558 (8)	0.0680 (9)	0.0684 (9)	-0.0167 (7)	0.0437 (7)	-0.0035 (7)
I2	0.0737 (6)	0.0268 (4)	0.0723 (7)	0.0048 (5)	0.0464 (5)	0.0017 (4)
Br3	0.0484 (7)	0.0636 (9)	0.0654 (9)	0.0047 (7)	0.0409 (7)	0.0002 (7)
C1	0.041 (7)	0.035 (7)	0.033 (6)	-0.012 (6)	0.027 (5)	-0.007 (5)
C2	0.043 (7)	0.017 (6)	0.035 (8)	0.002 (5)	0.024 (6)	0.000 (4)
C3	0.042 (6)	0.033 (7)	0.041 (7)	0.003 (5)	0.028 (6)	-0.004 (5)
C4	0.037 (7)	0.036 (8)	0.048 (8)	-0.005 (6)	0.027 (6)	-0.003 (6)
C5	0.046 (7)	0.023 (7)	0.040 (8)	0.005 (6)	0.015 (6)	-0.002 (5)
C6	0.036 (7)	0.064 (10)	0.045 (8)	-0.003 (7)	0.027 (6)	-0.016 (7)
N1	0.066 (8)	0.031 (7)	0.075 (9)	0.010 (7)	0.036 (7)	-0.001 (6)
O1	0.091 (8)	0.030 (6)	0.108 (9)	-0.003 (6)	0.053 (7)	0.003 (6)
O2	0.163 (12)	0.050 (7)	0.137 (11)	0.050 (8)	0.112 (10)	0.016 (6)
Br11	0.0522 (8)	0.0681 (9)	0.0685 (9)	0.0108 (7)	0.0404 (7)	-0.0033 (7)
I12	0.0755 (6)	0.0283 (4)	0.0735 (7)	-0.0069 (5)	0.0479 (5)	-0.0038 (4)
Br13	0.0488 (7)	0.0631 (9)	0.0703 (9)	-0.0088 (7)	0.0412 (7)	-0.0014 (7)
C11	0.043 (7)	0.035 (7)	0.041 (7)	-0.002 (6)	0.028 (6)	0.002 (6)
C12	0.041 (7)	0.033 (8)	0.039 (8)	0.007 (6)	0.030 (6)	0.004 (4)
C13	0.033 (6)	0.037 (8)	0.042 (7)	-0.005 (5)	0.022 (6)	-0.005 (6)
C14	0.051 (8)	0.029 (7)	0.044 (8)	0.008 (6)	0.025 (6)	0.000 (6)
C15	0.063 (9)	0.028 (7)	0.056 (9)	-0.015 (6)	0.045 (8)	-0.006 (5)
C16	0.046 (7)	0.031 (7)	0.042 (7)	-0.021 (6)	0.024 (6)	-0.015 (5)
N11	0.096 (10)	0.034 (7)	0.073 (9)	-0.018 (7)	0.057 (8)	-0.006 (6)
O11	0.101 (9)	0.029 (6)	0.147 (11)	-0.010 (6)	0.072 (8)	-0.005 (7)
O12	0.144 (11)	0.061 (7)	0.130 (10)	-0.042 (8)	0.106 (9)	-0.012 (6)

Geometric parameters (Å, °)

Br1—C1	1.894 (12)	Br11—C11	1.895 (14)
I2—C2	2.088 (12)	I12—C12	2.074 (14)
Br3—C3	1.875 (13)	Br13—C13	1.888 (13)
C1—C6	1.375 (18)	C11—C12	1.387 (17)
C1—C2	1.416 (17)	C11—C16	1.381 (18)
C2—C3	1.380 (17)	C12—C13	1.405 (17)
C3—C4	1.384 (16)	C13—C14	1.370 (16)
C4—C5	1.353 (18)	C14—C15	1.390 (19)
C4—H4A	0.9300	C14—H14A	0.9300
C5—C6	1.35 (2)	C15—C16	1.359 (19)
C5—N1	1.539 (18)	C15—N11	1.435 (19)
C6—H6A	0.9300	C16—H16A	0.9300
N1—O2	1.199 (17)	N11—O11	1.168 (19)
N1—O1	1.221 (19)	N11—O12	1.226 (18)
C6—C1—C2	120.8 (13)	C12—C11—C16	121.2 (14)

C6—C1—Br1	116.4 (11)	C12—C11—Br11	121.4 (11)
C2—C1—Br1	122.8 (10)	C16—C11—Br11	117.3 (11)
C3—C2—C1	118.1 (12)	C11—C12—C13	117.3 (13)
C3—C2—I2	123.6 (10)	C11—C12—I12	120.7 (11)
C1—C2—I2	118.4 (10)	C13—C12—I12	122.0 (10)
C2—C3—C4	122.0 (13)	C14—C13—C12	120.8 (13)
C2—C3—Br3	121.2 (10)	C14—C13—Br13	117.0 (11)
C4—C3—Br3	116.8 (11)	C12—C13—Br13	122.2 (10)
C5—C4—C3	115.9 (13)	C13—C14—C15	120.8 (14)
C5—C4—H4A	122.0	C13—C14—H14A	119.6
C3—C4—H4A	122.0	C15—C14—H14A	119.6
C4—C5—C6	126.6 (14)	C16—C15—C14	118.8 (14)
C4—C5—N1	116.2 (15)	C16—C15—N11	122.8 (14)
C6—C5—N1	117.2 (15)	C14—C15—N11	118.3 (15)
C5—C6—C1	116.7 (13)	C15—C16—C11	121.0 (14)
C5—C6—H6A	121.7	C15—C16—H16A	119.5
C1—C6—H6A	121.7	C11—C16—H16A	119.5
O2—N1—O1	126.4 (14)	O11—N11—O12	124.2 (16)
O2—N1—C5	117.6 (14)	O11—N11—C15	120.6 (18)
O1—N1—C5	115.9 (17)	O12—N11—C15	115.0 (15)
<hr/>			
C6—C1—C2—C3	0.0 (16)	C16—C11—C12—C13	-1.7 (16)
Br1—C1—C2—C3	179.7 (9)	Br11—C11—C12—C13	180.0 (9)
C6—C1—C2—I2	179.4 (9)	C16—C11—C12—I12	179.2 (9)
Br1—C1—C2—I2	-1.0 (12)	Br11—C11—C12—I12	0.8 (13)
C1—C2—C3—C4	-0.8 (17)	C11—C12—C13—C14	0.1 (17)
I2—C2—C3—C4	179.9 (9)	I12—C12—C13—C14	179.2 (9)
C1—C2—C3—Br3	-179.9 (9)	C11—C12—C13—Br13	-178.2 (9)
I2—C2—C3—Br3	0.7 (14)	I12—C12—C13—Br13	0.9 (14)
C2—C3—C4—C5	0.9 (18)	C12—C13—C14—C15	1.7 (19)
Br3—C3—C4—C5	-179.9 (9)	Br13—C13—C14—C15	-179.9 (10)
C3—C4—C5—C6	-0.2 (18)	C13—C14—C15—C16	-1.9 (18)
C3—C4—C5—N1	178.2 (11)	C13—C14—C15—N11	177.8 (12)
C4—C5—C6—C1	-0.5 (19)	C14—C15—C16—C11	0.3 (18)
N1—C5—C6—C1	-178.9 (10)	N11—C15—C16—C11	-179.5 (12)
C2—C1—C6—C5	0.6 (17)	C12—C11—C16—C15	1.6 (19)
Br1—C1—C6—C5	-179.1 (9)	Br11—C11—C16—C15	180.0 (10)
C4—C5—N1—O2	-171.0 (13)	C16—C15—N11—O11	175.7 (14)
C6—C5—N1—O2	7.6 (18)	C14—C15—N11—O11	-4 (2)
C4—C5—N1—O1	12.4 (17)	C16—C15—N11—O12	-8.3 (19)
C6—C5—N1—O1	-169.1 (12)	C14—C15—N11—O12	171.9 (13)
