



Crystal structure and Hirshfeld surface analysis of 2,6-di-iodo-4-nitro-toluene and 2,4,6-tri-bromo-toluene

Mohamed Larbi Medjroubi, Ali Boudjada, Noudjoud Hamdouni, Ouarda Brihi, Olivier Jeannin, Jean Meinel

► To cite this version:

Mohamed Larbi Medjroubi, Ali Boudjada, Noudjoud Hamdouni, Ouarda Brihi, Olivier Jeannin, et al.. Crystal structure and Hirshfeld surface analysis of 2,6-di-iodo-4-nitro-toluene and 2,4,6-tri-bromo-toluene. *Acta crystallographica Section E: Crystallographic communications* [2015-..], 2020, 76 (Pt 8), pp.1391-1397. 10.1107/S2056989020010270 . hal-02930250

HAL Id: hal-02930250

<https://hal.science/hal-02930250>

Submitted on 4 Sep 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution 4.0 International License

Crystal structure and Hirshfeld surface analysis of 2,6-diiodo-4-nitrotoluene and 2,4,6-tribromotoluene

Mohamed Larbi Medjroubi,^{a*} Ali Boudjada,^a Noudjoud Hamdouni,^a Ouarda Brihi,^a Olivier Jeannin^b and Jean Meinnel^b

Received 16 June 2020

Accepted 23 July 2020

Edited by G. Díaz de Delgado, Universidad de Los Andes, Venezuela

Keywords: X-ray diffraction; crystal structure; 2,6-diiodo-4-nitrotoluene; 2,4,6-tribromotoluene; Hirshfeld surface.

CCDC references: 2018692; 2018691

Supporting information: this article has supporting information at journals.iucr.org/e

^aLaboratoire de Cristallographie, Département de Physique, Université Mentouri-Constantine, 25000 Constantine, Algeria, and ^bUMR 6226 CNRS–Université Rennes 1 ‘Sciences Chimiques de Rennes’, Equipe ‘Matière Condensée et Systèmes Electroactifs’, Bâtiment 10C Campus de Beaulieu, 263 Avenue du Général Leclerc, F-35042 Rennes, France. *Correspondence e-mail: medjroubi-m@umc.edu.dz

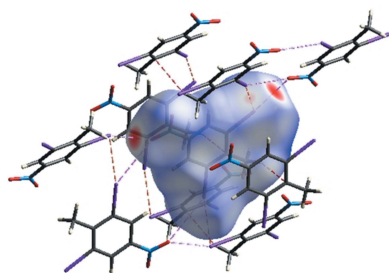
The title compounds, 2,6-diiodo-4-nitrotoluene (DINT, $C_7H_5I_2NO_2$) and 2,4,6-tribromotoluene (TBT, $C_7H_5Br_3$), are trisubstituted toluene molecules. Both molecules are planar, only the H atoms of the methyl group, and the nitro group in DINT, deviate significantly from the plane of the benzene ring. In the crystals of both compounds, molecules stack in columns up the shortest crystallographic axis, *viz.* the *a* axis in DINT and the *b* axis in TBT. In the crystal of DINT, molecules are linked *via* short $N\cdots O\cdots I$ contacts, forming chains along [100]. In TBT, molecules are linked by $C-H\cdots Br$ hydrogen bonds, forming chains along [010]. Hirshfeld surface analysis was used to explore the intermolecular contacts in the crystals of both DINT and TBT.

1. Chemical context

In order to understand the methyl radical behaviour of benzene molecules substituted by halogens and methyl groups, we have studied a number of halogenomesitylenes, such as triiodomesitylene (TIM; Boudjada *et al.*, 2001), trichloromesitylene (TCM; Tazi *et al.*, 1995), tribromomesitylene (TBM; Boudjada *et al.*, 1999) and dibromomesitylene (DBM; Hernandez *et al.*, 2003). In the solid state of these halogeno-methyl-benzene (HMB) compounds, the steric hindrance between the methyl group and the halogen atoms results in small out-of-plane deformations of the heavy atoms. In spite of the small amplitudes of the deformation, the impact on the rotational potential of the methyl group is considerable because of the contribution of the neighbouring halogen atoms on the methyl groups as observed in these planar structures. This study has now been extended to understand and identify the methyl-group behaviour of halogeno-toluene molecules, and we report herein on the crystal and molecular structures of the title compounds, 2,6-diiodo-4-nitrotoluene (DINT; systematic name: 1,3-diiodo-2-methyl-5-nitrobenzene) and 2,4,6-tribromotoluene (TBT; systematic name: 1,3,5-tribromo-2-methyl-benzene). Hirshfeld surface analysis was used to explore the intermolecular contacts in the crystals of both compounds.

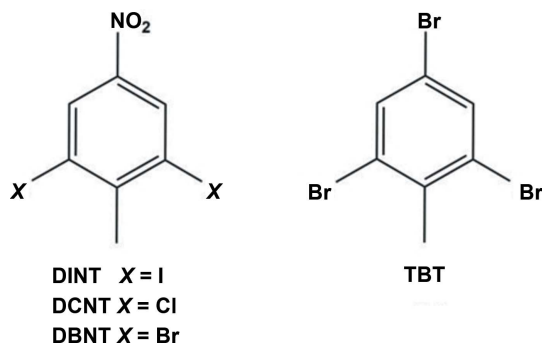
2. Structural commentary

The molecular structure of DINT is illustrated in Fig. 1, and that of TBT in Fig. 2. The structures of the title compounds are



OPEN ACCESS

compared with those of the dichloronitrotoluene (DCNT; Medjroubi *et al.*, 2017) and dibromonitrotoluene (DBNT; Medjroubi *et al.*, 2016) analogues, illustrated in Fig. 3.



In DBNT, the methyl group exhibits rotational disorder about the $C_{\text{ar}}-C_{\text{me}}$ axis. As in DCNT, the methyl group of DINT does not present any disorder. Hence, no significant steric hindrance of the methyl group by the *ortho* halogen atoms is observed. The longest bond lengths $C_{\text{ar}}-C_{\text{ar}}$ are adjacent to the $C_{\text{ar}}-C_{\text{me}}$ bond with an average value of 1.405 (4) Å. The bond-length values are close to those found in the literature. Moreover, in the crystal structure of DINT, the methyl group has a $C-H$ bond perpendicular to the mean plane with a torsion angle $C2-C1-C7-H7A = 90.0^\circ$, which has already previously been reported in the literature. The intermolecular $N1-O \cdots I$ [3.115 (3) Å] interactions are competing to ensure cohesion in the crystal, see Fig. 4. Atom I2 bonded to the atom C6, with the $C1-C6-I2$ angle of $121.7 (3)^\circ$ being greater than the angle $C5-C6-I2$ [$116.1 (2)^\circ$] located on the other side of the $C6-I2$ bond (Fig. 1). The aromatic ring is planar in DINT. The methyl C atom, the I atoms and the N atom of the nitro substituent, lie extremely close to the plane of the benzene ring; the deviations are 0.001 (1) Å for the methyl C atom, 0.097 (3) and $-0.097 (3)$ Å for the two I atoms, $-0.011 (2)$ Å for the nitro N atom, whereas for the oxygen atoms, which are located on

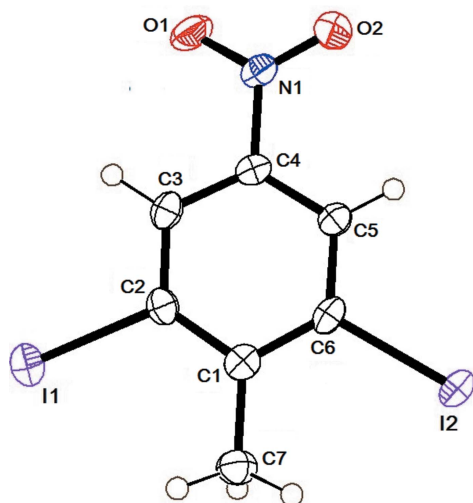


Figure 1
The molecular structure of DINT with the atom labelling and displacement ellipsoids drawn at the 50% probability level.

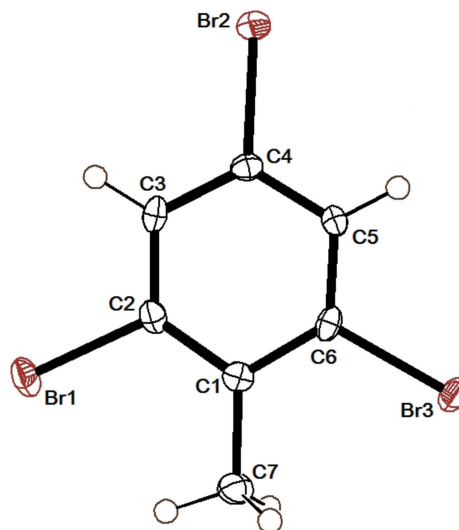


Figure 2
The molecular structure of TBT with the atom labelling and displacement ellipsoids drawn at the 50% probability level.

either side of the mean plane, the deviations are 0.293 (3) and $-0.283 (3)$ Å. In the crystal of DCNT, molecules are linked by weak $C-H \cdots O$ and $C-H \cdots Cl$ hydrogen bonds, forming layers parallel to the *ab* plane Fig. 5 (Medjroubi *et al.*, 2017).

The molecular structure of TBT is illustrated in Fig. 2. The structural study did not reveal any disorder and the intra-molecular interaction ensuring the cohesion in the crystal is $C-Br \cdots H7B$ (2.61 Å) as seen in Fig. 6 and Table 1. This

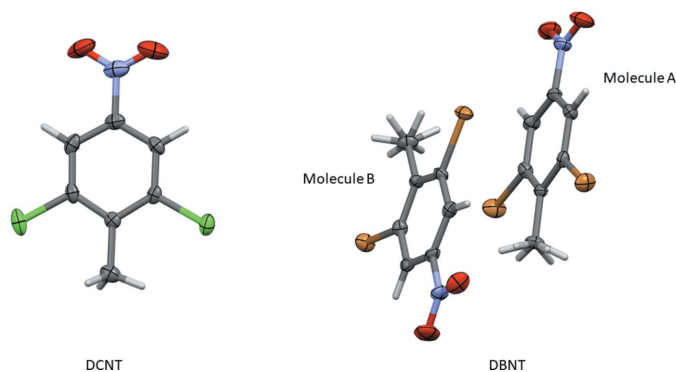


Figure 3
The molecular structures of DCNT and DBNT, with displacement ellipsoids drawn at the 50% probability level.

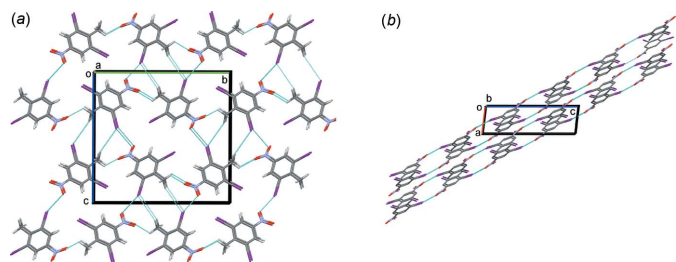


Figure 4
A view along the *a* and *b* axes of the crystal packing of DINT.

Table 1

Hydrogen bonds ($\text{\AA}$, $^\circ$) for (I) and (II).

Compound	$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
(I)	$C7-H7B\cdots I1$	0.98	2.82	3.333 (4)	113
	$C7-H7C\cdots I2$	0.98	2.84	3.331 (4)	112
(II)	$C7-H7B\cdots Br1$	0.98	2.61	3.199 (3)	118

conformation produces a significant steric effect between the hydrogen atoms of the methyl group and atom Br2 bonded to atom C6 with an angle $C1-C6-Br3 = 119.8 (2)^\circ$, which is clearly greater than the angle $C5-C6-Br3 = 116.5 (2)^\circ$ located on the other side of the $C6-Br1$ bond. This is the same case for the exocyclic angles $C6-C1-C7 = 121.9 (3)^\circ$ and $C2-C1-C7 = 123.6 (3)^\circ$ located on either side of the $C1-C7$ bond. As found in DINT and DCNT, the longest $C_{ar}-C_{ar}$ bond lengths are adjacent to the $C_{ar}-C_{me}$ bond (Fig. 2). The methyl C atom C7 is displaced from the benzene ring by

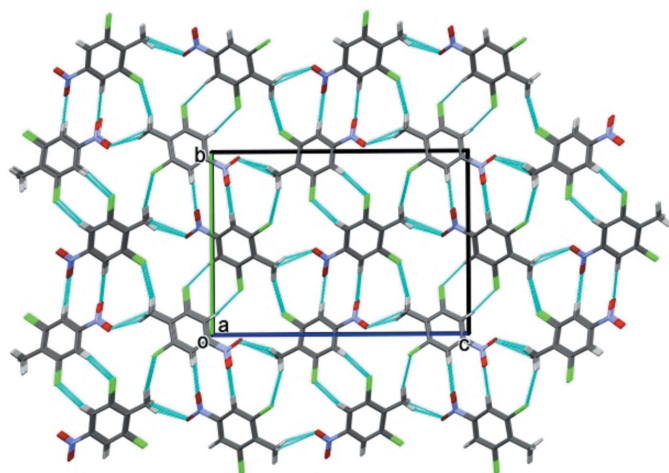


Figure 5

A view along the a axes of the crystal packing of 2,6-dichloro-4-nitrotoluene, DCNT.

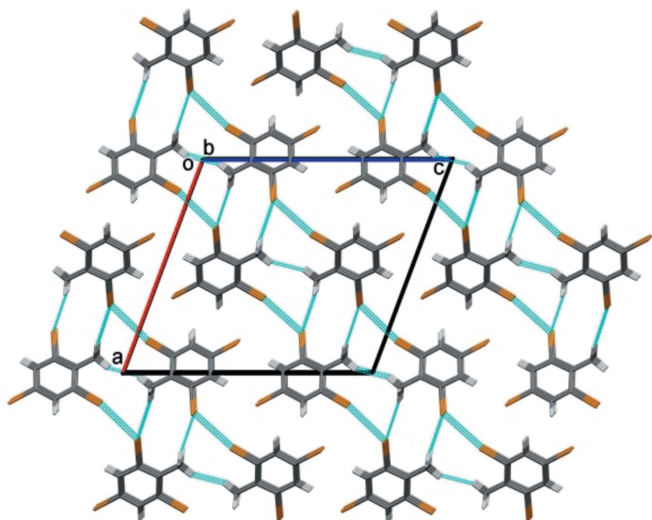


Figure 6

A view along the b axes of the crystal packing of 2,4,6-tribromotoluene, DBNT.

Table 2

Short contacts and contributions (%) to the Hirshfeld surface for DINT, DCNT and TBT.

DINT		DCNT		TBT	
Contact	%	Contact	%	Contact	%
$I\cdots H/H\cdots I$	25.7	$Cl\cdots H/H\cdots Cl$	26.8	$Br\cdots H/H\cdots Br$	42.7
$I\cdots O/O\cdots I$	16.0				
$O\cdots H/H\cdots O$	15.6	$O\cdots H/H\cdots O$	26.1		
$H\cdots H$	12.7	$H\cdots H$	9.1	$H\cdots H$	18.2
$C\cdots H/H\cdots C$	11.1	$C\cdots H/H\cdots C$	6.9	$C\cdots H/H\cdots C$	8.0
$O\cdots C/C\cdots O$	5.3				
$I\cdots I$	4.8	$Cl\cdots Cl$	5.9	$Br\cdots Br$	17.4
$C\cdots C$	3.4	$C\cdots C$	7.4	$C\cdots C$	7.3
		$Cl\cdots O/O\cdots Cl$	5.0		
		$Cl\cdots C/C\cdots Cl$	5.1	$Br\cdots C/C\cdots Br$	6.4

$-0.005 (1) \text{\AA}$, while the Br atoms lie almost in the plane of the benzene ring [deviations are $0.003 (3) \text{\AA}$ for atoms Br1 and Br3 and $-0.012 (3) \text{\AA}$ for atom Br2]. The CH_3 group presents an eclipsed $C-H$ bond with the mean plane of the molecule. A difference of 2° is found between the exocyclic angles $C_{ar}-C_{ar}-C_{me}$, which explains the importance of the interaction of this eclipsed bond with atom Br3. The endocyclic angle in front of the methyl group is equal to $116.6 (3)^\circ$ for DINT, $115.7 (2)^\circ$ for DCNT (Medjroubi *et al.*, 2017), $114.7 (3)^\circ$ for DBNT (Medjroubi *et al.*, 2016) and $114.5 (3)^\circ$ for TBT. The variation of this angle is very sensitive to the substitution of the halogen atoms surrounding the methyl groups of these different compounds.

3. Supramolecular features

In the crystal of DINT, the molecules are assembled into columns along the a -axis direction, the shortest crystallographic axis. Molecules are linked by $O\cdots I$ intermolecular interactions, with distance $I2\cdots O1^i = 3.12 (1) \text{\AA}$ [symmetry code (i): $x-1, -y+\frac{1}{2}, z+\frac{1}{2}$], leading to the formation of chains along the $[20\bar{1}]$ direction, see Fig. 4.

In the crystal of TBT, molecules stack in columns along the b -axis direction, again the shortest crystallographic axis. Molecules are linked by weak $Br\cdots Br$ interactions [$Br1\cdots Br3^{ii} = 3.5921 (5) \text{\AA}$; symmetry code (ii): $x+\frac{1}{2}, -y+\frac{3}{2}, z+\frac{1}{2}$], forming chains along the $[101]$ direction. $Br\cdots H$ short contacts are also present in the crystal of TBT [$Br1\cdots H7C^{ii} = 3.5921 (5) \text{\AA}$; symmetry code (iii): $x, -1+y, z$].

4. Analysis of the Hirshfeld surfaces of DINT and TBT

Additional insight into the intermolecular interactions was obtained from analysis of the Hirshfeld surface (HS) (Spackman & Jayatilaka, 2009) and the two-dimensional fingerprint plots (McKinnon *et al.*, 2007). The program *CystalExplorer* (Turner *et al.*, 2017) was used to generate Hirshfeld surfaces mapped over d_{norm} and the electrostatic potential for compounds TBT and DINT. The function d_{norm} is a ratio enclosing the distances of any surface point to the nearest interior (d_i) and exterior (d_e) atom and the van der Waals (vdW) radii of the atoms. The electrostatic potentials were

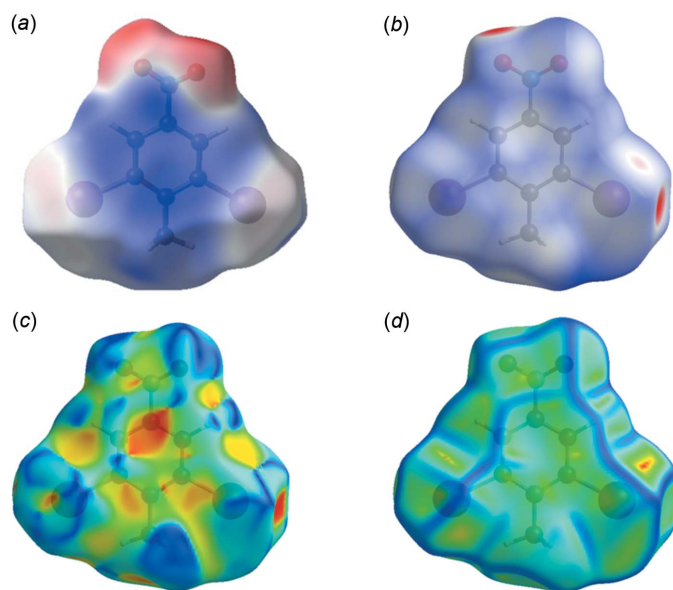


Figure 7
Hirshfeld surface for DINT mapped over (a) calculated electrostatic potential, (b) d_{norm} , (c) shape-index and (d) curvedness.

calculated using *TONTO* (Spackman & Jayatilaka, 2009) integrated into *CrystalExplorer*, using the crystal structure as the starting geometry. Short contacts and contributions to the Hirshfeld surface for DINT, DCNT (Medjroubi *et al.*, 2017) and TBT are given in Table 2. The Hirshfeld surface (HS) mapped over the electrostatic potential for DINT in the range $[-0.071$ to $+0.041]$, is shown in Fig. 7a where the red and blue regions represent negative and positive electrostatic potentials respectively. The Hirshfeld surface mapped over d_{norm} is depicted in Fig. 7b. The HS mapped over shape-index and curvedness are shown in Fig. 7c and 7d, respectively.

The crystal environment about a DINT molecule is illustrated in Fig. 8: the interactions are shown on the Hirshfeld surfaces with short contacts indicated in red. The two-dimensional fingerprint plots for all contacts are illustrated in Fig. 9a. The $\text{I} \cdots \text{O}/\text{O} \cdots \text{I}$ interaction ensures the cohesion of

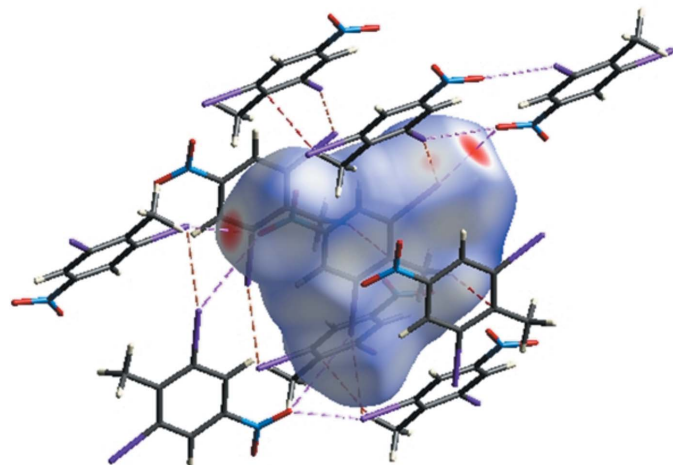


Figure 8
A view of the Hirshfeld surface of DINT mapped over d_{norm} , with interactions shown as dashed lines.

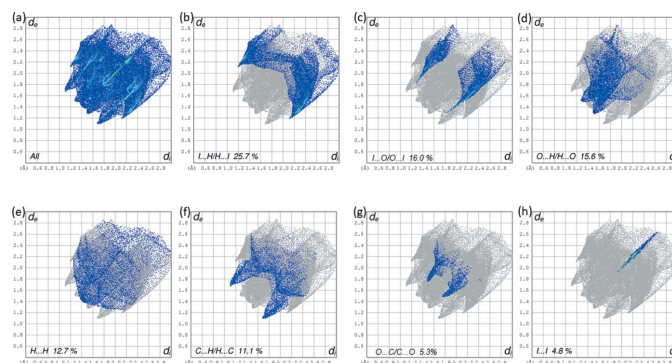


Figure 9
(a) The full two-dimensional fingerprint plot calculated for DINT and those delineated into (b) $\text{I} \cdots \text{H}/\text{H} \cdots \text{I}$ contacts, (c) $\text{I} \cdots \text{O}/\text{O} \cdots \text{I}$ contacts, (d) $\text{O} \cdots \text{H}/\text{H} \cdots \text{O}$ contacts, (e) $\text{H} \cdots \text{H}$ contacts, (f) $\text{C} \cdots \text{H}/\text{H} \cdots \text{C}$ contacts, (g) $\text{O} \cdots \text{C}/\text{C} \cdots \text{O}$ contacts and (h) $\text{I} \cdots \text{I}$ contacts.

the crystal with a contribution of 16% of all the interactions appearing in bright-red spots on the Hirshfeld surfaces mapped over d_{norm} . The fingerprint consists of two spikes with the ends at $d_e + d_i \simeq 3.1$ Å, Fig. 9c. The fingerprint of the $\text{C} \cdots \text{H}/\text{H} \cdots \text{C}$ interaction consists of two symmetrical peaks with a $d_e + d_i \simeq 2.8$ Å, Fig. 9f and almost equal to the sum of van der Waals radii. It is represented on the HS mapped with the shape-index property in the form of a pale-red spot, Fig. 7c. The $\text{I} \cdots \text{I}$ interaction is less important than $\text{O} \cdots \text{I}/\text{I} \cdots \text{O}$; however, it does contribute 4.8% to the total interactions, illustrating the equality of the $\text{I} \cdots \text{I}$ distance to the sum of van der Waals radii. The fingerprint is composed of a single peak in the form of a needle with $d_e + d_i \simeq 3.8$ Å, Fig. 9h. The absence of π - π stacking interactions is consistent with the low contributions of $\text{C} \cdots \text{C}$ contacts to the Hirshfeld surface (Table 2). The Hirshfeld surface analysis (Fig. 10b) and elec-

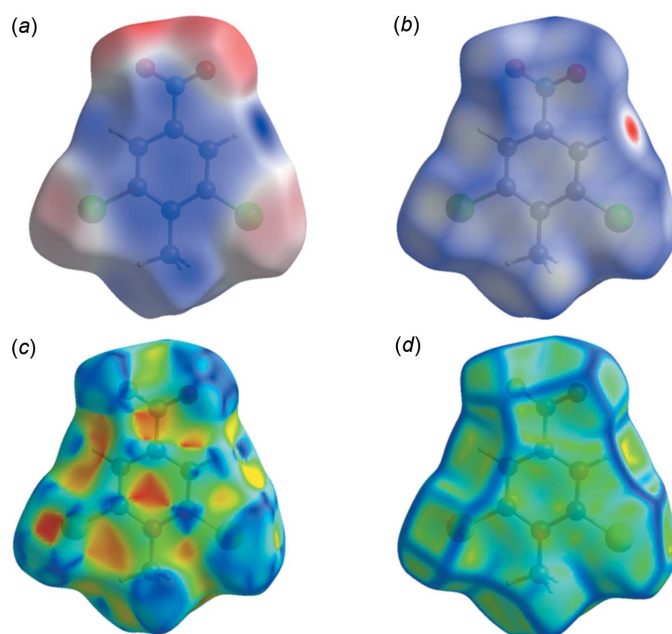


Figure 10
Hirshfeld surface for DCNT mapped over (a) calculated electrostatic potential, (b) d_{norm} , (c) shape-index and (d) curvedness.

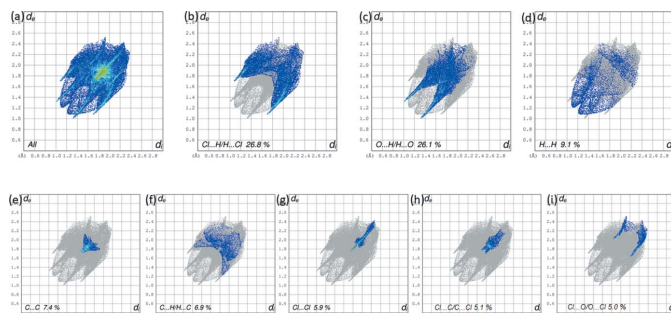


Figure 11

(a) The full two-dimensional fingerprint plot calculated for DCNT and those delineated into (b) Cl...H/H...Cl contacts, (c) O...H/H...O contacts, (d) H...H contacts, (e) C...C contacts, (f) C...H/H...C contacts, (g) Cl...Cl contacts, (h) Cl...C/C...Cl contacts and (i) Cl...O/O...Cl contacts.

trostatic potential surface (Fig. 10a) show the intermolecular interactions between different units in the crystalline environment of DCNT. The HS mapped over shape-index and curvedness are shown in Fig. 10c and d_i , respectively. The two-dimensional fingerprint plots for all contacts are illustrated in Fig. 11. The contributions of the major intermolecular contacts in the title compound are Cl...H/H...Cl (26.8%), O...H/H...O (26.1%), and H...H (10.6%) (Fig. 11a). Other contacts (e.g. C...C, H...C/C...H, Cl...Cl, Cl...C/C...Cl, Cl...O/O...Cl) make contributions of less than 7.5% to the HS. The graph shown in Fig. 11b represents the one-third of all the intermolecular contacts. All fingerprint points are located at distances with d_i equal to or greater than van der Waals distances, $d_e + d_i \approx 1.27$ Å, reflecting a zero tendency to form this intermolecular contact (Cl...H). The graph shown in Fig. 11c (O...H/H...O) shows the contact between the

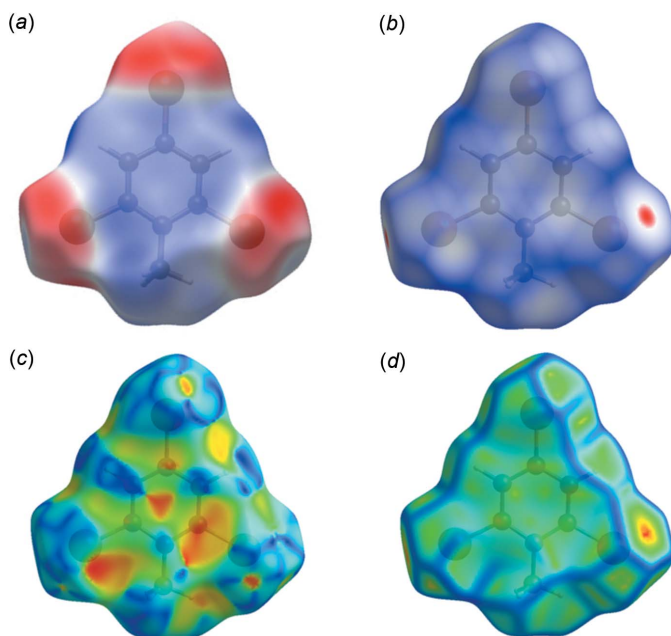


Figure 12

Hirshfeld surface for TBT mapped over (a) calculated electrostatic potential, (b) d_{norm} , (c) shape-index and (d) curvedness.

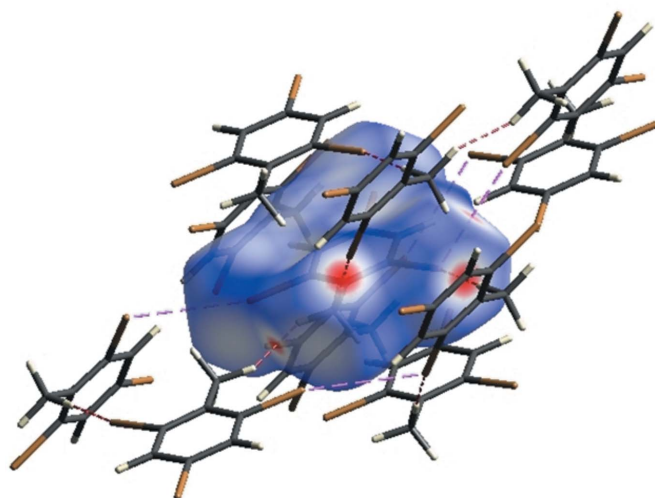


Figure 13

A view of the Hirshfeld surface of TBT mapped over d_{norm} , with interactions shown as dashed lines.

oxygen atoms inside the surface and the hydrogen atoms outside the surface, $d_e + d_i \approx 2.35$ Å, and has two symmetrical points at the top, bottom left and right. The graph shown in Fig. 11d (H...H; 10.6%) shows the two-dimensional fingerprint of the (d_i , d_e) points associated with hydrogen atoms, which has two symmetrical wings on the left and right with $d_e + d_i \approx 2.3$ Å.

The electrostatic potentials were mapped on the Hirshfeld surface using the STO-3G basis/Hartree–Fock level of theory over the range $[-0.016, 0.036]$ for TBT (Fig. 12). Atoms H7A, H7B and H7C of the methyl group and H3, H5 as donors, and the bromine atom acceptors, are also evident in Fig. 12a. The Hirshfeld surface mapped over d_{norm} is depicted in Fig. 12b. The overall 2D fingerprint plot is presented in Fig. 13a. The halogen–halogen (Br...Br) interaction contributes 17.4% to the HS and ensures the cohesion of the crystal and dictates the intermolecular stacking. The short intramolecular H...Br/Br...H contact between C3–H7B and Br1 (H7B...Br1 = 2.6 Å) can be recognized from the two neighbouring blue

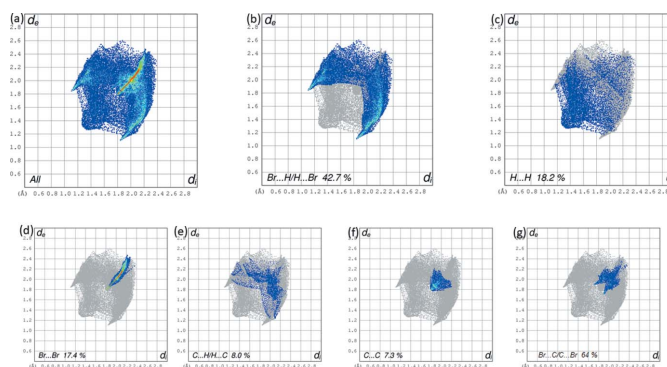


Figure 14

(a) The full two-dimensional fingerprint plot calculated for TBT and those delineated into (b) Br...H/H...Br contacts, (c) H...H contacts, (d) Br...Br contacts, (e) C...H/H...C contacts, (f) C...C contacts and (g) Br...C/C...Br contacts.

Table 3
Experimental details.

	DINT	TBT
Crystal data		
Chemical formula	C ₇ H ₅ I ₂ NO ₂	C ₇ H ₅ Br ₃
<i>M_r</i>	388.92	328.84
Crystal system, space group	Monoclinic, <i>P</i> 2 ₁ / <i>c</i>	Monoclinic, <i>P</i> 2 ₁ / <i>n</i>
Temperature (K)	150	150
<i>a</i> , <i>b</i> , <i>c</i> (Å)	4.3815 (2), 15.3348 (6), 14.5894 (6)	14.3484 (11), 3.9955 (3), 15.6975 (12)
β (°)	96.588 (1)	110.519 (2)
<i>V</i> (Å ³)	973.78 (7)	842.83 (11)
<i>Z</i>	4	4
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α
μ (mm ^{−1})	6.42	14.28
Crystal size (mm)	0.29 × 0.13 × 0.06	0.34 × 0.21 × 0.12
Data collection		
Diffractometer	Bruker APEXII	Bruker APEXII
Absorption correction	Multi-scan (<i>SADABS</i> ; Bruker, 2006)	Multi-scan (<i>SADABS</i> ; Bruker, 2006)
<i>T</i> _{min} , <i>T</i> _{max}	0.382, 0.680	0.496, 0.746
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	4104, 2244, 1850	6197, 1928, 1657
<i>R</i> _{int}	0.022	0.027
(sin θ/λ) _{max} (Å ^{−1})	0.651	0.650
Refinement		
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.024, 0.046, 0.98	0.025, 0.049, 1.08
No. of reflections	2244	1928
No. of parameters	110	93
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained
Δρ _{max} , Δρ _{min} (e Å ^{−3})	0.65, −0.55	0.70, −0.68

Computer programs: *APEX2* and *SAINT* (Bruker, 2006), *SIR2004* (Burla *et al.*, 2005), *SHELXL2018/3* (Sheldrick, 2015), *ORTEP-3 for Windows* and *WinGX* publication routines (Farrugia, 2012) and *Mercury* (Macrae *et al.*, 2020).

regions on the surface mapped with electrostatic potential in Fig. 14*c,d*. The two-dimensional fingerprint plot delineated into Br⋯H/H⋯Br has two peaks pointing to the pairs *d_e* + *d_i* ≈ 3.0 Å, slightly lower than or equal to the sum of van der Waals radii, Fig. 14*b*. These correspond to a 42.7% contribution to the Hirshfeld surface, and reflect the presence of intermolecular C7–H7C⋯Br3 interactions. The interatomic H⋯H contacts at distances greater than their van der Waals separation appear as scattered points in the greater part of the fingerprint plot Fig. 14*c*. The presence of C–H⋯π and H–C⋯π stacking interactions between the TBT rings is also apparent from the appearance of red and blue triangle pairs on the Hirshfeld surface mapped with shape-index property identified with arrows in Fig. 12*c*. The immediate environment about each molecule highlighting close contacts to the Hirshfeld surface by neighboring molecules is shown in Fig. 13. The relative contributions to the overall surface are given in Table 2.

5. Database survey

A search of the Cambridge Structural Database (CSD, Version 5.40, last update May 2019; Groom *et al.*, 2016) for 2,6-diiodo-4-nitrotoluene (DINT) and 2,4,6-tribromotoluene (TBT) gave five hits: 2,6-dichloro-4-nitrotoluene (DCNT; Medjroubi *et al.*, 2017), dibromonitrotoluene (DBNT; Medjroubi *et al.*, 2016), triiodomesitylene (TIM) (Boudjada *et al.*, 2001), tribromomesitylene (TBM; Boudjada *et al.*, 1999) and dibromomesitylene (DBM; Hernandez *et al.*, 2003). In DBNT

(Medjroubi *et al.*, 2016), there are two independent molecules per asymmetric unit and the methyl group H atoms are positionally disordered, as found for DBM (Hernandez *et al.*, 2003). While in the compounds DINT and DCNT (Medjroubi *et al.*, 2017), there is only one molecule in the asymmetric unit and no disorder is observed for the methyl group H atoms. In the molecule of DINT, a C_m–H (*m* = methyl) bond is perpendicular to the mean plane of the molecule, as found for triiodomesitylene (TIM; Boudjada *et al.*, 2001). The nitro group is inclined to the benzene ring by 16.72 (1)° in DINT, compared with 9.8 (3)° in DCNT, and 2.5 (5)° and 5.9 (4)° in DBNT. In the molecule of TBT, the CH₃ group presents an eclipsed C–H bond with the mean plane of the molecule. This also applies to DCNT (Medjroubi *et al.*, 2017), which does not present any disorder, as was also found in the case of tribromomesitylene TBM (Boudjada *et al.*, 1999). In 2,6-dihalogeno-4-nitrotoluene, as in the title compounds, the cohesion of the crystal is ensured by interactions of the type C–H⋯halogen and C–halogen⋯halogen.

6. Synthesis and crystallization

2,6-Diiodo-4-nitrotoluene (DINT): 4-nitrotoluene (0.68g, 5 mmol) was suspended in 90% (v/v) conc. H₂SO₄ (10 ml) at 298–303 K. While keeping the same temperature, the iodinating solution containing the I⁺ intermediate in *ca* 50% excess was added dropwise under stirring over 45 min. The stirring was continued at 298–303 K for a further 75 min. The final reaction mixture was poured, with stirring, into ice–water

(300 g). The crude solid obtained was recrystallized from ethanol (27 ml). On slow evaporation of the solvent, colourless prismatic crystals of DINT were obtained (yield 77%, 1.5 g).

2,4,6-Tribromotoluene (TBT) is commercially available (Sigma–Aldrich). It was recrystallized from ethanol solution, giving large colourless needle-like crystals, many of which were twinned.

7. Refinement details

Crystal data, data collection and structure refinement details for DINT and TBT are summarized in Table 3. The H atoms were included in calculated positions and refined as riding: C–H = 0.95–0.98 Å with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C-methyl})$ and $1.2U_{\text{eq}}(\text{C})$ for other H atoms.

Acknowledgements

We would like to thank the Centre de Diffractométrie de l'Université de Rennes 1 for the data collection.

References

- Boudjada, A., Hernandez, O., Meinel, J., Mani, M. & Paulus, W. (2001). *Acta Cryst.* **C57**, 1106–1108.
- Boudjada, F., Meinel, J., Cousson, A., Paulus, W., Mani, M. & Sanquer, M. (1999). *AIP Conf. Proc.* pp. 217–222.
- Bruker (2006). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Burla, M. C., Caliandro, R., Camalli, M., Carrozzini, B., Cascarano, G. L., De Caro, L., Giacovazzo, C., Polidori, G. & Spagna, R. (2005). *J. Appl. Cryst.* **38**, 381–388.
- Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
- Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* **B72**, 171–179.
- Hernandez, O., Cousson, A., Plazanet, M., Nierlich, M. & Meinel, J. (2003). *Acta Cryst.* **C59**, o445–o450.
- Macrae, C. F., Sovago, I., Cottrell, S. J., Galek, P. T. A., McCabe, P., Pidcock, E., Platings, M., Shields, G. P., Stevens, J. S., Towler, M. & Wood, P. A. (2020). *J. Appl. Cryst.* **53**, 226–235.
- McKinnon, J. J., Jayatilaka, D. & Spackman, M. A. (2007). *Chem. Commun.* pp. 3814.
- Medjroubi, M. L., Boudjada, A., Hamdouni, N., Jeannin, O. & Meinel, J. (2017). *IUCrData*, **2**, x170672.
- Medjroubi, M. L., Jeannin, O., Fourmigué, M., Boudjada, A. & Meinel, J. (2016). *IUCrData*, **1**, x160621.
- Sheldrick, G. M. (2015). *Acta Cryst.* **C71**, 3–8.
- Spackman, M. A. & Jayatilaka, D. (2009). *CrystEngComm*, **11**, 19–32.
- Tazi, M., Meinel, J., Sanquer, M., Nusimovici, M., Tonnard, F. & Carrie, R. (1995). *Acta Cryst.* **B51**, 838–847.
- Turner, M. J., McKinnon, J. J., Wolff, S. K., Grimwood, D. J., Spackman, P. R., Jayatilaka, D. & Spackman, M. A. (2017). *CrystalExplorer17*. University of Western Australia. <http://hirshfeldsurface.net>.

supporting information

Acta Cryst. (2020). E76, 1391-1397 [https://doi.org/10.1107/S2056989020010270]

Crystal structure and Hirshfeld surface analysis of 2,6-diiodo-4-nitrotoluene and 2,4,6-tribromotoluene

Mohamed Larbi Medjroubi, Ali Boudjada, Noudjoud Hamdouni, Ouarda Brihi, Olivier Jeannin and Jean Meinnel

Computing details

For both structures, data collection: *APEX2* (Bruker, 2006); cell refinement: *SAINT* (Bruker, 2006); data reduction: *SAINT* (Bruker, 2006); program(s) used to solve structure: *SIR2004* (Burla *et al.*, 2005). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 2015) for DINT; *SHELXL2018/3* (Sheldrick, 2015) for TBT. For both structures, molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *Mercury* (Macrae *et al.*, 2020); software used to prepare material for publication: *WinGX* publication routines (Farrugia, 2012).

2,6-Diiodo-4-nitrotoluene (DINT)

Crystal data

$C_7H_5I_2NO_2$
 $M_r = 388.92$
 Monoclinic, $P2_1/c$
 Hall symbol: -P 2ybc
 $a = 4.3815$ (2) Å
 $b = 15.3348$ (6) Å
 $c = 14.5894$ (6) Å
 $\beta = 96.588$ (1)°
 $V = 973.78$ (7) Å³
 $Z = 4$

$F(000) = 704$
 $D_x = 2.653$ Mg m⁻³
 Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
 Cell parameters from 3615 reflections
 $\theta = 2.8\text{--}27.4^\circ$
 $\mu = 6.42$ mm⁻¹
 $T = 150$ K
 Prism, colourless
 $0.29 \times 0.13 \times 0.06$ mm

Data collection

Bruker APEXII
 diffractometer
 CCD rotation images, thin slices scans
 Absorption correction: multi-scan
 (SADABS; Bruker, 2006)
 $T_{\min} = 0.382$, $T_{\max} = 0.680$
 4104 measured reflections

2244 independent reflections
 1850 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.022$
 $\theta_{\max} = 27.5^\circ$, $\theta_{\min} = 2.7^\circ$
 $h = -5 \rightarrow 5$
 $k = -19 \rightarrow 19$
 $l = 0 \rightarrow 18$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.024$
 $wR(F^2) = 0.046$
 $S = 0.98$
 2244 reflections
 110 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

$$w = 1/[\sigma^2(F_o^2) + (0.0064P)^2]$$

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

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

$$\Delta\rho_{\max} = 0.65 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.55 \text{ e } \text{\AA}^{-3}$$

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
I2	0.49927 (5)	0.16308 (2)	0.43507 (2)	0.02865 (8)
I1	0.61809 (6)	−0.09049 (2)	0.11508 (2)	0.03239 (8)
O2	1.0610 (7)	0.31383 (17)	0.16120 (19)	0.0439 (7)
O1	1.2265 (6)	0.21412 (17)	0.07502 (18)	0.0383 (6)
N1	1.0741 (6)	0.2380 (2)	0.1357 (2)	0.0270 (7)
C4	0.9021 (7)	0.1719 (2)	0.1809 (2)	0.0213 (7)
C5	0.7967 (7)	0.1926 (2)	0.2637 (2)	0.0226 (7)
C7	0.4089 (8)	−0.0220 (2)	0.3155 (3)	0.0311 (8)
C3	0.8521 (7)	0.0917 (2)	0.1389 (2)	0.0248 (8)
C6	0.6400 (7)	0.1288 (2)	0.3069 (2)	0.0223 (7)
C1	0.5769 (7)	0.0462 (2)	0.2676 (2)	0.0238 (8)
C2	0.6870 (7)	0.0302 (2)	0.1830 (2)	0.0243 (8)
H5	0.830322	0.248772	0.290300	0.027*
H3	0.927896	0.078917	0.081954	0.030*
H7A	0.556153	−0.056139	0.356537	0.047*
H7B	0.298926	−0.060732	0.269445	0.047*
H7C	0.261494	0.006076	0.351681	0.047*

Atomic displacement parameters ($\text{\AA}^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
I2	0.02982 (13)	0.03671 (15)	0.02075 (13)	0.00201 (11)	0.00862 (10)	−0.00039 (10)
I1	0.03450 (14)	0.02883 (14)	0.03341 (16)	−0.00032 (11)	0.00206 (11)	−0.00721 (11)
O2	0.0607 (19)	0.0330 (15)	0.0414 (18)	−0.0150 (14)	0.0212 (15)	−0.0067 (13)
O1	0.0426 (16)	0.0438 (16)	0.0318 (16)	0.0010 (13)	0.0189 (13)	0.0059 (13)
N1	0.0268 (15)	0.0334 (17)	0.0210 (16)	−0.0023 (14)	0.0039 (13)	0.0026 (14)
C4	0.0170 (16)	0.0263 (18)	0.0206 (18)	0.0018 (14)	0.0014 (13)	0.0045 (14)
C5	0.0216 (17)	0.0259 (18)	0.0200 (18)	0.0007 (14)	0.0009 (14)	0.0011 (15)
C7	0.0290 (19)	0.030 (2)	0.035 (2)	−0.0010 (17)	0.0083 (16)	0.0031 (17)
C3	0.0226 (17)	0.0310 (19)	0.0204 (19)	0.0045 (15)	0.0010 (14)	−0.0018 (15)
C6	0.0185 (16)	0.0330 (19)	0.0148 (18)	0.0066 (15)	−0.0007 (14)	0.0009 (15)
C1	0.0200 (16)	0.0279 (19)	0.0229 (19)	0.0055 (15)	−0.0003 (14)	0.0034 (15)
C2	0.0224 (17)	0.0233 (18)	0.026 (2)	0.0011 (15)	−0.0015 (15)	−0.0029 (15)

Geometric parameters ($\text{\AA}$, $^\circ$)

I2—C6	2.101 (3)	C7—C1	1.497 (5)
I1—C2	2.105 (3)	C7—H7A	0.9800
O2—N1	1.224 (4)	C7—H7B	0.9800
O1—N1	1.224 (4)	C7—H7C	0.9800
N1—C4	1.464 (4)	C3—C2	1.389 (5)

C4—C5	1.378 (5)	C3—H3	0.9500
C4—C3	1.381 (5)	C6—C1	1.404 (5)
C5—C6	1.388 (5)	C1—C2	1.398 (5)
C5—H5	0.9500		
O2—N1—O1	123.5 (3)	H7B—C7—H7C	109.5
O2—N1—C4	118.4 (3)	C4—C3—C2	117.6 (3)
O1—N1—C4	118.0 (3)	C4—C3—H3	121.2
C5—C4—C3	122.8 (3)	C2—C3—H3	121.2
C5—C4—N1	118.5 (3)	C5—C6—C1	122.3 (3)
C3—C4—N1	118.7 (3)	C5—C6—I2	116.1 (2)
C4—C5—C6	118.0 (3)	C1—C6—I2	121.7 (3)
C4—C5—H5	121.0	C2—C1—C6	116.5 (3)
C6—C5—H5	121.0	C2—C1—C7	121.8 (3)
C1—C7—H7A	109.5	C6—C1—C7	121.6 (3)
C1—C7—H7B	109.5	C3—C2—C1	122.7 (3)
H7A—C7—H7B	109.5	C3—C2—I1	115.7 (3)
C1—C7—H7C	109.5	C1—C2—I1	121.6 (3)
H7A—C7—H7C	109.5		
O2—N1—C4—C5	−15.8 (4)	C5—C6—C1—C2	1.5 (5)
O1—N1—C4—C5	163.4 (3)	I2—C6—C1—C2	−178.8 (2)
O2—N1—C4—C3	164.2 (3)	C5—C6—C1—C7	179.7 (3)
O1—N1—C4—C3	−16.7 (4)	I2—C6—C1—C7	−0.6 (4)
C3—C4—C5—C6	1.5 (5)	C4—C3—C2—C1	−1.2 (5)
N1—C4—C5—C6	−178.6 (3)	C4—C3—C2—I1	179.8 (2)
C5—C4—C3—C2	0.3 (5)	C6—C1—C2—C3	0.3 (5)
N1—C4—C3—C2	−179.7 (3)	C7—C1—C2—C3	−177.8 (3)
C4—C5—C6—C1	−2.4 (5)	C6—C1—C2—I1	179.2 (2)
C4—C5—C6—I2	177.9 (2)	C7—C1—C2—I1	1.1 (4)

2,4,6-Tribromotoluene (TBT)*Crystal data*C₇H₅Br₃ $M_r = 328.84$ Monoclinic, $P2_1/n$ $a = 14.3484$ (11) Å $b = 3.9955$ (3) Å $c = 15.6975$ (12) Å $\beta = 110.519$ (2)° $V = 842.83$ (11) Å³ $Z = 4$ $F(000) = 608$ $D_x = 2.592$ Mg m^{−3}Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 2989 reflections

 $\theta = 2.4$ – 27.5° $\mu = 14.28$ mm^{−1} $T = 150$ K

Prism, colourless

 $0.34 \times 0.21 \times 0.12$ mm*Data collection*

Bruker APEXII

diffractometer

CCD rotation images, thin slices scans

Absorption correction: multi-scan

(SADABS; Bruker, 2006)

 $T_{\min} = 0.496$, $T_{\max} = 0.746$

6197 measured reflections

1928 independent reflections

1657 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.027$

$\theta_{\max} = 27.5^\circ$, $\theta_{\min} = 2.4^\circ$
 $h = -18 \rightarrow 18$

$k = -4 \rightarrow 5$
 $l = -18 \rightarrow 20$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.025$
 $wR(F^2) = 0.049$
 $S = 1.08$
 1928 reflections
 93 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
 $w = 1/[\sigma^2(F_o^2) + (0.0154P)^2 + 1.1776P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.70 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.68 \text{ e } \text{\AA}^{-3}$
 Extinction correction: SHELXL-2018/3
 (Sheldrick 2015),
 $F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$
 Extinction coefficient: 0.00060 (17)

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 ($\text{\AA}^2$)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.68701 (2)	1.18762 (9)	0.84471 (2)	0.02351 (10)
Br2	0.36077 (2)	0.60522 (9)	0.90955 (2)	0.02044 (10)
Br3	0.35213 (2)	0.68698 (9)	0.55023 (2)	0.02088 (10)
C1	0.5156 (2)	0.9306 (8)	0.7029 (2)	0.0151 (7)
C2	0.5592 (2)	0.9823 (8)	0.7965 (2)	0.0165 (7)
C3	0.5158 (2)	0.8920 (8)	0.8588 (2)	0.0167 (7)
H3	0.548214	0.934507	0.921902	0.020*
C4	0.4234 (2)	0.7369 (8)	0.8266 (2)	0.0154 (7)
C5	0.3755 (2)	0.6790 (8)	0.7351 (2)	0.0148 (7)
H5	0.312062	0.574516	0.713540	0.018*
C6	0.4217 (2)	0.7759 (8)	0.6756 (2)	0.0156 (7)
C7	0.5638 (2)	1.0280 (9)	0.6357 (2)	0.0219 (8)
H7A	0.576650	0.826805	0.605878	0.033*
H7B	0.626764	1.142988	0.667500	0.033*
H7C	0.519404	1.177907	0.589887	0.033*

Atomic displacement parameters ($\text{\AA}^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.01425 (15)	0.0243 (2)	0.02664 (18)	−0.00447 (13)	0.00050 (13)	0.00205 (15)
Br2	0.02155 (16)	0.0246 (2)	0.01674 (16)	−0.00194 (14)	0.00871 (12)	0.00230 (14)
Br3	0.02070 (16)	0.0273 (2)	0.01272 (15)	−0.00059 (14)	0.00346 (12)	−0.00326 (14)
C1	0.0149 (14)	0.0130 (17)	0.0176 (15)	0.0034 (13)	0.0058 (12)	0.0028 (13)
C2	0.0139 (14)	0.0131 (17)	0.0191 (15)	−0.0009 (12)	0.0016 (12)	0.0024 (13)
C3	0.0176 (15)	0.0133 (17)	0.0146 (15)	0.0003 (13)	−0.0002 (12)	−0.0026 (13)

C4	0.0166 (14)	0.0153 (18)	0.0161 (15)	0.0033 (13)	0.0081 (12)	0.0007 (13)
C5	0.0123 (14)	0.0148 (17)	0.0163 (15)	−0.0015 (12)	0.0039 (12)	−0.0013 (13)
C6	0.0173 (14)	0.0134 (17)	0.0133 (14)	0.0030 (13)	0.0017 (12)	−0.0041 (13)
C7	0.0162 (15)	0.029 (2)	0.0213 (17)	0.0023 (14)	0.0074 (13)	0.0042 (15)

Geometric parameters (Å, °)

Br1—C2	1.907 (3)	C3—H3	0.9500
Br2—C4	1.898 (3)	C4—C5	1.377 (4)
Br3—C6	1.903 (3)	C5—C6	1.376 (5)
C1—C2	1.396 (4)	C5—H5	0.9500
C1—C6	1.405 (4)	C7—H7A	0.9800
C1—C7	1.502 (4)	C7—H7B	0.9800
C2—C3	1.379 (5)	C7—H7C	0.9800
C3—C4	1.389 (4)		
C2—C1—C6	114.5 (3)	C6—C5—C4	118.5 (3)
C2—C1—C7	123.6 (3)	C6—C5—H5	120.8
C6—C1—C7	121.9 (3)	C4—C5—H5	120.7
C3—C2—C1	124.1 (3)	C5—C6—C1	123.7 (3)
C3—C2—Br1	116.2 (2)	C5—C6—Br3	116.5 (2)
C1—C2—Br1	119.7 (2)	C1—C6—Br3	119.8 (2)
C2—C3—C4	118.0 (3)	C1—C7—H7A	109.5
C2—C3—H3	121.0	C1—C7—H7B	109.5
C4—C3—H3	121.0	H7A—C7—H7B	109.5
C5—C4—C3	121.2 (3)	C1—C7—H7C	109.5
C5—C4—Br2	119.1 (2)	H7A—C7—H7C	109.5
C3—C4—Br2	119.7 (2)	H7B—C7—H7C	109.5
C6—C1—C2—C3	0.0 (5)	C3—C4—C5—C6	0.5 (5)
C7—C1—C2—C3	−179.6 (3)	Br2—C4—C5—C6	179.9 (2)
C6—C1—C2—Br1	179.7 (2)	C4—C5—C6—C1	0.2 (5)
C7—C1—C2—Br1	0.1 (5)	C4—C5—C6—Br3	179.7 (2)
C1—C2—C3—C4	0.7 (5)	C2—C1—C6—C5	−0.5 (5)
Br1—C2—C3—C4	−179.0 (2)	C7—C1—C6—C5	179.2 (3)
C2—C3—C4—C5	−0.9 (5)	C2—C1—C6—Br3	−179.9 (2)
C2—C3—C4—Br2	179.7 (2)	C7—C1—C6—Br3	−0.3 (4)