

Crystal structures and Hirshfeld analysis of 4,6-dibromoindolenine and its quaternized salt

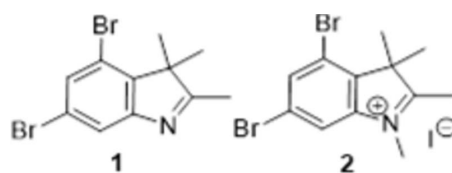
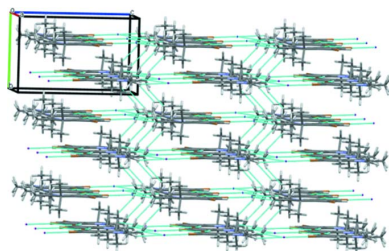
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4,6-Dibromo-2,3,3-trimethyl-3*H*-indole, C₁₁H₁₁Br₂N, exists as a neutral molecule in the asymmetric unit. The asymmetric unit of 4,6-dibromo-2,3,3-trimethyl-3*H*-indol-1-ium iodide, C₁₂H₁₄Br₂N⁺·I⁻, contains one organic cation and one iodine anion. The positive charge is localized on the quaternized nitrogen atom. In the crystal, molecules of 4,6-dibromoindolenine are linked by C—Br···π halogen bonds, forming zigzag chains propagating in the [001] direction. The molecules of the salt form layers parallel to the (010) plane where they are linked by C—H···Br hydrogen bonds, C—Br···Br and C—Br···I halogen bonds. The Hirshfeld surface analysis and two dimensional fingerprint plots were used to analyse the intermolecular contacts present in both crystals.

1. Chemical context

The structural analysis of 2,3,3-trimethyl-3*H*-indole (2,3,3-trimethylindolenine) and its quaternized salts (Lynch *et al.*, 2012; Connell *et al.*, 2014) plays a crucial role in understanding the mechanisms of the chemical reactions resulting in various functional products. These intermediates are promising scaffolds for the synthesis of indolenine-containing fluorescent dyes, including highly versatile cyanine (Sun *et al.*, 2016; Feng *et al.*, 2020) and squaraine dyes (Beverina & Salice, 2010). The incorporation of heavy atoms in the molecule, such as bromine and iodine, increases the generation of reactive species during photosensitization (Szaciłowski *et al.*, 2005; Semenova *et al.*, 2021). In particular, fluorescent dyes with bromine atoms are utilized for photodynamic therapy applications (Atchison *et al.*, 2017; Liu *et al.*, 2021). Moreover, cyanine with the 4,6-dibromoindolenine moiety indicates excellent properties for optical tumor imaging by its fluorescence (Guerrero *et al.*, 2017).



In this work, we carried out an X-ray diffraction and Hirshfeld surface analysis of 4,6-dibromoindolenine (**1**) and its quaternized salt (**2**), crystals of which were obtained by sequential synthesis starting from 3,5-dibromoaniline (**3**) by its diazotization with nitrosylsulfuric acid in sulfuric acid

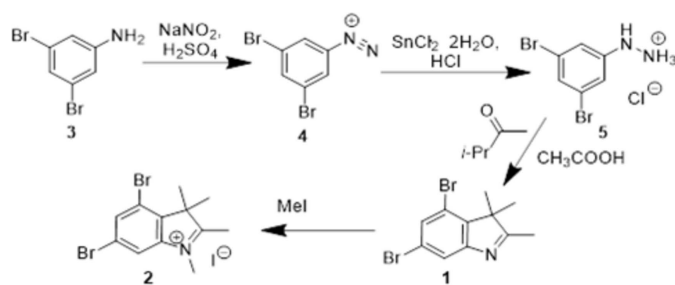


Figure 1
Synthesis of the title compounds **1** and **2**.

followed by reduction of the diazonium salt **4** with tin(II) chloride. The resulting 3,5-dibromophenylhydrazine was refluxed with 3-methyl-2-butanone in acetic acid to give 4,6-dibromoindolenine, **1**, which after *N*-alkylation with the excess of iodomethane in benzene solution forms crystals of the quaternized indolium salt **2** (Fig. 1).

2. Structural commentary

In the crystal, 4,6-dibromo-2,3,3-trimethyl-3*H*-indole, **1**, exists as one neutral molecule in the asymmetric unit (Fig. 2). The quaternized molecule **2** exists as a salt with an iodine anion in the crystal phase (Fig. 2). All atoms of the quaternized cation, with exception of the C9 atom and the hydrogen atoms of the C10H₃ and C11H₃ methyl groups are located in a special position relative to the symmetry plane. In compound **2**, the positive charge is localized on the nitrogen atom, which is caused by its quaternization. The N1–C11 bond is shortened to 1.460 (10) Å in comparison with the mean value of 1.485 Å for an N–C*sp*³ bond (Burgi & Dunitz, 1994). An analysis of the bond lengths in both structures showed that they are typical of those in similar compounds (Seiler *et al.*, 2018; Connell *et al.*, 2014; Holliman *et al.*, 2009; Bell  tete *et al.*, 1993).

3. Supramolecular features

In the crystal, molecules of **1** form zigzag chains in the [001] direction as a result of the formation of intermolecular C3–Br1···N1(π) and C3–Br1···C8(π) halogen bonds (Table 1, Fig. 3). Neighbouring chains are linked by weak C11–

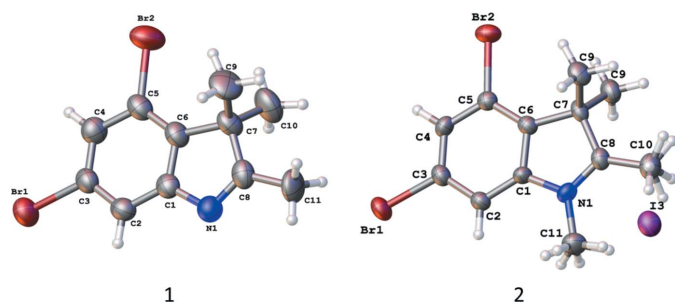


Figure 2
Molecular structure of compounds **1** and **2** with the atom labelling. Displacement ellipsoids are drawn at the 50% probability level.

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

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
C3–Br1···N1 ⁱ	1.89 (1)	3.19	5.283 (1)	166
C3–Br1···C8 ⁱ	1.89 (1)	3.53	5.046 (1)	153
C11–H11C···N1 ⁱⁱ	0.96	2.69	3.621 (1)	164

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

Table 2
Hydrogen-bond geometry (Å, °) for **2**.

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
C2–H2···Br2 ⁱ	0.93	3.05	3.872 (1)	149
C5–Br2···Br1 ⁱⁱ	1.88 (1)	3.58	5.397 (1)	162
C3–Br1···I1 ⁱⁱⁱ	1.90 (1)	3.62	5.514 (1)	176
C11–H11A···I1 ^{iv}	0.96	3.14	3.881 (1)	135

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

H11C···N1 hydrogen bonds (Table 1). It should be noted that only one of the bromine atoms participates in these interactions. The presence of the iodide anion in compound **2** leads to the complete involvement of both bromine atoms in the formation of intermolecular interactions. As a result, molecules of **2** form chains in the [100] direction as a result of the C2–H2···Br2 hydrogen bond and C5–Br2···Br1 halogen bond (Table 2, Fig. 4). Neighbouring chains are connected through the bridged iodide anion by the strong C3–Br1···I1 halogen bond and C11–H···I1 hydrogen bond. Layers parallel to the (010) plane can be recognized as a structural motif in the structure of **2** (Table 2).

4. Hirshfeld surface analysis

Crystal Explorer 17.5 (Turner *et al.*, 2017) was used to analyse the interactions in the structures and fingerprint plots mapped

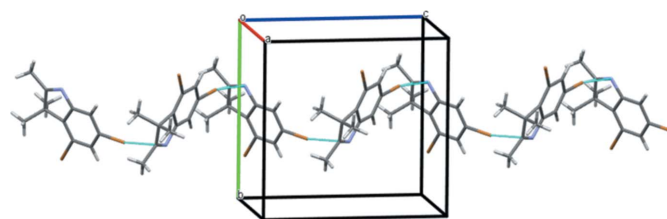


Figure 3
Zigzag chains in the crystal of compound **1**.

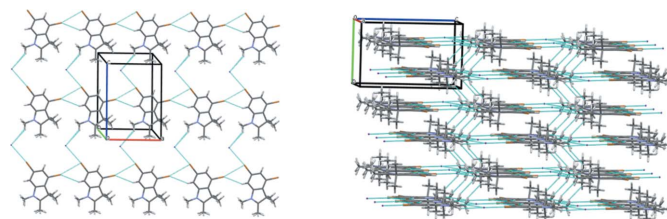


Figure 4
The chains (left) and layers (right) in the crystal of compound **2**.

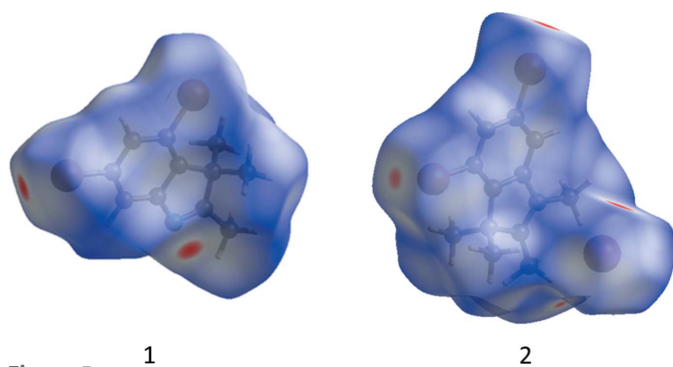


Figure 5
The Hirshfeld surface of compounds **1** and **2** mapped over d_{norm} .

over d_{norm} (Figs. 5–7) were generated. The molecular Hirshfeld surfaces were obtained using a standard (high) surface resolution with the three-dimensional d_{norm} surfaces mapped over a fixed colour scale of -0.1256 (red) to 1.401 (blue). The areas in red on the d_{norm} -mapped Hirshfeld surfaces (Fig. 5) correspond to contacts that are shorter than van der Waals radii sum of the closest atoms. As can be seen in Fig. 5, short contacts in **1** are present at the nitrogen and Br1 atoms. In **2**, the areas of short contacts are located at both the bromine atoms, the iodine atom and the hydrogen atoms of the methyl groups (Fig. 5). All of the intermolecular interactions of the title compounds are shown in the two-dimensional fingerprint plot presented in Figs. 6 and 7. The contribution of the $\text{Br} \cdots \text{H}/\text{H} \cdots \text{Br}$ contacts, corresponding to the $\text{C}-\text{H} \cdots \text{Br}$ interaction, is represented by a pair of sharp spikes. The interactions appear in the middle of the scattered points in the two-dimensional fingerprint plot with a contribution to the overall Hirshfeld surface of 30.3% (Fig. 7c) and 18.0% (Fig. 7c). The fingerprint plots indicate that the principal contributions are from $\text{H} \cdots \text{H}$ (38.3% (Fig. 6b) in **1**; 41.8% (Fig. 7b) in **2**), $\text{C} \cdots \text{H}/\text{H} \cdots \text{C}$ (13.3%; Fig. 6d in structure **1**) and $\text{I} \cdots \text{H}/\text{H} \cdots \text{I}$ (17.1%; Fig. 7d in structure **2**) contacts. The fingerprint plots also

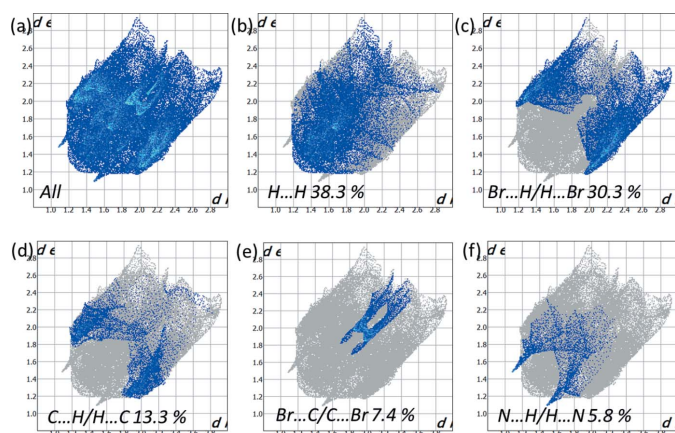


Figure 6
(a) The two-dimensional fingerprint plot for compound **1**, and those delineated into (b) $\text{H} \cdots \text{H}$ (38.3%), (c) $\text{Br} \cdots \text{H}/\text{H} \cdots \text{Br}$ (30.3%), (d) $\text{C} \cdots \text{H}/\text{H} \cdots \text{C}$ (13.3%), (e) $\text{Br} \cdots \text{C}/\text{C} \cdots \text{Br}$ (7.4%) and (f) $\text{N} \cdots \text{H}/\text{H} \cdots \text{N}$ (5.8%) contacts.

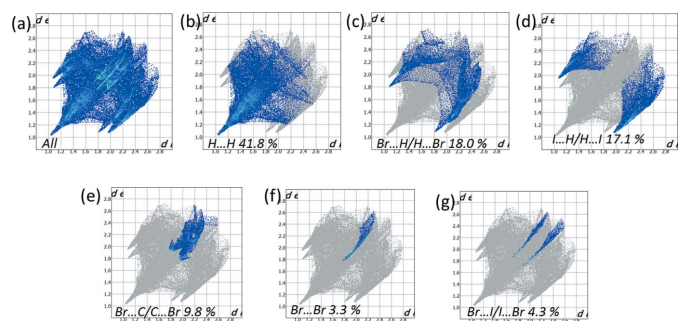


Figure 7
(a) The two-dimensional fingerprint plot for compound **2**, and those delineated into (b) $\text{H} \cdots \text{H}$ (41.8%), (c) $\text{Br} \cdots \text{H}/\text{H} \cdots \text{Br}$ (18.0%), (d) $\text{I} \cdots \text{H}/\text{H} \cdots \text{I}$ (17.1%), (e) $\text{Br} \cdots \text{C}/\text{C} \cdots \text{Br}$ (9.8%) (f) $\text{Br} \cdots \text{I}/\text{I} \cdots \text{Br}$ (4.3%) and $\text{Br} \cdots \text{Br}$ (3.3%) contacts.

indicate that all intermolecular interactions in the title compounds are rather weak.

5. Database survey

A search of the Cambridge Structural Database (CSD, Version 5.42, update of November 2020; Groom *et al.*, 2016) for the 2,3,3-trimethyl-3*H*-indole skeleton yielded 306 hits. The most similar to the title compounds are 5,7-dibromo-2,3,3-trimethyl-3*H*-indole (CSD refcode KOFRII; Holliman *et al.*, 2009) and 1,2,3,3-tetramethyl-3*H*-indolium iodide (NENZAJO1; Connell *et al.*, 2014). These compounds have a very similar molecular structure and differ only in the position of the substituents.

6. Synthesis and crystallization

Synthesis of 4,6-dibromo-2,3,3-trimethyl-3*H*-indole (**1**)

3,5-Dibromophenylhydrazine hydrochloride (**5**) (3.3 g, 11 mmol) and 3-methyl-2-butanone (1.8 mL, 16.8 mmol) were refluxed in 15 mL of acetic acid for 5 h. The acetic acid was evaporated and the residue was washed with a 5% aqueous solution Na_2CO_3 (20 mL) and then with water. Indole **1** was extracted using 3×25 mL of diethyl ether. The combined organic layers were dried over Na_2SO_4 and the ether was removed under reduced pressure by a rotary evaporator. After recrystallization from acetonitrile, light-brown crystals were obtained. Yield: 1.95 g (57%), ^1H NMR (400 MHz, $\text{DMSO}-d_6$), δ , ppm: 7.66 (1H, s, CH), 7.58 (1H, s, CH), 2.24 (3H, s, CH_3), 1.36 [6H, s, (CH_3)₂]. Analysis, %: found C, 41.69; H, 3.49; N, 4.45, $\text{C}_{11}\text{H}_{11}\text{Br}_2\text{N}$ requires C, 41.67; H, 3.50; N, 4.42, ESI-MS m/z found: $[\text{M} + \text{H}]^+$ 317.9; $\text{C}_{11}\text{H}_{12}\text{Br}_2\text{N}^+$ requires 317.9.

Synthesis of 4,6-dibromo-1,2,3,3-tetramethyl-3*H*-indol-1-ium iodide (**2**)

4,6-Dibromo-2,3,3-trimethyl-3*H*-indole (**1**) (0.3 g, 0.95 mmol) was dissolved in benzene (5 mL), iodomethane was added (0.5 mL, 8.03 mmol) and the mixture was left at room temperature for 24 h in a sealed tube. The beige crystals that formed were filtered off, washed with diethyl ether, dried,

Table 3
Experimental details.

	1	2
Crystal data		
Chemical formula	C ₁₁ H ₁₁ Br ₂ N	C ₁₂ H ₁₄ Br ₂ N ⁺ ·I ⁻
<i>M_r</i>	317.03	458.96
Crystal system, space group	Orthorhombic, <i>P2₁2₁2₁</i>	Monoclinic, <i>P2₁/m</i>
Temperature (K)	293	293
<i>a</i> , <i>b</i> , <i>c</i> (Å)	8.7761 (5), 11.3876 (7), 11.8654 (4)	8.3507 (6), 7.3719 (5), 11.7180 (8)
α , β , γ (°)	90, 90, 90	90, 92.755 (6), 90
<i>V</i> (Å ³)	1185.81 (11)	720.53 (9)
<i>Z</i>	4	2
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α
μ (mm ⁻¹)	6.80	7.74
Crystal size (mm)	0.4 × 0.3 × 0.3	0.4 × 0.2 × 0.1
Data collection		
Diffractometer	Xcalibur, Sapphire3	Xcalibur, Sapphire3
Absorption correction	Multi-scan (<i>CrysAlis PRO</i> ; Rigaku OD, 2018)	Multi-scan (<i>CrysAlis PRO</i> ; Rigaku OD, 2018)
<i>T_{min}</i> , <i>T_{max}</i>	0.682, 1.000	0.355, 1.000
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	8516, 2086, 1789	4499, 1374, 1242
<i>R_{int}</i>	0.081	0.083
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.595	0.595
Refinement		
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.047, 0.121, 1.07	0.046, 0.121, 1.05
No. of reflections	2086	1374
No. of parameters	130	97
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	0.44, -0.55	0.86, -0.91
Absolute structure	Flack <i>x</i> determined using 613 quotients [(<i>I</i> ⁺) - (<i>I</i> ⁻)] / [(<i>I</i> ⁺) + (<i>I</i> ⁻)] (Parsons et al., 2013)	-
Absolute structure parameter	0.05 (2)	-

Computer programs: *CrysAlis PRO* (Rigaku OD, 2018), *SHELXT2014/5* (Sheldrick, 2015a), *SHELXL2016/6* (Sheldrick, 2015b) and *OLEX2* (Dolomanov et al., 2009).

and were used without further purification. Yield: 300 mg (69%), ¹H NMR (400 MHz, DMSO-*d*₆), δ , ppm: 8.34 (1H, *s*, CH), 8.11 (1H, *s*, CH), 3.94 (3H, *s*, CH₃), 2.81 (3H, *s*, CH₃), 1.63 [6H, *s*, (CH₃)₂]. Analysis, %: found C, 31.34; H, 3.01; N, 3.08, C₁₂H₁₄Br₂IN requires C, 31.40; H, 3.07; N, 3.05, ESI-MS *m/z* found: [*M* - I]⁺ 331.9; C₁₂H₁₄Br₂N⁺ requires 332.0.

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. H atoms were included in calculated positions and treated as riding on their parent C atom: C-H = 0.93–0.98 Å with *U*_{iso}(H) = 1.5*U*_{eq}(C-methyl) or 1.2*U*_{eq}(C) for all other H atoms.

Funding information

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References

Atchison, J., Kamila, S., Nesbitt, H., Logan, K. A., Nicholas, D. M., Fowley, C., Davis, J., Callan, B., McHale, A. P. & Callan, J. F. (2017). *Chem. Commun.* **53**, 2009–2012.
 Belletête, M., Brisse, F., Durocher, G., Gravel, D., Héroux, A. & Popowycz, A. (1993). *J. Mol. Struct.* **297**, 63–80.
 Beverina, L. & Salice, P. (2010). *Eur. J. Org. Chem.* pp. 1207–1225.
 Burgi, H.-B. & Dunitz, J. D. (1994). *Structure correlation*, vol. 2, pp. 741–784. Weinheim: VCH.

Connell, A., Holliman, P. J., Davies, M. L., Gwenin, Ch. D., Weiss, S., Pitak, M. B., Horton, P. N., Coles, S. J. & Cooke, G. (2014). *J. Mater. Chem. A*, **2**, 4055–4066.
 Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.
 Feng, L., Chen, W., Ma, X., Liu, S. H. & Yin, J. (2020). *Org. Biomol. Chem.* **18**, 9385–9397.
 Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* **B72**, 171–179.
 Guerrero, Y., Singh, S. P., Mai, T., Murali, R. K., Tanikella, L., Zahedi, A., Kundra, V. & Anvari, B. (2017). *Appl. Mater. Interfaces*, **9**, 19601–19611.
 Holliman, P. J., Tizzard, G. J., Hursthouse, M. B. & Lamond, S. J. (2009). *University of Southampton, Crystal Structure Report Archive*, 1229.
 Liu, H., Yin, J., Xing, E., Du, Y., Su, Y., Feng, Y. & Meng, S. (2021). *Dyes Pigments*, **190**, 109327.
 Lynch, D. E., Kirkham, A. N., Chowdhury, M. Z. H., Wane, E. S. & Heptinstall, J. (2012). *Dyes Pigments*, **94**, 393–402.
 Parsons, S., Flack, H. D. & Wagner, T. (2013). *Acta Cryst.* **B69**, 249–259.
 Rigaku OD (2018). *CrysAlis PRO*. Rigaku Oxford Diffraction, Yarnton, England.
 Seiler, V. K., Callebaut, K., Robeyns, K., Tumanov, N., Wouters, J., Champagne, B. & Leyssens, T. (2018). *CrystEngComm*, **20**, 3318–3327.
 Semenova, O., Kobzev, D., Yazbak, F., Nakonechny, F., Kolosova, O., Tatars, A., Gellerman, G. & Patsenker, L. (2021). *Dyes Pigments*, **195**, 109745–109746.
 Sheldrick, G. M. (2015a). *Acta Cryst.* **A71**, 3–8.
 Sheldrick, G. M. (2015b). *Acta Cryst.* **C71**, 3–8.

Sun, W., Guo, Sh., Hu, Ch., Fan, J. & Peng, X. (2016). *Chem. Rev.* **116**, 7768–7817.

Szaciłowski, K., Macyk, W., Drzewiecka-Matuszek, A., Brindell, M. & Stochel, G. (2005). *Chem. Rev.* **105**, 2647–2694.

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

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Computing details

For both structures, data collection: *CrysAlis PRO* (Rigaku OD, 2018). Cell refinement: *CrysAlis PRO* (Rigaku OD, 2018) for (1). For both structures, data reduction: *CrysAlis PRO* (Rigaku OD, 2018); program(s) used to solve structure: *SHELXT2014/5* (Sheldrick, 2015b); program(s) used to refine structure: *SHELXL2016/6* (Sheldrick, 2015a); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009).

4,6-Dibromo-2,3,3-trimethyl-3H-indole (1)

Crystal data

$C_{11}H_{11}Br_2N$

$M_r = 317.03$

Orthorhombic, $P2_12_12_1$

$a = 8.7761$ (5) Å

$b = 11.3876$ (7) Å

$c = 11.8654$ (4) Å

$V = 1185.81$ (11) Å³

$Z = 4$

$F(000) = 616$

$D_x = 1.776$ Mg m⁻³

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

Cell parameters from 2796 reflections

$\theta = 3.6$ – 24.9°

$\mu = 6.80$ mm⁻¹

$T = 293$ K

Prism, red

$0.4 \times 0.3 \times 0.3$ mm

Data collection

Xcalibur, Sapphire3

diffractometer

Radiation source: fine-focus sealed X-ray tube,

Enhance (Mo) X-ray Source

Graphite monochromator

Detector resolution: 16.1827 pixels mm⁻¹

ω scans

Absorption correction: multi-scan

(*CrysAlisPro*; Rigaku OD, 2018)

$T_{\min} = 0.682$, $T_{\max} = 1.000$

8516 measured reflections

2086 independent reflections

1789 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.081$

$\theta_{\max} = 25.0^\circ$, $\theta_{\min} = 2.9^\circ$

$h = -10 \rightarrow 10$

$k = -13 \rightarrow 13$

$l = -14 \rightarrow 14$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.047$

$wR(F^2) = 0.121$

$S = 1.07$

2086 reflections

130 parameters

0 restraints

Primary atom site location: dual

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0554P)^2 + 0.295P]$$

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

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

$$\Delta\rho_{\max} = 0.44 \text{ e } \text{\AA}^{-3}$$

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

Absolute structure: Flack x determined using
613 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons et al.,
2013)

Absolute structure parameter: 0.05 (2)

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)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.24163 (11)	0.35819 (9)	0.83683 (7)	0.0630 (4)
Br2	0.73559 (14)	0.21032 (9)	0.56768 (8)	0.0769 (4)
N1	0.5082 (8)	0.6304 (7)	0.5315 (6)	0.0518 (18)
C1	0.4908 (9)	0.5231 (8)	0.5910 (6)	0.0432 (19)
C2	0.3837 (10)	0.5003 (7)	0.6734 (6)	0.047 (2)
H2	0.312700	0.556729	0.694752	0.056*
C3	0.3861 (9)	0.3912 (8)	0.7227 (6)	0.046 (2)
C4	0.4903 (9)	0.3063 (8)	0.6936 (7)	0.052 (2)
H4	0.489872	0.233692	0.729463	0.062*
C5	0.5979 (10)	0.3311 (8)	0.6085 (7)	0.049 (2)
C6	0.5999 (9)	0.4389 (8)	0.5579 (6)	0.046 (2)
C7	0.6962 (9)	0.4972 (8)	0.4670 (6)	0.050 (2)
C8	0.6202 (9)	0.6146 (8)	0.4635 (7)	0.051 (2)
C9	0.6811 (15)	0.4323 (11)	0.3518 (7)	0.077 (3)
H9A	0.719284	0.353684	0.359071	0.116*
H9B	0.738795	0.473434	0.295515	0.116*
H9C	0.575831	0.429848	0.329832	0.116*
C10	0.8638 (11)	0.5078 (11)	0.5014 (10)	0.079 (3)
H10A	0.870442	0.542173	0.575093	0.119*
H10B	0.916473	0.556660	0.448193	0.119*
H10C	0.909473	0.431228	0.502393	0.119*
C11	0.6680 (12)	0.7123 (9)	0.3846 (8)	0.072 (3)
H11A	0.597667	0.776545	0.390964	0.107*
H11B	0.668219	0.683767	0.308475	0.107*
H11C	0.768433	0.738629	0.404338	0.107*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0625 (6)	0.0687 (6)	0.0578 (5)	-0.0033 (6)	0.0196 (5)	0.0087 (4)
Br2	0.0836 (7)	0.0721 (7)	0.0750 (6)	0.0279 (7)	0.0213 (6)	0.0029 (5)
N1	0.054 (4)	0.052 (4)	0.050 (4)	-0.005 (4)	0.004 (3)	0.000 (4)
C1	0.042 (4)	0.048 (5)	0.040 (4)	-0.006 (4)	-0.002 (3)	-0.005 (4)
C2	0.045 (5)	0.048 (5)	0.047 (4)	0.002 (4)	0.003 (4)	-0.004 (4)

C3	0.039 (4)	0.052 (5)	0.045 (4)	-0.007 (4)	0.004 (4)	-0.004 (4)
C4	0.055 (5)	0.054 (6)	0.046 (4)	0.000 (5)	0.000 (4)	0.008 (4)
C5	0.043 (4)	0.063 (6)	0.041 (4)	-0.001 (4)	0.003 (4)	-0.001 (4)
C6	0.043 (5)	0.058 (5)	0.038 (4)	-0.003 (4)	0.005 (4)	0.001 (4)
C7	0.044 (5)	0.065 (6)	0.040 (4)	0.004 (4)	0.009 (3)	0.004 (4)
C8	0.045 (5)	0.063 (6)	0.047 (5)	-0.014 (4)	0.000 (4)	0.002 (4)
C9	0.095 (8)	0.092 (8)	0.046 (5)	-0.002 (7)	0.020 (5)	-0.016 (5)
C10	0.042 (6)	0.105 (10)	0.090 (7)	-0.003 (6)	0.008 (5)	0.013 (7)
C11	0.080 (7)	0.071 (7)	0.063 (5)	-0.019 (6)	0.023 (5)	0.020 (5)

Geometric parameters (Å, °)

Br1—C3	1.893 (8)	C7—C8	1.494 (13)
Br2—C5	1.894 (9)	C7—C9	1.560 (12)
N1—C1	1.419 (11)	C7—C10	1.531 (13)
N1—C8	1.284 (10)	C8—C11	1.514 (12)
C1—C2	1.381 (11)	C9—H9A	0.9600
C1—C6	1.411 (11)	C9—H9B	0.9600
C2—H2	0.9300	C9—H9C	0.9600
C2—C3	1.374 (11)	C10—H10A	0.9600
C3—C4	1.375 (11)	C10—H10B	0.9600
C4—H4	0.9300	C10—H10C	0.9600
C4—C5	1.412 (11)	C11—H11A	0.9600
C5—C6	1.367 (12)	C11—H11B	0.9600
C6—C7	1.522 (11)	C11—H11C	0.9600
C8—N1—C1	105.9 (8)	C8—C7—C10	111.5 (8)
C2—C1—N1	126.0 (8)	C10—C7—C9	110.6 (7)
C2—C1—C6	122.1 (8)	N1—C8—C7	116.7 (8)
C6—C1—N1	111.9 (7)	N1—C8—C11	119.8 (9)
C1—C2—H2	121.3	C7—C8—C11	123.4 (8)
C3—C2—C1	117.5 (8)	C7—C9—H9A	109.5
C3—C2—H2	121.3	C7—C9—H9B	109.5
C2—C3—Br1	118.3 (6)	C7—C9—H9C	109.5
C2—C3—C4	122.6 (7)	H9A—C9—H9B	109.5
C4—C3—Br1	119.1 (6)	H9A—C9—H9C	109.5
C3—C4—H4	120.5	H9B—C9—H9C	109.5
C3—C4—C5	119.0 (8)	C7—C10—H10A	109.5
C5—C4—H4	120.5	C7—C10—H10B	109.5
C4—C5—Br2	117.7 (7)	C7—C10—H10C	109.5
C6—C5—Br2	122.2 (6)	H10A—C10—H10B	109.5
C6—C5—C4	120.2 (8)	H10A—C10—H10C	109.5
C1—C6—C7	106.1 (7)	H10B—C10—H10C	109.5
C5—C6—C1	118.7 (7)	C8—C11—H11A	109.5
C5—C6—C7	135.2 (8)	C8—C11—H11B	109.5
C6—C7—C9	111.5 (8)	C8—C11—H11C	109.5
C6—C7—C10	112.3 (8)	H11A—C11—H11B	109.5
C8—C7—C6	99.3 (7)	H11A—C11—H11C	109.5

C8—C7—C9	111.2 (8)	H11B—C11—H11C	109.5
Br1—C3—C4—C5	-180.0 (6)	C3—C4—C5—Br2	-178.1 (6)
Br2—C5—C6—C1	178.3 (6)	C3—C4—C5—C6	1.4 (13)
Br2—C5—C6—C7	-1.3 (14)	C4—C5—C6—C1	-1.2 (12)
N1—C1—C2—C3	-179.1 (7)	C4—C5—C6—C7	179.2 (9)
N1—C1—C6—C5	179.6 (7)	C5—C6—C7—C8	179.9 (9)
N1—C1—C6—C7	-0.6 (9)	C5—C6—C7—C9	62.6 (13)
C1—N1—C8—C7	-0.7 (10)	C5—C6—C7—C10	-62.2 (13)
C1—N1—C8—C11	178.8 (8)	C6—C1—C2—C3	-0.3 (12)
C1—C2—C3—Br1	179.5 (6)	C6—C7—C8—N1	0.3 (9)
C1—C2—C3—C4	0.5 (12)	C6—C7—C8—C11	-179.2 (8)
C1—C6—C7—C8	0.2 (8)	C8—N1—C1—C2	179.8 (8)
C1—C6—C7—C9	-117.1 (8)	C8—N1—C1—C6	0.8 (9)
C1—C6—C7—C10	118.1 (9)	C9—C7—C8—N1	117.9 (8)
C2—C1—C6—C5	0.7 (12)	C9—C7—C8—C11	-61.7 (11)
C2—C1—C6—C7	-179.6 (7)	C10—C7—C8—N1	-118.2 (9)
C2—C3—C4—C5	-1.0 (13)	C10—C7—C8—C11	62.3 (11)

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C3—Br1 \cdots N1 ⁱ	1.89	3.19	5.283 (1)	166
C3—Br1 \cdots C8 ⁱ	1.89	3.53	5.046 (1)	153
C11—H11C \cdots N1 ⁱⁱ	0.96	2.69	3.621 (1)	164

Symmetry codes: (i) $-x+1/2, -y+1, z+1/2$; (ii) $x+1/2, -y+3/2, -z+1$.

4,6-Dibromo-2,3,3-trimethyl-3H-indol-1-ium iodide (2)

Crystal data

$C_{12}H_{14}Br_2N^+I^-$

$M_r = 458.96$

Monoclinic, $P2_1/m$

$a = 8.3507$ (6) \AA

$b = 7.3719$ (5) \AA

$c = 11.7180$ (8) \AA

$\beta = 92.755$ (6) $^\circ$

$V = 720.53$ (9) \AA^3

$Z = 2$

$F(000) = 432$

$D_x = 2.115$ Mg m^{-3}

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

Cell parameters from 1781 reflections

$\theta = 3.8\text{--}28.6^\circ$

$\mu = 7.74$ mm^{-1}

$T = 293$ K

Needle, red

$0.4 \times 0.2 \times 0.1$ mm

Data collection

Xcalibur, Sapphire3

diffractometer

Radiation source: fine-focus sealed X-ray tube,

Enhance (Mo) X-ray Source

Graphite monochromator

Detector resolution: 16.1827 pixels mm^{-1}

ω scans

Absorption correction: multi-scan

(CrysAlisPro; Rigaku OD, 2018)

$T_{\min} = 0.355$, $T_{\max} = 1.000$

4499 measured reflections

1374 independent reflections

1242 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.083$

$\theta_{\max} = 25.0^\circ$, $\theta_{\min} = 2.9^\circ$

$h = -9 \rightarrow 9$

$k = -8 \rightarrow 8$

$l = -12 \rightarrow 13$

*Refinement*Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.046$ $wR(F^2) = 0.121$ $S = 1.05$

1374 reflections

97 parameters

0 restraints

Primary atom site location: dual

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

 $w = 1/[\sigma^2(F_o^2) + (0.0732P)^2 + 0.1443P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} = 0.001$ $\Delta\rho_{\max} = 0.86 \text{ e } \text{\AA}^{-3}$ $\Delta\rho_{\min} = -0.91 \text{ e } \text{\AA}^{-3}$ *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>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
I1	0.70649 (6)	0.750000	0.12215 (4)	0.0481 (3)	
Br1	0.57546 (9)	0.250000	0.65282 (7)	0.0477 (3)	
Br2	1.19756 (8)	0.250000	0.49523 (7)	0.0455 (3)	
N1	0.7083 (7)	0.250000	0.2129 (5)	0.0333 (13)	
C1	0.7464 (7)	0.250000	0.3305 (5)	0.0310 (15)	
C2	0.6429 (8)	0.250000	0.4171 (6)	0.0339 (15)	
H2	0.532393	0.250000	0.402939	0.041*	
C3	0.7113 (9)	0.250000	0.5275 (6)	0.0361 (16)	
C4	0.8733 (8)	0.250000	0.5472 (6)	0.0334 (15)	
H4	0.915491	0.250000	0.622086	0.040*	
C5	0.9763 (8)	0.250000	0.4585 (6)	0.0321 (14)	
C6	0.9130 (8)	0.250000	0.3468 (6)	0.0317 (15)	
C7	0.9823 (9)	0.250000	0.2291 (6)	0.0328 (15)	
C8	0.8337 (9)	0.250000	0.1513 (6)	0.0347 (16)	
C9	1.0830 (6)	0.4194 (8)	0.2084 (5)	0.0446 (12)	
H9A	1.017880	0.525689	0.215897	0.067*	
H9B	1.122463	0.414922	0.132876	0.067*	
H9C	1.171753	0.423837	0.263544	0.067*	
C10	0.8300 (11)	0.250000	0.0265 (7)	0.0483 (19)	
H10A	0.929629	0.203613	0.001073	0.073*	0.5
H10B	0.814457	0.371640	-0.001140	0.073*	0.5
H10C	0.743463	0.174747	-0.002504	0.073*	0.5
C11	0.5431 (10)	0.250000	0.1659 (8)	0.051 (2)	
H11A	0.541464	0.284350	0.086856	0.077*	0.5
H11B	0.480906	0.334906	0.207372	0.077*	0.5
H11C	0.498349	0.130744	0.172659	0.077*	0.5

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
I1	0.0529 (4)	0.0457 (4)	0.0464 (4)	0.000	0.0092 (3)	0.000
Br1	0.0410 (5)	0.0658 (6)	0.0376 (5)	0.000	0.0156 (4)	0.000
Br2	0.0282 (5)	0.0547 (5)	0.0532 (5)	0.000	-0.0025 (4)	0.000
N1	0.034 (3)	0.038 (3)	0.028 (3)	0.000	-0.006 (2)	0.000
C1	0.024 (4)	0.042 (4)	0.027 (3)	0.000	-0.001 (3)	0.000
C2	0.028 (3)	0.041 (4)	0.033 (4)	0.000	0.004 (3)	0.000
C3	0.036 (4)	0.041 (4)	0.033 (4)	0.000	0.009 (3)	0.000
C4	0.038 (4)	0.038 (4)	0.024 (3)	0.000	-0.004 (3)	0.000
C5	0.031 (4)	0.034 (3)	0.032 (3)	0.000	0.001 (3)	0.000
C6	0.029 (4)	0.033 (4)	0.033 (4)	0.000	0.005 (3)	0.000
C7	0.038 (4)	0.031 (3)	0.030 (4)	0.000	0.014 (3)	0.000
C8	0.040 (4)	0.035 (4)	0.030 (4)	0.000	0.007 (3)	0.000
C9	0.046 (3)	0.047 (3)	0.042 (3)	-0.002 (2)	0.012 (2)	0.007 (2)
C10	0.058 (5)	0.052 (5)	0.036 (4)	0.000	0.006 (4)	0.000
C11	0.038 (5)	0.070 (6)	0.045 (5)	0.000	0.000 (4)	0.000

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

Br1—C3	1.899 (7)	C7—C8	1.504 (10)
Br2—C5	1.877 (7)	C7—C9	1.532 (7)
N1—C1	1.399 (8)	C7—C9 ⁱ	1.532 (7)
N1—C8	1.301 (9)	C8—C10	1.461 (10)
N1—C11	1.460 (10)	C9—H9A	0.9600
C1—C2	1.364 (10)	C9—H9B	0.9600
C1—C6	1.395 (9)	C9—H9C	0.9600
C2—H2	0.9300	C10—H10A	0.9600
C2—C3	1.389 (10)	C10—H10B	0.9600
C3—C4	1.361 (10)	C10—H10C	0.9600
C4—H4	0.9300	C11—H11A	0.9600
C4—C5	1.381 (10)	C11—H11B	0.9600
C5—C6	1.387 (10)	C11—H11C	0.9600
C6—C7	1.522 (9)		
C1—N1—C11	122.5 (6)	C8—C7—C9	110.3 (4)
C8—N1—C1	113.3 (6)	C8—C7—C9 ⁱ	110.3 (4)
C8—N1—C11	124.2 (7)	C9—C7—C9 ⁱ	109.3 (6)
C2—C1—N1	127.6 (6)	N1—C8—C7	109.0 (6)
C2—C1—C6	124.1 (6)	N1—C8—C10	125.2 (7)
C6—C1—N1	108.3 (6)	C10—C8—C7	125.7 (6)
C1—C2—H2	121.7	C7—C9—H9A	109.5
C1—C2—C3	116.5 (6)	C7—C9—H9B	109.5
C3—C2—H2	121.7	C7—C9—H9C	109.5
C2—C3—Br1	119.1 (5)	H9A—C9—H9B	109.5
C4—C3—Br1	119.6 (5)	H9A—C9—H9C	109.5
C4—C3—C2	121.3 (6)	H9B—C9—H9C	109.5

C3—C4—H4	119.3	C8—C10—H10A	109.5
C3—C4—C5	121.5 (6)	C8—C10—H10B	109.5
C5—C4—H4	119.3	C8—C10—H10C	109.5
C4—C5—Br2	118.0 (5)	H10A—C10—H10B	109.5
C4—C5—C6	119.1 (6)	H10A—C10—H10C	109.5
C6—C5—Br2	122.9 (5)	H10B—C10—H10C	109.5
C1—C6—C7	107.2 (6)	N1—C11—H11A	109.5
C5—C6—C1	117.5 (6)	N1—C11—H11B	109.5
C5—C6—C7	135.3 (6)	N1—C11—H11C	109.5
C6—C7—C9 ⁱ	112.3 (4)	H11A—C11—H11B	109.5
C6—C7—C9	112.3 (4)	H11A—C11—H11C	109.5
C8—C7—C6	102.2 (5)	H11B—C11—H11C	109.5
Br1—C3—C4—C5	180.000 (2)	C4—C5—C6—C1	0.000 (1)
Br2—C5—C6—C1	180.000 (1)	C4—C5—C6—C7	180.000 (1)
Br2—C5—C6—C7	0.000 (2)	C5—C6—C7—C8	180.000 (1)
N1—C1—C2—C3	180.000 (1)	C5—C6—C7—C9	-61.8 (4)
N1—C1—C6—C5	180.000 (1)	C5—C6—C7—C9 ⁱ	61.8 (4)
N1—C1—C6—C7	0.000 (1)	C6—C1—C2—C3	0.000 (1)
C1—N1—C8—C7	0.000 (1)	C6—C7—C8—N1	0.000 (1)
C1—N1—C8—C10	180.000 (1)	C6—C7—C8—C10	180.000 (1)
C1—C2—C3—Br1	180.000 (1)	C8—N1—C1—C2	180.000 (1)
C1—C2—C3—C4	0.000 (2)	C8—N1—C1—C6	0.000 (1)
C1—C6—C7—C8	0.000 (1)	C9 ⁱ —C7—C8—N1	119.6 (4)
C1—C6—C7—C9 ⁱ	-118.2 (4)	C9—C7—C8—N1	-119.6 (4)
C1—C6—C7—C9	118.2 (4)	C9 ⁱ —C7—C8—C10	-60.4 (4)
C2—C1—C6—C5	0.000 (1)	C9—C7—C8—C10	60.4 (4)
C2—C1—C6—C7	180.000 (1)	C11—N1—C1—C2	0.000 (1)
C2—C3—C4—C5	0.000 (2)	C11—N1—C1—C6	180.000 (1)
C3—C4—C5—Br2	180.000 (1)	C11—N1—C8—C7	180.000 (1)
C3—C4—C5—C6	0.000 (2)	C11—N1—C8—C10	0.000 (1)

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C2—H2 \cdots Br2 ⁱⁱ	0.93	3.05	3.872 (1)	149
C5—Br2 \cdots Br1 ⁱⁱⁱ	1.88 (1)	3.58	5.397 (1)	162
C3—Br1 \cdots I1 ^{iv}	1.90 (1)	3.62	5.514 (1)	176
C11—H11A \cdots I1 ^v	0.96	3.14	3.881 (1)	135

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