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

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4,6-Dibromo-2,3,3-trimethyl-3H-indole, \(\text{C}_{11}\text{H}_{11}\text{Br}_{2}\text{N}\), exists as a neutral molecule in the asymmetric unit. The asymmetric unit of 4,6-dibromo-2,3,3-trimethyl-3H-indol-1-ium iodide, \(\text{C}_{12}\text{H}_{14}\text{Br}_{2}\text{N}^+\text{I}^-\), 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 \(\text{C—Br}\) 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 \(\text{C—H}\cdots\text{Br}\) hydrogen bonds, \(\text{C—Br}\cdots\text{Br}\) and \(\text{C—Br}\cdots\text{I}\) 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-3H-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.
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-3H-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 C10H$_3$ and C11H$_3$ 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 by 0.029 (1) Å as a result of the formation of intermolecular interactions. As a result, molecular packing of 2 is determined by the presence of the iodide anion in compound 2 and 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).

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—H···Br2 and C12—H···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 [010] 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.
over $d_{\text{norm}}$ (Figs. 5–7) were generated. The molecular Hirshfeld surfaces were obtained using a standard (high) surface resolution with the three-dimensional $d_{\text{norm}}$ surfaces mapped over a fixed colour scale of $-0.1256$ (red) to 1.401 (blue). The areas in red on the $d_{\text{norm}}$-mapped Hirshfeld surfaces 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, 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 Br···H/\(H···Br\) contacts, corresponding to the C−H···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. 6c) and 18.0% (Fig. 7c). The fingerprint plots indicate that the principal contributions are from H···H (38.3% (Fig. 6b) in 1; 41.8% (Fig. 7b) in 2), C···H/\(H···C\) (13.3%; Fig. 6d in structure 1) and I···H/\(H···I\) (17.1%; Fig. 7d in structure 2) contacts. The fingerprint plots also 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-3H-indol-1-amine skeleton yielded 306 hits. The most similar to the title compounds are 5,7-dibromo-2,3,3-trimethyl-3H-indole (CSD refcode KOFRII; Holliman et al., 2009) and 1,2,3,3-tetramethyl-3H-indolium iodide (NENZAJ01; 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-3H-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 Na2CO₃ (20 mL) and then with water. Indole 1 was extracted using 3 × 25 mL of diethyl ether. The combined organic layers were dried over Na2SO4 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, DMSO-d₆), δ, ppm: 7.66 (1H, s, CH), 7.58 (1H, s, CH), 2.24 (3H, s, CH₃), 1.36 [6H, s, (CH₃)₂]. Analysis, %: found C, 41.69; H, 3.49; N, 4.45. C₁₁H₁₂Br₂N requires C, 41.67; H, 3.50; N, 4.42.

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

4,6-Dibromo-2,3,3-trimethyl-3H-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^-    |
| M_r         | 317.03                     | 458.96                      |
| Crystal system, space group | Orthorhombic, P2_12_2_1   | Monoclinic, P2_1/cm        |
| Temperature (K) | 293                        | 293                        |
| a, b, c (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         |
| V (Å^3)    | 1185.81 (11)                | 720.53 (9)                  |
| Z          | 4                          | 2                          |
| Radiation type | Mo Kα                      | Mo Kα                      |
| 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 (CrysAlis PRO; Rigaku OD, 2018) | Multi-scan (CrysAlis PRO; Rigaku OD, 2018) |
| T_{min}, T_{max} | 0.682, 1.000             | 0.355, 1.000                |
| No. of measured, independent and observed | 8516, 2086, 1789 | 4499, 1374, 1242 |
| R_{int}        | 0.081                     | 0.083                       |
| (sin θ/λ)_{max} (Å^-1) | 0.595                     | 0.595                       |

Refinement

| R(F^2) > 2σ(F^2), wR(F^2), S | 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 |
| Δρ_{max}, Δρ_{min} (e Å^-3) | 0.44, −0.55 | 0.86, −0.91 |
| Absolute structure | Flack x determined using 613 quotients | − |
| Absolute structure parameter | [I(I)−I(I)]/[I(I)+I(I)] (Parsons et al., 2013) | 0.05 (2) |

Chemical formula C_{11}H_{11}Br_{2}N and C_{12}H_{14}Br_{2}N+I^- 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, CH_3), 2.81 (3H, s, CH_3), 1.63 [6H, s, (CH_3)_2]. Analysis, %: found C, 31.34; H, 3.01; N, 3.05; ESI-MS m/z: C_{12}H_{14}Br_{2}N+ 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(eq)(H) = 1.5U(eq)(C-methyl) or 1.2U(eq)(C) for all other H atoms.

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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**

C₁₁H₁₁Br₂N

Mᵣ = 317.03

Orthorhombic, P2₁2₁2₁

a = 8.7761 (5) Å

b = 11.3876 (7) Å

μ = 6.80 mm⁻¹

φ = 3.6°–24.9°

Cell parameters from 2796 reflections

θ = 2.9°–24.9°

M = 1.776 Mg m⁻³

Mo Kα radiation, λ = 0.71073 Å

T = 293 K

Prism, red

0.4 × 0.3 × 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)

8516 measured reflections

2086 independent reflections

1789 reflections with I > 2σ(I)

Rint = 0.081

θmax = 25.0°, θmin = 2.9°

h = −10→10

k = −13→13

l = −14→14

**Refinement**

Refinement on F²

Least-squares matrix: full

R[F² > 2σ(F²)] = 0.047

wR(F²) = 0.121

S = 1.07

130 parameters

0 restraints

Primary atom site location: dual

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

supporting information
$w = 1/[\sigma^2(F_o^2) + (0.0554P)^2 + 0.295P]$  
where $P = (F_o^2 + 2F_c^2)/3$

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

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

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

**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 (Å$^2$)**

|       | $x$      | $y$      | $z$      | $U_{iso}/U_{eq}$ |
|-------|----------|----------|----------|------------------|
| 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 (Å$^2$)**

|       | $U_1^{11}$ | $U_2^{12}$ | $U_3^{13}$ | $U_1^{22}$ | $U_2^{23}$ | $U_3^{33}$ |
|-------|------------|------------|------------|------------|------------|------------|
| 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) |

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

Absolute structure parameter: 0.05 (2)
### Geometric parameters (Å, °)

|     |     |     |     |     |     |     |
|-----|-----|-----|-----|-----|-----|-----|
| 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) |

|     |     |     |     |     |     |     |
|-----|-----|-----|-----|-----|-----|-----|
| 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—C7 −1.3 (14)  C4—C5—C6—C1 −1.2 (12)
N1—C1—C2—C3 −179.1 (7)  C4—C5—C6—C7 179.9 (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 (Å, °)

\[
\begin{array}{cccc}
D—H···A & D—H & H···A & D···A \\
C3—Br1···N1i & 1.89 & 3.19 & 5.283 (1) & 166 \\
C3—Br1···C8i & 1.89 & 3.53 & 5.046 (1) & 153 \\
C11—H11C···N1ii & 0.96 & 2.69 & 3.621 (1) & 164 \\
\end{array}
\]

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

\(C_{12}H_{14}Br_2N^+\cdot I^-\)

\(M_r = 458.96\)

Monoclinic, \(P2_1/m\)

\(a = 8.3507 (6) \text{ Å}\

\(b = 7.3719 (5) \text{ Å}\

\(c = 11.7180 (8) \text{ Å}\

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

\(V = 720.53 (9) \text{ Å}^3\)

\(Z = 2\)

\(F(000) = 432\)

\(D_x = 2.115 \text{ Mg m}^{-3}\)

Mo \(K\alpha\) radiation, \(\lambda = 0.71073 \text{ Å}\)

Cell parameters from 1781 reflections

\(\theta = 3.8–28.6^\circ\)

\(\mu = 7.74 \text{ mm}^{-1}\)

\(T = 293 \text{ K}\)

Needle, red

\(T_{\text{min}} = 0.355, T_{\text{max}} = 1.000\)

4499 measured reflections

1374 independent reflections

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

\(R_{\text{int}} = 0.083\)

\(\theta_{\text{max}} = 25.0^\circ, \theta_{\text{min}} = 2.9^\circ\)

\(h = -9 \rightarrow 9\)

\(k = -8 \rightarrow 8\)

\(l = -12 \rightarrow 13\)

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\(^{-1}\)

\(\omega\) scans

Absorption correction: multi-scans

(CrysAlisPro; Rigaku OD, 2018)

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sup-4
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

\[
 w = 1/[\sigma(F_o^2) + (0.0732P)^2 + 0.1443P] \\
(\Delta/\sigma)_{\text{max}} = 0.001 \\
\Delta \rho_{\text{max}} = 0.86 \text{ e Å}^{-3} \\
\Delta \rho_{\text{min}} = -0.91 \text{ e Å}^{-3}
\]

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

|    | x    | y    | z    | \( U_{iso} \)/\( U_{eq} \) | 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 | 0.3305 (5) | 0.0310 (13) |
| C1 | 0.7464 (7) | 0.250000 | 0.4171 (6) | 0.0339 (15) |
| C2 | 0.6429 (8) | 0.250000 | 0.402939 | 0.041* |
| H2 | 0.53239 | 0.250000 | 0.5275 (6) | 0.0361 (16) |
| C3 | 0.7113 (9) | 0.250000 | 0.5472 (6) | 0.0334 (15) |
| C4 | 0.8733 (8) | 0.250000 | 0.622086 | 0.040* |
| H4 | 0.915491 | 0.250000 | 0.4585 (6) | 0.0321 (14) |
| C5 | 0.9763 (8) | 0.250000 | 0.3468 (6) | 0.0317 (15) |
| C6 | 0.9130 (8) | 0.250000 | 0.2291 (6) | 0.0328 (15) |
| C7 | 0.8337 (9) | 0.250000 | 0.1513 (6) | 0.0347 (16) |
| C8 | 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* |
| H10B | 0.814457 | 0.371640 | -0.001140 | 0.073* |
| H10C | 0.743463 | 0.174747 | -0.002504 | 0.073* |
| C11 | 0.5431 (10) | 0.250000 | 0.1659 (8) | 0.051 (2) |
| H11A | 0.541464 | 0.284350 | 0.086856 | 0.077* |
| H11B | 0.480906 | 0.334906 | 0.207372 | 0.077* |
| H11C | 0.498349 | 0.130744 | 0.172659 | 0.077* |
### Atomic displacement parameters (Å²)

|     | $U^{11}$   | $U^{22}$   | $U^{33}$   | $U^{12}$   | $U^{13}$   | $U^{23}$   |
|-----|------------|------------|------------|------------|------------|------------|
| I   | 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 (Å, °)

|        |          |          |          |          |          |          |
|--------|----------|----------|----------|----------|----------|----------|
| 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  | 122.5 (6) | C8—C7—C9 | 110.3 (4) |          |          |          |
| C8—N1  | 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—C6 | 127.6 (6) | N1—C8—C7  | 109.0 (6) |          |          |          |
| C6—C1—N1 | 108.3 (6) | C10—C8—C7  | 125.2 (7) |          |          |          |
| 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
C4—C5—C6—C1 0.000 (1) C4—C5—C6—C7 180.000 (1)
C4—C5—C6—C7 0.000 (2) C5—C6—C7—C9 −61.8 (4)
C5—C6—C7—C8 180.000 (1) C5—C6—C7—C9 180.000 (1)
C6—C7—C8—C9 −118.2 (4) C6—C7—C8—C9i 61.8 (4)
C1—C2—C3—Br1 180.000 (1) C1—C2—C3—C4 0.000 (2)
C1—C2—C3—C4 0.000 (2) C2—C3—C4—Br2 180.000 (1)
C1—C2—C3—C4 0.000 (2) C2—C3—C4—C5 0.000 (2)
C1—C2—C3—C4 0.000 (2) C3—C4—C5—Br2 180.000 (1)
C8—C7—C6 102.2 (5) C8—C7—C6 102.2 (5)
Symmetry code: (i) x, y, z.

Hydrogen-bond geometry (Å, °)

| D—H···A | D—H | H···A | D···A | D—H···A |
|---------|------|-------|-------|---------|
| C2—H2···Br2" | 0.93 | 3.05 | 3.872 (1) | 149 |
| C5—Br2···Br1"" | 1.88 (1) | 3.58 | 5.397 (1) | 162 |
| C3—Br1···I1iv | 1.90 (1) | 3.62 | 5.514 (1) | 176 |
| C11—H114···I1v | 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.