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Dibromonitrotoluene

Mohamed Larbi Medjroubi,[a]* Olivier Jeannin,[b] Marc Fourmigué,[b] Ali Boudjada[a] and Jean Meinnel[b]

[a]Laboratoire de Cristallographie, Département de Physique, Université Mentouri-Constantine, 25000 Constantine, Algeria, and [b]UMR 6226 CNRS–Université Rennes 1, 'Institut des 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: mlmedj@gmail.com

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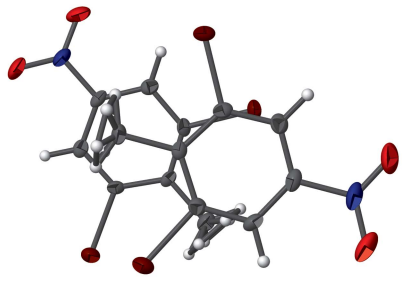
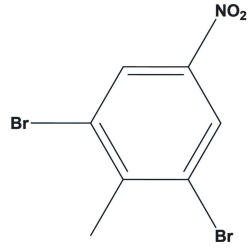
The title compound, $C_7H_5Br_2NO_2$ (common name: dibromonitrotoluene; systematic name: 1,3-dibromo-2-methyl-5-nitrobenzene) crystallizes with two independent molecules (*A* and *B*) in the asymmetric unit. In molecule *A*, the Br atoms lie almost in the plane of the benzene ring, with deviations of 0.012 (1) and 0.009 (1) Å, while for the methyl C atom the deviation is 0.038 (4) Å. In molecule *B*, the opposite is observed; for the methyl C atom the deviation is 0.003 (4) Å, while the two Br atoms deviate by 0.032 (1) and 0.025 (1) Å. In the crystal, the *B* molecules are linked *via* C—H···Br hydrogen bonds, forming chains along [101]. The *A* molecules are also aligned along the same direction, and there is a short Br···O contact of 3.101 (4) Å involving the *A* and *B* molecules. The molecules stack in layers parallel to (101) and are linked by weak π–π interactions [intercentroid distances = 3.564 (3) Å between *A* molecules and 3.662 (3) Å between *B* molecules].

3D view



Chemical scheme



Structure description

In trihalogeno-mesitylene molecules, for example 1,3,5-tribromo-2,4,6-trimethylbenzene (Bosch & Barnes, 2002), each methyl group is symmetrically surrounded by two halogens, the three potentials hindering the methyl-group rotation are rather large and different because they are mainly due to intramolecular interactions. The question was to know if the same is true for the title compound.

The title compound, Fig. 1, crystallizes with two independent molecules (*A* and *B*) in the asymmetric unit. The conformations of the two molecules are similar, as shown the by molecular overlap of molecule *B* inverted onto molecule *A* (Fig. 2). The nitro group (N4/O41/O42) is inclined to the benzene ring (C1–C6) by 2.5 (5)° in molecule *A* [the

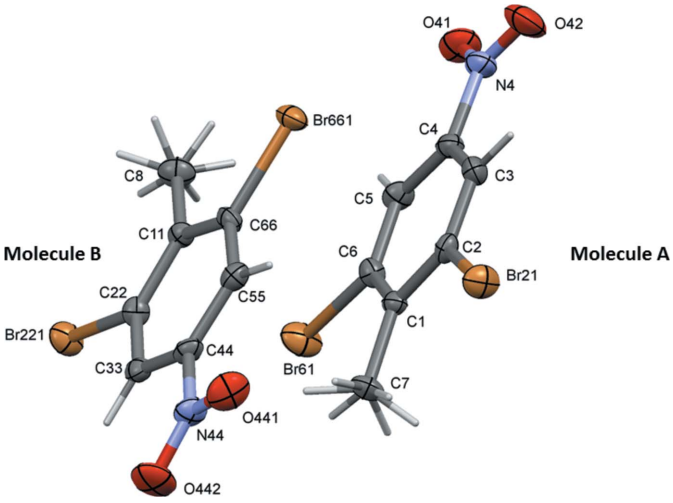


Figure 1
The molecular structure of the two independent molecules (*A* and *B*) of the title compound, showing the atom labelling. Displacement ellipsoids are drawn at the 50% probability level.

corresponding angle is 5.9 (4) ° in molecule *B*]. In molecule *A*, the methyl C atom (C7) is displaced from the benzene ring by 0.038 (4) Å, while the Br atoms lie almost in the plane of the benzene ring [deviations are −0.009 (1) Å for atom Br61 and −0.012 (1) Å for atom Br21]. In molecule *B*, the opposite is observed; atom C8 lies in the plane of the benzene ring [deviation = 0.003 (4) Å], while atoms Br661 and Br221 deviate by 0.032 (1) and 0.025 (1) Å, respectively. In a very similar compound, methyl 3,5-dibromo-4-methylbenzoate (Saeed *et al.*, 2010), the situation is slightly different; the methyl C atom deviates from the benzene ring by 0.026 (3) Å, while the two Br atoms deviate by 0.006 (1) and 0.067 (1) Å.

In molecule *A*, the cyclic C—C(CH$_3$)—C angle C2—C1—C6 is 114.7 (3) °, while the cyclic C—C(Br)—C angles are C1—C6—C5 = 123.6 (3) and C1—C2—C3 = 123.7 (3) °. In molecule *B*, the cyclic C—C(CH$_3$)—C angle C22—C11—C66 is 116.2 (3)°, while the cyclic C—C(Br)—C angles are C11—C66—C55 = 122.9 (3) and C11—C22—C33 =123.0 (3)°. This is similar to the situation in 1,3,5-tribromo-2,4,6-trimethylbenzene (Bosch & Barnes, 2002) and methyl 3,5-dibromo-4-

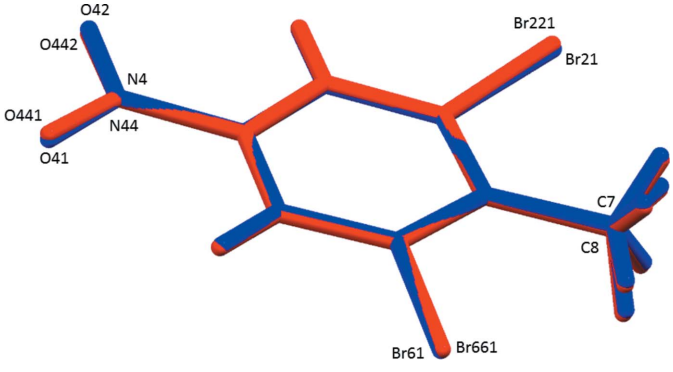


Figure 2
A view of the molecular overlap of the two independent molecules (*A* black and *B* red; *PLATON*; Spek, 2009).

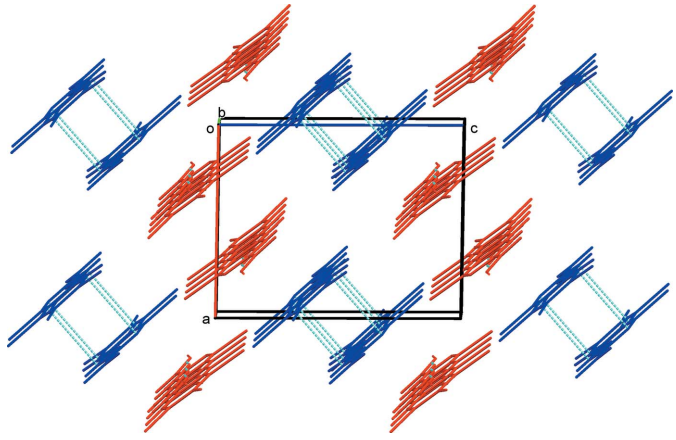


Figure 3
A view along the *b* axis of the crystal packing of the title compound, with the C—H···Br and shortest C$_{ar}$···C$_{ar}$ (ar = aromatic) interactions shown as dashed lines (molecule *A* blue and molecule *B* red).

methylbenzoate (Saeed *et al.*, 2010), where the cyclic C—C(CH$_3$)-C angles average *ca* 115.1°, and the cyclic C—C(Br)—C angles average *ca* 124.5°.

In the crystal, there is a short Br···O contact of 3.101 (4) Å involving the *A* and *B* molecules [Br661···O42^{i}; symmetry code (i): − *x* + 1, − *y* + 1, − *z* + 1]. The *B* molecules are linked by C—H···Br hydrogen bonds, forming chains along [101]; see Fig. 3 and Table 1. The *A* molecules also align along the same direction. The molecules stack in layers parallel to (101) and are linked by weak *π*–*π* interactions (Fig. 3): *Cg*1···*Cg*1^{ii} = 3.564 (3) Å, interplanar distance = 3.4396 (15) Å, slippage = 0.932 Å, symmetry code (ii): − *x* + 1, − *y*, − *z*; *Cg*2···*Cg*2^{iii} =

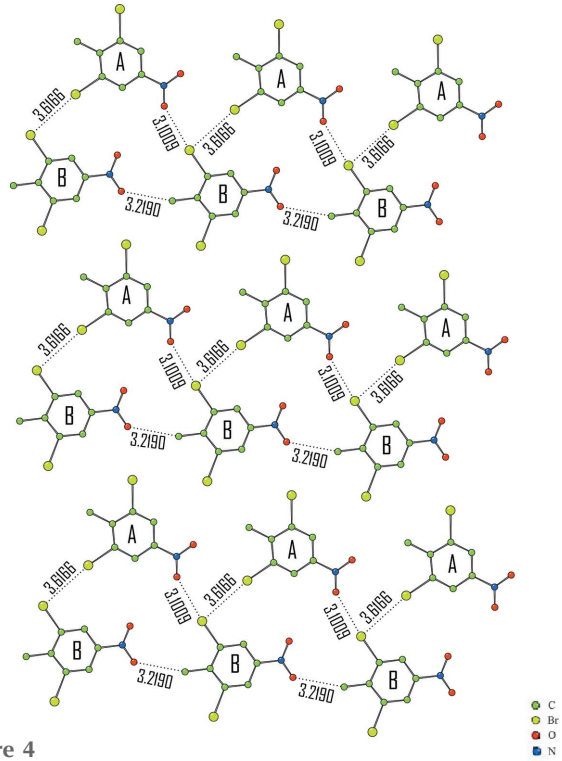


Figure 4
Intermolcular Br···O and Br···Br interactions.

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

D—H···A	D—H	H···A	D···A	D—H···A
C55—H551···Br21^{i}	0.96	2.92	3.799 (5)	153

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

3.662 (3) Å, interplanar distance = 3.3875 (16) Å, slippage = 1.391 Å, symmetry code (iii): $-x+2, -y+1, -z+1$; where *Cg*1 is the centroid of the benzene ring C1–C6 in molecule *A*, and *Cg*2 is the centroid of the benzene ring C11–C66 in molecule *B*. Intermolecular Br···O and Br···Br interactions of < 4 Å are shown in Fig. 4.

Synthesis and crystallization

The title compound is commercially available (Sigma–Aldrich). It was recrystallized from ethanol solution giving large needle-shaped single crystals, many of which were twinned.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The H atoms of the methyl groups are disordered over two positions, rotated by 60°.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_7H_5Br_2NO_2$
M_r	294.93
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	150
a, b, c (Å)	8.755 (5), 9.533 (5), 10.897 (5)
α, β, γ (°)	91.324 (5), 90.517 (5), 103.216 (5)
V (Å^3)	885.1 (8)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	9.12
Crystal size (mm)	0.34 × 0.21 × 0.12
Data collection	
Diffractometer	Bruker APEXII
Absorption correction	Multi-scan (*SADABS*; Bruker, 2006)
T_{min}, T_{max}	0.116, 0.335
No. of measured, independent and observed [$I > 3.0\sigma(I)$] reflections	8470, 4040, 3256
R_{int}	0.031
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.649
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.029, 0.053, 0.85
No. of reflections	3064
No. of parameters	218
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.63, −0.48

Computer programs: *APEX2* and *SAINT* (Bruker, 2006), *SIR2003* (Burla *et al.*, 2005), *CAMERON* (Watkin *et al.*, 1996), *Mercury* (Macrae *et al.*, 2008), *CRYSTALS* (Betteridge *et al.*, 2003) and *PLATON* (Spek, 2009).

Acknowledgements

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full crystallographic data

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1,3-Dibromo-2-methyl-5-nitrobenzene

Crystal data

$C_7H_5Br_2NO_2$
M_r = 294.93
Triclinic, $P\overline{1}$
Hall symbol: -P 1
a = 8.755 (5) Å
b = 9.533 (5) Å
c = 10.897 (5) Å
α = 91.324 (5)°
β = 90.517 (5)°
γ = 103.216 (5)°
V = 885.1 (8) Å^3
Z = 4
$F(000)$ = 560
D_x = 2.213 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71069 Å
Cell parameters from 3096 reflections
θ = 2.9–27.4°
μ = 9.12 mm^{-1}
T = 150 K
Block, colourless
0.34 × 0.21 × 0.12 mm

Data collection

Bruker APEXII diffractometer
Graphite monochromator
CCD rotation images, thin slices scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2006)
T_{min} = 0.116, T_{max} = 0.335
8470 measured reflections
4040 independent reflections
3256 reflections with $I > 3.0\sigma(I)$
R_{int} = 0.031
θ_{max} = 27.5°, θ_{min} = 1.9°
h = −11→9
k = −11→12
l = −13→14

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.053
S = 0.85
3064 reflections
218 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Hydrogen site location: difference Fourier map
H-atom parameters constrained
Method, part 1, Chebychev polynomial, [*w*eight] = 1.0/[A_0*T_0(x) + A_1*T_1(x) ··· + A_{n-1}]*T_{n-1}(x)] where A_i are the Chebychev coefficients listed below and x = *F* /*F*max Method = Robust Weighting W = [*w*eight] * [1-(delta*F*/6*sigma*F*)^2]^2 A_i are: 12.2 14.7 6.04
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.63 e Å^{-3}
$\Delta\rho_{min}$ = −0.48 e Å^{-3}

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

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Br21	0.73115 (5)	0.09978 (5)	0.53248 (4)	0.0289	
C2	0.8164 (4)	0.2686 (4)	0.4435 (3)	0.0187	

C3	0.7672 (5)	0.3919 (4)	0.4745 (3)	0.0224	
C4	0.8284 (5)	0.5151 (4)	0.4102 (4)	0.0217	
N4	0.7810 (4)	0.6497 (4)	0.4438 (3)	0.0303	
O41	0.8408 (4)	0.7582 (3)	0.3882 (3)	0.0405	
O42	0.6863 (5)	0.6461 (4)	0.5250 (3)	0.0474	
C5	0.9344 (5)	0.5165 (4)	0.3171 (4)	0.0221	
C6	0.9806 (4)	0.3910 (4)	0.2894 (3)	0.0197	
C1	0.9253 (4)	0.2614 (4)	0.3505 (3)	0.0173	
C7	0.9797 (5)	0.1263 (4)	0.3212 (4)	0.0236	
Br61	1.12679 (6)	0.39735 (5)	0.16074 (4)	0.0344	
Br661	0.45446 (5)	0.18993 (4)	0.27224 (4)	0.0245	
C66	0.5718 (4)	0.0850 (4)	0.1767 (3)	0.0185	
C55	0.5606 (4)	−0.0581 (4)	0.2075 (4)	0.0208	
C44	0.6430 (5)	−0.1374 (4)	0.1372 (4)	0.0206	
N44	0.6302 (4)	−0.2905 (3)	0.1650 (3)	0.0250	
O441	0.5369 (4)	−0.3445 (3)	0.2432 (3)	0.0360	
O442	0.7129 (4)	−0.3558 (3)	0.1075 (3)	0.0410	
C33	0.7364 (4)	−0.0797 (4)	0.0402 (3)	0.0194	
C22	0.7452 (4)	0.0633 (4)	0.0139 (3)	0.0180	
C11	0.6644 (4)	0.1508 (4)	0.0807 (3)	0.0173	
C8	0.6755 (5)	0.3058 (4)	0.0494 (4)	0.0281	
Br221	0.87104 (5)	0.13891 (4)	−0.12061 (4)	0.0275	
H31	0.6928	0.3923	0.5387	0.0500*	
H51	0.9747	0.6023	0.2728	0.0500*	
H551	0.4975	−0.1004	0.2747	0.0500*	
H331	0.7932	−0.1369	−0.0070	0.0500*	
H81	0.7431	0.3316	−0.0181	0.0500*	0.5000
H82	0.7156	0.3672	0.1185	0.0500*	0.5000
H83	0.5738	0.3198	0.0285	0.0500*	0.5000
H84	0.6130	0.3477	0.1045	0.0500*	0.5000
H85	0.7816	0.3590	0.0564	0.0500*	0.5000
H86	0.6385	0.3118	−0.0323	0.0500*	0.5000
H71	1.0530	0.1427	0.2558	0.0500*	0.5000
H72	1.0291	0.0972	0.3913	0.0500*	0.5000
H73	0.8926	0.0505	0.2965	0.0500*	0.5000
H74	0.9288	0.0504	0.3723	0.0500*	0.5000
H75	1.0905	0.1428	0.3337	0.0500*	0.5000
H76	0.9558	0.0976	0.2372	0.0500*	0.5000

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br21	0.0327 (2)	0.0265 (2)	0.0289 (2)	0.00771 (17)	0.01083 (17)	0.01296 (17)
C2	0.0211 (18)	0.0186 (18)	0.0155 (17)	0.0026 (14)	−0.0028 (14)	0.0031 (14)
C3	0.027 (2)	0.025 (2)	0.0169 (18)	0.0095 (16)	0.0003 (15)	−0.0027 (15)
C4	0.0235 (19)	0.0186 (19)	0.025 (2)	0.0095 (15)	−0.0067 (15)	−0.0047 (15)
N4	0.037 (2)	0.0242 (19)	0.033 (2)	0.0169 (16)	−0.0093 (17)	−0.0098 (15)
O41	0.052 (2)	0.0189 (16)	0.053 (2)	0.0135 (15)	−0.0124 (17)	−0.0046 (14)

O42	0.063 (2)	0.042 (2)	0.045 (2)	0.0311 (19)	0.0102 (18)	−0.0090 (16)
C5	0.026 (2)	0.0133 (17)	0.026 (2)	0.0026 (15)	−0.0017 (16)	0.0039 (15)
C6	0.0215 (19)	0.0189 (18)	0.0179 (18)	0.0030 (14)	0.0012 (14)	−0.0014 (14)
C1	0.0169 (17)	0.0166 (17)	0.0190 (17)	0.0055 (13)	−0.0024 (14)	−0.0023 (14)
C7	0.026 (2)	0.0174 (19)	0.029 (2)	0.0090 (15)	0.0044 (16)	−0.0022 (15)
Br61	0.0379 (3)	0.0332 (2)	0.0347 (2)	0.01147 (19)	0.0199 (2)	0.01220 (19)
Br661	0.0240 (2)	0.0237 (2)	0.0281 (2)	0.01057 (16)	0.00368 (16)	−0.00436 (15)
C66	0.0188 (17)	0.0168 (18)	0.0198 (18)	0.0044 (14)	−0.0006 (14)	−0.0067 (14)
C55	0.0204 (18)	0.0208 (19)	0.0211 (19)	0.0043 (15)	−0.0023 (15)	0.0036 (15)
C44	0.0239 (19)	0.0131 (17)	0.025 (2)	0.0059 (14)	−0.0058 (15)	0.0019 (14)
N44	0.0322 (19)	0.0147 (16)	0.0287 (18)	0.0071 (14)	−0.0044 (15)	0.0028 (13)
O441	0.0384 (18)	0.0256 (16)	0.0425 (19)	0.0024 (13)	0.0040 (15)	0.0169 (14)
O442	0.062 (2)	0.0196 (15)	0.048 (2)	0.0205 (15)	0.0084 (17)	0.0045 (14)
C33	0.0173 (17)	0.0191 (18)	0.0225 (19)	0.0061 (14)	−0.0047 (14)	−0.0011 (15)
C22	0.0181 (17)	0.0155 (17)	0.0182 (18)	−0.0010 (14)	0.0014 (14)	0.0024 (14)
C11	0.0191 (17)	0.0107 (16)	0.0212 (18)	0.0019 (13)	−0.0043 (14)	−0.0007 (13)
C8	0.029 (2)	0.0190 (19)	0.036 (2)	0.0057 (17)	0.0023 (18)	0.0027 (17)
Br221	0.0310 (2)	0.0247 (2)	0.0265 (2)	0.00517 (16)	0.01052 (17)	0.00595 (16)

Geometric parameters (Å, º)

Br21—C2	1.904 (4)	Br661—C66	1.892 (4)
C2—C3	1.377 (5)	C66—C55	1.395 (5)
C2—C1	1.408 (5)	C66—C11	1.398 (5)
C3—C4	1.384 (6)	C55—C44	1.382 (5)
C3—H31	0.961	C55—H551	0.961
C4—N4	1.476 (5)	C44—N44	1.476 (5)
C4—C5	1.380 (6)	C44—C33	1.387 (5)
N4—O41	1.224 (5)	N44—O441	1.225 (5)
N4—O42	1.213 (5)	N44—O442	1.225 (5)
C5—C6	1.376 (5)	C33—C22	1.385 (5)
C5—H51	0.957	C33—H331	0.962
C6—C1	1.406 (5)	C22—C11	1.406 (5)
C6—Br61	1.899 (4)	C22—Br221	1.897 (4)
C1—C7	1.501 (5)	C11—C8	1.506 (5)
C7—H71	0.955	C8—H81	0.949
C7—H72	0.952	C8—H82	0.955
C7—H73	0.955	C8—H83	0.956
C7—H74	0.953	C8—H84	0.956
C7—H75	0.954	C8—H85	0.953
C7—H76	0.957	C8—H86	0.952
Br21—C2—C3	117.4 (3)	Br661—C66—C55	116.6 (3)
Br21—C2—C1	118.9 (3)	Br661—C66—C11	120.5 (3)
C3—C2—C1	123.7 (3)	C55—C66—C11	122.9 (3)
C2—C3—C4	117.9 (4)	C66—C55—C44	117.5 (3)
C2—C3—H31	121.1	C66—C55—H551	121.3
C4—C3—H31	121.1	C44—C55—H551	121.2

C3—C4—N4	119.0 (4)	C55—C44—N44	118.9 (3)
C3—C4—C5	122.0 (3)	C55—C44—C33	122.8 (3)
N4—C4—C5	119.0 (4)	N44—C44—C33	118.3 (3)
C4—N4—O41	117.6 (4)	C44—N44—O441	118.1 (3)
C4—N4—O42	118.1 (4)	C44—N44—O442	117.8 (3)
O41—N4—O42	124.3 (4)	O441—N44—O442	124.1 (3)
C4—C5—C6	118.2 (3)	C44—C33—C22	117.7 (3)
C4—C5—H51	121.0	C44—C33—H331	121.2
C6—C5—H51	120.8	C22—C33—H331	121.1
C5—C6—C1	123.6 (3)	C33—C22—C11	123.0 (3)
C5—C6—Br61	116.9 (3)	C33—C22—Br221	116.9 (3)
C1—C6—Br61	119.5 (3)	C11—C22—Br221	120.2 (3)
C2—C1—C6	114.7 (3)	C22—C11—C66	116.2 (3)
C2—C1—C7	122.4 (3)	C22—C11—C8	121.8 (3)
C6—C1—C7	122.9 (3)	C66—C11—C8	122.0 (3)
C1—C7—H71	109.9	C11—C8—H81	110.3
C1—C7—H72	110.3	C11—C8—H82	109.9
H71—C7—H72	108.9	H81—C8—H82	109.1
C1—C7—H73	110.1	C11—C8—H83	110.0
H71—C7—H73	108.7	H81—C8—H83	109.0
H72—C7—H73	108.9	H82—C8—H83	108.5
C1—C7—H74	110.3	C11—C8—H84	109.9
H71—C7—H74	139.8	H81—C8—H84	139.9
H72—C7—H74	57.0	H82—C8—H84	55.2
H73—C7—H74	55.1	H83—C8—H84	56.4
C1—C7—H75	110.1	C11—C8—H85	110.1
H71—C7—H75	56.8	H81—C8—H85	55.6
H72—C7—H75	55.3	H82—C8—H85	56.8
H73—C7—H75	139.8	H83—C8—H85	139.9
H74—C7—H75	109.1	H84—C8—H85	108.8
C1—C7—H76	109.9	C11—C8—H86	110.2
H71—C7—H76	54.8	H81—C8—H86	56.7
H72—C7—H76	139.8	H82—C8—H86	139.9
H73—C7—H76	57.0	H83—C8—H86	55.5
H74—C7—H76	108.9	H84—C8—H86	108.8
H75—C7—H76	108.5	H85—C8—H86	109.1

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C55—H551···Br21^{i}	0.96	2.92	3.799 (5)	153

Symmetry code: (i) −*x*+1, −*y*, −*z*+1.