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The low-temperature phase of 1,3-dibromo-2,4,6-trimethylbenzene: a single-crystal neutron diffraction study at 120 and 14 K

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In the low-temperature phase of dibromomesitylene (1,3-dibromo-2,4,6-trimethylbenzene), $C_9H_{10}Br_2$, the molecule deviates significantly from the C_{3h} molecular symmetry encountered in tribromomesitylene (1,3,5-tribromo-2,4,6-trimethylbenzene), even for the endocyclic bond angles. An apparent C_{2v} molecular symmetry is observed. The angle between the normal to the molecular plane and the normal to the (100) plane is ~20°. The overall displacement was analysed at 120 K with rigid-body-motion tensor analysis. The methyl group located intermediate between the two Br atoms is rotationally disordered at both temperatures. This disorder was treated using two different approaches at 14 K, *viz.* the conventional split-atom model and a model using the special annular shapes of the atomic displacement parameters that are available in *CRYSTALS* [Watkin, Prout, Carruthers & Betteridge (1999). Issue 11. Chemical Crystallography Laboratory, Oxford, England], but only through the latter approach at 120 K. The disorder locally breaks the C_{2v} molecular symmetry at 14 K only. Intra- and intermolecular contacts are described and discussed in relation to this methyl-group disorder. The bidimensional pseudo-hexagonal structural topology of trihalogenomesitylenes is altered in dibromomesitylene insofar as the (100) molecular layers are undulated and are not coplanar as a result of an alternating tilt angle of ~34° propagating along the [011] and $[0\bar{1}\bar{1}]$ directions between successive antiferroelectric molecular columns oriented roughly along the *a* axis.

Comment

Halogenomethylbenzenes are considered as prototype systems for studying the quantum-rotational tunnelling behaviour (Prager & Heidemann, 1997) of methyl groups. The tunnel splitting, which acts as a local probe of molecular and crystal force fields, is used to test the relevance of numerical modelling (molecular dynamics and *ab initio* quantum-chemistry calculations) of intra- and intermolecular potentials. In this context, it is of great interest, as a prerequisite to any subsequent studies, not only to establish the crystal structures of these compounds at room temperature but also to determine the conformations of the methyl groups and the nuclear density of their H atoms at low temperature (typically below 30 K). The use of neutron diffraction in this endeavour is essential. We have focused our investigations first on the threefold symmetric trihalogenomesitylenes (1,3,5-trihalogeno-2,4,6-trimethylbenzenes), namely 1,3,5-trichloro-, 1,3,5-tribromo- and 1,3,5-triiodo-2,4,6-trimethylbenzene [trichloromesitylene (TCM; Tazi *et al.*, 1995), tribromomesitylene (TBM; Meinnel *et al.*, 2000) and triiodomesitylene (TIM; Boudjada *et al.*, 2001, 2002), respectively], which are triclinic at room temperature. Besides their interesting low-temperature dynamical properties, halogenomethylbenzenes are also studied because of their rich phase-transition properties. Orientational dynamic disorder is often encountered in the highest temperature phases ('plastic phases'; Kitaïgorodsky, 1973), and on heating or cooling, original phase transitions may occur (Fujiwara *et al.*, 1990; Tazi, 1990).

Replacing one halogen substituent in trihalogenomesitylenes by, for instance, an H atom lowers the molecular symmetry *via* the breaking of the C_3 symmetry axis of the isolated molecule (disregarding the methyl H atoms) and facilitates the study of the influence of the non-symmetric local molecular environment of the methyl groups on their quantum-rotational tunnelling behaviour. With these facts as background, we report here a structural study of 1,3-dibromo-2,4,6-trimethylbenzene (dibromomesitylene, DBM), (I), at 120 and 14 K from single-crystal neutron diffraction data. This work is the crystallographic counterpart of a numerical study of molecular structure and methyl-group rotational potential in halogenomesitylenes published elsewhere (Plazanet, 2000; Plazanet *et al.*, 2002). The methyl-group tunnelling behaviour of (I) was first studied by inelastic neutron scattering (INS; Meinnel *et al.*, 1995). A quasi-free quantum-rotor behaviour was evidenced for the methyl group intermediate between the two Br atoms, as reflected by a large tunnelling splitting of 0.39 meV, and a hindering potential with a predominant sixfold symmetry was proposed. In addition, (I) undergoes a reconstructive phase transition near room temperature (between 293 and 301 K); hence, both of the present structure determinations will refer to the low-temperature phase of the title compound, the structure of the high-temperature phase (probably a plastic phase) being unknown. The 14 K structure will be considered as the 'reference structure' of the low-temperature phase of (I); the following discussion will be based on the parameters of this phase unless otherwise noted.

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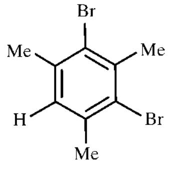
The conformation of (I) (Fig. 1, and Tables 1 and 2) is characterized mainly by a significant distortion of the endocyclic angles of the aromatic ring from ideal D_{6h} symmetry, the endocyclic angles being narrowed for a donor substituent such as Me and enlarged for a C_{ar} atom linked to an acceptor such as a halogen (Domenicano *et al.*, 1975). This deformation, which has already been encountered in TCM, TBM and TIM with C_{3h} symmetry, is much less symmetric here because of the inequivalence of the substituents at the 1-, 3- and 5-positions on the benzene ring. Indeed, C_{2v} symmetry can be discerned in (I) from the distortion of the endocyclic angles, *viz*. for atoms with methyl substituents, 117.08 (11)° (on average for atoms C4 and C6) and 115.77 (5)° (for atom C2), and for atoms bonded to bromine, 123.60 (7)° (on average for atoms C1 and C3); the angle is 122.87 (5)° for atom C5 linked to atom H51. In other words, it transpires that (disregarding the H_{Me} atoms) a molecular mirror plane perpendicular to the benzene ring runs through atoms C7, C2, C5 and H51. The intersection of this mirror plane with the plane of the ring is the twofold axis of the C_{2v} symmetry. Such a description in terms of simple symmetry considerations is roughly corroborated by the values of the exocyclic angles, which on either side of the C_2 axis are equal within 0.15°. Note that these slight deviations from the apparent C_{2v} symmetry concerning the exocyclic angles increase progressively on traversing the line from atom H51 to atom C7 (from ±0.006 to ±0.43°, respectively). The average intramolecular bond lengths [$C_{ar}—Br$ = 1.905 (3) Å, $C_{ar}—C_{ar}$ = 1.398 (2) Å and $C_{ar}—C_{Me}$ = 1.500 (2) Å], as well as the single $C_{ar}—H$ bond length [1.091 (2) Å], agree with the distances reported in the literature.



(I)

We have computed the best least-squares plane (unit weights) through the 12 non-H_{Me} atoms using the *MOLAX* routine in *CRYSTALS* (Watkin, Prout, Carruthers & Betteridge, 1999). The angle between the normal to the (100) plane and the normal to the molecular plane is 19.83°. While deviations from the latter plane are negligible for the benzene C atoms [mean absolute value = 0.005 (1) Å] and for atom H51 [0.010 (2) Å], atom Br2 deviates more significantly from the plane than atom Br1 [−0.032 (1) *versus* 0.009 (1) Å]; the same conclusion can be drawn for atom C9 of the methyl group *trans* to atom Br2 [−0.026 (1) *versus* 0.013 (1) and 0.009 (1) Å for atoms C7 and C8, respectively]. The refinement of the occupancies of the substituted groups, *i.e.* the Br atoms, atom H51 and the C_{Me} atoms, reveals no deviation (within the s.u. values) from the site-symmetry multiplicity. The low-temperature phase of (I) is therefore well ordered, without any orientational disorder of the whole molecule.

For the 120 K data, we performed a conventional **TLS** analysis using the *CRYSTALS* program (Watkin, Prout, Carruthers & Betteridge, 1999). The overall rigid-body-motion tensors **T**, **L** and **S** (Schomaker & Trueblood, 1968) were least-squares fitted to the individual anisotropic displacement parameters. In order to obtain a reasonably good overall *R* factor for U_{ij} (0.126), it was necessary to exclude all the H_{Me} atoms from the **TLS** calculation. Nevertheless, when atom H51 is removed from the calculation, the *R* factor for U_{ij} decreases significantly to 0.041, while the main **TLS** features remain unchanged. The diagonal values of the translational (**T**) and screw (**S**) tensors with respect to the principal axes of the librational (**L**) tensor are negligible, while those of the **L** tensor are $L_{11} = 1.4$, $L_{22} = 4.8$ and $L_{33} = 9.6°^2$. The centre of libration is close to the centre of gravity of the molecule. Axis 1 makes an angle of ~10° with the ring plane and is approximately perpendicular to the C5—C6 bond; axis 2 makes an angle of 42° with the normal to the ring plane and lies in a plane containing the C6—C9 bond; axis 3 makes an angle of 75° with the normal to the ring plane and lies in a plane perpendicular to the C3—C4 bond. At 14 K, the U_{ij} values are too small to permit convergence of the least-squares fitting.

The most striking crystallographic features of the low-temperature phase of (I) are the particular conformations of the three methyl groups with regard to the benzene ring and the nuclear density of the H_{Me} atoms. The experimental nuclear densities of the H atoms for each methyl group were determined by setting their occupancies to zero, refining the scale factor only and performing a difference Fourier synthesis in their plane [*e.g.* see Fig. 2 of Plazanet *et al.* (2002); the H-atom nuclear densities of the C7 methyl group at 120 and 14 K correspond to the observed structure factors multiplied by −1]. The H atoms of the C8 and C9 methyl groups appear localized around three sites, but their nuclear densities are much more diffuse than those of the C atoms to which they are linked; the H-atom U_{eq} parameters are 2.1–5.3 times larger than those of atoms C8 or C9. Both of these methyl groups are 'eclipsed', *i.e.* atoms H81 and H91 are located in the plane of the aromatic ring, with relevant torsion angles of 1.71 and 2.26°, respectively; atoms H81 and H91 point at atom H51 and

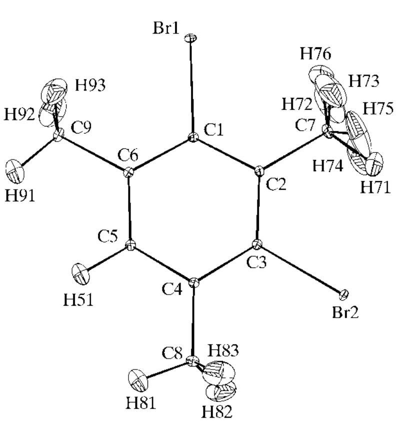


Figure 1
A view of (I) at 14 K, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

display the largest U_{eq} parameters of the methyl groups. This configuration allows the minimization of intramolecular $H_{Me}\cdots$Br interactions for the C8 and C9 methyl groups; the minimum contact distances are 2.996 (3) and 2.959 (3) Å for H82$\cdots$Br2 and H93$\cdots$Br1, respectively, compared with 2.586 (4) and 2.572 (6) Å for H71$\cdots$Br2 and H76$\cdots$Br1, respectively, involving the C7 methyl group. The aforementioned apparent C_{2v} symmetry is thus fulfilled here to a high degree of exactitude, as illustrated by the almost equal values of the C4—C8—H81 and C6—C9—H91 angles [110.75 (11) and 110.79 (9)°, respectively]. Note that, for trihalogenomesitylenes, C_{3h} and C_s symmetries are almost equally probable in isolated molecules and C_{2v} symmetry may be stabilized in the crystalline state, as encountered in TIM (Boudjada *et al.*, 2002). The C_{Me}—H bond length is systematically, though slightly, longer for staggered H atoms than for eclipsed ones [*e.g.* 1.0921 (19) and 1.0938 (18) Å for C8—H82 and C8—H83, respectively, *versus* 1.0890 (17) Å for C8—H81], and hence the C8 and C9 methyl groups do not exhibit perfect threefold symmetry; this deviation from threefold symmetry is predicted by density functional theory (DFT) and all quantum-mechanical calculations (Meinnel *et al.*, 2000; Boudjada *et al.*, 2002). On the other hand, the C7 methyl group situated intermediate between the two Br atoms behaves differently from the C8 and C9 methyl moieties. The H-atom nuclear density of the C7 group is, indeed, much more diffuse and strongly anisotropic (even at 14 K), in the sense that three damped maxima emerge from a distorted annulus. The split-atom model corresponds to two overlapped pseudo-methyl groups at 60° to one other, both eclipsed with the ring plane, *viz*. one with an average occupancy of $\sim\frac{2}{3}$ [mean value = 0.68 (2) for atoms H71, H72 and H73] and the other with an occupancy of $\sim\frac{1}{3}$ [mean value = 0.32 (2) for atoms H74, H75 and H76]. This description is equivalent to that obtained from the special-shape model [three split atoms (H71, H72 and H73) with a mean occupancy of 0.36 (2) plus a homogeneous ring with an occupancy of 1.92 (3)]. However, the real nuclear density along the H-atom rotational path, which is clearly inhomogeneous at 14 K and which is predicted to be divided among six sites for one methyl group from both INS experiments (Meinnel *et al.*, 1995) and DFT calculations (Plazanet *et al.*, 2002), is better accounted for by the split-atom model (for which the three H_{Me} sites lying between the principal congeners are refined with individual occupancies) than by the special-shape function. In any case, the apparent C_{2v} symmetry that is approximately fulfilled by the rest of the molecule is broken locally at 14 K by the H-atom nuclear density of the C7 methyl group. The occupancy of the H75(H74) site is approximately one-half that of the H73(H72) site; the two pairs of sites are thus not related by a mirror plane. In other words, at 14 K, the three most occupied H_{Me} sites (H71, H72 and H73) – which correspond to the three main maxima of Fig. 2(*b*) of Plazanet *et al.* (2002) – break the C_{2v} molecular symmetry because one of them, atom H71, is eclipsed and points towards atom Br2. However, this breaking of the molecular symmetry is not encountered at 120 K, insofar as the C7 methyl group H atoms are significantly delocalized, their nuclear densities forming an almost perfect ring (see Fig. 2*a* of Plazanet *et al.*, 2002). The delocalization of the H_{Me} atoms, although present at low temperature, is dynamic and reflects the quantum rotational tunnelling of the methyl groups coupled to their classical thermal motions and those of the whole molecule.

The structure of (I) can be described as a stacking of undulated molecular layers perpendicular to the *a* axis (at $x/a \simeq \frac{1}{4}$ and $\frac{3}{4}$), thus forming molecular columns propagated in the direction of that axis (Figs. 2 and 3). In these columns, the arrangement is 'antiferroelectric'; a given molecule is sandwiched between two molecules generated by as many inversion centres and belonging to adjacent layers. Atoms Br1 and Br2 are more or less directly below (*a*-projected shift $\simeq$ 0.75 Å) the C8 and C9 methyl groups, respectively, while, because the C_{Me}—H bond length is shorter than the C—Br bond, atom H51 is almost exactly below the disordered C7 methyl group. Such a structural topology is encountered at room temperature in triclinic TBM (Meinnel *et al.*, 2000) and TIM (Boudjada *et al.*, 2001, 2002), but in the latter two compounds, the molecular layers are flat, with each molecule lying in the (100) planes within 5°, while in the title compound, the normal to the ring plane is tilted by ~20° with respect to the *a* axis (see above). This tilt induces an undulation of the molecules within the (100) planes; along the [011] and [$0\bar{1}1$] directions, two successive *a*-axis-oriented antiferroelectric molecular columns are tilted by 34.30°. Consequently, the pseudo-hexagonal arrangement in the molecular layers that is typical of trihalogenomesitylenes (Boudjada *et al.*, 2002) and hexamethylbenzene (Hamilton *et al.*, 1969) is modified significantly in (I). Indeed, one molecule is surrounded by six neighbours in such a way that the C7, C8 and C9 methyl groups of neighbouring molecules are opposite one another, as are atoms Br1, Br2 and H51. However, because of the tilt of the molecules in (I), the triangular contacts differ from those in TBM and TIM (the symmetry operations for the atoms involved in these contacts can be found in the supplementary material); the Br$\cdots$Br contact distance is increased [3.767 (3) Å *versus* a mean of 3.572 Å in TBM], and the intermolecular C7$\cdots$C9 and C8$\cdots$C9 distances are shortened

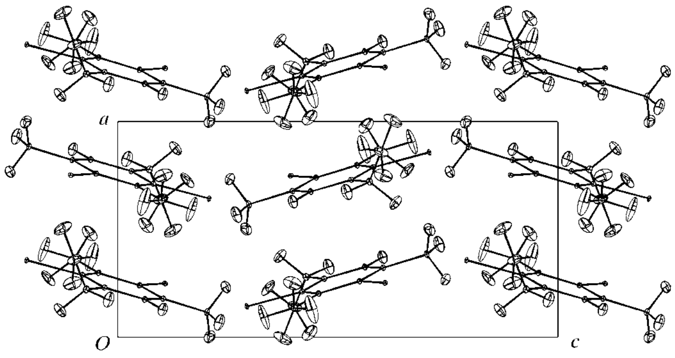


Figure 2
The packing of (I) at 14 K, viewed along the *c* axis. Displacement ellipsoids are drawn at the 30% probability level.

significantly, whereas the C7···C8 contact distance is almost unchanged [3.762 (4), 3.768 (4) and 4.084 (4) Å, respectively, *versus* a mean of 4.074 Å in TBM]. Atom H51 is 4.103 (4) and 3.114 (4) Å from atoms Br1 and Br2, respectively, of neighbouring molecules. More specifically, the eclipsed atoms H81 and H91 point towards atoms Br1 and Br2, respectively, of neighbouring molecules [contact distances = 3.199 (3) and 2.978 (3) Å compared with short intermolecular C8···Br1 and C9···Br2 contacts of 4.185 (4) and 3.963 (4) Å, respectively], while the shortest C7···Br contact distance in the (100) planes is 4.316 (6) Å. For molecules in different layers, it transpires that the minimum intermolecular distances, compared with the distances between molecules in the same layer, are significantly increased for the Br···Br and H51···Br contacts. The C7 and C8 methyl groups are involved in short H51···H_{Me} contacts [*e.g.* H51···H74 = 2.817 (5) Å and H51···H83 = 2.835 (3) Å], but the strongest van der Waals (vdW) interactions (Bondi, 1964) occur for H_{Me}···Br (sum of vdW radii = 3.05 Å); the minimum contact distances are 2.913 (4) and 2.952 (4) Å for H82···Br1 and H93···Br2, *versus* 3.029 (3) Å for H72···Br1. In summary, the differences between the C7 methyl group and its C8 and C9 analogues (from a structural point of view) can be explained by the symmetrical molecular and crystal environment of the C7 group. Indeed, this methyl group, which lies on the C_2 molecular symmetry axis, is flanked by two Br atoms in the molecule and is sandwiched between two H51 atoms in the molecular columns. The C7 methyl group therefore experiences stronger symmetric H_{Me}···Br intramolecular interactions. It should be stressed that the H_{Me}···Br intermolecular interactions are slightly weaker for the C7 methyl group than for the C8 and C9 groups. The significant Me···Me intermolecular coupling (sum of vdW radii = 2.40 Å) does not differ between the C7 and the C8 and C9 methyl groups but appears stronger than that in TBM [the minimum H_{Me}···H_{Me} intermolecular contact distance is 2.351 (5) Å in (I) for H75···H92 *versus* 2.764 Å in TBM].

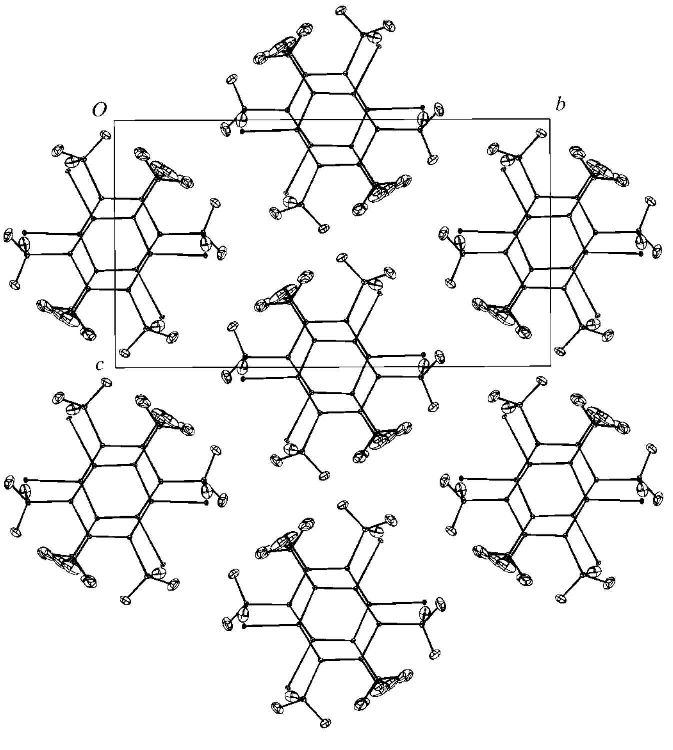


Figure 3
The packing of (I) at 14 K, viewed along the *a* axis. Displacement ellipsoids are drawn at the 30% probability level.

Experimental

Single crystals of (I) were grown by slow cooling (from 273 K) of a saturated solution of dibromomesitylene in chlorobenzene. A single crystal suitable for neutron diffraction data collection was kept below the phase-transition temperature (~297 K) throughout the experiment.

Compound (I) at 14 K

Crystal data

$C_9H_{10}Br_2$
M_r = 277.99
Monoclinic, $P2_1/n$
a = 7.691 (13) Å
b = 14.41 (2) Å
c = 8.909 (11) Å
β = 113.13 (2)°
V = 908 (2) Å^3
Z = 4
D_x = 2.034 Mg m^{-3}

Neutron radiation
λ = 0.8308 Å
Cell parameters from 12 reflections
θ = 36.0–42.0°
μ = 0.39 mm^{-1}
T = 14 (1) K
Prism, white
3.5 × 3.0 × 3.0 mm

Table 1
Selected geometric parameters (Å, °) for (I) at 14 K.

Br1—C1	1.9037 (19)	C7—H71	1.073 (2)
Br2—C3	1.906 (3)	C7—H72	1.0801 (18)
C1—C2	1.4025 (19)	C7—H73	1.092 (2)
C1—C6	1.3967 (14)	C7—H74	1.090 (2)
C2—C3	1.4038 (15)	C7—H75	1.085 (2)
C2—C7	1.4993 (15)	C7—H76	1.080 (2)
C3—C4	1.3962 (14)	C8—H81	1.0890 (17)
C4—C5	1.3943 (19)	C8—H82	1.0921 (19)
C4—C8	1.5008 (16)	C8—H83	1.0938 (18)
C5—C6	1.3939 (15)	C9—H91	1.0860 (18)
C5—H51	1.0911 (16)	C9—H92	1.0909 (17)
C6—C9	1.500 (2)	C9—H93	1.0912 (18)
Br1—C1—C2	119.34 (9)	C2—C7—H73	109.48 (14)
Br1—C1—C6	117.06 (9)	H71—C7—H73	108.0 (2)
C2—C1—C6	123.60 (5)	H72—C7—H73	106.7 (2)
C1—C2—C3	115.77 (5)	C2—C7—H74	108.5 (3)
C1—C2—C7	121.65 (5)	C2—C7—H75	111.0 (3)
C3—C2—C7	122.58 (9)	H74—C7—H75	107.4 (2)
Br2—C3—C2	119.02 (4)	C2—C7—H76	114.4 (3)
Br2—C3—C4	117.39 (4)	H74—C7—H76	107.5 (2)
C2—C3—C4	123.59 (9)	H75—C7—H76	107.8 (2)
C3—C4—C5	117.08 (11)	C4—C8—H81	110.75 (11)
C3—C4—C8	122.7 (1)	C4—C8—H82	111.55 (11)
C5—C4—C8	120.22 (5)	H81—C8—H82	108.10 (15)
C4—C5—C6	122.87 (5)	C4—C8—H83	110.69 (11)
C4—C5—H51	118.53 (8)	H81—C8—H83	108.84 (16)
C6—C5—H51	118.60 (11)	H82—C8—H83	106.77 (14)
C1—C6—C5	117.09 (11)	C6—C9—H91	110.79 (9)
C1—C6—C9	122.6 (1)	C6—C9—H92	110.8 (1)
C5—C6—C9	120.33 (9)	H91—C9—H92	108.30 (15)
C2—C7—H71	113.56 (17)	C6—C9—H93	111.69 (12)
C2—C7—H72	110.55 (16)	H91—C9—H93	108.44 (14)
H71—C7—H72	108.28 (17)	H92—C9—H93	106.67 (17)

Data collection

Orphée reactor (Saclay, France) 5C2 four-circle diffractometer
ω scans
3875 measured reflections
2998 independent reflections
2347 reflections with $I > 3\sigma(I)$

$R_{\rm int}$ = 0.017
$\theta_{\rm max}$ = 37.5°
$h = -11 \rightarrow 2$
$k = 0 \rightarrow 21$
$l = -12 \rightarrow 13$

Refinement

Refinement on F
R = 0.026
wR = 0.023
S = 1.16
2347 reflections
224 parameters
All H-atom parameters refined
Weighting: Chebychev polynomial with 4 parameters (Carruthers & Watkin, 1979)

$(\Delta/\sigma)_{\rm max}$ = 0.002
$\Delta\rho_{\rm max}$ = 0.65 Fm Å^{-3}
$\Delta\rho_{\rm min}$ = −0.97 Fm Å^{-3}
Extinction correction: equation (22) of Larson (1970)
Extinction coefficient: 17.4 (3)

Compound (I) at 120 K

Crystal data

$C_9H_{10}Br_2$
M_r = 277.99
Monoclinic, $P2_1/n$
a = 7.721 (14) Å
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μ = 0.39 mm^{-1}
T = 120 (1) K
Prism, white
3.5 × 3.0 × 3.0 mm

Data collection

Orphée reactor (Saclay, France) 5C2 four-circle diffractometer
ω scans
3242 measured reflections
2547 independent reflections
1490 reflections with $I > 3\sigma(I)$

$R_{\rm int}$ = 0.017
$\theta_{\rm max}$ = 35.0°
$h = -10 \rightarrow 2$
$k = 0 \rightarrow 19$
$l = -11 \rightarrow 12$

Table 2
Selected geometric parameters (Å, °) for (I) at 120 K.

Br1—C1	1.898 (2)	C5—C6	1.391 (2)
Br2—C3	1.904 (4)	C5—H51	1.091 (3)
C1—C2	1.403 (3)	C6—C9	1.501 (3)
C1—C6	1.392 (2)	C8—H81	1.089 (3)
C2—C3	1.399 (2)	C8—H82	1.090 (3)
C2—C7	1.497 (2)	C8—H83	1.086 (4)
C3—C4	1.392 (2)	C9—H91	1.088 (4)
C4—C5	1.391 (3)	C9—H92	1.091 (4)
C4—C8	1.498 (2)	C9—H93	1.091 (3)
Br1—C1—C2	119.50 (14)	C1—C6—C5	117.06 (16)
Br1—C1—C6	117.04 (14)	C1—C6—C9	122.69 (15)
C2—C1—C6	123.5 (1)	C5—C6—C9	120.25 (14)
C1—C2—C3	115.9 (1)	C4—C8—H81	110.8 (2)
C1—C2—C7	122.1 (1)	C4—C8—H82	111.7 (2)
C3—C2—C7	122.01 (14)	H81—C8—H82	107.8 (3)
Br2—C3—C2	118.84 (9)	C4—C8—H83	111.1 (2)
Br2—C3—C4	117.63 (9)	H81—C8—H83	108.8 (4)
C2—C3—C4	123.53 (14)	H82—C8—H83	106.4 (3)
C3—C4—C5	117.14 (16)	C6—C9—H91	110.8 (2)
C3—C4—C8	122.62 (15)	C6—C9—H92	110.8 (2)
C5—C4—C8	120.2 (1)	H91—C9—H92	108.1 (3)
C4—C5—C6	122.9 (1)	C6—C9—H93	111.4 (2)
C4—C5—H51	118.69 (18)	H91—C9—H93	108.5 (3)
C6—C5—H51	118.4 (2)	H92—C9—H93	107.1 (3)

Refinement

Refinement on F
R = 0.032
wR = 0.024
S = 1.06
1490 reflections
169 parameters
All H-atom parameters refined
Weighting: Chebychev polynomial with 4 parameters (Carruthers & Watkin, 1979)

$(\Delta/\sigma)_{\rm max}$ < 0.001
$\Delta\rho_{\rm max}$ = 1.42 Fm Å^{-3}
$\Delta\rho_{\rm min}$ = −1.17 Fm Å^{-3}
Extinction correction: equation (22) of Larson (1970)
Extinction coefficient: 13.2 (4)

The low-temperature structure of (I) was solved initially at 120 K from single-crystal X-ray diffraction data (Nonius KappaCCD diffractometer) by direct methods (*SHELXS*97; Sheldrick, 1997) and subsequent least-squares refinements (*CRYSTALS*; Watkin, Prout, Carruthers & Betteridge, 1999) [$P2_1/n$; a = 7.735 (2) Å, b = 14.477 (3) Å, c = 8.960 (2) Å and β = 112.87 (3)°; R = 0.059, wR = 0.067 and S = 1.04; $\Delta\rho_{\rm min}$ = −2.09 e Å^{-3} and $\Delta\rho_{\rm max}$ = 1.48 e Å^{-3}; 102 least-squares parameters *versus* 1489 independent reflections used]. The present structures of (I) at 120 and 14 K were refined from neutron diffraction data using the X-ray results as a starting model. The significant disorder affecting the H atoms of the C7 methyl group was treated at 14 K using two different approaches, *viz*. a conventional split-atom model and a model using the special shapes (ring) of the atomic displacement parameters (ADPs) that are available in *CRYSTALS* (Watkin, Prout, Carruthers & Betteridge, 1999), but only the latter approach was used at 120 K. At 14 K, the sum of the occupancies of the different pseudo-atoms was constrained to be equal to three, and the C—H distances were restricted to 1.09 Å. In the first approach (220 least-squares parameters), six sites were refined with conventional ADPs; in the second (200 least-squares parameters), only three sites with conventional ADPs were refined plus one site with a ring-shaped ADP defined by its thickness, radius [1.024 (2) Å], declination and azimuthal angles. The split-atom model, despite having a higher number of parameters, allows a better description of the H-atom nuclear densities at 14 K than the special-shape model ($\Delta\rho_{\rm min}$ = −0.97 *versus* −1.32 Fm Å^{-3}, respectively). On the other hand, at 120 K, only one site with a ring-shaped ADP can be properly described for the quasi-ideal ring-shaped nuclear densities of the three individually imperceptible C7 methyl group H atoms [radius of the ring = 1.030 (3) Å].

For compound (I) at both 14 and 120 K, data reduction: *PRON* (Scherf, 1998); program(s) used to refine structure: *CRYSTALS* (Watkin, Prout, Carruthers & Betteridge, 1999); scattering lengths from Sears (1992); molecular graphics: *CAMERON* (Watkin, Prout & Pearce, 1999); software used to prepare material for publication: *CRYSTALS*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA1013). Services for accessing these data are described at the back of the journal.

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