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2-Bromo-1,3-bis(bromomethyl)-benzene, with Z' = 1.5: whole-molecule disorder of one of the two independent molecules

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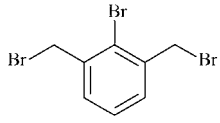
The title compound, $C_8H_7Br_3$, possesses normal geometrical parameters. There are two independent molecules; one shows whole-molecule disorder with respect to an inversion-symmetry-generated partner, while the other is undisordered. This results in the unusual situation of Z' = 1.5 and Z = 6 for a monoclinic crystal system. The undisordered molecule interacts with its neighbours by way of π–π stacking.

Comment

The title compound, (I), prepared earlier by Newcombe *et al.* (1977), was obtained during our ongoing studies to determine the philicity of aryl radicals by competitive cyclization reactions (Kirsop *et al.*, 2004*a*,*b*,*c*,*d*).



(I)

There are two independent molecules of (I) (Fig. 1). Both appear to possess their expected geometrical parameters, allowing for the rather low bond precisions obtained in this study. The C1-containing species is unexceptional. With respect to the mean plane of the C1–C6 benzene ring, one of the side-arm terminal Br atoms points 'up' [the displacement of Br2 is 1.790 (12) Å] and one points 'down' [the displacement of Br3 is −1.792 (12) Å].

The most interesting feature of the structure is the whole-molecule disorder displayed by the C11-containing molecule. This arises from inversion symmetry at the point (1, $\frac{1}{2}$, $\frac{1}{2}$) and symmetry-related locations. The resulting overlapped molecules (Fig. 2) are constrained by symmetry to have equal population parameters of 0.5 for all atoms in the molecule. As with the C1-containing molecule, the two side-arm terminal Br atoms are displaced in opposite senses with respect to the mean plane of the C11–C16 benzene ring [with displacements for Br12 and Br13 of 1.825 (16) and −1.74 (3) Å, respectively]. This situation of one ordered and one disordered molecule results in the atypical situation of Z' = 1.5 and Z = 6 for a monoclinic system.

As well as van der Waals forces, the crystal packing is influenced by π–π stacking interactions involving the C1-containing molecule (Fig. 3) generated by the *c*-glide symmetry operation. The $Cg\cdots Cg^{i}$ separation [Cg is the centroid of the C1–C6 ring; symmetry code: (i) $x, \frac{3}{2}-y, \frac{1}{2}+x$] is 3.755 (4) Å and the C1–C6/C1^{i}–C6^{i} interplanar separation is 3.411 Å. A *PLATON* (Spek, 2003) analysis of (I) revealed a slightly short Br1$\cdots$Br11^{ii} contact of 3.595 (2) Å [symmetry code: (ii) $2-x, 1-y, 1-z$], some 0.1 Å less than the van der Waals radius sum of 3.70 Å (Spek, 2003). Such Br$\cdots$Br contacts are quite common and their significance – specific attractive forces (Desiraju & Parthasarathy, 1989) or packing contacts (Eriksson & Hu, 2001) – has been debated.

The packing of (I) is shown in Fig. 4, indicating how the ordered and disordered molecules segregate into (010) sheets.

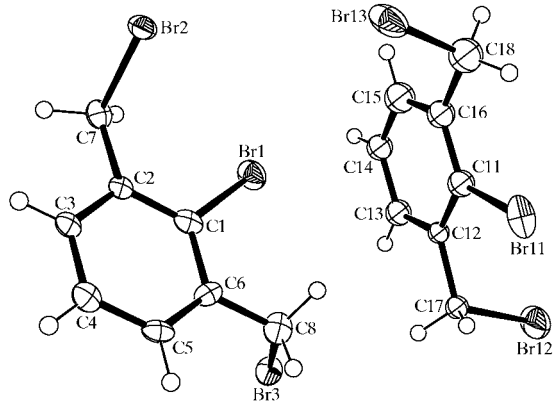


Figure 1
A view of (I), showing 50% probability displacement spheres and ellipsoids (H atoms are drawn as spheres of arbitrary radii).

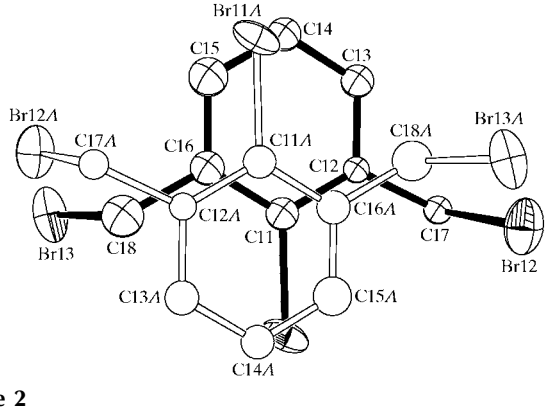


Figure 2
A detail of (I), showing the whole-molecule disorder of the C11-containing molecule (50% probability displacement spheres/ellipsoids; all H atoms have been omitted for clarity). Atoms with the suffix *A* are generated by the symmetry operation $(2-x, 1-y, 1-z)$.

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Because the C11-containing molecules are almost perpendicular to, and are sandwiched between, the π–π stacks of C1-containing molecules, there can be no π–π forces involving the former molecules [the dihedral angle between the C1–C6 and C11–C16 mean planes is 80.8 (6)°].

Aside from very simple molecules and fragments, whole-molecule disorder (WMD) is not particularly common. A classic example is the 10 π electron molecule azulene, $C_{10}H_8$, containing fused, planar, five- and seven-membered rings. After several conflicting studies it was concluded (Robertson *et al.*, 1962) that azulene shows WMD with the 5/7 and 7/5 conformations overlapped at random. More recently, Ichharam & Boeyens (2001) observed WMD in 2-(2-thienyl)-1-(2-pyrazinyl)ethene and 2-(2-thienyl)-1-(2-quinoxalinyl)-ethene. In both cases, the disordered components were related by pseudo-twofold axes. Cox & Wardell (2003) found WMD in 4,4′-sulfonylbis[*N*-(4-nitrophenylmethylene)benzenamine], with no (pseudo)symmetry relating the two slightly displaced disorder components.

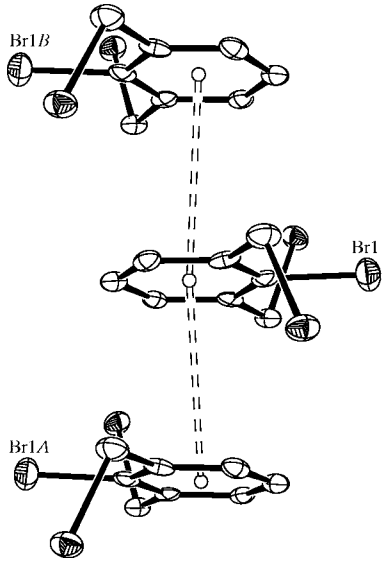

Figure 3
A detail of (I), showing the π–π stacking interaction involving the C1-containing molecule. The molecules containing atoms Br1*A* and Br1*B* are generated by the symmetry operations $(x, \frac{3}{2}-y, \frac{1}{2}+z)$ and $(x, \frac{3}{2}-y, z-\frac{1}{2})$, respectively.

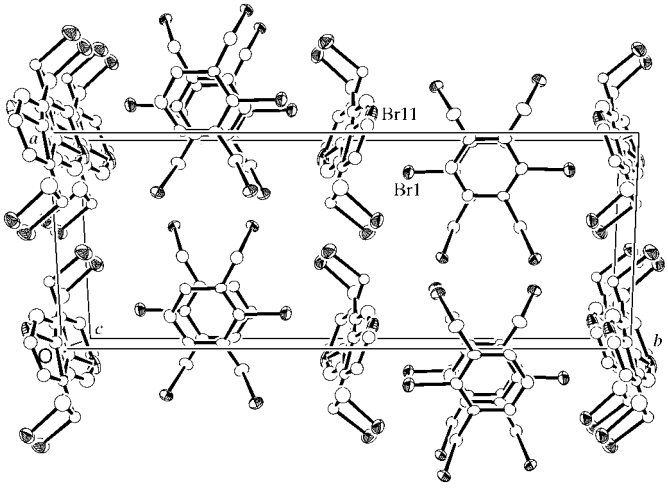

Figure 4
The packing in (I), viewed down [001], with H atoms omitted.

Experimental

2-Bromo-1,3-dimethylbenzene (5.0 g, 0.027 mol), *N*-bromosuccinamide (NBS, 9.6 g, 0.054 mol) and azobisisobutyronitrile (0.88 g, 0.0054 mol) were added to chloroform (100 ml). The mixture was stirred at reflux under a nitrogen atmosphere for 12 h. After cooling, the mixture was filtered and the solvent was removed at reduced pressure to give a yellow solid. Thin-layer chromatography (hexane) showed 2-bromo-1,3-bis(bromomethyl)benzene as a sharp spot at R_F = 0.21. The NBS residues were removed by flash column chromatography (20:1 hexane–ethyl acetate) and the solvent was removed. The product was washed with hexane, giving a white solid (4.9 g, 53%). A sample was recrystallized from hot hexane–ethyl acetate (20:1) to give clear needles of (I) [m.p. 371–373 K, literature (Newcombe *et al.*, 1977) 374–376 K]. ^{1}H NMR ($CDCl_3$): δ_H 4.64 (4H, *s*, 2 × CH_2), 7.28 (1H, *t*, *J* = 8.1 Hz, Ar–H), 7.41 (2H, *d*, *J* = 8.1 Hz, 2 × Ar–H); ^{13}C NMR ($CDCl_3$): δ_C 33.8, 126.6, 128.0, 131.3, 138.5.

Crystal data

$C_8H_7Br_3$
M_r = 342.87
Monoclinic, $P2_1/c$
a = 9.1114 (4) Å
b = 22.6016 (10) Å
c = 7.5004 (3) Å
β = 111.971 (3)°
V = 1432.40 (11) Å^3
Z = 6
D_x = 2.385 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 12.61 mm^{-1}
T = 120 (2) K
Blade, colourless
0.60 × 0.10 × 0.01 mm

Data collection

Nonius KappaCCD diffractometer
ω and φ scans
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
T_{min} = 0.049, T_{max} = 0.940
(expected range = 0.046–0.882)
14563 measured reflections
3266 independent reflections
2406 reflections with $I > 2\sigma(I)$
R_{int} = 0.099
θ_{max} = 27.6°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.084
$wR(F^2)$ = 0.253
S = 1.01
3266 reflections
146 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1847P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 1.89 e Å^{-3}
$\Delta\rho_{min}$ = −2.79 e Å^{-3}

The C1-containing molecule was located and refined straightforwardly. The C11-containing molecule evidently showed massive disorder. By careful analysis of difference maps, the disorder could be resolved into two overlapped symmetry-related molecules of (I) (as described in the *Comment*). The C atoms of the disordered molecule were refined isotropically. All H atoms were placed in calculated positions (C—H = 0.95–0.99 Å) and refined as riding, with U_{iso}(H) values of 1.2U_{eq}(C). The largest difference peak is 1.04 Å from atom Br2 and the deepest difference hole is 0.85 Å from the same atom. Attempts to model the crystal in lower-symmetry space groups were not successful.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* (Otwinowski & Minor, 1997), *SCALEPACK* and *SORTAV*

(Blessing, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3024). Services for accessing these data are described at the back of the journal.

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