1-(Dibromomethyl)-4-methoxy-2-methylbenzene

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The title compound, $C_9H_{10}Br_2O$, is a major product of the radical bromination of 4-methoxy-1,2-dimethylbenzene. Each Br atom is involved in a close contact with the O atom of a neighbouring molecule, forming a geometry that is suggestive of weak intermolecular O→Br charge-transfer interactions.

Comment

There are two recent reports that bromination of 4-methoxy-1,2-dimethylbenzene by excess *N*-bromosuccinimide under free-radical conditions affords 1,2-bis(bromomethyl)-4-methoxybenzene, (I), in >80% yield (Ohkawa *et al.*, 1997; Wang *et al.*, 1997). In our hands, the reported procedures both, in fact, form 1-(dibromomethyl)-4-methoxy-2-methylbenzene, (II), and 1-bromomethyl-4-methoxy-2-methylbenzene, (III) (Tanzawa *et al.*, 1995), in addition to (I), with yields of approximately 30% of (I), 25% of (II) and 15% of (III). The crystal structure of (II), a new compound, was undertaken in order to determine unambiguously which of the two methyl groups of the precursor had been doubly brominated.

(I)   (II)   (III)
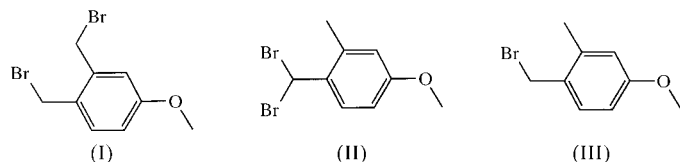
Interestingly, C10—Br12 [1.983 (4) Å] is substantially longer than C10—Br11 [1.948 (5) Å]. None of the three (dibromomethyl)arenes that have been structurally characterized previously exhibit this feature (García *et al.*, 1995; Stanger *et al.*, 1998; Sygula & Rabideau, 1998). It is suggestive that the lengthened C10—Br12 bond in (II) is almost perpendicular to the plane of the C1–C6 ring [C3—C4—C10—Br12 = 95.1 (4)°], which might conceivably reflect hyperconjugation between the C10—Br12 σ* orbital and the phenyl π-system. This would provide a convenient rationale for the lengthened C10—Br12 bond. However, static and energy-minimized *AM*1 calculations (CambridgeSoft, 1999) have demonstrated that Br12 makes no contribution to the π-orbitals of this compound,

which appears to rule out this explanation. All other bond lengths and angles within the molecule are unexceptional.

There are three unusually short intermolecular contacts in the lattice. Both Br atoms form a contact with O7 from a neighbouring molecule (Table 1). For both these interactions, the O7···Br[#]—C10[#] angle (# = i, ii; Table 1) is close to linear, while the disposition of C—O and O···Br[#] vectors about O7 forms a distorted tetrahedron [the angles about O7 not in Table 1 are C1—O7—C8 = 116.7 (4)° and Br11[i]···O7···Br12[ii] = 90.0 (2)°; the average angle about O7 including these intermolecular interactions is hence 108.3 (7)°]. These parameters are suggestive of weak intermolecular charge-transfer interactions between the lone pairs of O7 and the C—Br σ*-antibonding orbitals. There is also a close contact between H10 and Br12[iii], related by 1 − x, 1 − y, 1 − z, with C10···Br12[iii] = 3.712 (5), H10···Br12[iii] = 3.00 Å and C10—H10···Br12[iii] = 129°. A similar intramolecular C—H···Br interaction is observed in the structure of methyl 2,3-bis(dibromomethyl)benzoate (Stanger *et al.*, 1998). For comparison, the sum of the van der Waals radii of O and Br atoms is 3.35 Å, and of H and Br atoms is 3.15 Å (Pauling, 1960).

There are two intermolecular π–π interactions in the lattice, between molecules related by inversion at 1 − x, 2 − y, 1 − z (interplanar spacing 3.48 Å, centroid offset 3.6 Å), and by −x, 2 − y, 2 − z (interplanar spacing 3.70 Å, centroid offset 3.9 Å). In both these interactions, the stacked rings are strictly coplanar by symmetry, and have relative orientations that are consistent with an electrostatically attractive π–π interaction (Hunter & Sanders, 1990).
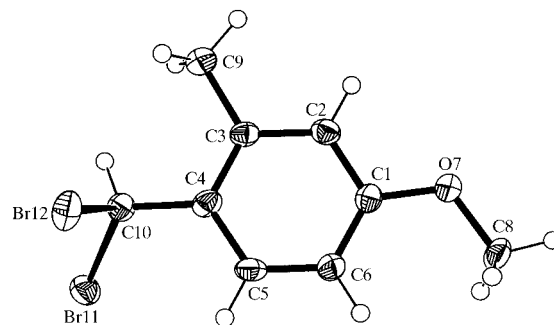

Figure 1
The molecular structure of (II) with 50% probability displacement ellipsoids, showing the atom-numbering scheme employed.

Experimental

1-Methoxy-3,4-dimethylbenzene (5.0 g, 36.3 mmol), *N*-bromosuccinimide (14.4 g, 80 mmol) and benzoylperoxide (0.04 g, 0.2 mmol) were mixed in CCl_4 (70 ml), and the resultant suspension refluxed for 30 min. Following cooling and filtration, evaporation of the solvent *in vacuo* yielded a pale brown oil that contained a mixture of compounds (I), (II) and (III), from thin-layer chromatography and ^1H NMR spectroscopy. Compound (II) was separated from the reaction mixture by fractional crystallization of the crude material from 1:1 diethyl ether–hexanes, which yielded moisture-sensitive white microcrystals. Recrystallization from the same solvent mixture yielded small colourless needles. ^1H NMR spectrum of (II) (CDCl$_3$, 250 MHz, 293 K): δ 7.76 (*d*, 8.8 Hz, 1H, Ph H^5), 6.88 (*s*, 1H, CHBr$_2$), 6.80 (*dd*, 2.8 and 8.8 Hz, 1H, Ph H^6), 6.63 (*d*, 2.8 Hz, 1H, Ph H^2), 3.81 (*s*, 3H, OCH$_3$), 2.42 (*s*, 3H, CH$_3$) p.p.m.

organic compounds

Crystal data

C$_9$H$_{10}$Br$_2$O
$M_r = 293.99$
Triclinic, $P\bar{1}$
$a = 7.4692\,(5)$ Å
$b = 8.7343\,(7)$ Å
$c = 8.9090\,(7)$ Å
$\alpha = 68.104\,(4)°$
$\beta = 77.038\,(4)°$
$\gamma = 67.310\,(4)°$
$V = 495.34\,(6)$ Å^3

$Z = 2$
$D_x = 1.971$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5761
  reflections
$\theta = 3.26–27.49°$
$\mu = 8.132$ mm^{-1}
$T = 150\,(2)$ K
Lath, colourless
$0.14 \times 0.07 \times 0.01$ mm

Data collection

Nonius KappaCCD area-detector
  diffractometer
Area-detector scans
Absorption correction: multi-scan
  (*SORTAV*; Blessing, 1995)
  $T_{min} = 0.396$, $T_{max} = 0.923$
5761 measured reflections

2258 independent reflections
1698 reflections with $I > 2\sigma(I)$
$R_{int} = 0.061$
$\theta_{max} = 27.49°$
$h = -9 \rightarrow 9$
$k = -11 \rightarrow 11$
$l = -10 \rightarrow 11$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.109$
$S = 1.013$
2258 reflections
112 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0469P)^2]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.968$ e Å^{-3}
$\Delta\rho_{min} = -0.77$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.012 (2)

Table 1
Selected distances (Å) and angles (°) for the close intermolecular O···Br contacts in (II) (# = i, ii).

Interaction	O7···Br	O7···Br$^{#}$—C10$^{#}$	C1—O7···Br$^{#}$	C8—O7···Br$^{#}$
O7···Br11^{i}	2.999 (5)	170.3 (3)	122.3 (3)	112.7 (3)
O7···Br12^{ii}	3.075 (5)	169.5 (3)	110.1 (3)	98.1 (3)

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

H atoms were placed in calculated positions and refined using a riding model. The C—H distances employed for the final refinement were 0.95 Å for the aryl H atoms, 0.98 Å for the methyl H atoms and 1.00 Å for the methine H10 atom.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1996); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEX* (McArdle, 1995); software used to prepare material for publication: local program.

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