

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

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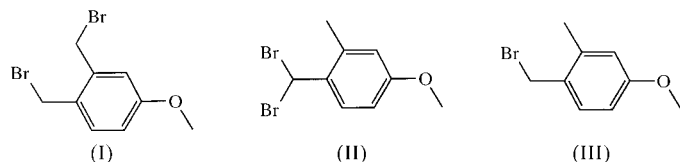
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The title compound, $C_9H_{10}Br_2O$, is a major product of the radical bromination of 4-methoxy-1,2-dimethylbenzene. Each Br atom is involved in a close contact with the O atom of a neighbouring molecule, forming a geometry that is suggestive of weak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



Interestingly, $C10-Br12$ [$1.983(4) \text{ \AA}$] is substantially longer than $C10-Br11$ [$1.948(5) \text{ \AA}$]. 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 [$C3-C4-C10-Br12 = 95.1(4)^\circ$], which might conceivably reflect hyperconjugation between the $C10-Br12 \sigma^*$ orbital and the phenyl π -system. This would provide a convenient rationale for the lengthened $C10-Br12$ bond. However, static and energy-minimized *AM1* 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 $O7 \cdots Br^{\#}-C10^{\#}$ angle ($\# = i, ii$; Table 1) is close to linear, while the disposition of $C-O$ and $O \cdots Br^{\#}$ vectors about O7 forms a distorted tetrahedron [the angles about O7 not in Table 1 are $C1-O7-C8 = 116.7(4)^\circ$ and $Br11^i \cdots O7 \cdots Br12^{ii} = 90.0(2)^\circ$; the average angle about O7 including these intermolecular interactions is hence $108.3(7)^\circ$]. These parameters are suggestive of weak intermolecular charge-transfer interactions between the lone pairs of O7 and the $C-Br \sigma^*$ -antibonding orbitals. There is also a close contact between H10 and $Br12^{iii}$, related by $1-x, 1-y, 1-z$, with $C10 \cdots Br12^{iii} = 3.712(5)$, $H10 \cdots Br12^{iii} = 3.00 \text{ \AA}$ and $C10-H10 \cdots Br12^{iii} = 129^\circ$. A similar intramolecular $C-H \cdots Br$ 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 \AA , and of H and Br atoms is 3.15 \AA (Pauling, 1960).

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

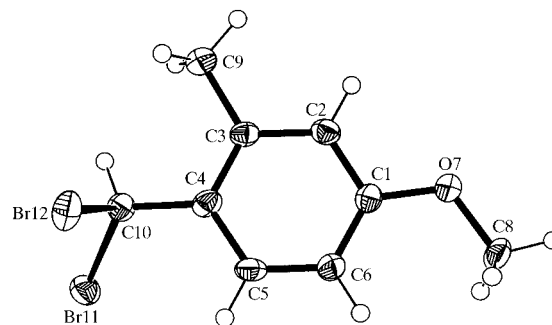


Figure 1

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.

Crystal data

$C_9H_{10}Br_2O$	$Z = 2$
$M_r = 293.99$	$D_x = 1.971 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 7.4692 (5) \text{ \AA}$	Cell parameters from 5761 reflections
$b = 8.7343 (7) \text{ \AA}$	$\theta = 3.26\text{--}27.49^\circ$
$c = 8.9090 (7) \text{ \AA}$	$\mu = 8.132 \text{ mm}^{-1}$
$\alpha = 68.104 (4)^\circ$	$T = 150 (2) \text{ K}$
$\beta = 77.038 (4)^\circ$	Lath, colourless
$\gamma = 67.310 (4)^\circ$	$0.14 \times 0.07 \times 0.01 \text{ mm}$
$V = 495.34 (6) \text{ \AA}^3$	

Data collection

Nonius KappaCCD area-detector diffractometer	2258 independent reflections
Area-detector scans	1698 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SORTAV; Blessing, 1995)	$R_{\text{int}} = 0.061$
$T_{\text{min}} = 0.396$, $T_{\text{max}} = 0.923$	$\theta_{\text{max}} = 27.49^\circ$
5761 measured reflections	$h = -9 \rightarrow 9$
	$k = -11 \rightarrow 11$
	$l = -10 \rightarrow 11$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0469P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.045$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.109$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.013$	$\Delta\rho_{\text{max}} = 0.968 \text{ e \AA}^{-3}$
2258 reflections	$\Delta\rho_{\text{min}} = -0.77 \text{ e \AA}^{-3}$
112 parameters	Extinction correction: <i>SHELXL97</i>
H-atom parameters constrained	Extinction coefficient: 0.012 (2)

Table 1

Selected distances (\AA) and angles ($^\circ$) for the close intermolecular $O \cdots Br$ contacts in (II) (# = i, ii).

Interaction	$O7 \cdots Br$	$O7 \cdots Br^{\#} - C10^{\#}$	$C1 - O7 \cdots Br^{\#}$	$C8 - O7 \cdots Br^{\#}$
$O7 \cdots Br11^i$	2.999 (5)	170.3 (3)	122.3 (3)	112.7 (3)
$O7 \cdots Br12^{ii}$	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 \AA for the aryl H atoms, 0.98 \AA for the methyl H atoms and 1.00 \AA 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: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP* (McArdle, 1995); software used to prepare material for publication: local program.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1445). Services for accessing these data are described at the back of the journal.

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