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1-(2-Bromo-1,1-dimethoxyethyl)-4-nitrobenzene

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Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.004 Å
R factor = 0.033
wR factor = 0.088
Data-to-parameter ratio = 17.6

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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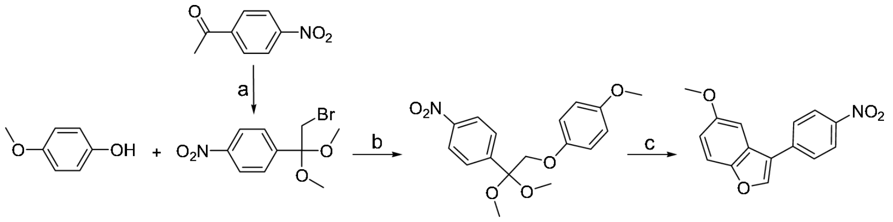
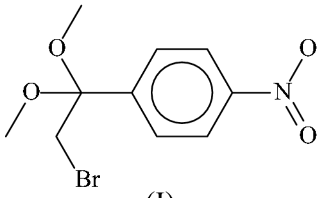
Methyl 4-nitrophenyl ketone was brominated by copper(II) bromide in methanol; the ketone reacts with the solvent *in situ* to yield the title compound, $C_{10}H_{12}BrNO_4$, which exists as a monomeric molecule.

Comment

Benzofurans are a class of heterocyclic compounds that possess a broad range of biological activity (Malamas *et al.*, 2000; Masubuchi *et al.*, 2001). Among the naturally occurring benzofurans, two have been identified as displaying mild cytotoxicity (Banskota *et al.*, 2000). We previously reported the structures of precursors that are used in the synthesis of biologically active compounds (Wu, An *et al.*, 2004; Wu, Zhou *et al.*, 2004). The present study similarly details the structure of the precursor for 5-methoxy-3-(4-nitrophenyl)benzofuran, whose synthesis has been facilitated by the ready preparation of the title diketal. This could be obtained directly from the reduction of copper(II) bromide by 1-(4-nitrophenyl)ethanone in methanol (pathway *a* in the first scheme below).



The reaction yields the title compound, (I) (Fig. 1), in high yield. In a subsequent nucleoplilic reaction, the 4-methoxyphenolate anion then displaces the Br atom to furnish (4-methoxylphenoxy)dimethoxymethyl-4-nitrobenzene, which cyclizes under the influence of Amberlyst 15 in boiling chlorobenzene to form the 3-substituted benzofuran (Shen, 2004). The synthesis is based on the synthesis of benzofurans that makes use of the aliphatic analog bromoacetaldehyde diethylacetal (Knölker & Fröhner, 1996).



(I)

The title compound exists as a monomer, and the bond dimensions are normal. Weak van der Waals interactions

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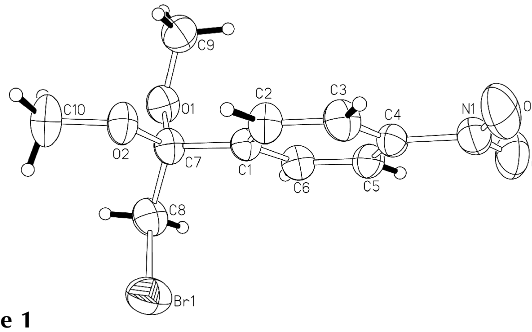

Figure 1
*ORTEP*II (Johnson, 1976) plot of $C_{10}H_{12}BrNO_4$. Displacement ellipsoids are drawn at the 50% probability level and H atoms are drawn as spheres of arbitrary radii.

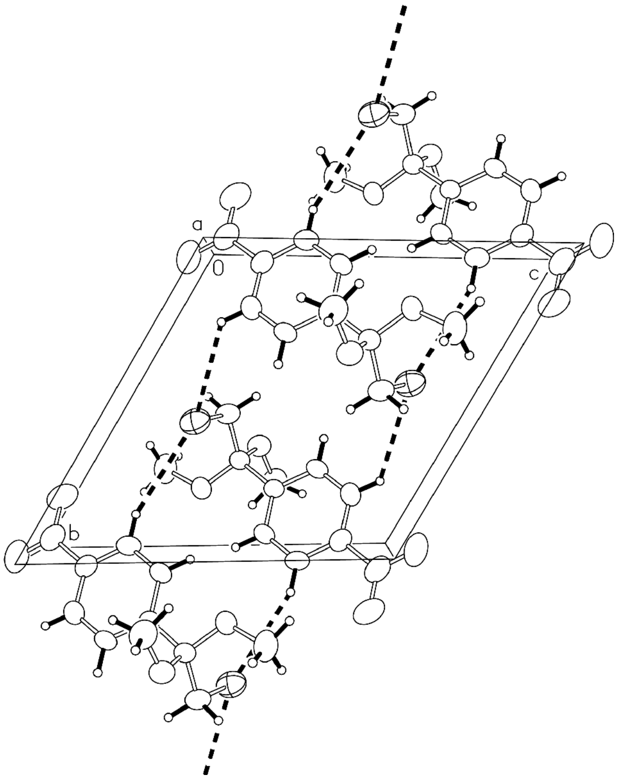

Figure 2
*ORTEP*II (Johnson, 1976) plot depicting the van der Waals interactions (dashed lines) involving the Br atom.

involving the Br atom [$Br1\cdots H3^{i} = 3.109$ (1) and $Br1\cdots H5^{ii} = 3.165$ (1) Å; symmetry codes: (i) $1-x, -y, 1-z$; (ii) $= 1-x, 1-y, 1-z$] link adjacent molecules into a chain running along the *b* axis (Fig. 2). A search of the Cambridge Structural Database (Version 5.25; Allen, 2002) shows that a small number of aromatic diketals, *e.g.* the diketals of phenyl triphenylmethyl ketone (Wo *et al.*, 1995) and of indolin-2,3-dione (De & Kitagawa, 1991), have been crystallographically characterized.

Experimental

Copper(II) bromide (33.5 g, 0.15 mol) was added to 1-(4-nitrophenyl)ethanone (12.4 g, 0.075 mol) that had been dissolved in methanol (200 ml), a small quantity at a time (approximately 1 h). The vigorously stirred solution was refluxed for 3 h. The reaction was followed by thin-layer chromatography. The solution was cooled and the copper(I) bromide was removed by filtration. The filtrate was decolorized by absorbite. The solvent was removed to give a solid that was recrystallized from petroleum ether. The formula was established by ^{1}H NMR (300 Hz, $CDCl_3$) spectroscopic analysis: δ 8.20 (*d*, $J = 9$ Hz, 2H), 7.66 (*d*, $J = 9$ Hz, 2H), 3.58 (*s*, 2H), 3.22 (*s*, $2CH_3$, 6H).

Crystal data

$C_{10}H_{12}BrNO_4$
$M_r = 290.12$
Triclinic, $P\overline{1}$
$a = 7.091$ (1) Å
$b = 9.906$ (1) Å
$c = 10.262$ (1) Å
$\alpha = 117.552$ (2)°
$\beta = 102.567$ (2)°
$\gamma = 97.488$ (2)°
$V = 601.1$ (1) Å^3

$Z = 2$
$D_x = 1.603$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 967 reflections
$\theta = 2.4$–27.0°
$\mu = 3.42$ mm^{-1}
$T = 295$ (2) K
Prism, colorless
$0.50 \times 0.36 \times 0.27$ mm

Data collection

Bruker SMART area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)
$T_{min} = 0.200$, $T_{max} = 0.397$
5175 measured reflections

2599 independent reflections
2238 reflections with $I > 2\sigma(I)$
$R_{int} = 0.024$
$\theta_{max} = 27.1°$
$h = -9 \rightarrow 9$
$k = -12 \rightarrow 12$
$l = -13 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.088$
$S = 1.02$
2599 reflections
148 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0389P)^2 + 0.3289P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.46$ e Å^{-3}
$\Delta\rho_{min} = -0.70$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.46 (1)

Table 1
Selected geometric parameters (Å, °).

Br1—C8	1.938 (3)	C1—C2	1.383 (3)
O1—C7	1.417 (3)	C1—C6	1.396 (3)
O1—C9	1.434 (3)	C1—C7	1.527 (3)
O2—C7	1.404 (3)	C2—C3	1.385 (3)
O2—C10	1.430 (3)	C3—C4	1.380 (3)
O3—N1	1.222 (3)	C4—C5	1.372 (3)
O4—N1	1.209 (3)	C5—C6	1.381 (3)
N1—C4	1.476 (3)	C7—C8	1.525 (3)
C7—O1—C9	114.8 (2)	C3—C4—N1	118.9 (2)
C7—O2—C10	116.4 (2)	C5—C4—N1	119.1 (2)
O3—N1—O4	123.7 (2)	C4—C5—C6	119.0 (2)
O3—N1—C4	117.9 (2)	C1—C6—C5	120.5 (2)
O4—N1—C4	118.4 (2)	O2—C7—O1	111.8 (2)
C2—C1—C6	119.1 (2)	O1—C7—C8	101.9 (2)
C2—C1—C7	121.9 (2)	O2—C7—C8	113.1 (2)
C6—C1—C7	119.0 (2)	O1—C7—C1	111.3 (2)
C1—C2—C3	120.8 (2)	O2—C7—C1	106.5 (2)
C2—C3—C4	118.6 (2)	C1—C7—C8	112.3 (2)
C3—C4—C5	122.0 (2)	C7—C8—Br1	111.8 (2)

H atoms were placed at calculated positions in the riding-model approximation ($C—H_{aromatic} = 0.93$ Å, $C—H_{methylene} = 0.96$ Å and $C—H_{methyl} = 0.97$ Å), with U_{iso}(H) values set to $1.2U_{eq}$ of the parent atoms for the aromatic and methylene atoms, and to $1.5U_{eq}$ for the methyl atoms.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

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