

2-Bromo-2-methyl-*N*-*p*-tolyl-propanamide

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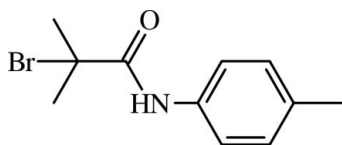
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Key indicators: single-crystal X-ray study; $T = 123$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.045; wR factor = 0.093; data-to-parameter ratio = 20.8.

In the title molecule, $\text{C}_{11}\text{H}_{14}\text{BrNO}$, there is twist between the mean plane of the amide group and the benzene ring [$\text{C}(\text{=O})-\text{N}-\text{C}\cdots\text{C}$ torsion angle = $-31.2(5)^\circ$]. In the crystal, intermolecular $\text{N}-\text{H}\cdots\text{O}$ and weak $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds link molecules into chains along $[100]$. The methyl group H atoms are disordered over two sets of sites with equal occupancy.

Related literature

For initiators in ATRP processes (polymerization by atom transfer radical), see: Matyjaszewski & Xia (2001); Kato *et al.* (1995); Pietrasik & Tsarevsky (2010). For a related structure, see: Moreno-Fuquen *et al.* (2011). For hydrogen-bond graph sets, see: Etter (1990).



Experimental

Crystal data

$\text{C}_{11}\text{H}_{14}\text{BrNO}$	$V = 2309.55(14) \text{ \AA}^3$
$M_r = 256.14$	$Z = 8$
Orthorhombic, $Pbca$	Mo $K\alpha$ radiation
$a = 10.0728(4) \text{ \AA}$	$\mu = 3.53 \text{ mm}^{-1}$
$b = 11.2577(4) \text{ \AA}$	$T = 123 \text{ K}$
$c = 20.3670(6) \text{ \AA}$	$0.25 \times 0.12 \times 0.05 \text{ mm}$

Data collection

Oxford Diffraction Xcalibur E diffractometer	10140 measured reflections
Absorption correction: multi-scan (<i>CrysAlis PRO</i> ; Oxford Diffraction, 2009)	2762 independent reflections
$T_{\min} = 0.751$, $T_{\max} = 1.000$	1819 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.049$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.045$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.093$	$\Delta\rho_{\text{max}} = 0.58 \text{ e \AA}^{-3}$
$S = 1.06$	$\Delta\rho_{\text{min}} = -0.46 \text{ e \AA}^{-3}$
2762 reflections	
133 parameters	

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N1}-\text{H1N}\cdots\text{O1}^i$	0.84 (2)	2.13 (2)	2.937 (3)	161 (3)
$\text{C1}-\text{H1C}\cdots\text{O1}^i$	0.98	2.44	3.382 (4)	162
$\text{C10}-\text{H10}\cdots\text{O1}^i$	0.95	2.57	3.321 (4)	137

Symmetry code: (i) $x - \frac{1}{2}, y, -z + \frac{1}{2}$.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2009); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis CCD*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PARST* (Nardelli, 1995).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH5254).

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supporting information

Acta Cryst. (2011). E67, o1543 [https://doi.org/10.1107/S1600536811019337]

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S1. Comment

The ATRP process (polymerization by atom transfer radical) allows control of the composition and functionality in polymerization reactions (Pietrasik & Tsarevsky, 2010). The use of functional initiators in these reactions allows the synthesis of new materials. Most initiators for ATRP processes are alkyl halides (Matyjaszewski & Xia, 2001; Kato *et al.*, 1995). As part of our work related to functional initiators in polymerization processes (Moreno-Fuquen *et al.*, 2011) we have determined the crystal structure of the title compound (I). The molecular structure of (I) is shown in Fig. 1. There is a twist between the mean plane of the amide group and benzene ring giving a C4—N1—C5—C6 torsion angle of $-31.2(5)^\circ$. In the crystal, intermolecular N—H $\cdots$ O and weak C—H $\cdots$ O hydrogen bonds link molecules into one-dimensional chains along [100] incorporating C(4) graph motifs (Etter, 1990) (see Table 1 and Fig. 2).

S2. Experimental

The initial reagents were purchased from Aldrich Chemical Co. and were used as received. In a 100mL round bottom flask 4-methylaniline (3.173 mmol, 0.340 g), triethylamine (0.635 mmol, 0.064 g) were mixed, then a solution of 2-bromo isobutiryl bromide (0.685 g) in anhydrous THF (5 ml) was added drop wise, under an argon stream. The reaction was carried out in a dry bag overnight under magnetic stirring. The solid was filtered off and dichloromethane (20 ml) added to the organic phase which was washed with brine (50 ml) followed by water (10 ml). The solution was concentrated at low pressure affording colourless crystals and recrystallized from a solution of hexane and ethyl acetate (80:20). M.p. 364 (1) K.

S3. Refinement

The H-atoms were placed geometrically with C—H = 0.95 Å for aromatic, C—H = 0.98 Å for methyl and $U_{\text{iso}}(\text{H})$ 1.2 and 1.5 times U_{eq} of the parent atom respectively. The methyl group H atoms are disordered over two sets of sites with equal occupancy.

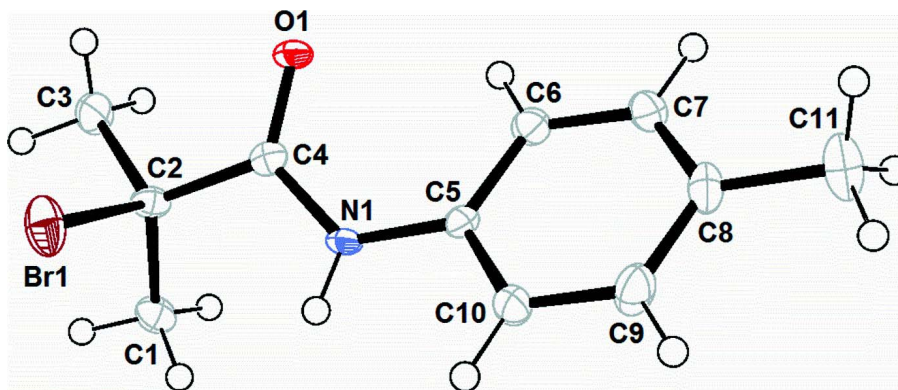


Figure 1

An ORTEP-3 (Farrugia, 1997) plot of (I) with displacement ellipsoids drawn at the 50% probability level. H atoms are shown as spheres of arbitrary radius.

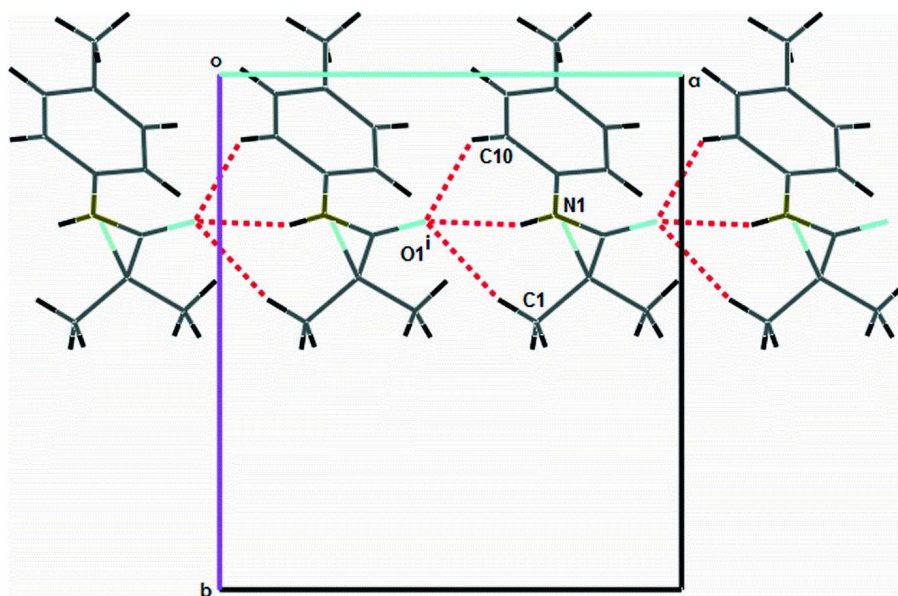


Figure 2

Part of the crystal structure of (I), showing the formation of a one dimensional chain along [100]. Symmetry code: (i) $x-1/2, +y, -z+1/2$.

2-Bromo-2-methyl-N-p-tolylpropanamide

Crystal data

$C_{11}H_{14}BrNO$

$M_r = 256.14$

Orthorhombic, $Pbca$

Hall symbol: $-P\ 2ac\ 2ab$

$a = 10.0728\ (4)\ \text{\AA}$

$b = 11.2577\ (4)\ \text{\AA}$

$c = 20.3670\ (6)\ \text{\AA}$

$V = 2309.55\ (14)\ \text{\AA}^3$

$Z = 8$

$F(000) = 1040$

$D_x = 1.473\ \text{Mg m}^{-3}$

Melting point: $385\ (1)\ \text{K}$

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 2266 reflections

$\theta = 3.4\text{--}29.5^\circ$

$\mu = 3.53\ \text{mm}^{-1}$

$T = 123\ \text{K}$

Tablet, colourless

$0.25 \times 0.12 \times 0.05\ \text{mm}$

Data collection

Oxford Diffraction Xcalibur E
diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
 ω scans
Absorption correction: multi-scan
(*CrysAlis PRO*; Oxford Diffraction, 2009)
 $T_{\min} = 0.751$, $T_{\max} = 1.000$

10140 measured reflections
2762 independent reflections
1819 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.049$
 $\theta_{\max} = 28.0^\circ$, $\theta_{\min} = 3.4^\circ$
 $h = -12 \rightarrow 13$
 $k = -10 \rightarrow 14$
 $l = -26 \rightarrow 22$

Refinement

Refinement on F^2
Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.045$
 $wR(F^2) = 0.093$
 $S = 1.06$
2762 reflections
133 parameters
0 restraints
Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map
Hydrogen site location: inferred from
neighbouring sites
H atoms treated by a mixture of independent
and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0316P)^2 + 0.7321P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.58 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.46 \text{ e } \text{\AA}^{-3}$

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2 , conventional R-factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F , and R-factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Br1	0.74332 (3)	0.28652 (3)	0.384590 (15)	0.02982 (13)	
O1	0.94616 (17)	0.2851 (2)	0.24129 (10)	0.0200 (5)	
N1	0.7262 (2)	0.2730 (3)	0.21911 (12)	0.0158 (6)	
C1	0.6864 (3)	0.4811 (3)	0.30022 (16)	0.0214 (7)	
H1A	0.7056	0.5288	0.2611	0.032*	
H1B	0.6768	0.5335	0.3384	0.032*	
H1C	0.6037	0.4368	0.2935	0.032*	
C2	0.7996 (3)	0.3946 (3)	0.31211 (15)	0.0173 (7)	
C3	0.9232 (3)	0.4587 (3)	0.33541 (16)	0.0287 (9)	
H3A	0.9914	0.4004	0.3472	0.043*	
H3B	0.9015	0.5073	0.3739	0.043*	
H3C	0.9565	0.5100	0.3002	0.043*	
C4	0.8312 (3)	0.3116 (3)	0.25448 (14)	0.0158 (7)	
C5	0.7307 (2)	0.1928 (3)	0.16557 (14)	0.0160 (7)	
C6	0.8384 (3)	0.1847 (3)	0.12261 (14)	0.0203 (7)	

H6	0.9135	0.2348	0.1281	0.024*	
C7	0.8347 (3)	0.1030 (3)	0.07213 (15)	0.0241 (8)	
H7	0.9082	0.0986	0.0431	0.029*	
C8	0.7285 (3)	0.0274 (3)	0.06198 (15)	0.0229 (8)	
C9	0.6210 (3)	0.0383 (3)	0.10438 (16)	0.0273 (8)	
H9	0.5457	−0.0113	0.0985	0.033*	
C10	0.6216 (3)	0.1202 (3)	0.15499 (15)	0.0225 (8)	
H10	0.5463	0.1267	0.1829	0.027*	
C11	0.7287 (3)	−0.0636 (4)	0.00758 (17)	0.0338 (9)	
H11A	0.6452	−0.1082	0.0085	0.051*	0.50
H11B	0.8033	−0.1184	0.0138	0.051*	0.50
H11C	0.7378	−0.0233	−0.0348	0.051*	0.50
H11D	0.8123	−0.0584	−0.0168	0.051*	0.50
H11E	0.6542	−0.0482	−0.0222	0.051*	0.50
H11F	0.7197	−0.1433	0.0264	0.051*	0.50
H1N	0.652 (2)	0.292 (3)	0.2342 (15)	0.032 (10)*	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0475 (2)	0.0235 (2)	0.01844 (18)	0.00201 (17)	0.00410 (15)	0.00302 (15)
O1	0.0101 (9)	0.0260 (14)	0.0240 (12)	0.0013 (10)	−0.0012 (8)	−0.0053 (11)
N1	0.0086 (12)	0.0198 (15)	0.0191 (13)	0.0006 (11)	0.0013 (9)	−0.0026 (11)
C1	0.0213 (16)	0.017 (2)	0.0254 (18)	0.0021 (13)	0.0028 (14)	−0.0020 (15)
C2	0.0131 (13)	0.0159 (19)	0.0228 (17)	−0.0020 (12)	0.0012 (12)	0.0001 (15)
C3	0.0218 (16)	0.037 (3)	0.0269 (19)	−0.0069 (16)	−0.0011 (14)	−0.0152 (18)
C4	0.0163 (14)	0.0137 (18)	0.0175 (15)	−0.0003 (12)	−0.0010 (12)	0.0051 (14)
C5	0.0137 (14)	0.0189 (18)	0.0153 (15)	0.0014 (13)	−0.0025 (11)	0.0010 (13)
C6	0.0172 (14)	0.025 (2)	0.0182 (16)	−0.0014 (13)	0.0012 (12)	0.0021 (15)
C7	0.0217 (16)	0.034 (2)	0.0165 (17)	0.0033 (15)	0.0025 (13)	−0.0009 (16)
C8	0.0334 (19)	0.020 (2)	0.0155 (16)	0.0022 (15)	−0.0021 (14)	−0.0022 (14)
C9	0.0275 (17)	0.031 (2)	0.0230 (18)	−0.0104 (15)	−0.0014 (14)	−0.0048 (16)
C10	0.0182 (15)	0.030 (2)	0.0192 (17)	−0.0032 (14)	0.0029 (13)	−0.0042 (16)
C11	0.051 (2)	0.029 (2)	0.0213 (18)	−0.0049 (17)	0.0051 (16)	−0.0064 (16)

Geometric parameters (Å, °)

Br1—C2	1.995 (3)	C6—C7	1.380 (4)
O1—C4	1.226 (3)	C6—H6	0.9500
N1—C4	1.352 (4)	C7—C8	1.382 (4)
N1—C5	1.416 (4)	C7—H7	0.9500
N1—H1N	0.840 (17)	C8—C9	1.391 (4)
C1—C2	1.519 (4)	C8—C11	1.509 (5)
C1—H1A	0.9800	C9—C10	1.382 (4)
C1—H1B	0.9800	C9—H9	0.9500
C1—H1C	0.9800	C10—H10	0.9500
C2—C3	1.515 (4)	C11—H11A	0.9800
C2—C4	1.533 (4)	C11—H11B	0.9800

C3—H3A	0.9800	C11—H11C	0.9800
C3—H3B	0.9800	C11—H11D	0.9800
C3—H3C	0.9800	C11—H11E	0.9800
C5—C10	1.387 (4)	C11—H11F	0.9800
C5—C6	1.397 (4)		
C4—N1—C5	126.2 (2)	C8—C7—H7	118.5
C4—N1—H1N	115 (2)	C7—C8—C9	117.1 (3)
C5—N1—H1N	118 (2)	C7—C8—C11	121.8 (3)
C2—C1—H1A	109.5	C9—C8—C11	121.1 (3)
C2—C1—H1B	109.5	C10—C9—C8	121.2 (3)
H1A—C1—H1B	109.5	C10—C9—H9	119.4
C2—C1—H1C	109.5	C8—C9—H9	119.4
H1A—C1—H1C	109.5	C9—C10—C5	120.8 (3)
H1B—C1—H1C	109.5	C9—C10—H10	119.6
C3—C2—C1	111.2 (3)	C5—C10—H10	119.6
C3—C2—C4	111.1 (2)	C8—C11—H11A	109.5
C1—C2—C4	115.1 (2)	C8—C11—H11B	109.5
C3—C2—Br1	107.0 (2)	H11A—C11—H11B	109.5
C1—C2—Br1	107.20 (19)	C8—C11—H11C	109.5
C4—C2—Br1	104.7 (2)	H11A—C11—H11C	109.5
C2—C3—H3A	109.5	H11B—C11—H11C	109.5
C2—C3—H3B	109.5	C8—C11—H11D	109.5
H3A—C3—H3B	109.5	H11A—C11—H11D	141.1
C2—C3—H3C	109.5	H11B—C11—H11D	56.3
H3A—C3—H3C	109.5	H11C—C11—H11D	56.3
H3B—C3—H3C	109.5	C8—C11—H11E	109.5
O1—C4—N1	123.0 (3)	H11A—C11—H11E	56.3
O1—C4—C2	120.8 (3)	H11B—C11—H11E	141.1
N1—C4—C2	116.2 (2)	H11C—C11—H11E	56.3
C10—C5—C6	118.7 (3)	H11D—C11—H11E	109.5
C10—C5—N1	118.1 (3)	C8—C11—H11F	109.5
C6—C5—N1	123.3 (3)	H11A—C11—H11F	56.3
C7—C6—C5	119.3 (3)	H11B—C11—H11F	56.3
C7—C6—H6	120.4	H11C—C11—H11F	141.1
C5—C6—H6	120.4	H11D—C11—H11F	109.5
C6—C7—C8	122.9 (3)	H11E—C11—H11F	109.5
C6—C7—H7	118.5		
C5—N1—C4—O1	4.0 (5)	C10—C5—C6—C7	−1.6 (5)
C5—N1—C4—C2	−177.5 (3)	N1—C5—C6—C7	179.3 (3)
C3—C2—C4—O1	14.6 (4)	C5—C6—C7—C8	−0.4 (5)
C1—C2—C4—O1	142.0 (3)	C6—C7—C8—C9	1.6 (5)
Br1—C2—C4—O1	−100.5 (3)	C6—C7—C8—C11	−178.2 (3)
C3—C2—C4—N1	−163.9 (3)	C7—C8—C9—C10	−1.0 (5)
C1—C2—C4—N1	−36.5 (4)	C11—C8—C9—C10	178.8 (3)
Br1—C2—C4—N1	81.0 (3)	C8—C9—C10—C5	−0.9 (5)
C4—N1—C5—C10	149.7 (3)	C6—C5—C10—C9	2.2 (5)

C4—N1—C5—C6	−31.2 (5)	N1—C5—C10—C9	−178.6 (3)
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Hydrogen-bond geometry (Å, °)

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
N1—H1N $\cdots$ O1 ⁱ	0.84 (2)	2.13 (2)	2.937 (3)	161 (3)
C1—H1C $\cdots$ O1 ⁱ	0.98	2.44	3.382 (4)	162
C10—H10 $\cdots$ O1 ⁱ	0.95	2.57	3.321 (4)	137

Symmetry code: (i) $x-1/2, y, -z+1/2$.