N,N′-(1,4-Phenylene)bis(2-bromo-2-methylpropanamide)

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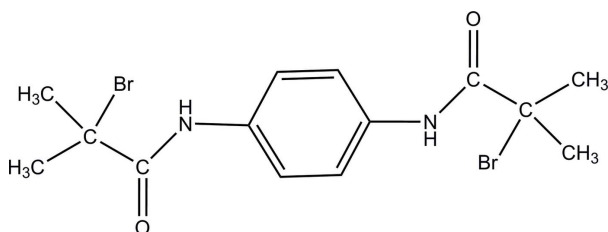Correspondence e-mail: damo@iitm.ac.in

The molecular structure of the title compound, $C_{14}H_{18}Br_2N_2O_2$, has one half-molecule in the asymmetric unit. The molecule has a crystallographic inversion centre in the middle of the benzene ring. The C—C—N—C torsion angle between the benzene ring and the bromoamide group is 149.2 (7)°. The crystal is stabilized by a strong intermolecular N—H···O bond and weak C—H···O interactions. These contacts give rise to a three-dimensional network.

Related literature

For the use of the title compound as an initiator in atom transfer radical polymerization and other polymerization studies, see: Ashraf *et al.* (1994); Domenicano *et al.* (1977); Kuipers *et al.* (1989); Matyjaszewski & Xia (2001); Miroshnikova *et al.* (2007); Rollison *et al.* (2006). For similar structures, see: Haridharan *et al.* (2010).

Experimental

Crystal data

$C_{14}H_{18}Br_2N_2O_2$	V = 823.2 (3) Å^3
M_r = 406.12	Z = 2
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
a = 13.834 (3) Å	μ = 4.93 mm^{-1}
b = 6.4746 (13) Å	T = 298 K
c = 9.4642 (18) Å	0.35 × 0.22 × 0.05 mm
β = 103.807 (9)°	

Data collection

Bruker APEXII CCD area-detector diffractometer	1834 measured reflections
Absorption correction: multi-scan (*SADABS*; Bruker, 2004)	1834 independent reflections
T_{min} = 0.278, T_{max} = 0.791	664 reflections with $I > 2\sigma(I)$
	R_{int} = 0.000

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.056	93 parameters
$wR(F^2)$ = 0.146	H-atom parameters constrained
S = 0.94	$\Delta\rho_{max}$ = 0.54 e Å^{-3}
1834 reflections	$\Delta\rho_{min}$ = −0.56 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···O1^i	0.86	2.23	3.057 (7)	162
C7—H7B···O1^i	0.96	2.57	3.503 (9)	164

Symmetry code: (i) $x, -y + \frac{3}{2}, z - \frac{1}{2}$.

Data collection: *APEX2* (Bruker, 2004); cell refinement: *APEX2* and *SAINT-Plus* (Bruker, 2004); data reduction: *SAINT-Plus* and *XPREP* (Bruker, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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supporting information

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S1. Comment

The title compound $C_{14}H_{18}Br_2N_2O_2$ is a difunctional aromatic amide based derivative, which is used as an initiator in Atom Transfer Radical Polymerization (ATRP) (Matyjaszewski *et al.*, 2001). We have already reported a similar ATRP initiator (Haridharan *et al.*, 2010). The title compound reported here is a similar derivative with a diamide functionality (Domenicano *et al.* (1977); Kuipers *et al.* (1989). It is mainly used as a component of engineering polymers and composites (Ashraf *et al.*, 1994). It is also an ingredient in hair dyes.

   p-Phenylenediamine is a precursor to aramid plastics and fibers such as Kevlar (Rollison *et al.*, 2006). *p*-Phenylenediamine is also used as a developing agent in the color photographic film development process, reacting with the silver grains in the film and creating the colored dyes that form the image. *p*-Phenylenediamine derivatives such as chloroquine are the most important and widely used class of drugs for treatment of malaria (Miroshnikova *et al.*, 2007). In the title compound $C_{14}H_{18}Br_2N_2O_2$, the torsion angle between the phenyl ring and the bromo amide group is 149.2 (7)° (C3—C1—N1—C4). The molecule has a crystallographic inversion centre in the middle of the phenyl ring. The crystal is stabilized by a strong intermolecular N—H⋯O bonding and weak C-H⋯O interactions. These contacts gives rise to a three dimensional network.

S2. Experimental

p-Phenylene diamine (5 g, 0.012 moles), triethylamine (12 g, 0.05 moles) and THF (400 ml) were placed in a 3-neck round bottomed flask. Bromoisobutyrl bromide (13.7 g, 0.05 moles) was added slowly, using a syringe, with stirring, upon which a brown precipitate of triethylammonium bromide was formed. The mixture was left to react for 12 h, with stirring. Subsequently, triethylammonium bromide, the precipitate was removed by filtration and the THF was removed by rotary evaporation. The resulting crude product was dissolved in ethyl acetate, washed with bicarbonate solution and then with water thrice followed by brine solution and dried over anhydrous sodium sulfate. The resulting solvent was removed by rotary evaporation. The product was purified by column chromatography technique using 10% ethyl acetate in hexane as the eluent to obtain pure initiator as a bright yellow solid. Recrystallization of the compound from hexane gave X-ray diffraction quality crystals of N,N′-(1,4-phenylene)bis(2-bromo-2-methylpropanamide).

S3. Refinement

All hydrogen atoms were fixed geometrically and allowed to ride on the parent carbon atoms, with aromatic C—H = 0.93 Å, methyl C—H = 0.96 Å and methylene C—H = 0.97 Å. The displacement parameters were set for phenyl and methylene H atoms at $U_{iso}(H) = 1.2U_{eq}(C)$ and methyl H atoms at $U_{iso}(H) = 1.5U_{eq}(C)$.

   The crystal data was collected up to 0.73 Å resolution, the crystal (the largest available) still diffracted quite weakly at high angle. On repeated crystallization we could get only small crystals which weakly diffracted. The data completeness we could get was only 93.6%.
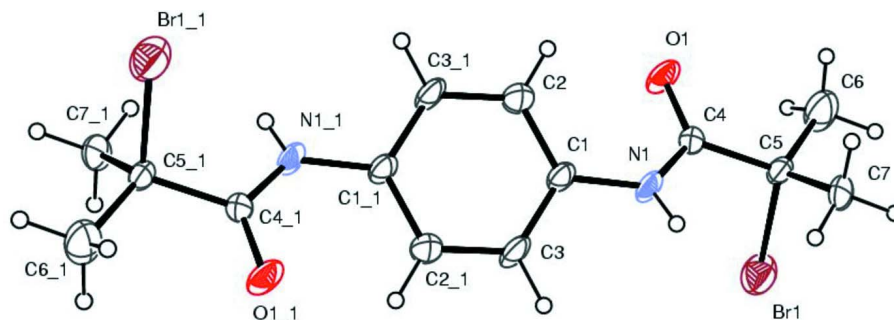
Figure 1

ORTEP of the molecule with atoms represented as 30% probability ellipsoids.

2-bromo-*N*-[4-(2-bromo-2-methylpropanamido)phenyl]-2-methylpropanamide

Crystal data

$C_{14}H_{18}Br_2N_2O_2$	$F(000) = 404$
$M_r = 406.12$	$D_x = 1.638$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 1219 reflections
$a = 13.834$ (3) Å	$\theta = 0.0$–$0.0°$
$b = 6.4746$ (13) Å	$\mu = 4.93$ mm^{-1}
$c = 9.4642$ (18) Å	$T = 298$ K
$\beta = 103.807$ (9)°	Block, colourless
$V = 823.2$ (3) Å^3	$0.35 \times 0.22 \times 0.05$ mm
$Z = 2$	

Data collection

Bruker APEXII CCD area-detector diffractometer	1834 measured reflections
	1834 independent reflections
Radiation source: fine-focus sealed tube	664 reflections with $I > 2\sigma(I)$
Graphite monochromator	$R_{int} = 0.000$
φ and ω scans	$\theta_{max} = 27.8°$, $\theta_{min} = 3.0°$
Absorption correction: multi-scan (*SADABS*; Bruker, 2004)	$h = -18 \rightarrow 17$
	$k = 0 \rightarrow 8$
$T_{min} = 0.278$, $T_{max} = 0.791$	$l = 0 \rightarrow 11$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.056$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.146$	
$S = 0.94$	H-atom parameters constrained
1834 reflections	$w = 1/[\sigma^2(F_o^2) + (0.0575P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
93 parameters	
0 restraints	$(\Delta/\sigma)_{max} < 0.001$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{max} = 0.54$ e Å^{-3}
	$\Delta\rho_{min} = -0.56$ e Å^{-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 $F^2 > 2\text{sigma}(F^2)$ 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 (Å²)

	x	y	z	$U_{iso}*/U_{eq}$
Br1	0.90343 (6)	0.80012 (14)	0.54184 (10)	0.0699 (4)
O1	0.7011 (3)	0.5876 (8)	0.6804 (5)	0.0520 (14)
N1	0.6647 (4)	0.7640 (8)	0.4699 (6)	0.0436 (16)
H1A	0.6809	0.7779	0.3882	0.052*
C1	0.5804 (5)	0.8774 (11)	0.4872 (7)	0.0364 (18)
C2	0.5188 (5)	0.8134 (11)	0.5735 (8)	0.050 (2)
H2	0.5308	0.6887	0.6234	0.060*
C3	0.5607 (5)	1.0646 (13)	0.4144 (7)	0.045 (2)
H3	0.6021	1.1089	0.3561	0.054*
C4	0.7212 (5)	0.6389 (10)	0.5664 (8)	0.0366 (18)
C5	0.8137 (4)	0.5549 (10)	0.5272 (7)	0.0387 (18)
C6	0.8682 (6)	0.4020 (14)	0.6398 (9)	0.079 (3)
H6A	0.8881	0.4692	0.7327	0.118*
H6B	0.9261	0.3518	0.6116	0.118*
H6C	0.8250	0.2884	0.6465	0.118*
C7	0.7975 (5)	0.4668 (11)	0.3732 (7)	0.051 (2)
H7A	0.8601	0.4226	0.3567	0.076*
H7B	0.7693	0.5714	0.3036	0.076*
H7C	0.7529	0.3512	0.3627	0.076*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0573 (6)	0.0714 (7)	0.0882 (8)	−0.0096 (5)	0.0316 (4)	−0.0175 (5)
O1	0.056 (3)	0.074 (4)	0.035 (3)	0.008 (3)	0.028 (3)	0.009 (3)
N1	0.053 (4)	0.056 (4)	0.032 (4)	0.018 (3)	0.028 (3)	0.011 (3)
C1	0.040 (4)	0.046 (5)	0.028 (4)	0.003 (3)	0.018 (3)	0.000 (4)
C2	0.056 (5)	0.050 (5)	0.052 (5)	0.013 (4)	0.027 (4)	0.018 (4)
C3	0.043 (4)	0.066 (6)	0.033 (5)	0.010 (4)	0.026 (3)	0.009 (4)
C4	0.045 (4)	0.032 (5)	0.038 (5)	0.007 (3)	0.021 (4)	0.004 (4)
C5	0.037 (4)	0.044 (5)	0.041 (5)	0.012 (4)	0.022 (3)	0.012 (4)
C6	0.095 (7)	0.092 (7)	0.062 (6)	0.042 (6)	0.044 (5)	0.028 (5)
C7	0.076 (5)	0.041 (5)	0.046 (5)	0.013 (4)	0.036 (4)	−0.006 (4)

Geometric parameters (Å, º)

Br1—C5	2.000 (7)	C3—H3	0.9300
O1—C4	1.223 (7)	C4—C5	1.516 (8)
N1—C4	1.326 (8)	C5—C6	1.517 (9)
N1—C1	1.421 (8)	C5—C7	1.531 (9)
N1—H1A	0.8600	C6—H6A	0.9600
C1—C2	1.377 (8)	C6—H6B	0.9600
C1—C3	1.389 (9)	C6—H6C	0.9600
C2—C3ⁱ	1.381 (9)	C7—H7A	0.9600
C2—H2	0.9300	C7—H7B	0.9600
C3—C2ⁱ	1.381 (9)	C7—H7C	0.9600
C4—N1—C1	127.0 (5)	C6—C5—C7	111.2 (6)
C4—N1—H1A	116.5	C4—C5—Br1	104.2 (4)
C1—N1—H1A	116.5	C6—C5—Br1	105.8 (5)
C2—C1—C3	118.8 (6)	C7—C5—Br1	108.0 (4)
C2—C1—N1	123.6 (7)	C5—C6—H6A	109.5
C3—C1—N1	117.6 (5)	C5—C6—H6B	109.5
C1—C2—C3ⁱ	119.7 (7)	H6A—C6—H6B	109.5
C1—C2—H2	120.2	C5—C6—H6C	109.5
C3ⁱ—C2—H2	120.2	H6A—C6—H6C	109.5
C2ⁱ—C3—C1	121.6 (6)	H6B—C6—H6C	109.5
C2ⁱ—C3—H3	119.2	C5—C7—H7A	109.5
C1—C3—H3	119.2	C5—C7—H7B	109.5
O1—C4—N1	123.5 (6)	H7A—C7—H7B	109.5
O1—C4—C5	120.1 (6)	C5—C7—H7C	109.5
N1—C4—C5	116.4 (6)	H7A—C7—H7C	109.5
C4—C5—C6	111.7 (5)	H7B—C7—H7C	109.5
C4—C5—C7	115.2 (6)		
C4—N1—C1—C2	−29.5 (11)	C1—N1—C4—C5	−173.4 (6)
C4—N1—C1—C3	149.4 (7)	O1—C4—C5—C6	2.8 (10)
C3—C1—C2—C3ⁱ	0.1 (12)	N1—C4—C5—C6	−175.8 (7)
N1—C1—C2—C3ⁱ	179.0 (6)	O1—C4—C5—C7	130.9 (7)
C2—C1—C3—C2ⁱ	−0.2 (12)	N1—C4—C5—C7	−47.8 (8)
N1—C1—C3—C2ⁱ	−179.1 (6)	O1—C4—C5—Br1	−111.0 (6)
C1—N1—C4—O1	8.0 (11)	N1—C4—C5—Br1	70.4 (7)

Symmetry code: (i) −*x*+1, −*y*+2, −*z*+1.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···O1ⁱⁱ	0.86	2.23	3.057 (7)	162
C7—H7*B*···O1ⁱⁱ	0.96	2.57	3.503 (9)	164

Symmetry code: (ii) *x*, −*y*+3/2, *z*−1/2.