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ISSN 2414-3146

N,*N*′-Bis(4-bromophenyl)-*N*,*N*′-dimethylurea

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Received 18 January 2018
Accepted 30 January 2018

Edited by J. Simpson, University of Otago, New Zealand

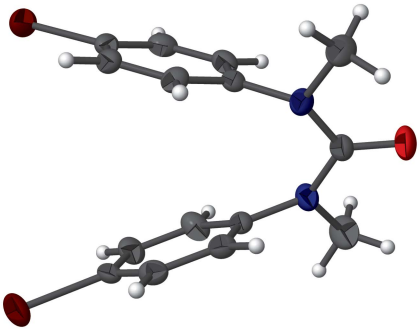
Keywords: crystal structure; urea; folding; instability on storage.

CCDC reference: 1820748

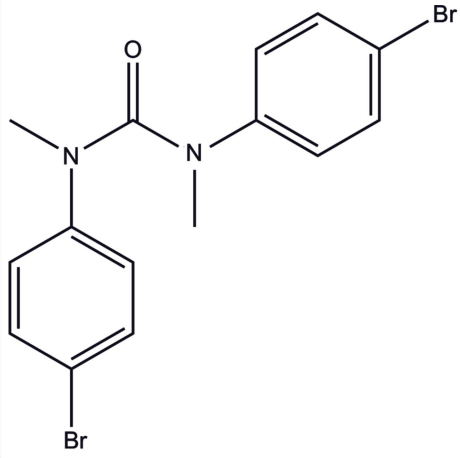
Structural data: full structural data are available from iucrdata.iucr.org

The structure of the title compound, $C_{15}H_{14}Br_2N_2O$, at 180 K has monoclinic ($P2_1/n$) symmetry. It was obtained unexpectedly from the decomposition of the parent 4-bromo-*N*-*tert*-butoxycarbonyl-*N*-methyl-aniline. It exhibits an '*endo*' conformation with angles between the two aromatic rings slightly lower than the average values found for similar compounds on the Cambridge Structural Database. In the crystal, C—H···O hydrogen bonds and short Br···Br halogen bonds [3.444 (1) Å] are observed.

3D view



Chemical scheme



Structure description

In the title compound, an 'endo' conformation is observed with the two aryl rings facing each other (Fig. 1). This structural feature has been observed previously and shown to be specific to *N*,*N*,*N*′,*N*′-tetrasubstituted-*N*,*N*′-diaryl urea derivatives (Clayden *et al.*, 2010; Hisamatsu *et al.*, 2011*a*,*b*; Hisamatsu *et al.*, 2012; Snape *et al.*, 2012). The planes of the two benzene rings are twisted by an angle of 29.51 (11)°, which compares moderately well with the average value found for similar structures in the CSD (Version 5.38, updated November 2016; Groom *et al.*, 2016). 44 structures were found, minimum angle 15.14°, maximum angle 81.25° with an average value of 33.59°. The C4—N1···N2—C10 torsion angle is 47.76° while the corresponding values obtained from the database for the 44 hits lie between 22.56 and 122.96° with an average value of 56.45°.

In the crystal, O2 acts as a bifurcated acceptor, forming C6—H6···O2 and C11—H11···O2 hydrogen bonds, Table 1. These combine with Br1···Br2^{iii} short contacts [3.444 (1) Å; symmetry code: (iii) $\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$] to generate a three-dimensional network, Fig. 2.

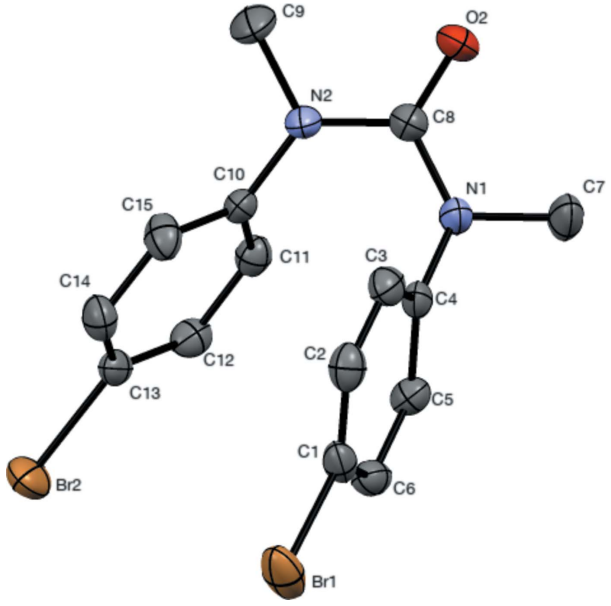


Figure 1
The molecular structure of the title compound showing the atom numbering with displacement ellipsoids drawn at the 50% probability level.

Synthesis and crystallization

Crystals of the title compound were obtained from 1 g of the oil of neat *tert*-butyl (4-bromophenyl)methylcarbamate (previously purified by column chromatography), upon standing in air for two months. This indicates the unprecedented instability of this Boc-protected aniline (Fig. 3). The crystals were washed with 10 mL of cyclohexane, providing 50 mg of crystals of the title compound.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

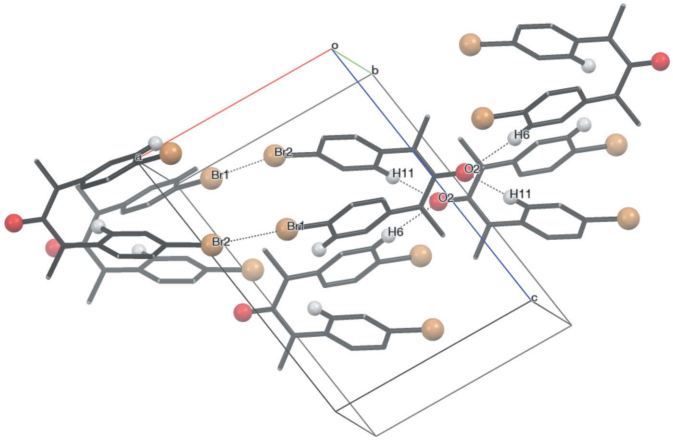


Figure 2
A view of the extended structure of the title compound with hydrogen bonds drawn as dashed lines. Hydrogen atoms not involved in hydrogen bonding have been omitted.

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

D—H···A	D—H	H···A	D···A	D—H···A
C6—H6···O2^{i}	0.95	2.59	3.526 (3)	170
C11—H11···O2^{ii}	0.95	2.42	3.365 (3)	178

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{15}H_{14}Br_2N_2O$
M_r	398.08
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	180
a, b, c (Å)	9.1622 (2), 12.8617 (4), 13.1863 (3)
β (°)	99.307 (3)
V (Å^3)	1533.44 (7)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	5.28
Crystal size (mm)	0.4 × 0.36 × 0.28
Data collection	
Diffractometer	Agilent Xcalibur, Eos, Gemini ultra
Absorption correction	Multi-scan (*CrysAlis PRO*; Agilent, 2014)
T_{min}, T_{max}	0.319, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	31347, 3484, 2771
R_{int}	0.043
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.649
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.033, 0.077, 1.05
No. of reflections	3484
No. of parameters	182
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.69, −0.77

Computer programs: *CrysAlis PRO* (Agilent, 2014), *SIR92* (Altomare *et al.*, 1994), *SHELXL2014* (Sheldrick, 2015) and *ORTEP-3 for Windows* and *WinGX* (Farrugia, 2012).

Funding information

The Association France Alzheimer and the Région Midi Pyrénées are acknowledged for financial support (PhD funding for AP).

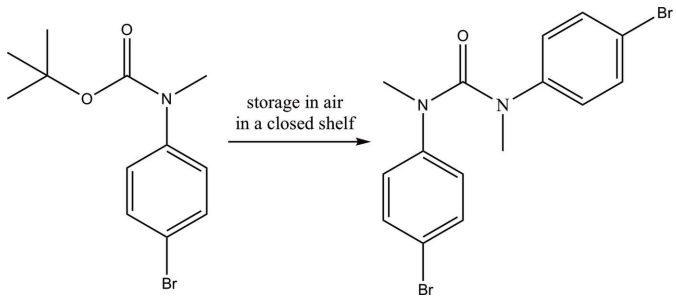


Figure 3
Chemical scheme showing the formation of the title compound from the corresponding Boc-protected aniline

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full crystallographic data

IUCrData (2018). **3**, x180186 [https://doi.org/10.1107/S2414314618001864]

N,*N*′-Bis(4-bromophenyl)-*N*,*N*′-dimethylurea

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Crystal data

$C_{15}H_{14}Br_2N_2O$
M_r = 398.08
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
a = 9.1622 (2) Å
b = 12.8617 (4) Å
c = 13.1863 (3) Å
β = 99.307 (3)°
V = 1533.44 (7) Å^3
Z = 4
$F(000)$ = 784
D_x = 1.724 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 7189 reflections
θ = 3.3–28.2°
μ = 5.28 mm^{-1}
T = 180 K
Block, colourless
0.4 × 0.36 × 0.28 mm

Data collection

Agilent Xcalibur, Eos, Gemini ultra diffractometer
Radiation source: Enhance (Mo) X-ray Source
Graphite monochromator
ω scans
Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2014)
T_{min} = 0.319, T_{max} = 1.000
31347 measured reflections
3484 independent reflections
2771 reflections with $I > 2\sigma(I)$
R_{int} = 0.043
θ_{max} = 27.5°, θ_{min} = 2.9°
h = −11→11
k = −16→16
l = −17→17

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.077
S = 1.05
3484 reflections
182 parameters
0 restraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0356P)^2 + 1.0497P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.69 e Å^{-3}
$\Delta\rho_{min}$ = −0.77 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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.5095 (3)	0.1833 (2)	0.44957 (19)	0.0284 (6)
C2	0.3728 (3)	0.1366 (2)	0.4417 (2)	0.0317 (6)
H2	0.3595	0.0667	0.4187	0.038*
C3	0.2553 (3)	0.1923 (2)	0.46768 (19)	0.0295 (6)
H3	0.1609	0.1605	0.4634	0.035*
C4	0.2753 (3)	0.2948 (2)	0.49998 (17)	0.0244 (5)
C5	0.4145 (3)	0.3395 (2)	0.50894 (19)	0.0268 (5)
H5	0.4287	0.409	0.5328	0.032*
C6	0.5329 (3)	0.2842 (2)	0.4835 (2)	0.0295 (6)
H6	0.6281	0.315	0.4894	0.035*
C7	0.1558 (3)	0.3762 (3)	0.6339 (2)	0.0401 (7)
H7A	0.0892	0.4344	0.641	0.06*
H7B	0.2565	0.3944	0.6661	0.06*
H7C	0.123	0.3145	0.6676	0.06*
C8	0.0184 (3)	0.3570 (2)	0.4626 (2)	0.0278 (6)
C9	−0.1240 (3)	0.3325 (3)	0.2923 (2)	0.0450 (8)
H9A	−0.1536	0.2599	0.299	0.068*
H9B	−0.1144	0.3467	0.2207	0.068*
H9C	−0.199	0.3785	0.3132	0.068*
C10	0.1394 (3)	0.3795 (2)	0.30935 (18)	0.0240 (5)
C11	0.2114 (3)	0.4727 (2)	0.33029 (19)	0.0269 (5)
H11	0.1798	0.5196	0.378	0.032*
C12	0.3302 (3)	0.4984 (2)	0.2819 (2)	0.0286 (6)
H12	0.3814	0.5622	0.2971	0.034*
C13	0.3732 (3)	0.4303 (2)	0.21162 (19)	0.0268 (6)
C14	0.3013 (3)	0.3378 (2)	0.1880 (2)	0.0329 (6)
H14	0.3312	0.292	0.1387	0.039*
C15	0.1840 (3)	0.3128 (2)	0.2376 (2)	0.0327 (6)
H15	0.1333	0.2489	0.2223	0.039*
N1	0.1540 (2)	0.35407 (18)	0.52462 (15)	0.0290 (5)
N2	0.0177 (2)	0.35073 (18)	0.35812 (16)	0.0304 (5)
O2	−0.0968 (2)	0.36539 (16)	0.49821 (15)	0.0374 (5)
Br1	0.66952 (4)	0.10678 (3)	0.41141 (2)	0.04620 (11)
Br2	0.53294 (3)	0.46621 (3)	0.14348 (2)	0.04781 (11)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0319 (14)	0.0326 (14)	0.0221 (12)	0.0102 (12)	0.0087 (11)	0.0044 (11)
C2	0.0430 (17)	0.0269 (14)	0.0253 (13)	0.0013 (12)	0.0054 (12)	0.0021 (11)
C3	0.0289 (14)	0.0340 (15)	0.0257 (13)	−0.0050 (11)	0.0047 (11)	0.0048 (11)
C4	0.0254 (13)	0.0315 (14)	0.0164 (11)	0.0029 (11)	0.0040 (9)	0.0026 (10)
C5	0.0257 (13)	0.0263 (14)	0.0268 (13)	0.0008 (10)	−0.0006 (10)	−0.0012 (10)
C6	0.0222 (13)	0.0363 (15)	0.0295 (13)	0.0011 (11)	0.0024 (10)	0.0073 (11)
C7	0.0395 (17)	0.059 (2)	0.0213 (13)	0.0147 (14)	0.0037 (12)	−0.0055 (13)

C8	0.0238 (13)	0.0339 (14)	0.0262 (13)	−0.0004 (11)	0.0052 (11)	0.0005 (11)
C9	0.0289 (15)	0.070 (2)	0.0338 (16)	−0.0149 (15)	−0.0035 (12)	−0.0055 (15)
C10	0.0202 (12)	0.0323 (14)	0.0187 (11)	0.0006 (10)	0.0004 (9)	0.0021 (10)
C11	0.0300 (14)	0.0262 (13)	0.0239 (12)	0.0036 (11)	0.0018 (10)	0.0009 (10)
C12	0.0278 (14)	0.0255 (13)	0.0308 (14)	−0.0041 (11)	0.0001 (11)	0.0051 (11)
C13	0.0228 (13)	0.0362 (14)	0.0212 (12)	0.0002 (11)	0.0030 (10)	0.0109 (11)
C14	0.0390 (16)	0.0375 (16)	0.0241 (13)	0.0018 (12)	0.0106 (12)	−0.0023 (11)
C15	0.0404 (16)	0.0317 (15)	0.0268 (13)	−0.0103 (12)	0.0082 (12)	−0.0057 (11)
N1	0.0246 (11)	0.0430 (13)	0.0192 (10)	0.0068 (10)	0.0034 (9)	−0.0026 (9)
N2	0.0193 (11)	0.0485 (14)	0.0229 (11)	−0.0060 (10)	0.0016 (9)	0.0007 (10)
O2	0.0232 (10)	0.0557 (13)	0.0353 (10)	0.0000 (9)	0.0110 (8)	−0.0047 (9)
Br1	0.0511 (2)	0.0519 (2)	0.04037 (18)	0.02521 (15)	0.02171 (14)	0.00926 (14)
Br2	0.03153 (17)	0.0754 (3)	0.03916 (18)	−0.00702 (15)	0.01386 (13)	0.01359 (15)

Geometric parameters (Å, º)

C1—C2	1.377 (4)	C8—N2	1.379 (3)
C1—C6	1.377 (4)	C9—N2	1.459 (3)
C1—Br1	1.900 (2)	C9—H9A	0.98
C2—C3	1.382 (4)	C9—H9B	0.98
C2—H2	0.95	C9—H9C	0.98
C3—C4	1.388 (4)	C10—C11	1.375 (4)
C3—H3	0.95	C10—C15	1.387 (4)
C4—C5	1.386 (4)	C10—N2	1.424 (3)
C4—N1	1.429 (3)	C11—C12	1.388 (4)
C5—C6	1.383 (4)	C11—H11	0.95
C5—H5	0.95	C12—C13	1.379 (4)
C6—H6	0.95	C12—H12	0.95
C7—N1	1.466 (3)	C13—C14	1.371 (4)
C7—H7A	0.98	C13—Br2	1.894 (2)
C7—H7B	0.98	C14—C15	1.383 (4)
C7—H7C	0.98	C14—H14	0.95
C8—O2	1.227 (3)	C15—H15	0.95
C8—N1	1.373 (3)	Br1—Br2^{i}	3.4443 (4)
C2—C1—C6	121.8 (2)	N2—C9—H9C	109.5
C2—C1—Br1	119.0 (2)	H9A—C9—H9C	109.5
C6—C1—Br1	119.2 (2)	H9B—C9—H9C	109.5
C1—C2—C3	119.3 (2)	C11—C10—C15	119.5 (2)
C1—C2—H2	120.3	C11—C10—N2	121.4 (2)
C3—C2—H2	120.3	C15—C10—N2	119.1 (2)
C2—C3—C4	119.9 (2)	C10—C11—C12	120.1 (2)
C2—C3—H3	120	C10—C11—H11	119.9
C4—C3—H3	120	C12—C11—H11	119.9
C5—C4—C3	119.6 (2)	C13—C12—C11	119.2 (2)
C5—C4—N1	119.9 (2)	C13—C12—H12	120.4
C3—C4—N1	120.5 (2)	C11—C12—H12	120.4
C6—C5—C4	120.8 (2)	C14—C13—C12	121.7 (2)

C6—C5—H5	119.6	C14—C13—Br2	118.9 (2)
C4—C5—H5	119.6	C12—C13—Br2	119.4 (2)
C1—C6—C5	118.4 (2)	C13—C14—C15	118.4 (2)
C1—C6—H6	120.8	C13—C14—H14	120.8
C5—C6—H6	120.8	C15—C14—H14	120.8
N1—C7—H7A	109.5	C14—C15—C10	121.1 (2)
N1—C7—H7B	109.5	C14—C15—H15	119.5
H7A—C7—H7B	109.5	C10—C15—H15	119.5
N1—C7—H7C	109.5	C8—N1—C4	122.8 (2)
H7A—C7—H7C	109.5	C8—N1—C7	116.5 (2)
H7B—C7—H7C	109.5	C4—N1—C7	116.2 (2)
O2—C8—N1	121.7 (2)	C8—N2—C10	124.0 (2)
O2—C8—N2	121.5 (2)	C8—N2—C9	117.6 (2)
N1—C8—N2	116.8 (2)	C10—N2—C9	117.4 (2)
N2—C9—H9A	109.5	C1—Br1—Br2^{i}	176.83 (8)
N2—C9—H9B	109.5	C13—Br2—Br1^{i}	90.26 (8)
H9A—C9—H9B	109.5		

Symmetry code: (i) $-x+3/2$, $y-1/2$, $-z+1/2$.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C6—H6···O2^{ii}	0.95	2.59	3.526 (3)	170
C11—H11···O2^{iii}	0.95	2.42	3.365 (3)	178

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