Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

3-[1-(4-Bromophenyl)ethoxy]-2,2,5-trimethyl-4-phenyl-3-azahexane

Praveen Pitliya,[a] Ray J. Butcher,[a]* A. Karim,[b] Paul F. Hudrlik,[a] Anne M. Hudrlik[a] and D. Raghavan[a]

[a]Department of Chemistry, Howard University, 525 College Street NW, Washington, DC 20059, USA, and [b]Department of Polymer Engineering, University of Akron, Akron, OH, USA
Correspondence e-mail: rbutcher99@yahoo.com

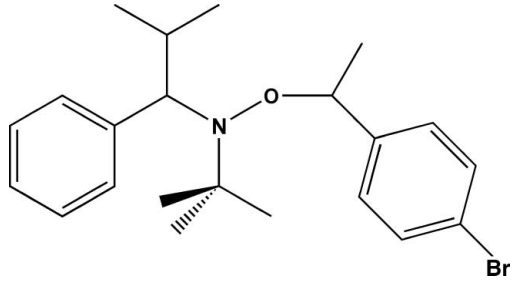
Received 27 September 2013; accepted 1 November 2013

Key indicators: single-crystal X-ray study; T = 123 K; mean σ(C–C) = 0.002 Å; disorder in main residue; R factor = 0.066; wR factor = 0.123; data-to-parameter ratio = 54.9.

The title compound, $C_{22}H_{30}BrNO$, is an alkoxyamine compound, an effective initiator in nitroxide-mediated free radical polymerization. It was prepared as a mixture of two diasteromers; the crystal for the X-ray analysis showed one of these as a pair of *R*,*S* and *S*,*R* enantiomers. The *tert*-butyl and isopropyl groups are in an almost *anti* conformation in the crystal [C—N—C—C torsion angle = −168.8 (1)°], and the methyl group of the ethoxy group is in an approximate *anti* relationship to the *tert*-butyl group. The dihedral angle between the phenyl and benzene rings is 33.12 (7)°. The Br atom is disordered over two positions, with occupancies of 0.9139 (16) and 0.0861 (16). In the crystal, weak C—H···Br contacts link the molecules into chains along [$\bar{1}$10].

Related literature

For the use of TIPNO-based alkoxyamine in polymer synthesis (TIPNO = 2,2,5-trimethyl-4-phenyl-3-azahexane-3-nitroxide), see: Benoit *et al.* (1999). For the synthesis of the title compound, see: Kaul *et al.* (2010). For the use of the title compound in block copolymer synthesis, see: Richard *et al.* (2008); Kaul *et al.* (2010); Stalmach *et al.* (2001); van der Veen *et al.* (2004); Widin *et al.* (2013). For properties of alkoxyamines, see: Benoit *et al.* (1999); Wetter *et al.* (2004); Rodlert *et al.* (2000); Nilsen & Braslau (2006). For synthesis of 1-(4-bromophenyl) ethylbromide, see: Kodama *et al.* (2011); Thompson *et al.* (2011). For standard bond lengths, see: Allen *et al.* (1987).



Experimental

Crystal data

$C_{22}H_{30}BrNO$
M_r = 404.38
Triclinic, $P\overline{1}$
a = 8.2595 (4) Å
b = 10.0175 (4) Å
c = 12.5257 (6) Å
α = 88.798 (4)°
β = 78.824 (4)°
γ = 89.220 (3)°
V = 1016.45 (8) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 2.03 mm^{-1}
T = 123 K
0.51 × 0.35 × 0.06 mm

Data collection

Agilent Xcalibur (Ruby, Gemini) diffractometer
Absorption correction: analytical [*CrysAlis PRO* (Agilent, 2012), based on expressions derived by Clark & Reid (1995)]
T_{min} = 0.375, T_{max} = 0.888
23820 measured reflections
13014 independent reflections
7448 reflections with $I > 2\sigma(I)$
R_{int} = 0.040

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.066
$wR(F^2)$ = 0.123
S = 1.08
13014 reflections
237 parameters
14 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.71 e Å^{-3}
$\Delta\rho_{min}$ = −0.78 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
C11—H11B···Br1A^{i}	0.98	3.12	3.9782 (16)	148
C13—H13A···Br1A^{ii}	1.00	3.07	4.0358 (13)	163
C13—H13A···Br1B^{ii}	1.00	3.02	3.970 (2)	159
C15—H15B···Br1B^{ii}	0.98	3.14	4.017 (3)	149

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

Data collection: *CrysAlis PRO* (Agilent, 2012); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

DR and AK would like to thank the US Department of Energy, Division of Basic Energy Sciences under contract No. DE–FG02-10ER4779. RJB wishes to acknowledge the NSF–MRI program (grant CHE-0619278) for funds to purchase the diffractometer and the Howard University Nanoscience Facility for access to liquid nitrogen.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HG5350).

References

Agilent (2012). *CrysAlis PRO* and *CrysAlis RED*. Agilent Technologies, Yarnton, England.

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.

Benoit, D., Chaplinski, V., Braslau, R. & Hawker, C. J. (1999). *J. Am. Chem. Soc.* **121**, 3904–3920.

Clark, R. C. & Reid, J. S. (1995). *Acta Cryst.* A**51**, 887–897.

Kaul, E., Senkovskyy, V., Tkachov, R., Bocharova, V., Komber, H., Stamm, M. & Kiriy, A. (2010). *Macromolecules*, **43**, 77–81.

Kodama, S., Hashidate, S., Nomoto, A., Yano, S., Ueshima, M. & Ogawa, A. (2011). *Chem. Lett.* **40**, 495–497.

Nilsen, A. & Braslau, R. (2006). *J. Polym. Sci. Part A Polym. Chem.* **44**, 697–717.

Richard, F., Brochon, C., Leclerc, N., Eckhardt, D., Heiser, T. & Hadziioannou, G. (2008). *Macromol. Rapid Commun.* **29**, 885–891.

Rodlert, M., Harth, E., Rees, I. & Hawker, C. J. (2000). *J. Polym. Sci. Part A Polym. Chem.* **38**, 4749–4763.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Stalmach, U., de Boer, B., Post, A. D., van Hutten, P. F. & Hadziioannou, G. (2001). *Angew. Chem. Int. Ed.* **40**, 428–430.

Thompson, A. M., Sutherland, H. S., Palmer, B. D., Kmentova, I., Blaser, A., Franzblau, S. G., Wan, B., Wang, Y., Ma, Z. & Denny, W. A. (2011). *J. Med. Chem.* **54**, 6563–6585.

Veen, M. H. van der, de Boer, B., Stalmach, U., van de Wetering, K. I. & Hadziioannou, G. (2004). *Macromolecules*, **37**, 3673–3684.

Wetter, C., Gierlich, J., Knoop, C. A., Müller, C., Schulte, T. & Studer, A. (2004). *Chem. Eur. J.* **10**, 1156–1166.

Widin, J. M., Kim, M., Schmitt, A. K., Han, E., Gopalan, P. & Mahanthappa, M. K. (2013). *Macromolecules*, **46**, 4472–4480.

supporting information

Acta Cryst. (2013). E**69**, o1792–o1793 [doi:10.1107/S1600536813029966]

3-[1-(4-Bromophenyl)ethoxy]-2,2,5-trimethyl-4-phenyl-3-azahexane

Praveen Pitliya, Ray J. Butcher, A. Karim, Paul F. Hudrlik, Anne M. Hudrlik and D. Raghavan

S1. Comment

Nitroxide-mediated radical polymerization (NMRP) has been widely used under mild conditions to synthesize polymers and block copolymers with controlled molecular weight, polydispersity, and end group functionality (Benoit *et al.*, 1999; Wetter *et al.*, 2004). In NMRP, an alkoxyamine is used to initiate and mediate polymerization. The C–O bond of an alkoxyamine is stable to normal purification and handling procedures as well as variety of reaction conditions (Rodlert *et al.*, 2000). However, under appropriate conditions, homolysis of the C—O bond occurs, giving a (relatively stable) nitroxide radical and carbon radical which can initiate radical polymerization. The nitroxides are kinetically persistent radicals, and act as reversible traps for the less stable radical intermediates in the polymerization (Nilsen & Braslau, 2006).

Alkoxyamines based on 2,2,5-trimethyl-4-phenyl-3-azahexane-3-nitroxide (TIPNO) have been widely used as initiators/mediators to synthesize a variety of linear polymers and block copolymers (van der Veen *et al.*, 2004; Widin *et al.*, 2013). In particular, alkoxyamine **2** (*X* = H; Figure 4), was found to be especially useful in NMRP (Benoit *et al.*, 1999). The title compound, bromo analog **1** (*X* = Br) was developed so that **2** could be attached to a polymer, to give a macroinitiator for block copolymer synthesis (Stalmach *et al.*, 2001). It has been used successfully in a number of block copolymer syntheses including polystyrene-b-poly(3-hexylthiophene) (PS-b-P3HT) (Kaul *et al.*, 2010), poly(phenylenevinylene)-b-poly(butylacrylate) (PPV-b-PBA) (Stalmach *et al.*, 2001), and poly(3-hexylthiophene)-b-poly(butylacrylate-stat-C60methylstyrene {P3HT-b-[P(BA-stat-C60MS)]} (Richard *et al.*, 2008). Examples of block copolymers, prepared by TIPNO-mediated polymerizations, that have been successfully utilized in photovoltaic application are poly[(2,5-di(2'ethyl)hexyloxy)-1,4-phenylenevinylene]-b-poly(butylacrylate-stat-C60methylstyrene) [DEH-PPV-b-P(BA-stat-C60MS)], poly(vinyltriphenylamine)-b-poly(perylene bisimide acrylate) (PvTPA-b-PPerAcr) and poly(3-hexylthiophene)-b-poly(perylene bisimide acrylate (P3HT-b-PPerAcr).

The title compound was prepared as a mixture of two diastereomers in nearly equal amounts, as can be seen by the NMR spectrum (Figure 3). The crystal for the X-ray analysis showed one of the diastereomers (Figure 1), a pair of *R*,*S* and S,*R* (at C7 and C13) enantiomers. The *tert*-butyl group and isopropyl group are in a nearly *anti* conformation in the crystal (dihedral angle C9, N1, C13, C14 = -168.8 (1)°). The C—Me bond (C7, C8) and N-*tert*-Bu bond (N1, C9) are in an *anti* relationship (C8, C7, N1, C9 = 172.3 (1)°), and the C—Me bond (C7, C8) and *C*-isopropyl bond (C13, C14) are in a *syn* relationship (C8, C7, C13, C14 = 4.6 (1) degrees). The dihedral angle between the planes of the phenyl groups is 33.12 (7)°.

The bromine atom was disordered over two positions with occupancies of 0.9139 (16) and 0.0961 (16). The central N is pyramidal and all the bond lengths and angles are in the normal ranges (Allen *et al.*, 1987). There are weak C—H···Br intermolecular contacts which link the molecules into chains in the [$\bar{1}$ 1 0] direction.

S2. Experimental

(*a*) 1-(4-Bromophenyl)ethylbromide

1-(4-Bromophenyl)ethylbromide was synthesized according to previously reported procedures. 4-Bromoacetophenone was reduced to 1-(4-bromophenyl)ethanol by sodium borohydride (Kodama *et al.*, 2011), and the product was treated with PBr_3 using a procedure of Thompson (Thompson *et al.*, 2011). 1-(4-Bromophenyl)ethylbromide (Kaul *et al.*, 2010) was obtained as colorless liquid in 70% overall yield.

(*b*) 3-[1-(4-Bromophenyl)ethoxy]-2,2,5-trimethyl-4-phenyl-3-azahexane (1)

3-[1-(4-Bromophenyl)ethoxy]-2,2,5-trimethyl-4-phenyl-3-azahexane was synthesized according to a previously reported method [Kaul *et al.*, 2010] with a modification of the time and temperature. Synthesized 1-(4-bromophenyl) ethylbromide and commercially available 2,2,5-trimethyl-4-phenyl-3-azahexane-3-nitroxide (TIPNO) were reacted in the presence of CuBr and *N*,*N*,*N*′′,*N*′,*N*′′-pentamethyldiethylenetriamine (PMDETA) in toluene at 75 °C for 17 hr to form the title compound (**1**), 3-[1-(4-bromophenyl)ethoxy]-2,2,5-trimethyl-4-phenyl-3-azahexane, in 80% yield as a viscous colorless oil which slowly crystallized in the refrigerator. The synthesized compound was characterized by ^{1}H NMR and its crystal structure was determined by X-ray crystallography. The ^{1}H NMR spectrum (Figure 3) showed the presence of two diastereomers in nearly equal amounts, and was in agreement with the published spectrum (Kaul *et al.*, 2010). A crystal was taken for X-ray crystallography.

^{1}H NMR (400 MHz, $CDCl_3$) (mixture of two diastereomers): δ = 7.55–7.15 (HAr), 4.89 (H5 and H5′), 3.43 (H3), 3.31 (H3′), 2.31 (H2), 1.58 (H6), 1.53 (H6′), 1.42 (H2′), 1.26 (H1), 1.04 (H4′), 0.93 (H1′), 0.78 (H4), 0.54 (H1), 0.25 (H1′).

S3. Refinement

Carbon-bonded hydrogen atoms were included in idealized positions and set to ride on the parent atoms. The bromine atom was disordered over two positions with occupancies of 0.9139 (16) and 0.0961 (16).

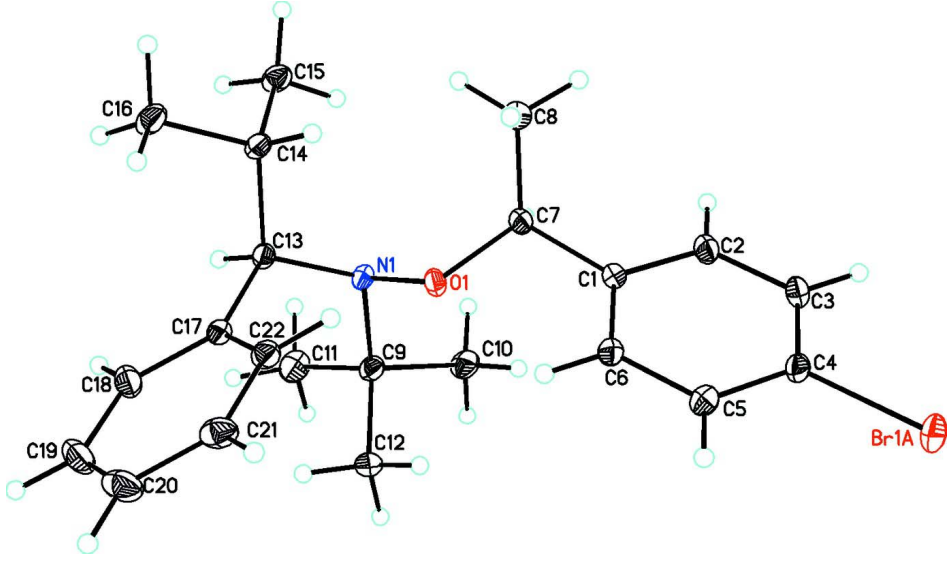


Figure 1

Structural diagram of the title compound. Atomic displacement parameters are at the 30% probability level.

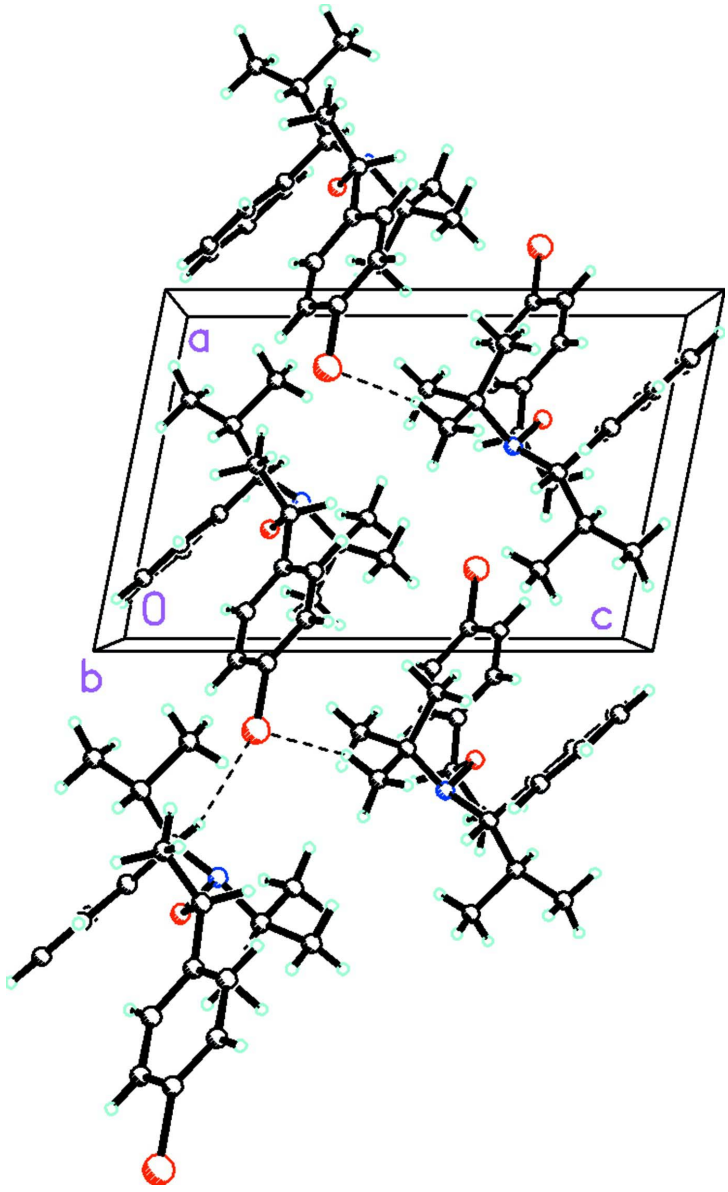


Figure 2

Packing diagram of the title compound viewed along the *a* axis.

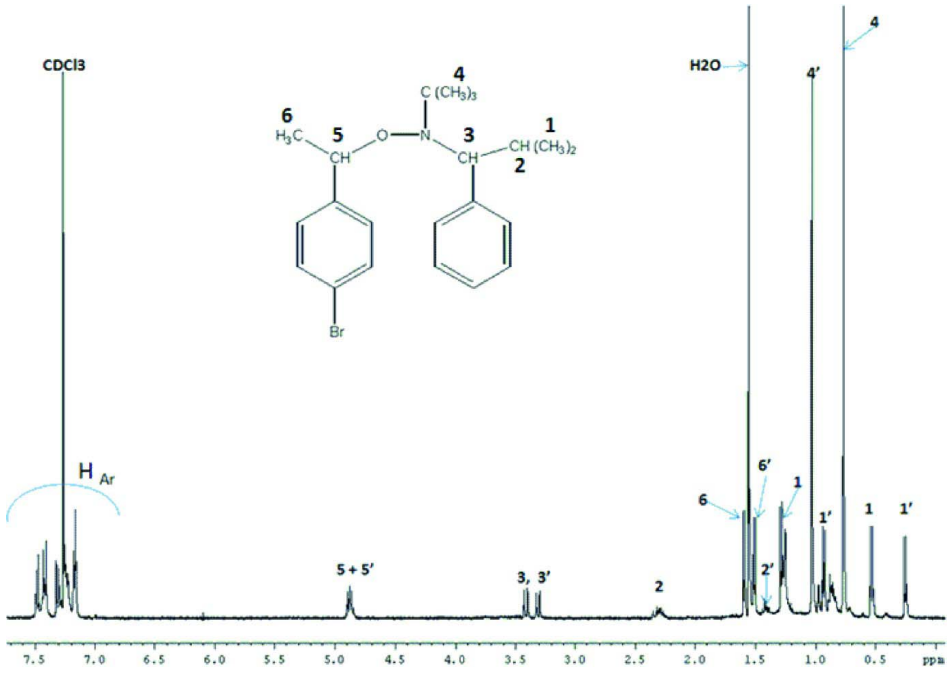
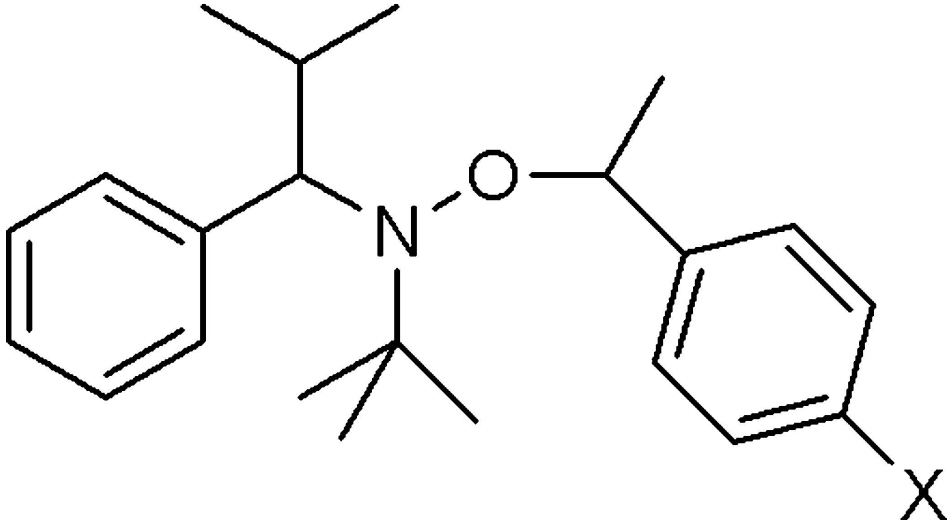


Figure 3

^{1}H NMR spectrum of 3-[1-(4-bromophenyl)ethoxy]-2,2,5-trimethyl-4-phenyl-3-azahexane (two diastereomers) in $CDCl_3$



1 X = Br

2 X = H

Figure 4

Alkoxyamine **2** (X = H) and the title compound, bromo analog **1** (X = Br).

3-[1-(4-Bromophenyl)ethoxy]-2,2,5-trimethyl-4-phenyl-3-azahexane

Crystal data

$C_{22}H_{30}BrNO$
$M_r = 404.38$
Triclinic, $P\overline{1}$
Hall symbol: -P 1
$a = 8.2595$ (4) Å
$b = 10.0175$ (4) Å
$c = 12.5257$ (6) Å
$\alpha = 88.798$ (4)°
$\beta = 78.824$ (4)°
$\gamma = 89.220$ (3)°
$V = 1016.45$ (8) Å^3
$Z = 2$
$F(000) = 424$
$D_x = 1.321$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 4369 reflections
$\theta = 3.2$–$40.9°$
$\mu = 2.03$ mm^{-1}
$T = 123$ K
Diamond shaped plate, colorless
0.51 × 0.35 × 0.06 mm

Data collection

Agilent Xcalibur (Ruby, Gemini) diffractometer
Radiation source: Enhance (Mo) X-ray Source
Graphite monochromator
Detector resolution: 10.5081 pixels mm^{-1}
ω scans
Absorption correction: analytical [*CrysAlis PRO* (Agilent, 2012), based on expressions derived by Clark & Reid (1995)]
$T_{min} = 0.375$, $T_{max} = 0.888$
23820 measured reflections
13014 independent reflections
7448 reflections with $I > 2\sigma(I)$
$R_{int} = 0.040$
$\theta_{max} = 41.0°$, $\theta_{min} = 3.2°$
$h = -13 \rightarrow 15$
$k = -18 \rightarrow 18$
$l = -16 \rightarrow 22$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.066$
$wR(F^2) = 0.123$
$S = 1.08$
13014 reflections
237 parameters
14 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0319P)^2 + 0.3044P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.71$ e Å^{-3}
$\Delta\rho_{min} = -0.78$ e Å^{-3}

Special details

Experimental. CrysAlisPro (Agilent, 2012) Analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid. (Clark & Reid, 1995)

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s 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 $F^2 > \sigma(F^2)$ 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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Br1A	−0.21657 (3)	1.03569 (3)	0.31920 (3)	0.03904 (8)	0.9139 (16)

Br1B	−0.2097 (3)	1.0344 (3)	0.2954 (4)	0.03904 (8)	0.0861 (16)
O1	0.33888 (11)	0.52249 (9)	0.26150 (7)	0.02013 (18)	
N1	0.42054 (13)	0.41412 (11)	0.31003 (9)	0.0184 (2)	
C1	0.22930 (16)	0.73932 (14)	0.30589 (11)	0.0213 (2)	
C2	0.21935 (18)	0.85614 (15)	0.36510 (12)	0.0263 (3)	
H2A	0.3043	0.8757	0.4036	0.032*	
C3	0.08780 (19)	0.94442 (15)	0.36896 (13)	0.0282 (3)	
H3A	0.0825	1.0244	0.4089	0.034*	
C4	−0.03621 (15)	0.91347 (13)	0.31314 (12)	0.0255 (3)	
C5	−0.03140 (18)	0.79814 (15)	0.25483 (12)	0.0260 (3)	
H5A	−0.1177	0.7784	0.2175	0.031*	
C6	0.10213 (17)	0.71062 (15)	0.25143 (11)	0.0235 (3)	
H6A	0.1066	0.6306	0.2116	0.028*	
C7	0.38199 (16)	0.65120 (14)	0.29630 (12)	0.0243 (3)	
H7A	0.4127	0.6411	0.3695	0.029*	
C8	0.5227 (2)	0.71609 (18)	0.21809 (15)	0.0361 (4)	
H8A	0.6227	0.6610	0.2138	0.054*	
H8B	0.5424	0.8050	0.2440	0.054*	
H8C	0.4943	0.7243	0.1458	0.054*	
C9	0.29326 (17)	0.35139 (15)	0.39863 (11)	0.0228 (3)	
C10	0.25278 (19)	0.45110 (17)	0.49164 (12)	0.0297 (3)	
H10A	0.1974	0.5298	0.4670	0.045*	
H10B	0.3551	0.4782	0.5133	0.045*	
H10C	0.1800	0.4089	0.5539	0.045*	
C11	0.3726 (2)	0.22698 (17)	0.44159 (13)	0.0338 (4)	
H11A	0.3849	0.1568	0.3872	0.051*	
H11B	0.3021	0.1950	0.5092	0.051*	
H11C	0.4813	0.2497	0.4559	0.051*	
C12	0.13032 (17)	0.31498 (16)	0.36504 (13)	0.0276 (3)	
H12A	0.1510	0.2450	0.3104	0.041*	
H12B	0.0841	0.3942	0.3342	0.041*	
H12C	0.0520	0.2825	0.4290	0.041*	
C13	0.49844 (15)	0.32510 (13)	0.21998 (10)	0.0188 (2)	
H13A	0.5453	0.2479	0.2563	0.023*	
C14	0.64814 (15)	0.39403 (15)	0.14855 (10)	0.0209 (2)	
H14A	0.6102	0.4801	0.1192	0.025*	
C15	0.77943 (17)	0.42426 (17)	0.21525 (12)	0.0273 (3)	
H15A	0.8661	0.4789	0.1713	0.041*	
H15B	0.8277	0.3404	0.2367	0.041*	
H15C	0.7287	0.4729	0.2805	0.041*	
C16	0.72633 (18)	0.30662 (18)	0.05259 (12)	0.0303 (3)	
H16A	0.8242	0.3510	0.0108	0.045*	
H16B	0.6463	0.2931	0.0055	0.045*	
H16C	0.7585	0.2200	0.0802	0.045*	
C17	0.38509 (16)	0.26336 (14)	0.15192 (10)	0.0203 (2)	
C18	0.3761 (2)	0.12507 (16)	0.14801 (12)	0.0283 (3)	
H18A	0.4397	0.0712	0.1881	0.034*	
C19	0.2754 (2)	0.06402 (18)	0.08627 (13)	0.0363 (4)	

H19A	0.2704	−0.0306	0.0847	0.044*
C20	0.1827 (2)	0.1417 (2)	0.02737 (13)	0.0372 (4)
H20A	0.1125	0.1007	−0.0138	0.045*
C21	0.19305 (18)	0.27933 (18)	0.02873 (12)	0.0299 (3)
H21A	0.1304	0.3327	−0.0124	0.036*
C22	0.29426 (17)	0.34049 (15)	0.08968 (11)	0.0232 (3)
H22A	0.3016	0.4351	0.0890	0.028*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1A	0.03220 (8)	0.02458 (8)	0.0589 (2)	0.01144 (6)	−0.00651 (9)	0.00285 (9)
Br1B	0.03220 (8)	0.02458 (8)	0.0589 (2)	0.01144 (6)	−0.00651 (9)	0.00285 (9)
O1	0.0218 (4)	0.0146 (4)	0.0256 (4)	0.0023 (3)	−0.0084 (3)	−0.0031 (3)
N1	0.0176 (4)	0.0182 (5)	0.0187 (5)	0.0036 (4)	−0.0019 (4)	−0.0007 (4)
C1	0.0193 (5)	0.0165 (5)	0.0273 (6)	−0.0007 (4)	−0.0026 (5)	−0.0019 (5)
C2	0.0260 (6)	0.0197 (6)	0.0342 (7)	0.0003 (5)	−0.0079 (5)	−0.0059 (5)
C3	0.0305 (7)	0.0169 (6)	0.0357 (7)	0.0018 (5)	−0.0020 (6)	−0.0042 (5)
C4	0.0219 (6)	0.0173 (6)	0.0346 (7)	0.0035 (5)	0.0004 (5)	0.0046 (5)
C5	0.0217 (6)	0.0256 (7)	0.0310 (7)	0.0031 (5)	−0.0061 (5)	−0.0009 (5)
C6	0.0204 (5)	0.0207 (6)	0.0295 (6)	0.0011 (5)	−0.0043 (5)	−0.0060 (5)
C7	0.0187 (5)	0.0182 (6)	0.0367 (7)	−0.0001 (5)	−0.0067 (5)	−0.0058 (5)
C8	0.0243 (7)	0.0267 (8)	0.0543 (10)	−0.0028 (6)	0.0009 (7)	−0.0064 (7)
C9	0.0204 (5)	0.0230 (6)	0.0229 (6)	0.0009 (5)	0.0011 (5)	0.0002 (5)
C10	0.0278 (7)	0.0352 (8)	0.0232 (6)	−0.0001 (6)	0.0025 (5)	−0.0050 (6)
C11	0.0355 (8)	0.0317 (8)	0.0307 (7)	0.0048 (7)	0.0008 (6)	0.0089 (6)
C12	0.0206 (6)	0.0255 (7)	0.0342 (7)	−0.0038 (5)	0.0018 (5)	−0.0030 (6)
C13	0.0181 (5)	0.0182 (5)	0.0200 (5)	0.0024 (4)	−0.0036 (4)	−0.0023 (4)
C14	0.0165 (5)	0.0248 (6)	0.0208 (6)	0.0017 (5)	−0.0024 (4)	−0.0032 (5)
C15	0.0188 (5)	0.0360 (8)	0.0281 (7)	0.0005 (5)	−0.0060 (5)	−0.0057 (6)
C16	0.0221 (6)	0.0413 (9)	0.0260 (7)	0.0020 (6)	−0.0001 (5)	−0.0110 (6)
C17	0.0179 (5)	0.0213 (6)	0.0209 (6)	−0.0003 (5)	−0.0012 (4)	−0.0039 (4)
C18	0.0334 (7)	0.0221 (6)	0.0289 (7)	−0.0010 (6)	−0.0047 (6)	−0.0042 (5)
C19	0.0455 (9)	0.0276 (8)	0.0352 (8)	−0.0129 (7)	−0.0048 (7)	−0.0080 (6)
C20	0.0352 (8)	0.0463 (10)	0.0315 (8)	−0.0160 (7)	−0.0075 (6)	−0.0078 (7)
C21	0.0232 (6)	0.0421 (9)	0.0253 (7)	−0.0041 (6)	−0.0067 (5)	−0.0032 (6)
C22	0.0206 (5)	0.0266 (7)	0.0222 (6)	0.0001 (5)	−0.0031 (5)	−0.0035 (5)

Geometric parameters (Å, º)

Br1A—C4	1.9064 (11)	C11—H11B	0.9800
Br1B—C4	1.9064 (15)	C11—H11C	0.9800
O1—C7	1.4406 (17)	C12—H12A	0.9800
O1—N1	1.4540 (14)	C12—H12B	0.9800
N1—C13	1.4922 (16)	C12—H12C	0.9800
N1—C9	1.5061 (18)	C13—C17	1.5274 (18)
C1—C2	1.3916 (19)	C13—C14	1.5409 (19)
C1—C6	1.3948 (19)	C13—H13A	1.0000

C1—C7	1.5165 (18)	C14—C15	1.5285 (19)
C2—C3	1.386 (2)	C14—C16	1.5350 (19)
C2—H2A	0.9500	C14—H14A	1.0000
C3—C4	1.389 (2)	C15—H15A	0.9800
C3—H3A	0.9500	C15—H15B	0.9800
C4—C5	1.376 (2)	C15—H15C	0.9800
C5—C6	1.3942 (19)	C16—H16A	0.9800
C5—H5A	0.9500	C16—H16B	0.9800
C6—H6A	0.9500	C16—H16C	0.9800
C7—C8	1.512 (2)	C17—C18	1.391 (2)
C7—H7A	1.0000	C17—C22	1.3975 (19)
C8—H8A	0.9800	C18—C19	1.396 (2)
C8—H8B	0.9800	C18—H18A	0.9500
C8—H8C	0.9800	C19—C20	1.383 (3)
C9—C10	1.535 (2)	C19—H19A	0.9500
C9—C11	1.536 (2)	C20—C21	1.384 (3)
C9—C12	1.536 (2)	C20—H20A	0.9500
C10—H10A	0.9800	C21—C22	1.392 (2)
C10—H10B	0.9800	C21—H21A	0.9500
C10—H10C	0.9800	C22—H22A	0.9500
C11—H11A	0.9800		

C7—O1—N1	111.94 (9)	C9—C11—H11C	109.5
O1—N1—C13	107.20 (9)	H11A—C11—H11C	109.5
O1—N1—C9	107.14 (9)	H11B—C11—H11C	109.5
C13—N1—C9	116.38 (11)	C9—C12—H12A	109.5
C2—C1—C6	118.76 (12)	C9—C12—H12B	109.5
C2—C1—C7	119.47 (12)	H12A—C12—H12B	109.5
C6—C1—C7	121.66 (12)	C9—C12—H12C	109.5
C3—C2—C1	121.23 (14)	H12A—C12—H12C	109.5
C3—C2—H2A	119.4	H12B—C12—H12C	109.5
C1—C2—H2A	119.4	N1—C13—C17	117.31 (10)
C2—C3—C4	118.61 (13)	N1—C13—C14	110.32 (11)
C2—C3—H3A	120.7	C17—C13—C14	112.06 (10)
C4—C3—H3A	120.7	N1—C13—H13A	105.4
C5—C4—C3	121.74 (11)	C17—C13—H13A	105.4
C5—C4—Br1A	120.07 (11)	C14—C13—H13A	105.4
C3—C4—Br1A	118.19 (11)	C15—C14—C16	108.65 (11)
C5—C4—Br1B	114.39 (18)	C15—C14—C13	110.80 (11)
C3—C4—Br1B	123.43 (18)	C16—C14—C13	111.31 (12)
Br1A—C4—Br1B	8.81 (16)	C15—C14—H14A	108.7
C4—C5—C6	118.94 (13)	C16—C14—H14A	108.7
C4—C5—H5A	120.5	C13—C14—H14A	108.7
C6—C5—H5A	120.5	C14—C15—H15A	109.5
C5—C6—C1	120.72 (13)	C14—C15—H15B	109.5
C5—C6—H6A	119.6	H15A—C15—H15B	109.5
C1—C6—H6A	119.6	C14—C15—H15C	109.5
O1—C7—C8	113.22 (12)	H15A—C15—H15C	109.5

O1—C7—C1	106.94 (10)	H15B—C15—H15C	109.5
C8—C7—C1	109.28 (12)	C14—C16—H16A	109.5
O1—C7—H7A	109.1	C14—C16—H16B	109.5
C8—C7—H7A	109.1	H16A—C16—H16B	109.5
C1—C7—H7A	109.1	C14—C16—H16C	109.5
C7—C8—H8A	109.5	H16A—C16—H16C	109.5
C7—C8—H8B	109.5	H16B—C16—H16C	109.5
H8A—C8—H8B	109.5	C18—C17—C22	118.35 (13)
C7—C8—H8C	109.5	C18—C17—C13	119.09 (12)
H8A—C8—H8C	109.5	C22—C17—C13	122.51 (12)
H8B—C8—H8C	109.5	C17—C18—C19	121.19 (15)
N1—C9—C10	107.73 (12)	C17—C18—H18A	119.4
N1—C9—C11	107.59 (11)	C19—C18—H18A	119.4
C10—C9—C11	108.01 (12)	C20—C19—C18	119.81 (16)
N1—C9—C12	115.25 (11)	C20—C19—H19A	120.1
C10—C9—C12	107.66 (11)	C18—C19—H19A	120.1
C11—C9—C12	110.36 (13)	C19—C20—C21	119.62 (15)
C9—C10—H10A	109.5	C19—C20—H20A	120.2
C9—C10—H10B	109.5	C21—C20—H20A	120.2
H10A—C10—H10B	109.5	C20—C21—C22	120.69 (15)
C9—C10—H10C	109.5	C20—C21—H21A	119.7
H10A—C10—H10C	109.5	C22—C21—H21A	119.7
H10B—C10—H10C	109.5	C21—C22—C17	120.29 (15)
C9—C11—H11A	109.5	C21—C22—H22A	119.9
C9—C11—H11B	109.5	C17—C22—H22A	119.9
H11A—C11—H11B	109.5		

C7—O1—N1—C13	−130.22 (11)	O1—N1—C9—C12	50.03 (14)
C7—O1—N1—C9	104.18 (12)	C13—N1—C9—C12	−69.86 (15)
C6—C1—C2—C3	−1.2 (2)	O1—N1—C13—C17	−58.63 (14)
C7—C1—C2—C3	175.04 (14)	C9—N1—C13—C17	61.23 (15)
C1—C2—C3—C4	0.7 (2)	O1—N1—C13—C14	71.30 (12)
C2—C3—C4—C5	0.1 (2)	C9—N1—C13—C14	−168.84 (10)
C2—C3—C4—Br1A	179.95 (11)	N1—C13—C14—C15	61.24 (14)
C2—C3—C4—Br1B	−171.8 (2)	C17—C13—C14—C15	−166.09 (11)
C3—C4—C5—C6	−0.3 (2)	N1—C13—C14—C16	−177.74 (11)
Br1A—C4—C5—C6	179.81 (11)	C17—C13—C14—C16	−45.06 (15)
Br1B—C4—C5—C6	172.24 (17)	N1—C13—C17—C18	−120.29 (14)
C4—C5—C6—C1	−0.2 (2)	C14—C13—C17—C18	110.60 (14)
C2—C1—C6—C5	0.9 (2)	N1—C13—C17—C22	62.25 (17)
C7—C1—C6—C5	−175.21 (14)	C14—C13—C17—C22	−66.86 (15)
N1—O1—C7—C8	95.05 (14)	C22—C17—C18—C19	−1.9 (2)
N1—O1—C7—C1	−144.54 (10)	C13—C17—C18—C19	−179.49 (14)
C2—C1—C7—O1	162.77 (13)	C17—C18—C19—C20	0.2 (2)
C6—C1—C7—O1	−21.13 (18)	C18—C19—C20—C21	1.1 (3)
C2—C1—C7—C8	−74.34 (17)	C19—C20—C21—C22	−0.7 (2)
C6—C1—C7—C8	101.77 (16)	C20—C21—C22—C17	−1.0 (2)
O1—N1—C9—C10	−70.17 (13)	C18—C17—C22—C21	2.3 (2)

C13—N1—C9—C10	169.94 (11)	C13—C17—C22—C21	179.79 (12)
O1—N1—C9—C11	173.61 (11)	C8—C7—C13—C14	4.56 (11)
C13—N1—C9—C11	53.72 (15)	C8—C7—N1—C9	172.28 (12)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C11—H11*B*···Br1*A*^{i}	0.98	3.12	3.9782 (16)	148
C13—H13*A*···Br1*A*^{ii}	1.00	3.07	4.0358 (13)	163
C13—H13*A*···Br1*B*^{ii}	1.00	3.02	3.970 (2)	159
C15—H15*B*···Br1*B*^{ii}	0.98	3.14	4.017 (3)	149

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