organic compounds

4,6-Dibromo-N-{3-[(4,6-dibromo-2,3-dimethylphenyl)imino]butan-2-ylidene}-2,3-dimethylaniline

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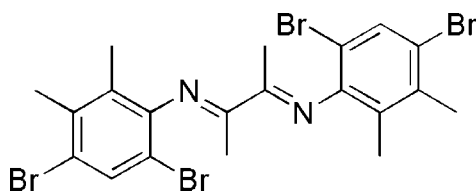Correspondence e-mail: clinton_du@126.com

The title compound, $C_{20}H_{20}Br_4N_2$, is a product of the condensation reaction of 4,6-dibromo-2,3-dimethylaniline and butane-2,3-dione. The molecule has a center of symmetry at the mid-point of the central C—C bond. The dihedral angle between the benzene ring and the 1,4-diazabutadiene plane is 78.3 (2)°. Niether hydrogen bonding nor aromatic stacking is observed in the crystal structure.

Related literature

For applications of diimine–metal catalysts, see: Johnson *et al.* (1995). For related structures, see: Gao *et al.* (2012); Sun *et al.* (2012); Popeney *et al.* (2012); Shi *et al.* (2012); Zhang & Ye (2012); Killian *et al.* (1996); Yuan *et al.* (2005, 2011).

Experimental

Crystal data

$C_{20}H_{20}Br_4N_2$	a = 5.5582 (6) Å
M_r = 607.98	b = 12.8881 (15) Å
Monoclinic, $P2_1/n$	c = 14.8377 (11) Å
β = 98.782 (8)°	μ = 9.40 mm^{-1}
V = 1050.43 (19) Å^3	T = 150 K
Z = 2	0.29 × 0.17 × 0.16 mm
Cu $K\alpha$ radiation	

Data collection

Agilent SuperNova (Dual, Cu at zero, Eos) diffractometer	4675 measured reflections
	1921 independent reflections
Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2013) T_{min} = 0.688, T_{max} = 1.000	1777 reflections with $I > 2\sigma(I)$
	R_{int} = 0.029

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.044	121 parameters
$wR(F^2)$ = 0.135	H-atom parameters constrained
S = 1.11	$\Delta\rho_{max}$ = 0.70 e Å^{-3}
1921 reflections	$\Delta\rho_{min}$ = −1.04 e Å^{-3}

Data collection: *CrysAlis PRO* (Agilent, 2013); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis RED* (Agilent, 2013); program(s) used to solve structure: *SUPERFLIP* (Palatinus & Chapuis, 2007); program(s) used to refine structure: *OLEX2* (Dolomanov *et al.*, 2009); molecular graphics: *OLEX2*; software used to prepare material for publication: *OLEX2*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: RK2409).

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supporting information

4,6-Dibromo-*N*-{3-[(4,6-dibromo-2,3-dimethylphenyl)imino]butan-2-ylidene}-2,3-dimethylaniline

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S1. Comment

Since Brookhart and co–workers discovered nickel and palladium(II) aryl–substituted *α*–diimine catalysts for olefin polymerization (Johnson *et al.*, 1995), late transition metal catalysis has attracted increasing attention due to their high functional group tolerance and their ability to produce branched or dendritic polymer (Gao *et al.*, 2012; Sun *et al.*, 2012; Popeney *et al.*, 2012; Shi *et al.*, 2012; Zhang & Ye, 2012; Killian *et al.*, 1996; Yuan *et al.*, 2005;2011). In this study, we designed and synthesized the title compound as abidentate ligand (Fig. 1).

The title molecule placed in center of symmetry (middle of C6—C6^i bond). The dihedral angle between the benzene ring and 1,4–diazabutadiene plane is 78.3 (2)°. Niether hydrogen bonding nor aromatic stacking are observed in the crystal structure.

S2. Experimental

Formic acid (0.5 ml) was added to a stirred solution of 2,3–butanedione (0.09 g, 1.00 mmol) and 4,6–dibromo–2,3–di-methylaniline (0.61 g, 2.2 mmol) in ethanol (10 ml) (Fig. 2). The mixture was refluxed for 24 h, and then cooled and the precipitate was separated by filtration. The solid was recrystallized from *Et*OH/CH$_2$Cl$_2$ (*v*:*v* = 10:1), washed with cold ethanol and dried under vacuum to give the title compound1. Yield is 0.50 g (82%). Crystals suitable for X–ray structure determination were grown from a cyclohexane/dichloromethane (*v*:*v* = 1:2) solution. Anal. Calcd. for C$_{20}$H$_{20}$Br$_4$N$_2$: C, 39.51; H, 3.32; Br, 52.57; N, 4.61. Found: C, 39.49; H, 3.31; Br, 52.60 N, 4.60.

S3. Refinement

All hydrogen atoms were placed in calculated positions with C—H distances of 0.93Å and 0.96Å for aryl and methyl H atoms. They were included in the refinement in a riding model approximation, respectively. The H atoms were assigned $U_{iso} = 1.2U_{eq}(C)$ for aryl H and $U_{iso} = 1.5U_{eq}(C)$ for methyl H.
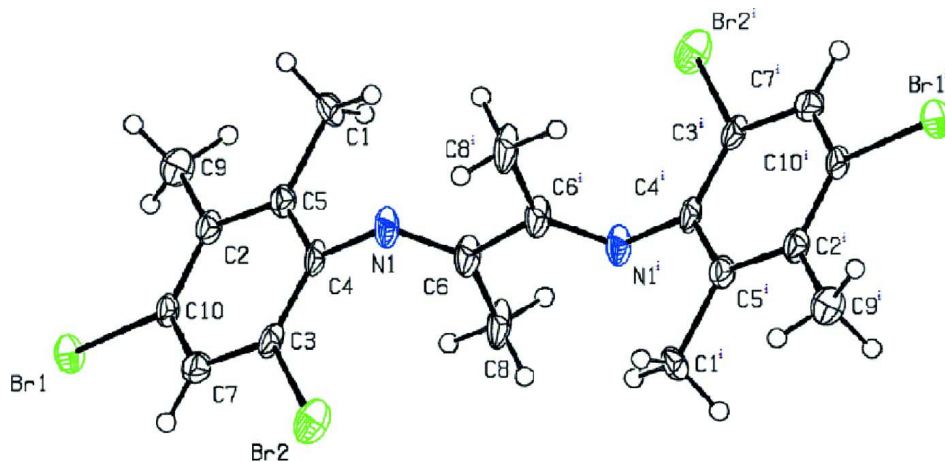
Figure 1

Molecular structure of title compound with the atom numbering scheme. Displacement ellipsoids are shown at the 50% probability level. H atoms are presented as a small spheres of arbitrary radius. Symmetry code: (i) -*x*+1, -*y*+1, -*z*+1.
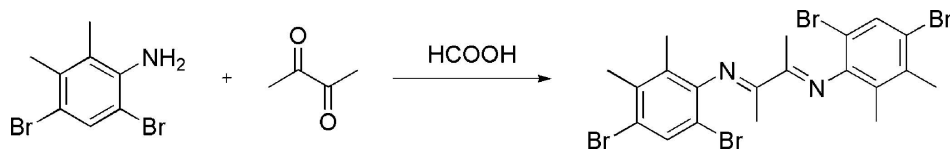
Figure 2

A condensation reaction of 2,3–butanedione and 4,6–dibromo-2,3–dimethylaniline.

4,6-Dibromo-*N*-{3-[(4,6-dibromo-2,3-dimethylphenyl)imino]butan-2-ylidene}-2,3-dimethylaniline

Crystal data

$C_{20}H_{20}Br_4N_2$	$F(000) = 588$
$M_r = 607.98$	$D_x = 1.922$ Mg m^{-3}
Monoclinic, $P2_1/n$	Cu $K\alpha$ radiation, $\lambda = 1.5418$ Å
$a = 5.5582$ (6) Å	Cell parameters from 2210 reflections
$b = 12.8881$ (15) Å	$\theta = 3.4–70.4°$
$c = 14.8377$ (11) Å	$\mu = 9.40$ mm^{-1}
$\beta = 98.782$ (8)°	$T = 150$ K
$V = 1050.43$ (19) Å^3	Block, clear light yellow
$Z = 2$	$0.29 \times 0.17 \times 0.16$ mm

Data collection

Agilent SuperNova (Dual, Cu at zero, Eos) diffractometer	$T_{min} = 0.688$, $T_{max} = 1.000$
	4675 measured reflections
Radiation source: SuperNova (Cu) X-ray Source	1921 independent reflections
	1777 reflections with $I > 2\sigma(I)$
Mirror monochromator	$R_{int} = 0.029$
Detector resolution: 16.0733 pixels mm^{-1}	$\theta_{max} = 68.2°$, $\theta_{min} = 4.6°$
ω–scans	$h = -6 \rightarrow 4$
Absorption correction: multi-scan	$k = -15 \rightarrow 15$
(*CrysAlis PRO*; Agilent, 2013)	$l = -17 \rightarrow 17$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier
Least-squares matrix: full	map
$R[F^2 > 2\sigma(F^2)] = 0.044$	Hydrogen site location: inferred from
$wR(F^2) = 0.135$	neighbouring sites
$S = 1.11$	H-atom parameters constrained
1921 reflections	$w = 1/[\sigma^2(F_o^2) + (0.0802P)^2 + 2.2115P]$
121 parameters	where $P = (F_o^2 + 2F_c^2)/3$
0 restraints	$(\Delta/\sigma)_{max} < 0.001$
Primary atom site location: structure-invariant	$\Delta\rho_{max} = 0.70$ e Å^{-3}
direct methods	$\Delta\rho_{min} = -1.04$ e Å^{-3}

Special details

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'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*	$U_{iso}*/U_{eq}$
Br2	0.84461 (11)	0.31214 (5)	0.68427 (4)	0.0431 (2)
N1	0.5517 (8)	0.5134 (4)	0.6182 (3)	0.0327 (9)
C2	0.2754 (9)	0.4881 (4)	0.8311 (3)	0.0269 (9)
C3	0.6169 (9)	0.3862 (4)	0.7425 (3)	0.0277 (10)
C4	0.4939 (9)	0.4723 (4)	0.7012 (3)	0.0275 (10)
C5	0.3261 (10)	0.5238 (4)	0.7464 (3)	0.0296 (10)
C6	0.4633 (10)	0.4739 (4)	0.5417 (3)	0.0341 (11)
C7	0.5762 (9)	0.3504 (4)	0.8271 (3)	0.0293 (10)
H7	0.6616	0.2939	0.8548	0.035*
C1	0.1862 (10)	0.6189 (4)	0.7022 (3)	0.0341 (11)
H1A	0.0200	0.5999	0.6813	0.051*
H1B	0.2604	0.6422	0.6515	0.051*
H1C	0.1912	0.6736	0.7463	0.051*
C8	0.2980 (12)	0.3814 (5)	0.5268 (3)	0.0438 (14)
H8A	0.1479	0.4010	0.4898	0.066*
H8B	0.2654	0.3560	0.5845	0.066*
H8C	0.3751	0.3278	0.4964	0.066*
C9	0.0867 (10)	0.5414 (4)	0.8773 (4)	0.0378 (12)
H9A	0.1616	0.5968	0.9148	0.057*
H9B	0.0170	0.4924	0.9146	0.057*
H9C	−0.0388	0.5691	0.8321	0.057*
C10	0.4039 (9)	0.4017 (4)	0.8689 (3)	0.0277 (10)
Br1	0.34078 (11)	0.34478 (4)	0.98167 (3)	0.0379 (2)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br2	0.0473 (4)	0.0546 (4)	0.0317 (3)	−0.0012 (3)	0.0199 (3)	−0.0110 (2)
N1	0.043 (2)	0.043 (2)	0.0129 (18)	−0.0155 (19)	0.0064 (16)	0.0029 (17)
C2	0.035 (2)	0.030 (2)	0.017 (2)	−0.0044 (19)	0.0075 (17)	−0.0020 (17)
C3	0.038 (2)	0.032 (2)	0.015 (2)	−0.005 (2)	0.0109 (17)	−0.0075 (18)
C4	0.042 (3)	0.032 (2)	0.0096 (19)	−0.012 (2)	0.0066 (17)	−0.0023 (17)
C5	0.047 (3)	0.026 (2)	0.015 (2)	−0.006 (2)	0.0046 (19)	0.0011 (18)
C6	0.047 (3)	0.044 (3)	0.013 (2)	−0.016 (2)	0.0102 (19)	0.001 (2)
C7	0.042 (3)	0.025 (2)	0.022 (2)	−0.003 (2)	0.007 (2)	−0.0012 (17)
C1	0.053 (3)	0.029 (2)	0.019 (2)	−0.004 (2)	0.001 (2)	0.0107 (19)
C8	0.061 (4)	0.058 (3)	0.013 (2)	−0.031 (3)	0.007 (2)	0.000 (2)
C9	0.045 (3)	0.042 (3)	0.029 (3)	0.005 (2)	0.015 (2)	−0.003 (2)
C10	0.044 (3)	0.030 (2)	0.0102 (18)	−0.004 (2)	0.0077 (17)	0.0000 (17)
Br1	0.0605 (4)	0.0407 (4)	0.0159 (3)	0.0013 (2)	0.0171 (2)	0.00654 (19)

Geometric parameters (Å, º)

Br2—C3	1.895 (5)	C7—H7	0.9300
N1—C4	1.422 (6)	C7—C10	1.385 (7)
N1—C6	1.273 (6)	C1—H1A	0.9600
C2—C5	1.406 (6)	C1—H1B	0.9600
C2—C9	1.504 (7)	C1—H1C	0.9600
C2—C10	1.395 (7)	C8—H8A	0.9600
C3—C4	1.395 (7)	C8—H8B	0.9600
C3—C7	1.388 (6)	C8—H8C	0.9600
C4—C5	1.397 (7)	C9—H9A	0.9600
C5—C1	1.543 (7)	C9—H9B	0.9600
C6—C6ⁱ	1.518 (9)	C9—H9C	0.9600
C6—C8	1.501 (7)	C10—Br1	1.908 (4)
C6—N1—C4	121.1 (4)	C5—C1—H1B	109.5
C5—C2—C9	120.5 (5)	C5—C1—H1C	109.5
C10—C2—C5	117.4 (4)	H1A—C1—H1B	109.5
C10—C2—C9	122.1 (4)	H1A—C1—H1C	109.5
C4—C3—Br2	121.1 (3)	H1B—C1—H1C	109.5
C7—C3—Br2	117.2 (4)	C6—C8—H8A	109.5
C7—C3—C4	121.6 (4)	C6—C8—H8B	109.5
C3—C4—N1	121.1 (4)	C6—C8—H8C	109.5
C3—C4—C5	119.1 (4)	H8A—C8—H8B	109.5
C5—C4—N1	119.6 (4)	H8A—C8—H8C	109.5
C2—C5—C1	118.9 (5)	H8B—C8—H8C	109.5
C4—C5—C2	120.9 (4)	C2—C9—H9A	109.5
C4—C5—C1	120.2 (4)	C2—C9—H9B	109.5
N1—C6—C6ⁱ	115.8 (6)	C2—C9—H9C	109.5
N1—C6—C8	126.4 (4)	H9A—C9—H9B	109.5
C8—C6—C6ⁱ	117.8 (5)	H9A—C9—H9C	109.5

C3—C7—H7	121.1	H9B—C9—H9C	109.5
C10—C7—C3	117.8 (5)	C2—C10—Br1	120.6 (4)
C10—C7—H7	121.1	C7—C10—C2	123.2 (4)
C5—C1—H1A	109.5	C7—C10—Br1	116.2 (4)
Br2—C3—C4—N1	−6.1 (6)	C5—C2—C10—C7	−0.1 (7)
Br2—C3—C4—C5	179.4 (3)	C5—C2—C10—Br1	−178.0 (4)
Br2—C3—C7—C10	−177.8 (4)	C6—N1—C4—C3	82.4 (7)
N1—C4—C5—C2	−176.5 (4)	C6—N1—C4—C5	−103.1 (6)
N1—C4—C5—C1	5.7 (7)	C7—C3—C4—N1	174.7 (4)
C3—C4—C5—C2	−1.9 (7)	C7—C3—C4—C5	0.2 (7)
C3—C4—C5—C1	−179.7 (4)	C9—C2—C5—C4	−177.4 (5)
C3—C7—C10—C2	−1.5 (7)	C9—C2—C5—C1	0.4 (7)
C3—C7—C10—Br1	176.5 (4)	C9—C2—C10—C7	179.1 (5)
C4—N1—C6—C6^i	179.2 (6)	C9—C2—C10—Br1	1.2 (7)
C4—N1—C6—C8	−1.5 (10)	C10—C2—C5—C4	1.8 (7)
C4—C3—C7—C10	1.5 (7)	C10—C2—C5—C1	179.6 (4)

Symmetry code: (i) −x+1, −y+1, −z+1.