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

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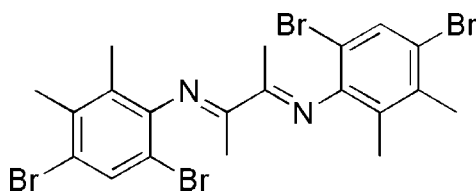
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Key indicators: single-crystal X-ray study; $T = 150$ K; mean $\sigma(\text{C}-\text{C}) = 0.007$ Å; R factor = 0.044; wR factor = 0.135; data-to-parameter ratio = 15.9.

The title compound, $\text{C}_{20}\text{H}_{20}\text{Br}_4\text{N}_2$, 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 $\text{C}-\text{C}$ bond. The dihedral angle between the benzene ring and the 1,4-diazabutadiene plane is $78.3(2)^\circ$. Neither 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

$\text{C}_{20}\text{H}_{20}\text{Br}_4\text{N}_2$
 $M_r = 607.98$
 Monoclinic, $P2_1/n$

$a = 5.5582(6)$ Å
 $b = 12.8881(15)$ Å
 $c = 14.8377(11)$ Å

$\beta = 98.782(8)^\circ$
 $V = 1050.43(19)$ Å³
 $Z = 2$
 Cu $K\alpha$ radiation

$\mu = 9.40$ mm⁻¹
 $T = 150$ K
 $0.29 \times 0.17 \times 0.16$ mm

Data collection

Agilent SuperNova (Dual, Cu at zero, Eos) diffractometer
 Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2013)
 $T_{\min} = 0.688$, $T_{\max} = 1.000$

4675 measured reflections
 1921 independent reflections
 1777 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.029$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.044$
 $wR(F^2) = 0.135$
 $S = 1.11$
 1921 reflections

121 parameters
 H-atom parameters constrained
 $\Delta\rho_{\max} = 0.70$ e Å⁻³
 $\Delta\rho_{\min} = -1.04$ 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*.

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

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supplementary materials

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

Lina Huang, Zhengyin Du, Wei Liu and Fushou Che

1. 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' bond). The dihedral angle between the benzene ring and 1,4-diazabutadiene plane is 78.3 (2)°. Neither hydrogen bonding nor aromatic stacking are observed in the crystal structure.

2. Experimental

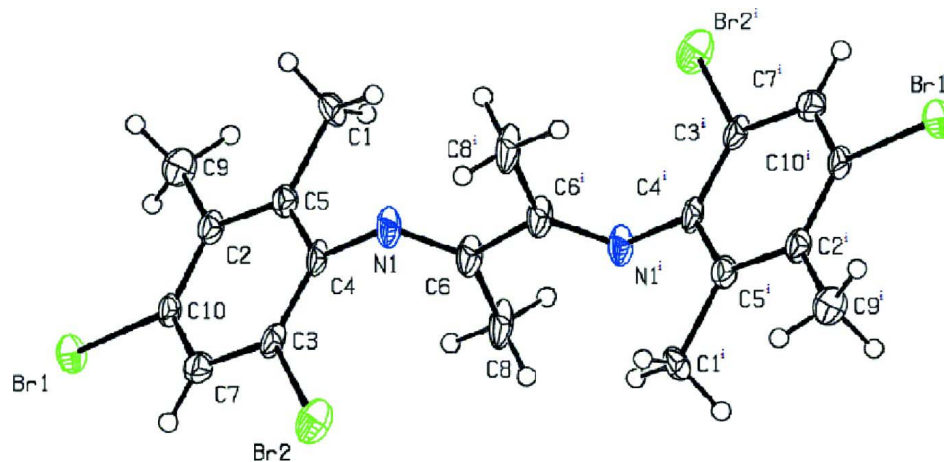
Formic acid (0.5 ml) was added to a stirred solution of 2,3-butanedione (0.09 g, 1.00 mmol) and 4,6-dibromo-2,3-dimethylaniline (0.61 g, 2.2 mmol) in ethanol (10 ml) (Fig. 2). The mixture was refluxed for 24 h, and then cooled and the precipitate was separated by filtration. The solid was recrystallized from *EtOH*/*CH₂Cl₂* (*v:v* = 10:1), washed with cold ethanol and dried under vacuum to give the title compound 1. 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 C₂₀H₂₀Br₄N₂: 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.

3. Refinement

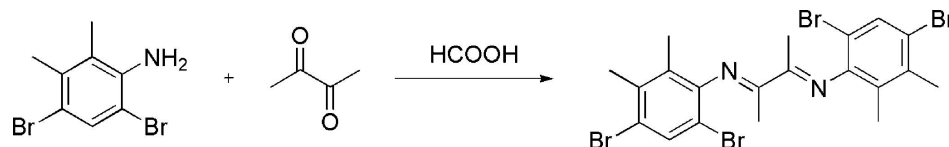
All hydrogen atoms were placed in calculated positions with C—H distances of 0.93 Å and 0.96 Å for aryl and methyl H atoms. They were included in the refinement in a riding model approximation, respectively. The H atoms were assigned $U_{\text{iso}} = 1.2U_{\text{eq}}(\text{C})$ for aryl H and $U_{\text{iso}}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

Computing details

Data collection: *CrysAlis PRO* (Agilent, 2013); cell refinement: *CrysAlis PRO* (Agilent, 2013); 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* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009).


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

$C_{20}H_{20}Br_4N_2$

$M_r = 607.98$

Monoclinic, $P2_1/n$

$a = 5.5582$ (6) Å

$b = 12.8881$ (15) Å

$c = 14.8377$ (11) Å

$\beta = 98.782$ (8)°

$V = 1050.43$ (19) Å³

$Z = 2$

$F(000) = 588$

$D_x = 1.922$ Mg m⁻³

Cu $K\alpha$ radiation, $\lambda = 1.5418$ Å

Cell parameters from 2210 reflections

$\theta = 3.4$ – 70.4 °

$\mu = 9.40$ mm⁻¹

$T = 150$ K

Block, clear light yellow

$0.29 \times 0.17 \times 0.16$ mm

Data collection

Agilent SuperNova (Dual, Cu at zero, Eos) diffractometer

Radiation source: SuperNova (Cu) X-ray Source

Mirror monochromator

Detector resolution: 16.0733 pixels mm⁻¹

ω -scans

Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2013)

$T_{\min} = 0.688$, $T_{\max} = 1.000$

4675 measured reflections

1921 independent reflections

1777 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.029$

$\theta_{\max} = 68.2$ °, $\theta_{\min} = 4.6$ °

$h = -6 \rightarrow 4$

$k = -15 \rightarrow 15$

$l = -17 \rightarrow 17$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.044$
 $wR(F^2) = 0.135$
 $S = 1.11$
 1921 reflections
 121 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-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0802P)^2 + 2.2115P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.70 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -1.04 \text{ e } \text{\AA}^{-3}$

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
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 (\AA^2)

	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 (\AA , $^\circ$)

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—C6 ⁱ	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—C6 ⁱ	115.8 (6)	C2—C9—H9C	109.5
N1—C6—C8	126.4 (4)	H9A—C9—H9B	109.5
C8—C6—C6 ⁱ	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) $-x+1, -y+1, -z+1$.