

Crystal structure of 1,2-bis[(2-*tert*-butylphenyl)imino]ethane

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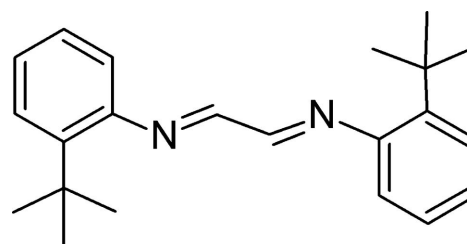
The whole molecule of the title compound, $C_{22}H_{28}N_2$, (I), is generated by inversion symmetry. The molecule is rather similar to that of 2,3-bis[(2-*tert*-butylphenyl)imino]butane, (II), a diimine ligand comprising similar structural features [Ferreira *et al.* (2006). *Acta Cryst. E* **62**, o4282–o4284]. Both ligands crystallize with the $-N=C(R)-C(R)=N-$ group around an inversion centre, in a *trans* configuration. Comparing the two structures, it may be noted that the independent planar groups in both molecules [the central link, $-N=C(R)-C(R)=N-$, and the terminal aromatic ring] subtend an angle of $69.6(1)^\circ$ in (II) and $49.4(2)^\circ$ in (I). Ferreira and co-workers proposed that such angle deviation may be ascribed to the presence of two non-classical intramolecular hydrogen bonds and steric factors. In fact, in (I), similar non-classical hydrogen bonds are observed, and the larger angular deviation in (II) may be assigned to the presence of methyl groups in the diimino fragment, which can cause steric hindrance due to the presence of bulky *tert*-butyl substituents in the aromatic rings. The $C=N$ bond lengths are similar in both compounds and agree with commonly accepted values.

Keywords: crystal structure; diimine; non-classical hydrogen bonds; DNA.

CCDC reference: 1062877

1. Related literature

For general properties of diimines, see: Rix & Brookhart (1995); Hissler *et al.* (2000); Ramakrishnan *et al.* (2011a). For the interaction of diimine–metal complexes with DNA, see: Wang *et al.* (2004); Tan *et al.* (2008); Ramakrishnan *et al.* (2011b). For a related structure, see: Ferreira *et al.* (2006).



2. Experimental

2.1. Crystal data

$C_{22}H_{28}N_2$	$V = 995.5(3) \text{ \AA}^3$
$M_r = 320.46$	$Z = 2$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 12.333(3) \text{ \AA}$	$\mu = 0.06 \text{ mm}^{-1}$
$b = 6.4740(13) \text{ \AA}$	$T = 293 \text{ K}$
$c = 12.519(3) \text{ \AA}$	$0.3 \times 0.17 \times 0.07 \text{ mm}$
$\beta = 95.22(3)^\circ$	

2.2. Data collection

Nonius KappaCCD diffractometer	1284 reflections with $I > 2\sigma(I)$
21498 measured reflections	$R_{int} = 0.072$
1811 independent reflections	

2.3. Refinement

$R[F^2 > 2\sigma(F^2)] = 0.049$	109 parameters
$wR(F^2) = 0.119$	H-atom parameters constrained
$S = 1.06$	$\Delta\rho_{max} = 0.13 \text{ e \AA}^{-3}$
1811 reflections	$\Delta\rho_{min} = -0.15 \text{ e \AA}^{-3}$

Table 1

Hydrogen-bond geometry (\AA , $^\circ$).

D—H...A	D—H	H...A	D...A	D—H...A
C10—H10B...N1	0.960	2.405(2)	3.055(3)	124.8(3)
C11—H11C...N1	0.960	2.414(2)	3.064(3)	124.6(2)

Data collection: *COLLECT* (Nonius, 2004); cell refinement: *DIRAX/LSQ* (Duisenberg, 1992); data reduction: *EVALCCD* (Duisenberg *et al.*, 2003); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *WinGX* (Farrugia, 2012).

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Supporting information for this paper is available from the IUCr electronic archives (Reference: BG2548).

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supporting information

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Crystal structure of 1,2-bis[(2-*tert*-butylphenyl)imino]ethane

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S1. Chemical context

The design and development of effective anticancer metallodrugs has become one of the more important areas in pharmaceutical industry and academia. Nonetheless, side effects associated with these complexes and the development of tumor resistance has led to the search for new generations of metal based anticancer agents. Diimine compounds have been employed in many applications, including olefin polymerization, luminescence studies and metallodrug synthesis. (Rix & Brookhart, 1995; Hissler *et al.*, 2000; Ramakrishnan *et al.*, 2011a) The interaction of diimine Cobalt, Ruthenium and Iron complexes with DNA has attracted much attention during the last decade. (Wang *et al.*, 2004; Tan *et al.* 2008; Ramakrishnan *et al.*, 2011b). The antitumoral screening activity of potential metallodrugs with distinct nitrogen based ligands has helped researchers to understand how factors as size, geometry and electronic structure can contribute to DNA binding thus allowing to categorize which factors are important to enhance metallodrug performance. We report herein on the crystal structure of C₂₂H₂₈N₂ (I)

S2. Structural commentary

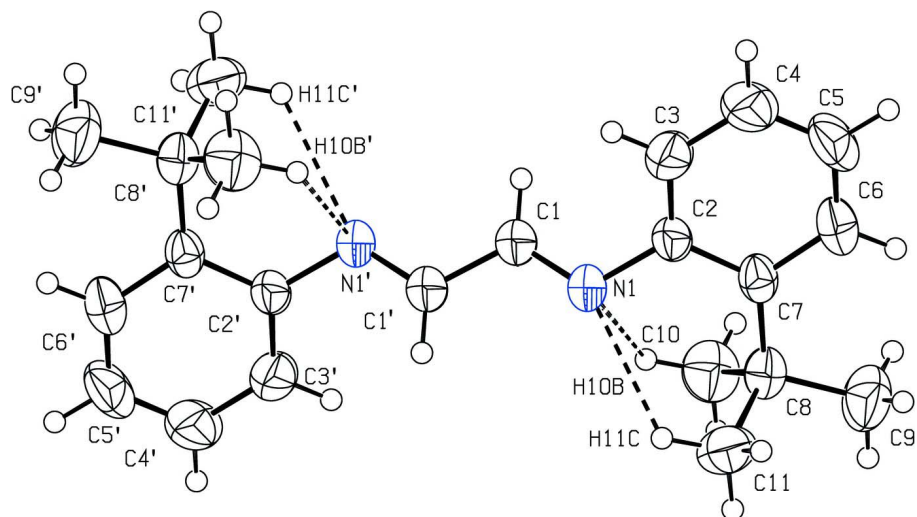
The crystal structure of 2,3-Bis(2-*tert*-butylphenylimino)butane, C₂₄H₃₂N₂ (II), a diimine ligand comprising similar structural features was already reported. (Ferreira *et al.*, 2006). Both ligands crystallize with the –N=C(R)—C(R)=N– group around an inversion centre, in a trans configuration. Comparing the two structures, it may be noted that the independent planar groups in both molecules (the central link, –N=C(R)—C(R)=N–, and the terminal aromatic ring) subtend an angle of 69.6 (1)° in (II) and 49.4 (2)° in (I). Ferreira and co-workers proposed that such angle deviation may be ascribed to the presence of two non classical hydrogen bonds and steric factors. In fact, in the title compound, similar non-classical hydrogen bonds were observed: C10—H10B···N1 and C11—H11C···N1. (Fig 1 and Table 1) The greater angle deviation in (II) may be assigned to the presence of methyl groups in the diimino fragment, which can cause steric hindrance due to the presence of bulky *tert*-butyl substituents in the aromatic rings. The C=N bond lengths are similar to the corresponding ones in (II) and agree well with what is expected for this bonding mode.

S3. Synthesis and crystallization

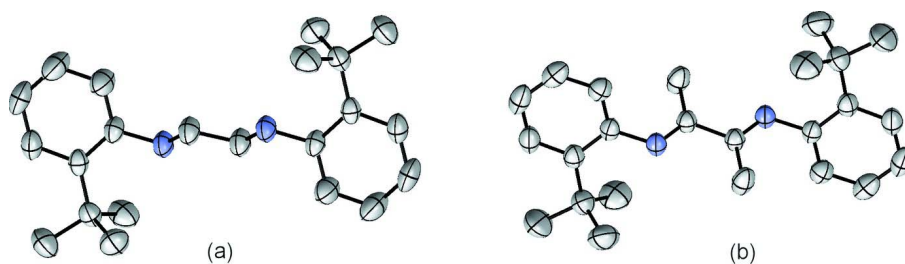
To a solution of 2-*tert*-butylaniline (3.6 g; 26 mmol) in 15 mL de methanol, 1.5 mL of glyoxal solution (40 % in water; 13 mmol) was added. The resulting mixture was stirred overnight at room temperature. The yellow precipitate was filtered off, dried under vacuum for 2 days. Slow evaporation of the filtrate gave crystals suitable for single-crystal XRD studies. (Yield: 90 %)

S4. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. The H atoms were placed into the calculated idealized positions. All H atoms were refined with fixed individual displacement parameters [$U_{iso}(H) = 1.2U_{eq}(Csp^2)$ or $1.5U_{eq}(methyl\ group)$] using a riding model.

**Figure 1**

View of (I) (50% probability displacement ellipsoids). The dashed lines indicate the proposed non-classical intramolecular hydrogen bonds. [Symmetry code: (') $1 - x, 1 - y, -z$.]

**Figure 2**

Comparison of the structures of (a) (I) and (b) (II).

2-*tert*-Butyl-*N*-{2-[(2-*tert*-butylphenyl)imino]ethylidene}aniline

Crystal data

$C_{22}H_{28}N_2$

$M_r = 320.46$

Monoclinic, $P2_1/n$

Hall symbol: $-P 2_1n$

$a = 12.333 (3) \text{ \AA}$

$b = 6.4740 (13) \text{ \AA}$

$c = 12.519 (3) \text{ \AA}$

$\beta = 95.22 (3)^\circ$

$V = 995.5 (3) \text{ \AA}^3$

$Z = 2$

$F(000) = 348$

$D_x = 1.069 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 21498 reflections

$\theta = 3.6\text{--}25.4^\circ$

$\mu = 0.06 \text{ mm}^{-1}$

$T = 293 \text{ K}$

Plate, yellow

$0.3 \times 0.17 \times 0.07 \text{ mm}$

Data collection

Nonius KappaCCD

diffractometer

Horizontally mounted graphite crystal

monochromator

Detector resolution: 9 pixels mm^{-1}

CCD scans

21498 measured reflections

1811 independent reflections

1284 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.072$

$\theta_{\max} = 25.4^\circ$, $\theta_{\min} = 3.6^\circ$
 $h = -14 \rightarrow 14$

$k = -7 \rightarrow 7$
 $l = -15 \rightarrow 15$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.049$
 $wR(F^2) = 0.119$
 $S = 1.06$
 1811 reflections
 109 parameters
 0 restraints

Hydrogen site location: inferred from
 neighbouring sites
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0452P)^2 + 0.2479P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.13 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.15 \text{ e } \text{\AA}^{-3}$

Special details

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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	0.46712 (12)	0.1526 (2)	0.10801 (11)	0.0485 (4)
C1	0.47499 (15)	0.0981 (3)	0.01174 (14)	0.0520 (5)
H1	0.4486	0.1842	-0.0442	0.062*
C2	0.41192 (14)	0.3400 (3)	0.12810 (12)	0.0440 (4)
C3	0.31398 (16)	0.3836 (3)	0.06876 (15)	0.0622 (6)
H3	0.2873	0.292	0.0155	0.075*
C4	0.25541 (18)	0.5595 (4)	0.08691 (17)	0.0736 (7)
H4	0.19	0.587	0.0465	0.088*
C5	0.29551 (17)	0.6930 (3)	0.16573 (18)	0.0694 (6)
H5	0.2576	0.8134	0.1783	0.083*
C6	0.39173 (16)	0.6496 (3)	0.22646 (15)	0.0559 (5)
H6	0.4171	0.7428	0.2795	0.067*
C7	0.45274 (13)	0.4721 (2)	0.21188 (13)	0.0413 (4)
C8	0.55778 (14)	0.4249 (3)	0.28333 (14)	0.0476 (4)
C9	0.58580 (19)	0.5962 (4)	0.36621 (18)	0.0777 (7)
H9A	0.5955	0.7244	0.3298	0.117*
H9B	0.6518	0.5612	0.409	0.117*
H9C	0.5276	0.6101	0.4117	0.117*
C10	0.65538 (15)	0.4063 (4)	0.21568 (17)	0.0701 (6)
H10A	0.6639	0.533	0.1775	0.105*
H10B	0.6429	0.295	0.1654	0.105*
H10C	0.7203	0.3791	0.2619	0.105*
C11	0.54410 (18)	0.2230 (3)	0.34482 (16)	0.0684 (6)
H11A	0.4834	0.2354	0.3872	0.103*
H11B	0.6091	0.1959	0.3909	0.103*
H11C	0.5313	0.1113	0.2948	0.103*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0604 (9)	0.0429 (9)	0.0420 (8)	0.0096 (7)	0.0034 (7)	-0.0089 (7)
C1	0.0685 (12)	0.0456 (10)	0.0416 (10)	0.0134 (9)	0.0028 (8)	-0.0051 (8)
C2	0.0546 (10)	0.0405 (10)	0.0380 (9)	0.0103 (8)	0.0092 (7)	-0.0021 (7)
C3	0.0662 (13)	0.0709 (14)	0.0482 (11)	0.0188 (11)	-0.0016 (9)	-0.0108 (10)
C4	0.0681 (14)	0.0872 (17)	0.0650 (13)	0.0346 (13)	0.0029 (11)	0.0000 (12)
C5	0.0734 (14)	0.0550 (13)	0.0827 (15)	0.0288 (11)	0.0235 (12)	0.0000 (11)
C6	0.0639 (12)	0.0415 (11)	0.0650 (12)	0.0040 (9)	0.0201 (10)	-0.0096 (9)
C7	0.0496 (10)	0.0348 (9)	0.0417 (9)	-0.0007 (8)	0.0171 (7)	-0.0024 (7)
C8	0.0514 (10)	0.0432 (10)	0.0489 (10)	-0.0055 (8)	0.0089 (8)	-0.0081 (8)
C9	0.0799 (15)	0.0730 (15)	0.0787 (15)	-0.0088 (12)	-0.0013 (12)	-0.0280 (12)
C10	0.0513 (11)	0.0795 (16)	0.0811 (15)	0.0017 (11)	0.0144 (10)	-0.0068 (12)
C11	0.0809 (14)	0.0659 (14)	0.0554 (12)	-0.0091 (12)	-0.0105 (10)	0.0094 (10)

Geometric parameters (\AA , $^\circ$)

N1—C1	1.268 (2)	C7—C8	1.536 (2)
N1—C2	1.425 (2)	C8—C9	1.537 (2)
C1—H1	0.93	C9—H9A	0.96
C1—C1 ⁱ	1.454 (3)	C9—H9B	0.96
C2—C3	1.388 (2)	C9—H9C	0.96
C2—C7	1.410 (2)	C8—C10	1.538 (2)
C3—C4	1.378 (3)	C10—H10A	0.96
C3—H3	0.93	C10—H10B	0.96
C4—C5	1.370 (3)	C10—H10C	0.96
C5—H5	0.93	C8—C11	1.534 (3)
C4—H4	0.93	C11—H11A	0.96
C5—C6	1.379 (3)	C11—H11B	0.96
C6—C7	1.395 (2)	C11—H11C	0.96
C6—H6	0.93		
C1—N1—C2	118.93 (15)	C11—C8—C9	107.72 (16)
N1—C1—C1 ⁱ	120.4 (2)	C7—C8—C9	112.06 (15)
N1—C1—H1	119.8	C11—C8—C10	109.68 (16)
C1 ⁱ —C1—H1	119.8	C7—C8—C10	110.83 (14)
C3—C2—C7	120.59 (16)	C9—C8—C10	106.81 (16)
C3—C2—N1	119.03 (15)	C8—C9—H9A	109.5
C7—C2—N1	120.24 (15)	C8—C9—H9B	109.5
C4—C3—C2	121.56 (19)	H9A—C9—H9B	109.5
C4—C3—H3	119.2	C8—C9—H9C	109.5
C2—C3—H3	119.2	H9A—C9—H9C	109.5
C5—C4—C3	118.67 (19)	H9B—C9—H9C	109.5
C5—C4—H4	120.7	C8—C10—H10A	109.5
C3—C4—H4	120.7	C8—C10—H10B	109.5
C4—C5—C6	120.33 (19)	H10A—C10—H10B	109.5
C4—C5—H5	119.8	C8—C10—H10C	109.5

C6—C5—H5	119.8	H10A—C10—H10C	109.5
C5—C6—C7	122.91 (18)	H10B—C10—H10C	109.5
C5—C6—H6	118.5	C8—C11—H11A	109.5
C7—C6—H6	118.5	C8—C11—H11B	109.5
C6—C7—C2	115.89 (16)	H11A—C11—H11B	109.5
C6—C7—C8	121.60 (15)	C8—C11—H11C	109.5
C2—C7—C8	122.51 (14)	H11A—C11—H11C	109.5
C11—C8—C7	109.64 (14)	H11B—C11—H11C	109.5
C2—N1—C1—C1 ⁱ	-176.3 (2)	C3—C2—C7—C6	-3.0 (2)
C1—N1—C2—C3	44.2 (2)	N1—C2—C7—C6	-178.76 (15)
C1—N1—C2—C7	-139.97 (18)	C3—C2—C7—C8	176.94 (17)
C7—C2—C3—C4	2.2 (3)	N1—C2—C7—C8	1.2 (2)
N1—C2—C3—C4	178.05 (18)	C6—C7—C8—C11	117.87 (18)
C2—C3—C4—C5	-0.1 (3)	C2—C7—C8—C11	-62.0 (2)
C3—C4—C5—C6	-1.0 (3)	C6—C7—C8—C9	-1.7 (2)
C4—C5—C6—C7	0.1 (3)	C2—C7—C8—C9	178.39 (16)
C5—C6—C7—C2	1.9 (3)	C6—C7—C8—C10	-120.91 (18)
C5—C6—C7—C8	-178.02 (17)	C2—C7—C8—C10	59.2 (2)

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