

(1*R*,2*R*)-(–)-1,2-Dibenzamidino-cyclohexane**Jian-Feng Li,^a Lin-Hong Weng,^b
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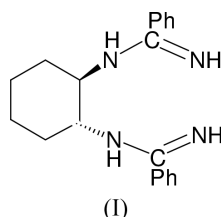
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Key indicatorsSingle-crystal X-ray study
T = 173 K
Mean $\sigma(\text{C}-\text{C}) = 0.006 \text{ \AA}$
R factor = 0.059
wR factor = 0.119
Data-to-parameter ratio = 7.6For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

The title compound, (1*R*,2*R*)-(–)-1,2-[N(H)=C(Ph)N(H)]₂-C₆H₁₀, C₂₀H₂₄N₄, was prepared and its structure determined. The molecule has two N–C–N fragments which are twisted out of the phenyl planes. The single and double C–N bonds are essentially localized.

Comment

Bis(amidinate) compounds, $\{[\text{RC}(\text{NR}')_2]_2\}^{2-}$, are extensively used as ligands for transition metals, lanthanides and main group elements, towards which they act most frequently as tetradentate 8-electron donors (Barker & Kilner, 1994; Edlmann, 1994). Recently, linked bis(amidinate) compounds, in which the two anionic moieties are linked by a covalent bridge, have received increasing attention, because of their unusual ligand geometry and different coordination behavior (Whitener *et al.*, 1999). This kind of dianion also exhibits versatility in its binding modes and, through varying the substituents, presents a flexible system in steric bulk and electronic properties of the ligands and their complexes. In addition to the two previously reported examples (Hagadorn & Arnold, 1998; Bambirra *et al.*, 2001), we also developed a method to prepare a new kind of linked bis(amidinate) ligand and investigated its chemistry (Li, Weng, Wei & Liu, 2002). Neutral multidentate ligands bearing nitrogen donor atoms, including porphyrins, metalloporphyrins (Ellis & Lyons, 1990), and 1,1-dimethylbiguanide (Lemoine *et al.*, 1996), are promising systems for applications in catalysis. We describe here the synthesis of a new neutral, chiral linked bis-(benzamidinate) ligand derived from a lithium complex. The title compound, (I), has four nitrogen donor atoms and its crystal structure is presented here.



Selected geometric parameters of (I) are listed in Table 1. The molecular structure is illustrated in Fig. 1. The cyclohexane ring adopts a chair conformation. The two N–C–N fragments are nearly coplanar with the ring atoms to which they are attached, with torsion angles $-3.0 (5)$ and $-9.2 (5)^\circ$. The dihedral angles between the N–C–N fragments and the phenyl rings are $35.9 (3)$ and $32.5 (4)^\circ$.

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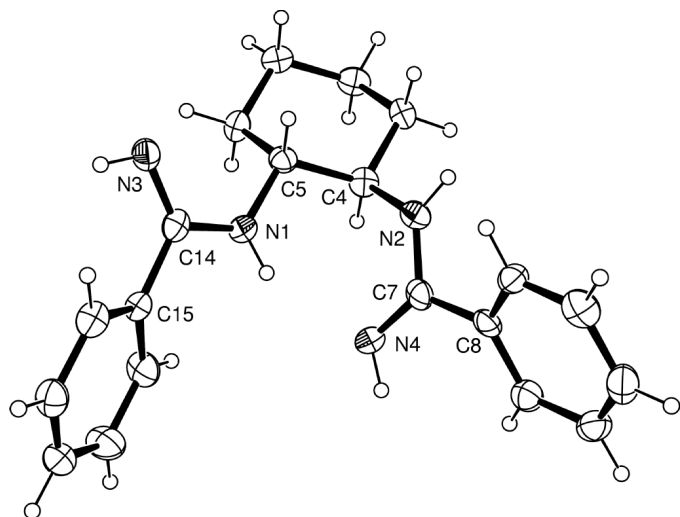


Figure 1
View of the molecule of (I), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by small spheres of arbitrary radii.

The two N atoms linked to the cyclohexane ring are both sp^2 -hybridized (sum of angles around N1 and N2 are 358.9 and 359.6° , respectively). The other two N atoms, N3 and N4, are attached to the amidinate C atoms with double bonds. These double bonds, N4=C7 [$1.293(5) \text{ \AA}$] and N3=C14 [$1.301(5) \text{ \AA}$], are considerably shorter than the single bonds, N2=C4 [$1.476(5) \text{ \AA}$] and N1=C5 [$1.476(5) \text{ \AA}$]. By contrast, in the analogous $\text{Li}[(1R,2R)\text{-}(-)\text{-}1\text{-}\{\text{NC}(\text{Ph})\text{N}(\text{SiMe}_3)\}\text{-}2\text{-}(\text{NHSiMe}_3)\text{-C}_6\text{H}_{10}]$ (II) (Li, Weng, Wei & Liu, 2002), the anionic N—C—N fragment has some degree of π -electron delocalization and the bond distances between nitrogen and carbon are similar [$1.337(2)$ and $1.325(12) \text{ \AA}$]. These values are intermediate between the C—N bond lengths in (I). In addition, the bonds C7—C8 [$1.503(6) \text{ \AA}$] and C14—C15 [$1.501(5) \text{ \AA}$] are a little shorter than the corresponding bonds in (II) [$1.513(16) \text{ \AA}$], in accordance with conjugation between the C=N double bonds and the phenyl groups.

Experimental

Distilled water was added dropwise to a stirred solution of $\text{Li}_2[(1R,2R)\text{-}(-)\text{-}1,2\text{-}\{\text{NC}(\text{Ph})\text{N}(\text{SiMe}_3)\}\text{-C}_6\text{H}_{10}]$ (synthesized according to Li, Weng, Wei & Liu, 2002) in hexane (in the mole ratio 4:1). After overnight reaction, the pale yellow mixture was filtered, then the solvent was removed in vacuum and the residual solid was redissolved in chloroform. After filtration, the filtrate was left at room temperature and colorless crystals of (I) grew at the bottom of the flask after 2 d. Elemental analysis and NMR spectra are completely in agreement with the structural composition of (I). Spectroscopic analysis: ^1H NMR (CDCl_3 , δ , p.p.m.): 1.42 (*d*, 4H, CH), 1.78 (*m*, 2H, CH), 2.26 (*m*, 2H, CH), 3.97 (*m*, 2H, CH), 5.89 (*s*, 4H, NH), 7.35 (*m*, 3H, phenyl), 7.48 (*m*, 2H, phenyl); ^{13}C NMR (CDCl_3 , δ , p.p.m.): 25.59, 32.98, 57.15, 126.98, 128.63, 129.22, 129.65, 131.24, 138.30, 169.33.

Crystal data

$\text{C}_{20}\text{H}_{24}\text{N}_4$
 $M_r = 320.43$
Orthorhombic, $P2_12_12_1$
 $a = 8.696(5) \text{ \AA}$
 $b = 8.698(5) \text{ \AA}$
 $c = 22.806(13) \text{ \AA}$
 $V = 1725.1(17) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.234 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation
Cell parameters from 9871 reflections
 $\theta = 2.5\text{--}19.5^\circ$
 $\mu = 0.08 \text{ mm}^{-1}$
 $T = 173(2) \text{ K}$
Block, colorless
 $0.20 \times 0.10 \times 0.10 \text{ mm}$

Data collection

Siemens SMART CCD diffractometer
 ω scans
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\text{min}} = 0.985$, $T_{\text{max}} = 0.993$
7152 measured reflections

1773 independent reflections
1505 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.098$
 $\theta_{\text{max}} = 25.0^\circ$
 $h = -10 \rightarrow 8$
 $k = -10 \rightarrow 10$
 $l = -27 \rightarrow 25$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.059$
 $wR(F^2) = 0.119$
 $S = 1.06$
1773 reflections
233 parameters

H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0443P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.19 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.21 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (\AA , $^\circ$).

C4—N2	1.476 (5)	C7—C8	1.503 (6)
C4—C5	1.537 (5)	C14—N3	1.301 (5)
C5—N1	1.467 (5)	C14—N1	1.352 (5)
C7—N4	1.293 (5)	C14—C15	1.501 (5)
C7—N2	1.352 (5)		
N2—C4—C5	111.9 (3)	N3—C14—N1	120.4 (4)
N1—C5—C4	109.8 (3)	N3—C14—C15	124.3 (4)
N4—C7—N2	120.5 (4)	N1—C14—C15	115.2 (3)
N4—C7—C8	124.2 (4)	C14—N1—C5	123.3 (3)
N2—C7—C8	115.4 (3)	C7—N2—C4	121.9 (3)
N2—C4—C5—N1	−58.8 (4)	N4—C7—N2—C4	−9.2 (5)
N3—C14—N1—C5	−3.0 (5)	C8—C7—N2—C4	171.1 (3)
C15—C14—N1—C5	175.8 (3)	C5—C4—N2—C7	92.1 (4)
C4—C5—N1—C14	162.9 (3)		

Table 2

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

$D\text{--}H\cdots A$	$D\text{--}H$	$H\cdots A$	$D\cdots A$	$D\text{--}H\cdots A$
N2—H2 \cdots N3 ⁱ	0.91 (4)	2.12 (5)	3.024 (5)	172 (4)
N1—H1 \cdots N4	0.83 (4)	2.14 (4)	2.898 (5)	151 (3)

Symmetry code: (i) $x - \frac{1}{2}, \frac{3}{2} - y, -z$.

All H atoms were initially located in a difference Fourier map. The methyl H atoms were then constrained to an ideal geometry with C—H distances of 0.98 \AA and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$, but each group was allowed to rotate freely about its C—C bond. The positions of the amine H atoms were refined freely along with isotropic displacement parameters. All other H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms with C—H distances in the range $0.95\text{--}1.00 \text{ \AA}$ and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Anomalous dispersion effects are negligible, and Friedel pairs were merged in the refinement. The absolute configuration was assumed from the known (*R,R*) configuration of the starting lithium salt (Li, Weng, Wei & Liu, 2002). Furthermore, [(1*R*,2*R*)-(–)-1,2-(*NSiMe*₃)₂-C₆H₁₀]₂Zr, derived from the same starting lithium salt, has been examined and its absolute configuration confirmed, with a Flack (1983) parameter of essentially zero (Li, Weng, Huang *et al.*, 2002).

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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