organic compounds

1,3-Bis{(+)-(S)-[1-(1-naphthyl)ethyl]iminomethyl}benzene dichloromethane solvate

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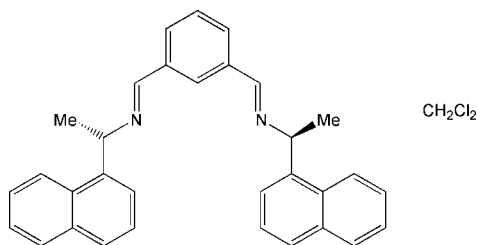
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In the title compound, $C_{32}H_{28}N_2 \cdot CH_2Cl_2$, the complete Schiff base and solvent molecules are both generated by crystallographic twofold axes, with the two C atoms of the former and the C atom of the latter lying on the rotation axis. The central benzene ring is substituted with two chiral groups including imine functionalities, with the common E configuration. The dihedral angle between the central benzene ring and the terminal naphthalene ring is 45.42 (9)° and that between the two naphthalene rings is 89.16 (8)°. The conformation of the Schiff base allows solvent molecules to fill the voids in the crystal, affording a stable 1:1 solvate, but the solvent interacts poorly with the Schiff base, as reflected by its rather high displacement parameters.

Related literature

For solvent-free synthesis in organic chemistry, see: Jeon *et al.* (2005); Noyori (2005); Tanaka & Toda (2000). For related chiral Schiff bases synthesized using similar routes, see: Tovar *et al.* (2007).

Experimental

Crystal data

$C_{32}H_{28}N_2 \cdot CH_2Cl_2$	V = 1411.3 (7) Å^3
M_r = 525.49	Z = 2
Orthorhombic, $P2_12_12$	Mo $K\alpha$ radiation
a = 8.550 (2) Å	μ = 0.25 mm^{-1}
b = 20.706 (6) Å	T = 298 K
c = 7.972 (3) Å	0.40 × 0.24 × 0.20 mm

Data collection

Siemens P4 diffractometer	1428 reflections with $I > 2\sigma(I)$
Absorption correction: gaussian	R_{int} = 0.060
(*XSCANS*; Siemens, 1996)	3 standard reflections
T_{min} = 0.933, T_{max} = 0.954	every 97 reflections
6308 measured reflections	intensity decay: 2.3%
2497 independent reflections	

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.060	$\Delta\rho_{max}$ = 0.19 e Å^{-3}
$wR(F^2)$ = 0.186	$\Delta\rho_{min}$ = −0.16 e Å^{-3}
S = 1.06	Absolute structure: Flack (1983),
2497 reflections	1028 Friedel pairs
172 parameters	Flack parameter: 0.0 (2)
H-atom parameters constrained	

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXL97*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FJ2198).

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supporting information

1,3-Bis{(+)-(*S*)-[1-(1-naphthyl)ethyl]iminomethyl}benzene dichloromethane solvate

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S1. Comment

During the last few decades, a central objective in synthetic organic chemistry has been to develop greener and more economically competitive processes for the efficient synthesis of compounds with potential applications in diverse fields. In this context, the solvent-free approach is simple with amazing versatility because it reduces the use of organic solvents and minimizes the formation of other waste. Likewise, the reactions occur under mild conditions and usually require easier workup procedures and simpler equipment. Moreover, it may allow access to compounds that require harsh reaction conditions under traditional approaches or when the yields are too low to be of practical convenience (Jeon *et al.*, 2005; Noyori, 2005; Tanaka & Toda, 2000).

On the other hand, bisimines have lately attracted much attention, mostly due to their versatile coordination behavior and the interesting properties of their metal complexes. These compounds are particularly interesting since they can potentially act in a variety of coordination modes.
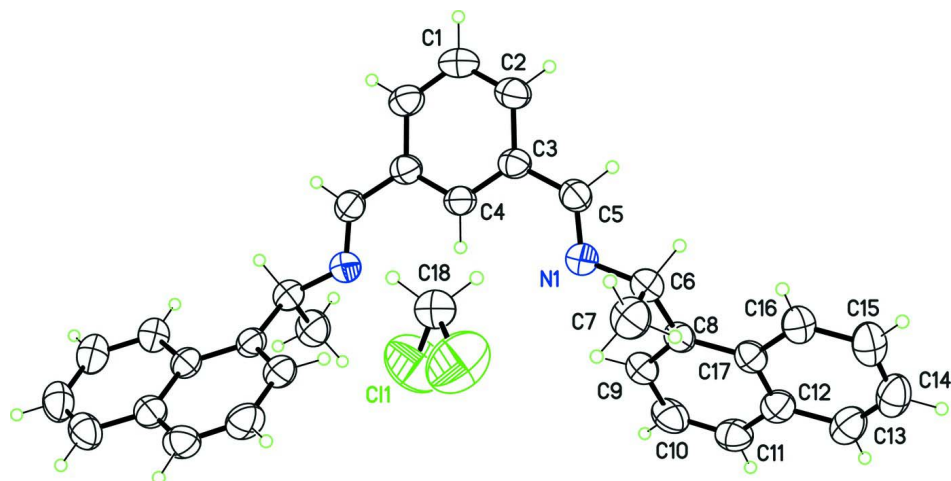
Continuing our work on the synthesis of chiral imines (Tovar *et al.*, 2007), we synthesized the title Schiff base under solvent-free conditions and report here its X-ray structure. The asymmetric unit contains one half-molecule and one half dichloromethane molecule, both placed on binary axis (Fig. 1). This arrangement is probably favored by the presence of a chiral center, C6, allowing to orient the substituents of the imine functionality towards the opposite faces of the central benzene core. The crystal is further stabilized by the inclusion of lattice solvent, resulting in a 1:1 solvate. Indeed, the shape of the Schiff base is suitable for the formation of a guest-host complex (Fig. 2). However, as no efficient hydrogen bonds are formed, the solvent molecule presents high displacement parameters, compared to the host (See Fig. 1).

S2. Experimental

Under solvent-free conditions, a mixture of benzene-1,3-dicarboxaldehyde (0.12 g, 0.9 mmol) and (*S*)-(-)-1-naphthyl-ethylamine (0.32 g, 1.8 mmol) were mixed at 298 K, giving a white solid. The crude material was recrystallized from CH_2Cl_2, affording colorless crystals of the title solvate (Yield: 98%; m.p. 343–345 K. $[\alpha]^{25}_D$=+253.7 (*c*=1, CHCl₃). IR and NMR data are consistent with the X-ray structure (see archived CIF).

S3. Refinement

All H atoms were placed in idealized positions and refined as riding to their carrier C atoms, with bond lengths fixed to 0.93 (aromatic CH), 0.96 (methyl CH₃), 0.97 (methylene CH₂) and 0.98 Å (methine CH). isotropic displacement parameters were calculated as $U_{iso}(H) = 1.5 U_{eq}$(carrier atom) for the methyl group and $U_{iso}(H) = 1.2 U_{eq}$(carrier atom) otherwise.

Figure 1

Molecular structure of the title compound, with 30% probability level displacement ellipsoids for non-H atoms. Non-labeled atoms are generated through the symmetry operation 2 - x, 1 - y, z.

Figure 2

A part of the crystal structure of the title compound along [100], showing the lattice solvent molecules with a space-filling representation.

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Crystal data

$C_{32}H_{28}N_2 \cdot CH_2Cl_2$	$c = 7.972$ (3) Å
$M_r = 525.49$	$V = 1411.3$ (7) Å³
Orthorhombic, $P2_12_12$	$Z = 2$
Hall symbol: P 2 2ab	$F(000) = 552$
$a = 8.550$ (2) Å	$D_x = 1.237$ Mg m⁻³
$b = 20.706$ (6) Å	Melting point: 343 K

Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 51 reflections
θ = 4.0–11.9°
μ = 0.25 mm⁻¹

T = 298 K
Prism, yellow
0.40 × 0.24 × 0.20 mm

Data collection

Siemens P4
    diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
2*θ*/*ω* scans
Absorption correction: gaussian
    (*XSCANS*; Siemens, 1996)
T_{min} = 0.933, T_{max} = 0.954
6308 measured reflections

2497 independent reflections
1428 reflections with $I > 2\sigma(I)$
R_{int} = 0.060
θ_{max} = 25.0°, θ_{min} = 2.0°
$h = -10 \rightarrow 10$
$k = -24 \rightarrow 24$
$l = -9 \rightarrow 9$
3 standard reflections every 97 reflections
intensity decay: 2.3%

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.060
$wR(F^2)$ = 0.186
S = 1.06
2497 reflections
172 parameters
0 restraints
0 constraints
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
$w = 1/[\sigma^2(F_o^2) + (0.0833P)^2 + 0.2257P]$
    where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.19 e Å⁻³
$\Delta\rho_{min}$ = −0.16 e Å⁻³
Extinction correction: *SHELXL97* (Sheldrick,
    2008), Fc*=kFc[1+0.001xFc²λ³/sin(2θ)]⁻¹ᐟ⁴
Extinction coefficient: 0.036 (6)
Absolute structure: Flack (1983), 1028 Friedel
    pairs
Absolute structure parameter: 0.0 (2)

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
N1	0.8943 (5)	0.38124 (15)	1.0214 (4)	0.0789 (10)
C1	1.0000	0.5000	1.5231 (7)	0.0904 (19)
H1A	1.0000	0.5000	1.6398	0.108*
C2	0.9506 (5)	0.4463 (2)	1.4376 (5)	0.0800 (12)
H2A	0.9166	0.4102	1.4968	0.096*
C3	0.9508 (4)	0.44531 (18)	1.2633 (5)	0.0660 (10)
C4	1.0000	0.5000	1.1777 (7)	0.0682 (14)
H4A	1.0000	0.5000	1.0611	0.082*
C5	0.9004 (5)	0.38667 (18)	1.1771 (5)	0.0711 (10)
H5A	0.8711	0.3514	1.2420	0.085*
C6	0.8370 (5)	0.32020 (18)	0.9537 (5)	0.0747 (11)
H6A	0.8222	0.2897	1.0464	0.090*
C7	0.6791 (5)	0.3332 (2)	0.8717 (6)	0.0947 (14)
H7A	0.6077	0.3499	0.9539	0.142*
H7B	0.6383	0.2937	0.8262	0.142*
H7C	0.6918	0.3642	0.7832	0.142*
C8	0.9507 (5)	0.29178 (16)	0.8309 (5)	0.0646 (9)

C9	1.0643 (5)	0.32880 (18)	0.7563 (5)	0.0760 (11)
H9A	1.0740	0.3720	0.7868	0.091*
C10	1.1656 (6)	0.3034 (2)	0.6361 (6)	0.0924 (14)
H10A	1.2430	0.3295	0.5899	0.111*
C11	1.1527 (6)	0.2419 (2)	0.5865 (5)	0.0851 (12)
H11A	1.2184	0.2263	0.5028	0.102*
C12	1.0413 (5)	0.20049 (19)	0.6592 (5)	0.0751 (11)
C13	1.0297 (6)	0.1351 (2)	0.6116 (6)	0.0911 (13)
H13A	1.0960	0.1188	0.5293	0.109*
C14	0.9225 (6)	0.0957 (2)	0.6848 (7)	0.0973 (15)
H14A	0.9158	0.0527	0.6524	0.117*
C15	0.8233 (5)	0.1194 (2)	0.8073 (7)	0.0909 (14)
H15A	0.7514	0.0919	0.8578	0.109*
C16	0.8295 (5)	0.18255 (17)	0.8549 (6)	0.0749 (11)
H16A	0.7615	0.1975	0.9371	0.090*
C17	0.9380 (4)	0.22579 (17)	0.7812 (5)	0.0652 (9)
C18	0.5000	0.5000	0.8916 (9)	0.123 (3)
H18A	0.4641	0.5349	0.9629	0.148*
Cl1	0.6505 (3)	0.52641 (11)	0.7706 (3)	0.1852 (10)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.102 (3)	0.0685 (19)	0.067 (2)	−0.0018 (18)	0.003 (2)	0.0003 (16)
C1	0.099 (5)	0.115 (5)	0.057 (3)	0.000 (4)	0.000	0.000
C2	0.084 (3)	0.090 (3)	0.066 (2)	0.004 (3)	0.008 (2)	0.008 (2)
C3	0.062 (2)	0.076 (2)	0.060 (2)	0.0110 (19)	0.0047 (19)	0.0017 (19)
C4	0.073 (3)	0.075 (3)	0.056 (3)	0.015 (3)	0.000	0.000
C5	0.073 (2)	0.070 (2)	0.070 (3)	0.008 (2)	0.007 (2)	0.008 (2)
C6	0.085 (3)	0.070 (2)	0.069 (2)	−0.001 (2)	0.003 (2)	0.0066 (19)
C7	0.080 (3)	0.099 (3)	0.105 (3)	0.016 (3)	0.008 (3)	0.000 (3)
C8	0.069 (2)	0.064 (2)	0.060 (2)	0.0002 (18)	0.003 (2)	0.0087 (17)
C9	0.085 (3)	0.072 (2)	0.071 (2)	−0.006 (2)	0.005 (2)	0.009 (2)
C10	0.091 (3)	0.100 (3)	0.086 (3)	−0.005 (3)	0.026 (3)	0.022 (3)
C11	0.082 (3)	0.102 (3)	0.072 (3)	0.013 (3)	0.011 (2)	0.003 (2)
C12	0.071 (2)	0.081 (2)	0.073 (2)	0.010 (2)	−0.014 (2)	−0.004 (2)
C13	0.089 (3)	0.090 (3)	0.095 (3)	0.020 (3)	−0.019 (3)	−0.019 (3)
C14	0.097 (3)	0.076 (3)	0.120 (4)	0.012 (3)	−0.030 (4)	−0.010 (3)
C15	0.078 (3)	0.075 (3)	0.120 (4)	−0.005 (2)	−0.024 (3)	0.007 (3)
C16	0.066 (2)	0.072 (2)	0.087 (3)	−0.004 (2)	−0.004 (2)	0.002 (2)
C17	0.059 (2)	0.069 (2)	0.068 (2)	0.0022 (18)	−0.007 (2)	0.0072 (18)
C18	0.192 (10)	0.094 (5)	0.084 (4)	−0.003 (5)	0.000	0.000
Cl1	0.1454 (16)	0.208 (2)	0.202 (2)	−0.0442 (14)	0.0100 (17)	0.0547 (16)

Geometric parameters (Å, °)

N1—C5	1.248 (5)	C9—C10	1.395 (6)
N1—C6	1.459 (5)	C9—H9A	0.9300

C1—C2	1.371 (5)	C10—C11	1.338 (6)
C1—C2ⁱ	1.371 (5)	C10—H10A	0.9300
C1—H1A	0.9300	C11—C12	1.407 (6)
C2—C3	1.390 (5)	C11—H11A	0.9300
C2—H2A	0.9300	C12—C13	1.410 (6)
C3—C4	1.387 (4)	C12—C17	1.414 (5)
C3—C5	1.460 (5)	C13—C14	1.359 (7)
C4—C3ⁱ	1.387 (4)	C13—H13A	0.9300
C4—H4A	0.9300	C14—C15	1.384 (7)
C5—H5A	0.9300	C14—H14A	0.9300
C6—C8	1.500 (5)	C15—C16	1.363 (5)
C6—C7	1.524 (6)	C15—H15A	0.9300
C6—H6A	0.9800	C16—C17	1.416 (5)
C7—H7A	0.9600	C16—H16A	0.9300
C7—H7B	0.9600	C18—Cl1ⁱⁱ	1.699 (5)
C7—H7C	0.9600	C18—Cl1	1.699 (5)
C8—C9	1.373 (5)	C18—H18A	0.9698
C8—C17	1.427 (5)		
C5—N1—C6	117.4 (3)	C8—C9—C10	121.8 (4)
C2—C1—C2ⁱ	120.4 (6)	C8—C9—H9A	119.1
C2—C1—H1A	119.8	C10—C9—H9A	119.1
C2ⁱ—C1—H1A	119.8	C11—C10—C9	120.7 (4)
C1—C2—C3	120.6 (4)	C11—C10—H10A	119.7
C1—C2—H2A	119.7	C9—C10—H10A	119.7
C3—C2—H2A	119.7	C10—C11—C12	121.0 (4)
C4—C3—C2	118.7 (4)	C10—C11—H11A	119.5
C4—C3—C5	122.5 (4)	C12—C11—H11A	119.5
C2—C3—C5	118.8 (4)	C11—C12—C13	121.5 (4)
C3—C4—C3ⁱ	121.1 (5)	C11—C12—C17	118.7 (4)
C3—C4—H4A	119.4	C13—C12—C17	119.8 (4)
C3ⁱ—C4—H4A	119.4	C14—C13—C12	120.5 (5)
N1—C5—C3	123.7 (4)	C14—C13—H13A	119.7
N1—C5—H5A	118.1	C12—C13—H13A	119.7
C3—C5—H5A	118.1	C13—C14—C15	120.3 (4)
N1—C6—C8	111.3 (3)	C13—C14—H14A	119.9
N1—C6—C7	107.6 (3)	C15—C14—H14A	119.9
C8—C6—C7	111.3 (3)	C16—C15—C14	120.8 (5)
N1—C6—H6A	108.8	C16—C15—H15A	119.6
C8—C6—H6A	108.8	C14—C15—H15A	119.6
C7—C6—H6A	108.8	C15—C16—C17	121.1 (4)
C6—C7—H7A	109.5	C15—C16—H16A	119.4
C6—C7—H7B	109.5	C17—C16—H16A	119.4
H7A—C7—H7B	109.5	C12—C17—C16	117.4 (4)
C6—C7—H7C	109.5	C12—C17—C8	119.9 (3)
H7A—C7—H7C	109.5	C16—C17—C8	122.7 (4)
H7B—C7—H7C	109.5	Cl1ⁱⁱ—C18—Cl1	110.8 (4)
C9—C8—C17	117.9 (4)	Cl1ⁱⁱ—C18—H18A	109.4

C9—C8—C6	121.5 (3)	Cl1—C18—H18A	109.4
C17—C8—C6	120.5 (3)		
C2ⁱ—C1—C2—C3	0.4 (3)	C10—C11—C12—C13	−178.1 (4)
C1—C2—C3—C4	−0.9 (6)	C10—C11—C12—C17	2.7 (6)
C1—C2—C3—C5	178.7 (3)	C11—C12—C13—C14	179.2 (4)
C2—C3—C4—C3ⁱ	0.4 (3)	C17—C12—C13—C14	−1.6 (6)
C5—C3—C4—C3ⁱ	−179.1 (4)	C12—C13—C14—C15	0.0 (7)
C6—N1—C5—C3	−178.2 (4)	C13—C14—C15—C16	1.0 (7)
C4—C3—C5—N1	−1.5 (6)	C14—C15—C16—C17	−0.3 (6)
C2—C3—C5—N1	179.0 (4)	C11—C12—C17—C16	−178.6 (4)
C5—N1—C6—C8	−126.4 (4)	C13—C12—C17—C16	2.2 (5)
C5—N1—C6—C7	111.4 (4)	C11—C12—C17—C8	−1.5 (5)
N1—C6—C8—C9	−19.0 (5)	C13—C12—C17—C8	179.3 (4)
C7—C6—C8—C9	101.1 (4)	C15—C16—C17—C12	−1.3 (6)
N1—C6—C8—C17	164.5 (3)	C15—C16—C17—C8	−178.3 (4)
C7—C6—C8—C17	−75.4 (4)	C9—C8—C17—C12	0.3 (5)
C17—C8—C9—C10	−0.3 (6)	C6—C8—C17—C12	177.0 (3)
C6—C8—C9—C10	−176.9 (4)	C9—C8—C17—C16	177.2 (3)
C8—C9—C10—C11	1.5 (7)	C6—C8—C17—C16	−6.1 (5)
C9—C10—C11—C12	−2.7 (7)		

Symmetry codes: (i) −*x*+2, −*y*+1, *z*; (ii) −*x*+1, −*y*+1, *z*.