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Crystal structure of racemic *cis*-2-amino-1,2-diphenylethanol (ADE)

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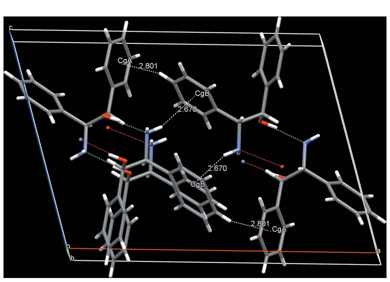

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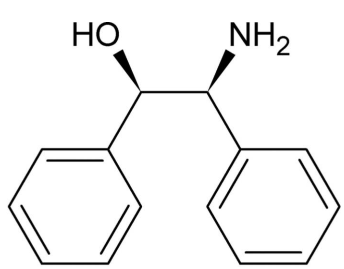
In the title racemic compound, $C_{14}H_{15}NO$, the hydroxy and amino groups form a bent tweezer-like motif towards the phenyl groups. In the crystal, enantiomers aggregate with each other and are linked by O—H···N hydrogen bonds, forming chiral 2_1-helical columnar structures from *C*(5) chains along the *b*-axis direction. Left- and right-handed 2_1 helices are formed from (1*S*,2*R*)-2-amino-1,2-diphenylethanol and (1*R*,2*S*)-2-amino-1,2-diphenylethanol, respectively.

1. Chemical context

The production of chiral compounds has great importance in the pharmaceutical industry, and diastereomer salt separation is still widely applied in the process. An optical resolving agent, chiral 2-amino-1,2-diphenylethanol (ADE) (Read & Steele, 1927), has been widely tried and used in diastereomer salt separation methods; for example, chiral discrimination of 2-arylalkanoic acids by (1*R*,2*S*)-ADE (*cis*-isomer) (Kinbara *et al.*, 1998). The ADE molecule with two adjacent stereogenic centers exists as diastereoisomers (and more, enantiomers of *cis*- and *trans*-forms), and can be purchased without difficulty. It was considered that *cis*- and *trans*-ADE have different properties and play different roles in diastereomer salt separations. In fact, co-crystal structures with *cis*-ADE enantiomers have been found in previous reports. The racemic structure of *trans*-ADE has been reported (Bari *et al.*, 2012), but that of *cis*-ADE has not. The crystal structure of racemic *cis*-ADE is reported on herein.



2. Structural commentary

In the title compound (*cis*-ADE), Fig. 1, the hydroxy and amino groups form a tweezer-like motif. Selected geometrical parameters are given in Table 1. The dihedral angle between the phenyl rings is 50.29 (6)° and the torsion angle O1—C1—C2—N1 is 59.72 (11)°. These values are similar to those observed for *trans*-ADE (Bari *et al.*, 2012), *viz*. 48.05 (5) and 54.01 (10)°, respectively. However, in *cis*-ADE the hydroxyl group against the opposed phenyl ring adopts a *gauche*

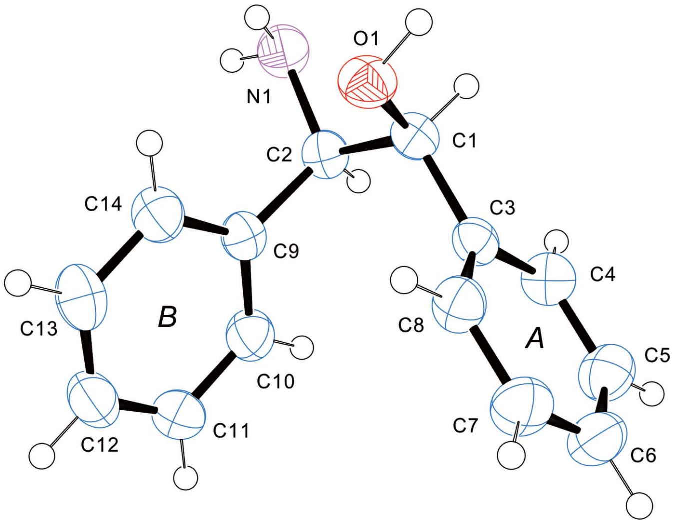


Figure 1
A view of the molecular structure of *cis-(1S,2R)*-ADE, with atom and ring labelling. Displacement ellipsoids are drawn at the 50% probability level.

conformation [O1—C1—C2—C9 = −67.39 (11)°] compared to a *trans* conformation in *trans*-ADE. Thus a tweezer-like motif bent against the phenyl groups is seen in *cis*-ADE *versus* a projected motif in *trans*-ADE. The arrangements are similar to those found in the diastereomer salts with *cis*-enantiomers, except for (1*R*,2*S*)-2-ammonio-1,2-diphenylethanol (Imai *et al.*, 2008).

3. Supramolecular features

In the crystal, enantiomers aggregate separately and are linked by O1—H13···N1 = [2.7977 (16) Å] hydrogen bonds, forming chiral 2_1-helical columnar structures from *C*(5) chains along the *b*-axis direction (Table 2 and Fig. 2): Left- and right-handed 2_1 helices are formed from (1*S*, 2*R*)-ADE and (1*R*, 2*S*)-ADE, respectively. The hydrophobic columnar structures surrounded by phenyl groups are consolidated by the C—H···π and N—H···π interactions, forming slabs parallel to the *ab* plane (Table 2 and Fig. 2). This is in contrast to the columnar structure stacking of racemic $R_2^2(10)$ ring dimers from the O—H···N hydrogen bonds observed in the crystal structure of *trans*-ADE (Bari *et al.*, 2012).

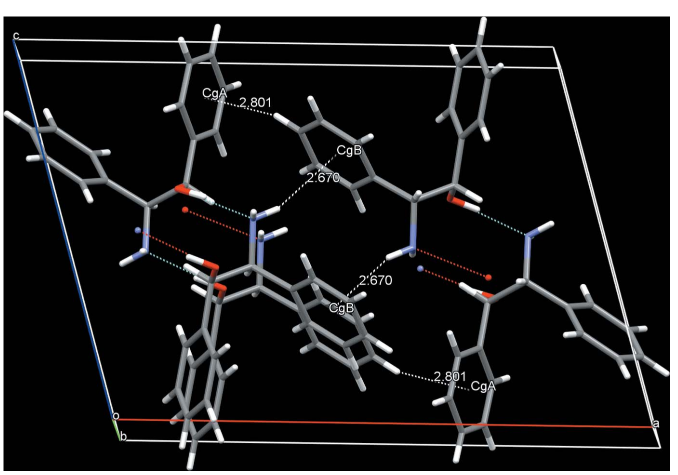


Figure 2
A partial view of the crystal packing of the title compound. Dashed lines indicate the hydrogen bonds, and C—H···π and N—H···π interactions (see Table 2).

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.4213 (14)	N1—C2	1.4732 (15)
O1—C1—C3	112.57 (9)	N1—C2—C9	115.19 (9)
O1—C1—C2	107.90 (9)	N1—C2—C1	106.72 (9)
O1—C1—C2—N1	59.72 (11)	C3—C1—C2—N1	−175.47 (9)
O1—C1—C2—C9	−67.39 (11)	C3—C1—C2—C9	57.42 (12)

Table 2
Hydrogen-bond geometry (Å, °).

CgA and *CgB* are the centroids of rings C3–C8 and C9–C14, respectively.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H13···N1^{i}	0.95 (2)	1.86 (2)	2.7977 (16)	173.1 (16)
N1—H15···*CgB*^{ii}	0.88 (2)	2.670 (19)	3.5125 (14)	160.3 (15)
C12—H10···*CgA*^{iii}	0.93	2.80	3.6780 (17)	158

Symmetry codes: (i) $-x+\frac{3}{2}, y+\frac{1}{2}, -z+1$; (ii) $-x+2, -y+1, -z+1$; (iii) $x+\frac{1}{2}, -y+\frac{3}{2}, z$.

Table 3
Experimental details.

Crystal data	
Chemical formula	$C_{14}H_{15}NO$
M_r	213.27
Crystal system, space group	Monoclinic, $P2_1/a$
Temperature (K)	297
a, *b*, *c* (Å)	16.7752 (17), 5.7573 (10), 12.2887 (13)
β (°)	105.680 (7)
V (Å^3)	1142.7 (3)
Z	4
Radiation type	Cu *K*α
μ (mm^{-1})	0.61
Crystal size (mm)	0.30 × 0.30 × 0.20
Data collection	
Diffractometer	Entaf–Nonius CAD-4
Absorption correction	ψ scan (North *et al.*, 1968)
T_{min}, T_{max}	0.83, 0.90
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	2442, 2354, 2058
R_{int}	0.019
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.626
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.037, 0.105, 1.03
No. of reflections	2354
No. of parameters	158
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.22, −0.18

Computer programs: *CAD-4 Software* (Enraf–Nonius, 1989), *XCAD4* (Harms & Wocadlo, 1995), *SHELXS97* (Sheldrick, 2008), *SHELXL2014/7* (Sheldrick, 2015), *ORTEP-3 for Windows* and *WinGX* (Farrugia, 2012), *Mercury* (Macrae *et al.*, 2008), *PLATON* (Spek, 2009) and *publCIF* (Westrip, 2010).

4. Synthesis and crystallization

cis-Enantiomers of 2-amino-1,2-diphenylethanol (ADE) were purchased from Sigma–Aldrich Co. Ltd. Equivalent weights were mixed in a bottle. Plate-like colourless crystals of the title racemic compound were obtained by vapour-phase diffusion of an aqueous ethanol solution at 297 K.

5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. All H atoms were located in difference Fourier maps. The NH_2 and OH H atoms were freely refined. The C-bound H atoms were included in calculated positions and treated as riding atoms: C—H = 0.93–0.98 Å with $U_{iso}(H) = 1.2U_{eq}(C)$.

Acknowledgements

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supporting information

Acta Cryst. (2015). E**71**, 1539-1541 [doi:10.1107/S2056989015022318]

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Isao Fujii

Computing details

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software* (Enraf–Nonius, 1989); data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014/7* (Sheldrick, 2015); molecular graphics: *ORTEP-3* for Windows (Farrugia, 2012) and *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *PLATON* (Spek, 2009), *publCIF* (Westrip, 2010), and *WinGX* (Farrugia, 2012).

cis-2-Amino-1,2-diphenylethanol

Crystal data

$C_{14}H_{15}NO$
M_r = 213.27
Monoclinic, $P2_1/a$
Hall symbol: -P 2yab
a = 16.7752 (17) Å
b = 5.7573 (10) Å
c = 12.2887 (13) Å
β = 105.680 (7)°
V = 1142.7 (3) Å^3
Z = 4
$F(000)$ = 456
D_x = 1.240 Mg m^{-3}
Cu $K\alpha$ radiation, λ = 1.54178 Å
Cell parameters from 25 reflections
θ = 20–25°
μ = 0.61 mm^{-1}
T = 297 K
Plate, colourless
0.30 × 0.30 × 0.20 mm

Data collection

Entaf–Nonius CAD-4 diffractometer
Radiation source: tube sealed
Graphite monochromator
2θ–ω scan
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.83, T_{max} = 0.90
2442 measured reflections
2354 independent reflections
2058 reflections with $I > 2\sigma(I)$
R_{int} = 0.019
θ_{max} = 74.9°, θ_{min} = 3.7°
h = −21→0
k = −7→0
l = −14→15
3 standard reflections every 300 reflections
intensity decay: none

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.105
S = 1.03
2354 reflections
158 parameters
0 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
W = $1/[\Sigma^2(FO^2) + (0.0588P)^2 + 0.2117P]$ WHERE $P = (FO^2 + 2FC^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.22 e Å^{-3}
$\Delta\rho_{min}$ = −0.18 e Å^{-3}

Extinction correction: *SHELXL2014/7* (Sheldrick, 2015), FC*=KFC[1+0.001XFC²Λ³/SIN(2Θ)]^-1/4

Extinction coefficient: 0.0107 (9)

Absolute structure: see text

Special details

Geometry. Bond distances, angles *etc*. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

Refinement. Refinement on F^2 for ALL reflections except those flagged by the user for potential systematic errors. Weighted *R*-factors *wR* and all goodnesses 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 observed criterion of $F^2 > \sigma(F^2)$ is used only for calculating -*R*-factor-obs *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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.76749 (6)	0.89601 (14)	0.38299 (7)	0.0445 (3)
N1	0.85894 (7)	0.5703 (2)	0.53117 (9)	0.0478 (3)
C1	0.75159 (7)	0.65596 (19)	0.36005 (9)	0.0359 (3)
C2	0.83327 (6)	0.5226 (2)	0.40885 (9)	0.0370 (3)
C3	0.71413 (6)	0.60757 (19)	0.23561 (9)	0.0347 (3)
C4	0.67124 (8)	0.4020 (2)	0.20194 (10)	0.0438 (3)
C5	0.63480 (9)	0.3576 (2)	0.08879 (12)	0.0514 (4)
C6	0.64086 (8)	0.5178 (3)	0.00766 (10)	0.0527 (4)
C7	0.68404 (8)	0.7206 (3)	0.04003 (10)	0.0516 (4)
C8	0.72072 (7)	0.7658 (2)	0.15340 (10)	0.0427 (3)
C9	0.89766 (6)	0.57714 (19)	0.34642 (9)	0.0352 (3)
C10	0.91137 (8)	0.4216 (2)	0.26755 (11)	0.0458 (4)
C11	0.96758 (8)	0.4696 (3)	0.20612 (11)	0.0552 (4)
C12	1.01117 (8)	0.6743 (3)	0.22244 (11)	0.0521 (4)
C13	0.99884 (8)	0.8302 (2)	0.30109 (12)	0.0517 (4)
C14	0.94275 (8)	0.7827 (2)	0.36305 (11)	0.0454 (4)
H1	0.71190	0.60500	0.40080	0.0430*
H2	0.82070	0.35640	0.39920	0.0440*
H3	0.66700	0.29320	0.25600	0.0530*
H4	0.60610	0.21950	0.06720	0.0620*
H5	0.61590	0.48860	−0.06840	0.0630*
H6	0.68870	0.82810	−0.01440	0.0620*
H7	0.74990	0.90330	0.17440	0.0510*
H8	0.88230	0.28220	0.25550	0.0550*
H9	0.97580	0.36260	0.15350	0.0660*
H10	1.04860	0.70720	0.18080	0.0630*
H11	1.02840	0.96890	0.31290	0.0620*
H12	0.93530	0.88950	0.41620	0.0540*
H13	0.7225 (12)	0.959 (3)	0.4061 (15)	0.077 (5)*
H14	0.8637 (12)	0.732 (4)	0.5400 (16)	0.085 (6)*
H15	0.9080 (12)	0.508 (3)	0.5611 (15)	0.074 (5)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0495 (5)	0.0365 (4)	0.0494 (5)	0.0033 (4)	0.0169 (4)	−0.0058 (3)
N1	0.0460 (6)	0.0600 (7)	0.0362 (5)	−0.0006 (5)	0.0089 (4)	0.0094 (5)
C1	0.0370 (5)	0.0355 (5)	0.0375 (5)	0.0012 (4)	0.0138 (4)	0.0019 (4)
C2	0.0378 (6)	0.0353 (6)	0.0381 (5)	0.0000 (4)	0.0106 (4)	0.0049 (4)
C3	0.0315 (5)	0.0362 (6)	0.0374 (5)	0.0048 (4)	0.0108 (4)	0.0026 (4)
C4	0.0496 (6)	0.0368 (6)	0.0456 (6)	−0.0001 (5)	0.0140 (5)	0.0032 (5)
C5	0.0540 (7)	0.0442 (7)	0.0536 (7)	−0.0054 (6)	0.0102 (6)	−0.0083 (6)
C6	0.0535 (7)	0.0617 (8)	0.0390 (6)	0.0018 (6)	0.0059 (5)	−0.0046 (6)
C7	0.0566 (7)	0.0565 (8)	0.0400 (6)	−0.0017 (6)	0.0104 (5)	0.0096 (6)
C8	0.0430 (6)	0.0419 (6)	0.0427 (6)	−0.0041 (5)	0.0108 (5)	0.0047 (5)
C9	0.0321 (5)	0.0346 (5)	0.0378 (5)	0.0039 (4)	0.0077 (4)	0.0051 (4)
C10	0.0417 (6)	0.0437 (7)	0.0525 (7)	−0.0027 (5)	0.0138 (5)	−0.0079 (5)
C11	0.0465 (7)	0.0714 (9)	0.0508 (7)	−0.0004 (6)	0.0186 (6)	−0.0137 (7)
C12	0.0375 (6)	0.0719 (9)	0.0495 (7)	0.0009 (6)	0.0162 (5)	0.0087 (6)
C13	0.0431 (6)	0.0468 (7)	0.0669 (8)	−0.0062 (5)	0.0176 (6)	0.0070 (6)
C14	0.0453 (6)	0.0382 (6)	0.0548 (7)	−0.0019 (5)	0.0171 (5)	−0.0028 (5)

Geometric parameters (Å, º)

O1—C1	1.4213 (14)	C10—C11	1.386 (2)
N1—C2	1.4732 (15)	C11—C12	1.373 (2)
O1—H13	0.95 (2)	C12—C13	1.375 (2)
C1—C3	1.5138 (15)	C13—C14	1.388 (2)
N1—H15	0.88 (2)	C1—H1	0.9800
N1—H14	0.94 (2)	C2—H2	0.9800
C1—C2	1.5435 (16)	C4—H3	0.9300
C2—C9	1.5172 (15)	C5—H4	0.9300
C3—C8	1.3868 (16)	C6—H5	0.9300
C3—C4	1.3888 (16)	C7—H6	0.9300
C4—C5	1.3831 (19)	C8—H7	0.9300
C5—C6	1.382 (2)	C10—H8	0.9300
C6—C7	1.375 (2)	C11—H9	0.9300
C7—C8	1.3870 (17)	C12—H10	0.9300
C9—C14	1.3896 (16)	C13—H11	0.9300
C9—C10	1.3837 (17)	C14—H12	0.9300
C1—O1—H13	108.0 (11)	O1—C1—H1	108.00
O1—C1—C3	112.57 (9)	C2—C1—H1	108.00
C2—C1—C3	112.55 (9)	C3—C1—H1	108.00
H14—N1—H15	108.3 (17)	N1—C2—H2	107.00
O1—C1—C2	107.90 (9)	C1—C2—H2	107.00
C2—N1—H14	107.2 (12)	C9—C2—H2	107.00
C2—N1—H15	109.4 (12)	C3—C4—H3	120.00
N1—C2—C9	115.19 (9)	C5—C4—H3	120.00
C1—C2—C9	112.28 (9)	C4—C5—H4	120.00

N1—C2—C1	106.72 (9)	C6—C5—H4	120.00
C1—C3—C4	119.87 (10)	C5—C6—H5	120.00
C1—C3—C8	121.46 (10)	C7—C6—H5	120.00
C4—C3—C8	118.66 (10)	C6—C7—H6	120.00
C3—C4—C5	120.64 (11)	C8—C7—H6	120.00
C4—C5—C6	120.21 (12)	C3—C8—H7	120.00
C5—C6—C7	119.59 (12)	C7—C8—H7	120.00
C6—C7—C8	120.39 (13)	C9—C10—H8	119.00
C3—C8—C7	120.49 (12)	C11—C10—H8	119.00
C2—C9—C10	119.74 (10)	C10—C11—H9	120.00
C2—C9—C14	122.38 (10)	C12—C11—H9	120.00
C10—C9—C14	117.86 (11)	C11—C12—H10	120.00
C9—C10—C11	121.26 (12)	C13—C12—H10	120.00
C10—C11—C12	120.37 (13)	C12—C13—H11	120.00
C11—C12—C13	119.19 (13)	C14—C13—H11	120.00
C12—C13—C14	120.66 (12)	C9—C14—H12	120.00
C9—C14—C13	120.65 (11)	C13—C14—H12	120.00
O1—C1—C2—N1	59.72 (11)	C1—C3—C8—C7	−178.29 (12)
O1—C1—C2—C9	−67.39 (11)	C4—C3—C8—C7	0.98 (18)
C3—C1—C2—N1	−175.47 (9)	C3—C4—C5—C6	0.1 (2)
C3—C1—C2—C9	57.42 (12)	C4—C5—C6—C7	0.6 (2)
O1—C1—C3—C4	−159.70 (11)	C5—C6—C7—C8	−0.6 (2)
O1—C1—C3—C8	19.56 (15)	C6—C7—C8—C3	−0.2 (2)
C2—C1—C3—C4	78.10 (13)	C2—C9—C10—C11	177.69 (11)
C2—C1—C3—C8	−102.65 (12)	C14—C9—C10—C11	−0.64 (18)
N1—C2—C9—C10	136.09 (11)	C2—C9—C14—C13	−177.49 (11)
N1—C2—C9—C14	−45.66 (15)	C10—C9—C14—C13	0.80 (18)
C1—C2—C9—C10	−101.48 (12)	C9—C10—C11—C12	0.0 (2)
C1—C2—C9—C14	76.77 (13)	C10—C11—C12—C13	0.5 (2)
C1—C3—C4—C5	178.33 (12)	C11—C12—C13—C14	−0.4 (2)
C8—C3—C4—C5	−0.94 (19)	C12—C13—C14—C9	−0.3 (2)

Hydrogen-bond geometry (Å, º)

CgA and *CgB* are the centroids of rings C3–C8 and C9–C14, respectively.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H13···N1^{i}	0.95 (2)	1.86 (2)	2.7977 (16)	173.1 (16)
N1—H15···*CgB*^{ii}	0.88 (2)	2.670 (19)	3.5125 (14)	160.3 (15)
C12—H10···*CgA*^{iii}	0.93	2.80	3.6780 (17)	158

Symmetry codes: (i) $-x+3/2$, $y+1/2$, $-z+1$; (ii) $-x+2$, $-y+1$, $-z+1$; (iii) $x+1/2$, $-y+3/2$, z.