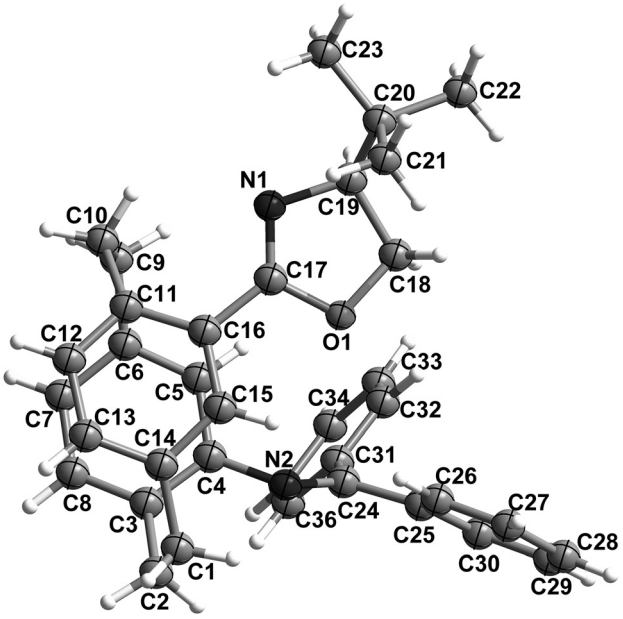
Zhen Chen, Yanwen Sun*, Chao Chen, Nuo Xu, Xiaozhong Wang and Sijun Li

The crystal structure of (*S*, R_p)-4–benzhydrylideneamino-12-(4-*tert*-butyl oxazolin-2-yl)[2.2]paracyclophane, $C_{36}H_{36}N_2O$



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Abstract

$C_{36}H_{36}N_2O$, orthorhombic, $P2_12_12_1$ (no. 19), a = 11.849(2) Å, b = 14.373(3) Å, c = 17.183(3) Å, V = 2926.4(10) Å^3, Z = 4, $R_{gt}(F)$ = 0.0514, wR_{ref} (F^2) = 0.1272, T = 296(2) K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	0.20 × 0.20 × 0.15 mm
Wavelength:	Cu *K*α radiation (1.54178 Å)
μ:	0.53 mm^{-1}
Diffractometer, scan mode:	Bruker Smart Apex II, φ and ω
θ_{max}, completeness:	63.9°, 99 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	13,540, 4716, 0.068
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 3141
$N(param)_{refined}$:	411
Programs:	Bruker [1], Olex2 [2], SHELX [3, 4], Diamond [5]

1 Source of materials

We started the synthesis of 4–Benzhydrylideneamino-12-(4-*tert*-butyl oxazolin-2-yl)[2.2]paracyclophane from 4-bromo-12-(4-*tert*-butyl oxazolin-2-yl) [2.2]paracyclophane diastereomers, which were prepared from racemic 4,12-dibromo[2.2]paracyclophane according to the literature [6, 7]. The (*S*, S_p)-diastereomer-dominated and (*S*, R_p)-diastereomer-dominated products were obtained by column chromatography of separation (ethyl acetate: petroleum ether = 1:25 and a small amount of triethylamine 5 drops/500 mL). For (*S*, R_p)-diastereomer based products, a small amount of (*S*, S_p)-diastereomer was further removed by ethanol recrystallization. The remaining (*S*, R_p)-product was recrystallized with n-hexane affording yellow crystals.

2 Experimental details

The structure was solved by Direct Methods with the SHELX [3]. All H-atoms were positioned geometrically and refined using a riding model with d(C–H) = 0.93 Å, U_{iso} = 1.2U_{eq} (C) for aromatic, 0.97 Å, U_{iso} = 1.2U_{eq} (C) for CH_2, 0.98 Å, U_{iso} = 1.2 U_{eq} (C) for CH, 0.96 Å, U_{iso} = 1.5 U_{eq} (C) for CH_3 atoms.

***Corresponding author: Yanwen Sun**, School of Chemistry and Chemical Engineering, Hebei Normal University For Nationalities, Higher Education Park, Chengde 067000, P. R. China, E-mail: sunyanwen0702@126.com
Zhen Chen, Nuo Xu, Xiaozhong Wang and Sijun Li, School of Chemistry and Chemical Engineering, Hebei Normal University For Nationalities, Higher Education Park, Chengde 067000, P. R. China. https://orcid.org/0000-0001-5299-7365 (Z. Chen)
Chao Chen, Methanol Branch of Daqing Oilfield Chemical Co., Ltd., Daqing 163411, P. R. China

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
O1	−0.7987 (3)	−0.1290 (3)	−0.08036 (18)	0.0792 (11)
N1	−0.7140 (4)	−0.0590 (3)	−0.1808 (2)	0.0703 (12)
N2	−0.8916 (3)	−0.3639 (3)	−0.0840 (2)	0.0552 (9)
C1	−1.1319 (5)	−0.3073 (4)	−0.1626 (3)	0.0693 (14)
H1A	−1.127 (4)	−0.294 (3)	−0.108 (3)	0.055 (12)*
H1B	−1.210 (6)	−0.309 (4)	−0.185 (4)	0.11 (2)*
C2	−1.0815 (5)	−0.4074 (4)	−0.1788 (3)	0.0660 (13)
H2A	−1.083 (4)	−0.438 (3)	−0.133 (3)	0.054 (12)*
H2B	−1.136 (5)	−0.434 (4)	−0.216 (3)	0.10 (2)*
C3	−0.9640 (4)	−0.4046 (3)	−0.2107 (3)	0.0577 (11)
C4	−0.8721 (4)	−0.3751 (3)	−0.1654 (2)	0.0532 (11)
C5	−0.7783 (4)	−0.3360 (3)	−0.2007 (3)	0.0586 (12)
H5	−0.725 (4)	−0.308 (3)	−0.172 (3)	0.065 (15)*
C6	−0.7710 (4)	−0.3245 (4)	−0.2806 (3)	0.0628 (13)
C7	−0.8501 (5)	−0.3735 (4)	−0.3251 (3)	0.0673 (14)
H7	−0.844 (4)	−0.370 (4)	−0.384 (3)	0.090 (18)*
C8	−0.9428 (5)	−0.4133 (4)	−0.2903 (3)	0.0650 (13)
H8	−0.999 (4)	−0.437 (3)	−0.323 (3)	0.069 (15)*
C9	−0.7016 (5)	−0.2461 (4)	−0.3144 (3)	0.0752 (15)
H9A	−0.670 (4)	−0.272 (4)	−0.367 (3)	0.077 (16)*
H9B	−0.638 (6)	−0.229 (5)	−0.281 (4)	0.12 (2)*
C10	−0.7730 (5)	−0.1561 (4)	−0.3305 (3)	0.0671 (14)
H10A	−0.726 (5)	−0.104 (4)	−0.318 (3)	0.072 (16)*
H10B	−0.790 (4)	−0.158 (3)	−0.384 (3)	0.068 (14)*
C11	−0.8827 (4)	−0.1537 (3)	−0.2854 (3)	0.0561 (11)
C12	−0.9810 (5)	−0.1830 (4)	−0.3229 (3)	0.0658 (14)
H12	−0.980 (3)	−0.184 (3)	−0.373 (3)	0.044 (12)*
C13	−1.0713 (5)	−0.2207 (4)	−0.2831 (3)	0.0641 (13)
H13	−1.127 (5)	−0.247 (3)	−0.313 (3)	0.067 (15)*
C14	−1.0664 (4)	−0.2327 (3)	−0.2033 (3)	0.0582 (11)
C15	−0.9804 (4)	−0.1840 (3)	−0.1647 (3)	0.0543 (11)
H15	−0.974 (4)	−0.183 (3)	−0.108 (3)	0.058 (13)*
C16	−0.8896 (4)	−0.1458 (3)	−0.2038 (3)	0.0531 (11)
C17	−0.7960 (4)	−0.1078 (3)	−0.1573 (2)	0.0558 (11)
C18	−0.6972 (5)	−0.0903 (4)	−0.0473 (3)	0.0728 (14)
H18A	−0.648022	−0.139299	−0.028449	0.087*
H18B	−0.715134	−0.048987	−0.004421	0.087*
C19	−0.6414 (4)	−0.0371 (3)	−0.1131 (3)	0.0625 (12)
H19	−0.566449	−0.063733	−0.122212	0.075*
C20	−0.6288 (5)	0.0673 (4)	−0.1009 (3)	0.0718 (13)
C21	−0.7428 (6)	0.1122 (5)	−0.0823 (5)	0.113 (3)
H21A	−0.793416	0.103069	−0.125306	0.169*
H21B	−0.732519	0.177566	−0.073566	0.169*
H21C	−0.774002	0.083961	−0.036488	0.169*
C22	−0.5459 (5)	0.0844 (4)	−0.0345 (3)	0.0850 (17)
H22A	−0.575949	0.058888	0.012831	0.128*
H22B	−0.534395	0.150071	−0.028218	0.128*
H22C	−0.475216	0.054925	−0.046224	0.128*
C23	−0.5800 (7)	0.1095 (5)	−0.1745 (4)	0.118 (3)
H23A	−0.512542	0.076661	−0.188707	0.177*
H23B	−0.562488	0.173780	−0.165514	0.177*
H23C	−0.634204	0.104654	−0.215858	0.177*
C24	−0.8218 (4)	−0.3921 (3)	−0.0318 (2)	0.0522 (10)
C25	−0.8458 (4)	−0.3661 (3)	0.0498 (3)	0.0549 (11)
C26	−0.9105 (4)	−0.2879 (3)	0.0664 (3)	0.0597 (12)
H26	−0.934721	−0.249822	0.025945	0.072*
C27	−0.9393 (5)	−0.2661 (4)	0.1421 (3)	0.0717 (14)
H27	−0.982847	−0.213653	0.152456	0.086*
C28	−0.9032 (5)	−0.3224 (4)	0.2025 (3)	0.0793 (16)
H28	−0.924475	−0.308724	0.253297	0.095*
C29	−0.8364 (5)	−0.3981 (4)	0.1877 (3)	0.0763 (15)
H29	−0.810673	−0.434790	0.228636	0.092*
C30	−0.8072 (4)	−0.4200 (4)	0.1118 (3)	0.0669 (13)
H30	−0.761243	−0.471152	0.102143	0.080*
C31	−0.7229 (4)	−0.4537 (3)	−0.0469 (2)	0.0559 (11)
C32	−0.6169 (5)	−0.4267 (5)	−0.0226 (3)	0.0838 (17)
H32	−0.607411	−0.369694	0.002154	0.101*
C33	−0.5247 (6)	−0.4836 (6)	−0.0349 (5)	0.119 (3)
H33	−0.453098	−0.464117	−0.019855	0.143*
C34	−0.5391 (7)	−0.5698 (6)	−0.0696 (4)	0.117 (3)
H34	−0.477698	−0.609107	−0.077033	0.140*
C35	−0.6460 (7)	−0.5967 (5)	−0.0932 (4)	0.097 (2)
H35	−0.656317	−0.654524	−0.116411	0.117*
C36	−0.7372 (5)	−0.5385 (4)	−0.0825 (3)	0.0714 (14)
H36	−0.808385	−0.556655	−0.099458	0.086*

3 Comment

The [2.2]paracyclophane derivatives play an important role in asymmetric catalysis [8]. Substituted [2.2]paracyclophanes with planar chirality used as ligands and proceed in asymmetric catalysis were first reported in 1997 [9]. Since then, many planar chiral [2.2]paracyclophane derivatives have been synthesized and applied in all kinds of asymmetric transformations. The synthesis of double chiral ligands with a planar chiral [2.2]paracyclophane is a hot topic. It is a good strategy to construct bichiral ligands by introducing oxazoline derivatives which have excellent coordination ability and center chirality to [2.2]paracyclophane skeleton. It is important to study the crystal structure of double-chiral ligands for the study of its catalytic mechanism. We previously reported a crystal structure of (*S*, S_p)*tert*-butyl 2-(4-(12-bromo [2.2]-paracyclophanyl) carbamoyl) pyrrolidine-1-carboxylate.

The structure of the title compound is illustrated in the figure, its absolute conguration of the [2.2]paracyclophane moiety is established as (R_p) by comparison with the known conguration of the *S*-oxazoline moiety. The single-crystal structure verifies that all bond lengths are in normal ranges. The constrained [2.2]paracyclophane core gives boatlike conformation as well as the similar pseudo-para substituted structure [10], but the direction of methylene bonds C1–C2

and C9–C10 is twisted rather than parallel, the nonbonded C–C distance between the ipso carbons, C3 and C14 (2.75 Å) is also not exactly same with C6 and C11(2.79 Å). The two planes across C4/C5/C7/C8 and C12/C13/C15/C16 are not parallel like pseudo-para substituted structure [10], the dihedral angles up to 2.75(3)° which is the same than in the similar pseudo-ortho substituted structure (2.79(4)°) [11]. Additionally, the side with substituents C4/C5 and C15/C16 are closer to each other than the other side which is similar to (S_p, *S*) *tert*-butyl 2-(4-(12-bromo [2.2]paracyclophanyl) carbamoyl) pyrrolidine-1-carboxylate and unusual to other similar structures [11–13]. This may be due to the involvement of substituents in intermolecular interactions. There are only intermolecular interactions and non-classical hydrogen bonds in this molecule. The presence of non-classical hydrogen bonds between C–H donors and the aromatic C atom from other molecules [C_{30}–$H_{30}\cdots C_7^i$ symmetry code i: $-3/2-x$, $-1-y$, $1/2+z$] results in the formation of one-dimensional chain-like structure along the [001] direction. The one-dimensional structures are further connected by non-classical hydrogen bonds [C_{19}–$H_{19}\cdots C_{27}^{ii}$ or C_{28}^{ii} symmetry code ii: $1/2+x$, $-1/2-y$, $-z$] forming three-dimensional supramolecular structure.

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Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

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