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## (S)-Perillaldehyde azine

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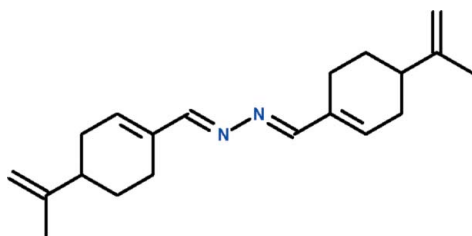
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Key indicators: single-crystal X-ray study;  $T = 173$  K; mean  $\sigma(\text{C}-\text{C}) = 0.004$  Å;  $R$  factor = 0.046;  $wR$  factor = 0.141; data-to-parameter ratio = 10.0.

The C=N-N=C linkage [torsion angle  $-172.5$  (2)°] in the title azine, C<sub>20</sub>H<sub>28</sub>N<sub>2</sub>, adopts a *trans* conformation. The six-membered rings adopt sofa conformations.

## Related literature

A previous study reported the oxime derivative of *S*-perillaldehyde; see Yuan *et al.* (2009). Only few crystal structures of azines have been reported, see: Berthou *et al.* (1970); Kim & Lee (2008); Marek *et al.* (1997); Rizal *et al.* (2008); Sanz *et al.* (1999).



## Experimental

## Crystal data

C<sub>20</sub>H<sub>28</sub>N<sub>2</sub> $M_r = 296.44$ 

Monoclinic,  $P2_1$   
 $a = 8.8200$  (5) Å  
 $b = 9.7603$  (6) Å  
 $c = 10.1710$  (6) Å  
 $\beta = 94.970$  (1)°  
 $V = 872.29$  (9) Å<sup>3</sup>

$Z = 2$   
 Mo  $K\alpha$  radiation  
 $\mu = 0.07$  mm<sup>-1</sup>  
 $T = 173$  K  
 $0.48 \times 0.46 \times 0.21$  mm

## Data collection

Bruker SMART APEX  
 diffractometer  
 7179 measured reflections

2013 independent reflections  
 1802 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.035$

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.046$   
 $wR(F^2) = 0.141$   
 $S = 1.12$   
 2013 reflections  
 201 parameters

1 restraint  
 H-atom parameters constrained  
 $\Delta\rho_{\text{max}} = 0.22$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.23$  e Å<sup>-3</sup>

Data collection: *SMART* (Bruker, 2003); cell refinement: *SAINTE* (Bruker, 2003); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *publCIF* (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT5184).

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**supplementary materials**

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## (S)-Perillaldehyde azine

L.-L. Han, J.-H. Shi, D.-P. Yan and S. W. Ng

### Experimental

An ethanol solution (10 ml) of hydrazinium hydroxide (0.5 g, 0.01 mol) was added to a 50% ethanol solution (50 ml) of perillaldehyde (3 g, 0.02 mol); acetic acid (2 ml) was then added. The mixture was heated for two hours. The product was recrystallized from ethyl acetate to afford light-yellow crystals (yield 70%).

### Refinement

Carbon-bound H-atoms were placed in calculated positions (C—H 0.95–1.00 Å) and were included in the refinement in the riding model approximation, with  $U(\text{H})$  set to  $1.2U(\text{C})$ . In the absence of anomalous scatterers Friedel pairs were merged. The chiral carbon atoms were assumed to have an *S*-configuration, i.e., the configuration of perillaldehyde itself.

### Figures

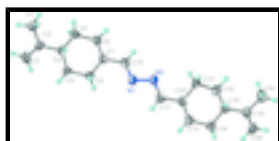


Fig. 1. Anisotropic displacement ellipsoid plot (Barbour, 2001) of  $\text{C}_{20}\text{H}_{28}\text{N}_2$  at the 70% probability level; hydrogen atoms are shown as spheres of arbitrary radius.

## (S)-Perillaldehyde azine

### Crystal data

$\text{C}_{20}\text{H}_{28}\text{N}_2$	$F(000) = 324$
$M_r = 296.44$	$D_x = 1.129 \text{ Mg m}^{-3}$
Monoclinic, $P2_1$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
Hall symbol: P 2yb	Cell parameters from 4048 reflections
$a = 8.8200 (5) \text{ \AA}$	$\theta = 2.3\text{--}27.2^\circ$
$b = 9.7603 (6) \text{ \AA}$	$\mu = 0.07 \text{ mm}^{-1}$
$c = 10.1710 (6) \text{ \AA}$	$T = 173 \text{ K}$
$\beta = 94.970 (1)^\circ$	Block, yellow
$V = 872.29 (9) \text{ \AA}^3$	$0.48 \times 0.46 \times 0.21 \text{ mm}$
$Z = 2$	

### Data collection

Bruker SMART APEX diffractometer	1802 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	$R_{\text{int}} = 0.035$

# supplementary materials

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graphite  $\theta_{\max} = 27.2^\circ$ ,  $\theta_{\min} = 2.0^\circ$   
 $\omega$  scans  $h = -11 \rightarrow 11$   
7179 measured reflections  $k = -12 \rightarrow 12$   
2013 independent reflections  $l = -12 \rightarrow 12$

## Refinement

Refinement on  $F^2$  Primary atom site location: structure-invariant direct methods  
Least-squares matrix: full Secondary atom site location: difference Fourier map  
 $R[F^2 > 2\sigma(F^2)] = 0.046$  Hydrogen site location: inferred from neighbouring sites  
 $wR(F^2) = 0.141$  H-atom parameters constrained  
 $S = 1.12$   $w = 1/[\sigma^2(F_o^2) + (0.074P)^2 + 0.242P]$   
2013 reflections where  $P = (F_o^2 + 2F_c^2)/3$   
201 parameters  $(\Delta/\sigma)_{\max} = 0.001$   
1 restraint  $\Delta\rho_{\max} = 0.22 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.23 \text{ e } \text{\AA}^{-3}$

## Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	1.1573 (3)	0.4999 (3)	0.9681 (2)	0.0344 (5)
N2	1.2864 (3)	0.5570 (3)	1.0416 (2)	0.0340 (5)
C1	0.3418 (3)	0.5570 (4)	0.6676 (3)	0.0432 (7)
H1A	0.2556	0.5311	0.6053	0.065*
H1B	0.3581	0.6561	0.6631	0.065*
H1C	0.3200	0.5317	0.7573	0.065*
C2	0.4821 (3)	0.4836 (3)	0.6326 (3)	0.0335 (6)
C3	0.4827 (4)	0.4131 (4)	0.5213 (3)	0.0451 (8)
H3A	0.3933	0.4085	0.4623	0.054*
H3B	0.5725	0.3672	0.5006	0.054*
C4	0.6201 (3)	0.4954 (3)	0.7323 (3)	0.0303 (6)
H4	0.5881	0.4606	0.8182	0.036*
C5	0.6657 (4)	0.6461 (3)	0.7542 (3)	0.0403 (7)
H5A	0.6717	0.6907	0.6674	0.048*
H5B	0.5856	0.6933	0.7995	0.048*
C6	0.8147 (3)	0.6631 (3)	0.8341 (3)	0.0369 (6)
H6	0.8407	0.7518	0.8673	0.044*
C7	0.9134 (3)	0.5613 (3)	0.8618 (3)	0.0302 (6)
C8	0.8822 (3)	0.4179 (3)	0.8139 (3)	0.0373 (7)
H8A	0.8524	0.3612	0.8882	0.045*
H8B	0.9767	0.3785	0.7837	0.045*
C9	0.7568 (3)	0.4114 (3)	0.7014 (3)	0.0356 (6)
H9A	0.7962	0.4465	0.6196	0.043*
H9B	0.7255	0.3149	0.6860	0.043*
C10	1.0558 (3)	0.5917 (3)	0.9402 (3)	0.0325 (6)
H10	1.0739	0.6824	0.9716	0.039*

C11	1.3954 (3)	0.4699 (3)	1.0567 (3)	0.0321 (6)
H11	1.3816	0.3810	1.0195	0.038*
C12	1.5398 (3)	0.5041 (3)	1.1296 (3)	0.0302 (6)
C13	1.6523 (3)	0.4117 (3)	1.1373 (3)	0.0340 (6)
H13	1.6335	0.3259	1.0948	0.041*
C14	1.8062 (3)	0.4349 (3)	1.2089 (3)	0.0349 (6)
H14A	1.8814	0.4500	1.1436	0.042*
H14B	1.8370	0.3517	1.2603	0.042*
C15	1.8082 (3)	0.5578 (3)	1.3023 (3)	0.0318 (6)
H15	1.7472	0.5319	1.3769	0.038*
C16	1.7255 (3)	0.6772 (3)	1.2292 (3)	0.0370 (7)
H16A	1.7332	0.7600	1.2855	0.044*
H16B	1.7748	0.6974	1.1475	0.044*
C17	1.5580 (3)	0.6425 (3)	1.1939 (3)	0.0384 (7)
H17A	1.5035	0.6437	1.2750	0.046*
H17B	1.5116	0.7131	1.1331	0.046*
C18	1.9656 (3)	0.5985 (3)	1.3620 (3)	0.0342 (6)
C19	1.9691 (4)	0.7035 (4)	1.4708 (3)	0.0460 (8)
H19A	2.0750	0.7240	1.5018	0.069*
H19B	1.9160	0.6674	1.5442	0.069*
H19C	1.9186	0.7875	1.4373	0.069*
C20	2.0927 (3)	0.5473 (4)	1.3233 (3)	0.0407 (7)
H20A	2.1881	0.5766	1.3641	0.049*
H20B	2.0888	0.4812	1.2546	0.049*

Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
N1	0.0284 (11)	0.0386 (13)	0.0355 (12)	-0.0022 (11)	-0.0012 (9)	-0.0030 (11)
N2	0.0286 (12)	0.0386 (13)	0.0342 (11)	-0.0017 (11)	-0.0011 (9)	-0.0028 (11)
C1	0.0339 (15)	0.0515 (18)	0.0434 (15)	0.0057 (15)	-0.0007 (12)	-0.0029 (15)
C2	0.0291 (13)	0.0356 (15)	0.0352 (13)	-0.0007 (13)	-0.0007 (11)	0.0034 (12)
C3	0.0401 (16)	0.052 (2)	0.0420 (17)	0.0017 (16)	-0.0050 (13)	-0.0098 (16)
C4	0.0303 (13)	0.0304 (13)	0.0297 (12)	0.0008 (12)	-0.0003 (10)	-0.0007 (11)
C5	0.0366 (16)	0.0284 (14)	0.0547 (17)	0.0077 (13)	-0.0036 (13)	-0.0055 (14)
C6	0.0350 (15)	0.0281 (14)	0.0466 (15)	-0.0013 (12)	-0.0019 (12)	-0.0054 (13)
C7	0.0287 (13)	0.0328 (14)	0.0289 (12)	-0.0008 (12)	0.0010 (10)	-0.0031 (11)
C8	0.0349 (15)	0.0314 (15)	0.0438 (15)	0.0055 (13)	-0.0064 (12)	-0.0025 (14)
C9	0.0356 (14)	0.0275 (14)	0.0426 (15)	0.0031 (12)	-0.0031 (12)	-0.0060 (13)
C10	0.0316 (14)	0.0328 (15)	0.0334 (13)	-0.0029 (12)	0.0038 (11)	-0.0045 (11)
C11	0.0336 (14)	0.0330 (16)	0.0296 (13)	-0.0038 (12)	0.0029 (10)	0.0011 (11)
C12	0.0299 (13)	0.0320 (14)	0.0288 (12)	-0.0032 (12)	0.0037 (10)	0.0027 (11)
C13	0.0343 (14)	0.0320 (14)	0.0349 (13)	-0.0020 (13)	-0.0015 (11)	0.0011 (12)
C14	0.0309 (14)	0.0318 (15)	0.0411 (15)	0.0020 (12)	-0.0027 (11)	0.0006 (12)
C15	0.0290 (13)	0.0362 (15)	0.0302 (12)	-0.0040 (12)	0.0027 (10)	0.0031 (12)
C16	0.0342 (15)	0.0318 (15)	0.0434 (15)	-0.0035 (12)	-0.0054 (12)	-0.0012 (12)
C17	0.0335 (15)	0.0349 (16)	0.0451 (16)	0.0027 (13)	-0.0061 (12)	-0.0021 (14)
C18	0.0351 (15)	0.0372 (16)	0.0296 (13)	-0.0048 (12)	-0.0011 (11)	0.0054 (11)

## supplementary materials

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C19	0.0404 (17)	0.059 (2)	0.0382 (16)	-0.0084 (16)	0.0010 (12)	-0.0103 (15)
C20	0.0319 (15)	0.0471 (18)	0.0416 (15)	-0.0016 (14)	-0.0048 (12)	0.0004 (15)

### *Geometric parameters (Å, °)*

N1—C10	1.280 (4)	C10—H10	0.9500
N1—N2	1.421 (3)	C11—C12	1.456 (4)
N2—C11	1.282 (4)	C11—H11	0.9500
C1—C2	1.499 (4)	C12—C13	1.338 (4)
C1—H1A	0.9800	C12—C17	1.503 (4)
C1—H1B	0.9800	C13—C14	1.501 (4)
C1—H1C	0.9800	C13—H13	0.9500
C2—C3	1.325 (4)	C14—C15	1.529 (4)
C2—C4	1.519 (4)	C14—H14A	0.9900
C3—H3A	0.9500	C14—H14B	0.9900
C3—H3B	0.9500	C15—C18	1.519 (4)
C4—C9	1.513 (4)	C15—C16	1.533 (4)
C4—C5	1.537 (4)	C15—H15	1.0000
C4—H4	1.0000	C16—C17	1.528 (4)
C5—C6	1.493 (4)	C16—H16A	0.9900
C5—H5A	0.9900	C16—H16B	0.9900
C5—H5B	0.9900	C17—H17A	0.9900
C6—C7	1.335 (4)	C17—H17B	0.9900
C6—H6	0.9500	C18—C20	1.318 (4)
C7—C10	1.459 (4)	C18—C19	1.507 (4)
C7—C8	1.500 (4)	C19—H19A	0.9800
C8—C9	1.523 (4)	C19—H19B	0.9800
C8—H8A	0.9900	C19—H19C	0.9800
C8—H8B	0.9900	C20—H20A	0.9500
C9—H9A	0.9900	C20—H20B	0.9500
C9—H9B	0.9900		
C10—N1—N2	110.8 (3)	C7—C10—H10	119.0
C11—N2—N1	111.2 (2)	N2—C11—C12	121.5 (3)
C2—C1—H1A	109.5	N2—C11—H11	119.3
C2—C1—H1B	109.5	C12—C11—H11	119.3
H1A—C1—H1B	109.5	C13—C12—C11	119.1 (3)
C2—C1—H1C	109.5	C13—C12—C17	122.0 (3)
H1A—C1—H1C	109.5	C11—C12—C17	118.9 (3)
H1B—C1—H1C	109.5	C12—C13—C14	124.2 (3)
C3—C2—C1	121.0 (3)	C12—C13—H13	117.9
C3—C2—C4	123.2 (3)	C14—C13—H13	117.9
C1—C2—C4	115.8 (3)	C13—C14—C15	112.4 (2)
C2—C3—H3A	120.0	C13—C14—H14A	109.1
C2—C3—H3B	120.0	C15—C14—H14A	109.1
H3A—C3—H3B	120.0	C13—C14—H14B	109.1
C9—C4—C2	115.3 (2)	C15—C14—H14B	109.1
C9—C4—C5	110.2 (2)	H14A—C14—H14B	107.9
C2—C4—C5	110.7 (2)	C18—C15—C14	114.5 (2)
C9—C4—H4	106.7	C18—C15—C16	112.0 (2)

C2—C4—H4	106.7	C14—C15—C16	108.4 (2)
C5—C4—H4	106.7	C18—C15—H15	107.2
C6—C5—C4	113.1 (2)	C14—C15—H15	107.2
C6—C5—H5A	108.9	C16—C15—H15	107.2
C4—C5—H5A	108.9	C17—C16—C15	110.8 (2)
C6—C5—H5B	108.9	C17—C16—H16A	109.5
C4—C5—H5B	108.9	C15—C16—H16A	109.5
H5A—C5—H5B	107.8	C17—C16—H16B	109.5
C7—C6—C5	124.0 (3)	C15—C16—H16B	109.5
C7—C6—H6	118.0	H16A—C16—H16B	108.1
C5—C6—H6	118.0	C12—C17—C16	111.4 (3)
C6—C7—C10	118.6 (3)	C12—C17—H17A	109.3
C6—C7—C8	121.9 (2)	C16—C17—H17A	109.3
C10—C7—C8	119.5 (3)	C12—C17—H17B	109.3
C7—C8—C9	112.5 (2)	C16—C17—H17B	109.3
C7—C8—H8A	109.1	H17A—C17—H17B	108.0
C9—C8—H8A	109.1	C20—C18—C19	120.9 (3)
C7—C8—H8B	109.1	C20—C18—C15	123.6 (3)
C9—C8—H8B	109.1	C19—C18—C15	115.6 (3)
H8A—C8—H8B	107.8	C18—C19—H19A	109.5
C4—C9—C8	111.2 (2)	C18—C19—H19B	109.5
C4—C9—H9A	109.4	H19A—C19—H19B	109.5
C8—C9—H9A	109.4	C18—C19—H19C	109.5
C4—C9—H9B	109.4	H19A—C19—H19C	109.5
C8—C9—H9B	109.4	H19B—C19—H19C	109.5
H9A—C9—H9B	108.0	C18—C20—H20A	120.0
N1—C10—C7	122.1 (3)	C18—C20—H20B	120.0
N1—C10—H10	119.0	H20A—C20—H20B	120.0
C10—N1—N2—C11	-172.5 (2)	N1—N2—C11—C12	-179.6 (2)
C3—C2—C4—C9	-4.6 (4)	N2—C11—C12—C13	-176.9 (3)
C1—C2—C4—C9	175.2 (3)	N2—C11—C12—C17	3.0 (4)
C3—C2—C4—C5	121.3 (4)	C11—C12—C13—C14	179.7 (2)
C1—C2—C4—C5	-58.9 (4)	C17—C12—C13—C14	-0.2 (4)
C9—C4—C5—C6	-42.0 (3)	C12—C13—C14—C15	15.4 (4)
C2—C4—C5—C6	-170.7 (2)	C13—C14—C15—C18	-171.5 (2)
C4—C5—C6—C7	12.8 (4)	C13—C14—C15—C16	-45.7 (3)
C5—C6—C7—C10	179.6 (3)	C18—C15—C16—C17	-168.8 (2)
C5—C6—C7—C8	-0.1 (5)	C14—C15—C16—C17	63.9 (3)
C6—C7—C8—C9	17.4 (4)	C13—C12—C17—C16	16.9 (4)
C10—C7—C8—C9	-162.3 (2)	C11—C12—C17—C16	-163.0 (2)
C2—C4—C9—C8	-173.8 (3)	C15—C16—C17—C12	-48.7 (3)
C5—C4—C9—C8	60.0 (3)	C14—C15—C18—C20	9.7 (4)
C7—C8—C9—C4	-47.3 (4)	C16—C15—C18—C20	-114.2 (3)
N2—N1—C10—C7	178.1 (2)	C14—C15—C18—C19	-170.4 (3)
C6—C7—C10—N1	-178.4 (3)	C16—C15—C18—C19	65.7 (3)
C8—C7—C10—N1	1.2 (4)		

Fig. 1

