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10-Ethyl-10*H*-phenothiazine-3-carbaldehyde

Dao-Hui Yu, Jian-Qing Wang, Lin Kong* and Zhao-di Liu

Department of Chemistry, Anhui University, Hefei 230039, People's Republic of China, and Key Laboratory of Functional Inorganic Materials, Chemistry, Hefei 230039, People's Republic of China
Correspondence e-mail: kong_lin2009@126.com

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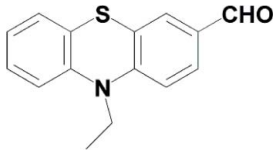
Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.003 Å; R factor = 0.041; wR factor = 0.109; data-to-parameter ratio = 13.3.

In the title molecule, $C_{15}H_{13}NOS$, the two benzene rings of the tricyclic fused-ring system are inclined at 21.1 (1)°. In the crystal, weak C—H···O hydrogen bonds link the molecules into chains along [001]. The crystal packing also exhibits π–π interactions with a distance of 3.801 (5) Å between the centroids of the benzene rings of neighbouring molecules.

Related literature

For related structures, see: Chu & Van der Helm (1975); Hdii *et al.* (1998); Li *et al.* (2009*a*,*b*).



Experimental

Crystal data

$C_{15}H_{13}NOS$
M_r = 255.32
Orthorhombic, *Pbca*
a = 8.0867 (1) Å
b = 15.3271 (3) Å
c = 20.3369 (4) Å
V = 2520.67 (8) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.24 mm^{-1}
T = 296 K
0.20 × 0.10 × 0.10 mm

Data collection

Bruker SMART APEX diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.953, T_{max} = 0.976
17210 measured reflections
2225 independent reflections
1909 reflections with $I > 2\sigma(I)$
R_{int} = 0.028

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.109
S = 1.08
2225 reflections
167 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.40 e Å^{-3}
$\Delta\rho_{min}$ = −0.42 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C14—H14A···O1^{i}	0.97	2.64	3.563 (3)	158

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

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CV5184).

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supporting information

Acta Cryst. (2011). E**67**, o3344 [https://doi.org/10.1107/S1600536811047799]

10-Ethyl-10*H*-phenothiazine-3-carbaldehyde

Dao-Hui Yu, Jian-Qing Wang, Lin Kong and Zhao-di Liu

S1. Comment

The title compound (I) is often used as intermediate in the synthesis of organic compounds with optical properties (Li *et al.*, 2009*a, b*). Herewith we present its crystal structure.

In (I) (Fig.1), two benzene rings form the dihedral angles of 10.0 (8)° and 12.0 (8)°, respectively, with the thiomorpholine mean plane. The folding of the molecule is characterized by dihedral angle formed by two benzene rings, which is 21.1 (1) °. In the related compounds, 10-ethylphenothiazine (Chu *et al.*, 1975) and 10-ethyl-3-nitrophenothiazine (Hdii *et al.*, 1998), the corresponding dihedral angle is 44.9 (1) and 22.8 (1) °, respectively, showing that any substitution added to benzene ring flattens the tricycle. This tendency also observed in the structure of (*E*)-3-(10-ethyl-10*H*-phenothiazin-3-yl)acrylic acid (Li *et al.*, 2009*b*), where these dihedral angles in two independent molecules are 25.3 (9) ° and 29.8 (8) °, respectively. The ethyl group in (I) is almost orthogonal to the thiazine ring, the torsion angle C6–N1—Cl4–C15 is 85.6 (1)°. While in 10-ethylphenothiazine (Chu *et al.*, 1975), the corresponding angle is 146.1 (4) °, and in 10-ethyl-3-nitrophenothiazine (Hon *et al.*, 1998) this angle is -84.9 (2)°. The aldehyde group is almost coplanar with its attached phenyl ring, the torsion angle C12–C11–C13–O1 being -2.59 °.

In the crystal, weak intermolecular C—H···O hydrogen bonds (Table 1) link molecules into chains along [001]. The crystal packing exhibits $\pi\cdots\pi$ interactions with the distance of 3.801 (5) Å between the centroids of benzene rings from the neighbouring molecules.

S2. Experimental

NaH (4.08 g, 0.17 mol) and DMF (5 ml) were added to a three-necked flask equipped with a magnetic stirrer and a reflux condenser, and then phenothiazine (20.0 g, 0.1 mol), DMF (10 ml) were added dropwisely (about 30 min), refluxed for another 20 min. Then C_2H_5Br (17 ml) was dropped into the mixture and refluxed for 2 h with TLC detection. The pH of the solution was adjusted to acidic with hydrochloric acid then extracted with 500 ml of ethyl acetate, washed three times with distilled water, and dried with anhydrous magnesium sulfate. It was then filtered and concentrated to produce 18.2 g needle crystals in 80% yield.

N-ethyl-phenothiazine (11.35 g, 0.05 mol) and DMF (39 ml) were added to a three-necked flask in ice equipped with a magnetic stirrer and a reflux condenser, then $POCl_3$ (92 ml) was added dropwisely (about 30 min), the mixture was refluxed for 1 h. Then the mixture was poured into ice to get light yellow solid. The pH of the mixture was adjusted to neutral with NaOH and extracted three times with 150 ml of ethyl acetate. The organic layer was washed with distilled water and then saturated brine. The organic extracts were dried with anhydrous magnesium sulfate. The solvent was removed *in vacuo*. The residue was purified by column chromatography on silica gel with petroleum ether as eluent to give 7.6 g titled compound as a yellow solid in 60% yield. ^{1}H NMR (400 MHz, $CDCl_3$) 7.569 (s, 1H), 7.157 (t, 1H), 7.097 (d, J = 7.8 Hz, 1H), 6.912 (d, J = 6.4 Hz, 1H), 6.896 (d, J = 6.2 Hz, 1H), 3.974 (q, 2H), 1.447 (t,3*H*). ^{13}C NMR (100 MHz). 89, 42.47, 114.40, 115.58, 123.30, 123.56, 124.51, 127.49, 127.59, 128.25, 130.16, 131.04, 189.98.

S3. Refinement

The methine H atoms was located on a difference map and isotropically refined. All the rest H atoms were placed in geometrically idealized positions (C—H = 0.93 - 0.97 Å) and constrained to ride on their parent atoms, with U_{iso}(H) = 1.2-1.5 U_{eq}(C).

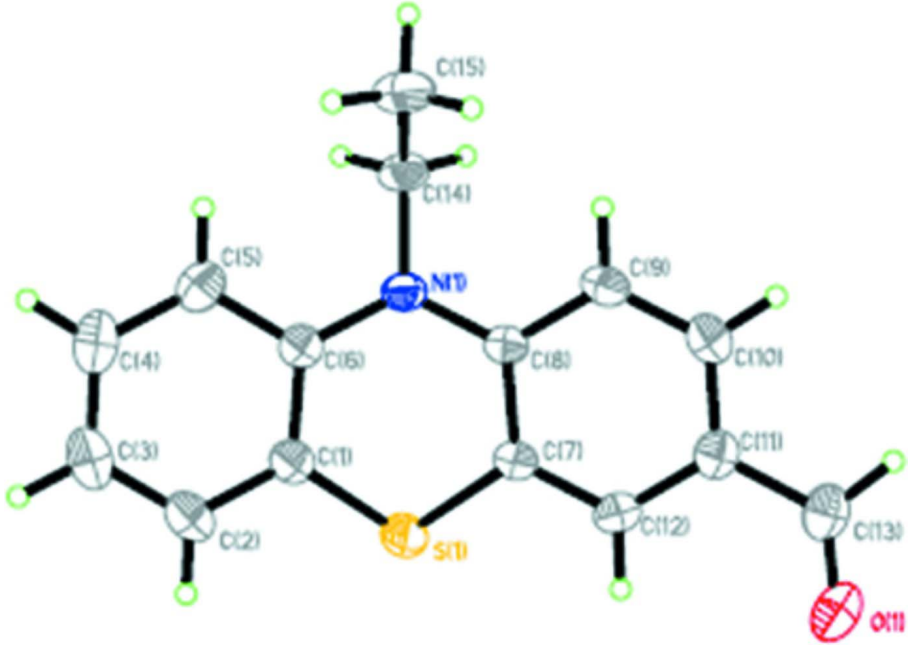

Figure 1

The molecular structure of the title molecule with 50% probability displacement ellipsoids.

10-Ethyl-10*H*-phenothiazine-3-carbaldehyde

Crystal data

$C_{15}H_{13}NOS$
M_r = 255.32
Orthorhombic, *Pbca*
Hall symbol: -P 2ac 2ab
a = 8.0867 (1) Å
b = 15.3271 (3) Å
c = 20.3369 (4) Å
V = 2520.67 (8) Å^3
Z = 8
F(000) = 1072
D_x = 1.346 Mg m^{-3}
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 7387 reflections
θ = 2.7–27.1°
μ = 0.24 mm^{-1}
T = 296 K
Needle, yellow
0.20 × 0.10 × 0.10 mm

Data collection

Bruker SMART APEX diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
phi and *ω* scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.953, T_{max} = 0.976
17210 measured reflections
2225 independent reflections
1909 reflections with $I > 2\sigma(I)$
R_{int} = 0.028
θ_{max} = 25.0°, θ_{min} = 2.0°
h = −9→9
k = −17→18
l = −22→24

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.109$
$S = 1.08$
2225 reflections
167 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.048P)^2 + 1.0328P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.030$
$\Delta\rho_{max} = 0.40$ e Å^{-3}
$\Delta\rho_{min} = -0.42$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0062 (8)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness 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 threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.24520 (8)	0.67345 (3)	0.06193 (3)	0.0654 (2)
C6	0.0560 (2)	0.57828 (11)	0.14810 (8)	0.0434 (4)
N1	0.13723 (18)	0.50268 (9)	0.12517 (7)	0.0460 (4)
C1	0.0870 (2)	0.66009 (11)	0.12020 (9)	0.0473 (4)
C8	0.1974 (2)	0.49538 (11)	0.06126 (8)	0.0415 (4)
O1	0.4535 (2)	0.53800 (12)	−0.16387 (7)	0.0733 (4)
C12	0.3099 (2)	0.56256 (12)	−0.03694 (9)	0.0480 (4)
H12	0.3371	0.6129	−0.0601	0.058*
C11	0.3359 (2)	0.48174 (13)	−0.06591 (8)	0.0488 (4)
C14	0.1335 (2)	0.42393 (12)	0.16677 (10)	0.0541 (5)
H14A	0.1398	0.4419	0.2124	0.065*
H14B	0.2313	0.3894	0.1574	0.065*
C7	0.2448 (2)	0.56995 (11)	0.02515 (9)	0.0434 (4)
C2	0.0052 (3)	0.73369 (13)	0.14222 (10)	0.0583 (5)
H2	0.0247	0.7871	0.1219	0.070*
C5	−0.0556 (2)	0.57511 (13)	0.20039 (10)	0.0554 (5)
H5	−0.0786	0.5219	0.2204	0.066*
C13	0.4132 (3)	0.47568 (17)	−0.13082 (10)	0.0598 (5)
C9	0.2197 (2)	0.41474 (12)	0.03065 (10)	0.0506 (5)
H9	0.1869	0.3643	0.0525	0.061*
C10	0.2888 (2)	0.40786 (13)	−0.03095 (10)	0.0540 (5)
H10	0.3043	0.3530	−0.0495	0.065*
C15	−0.0183 (3)	0.36605 (15)	0.15823 (12)	0.0694 (6)

H15A	−0.1153	0.3976	0.1714	0.104*
H15B	−0.0068	0.3148	0.1850	0.104*
H15C	−0.0282	0.3492	0.1129	0.104*
C4	−0.1325 (3)	0.64997 (17)	0.22290 (11)	0.0677 (6)
H4	−0.2044	0.6465	0.2585	0.081*
C3	−0.1046 (3)	0.72895 (16)	0.19376 (11)	0.0679 (6)
H3	−0.1590	0.7787	0.2085	0.081*
H13	0.429 (4)	0.4148 (18)	−0.1460 (14)	0.102*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0860 (4)	0.0370 (3)	0.0734 (4)	−0.0115 (2)	0.0224 (3)	−0.0011 (2)
C6	0.0406 (9)	0.0475 (10)	0.0421 (9)	0.0007 (7)	−0.0072 (7)	0.0005 (7)
N1	0.0503 (8)	0.0407 (8)	0.0471 (8)	0.0021 (6)	0.0024 (7)	0.0102 (6)
C1	0.0509 (10)	0.0449 (10)	0.0461 (10)	0.0015 (8)	−0.0072 (8)	−0.0011 (8)
C8	0.0400 (8)	0.0382 (9)	0.0464 (9)	−0.0009 (7)	−0.0030 (7)	0.0056 (7)
O1	0.0770 (10)	0.0945 (12)	0.0485 (8)	−0.0086 (9)	0.0078 (7)	−0.0013 (8)
C12	0.0490 (10)	0.0496 (10)	0.0455 (10)	−0.0053 (8)	−0.0021 (8)	0.0086 (8)
C11	0.0427 (10)	0.0585 (12)	0.0453 (10)	0.0012 (8)	−0.0057 (7)	−0.0019 (8)
C14	0.0547 (11)	0.0518 (11)	0.0558 (11)	0.0035 (9)	−0.0008 (9)	0.0213 (8)
C7	0.0452 (10)	0.0373 (9)	0.0476 (10)	−0.0012 (7)	−0.0013 (8)	0.0041 (7)
C2	0.0629 (12)	0.0484 (11)	0.0635 (12)	0.0078 (9)	−0.0119 (10)	−0.0070 (9)
C5	0.0503 (10)	0.0677 (13)	0.0481 (10)	−0.0041 (9)	−0.0001 (9)	0.0016 (9)
C13	0.0505 (11)	0.0781 (15)	0.0508 (11)	0.0003 (11)	−0.0066 (9)	−0.0080 (11)
C9	0.0541 (11)	0.0371 (9)	0.0607 (12)	−0.0007 (8)	0.0000 (9)	0.0055 (8)
C10	0.0545 (11)	0.0474 (11)	0.0600 (12)	0.0036 (9)	−0.0063 (9)	−0.0085 (9)
C15	0.0670 (13)	0.0598 (13)	0.0813 (15)	−0.0072 (10)	0.0038 (11)	0.0263 (11)
C4	0.0539 (12)	0.0902 (17)	0.0589 (12)	0.0050 (11)	0.0047 (10)	−0.0172 (12)
C3	0.0597 (12)	0.0707 (14)	0.0732 (14)	0.0152 (11)	−0.0059 (11)	−0.0206 (12)

Geometric parameters (Å, º)

S1—C7	1.7538 (18)	C14—H14A	0.9700
S1—C1	1.756 (2)	C14—H14B	0.9700
C6—C5	1.396 (3)	C2—C3	1.376 (3)
C6—C1	1.399 (2)	C2—H2	0.9300
C6—N1	1.411 (2)	C5—C4	1.383 (3)
N1—C8	1.392 (2)	C5—H5	0.9300
N1—C14	1.474 (2)	C13—H13	0.99 (3)
C1—C2	1.382 (3)	C9—C10	1.376 (3)
C8—C9	1.396 (3)	C9—H9	0.9300
C8—C7	1.412 (2)	C10—H10	0.9300
O1—C13	1.212 (3)	C15—H15A	0.9600
C12—C7	1.372 (3)	C15—H15B	0.9600
C12—C11	1.388 (3)	C15—H15C	0.9600
C12—H12	0.9300	C4—C3	1.366 (3)
C11—C10	1.390 (3)	C4—H4	0.9300

C11—C13	1.463 (3)	C3—H3	0.9300
C14—C15	1.524 (3)		

C7—S1—C1	100.44 (8)	C3—C2—C1	120.8 (2)
C5—C6—C1	117.13 (17)	C3—C2—H2	119.6
C5—C6—N1	121.61 (16)	C1—C2—H2	119.6
C1—C6—N1	121.24 (16)	C4—C5—C6	120.93 (19)
C8—N1—C6	122.48 (14)	C4—C5—H5	119.5
C8—N1—C14	118.49 (15)	C6—C5—H5	119.5
C6—N1—C14	118.24 (15)	O1—C13—C11	124.4 (2)
C2—C1—C6	120.97 (18)	O1—C13—H13	122.3 (17)
C2—C1—S1	118.17 (15)	C11—C13—H13	113.3 (17)
C6—C1—S1	120.58 (14)	C10—C9—C8	121.78 (17)
N1—C8—C9	122.20 (15)	C10—C9—H9	119.1
N1—C8—C7	121.03 (15)	C8—C9—H9	119.1
C9—C8—C7	116.73 (16)	C9—C10—C11	120.97 (18)
C7—C12—C11	121.50 (17)	C9—C10—H10	119.5
C7—C12—H12	119.3	C11—C10—H10	119.5
C11—C12—H12	119.3	C14—C15—H15A	109.5
C12—C11—C10	117.92 (17)	C14—C15—H15B	109.5
C12—C11—C13	120.29 (19)	H15A—C15—H15B	109.5
C10—C11—C13	121.78 (19)	C14—C15—H15C	109.5
N1—C14—C15	115.30 (16)	H15A—C15—H15C	109.5
N1—C14—H14A	108.4	H15B—C15—H15C	109.5
C15—C14—H14A	108.4	C3—C4—C5	121.2 (2)
N1—C14—H14B	108.4	C3—C4—H4	119.4
C15—C14—H14B	108.4	C5—C4—H4	119.4
H14A—C14—H14B	107.5	C4—C3—C2	118.9 (2)
C12—C7—C8	121.06 (16)	C4—C3—H3	120.5
C12—C7—S1	117.80 (13)	C2—C3—H3	120.5
C8—C7—S1	120.72 (14)		

C5—C6—N1—C8	155.35 (17)	N1—C8—C7—C12	177.55 (16)
C1—C6—N1—C8	−26.1 (2)	C9—C8—C7—C12	−0.1 (3)
C5—C6—N1—C14	−14.3 (2)	N1—C8—C7—S1	5.2 (2)
C1—C6—N1—C14	164.21 (16)	C9—C8—C7—S1	−172.52 (13)
C5—C6—C1—C2	−2.4 (3)	C1—S1—C7—C12	157.90 (15)
N1—C6—C1—C2	179.03 (16)	C1—S1—C7—C8	−29.47 (16)
C5—C6—C1—S1	171.37 (14)	C6—C1—C2—C3	2.3 (3)
N1—C6—C1—S1	−7.2 (2)	S1—C1—C2—C3	−171.58 (16)
C7—S1—C1—C2	−155.68 (15)	C1—C6—C5—C4	0.5 (3)
C7—S1—C1—C6	30.42 (16)	N1—C6—C5—C4	179.09 (17)
C6—N1—C8—C9	−155.31 (17)	C12—C11—C13—O1	−2.6 (3)
C14—N1—C8—C9	14.4 (3)	C10—C11—C13—O1	178.44 (19)
C6—N1—C8—C7	27.1 (2)	N1—C8—C9—C10	−175.86 (17)
C14—N1—C8—C7	−163.21 (16)	C7—C8—C9—C10	1.8 (3)
C7—C12—C11—C10	2.1 (3)	C8—C9—C10—C11	−1.5 (3)
C7—C12—C11—C13	−176.89 (17)	C12—C11—C10—C9	−0.5 (3)

C8—N1—C14—C15	−84.5 (2)	C13—C11—C10—C9	178.53 (18)
C6—N1—C14—C15	85.6 (2)	C6—C5—C4—C3	1.5 (3)
C11—C12—C7—C8	−1.8 (3)	C5—C4—C3—C2	−1.6 (3)
C11—C12—C7—S1	170.76 (14)	C1—C2—C3—C4	−0.3 (3)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C14—H14*A*···O1^{i}	0.97	2.64	3.563 (3)	158

Symmetry code: (i) −*x*+1/2, −*y*+1, *z*+1/2.