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10-[(4-Nitrophenyl)ethynyl]-10*H*-phenothiazine

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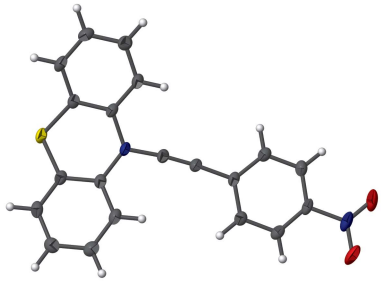
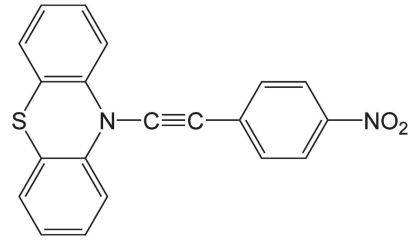
Structural data: full structural data are available from iucrdata.iucr.org

The title compound, $C_{20}H_{12}N_2OS$, is a 10-ethynyl-10*H*-phenothiazine derivative. The phenothiazine unit has a butterfly shape, where the folding angle between the two benzene rings is 153.87 (7)°, which is almost as in other reported phenothiazine derivatives. The dihedral angle between the mean plane including the C atoms bonded to the phenothiazine N atom and the benzene ring of the nitrobenzene group is 10.34 (5)°. The near planar geometry of the molecule is reasonably explained by intramolecular charge-transfer interactions.

3D view



Chemical scheme



Structure description

Phenothiazines are known to be good electron donors and have attracted interest from the point of view of photo-induced electron transfer or magnetism (Sun *et al.*, 2004; Okamoto *et al.*, 2004; Okada *et al.*, 1996). A phenothiazine derivative, 10-(prop-1-yn-1-yl)-10*H*-phenothiazine, which incorporates an ynamine moiety, is well known as the first reported ynamine compound (Zaugg *et al.*, 1958), and its structure has already been studied (Umezono & Okuno, 2012). Other structures of some related derivatives have also been analysed (Umezono & Okuno, 2013; Umezono *et al.*, 2013).

In the title compound, the phenothiazine moiety has a butterfly structure, as shown in Fig. 1, in which the dihedral angle between the two benzene rings (the C1–C6 and C7–C12 mean planes) is 153.87 (7)°. The central six-membered ring has a boat conformation, in which the S1···N1 separation is 3.0565 (14) Å. The structure around the phenothiazine nitrogen atom is pyramidal, with atom N1 located 0.1271 (16) Å above the C1/C12/C13 plane. The dihedral angle between the C1/C12/C13 plane and the C15–C20 benzene ring is 10.34 (5)°. The molecule is thus almost planar, and this feature is reasonably explained by intramolecular charge-transfer interactions between phenothiazine and nitrophenyl units.

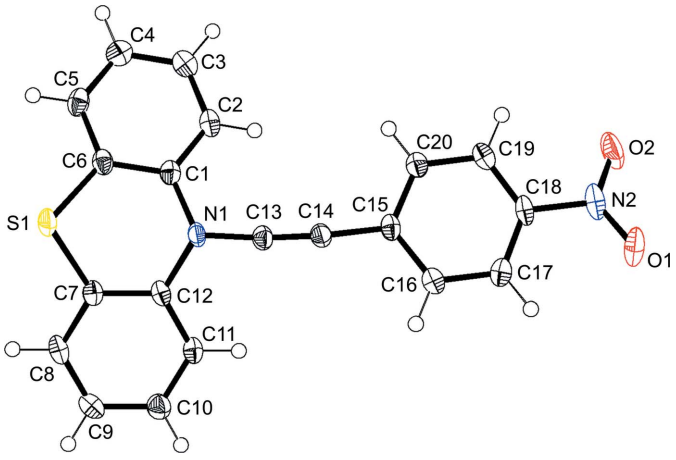


Figure 1
ORTEP view of the title compound with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

Synthesis and crystallization

Single crystals suitable for X-ray analysis were obtained by concentration of a dichloromethane solution. The title compound was prepared through the Sonogashira-coupling reaction between 1-iodo-4-nitrobenzene and 10-ethynyl-10*H*-phenothiazine, as follows: to a solution of 1-iodo-4-nitrobenzene (0.33 g, 1.3 mmol) and 10-ethynyl-10*H*-phenothiazine (0.30 g, 1.3 mmol) in 13 ml of THF and triethylamine (1:1 *v*/*v*), tetrakis(triphenylphosphine)palladium(0) (0.093 g, 0.080 mmol) and copper(I) iodide (8.0 mg, 0.040 mmol) were added. The solution was stirred for 20 h and filtrated. The filtrate was concentrated and the residue was extracted with $CHCl_3$. The organic layer was washed with water, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by gel permeation chromatography to give 32 mg (6.9% yield) of the title compound, as pale-red crystals. ^{1}H NMR ($CDCl_3$): δ = 8.21 (*d*, *J* = 9.0 Hz, 0.8 Hz, 2H), 7.58 (*d*, *J* = 9.0 Hz, 2H), 7.48 (*d*, *J* = 7.3 Hz, 2H), 7.26 (*t*, *J* = 7.3 Hz, 2H), 7.17 (*d*, *J* = 6.5 Hz, 2H), 7.10 (*t*, *J* = 6.5 Hz, 2H).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1.

Funding information

This work was supported by the Adaptable and Seamless Technology Transfer Program through Target-driven R&D from the Japan Science and Technology Agency (JST).

Table 1
Experimental details.

Crystal data	
Chemical formula	$C_{20}H_{12}N_2O_2S$
M_r	344.39
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	93
a, *b*, *c* (Å)	8.1891 (15), 8.2417 (15), 12.813 (3)
α, β, γ (°)	81.632 (9), 81.394 (10), 66.649 (8)
V (Å^3)	781.4 (3)
Z	2
Radiation type	Mo *K*α
μ (mm^{-1})	0.22
Crystal size (mm)	0.15 × 0.12 × 0.05
Data collection	
Diffractometer	Rigaku Saturn724+
Absorption correction	Numerical (*NUMABS*; Rigaku, 1999)
T_{min}, T_{max}	0.977, 0.988
No. of measured, independent and observed [$F^2 > 2.0\sigma(F^2)$] reflections	5406, 2701, 2234
R_{int}	0.021
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.595
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.037, 0.100, 1.09
No. of reflections	2701
No. of parameters	226
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.24, −0.22

Computer programs: *CrystalClear* (Rigaku, 2008), *SHELXD2013/2* (Sheldrick, 2008), *SHELXL2014/7* (Sheldrick, 2015), *ORTEP-3 for Windows* (Farrugia, 2012) and *CrystalStructure* (Rigaku, 2019).

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full crystallographic data

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Crystal data

$C_{20}H_{12}N_2O_2S$
M_r = 344.39
Triclinic, $P\overline{1}$
a = 8.1891 (15) Å
b = 8.2417 (15) Å
c = 12.813 (3) Å
α = 81.632 (9)°
β = 81.394 (10)°
γ = 66.649 (8)°
V = 781.4 (3) Å^3
Z = 2
$F(000)$ = 356.00
D_x = 1.464 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71075 Å
Cell parameters from 2498 reflections
θ = 1.6–31.3°
μ = 0.22 mm^{-1}
T = 93 K
Block, red
0.15 × 0.12 × 0.05 mm

Data collection

Rigaku Saturn724+ diffractometer
Detector resolution: 7.111 pixels mm^{-1}
ω scans
Absorption correction: numerical (NUMABS; Rigaku, 1999)
T_{min} = 0.977, T_{max} = 0.988
5406 measured reflections
2701 independent reflections
2234 reflections with $F^2 > 2.0\sigma(F^2)$
R_{int} = 0.021
θ_{max} = 25.0°, θ_{min} = 1.6°
h = −9→9
k = −9→9
l = −11→15

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.100
S = 1.09
2701 reflections
226 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-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0537P)^2 + 0.2098P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.24 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-3}

Special details

Refinement. The C-bound H atoms were placed in ideal positions and were refined as riding on their parent C atoms. U_{iso}(H) values of the H atoms were set at 1.2U_{eq}(parent atom).

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

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	−0.18967 (6)	1.42062 (6)	0.10364 (4)	0.02912 (16)
O1	0.67949 (19)	−0.06179 (18)	0.41540 (13)	0.0439 (4)
O2	0.5066 (2)	−0.10830 (18)	0.32062 (13)	0.0465 (4)
N1	−0.02003 (19)	1.04512 (18)	0.21162 (11)	0.0224 (3)
N2	0.5590 (2)	−0.0089 (2)	0.35670 (14)	0.0341 (4)
C1	−0.1331 (2)	1.0636 (2)	0.13171 (13)	0.0211 (4)
C2	−0.1530 (2)	0.9172 (2)	0.10350 (14)	0.0256 (4)
H2	−0.0962	0.8040	0.1403	0.031*
C3	−0.2544 (2)	0.9333 (3)	0.02236 (15)	0.0283 (4)
H3	−0.2634	0.8309	0.0022	0.034*
C4	−0.3429 (2)	1.0989 (2)	−0.02954 (15)	0.0279 (4)
H4	−0.4134	1.1107	−0.0849	0.034*
C5	−0.3276 (2)	1.2470 (2)	0.00017 (14)	0.0262 (4)
H5	−0.3903	1.3608	−0.0341	0.031*
C6	−0.2220 (2)	1.2315 (2)	0.07908 (14)	0.0231 (4)
C7	−0.1384 (2)	1.3617 (2)	0.23645 (14)	0.0224 (4)
C8	−0.1760 (2)	1.4970 (2)	0.30086 (15)	0.0263 (4)
H8	−0.2378	1.6169	0.2748	0.032*
C9	−0.1241 (2)	1.4584 (2)	0.40224 (15)	0.0274 (4)
H9	−0.1490	1.5515	0.4454	0.033*
C10	−0.0355 (2)	1.2829 (2)	0.44086 (15)	0.0283 (4)
H10	0.0026	1.2558	0.5100	0.034*
C11	−0.0028 (2)	1.1470 (2)	0.37808 (14)	0.0244 (4)
H11	0.0552	1.0270	0.4053	0.029*
C12	−0.0541 (2)	1.1850 (2)	0.27614 (14)	0.0216 (4)
C13	0.0882 (2)	0.8781 (2)	0.24405 (13)	0.0226 (4)
C14	0.1838 (2)	0.7265 (2)	0.26460 (14)	0.0234 (4)
C15	0.2884 (2)	0.5416 (2)	0.28480 (13)	0.0217 (4)
C16	0.4081 (2)	0.4783 (2)	0.36260 (14)	0.0255 (4)
H16	0.4267	0.5599	0.4001	0.031*
C17	0.4991 (2)	0.2982 (2)	0.38510 (15)	0.0268 (4)
H17	0.5802	0.2548	0.4379	0.032*
C18	0.4703 (2)	0.1825 (2)	0.32941 (15)	0.0251 (4)
C19	0.3582 (2)	0.2398 (2)	0.24936 (15)	0.0255 (4)
H19	0.3436	0.1570	0.2110	0.031*
C20	0.2681 (2)	0.4202 (2)	0.22653 (14)	0.0244 (4)
H20	0.1919	0.4623	0.1711	0.029*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0395 (3)	0.0158 (2)	0.0288 (3)	−0.0084 (2)	−0.0061 (2)	0.00428 (18)
O1	0.0330 (8)	0.0244 (7)	0.0613 (10)	0.0006 (6)	−0.0119 (7)	0.0094 (7)
O2	0.0478 (9)	0.0152 (7)	0.0734 (12)	−0.0077 (6)	−0.0084 (8)	−0.0054 (7)
N1	0.0264 (8)	0.0130 (7)	0.0236 (8)	−0.0034 (6)	−0.0026 (6)	−0.0003 (6)

N2	0.0272 (9)	0.0167 (8)	0.0481 (11)	−0.0020 (7)	0.0046 (8)	0.0011 (8)
C1	0.0190 (8)	0.0194 (9)	0.0211 (9)	−0.0052 (7)	0.0021 (7)	−0.0009 (7)
C2	0.0245 (9)	0.0182 (9)	0.0299 (10)	−0.0057 (7)	0.0014 (8)	−0.0004 (7)
C3	0.0262 (9)	0.0263 (10)	0.0327 (10)	−0.0113 (8)	0.0024 (8)	−0.0056 (8)
C4	0.0221 (9)	0.0333 (10)	0.0272 (10)	−0.0098 (8)	−0.0005 (7)	−0.0033 (8)
C5	0.0213 (9)	0.0238 (9)	0.0260 (10)	−0.0033 (8)	0.0007 (7)	0.0026 (7)
C6	0.0235 (9)	0.0187 (9)	0.0228 (9)	−0.0055 (7)	0.0023 (7)	−0.0012 (7)
C7	0.0221 (9)	0.0183 (9)	0.0251 (9)	−0.0074 (7)	−0.0011 (7)	0.0007 (7)
C8	0.0253 (9)	0.0152 (9)	0.0356 (11)	−0.0067 (7)	0.0013 (8)	−0.0013 (7)
C9	0.0298 (10)	0.0238 (10)	0.0314 (10)	−0.0131 (8)	0.0025 (8)	−0.0083 (8)
C10	0.0328 (10)	0.0252 (10)	0.0274 (10)	−0.0122 (8)	−0.0028 (8)	−0.0012 (8)
C11	0.0261 (9)	0.0174 (9)	0.0268 (10)	−0.0068 (7)	−0.0019 (7)	0.0016 (7)
C12	0.0207 (8)	0.0155 (8)	0.0259 (9)	−0.0054 (7)	0.0016 (7)	−0.0024 (7)
C13	0.0257 (9)	0.0181 (9)	0.0212 (9)	−0.0068 (8)	−0.0008 (7)	0.0002 (7)
C14	0.0270 (9)	0.0183 (9)	0.0228 (9)	−0.0067 (8)	−0.0022 (7)	−0.0018 (7)
C15	0.0213 (9)	0.0166 (8)	0.0230 (9)	−0.0052 (7)	0.0025 (7)	0.0004 (7)
C16	0.0257 (9)	0.0203 (9)	0.0290 (10)	−0.0074 (8)	−0.0005 (8)	−0.0036 (7)
C17	0.0222 (9)	0.0230 (9)	0.0302 (10)	−0.0045 (8)	−0.0034 (8)	0.0016 (8)
C18	0.0205 (9)	0.0142 (9)	0.0338 (10)	−0.0021 (7)	0.0026 (8)	−0.0003 (7)
C19	0.0245 (9)	0.0194 (9)	0.0309 (10)	−0.0073 (8)	0.0030 (8)	−0.0060 (7)
C20	0.0241 (9)	0.0209 (9)	0.0256 (9)	−0.0066 (7)	−0.0007 (7)	−0.0020 (7)

Geometric parameters (Å, º)

S1—C6	1.7591 (19)	C8—C9	1.381 (3)
S1—C7	1.7661 (19)	C8—H8	0.9500
O1—N2	1.231 (2)	C9—C10	1.390 (3)
O2—N2	1.232 (2)	C9—H9	0.9500
N1—C13	1.353 (2)	C10—C11	1.390 (3)
N1—C12	1.430 (2)	C10—H10	0.9500
N1—C1	1.434 (2)	C11—C12	1.386 (3)
N2—C18	1.464 (2)	C11—H11	0.9500
C1—C2	1.383 (3)	C13—C14	1.198 (2)
C1—C6	1.406 (2)	C14—C15	1.428 (2)
C2—C3	1.385 (3)	C15—C16	1.401 (3)
C2—H2	0.9500	C15—C20	1.405 (2)
C3—C4	1.388 (3)	C16—C17	1.380 (2)
C3—H3	0.9500	C16—H16	0.9500
C4—C5	1.386 (3)	C17—C18	1.379 (3)
C4—H4	0.9500	C17—H17	0.9500
C5—C6	1.386 (3)	C18—C19	1.384 (3)
C5—H5	0.9500	C19—C20	1.382 (2)
C7—C8	1.392 (2)	C19—H19	0.9500
C7—C12	1.396 (2)	C20—H20	0.9500
C6—S1—C7	100.18 (8)	C8—C9—H9	120.1
C13—N1—C12	118.98 (15)	C10—C9—H9	120.1
C13—N1—C1	116.86 (15)	C9—C10—C11	119.86 (17)

C12—N1—C1	121.74 (13)	C9—C10—H10	120.1
O1—N2—O2	123.51 (16)	C11—C10—H10	120.1
O1—N2—C18	118.62 (17)	C12—C11—C10	120.61 (16)
O2—N2—C18	117.86 (17)	C12—C11—H11	119.7
C2—C1—C6	119.15 (17)	C10—C11—H11	119.7
C2—C1—N1	120.85 (15)	C11—C12—C7	119.39 (16)
C6—C1—N1	119.98 (16)	C11—C12—N1	120.54 (15)
C1—C2—C3	120.95 (17)	C7—C12—N1	120.07 (16)
C1—C2—H2	119.5	C14—C13—N1	174.55 (19)
C3—C2—H2	119.5	C13—C14—C15	175.25 (19)
C2—C3—C4	120.04 (18)	C16—C15—C20	119.27 (15)
C2—C3—H3	120.0	C16—C15—C14	121.62 (16)
C4—C3—H3	120.0	C20—C15—C14	119.10 (16)
C5—C4—C3	119.34 (18)	C17—C16—C15	120.40 (17)
C5—C4—H4	120.3	C17—C16—H16	119.8
C3—C4—H4	120.3	C15—C16—H16	119.8
C4—C5—C6	121.03 (16)	C18—C17—C16	118.75 (17)
C4—C5—H5	119.5	C18—C17—H17	120.6
C6—C5—H5	119.5	C16—C17—H17	120.6
C5—C6—C1	119.45 (17)	C17—C18—C19	122.61 (16)
C5—C6—S1	118.75 (13)	C17—C18—N2	119.09 (17)
C1—C6—S1	121.63 (14)	C19—C18—N2	118.29 (17)
C8—C7—C12	119.73 (17)	C20—C19—C18	118.49 (17)
C8—C7—S1	118.41 (13)	C20—C19—H19	120.8
C12—C7—S1	121.78 (14)	C18—C19—H19	120.8
C9—C8—C7	120.60 (16)	C19—C20—C15	120.37 (17)
C9—C8—H8	119.7	C19—C20—H20	119.8
C7—C8—H8	119.7	C15—C20—H20	119.8
C8—C9—C10	119.75 (17)		

C13—N1—C1—C2	11.1 (2)	C10—C11—C12—C7	0.3 (3)
C12—N1—C1—C2	−151.03 (16)	C10—C11—C12—N1	179.89 (16)
C13—N1—C1—C6	−167.32 (15)	C8—C7—C12—C11	−2.3 (3)
C12—N1—C1—C6	30.6 (2)	S1—C7—C12—C11	174.37 (13)
C6—C1—C2—C3	2.0 (3)	C8—C7—C12—N1	178.07 (16)
N1—C1—C2—C3	−176.47 (15)	S1—C7—C12—N1	−5.2 (2)
C1—C2—C3—C4	−2.2 (3)	C13—N1—C12—C11	−10.9 (2)
C2—C3—C4—C5	0.5 (3)	C1—N1—C12—C11	150.89 (16)
C3—C4—C5—C6	1.5 (3)	C13—N1—C12—C7	168.71 (15)
C4—C5—C6—C1	−1.7 (3)	C1—N1—C12—C7	−29.5 (2)
C4—C5—C6—S1	173.52 (13)	C20—C15—C16—C17	−2.9 (3)
C2—C1—C6—C5	0.0 (2)	C14—C15—C16—C17	175.91 (16)
N1—C1—C6—C5	178.45 (15)	C15—C16—C17—C18	0.2 (3)
C2—C1—C6—S1	−175.11 (13)	C16—C17—C18—C19	2.3 (3)
N1—C1—C6—S1	3.3 (2)	C16—C17—C18—N2	−176.74 (15)
C7—S1—C6—C5	155.97 (14)	O1—N2—C18—C17	−12.3 (2)
C7—S1—C6—C1	−28.87 (16)	O2—N2—C18—C17	166.68 (17)
C6—S1—C7—C8	−153.28 (14)	O1—N2—C18—C19	168.69 (17)

C6—S1—C7—C12	29.96 (16)	O2—N2—C18—C19	−12.4 (2)
C12—C7—C8—C9	2.6 (3)	C17—C18—C19—C20	−1.8 (3)
S1—C7—C8—C9	−174.25 (14)	N2—C18—C19—C20	177.16 (15)
C7—C8—C9—C10	−0.7 (3)	C18—C19—C20—C15	−1.0 (2)
C8—C9—C10—C11	−1.3 (3)	C16—C15—C20—C19	3.3 (3)
C9—C10—C11—C12	1.5 (3)	C14—C15—C20—C19	−175.53 (16)