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(*E*)-*N*-(3,4-Dimethylphenyl)-1-[5-(phenylethynyl)-thiophen-2-yl]methanimine

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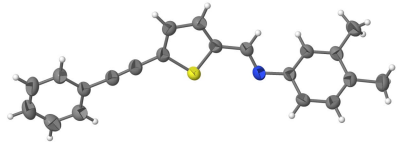
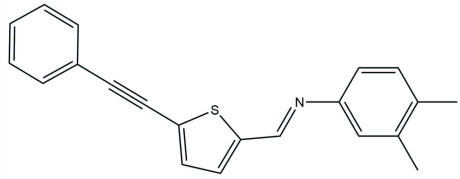
The title compound, $C_{21}H_{17}NS$, was synthesized *via* the reaction of 5-(2-phenyleth-1-ynyl)thiophene-2-carbaldehyde and 3,4-dimethylaniline using ammonium bifluoride (NH_4HF_2) as an acid catalyst in methanol. The molecule has three aryl rings: a phenyl (A), a thiophene (B), and a dimethylbenzene ring (C). The dihedral angles between the mean planes defined by these individual rings are 14.88 (6)° for A/B and 43.93 (4)° for B/C.

3D view



Chemical scheme



Structure description

Imine formation between thiophenecarbaldehydes and anilines are prevalent in the chemical literature. Not only are they of interest as potential drug candidates, as anti-bacterial and/or antifungal agents (Shanty *et al.*, 2017), but they are also interesting ligands (Belkhiria *et al.*, 2018). Our interests are in quinoxaline formation. The synthetic method using ammonium bifluoride as an acid catalyst outlined by Lassagne and co-workers (Lassagne *et al.*, 2015) has proven to be a clean high-yielding method for the synthesis quinoxalines and in addition for the production of imines. This reaction is proof for the clean high-yield production of imines as well.

In the molecule (Fig. 1), all bond lengths and angles are within expected values. Molecules associated by inversion have intermolecular contacts between the imine nitrogen (N1) and a hydrogen on a neighboring methyl group (C20). The overall packing (Fig. 2) resembles the classic herringbone pattern.

Synthesis and crystallization

To a 50 ml Erlenmeyer flask, 1.00 mmol of 5-(2-phenyleth-1-ynyl)thiophene-2-carbaldehyde (212 mg) was stirred into 10 ml of 2.5 × 10^{-3} mol l^{-1} solution of NH_4HF_2 in methanol. After the solid aldehyde had dissolved, 1.00 mmol of 3,4-dimethylaniline (121 mg) was added. Within the first 5 min, the amine also dissolved; however, within an

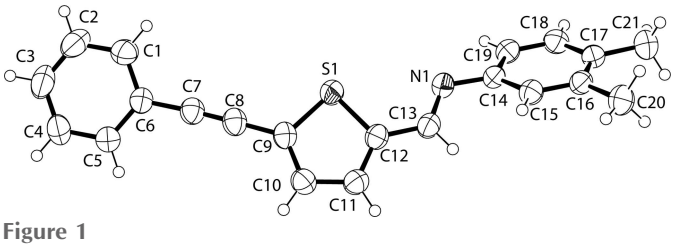


Figure 1
ORTEP view of the title compound, with 50% probability displacement ellipsoids.

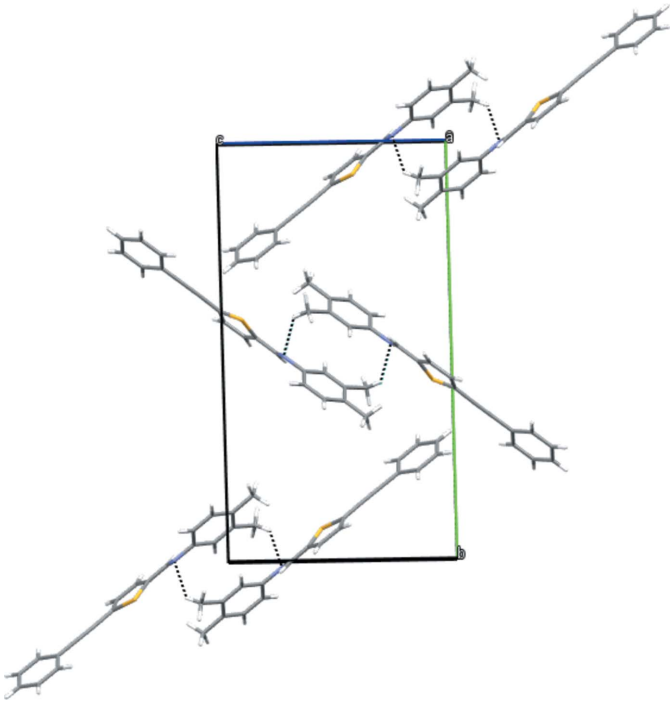


Figure 2
A view along [100] showing short packing contacts between imine N atoms and methyl H atoms on neighboring molecules (Macrae *et al.*, 2008).

hour, the product had begun to precipitate. The reaction was allowed to continue stirring overnight to ensure completion. Once filtered, the yellow solid product was washed with two 2 ml aliquots of ice cold 50:50 methanol–water, and once dried, 287 mg of product was formed (91.0% yield). This procedure is similar, though not identical, to a method used by Lassagne and co-workers to form quinoxalines and pyrido[2,3-*b*]pyrazines (Lassagne *et al.*, 2015). Crystals for diffraction study were crystallized from methylene chloride (m.p. 410 K). ATR–IR (cm^{-1}): 3059, 2971, 2918, 1882, 1612, 1486, 1440, 1020, 826, 806. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.54 (*s*, 1H), 7.58 (*m*, 2H), 7.40 (*m*, 4H), 7.30 (*t*, 1H), 7.17 (*d*, 1H), 7.08 (*d*, 1H), 7.04 (*dd*, 1H), 2.31 (*d*, 6H). ^{13}C (75 MHz, $CDCl_3$): δ 151.17, 148.88, 144.11, 137.42, 134.96, 132.37, 131.58, 131.40, 130.32, 128.83, 128.46, 127.35, 122.56, 118.24, 95.68, 82.86, 19.86, 19.40. F T–IR, ^{1}H NMR, COSY and ^{13}C NMR are given in the supporting information.

Table 1
Experimental details.

Crystal data	
Chemical formula	$C_{21}H_{17}NS$
M_r	315.42
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	293
a, b, c (Å)	5.9435 (3), 22.7785 (7), 15.0910 (9)
β (°)	124.087 (8)
V (Å^3)	1692.06 (14)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.19
Crystal size (mm)	0.49 × 0.43 × 0.23
Data collection	
Diffractometer	Rigaku Xcalibur Sapphire3
Absorption correction	Multi-scan (*CrysAlis PRO*; Rigaku OD, 2015)
T_{min}, T_{max}	0.754, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	42768, 6330, 4181
R_{int}	0.035
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.779
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.046, 0.131, 1.03
No. of reflections	6330
No. of parameters	210
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.21, −0.23

Computer programs: *CrysAlis PRO* (Rigaku OD, 2015), *SHELXT* (Sheldrick, 2015*a*), *SHELXL* (Sheldrick, 2015*b*) and *OLEX2* (Dolomanov *et al.*, 2009).

Refinement

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

Acknowledgements

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full crystallographic data

IUCrData (2019). **4**, x190363 [https://doi.org/10.1107/S2414314619003638]

(*E*)-*N*-(3,4-Dimethylphenyl)-1-[5-(phenylethynyl)thiophen-2-yl]methanimine

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Crystal data

$C_{21}H_{17}NS$
M_r = 315.42
Monoclinic, $P2_1/c$
a = 5.9435 (3) Å
b = 22.7785 (7) Å
c = 15.0910 (9) Å
β = 124.087 (8)°
V = 1692.06 (14) Å^3
Z = 4
$F(000)$ = 664
D_x = 1.238 Mg m^{-3}
Melting point: 410 K
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 8633 reflections
θ = 4.2–31.1°
μ = 0.19 mm^{-1}
T = 293 K
Plate, yellow
0.49 × 0.43 × 0.23 mm

Data collection

Xcalibur, Sapphire3 diffractometer
Radiation source: fine-focus sealed X-ray tube, Enhance (Mo) X-ray Source
Graphite monochromator
Detector resolution: 16.1790 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (CrysAlis PRO; Rigaku OD, 2015)
T_{min} = 0.754, T_{max} = 1.000
42768 measured reflections
6330 independent reflections
4181 reflections with $I > 2\sigma(I)$
R_{int} = 0.035
θ_{max} = 33.6°, θ_{min} = 4.2°
h = −9→9
k = −35→35
l = −23→23

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.131
S = 1.03
6330 reflections
210 parameters
0 restraints
Primary atom site location: dual
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0574P)^2 + 0.2177P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.21 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}

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

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.4721 (3)	0.73831 (6)	−0.25547 (12)	0.0574 (3)
H1	0.6539	0.7351	−0.1992	0.069*
C2	0.3977 (4)	0.77446 (7)	−0.34126 (14)	0.0692 (4)

H2	0.5296	0.7957	−0.3424	0.083*
C3	0.1302 (4)	0.77907 (7)	−0.42473 (14)	0.0712 (4)
H3	0.0812	0.8035	−0.4823	0.085*
C4	−0.0653 (3)	0.74777 (7)	−0.42359 (13)	0.0678 (4)
H4	−0.2463	0.7509	−0.4806	0.081*
C5	0.0053 (3)	0.71160 (6)	−0.33820 (11)	0.0538 (3)
H5	−0.1283	0.6906	−0.3378	0.065*
C6	0.2751 (3)	0.70658 (5)	−0.25309 (9)	0.0442 (3)
C7	0.3453 (3)	0.66938 (6)	−0.16471 (10)	0.0491 (3)
C8	0.3928 (3)	0.63856 (6)	−0.09161 (10)	0.0496 (3)
C9	0.4458 (3)	0.60085 (5)	−0.00742 (9)	0.0445 (3)
C10	0.2630 (3)	0.57639 (6)	0.00958 (11)	0.0505 (3)
H10	0.0772	0.5837	−0.0334	0.061*
C11	0.3859 (3)	0.53910 (6)	0.09894 (11)	0.0500 (3)
H11	0.2902	0.5195	0.1219	0.060*
C12	0.6603 (3)	0.53453 (5)	0.14866 (10)	0.0436 (3)
C13	0.8443 (3)	0.49621 (5)	0.23642 (10)	0.0458 (3)
H13	0.7823	0.4768	0.2731	0.055*
C14	1.2578 (2)	0.45061 (5)	0.35353 (10)	0.0427 (2)
C15	1.2450 (3)	0.44648 (6)	0.44287 (10)	0.0458 (3)
H15	1.1172	0.4688	0.4451	0.055*
C16	1.4172 (3)	0.41012 (5)	0.52816 (10)	0.0454 (3)
C17	1.6122 (3)	0.37701 (5)	0.52561 (10)	0.0475 (3)
C18	1.6256 (3)	0.38167 (6)	0.43691 (11)	0.0511 (3)
H18	1.7548	0.3599	0.4348	0.061*
C19	1.4519 (3)	0.41790 (6)	0.35167 (11)	0.0484 (3)
H19	1.4652	0.4203	0.2932	0.058*
C20	1.3950 (3)	0.40764 (8)	0.62267 (12)	0.0634 (4)
H20A	1.5619	0.4210	0.6855	0.095*
H20B	1.3602	0.3680	0.6332	0.095*
H20C	1.2486	0.4324	0.6096	0.095*
C21	1.8056 (3)	0.33707 (8)	0.61696 (13)	0.0674 (4)
H21A	1.9227	0.3601	0.6799	0.101*
H21B	1.9131	0.3156	0.5986	0.101*
H21C	1.7042	0.3101	0.6305	0.101*
N1	1.0880 (2)	0.48807 (5)	0.26526 (8)	0.0469 (2)
S1	0.77294 (7)	0.578178 (15)	0.08798 (3)	0.04885 (10)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0533 (8)	0.0607 (8)	0.0519 (7)	−0.0092 (6)	0.0255 (6)	−0.0024 (6)
C2	0.0825 (11)	0.0612 (9)	0.0725 (10)	−0.0169 (8)	0.0487 (9)	0.0023 (8)
C3	0.0916 (12)	0.0555 (8)	0.0620 (9)	0.0016 (8)	0.0402 (9)	0.0168 (7)
C4	0.0609 (9)	0.0654 (9)	0.0572 (9)	0.0076 (7)	0.0208 (7)	0.0174 (7)
C5	0.0488 (7)	0.0535 (7)	0.0527 (7)	−0.0009 (6)	0.0246 (6)	0.0068 (6)
C6	0.0510 (7)	0.0400 (6)	0.0396 (6)	−0.0003 (5)	0.0242 (5)	−0.0015 (4)
C7	0.0533 (7)	0.0476 (6)	0.0422 (6)	−0.0008 (5)	0.0242 (6)	−0.0013 (5)

C8	0.0549 (7)	0.0470 (6)	0.0416 (6)	0.0017 (5)	0.0238 (6)	−0.0011 (5)
C9	0.0516 (7)	0.0426 (6)	0.0374 (5)	0.0029 (5)	0.0238 (5)	−0.0018 (5)
C10	0.0455 (7)	0.0518 (7)	0.0509 (7)	0.0035 (5)	0.0250 (6)	0.0023 (6)
C11	0.0497 (7)	0.0507 (7)	0.0540 (7)	−0.0002 (5)	0.0317 (6)	0.0042 (6)
C12	0.0502 (7)	0.0426 (6)	0.0420 (6)	0.0006 (5)	0.0284 (5)	0.0004 (5)
C13	0.0514 (7)	0.0450 (6)	0.0437 (6)	−0.0014 (5)	0.0283 (6)	0.0039 (5)
C14	0.0433 (6)	0.0425 (6)	0.0413 (6)	−0.0043 (5)	0.0229 (5)	0.0037 (5)
C15	0.0488 (7)	0.0460 (6)	0.0442 (6)	−0.0003 (5)	0.0270 (6)	0.0006 (5)
C16	0.0487 (7)	0.0458 (6)	0.0393 (6)	−0.0086 (5)	0.0231 (5)	−0.0007 (5)
C17	0.0433 (6)	0.0455 (6)	0.0455 (6)	−0.0052 (5)	0.0200 (5)	0.0040 (5)
C18	0.0452 (7)	0.0537 (7)	0.0551 (7)	0.0020 (5)	0.0284 (6)	0.0027 (6)
C19	0.0485 (7)	0.0551 (7)	0.0478 (7)	−0.0014 (5)	0.0308 (6)	0.0036 (5)
C20	0.0668 (9)	0.0800 (10)	0.0464 (7)	−0.0015 (8)	0.0336 (7)	0.0066 (7)
C21	0.0597 (9)	0.0708 (10)	0.0608 (9)	0.0082 (7)	0.0271 (8)	0.0204 (8)
N1	0.0496 (6)	0.0479 (5)	0.0422 (5)	−0.0003 (4)	0.0251 (5)	0.0063 (4)
S1	0.04729 (18)	0.05599 (19)	0.04635 (18)	0.00247 (13)	0.02812 (15)	0.00812 (13)

Geometric parameters (Å, º)

C1—H1	0.9300	C12—S1	1.7210 (12)
C1—C2	1.381 (2)	C13—H13	0.9300
C1—C6	1.3933 (19)	C13—N1	1.2706 (16)
C2—H2	0.9300	C14—C15	1.3956 (17)
C2—C3	1.372 (3)	C14—C19	1.3866 (18)
C3—H3	0.9300	C14—N1	1.4192 (15)
C3—C4	1.372 (2)	C15—H15	0.9300
C4—H4	0.9300	C15—C16	1.3835 (17)
C4—C5	1.3818 (19)	C16—C17	1.4013 (19)
C5—H5	0.9300	C16—C20	1.5054 (18)
C5—C6	1.3880 (18)	C17—C18	1.3889 (19)
C6—C7	1.4308 (17)	C17—C21	1.5076 (19)
C7—C8	1.2002 (18)	C18—H18	0.9300
C8—C9	1.4151 (17)	C18—C19	1.3833 (18)
C9—C10	1.3673 (19)	C19—H19	0.9300
C9—S1	1.7270 (13)	C20—H20A	0.9600
C10—H10	0.9300	C20—H20B	0.9600
C10—C11	1.4033 (18)	C20—H20C	0.9600
C11—H11	0.9300	C21—H21A	0.9600
C11—C12	1.3647 (18)	C21—H21B	0.9600
C12—C13	1.4452 (17)	C21—H21C	0.9600
C2—C1—H1	120.0	N1—C13—H13	118.9
C2—C1—C6	120.08 (14)	C15—C14—N1	123.50 (11)
C6—C1—H1	120.0	C19—C14—C15	118.68 (11)
C1—C2—H2	119.9	C19—C14—N1	117.79 (11)
C3—C2—C1	120.24 (15)	C14—C15—H15	119.1
C3—C2—H2	119.9	C16—C15—C14	121.77 (12)
C2—C3—H3	119.9	C16—C15—H15	119.1

C4—C3—C2	120.20 (14)	C15—C16—C17	119.26 (12)
C4—C3—H3	119.9	C15—C16—C20	119.46 (13)
C3—C4—H4	119.8	C17—C16—C20	121.26 (12)
C3—C4—C5	120.33 (15)	C16—C17—C21	121.21 (12)
C5—C4—H4	119.8	C18—C17—C16	118.71 (12)
C4—C5—H5	119.9	C18—C17—C21	120.08 (13)
C4—C5—C6	120.10 (13)	C17—C18—H18	119.1
C6—C5—H5	119.9	C19—C18—C17	121.72 (12)
C1—C6—C7	121.40 (12)	C19—C18—H18	119.1
C5—C6—C1	119.04 (12)	C14—C19—H19	120.1
C5—C6—C7	119.56 (12)	C18—C19—C14	119.84 (12)
C8—C7—C6	177.09 (15)	C18—C19—H19	120.1
C7—C8—C9	178.38 (14)	C16—C20—H20A	109.5
C8—C9—S1	120.67 (10)	C16—C20—H20B	109.5
C10—C9—C8	127.98 (12)	C16—C20—H20C	109.5
C10—C9—S1	111.32 (10)	H20A—C20—H20B	109.5
C9—C10—H10	123.6	H20A—C20—H20C	109.5
C9—C10—C11	112.74 (12)	H20B—C20—H20C	109.5
C11—C10—H10	123.6	C17—C21—H21A	109.5
C10—C11—H11	123.4	C17—C21—H21B	109.5
C12—C11—C10	113.12 (12)	C17—C21—H21C	109.5
C12—C11—H11	123.4	H21A—C21—H21B	109.5
C11—C12—C13	127.39 (11)	H21A—C21—H21C	109.5
C11—C12—S1	111.39 (9)	H21B—C21—H21C	109.5
C13—C12—S1	121.09 (10)	C13—N1—C14	118.94 (10)
C12—C13—H13	118.9	C12—S1—C9	91.40 (6)
N1—C13—C12	122.27 (11)		