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2-(2-Nitroanilino)-4,5,6,7-tetrahydrobenzo[*b*]thiophene-3-carbonitrile

Francisco J.B. Mendonça Junior,[a] Maria do Carmo A. de Lima,[b] Suely L. Galdino,[b] Ivan R. Pitta[b] and Carlos A. de Simone[c]*

[a]Laboratório de Síntese e Vetorização de Moléculas Bioativas, Universidade Estadual da Paraíba, 58020-540 João Pessoa, PB, Brazil, [b]Laboratório de Síntese e Planejamento de Fármacos, Departamento de Antibióticos, Universidade Federal de Pernambuco, 50670-910 Recife, PE, Brazil, and [c]Departamento de Física e Informática, Instituto de Física de São Carlos, Universidade de São Paulo - USP, 13560-970 São Carlos, SP, Brazil
Correspondence e-mail: casimone@ifsc.usp.br

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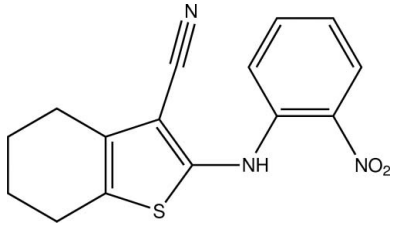
Key indicators: single-crystal X-ray study; T = 295 K; mean σ(C–C) = 0.004 Å; R factor = 0.057; wR factor = 0.174; data-to-parameter ratio = 16.9.

The title compound, $C_{15}H_{13}N_3O_2S$, was synthesized by the reaction of 2-amino-5,6,7,8-tetrahydro-4*H*-cyclohepta[*b*]thiophene-3-carbonitrile and *o*-fluoronitrobenzene. The dihedral angle between the thiophene and nitrophenyl rings is 75.15 (2)°. In the crystal, intermolecular N—H···N and C—H···O interactions lead to the formation of a supramolecular chain extending along the *c*-axis direction.

Related literature

For background to 2-substituted thiophenes, see: Puterová *et al.* (2009). For the biological activity of 2-amino-benzo[*b*]-thiophene derivatives, see: Fakhr *et al.* (2008); Baraldi *et al.* (2006). For the synthesis of 2-amino thiophenes, see: Gewald *et al.* (1966). For puckering parameters, see: Cremer & Pople (1975).



Experimental

Crystal data

$C_{15}H_{13}N_3O_2S$ M_r = 299.34
Monoclinic, $P2_1/c$
a = 13.2764 (4) Å
b = 13.4447 (7) Å
c = 8.2237 (4) Å
β = 106.794 (2)°
V = 1405.30 (11) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.24 mm^{-1}
T = 295 K
0.27 × 0.19 × 0.17 mm

Data collection

Nonius KappaCCD diffractometer
9590 measured reflections
3241 independent reflections
2351 reflections with $I > 2\sigma(I)$
R_{int} = 0.051

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.057
$wR(F^2)$ = 0.174
S = 1.06
3241 reflections
192 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.45 e Å^{-3}
$\Delta\rho_{min}$ = −0.38 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2···N1^{i}	0.86	2.48	3.093 (3)	129
C11—H11···O1^{ii}	0.93	2.56	3.351 (3)	143

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

Data collection: *COLLECT* (Nonius, 1997); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: TK2704).

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2-(2-Nitroanilino)-4,5,6,7-tetrahydrobenzo[*b*]thiophene-3-carbonitrile

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S1. Comment

The various uses of 2-substituted thiophenes have been well documented (Puterová *et al.*, 2009). Amongst these applications, some 2-substituted benzo[*b*]thiophenes derivatives present anti-inflammatory and analgesic activities (Fakhr *et al.*, 2008), and others are adenosine A1 allosteric enhancers (Baraldi *et al.*, 2006). In this work, we report the structure of the title compound prepared by the reaction of 2-amino-5,6,7,8-tetrahydro-*4H*-cyclohepta[*b*]thiophene-3-carbonitrile and *o*-fluoro-nitrobenzene.

In the title compound, Fig. 1, the dihedral angle between least-squares planes passing through atoms of thiophene and nitrophenyl rings is 75.15 (2) °. The cyclohexane ring adopts a half-chair conformation with calculated puckering parameters of: q_2 = 0.285 (5) Å, q_3 = -0.240 (3) Å, Q_T = 0.373 (4) Å, θ = 130.2 (3) °, φ = -27.5 (6) ° (Cremer & Pople, 1975). In the packing, intermolecular N–H···N and C—H··· O interactions lead to the formation a supramolecular polymeric chain that extends along the *c* direction; Table 2 & Fig.2.

S2. Experimental

Under nitrogen and at 273 K, a dry THF solution (80 ml) of 2-amino-4,5,6,7- tetrahydro-*4H*-benzo[*b*]thiophene-3-carbonitrile (0.07 mol) and *o*-fluoro-nitrobenzene (0.07 mol) was added drop wise to a stirred suspension of NaH (0.105 mol) in dry THF (20 ml). The reaction mixture was stirred at room temperature for 24 h. The resulting mixture was adjusted to pH = 5 with 2 N HCl and then extracted with $CHCl_3$. The extract was washed with aqueous Na_2CO_3 and water, dried over $CaCl_2$, and evaporated under reduced pressure. The dark-red solid obtained was purified by recrystallization from absolute ethanol, affording the title compound as red crystals; yield 11.72 g (56%), m.pt 275–276 K (Gewald *et al.*, 1966). Crystals were grown by evaporation at room temperature of its dichloromethane solution.

NMR ^{1}H (200 MHz, $CDCl_3$) δ: 1.84–1.87 (m, 4H), 2.63–2.73 (m, 4H), 6.91 (dt, 1H, J = 8.6, 1.4 Hz), 7.18 (dd, 1H, J = 8.6, 1.0 Hz), 7.51 (dt, 1H, J = 8.6, 8.2, 7.4 Hz), 8.22 (dd, 1H, J = 8.4, 1.4 Hz), 9.6 (s, 1H) p.p.m.

S3. Refinement

All H atoms attached were fixed geometrically and treated as riding with C—H = 0.93 Å (aromatic) or 0.97 Å (methylene) and N—H = 0.86 Å, and with U_{iso}(H) = 1.2U_{eq}(C or N).

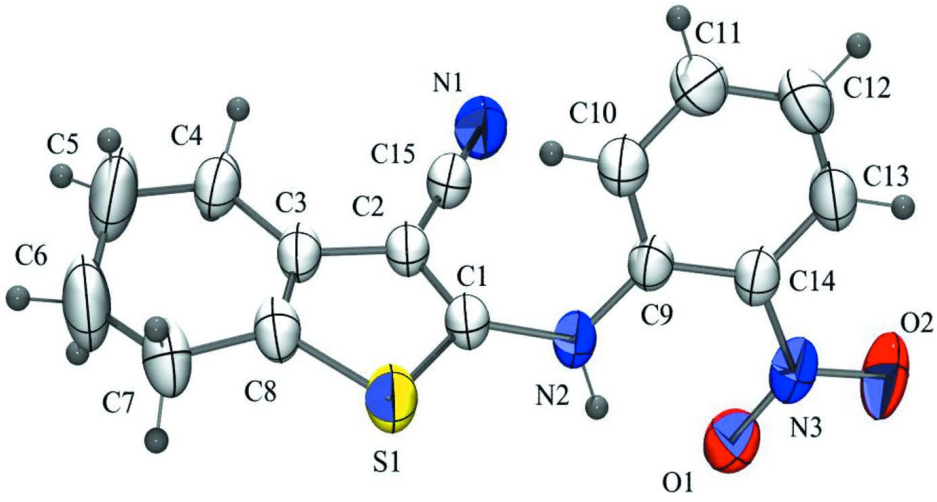

Figure 1

Projection of $C_{15}H_{13}N_3O_2S$, showing atom labelling and 50% probability displacement ellipsoids.

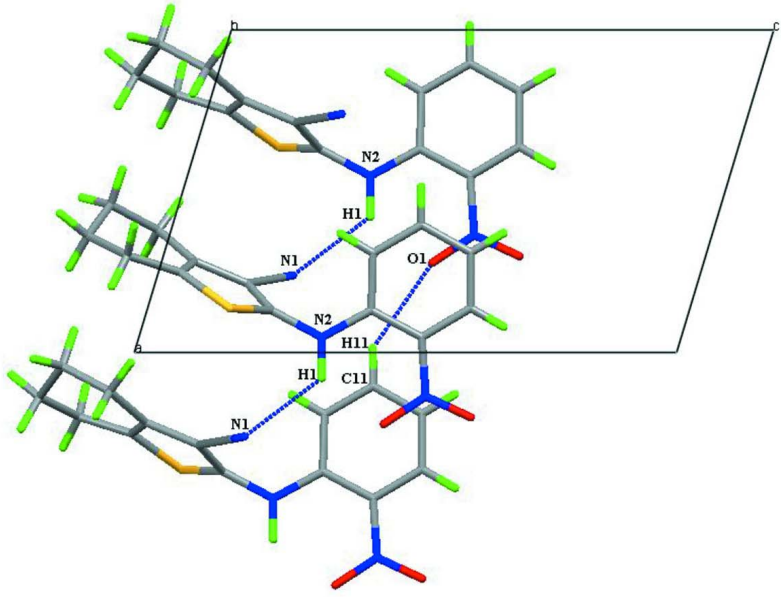

Figure 2

View of the packing along *b* axis showing intermolecular interactions as blue dashed lines.

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Crystal data

$C_{15}H_{13}N_3O_2S$
$M_r = 299.34$
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a = 13.2764$ (4) Å
$b = 13.4447$ (7) Å
$c = 8.2237$ (4) Å
$\beta = 106.794$ (2)°
$V = 1405.30$ (11) Å^3
$Z = 4$
$F(000) = 624$
$D_x = 1.415$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 4953 reflections
$\theta = 2.9$–27.5°
$\mu = 0.24$ mm^{-1}

T = 295 K
Prism, yellow

0.27 × 0.19 × 0.17 mm

Data collection

Nonius KappaCCD diffractometer
Radiation source: Enraf Nonius FR590
Horizonally mounted graphite crystal monochromator
Detector resolution: 9 pixels mm^{-1}
CCD rotation images,thick slices scans
9590 measured reflections

3241 independent reflections
2351 reflections with $I > 2\sigma(I)$
R_{int} = 0.051
θ_{max} = 27.5°, θ_{min} = 3.0°
h = −17→17
k = −17→17
l = −9→10

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.057
$wR(F^2)$ = 0.174
S = 1.06
3241 reflections
192 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
$w = 1/[\sigma^2(F_o^2) + (0.1015P)^2 + 0.2662P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.45 e Å^{-3}
$\Delta\rho_{min}$ = −0.38 e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.133 (13)

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}
C1	−0.22931 (15)	−0.11377 (16)	−0.8690 (3)	0.0489 (5)
C2	−0.17013 (15)	−0.19140 (16)	−0.7859 (2)	0.0470 (5)
C3	−0.06070 (15)	−0.16847 (17)	−0.7171 (3)	0.0494 (5)
C4	0.02377 (17)	−0.2391 (2)	−0.6205 (3)	0.0620 (6)
H4A	0.0009	−0.2717	−0.5322	0.074*
H4B	0.0352	−0.2898	−0.6972	0.074*
C5	0.1254 (2)	−0.1846 (3)	−0.5417 (5)	0.1058 (12)
H5A	0.1231	−0.1586	−0.4328	0.127*
H5B	0.1823	−0.2325	−0.5196	0.127*
C6	0.1505 (2)	−0.1041 (3)	−0.6378 (6)	0.1056 (13)
H6A	0.1667	−0.1319	−0.7362	0.127*
H6B	0.2138	−0.0720	−0.5686	0.127*
C7	0.06661 (19)	−0.0251 (2)	−0.6990 (4)	0.0700 (7)

H7A	0.0705	0.0225	−0.6088	0.084*
H7B	0.0783	0.0102	−0.7948	0.084*
C8	−0.04015 (15)	−0.07297 (18)	−0.7510 (3)	0.0540 (5)
C9	−0.41366 (15)	−0.11662 (14)	−0.8689 (3)	0.0449 (5)
C10	−0.38494 (18)	−0.10942 (18)	−0.6915 (3)	0.0560 (6)
H10	−0.3142	−0.1031	−0.6314	0.067*
C11	−0.4588 (2)	−0.1114 (2)	−0.6043 (3)	0.0649 (6)
H11	−0.4374	−0.1062	−0.4865	0.078*
C12	−0.5649 (2)	−0.1210 (2)	−0.6897 (4)	0.0703 (7)
H12	−0.6145	−0.1229	−0.6298	0.084*
C13	−0.59545 (18)	−0.12779 (18)	−0.8620 (4)	0.0622 (6)
H13	−0.6665	−0.1338	−0.9202	0.075*
C14	−0.52138 (16)	−0.12570 (15)	−0.9526 (3)	0.0486 (5)
C15	−0.21465 (15)	−0.28666 (18)	−0.7727 (3)	0.0519 (5)
N1	−0.25004 (17)	−0.36281 (16)	−0.7606 (3)	0.0673 (6)
N2	−0.33714 (13)	−0.11309 (15)	−0.9523 (2)	0.0524 (5)
H2	−0.3569	−0.1103	−1.0614	0.063*
N3	−0.56173 (15)	−0.13233 (14)	−1.1361 (3)	0.0572 (5)
O1	−0.49971 (14)	−0.12880 (15)	−1.2218 (2)	0.0713 (5)
O2	−0.65641 (14)	−0.14080 (17)	−1.2012 (3)	0.0866 (6)
S1	−0.15219 (4)	−0.01029 (5)	−0.86321 (8)	0.0610 (3)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0350 (10)	0.0626 (12)	0.0490 (11)	0.0004 (8)	0.0119 (8)	0.0021 (9)
C2	0.0348 (9)	0.0602 (12)	0.0452 (10)	0.0001 (8)	0.0105 (8)	0.0005 (9)
C3	0.0342 (10)	0.0649 (12)	0.0479 (10)	0.0015 (8)	0.0103 (8)	−0.0039 (9)
C4	0.0414 (11)	0.0756 (15)	0.0637 (13)	0.0065 (10)	0.0066 (10)	0.0019 (12)
C5	0.0452 (15)	0.113 (3)	0.134 (3)	0.0006 (15)	−0.0129 (17)	0.017 (2)
C6	0.0401 (14)	0.111 (3)	0.155 (4)	−0.0094 (14)	0.0110 (17)	0.012 (2)
C7	0.0415 (11)	0.0811 (17)	0.0843 (17)	−0.0116 (11)	0.0133 (11)	−0.0086 (14)
C8	0.0371 (10)	0.0652 (13)	0.0598 (12)	−0.0011 (9)	0.0140 (9)	−0.0044 (10)
C9	0.0365 (9)	0.0465 (10)	0.0504 (10)	0.0035 (7)	0.0104 (8)	0.0042 (8)
C10	0.0433 (11)	0.0699 (14)	0.0537 (12)	0.0050 (10)	0.0123 (9)	0.0017 (10)
C11	0.0588 (14)	0.0817 (17)	0.0590 (13)	0.0141 (12)	0.0246 (11)	0.0063 (12)
C12	0.0552 (14)	0.0834 (18)	0.0825 (18)	0.0101 (12)	0.0363 (13)	0.0121 (14)
C13	0.0391 (11)	0.0643 (14)	0.0836 (17)	0.0018 (9)	0.0182 (11)	0.0075 (12)
C14	0.0375 (10)	0.0461 (10)	0.0590 (12)	0.0030 (8)	0.0088 (9)	0.0038 (9)
C15	0.0373 (10)	0.0654 (13)	0.0502 (11)	0.0030 (9)	0.0081 (8)	0.0052 (10)
N1	0.0534 (11)	0.0684 (13)	0.0759 (13)	−0.0033 (10)	0.0121 (10)	0.0102 (10)
N2	0.0335 (8)	0.0765 (12)	0.0444 (9)	0.0030 (8)	0.0069 (7)	0.0035 (8)
N3	0.0420 (9)	0.0574 (11)	0.0631 (11)	0.0020 (8)	0.0010 (8)	−0.0018 (9)
O1	0.0580 (10)	0.0953 (14)	0.0540 (9)	−0.0013 (9)	0.0056 (8)	0.0017 (9)
O2	0.0413 (9)	0.1135 (16)	0.0871 (13)	0.0028 (9)	−0.0099 (9)	−0.0141 (11)
S1	0.0445 (4)	0.0594 (4)	0.0757 (5)	−0.0014 (2)	0.0119 (3)	0.0052 (3)

Geometric parameters (Å, º)

C1—C2	1.365 (3)	C7—H7B	0.9700
C1—N2	1.397 (2)	C8—S1	1.727 (2)
C1—S1	1.720 (2)	C9—N2	1.381 (2)
C2—C15	1.428 (3)	C9—C10	1.401 (3)
C2—C3	1.432 (3)	C9—C14	1.402 (3)
C3—C8	1.358 (3)	C10—C11	1.372 (3)
C3—C4	1.508 (3)	C10—H10	0.9300
C4—C5	1.507 (4)	C11—C12	1.386 (4)
C4—H4A	0.9700	C11—H11	0.9300
C4—H4B	0.9700	C12—C13	1.360 (4)
C5—C6	1.436 (5)	C12—H12	0.9300
C5—H5A	0.9700	C13—C14	1.395 (3)
C5—H5B	0.9700	C13—H13	0.9300
C6—C7	1.516 (4)	C14—N3	1.451 (3)
C6—H6A	0.9700	C15—N1	1.143 (3)
C6—H6B	0.9700	N2—H2	0.8600
C7—C8	1.502 (3)	N3—O2	1.221 (3)
C7—H7A	0.9700	N3—O1	1.230 (3)
C2—C1—N2	127.62 (19)	C6—C7—H7B	109.7
C2—C1—S1	110.65 (15)	H7A—C7—H7B	108.2
N2—C1—S1	121.72 (16)	C3—C8—C7	125.1 (2)
C1—C2—C15	122.20 (18)	C3—C8—S1	112.21 (15)
C1—C2—C3	113.87 (19)	C7—C8—S1	122.6 (2)
C15—C2—C3	123.92 (19)	N2—C9—C10	119.80 (18)
C8—C3—C2	111.30 (19)	N2—C9—C14	123.48 (19)
C8—C3—C4	122.69 (19)	C10—C9—C14	116.71 (19)
C2—C3—C4	126.0 (2)	C11—C10—C9	121.5 (2)
C5—C4—C3	111.0 (2)	C11—C10—H10	119.2
C5—C4—H4A	109.4	C9—C10—H10	119.2
C3—C4—H4A	109.4	C10—C11—C12	120.8 (2)
C5—C4—H4B	109.4	C10—C11—H11	119.6
C3—C4—H4B	109.4	C12—C11—H11	119.6
H4A—C4—H4B	108.0	C13—C12—C11	119.2 (2)
C6—C5—C4	116.8 (3)	C13—C12—H12	120.4
C6—C5—H5A	108.1	C11—C12—H12	120.4
C4—C5—H5A	108.1	C12—C13—C14	120.7 (2)
C6—C5—H5B	108.1	C12—C13—H13	119.6
C4—C5—H5B	108.1	C14—C13—H13	119.6
H5A—C5—H5B	107.3	C13—C14—C9	121.1 (2)
C5—C6—C7	116.4 (3)	C13—C14—N3	116.7 (2)
C5—C6—H6A	108.2	C9—C14—N3	122.25 (19)
C7—C6—H6A	108.2	N1—C15—C2	179.4 (2)
C5—C6—H6B	108.2	C9—N2—C1	123.57 (17)
C7—C6—H6B	108.2	C9—N2—H2	118.2
H6A—C6—H6B	107.3	C1—N2—H2	118.2

C8—C7—C6	109.7 (2)	O2—N3—O1	121.8 (2)
C8—C7—H7A	109.7	O2—N3—C14	119.0 (2)
C6—C7—H7A	109.7	O1—N3—C14	119.12 (18)
C8—C7—H7B	109.7	C1—S1—C8	91.95 (10)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···N1^{i}	0.86	2.48	3.093 (3)	129
C11—H11···O1^{ii}	0.93	2.56	3.351 (3)	143

Symmetry codes: (i) x, $-y-1/2$, $z-1/2$; (ii) x, y, $z+1$.