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2-Amino-4-(2-naphthyl)thiophene-3-carbonitrile

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
R factor = 0.042
wR factor = 0.070
Data-to-parameter ratio = 17.0

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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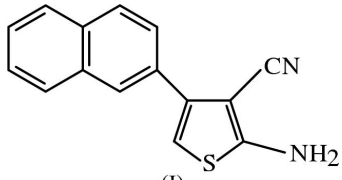
A new type of thiophene derivative with potential pharmacological activity, *viz*. 2-amino-4-(2-naphthalyl)thiophene-3-carbonitrile, $C_{15}H_{10}N_2S$, has been prepared and studied by NMR and single-crystal X-ray diffraction techniques. The molecule contains two different groups, naphthalene and thiophene, which are nearly perpendicular to one another. In the crystal structure, a hydrogen bond, with a $D\cdots A$ distance of 3.033 (3) Å, is present between the amino substituent and the carbonitrile N atom of a symmetry-related molecule. The crystal structure also includes one C—H$\cdots\pi$ interaction.

Comment

The design of compounds that possess important pharmacological properties, such as antibacterial, anticancer, anti-inflammatory and antitoxic activities, is an important area of research, and highly substituted thiophenes from an integral part of numerous natural products (Koike *et al.*, 1997) and pharmaceuticals, which have been found to exhibit these activities. These compounds are often used as novel conducting polymers (Press & Pelkey, 1997) and isostatic replacements for phenyl groups in medicinal chemistry (Jarvest *et al.*, 1999). The electronic and optical properties of polythiophene and its derivatives have been the subject of many investigations (Roncali, 1997; Ekinci *et al.*, 2002).



(I)

Azo dyes with heterocyclic diazo components led to commercial products to replace the conventional azobenzene disperse dyes (Annen *et al.*, 1987; ICI, 1958). Some derivatives, obtained by the coupling of 2-aminothiophenes and 2-aminothiazide groups, were distinguished by their high color strength and brilliant shades (BASF, 1979*a*,*b*). Since the first report of the preparation of 2-aminothiophene (Stadler, 1885), the synthesis of highly functionalized aminothiophenes has been studied extensively (Norris, 1986).

The title compound, (I), contains two different cyclic groups, naphthalene and thiophene, as seen in Fig. 1. The thiophene ring exhibits normal geometry and is planar, with a maximum deviation of 0.011 (2) Å for atom C2. Similar arrangements have been observed previously (Çoruh, Ustabaş, Tümer *et al.*, 2003; Çoruh, Ustabaş, Yılmaz & Yavuz, 2003; Vasu *et al.*, 2004*a*,*b*). However, atoms N1 and C1 of the

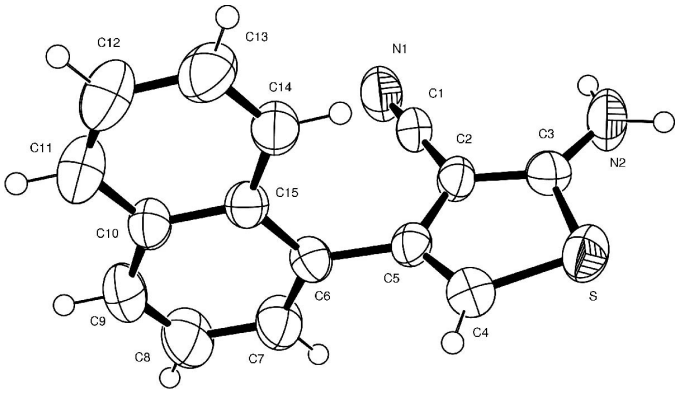


Figure 1
A view of the molecular structure of (I), with the atomic numbering scheme and displacement ellipsoids drawn at the 50% probability level.

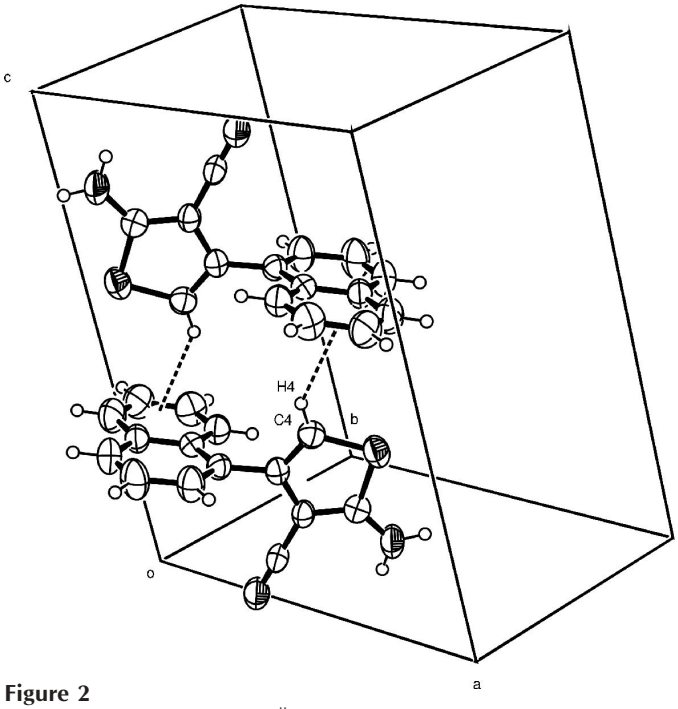


Figure 2
A view of the C4—H4···$Cg3^{ii}$ interaction in (I), shown as dashed lines [symmetry code: (ii) $-x, 1-y, -z$].

carbonitrile substituent deviate from this plane by 0.194 (2) and 0.101 (3) Å, respectively. The naphthalene system is also planar, with a maximum deviation of 0.041 (3) Å for atom C8. The two groups are nearly perpendicular to one another, with a dihedral angle of 85.88 (7)°.

The crystal structure of (I) exhibits a C—H···π hydrogen bond in addition to an intermolecular N—H···N hydrogen bond, and details are given in Table 2. It is thought that these interactions may have some influence on the overall molecular conformation. Atom C4 of the thiophene ring acts as a hydrogen-bond donor, *via* atom H4, to the C10–C15 ring (*Cg*3) in the molecule at $(-x, 1-y, -z)$ (see Fig. 2). The intermolecular hydrogen bond occurs between the amino group, *via* atom H2*A*, and carbonitrile atom $N1^{i}$ of a symmetry-related molecule, as shown in Fig. 3 (symmetry code in Table 2).

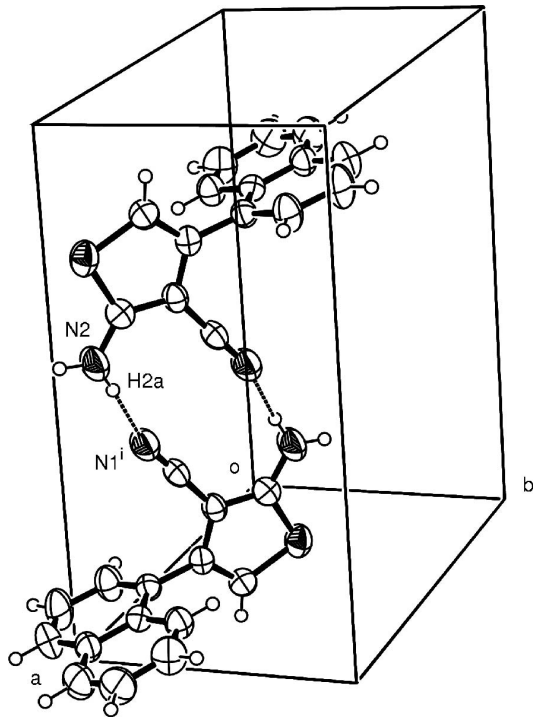


Figure 3
The crystal packing of (I), showing the formation of the hydrogen-bonded (dashed lines) dimer [symmetry code: (i) $1-x, -y, -z$].

All of these interactions (see Table 2) stabilize crystal structure and generate infinite chains parallel to the *a* axis, and seem to force the molecule to adopt a twisted conformation.

Experimental

2-[2-Bromo-1-(2-naphthyl)ethylidene]malononitrile (0.94 g, 5 mmol) was dissolved in a solution of dioxane (5 ml) and absolute ethanol (20 ml). The solution was stirred and cooled to 273 K using an ice–salt bath and then a suspension of NaSH (0.3 g), in absolute ethanol (10 ml) was added dropwise over a period of 30 min. The resulting reaction mixture was stirred for an additional 1 h at room temperature. After removal of the solvent, the residue was filtered on a short Al_2O_3 column, eluting with hexane–ethyl acetate (7:3). After removing the solvent, the residue was crystallized from chloroform to yield 2-amino-4-(2-naphthyl)thiophene-3-carbonitrile, (I) (yield 74%, colorless crystals, m.p. 402–403 K). ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.09 (*s*, 1H, ArH), 7.92–7.48 (*m*, 6H, ArH), 6.47 (*s*, 1H, H_5), 4.96 (*bs*, 2H, NH_2); ^{13}C NMR (50 MHz, $CDCl_3$): δ 165.55, 141.98, 135.39, 134.99, 133.52, 130.52, 130.31, 129.67, 128.49, 128.38, 128.09, 127.15, 117.83, 108.38, 90.84; IR ($CHCl_3$): ν 3428, 3326, 3122, 3054, 2204, 1640, 1619, 1514, 1402, 1198.

Crystal data

$C_{15}H_{10}N_2S$
M_r = 250.31
Monoclinic, $P2_1/n$
a = 12.3075 (14) Å
b = 7.4751 (9) Å
c = 13.6676 (17) Å
β = 94.046 (3)°
V = 1254.3 (3) Å^3
Z = 4
D_x = 1.326 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 6485 reflections
θ = 2–28.1°
μ = 0.24 mm^{-1}
T = 293 (2) K
Prism, colorless
0.25 × 0.10 × 0.10 mm

Data collection

Bruker SMART CCD area-detector diffractometer	930 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.063$
Absorption correction: none	$\theta_{max} = 27.1^\circ$
6485 measured reflections	$h = -16 \rightarrow 14$
2769 independent reflections	$k = -9 \rightarrow 5$
	$l = -18 \rightarrow 14$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.042$	$w = 1/[\sigma^2(F_o^2) + (0.0119P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.070$	$(\Delta/\sigma)_{max} < 0.001$
$S = 0.72$	$\Delta\rho_{max} = 0.15$ e Å^{-3}
2769 reflections	$\Delta\rho_{min} = -0.16$ e Å^{-3}
163 parameters	

Table 1
Selected geometric parameters (Å, °).

S—C3	1.730 (3)	C3—N2	1.345 (3)
S—C4	1.733 (2)	N1—C1	1.142 (3)
C3—S—C4	91.61 (13)	C2—C3—S	110.3 (2)
N2—C3—C2	128.6 (3)	N1—C1—C2	178.6 (3)
N2—C3—S	121.1 (2)	C5—C4—S	112.4 (2)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2A···N1^{i}	0.86	2.21	3.033 (3)	161
C4—H4···$Cg3^{ii}$	0.93	2.75	3.564 (3)	146

Symmetry codes: (i) $1-x, -y, -z$; (ii) $-x, 1-y, -z$. Note: $Cg3$ is the centroid of the C10–C15 ring.

All the H atoms were positioned geometrically and refined using a riding model. The C—H bond lengths were 0.93 Å (aromatic and methine) and N—H = 0.86 Å, with U_{iso}(H) values of $1.5U_{eq}$(C) and $1.2U_{eq}$(N).

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*, *PARST* (Nardelli, 1995) and *WinGX* (Farrugia, 1999).

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