Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

2-Amino-4-methylthiophene-3-carbonitrile

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Received 30 July 2003
Accepted 7 August 2003
Online 23 August 2003

The title compound, $C_6H_6N_2S$, consists of a thiophene ring carrying three substitutent groups. Two N—H···N intermolecular hydrogen bonds link neighboring molecules into a three-dimensional network.

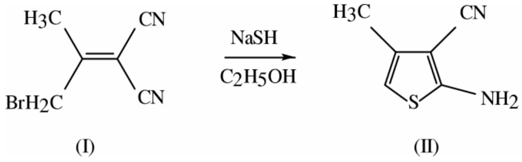
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.005 Å
R factor = 0.052
wR factor = 0.154
Data-to-parameter ratio = 13.8

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

Comment

Highly substituted thiophenes form an important part of numerous natural products (Koike *et al.*, 1997) and pharmaceuticals (World Drug Index, 2000). They are often used as novel conducting polymers 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 & Demir, 2002).



The title compound, (II) (Fig. 1), consists of a thiophene ring carrying three subtituents, *viz.* an amino group, a methyl group and a cyano group. The S—C bond lengths, 1.728 (4) and 1.725 (4) Å, are in good agreement with those in the literature, *e.g.* 1.734 (2) and 1.721 (3) Å (Han & Choi, 2000), 1.727 (1) and 1.729 (2) Å (Elerman & Elmalı, 1998), and 1.723 (2) and 1.735 (3) Å (Wouters *et al.*, 1997). The C1≡N1 bond distance is 1.153 (4) Å, typical of such a triple bond. This value agrees well with similar bonds reported in the literature, *e.g.* 1.132 (2) Å (Elerman & Elmalı, 1998), 1.130 (5) and 1.142 (5) Å (Çoruh *et al.*, 2002), and 1.148 (2) Å (Boitsov *et al.*, 2002). The molecule of (II) is planar, the maximum deviation from the least-squares plane being 0.0074 (33) Å for atom C4.

A packing diagram of (II) is shown Fig. 2. The molecules are stacked such that there are no ring–ring or X—H···π interactions between molecules in the stacks; the distance between planes of molecules in the stacks is 5.671 (7) Å. The crystal structure of (II) is stabilized by two N—H···N intermolecular hydrogen bonds (Table 3 and Fig. 2).

Experimental

2-(2-Bromo-1-methylethylidene)malononitrile (0.94 g, 5 mmol) was dissolved in a solution of dioxane (5 ml) and absolute ethanol (20 ml). The stirred solution was cooled to 273 K in an ice-salt bath, and a suspension of NaSH (0.3 g) in 10 ml of absolute ethanol was then added dropwise over a period of 30 min. The resulting reaction

DOI: 10.1107/S1600536803017549

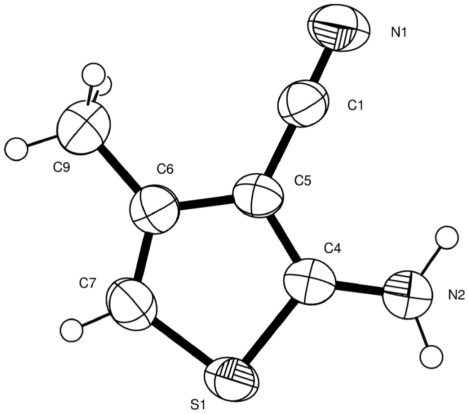


Figure 1
View of the title compound, with the atom numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level.

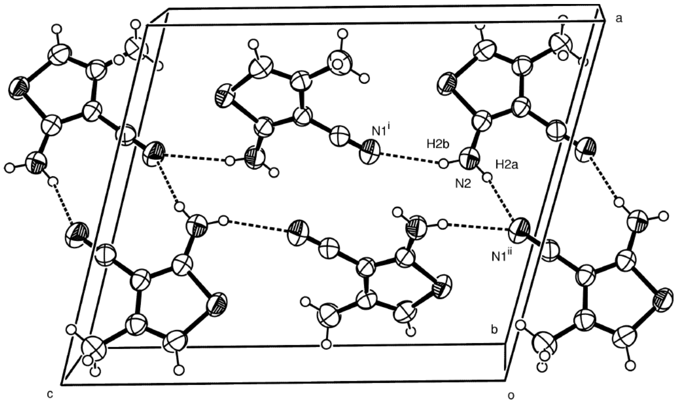


Figure 2
The hydrogen-bond network in (II), viewed approximately along the [010] direction. Hydrogen bonds are indicated by dashed lines.

mixture was stirred for a further 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). The solvent was removed and the residue crystallized from chloroform to yield (556 mg, 81%) 2-amino-4-methylthiophene-3-carbonitrile (light pink crystals, mp 391–392 K). ^{1}H NMR (200 MHz, $CDCl_3$): δ 5.59 (*s*, 1H, H_5), 4.81 (*bs*, 2H, NH_2), 2.11 (*s*, 3H, CH_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ 162.44, 135.91, 115.52, 105.32, 91.03, 15.53. IR ($CHCl_3$) 3417, 3212, 3097, 2977, 2202, 1627, 1558, 1446, 1300, 1191, 1068, 836.

Crystal data

$C_6H_6N_2S$
$M_r = 138.20$
Monoclinic, $P2_1/c$
$a = 11.900$ (5) Å
$b = 4.130$ (5) Å
$c = 14.085$ (5) Å
$\beta = 105.562$ (5)°
$V = 666.9$ (9) Å^3
$Z = 4$

$D_x = 1.376$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1153 reflections
$\theta = 1.8$–25.2°
$\mu = 0.39$ mm^{-1}
$T = 293$ K
Block, pink
0.20 × 0.15 × 0.10 mm

Data collection

Nonius KappaCCD diffractometer
φ and ω scans
Absorption correction: none
1849 measured reflections
1135 independent reflections
789 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.060$
$\theta_{\rm max} = 25.2°$
$h = -13 \rightarrow 13$
$k = -4 \rightarrow 4$
$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.052$
$wR(F^2) = 0.154$
$S = 1.00$
1135 reflections
82 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.087P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.33$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.31$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S1—C4	1.728 (4)	N1—C1	1.153 (4)
S1—C7	1.725 (4)	N2—C4	1.354 (5)
C4—S1—C7	91.95 (15)	S1—C4—C5	110.3 (3)
N1—C1—C5	179.2 (4)	N2—C4—C5	128.8 (3)
S1—C4—N2	120.9 (2)	S1—C7—C6	112.9 (3)

Table 2
Contact distances (Å, °).

S1···N1^{i}	3.401 (5)	N1···N2^{ii}	3.117 (6)

Table 3
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2*B*···N1^{i}	0.86	2.48	3.276 (5)	155
N2—H2*A*···N1^{ii}	0.86	2.31	3.117 (6)	157

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

All H atoms were positioned geometrically and refined in riding mode, with methyl C—H = 0.96 Å, other C—H = 0.93 Å, and N—H = 0.86 Å. For methyl H, $U_{\rm iso}$ values were set equal to $1.5U_{\rm eq}$ of the carrier C atom. For other N—H and other C—H, $U_{\rm iso}$(H) values were set equal to $1.2U_{\rm eq}$ of the carrier atom.

Data collection: *COLLECT* (Nonius BV, 1997–2000); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997) and *PLATON* (Spek, 1997); software used to prepare material for publication: *SHELXL*97 and *WinGX* (Farrugia, 1999).

We thank the Spanish MCyT (BQU2000-0219) and FICYT (PR-01-GE-4) for financial support.

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