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6-Amino-4-(methylsulfanyl)-2-oxo-1-tolyl-1,2-dihydropyridine-3,5-dicarbonitrile

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Key indicators

Single-crystal X-ray study
T = 173 K
Mean σ(C–C) = 0.002 Å
R factor = 0.033
wR factor = 0.089
Data-to-parameter ratio = 12.7

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

In the title compound, $C_{15}H_{12}N_4OS$, the bond lengths at the heterocyclic N atom are N—C_{Ph} = 1.454 (2) Å, N—C(═O) = 1.416 (2) Å and N—C(NH_2) = 1.369 (2) Å. The interplanar angle between the two rings is 85.56 (4)°. The molecules are associated in layers parallel to $(10\overline{1})$ by two hydrogen bonds involving the NH_2 group.

Comment

In the course of our studies aimed at the development of efficient and simple procedures for the synthesis of anti-metabolic agents (Elgemeie & Sood, 2001; Elgemeie & El-Aziz, 2002; Elgemeie *et al.*, 2003; Elgemeie & Elkaradawy, 2004), we have carried out the reaction of the 1,3-dithiolane derivative (1) with [bis(methylthio)methylene]malononitrile, (2), in boiling ethanol containing a catalytic amount of piperidine, leading to the *N*-aryl-4-methylsulfanyl-2-pyridone (3) rather than the expected pyranodithiolane derivative (6). The structure of (3) was established on the basis of its elemental analysis and spectroscopic data (MS, IR and ^{1}H NMR). Moreover, (3) was shown to be the same as the product obtained from our previously reported reaction of (1) with (7) by their melting points and spectroscopic data (Elgemeie *et al.*, 2000). The formation of (3) from (1) and (7) is assumed to proceed *via* (5), which was cyclized to yield the final novel *N*-aryl-4-methylsulfanyl-2-pyridone derivative (3). The formation of (3) from (1) and (2) is assumed to proceed first *via* hydrolysis of (1) to yield the *N*-arylcyanoacetamide derivative (7), which reacts with (2) to yield the product (3).

The molecular structure of (3) is shown in Fig. 1. The molecular dimensions (Table 1) are similar to those of a related ring system reported by Arévalo *et al.* (2000) [Cambridge Structural Database (Allen, 2002) refcode DOCKIP]. The thiosulfanyl group is rotated out of the heterocyclic ring plane by 51.2 (2)°. The interplanar angle between the two rings is 85.56 (4)°.

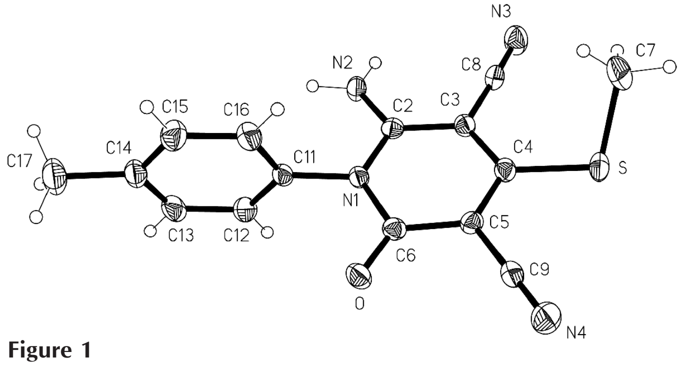
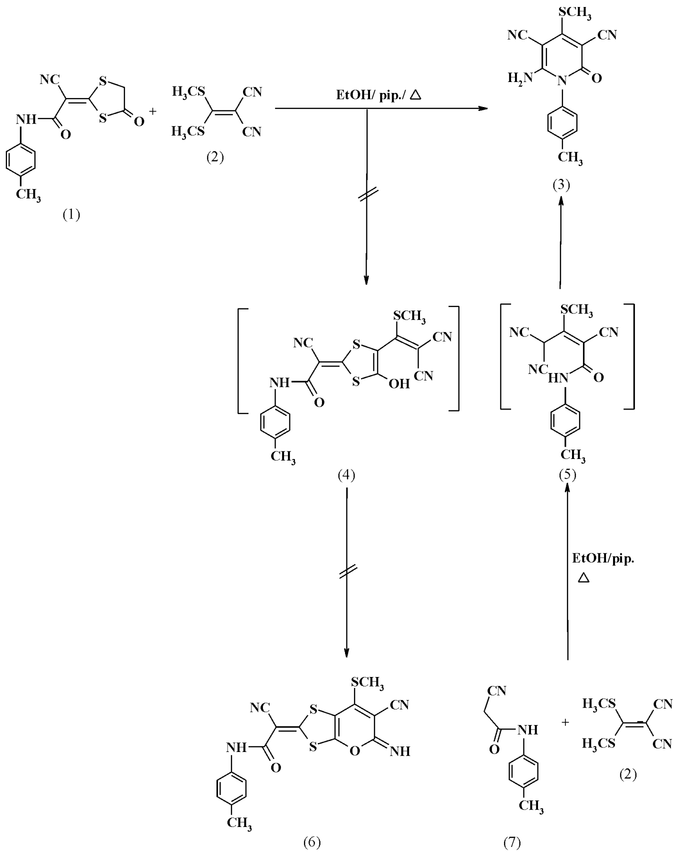


Figure 1
The molecule of (3) in the crystal structure. Displacement ellipsoids are shown at the 50% probability level and H atom radii are arbitrary.

The NH_2 group acts as donor in two classical intermolecular hydrogen bonds, to the carbonyl O and one nitrile N atom (Table 2), the net effect of which is to form layers of molecules parallel to $(10\overline{1})$ (Fig. 2).



Experimental

Method A: A mixture of (1) (0.01 mol) and (2) (0.01 mol) was heated in ethanol (30 ml) in the presence of catalytic amounts of piperidine for 30 min and then cooled. The precipitated product was filtered off and recrystallized from ethanol in 70% yield (m.p. 531–533 K).

Method B: A mixture of (2) and (7) was heated in ethanol (40 ml) in the presence of catalytic amounts of piperidine for 1 h and then cooled. The precipitated product was filtered off and recrystallized from ethanol in 80% yield (m.p. 531–533 K).

Crystal data

$C_{15}H_{12}N_4OS$
$M_r = 296.35$
Monoclinic, $P2_1/n$
$a = 8.5598$ (6) Å
$b = 9.6111$ (5) Å
$c = 17.9319$ (9) Å
$\beta = 100.364$ (4)°
$V = 1451.17$ (15) Å^3
$Z = 4$
$D_x = 1.356$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 63 reflections
$\theta = 10.2$–25.0°
$\mu = 0.23$ mm^{-1}
$T = 173$ (2) K
Tablet, pale brown
0.60 × 0.50 × 0.15 mm

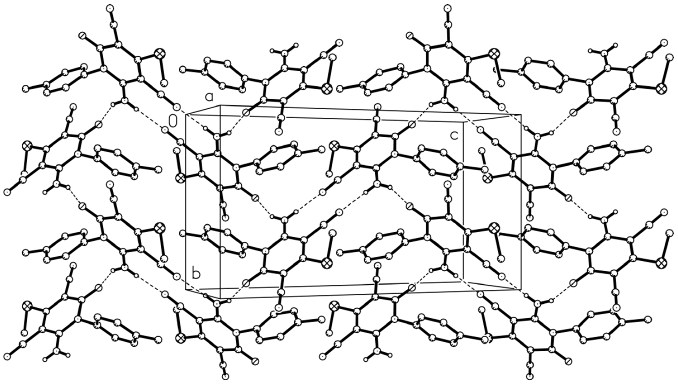


Figure 2
A packing diagram of (3), with the view direction perpendicular to $(10\overline{1})$. For clarity, H atoms not involved in hydrogen bonding have been omitted. Dashed lines represent hydrogen bonds.

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction: none
4858 measured reflections
2547 independent reflections
2093 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.024$
$\theta_{\max} = 25.0°$
$h = -10 \rightarrow 8$
$k = 0 \rightarrow 11$
$l = -21 \rightarrow 21$
3 standard reflections every 247 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.089$
$S = 1.03$
2547 reflections
200 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0519P)^2 + 0.2627P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 0.19$ e Å^{-3}
$\Delta\rho_{\min} = -0.32$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S—C4	1.7654 (16)	N1—C6	1.416 (2)
S—C7	1.808 (2)	N1—C11	1.454 (2)
N1—C2	1.369 (2)	N2—C2	1.321 (2)
C4—S—C7	103.21 (8)		
C7—S—C4—C3	51.21 (16)		

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N2—H01⋯O$^{\rm i}$	0.88 (2)	2.06 (2)	2.8763 (18)	153.1 (18)
N2—H02⋯N3$^{\rm ii}$	0.83 (2)	2.20 (2)	2.988 (2)	158.4 (18)
C7—H7C⋯O$^{\rm iii}$	0.98	2.56	3.338 (2)	136
C16—H16⋯N4$^{\rm iii}$	0.95	2.63	3.442 (2)	144

Symmetry codes: (i) $\frac{3}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$; (ii) $1-x, -y, -z$; (iii) $\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$.

H atoms attached to N atoms were refined freely. H atoms of the methyl groups were identified in a difference synthesis, idealized and refined as rigid groups (C—H = 0.98 Å and H—C—H = 109.5°) allowed to rotate but not to tip. Other C-bound H atoms were included using a riding model, with fixed C—H bond lengths of 0.95 Å; all $U_{\rm iso}$(H) values were fixed at 1.2 times $U_{\rm eq}$ of the parent C atom.

Data collection: *XSCANS* (Fait, 1991); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1994); software used to prepare material for publication: *SHELXL*97.

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