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The crystal structure of 2-((3-methylthiophen-2-yl)methylene)malononitrile, $C_9H_6N_2S$

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Abstract

$C_9H_6N_2S$, triclinic, $P\bar{1}$ (no. 2), $a = 3.9497(4)$ Å, $b = 9.0268(13)$ Å, $c = 12.2935(16)$ Å, $V = 431.37(10)$ Å³, $Z = 2$, $R_{gt}(F) = 0.0496$, $wR_{ref}(F^2) = 0.0747$, $T = 296(2)$ K.

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The crystal structure is shown in the figure (upper part: ORTEP labelled diagram where thermal ellipsoids were drawn at 50% probability level; middle part: non classical hydrogen

bonds). Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

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Table 1: Data collection and handling.

Crystal:	Orange plate
Size:	0.40 × 0.18 × 0.03 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.32 mm ⁻¹
Diffractometer, scan mode:	SuperNova, ω
θ_{max} , completeness:	29.1°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	3141, 2002, 0.018
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 1432
$N(param)_{refined}$:	110
Programs:	CrysAlis ^{PRO} [1], SHELX [2, 3], WinGX [4]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
C1	0.8402(5)	0.1934(3)	0.76250(17)	0.0406(5)
C2	0.7663(6)	0.3487(3)	0.74636(18)	0.0457(6)
C3	0.5738(6)	0.4145(3)	0.8356(2)	0.0573(7)
H3	0.499989	0.517416	0.838691	0.069*
C4	0.5069(7)	0.3136(3)	0.9160(2)	0.0599(7)
H4	0.382893	0.339822	0.980138	0.072*
C5	1.0300(5)	0.0960(3)	0.68699(17)	0.0417(5)
H5	1.115141	0.144226	0.625061	0.050*
C6	1.1072(5)	−0.0561(3)	0.69057(17)	0.0418(5)
C7	1.3052(6)	−0.1318(3)	0.60350(19)	0.0478(6)
C8	0.9981(6)	−0.1540(3)	0.7767(2)	0.0517(6)
C9	0.8726(7)	0.4370(3)	0.6469(2)	0.0596(7)
H9A	1.088037	0.387309	0.617444	0.089*
H9B	0.896778	0.536081	0.666167	0.089*
H9C	0.701171	0.444003	0.593236	0.089*
N1	1.4635(6)	−0.1930(3)	0.53487(19)	0.0657(6)
N2	0.9128(7)	−0.2348(3)	0.8435(2)	0.0810(8)
S1	0.67250(16)	0.13381(8)	0.88799(5)	0.0529(2)

Source of material

The title compound was synthesized by Knoevenagel reaction. To a mixture of 3-methylthiophene-2-carbaldehyde (10 mmol) and malononitrile (10 mmol) in ethanol (100 mL) was added 2 drops of piperidine, stirred for 1–2 h and then cooled to room temperature. The obtained precipitate was filtered off, washed with ethanol and then dried.

Experimental details

The data collection was accomplished using the CrysAlisPro software [1]. The figures were generated through ORTEP and PLATON [4, 5]. All the aromatic C–H hydrogen atoms were positioned geometrically with C–H = 0.93 Å and treated as riding atoms with *U*_{iso}(H) was set to 1.2 *U*_{eq}(C). Similarly, methyl hydrogen atoms were also positioned geometrically with C–H = 0.96 Å and treated as riding atoms with *U*_{iso}(H) was set to 1.5 *U*_{eq}(C) for methyl carbon atoms.

Comment

Owing to its multiple biological and electronic properties, thiophene and its derivatives have attracted widespread attention and are treated as important classes of heterocycles due to their existence in a broad spectrum of natural and synthetic organic compounds [6–8]. Apart from biological activity, due to their structural and electronic properties, compounds having a thiophene core are promising candidates for materials-related applications such as functional materials biosensors, organic field

effect transistors (OFETs), organic light-emitting diodes (OLEDs).

In the crystal structure of the title compound (*cf.* the upper part of the figure), the cyano group is connected to the 3-methyl thiophene moiety through double bond. The molecule is planar as the root mean square (r.m.s.) deviation value of the plane produced from the fitted non-hydrogen atoms of molecules is 0.0408 Å. The largest deviations were observed from the S = 0.0885(1) Å and N = −0.0608(2) Å atoms. The dihedral angle between the thiophene and malononitrile moieties is 4.65(4)°. The crystal structure of the compound is further stabilized by the intermolecular hydrogen bonding interactions (middle and lower part of the figure). These two C–H···N type weak interactions connect the molecules along the diagonal of *ac*-plane. The carbon atom C5 at (*x*, *y*, *z*) position contributes *via* its hydrogen atom to N1 atom at (−*x* + 3, −*y*, −*z* + 1) and generates a 10 membered ring motif *R*²₂(10). Similarly, carbon atom C4 at (*x*, *y*, *z*) position contributes as donor atom *via* its hydrogen atom to N2 atom at (−*x* + 1, −*y*, −*z* + 2) and generates a 16 membered ring motif *R*²₂(16) (middle and lower part of the figure).

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