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Key indicators

Single-crystal X-ray study
T = 295 K
Mean $\sigma(\text{C}-\text{C}) = 0.003 \text{ \AA}$
R factor = 0.049
wR factor = 0.147
Data-to-parameter ratio = 16.4

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

Dimethyl 2-(4-fluorophenyl)-3-(methylamino)-
furan-4,5-dicarboxylate

The title compound, $\text{C}_{15}\text{H}_{14}\text{FNO}_5$, was synthesized *via* a thiazole-carbene-mediated multicomponent reaction. In the crystal structure, the dihedral angle between the benzene and furan rings is $17.58 (11)^\circ$. Non-classical C—H...O hydrogen bonds link the molecules in the crystal structure into infinite chains.

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Comment

Substituted furans play an important role in organic chemistry, not only as key structural units in many natural products and important pharmaceuticals (Dean, 1963; Nakanishi *et al.*, 1974), but as useful building blocks in synthetic chemistry (Lipshutz, 1986; Raczko & Jurcak, 1995). Recently, we reported a facile synthesis of polysubstituted 3-aminofurans *via* a thiazole-carbene-mediated multi-component reaction (Ma & Yang, 2005). In this paper, we report the crystal structure of 2-(4-fluorophenyl)-3-(methylamino)furan-4,5-dicarboxylate, (1).

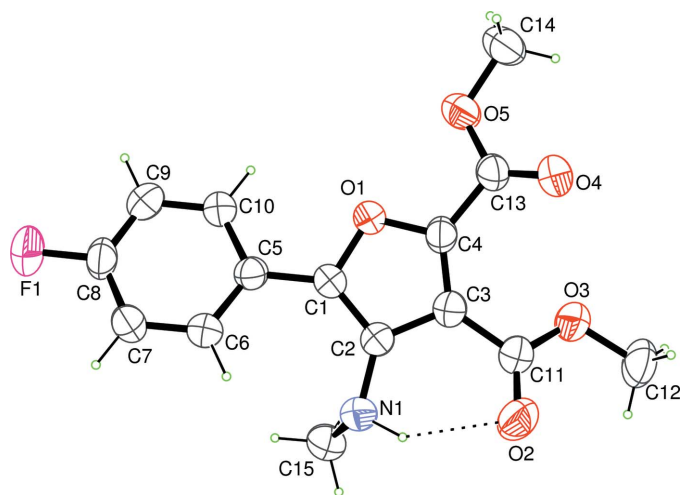
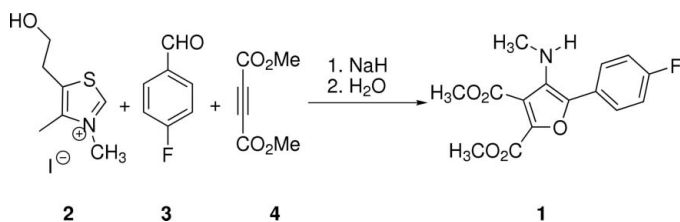


Figure 1

The molecule of compound (1) in the crystal structure. Displacement ellipsoids are drawn at the 50% probability level. The dotted line indicates the intramolecular hydrogen bond.

The molecular structure of (1) is shown in Fig. 1. The benzene ring and the furan moiety are inclined to one another at an angle of 17.58 (11)°.

In the crystal structure, non-classical C—H···O hydrogen bonds play an important role in the formation of polymeric chains (Fig. 2). Hydrogen-bond parameters are listed in Table 1.

Experimental

To a suspension of NaH (1.5 mmol) in anhydrous CH₂Cl₂ (3 ml) was added a solution of the thiazolium salt (2) (1.0 mmol) in dry CH₂Cl₂ (2 ml) at 195 K under nitrogen. After 10–15 min, a mixture of *p*-fluorobenzaldehyde, (3) (0.5 mmol), and dimethyl acetylenedicarboxylate, (4) (0.75 mmol), in CH₂Cl₂ (2 ml) was added over a period of 10 min and the mixture stirred for 2 h. After this, the reaction temperature was raised to 273 K and kept at this temperature for an additional 2 h. The resulting mixture was carefully poured onto an ice-cooled solution of NaHCO₃ (1 M) and then extracted with CH₂Cl₂. The combined organic phase was washed with brine and dried over anhydrous Na₂SO₄. The solvent was removed under reduced pressure and the resulting oil was purified by column chromatography to afford the product, (1) (110 mg, yield 72%). Compound (1) was recrystallized from solution in AcOEt as pale-yellow crystals (m.p. 349–350 K). Spectroscopic analysis: ¹H NMR (500 MHz, CDCl₃, δ, p.p.m.): 7.76–7.74 (*m*, 2H), 7.11 (*t*, 2H, *J* = 8.5 Hz), 3.93 (*s*, 3H), 3.91 (*s*, 3H), 2.66 (*s*, 3H); ¹³C NMR (125 MHz, CDCl₃, δ, p.p.m.): 164.0 (*d*, *J*_{CF} = 66.6 Hz), 161.5, 158.5, 141.4, 140.9, 134.6, 128.2 (*d*, *J*_{CF} = 8.0 Hz), 126.3 (*d*, *J*_{CF} = 3.0 Hz), 118.8, 115.8 (*d*, *J*_{CF} = 21.6 Hz), 52.5, 52.5, 34.9; HRMS (ESI): *m/z*, calculated for [C₂₁H₁₈FNO₅+Na]⁺: 308.0929; found: 308.0924; IR (KBr, ν, cm⁻¹): 2954, 1725, 1704, 1590, 1498, 1443, 1334, 1233, 1204.

Crystal data

C ₁₅ H ₁₄ FNO ₅	<i>D</i> _x = 1.420 Mg m ⁻³
<i>M</i> _r = 307.28	Mo Kα radiation
Monoclinic, C2/c	Cell parameters from 8846 reflections
<i>a</i> = 17.3249 (8) Å	<i>θ</i> = 2.6–27.4°
<i>b</i> = 9.4165 (4) Å	<i>μ</i> = 0.12 mm ⁻¹
<i>c</i> = 18.2202 (10) Å	<i>T</i> = 295 (1) K
<i>β</i> = 104.7530 (6)°	Prism, yellow
<i>V</i> = 2874.4 (2) Å ³	0.60 × 0.48 × 0.46 mm
<i>Z</i> = 8	

Data collection

Rigaku R-AXIS RAPID diffractometer	3283 independent reflections
<i>ω</i> scans	1935 reflections with <i>F</i> ² > 2σ(<i>F</i> ²)
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)	<i>R</i> _{int} = 0.031
<i>T</i> _{min} = 0.914, <i>T</i> _{max} = 0.948	<i>θ</i> _{max} = 27.5°
12161 measured reflections	<i>h</i> = -22 → 22
	<i>k</i> = -12 → 12
	<i>l</i> = -23 → 21

Refinement

Refinement on <i>F</i> ²	<i>w</i> = 1/[0.0017 <i>F</i> _o ² + σ(<i>F</i> _o ²)]/(4 <i>F</i> _o ²)
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.049	(Δ/σ) _{max} < 0.001
<i>wR</i> (<i>F</i> ²) = 0.147	Δρ _{max} = 0.48 e Å ⁻³
<i>S</i> = 1.01	Δρ _{min} = -0.34 e Å ⁻³
3283 reflections	Extinction correction: Larson (1970), equation 22
200 parameters	Extinction coefficient: 19 (2)
H-atom parameters constrained	

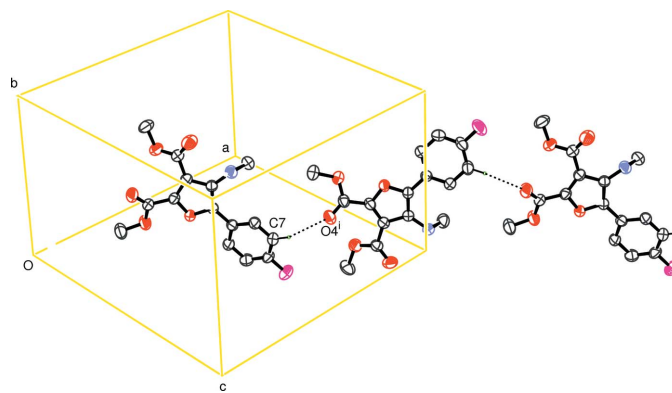


Figure 2

The molecular packing of (1). Dashed lines indicate the intermolecular hydrogen-bonding interactions (see Table 1 for symmetry code). H atoms not involved in hydrogen bonding have been omitted.

Table 1

Hydrogen-bond geometry (Å, °).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
N1—H101···O2	0.98	2.12	2.901 (3)	136
C7—H7···O4 ⁱ	0.97	2.56	3.478 (3)	157

Symmetry code: (i) +*x* + $\frac{1}{2}$, -*y* + $\frac{1}{2}$, +*z* + $\frac{1}{2}$.

All H atoms were placed in calculated positions, with N—H = 0.98 Å and C—H = 0.97 Å, and included in the final cycles of refinement in the riding-model approximation, with *U*_{iso}(H) = 1.2*U*_{eq}(C,N).

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MS, 2004); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 1996); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *CrystalStructure* and *PLATON* (Spek, 2003).

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