Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

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

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Received 27 September 2005
Accepted 10 October 2005
Online 15 October 2005

Key indicators

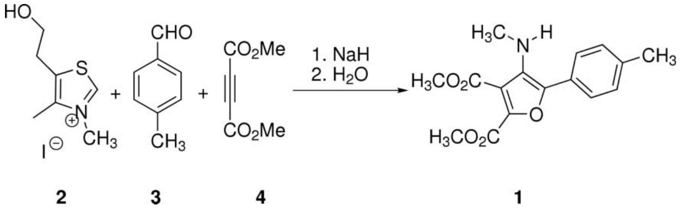
Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.004 Å
R factor = 0.053
wR factor = 0.159
Data-to-parameter ratio = 17.6

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

The title compound, $C_{16}H_{17}NO_5$, crystallizes with two molecules in the asymmetric unit. The dihedral angles between the furan and benzene rings are 26.38 (13) and 28.52 (14)°. The molecules are linked by N—H···O hydrogen bonds, leading to dimers.

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 also 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 multicomponent reaction (Ma & Yang, 2005). In this paper, we report the crystal structure of the title compound, (1).



The molecular structure of (1) is shown in Fig. 1. The compound crystallizes in space group $P2_1/c$ with two molecules in the asymmetric unit. There are no significant differences between the bond lengths and angles of the two molecules; however, there are significant differences in the magnitudes of some of the equivalent torsion angles involving the furan ring and its substituents (Table 1). The dihedral angles between the furan and benzene rings are 26.38 (13) and 28.52 (14)°. In the crystal structure, hydrogen bonding leads to dimerization (Table 2). As a result, a ten-membered ring is formed between molecules (Fig. 2), whose topological motif corresponds to the first level graph-set descriptor $R_2^2(10)$ (Bernstein *et al.*, 1995).

Experimental

To a suspension of NaH (1.5 mmol) in anhydrous CH_2Cl_2 (3 ml) was added a solution of the thiazolium salt (2) (1.0 mmol) in dry CH_2Cl_2 (2 ml) at 195 K under nitrogen. After 10–15 min, a mixture of *p*-tolualdehyde (3) (0.5 mmol) and dimethyl acetylenedicarboxylate (4) (0.75 mmol) in CH_2Cl_2 (2 ml) was added over a period of 10 min, then stirred for 2 h. The reaction temperature was then raised to 273 K and kept at this temperature for an additional 2 h. The resulting mixture was poured carefully on to an ice-cooled solution of $NaHCO_3$ and then extracted with CH_2Cl_2. The combined organic

doi:10.1107/S1600536805032307

phase was washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the resulting oil was purified by column chromatography to afford the product (1) (62 mg, yield 41%). Compound (1) was recrystallized from ethyl acetate as pale-yellow crystals (m.p. 354–355 K). ^{1}H NMR (500 MHz, $CDCl_3$, δ, p.p.m.): 7.66 (*d*, 2H, $J = 8.1$ Hz), 7.22 (*d*, 2H, $J = 7.9$ Hz), 3.93 (*s*, 3H), 3.91 (*s*, 3H), 2.68 (*s*, 3H), 2.37 (*s*, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, δ, p.p.m.): 164.1, 158.5, 142.5, 140.5, 138.1, 134.3, 129.3, 127.2, 126.2, 118.9, 52.4, 52.3, 34.8, 21.5; HRMS (ESI): *m*/*z*, calculated for $[C_{16}H_{17}NO_5+H]^+$: 304.1179; found: 304.1176; IR (KBr): 3369, 2951, 1726, 1703, 1608, 1509, 1445, 1335, 1236,1211 cm^{-1}.

Crystal data

$C_{16}H_{17}NO_5$
$M_r = 303.31$
Monoclinic, $P2_1/c$
$a = 15.5390$ (2) Å
$b = 17.8363$ (3) Å
$c = 11.6349$ (3) Å
$\beta = 108.6580$ (7)°
$V = 3055.23$ (10) Å^3
$Z = 8$

$D_x = 1.319$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 12870 reflections
$\theta = 1.8$–27.5°
$\mu = 0.10$ mm^{-1}
$T = 295$ (1) K
Prism, yellow
0.30 × 0.20 × 0.10 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.943$, $T_{max} = 0.990$
28950 measured reflections

6994 independent reflections
3442 reflections with $F^2 > 2\sigma(F^2)$
$R_{int} = 0.050$
$\theta_{max} = 27.5°$
$h = -20 \rightarrow 20$
$k = -23 \rightarrow 23$
$l = -15 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.053$
$wR(F^2) = 0.159$
$S = 1.01$
6992 reflections
397 parameters

H-atom parameters constrained
$w = 1/[0.0014F_o^2 + 1\sigma(F_o^2)]/(4F_o^2)$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.57$ e Å^{-3}
$\Delta\rho_{min} = -0.59$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.386 (3)	N1—C2	1.400 (3)
O2—C12	1.211 (3)	N1—C16	1.463 (3)
O6—C17	1.383 (3)	N2—C18	1.390 (3)
O7—C28	1.202 (3)	N2—C32	1.445 (3)
C2—N1—C16	117.6 (2)	O1—C1—C2	109.3 (2)
C18—N2—C32	118.9 (2)	O6—C17—C18	109.4 (2)
C16—N1—C2—C1	57.1 (3)	O1—C4—C14—O5	−21.6 (2)
C32—N2—C18—C17	53.0 (3)	O6—C17—C21—C22	28.0 (3)
O1—C1—C5—C6	23.9 (3)	C20—C19—C28—O8	−33.8 (3)
C4—C3—C12—O3	−36.3 (3)	O6—C20—C30—O10	−18.3 (2)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H101···O7^i	0.86	2.38	3.089 (3)	140
N2—H201···O2^{ii}	0.86	2.64	3.253 (2)	129

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

Atoms H101 and H201 were found in a difference Fourier map and refined as riding, with N—H = 0.86 Å and $U_{iso}(H) = 11.2U_{eq}(N)$. The other H atoms were placed in calculated positions, with $U_{iso}(H) =$

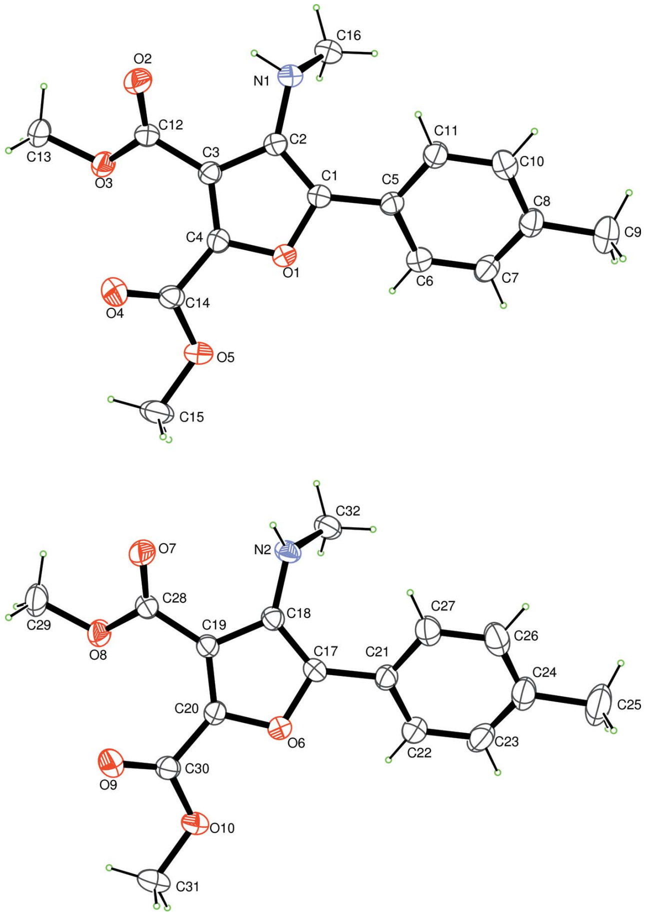


Figure 1
Views of the two molecules of (1), with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

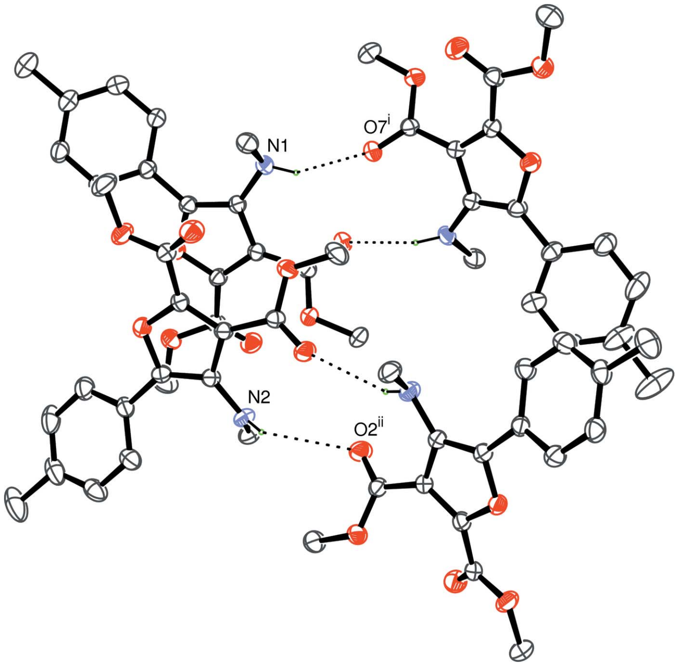


Figure 2
A view of the dimers formed by paired N—H···O hydrogen bonds (dashed lines) in the crystal structure of (I). H atoms not involved in hydrogen bonds have been omitted for clarity.

$1.2U_{eq}$(C) and C—H = 0.93 or 0.96 Å, and included in the final cycles of refinement in the riding-model approximation.

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

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