organic papers

N-(2,6-Difluorobenzoyl)-N'-(4,6-dimethoxy-pyrimidin-2-yl)urea

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In the title compound, $C_{14}H_{12}F_2N_4O_4$, an intramolecular N—H···N hydrogen bond forms a six-membered ring within the urea bridge.

Comment

The title compound has been obtained in the course of our studies of biological activities of the substituted benzoylurea derivatives containing substituted pyrimidine. Many acylurea compounds show high insecticidal activity (Zhao *et al.*, 2003), and investigation of acylureas as insecticides has become the subject of intensive research, leading to many novel substituted benzoylurea insecticides in the literature (Leighton *et al.*, 1981; Xue *et al.*, 1998; Zhao *et al.*, 2003; Wang *et al.*, 1998). We have developed the synthesis of (4) (see scheme), and report here its crystal structure. The key feature of this benzoylurea is that the 2,6-difluorobenzoyl group is linked to the urea bridge by an amide bond, and the pyrimidine ring, substituted in both *meta* positions, is attached to the distal N atom of urea. This might provide an opportunity for the study of the cooperative effect of combining these biologically active components in a single molecule.
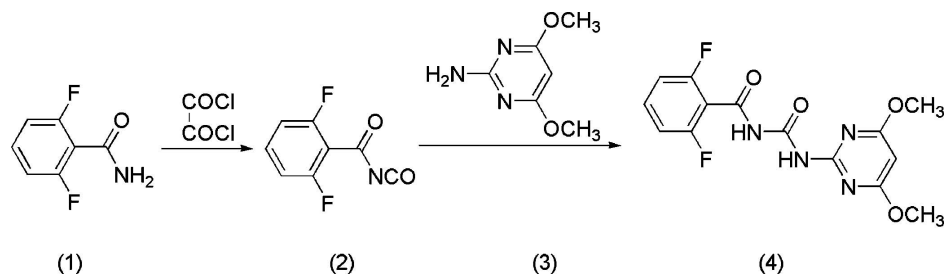
The molecular structure of (4) is shown in Fig. 1, and some geometric parameters are shown in Table 1. The intramolecular hydrogen bond (N1—H4···N4) forms a six-membered ring within the urea bridge (Table 2).

Experimental

Excluding moisture, oxalyl dichloride (2.62 ml, 0.03 mol) was added slowly to a stirred solution of 2,6-difluorobenzamide (1.57 g, 0.01 mol) in toluene (15 ml) and the mixture was refluxed and stirred for another 2 h at 333 K. After evaporation of the excess oxalyl dichloride under vacuum, a solution of 4,6-dimethoxypyrimidin-2-amine (1.55 g, 0.01 mol) in chloroform (10 ml) was added to the residue with stirring; the mixture was refluxed and stirred for another 3 h at 323 K, then allowed to stand at room temperature for 10 h. The separated white crystalline precipitate (4) was filtered off under suction. Crystals suitable for single-crystal X-ray diffraction were

obtained by slow evaporation of a solution of (4) in acetonitrile–ethanol (1:2.5 v/v) at room temperature. M.p. 432–433 K. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 3.92 (s, 6 H, OCH$_3$), 5.80 (s, 1 H, py-H), 6.97–7.44 (m, 3 H, ph-H).

Crystal data

C$_{14}$H$_{12}$F$_2$N$_4$O$_4$	$Z = 4$
$M_r = 338.28$	$D_x = 1.487$ Mg m^{-3}
Monoclinic, Cc	Mo $K\alpha$ radiation
$a = 7.6870$ (8) Å	$\mu = 0.13$ mm^{-1}
$b = 31.097$ (3) Å	$T = 298$ K
$c = 6.7432$ (7) Å	Block, colorless
$\beta = 110.371$ (2)°	$0.22 \times 0.20 \times 0.18$ mm
$V = 1511.1$ (3) Å^3	

Data collection

Bruker SMART CCD diffractometer	1809 independent reflections
	1314 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.054$
Absorption correction: none	$\theta_{max} = 28.3°$
6669 measured reflections	

Refinement

Refinement on F^2	where T_i are the Chebychev
$R[F^2 > 2\sigma(F^2)] = 0.036$	polynomials and $x = F_c/F_{max}$
$wR(F^2) = 0.075$	(Prince, 1982; Watkin, 1994)
$S = 0.96$	$(\Delta/\sigma)_{max} < 0.001$
1801 reflections	$\Delta\rho_{max} = 0.22$ e Å^{-3}
218 parameters	$\Delta\rho_{min} = -0.18$ e Å^{-3}
H-atom parameters constrained	Extinction correction: Larson
$w = [1 - (F_o - F_c)^2/36\sigma^2(F)]^2/$	(1970), equation 22
$[7.65T_0(x) + 9.99T_1(x) +$	Extinction coefficient: 0.6 (1) x 10^2
$2.89T_2(x)]$,	

Table 1
Selected geometric parameters (Å, °).

N1—C7	1.374 (4)	N2—C9	1.386 (4)
N1—C8	1.381 (4)	O1—C7	1.199 (4)
N2—C8	1.375 (4)	O2—C8	1.203 (4)
C7—N1—C8	127.6 (3)	C1—C7—N1	119.5 (3)
C8—N2—C9	132.8 (3)	N1—C8—N2	115.1 (3)

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H4$\cdots$N4	0.87	2.07	2.689 (3)	127

Because the data were collected with Mo $K\alpha$ radiation, there were no measurable anomalous differences, and Friedel pairs were merged in the final cycles of refinement. The H atoms were all visible in
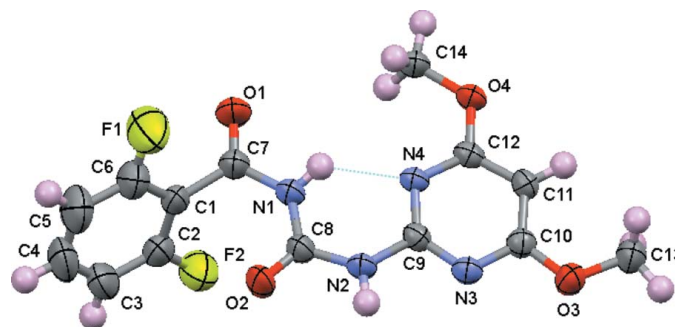
Figure 1
Molecular structure of (4), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level for non-H atoms. The dashed line represents the N—H$\cdots$N hydrogen bond.

difference Fourier maps, but those attached to C atoms were repositioned geometrically. The H atoms were initially refined with soft restraints on the bond lengths and angles to regularize their geometry (C—H = 0.93–0.98 Å and N—H = 0.86–0.89 Å) and isotropic displacement parameters [U_{iso}(H) in the range 1.2–1.5 times U_{eq} of the parent atom], after which they were refined with riding constraints.

Data collection: *SMART* (Siemens, 1993); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS86* (Sheldrick, 1986); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics: *MERCURY* (Macrae *et al.*, 2006); software used to prepare material for publication: *CRYSTALS*.

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