

C—H···O hydrogen-bonding and C—H··· π interactions in 3-(4-fluorophenyl)-1,5,7-trimethyl-1,2,3,4-tetrahydropyrido[2,3-*d*]pyrimidine-2,4-dione

Urmila H. Patel,^{a*} Pinal D. Patel^a and Neha Thakker^b

^aDepartment of Physics, Sardar Patel University, Vallabh Vidya Nagar, Gujarat 388 120, India, and ^bDepartment of Chemistry, Gujarat University, Ahmedabad, Gujarat 380 009, India

Correspondence e-mail: u_h_patel@yahoo.com

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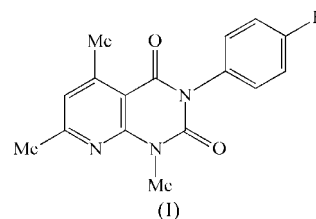
In the title compound, C₁₆H₁₄FN₃O₂, a diverse set of weak intermolecular C—H··· π , π – π and C—H···O interactions link the molecules into sheets. The C—H···O interactions generate centrosymmetric rings with a graph-set motif of *R*₂²(14) and chains with a *C*(8) motif.

Comment

Fused pyrido[2,3-*d*]pyrimidines, the 5-deza analogues of pteridines, are known to possess a variety of biological properties (Heber *et al.*, 1993) and have been reported as dihydrofolate reductase inhibitors and antitumor and anti-hypertensive agents (Cody *et al.*, 2002; Ellingboe, 1995; Dave & Shukla, 2000). In the absence of potential donor and acceptor groups in the heterocyclic compound, nonconventional weak intermolecular forces, such as C—H··· π and π – π interactions, contribute to the stability of the molecular structure.

As part of a systematic investigation of heterocyclic compounds (Patel *et al.*, 2002; Jotani *et al.*, 2006), in the present study, we report the molecular structure of the title compound, (I). A view of the molecule is shown in Fig. 1. The molecule contains a fused ring system composed of pyridine and pyrimidine; the C—N distances range from 1.332 (3) to 1.470 (3) Å and the endocyclic angles at the N atoms range from 116.88 (19) to 125.28 (17)° (Table 1). A similar structural feature is also reported for piromidic acid (Song *et al.*, 1998) and pipemidic acid (Fonseca *et al.*, 1986). Least-squares plane calculations show that the fused pyridopyrimidine ring system is planar; the dihedral angle between the two ring planes is 3.26 (11)°. The r.m.s. deviation of the atoms of the fused rings from the mean plane through the rings is 0.033 Å, with a maximum deviation of 0.0599 (16) Å for atom N7.

All three methyl groups and the two O-atom substituents almost share the plane of the ring to which they are bonded, as shown by the torsion angles in Table 1. The plane of the fluorenyl ring (C16–C21) is almost orthogonal [75.21 (10)°] to that of the fused ring system, thus minimizing intramolecular interactions with this unit. The F atom is not involved in any intermolecular interactions, unlike the Br··· π interactions reported in the lattice inclusion compounds of 1,4,8,11-tetrabromo-5 β ,6,12 β ,13-tetrahydropentaleno[1,2-*b*:4,5-*b'*]diquinoline (Rahman *et al.*, 2004). The closest approach to atom F22 in (I) is by methyl atom C15 [F22···C15(*x*, *y*, *z* – 1) = 3.158 (4) Å].



The packing (Fig. 2) of the molecules is mainly stabilized by C—H···O and C—H··· π interactions (Table 2). Two significant C—H··· π interactions exist between the C12 and C15 methyl groups and the π -electron clouds of the fluorenyl ring and the pyrimidine ring (C5/C6/N7/C8/N9/C10), respectively, in neighbouring molecules. According to a classification of Malone *et al.* (1997), one of the C—H··· π interactions, *viz.* C15—H153···Cg1^{iv} (Cg1 is the centre of gravity of the pyrimidine ring; all symmetry codes are as in Table 2), very much belongs to the classical geometry type-I interaction, *i.e.* the type T interaction with the C15—H153 bond pointing towards the centre of the acceptor ring; the H153···Cg1^{iv} distance is 2.71 Å, the C15—H153···Cg1^{iv} angle is 158°, the angle of approach of the H153···Cg1^{iv} vector to the plane of the aromatic ring is 84.3° and the distance of the projection of the H153···Cg1^{iv} vector on to the ring plane from the centre of the ring is 0.029 Å. In the other C—H··· π interaction, which involves the π system of the fluorophenyl ring, C12—H123···Cg2ⁱ (Cg2 is the centre of gravity of the fluorophenyl

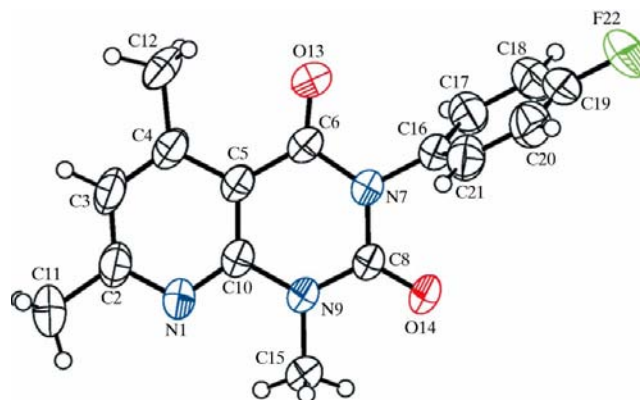


Figure 1

The molecular structure of (I), showing the atom-labelling scheme and 50% probability displacement ellipsoids.

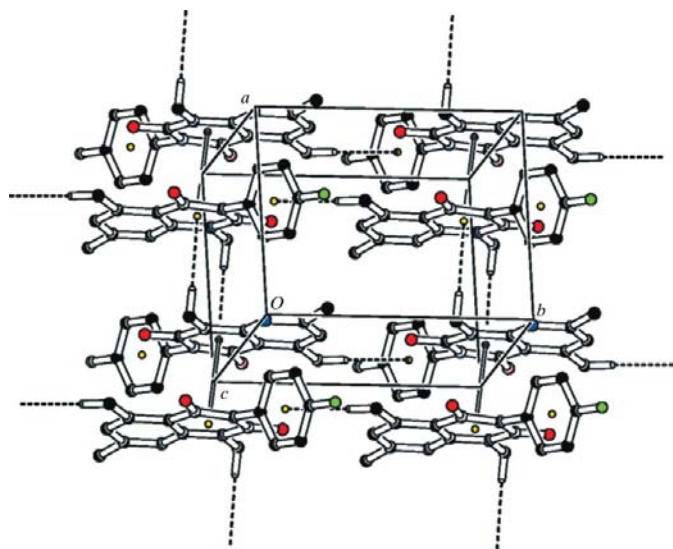


Figure 2

The molecular packing of (I), showing the C—H \cdots π interactions as dashed lines and π — π interactions as solid lines. H atoms not involved in these interactions have been omitted.

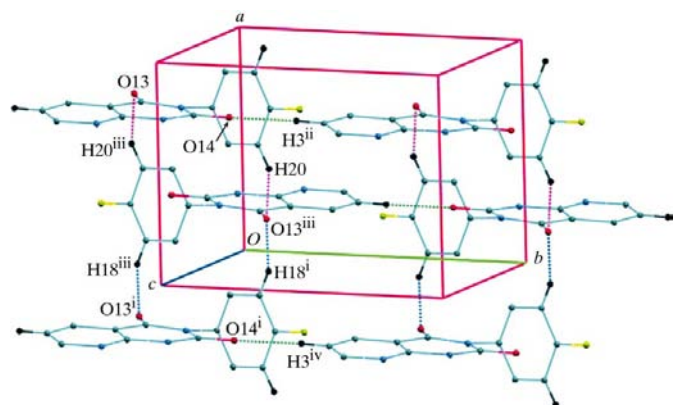


Figure 3

The crystal packing of (I), showing the formation of rings, chains and sheets *via* C—H \cdots O interactions. H atoms not involved in these interactions have been omitted. [Symmetry codes: (iii) $-x + 1, -y, -z + 1$; (v) $x - 1, y, z$; (vi) $x, y + 1, z$; (vii) $x - 1, y + 1, z$.]

ring) forms a type-III geometry; the H123 \cdots Cg2ⁱ distance is 3.00 Å, the C12—H123 \cdots Cg2ⁱ angle is 133°, the angle of approach of the H123 \cdots Cg2ⁱ vector to the plane of the fluorophenyl ring is 86.6° and the distance of projection of the H123 \cdots Cg2ⁱ vector on to the ring plane from the centre of the ring is 0.189 Å.

Parallel to the [100] direction, each molecule is connected on each side by a pair of centrosymmetrically related C—H \cdots O interactions to its neighbour. On one side of the reference molecule, the C18—H18 \cdots O13ⁱⁱ and C18ⁱⁱ—H18ⁱⁱ \cdots O13 interactions complete a ring, which can be described by a graph-set motif of $R_2^2(14)$ (Fig. 3) (Bernstein *et al.*, 1995). On the other side of the reference molecule, the C20—H20 \cdots O13ⁱⁱⁱ and C20ⁱⁱⁱ—H20ⁱⁱⁱ \cdots O13 interactions complete another ring of the same size. Together, the inter-

actions link the molecules into a ladder that runs parallel to the [100] direction. In addition, the molecules are linked by the C3—H3 \cdots O14ⁱ interaction into chains that run along [010] and can be described by a C(8) graph-set motif. The described chains and rings combine to form molecular sheets, which lie parallel to the (001) plane. π — π and C—H \cdots π interactions also occur within these sheets. The π — π interaction involves two centrosymmetrically related pyrimidine rings [at (x, y, z) and $(-x + 2, -y, -z + 2)$], where the centroids of the two rings are separated by 3.871 (4) Å (Fig. 2).

Experimental

The synthesis of the title compound was reported by Thaker (2004). Single crystals (m.p. 483 K) were grown by slow evaporation from a solution of the compound in ethyl acetate with a layer of ethyl alcohol and a few traces of dimethylformamide over it. The crystal density was measured by flotation in aqueous potassium iodide.

Crystal data

C ₁₆ H ₁₄ FN ₃ O ₂	$\gamma = 93.96$ (5)°
$M_r = 299.30$	$V = 727.5$ (8) Å ³
Triclinic, $P\bar{1}$	$Z = 2$
$a = 7.358$ (7) Å	Mo K α radiation
$b = 9.377$ (3) Å	$\mu = 0.10$ mm ⁻¹
$c = 10.758$ (4) Å	$T = 293$ (2) K
$\alpha = 97.53$ (3)°	$0.3 \times 0.2 \times 0.2$ mm
$\beta = 97.09$ (3)°	

Data collection

Enraf–Nonius CAD-4 diffractometer	2559 independent reflections
Absorption correction: ψ scan (North <i>et al.</i> , 1968)	1765 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.955, T_{\max} = 0.996$	$R_{\text{int}} = 0.010$
2776 measured reflections	2 standard reflections
	frequency: 60 min
	intensity decay: none

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.054$	202 parameters
$wR(F^2) = 0.167$	H-atom parameters constrained
$S = 1.03$	$\Delta\rho_{\text{max}} = 0.19$ e Å ⁻³
2559 reflections	$\Delta\rho_{\text{min}} = -0.29$ e Å ⁻³

Table 1

Selected geometric parameters (Å, °).

N1—C10	1.332 (3)	N7—C16	1.450 (3)
N1—C2	1.346 (3)	N9—C8	1.371 (3)
N7—C8	1.397 (3)	N9—C10	1.399 (3)
N7—C6	1.404 (3)	N9—C15	1.470 (3)
C10—N1—C2	116.88 (19)	N1—C10—N9	115.49 (18)
C8—N7—C6	125.28 (17)	N1—C10—C5	124.89 (18)
C8—N9—C10	123.17 (18)	N9—C10—C5	119.63 (19)
C11—C2—C3—C4	177.1 (2)	C15—N9—C8—N7	-177.94 (18)
C12—C4—C5—C10	-178.3 (2)	C6—C5—C10—N1	176.16 (19)
C8—N7—C6—O13	-176.4 (2)	C4—C5—C10—N9	178.52 (18)
C16—N7—C6—C5	-173.85 (18)	C8—N7—C16—C17	105.8 (3)
C15—N9—C8—O14	1.9 (3)	C6—N7—C16—C21	102.9 (2)

All H atoms were placed in geometrically idealized positions, with C—H distances of 0.96 (methyl) or 0.93 Å (aromatic), and constrained to ride on their parent atoms, with $U_{\text{iso}}(\text{H})$ values of

Table 2

Hydrogen-bond geometry (Å, °).

Cg1 and Cg2 are the centres of gravity of the pyrimidine and fluorophenyl rings, respectively.

<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>
C3—H3...O14 ⁱ	0.93	2.36	3.280 (4)	168
C18—H18...O13 ⁱⁱ	0.93	2.45	3.305 (5)	153
C20—H20...O13 ⁱⁱⁱ	0.93	2.49	3.274 (5)	142
C15—H153...Cg1 ^{iv}	0.96	2.71	3.617 (4)	158
C12—H123...Cg2 ⁱ	0.96	3.00	3.716 (5)	133

Symmetry codes: (i) $x, y - 1, z$; (ii) $-x + 2, -y, -z + 1$; (iii) $-x + 1, -y, -z + 1$; (iv) $-x + 1, -y, -z + 2$.1.2 $U_{eq}(C)$ for the phenyl H atoms and 1.5 $U_{eq}(C)$ for the methyl H atoms.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *XCAD4* in *WinGX* (Farrugia, 1999); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN3041). Services for accessing these data are described at the back of the journal.

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