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6-Methyl-4-phenylthieno[2,3-*b*]pyridine-2,5-dicarboxylic acid

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.006 Å
R factor = 0.055
wR factor = 0.167
Data-to-parameter ratio = 12.5

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

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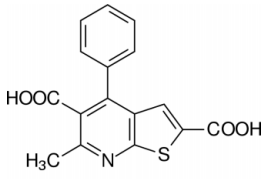
The crystal structure of the title compound, $C_{16}H_{11}NO_4S$, is stabilized by intermolecular hydrogen bonds of the types O—H···O, O—H···N and C—H···O. The thieno[2,3-*b*]pyridine moiety is planar.

Comment

Thieno[2,3-*b*]pyridine derivatives form a class of fused heterocyclic compounds with interesting bio- and pharmacological properties. The activity of some dihydrothieno[2,3-*b*]-pyridine derivatives has been thoroughly investigated as calcium antagonists in the treatment of cardiovascular diseases (Dessy *et al.*, 1993). Also, the enantioselective synthesis of a thieno[2,3-*b*]pyridine as a 5-lipoxygenase (5-LO) inhibitor has been reported (Rohloff *et al.*, 1994). In previous work, we described the crystal structures of two different dihydrothieno[2,3-*b*]pyridines (Duque *et al.*, 1998, 2000) and recently we reported the crystal structure of 2,5-diethoxycarbonyl-6-methyl-4-phenylthieno[2,3-*b*]pyridine (Novoa de Armas *et al.*, 2003*a*) and its substituted 4-(4-bromophenyl) analog (Novoa de Armas *et al.*, 2003*b*). Saponification of the two ester groups yields the title compound, (I), as a crystalline solid. In (I), the thieno[2,3-*b*]pyridine moiety is planar and the dihedral angle between the least-squares plane of the thieno[2,3-*b*]pyridine moiety and the 4-phenyl ring is 46.3 (2)°. The carboxyl group C21/O22/O23 is nearly coplanar with the thieno[2,3-*b*]pyridine moiety [C3—C2—C21—O22 = 3.2 (7)°], while the other carboxyl group, C51/O52/O53, is not [C4—C5—C51—O52 = 71.2 (6)°]. The mean Csp^2—Csp^2 bond length within the 4-phenyl ring is 1.383 (4) Å. The crystal structure is stabilized by hydrogen bonds of the types O—H···O, O—H···N and C—H···O (Table 2). The difference between the ester 2,5-diethoxycarbonyl-6-methyl-4-phenylthieno[2,3-*b*]pyridine and (I) is the presence of the intermolecular O—H···O hydrogen bonds in the latter.



(I)

Experimental

Diethyl 4-phenylthieno[2,3-*b*]pyridine-2,5-dicarboxylate (2 mmol) was mixed with 20 ml of 10% aqueous sodium hydroxide and the mixture was refluxed vigorously until all the solid ester had dissolved

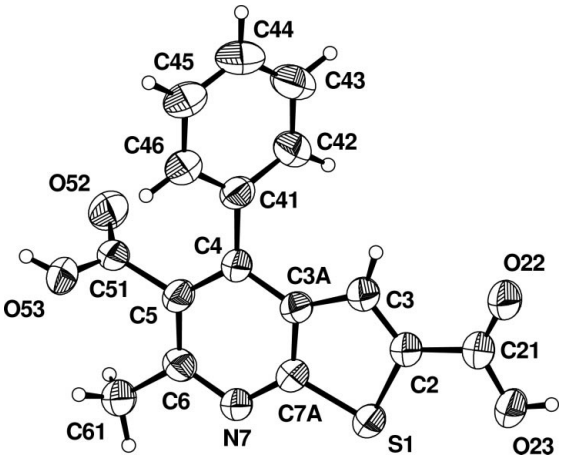


Figure 1
Plot showing the atomic numbering scheme for the title compound. Displacement ellipsoids are drawn at the 50% probability level for non-H atoms.

(about 1 h). The saponification mixture was then cooled and the aqueous solution was separated from any oil present. Afterwards, the solution was acidified to Congo red paper with 10% sulfuric acid. Compound (I) was collected by filtration and washed thoroughly with water, then dried (yield 86%; m.p. 638 K). IR (KBr, cm^{-1}): 3384 (OH), 1724 (C═O), 1685 (C═O), 1600 (C═C); ^{1}H NMR (DMSO-d_6, p.p.m.): 7.58–7.51 (*m*, 5H, Ph), 7.49 (*s*, 1H, ═CH), 3.44 (*br s*, 2H, OH), 2.66 (*s*, 3H, CH_3); ^{13}C NMR (DMSO-d_6, p.p.m.): 168.6 (CO), 162.2 (CO), 161.1 (C6), 154.2 (C4), 143.0 (C1′), 134.9 (C2), 133.8 (C7a), 128.9 (C4′), 128.6 (C3a), 128.4 (C3′ and C5′), 128.3 (C2′ and C6′), 127.1 (C3), 126.4 (C5), 22.7 (CH_3); MS, *m*/*Z* (intensity %): 313 (M^+, 100), 296 (30), 295 (50), 222 (12), 78 (19), 63 (38). Crystals suitable for X-ray analysis were obtained by slow evaporation from methanol.

Crystal data

$C_{16}H_{11}NO_4S$
M_r = 313.32
Monoclinic, $P2_1/c$
a = 13.3208 (5) Å
b = 12.5015 (4) Å
c = 8.9448 (4) Å
β = 102.859 (3)°
V = 1452.22 (8) Å^3
Z = 4
D_x = 1.433 Mg m^{-3}
Cu Kα radiation
Cell parameters from 39 reflections
θ = 6.8–27.9°
μ = 2.15 mm^{-1}
T = 293 K
Plate, colourless
0.40 × 0.20 × 0.02 mm

Data collection

Siemens *P*4 four-circle diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.627, T_{max} = 0.958
3514 measured reflections
2535 independent reflections
1565 reflections with $F^2 > 2\sigma(F^2)$
R_{int} = 0.042
θ_{max} = 69.3°
$h = -16 \rightarrow 16$
$k = -15 \rightarrow 1$
$l = -1 \rightarrow 10$
3 standard reflections
every 100 reflections
intensity decay: 2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.055
$wR(F^2)$ = 0.167
S = 1.11
2535 reflections
203 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0433P)^2 + 2.354P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.33 e Å^{-3}
$\Delta\rho_{min}$ = −0.27 e Å^{-3}
Extinction correction: *SHELXL*97′
Extinction coefficient: 0.0050 (5)

Table 1
Selected geometric parameters (Å, °).

S1—C2	1.732 (4)	O52—C51	1.203 (5)
S1—C7*A*	1.730 (4)	O53—C51	1.322 (5)
O22—C21	1.231 (5)	N7—C6	1.343 (5)
O23—C21	1.309 (5)	N7—C7*A*	1.341 (5)
C2—S1—C7*A*	89.7 (2)	N7—C7*A*—C3*A*	125.4 (4)
C6—N7—C7*A*	117.1 (3)	O23—C21—C2	113.8 (4)
S1—C2—C21	121.2 (3)	O22—C21—C2	121.6 (3)
S1—C2—C3	114.2 (3)	O22—C21—O23	124.6 (4)
N7—C6—C61	115.6 (3)	O53—C51—C5	112.5 (3)
N7—C6—C5	121.8 (4)	O52—C51—O53	124.8 (4)
S1—C7*A*—C3*A*	113.0 (3)	O52—C51—C5	122.7 (4)
S1—C7*A*—N7	121.6 (3)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O23—H23···O22^{i}	0.82	1.81	2.633 (5)	176
O53—H53···N7^{ii}	0.82	1.88	2.688 (4)	170
C45—H45···O52^{iii}	0.93	2.48	3.362 (6)	158

Symmetry codes: (i) $1-x, 1-y, 2-z$; (ii) $2-x, y-\frac{1}{2}, \frac{3}{2}-z$; (iii) $x, -\frac{1}{2}-y, \frac{1}{2}+z$.

H atoms were positioned geometrically and included in the refinement, but were constrained to ride on their parent atoms, with U_{iso}(H) values fixed at 1.3U_{eq} of their parent atoms.

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Bergerhoff, 1996); software used to prepare material for publication: *PLATON* (Spek, 2003), *PARST* (Nardelli, 1995) and *PARSTCIF* (Nardelli, 1991).

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