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2,5-Diethoxycarbonyl-6-methyl-4-phenyl-thieno[2,3-*b*]pyridine

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In the title compound, $C_{20}H_{19}NO_4S$, the structure is stabilized by intermolecular and intramolecular C—H⋯O hydrogen bonds. The thieno[2,3-*b*]pyridine moiety is planar.

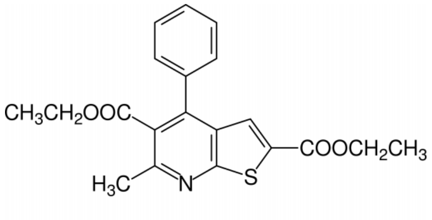
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
R factor = 0.051
wR factor = 0.148
Data-to-parameter ratio = 14.3

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

Comment

Research on 1,4-dihydropyridine (1,4-DHP) systems is of high interest owing to their biological properties. Recently the pharmacological properties of some 1,4-DHP derivatives (Yagupolskii *et al.*, 2001) have been reported. In addition, some thieno[2,3-*b*]pyridines with a different substitution pattern have shown interesting anti-arteriosclerotic effects (Saito *et al.*, 1993). In previous studies, we have described the crystal structures of two different dihydrothieno[2,3-*b*]-pyridines (Duque *et al.*, 1998, 2000). They were obtained by an expeditious synthetic pathway (Suárez *et al.*, 1997), involving reaction of the appropriate alkyl 4-aryl-6-chloro-5-formyl-2-methyl-1,4-dihydropyridine-3-carboxylate (Verdecia *et al.*, 1996) with an equimolar amount of ethyl mercaptoacetate in the presence of sodium ethoxide and dry ethanol. Further oxidation of these dihydro-derivatives produces the corresponding thieno[2,3-*b*]pyridines, such as the title compound, (I). In (I), the thieno[2,3-*b*]pyridine moiety is planar and the dihedral angle between its least-squares plane and that of the 4-phenyl ring is 58.07 (10)°. The ester groups are nearly coplanar with the thieno[2,3-*b*]pyridine moiety. The mean Csp^2—Csp^2 bond length within the 4-phenyl ring is 1.384 (2) Å. The structure is stabilized by two intermolecular and two intramolecular hydrogen-bonds of the type C—H⋯O.



(I)

Experimental

A solution of ceric ammonium nitrate (2 mmol) in water (5 ml) was added dropwise to a stirred solution of diethyl 6-methyl-4-phenyl-dihydrothieno[2,3-*b*]pyridine-2,5-dicarboxylate (1 mmol) in acetone (10 ml). Stirring was continued for 0.5 h, and the reaction mixture was partitioned between ethyl acetate and water. Afterwards, the crude product, (I), was purified by column chromatography on silica gel (20 g), using hexane:ethyl acetate (4:1) as eluent (yield 91%; m.p.

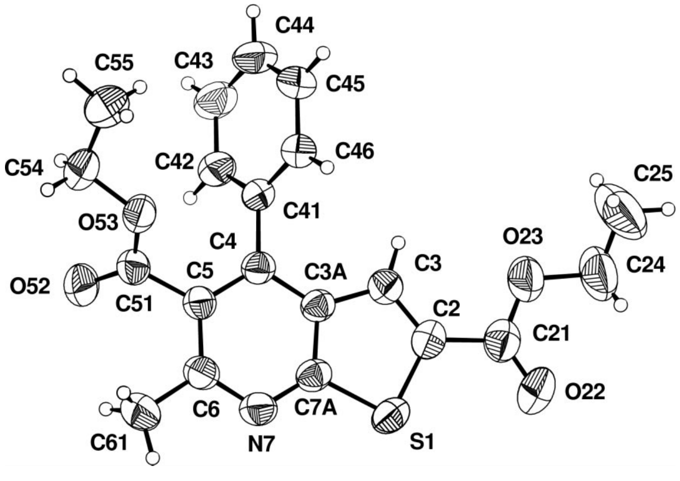


Figure 1
View of the title compound, showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level for non-H atoms.

400–401 K). IR (KBr, cm^{-1}): 1706 (C═O), 1654 (C═O), 1629 (C═C); ^{1}H-NMR (DMSO-d_6, p.p.m.): 7.59 (*s*, 1H, = CH), 7.57–7.43 (*m*, 5H, Ph), 4.32 (*q*, 2H, CH$_2$), 4.06 (*q*, 2H, CH$_2$), 2.66 (*s*, 3H, CH$_3$), 1.29 (*t*, 3H, CH$_3$), 0.89 (*t*, 3H, CH$_3$); ^{13}C-NMR (DMSO-d_6, p.p.m.): 167.6 (CO), 162.2 (CO), 161.7 (C6), 155.7 (C4), 145.0 (C41), 135.4 (C2), 133.0 (C7a), 129.6 (C3a), 129.1 (C43, C45), 129.1 (C44), 128.7 (C42, C46), 127.4 (C3), 126.2 (C5), 62.3 (CH2), 61.7 (CH2), 23.3 (CH3), 14.4 (CH3), 13.7 (CH3); MS, *m*/*z* (intensity %): 369 (M^+, 100), 341 (7), 296 (23), 223 (11). Crystals suitable for X-ray analysis were obtained by slow evaporation from methanol.

Crystal data

$C_{20}H_{19}NO_4S$
$M_r = 369.42$
Monoclinic, $P2_1/n$
$a = 7.7809$ (4) Å
$b = 9.8572$ (4) Å
$c = 24.548$ (1) Å
$\beta = 97.222$ (5)°
$V = 1867.8$ (2) Å^3
$Z = 4$

$D_x = 1.314$ Mg m^{-3}
Cu Kα radiation
Cell parameters from 38 reflections
$\theta = 11.0$–$28.0°$
$\mu = 1.75$ mm^{-1}
$T = 293$ K
Prism, colourless
0.40 × 0.20 × 0.18 mm

Data collection

Siemens *P*4 four-circle diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.529$, $T_{\max} = 0.730$
4884 measured reflections
3411 independent reflections
2824 reflections with $F^2 > 2\sigma(F^2)$

$R_{\rm int} = 0.047$
$\theta_{\max} = 69.3°$
$h = -1 \rightarrow 9$
$k = -11 \rightarrow 1$
$l = -29 \rightarrow 29$
3 standard reflections every 100 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.051$
$wR(F^2) = 0.148$
$S = 1.05$
3411 reflections
239 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (.069P)^2 +.\,8481P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.29$ e Å^{-3}
$\Delta\rho_{\min} = -0.39$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0043 (4)

Table 1
Selected geometric parameters (Å, °).

S1—C2	1.732 (3)	C41—C46	1.393 (3)
S1—C7*A*	1.727 (2)	C42—C43	1.384 (4)
C2—C21	1.470 (4)	C43—C44	1.372 (5)
C2—C3	1.358 (3)	C44—C45	1.373 (5)
C21—O22	1.202 (4)	C45—C46	1.383 (4)
C21—O23	1.332 (4)	C5—C51	1.496 (3)
O23—C24	1.454 (5)	C5—C6	1.414 (3)
C24—C25	1.334 (6)	C51—O52	1.203 (3)
C3—C3*A*	1.426 (3)	C51—O53	1.324 (3)
C3*A*—C4	1.406 (3)	O53—C54	1.451 (3)
C3*A*—C7*A*	1.410 (3)	C54—C55	1.469 (5)
C4—C41	1.485 (3)	C6—C61	1.503 (4)
C4—C5	1.399 (3)	C6—N7	1.337 (3)
C41—C42	1.391 (4)	N7—C7*A*	1.337 (3)
C2—S1—C7*A*	90.10 (10)	C42—C43—C44	120.3 (3)
S1—C2—C21	117.0 (2)	C43—C44—C45	120.1 (3)
S1—C2—C3	113.8 (2)	C44—C45—C46	120.6 (3)
C21—C2—C3	129.1 (2)	C41—C46—C45	119.7 (2)
C2—C21—O22	124.1 (3)	C4—C5—C51	121.0 (2)
C2—C21—O23	111.3 (3)	C4—C5—C6	120.9 (2)
O22—C21—O23	124.6 (3)	C51—C5—C6	118.1 (2)
C21—O23—C24	116.0 (3)	C5—C51—O52	124.9 (2)
O23—C24—C25	111.9 (3)	C5—C51—O53	110.9 (2)
C2—C3—C3*A*	112.4 (2)	O52—C51—O53	124.2 (2)
C3—C3*A*—C4	131.4 (2)	C51—O53—C54	118.4 (2)
C3—C3*A*—C7*A*	111.0 (2)	O53—C54—C55	106.5 (2)
C4—C3*A*—C7*A*	117.7 (2)	C5—C6—C61	122.8 (2)
C3*A*—C4—C41	121.0 (2)	C5—C6—N7	122.6 (2)
C3*A*—C4—C5	116.7 (2)	C61—C6—N7	114.5 (2)
C41—C4—C5	122.4 (2)	C6—N7—C7*A*	116.1 (2)
C4—C41—C42	120.4 (2)	S1—C7*A*—C3*A*	112.6 (2)
C4—C41—C46	120.4 (2)	S1—C7*A*—N7	121.4 (2)
C42—C41—C46	119.2 (2)	C3*A*—C7*A*—N7	126.0 (2)
C41—C42—C43	120.1 (2)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C42—H42···O22$^{\rm i}$	0.93	2.57	3.455 (4)	159
C43—H43···O52$^{\rm ii}$	0.93	2.54	3.403 (3)	155
C61—H61*A*···O52	0.96	2.55	2.987 (4)	108
C24—H24···O22	0.97	2.39	2.670 (5)	96

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

The short distance for C24—C25 = 1.334 (6) Å is the the result of some disorder in atom C25 of the terminal methyl group, as indicated by rather high anisotropic displacement parameters. H atoms were positioned geometrically and included in the refinement, but were constrained to ride on their parent atoms, with U(H) fixed at $1.3U_{\rm eq}$ 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, 1990), *PARST* (Nardelli, 1995), *PARSTCIF* (Nardelli, 1991).

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