

Ethyl 4*H*-thieno[3,2-*b*]pyrrole-5-carboxylateJanine T Chantson and
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Key indicators

Single-crystal X-ray study
T = 293 K
Mean $\sigma(\text{C}-\text{C}) = 0.002 \text{ \AA}$
R factor = 0.040
wR factor = 0.113
Data-to-parameter ratio = 11.8For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Ethyl 4*H*-thieno[3,2-*b*]pyrrole-5-carboxylate, C₉H₉NO₂S, is derived from thiophene-3-carboxaldehyde and ethyl azidoacetate. The crystal structure is composed of an ethyl carboxylate group attached to a planar thieno[3,2-*b*]pyrrole ring system.

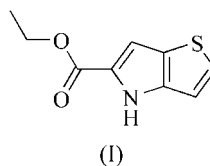
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Comment

During the past few decades the optical and electronic properties of conjugated organic polymers have received considerable interest. These polymers are often based on heteroaromatic components and several fused-ring systems based on thiophene–pyrazine, thiophene–thiophene, thiophene–pyrrole and pyrrole–pyrrole moieties have been investigated as possible polymer precursors (Roncali, 1992; Pagani, 1994). While the preparation of thieno[3,2-*b*]pyrrole was described several decades ago (Gronomitz *et al.*, 1976; Farnier *et al.*, 1976), no experimental data on the molecular geometry of substituted or unsubstituted thieno[3,2-*b*]pyrroles have been reported. However, the structures of ethyl 4*H*-furo[3,2-*b*]pyrrole-5-carboxylate (Sivý *et al.*, 1988) and unsubstituted plus a number of substituted methyl 4*H*-furo[3,2-*b*]pyrrole-5-carboxylates (Cryanski *et al.*, 2001) have been published. Also the crystal structures of *N*-octyl, *N*-*tert*-butyl, and *N*-*p*-hexylphenyl-functionalized dithieno[3,2-*b*:2',3'-*d*]pyrroles have recently been described (Ogawa & Rasmussen, 2003). In this paper, we report the X-ray crystal structure of ethyl 4*H*-thieno[3,2-*b*]pyrrole-5-carboxylate, (I).



The molecular structure of (I) is shown in Fig. 1. The thienopyrrole ring is planar (r.m.s. deviation of the ring atoms from the least-squares plane = 0.002 Å). The C4–S1–C1 angle [90.68 (8)°] is similar to the corresponding angle at the S atoms in several *N*-functionalized dithieno[3,2-*b*:2',3'-*d*]pyrroles [C–S–C = 90.07–90.74°, mean = 90.4 (2)°; Ogawa & Rasmussen, 2003]. The C3–N1–C6 angle [108.40 (13)°] is, in turn, similar to the corresponding angle [108.5 (3)°] in ethyl 4*H*-furo[3,2-*b*]pyrrole-5-carboxylate (Sivý *et al.*, 1988), but somewhat larger than the corresponding angles found in some methyl 2*R*-3*R'*-4*H*-furo[3,2-*b*]pyrrole-5-carboxylates [107.61 (11)°, *R* = *R'* = H; 107.36 (11)°, *R* = *R'* = Me; 107.81 (13)° *R* = CHO, *R'* = H; Cryanski *et al.*, 2001]. The C–C bond shared by the two rings is somewhat longer [1.387 (2) Å] than the corresponding bond in a range of 4*H*-furo[3,2-*b*]-

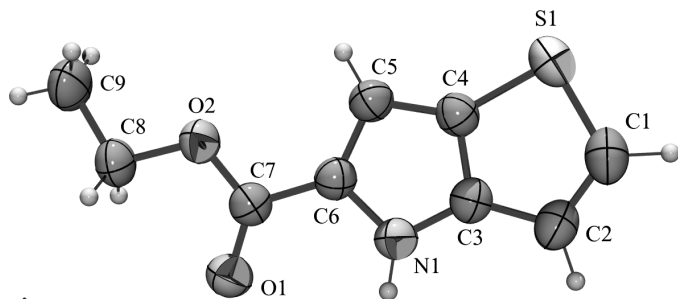


Figure 1
The molecular structure of (I), with displacement ellipsoids drawn at the 50% probability level and H atoms drawn as spheres of arbitrary radius.

pyrrole carboxylates [1.361–1.380 Å, mean = 1.373 (8) Å; Cryanski *et al.*, 2001; Sivý *et al.*, 1988] and is at the upper end of the range of the corresponding bond length in a number of *N*-functionalized dithieno[3,2-*b*:2',3'-*d*]pyrroles [1.371–1.389 Å, mean = 1.381 (6) Å; Ogawa & Rasmussen, 2003].

Experimental

Compound (I) was prepared by adjusting a previously reported method (Hemetsberger & Knittel, 1972). Ethyl azidoacetate and 2-thiophenecarboxaldehyde were added to a solution of sodium in ethanol at 253 K for 90 min. After work-up the resultant yellow oil was refluxed in xylene for 1 h. Following work-up and crystallization, (I) was obtained as a colourless solid (yield: 60%; m.p. 402–403 K). ¹H NMR (CDCl₃, 298 K): δ 1.37 (*t*, ³*J*_{H,H} = 7.1, 3H, CH₃), 4.35 (*q*, ³*J*_{H,H} = 7.1 Hz, 2H, CH₂), 6.94 (*d*, ³*J*_{H,H} = 5.2 Hz, 1H, CH), 7.12 (*d*, ⁴*J*_{H,H} = 1.6 Hz, 1H, CH), 7.31 (*d*, ³*J*_{H,H} = 5.2 Hz, 1H, CH), 8.99 (*br s*, 1H, NH). ¹³C NMR (CDCl₃, 298 K): δ 14.5 (CH₃), 60.7 (CH₂), 107.5 (CH), 111.0 (CH), 127.1 and 124.7 (*ipso*-C), 129.4 (CH), 141.4 (*ipso*-C). FAB-MS: accurate mass 195.035400 (calculated), 195.035412 (observed); *m/z* 195 [*M*⁺, 67%], 150 [*M*⁺ – EtO, 26%], 149 [*M*⁺ – EtOH, 100%], 122 [*M*⁺ – CO₂Et, 11%], 121 [*M*⁺ – HCO₂Et, 28%], 95 [*M*⁺ – HCO₂Et – C₂H₂, 15%].

Crystal data

C₉H₉NO₂S
M_r = 195.23
 Monoclinic, *P*₂₁/*n*
a = 5.9572 (4) Å
b = 12.9894 (9) Å
c = 12.1234 (9) Å
 β = 98.169 (1)°
V = 928.60 (11) Å³
Z = 4

D_x = 1.396 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 3284 reflections
 θ = 3.1–26.4°
 μ = 0.31 mm⁻¹
T = 293 (2) K
 Rectangular prism, colourless
 0.41 × 0.26 × 0.15 mm

Data collection

Bruker *P4*/SMART 1000 CCD diffractometer
 φ and ω scans
 Absorption correction: multi-scan (*SADABS*; Bruker, 2001)
*T*_{min} = 0.796, *T*_{max} = 0.954
 4919 measured reflections

1762 independent reflections
 1550 reflections with *I* > 2σ(*I*)
*R*_{int} = 0.028
 θ _{max} = 26.6°
h = –3 → 7
k = –14 → 15
l = –13 → 14

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.040
wR(*F*²) = 0.113
S = 1.08
 1762 reflections
 149 parameters
 All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0707P)^2 + 0.0977P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.19 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.21 \text{ e \AA}^{-3}$
 Extinction correction: *SHELXTL*
 Extinction coefficient: 0.019 (4)

Table 1

Selected geometric parameters (Å, °).

S1–C4	1.7256 (16)	C2–C3	1.413 (2)
S1–C1	1.732 (2)	C3–C4	1.387 (2)
N1–C3	1.357 (2)	C4–C5	1.408 (2)
N1–C6	1.374 (2)	C5–C6	1.380 (2)
C1–C2	1.350 (3)		
C4–S1–C1	90.68 (8)	C4–C3–C2	114.84 (14)
C3–N1–C6	108.40 (13)	C3–C4–C5	108.33 (13)
C2–C1–S1	114.26 (14)	C3–C4–S1	110.13 (12)
C1–C2–C3	110.08 (16)	C5–C4–S1	141.54 (13)
N1–C3–C4	108.04 (13)	C6–C5–C4	105.58 (14)
N1–C3–C2	137.12 (15)	N1–C6–C5	109.65 (14)

All H-atom positions were obtained from difference Fourier syntheses and were refined unconstrained with individual isotropic displacement parameters.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *ORTEP-3* (Farrugia, 1997) and *POV-Ray* (The POV-Ray Team, 2004); software used to prepare material for publication: *SHELXTL*.

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References

- Bruker (2001). *SMART*, *SAINT*, *SADABS* and *SHELXTL* (Version 6.12). Bruker AXS Inc., Madison, Wisconsin, USA.
- Cryanski, M. K., Krygowski, T. M., Krutosikova, A. & Slezziak, R. (2001). *Tetrahedron*, **57**, 8867–8873.
- Farnier, M., Soth, S. & Fournari, P. (1976). *Can. J. Chem.* **54**, 1074–1082.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Gronowitz, S., Westerlund, C. & Hörnfeldt, A.-B. (1976). *Acta Chem. Scand. Ser. B*, **30**, 391–396.
- Hemetsberger, H. & Knittel, D. (1972). *Monatsh. Chem.* **103**, 194–204.
- Ogawa, K. & Rasmussen, S. C. (2003). *J. Org. Chem.* **68**, 2921–2928.
- Pagani, G. A. (1994). *Heterocycles*, **37**, 2069–2086.
- The POV-Ray Team (2004). *POV-Ray*. URL: <http://www.povray.org/download/>.
- Roncali, J. (1992). *Chem. Rev.* **92**, 711–738.
- Sivý, P., Koren, B., Valach, F. & Krutosikova, A. (1988). *Acta Cryst.* **C44**, 2032–2033.