

trans disposition (Foces-Foces, Cano & Garcia-Blanco, 1980).

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Structure of Ethyl 2-Amino-4,5,6,7-tetrahydrobenzo[*b*]thiophene-3-carboxylate at 163 K

BY S. B. LARSON* AND S. H. SIMONSEN

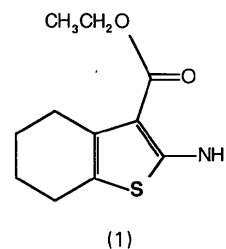
Department of Chemistry, University of Texas at Austin, Austin, TX 78712, USA

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Abstract. C₁₁H₁₅NO₂S, *M_r* = 225.31, monoclinic, *P*2₁/*c*, *a* = 8.2996 (13), *b* = 9.5307 (12), *c* = 14.6009 (20) Å, β = 105.818 (13)°, *V* = 1111.2 (3) Å³, *Z* = 4, *D_x*(163 K) = 1.347, *D_m*(295 K) = 1.310 (1) g cm⁻³, λ(MoKα) = 0.71069 Å, μ = 2.68 cm⁻¹, *F*(000) = 480, *R* = 0.0407 for 2527 reflections [*F_o* ≥ 4σ(*F_o*)]. The thiophene ring is planar [max. deviation: C(9), 0.007 (2) Å] as is the carboxyl group, C(3), C(10), O(1), O(2) [max. deviation: C(10), 0.001 (2) Å]; the twist between these planes is only 0.96 (7)°. Planarity of the N, C(2), C(3), C(10), O(1), O(2), C(11) fragment is favored because of the intramolecular hydrogen bond [O(1)⋯H(N)B, 2.08 (3) Å]; and conjugation which is evident in the short single bonds [C(2)–N and C(3)–C(10)] and long double bonds [C(2)–C(3) and C(10)–O(1)] in this fragment. The N is slightly pyramidal [max. deviation: N, –0.105 (2) Å]. The intermolecular hydrogen bonding [O(1)⋯H(N)A (1–*x*, ½+*y*, ½–*z*), 2.01 (2) Å] connects the molecules along the *b* axis. All other intermolecular contacts are not less than the sum of the respective van der Waals radii.

Experimental. Large colorless, transparent prismatic crystals of (1) were obtained by sublimation from a

sample purchased from Aldrich Chemical Co. Density was measured by flotation in aqueous ZnCl₂. Table 1 is a summary of data collection and structural refinement.



The structure was solved by *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), and refined by full-matrix least squares (*SHELX76*, Sheldrick, 1976). Scattering factors and anomalous-dispersion corrections for non-H atoms were taken from *International Tables for X-ray Crystallography* (1974); H from Stewart, Davidson & Simpson (1965). All atomic positional parameters were refined. Non-H atoms were refined anisotropically; H atoms isotropically. The H atoms were located in an electron density difference map as peaks of 0.60–0.94 e Å⁻³. Atom labeling, bond lengths and bond angles are shown in Fig. 1. Fig. 2 illustrates the molecular packing and

* Current address: Nucleic Acid Research Institute, 3300 Hyland Avenue, Costa Mesa, CA 92626, USA.

Table 1. Summary of data collection and structural refinement for C₁₁H₁₅NO₂S

(a) Data collection (163 K)*†	
Radiation, λ (Å)	Mo K α , 0.71069
Mode	ω scan
Scan range	Symmetrically over 1° about $K\alpha_{1,2}$ maximum
Background	Offset $\pm 1^\circ$ in ω from $K\alpha_{1,2}$ maximum
Scan rate (° min ⁻¹)	3.0–6.0
Stability analysis	
Computed s, t	–0.000171, 0.0
Correction range on l	0.4% (not applied)
Standard reflections	004, 020, 210, 213
2 θ range (°)	4.0–60.0
Total reflections measured, unique	3250, 3250
Crystal dimensions (mm)	0.46 × 0.31 × 0.14
Crystal volume (mm ³)	0.0185
Crystal faces	{011}, {0 $\bar{1}$ 1}, {011}, {0 $\bar{2}$ 1}, {100}
	{111}, {111}, {001} + fragment face
Transmission-factor range	0.923–0.968
(b) Structure refinement‡	
Instability factor, p	0.04
Reflections used, m [$F \geq 4\sigma(F_o)$]	2527
No. of variables, n	196
Goodness of fit, S	1.307
R, wR	0.0407, 0.0458
R_{int}	0.0573
Max. $ \Delta / \sigma $	0.017
Max. peak in difference map (e Å ⁻³)	0.35 [near C(5), disordered]
Min. density in difference map (e Å ⁻³)	–0.29

* Unit-cell parameters were obtained by least-squares refinement of the setting angles of 45 reflections with $21.6 < 2\theta < 27.8^\circ$.

† Syntax P2, diffractometer with a graphite monochromator and Syntex LT-1 inert-gas (N₂) low-temperature delivery system. Data reduction was carried out as described in Riley & Davis (1976). Crystal and instrument stability were monitored by remeasurement of 4 check reflections after every 96 reflections. As detailed by Henslee & Davis (1975), these data were analyzed to relate intensity to exposure time by the equation $y = 1.0 + sx + tx^2$, where x is exposure time (hours), y is fractional intensity relative to $x = 0$ and s and t are coefficients determined by least squares.

‡ Function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = 1/(\sigma(F_o))^2$; $\sigma(F_o) = \{F_o[\sigma(D)]/2I\}$; $\sigma(D) = \{N_{pk} + N_{bg1} + N_{bg2} + (pI)^2\}^{1/2}$.

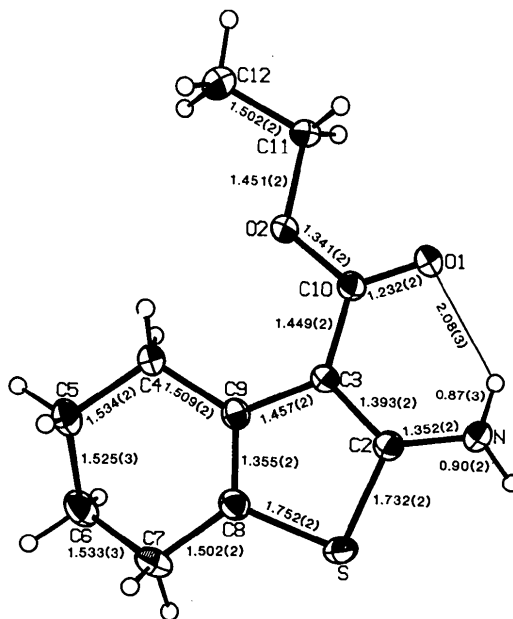
Table 2. Positions and U/U_{eq} for atoms in C₁₁H₁₅NO₂S

For non-H atoms, the U value is U_{eq} , calculated as $U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* A_{ij}$, where A_{ij} is the dot product of the i th and j th direct-space unit-cell vectors.

	x	y	z	U/U_{eq} (Å ²)
S	0.21135 (6)	0.19052 (4)	0.11119 (3)	0.02407 (13)
O(1)	0.4743 (2)	0.61395 (12)	0.15385 (8)	0.0243 (4)
O(2)	0.34005 (15)	0.65153 (12)	–0.00009 (8)	0.0213 (3)
N	0.4190 (2)	0.3646 (2)	0.23326 (10)	0.0294 (5)
C(2)	0.3226 (2)	0.3449 (2)	0.14327 (11)	0.0208 (5)
C(3)	0.2935 (2)	0.4378 (2)	0.06691 (11)	0.0177 (4)
C(4)	0.1202 (2)	0.4535 (2)	–0.11405 (11)	0.0198 (5)
C(5)	–0.0183 (2)	0.3713 (2)	–0.18473 (12)	0.0271 (5)
C(6)	0.0113 (3)	0.2132 (2)	–0.17851 (13)	0.0283 (6)
C(7)	0.0117 (2)	0.1590 (2)	–0.07961 (13)	0.0252 (5)
C(8)	0.1253 (2)	0.2500 (2)	–0.00547 (11)	0.0198 (5)
C(9)	0.1771 (2)	0.3815 (2)	–0.01859 (11)	0.0175 (4)
C(10)	0.3774 (2)	0.5726 (2)	0.07894 (11)	0.0177 (4)
C(11)	0.4159 (2)	0.7897 (2)	0.00623 (12)	0.0208 (5)
C(12)	0.3404 (2)	0.8589 (2)	–0.08812 (13)	0.0286 (6)
H(N)A	0.452 (3)	0.292 (3)	0.272 (2)	0.042 (6)
H(N)B	0.482 (3)	0.439 (3)	0.241 (2)	0.044 (7)
H(4)A	0.221 (2)	0.465 (2)	–0.1399 (12)	0.019 (5)
H(4)B	0.081 (3)	0.545 (2)	–0.1089 (14)	0.032 (6)
H(5)A	–0.025 (3)	0.404 (2)	–0.251 (2)	0.036 (6)
H(5)B	–0.132 (3)	0.394 (2)	–0.1720 (14)	0.032 (5)
H(6)A	0.121 (3)	0.194 (2)	–0.193 (2)	0.037 (6)
H(6)B	–0.078 (3)	0.163 (2)	–0.223 (2)	0.044 (6)
H(7)A	–0.106 (3)	0.160 (2)	–0.0740 (14)	0.031 (5)
H(7)B	0.053 (3)	0.062 (2)	–0.0711 (14)	0.034 (6)

Table 2 (cont.)

	x	y	z	U/U_{eq} (Å ²)
H(11)A	0.538 (2)	0.778 (2)	0.0217 (13)	0.022 (5)
H(11)B	0.387 (2)	0.841 (2)	0.0558 (14)	0.023 (5)
H(12)A	0.373 (3)	0.809 (2)	–0.143 (2)	0.036 (6)
H(12)B	0.223 (3)	0.862 (2)	–0.099 (2)	0.037 (6)
H(12)C	0.385 (3)	0.953 (2)	–0.0875 (15)	0.037 (6)



N–C(2)–S	120.8	C(5)–C(4)–C(9)	112.2
N–C(2)–C(3)	128.1	C(4)–C(9)–C(8)	121.3
C(2)–S–C(8)	92.0	C(9)–C(8)–C(7)	126.4
S–C(8)–C(9)	112.1	C(4)–C(9)–C(3)	126.2
C(8)–C(9)–C(3)	112.4	C(9)–C(3)–C(10)	128.0
C(9)–C(3)–C(2)	112.4	C(2)–C(3)–C(10)	119.6
C(3)–C(2)–S	111.1	C(3)–C(10)–O(1)	124.5
S–C(8)–C(7)	121.6	C(3)–C(10)–O(2)	113.7
C(8)–C(7)–C(6)	108.9	O(1)–C(10)–O(2)	121.8
C(7)–C(6)–C(5)	110.4	C(10)–O(2)–C(11)	117.4
C(6)–C(5)–C(4)	112.6	O(2)–C(11)–C(12)	106.0

Fig. 1. View of the title compound illustrating atom labeling and bond lengths (Å) and e.s.d.'s. Thermal ellipsoids scaled to 50% probability. Bond angles (°) with e.s.d.'s in the range 0.1–0.2°.

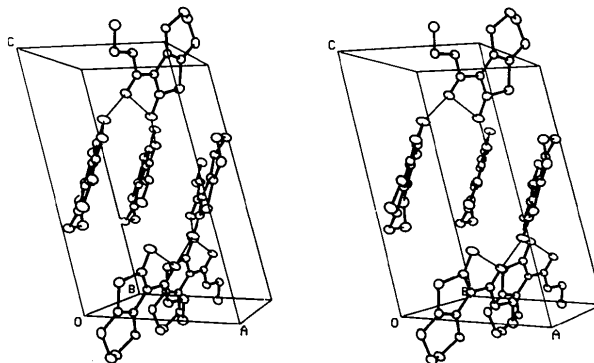


Fig. 2. Stereoview of the molecular packing.

the planarity of the entire system [excluding C(5) and C(6)]. Atomic parameters are given in Table 2.* Principal computer programs are cited in Gadol & Davis (1982); the least-squares-planes program was written by Cordes (1983).

Related literature. The structure was previously reported (Simonsen, 1972), but there was some difficulty with disorder in the cyclohexeno ring. In the present structure determination, the disorder shows up in the final electron density difference map in which peaks of 0.35 and 0.31 e Å⁻³ form a reasonable C(4)—C(5)—C(6)—C(7) chain with C—C distances of 1.66, 1.63 and 1.45 Å through the sequence. This fraction, amounting to approximately 5%, was ignored. The angle between the thiophene ring and the carboxyl group in the title compound differs greatly from the 79° found in 2-(*N,N*-diethylamino)-3-carbomethoxy-naphtho[2,3-*b*]thiophene-4,9-dione (DCMT) (Gibbons, Lerbscher & Trotter, 1972). DCMT cannot hydrogen

bond intramolecularly and, in fact, severe steric interactions prevent the carbomethoxy group from being coplanar with the thiophene ring.

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* Tables of anisotropic thermal parameters, bond lengths and angles involving H atoms, torsion angles, least-squares planes and structure-factor amplitudes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51190 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure of a 2,4-Dithiinopyran Derivative

BY JOCHEN ANTEL AND GEORGE M. SHELDRIK

Institut für Anorganische Chemie der Universität, Tammannstrasse 4, D-3400 Göttingen, Federal Republic of Germany

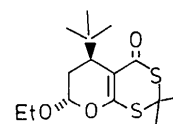
AND PETER SCHÄFER AND LUTZ-F. TIETZE

Institut für Organische Chemie der Universität, Tammannstrasse 2, D-3400 Göttingen, Federal Republic of Germany

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Abstract. (5*SR*,7*RS*)-7-Ethoxy-5,6-dihydro-2,2-dimethyl-5-*tert*-butyl-8*H*-[1,3]dithiinol[4,5-*b*]pyran-4-one, C₁₅H₂₄O₃S₂, *M_r* = 316.47, monoclinic, *P*2₁/*c*, *a* = 10.233 (2), *b* = 12.647 (2), *c* = 12.898 (3) Å, β = 95.12 (3)°, *V* = 1662.42 Å³, *Z* = 4, *D_x* = 1.264 Mg m⁻³, λ(Mo *K*α) = 0.71069 Å, μ = 0.31 mm⁻¹, *F*(000) = 680, *T* = 298 K, *R* = 0.038 for 2580 observed reflections. The structure was investigated to determine the relative configuration, which could not be established unambiguously by NMR.

Experimental. Title compound (I): crystal size 0.2 × 0.3 × 0.4 mm. Stoe–Siemens four-circle diffractometer, monochromated Mo *K*α radiation, profile-



(I)