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## Structure of Ethyl 2-Amino-4-phenylthiophene-3-carboxylate

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**Abstract.**  $C_{13}H_{13}NO_2S$ ,  $M_r = 247.3$ , monoclinic,  $P2_1/c$ ,  $a = 10.650$  (1),  $b = 13.942$  (2),  $c = 9.273$  (1) Å,  $\beta = 115.07$  (1)°,  $V = 1247.1$  (4) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.320$  (3) Mg m<sup>-3</sup>,  $\lambda(\text{Cu } K\alpha) = 1.5418$  Å,  $\mu = 2.18$  mm<sup>-1</sup>,  $F(000) = 520$ ,  $T = 295$  K,  $R = 0.05$  for 1664 observed reflections [ $I > 2\sigma(I)$ ]. Molecular geometry is within the normal limits. The thiophene ring is planar. The steric repulsion between the phenyl ring and the ethoxycarbonyl group is minimized by (i) the rotation of the phenyl ring [dihedral angle 70.2 (1)° between the phenyl and thiophene rings] and (ii) the widening of the external angle at C(4) by 8.2 (4)° [the difference between the angles C(3)—C(4)—C(41) and C(5)—C(4)—C(41)]. The molecule exhibits both intra- and intermolecular N—H...O hydrogen bonding.

**Experimental.** The title compound was prepared by the following procedure: acetophenone was allowed to undergo a Cope reaction (Cope, Hoffmann, Wyckoff & Hardenbergh, 1941) with ethyl cyanoacetate, followed by a Gewald reaction (Gewald 1962, 1965; Gewald, Schinke & Bottcher, 1966) in the presence of sulfur to form ethyl 2-amino-4-phenylthiophene-3-carboxylate as a crystalline solid.

This was filtered, washed with ethanol and recrystallized from chloroform; pale-brown needles were obtained.

A specimen of dimensions 0.3 × 0.4 × 0.3 mm was chosen. Lattice parameters and their e.s.d.'s were derived from a least-squares treatment of 25 reflections ( $6 < \theta < 33^\circ$ ). Intensity data were collected on an Enraf-Nonius CAD-4 single-crystal X-ray diffractometer, graphite-monochromated Cu  $K\alpha$  radiation,  $\omega/2\theta$  scan mode for  $h - 10 \rightarrow 10$ ,  $k 0 \rightarrow 15$ ,  $l 0 \rightarrow 10$ ,  $2\theta_{\text{max}} = 120^\circ$ . Three standard reflections monitored every 100 measurements showed no significant variation in the intensities. Of the 2076 unique reflections collected, 1664 were judged significant,  $I > 2\sigma(I)$ ,  $R_{\text{int}} = 0.04$ . Intensities were corrected for Lp effects. An empirical-absorption correction based on a series of  $\psi$  scans was applied. Transmission coefficient ranged from 0.847 to 0.994. Structure was solved by direct methods using *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). 15 non-H atoms were located from an  $E$  map. The remaining atoms, including H atoms, were located from succeeding difference Fourier syntheses. Positional and thermal parameters of non-H atoms were refined by full-matrix least-squares refinement on  $F$  using *SHELX76* (Sheldrick, 1976). The H atoms were refined with an individual isotropic temperature factor (fixed in the final cycles). At the final stage of

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Table 1. Fractional atomic coordinates ( $\times 10^4$ ) and equivalent isotropic thermal parameters ( $\times 10^4$ ) for non-H atoms in  $C_{13}H_{13}NO_2S$  with their e.s.d.'s in parentheses

$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$U_{eq}(\text{\AA}^2)$
S(1)	2888.8 (7)	1706.7 (6)	11879.5 (8)	413 (3)
O(1)	4870 (2)	1358 (1)	8444 (2)	339 (6)
O(2)	3396 (2)	135 (1)	7412 (2)	344 (6)
N(1)	4836 (2)	2318 (2)	10986 (3)	368 (8)
C(2)	3792 (3)	1683 (2)	10714 (3)	318 (8)
C(3)	3328 (2)	953 (2)	9577 (3)	281 (7)
C(4)	2229 (2)	396 (2)	9707 (3)	335 (9)
C(5)	1912 (3)	722 (2)	10887 (3)	440 (11)
C(6)	3939 (2)	845 (2)	8467 (3)	296 (7)
C(7)	3965 (3)	11 (2)	6254 (3)	379 (10)
C(8)	3246 (3)	-842 (2)	5260 (4)	457 (12)
C(41)	1479 (3)	-445 (2)	8739 (3)	357 (9)
C(42)	513 (3)	-354 (2)	7179 (3)	428 (11)
C(43)	-256 (3)	-1131 (3)	6333 (3)	519 (11)
C(44)	-64 (3)	-2010 (3)	7025 (4)	540 (12)
C(45)	876 (3)	-2124 (2)	8582 (5)	597 (15)
C(46)	1652 (3)	-1347 (2)	9446 (4)	504 (12)

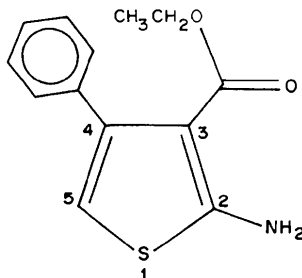


Fig. 1. Structural formula with atomic numbering.

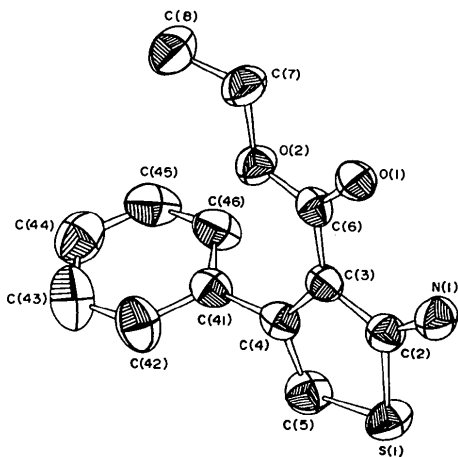


Fig. 2. Perspective view of the molecule with crystallographic numbering scheme.

refinement weights were introduced resulting in  $R = 0.05$  and  $wR = 0.08$ , where  $w = 1/\sigma^2(F_o)$ , shift/e.s.d. = 0.1 for 194 parameters. The final difference map was featureless within  $0.59 \text{ e \AA}^{-3}$ . The atomic scattering factors used for all the atoms were taken from

Table 2. Bond lengths ( $\text{\AA}$ ), bond angles ( $^\circ$ ) and selected torsion angles ( $^\circ$ ) with e.s.d.'s in parentheses

S(1)—C(2)	1.725 (3)	O(2)—C(7)	1.450 (4)
C(5)—S(1)	1.733 (3)	C(7)—C(8)	1.501 (4)
C(2)—C(3)	1.396 (4)	C(4)—C(41)	1.487 (4)
C(3)—C(4)	1.452 (4)	C(41)—C(42)	1.381 (4)
C(4)—C(5)	1.353 (4)	C(42)—C(43)	1.384 (5)
C(2)—N(1)	1.359 (4)	C(43)—C(44)	1.358 (6)
C(3)—C(6)	1.440 (3)	C(44)—C(45)	1.374 (5)
C(6)—O(1)	1.230 (3)	C(45)—C(46)	1.392 (5)
C(6)—O(2)	1.339 (3)	C(46)—C(41)	1.394 (4)
C(5)—S(1)—C(2)	91.2 (1)	O(2)—C(7)—C(8)	106.5 (2)
S(1)—C(2)—C(3)	112.0 (2)	C(3)—C(4)—C(41)	128.1 (2)
C(2)—C(3)—C(4)	111.5 (2)	C(5)—C(4)—C(41)	119.9 (2)
C(3)—C(4)—C(5)	111.9 (2)	C(4)—C(41)—C(42)	122.1 (3)
C(4)—C(5)—S(1)	113.3 (2)	C(4)—C(41)—C(46)	119.8 (3)
S(1)—C(2)—N(1)	120.1 (2)	C(4)—C(3)—C(6)	128.9 (2)
N(1)—C(2)—C(3)	127.9 (3)	C(41)—C(42)—C(43)	121.4 (3)
C(2)—C(3)—C(6)	119.6 (2)	C(42)—C(43)—C(44)	120.3 (3)
C(3)—C(6)—O(1)	124.3 (2)	C(43)—C(44)—C(45)	119.8 (3)
C(3)—C(6)—O(2)	114.4 (2)	C(44)—C(45)—C(46)	120.4 (3)
O(1)—C(6)—O(2)	121.3 (2)	C(45)—C(46)—C(41)	120.2 (3)
C(6)—O(2)—C(7)	116.3 (2)	C(46)—C(41)—C(42)	117.8 (3)
C(5)—S(1)—C(2)—C(3)	1.4 (2)	C(6)—C(3)—C(4)—C(41)	1.5 (5)
C(2)—S(1)—C(5)—C(4)	-1.1 (2)	C(4)—C(3)—C(6)—O(1)	179.7 (3)
S(1)—C(2)—C(3)—C(4)	-1.3 (3)	C(2)—C(3)—C(6)—O(1)	0.3 (4)
C(2)—C(3)—C(4)—C(5)	0.5 (3)	C(4)—C(3)—C(6)—O(2)	0.6 (4)
C(3)—C(4)—C(5)—S(1)	0.5 (3)	C(3)—C(4)—C(41)—C(46)	112.8 (3)

*International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B). Table 1\* lists the final atomic coordinates and equivalent isotropic thermal parameters for non-H atoms. Fig. 1 illustrates the structural formula with atomic numbering. The crystallographic numbering scheme and molecular connectivity are given in a perspective view of the molecule (Fig. 2). The bond lengths, bond angles and selected torsion angles are listed in Table 2.

**Related literature.** The rotation of the phenyl ring with respect to the thiophene ring is  $54.9(1)^\circ$  in 2-amino-4-methyl-5-phenylthiophene-3-carboxamide (Joseph, Selladurai, Kannan & Parthasarathi, 1991). In tetraphenylthieno[3,4-c]thiophene (Glick & Cook, 1972), the two phenyl rings are rotated out of the dithiophene plane by  $39.6$  and  $58.4^\circ$  respectively.

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\* Tables of anisotropic thermal parameters, positional parameters for H atoms, bond lengths and angles involving H atoms, additional torsion angles, least-squares planes, H-bonding geometry and structure factor amplitudes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53916 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## 1,2,7a-Trihydroxy-2-methylperhydro-1-phosphaindene 1-Oxide

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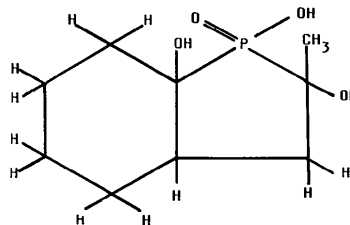
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(Received 11 November 1990; accepted 10 January 1991)

**Abstract.**  $C_9H_{17}O_4P$ ,  $M_r = 220.20$ , monoclinic,  $P2_1$ ,  $a = 12.385$  (4),  $b = 6.590$  (3),  $c = 13.394$  (4) Å,  $\beta = 98.00$  (3)°,  $V = 1082.54$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.351$  g cm<sup>-3</sup>,  $\lambda(\text{Cu } K\alpha) = 1.54178$  Å,  $\mu = 21.9$  cm<sup>-1</sup>,  $F(000) = 472$ ,  $T = 296$  K,  $R_F = 0.044$ ,  $wR_F = 0.048$  for 1850 observed reflections [ $I_o > 3\sigma(I_o)$ ] and 253 parameters. The asymmetric unit consists of two independent molecules which have almost identical but inverted conformations. Molecule 1: The five-membered phospholane ring exists in an envelope conformation with C(3) at the flap [the asymmetry parameter  $\Delta C_s^{C(9)} = 2.35$  (6)°]. The six-membered cyclohexane ring is a slightly twisted chair [ $\Delta C_s^{C(5)} = 1.93$  (6),  $\Delta C_2^{C(3),C(4)} = 6.33$  (6)°]. The rings are *trans*-fused and the hydroxyl group O(4) is *anti* to the phosphoryl group P(1)—O(1). Molecule 2: The five-membered phospholane ring is a slightly twisted envelope with C(13) at the flap [ $\Delta C_s^{C(13)} = 3.85$  (6)°]. The fused six-membered cyclohexane ring is almost an ideal chair [ $\Delta C_s^{C(14),C(17)} = 1.08$  (6),  $\Delta C_2^{C(13),C(18)} = 0.16$  (6)°]. The rings are *trans*-fused and the hydroxyl group O(14) is *anti* to the phosphoryl group P(2)—O(11).

**Experimental.** Colourless crystals of (I) from methanol/ethanol (1/1), 0.25 × 0.25 × 0.50 mm; CAD-4 diffractometer with graphite mono-

chromator; lattice parameters from the least-squares refinement of the setting angles of 22 reflections in the  $\theta$  range 10–39°. Intensity data were collected by the  $\omega$ -2 $\theta$  scan method with an  $\omega$ -scan width of (1.80 + 0.14tan $\theta$ )° and a variable scan speed of 1.5–5.5° min<sup>-1</sup> using graphite-monochromatized Cu  $K\alpha$  radiation with indices  $h - 1$  to 15,  $k - 1$  to 8 and  $l - 16$  to 16 in the  $\theta$  range 0–70°. The intensities of three standard reflections (312, 004, 215) measured every hour showed no evidence of crystal decay. Intensities of 2228 reflections were measured of which 1902 had  $I > 3\sigma(I)$ , and were used in the structure solution and refinement. Lorentz-polarization corrections and  $\psi$ -scan-based empirical absorption corrections were applied.



(I)

The structure was solved by direct methods using *SHELXS86* (Sheldrick, 1985). Refinement of the structure was by full-matrix least-squares calculations. At an intermediate stage in the refinement, a difference map revealed all the H atoms which were included in the subsequent cycles of refinement at

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