

*Acta Cryst.* (1995). **C51**, 2444–2446

# 1-(*p*-Chlorophenyl)-5 $\alpha$ -methoxycarbonylmethyl-4 $\beta$ -(2-thienyl)pyrrolidin-2-one

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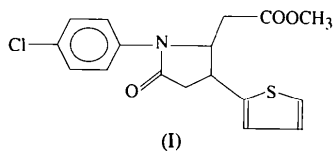
(Received 29 November 1994; accepted 10 May 1995)

## Abstract

The chlorophenyl ring, thiophene ring and the acetate side chain of the title ester, methyl 1-(4-chlorophenyl)-5-oxo-3 $\beta$ -(2-thienyl)-2 $\alpha$ -pyrrolidineacetate, C<sub>17</sub>H<sub>16</sub>ClNO<sub>3</sub>S, are individually planar. The pyrrolidine ring adopts a conformation between envelope and half-chair. The possibility of rotation of the thiophene ring by 180° is observed in the molecule. The crystal structure is stabilized by van der Waals forces.

## Comment

The antibacterial activities of *N*-phenyl (or *p*-chlorophenyl)  $\gamma$ -lactam derivatives are found to be pronounced in the presence of an acidic environment (Ray, Sami, Kar, Roy & Brahma, 1995). Moreover, the disposition of the —CH<sub>2</sub>COOR and thiophene groups is important in predicting bioactivities. It was observed that arylaminomalonates produce  $\gamma$ -lactam diesters with arylacryloyl chlorides in the presence of bases (Kar, Chatterjee & Ray, 1993). Molecules containing a thiophene moiety are new to this class of compounds. Preliminary biological data for these compounds encouraged us to investigate their structural details, particularly their stereochemistry, and hence the X-ray structure analysis of the title compound, (I), was carried out.



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The chlorophenyl ring (*A*), the thiophene ring (*B*) and the acetate side chain (*C*) at C10 are all planar; the dihedral angle between the *A* and *B* planes is 87.11 (6)°, that between *A* and *C* is 78.99 (7)° and that between *B* and *C* is 9.09 (6)°. The chlorophenyl ring lies almost in the best plane of the pyrrolidine ring, and the thiophene ring and the acetate side chain are perpendicular to this plane, oriented in opposite directions. The pyrrolidine ring has a conformation between envelope and half-chair, with asymmetry parameters  $\Delta C_5(C9) = 0.020(1)$  and  $\Delta C_2(C7) = 0.039(1)$  (Nardelli, 1983*a*). The deviations of atoms C9 and C10 from the plane defined by N1, C7 and C8 are  $-0.423(2)$  and  $0.079(2)$  Å, respectively.

The bond lengths and angles in this structure are generally normal except for the following: the two N—C<sub>sp<sup>2</sup></sub> bond lengths, N1—C6 1.416(2) and N1—C7 1.383(2) Å, are significantly different, the shortened value of the latter possibly being due to the carbonyl O atom O1 at C7; the C—O distances, C12—O3 1.331(2) and C13—O3 1.441(3) Å, are asymmetrical.

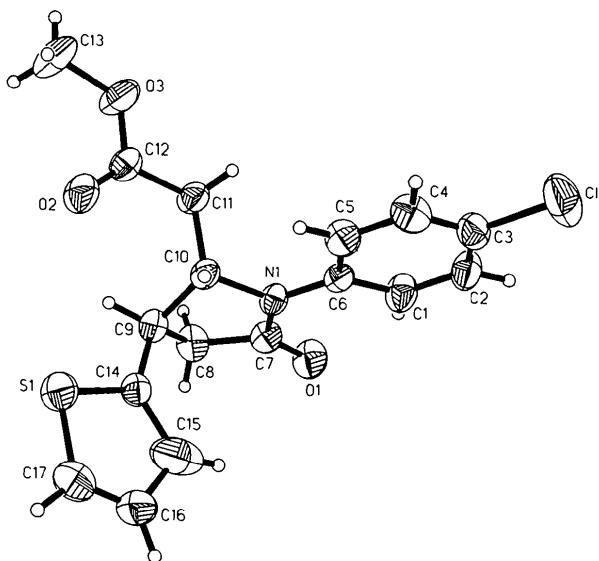


Fig. 1. The structure of the title compound showing 50% probability displacement ellipsoids and the numbering scheme. The major conformer is shown.

## Experimental

The base-catalysed hydrolysis/decarboxylation generated exclusively *trans* acid, which on Arndt Eistert's synthesis produced the title  $\gamma$ -lactam derivative (Kar, Chatterjee & Ray, 1993). Single crystals were grown by slow evaporation of a 2-propanol solution of the compound.

### Crystal data

C<sub>17</sub>H<sub>16</sub>ClNO<sub>3</sub>S  
M<sub>r</sub> = 349.82

Mo K $\alpha$  radiation  
 $\lambda = 0.71073$  Å

Monoclinic  
 $P2_1/c$   
 $a = 9.632 (1) \text{ \AA}$   
 $b = 13.094 (1) \text{ \AA}$   
 $c = 13.226 (1) \text{ \AA}$   
 $\beta = 101.65 (1)^\circ$   
 $V = 1633.7 (2) \text{ \AA}^3$   
 $Z = 4$   
 $D_x = 1.422 \text{ Mg m}^{-3}$

**Data collection**

Siemens P4 four-circle  
 diffractometer  
 $\theta-2\theta$  scans  
 Absorption correction:  
 none  
 4771 measured reflections  
 3741 independent reflections  
 2837 observed reflections  
 $[I > 2\sigma(I)]$

**Refinement**

Refinement on  $F^2$   
 $R(F) = 0.0424$   
 $wR(F^2) = 0.1266$   
 $S = 1.082$   
 3741 reflections  
 279 parameters  
 All H-atom parameters  
 refined  
 $w = 1/[\sigma^2(F_o^2) + (0.0657P)^2 + 0.1977P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

**Cell parameters from 25 reflections**

$\theta = 8-25^\circ$   
 $\mu = 0.375 \text{ mm}^{-1}$   
 $T = 293 (2) \text{ K}$   
 Block  
 $0.56 \times 0.52 \times 0.38 \text{ mm}$   
 Colourless, transparent

$R_{\text{int}} = 0.0260$   
 $\theta_{\text{max}} = 27.50^\circ$   
 $h = -1 \rightarrow 12$   
 $k = -1 \rightarrow 17$   
 $l = -17 \rightarrow 17$   
 3 standard reflections  
 monitored every 100  
 reflections  
 intensity decay:  $<2\%$

$(\Delta/\sigma)_{\text{max}} = -0.001$   
 $\Delta\rho_{\text{max}} = 0.257 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.356 \text{ e \AA}^{-3}$   
 Atomic scattering factors  
 from *International Tables  
 for Crystallography* (1992,  
 Vol. C, Tables 4.2.6.8 and  
 6.1.1.4)

**Table 2. Selected geometric parameters ( $\text{\AA}, ^\circ$ )**

C11—C3	1.737 (2)	C3—C4	1.372 (3)
S1—C17	1.686 (2)	C4—C5	1.377 (3)
S1—C14	1.714 (2)	C5—C6	1.395 (2)
O1—C7	1.213 (2)	C7—C8	1.505 (3)
O2—C12	1.198 (2)	C8—C9	1.534 (2)
O3—C12	1.331 (2)	C9—C14	1.500 (2)
O3—C13	1.441 (3)	C9—C10	1.547 (2)
N1—C7	1.383 (2)	C10—C11	1.523 (2)
N1—C6	1.416 (2)	C11—C12	1.498 (2)
N1—C10	1.475 (2)	C14—C15	1.392 (3)
C1—C2	1.380 (3)	C15—C16	1.418 (3)
C1—C6	1.392 (2)	C16—C17	1.340 (3)
C2—C3	1.371 (3)		
C17—S1—C14	92.69 (10)	C7—C8—C9	105.11 (14)
C12—O3—C13	116.4 (2)	C14—C9—C8	113.2 (2)
C7—N1—C6	125.70 (13)	C14—C9—C10	111.82 (14)
C7—N1—C10	112.12 (13)	C8—C9—C10	102.29 (14)
C6—N1—C10	121.85 (13)	N1—C10—C11	110.64 (13)
C2—C1—C6	121.0 (2)	N1—C10—C9	103.07 (13)
C3—C2—C1	120.0 (2)	C11—C10—C9	112.84 (15)
C2—C3—C4	120.2 (2)	C12—C11—C10	113.17 (15)
C2—C3—C11	119.2 (2)	O2—C12—O3	124.0 (2)
C4—C3—C11	120.6 (2)	O2—C12—C11	125.3 (2)
C3—C4—C5	120.1 (2)	O3—C12—C11	110.7 (2)
C4—C5—C6	120.9 (2)	C15—C14—C9	130.5 (2)
C1—C6—C5	117.8 (2)	C15—C14—S1	109.19 (15)
C1—C6—N1	121.87 (15)	C9—C14—S1	120.27 (12)
C5—C6—N1	120.38 (15)	C14—C15—C16	113.2 (2)
O1—C7—N1	126.8 (2)	C17—C16—C15	111.6 (2)
O1—C7—C8	125.4 (2)	C16—C17—S1	113.3 (2)
N1—C7—C8	107.74 (14)		

The structure was solved by direct methods and refined by a full-matrix least-squares technique. All H atoms except H15 (attached to C15) were located from a difference Fourier map and refined isotropically. H15 was also located from a difference Fourier map, but on refinement started moving closer to C15, so it was allowed to ride on C15. At this stage, the  $R$  value was 0.053 ( $wR = 0.163$ ) and the difference Fourier map showed an electron cloud of approximately  $0.60 \text{ e \AA}^{-3}$  around C15; the C14—C15 distance was  $1.450 \text{ \AA}$ . This led us to think about the possibility of a  $180^\circ$  rotation of the thiophene ring with respect to the C9—C14 single bond. Hence, it was decided to refine the structure with S1' and C15' positions and this resulted in a better  $R$  value of 0.042 ( $wR = 0.121$ ). The populations were 89 and 11% for the regular and rotated conformations, respectively. Also, the electron cloud at C15 disappeared in the final difference map and was featureless with a maximum of  $0.25 \text{ e \AA}^{-3}$ .

Data collection: XSCANS (Siemens, 1991). Cell refinement: XSCANS. Data reduction: XSCANS. Program(s) used to solve structure: SHELXS86 (Sheldrick, 1990a). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: SHELXTL/PC (Sheldrick, 1990b). Software used to prepare material for publication: SHELXL93. Geometric calculations: PARST (Nardelli, 1983b).

The authors would like to thank the Malaysian Government and the Universiti Sains Malaysia for research grant R&D No. 123-3417-2201. One of the authors (KS) thanks the Universiti Sains Malaysia for a Visiting Post Doctoral Research Fellowship.

**Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ )**

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

	$x$	$y$	$z$	$U_{\text{eq}}$
C11	0.45189 (8)	0.93742 (5)	0.37594 (6)	0.0762 (2)
S1 †	0.08811 (7)	0.25578 (5)	0.42483 (5)	0.0511 (2)
S1' †	0.2859 (5)	0.3111 (5)	0.2865 (5)	0.0511 (2)
O1	0.1932 (2)	0.52573 (12)	0.08627 (9)	0.0537 (4)
O2	-0.1626 (2)	0.46190 (12)	0.42664 (10)	0.0543 (4)
O3	-0.30253 (15)	0.59026 (13)	0.35697 (12)	0.0589 (4)
N1	0.13951 (15)	0.55281 (11)	0.24761 (10)	0.0333 (3)
C1	0.2880 (2)	0.6955 (2)	0.21245 (15)	0.0466 (5)
C2	0.3597 (2)	0.7852 (2)	0.2429 (2)	0.0506 (5)
C3	0.3617 (2)	0.82415 (15)	0.3394 (2)	0.0456 (4)
C4	0.2916 (2)	0.7747 (2)	0.4057 (2)	0.0487 (5)
C5	0.2195 (2)	0.6853 (2)	0.37572 (14)	0.0428 (4)
C6	0.2154 (2)	0.64405 (13)	0.27794 (12)	0.0330 (3)
C7	0.1325 (2)	0.50250 (14)	0.15480 (12)	0.0381 (4)
C8	0.0340 (2)	0.4130 (2)	0.15277 (14)	0.0441 (4)
C9	0.0203 (2)	0.39780 (13)	0.26534 (13)	0.0361 (4)
C10	0.0444 (2)	0.50713 (13)	0.30972 (12)	0.0327 (3)
C11	-0.0924 (2)	0.5683 (2)	0.29808 (15)	0.0415 (4)
C12	-0.1867 (2)	0.53251 (15)	0.36816 (13)	0.0394 (4)
C13	-0.4033 (3)	0.5636 (3)	0.4197 (3)	0.0753 (8)
C14	0.1262 (2)	0.32366 (13)	0.32304 (12)	0.0366 (4)
C15	0.2623 (3)	0.2991 (2)	0.3107 (2)	0.0449 (5)
C15' †	0.1261 (10)	0.2559 (15)	0.4041 (14)	0.0449 (5)
C16	0.3288 (2)	0.2238 (2)	0.3812 (2)	0.0561 (5)
C17	0.2462 (3)	0.1957 (2)	0.4466 (2)	0.0560 (5)

† Partial occupancy due to rotational disorder (see below).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KH1028). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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*Acta Cryst.* (1995). **C51**, 2446–2450

## Symmetrically Substituted Thiourea Derivatives

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(Received 22 February 1995; accepted 9 May 1995)

## Abstract

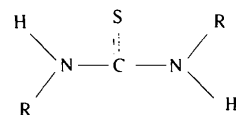
The crystal structures of three symmetrically substituted thiourea derivatives, 1,3-diethylthiourea (DETU), C<sub>5</sub>H<sub>12</sub>N<sub>2</sub>S, 1,3-diisopropylthiourea (DIPTU), C<sub>7</sub>H<sub>16</sub>N<sub>2</sub>S, and 1,3-diphenylthiourea (DPTU), C<sub>13</sub>H<sub>12</sub>N<sub>2</sub>S, are reported. N—H...S hydrogen bonds link the molecules into two-dimensional networks in DETU and DIPTU

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and into one-dimensional chains in DPTU. DETU and DIPTU have the same mode of packing in the crystal lattice.

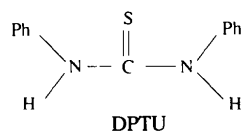
## Comment

In the past, many crystal structure analyses of metal complexes of thiourea, but only a few with substituted thioureas, have been reported. There is no structural report exclusively on substituted thiourea derivatives. This may be due to the difficulty in obtaining crystals suitable for X-ray diffraction studies. The preparation of these compounds involves a novel cost-effective synthetic procedure (Ramadas & Janarthanan, 1995) and they have applications as rubber accelerators and as intermediates in dye preparation. They are also used for the synthesis of unsymmetrical thioureas (Ramadas, Srinivasan & Janarthanan, 1993), which are very useful agrochemical intermediates. We are interested in the molecular conformations and the details of the N—H...S hydrogen-bond formation of these ligands in the solid state. In this paper, we report the crystal structure determinations of three symmetrically substituted thiourea derivatives, namely 1,3-diethylthiourea (DETU), 1,3-diisopropylthiourea (DIPTU) and 1,3-diphenylthiourea (DPTU). The *ORTEP* (Johnson, 1965) plots of these molecules together with their numbering schemes are shown in Fig. 1.



DETU: R = CH<sub>2</sub>CH<sub>3</sub>

DIPTU: R = CH(CH<sub>3</sub>)<sub>2</sub>



DPTU

The molecule of DETU shows thermal disorder, with the ethyl C atoms having high thermal vibrations. One of the ethyl groups in particular (atoms C2 and C3) shows major disorder. The best model finally adopted was one with an occupancy of one site, but with relatively large displacement parameters and an unusual C2—C3 bond distance [1.366(6) Å]. Such disorder has been observed previously in one of the DETU ligands in the structure of tetrakis(*N,N'*-DETU)cobalt(II) diperchlorate (Fawcett, Fehskens, Potenza, Schugar & Lalancette, 1979). The S=C1 bond length is between the mean value observed in DETU–metal complexes (1.734 Å) and the unweighted mean value (1.681 Å) given for C=S in thioureas (Allen *et al.*, 1987). The increase in the C=S bond length is reflected in the shortening of