$C_{20}H_{21}NO_5S$

Diethyl 5-Oxo-1-phenyl-3-(2-thienyl)-pyrrolidine-2,2-dicarboxylate, $C_{20}H_{21}NO_5S$

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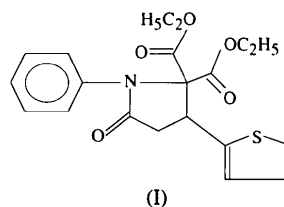
Abstract

The possibility of the 180° rotation of the thiophene ring is observed. The phenyl ring is almost perpendicular to the pyrrolidine ring. The structure is stabilized by van der Waals interactions.

Comment

Recently we observed that *N*-phenyl γ-lactam derivatives exhibited Gram-positive and Gram-negative antibacterial activities (Ray, Sami, Kar, Roy & Brahma, 1995). This opens up the subject of a new structure–activity relationship for γ-lactam antibacterial derivatives. It is now believed that the bioactivity of the lactam compounds depends on the acylating ability of several proteins to inhibit the cross-linking of bacterial cell wall (Baldwin, Lynch & Pitlik, 1991), which again is dependent on a suitably substituted and activated lactam ring (Baldwin, Chan, Gallecher & Otsnka, 1984). The type of structural moiety that causes maximum bioactivity is a problem that requires urgent attention. In this endeavour we have synthesized some 5,5-ethoxycarbonyl-*N*-phenyl-4-(2-thienyl)pyrrolidin-2-one derivatives by a novel one-step condensation of arylaminomalonates with thienylacryl-oyl chlorides through intermolecular Michael addition, followed by intramolecular amidification (Kar, Chatterjee & Ray, 1993; Roy & Ray, 1994). The crystal structure determination of the title compound, (I), one of the above derivatives, was carried out in order to elucidate the molecular conformation.

(I)

An *ORTEP*II (Johnson, 1976) plot of the molecule with the numbering scheme is shown in Fig. 1. In general, the bond lengths and angles in this structure are normal. The increased C17=C18 length [1.418 (3) Å] and shortened C18—C19 length [1.443 (3) Å] are justified from the point of view of the rotation of the thiophene ring with respect to the C9—C17 single bond (as explained in the *Experimental*).
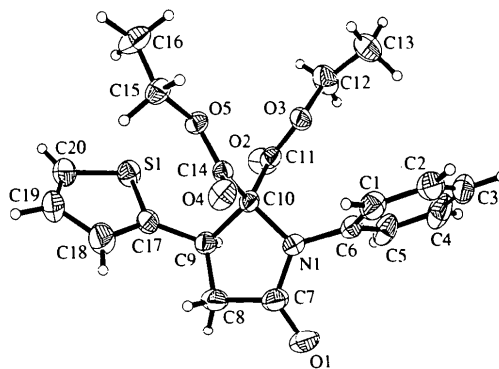

Fig. 1. *ORTEP*II (Johnson, 1976) drawing of the title compound with atom-labelling scheme, showing 50% probability displacement ellipsoids.

The phenyl ring and the thiophene ring are planar. Whereas one of the ethoxycarbonyl side chains [C14(O4)—O5—C15—C16] is planar, the other [C11(O2)—O3—C12—C13] is not, due to steric interations. The dihedral angle between the planes of the phenyl and thiophene rings is 63.15 (7)°. The phenyl ring lies almost perpendicular [93.39 (6)°] to the best plane of the pyrrolidine ring, whereas the thiophene ring makes an angle of 56.68 (6)° with it. The planar ethoxycarbonyl side chain is also perpendicular to the pyrrolidine ring [91.48 (8)°], while the other ethoxycarbonyl (non-planar) chain makes an angle of 64.61 (9)° in the opposite direction. The two ethoxycarbonyl planes make angles of 103.18 (6) and 40.00 (9)° with the phenyl ring plane, and 142.38 (7) and 72.53 (7)° with the thiophene ring plane. The pyrrolidine ring is in a conformation between envelope and half-chair; the asymmetry parameters defined by Nardelli (1983*a*) are *DS*(C9) = 0.030 (1) and *D2*(C7) = 0.032 (1).

Experimental

Single crystals were grown by dissolving the compound in 2-propanol and then by a slow evaporation technique at room temperature.

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Crystal data

$C_{20}H_{21}NO_5S$	Mo $K\alpha$ radiation
$M_r = 387.44$	$\lambda = 0.71073$ Å
Monoclinic	Cell parameters from 25
$P2_1/n$	reflections
$a = 10.872\,(1)$ Å	$\theta = 8\text{–}25°$
$b = 14.559\,(1)$ Å	$\mu = 0.194$ mm^{-1}
$c = 12.674\,(1)$ Å	$T = 293\,(2)$ K
$\beta = 100.27\,(1)°$	Transparent block
$V = 1974.0\,(3)$ Å^3	$0.54 \times 0.48 \times 0.24$ mm
$Z = 4$	Colourless
$D_x = 1.304$ Mg m^{-3}	

Data collection

Siemens $P4$ diffractometer	$\theta_{max} = 27.50°$
$\theta/2\theta$ scans	$h = -1 \rightarrow 11$
Absorption correction:	$k = -1 \rightarrow 18$
none	$l = -16 \rightarrow 16$
5373 measured reflections	3 standard reflections
4301 independent reflections	monitored every 100
2689 observed reflections	reflections
$[I > 2\sigma(I)]$	intensity decay: $< 0.3\%$
$R_{int} = 0.0222$	

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} < 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.0425$	$\Delta\rho_{max} = 0.220$ e Å^{-3}
$wR(F^2) = 0.1071$	$\Delta\rho_{min} = -0.232$ e Å^{-3}
$S = 1.096$	Extinction correction: none
4301 reflections	Atomic scattering factors
329 parameters	from *International Tables*
All H-atom parameters	*for Crystallography* (1992,
refined	Vol. C, Tables 4.2.6.8 and
$w = 1/[\sigma^2(F_o^2) + (0.0648P)^2]$	6.1.1.4)
where $P = (F_o^2 + 2F_c^2)/3$	

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
S1†	0.06296 (6)	0.52119 (4)	0.70111 (5)	0.0640 (2)
S1'†	0.3048 (2)	0.51663 (13)	0.7423 (2)	0.0840 (8)
O1	0.3845 (2)	0.42943 (11)	1.15990 (11)	0.0864 (5)
O2	−0.04858 (13)	0.40632 (10)	0.90447 (12)	0.0749 (4)
O3	0.01609 (11)	0.25984 (9)	0.91074 (9)	0.0528 (3)
O4	0.34648 (12)	0.29231 (10)	0.87512 (10)	0.0630 (4)
O5	0.16569 (11)	0.30170 (8)	0.75842 (9)	0.0469 (3)
N1	0.23041 (13)	0.36259 (10)	1.03832 (10)	0.0477 (3)
C1	0.2613 (2)	0.20459 (14)	1.1027 (2)	0.0620 (5)
C2	0.2295 (3)	0.1338 (2)	1.1631 (2)	0.0838 (7)
C3	0.1406 (3)	0.1462 (3)	1.2260 (2)	0.0948 (10)
C4	0.0844 (3)	0.2298 (3)	1.2297 (2)	0.0925 (10)
C5	0.1154 (2)	0.3013 (2)	1.1688 (2)	0.0682 (6)
C6	0.2030 (2)	0.28802 (12)	1.10459 (12)	0.0461 (4)
C7	0.3171 (2)	0.42835 (13)	1.07233 (15)	0.0625 (5)
C8	0.3167 (3)	0.4960 (2)	0.9832 (2)	0.0754 (7)
C9	0.1962 (2)	0.47691 (12)	0.90519 (14)	0.0513 (4)
C10	0.17227 (15)	0.37297 (11)	0.92525 (12)	0.0422 (4)
C11	0.0322 (2)	0.34983 (13)	0.91064 (12)	0.0480 (4)
C12	−0.1109 (2)	0.2262 (2)	0.9050 (3)	0.0823 (8)
C13	−0.1059 (3)	0.1285 (2)	0.9314 (3)	0.0917 (8)
C14	0.2394 (2)	0.31512 (11)	0.85215 (13)	0.0419 (4)
C15	0.2211 (2)	0.2620 (2)	0.67244 (15)	0.0573 (5)
C16	0.1202 (3)	0.2547 (2)	0.5775 (2)	0.0811 (8)
C17	0.1984 (2)	0.50357 (11)	0.79094 (15)	0.0511 (4)
C18†	0.3048 (2)	0.51663 (13)	0.7423 (2)	0.0840 (8)

C18'†	0.06296 (6)	0.52119 (4)	0.70111 (5)	0.0640 (2)
C19	0.2628 (3)	0.5419 (2)	0.6316 (2)	0.0767 (6)
C20	0.1407 (3)	0.5464 (2)	0.6014 (2)	0.0752 (6)

† Partially occupied due to rotational disorder of the thiophene ring (see below).

Table 2. *Selected geometric parameters* (Å, °)

S1—C20	1.681 (2)	C3—C4	1.366 (4)
S1—C17	1.713 (2)	C4—C5	1.373 (4)
O1—C7	1.216 (2)	C5—C6	1.372 (3)
O2—C11	1.196 (2)	C7—C8	1.498 (3)
O3—C11	1.322 (2)	C8—C9	1.520 (3)
O3—C12	1.454 (3)	C9—C17	1.504 (3)
O4—C14	1.195 (2)	C9—C10	1.564 (2)
O5—C14	1.324 (2)	C10—C14	1.530 (2)
O5—C15	1.456 (2)	C10—C11	1.538 (2)
N1—C7	1.358 (2)	C12—C13	1.461 (4)
N1—C6	1.436 (2)	C15—C16	1.481 (3)
N1—C10	1.467 (2)	C17—C18	1.418 (3)
C1—C2	1.364 (3)	C18—C19	1.443 (3)
C1—C6	1.372 (3)	C19—C20	1.317 (4)
C2—C3	1.371 (4)		
C20—S1—C17	92.54 (12)	N1—C10—C14	111.45 (13)
C11—O3—C12	117.3 (2)	N1—C10—C11	109.87 (13)
C14—O5—C15	117.71 (14)	N1—C10—C11	112.05 (13)
C7—N1—C6	123.50 (14)	N1—C10—C9	101.73 (12)
C7—N1—C10	113.01 (14)	C14—C10—C9	108.86 (13)
C6—N1—C10	123.42 (13)	C11—C10—C9	112.46 (15)
C2—C1—C6	119.7 (2)	O2—C11—O3	125.9 (2)
C1—C2—C3	120.2 (3)	O2—C11—C10	123.9 (2)
C4—C3—C2	120.2 (2)	O3—C11—C10	110.23 (15)
C3—C4—C5	120.0 (3)	O3—C12—C13	108.7 (2)
C6—C5—C4	119.5 (3)	O4—C14—O5	125.81 (15)
C5—C6—C1	120.4 (2)	O4—C14—C10	123.7 (2)
C5—C6—N1	118.6 (2)	O5—C14—C10	110.28 (14)
C1—C6—N1	121.0 (2)	O5—C15—C16	106.9 (2)
O1—C7—N1	124.7 (2)	C18—C17—C9	127.5 (2)
O1—C7—C8	126.8 (2)	C18—C17—S1	111.25 (14)
N1—C7—C8	108.4 (2)	C9—C17—S1	121.28 (14)
C7—C8—C9	104.9 (2)	C17—C18—C19	108.4 (2)
C17—C9—C8	114.8 (2)	C20—C19—C18	115.1 (2)
C17—C9—C10	115.98 (14)	C19—C20—S1	112.7 (2)
C8—C9—C10	102.72 (15)		
C10—N1—C7—C8	4.8 (2)	C7—N1—C10—C9	−21.9 (2)
N1—C7—C8—C9	15.2 (3)	C8—C9—C10—N1	29.3 (2)
C7—C8—C9—C10	−27.4 (2)		

The structure was solved by direct methods and refined by full-matrix least-squares techniques on F^2. All H atoms were located from a difference Fourier map. The refinement at this stage did not lead to good convergence ($R = 0.049$ and $wR = 0.158$) and the difference Fourier map showed an electron cloud of approximately 0.50 e Å^{-3} near C18. Based on our earlier experiences, this was interpreted as due to the possible rotation of the thiophene ring through 180° about the C9—C17 single bond. This would make S1 and C18 interchange their positions. Hence, it was decided to refine the structure on this basis (with S1' at C18 and C18' at S1 positions); this resulted in very good convergence with the final R values as reported above. The regular and rotated conformations are 87 and 13%, respectively. All H atoms were refined isotropically and the electron cloud near C18 disappeared in the final difference map, which was featureless. The consideration of the rotation of the thiophene ring in the refinement led to better e.s.d.'s for the refined parameters and hence to the structural parameters.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1990). Software used

to prepare material for publication: *SHELXL93*. Geometric calculations: *PARST* (Nardelli, 1983*b*).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AS1174). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Comment

Recently, we reported the first examples of a transition metal-catalyzed intramolecular homo-Diels–Alder reaction (Lautens, Tam & Edwards, 1992; Lautens, Lautens & Smith, 1990). Pentacyclene, (1), was synthesized *via* this method. Hydroboration of pentacyclene, (1), with 9-borabicyclo[3.3.1]nonane (9-BBN), followed by oxidative work-up, afforded alcohol (2) as a single regio- and stereoisomer with unusual *trans*-fused cyclopentane rings (Motherwell & Shipman, 1990). In order to confirm that the cyclopentane ring junctions are *trans* fused, alcohol (2) was converted into ester (3) and the structure determined by X-ray diffraction analysis.

(1)   (2)   (3)

9-BBN - 9-borabicyclo[3.3.1]nonane
DCC = *N,N'*-dicyclohexylcarbodiimide
DMAP = 4-(dimethylamino)pyridine

The effects of strain are reflected in the the bond lengths and angles of the molecule. This can be observed for the C_{sp^3} atoms. The bond length C9—C10 is 1.505 (4) Å, while C7—C8 is significantly longer at 1.568 (4) Å. The smallest angle is 59.2 (2)° for C10—C12—C11, while the largest is 128.4 (2)° for C8—C1—C2. The structure of one other molecule containing a *trans*-fused system of rings has been reported (Van Hijfte, Little, Peterson & Moeller, 1987).

An Unusual *trans*-Fused Cyclopentane Ring System at 158 K

MARK LAUTENS, ALAN J. LOUGH AND WILLIAM TAM

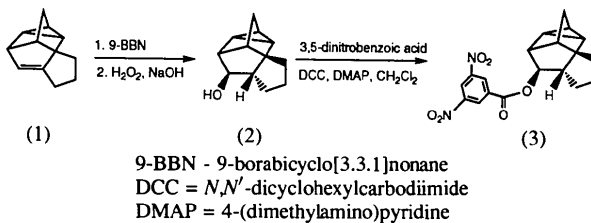*Department of Chemistry, University of Toronto, Toronto, Ontario M5S 1A1, Canada*

Abstract

The crystal structure of the title compound, pentacyclo[6.4.0^{1,5}.0^{1,8}.0^{7,11}.0^{10,12}]dodecan-6-yl 3,5-dinitrobenzoate, $C_{19}H_{18}N_2O_6$, establishes the cyclopentane ring junctions in the molecule to be *trans* fused. The C_{sp^3}—C_{sp^3} bond lengths range from 1.505 (4) to 1.568 (4) Å.
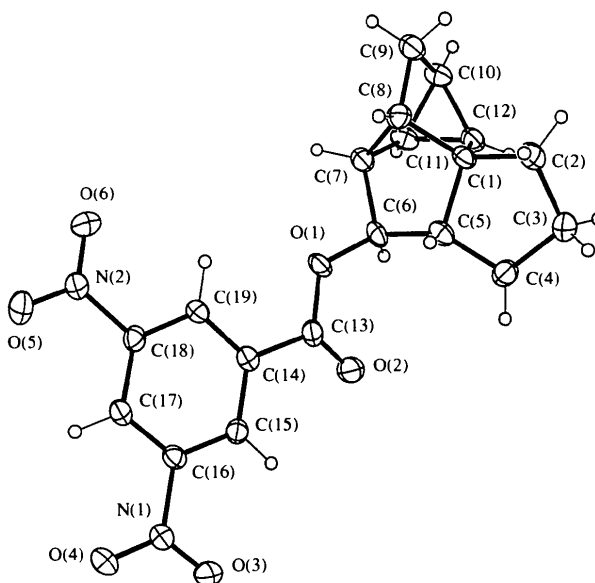
Fig. 1. View of compound (3) with the crystallographic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are drawn as small spheres. The junction of the *trans*-fused cyclopentane rings is the C1—C5 bond.