$\omega/2\theta$ scans
Absorption correction:
by integration (*ABSORP* in *NRCVAX*; Gabe *et al.*, 1989)
$T_{min} = 0.831$, $T_{max} = 0.939$
19 833 measured reflections
5062 independent reflections (including Friedel pairs)

$R_{int} = 0.045$
$\theta_{max} = 69.81°$
$h = -9 \rightarrow 9$
$k = -14 \rightarrow 14$
$l = -35 \rightarrow 35$
4 standard reflections
frequency: 30 min
intensity variation: 4.0%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.068$
$S = 0.888$
5062 reflections
434 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0208P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.046$
$\Delta\rho_{max} = 0.138$ e Å^{-3}
$\Delta\rho_{min} = -0.134$ e Å^{-3}

Extinction correction: *SHELXL*96 (Sheldrick, 1996)
Extinction coefficient: 0.00065 (5)
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = 0.1 (3)

Table 1. *Hydrogen-bonding geometry (Å, °)*

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O7—H7$A\cdots$O12^{i}	0.82	2.45	3.204 (3)	152.9
O12—H12$A\cdots$O7^{ii}	0.82	2.46	3.204 (3)	150.6

Symmetry codes: (i) $\frac{1}{2}+x, \frac{3}{2}-y, 2-z$; (ii) $x-\frac{1}{2}, \frac{3}{2}-y, 2-z$.

H atoms were constrained to their parent sites using a riding model [*SHELXL*96 (Sheldrick, 1996) defaults; C—H 0.93 to 0.98 and O—H 0.82 Å]. The H-atom isotropic displacement parameters, U_{iso}, were adjusted to be 50% greater than the displacement parameters of the parent site for the methyl and hydroxyl H atoms, and 20% greater for the remaining H atoms. A final verification of possible voids was performed using the *VOID* routine of the *PLATON* program (Spek, 1995).

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *NRC*-2 and *NRC*-2*A* (Ahmed *et al.*, 1973). Program(s) used to solve structure: *SHELXS*96 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*96. Molecular graphics: *ORTEP*II (Johnson, 1976) in *NRCVAX* (Gabe *et al.*, 1989). Software used to prepare material for publication: *NRCVAX* and *SHELXL*96.

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Methyl 2-(2-Methoxyphenyl)-2,3,3a,4,6,6a-hexahydro-1*H*-thieno[3,4-*b*]pyrrole-6a-carboxylate

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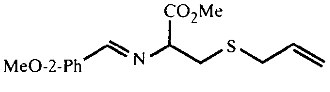
Abstract

The title compound, $C_{15}H_{19}NO_3S$, has *cis* stereochemistry at the ring junction, resulting from an *exo* intramolecular 1,3-dipolar cycloaddition. It crystallizes as a racemate. The tetrahydrothieno ring has an S-envelope form and the pyrrole ring adopts a half-chair conformation. The amino H atom is shared in a bifurcated intramolecular hydrogen bond between the bare O atoms of the carboxylate and methoxy groups. Cohesion of the structure is achieved through weak intermolecular interactions only.

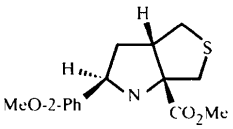
Comment

Intramolecular 1,3-dipolar cycloaddition is an important method for the construction of fused-ring heterocycles. The prototropic generation of azomethine ylides from the imines of α-amino acid esters is an example of this type of process (Grigg, 1987). We have previously reported the synthesis of a tetrahydro-1*H*-thieno-[3,4-*b*]pyrrole-3a,6a-dicarboxylate derivative through an intramolecular 1,3-dipolar cycloaddition of the azomethine ylide which was generated from a Schiff base by proton transfer (Barkley *et al.*, 1995). Dipolar cycloaddition of azomethine ylides derived from Schiff bases of *S*-allylcysteine methyl ester has also been observed (Grigg, 1985; Grigg *et al.*, 1989). We decided to investigate the possibility of making more extensive use of this type of reaction and gather more consistent structural information on the products which are of potential pharmacological importance (Garcia & Galvez, 1985).

The title compound, (II), was prepared from imine (I) and a single-crystal X-ray diffraction study was undertaken in order to determine the complete stereochemistry. It crystallizes as a racemate and the unit cell contains two enantiomer molecules related by the inversion center. The enantiomer represented in Fig. 1 has four chiral centers with the following configurations: C1(*R*), C2(*S*), C4(*R*) and N1(*R*). The molecule has *cis* stereochemistry at the ring junction resulting from an *exo* intramolecular 1,3-dipolar cycloaddition. The dihedral angle between the least-squares planes of the tetrahydrothieno and pyrrole rings is 50.8 (5)°. The four C atoms of the tetrahydrothieno ring are approximately coplanar and atom S1 lies 0.763 (1) Å from this plane. This ring has an approximate S1-envelope form, the Cremer & Pople (1975) ring-puckering amplitudes being q_2 = 0.466 (2) Å and φ_2 = 5.6 (2)°. The pyrrole ring deviates significantly from planarity and has a conformation that can be described as half-chair (Duax *et al.*, 1976) with a local pseudo-twofold axis running along C1 and the midpoint of the C2—C3 bond, as shown by the ring-puckering amplitudes q_2 = 0.371 (2) Å and φ_2 = −47.1 (3)° (pivot atom N1). The bond lengths and angles in the thienopyrrole ring system compare well with values found in similar compounds (Barkley *et al.*, 1995; Mackay *et al.*, 1995). The methoxy group lies close to the plane of the phenyl ring [dihedral angle 4.5 (2)°].



(I)



(II)

The amino H atom participates in an intramolecular bifurcated hydrogen-bond system linking N1 to both O1 and O3, and lying approximately in a plane; the sum of the three bond angles around the H atom is 354 (3)°. A weaker C—H···O intramolecular interaction exists between atoms C3 and O3.

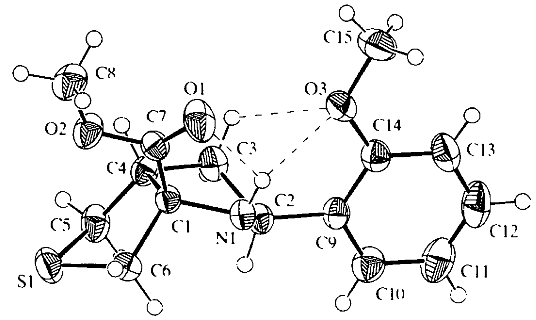


Fig. 1. *ORTEP*II (Johnson, 1976) plot of the title compound. Displacement ellipsoids are drawn at the 50% probability level, except for H atoms, which are shown as spheres of arbitrary radii. The dashed lines show the intramolecular hydrogen bonds.

Experimental

The intramolecular cycloaddition was achieved by heating a solution of the imine (I) (2 mmol) in xylene (10 ml) under reflux under N_2 for 24 h. The solvent was evaporated and the crude product purified by crystallization from ethyl ether–petroleum ether (313–333 K). Final yield: 67%; m.p. 388 (2) K; ^{1}H NMR (300 MHz, $CDCl_3$) δ (p.p.m.): 2.07–2.21 (2H, *m*), 2.75 (1H, *dd*, *J* = 4.4 and 11.7 Hz), 2.88 (1H, *d*, *J* = 12.2 Hz), 2.96 (1H, *brs*, NH), 3.19 (1H, *dd*, *J* = 7.5 and 11.7 Hz), 3.30 (1H, *d*, *J* = 12.2 Hz), 3.33–3.39 (1H, *m*), 3.64 (3H, *s*, CO_2CH_3), 3.83 (3H, *s*), 4.76 (1H, *t*, *J* = 6.8 Hz), 6.82–6.93 (2H, *m*, ArH), 7.18–7.24 (1H, *m*, ArH) and 7.31 (1H, *dd*, *J* = 1.4 and 7.5 Hz, ArH); MS (*m*/*z*): 293 (M^+, 4%) 234 (98), 220 (60), 186 (37), 149 (100), 134 (94). Analysis calculated for $C_{15}H_{19}NO_3S$: C 61.41, H 6.33, N 4.79, S 10.93%; found: C 61.47, H 6.43, N 4.22, S 10.40%.

Crystal data

$C_{15}H_{19}NO_3S$
M_r = 293.37
Triclinic
$P\overline{1}$
a = 7.7869 (12) Å
b = 9.6947 (13) Å
c = 9.849 (2) Å
α = 93.036 (14)°
β = 102.402 (15)°
γ = 98.478 (13)°
V = 715.5 (2) Å^3
Z = 2
D_x = 1.362 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 10.4–19.5°
μ = 0.233 mm^{-1}
T = 293 (2) K
Prismatic
0.40 × 0.38 × 0.38 mm
Translucent yellow

Data collection

Enraf–Nonius CAD-4 diffractometer

$R_{\rm int}$ = 0.012
$\theta_{\rm max}$ = 25°

Profile data from ω–2θ scans
Absorption correction: none
3030 measured reflections
2510 independent reflections
2095 reflections with $I > 2\sigma(I)$
$h = -9 \rightarrow 9$
$k = -11 \rightarrow 11$
$l = -11 \rightarrow 1$
3 standard reflections
frequency: 300 min
intensity decay: 1.2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.090$
$S = 1.027$
2510 reflections
186 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0391P)^2 + 0.3614P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.210$ e Å^{-3}
$\Delta\rho_{\min} = -0.220$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

S1—C6	1.803 (2)	N1—C1	1.471 (2)
S1—C5	1.803 (2)	N1—C2	1.476 (2)
C6—S1—C5	90.18 (8)	C5—C4—C3	113.06 (15)
C1—N1—C2	105.84 (13)	C3—C4—C1	103.52 (13)
N1—C1—C4	107.73 (13)	C4—C5—S1	107.13 (12)
N1—C2—C3	105.20 (13)	C1—C6—S1	108.33 (12)
C4—C3—C2	102.88 (14)		
C6—C1—C4—C3	−125.73 (15)	C4—C1—C7—O1	−117.9 (2)
C6—C1—C7—O1	122.0 (2)		

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1	0.82 (2)	2.24 (2)	2.703 (2)	115 (2)
N1—H1···O3	0.82 (2)	2.30 (2)	2.899 (2)	130 (2)
C3—H3*A*···O3	0.97	2.55	3.108 (2)	117

The H atoms of the organic moiety were placed in calculated positions and refined as riding using *SHELXL*97 defaults (Sheldrick, 1997), except for the amino H atom, which was located from a difference Fourier synthesis and refined with $U_{eq} = 1.2U_{eq}(\mathrm{N1})$. Examination of the crystal structure with *PLATON* (Spek, 1995) showed that there were no significant empty cavities in the crystal packing. All calculations were performed on a Pentium 150 MHz PC running LINUX.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *SDP-Plus* (Frenz, 1985). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*97.

We are indebted to Dr José Carlos Prata Pina for helpful assistance with our CAD-4 automatic diffractometer which enabled the experimental work to be carried out. This work was supported by project PRAXIS XXI 2/2.1/QUI/390/94 and Chymiotechnon. We thank Faculdade de Farmácia, University of Coimbra, Portugal, for the leave of absence of AMTDPVC.

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N,*N*′-Diphenylguanidinium Nitrate

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Abstract

The cation of the title salt, $C_{13}H_{14}N_3^+.NO_3^-$, is found to have a conformation with both phenyl rings lying in *syn* positions with respect to the unsubstituted N atom. The geometry of the guanidinium group is close to that expected for a central C_{sp^2} atom. The structure is stabilized by a two-dimensional network of hydrogen bonds in the (100) plane, where the O atoms of the anion are acceptors from the N—H guanidinium groups.

Comment

Certain *N*,*N*′-diarylguanidines are reported to have neuroprotective properties against glutamate-induced neuronal cell depth (Olney *et al.*, 1989). *N*,*N*′-Di-*o*-tolylguanidine and its congeners were shown to be selective ligands for the haloperidol-sensitive σ receptors, and neuroleptic and antihypersensitive activities of these

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1332). Services for accessing these data are described at the back of the journal.