Monoclinic
$P2_1/c$
a = 12.748 (2) Å
b = 6.110 (3) Å
c = 14.870 (6) Å
β = 99.51 (2)°
V = 1142 (1) Å^3
Z = 4
D_x = 1.443 Mg m^{-3}
D_m not measured

Cell parameters from 25 reflections
θ = 11–19°
μ = 0.105 mm^{-1}
T = 100 K
Needle fragment
0.57 × 0.55 × 0.18 mm
Colorless

Data collection

Enraf–Nonius CAD-4 diffractometer (with Oxford Cryostream cooler)
$\theta/2\theta$ scans
Absorption correction: none
6069 measured reflections
3454 independent reflections
2926 reflections with $I > \sigma(I)$

R_{int} = 0.030
θ_{max} = 30.0°
$h = -17 \rightarrow 16$
$k = 0 \rightarrow 8$
$l = -19 \rightarrow 19$
3 standard reflections
frequency: 60 min
intensity decay: 1.8%

Refinement

Refinement on F^2
$R(F)$ = 0.050
$wR(F^2)$ = 0.055
S = 1.976
2926 reflections
212 parameters
All H atoms refined
$w = 4F_o^2/[\sigma^2(F_o^2) + 0.0004F_o^4]$

$(\Delta/\sigma)_{max}$ = 0.026
$\Delta\rho_{max}$ = 0.40 e Å^{-3}
$\Delta\rho_{min}$ = −0.33 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

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

O1′—C2′	1.373 (2)	C3a—C6a	1.555 (2)
O1′—C5′	1.436 (2)	C3—C7	1.332 (2)
O1—C2	1.351 (2)	C3′—C4′	1.313 (2)
O1—C6a	1.462 (2)	C4—C5	1.337 (2)
O2—C2	1.211 (2)		
C2—O1—C6a	111.7 (1)	C3a—C4—C5	112.4 (1)
O1—C2—C3	109.3 (1)	C4—C5—C6	112.4 (1)
C3—C3a—C6a	102.3 (1)	O1—C6a—C3a	105.9 (1)
C4—C3a—C6a	102.8 (1)	C3a—C6a—C6	107.0 (1)
C2—C3—C3a	108.8 (1)	C5—C6—C6a	104.1 (1)
C7—O3—C5′—C4′	176.5 (1)	C2—C3—C7—O3	−179.7 (1)
C5′—O3—C7—C3	170.4 (1)		

C—H distances range from 0.91 (2) to 1.00 (2) Å, while B_{iso} values for H atoms range from 0.9 (3) to 5.2 (6) Å^2.

Data collection: *CAD-4 Operations Manual* (Enraf–Nonius, 1994). Cell refinement: *CAD-4 Operations Manual*. Data reduction: *PROCESS* in *MolEN* (Fair, 1990). Program(s) used to solve structure: Direct methods *SIR* (Burla *et al.*, 1989). Program(s) used to refine structure: *LSFM* in *MolEN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *BTABLE PTABLE CIF IN* in *MolEN*.

The purchase of the diffractometer was made possible by a National Science Foundation chemical instrumentation grant, which we gratefully acknowledge. Improvements to the LSU X-ray Crystallography Facility were supported by grant No. LEQSF(1996–97)-ENH-TR-10, administered by the Louisiana Board of Regents. IMW acknowledges support by a National Institutes of Health grant (GM 39844). JKR is supported by Rockefeller Foundation postdoctoral fellowship (RF 94027 #600).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SX1062). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1999). C**55**, 761–764

Two novel 3,4-disubstituted 1,2,4-oxadiazole-5(4*H*)-thiones

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(*Received 30 June 1998; accepted 11 January 1999*)

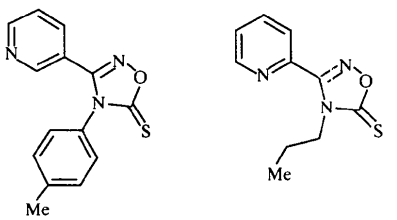
Abstract

Compound (1), 3-(3-pyridyl)-4-*p*-tolyl-1,2,4-oxadiazole-5(4*H*)-thione, $C_{14}H_{11}N_3OS$, and compound (2), 3-(2-pyridyl)-4-propyl-1,2,4-oxadiazole-5(4*H*)-thione,

$C_{10}H_{11}N_3OS$, both contain planar oxadiazole rings. The C=S distance is 1.614 (3) Å in compound (1) and 1.634 (1) Å in compound (2).

Comment

Heterocycles bearing nitrogen and sulfur are known to show significant biological activity against various bacteria and fungi species. In this regard, 3,4-disubstituted 1,2,4-oxadiazole-5(4*H*)-thiones were synthesized (Dürüşt *et al.*, 1991) and their spectroscopic behavior published previously (Dürüşt & Dürüşt, 1992; Dürüşt & Faggi, 1997; Dürüşt, 1998). 3-(2-Pyridyl)-4-*n*-propyl-1,2,4-oxadiazole-5(4*H*)-thione, (2), and 3-(3-pyridyl)-4-*p*-tolyl-1,2,4-oxadiazole-5(4*H*)-thione, (1), were investigated against bacteria and fungi species, and they were found to have considerable activity against both (Gümüs *et al.*, 1993).



(1) (2)

A search of the Cambridge Structural Database (Allen & Kennard, 1993; version of June 1998, *ca* 181 000 entries), for the 1,2,4-oxadiazole-5-thione subunit yielded no hits, and a search for the 1,2,4-oxadiazole-5-one subunit with C substituents at the 3 and 4 positions yielded but two hits (Cheng *et al.*, 1982; Amor *et al.*, 1987). As there is a lack of structural data in the literature for this class of compound, we have determined the structures of these novel 3,4-disubstituted 1,2,4-oxadiazole-5(4*H*)-thione heterocycles, at room temperature for (1), and at 100 K for (2). Much of the structural data available for similar heterocycles involves rings containing sp^3-hybridized C atoms (Balsamini *et al.*, 1992; Ruiz-Valero *et al.*, 1985), rather than Csp^2 atoms like the structures we report here. While we were able to obtain an excellent crystal of compound (2), crystals of (1) are thin plates of lower quality, which decayed 18.8% in intensity during data collection, and thus the structure determination of (1) is of lower precision. Due to the dearth of structural data for 1,2,4-oxadiazoline-5-thiones, we include both determinations here.

The structures of both (1) and (2) contain essentially planar, five-membered oxadiazole rings. That of (1) has a mean deviation of 0.001 (1) Å amongst its atoms and (2) has a mean deviation of 0.004 (4) Å. This planarity appears in similar structures with sp^2-hybridized C atoms in the ring (Amor *et al.*, 1987) while those with Csp^3 atoms exhibit envelope and twist conformations (Balsamini *et al.*, 1992; Ruiz-Valero *et al.*, 1985). In addition, the S atom of the thione substituent is nearly coplanar with the ring in both structures, deviating by 0.0042 (4) in (2) and 0.014 (5) Å in (1). All bond distances and angles within the rings agree with similar structures within experimental error (Amor *et al.*, 1987).

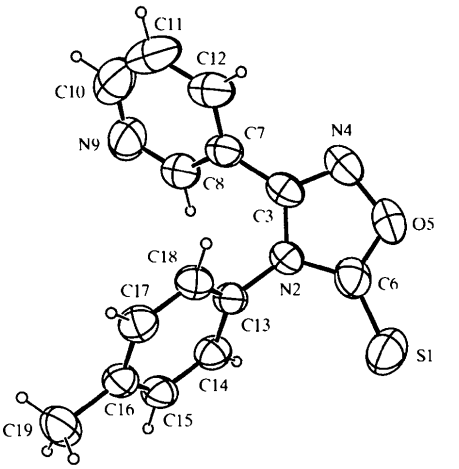


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of (1) with ellipsoids at the 50% probability level.

Similar characteristics exist between the substituents of the oxadiazole rings in the two structures. The observed C=S bond distance in (1) is slightly shorter at 1.614 (3) Å than in (2) where it is 1.634 (1) Å. Both have a pyridine ring bonded at comparable distances to the oxadiazole [1.483 (4) in (1) and 1.473 (2) Å in (2)]. In both cases, the pyridyl-C atom bonded to the heterocycle lies slightly out of the plane of the heterocycle, deviating 0.036 (5) and 0.012 (2) Å from the ring plane in (1) and (2), respectively. The 2-pyridyl substituent of (2) is nearly coplanar with the

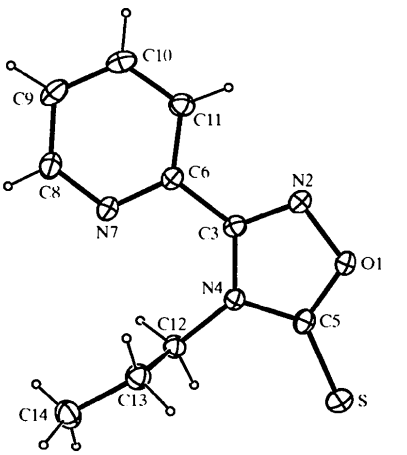


Fig. 2. *ORTEP*II (Johnson, 1976) drawing of (2) with ellipsoids at the 50% probability level.

oxadiazole ring [N4—C3—C6—N7 3.3 (2)°], while the 3-pyridyl substituent of (1) deviates markedly from coplanarity [N2—C3—C7—C8 −57.1 (5)°]. This may be understood as resulting from favorable intramolecular interactions of H atoms with N lone pairs in (2) [H12*b*···N7 2.41 (2) Å; H11···N2 2.51 (2) Å], *versus* unfavorable potential H···H interactions between the pyridyl and tolyl substituents in (1). To avoid such contacts, the tolyl ring is also twisted −60.9 (3)° (C3—N2—C13—C18) out of the heterocyclic plane, and there is a twist of −11.1 (4)° about the C3—N2 bond carrying the two substituents. The corresponding torsion angle in (2) (C12—N4—C3—C6) is 1.1 (2)°, showing no such distortion.

Experimental

Synthesis of (1): a solution of redistilled thiophosgene in chloroform was added dropwise to an ice-cooled solution of *N*-*p*-tolylpyridine-3-carboxamidoxime and pyridine. The reaction mixture was stirred at room temperature for 3 d. The solvent was evaporated under reduced pressure, and the crude product was crystallized from ethanol to give (1) (m.p. 432–433 K).

Synthesis of (2): as for (1), substituting *n*-propyl for *p*-tolyl in *N*-*p*-tolylpyridine-3-carboxamidoxime and crystallization from *n*-pentane instead of ethanol. The m.p. for (2) is 337–338 K.

Compound (1)

Crystal data

$C_{14}H_{11}N_3OS$
M_r = 269.32
Monoclinic
$P2_1/c$
a = 16.234 (3) Å
b = 11.017 (2) Å
c = 7.1954 (14) Å
β = 93.15 (3)°
V = 1285.0 (4) Å^3
Z = 4
D_x = 1.392 Mg m^{-3}
D_m not measured
Cu $K\alpha$ radiation
λ = 1.54184 Å
Cell parameters from 25 reflections
θ = 15.8–23.1°
μ = 2.10 mm^{-1}
T = 293 K
Plate
0.30 × 0.23 × 0.05 mm
Colorless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.49, T_{max} = 0.90
5232 measured reflections
2637 independent reflections
1833 reflections with $I > 2\sigma(I)$
R_{int} = 0.086
θ_{max} = 75.0°
$h = 0 \rightarrow 20$
$k = -13 \rightarrow 13$
$l = -9 \rightarrow 9$
3 standard reflections
frequency: 120 min
intensity decay: 18.8%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.070
$wR(F^2)$ = 0.201
S = 1.069
2637 reflections
174 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.07P)^2 + 0.2054P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = −0.03
$\Delta\rho_{max}$ = 0.29 e Å^{-3}
$\Delta\rho_{min}$ = −0.45 e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.040 (5)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

S1—C6	1.614 (3)	N2—C6	1.376 (4)
O5—C6	1.366 (4)	N2—C13	1.433 (3)
O5—N4	1.446 (3)	N4—C3	1.283 (4)
N2—C3	1.369 (3)	C3—C7	1.483 (4)
C6—O5—N4	108.6 (2)	N4—C3—N2	112.8 (3)
C3—N2—C6	107.5 (2)	O5—C6—N2	106.1 (2)
C3—N4—O5	104.9 (2)		
C13—N2—C3—C7	−11.1 (4)	N2—C3—C7—C8	−57.1 (5)
C13—N2—C6—S1	8.8 (4)	C3—N2—C13—C18	−60.9 (3)

Compound (2)

Crystal data

$C_{10}H_{11}N_3OS$
M_r = 221.28
Triclinic
$P\bar{1}$
a = 7.728 (1) Å
b = 8.826 (2) Å
c = 9.3699 (9) Å
α = 112.89 (1)°
β = 112.029 (9)°
γ = 94.84 (1)°
V = 525.6 (4) Å^3
Z = 2
D_x = 1.399 Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 11.6–18.2°
μ = 0.271 mm^{-1}
T = 100 K
Fragment
0.50 × 0.42 × 0.30 mm
Colorless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.88, T_{max} = 0.92
5166 measured reflections
3063 independent reflections
2753 reflections with $I > \sigma(I)$
R_{int} = 0.012
θ_{max} = 30.0°
$h = -10 \rightarrow 10$
$k = -10 \rightarrow 12$
$l = -13 \rightarrow 12$
3 standard reflections
frequency: 60 min
intensity decay: 0.1%

Refinement

Refinement on F
R = 0.044
wR = 0.058
$wR(F^2)$ = 0.058
S = 1.955
2753 reflections
180 parameters
All H-atom parameters refined
$w = 4F_o^2/[\sigma^2(F_o^2) + 0.0004F_o^4]$
$(\Delta/\sigma)_{max}$ = 0.02
$\Delta\rho_{max}$ = 0.53 e Å^{-3}
$\Delta\rho_{min}$ = −0.49 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

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

S—C5	1.634 (1)	N4—C3	1.384 (1)
O1—N2	1.421 (1)	N4—C5	1.360 (2)
O1—C5	1.350 (2)	C3—C6	1.473 (2)
N2—C3	1.298 (2)		
N2—O1—C5	109.7 (1)	N2—C3—N4	112.0 (1)
O1—N2—C3	104.60 (9)	O1—C5—N4	106.86 (9)
C3—N4—C5	106.8 (1)		
C12—N4—C3—C6	1.1 (2)	N4—C3—C6—N7	3.3 (2)
C12—N4—C5—S	−0.1 (2)	N4—C12—C13—C14	170.0 (1)
C3—N4—C12—C13	−86.6 (2)		

The H atoms of (1) were placed in calculated positions with C—H 0.93 Å and isotropic displacement parameters at $1.2U_{eq}$ of the bonded C atom. H atoms of the methyl group at C19 were calculated with C—H 0.96 Å in idealized positions of maximum total electron density. A torsional parameter specifying the conformation of the methyl group was refined. All other H atoms were allowed to ride on the attached C atom. H atoms of (2) were refined with isotropic displacement parameters. C—H distances are in the range 0.87 (2)–1.01 (2) Å, while U_{iso} values are in the range 0.024 (5)–0.042 (7) Å^2.

For both compounds, data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1993); cell refinement: *CAD-4 EXPRESS*. Data reduction: *XCAD4* (Harms & Wocadlo, 1996) for (1); *PROCESS* in *MolEN* (Fair, 1990) for (2). Program(s) used to solve structures: *SHELXS86* (Sheldrick, 1990) for (1); *SIR* (direct methods) (Burla *et al.*, 1989) for (2). Program(s) used to refine structures: *SHELXL93* (Sheldrick, 1993) for (1); *LSFM* in *MolEN* for (2). For both compounds, molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *SHELXTL* for (1); *CIF IN* in *MolEN* for (2).

The purchase of the diffractometer was made possible by a National Science Foundation chemical instrumentation grant, which we gratefully acknowledge. Improvements to the LSU X-ray Crystallography Facility were supported by grant No. LEQSF(1996–97)-ENH-TR-10, administered by the Louisiana Board of Regents. DRB wishes to acknowledge the Chancellor's Student Aid Fund and the Howard Hughes Research Institute Summer Research Program which made these structure determinations possible.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1041). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1999). C**55**, 764–766

N-Methyl-2′-nitrocinnamanilide

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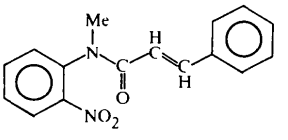
(*Received 22 September 1998; accepted 21 December 1998*)

Abstract

An inversion centre relates two molecules of the title compound, $C_{16}H_{14}N_2O_3$, which form a dimer through C—H···O hydrogen bonds. The inversion centre lies almost in the plane of the dimer. This study provides a good example of C—H···O interactions leading to dimeric coupling of molecules.

Comment

The title compound, (I), is an intermediate in the synthesis of substituted indole steroids. An interesting aspect of the structure is the occurrence of an inversion-related dimer linked by C—H···O hydrogen bonds.



(I)