Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Two *N*-substituted 3,5-diphenyl-2-pyrazoline-1-thiocarboxamides

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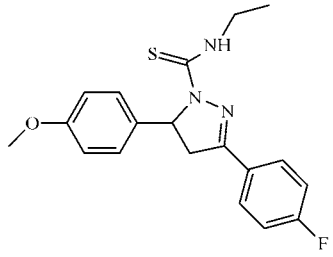
Received 11 July 2005
Accepted 21 July 2005
Online 10 August 2005

The structures of *N*-ethyl-3-(4-fluorophenyl)-5-(4-methoxyphenyl)-2-pyrazoline-1-thiocarboxamide, $C_{19}H_{20}FN_3OS$, (I), and 3-(4-fluorophenyl)-*N*-methyl-5-(4-methylphenyl)-2-pyrazoline-1-thiocarboxamide, $C_{18}H_{18}FN_3S$, (II), have similar geometric parameters. The methoxy/methyl-substituted phenyl groups are almost perpendicular to the pyrazoline (pyraz) ring [interplanar angles of 89.29 (8) and 80.39 (10)° for (I) and (II), respectively], which is coplanar with the fluorophenyl ring [interplanar angles of 5.72 (9) and 10.48 (10)°]. The pyrazoline ring approximates an envelope conformation in both structures, with the two-coordinate N atom involved in an intramolecular $N-H\cdots N_{pyraz}$ interaction. In (I), $N-H\cdots O$ and $C-H\cdots S$ intermolecular hydrogen bonds are the primary interactions, whereas in (II), there are no intermolecular hydrogen bonds.

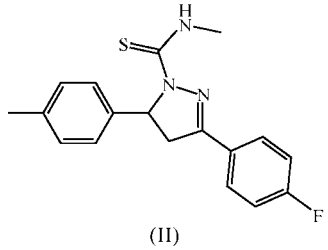
Comment

Prodrug-based monoamine oxidase (MAO) inhibitors display important antidepressant activity. Previous studies have demonstrated the MAO inhibitory activities of 1,3,5-triphenyl-2-pyrazolines (Soni *et al.*, 1987; Chimenti *et al.*, 2004). We have previously synthesized several phenyl-2-pyrazoline derivatives (Bilgin *et al.*, 1993; Palaska *et al.*, 1996, 2001), and we report here the structures of two 5-aryl-3-(4-fluorophenyl)-1-(*N*-substituted thiocarbamoyl)-2-pyrazolines (Figs. 1–3 and Tables 1 and 2).

In (I), the five-membered pyrazoline ring has an envelope conformation, with atom C8 forming the flap. Atoms N1, N2, C9 and C10 coplanar, with a maximum deviation of 0.069 (2) Å for atom C9; atom C8 is 0.18 (2) Å from this plane [the puckering parameters (Cremer & Pople, 1975) are q_2 = 0.15 (2) Å and φ = 89.36 (6)°]. Compound (II) is similar, although it shows a slight envelope-like distortion; atom C8 is 0.12 (2) Å from the mean plane [q_2 = 0.24 (3) Å and φ = 84.16 (7)°]. The bond lengths and angles in the five-membered rings in both compounds are in agreement with expected values (Allen, 2002; Krishnakumar *et al.*, 2004). The pyrazoline ring N—N bond lengths are similar, *viz.* 1.3886 (16) Å in (I) and 1.395 (2) Å in (II), and are influenced by the degree of conjugation within the C=N double bond of the pyrazoline ring.



(I)



(II)

The bond lengths and angles of the thiocarbamoyl groups of (I) and (II) are comparable to those of the related compound *O*-(2-*tert*-butyl-6-dimethylthiocarbamoyl-4-methylphenyl) *N*,*N*-diethylthiocarbamate (Castillo *et al.*, 2003). In (I) and (II), the thiocarbamoyl S1=C7 and pyrazoline N2=C10 bonds are well defined double bonds. The N—C=S bond angles around the C atoms of the thiocarbamoyl moieties are similar, with values of 120.75 (10)° for (I) and 121.31 (14)° for (II). The N—C—N(H)—C torsion angle is −175.44 (13)° for (I) and −170.43 (17)° for (II). In each compound, the methoxyphenyl or methylphenyl group occupies a pseudo-axial position and, as a result, is approximately perpendicular to the mean plane of the pyrazoline ring [the interplanar angle is 89.29 (8)° in (I) and 80.39 (10)° in (II)].

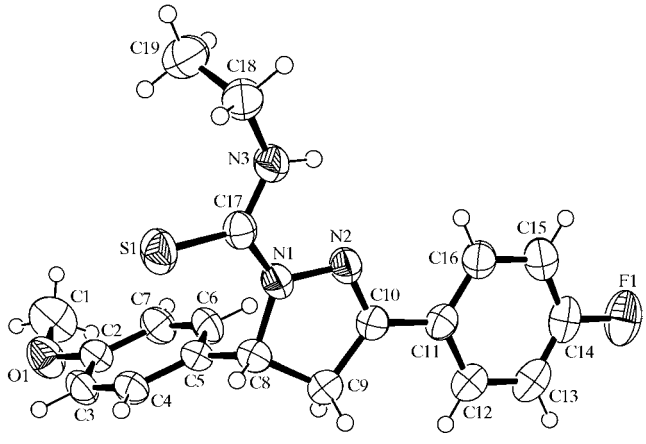


Figure 1
The structure of (I), with displacement ellipsoids drawn at the 50% probability level.

  DOI: 10.1107/S0108270105023255

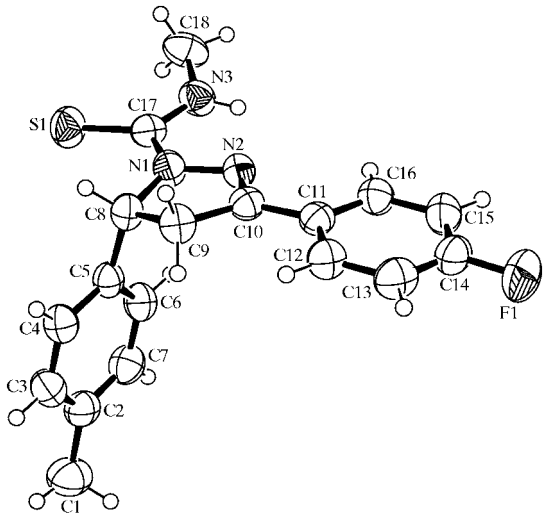


Figure 2
The structure of (II), with displacement ellipsoids drawn at the 50% probability level.

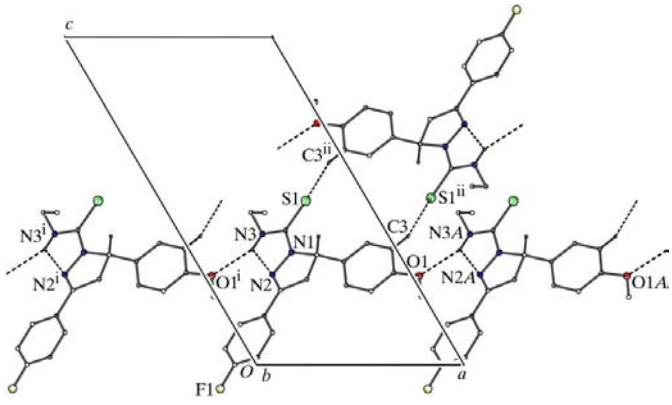


Figure 3
The hydrogen-bond interactions (dashed lines) in (I), depicted with the unit cell. Only H atoms involved in interactions and atom H8 are shown. [Symmetry codes are as in Table 2, with the addition of (*A*) 1 + *x*, *y*, *z*.]

In (I), the carbamoyl N—H H atom forms a bifurcated hydrogen bond involving an intramolecular interaction with atom N2 of the pyrazoline group [graph set *S*(5); Bernstein *et al.*, 1995] and an intermolecular hydrogen bond with methoxy atom O1 [N3—H20···O1^{i}, with graph set *C*(11); symmetry code: (i) *x* − 1, *y*, *z*; Table 1]. The latter interaction links the molecules into a one-dimensional chain along (100) (Fig. 3). Intermolecular C3—H3···S1^{ii} hydrogen bonds [symmetry code: (ii) −*x* + 2, −*y* + 2, −*z* + 1] further link the chains across inversion centres, forming rings with graph set $R_2^2(16)$ (Bernstein *et al.*, 1995). In (II), only relatively weak intramolecular hydrogen bonds are present (Table 2).

Experimental

Hydrazine hydrate (0.02 mol) was added to an ethanol solution of 1-(4-fluorophenyl)-3-(4-methylphenyl)-2-propenone or 1-(4-fluorophenyl)-3-(4-methoxyphenyl)-2-propenone (0.01 mol) and refluxed for 2 h. The reaction mixture was cooled to 255 K, and the solid mass that separated out was filtered off and dissolved in dry diethyl ether. Substituted ethyl or methyl isothiocyanate (0.01 mol) and three drops of Et_3N were added and stirred for 4 h. The reaction mixture was evaporated to dryness and the solid mass was crystallized from ethanol in the case of (I) and methanol for (II). Compound (I) was crystallized from ethanol (yield 50.4%, m.p. 412 K). IR (KBr, cm^{-1}): 3342 (N—H), 1606 (C═N), 1440 (C═C), 1387 (C_4—H), 1320 (C═S), 1033 (C_5—N_1). ^{1}H NMR ($CDCl_3$, p.p.m.): 1.28 (*t*, 3H, CH_2—CH_3), 3.11 (*dd*, 1H, pyrazoline H_4), 3.72 (*m*, 2H, CH_2—CH_3), 3.75 (*m*, 4H, –OCH_3, pyrazoline H_4), 6.03 (*dd*, 1H, pyrazoline H_5), 6.83–7.74 (*m*, 8H, aromatic). Compound (II) was crystallized from methanol (yield 45.8%, m.p. 422 K). IR (KBr, cm^{-1}): 3362 (N—H), 1602 (C═N), 1419 (C═C), 1320 (C═S), 1004 (C_5—N_1). ^{1}H NMR ($CDCl_3$, p.p.m.): 2.30 (*s*, 3H, Ar—CH_3), 3.19 (*s*, 3H, NH—CH_3), 3.12 (*dd*, 1H, pyrazoline H_4), 3.76 (*dd*, 1H, pyrazoline H_4), 6.05 (*dd*, 1H, pyrazoline H_5), 7.09–7.73 (*m*, 8H, aromatic).

Compound (I)

Crystal data

$C_{19}H_{20}FN_3OS$
M_r = 357.44
Monoclinic, $P2_1/c$
a = 9.706 (5) Å
b = 12.141 (5) Å
c = 17.753 (5) Å
β = 120.372 (17)°
V = 1804.9 (13) Å^3
Z = 4
D_x = 1.315 Mg m^{-3}
Mo *K*α radiation
Cell parameters from 10785 reflections
θ = 1.3–26.7°
μ = 0.20 mm^{-1}
T = 293 (2) K
Prism, yellow
0.60 × 0.54 × 0.30 mm

Data collection

Stoe IPDS-II diffractometer
ω scans
12891 measured reflections
3622 independent reflections
2785 reflections with $I > 2\sigma(I)$
R_{int} = 0.043
θ_{max} = 26.3°
h = −12 → 12
k = −15 → 15
l = −22 → 22

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.092
S = 1.03
3622 reflections
234 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0499P)^2 + 0.0998P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.14 e Å^{-3}
$\Delta\rho_{min}$ = −0.15 e Å^{-3}

Table 1
Hydrogen-bond and contact geometry (Å, °) for (I).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H20···O1^{i}	0.87 (2)	2.32 (2)	3.092 (2)	149 (2)
N3—H20···N2	0.87 (2)	2.21 (2)	2.6187 (18)	109 (1)
C3—H3···S1^{ii}	0.93	2.79	3.5471 (18)	140
C18—H18*B*···S1	0.97	2.75	3.088 (2)	101

Symmetry codes: (i) *x* − 1, *y*, *z*; (ii) −*x* + 2, −*y* + 2, −*z* + 1.

Compound (II)

Crystal data

$C_{18}H_{18}FN_3S$
M_r = 327.41
Monoclinic, $P2_1/c$
a = 9.4191 (17) Å
b = 12.2032 (11) Å
c = 14.673 (2) Å
β = 103.063 (14)°
V = 1642.9 (4) Å^3
Z = 4
D_x = 1.324 Mg m^{-3}
Mo *K*α radiation
Cell parameters from 8856 reflections
θ = 1.4–26.7°
μ = 0.21 mm^{-1}
T = 293 (2) K
Prism, yellow
0.60 × 0.46 × 0.25 mm

Data collection

Stoe IPDS-II diffractometer
ω scan
Absorption correction: integration (*X-RED32*; Stoe & Cie, 2002)
T_{min} = 0.885, T_{max} = 0.954
10474 measured reflections
3429 independent reflections
2655 reflections with $I > 2\sigma(I)$
R_{int} = 0.051
θ_{max} = 26.6°
$h = -11 \rightarrow 11$
$k = -14 \rightarrow 15$
$l = -18 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.140
S = 1.08
3429 reflections
214 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0738P)^2 + 0.2481P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.23 e Å^{-3}
$\Delta\rho_{min}$ = −0.30 e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.041 (5)

Table 2
Hydrogen-bond and short-contact geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3···N2	0.86	2.20	2.602 (2)	108
C6—H6···N1	0.93	2.53	2.866 (3)	102

Atoms H8 and H20 of (I) and atom H18 of (II) were located in difference Fourier maps and refined independently, with isotropic displacement parameters [C8—H8 = 1.001 (16) Å, N3—H20 = 0.865 (16) Å and C8—H18 = 0.94 (2) Å]. The remaining H atoms were positioned geometrically and refined using a riding model, fixing the aromatic C—H distances at 0.93 Å, the CH_2 C—H distances at 0.97 Å and the methyl C—H distances at 0.96 Å [U_{iso}(H) = 1.2U_{eq}(C,N) or 1.5U_{eq}(methyl C)].

For both compounds, data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED32* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996); publication software: *WinGX* (Farrugia, 1999) and *PARST* (Nardelli, 1995).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1282). Services for accessing these data are described at the back of the journal.

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Bernstein, J., Davies, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Bilgin, A. A., Palaska, E. & Sunal, R. (1993). *Arzneim. Forsch. Drug Res.* **43**, 1041–1044.
Burnett, M. N. & Johnson, C. K. (1996). *ORTEPIII*. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.
Castillo, I., Flores-Figuerro, A. & Ortega, S. H. (2003). *Acta Cryst.* C**59**, o577–o579.
Chimenti, F., Bolasco, A., Manna, F., Secci, D., Chimenti, P., Befani, O., Turini, P., Giovannini, V., Mondovi, B., Cirilli, R. & La Torre, F. (2004). *J. Med. Chem.* pp. 2071–2074.
Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Krishnakumar, R. V., Vijayabaskar, V., Perumal, S., Selvaraj, S. & Natarajan, S. (2004). *Acta Cryst.* E**60**, o476–o478.
Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.
Palaska, E., Aytemir, M., Uzbay, I. T. & Erol, D. (2001). *Eur. J. Med. Chem.* **36**, 539–543.
Palaska, E., Erol, D. & Demirdamar, R. (1996). *Eur. J. Med. Chem.* **31**, 43–47.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Soni, N., Pande, K., Kalsi, R., Gupta, T. K., Parmar, S. S. & Barthwal, J. P. (1987). *Res. Commun. Chem. Pathol. Pharmacol.* **56**, 129–132.
Stoe & Cie (2002). *X-AREA* (Version 1.18) and *X-RED32* (Version 1.04). Stoe & Cie, Darmstadt, Germany.