8226 reflections
914 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.079P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = 0.00 (5)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H1*WA*···N22*D*	0.83 (2)	2.17 (2)	2.985 (5)	168 (2)
O1*W*—H1*WB*···O8*WA*	0.84 (4)	1.98 (5)	2.81 (4)	168 (4)
O1*W*—H1*WB*···O8*WB*	0.84 (4)	2.05 (5)	2.79 (4)	147 (4)
O2*W*—H2*WA*···N19*D*	0.82 (4)	2.12 (4)	2.923 (6)	167 (4)
O2*W*—H2*WB*···O1*W*	0.83 (7)	2.02 (6)	2.836 (6)	168 (6)
O3*W*—H3*WA*···N18*B*	0.84 (3)	1.98 (2)	2.808 (5)	166 (2)

Table 2. *Contact distances (Å)*

O4*W*···O6*W*	2.917 (8)	O6*W*···O7*WB*^{iv}	2.68 (2)
O2*W*···O3*W*^{i}	2.781 (6)	O8*WA*···N19*B*^{i}	2.90 (3)
O3*W*···O5*W*^{iii}	2.812 (6)	O8*WA*···N18*D*^{vi}	2.91 (2)
O4*W*···O5*W*^{iii}	2.799 (6)	O8*WB*···N19*B*^{i}	2.82 (2)
O6*W*···O7*WA*^{iv}	2.829 (8)	O8*WB*···N18*D*^{vi}	2.94 (3)

Symmetry codes: (i) $1 + x, 1 + y, z - 1$; (ii) $x - 1, y - 1, z$; (iii) $x - 1, y - 1, 1 + z$; (iv) $1 + x, y, z$; (v) $x, 1 + y, z - 1$; (vi) $x - 1, y, z$.

The conspicuous pseudocentrosymmetry was thoroughly checked by refinement of a model in $P\bar{1}$ but this proved fruitless. Two water molecules (O7*W* and O8*W*) out of the eight independent ones in the structure showed disorder and were refined with a split model. The H atoms of these two water molecules could not be located and nor could those for the O6*W* molecule and three others corresponding to molecules O3*W*, O4*W* and O5*W*, respectively. The remaining H atoms were found in late difference Fourier maps and were refined with geometric constraints and independent isotropic displacement parameters. H atoms attached to C atoms were placed at their calculated sites and allowed to ride on their hosts.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *MSC/AFC Diffractometer Control Software*. Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*a*). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*b*). Molecular graphics: *XP* in *SHELXTL/PC* (Sheldrick, 1994). Software used to prepare material for publication: *PARST* (Nardelli, 1983*b*) and CSD (Allen & Kennard, 1993).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SX1085). Services for accessing these data are described at the back of the journal.

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5-[(Dimethylamino)methyleneamino]-3-methyl-1-phenylpyrazole

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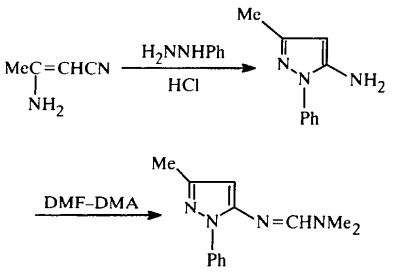
Abstract

The title substituted pyrazole, $C_{13}H_{16}N_4$, was prepared in order to study some specifics relating to the C—N bond. The dihedral angle between the pyrazole and phenyl planes is 22.75 (8)°. A better coplanarity of the pyrazole and phenyl planes is observed in the title compound in comparison with that of similar systems.

Comment

This work is part of an ongoing study of the synthesis of compounds which are characterized by the presence of a pyrazole ring with different substituents. More than 209 structures of neutral pyrazoles have been analysed (Llamas-Saiz *et al.*, 1994). The structures of these pyrazoles were classified according to the substituent on the N atom at position 1. The structure determination of 5-[(dimethylamino)methyleneamino]-

3-methyl-1-phenylpyrazole, (I), was undertaken in order to establish its molecular conformation in the solid state and to analyse the degree of coplanarity of the pyrazole and phenyl planes.



(I)

The synthesis of compound (I) has been reported previously by Lamartina & Migliara (1990). The crystal structure of pyrazole as a free molecule has been reported by Larsen *et al.* (1970). Other molecules similar to the present structure were used to compare their molecular parameters with those of the title compound. From the Cambridge Structural Database (Allen *et al.*, 1991), two similar systems containing the pyrazole and phenyl groups, 1-phenyl-5-methyl-3-pyrazolone (PMPYZL; Bechtel *et al.*, 1973) and ethyl 10-methyl-12-phenyl-4-*p*-tolyl-5-*p*-tolylimino-2,4,6,11,12-pentaazatricyclo[7.3.0.$0^{3,6}$]dodeca-1(9),2,7,10-tetraene-7-carboxylate (SOZCAL; Molina *et al.*, 1992), were found and were also used for comparison with (I).

When comparing the bond lengths of the pyrazole moiety in (I) with those in free pyrazole (two independent molecules) it is found that the N1—N2 distance changes from 1.379 (2) to 1.338 and 1.344 Å and the N1—C7 bond length changes from 1.372 (2) to 1.339 and 1.325 Å, respectively (Larsen *et al.*, 1970). These differences can be explained by the presence of different substituents at N1 or C7. Other bond lengths in (I) and the free molecule are comparable. The N1—C7 bond length and C7—C12—C11 and N1—C7—C12 bond angles are moderately different in (I) from the values in the 209 pyrazole systems (average values of 1.356 Å and 105.2 and 107.2°, respectively) which are reported in the literature (Llamas-Saiz *et al.*, 1994). Other bond lengths and angles of the pyrazole ring are comparable with the average values reported by Llamas-Saiz *et al.* (1994).

Comparison of the molecular parameters of compound (I) with those of PMPYZL and SOZCAL shows that the bond lengths and angles are very similar. The N3—C8 bond is *cis* oriented with respect to the C7—C12 bond. The C12—C7—N3—C8 torsion angle is −36.4 (3)°. This particular conformation is adopted in (I) as a consequence of the presence of the bulky substituent at N1. The dihedral angle between the pyrazole and phenyl rings in (I) is 22.75 (8)°, whereas the dihedral angles for the SOZCAL and PMPYZL compounds are 44.3 (2) and 44.3 (1)°, respectively. These values suggest a better coplanarity and therefore a better resonance between the pyrazole and phenyl rings and a shorter C1—N1 bond for compound (I).

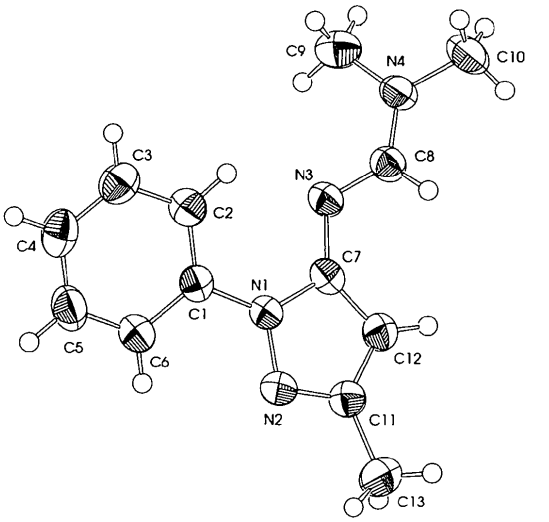


Fig. 1. A perspective view (*ZORTEP*; Zsolnai, 1995) of (I) with the atomic labelling scheme. Displacement ellipsoids are plotted at the 50% probability level and H atoms are shown as circles of an arbitrary radius.

Experimental

5-Amino-3-methyl-1-phenylpyrazole (1 mmol) in *N,N*-dimethylformamide–dimethyl acetal (DMF–DMA) (20% *w/w*) was heated to reflux for 10 h. After evaporation of the solvent under reduced pressure, the residue, (I), was washed with ethanol, filtered and washed with ethanol again [yield 80%; m.p. 387 (1) K]. Spectroscopic analysis: ^{1}H NMR ($CDCl_3$, δ, p.p.m.): 2.29 (3H, *s*, CH_3), 2.98 [6H, *s*, $N(CH_3)_2$], 5.66 (1H, *s*, H4), 7.68 (1H, *s*, N=CH), 7.20–7.86 (5H, *m*, 1-Ph); ^{13}C NMR ($CDCl_3$, δ, p.p.m.): 14.3 (CH_3), 34.2 and 39.8 [$N(CH_3)_2$], 91.0 (C4), 122.5 and 127.8 ($C_{o,m}$), 125.6 (C_p), 140.0 (C_i), 148.4 (N=CH), 151.8 (C5), 154.2 (C2).

Crystal data

$C_{13}H_{16}N_4$
M_r = 228.30
Monoclinic
$P2_1/n$
a = 9.1149 (6) Å
b = 7.5153 (4) Å
c = 18.1463 (8) Å
β = 92.03 (1)°
V = 1242.3 (1) Å^3
Z = 4
D_x = 1.221 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 10.4–18.2°
μ = 0.077 mm^{-1}
T = 293 K
Prism
0.25 × 0.10 × 0.10 mm
Yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2692 measured reflections
2528 independent reflections
1943 reflections with $I > 2\sigma(I)$
$R_{int} = 0.013$
$\theta_{max} = 26.3°$
$h = -11 \rightarrow 0$
$k = 0 \rightarrow 9$
$l = -22 \rightarrow 22$
3 standard reflections
frequency: 120 min
intensity decay: 0.7%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.157$
$S = 1.097$
2527 reflections
156 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0763P)^2 + 0.3950P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = -0.004$
$\Delta\rho_{max} = 0.25$ e Å^{-3}
$\Delta\rho_{min} = -0.23$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.032 (4)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

N1—C7	1.372 (2)	N3—C8	1.289 (2)
N1—N2	1.379 (2)	C7—C12	1.376 (3)
N1—C1	1.419 (2)	C11—C12	1.399 (3)
N2—C11	1.323 (2)		
C7—C12—C11	106.2 (2)		
C8—N3—C7—C12	−36.4 (3)	C9—N4—C8—N3	1.1 (3)

The pyrazole ring and methyl H atoms were added at calculated positions. The remaining H atoms were treated with a riding model with *SHELXL*93 (Sheldrick, 1993) defaults (C—H 0.93–0.96 Å) and were not refined; $U_{iso} = 0.076$ Å^2 was assigned to all H atoms.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *CAD-4 SDP* (Frenz, 1978). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93. Molecular graphics: *ZORTEP* (Zsolnai, 1995). Software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1200). Services for accessing these data are described at the back of the journal.

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4-(4-Methylphenyl)-3-(4-pyridyl)-1*H*-1,2,4-triazole-5(4*H*)-thione

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Abstract

The title compound, $C_{14}H_{12}N_4S$, crystallizes with two independent molecules which differ slightly in conformation. The methyl-substituted phenyl ring is inclined at angles of 67 (1) and 76 (1)° with respect to the 1,2,4-triazole moiety in molecules 1 and 2, respectively. The dihedral angles between the substituted pyridyl and phenyl rings are 73 (1) and 71 (1)°, respectively, in the two molecules. The two molecules are linked by N—H···N hydrogen bonds.

Comment

1,2,4-Triazole derivatives have antibacterial (Jantová *et al.*, 1998), antimicrobial, antiviral, antifungal (Holla *et al.*, 1996), antioxidant and antiradical activities (Dunaev *et al.*, 1996). These derivatives are also used as adenosine deaminase (Volpini *et al.*, 1997) and aromatase inhibitors (Okada *et al.*, 1997). Condensed [1,2,4]-triazoles are biologically interesting products (Kottke *et al.*, 1983;