Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

3-*tert*-Butyl-5-[(4-methoxybenzylidene)amino]-1-phenylpyrazole

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Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.003 Å
R factor = 0.052
wR factor = 0.135
Data-to-parameter ratio = 16.4

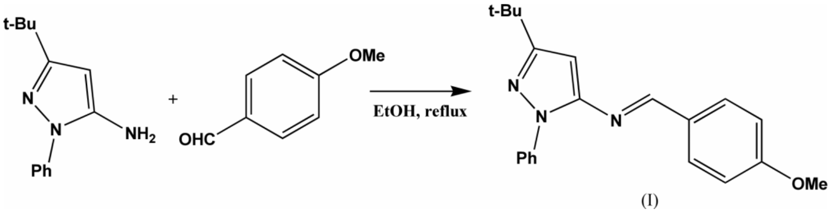
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 14 January 2003
Accepted 21 January 2003
Online 31 January 2003

The title compound, $C_{21}H_{23}N_3O$, has a supramolecular structure which is determined by a very weak C—H···O(methoxy) hydrogen bond and a similarly weak C—H···π interaction.

Comment

The title compound, (I), was prepared as an intermediate in the preparation of new fused-pyrazole derivatives (see *Scheme* below).



(I)

There are no unusual bonds or angles (Table 1) in the pyrazole ring, which is planar within experimental error. [Note that the atom numbering used for the title molecule does not follow normal IUPAC conventions.]

The mean plane of the phenyl ring attached to N2 is tilted at 26.70 (9)° to the mean plane of the pyrazole ring. The torsion angles involving the methoxy carbon, C341, show that the

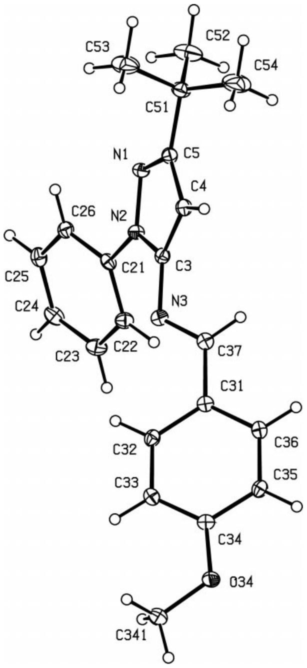


Figure 1
A view of (I) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

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DOI: 10.1107/S1600536803001909

methoxy group is almost, but not quite, coplanar with the phenyl ring to which it is attached [C33—C34—O34—C341 = 5.1 (2)°]; there is a tendency for methoxy groups to be coplanar with the phenyl ring in anisoles [see Domiano *et al.* (1979)]

The supramolecular structure is determined by two very weak interactions involving phenyl H atoms (Table 2). The C4—H4···O34 bond links the molecules at (x, y, z) and ($1 - x$, $-y$, $-z$) into a head-to-tail centrosymmetric $R_2^2(20)$ dimer (Bernstein *et al.*, 1995), formed about the centre of symmetry at ($\frac{1}{2}$, 0,0) (Fig. 2). These dimers are then linked by a C—H···π interaction into a ribbon which runs parallel to the b axis; this is formed by the interaction C25—H25···centroid of the phenyl ring attached to N2 (Fig. 3).

Examination of the structure with *PLATON* (Spek, 2002) showed that there were no solvent-accessible voids in the crystal lattice.

Experimental

A mixture of 5-amino-3-(*tert*-butyl)-1-phenyl-1*H*-pyrazole (0.11 g, 0.512 mmol), *p*-methoxybenzaldehyde (0.07 g, 0.514 mmol) and ethanol (10 ml) was heated to reflux for 5 min. After cooling, the pale yellow solid which formed was filtered off and washed with ethanol (85% yield; m.p. 394 K). ^{1}H NMR (300 MHz, CDCl$_3$, p.p.m.): 1.39 (9H, *s*), 3.85 (3H, *s*), 6.20 (1H, *s*), 6.95 (2H, *d*, J = 9.0 Hz), 7.26 (1H, *t*, J = 9.0 Hz), 7.42 (2H, *br t*), 7.79 (4H, *br d*), 8.58 (1H, *s*, N═CH); ^{13}C NMR (75 MHz, CDCl$_3$, p.p.m.): 30.4, 32.5, 55.4, 89.7, 114.3, 124.1, 126.1, 128.4, 129.0, 130.8, 139.9, 150.4, 159.2 (N═CH), 162.1, 162.6; MS (70 eV): *m*/*e* (%) 333 (95), 318 (73), 291 (44), 77 (100), 51 (48), 41 (77). Crystals suitable for single-crystal X-ray diffraction were grown from a solution in ethanol.

Crystal data

$C_{21}H_{23}N_3O$
$M_r = 333.42$
Monoclinic, $P2_1/c$
$a = 10.0744\ (3)$ Å
$b = 6.2583\ (2)$ Å
$c = 28.9244\ (9)$ Å
$\beta = 101.0410\ (13)°$
$V = 1789.89\ (10)$ Å^3
$Z = 4$
$D_x = 1.237$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3762 reflections
$\theta = 3.2$–$27.5°$
$\mu = 0.08$ mm^{-1}
$T = 120\ (1)$ K
Block, brown
0.40 × 0.20 × 0.10 mm

Data collection

Nonius KappaCCD diffractometer
φ scans and ω scans with κ offsets
Absorption correction: multi-scan (*DENZO–SMN*; Otwinowski & Minor, 1997)
$T_{\min} = 0.970$, $T_{\max} = 0.992$
9156 measured reflections
3762 independent reflections
2710 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.056$
$\theta_{\max} = 27.5°$
$h = -11 \rightarrow 13$
$k = -8 \rightarrow 4$
$l = -37 \rightarrow 31$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.052$
$wR(F^2) = 0.135$
$S = 1.04$
3762 reflections
230 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0575P)^2 + 0.7158P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.46$ e Å^{-3}
$\Delta\rho_{\min} = -0.33$ e Å^{-3}

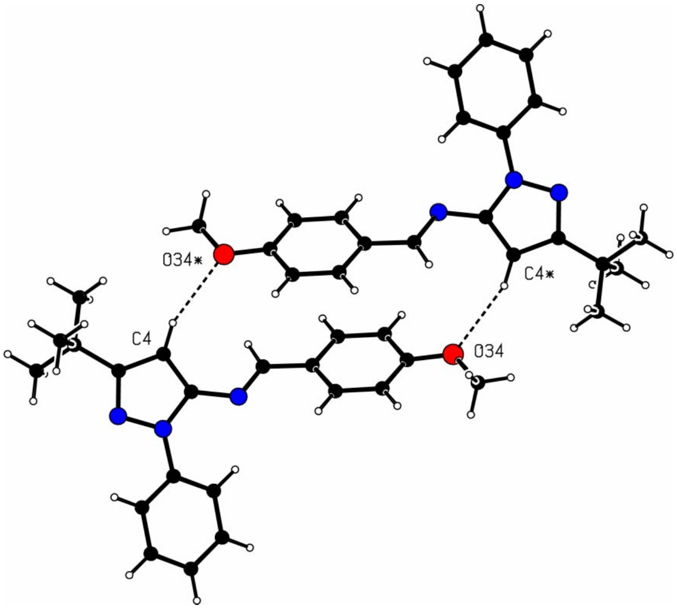

Figure 2
A view of the the $R_2^2(20)$ centrosymmetric dimer.

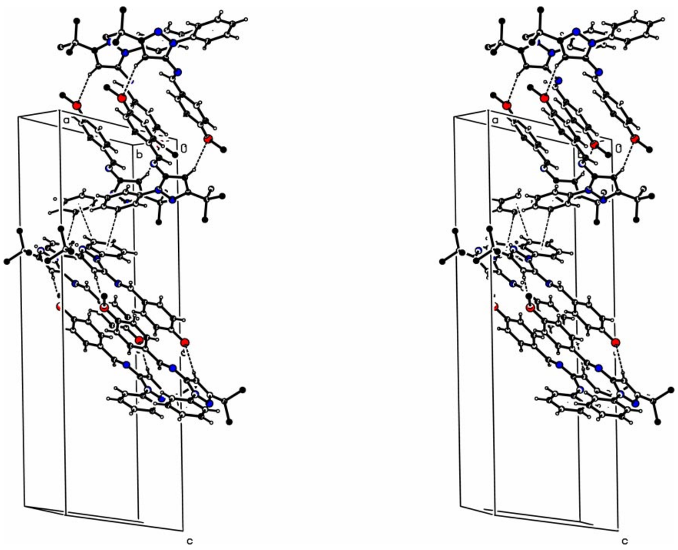

Figure 3
Stereoview showing the dimers linked by the C—H···π interaction. Methyl H atoms have been omitted for clarity.

Table 1
Selected geometric parameters (Å, °).

N1—C5	1.330 (2)	C3—N3	1.394 (2)
N1—N2	1.369 (2)	N3—C37	1.283 (2)
N2—C3	1.367 (2)	C37—C31	1.455 (2)
C3—C4	1.375 (2)	C4—C5	1.404 (2)
C5—N1—N2	105.23 (14)	C3—C4—C5	105.61 (16)
C3—N2—N1	111.23 (13)	N1—C5—C4	111.28 (15)
N2—C3—C4	106.64 (15)		
C3—N2—C21—C22	−25.9 (3)	C3—N3—C37—C31	173.83 (15)
N1—N2—C21—C22	151.18 (16)	N3—C37—C31—C32	−11.9 (3)
C3—N2—C21—C26	155.84 (17)	N3—C37—C31—C36	170.00 (16)
N1—N2—C21—C26	−27.0 (2)	C33—C34—O34—C341	5.1 (2)
N2—C3—N3—C37	146.59 (16)	C35—C34—O34—C341	−175.37 (15)
C4—C3—N3—C37	−40.1 (3)		

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

*Cg*1 is the centroid of the C21–C26 ring.

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
C4—H4⋯O34^{i}	0.95	2.59	3.487 (2)	157
C25—H25⋯*Cg*1^{ii}	0.95	2.73	3.472 (2)	135

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

H atoms were treated as riding atoms, with C—H distances in the range 0.95–0.98 Å. The data shows a completness of 0.92 at θ of 27.50° and 0.933 at θ of 25.00°; examination of the data shows that data at high θ values are very weak or absent. The methyl atoms of the *tert*-butyl group, particularly C54, have higher displacement parameters than the other atoms in the structure, indicating a degree of rotational disorder in this group.

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976) and *PLATON* (Spek, 2002); software used to prepare material for publication: *SHELXL*97 and *WordPerfect* macro *PRPKAPPA* (Ferguson, 1999).

X-ray data were collected at the EPSRC X-ray Crystallographic Service, University of Southampton; the authors thank the staff for all their help and advice. MN, AS and JC thank the Ministerio de Educación Cultura y Deportes, (Programa de Cooperación con Iberoamérica, AECI) of Spain for financial support for this work. RA thanks COLCIENCIAS and Universidad del Valle for financial support.

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