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N-(3-*tert*-Butyl-1-phenyl-1*H*-pyrazol-5-yl)-*N*-(4-methoxybenzyl)acetamide: a hydrogen-bonded chain of centrosymmetric rings

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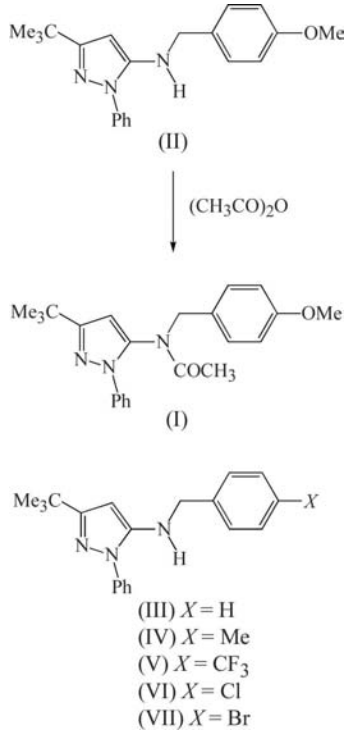
The molecule of the title compound, $C_{23}H_{27}N_3O_2$, adopts a conformation having no internal symmetry so that the compound exhibits conformational chirality. The molecules are linked by a combination of C—H···O and C—H···π(arene) hydrogen bonds into a chain of rings in which two types of centrosymmetric ring alternate.

Comment

We report here the structure and supramolecular aggregation of the title compound, (I) (Fig. 1); this compound was prepared by acetylation of the amine, (II) (see scheme), whose structure was reported several years ago (Abonía *et al.*, 2007). Compound (I) was originally prepared as a possible intermediate for the synthesis of new fused pyrazolobenzazepine derivatives with potential biological applications (Lucács *et al.*, 2001; Wikström *et al.*, 2002; Crecente-Campo *et al.*, 2009), and here we compare its structure with those of the precursor, (II), and some analogues of (II) (Castillo *et al.*, 2009).

The molecular conformation of compound (I) can conveniently be considered in terms of the orientations of the three substituents bonded to the pyrazole ring relative to the plane of the pyrazole ring itself, as indicated by the leading torsion angles (Table 1). The unsubstituted ring makes a dihedral angle of 50.3 (2)° with the pyrazole ring; coplanarity of these two rings would lead to some short nonbonded contacts, in particular between the H atom bonded to atom C12 (Fig. 1) and the atoms of the amide group. As often found in systems of this type (Abonía *et al.*, 2007; Castillo *et al.*, 2009), the *tert*-butyl group adopts an orientation in which one of the methyl C atoms, here C32, is close to, but not precisely in, the plane of the adjacent pyrazole ring: in (I), atom C32 is displaced by only 0.111 (2) Å from the plane of the pyrazole ring. Although the amide unit based on atoms N51 and C58 is planar, this plane is almost orthogonal to that of the pyrazole ring, as the torsion angles N1—C5—N51—C57 and N1—C5—N51—C58 show (Table 1). On the other hand, the methoxy group is almost coplanar with the adjacent benzene ring and methyl atom C541 is displaced from the plane of this ring by only 0.100 (2) Å. Accordingly, the exocyclic bond angles at atom C54 differ by almost 10° (Table 1). The remaining bond distances and angles present no unusual values.



The conformation means that the molecules of compound (I) exhibit no internal symmetry and hence they are conformationally chiral; however, the centrosymmetric space group accommodates equal numbers of the two conformational enantiomers. The non-acylated precursor, (II), adopts a rather similar conformation to that of (I) but it crystallizes in the enantiomeric pair of space groups $P4_12_12$ and $P4_32_12$, so that each crystal contains only a single conformational enantiomer (Abonía *et al.*, 2007). While it was not possible to determine the correct space group for the crystal selected for data collection because of the absence of significant resonant scattering, it was concluded that the distribution of the crystalline products between the two space groups was essentially statistical. Despite their very close similarities in constitution and conformation, the series of compounds (II)–(VII) (Abonía *et al.*, 2007; Castillo *et al.*, 2009) exhibit a wide range of crystallization behaviour and some unexpected isomorphisms. Thus, compounds (II) (X = OMe) and (IV) (X = Me) are isomorphous in the enantiomeric space groups $P4_12_12$ and $P4_32_12$, and compounds (III) (X = H), (V) (X = CF_3) and (VII)

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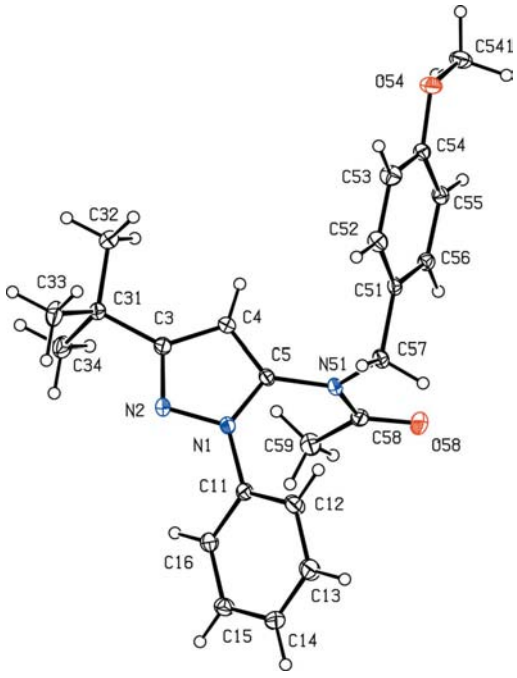

Figure 1
The molecular structure of compound (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

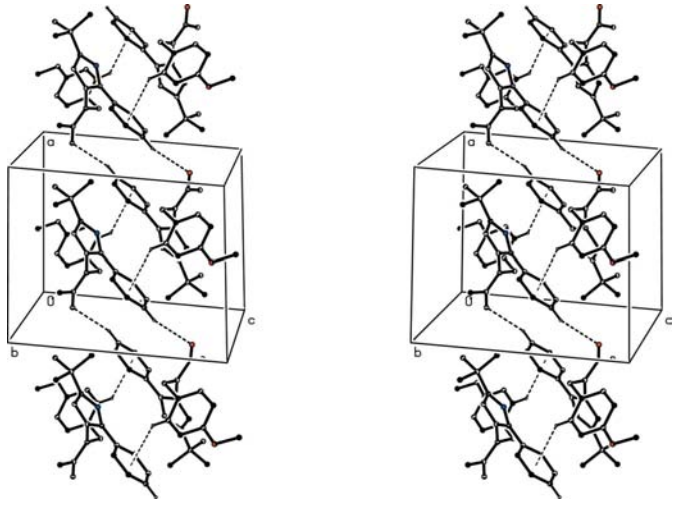

Figure 2
A stereoview of part of the crystal structure of compound (I), showing the formation of a chain of hydrogen-bonded rings running parallel to the [100] direction. For the sake of clarity, H atoms not involved in the motifs shown have been omitted.

(X = Br) are isomorphous in space group $C2/c$, but compound (VI) (X = Cl) is isomorphous with neither (IV) nor (VII).

The molecules of compound (I) are linked into a chain of centrosymmetric edge-fused rings by a combination of one C—H···O hydrogen bond and one C—H···π(arene) hydrogen bond (Table 2), in which the unsubstituted phenyl ring (C11–C16) provides the donor in the C—H···O hydrogen bond as well as acting as the acceptor in the C—H···π(arene) hydrogen bond. This latter interaction may be an important influence on the orientation of the phenyl ring relative to the pyrazole core of the molecule.

In the first of these interactions, aryl atom C14 in the molecule at (x, y, z) acts as hydrogen-bond donor to carbonyl atom O58 in the molecule at ($-x$, $1-y$, $1-z$), so forming a centrosymmetric $R_2^2(20)$ (Bernstein *et al.*, 1995) ring, centred at (0, $\frac{1}{2}$, $\frac{1}{2}$). In the second interaction, aryl atom C52 at (x, y, z) acts as hydrogen-bond donor to aryl ring C11–C16 in the molecule at ($1-x$, $1-y$, $1-z$), so forming a second centrosymmetric ring, this time centred at ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$). Propagation by inversion of these two motifs thus generates a chain of edge-fused rings running parallel to the [100] direction, with the rings built from paired C—H···O hydrogen bonds centred at (n, $\frac{1}{2}$, $\frac{1}{2}$), where n represents an integer, and those built from paired C—H···π(arene) hydrogen bonds centred at ($n+\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$), where n again represents an integer (Fig. 2).

The supramolecular aggregation in compound (I) may be briefly contrasted with that in compounds (II)–(VII) (Abonía *et al.*, 2007; Castillo *et al.*, 2009). In each of compounds (III)–(VII), the crystal structures are dominated by N—H···π hydrogen bonds, often accompanied by C—H···π hydrogen bonds, leading to the formation of a finite dimer in compound (IV), a simple chain in (III), a chain of rings in (VI), and sheets in both (V) and (VII). In compound (II), however, the N—H bond plays no role in the intermolecular aggregation, which instead is determined by a single C—H···N hydrogen bond, which forms a simple $C(9)$ chain.

Experimental

Sodium borohydride (3.8 mmol) was added portionwise over a period of 1 h to a solution of (*E*)-5-amino-3-*tert*-butyl-*N*-(4-methoxybenzylidene)-1-phenyl-1*H*-pyrazole (1.50 mmol) in methanol (10 ml). After the reduction was complete, the volume of the solution was reduced to around 3 ml under reduced pressure, and water (5 ml) was then added. The resulting mixture was extracted with ethyl acetate (2 × 5 ml) and the combined extracts were dried with anhydrous sodium sulfate; the solvent was then removed to give the pure amine intermediate, (II) (see scheme), in 98% isolated yield. A mixture of (II) (0.89 mmol) and acetic anhydride (0.18 g, 2.0 mmol) was heated to 373 K in an oil bath for 10 min. After the reaction was complete, the mixture was cooled to ambient temperature and water (3 ml) was added. The resulting solid product, (I), was collected by filtration in quantitative yield. Colourless crystals suitable for single-crystal X-ray diffraction were grown by slow evaporation of a solution in methanol (m.p. 390 K). MS (IE 70 eV) m/z (%): 377 (7 [M^+]), 121 (100), 77 (6). Analysis found: C 73.1, H 7.4, N 11.12%; $C_{23}H_{27}N_3O_2$ requires C 73.2, H 7.2, N 11.1%.

Crystal data

$C_{23}H_{27}N_3O_2$
M_r = 377.48
Triclinic, $P\overline{1}$
a = 9.8325 (3) Å
b = 9.8649 (4) Å
c = 12.0365 (3) Å
α = 97.468 (2)°
β = 95.512 (2)°
γ = 114.643 (1)°
V = 1037.44 (5) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.08 mm^{-1}
T = 120 K
0.18 × 0.12 × 0.10 mm

Data collection

Bruker–Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.986, T_{max} = 0.992
18936 measured reflections
4079 independent reflections
3269 reflections with $I > 2\sigma(I)$
R_{int} = 0.047

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.102
S = 1.05
4079 reflections
259 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.20 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}

Table 1
Selected bond and torsion angles (°).

O54—C54—C53	115.54 (13)	C54—O54—C541	116.67 (11)
O54—C54—C55	124.75 (13)		
N2—N1—C11—C12	−133.97 (14)	N1—C5—N51—C57	−100.84 (15)
N2—C3—C31—C32	172.69 (13)	N1—C5—N51—C58	83.16 (17)
N2—C3—C31—C33	51.01 (18)	C5—N51—C57—C51	−80.52 (15)
N2—C3—C31—C34	−68.09 (17)	N51—C57—C51—C52	118.10 (14)
C53—C54—O54—C541	−177.94 (13)	C5—N51—C58—O58	176.99 (13)

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

D—H···A	D—H	H···A	D···A	D—H···A
C14—H14···O58^{i}	0.95	2.55	3.389 (2)	147
C52—H52···Cg^{ii}	0.95	2.75	3.544 (2)	142

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

All H atoms were located in difference maps and then treated as riding atoms in geometrically idealized positions, with C—H distances of 0.95 (aromatic and pyrazole), 0.98 (CH_3) or 0.99 Å (CH_2), and with U_{iso}(H) = kU_{eq}(C), where k = 1.5 for the methyl groups, which were permitted to rotate but not to tilt, and 1.2 for all other H atoms.

Data collection: *COLLECT* (Hooft, 1999); cell refinement: *DIRAX*/*LSQ* (Duisenberg *et al.*, 2000); data reduction: *EVALCCD* (Duisenberg *et al.*, 2003); program(s) used to solve structure: *SIR2004* (Burla *et al.*, 2005); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL97* and *PLATON*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3357). Services for accessing these data are described at the back of the journal.

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