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Seven 5-benzylamino-3-*tert*-butyl-1-phenyl-1*H*-pyrazoles: unexpected isomorphisms, and hydrogen-bonded supramolecular structures in zero, one and two dimensions

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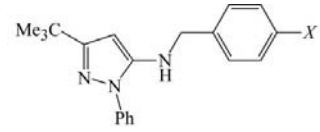
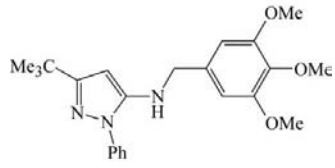
5-Benzylamino-3-*tert*-butyl-1-phenyl-1*H*-pyrazole, $C_{20}H_{23}N_3$, (I), and its 5-[4-(trifluoromethyl)benzyl]-, $C_{21}H_{22}F_3N_3$, (III), and 5-(4-bromobenzyl)-, $C_{20}H_{22}BrN_3$, (V), analogues, are isomorphous in the space group *C*2/*c*, but not strictly isostructural; molecules of (I) form hydrogen-bonded chains, while those of (III) and (V) form hydrogen-bonded sheets, albeit with slightly different architectures. Molecules of 3-*tert*-butyl-5-(4-methylbenzylamino)-1-phenyl-1*H*-pyrazole, $C_{21}H_{25}N_3$, (II), are linked into hydrogen-bonded dimers by a combination of N—H···π(arene) and C—H···π(arene) hydrogen bonds, while those of 3-*tert*-butyl-5-(4-chlorobenzylamino)-1-phenyl-1*H*-pyrazole, $C_{20}H_{22}ClN_3$, (IV), form hydrogen-bonded chains of rings which are themselves linked into sheets by an aromatic π–π stacking interaction. Simple hydrogen-bonded chains built from a single N—H···O hydrogen bond are formed in 3-*tert*-butyl-5-(4-nitrobenzylamino)-1-phenyl-1*H*-pyrazole, $C_{20}H_{22}N_4O_2$, (VI), while in 3-*tert*-butyl-5-(3,4,5-trimethoxybenzylamino)-1-phenyl-1*H*-pyrazole, $C_{23}H_{29}N_3O_3$, (VII), which crystallizes with $Z' = 2$ in the space group $P\overline{1}$, pairs of molecules are linked into two independent centrosymmetric dimers, one generated by a three-centre N—H···$(O)_2$ hydrogen bond and the other by a two-centre N—H···O hydrogen bond.

Comment

Pyrazoles are a class of heterocyclic compounds whose members exhibit a wide range of interesting properties, including drug and pesticide activity, as well as forming the basis for new materials (Elguero, 1984, 1996). We have recently determined the structures of a number of new (*E*)-5-arylideneamino-3-*tert*-butyl-1-phenyl-1*H*-pyrazoles, which are the first intermediates isolated in a synthetic pathway developed as a route to new fused heterocyclic compounds containing the pyrazole unit (Castillo *et al.*, 2009). The next step in this pathway requires the reduction of the imine derivatives to give the corresponding 5-arylmethylamino-3-*tert*-butyl-1-phenyl-1*H*-pyrazoles, and we report here the molecular and supramolecular structures of seven compounds of this type, namely 5-benzylamino-3-*tert*-butyl-1-phenyl-1*H*-pyrazole, (I), and its 4-methylbenzyl, 4-(trifluoromethyl)-benzyl, 4-chlorobenzyl, 4-bromobenzyl and 4-nitrobenzyl analogues, denoted (II)–(VI), and the 3,4,5-trimethoxybenzyl analogue, (VII), which we compare with the 4-methoxybenzyl derivative, (VIII), whose structure was reported several years ago (Abonía *et al.*, 2007) (see scheme below and Fig. 1).



(I) X = H
(II) X = Me
(III) X = CF_3
(IV) X = Cl
(V) X = Br
(VI) X = NO_2
(VIII) X = OMe



(VII)

The crystallization characteristics of the benzylamino series composed of compounds (I)–(VII) show some unexpected features. It is not infrequently found that the corresponding 4-methylphenyl and 4-chlorophenyl derivatives in a particular series are isomorphous and isostructural; likewise the corresponding 4-chlorophenyl and 4-bromophenyl analogues in other series are not infrequently found to be isomorphous. However, in the present series of compounds, no two of these derivatives, *viz.* compounds (II), (IV) and (V), are isomorphous. By contrast, and somewhat unexpectedly, the unsubstituted benzyl compound, (I), was found to be isomorphous with both the 4-trifluorobenzyl, (III), and 4-bromobenzyl, (V), compounds. These three compounds all crystallize in the space group *C*2/*c* with very similar cell dimensions and very similar values of the coordinates of corresponding atoms. However, the 4-chlorobenzyl analogue, (IV), in the space group $P\overline{1}$, is isomorphous neither with 4-methylbenzyl compound (II) nor 4-bromobenzyl compound (V).

4-Methylbenzyl compound (II) and its 4-methoxy analogue, (VIII) (Abonía *et al.*, 2007), are effectively isomorphous, with close correspondence between the two sets of atomic coordinates, although the cell dimensions are slightly larger for (VIII) [a = 10.9665 (14) Å and c = 30.976 (6) Å]. For neither of these compounds was it possible to establish whether the correct space group for the crystal selected for data collection

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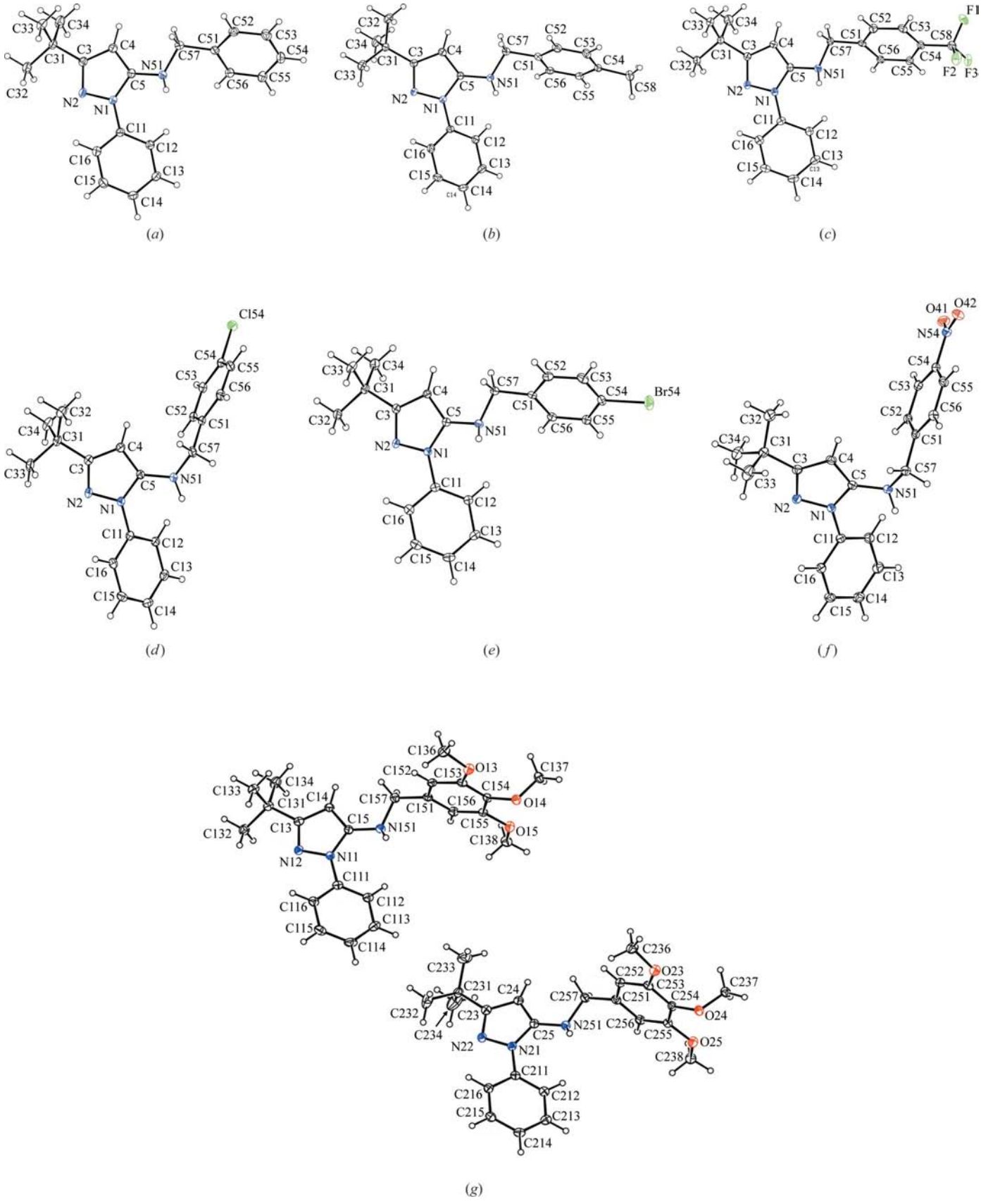

Figure 1
The molecular structures of compounds (I)–(VIII), showing the atom-labelling schemes: (*a*) compound (I), (*b*) compound (II), (*c*) compound (III), (*d*) compound (IV), (*e*) compound (V), (*f*) compound (VI) and (*g*) the two independent molecules of compound (VII). Displacement ellipsoids are drawn at the 30% probability level.

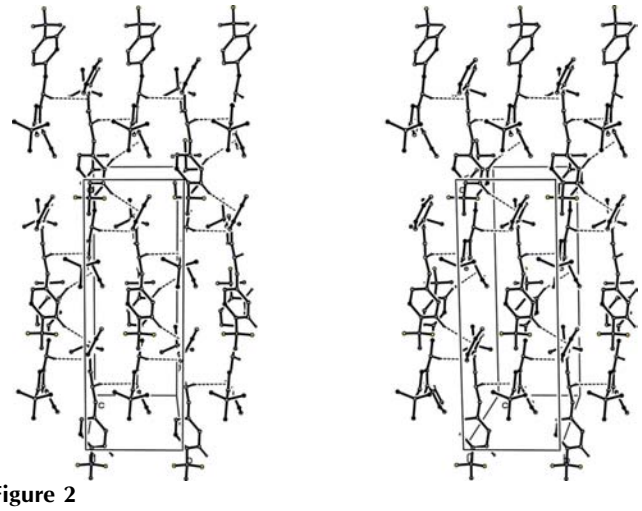

Figure 2
A stereoview of part of the crystal structure of compound (III), showing the formation of a sheet parallel to (001) containing N—H···π(pyrazole) and C—H···π(arene) interactions. For the sake of clarity, H atoms bonded to C atoms not involved in the motifs shown have been omitted.

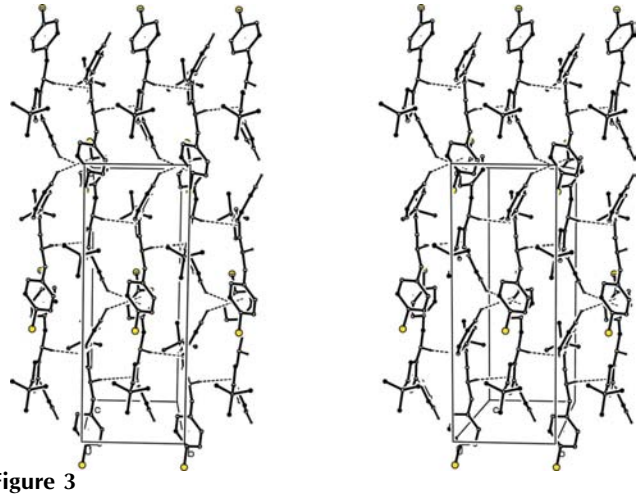

Figure 3
A stereoview of part of the crystal structure of compound (V), showing the formation of a sheet parallel to (001) containing N—H···π(pyrazole) and C—H···π(arene) interactions. For the sake of clarity, H atoms bonded to C atoms not involved in the motifs shown have been omitted.

was $P4_12_12$ or $P4_32_12$, and hence the correct conformational enantiomorphs present in these crystals could not be determined, although this identification has no chemical significance. For (VIII), the authors concluded that the distribution between the two space groups was probably statistical, as was the distribution of the two conformational enantiomorphs. Since compounds (I) and (III)–(VII) all crystallize in centrosymmetric space groups as racemic mixtures of conformational enantiomorphs, this conclusion concerning the space groups seems appropriate for compound (II) also.

All of the compounds studied here crystallize with $Z' = 1$, with the exception of 3,4,5-trimethoxybenzyl derivative (VII), which crystallizes in $P\overline{1}$ with $Z' = 2$. The various ADDSYM routines in *PLATON* (Spek, 2009) all showed that no additional symmetry was present. However, the two molecules in the selected asymmetric unit, which were chosen to have the same orientation of the 1-phenyl group relative to the pyrazole ring, are approximately related by a noncrystallographic translation of $(\frac{1}{2}, 0, \frac{1}{2})$. As discussed below, the conformations adopted by the *tert*-butyl groups in the two independent molecules definitively rule out the possibility of any further crystallographic symmetry.

With the exception of the polyatomic substituent groups in the benzyl unit, the overall molecular conformations of compounds (I)–(VII) can be defined in terms of just five torsion angles (Table 1). The orientation of the unsubstituted phenyl ring, as defined by the torsion angles N*x*2—N*x*1—C*x*11—C*x*12 [where *x* is nul for compounds (I)–(VI), and *x* = 1 or 2 for compound (VII)], and the location of the benzyl methylene unit, as defined by the torsion angles N*x*1—C*x*5—N*x*51—C*x*57, show only modest variation across the whole series. In all compounds except (IV) and (VII), there is an intramolecular C—H···N contact from atom C12 (Table 2): however, the orientation of the unsubstituted phenyl ring does not seem to be significantly influenced by the presence or absence of this contact. The other torsion angles show some interesting variations; in particular, both the position of the substituted aryl ring, as defined by C*x*5—N*x*51—C*x*57—C*x*51, and the orientation of this ring, as defined by N*x*51—C*x*57—C*x*51—C*x*52, differ markedly in compounds (IV) and (VI) from those in the remainder. In a similar manner, the orientation of the *tert*-butyl groups in compounds (I), (III) and (V) is such that one methyl group is fairly close to the plane of the pyrazole ring, although by no means coincident with it, while in the other compounds, the projection of one of the C—C bonds in this group is almost normal to the plane of the pyrazole ring. The two independent molecules in compound (VII) have almost identical conformations, apart from their *tert*-butyl groups, which are rotated in the opposite senses relative to the pyrazole ring. The *tert*-butyl groups in compounds (I)–(VII) are directly bonded to a planar ring, so that the rotational barriers about the exocyclic C—C bonds will be a close approximation to an idealized sixfold barrier, long known to be extremely low, *ca* a few tens of J mol^{-1} (Tannenbaum *et al.*, 1956; Naylor & Wilson, 1957); accordingly, the *tert*-butyl groups may be acting here essentially as space fillers, adopting whatever orientations are best adapted to the spaces available between the molecules, once the direction-specific intermolecular forces have been accommodated.

A variety of direction-specific intermolecular interactions are present in the structures of compounds (I)–(VII), in particular *X*—H···π(arene) and *X*—H···π(pyrazole) hydrogen bonds, both for *X* = C and N, as well as N—H···O hydrogen bonds in both (VI) and (VII) (Table 2). These interactions link the molecules into supramolecular aggregations ranging from finite (zero-dimensional) dimer units in each of (II) and (VII), *via* simple chains in (I) and (VI), and chains of rings π-stacked into sheets in (IV), to hydrogen-bonded sheets in each of (III) and (V).

Compounds (I), (III) and (V) are isomorphous, and in each compound molecules related by a 2_1 screw axis along $(\frac{3}{4}, y, \frac{1}{4})$ are linked into chains by an N—H···π(pyrazole) hydrogen bond. While the molecules of the three compounds are

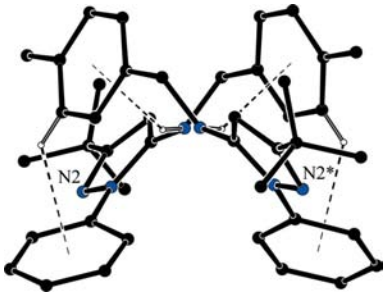

Figure 4
Part of the crystal structure of compound (II), showing the formation of a dimeric aggregate of molecules related by a twofold rotation axis. For the sake of clarity, the unit-cell outline and H atoms bonded to C atoms not involved in the motifs shown have been omitted. The atom marked with an asterisk (*) is at the symmetry position (y, x, $1-z$).

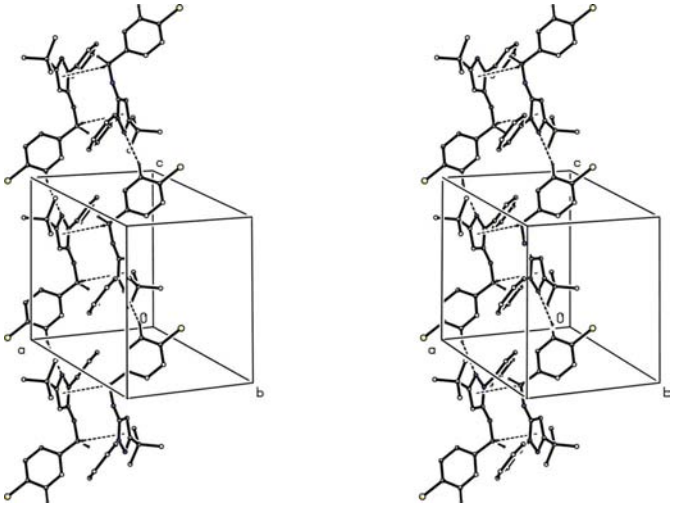

Figure 5
A stereoview of part of the crystal structure of compound (IV), showing the formation of a chain of centrosymmetric rings running parallel to the [001] direction and containing C—H···N and C—H···π(arene) hydrogen bonds. For the sake of clarity, H atoms bonded to C or N atoms not involved in the motifs shown have been omitted.

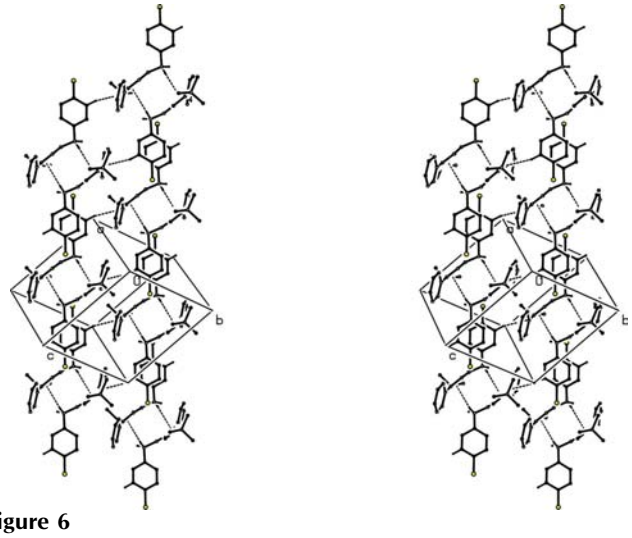

Figure 6
A stereoview of part of the crystal structure of compound (IV), showing the aromatic π–π stacking interaction which links chains of rings into sheets parallel to (100). For the sake of clarity, H atoms bonded to C or N atoms not involved in the motifs shown have been omitted.

arranged almost identically in their unit cells, the weak intermolecular forces show some differences from one compound to another. Thus, in (III), a C—H···π(arene) interaction involving the C11–C16 ring links the initial chains into sheets parallel to (001) (Fig. 2), while in (V), the (001) sheet is generated by a C—H···π(arene) hydrogen bond involving the C51–C56 ring (Fig. 3). In each of (III) and (V), the reference sheet lies in the domain $0 < z < \frac{1}{2}$, with a further sheet, which is related to the first by inversion, lying in the domain $\frac{1}{2} < z < 1.0$; however, there are no direction-specific interactions between adjacent sheets.

Minor changes in the unit-cell dimensions from one compound to another in this group are apparently sufficient to bring different weak interactions into play; this does not, however, detract from the fact that the overall molecular arrangements within this group are effectively the same. Thus, while this group can be regarded as isostructural in terms of the overall molecular arrangement, they are not strictly isostructural in terms of the direction-specific intermolecular interactions which appear to be operative. We have recently reported (Acosta *et al.*, 2009) another series of compounds which similarly are isomorphous in terms of only small changes in their unit-cell dimensions, as well as in their atomic coordinates, but where these changes in cell dimension are sufficient to influence which of the intermolecular interactions are structurally significant, so that those compounds are not strictly isostructural.

In compound (II), the combination of one N—H···π(arene) hydrogen bond and one C—H···π(arene) hydrogen bond, each involving a different arene ring, links pairs of molecules related by the twofold rotation axis along $x = y$ at $z = \frac{1}{2}$ into a finite dimeric unit (Fig. 4). There are four of these dimeric units in each unit cell, each lying across a different rotation axis, but there are no direction-specific interactions between the dimers; in particular, aromatic π–π stacking interactions are absent. The supramolecular aggregation in compound (II) is thus significantly different from that in the isomorphous 4-methoxybenzyl analogue (VIII) (Abonía *et al.*, 2007), where a single C—H···N hydrogen bond links molecules related by translation into simple $C(9)$ chains: N—H···π and C—H···π interactions are, however, absent from the structure of (VIII).

The only possible acceptor within hydrogen-bonding range of the N—H bond in compound (IV) is the Cl atom of the molecule at $(1-x, 1-y, 2-z)$. However, it has been concluded that such contacts involving covalently bound Cl are probably no more than van der Waals contacts, and that geometrically they are certainly at the outer limit of what could conceivably be described as a hydrogen bond (Aakeröy *et al.*, 1999; Brammer *et al.*, 2001; Thallapally & Nangia, 2001). Accordingly, we have discounted this contact as it seems unlikely to be of structural significance.

A C—H···N hydrogen bond links molecules of (IV) which are related by translation into a $C(9)$ (Bernstein *et al.*, 1995) chain running parallel to the [001] direction (Fig. 5). Antiparallel pairs of such chains, related by inversion, are then linked into a chain of edge-fused rings along $(\frac{1}{2}, 0, z)$ (Fig. 5).

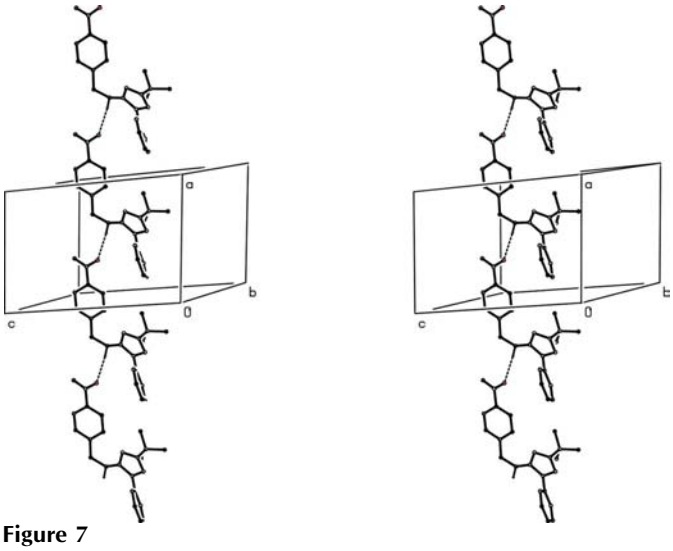

Figure 7
A stereoview of part of the crystal structure of compound (VI), showing the formation of a hydrogen-bonded $C(9)$ chain running parallel to the [100] direction and containing N—H···O hydrogen bonds. For the sake of clarity, H atoms bonded to C atoms have all been omitted.

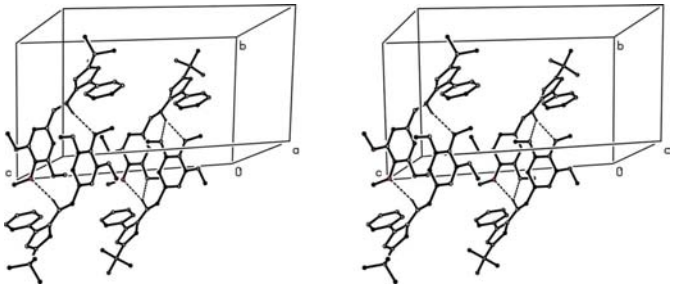

Figure 8
A stereoview of part of the crystal structure of compound (VII), showing the location of the two independent hydrogen-bonded dimers within the unit cell. For the sake of clarity, H atoms bonded to C atoms have all been omitted.

The 4-chlorophenyl rings of the molecules at (x, y, z) and ($1-x$, $1-y$, $2-z$) are strictly parallel within an interplanar spacing of 3.474 (2) Å; the ring-centroid separation is 3.773 (2) Å, corresponding to a near-ideal ring-centroid offset of 1.472 (2) Å (Fig. 6). The two molecules involved in this π-stacking interaction form parts of the hydrogen-bonded chains along ($\frac{1}{2}$, 0, z) and ($\frac{1}{2}$, 1, z), so that this interaction links hydrogen-bonded chains of rings into a sheet parallel to (100). By contrast, the supramolecular aggregation in compound (VI) depends upon just a single N—H···O hydrogen bond, which links molecules related by translation into a simple chain running parallel to the [100] direction (Fig. 7).

The supramolecular aggregation in 3,4,5-trimethoxybenzyl derivative (VII) depends solely upon N—H···O hydrogen bonds, which generate two independent centrosymmetric dimers. The dimer formed by the type 1 molecules contains an asymmetric three-centre N—H···$(O)_2$ interaction, which generates a centrosymmetric $R_2^2(14)$ ring flanked by two symmetry-related $R_1^2(5)$ rings, while the dimer formed by the type 2 molecules contains a single $R_2^2(16)$ ring (Fig. 8). These two dimers are centred respectively across ($\frac{1}{2}$, 0, $\frac{1}{2}$) and (1, 0, 1), illustrating again the pseudo-translational relationship between the two independent molecules in this structure. As with the conformations of the *tert*-butyl groups discussed above, so too the different N—H···O interactions within the two independent dimers rules out the possibility of any additional crystallographic symmetry.

Experimental

To a solution of the appropriate (*E*)-5-arylideneamino-3-*tert*-butyl-1-phenyl-1*H*-pyrazole (100 mg) in methanol (3–4 ml), solid sodium borohydride (2.5 mmol) was added portionwise with stirring over a period of 5 min, and after 1 h at ambient temperature the volume of the reaction mixture was reduced under reduced pressure to 1 ml, followed by the addition of water (5 ml). The aqueous solution was extracted with ethyl acetate (2 × 5 ml) and the combined organic extracts were dried over anhydrous sodium sulfate; after removal of the solvent the resulting products were crystallized from ethanol, except for (I), which was crystallized from hexane. Compound (I): colourless, 91% yield, m.p. 351 K; MS (70 eV) *m*/*z* (%): 305 (100) [M^+], 290 (59) [$M-15$], 263 (69) [$M-42$], 91 (34), 77 (13) [Ph]; analysis found: C 78.5, H 7.8, N 13.7%; $C_{20}H_{23}N_3$ requires C 78.7, H 7.6, N 13.8%. (II): colourless, 85% yield, m.p. 372–373 K; MS (70 eV) *m*/*z* (%): 319 (76) [M^+], 304 (18) [$M-15$], 277 (30) [$M-42$], 105 (100) [C_8H_9], 77 (8) [Ph]; analysis found: C 78.7, H 8.1, N 12.9%; $C_{21}H_{25}N_3$ requires C 79.0, H 7.9, N 13.2%. (III): yellow, 77% yield, m.p. 370–371 K; MS 70 (eV) *m*/*z* (%): 373 (100) [M^+], 358 (84) [$M-15$], 331 (98) [$M-42$], 214 (19), 159 (38) [$C_8H_6F_3$], 77 (10); analysis found: C 67.4, H 5.9, N 11.2%; $C_{21}H_{22}F_3N_3$ requires C 67.6, H 5.9, N 11.3%. (IV) colourless, 89% yield, m.p. 386–388 K; MS (70 eV) *m*/*z* (%): 341/339 (28/84) [M^+], 326/324 (13/35) [$M-15$], 299/297 (20/58) [$M-42$], 214 (37), 158 (38), 127/125 (29/100) [C_7H_6Cl], 77 (63) [Ph]; analysis found: C 70.5, H 6.7, N 12.3%; $C_{20}H_{22}ClN_3$ requires C 70.7, H 6.5, N 12.4%. (V): yellow, 83% yield, m.p. 365–366 K; MS (70 eV) *m*/*z* (%): 385/383 (96/100) [M^+], 370/368 (45/44) [$M-15$], 343/341 (70/73) [$M-42$], 214 (70), 171/169 (72/67) [C_7H_6Br]; analysis found: C 62.3, H 5.9, N 11.0%; $C_{20}H_{22}BrN_3$ requires C 62.5, H 5.8, N 10.9%. (VI): yellow, 84% yield, m.p. 375–377 K; MS (70 eV) *m*/*z* (%): 350 (95) [M^+], 335 (85) [$M-15$], 308 (100) [$M-42$], 214 (15), 158 (15); analysis found: C 68.2, H 6.3, N 16.0%; $C_{20}H_{22}N_4O_2$ requires C 68.6, H 6.3, N 16.0%. (VII): colourless, 83% yield, m.p. 392–394 K; MS 70 (eV) *m*/*z* (%): 395 (8) [M^+], 181 (100) [$C_{10}H_{13}O_3$]; analysis found: C 69.9, H 7.3, N 10.7%; $C_{23}H_{29}N_3O_3$ requires C 69.9, H 7.4, N 10.6%.

Compound (I)

Crystal data

$C_{20}H_{23}N_3$
M_r = 305.41
Monoclinic, $C2/c$
a = 20.038 (4) Å
b = 7.3732 (12) Å
c = 23.444 (3) Å
β = 106.007 (13)°
V = 3329.4 (10) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.07 mm^{-1}
T = 120 (2) K
0.31 × 0.26 × 0.21 mm

Data collection

Bruker–Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.967, T_{max} = 0.985
30597 measured reflections
3813 independent reflections
2464 reflections with $I > 2\sigma(I)$
R_{int} = 0.075

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.052$
$wR(F^2) = 0.129$
$S = 1.06$
3813 reflections
211 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.21$ e Å^{-3}
$\Delta\rho_{min} = -0.36$ e Å^{-3}

Compound (II)

Crystal data

$C_{21}H_{25}N_3$
$M_r = 319.44$
Tetragonal, $P4_32_12$
$a = 10.7749$ (13) Å
$c = 30.868$ (3) Å
$V = 3583.6$ (7) Å^3
$Z = 8$
Mo $K\alpha$ radiation
$\mu = 0.07$ mm^{-1}
$T = 120$ (2) K
0.37 × 0.27 × 0.24 mm

Data collection

Bruker–Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{min} = 0.949$, $T_{max} = 0.983$
22266 measured reflections
2412 independent reflections
1598 reflections with $I > 2\sigma(I)$
$R_{int} = 0.075$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.052$
$wR(F^2) = 0.119$
$S = 1.12$
2412 reflections
221 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.20$ e Å^{-3}
$\Delta\rho_{min} = -0.30$ e Å^{-3}

Compound (III)

Crystal data

$C_{21}H_{22}F_3N_3$
$M_r = 373.42$
Monoclinic, $C2/c$
$a = 20.824$ (3) Å
$b = 7.3429$ (11) Å
$c = 24.225$ (4) Å
$\beta = 97.275$ (11)°
$V = 3674.3$ (10) Å^3
$Z = 8$
Mo $K\alpha$ radiation
$\mu = 0.10$ mm^{-1}
$T = 120$ (2) K
0.36 × 0.09 × 0.04 mm

Data collection

Bruker–Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{min} = 0.946$, $T_{max} = 0.996$
21869 measured reflections
4218 independent reflections
2014 reflections with $I > 2\sigma(I)$
$R_{int} = 0.151$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.083$
$wR(F^2) = 0.196$
$S = 1.08$
4218 reflections
247 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.29$ e Å^{-3}
$\Delta\rho_{min} = -0.47$ e Å^{-3}

Compound (IV)

Crystal data

$C_{20}H_{22}ClN_3$
$M_r = 339.86$
Triclinic, $P\overline{1}$
$a = 9.385$ (3) Å
$b = 9.7584$ (19) Å
$c = 10.6014$ (17) Å
$\alpha = 112.459$ (13)°
$\beta = 95.721$ (18)°
$\gamma = 99.735$ (19)°
$V = 869.8$ (4) Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 0.23$ mm^{-1}
$T = 120$ (2) K
0.25 × 0.10 × 0.05 mm

Data collection

Bruker–Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{min} = 0.958$, $T_{max} = 0.989$
25011 measured reflections
3991 independent reflections
2811 reflections with $I > 2\sigma(I)$
$R_{int} = 0.059$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.113$
$S = 1.08$
3991 reflections
220 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.23$ e Å^{-3}
$\Delta\rho_{min} = -0.28$ e Å^{-3}

Compound (V)

Crystal data

$C_{20}H_{22}BrN_3$
$M_r = 384.32$
Monoclinic, $C2/c$
$a = 20.1981$ (6) Å
$b = 7.3960$ (9) Å
$c = 24.171$ (4) Å
$\beta = 98.634$ (7)°
$V = 3569.9$ (7) Å^3
$Z = 8$
Mo $K\alpha$ radiation
$\mu = 2.31$ mm^{-1}
$T = 120$ (2) K
0.44 × 0.13 × 0.11 mm

Data collection

Bruker–Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{min} = 0.499$, $T_{max} = 0.785$
28981 measured reflections
4071 independent reflections
2871 reflections with $I > 2\sigma(I)$
$R_{int} = 0.051$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.137$
$S = 1.10$
4071 reflections
220 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.41$ e Å^{-3}
$\Delta\rho_{min} = -0.63$ e Å^{-3}

Compound (VI)

Crystal data

$C_{20}H_{22}N_4O_2$
$M_r = 350.42$
Monoclinic, $P2_1/n$
$a = 9.6594$ (11) Å
$b = 12.3991$ (11) Å
$c = 15.4338$ (15) Å
$\beta = 97.744$ (8)°
$V = 1831.6$ (3) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.09$ mm^{-1}
$T = 120$ (2) K
0.29 × 0.27 × 0.24 mm

Data collection

Bruker–Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{min} = 0.959$, $T_{max} = 0.980$
29100 measured reflections
4192 independent reflections
2657 reflections with $I > 2\sigma(I)$
$R_{int} = 0.078$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.062$
$wR(F^2) = 0.169$
$S = 1.06$
4192 reflections
239 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.66$ e Å^{-3}
$\Delta\rho_{min} = -0.33$ e Å^{-3}

Compound (VII)

Crystal data

$C_{23}H_{29}N_3O_3$
M_r = 395.49
Triclinic, $P\overline{1}$
a = 10.1533 (11) Å
b = 11.1645 (10) Å
c = 20.927 (2) Å
α = 84.820 (8)°
β = 82.988 (8)°
γ = 63.153 (7)°
V = 2099.0 (4) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.08 mm^{-1}
T = 120 (2) K
0.48 × 0.35 × 0.25 mm

Data collection

Bruker–Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.961, T_{max} = 0.986
50489 measured reflections
9621 independent reflections
5050 reflections with $I > 2\sigma(I)$
R_{int} = 0.094

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.064
$wR(F^2)$ = 0.174
S = 1.02
9621 reflections
535 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.48 e Å^{-3}
$\Delta\rho_{min}$ = −0.35 e Å^{-3}

Table 1
Selected torsion angles (°) for compounds (I)–(VII).

	θ_1	θ_2	θ_3	θ_4	θ_5
(I)	144.31 (16)	173.57 (18)	−171.61 (16)	−162.80 (15)	−148.74 (17)
(II)	151.7 (3)	−26.5 (4)	−175.7 (3)	−177.0 (3)	−130.1 (3)
(III)	149.2 (3)	178.4 (3)	−170.8 (3)	−169.5 (3)	−140.2 (3)
(IV)	139.50 (17)	−29.2 (3)	−163.66 (16)	−89.3 (2)	−0.6 (2)
(V)	147.0 (3)	176.9 (3)	−171.9 (3)	−166.3 (3)	−142.8 (3)
(VI)	137.9 (2)	21.8 (4)	−159.4 (2)	−86.6 (3)	1.1 (3)
(VII)	Molecule 1				
	152.5 (2)	156.6 (3)	−173.7 (2)	169.7 (2)	−103.8 (3)
(VII)	Molecule 2				
	154.8 (2)	−149.7 (3)	−173.6 (2)	168.0 (2)	−103.3 (3)

Notes: θ_1 represents the angle N*x*2—N*x*1—C*x*11—C*x*12, θ_2 represents the angle C*x*4—C*x*3—C*x*31—C*x*32, θ_3 represents the angle N*x*1—C*x*5—N*x*51—C*x*57, θ_4 represents the angle C*x*5—N*x*51—C*x*57—C*x*51 and θ_5 represents the angle N*x*51—C*x*57—C*x*51—C*x*52. For compounds (I)–(VI), *x* is nul; for compound (VII), where Z' = 2, *x* = 1 or 2.

All H atoms were located in difference maps and then treated as riding atoms with distances C—H = 0.95 (aromatic and pyrazole), 0.98 (CH_3) or 0.99 Å (CH_2) and N—H = 0.88 Å, with U_{iso}(H) = kU_{eq}(carrier), where k = 1.5 for the methyl groups, which were permitted to rotate but not to tilt, and k = 1.2 for all other H atoms. For the compounds which crystallize in centrosymmetric space groups, the reference molecules were all selected to have the same orientation of the 1-phenyl group, as defined by the sign of the torsion angle N2—N1—C11—C12. In the absence of significant resonant scattering, it was not possible, for compound (II), to distinguish between the possible enantiomeric space groups $P4_12_12$ and $P4_32_12$; for consistency of configuration, $P4_32_12$ was selected and the Friedel-equivalent reflections were merged prior to the final refinements. The final R index for compound (III) was rather high, despite the residuals in the final difference map being lower in this compound than for several others in this series; the crystal quality for (III) was consistently poor, as indicated by the high merging index of 0.158. In compound (VI), the largest maxima in the final difference maps, with heights 0.65, 0.62 and 0.40 e Å^{-3} were located, respectively, 1.37 Å from C33, 1.07 Å from C34 and 1.12 Å from C32, consistent with some librational motion of this group about the C3—C31 bond.

Table 2
Hydrogen bonds and short intra- and intermolecular contacts (Å, °) for compounds (I)–(VII).

*Cg*1 represents the centroid of the N1/N2/C3–C5 ring, *Cg*2 represents the centroid of the C11–C16 ring and *Cg*3 represents the centroid of the C51–C56 ring.

Compound	D—H···A	D—H	H···A	D···A	D—H···A
(I)	C12—H12···N51	0.95	2.55	3.011 (2)	110
	N51—H51···*Cg*1^{i}	0.88	2.82	3.523 (2)	138
(II)	C12—H12···N51	0.95	2.54	3.009 (4)	111
	N51—H51···*Cg*3^{ii}	0.88	2.95	3.718 (2)	147
	C55—H55···*Cg*2^{ii}	0.95	2.70	3.444 (3)	136
(III)	C12—H12···N51	0.95	2.51	2.995 (5)	112
	N51—H51···*Cg*1^{i}	0.88	2.80	3.470 (3)	134
	C53—H53···*Cg*2^{iii}	0.95	2.91	3.809 (4)	157
(IV)	N51—H51···Cl54^{iv}	0.88	2.83	3.486 (2)	133
	C55—H55···N2^{v}	0.95	2.49	3.410 (3)	163
	C57—H572···*Cg*1^{vi}	0.99	2.88	3.557 (2)	126
(V)	C12—H12···N51	0.95	2.51	2.980 (4)	111
	N51—H51···*Cg*1^{i}	0.88	2.72	3.504 (3)	148
	C15—H15···*Cg*3^{vii}	0.95	2.95	3.687 (4)	135
(VI)	C12—H12···N51	0.95	2.62	3.026 (3)	106
	N51—H51···O41^{viii}	0.88	2.19	3.025 (3)	158
(VII)	C112—H112···N151	0.95	2.48	3.004 (4)	115
	C212—H212···N251	0.95	2.46	3.002 (4)	116
	N151—H151···O13^{vi}	0.88	2.57	3.316 (3)	144
	N151—H151···O14^{vi}	0.88	2.30	3.095 (3)	150
	N251—H251···O24^{ix}	0.88	2.38	3.150 (3)	147

Symmetry codes: (i) $\frac{3}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; (ii) $y, x, 1-z$; (iii) $-\frac{1}{2}+x, \frac{1}{2}+y, z$; (iv) $1-x, 1-y, 2-z$; (v) $x, y, 1+z$; (vi) $1-x, -y, 1-z$; (vii) $\frac{1}{2}+y, \frac{1}{2}+y, z$; (viii) $-1+x, y, z$; (ix) $2-x, -y, 2-z$.

For all compounds, 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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