

Two isomeric pairs of dihydrobenzo-pyrazoloquinazolines: centrosymmetric dimers, chains and sheets built from C—H···N and C—H··· π (arene) hydrogen bonds and π – π stacking interactions

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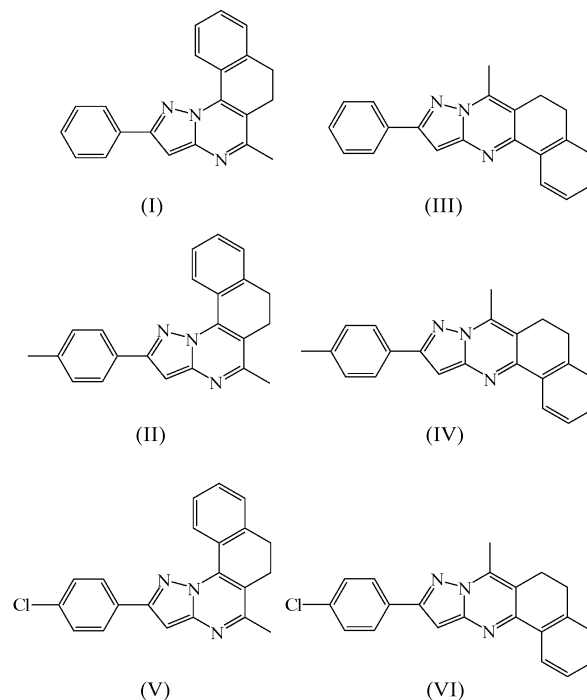
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Molecules of 5-methyl-2-phenyl-6,7-dihydrobenzo[*h*]pyrazolo[1,5-*a*]quinazoline, C₂₁H₁₇N₃, (I), are linked into chains by a combination of a C—H··· π (arene) hydrogen bond and a π – π stacking interaction; in the closely related 5-methyl-2-(4-methylphenyl)-6,7-dihydrobenzo[*h*]pyrazolo[1,5-*a*]quinazoline, C₂₂H₁₉N₃, (II), there are no hydrogen bonds and the molecules are linked into centrosymmetric dimers by a π – π stacking interaction. 7-Methyl-10-phenyl-5,6-dihydrobenzo[*h*]pyrazolo[5,1-*b*]quinazoline, C₂₁H₁₇N₃, (III), is isomeric with (I), and the molecules of (III) are linked into sheets by a combination of C—H···N and C—H··· π (arene) hydrogen bonds. 7-Methyl-10-(4-methylphenyl)-5,6-dihydrobenzo[*h*]pyrazolo[5,1-*b*]quinazoline, C₂₂H₁₉N₃, (IV), is isomeric with (II), and molecules of (IV) are linked into centrosymmetric dimers by a C—H··· π (arene) hydrogen bond, augmented by π – π stacking interactions.

Comment

As part of a wider study of fused quinazoline systems, which are important pharmacophores (Fry *et al.*, 1994), we have recently reported the structures of two pyrazoloquinazolines (Low *et al.*, 2004). Similar systems have been shown to be potent amino-acid antagonists (McQuaid *et al.*, 1992), as well as being immunosuppressants and anti-inflammatory, anti-asthmatic and anti-allergenic agents (Casey *et al.*, 1980). We describe here two isomeric pairs of dihydrobenzopyrazoloquinazolines; the benzo[*h*]pyrazolo[1,5-*a*]quinazolines (I) and (II) (see scheme) are isomeric with the

benzo[*h*]pyrazolo[5,1-*b*]quinazolines (III) and (IV). Each pair of isomers was obtained from the corresponding 5-amino-pyrazole and 2-acetyltetralone using solvent-free cyclocondensation reactions under microwave irradiation.



The corresponding bond lengths within the heterobicyclic fragments in (I)–(IV) [Figs. 1–4, where the atom-numbering in (III) and (IV) is necessarily different from that in (I) and (II)] are very similar (Table 4), but the patterns of these bond distances show some interesting properties. In each of (I)–(IV), the N1–C2 bond, which is formally a double bond, is not significantly shorter than either the C3A–N4 bonds, or the C11B–N11C bonds in (I) and (II) or the C11–N11A bond in (IV), all of which are formally single bonds; at the same time, the cross-ring bonds are by far the longest C–N bonds in either molecule. These observations, together with the clear bond fixation in the pyrimidine ring, suggest that the ten π electrons of the pyrazolopyrimidine units are not fully delocalized around the periphery, but instead adopt a more characteristic arrangement reminiscent of that in naphthalene.

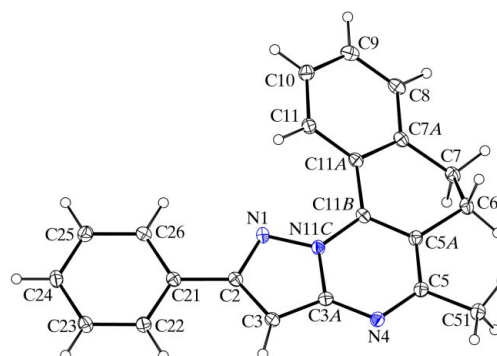


Figure 1
The molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

In each compound, the non-aromatic carbocyclic ring, containing atoms C6 and C7 in (I) and (II), and C9 and C10 in (III) and (IV), adopts a screw-boat conformation. The total puckering amplitudes Q (Cremer & Pople, 1975) are all very similar, at 0.476 (2), 0.467 (3), 0.426 (2) and 0.476 (2) Å for (I)–(IV), respectively, and the ring-puckering parameters in (I) and (II) are, for the atom sequence C5A–C6–C7–C11A–C11B, $\theta = 68.9$ (2)° and $\varphi = 93.6$ (2)° for (I), and $\theta = 68.1$ (4)° and $\varphi = 99.4$ (4)° for (II); these parameters are $\theta = 67.8$ (2)° and $\varphi = 202.5$ (2)° for (III), and $\theta = 65.8$ (2)° and $\varphi = 211.5$ (2)° for (IV), for the atom-sequence C4A–C4B–C8A–C9–C10–C10A. The ideal parameters for this conformation are $\theta = 67.5^\circ$ and $\varphi = (60n + 30)^\circ$, so that $n = 1$ in

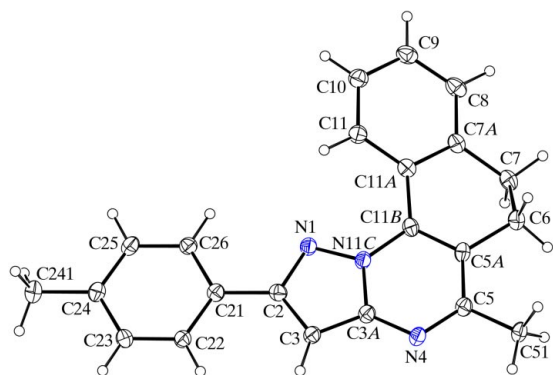


Figure 2
The molecule of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

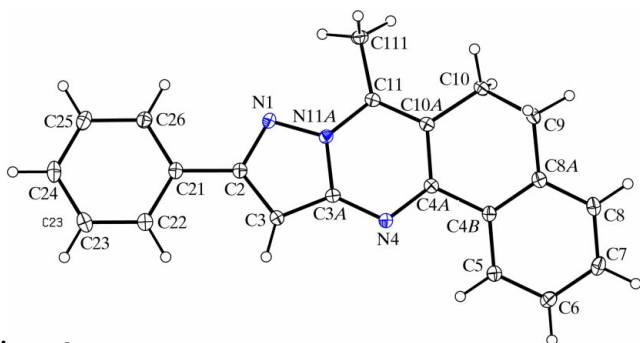


Figure 3
The molecule of (III), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

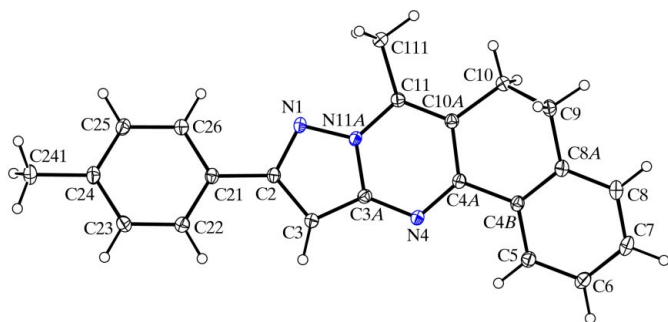


Figure 4
The molecule of (IV), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

each of (I) and (II), and $n = 3$ in each of (III) and (IV) (Evans & Boeyens, 1989). Associated with these ring puckerings, the pyrimidine rings are not coplanar with the adjacent aryl rings, with dihedral angles between these rings of 24.83 (7)° in (I), 22.4 (2)° in (II), 18.75 (5)° in (III) and 18.45 (5)° in (IV). By contrast, the pendent aryl ring C21–C26 is nearly coplanar with the pyrazole ring in each of (I)–(III), where the relevant dihedral angles are 2.21 (8), 0.6 (2) and 1.11 (6)°, respectively, although this angle is 14.71 (6)° in (IV).

Despite the close similarity between compounds (I)–(IV) (Figs. 1–4) in terms both of their overall constitutions and of their detailed molecular geometries, there are some significant variations in the nature of the supramolecular aggregation. In (I), the molecules are linked into chains by a single C–H... π (arene) hydrogen bond (Table 1), and the chain formation is reinforced by a π – π stacking interaction. Atom C6 in the molecule at (x, y, z) acts as a hydrogen-bond donor, *via* H6A, to the pyrimidine ring of the molecule at $(\frac{1}{2} + x, \frac{1}{2} - y, 1 - z)$, so forming a chain running parallel to the [100] direction and generated by the 2_1 screw axis along $(x, \frac{1}{4}, \frac{1}{2})$ (Fig. 5). Within this chain, the pyrimidine ring in the molecule at (x, y, z) and the C21–C26 aryl ring of the molecule at $(1 + x, y, z)$ are almost parallel, with a dihedral angle of only 3.3 (2)° between them; the interplanar spacing is *ca* 3.46 Å, and the ring-centroid separation is 3.630 (2) Å, corresponding to a ring offset of *ca* 1.10 Å. Four chains of this type pass through each unit cell, but there are no direction-specific interactions between adjacent chains; in particular, C–H...N hydrogen bonds are absent.

By contrast, in the very closely related (II), there are no hydrogen bonds at all, and the molecules are simply linked into centrosymmetric dimers by a single π – π stacking interaction. The aryl rings (C7A/C8/C9/C10/C11/C11A) (Fig. 2) in the molecules at (x, y, z) and $(1 - x, 1 - y, -z)$ are strictly parallel, with an interplanar spacing of 3.434 (2) Å; the ring-centroid separation is 3.635 (2) Å, corresponding to a ring offset of 1.190 (2) Å (Fig. 6).

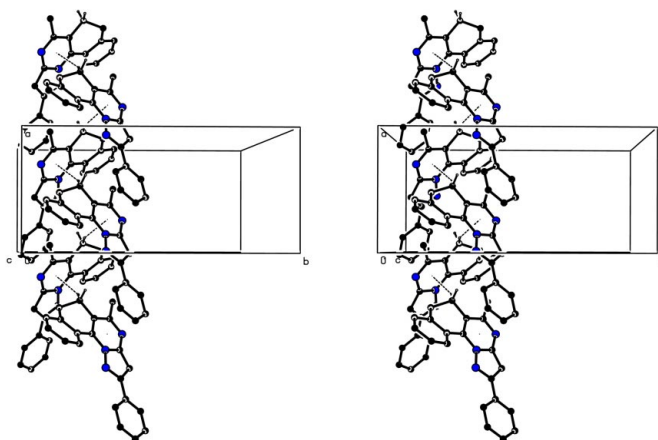


Figure 5
Stereoview of part of the crystal structure of (I), showing the formation of a [100] chain built from C–H... π (arene) hydrogen bonds and π – π stacking interactions. For clarity, H atoms bonded to C atoms that are not involved in the motif shown have been omitted.

Compound (III) is an isomer of (I), but the supramolecular aggregation is entirely different. The molecules are linked by a combination of C—H···N and C—H··· π (arene) hydrogen bonds (Table 2) into sheets of some complexity, whose formation is, however, readily analysed in terms of two one-dimensional substructures. One substructure, involving two

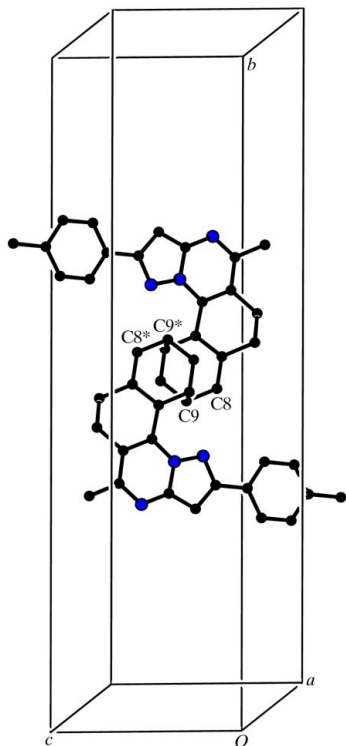


Figure 6
Part of the crystal structure of (II), showing the formation of a centrosymmetric π -stacked dimer. For clarity, all H atoms have been omitted. Atoms marked with an asterisk (*) are at the symmetry position $(1 - x, 1 - y, 1 - z)$.

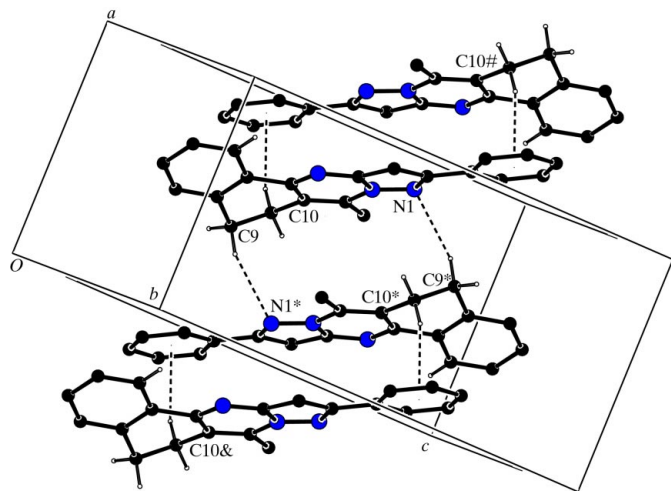


Figure 7
Part of the crystal structure of (III), showing the formation of a [100] chain of edge-fused rings. For clarity, H atoms not involved in hydrogen bonding have been omitted. Atoms marked with an asterisk (*), a hash (#) or an ampersand (&) are at the symmetry positions $(1 - x, 1 - y, 1 - z)$, $(2 - x, 1 - y, 1 - z)$ and $(-1 + x, y, z)$, respectively.

types of hydrogen bond, takes the form of a chain of edge-fused rings. Atom C9 in the molecule at (x, y, z) acts as a hydrogen-bond donor, *via* H9B, to atom N1 in the molecule at $(1 - x, 1 - y, 1 - z)$, so generating a centrosymmetric $R_2^2(14)$ ring centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ (Fig. 7). In addition, atom C10 in the molecule at (x, y, z) , part of the $R_2^2(14)$ dimer at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, acts as a hydrogen-bond donor, *via* H10B, to the C21–C26 aryl ring of the molecule at $(2 - x, 1 - y, 1 - z)$, which itself forms part of the $R_2^2(14)$ dimer centred at $(1, \frac{1}{2}, \frac{1}{2})$. Propagation by inversion of these two hydrogen bonds then generates a chain of edge-fused rings along $(x, \frac{1}{2}, \frac{1}{2})$ (Fig. 7). In the second one-dimensional substructure, atom C5 in the molecule at (x, y, z) acts as a hydrogen-bond donor to the C21–C26 aryl ring in the molecule at $(x, \frac{3}{2} - y, -\frac{1}{2} + z)$, so forming a chain running parallel to the [001] direction and generated by the *c*-glide plane at $y = 0.75$ (Fig. 8). The rings of type C21–C26 thus accept a C—H··· π (arene) hydrogen bond on each face. The combination of [100] and [001] chains then generates a complex sheet parallel to (010).

In (IV), which is an isomer of (II), the molecules are again linked into centrosymmetric dimers, but this time the dimer formation is dominated by a C—H··· π (arene) hydrogen bond (Table 3). Atom C10 in the molecule at (x, y, z) acts as a

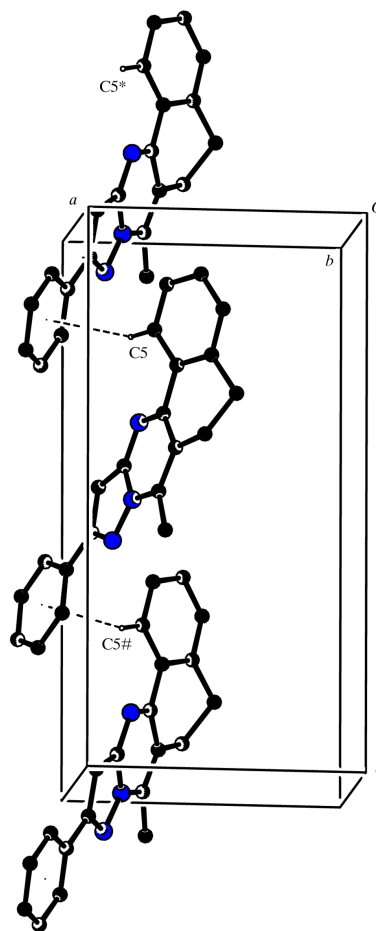


Figure 8
Part of the crystal structure of (III), showing the formation of a [001] chain. For clarity, H atoms that are not involved in the motif shown have been omitted. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(x, \frac{3}{2} - y, -\frac{1}{2} + z)$ and $(x, \frac{3}{2} - y, \frac{1}{2} + z)$, respectively.

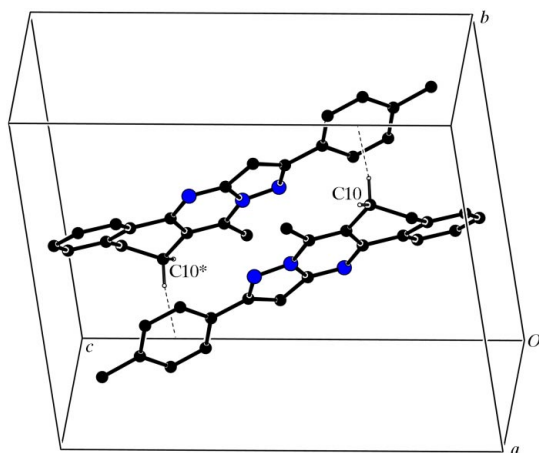


Figure 9

Part of the crystal structure of (IV), showing the formation of a centrosymmetric hydrogen-bonded dimer. For clarity, H atoms bonded to the C atoms that are not involved in the motif shown have been omitted. Atoms marked with an asterisk (*) are at the symmetry position $(1 - x, 1 - y, 1 - z)$.

hydrogen-bond donor, *via* H10B, to the C21–C26 aryl ring of the molecule at $(1 - x, 1 - y, 1 - z)$, so generating a dimer centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ (Fig. 9). In addition, there are a number of π – π stacking interactions, which assist in the stabilization of this dimer. The two pyrazole rings within the dimer are strictly parallel, with an interplanar spacing of 3.410 (2) Å; the ring-centroid separation is 3.704 (2) Å, corresponding to a ring offset of 1.446 (2) Å. The pyrazole ring in the molecule at (x, y, z) is nearly parallel to the pyrimidine ring of the molecule at $(1 - x, 1 - y, 1 - z)$; the dihedral angle between these planes is only 1.3 (2)°, and the interplanar spacing is *ca* 3.42 Å. The corresponding ring-centroid separation is 3.704 (2) Å, giving a ring offset here of *ca* 1.42 Å. Thus, the pyrazole ring in each component of the dimer overlaps equally the pyrazole and pyrimidine rings of the other component (Fig. 9).

The pairs of isomers (I)/(III) and (III)/(IV) may be briefly compared with the corresponding pair of isomers (V) and (VI) (see scheme) containing 4-chlorophenyl substituents (Low *et al.*, 2004). Neither of the 4-chlorophenyl compounds (V) or (VI) is isomorphous with the corresponding 4-methylphenyl compound. In (V), which crystallizes in the space group $P\bar{1}$ with $Z' = 2$, the molecules are linked into chains by π – π stacking interactions, whereas in (VI), which has $Z' = 1$ in $P\bar{1}$, the molecules are linked into isolated centrosymmetric dimers by means of paired C–H... π (arene) hydrogen bonds.

Experimental

For the synthesis of the isomeric pair of compounds (I) and (III), equimolar amounts of 5-amino-3-phenyl-1H-pyrazole (2.6 mmol) and 2-acetyltetralone (2.6 mmol) were placed in Pyrex glass open vessels and irradiated in a domestic microwave oven for 1.5 min (at 600 Watts). The reaction mixture was treated with ethanol. After the solvent had been removed, the products were separated by column chromatography on silica gel, using hexane/ethyl acetate (3:1 *v/v*) as eluant. The first fraction eluted contained compound (III) (yield 20%, m.p. 430–431 K, brown crystals). MS (EI 30 eV) *m/z* (%): 311 (100, M^+), 296 (3), 269 (8). The second fraction (main product)

contained (I) (yield 74%, m.p. 450–451 K, yellow crystals). MS (EI 30 eV) *m/z* (%): 311 (100, M^+), 296 (4), 269 (12). For the synthesis of the isomeric pair of compounds (II) and (IV), equimolar amounts of 5-amino-3-(4-methylphenyl)-1H-pyrazole (2.6 mmol) and 2-acetyltetralone (2.6 mmol) were placed in Pyrex glass open vessels and irradiated in a domestic microwave oven for 1.5 min (at 600 Watts). The reaction mixture was treated with ethanol. After the solvent had been removed, the products were separated by column chromatography on silica gel, using hexane/ethyl acetate (3:1 *v/v*) as eluant. The first fraction eluted contained compound (IV) (yield 17%, m.p. 453–454 K, brown crystals). MS (EI 30 eV) *m/z* (%): 325 (100, M^+), 310 (7), 283 (10). The second fraction (main product) contained (II) (yield 71%, m.p. 478–479 K, yellow crystals). MS (EI 30 eV) *m/z* (%): 325 (100, M^+), 310 (9), 283 (12). Crystals suitable for single-crystal X-ray diffraction were selected directly from the samples purified by chromatography as described.

Compound (I)

Crystal data

$C_{21}H_{17}N_3$
 $M_r = 311.38$
 Orthorhombic, $Pbca$
 $a = 7.6223$ (2) Å
 $b = 16.7937$ (7) Å
 $c = 24.4900$ (9) Å
 $V = 3134.88$ (19) Å³
 $Z = 8$
 $D_x = 1.319$ Mg m⁻³

Mo $K\alpha$ radiation
 Cell parameters from 3577 reflections
 $\theta = 3.1$ – 27.5°
 $\mu = 0.08$ mm⁻¹
 $T = 120$ (2) K
 Needle, yellow
 $0.90 \times 0.08 \times 0.06$ mm

Data collection

Nonius KappaCCD diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 2003)
 $T_{\min} = 0.923$, $T_{\max} = 0.995$
 19 065 measured reflections
 3577 independent reflections

2438 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.056$
 $\theta_{\max} = 27.5^\circ$
 $h = -9 \rightarrow 9$
 $k = -20 \rightarrow 21$
 $l = -30 \rightarrow 31$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.049$
 $wR(F^2) = 0.121$
 $S = 1.07$
 3577 reflections
 218 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0634P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.25$ e Å⁻³
 $\Delta\rho_{\min} = -0.30$ e Å⁻³

Compound (II)

Crystal data

$C_{22}H_{19}N_3$
 $M_r = 325.40$
 Monoclinic, $P2_1/n$
 $a = 7.2767$ (13) Å
 $b = 29.924$ (6) Å
 $c = 8.0463$ (12) Å
 $\beta = 112.590$ (6)°
 $V = 1617.6$ (5) Å³
 $Z = 4$

$D_x = 1.336$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 2701 reflections
 $\theta = 3.1$ – 25.0°
 $\mu = 0.08$ mm⁻¹
 $T = 120$ (2) K
 Block, yellow
 $0.18 \times 0.16 \times 0.12$ mm

Table 1

Hydrogen-bond geometry (Å, °) for (I).

Cg1 is the centroid of the pyrimidine ring.

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
C6–H6A...Cg1 ¹	0.99	2.75	3.644 (2)	150

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

Data collection

Nonius KappaCCD diffractometer
 φ and ω scans
 Absorption correction: multi-scan
 (SADABS; Sheldrick, 2003)
 $T_{\min} = 0.978$, $T_{\max} = 0.991$
 7247 measured reflections
 2701 independent reflections

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.078$
 $wR(F^2) = 0.248$
 $S = 1.05$
 2701 reflections
 228 parameters
 H-atom parameters constrained

2214 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.051$
 $\theta_{\text{max}} = 25.0^\circ$
 $h = -8 \rightarrow 8$
 $k = -35 \rightarrow 34$
 $l = -9 \rightarrow 9$
 $w = 1/[\sigma^2(F_o^2) + (0.1774P)^2 + 0.6771P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.007$
 $\Delta\rho_{\text{max}} = 0.36 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.42 \text{ e } \text{\AA}^{-3}$

Table 2

Hydrogen-bond geometry (\AA , $^\circ$) for (III).

Cg2 is the centroid of ring C21–C26.

D—H...A	D—H	H...A	D...A	D—H...A
C5—H5...Cg2 ⁱⁱ	0.95	2.67	3.5129 (12)	148
C9—H9B...N1 ⁱⁱⁱ	0.99	2.58	3.4003 (14)	140
C10—H10B...Cg2 ^{iv}	0.99	2.55	3.4676 (12)	154

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

Compound (III)

Crystal data

$C_{21}H_{17}N_3$
 $M_r = 311.38$
 Monoclinic, $P2_1/c$
 $a = 8.1092$ (1) \AA
 $b = 11.7265$ (2) \AA
 $c = 16.3486$ (3) \AA
 $\beta = 90.9010$ (12) $^\circ$
 $V = 1554.44$ (4) \AA^3
 $Z = 4$

$D_x = 1.331 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 3555 reflections
 $\theta = 3.1\text{--}27.5^\circ$
 $\mu = 0.08 \text{ mm}^{-1}$
 $T = 120$ (2) K
 Plate, brown
 $0.40 \times 0.10 \times 0.10 \text{ mm}$

Data collection

Nonius KappaCCD diffractometer
 φ and ω scans
 Absorption correction: multi-scan
 (SADABS; Sheldrick, 2003)
 $T_{\min} = 0.981$, $T_{\max} = 0.992$
 28 824 measured reflections
 3555 independent reflections

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.039$
 $wR(F^2) = 0.102$
 $S = 1.04$
 3555 reflections
 218 parameters
 H-atom parameters constrained

3093 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.031$
 $\theta_{\text{max}} = 27.5^\circ$
 $h = -10 \rightarrow 9$
 $k = -15 \rightarrow 15$
 $l = -21 \rightarrow 21$
 $w = 1/[\sigma^2(F_o^2) + (0.0488P)^2 + 0.5945P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.25 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.32 \text{ e } \text{\AA}^{-3}$

Table 3

Hydrogen-bond geometry (\AA , $^\circ$) for (IV).

Cg2 is the centroid of ring C21–C26.

D—H...A	D—H	H...A	D...A	D—H...A
C10—H10B...Cg2 ⁱⁱⁱ	0.99	2.80	3.691 (2)	151

Symmetry code: (iii) $-x + 1, -y + 1, -z + 1$.

Compound (IV)

Crystal data

$C_{22}H_{16}N_3$
 $M_r = 325.40$
 Monoclinic, $P2_1/c$
 $a = 7.9037$ (7) \AA
 $b = 13.1038$ (10) \AA
 $c = 16.0576$ (13) \AA
 $\beta = 99.199$ (6) $^\circ$
 $V = 1641.7$ (2) \AA^3
 $Z = 4$

$D_x = 1.317 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 3765 reflections
 $\theta = 3.0\text{--}27.6^\circ$
 $\mu = 0.08 \text{ mm}^{-1}$
 $T = 120$ (2) K
 Block, brown
 $0.50 \times 0.40 \times 0.35 \text{ mm}$

Data collection

Nonius KappaCCD diffractometer
 φ and ω scans
 Absorption correction: multi-scan
 (SADABS; Sheldrick, 2003)
 $T_{\min} = 0.956$, $T_{\max} = 0.973$
 22 738 measured reflections
 3765 independent reflections

3274 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.027$
 $\theta_{\text{max}} = 27.6^\circ$
 $h = -10 \rightarrow 10$
 $k = -17 \rightarrow 16$
 $l = -20 \rightarrow 20$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.045$
 $wR(F^2) = 0.124$
 $S = 1.06$
 3765 reflections
 229 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0742P)^2 + 0.428P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.34 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.35 \text{ e } \text{\AA}^{-3}$
 Extinction correction: *SHELXL97*
 Extinction coefficient: 0.073 (7)

Table 4

Selected bond lengths (\AA) for compounds (I)–(IV).

	(I)	(II)	(III)	(IV)	
N1—C2	1.3493 (19)	1.349 (3)	N1—C2	1.3524 (14)	1.3446 (15)
C2—C3	1.397 (2)	1.392 (4)	C2—C3	1.4000 (15)	1.3989 (15)
C3—C3A	1.383 (2)	1.380 (4)	C3—C3A	1.3878 (15)	1.3863 (16)
C3A—N4	1.3550 (17)	1.361 (3)	C3A—N4	1.3467 (14)	1.3504 (14)
N4—C5	1.3252 (19)	1.318 (4)	N4—C4A	1.3259 (14)	1.3201 (15)
C5—C5A	1.428 (2)	1.425 (4)	C4A—C10A	1.4344 (15)	1.4350 (15)
C5A—C11B	1.3790 (19)	1.385 (4)	C10A—C11	1.3723 (15)	1.3685 (15)
C11B—N11C	1.3808 (18)	1.383 (3)	C11—N11A	1.3726 (14)	1.3662 (14)
N11C—N1	1.3626 (16)	1.361 (3)	N11A—N1	1.3595 (12)	1.3534 (12)
C3A—N11C	1.3957 (19)	1.386 (4)	C3A—N11A	1.3905 (14)	1.3854 (14)

The space groups *Pbca*, $P2_1/n$, $P2_1/c$ and $P2_1/c$ for compounds (I)–(IV), respectively, were all uniquely assigned from the systematic absences. All H atoms were located from difference maps in fully ordered sites; they were then treated as riding atoms, with C–H distances of 0.95 (aromatic), 0.98 (methyl) or 0.99 \AA (CH_2), and with $U_{\text{iso}}(\text{H})$ values of $1.2U_{\text{eq}}(\text{C})$, or $1.5U_{\text{eq}}(\text{C})$ for the methyl groups. Compound (I) crystallized in the form of long very fine needles. All attempts to cut suitably small fragments from these needles caused irretrievable shattering, and hence the shortest needle in the sample was selected for data collection without modification.

For all compounds, data collection: *COLLECT* (Hooft, 1999); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; data reduction: *DENZO* and *COLLECT*; structure solution: *OSCAIL* (McArdle, 2003) and *SHELXS97* (Sheldrick, 1997); structure refinement: *OSCAIL* and *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1841). Services for accessing these data are described at the back of the journal.

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