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Hydrogen-bonded assembly in six closely related pyrazolo[3,4-*b*]-pyridine derivatives; a simple chain, three types of chains of rings and a complex sheet structure

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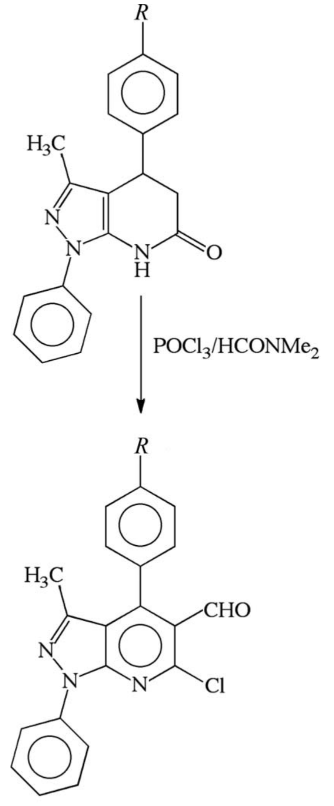
Six closely related pyrazolo[3,4-*b*]pyridine derivatives, namely 6-chloro-3-methyl-1,4-diphenylpyrazolo[3,4-*b*]pyridine-5-carbaldehyde, $C_{20}H_{14}ClN_3O$, (I), 6-chloro-3-methyl-4-(4-methylphenyl)-1-phenylpyrazolo[3,4-*b*]pyridine-5-carbaldehyde, $C_{21}H_{16}ClN_3O$, (II), 6-chloro-4-(4-chlorophenyl)-3-methyl-1-phenylpyrazolo[3,4-*b*]pyridine-5-carbaldehyde, $C_{20}H_{13}Cl_2N_3O$, (III), 4-(4-bromophenyl)-6-chloro-3-methyl-1-phenylpyrazolo[3,4-*b*]pyridine-5-carbaldehyde, $C_{20}H_{13}BrClN_3O$, (IV), 6-chloro-4-(4-methoxyphenyl)-3-methyl-1-phenylpyrazolo[3,4-*b*]pyridine-5-carbaldehyde, $C_{21}H_{16}ClN_3O_2$, (V), and 6-chloro-3-methyl-4-(4-nitrophenyl)-1-phenylpyrazolo[3,4-*b*]pyridine-5-carbaldehyde, $C_{20}H_{13}ClN_4O_3$, (VI), which differ only in the identity of a single small substituent on one of the aryl rings, crystallize in four different space groups spanning three crystal systems. The molecules of (I) are linked into a chain of rings by a combination of C—H···N and C—H···π(arene) hydrogen bonds; those of (II), (IV) and (V), which all crystallize in the space group $P\overline{1}$, are each linked by two independent C—H···O hydrogen bonds to form chains of edge-fused rings running in different directions through the three unit cells; the molecules of (III) are linked into complex sheets by a combination of two C—H···O hydrogen bonds and one C—H···π(arene) hydrogen bond; finally, the molecules of (VI) are linked by a single C—H···O hydrogen bond to form a simple chain.

Comment

We have recently described the preparation of a series of 6-chloropyrazolo[3,4-*b*]pyridine-5-carbaldehydes *via* tandem chlorination–formylation of pyrazolopyridinones under Vilsmeier–Haack conditions (Quiroga *et al.*, 2010). These compounds are intended for use as precursors in the synthesis of new fused heterocyclic systems with potential bioactivity. We report here the molecular and supramolecular structures of six closely-related 4-aryl-6-chloro-3-methyl-1-phenyl-pyrazolo-[3,4-*b*]pyridine-5-carbaldehydes, (I)–(VI) (Figs. 1–6).



(I) $R = H$
(II) $R = Me$
(III) $R = Cl$
(IV) $R = Br$
(V) $R = OMe$
(VI) $R = NO_2$

Despite differing by only the single substituent *R* at atom C44 (see Scheme and Figs. 1–6), compounds (I)–(VI) show some interesting variations in their crystallization characteristics. Compound (III), where *R* = Cl, might well be expected to be isomorphous either with (II), where *R* = Me, or with (IV), where *R* = Br. In the event, (III) crystallizes in the orthorhombic space group *Pbcn*, while (II) and (IV) both crystallize in the triclinic space group $P\overline{1}$, as does (V), where *R* = OMe, while the nitro derivative (VI) crystallizes in the monoclinic space group $P2_1/c$. Thus, these six rather similar compounds crystallize in no fewer than four different space groups ($P\overline{1}$, $P2_1/c$, $C2/c$ and *Pbcn*) spanning three crystal systems. Despite their common space group, the unit-cell dimensions of (II) and (IV) differ in that (II) has all the unit-cell angles less than 90° and quite similar in value, while (IV) has all the unit-cell angles greater than 90° and spanning a range of *ca* 17°. Despite their different space groups, the effective molecular volumes for (II), *R* = Me, and (III), *R* = Cl, as calculated from $V_{\rm cell}/Z$ (see *Crystal data*), are identical within experimental uncertainty, while the molecular volume of (IV) (*R* = Br) is greater by only *ca* 2.4%.

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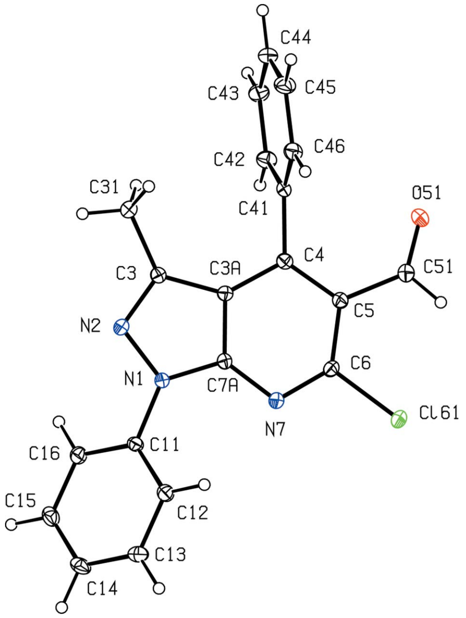

Figure 1
The molecular structure of (I) (R = H), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

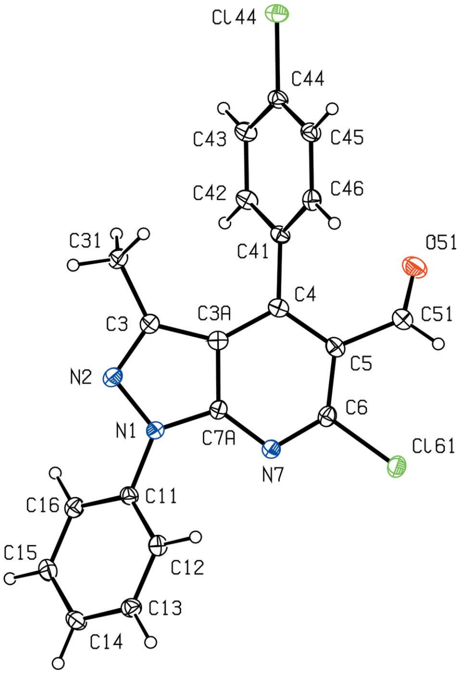

Figure 3
The molecular structure of (III) (R = Cl), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

None of the molecules of (I)–(VI) exhibit any internal symmetry and all of them are conformationally chiral. However, the centrosymmetric space groups all accommodate equal numbers of the two conformational enantiomers. The reference molecules of (I)–(VI) were selected to have the same sign for the torsion angles N2—N1—C11—C12 defining the orientation of the C11–C16 ring relative to the fused ring system (Table 1 and Figs. 1–6), where the individual values span a range of *ca* 40°. Similarly, the torsion angles C3*A*—C4—C41—C42, defining the orientation of the C41–C46 ring relative to the fused ring system, vary quite widely, spanning a range of *ca* 60°. While it is perhaps tempting to associate the variable orientation of the substituted C41–C46 aryl ring with the fact that donors forming part of this ring participate in hydrogen bonding in each of (I)–(VI), such an interpretation could not be convincingly applied to the orientation of the unsubstituted C11–C16 aryl ring, since the location of the

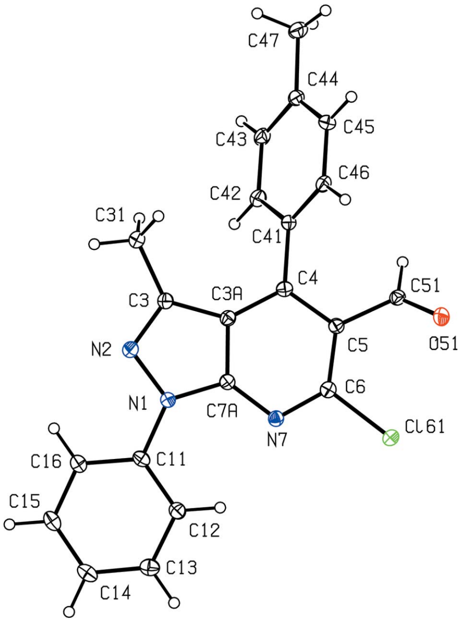

Figure 2
The molecular structure of (II) (R = Me), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

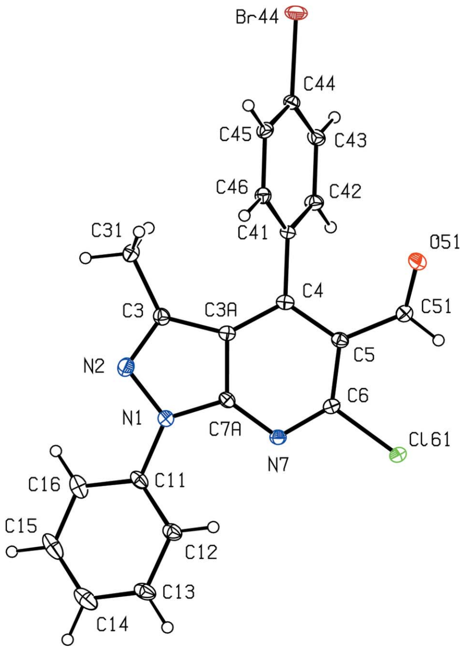

Figure 4
The molecular structure of (IV) (R = Br), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

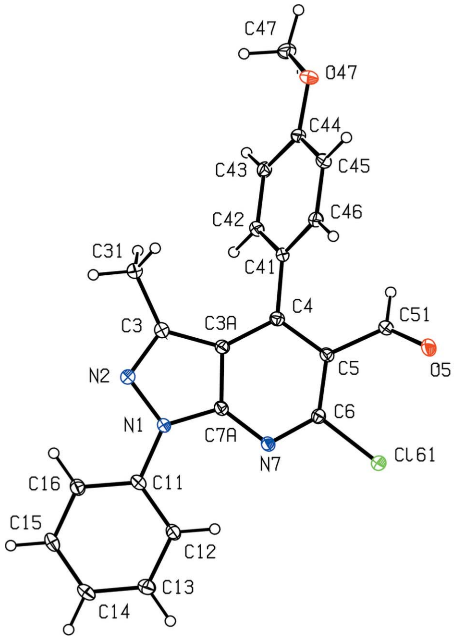

Figure 5
The molecular structure of (V) (R = OMe), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

donor unit C14—H14, active in (II), (IV) and (V), is unaffected by the value of the N2—N1—C11—C12 torsion angle.

Perhaps the most striking feature of the molecular conformations in (I)–(VI) concerns the orientation of the formyl group (Table 1 and Figs. 1–6), where the formyl O atom is directed towards atom Cl61 in (II) and (V) but away from it in all the other compounds. This type of behaviour has been noted previously in a series of N^6-substituted 2-amino-4-chloro-5-formylpyrimidines (Cobo *et al.*, 2008). A number of factors, including intra- and intermolecular hydrogen bonds and electrostatic factors, were considered as possibly underlying the occurrence of the two different formyl conformations, but no single factor was regarded in that work as providing a fully satisfactory interpretation of the observed behaviour. Likewise for (I)–(VI) here, no clear and simple interpretation of the formyl orientation presents itself.

The supramolecular assembly in (I)–(VI) is dominated by C—H···O hydrogen bonds (Table 2), but there is a C—H···N hydrogen bond in (I) and there are C—H···π(arene) hydrogen bonds in (I) and (III), where both compounds utilize the C11–C16 aryl ring as the acceptor. Intermolecular contacts of C—H···O type have been regarded as structurally insignificant if: (*a*) the H···O distance exceeds 2.60 Å (*cf.* Bondi, 1964; Rowland & Taylor, 1996), (*b*) the C—H···O angle is less than 130° (*cf.* Wood *et al.*, 2009) or (*c*) if the C—H bond concerned forms part of a methyl group. Such C—H bonds are of low acidity, and methyl groups $H_3C—E$ are likely to be undergoing very rapid rotation about the C—E bonds (Riddell & Rogerson, 1996, 1997), particularly when bonded to aryl rings, where the sixfold rotational barriers are typically only a few J mol^{-1} (Tannenbaum *et al.*, 1956; Naylor & Wilson, 1957). For compounds crystallizing in different space groups, very different patterns of supramolecular assembly are observed, but the three compounds which crystallize in the space group $P\overline{1}$, (II), (IV) and (V), all have rather similar hydrogen-bonded structures, albeit with differences in detail.

In the structure of (I), in the space group $C2/c$, a combination of one C—H···N and one C—H···π(arene) hydrogen bond links molecules related by the 2_1 screw axis along ($\frac{3}{4}$, y, $\frac{1}{4}$)

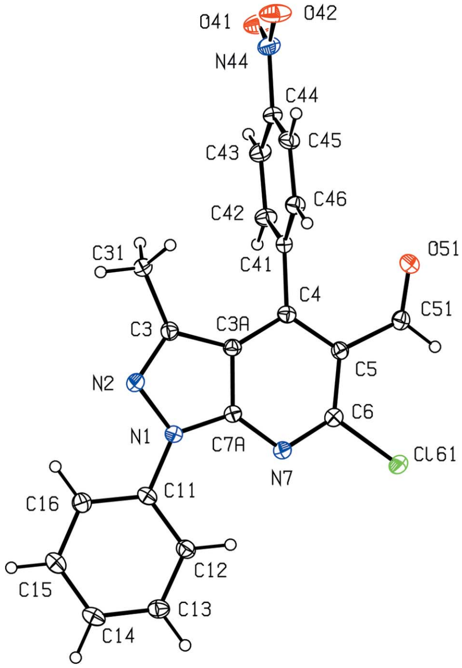

Figure 6
The molecular structure of (VI) (R = NO$_2$), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

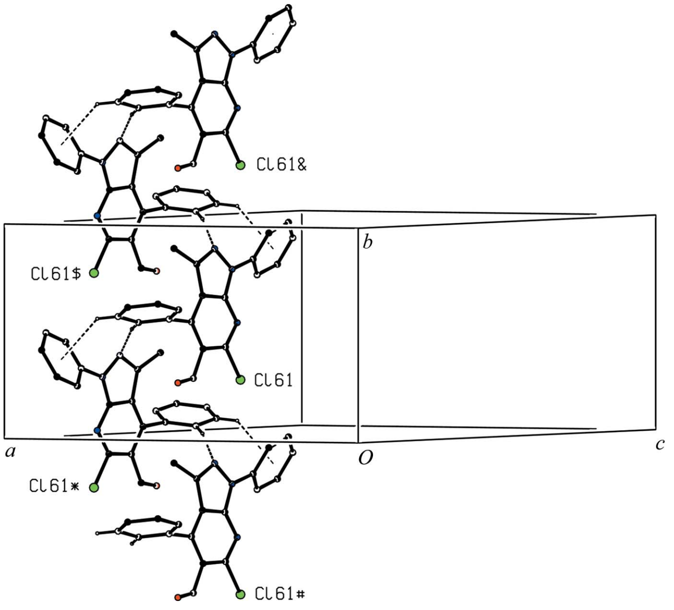

Figure 7
Part of the crystal structure of (I), showing the formation of a chain of rings along [010]. For the sake of clarity, H atoms not involved in the motif shown have been omitted. Atoms marked with an asterisk (*), hash (#), dollar sign ($) or ampersand (&) are at the symmetry positions ($-x+\frac{3}{2}$, $y-\frac{1}{2}$, $-z+\frac{1}{2}$), (x, $y-1$, z), ($-x+\frac{3}{2}$, $y+\frac{1}{2}$, $-z+\frac{1}{2}$) and (x, $y+1$, z), respectively.

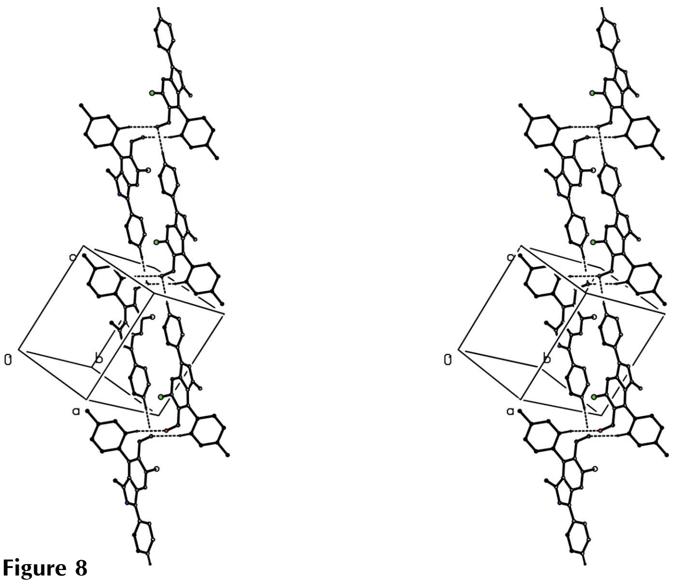

Figure 8
A stereoview of part of the crystal structure of (II), showing the formation of a chain of edge-fused $R^2_2(14)$ and $R^2_4(26)$ rings along $[10\overline{1}]$. For the sake of clarity, H atoms not involved in the motif shown have been omitted.

to form a chain of rings running parallel to the [010] direction (Fig. 7). Four chains of this type, each containing molecules related to one another by one of the four screw axes along $(\frac{1}{4}, y, \frac{1}{4})$, $(\frac{1}{4}, y, \frac{3}{4})$, $(\frac{3}{4}, y, \frac{1}{4})$ and $(\frac{3}{4}, y, \frac{3}{4})$, pass through each unit cell, but there are no direction-specific interactions between adjacent chains.

There are two C—H$\cdots$O hydrogen bonds in the structures of each of (II), (IV) and (V) (Table 2). One of these hydrogen bonds, where the donor forms part of the C41–C46 ring, links pairs of molecules related by inversion, forming centrosymmetric $R^2_2(14)$ (Bernstein *et al.*, 1995) rings in each of (II) and (V) (Figs. 8 and 12) and a centrosymmetric $R^2_2(16)$ ring in (IV) (Fig. 11). The second hydrogen bond, which utilizes the same donor atom in each of the three compounds, links molecules related by translation into $C(12)$ chains running parallel to the $[10\overline{1}]$, [110] and $[1\overline{1}0]$ directions in (II), (IV) and (V), respectively. The combination of the two C—H$\cdots$O hydrogen bonds leads in each case to the formation of a chain of edge-fused rings. In (II), this chain of rings contains $R^2_2(14)$ rings centred at $(\frac{1}{2} + n, \frac{1}{2}, 1 - n)$, where n represents an integer, alternating with $R^2_4(26)$ rings centred at $(n, \frac{1}{2}, \frac{3}{2} - n)$ (Fig. 8); in (IV), $R^2_2(16)$ rings centred at $(n, n, 0)$ alternate with $R^2_4(28)$ rings centred at $(\frac{1}{2} + n, \frac{1}{2} + n, \frac{1}{2})$ (Fig. 11); and in (V), $R^2_2(14)$ rings centred at $(\frac{1}{2} + n, -n, 0)$ alternate with $R^2_4(26)$ rings centred at $(n, \frac{1}{2} - n, \frac{1}{2})$ (Fig. 12), where in every case n represents an integer.

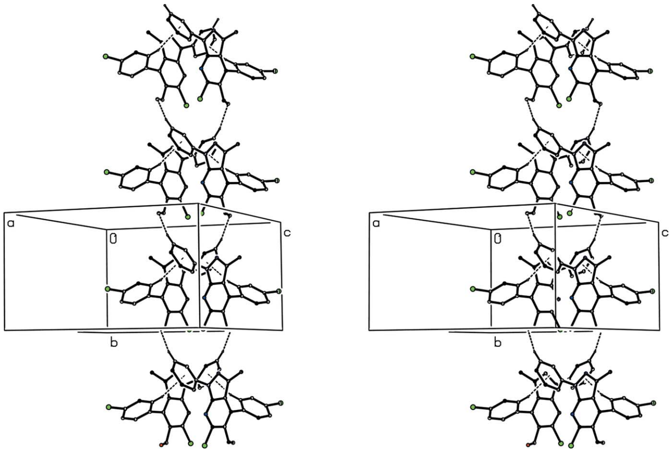

Figure 9
A stereoview of part of the crystal structure of (III), showing the formation of two translation-related $C(11)$ chains around $(\frac{1}{2}, y, \frac{3}{4})$, built from C—H$\cdots$O hydrogen bonds and linked by a C—H$\cdots\pi$(arene) hydrogen bond. For the sake of clarity, H atoms not involved in the motif shown have been omitted.

The hydrogen-bonded assembly in (III) is two-dimensional and of considerably greater complexity than the other hydrogen-bonded structures reported here. However, it can be straightforwardly analysed in terms of a one-dimensional substructure. Atom C15 in the molecule at (x, y, z) acts as hydrogen-bond donor to atom O51 in the molecule at $(-x + 1, y - 1, -z + \frac{3}{2})$, while atom C15 at $(-x + 1, y - 1, -z + \frac{3}{2})$ in turn acts as donor to atom O51 at $(x, y - 2, z)$, so forming a $C(11)$ chain running parallel to the [010] direction. There are, in fact, two such chains around the 2_1 screw axis along $(\frac{1}{2}, y, \frac{3}{4})$, related to one another by a unit translation along [010], and these two chains are linked to one another by a C—H$\cdots\pi$(arene)$(-x + 1, y, -z + \frac{3}{2})$ hydrogen bond to form a one-dimensional substructure (Fig. 9).

The action of the second C—H$\cdots$O hydrogen bond in (III) is to link the double chains which run parallel to [010] into a sheet. Atoms C43 in the molecules at (x, y, z) and $(-x + 1, y - 1, -z + \frac{3}{2})$, which are both components of a chain along $(\frac{1}{2}, y, \frac{1}{2})$, act as hydrogen-bond donors to atoms O51 in the molecules at $(-x + \frac{3}{2}, y - \frac{1}{2}, z)$ and $(x - \frac{1}{2}, y - \frac{3}{2}, -z + \frac{3}{2})$, respectively, which themselves form parts of $C(11)$ chains along $(1, y, \frac{3}{4})$ and $(0, y, \frac{3}{4})$, respectively, so leading to the formation of a sheet lying parallel to (001) (Fig. 10). This sheet lies in the domain $\frac{1}{2} < z < 1.0$, and a second sheet, related to the first by inversion, lies in the domain $0 < z < \frac{1}{2}$, but there are no direction-specific interactions between adjacent sheets. Thus, compound (III), despite having a constitution and steric

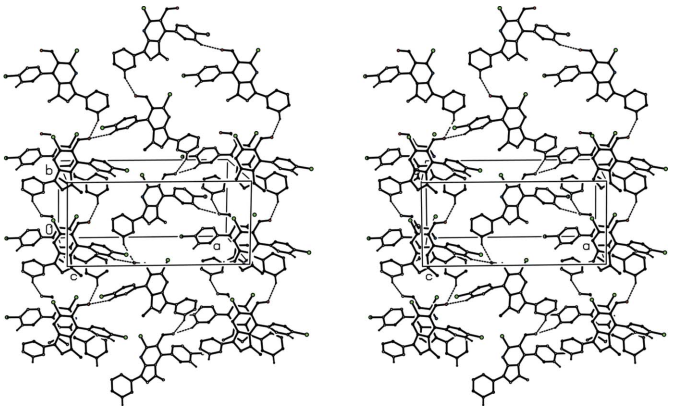

Figure 10
A stereoview of part of the crystal structure of (III), showing the linking of the chains along [010] to form a sheet lying parallel to (001). For the sake of clarity, H atoms not involved in the motif shown have been omitted.

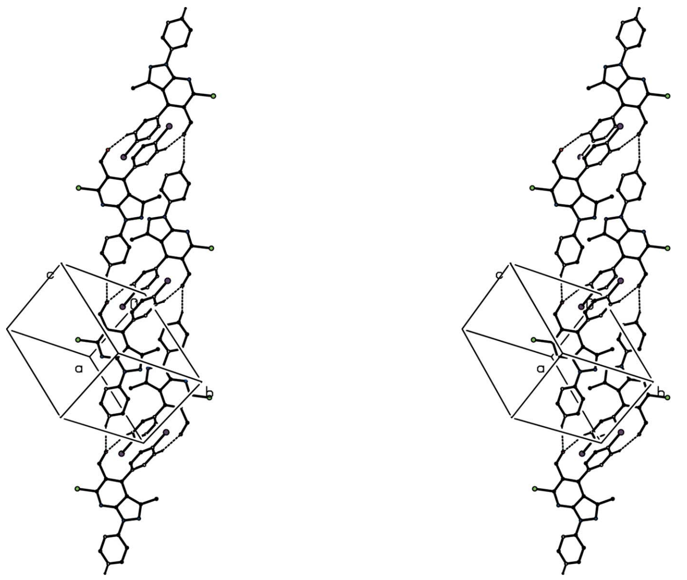

Figure 11
A stereoview of part of the crystal structure of (IV), showing the formation of a chain of edge-fused $R_2^2(16)$ and $R_4^2(28)$ rings along [110]. For the sake of clarity, H atoms not involved in the motif shown have been omitted.

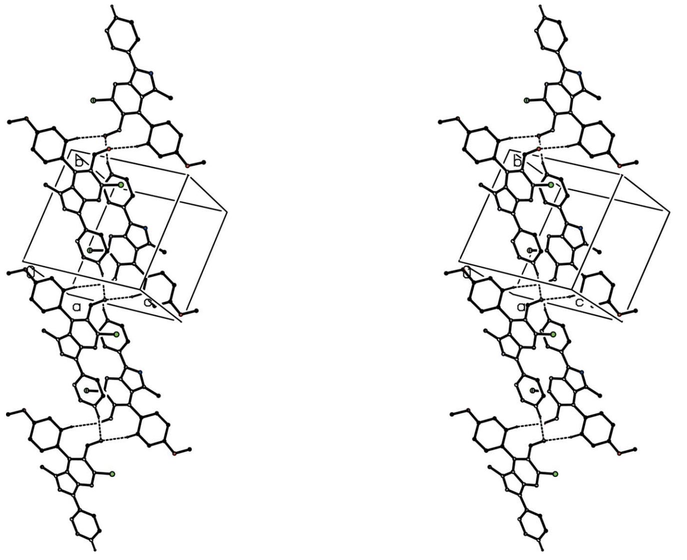

Figure 12
A stereoview of part of the crystal structure of (V), showing the formation of a chain of edge-fused $R_2^2(14)$ and $R_4^2(26)$ rings along [$1\bar{1}0$]. For the sake of clarity, H atoms not involved in the motif shown have been omitted.

properties, as manifested by the molecular volume, very similar to those of (II) and (IV), not only crystallizes in a different crystal system but also adopts a very different, and much more complex, pattern of supramolecular assembly.

In the structure of (VI), in the space group $P2_1/c$, a single C—H···O hydrogen bond links molecules related by the 2_1 screw axis along $(0, y, \frac{1}{4})$ into a simple $C(8)$ chain. Two such chains, related to one another by inversion, pass through each unit cell, but there are no direction-specific interactions between adjacent chains. It is interesting to note that (VI), where R = NO_2 and thus having the largest number of potential hydrogen-bond acceptors within each molecule, in fact has the simplest hydrogen-bonded structure in this series.

The wide range of space groups observed here, together with the different modes of hydrogen-bonded assembly, certainly suggest that series of this type might provide an interesting challenge for structure-prediction algorithms (Day *et al.*, 2005, 2009).

Experimental

A suspension of the appropriate 4-aryl-3-methyl-1-phenyl-4,5-dihydro-1*H*-pyrazolo[3,4-*b*]pyridin-6(7*H*)-one (1 mmol) in dimethylformamide (2 ml) was cooled using an ice–water bath, and then phosphoryl chloride (0.2 ml, 2.1 mmol) was added dropwise. Each reaction mixture was stirred for 30 min at ambient temperature and subsequently heated at 373 K for 5 h. After cooling to ambient temperature by the addition of ice, the reaction mixture was neutralized using sodium hydrogen carbonate solution with vigorous stirring. In each case, the resulting yellow precipitate was collected by filtration, dried and recrystallized from dimethylformamide to afford yellow crystals suitable for single-crystal X-ray diffraction.

Compound (I)

Crystal data

$C_{20}H_{14}ClN_3O$
M_r = 347.79
Monoclinic, $C2/c$
a = 16.784 (3) Å
b = 9.6380 (8) Å
c = 21.699 (4) Å
β = 108.820 (12)°
V = 3322.5 (9) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.24 mm^{-1}
T = 120 K
0.36 × 0.32 × 0.12 mm

Data collection

Bruker–Nonius KappaCCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{\min}$ = 0.918, $T_{\max}$ = 0.972
24328 measured reflections
3829 independent reflections
2899 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.042

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.100
S = 1.05
3829 reflections
227 parameters
H-atom parameters constrained
$\Delta\rho_{\max}$ = 0.49 e Å^{-3}
$\Delta\rho_{\min}$ = −0.37 e Å^{-3}

Compound (II)

Crystal data

$C_{21}H_{16}ClN_3O$
M_r = 361.82
Triclinic, $P\bar{1}$
a = 8.2898 (8) Å
b = 9.9191 (14) Å
c = 10.3666 (10) Å
α = 87.108 (11)°
β = 86.808 (8)°
γ = 85.088 (12)°
V = 847.08 (17) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.24 mm^{-1}
T = 120 K
0.31 × 0.26 × 0.20 mm

Data collection

Bruker–Nonius KappaCCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{\min}$ = 0.929, $T_{\max}$ = 0.953
21387 measured reflections
3880 independent reflections
2544 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.074

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.130$
$S = 1.03$
3880 reflections
237 parameters
H-atom parameters constrained
$\Delta\rho_{\max} = 0.31$ e Å^{-3}
$\Delta\rho_{\min} = -0.30$ e Å^{-3}

Compound (III)

Crystal data

$C_{20}H_{13}Cl_2N_3O$
$M_r = 382.23$
Orthorhombic, *Pbcn*
$a = 20.868$ (3) Å
$b = 9.603$ (4) Å
$c = 16.924$ (9) Å
$V = 3391$ (2) Å^3
$Z = 8$
Mo $K\alpha$ radiation
$\mu = 0.40$ mm^{-1}
$T = 120$ K
0.40 × 0.37 × 0.28 mm

Data collection

Bruker–Nonius KappaCCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{\min} = 0.857$, $T_{\max} = 0.897$
34307 measured reflections
3898 independent reflections
2444 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.080$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.053$
$wR(F^2) = 0.147$
$S = 1.08$
3898 reflections
236 parameters
H-atom parameters constrained
$\Delta\rho_{\max} = 0.62$ e Å^{-3}
$\Delta\rho_{\min} = -0.46$ e Å^{-3}

Compound (IV)

Crystal data

$C_{20}H_{13}BrClN_3O$
$M_r = 426.68$
Triclinic, $P\overline{1}$
$a = 9.3826$ (11) Å
$b = 9.7781$ (12) Å
$c = 10.1072$ (6) Å
$\alpha = 108.077$ (10)°
$\beta = 99.353$ (9)°
$\gamma = 90.911$ (10)°
$V = 867.61$ (16) Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 2.54$ mm^{-1}
$T = 120$ K
0.36 × 0.27 × 0.20 mm

Data collection

Bruker–Nonius KappaCCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{\min} = 0.440$, $T_{\max} = 0.604$
23897 measured reflections
3981 independent reflections
3098 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.048$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.077$
$S = 1.05$
3981 reflections
236 parameters
H-atom parameters constrained
$\Delta\rho_{\max} = 0.63$ e Å^{-3}
$\Delta\rho_{\min} = -0.42$ e Å^{-3}

Compound (V)

Crystal data

$C_{21}H_{16}ClN_3O_2$
$M_r = 377.82$
Triclinic, $P\overline{1}$
$a = 8.6972$ (8) Å
$b = 10.039$ (2) Å
$c = 10.090$ (2) Å
$\alpha = 85.23$ (2)°
$\beta = 80.856$ (16)°
$\gamma = 86.665$ (16)°
$V = 865.9$ (3) Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 0.24$ mm^{-1}
$T = 120$ K
0.28 × 0.19 × 0.14 mm

Data collection

Bruker–Nonius KappaCCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{\min} = 0.935$, $T_{\max} = 0.968$
21671 measured reflections
3975 independent reflections
3265 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.038$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.090$
$S = 1.06$
3975 reflections
246 parameters
H-atom parameters constrained
$\Delta\rho_{\max} = 0.30$ e Å^{-3}
$\Delta\rho_{\min} = -0.34$ e Å^{-3}

Compound (VI)

Crystal data

$C_{20}H_{13}ClN_4O_3$
$M_r = 392.79$
Monoclinic, $P2_1/c$
$a = 11.7839$ (13) Å
$b = 9.9890$ (4) Å
$c = 15.71$ (2) Å
$\beta = 106.084$ (8)°
$V = 1776$ (2) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.25$ mm^{-1}
$T = 120$ K
0.39 × 0.29 × 0.14 mm

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

Compound	N2—N1—C11—C12	C3*A*—C4—C41—C42	C4—C5—C51—O51
(I)	−140.93 (16)	−73.6 (2)	−10.2 (3)
(II)	−173.2 (2)	−53.6 (3)	147.5 (2)
(III)	−135.7 (3)	−56.7 (4)	−24.9 (5)
(IV)	−155.9 (2)	−115.5 (3)	13.8 (4)
(V)	−177.26 (14)	−55.9 (2)	150.72 (16)
(VI)	−167.68 (18)	−88.6 (2)	1.8 (3)

Table 2
Geometry of hydrogen bonds and short intramolecular contacts (Å, °) for (I)–(VI).

*Cg*1 represents the centroid of the C11–C16 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
(I)				
C46—H46···N2$^{\rm i}$	0.95	2.58	3.515 (2)	169
C45—H45···*Cg*1$^{\rm i}$	0.95	2.76	3.508 (2)	136
(II)				
C14—H14···O51$^{\rm ii}$	0.95	2.46	3.319 (3)	150
C46—H46···O51$^{\rm iii}$	0.95	2.41	3.348 (3)	170
(III)				
C15—H15···O51$^{\rm iv}$	0.95	2.56	3.433 (4)	153
C43—H43···O51$^{\rm v}$	0.95	2.50	3.381 (4)	154
C42—H42···*Cg*1$^{\rm vi}$	0.95	2.75	3.653 (4)	160
(IV)				
C14—H14···O51$^{\rm vii}$	0.95	2.55	3.448 (4)	157
C45—H45···O51$^{\rm viii}$	0.95	2.49	3.397 (3)	160
(V)				
C14—H14···O51$^{\rm ix}$	0.95	2.43	3.312 (2)	154
C46—H46···O51^{x}	0.95	2.36	3.300 (2)	171
(VI)				
C45—H45···O51$^{\rm xi}$	0.95	2.41	3.261 (2)	150

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

Data collection

Bruker–Nonius KappaCCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{\rm min} = 0.910$, $T_{\rm max} = 0.966$
25554 measured reflections
4073 independent reflections
2914 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.049$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.134$
$S = 1.09$
4073 reflections
254 parameters
H-atom parameters constrained
$\Delta\rho_{\rm max} = 0.42$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.34$ e Å^{-3}

All H atoms were located in difference maps and then treated as riding atoms in geometrically idealized positions, with C—H = 0.95 (aromatic and formyl H) or 0.98 Å (methyl H), and with $U_{\rm iso}({\rm H}) = kU_{\rm eq}({\rm C})$, 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.

For all compounds, data collection: *COLLECT* (Nonius, 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: YF3009). Services for accessing these data are described at the back of the journal.

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