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Four N^7-benzyl-substituted 4,5,6,7-tetrahydro-1*H*-pyrazolo[3,4-*b*]pyri-]pyridine-5-spiro-1′-cyclohexane-2′,6′-diones as ethanol hemisolvates: similar molecular constitutions but different crystal structures

Silvia Cruz,[a] Jorge Trilleras,[b] Justo Cobo,[c] John N. Low[d] and Christopher Glidewell[e]*

[a]Departamento de Química, Universidad de Nariño, Ciudad Universitaria, Torobajo, AA 1175 Pasto, Colombia, [b]Grupo de Investigación de Compuestos Heterocíclicos, Departamento de Química, Universidad de Valle, AA 25360 Cali, Colombia, [c]Departamento de Química Inorgánica y Orgánica, Universidad de Jaén, 23071 Jaén, Spain, [d]Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen AB24 3UE, Scotland, and [e]School of Chemistry, University of St Andrews, Fife KY16 9ST, Scotland
Correspondence e-mail: cg@st-andrews.ac.uk

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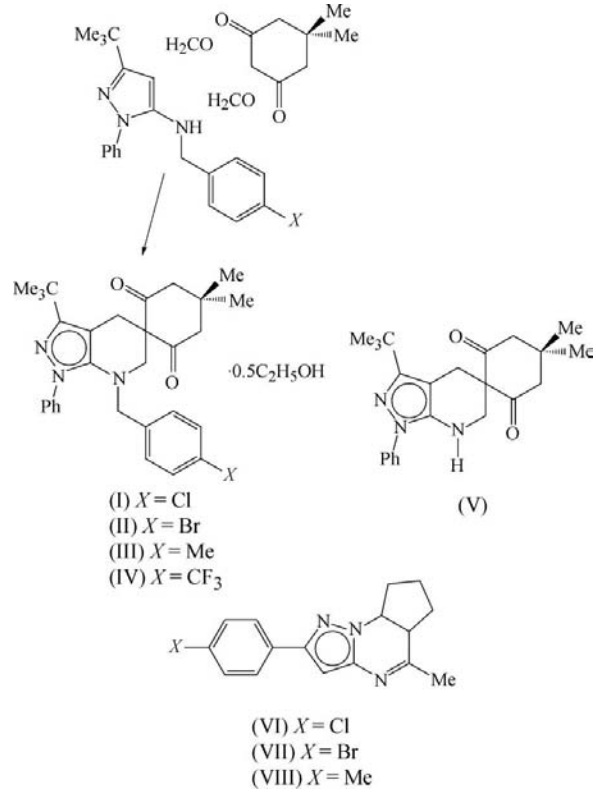
3-*tert*-Butyl-7-(4-chlorobenzyl)-4′,4′-dimethyl-1-phenyl-4,5,6,7-tetrahydro-1*H*-pyrazolo[3,4-*b*]pyridine-5-spiro-1′-cyclohexane-2′,6′-dione ethanol hemisolvate, $C_{30}H_{34}ClN_3O_2\cdot 0.5C_2H_6O$, (I), its 7-(4-bromobenzyl)- analogue, $C_{30}H_{34}BrN_3O_2\cdot 0.5C_2H_6O$, (II), and its 7-(4-methylbenzyl)- analogue, $C_{31}H_{37}N_3O_2\cdot 0.5C_2H_6O$, (III), are isomorphous, with the ethanol component disordered across a twofold rotation axis in the space group *C*2/*c*. In the corresponding 7-[4-(trifluoromethyl)benzyl]- compound, $C_{31}H_{34}F_3N_3O_2\cdot 0.5C_2H_6O$, (IV), the ethanol component is disordered across a centre of inversion in the space group $P\overline{1}$. In each of (I)–(IV), the reduced pyridine ring adopts a half-chair conformation. The heterocyclic components in (I)–(III) are linked into centrosymmetric dimers by a single C—H$\cdots\pi$ interaction, with the half-occupancy ethanol component linked to the dimer by a combination of C—H$\cdots$O and O—H$\cdots\pi$(arene) hydrogen bonds. The heterocyclic molecules in (IV) are linked into chains of centrosymmetric rings by C—H$\cdots$O and C—H$\cdots\pi$ hydrogen bonds, again with the half-occupancy ethanol component pendent from the chain. The significance of this study lies in the isomorphism of the related derivatives (I)–(III), in the stoichiometric hemisolvation by ethanol, where the disordered solvent molecule is linked to the heterocyclic component by a two-point linkage, and in the differences between the crystal structures of (I)–(III) and that of (IV).

Comment

Spiranes are rather rigid structures which are useful as frameworks for the attachment of functional groups incorporating pharmacophoric or metal-coordinating moieties. Spiro skeletons are not only present in numerous naturally occurring alkaloids, but have also been used in drug discovery and in the development of combinatorial libraries (Bazgir *et al.*, 2008). The development of new routes for the synthesis of these frameworks has attracted considerable attention and several distinct approaches have been reported for the preparation of heterocyclic spiranes. These include palladium-promoted spiroannulations onto carbocyclic or heterocyclic substrates (Møller & Undheim, 2003), spirocyclizations mediated by BF_3–Et_2O (Caputo *et al.*, 2003), spiroannulation of carboxylic acids (Rahimizadeh *et al.*, 2007), and oxidative rearrangement sequences and intramolecular Mannich reactions (Marti & Carreira, 2003).



We report here the structures of four closely related compounds, (I)–(IV), all obtained using three-component cyclocondensations induced by microwave irradiation, and all crystallizing as ethanol hemisolvates. We have been investigating such cyclocondensations as part of a programme for the synthesis of fused pyrazolo derivatives (Quiroga *et al.*, 1999), and we have recently reported (Low *et al.*, 2004) the structure of compound (V), obtained from the condensation reaction between 5-amino-3-*tert*-butyl-1-phenylpyrazole, 5,5-dimethylcyclohexane-1,3-dione (dimedone) and formaldehyde. The constitution of the heterocyclic component in (I)–(IV) differs from that in (V) in having a substituted benzyl group at position N7, rather than a H atom. Compounds (I)–(IV) were synthesized using a straightforward modification of the

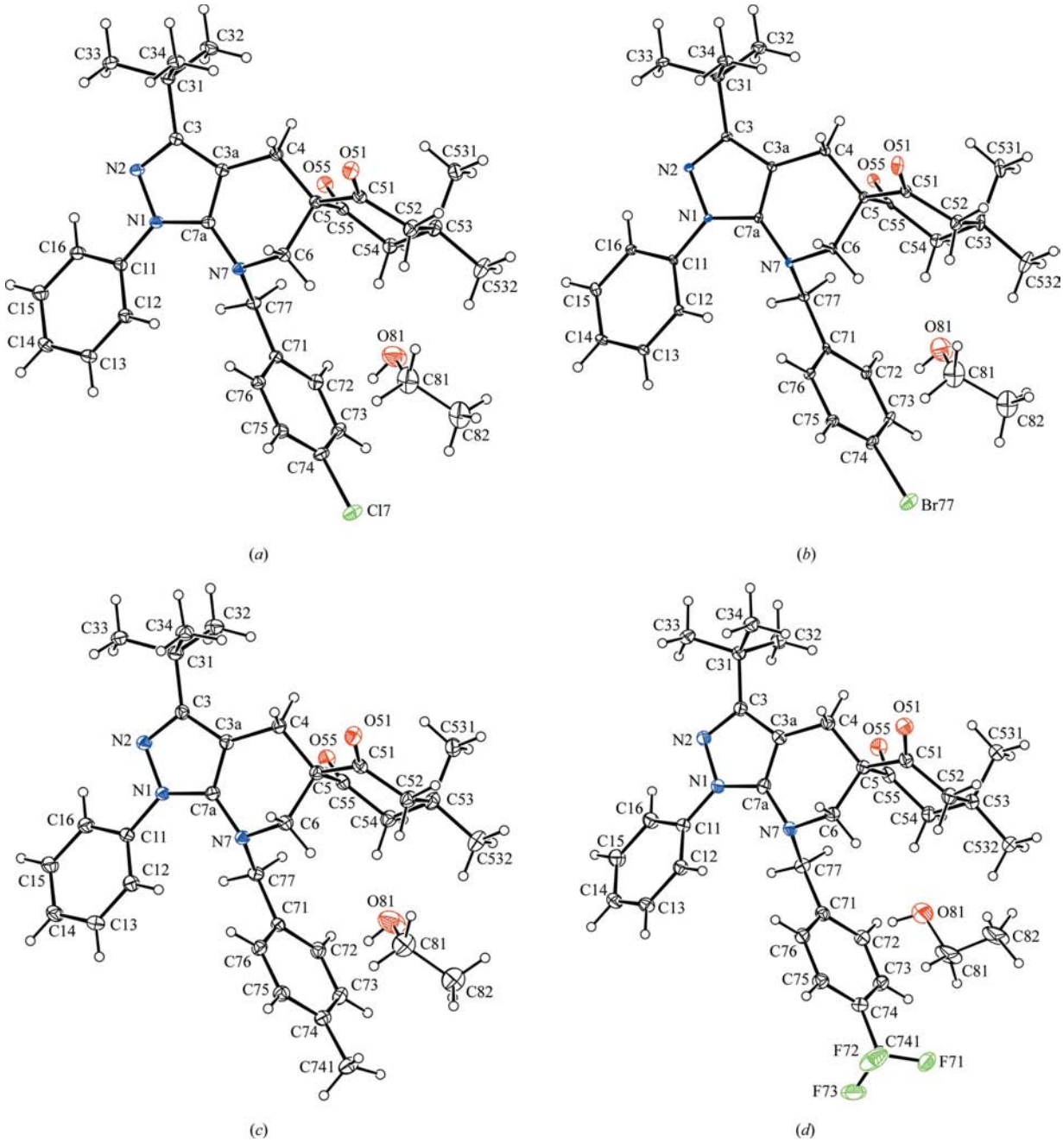


Figure 1
The independent molecular components in (*a*) compound (I), (*b*) (II), (*c*) (III) and (*d*) (IV). The ethanol components all have 0.5 occupancy, so that only half of the heterocyclic molecules are linked to ethanol molecules *via* hydrogen bonds (see *Comment*). Displacement ellipsoids are drawn at the 30% probability level.

synthetic method employed earlier, but employing in each case an appropriately substituted 5-benzylamino-3-*tert*-butyl-1-phenylpyrazole as the amino component (see scheme).

Compounds (I)–(IV) (Fig. 1) all crystallize as stoichiometric ethanol hemisolvates, with the ethanol disordered across a twofold rotation axis in (I)–(III) and across a centre of inversion in (IV). Compounds (I)–(III) are isomorphous in the space group $C2/c$, while (IV) crystallizes in the space group $P\overline{1}$ with very different unit-cell dimensions. Examination of the refined structures using *PLATON* (Spek, 2003) showed that artificial removal of the ethanol component from the structures gave rise to four voids per unit cell in (I)–(III), with volumes ranging from 72 Å^3 per void in (I) to 66 Å^3 per void in (II) and (III), amounting in total to *ca* 5% of the unit-cell volume, and located near $(\frac{1}{2}, \frac{2}{3}, \frac{3}{4})$ and the symmetry-related equivalent positions. In (IV), a similar investigation found a single void centred at $(\frac{1}{2}, \frac{1}{2}, 1)$ and accounting for *ca* 6.3% of the unit-cell volume. It is possible that the structural role of the ethanol is simply to occupy what would otherwise be void space; this is certainly consistent with its very limited partici-

pation in the supramolecular aggregation in the structures of (I)–(IV).

Thus, in each of the two distinct structures, the half-occupancy ethanol component is linked to the heterocyclic component by a combination of a C—H···O hydrogen bond and an O—H···π(arene) hydrogen bond in which the aryl ring of the benzyl substituent acts as the acceptor (Table 2). Statistically, the pairs of heterocyclic molecules related by a twofold axis in (I)–(III) or by inversion in (IV) are each associated with a disordered ethanol molecule lying across the symmetry element in question. However, at the local level, each ethanol site is occupied by a single molecule with a definite orientation, although the two alternative orientations occur with equal probability. Thus, for each ethanol location, one set of atomic sites is fully occupied while the other is vacant. Hence, a specific ethanol molecule is either linked to the heterocycle at (x, y, z) or to its symmetry-related companion, but it cannot be linked to two such heterocycles. Thus, the ethanol component plays no further role in the supramolecular aggregation.

The isomorphism of (I)–(III) may be compared with the isomorphous series (VI)–(VIII) (Portilla *et al.*, 2005). On the other hand, in the closely-related 7-arylbenzo[*h*]pyrazolo-[3,4-*b*]quinolines, the 4-chlorophenyl and 4-methylphenyl derivatives are isomorphous, while in the isomeric 11-arylbenzo[*f*]pyrazolo[3,4-*b*]quinolines, the corresponding derivatives are not isomorphous (Portilla *et al.*, 2008), although the 4-chlorophenyl compound is isomorphous with the 4-bromophenyl derivative (Serrano *et al.*, 2005*a*,*b*).

In each of (I)–(IV), the reduced pyridine ring adopts a half-chair conformation, as shown by the ring-puckering parameters (Table 1; Cremer & Pople, 1975). For an idealized half-chair ring with equal bond lengths throughout, the ring-puckering angles are $\theta = 50.8^\circ$ and $\varphi = (60k + 30)^\circ$, where k represents an integer. The similarity between the corresponding parameters is very high for the isomorphous compounds (I)–(III), while the parameters for (IV) differ slightly.

The rest of the molecular conformation is determined by the orientation of the three pendent substituents relative to the heterocyclic molecular core, and these orientations can be defined in terms of just six torsion angles (Table 1). The *tert*-butyl substituent is always slightly rotated about the C3—C31 bond so that atom C33 lies just out of the plane of the pyrazole ring. As with the ring-puckering angles for the pyridine ring, the corresponding torsion angles in the isomorphous compounds (I)–(III) are all very similar, while the out-of-plane rotation of the *tert*-butyl group is significantly larger in (IV). The observed conformations, together with the pyramidal coordination at atom N7, mean that the molecules have no internal symmetry and hence that they are chiral, although the space group in all cases accommodates a racemic mixture of enantiomers.

The supramolecular aggregation depends upon hydrogen-bond formation between the heterocyclic molecules, and the ethanol components are simply pendent from the resulting hydrogen-bonded aggregates. The aggregation is dominated by hydrogen bonds of C—H···π type, augmented in the case of (IV) by a C—H···O hydrogen bond (Table 2). Of the short intermolecular contacts indicated by *PLATON* (Spek, 2003) as possible hydrogen bonds, we have discounted all those involving methyl C—H bonds as potential donors. Not only are methyl C—H bonds expected to be of rather low acidity but, in general, methyl groups CH_3—E undergo extremely fast rotation about the C—E bond even in the solid state, as shown by solid-state NMR spectroscopy (Riddell & Rogerson, 1996, 1997). Such contacts of C—H···O type occur in (I)–(III). In each case, however, the fast rotation of the methyl groups about the C—C bonds will render such contacts structurally insignificant. In addition, we have discarded intermolecular C—H···O contacts in which the H···O distance exceeds 2.50 Å, and all contacts where the D—H···A angle is less than 125°. Finally, we have excluded from consideration the intermolecular C—H···Cl and C—H···Br contacts in (I) and (II), as it has been concluded that such contacts involving covalently bound Cl or Br 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).

In compounds (I)–(III) a single C—H···π interaction (Table 2) links pairs of pyrazolopyridine units into a centrosymmetric dimer (Fig. 2), but there are no direction-specific interactions between these dimers, so that the supramolecular structure can be regarded as finite or zero-dimensional.

By contrast, in compound (IV), where an entirely equivalent dimer is formed by paired C—H···π interactions, these dimeric units are further linked by a C—H···O hydrogen

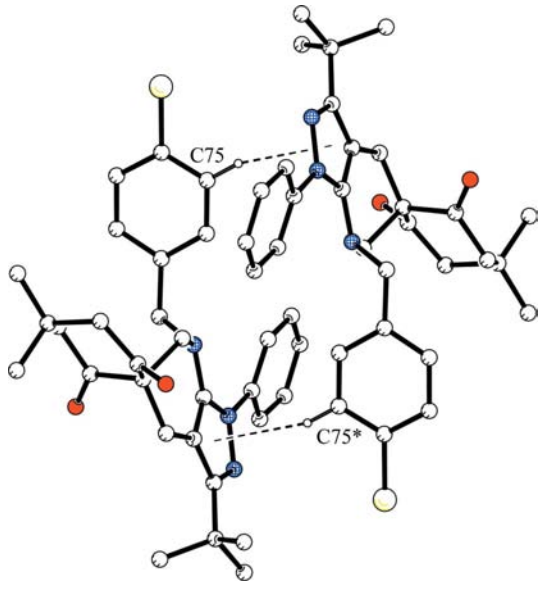


Figure 2
The centrosymmetric hydrogen-bonded dimer formed in each of the isomorphous compounds (I)–(III). For the sake of clarity, the half-occupancy ethanol molecules, H atoms not involved in the hydrogen-bonded motif shown, and the unit-cell outline have all been omitted. The atom marked with an asterisk (*) is at the symmetry position ($\frac{1}{2} - x, \frac{3}{2} - y, 1 - z$).

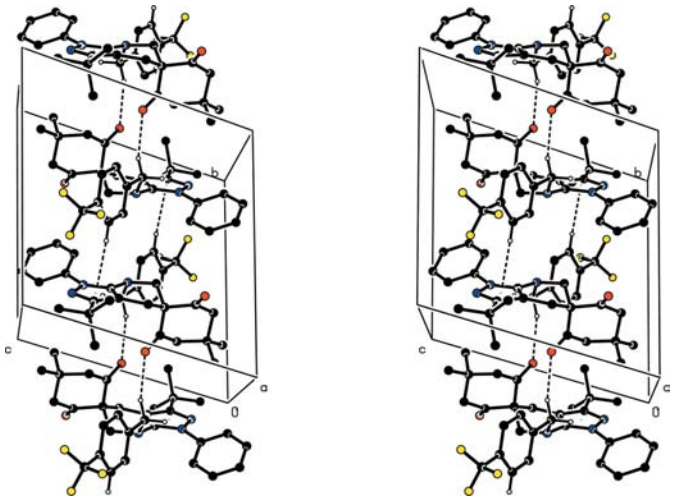


Figure 3
A stereoview of part of the crystal structure of (IV), showing the formation of a chain of centrosymmetric hydrogen-bonded rings along [010] built from C—H···O and C—H···π hydrogen bonds. For the sake of clarity, the half-occupancy ethanol molecules and H atoms not involved in the motifs shown have been omitted.

bond (Table 2) into a chain of centrosymmetric rings running parallel to the [010] direction (Fig. 3). Rings of $R_2^2(14)$ type (Bernstein *et al.*, 1995) formed by pairs of C—H···O hydrogen bonds are centred at $(\frac{1}{2}, n, \frac{1}{2})$, where n represents an integer, while the rings formed by pairs of C—H···π interactions are centred at $(\frac{1}{2}, \frac{1}{2}+n, \frac{1}{2})$, where n represents an integer. There are no direction-specific interactions between these chains of rings, so that the supramolecular structure is one-dimensional.

Compounds (I)–(IV) are thus similar in constitution and their heterocyclic components are very similar in both configuration and conformation. Despite these close resemblances, the range of direction-specific intermolecular interactions and the crystal structures differ between those of the isomorphous compounds (I)–(III) on the one hand and compound (IV) on the other. The contrast between compounds (III) and (IV) is particularly striking, as their compositions differ only in the formal replacement of a CH_3 group in (III) by a CF_3 group in (IV), and as neither of these substituents plays any direct role in the supramolecular aggregation. The prediction of the crystal structures of molecular compounds remains an extremely difficult undertaking which has so far met with very limited success (Day *et al.*, 2005). Any attempts at the present time to explain the structural differences found here between compounds (III) and (IV) are thus likely to be largely speculative.

Experimental

Microwave-induced syntheses were carried out using a focused microwave reactor (CEM Discover). A mixture of the appropriately substituted aminopyrazole (see scheme; 2 mmol), 5,5-dimethylcyclohexane-1,3-dione (2 mmol) and an excess of paraformaldehyde (80–100 mg) was exposed to microwave radiation at 473 K with a maximum power of 300 W for 25 min. The reaction mixtures were then dissolved in hot ethanol. After cooling, the solid products were collected by filtration and washed with ethanol and then hexane (2 × 5 ml) to afford the pure products, (I)–(IV), as colourless crystals. For (I), yield 85%, m.p. 453–455 K; HRMS found 503.2336; $C_{30}H_{34}ClN_3O_2$ requires 503.2340. For (II), yield 77%, m.p. 439–441 K; HRMS found 547.1828, $C_{30}H_{34}BrN_3O_2$ requires 547.1834. For (III), yield 75%, m.p. 472–474 K; HRMS found 483.2894, $C_{31}H_{37}N_3O_2$ requires 483.2886. For (IV), yield 85%, m.p. 418–420 K; HRMS found 537.2610, $C_{31}H_{34}F_3N_3O_2$ requires 537.2603.

Compound (I)

Crystal data

$C_{30}H_{34}ClN_3O_2\cdot0.5C_2H_6O$
M_r = 527.09
Monoclinic, $C2/c$
a = 27.419 (4) Å
b = 10.5860 (13) Å
c = 21.580 (3) Å
β = 122.625 (11)°
V = 5275.5 (14) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.18 mm^{-1}
T = 120 (2) K
0.32 × 0.23 × 0.22 mm

Data collection

Bruker–Nonius KappaCCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.954, T_{max} = 0.961
36250 measured reflections
6021 independent reflections
4812 reflections with $I > 2\sigma(I)$
R_{int} = 0.059

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.051
$wR(F^2)$ = 0.132
S = 1.08
6021 reflections
352 parameters
3 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.55 e Å^{-3}
$\Delta\rho_{min}$ = −0.52 e Å^{-3}

Compound (II)

Crystal data

$C_{30}H_{34}BrN_3O_2\cdot0.5C_2H_6O$
M_r = 571.55
Monoclinic, $C2/c$
a = 27.4453 (7) Å
b = 10.5519 (8) Å
c = 21.715 (2) Å
β = 122.484 (7)°
V = 5304.8 (8) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 1.59 mm^{-1}
T = 120 (2) K
0.45 × 0.35 × 0.25 mm

Table 1
Selected geometric parameters (Å, °) for compounds (I)–(IV).

Ring-puckering parameters are specified for the atom sequence N7—C6—C5—C4—C3a—C7a.

	(I)	(II)	(III)	(IV)
Ring-puckering parameters				
Q	0.482 (2)	0.483 (5)	0.477 (3)	0.475 (5)
θ	53.6 (2)	53.3 (6)	53.1 (4)	50.2 (4)
φ	87.9 (3)	86.7 (7)	88.0 (4)	100.9 (4)
Torsion angles				
N2—C3—C31—C32	−118.00 (19)	−119.2 (5)	−115.3 (3)	−106.4 (3)
N2—C3—C31—C33	2.7 (3)	1.4 (6)	4.8 (3)	13.4 (4)
N2—C3—C31—C34	122.09 (19)	121.1 (5)	124.5 (3)	134.3 (3)
N2—N1—C11—C12	−151.77 (18)	−152.4 (4)	−151.1 (2)	−147.9 (3)
C6—N7—C77—C71	60.3 (2)	59.9 (5)	58.6 (3)	60.1 (3)
N7—C77—C71—C72	−146.42 (17)	−145.7 (4)	−143.4 (2)	−139.9 (3)

Data collection

Bruker–Nonius KappaCCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.499, T_{max} = 0.673
46446 measured reflections
6083 independent reflections
3856 reflections with $I > 2\sigma(I)$
R_{int} = 0.091

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.069
$wR(F^2)$ = 0.206
S = 1.04
6083 reflections
351 parameters
3 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.87 e Å^{-3}
$\Delta\rho_{min}$ = −1.30 e Å^{-3}

Compound (III)

Crystal data

$C_{31}H_{37}N_3O_2{\cdot}0.5C_2H_6O$
M_r = 506.67
Monoclinic, $C2/c$
a = 27.281 (5) Å
b = 10.6438 (15) Å
c = 21.567 (3) Å
β = 122.082 (12)°
V = 5306.1 (16) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.08 mm^{-1}
T = 120 (2) K
0.51 × 0.30 × 0.07 mm

Data collection

Bruker–Nonius KappaCCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.966, T_{max} = 0.994
48672 measured reflections
6079 independent reflections
3421 reflections with $I > 2\sigma(I)$
R_{int} = 0.118

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.064
$wR(F^2)$ = 0.178
S = 1.03
6079 reflections
353 parameters
3 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.33 e Å^{-3}
$\Delta\rho_{min}$ = −0.42 e Å^{-3}

Compound (IV)

Crystal data

$C_{31}H_{34}F_3N_3O_2{\cdot}0.5C_2H_6O$
M_r = 560.65
Triclinic, $P\overline{1}$
a = 10.3270 (12) Å
b = 11.9970 (14) Å
c = 12.427 (3) Å
α = 75.016 (13)°
β = 70.059 (11)°
γ = 84.481 (9)°
V = 1398.0 (4) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.10 mm^{-1}
T = 120 (2) K
0.47 × 0.35 × 0.28 mm

Data collection

Bruker–Nonius KappaCCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.963, T_{max} = 0.973
39346 measured reflections
6424 independent reflections
3353 reflections with $I > 2\sigma(I)$
R_{int} = 0.092

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.069
$wR(F^2)$ = 0.224
S = 1.05
6424 reflections
378 parameters
3 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.46 e Å^{-3}
$\Delta\rho_{min}$ = −0.53 e Å^{-3}

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

Because of the ethanol disorder, only half of the heterocyclic molecules in each compound form hydrogen bonds to an ethanol molecule (see *Comment*). *Cg*1 represents the centroid of the C71–C76 ring and *Cg*2 represents the centroid of the N1/N2/C3/C3a/C7a ring.

Compound	D—H···A	D—H	H···A	D···A	D—H···A
(I)	O81—H81···*Cg*1	0.84	2.32	3.116 (5)	157
	C52—H52*A*···O81	0.99	2.27	3.188 (5)	154
	C75—H75···*Cg*2^{i}	0.95	2.55	3.469 (2)	163
(II)	O81—H81···*Cg*1	0.84	2.25	3.060 (13)	163
	C52—H52*A*···O81	0.99	2.31	3.224 (12)	153
	C75—H75···*Cg*2^{i}	0.95	2.58	3.498 (6)	164
(III)	O81—H81···*Cg*1	0.84	2.23	3.057 (7)	166
	C52—H52*A*···O81	0.99	2.22	3.145 (6)	155
	C75—H75···*Cg*2^{i}	0.95	2.59	3.519 (3)	167
(IV)	O81—H81···*Cg*1	0.84	2.58	3.245 (6)	137
	C52—H52*A*···O81	0.99	2.31	3.285 (8)	170
	C75—H75···*Cg*2^{ii}	0.95	2.67	3.544 (4)	154
	C77—H77*A*···O55^{iii}	0.99	2.42	3.352 (3)	157

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

For compounds (I)–(III), the systematic absences permitted *Cc* or *C*2/*c* as possible space groups; *C*2/*c* was selected and confirmed by the structure analysis. Crystals of compound (IV) are triclinic; space group $P\overline{1}$ was selected and confirmed by the structure analysis. All H atoms were located in difference maps and then treated as riding atoms in geometrically idealized positions, with C—H = 0.95 (aromatic), 0.98 (CH_3) or 0.99 Å (CH_2) and O—H = 0.84 Å, and with U_{iso}(H) = kU_{eq}(carrier), where k = 1.5 for the methyl and hydroxyl H atoms, and 1.2 for all other H atoms. In (I)–(III), the ethanol component was disordered across a twofold axis, selected as that along ($\frac{1}{2}$, y, $\frac{3}{4}$), while in (IV) this component was disordered across a centre of inversion, selected as that at ($\frac{1}{2}$, $\frac{1}{2}$, 1). For each compound, it proved necessary to apply restraints to the C—C and C—O distances of 1.540 (1) and 1.420 (1) Å, respectively, and to the nonbonded C···O distance of 2.418 (2) Å in the disordered ethanol component. The reference heterocyclic molecule in (IV) was selected to be of the same hand as those in (I)–(III).

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: *OSCAIL* (McArdle, 2003) and *SHELXL97* (Sheldrick, 2008); 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: GA3109). Services for accessing these data are described at the back of the journal.

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